ESTIMATES OF OCCUPATIONAL SAFETY AND HEALTH **IMPACTS RESULTING FROM LARGE-SCALE PRODUCTION OF MAJOR PHOTOVOLTAIC TECHNOLOGIES**

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NATIONAL CENTER FOR ANALYSIS OF ENERGY SYSTEMS DEPARTMENT OF ENERGY AND ENVIRONMENT

BROOKHAVEN NATIONAL LABORATORY UPTON, NEW YORK 11973

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BNL 51324 UC-63 (Photovoltaic Conversion – TIC-4500)

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August 1980

BIOMEDICAL AND ENVIRONMENTAL ASSESSMENT DIVISION NATIONAL CENTER FOR ANALYSIS OF ENERGY SYSTEMS DEPARTMENT OF ENERGY AND ENVIRONMENT BROOKHAVEN NATIONAL LABORATORY ASSOCIATED UNIVERSITIES, INC.

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SECTION 1

SUMMARY

The purpose of this study is to estimate both quantitatively and qualitatively, the worker and societal risks attributable to four photovoltaic cell (solar cell) production processes. Quantitative risk values were determined by use of statistics from the California semiconductor industry. The qualitative risk assessment was performed using a variety of both governmental and private sources of data.

The occupational health statistics derived from the semiconductor industry were used to predict injury and fatality levels associated with photovoltaic cell manufacturing. The use of these statistics to characterize the two silicon processes described herein is defensible from the standpoint that many of the same process steps and materials are used in both the semiconductor and photovoltaic industries. These health statistics are less applicable to the gallium arsenide and cadmium sulfide manufacturing processes, primarily because of differences in the materials utilized. Although such differences tend to discourage any absolute comparisons among the four photovoltaic cell production processes, certain relative comparisons are warranted.

To facilitate a risk comparison of the four processes, the number and severity of process-related chemical hazards were assessed. This qualitative hazard assessment addresses both the relative toxicity and the exposure potential of substances in the workplace. In addition to the worker-related hazards, estimates of process-related emissions and wastes are also provided.

- 1 ==

1.1 QUANTITATIVE ASSESSMENT

The occupational health hazards associated with production of photovoltaic devices are expressed in two formats. The first format is absolute risk to society, expressed in terms of total lost workdays or fatalities for the entire 100 MW/yr production process being discussed. The second format is the relative risk to process workers, expressed in terms of lost workdays or fatalities per 100 employee-years of labor. The societal and worker-related indices for lost workdays are presented in Figure 1.1-1. The societal and worker-related fatality indices are presented in Figure 1.1-2.

Figure 1.1-1a presents the total lost workdays for 100-MW/yr plants using the various photovoltaic cell production processes (unshaded). The figure also shows the total lost workdays associated with the various base-material industries (shaded). The magnitude of the lost workday value for the photovoltaic portion of each process is most directly related to the estimated labor requirements, rather than to a variation in the worker-related risks (Figure 1.1-1b). The magnitude of lost workdays associated with the silicon I process can be attributed to the more labor-intensive nature of this technology. The silicon II process, which is more automated, shows a lower value for total lost workdays.

In a similar sense the lower value for the cadmium sulfide process is attributable to its greater emphasis on automation than either the silicon I or silicon II processes.

The number of lost workdays associated with the gallium arsenide process is related to the increased labor requirements resulting from the large number of process steps comprising the production sequence. The production sequence used for the gallium arsenide process is similar in complexity to that used for silicon I photovoltaic cell manufacturing. The gallium arsenide process, in addition to its complexity, is the least well defined of the four processes.

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Figure 1.1-1. Lost workday risks.

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Figure 1.1-2b. Worker related fatality risks.

Figure 1.1-2. Fatality risks.

- 4 - Figure 1.1-2a presents the fatality figures for 100-MW/yr plants. The number of fatalities associated with the photo-voltaic cell production portions of each process, like the number of lost workdays, is more closely attributable to labor requirements of the process than to worker-related risks (Figure 1.1-2b).

In general, the degree of automation achieved in a particular photovoltaic manufacturing process will dictate the process labor requirements and to a significant degree the magnitude of the resulting injuries, illnesses, and fatalities.

The silicon II and cadmium sulfide production processes exhibit the lowest values for total fatalities. These lower values are attributable to a greater degree of automation and, with respect to cadmium sulfide, a simplification of the processing steps. The total-fatality figure calculated for the silicon I process can be explained by the more labor-intensive character of many of its process steps, despite the somewhat lower fatality rate for silicon I (Figure 1.1-2b). The high total-fatality figure for the gallium arsenide process is attributable to both the complex nature of the technology (analogous to the Silicon I process), and an increase in worker related risk.

The occupational health statistics determined for the photovoltaic industry have no direct counterpart within the pool of published labor statistics. Although data is collected from the photovoltaic industry, the information is compiled with data from related businesses to produce a descriptive statistic reflecting a broader group of industrial activities. The photovoltaic industry is part of a larger industrial classification described as the semiconductor and related devices industry. The national figure for injury, illness, and fatality related lost workdays for the semiconductor and related devices industry in 1977 was 30.8 lost workdays per 100 employee-years (U.S. Dept. of Labor, 1979,b). The 1977 California statistic for this industrial group was 39.4 lost workdays per 100 employee-years

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(California Department of Industrial Relations, 1979). These published statistics can be compared to the lost workday statistics determined for the four photovoltaic processes as presented in Table 1.1-1.

A similar problem arises when trying to compare the fatality rates determined for the four photovoltaic processes to a published statistic. The national figure for fatalities associated with all manufacturing activities in 1977 was 4.5×10^{-3} fatalities per 100 employee-years (U.S. Department of Labor, 1979a). The 1977 statistic for the electronic components and accessories industry, an industry group comprising semiconductors and related devices, was 1.2×10^{-3} fatalities per 100 employee-years (Curran, 1980). These published figures can be compared to the fatality statistics determined for the four photovaltaic processes as presented in Table 1.1-1.

1.2 QUALITATIVE ASSESSMENT

The qualitative assessment of each process is based on its potential to produce a chemical or physical exposure to workers and on the relative toxicity of the substances involved. The product of this qualitative assessment is a numerical ranking that indicates the degree of hazard associated with each process step.

None of the photovoltaic processes shows an extremely high ranking for acute or chronic hazard of any of the materials used; however, a similar evaluation of the production of base materials does reveal one extremely high hazard situation per process. In the silicon I and silicon II processes, the hazard rating for chronic exposure to silica during sand and gravel mining indicates a potentially serious problem; in the cadmium sulfide process, chronic exposure to cadmium dusts during refining is also considered hazardous; and in the gallium arsenide process, the hazard consists of chronic exposure to arsenic trioxide during arsenic smelting.

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Production process	Lost workdays per 100 employee-years	Fatalities per 100 employee-years
Silicon I	47.5	1.9×10^{-3}
Silicon II	44.9	2.1×10^{-3}
Cadmium sulfide	45.8	2.1×10^{-3}
Gallium arsenide	49.2	2.5×10^{-3}

TABLE 1.1-1. OCCUPATIONAL HEALTH STATISTICS DETERMINED FOR THE FOUR PHOTOVOLTAIC PROCESSES

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One can compare the photovoltaic processes by the number of major acute or chronic hazards that have been determined. The results of such a comparison show that the silicon I process has the greatest number of potentially hazardous acute situations, followed by gallium arsenide, cadmium sulfide, and silicon II processes, in that order. Comparison of chronic hazards in the same manner indicates that the cadmium sulfide process leads, followed by gallium arsenide, silicon I, and silicon II. In addition to the qualitative assessment of acute and chronic hazards, the materials used in each process that are suspected carcinogens or teratogens are tallied. The frequency of usage of these substances is the basis of an additional comparison, which shows that the gallium arsenide and cadmium sulfide processes use an equal number of carcinogenic or teratogenic substances, followed in order by the silicon I and silicon II processes.

Preparation of the qualitative assessment indicated that little or no toxicological information is available to characterize many substances. This problem of data limitation is compounded by the inadequate characterization of many of the process steps, especially with respect to the chemical reactions involved and the byproducts produced.

The photovoltaic production processes used in assessment of both the quantitative and qualitative risks are considered to be examples of current industrial technology and of foreseeable changes in the state-of-the-art. The production processes that were constructed for use in this study may not accurately depict the commercial facilities of the future (5 to 10 years). This is especially true of the gallium arsenide process, which is in a very early stage of development.

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SECTION 2

INTRODUCTION

In the design, development, and acceptance of new energy technologies, our concern with safety, health, and environmental factors have assumed increasing importance. One such emerging energy technology is photovoltaics, in which sunlight is converted directly into electrical energy through photoconductive materials. Materials receiving the major focus for use in fabrication of photovoltaic cells are silicon, cadmium sulfide, and gallium arsenide.

The industry is young, and production of photovoltaic cells on a large scale has yet to be attempted. Within this decade, however, it is expected that solar cells will be mass-produced at costs that will make them competitive with conventional energy resources.

Because of the rapid growth expected in the photovoltaic industry, it is important to examine in detail the potential risks associated with mass production of solar cells in terms of safety, health, and the environment. Such a risk evaluation is the purpose of this report. A qualitative assessment is performed, and an attempt is made to quantitatively assess the magnitude of injuries and deaths that might be expected in the industry. Because no large-scale photovoltaic production facility is now in operation, the quantitative data were developed by use of morbidity and mortality statistics from the semiconductor industry in California. The semiconductor industry was selected because many of the same or similar processes and materials used in that industry will also be used in solar cell production; it should be noted, however, that in many instances photovoltaic

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cell production will require less rigorous quality control. This change in quality control will result in more automation, less manual labor, and less worker interaction with the processes. California data were used because a large percentage of the semiconductor industry is established there, and because the State's system for collecting Workman's Compensation statistics also alows for retrieval and arrangement of the data base. The methodologies used to determine the statistics on occupational injury, illness, and fatality are presented in Section 3.1.

The report deals with four production processes, depicted in Figures 2.1 to 2.4. These processes were selected because they produce cells that are relatively more highly developed and for which mass production techniques are more clearly defined. Two processes are described for production of single-crystal silicon cells. The silicon I process uses a more conventional approach to production and processing (Section 4), whereas the silicon II process uses more advanced techniques in several instances (Section 5).

A spray process for the production of cadmium sulfide/ copper sulfide (CdS/Cu_xS) cells is discussed in Section 6. The company producing these cells hopes to have a 5-MW/yr production plant on-line in 1981. Because this effort is privately funded, many aspects of the process are considered to be proprietary. The proprietary information used to develop manpower requirements or risk assessment data for this report is not included.

The fourth process discussed (Section 7) involves production of single-crystal gallium arsenide (GaAs) concentrator cells. Of the four processes, the GaAs process is the least developed with respect to production techniques. The data given with respect of this process are based on a high-throughput pilot process in which a pulse liquid-phase epitaxy (LPE) technique is used to grow the necessary layers on the GaAs substrate. Data developed for this process were obtained from the literature when possible; where published data were not available, comparisons were made with the silicon-I process.



Figure 2-1. Single-crystal silicon process - I.

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Figure 2-2. Single-crystal silicon process - II.

- 12 -



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Figure 2-3. Production of cadmium sulfide/copper sulfide backwall cell.

1 1.3

SINGLE CRYSTAL GALLIUM ARSENIDE



Figure 2-4. Single-crystal gallium arsenide process.

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Comparisons of this nature are warranted because several of the single-crystal GaAs processing techniques parallel those in the silicon-I process.

It should be noted that great advances have been made in production of thin-film GaAs cells by organometallic chemical vapor deposition (OM-CVD) techniques. Although many believe that this may be the process best suitable for production of GaAs cells on a large scale, progress at this time in highthroughput production is no more advanced than with LPE processes.

The scope of each process review includes mining and/or refining of selected base materials through cell production and construction of the finished module. The base materials selected for consideration (i.e., 'silica, silicon, cadmium. gallium, and arsenic) are those involved in the production of substances central to the operation of the photovoltaic cells. The selected base materials do not necessarily constitute a major portion of the finished product. A truly comprehensive assessment of all base materials would involve the analysis of many additional substances and would require an effort beyond the scope of this project.

For each production step within a given process the report presents a line description; an analysis of material and manpower requirements; a determination of emissions, wastes, and controls; and a calculation of occupational hazards and risks. In addition to the statistical risk assessment, the relative toxicities of the various process materials were determined. The toxicity assessments are based upon a ranking scheme described in Section 3.2, Evaluation of Chemical Toxicity.

2

Finally, Section 8 presents an overall summary of projected material requirements, manpower needs, injuries, and deaths for each process at both a 5.57-MW/yr and a 100-MW/yr production level. In addition to the overall summary, a statistical risk assessment and chemical hazard analysis are presented. The statistical risk assessment provides a quantitative picture of

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hazards associated with each process. The chemical analysis provides a more qualitative assessment of chemical toxicity and exposure potential within each process. Finally, risk data for all four processes are compared and discussed. An appendix gives details of the calculations used to determine material requirements for each photovoltaic cell production process.

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SECTION 3

METHODOLOGIES FOR DETERMINING OCCUPATIONAL HEALTH STATISTICS AND EVALUATING CHEMICAL TOXICITY

Occupational injury, illness, and fatality statistics were determined for application to the four photovoltaic processes. A scheme was constructed for evaluating the relative toxicity of chemical substances used in the four processes. The methodologies for both the determination of occupational and health statistics and the evaluation of chemical toxicity are presented in this section. The occupational health statistics will be used in Sections 4 through 7 to perform process specific risk assessments. The toxicity evaluation along with the process risk assessments will be used as raw analytical data for Section 8, Hazard Analysis and Risk Assessment.

3.1 OCCUPATIONAL INJURY, ILLNESS, AND FATALITY STATISTICS

Occupational health statistics characterizing the injury, illness, and fatality levels associated with occupations in the photovoltaics industry are not available from any private or governmental organizations. Individual private firms involved in the production of photovoltaic devices are reluctant to provide health-related information. Governmental organizations responsible for collecting occupational-health-related statistics do not have the capability to identify and retrieve data at a level of detail that would characterize a single industry. For these reasons we have had to estimate occupational health statistics for the photovoltaic industry from data relating to larger industrial classifications. Occupational health statistics are available to characterize injury, illness, and fatality levels associated with base material industries. The base material industries are those that supply key raw material to a photovoltaic process.

Problems also exist with the types of occupational information available, particularly some of the standard descriptive statistics used to assess occupational health hazards; i.e., fatality rates, frequency rates, and severity rates. Because these forms of information are unavailable, the statistics must be developed from other types of data. Data on lost-workday cases, fatality indexes, and average number of lost workdays are used in estimates of descriptive health statistics for occupations in the photovoltaics industry.

This section of the report describes the manipulative procedures and arithmetic calculations used to derive these descriptive statistics. Results of the data handling and the statistical calculations for the photovoltaic industry are presented in the final subsection along with statistics used to characterize the base material industries. Potential sources of error associated with the statistics and the limits of their application are discussed briefly.

3.1.1 Occupational Employment

Development of occupational health statistics (illness, injury, and fatality rates) requires an estimate of employment by individual occupation. Where employment figures are not available for specific occupations, the occupations can be grouped into larger occupational categories for which employment data is available.

Total employment figures for the California semiconductor industry in 1978 are available from the Employment Data and Research Development Department (CEDD, 1980). Data on employment by individual occupation are not available for the semiconductor industry or any other four-digit Standard Industrial

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Classification (SIC). The CEDD does provide occupational employment statistics for larger three-digit SIC industrial categories (CEDD, 1979). For example, data are available for the electronic components and accessories industrial category (SIC 367), of which the semiconductor industries are a subset.

The breakdown of occupational employment for the electronic components category is used to apportion employment to occupations within the semiconductor industry. Although this method of apportionment produces somewhat coarse estimates of employment, the technique seems appropriate for two reasons: (1) the electronic components category is the smallest industry classification for which a complete occupational breakdown is available, and (2) 1978 employment statistics show that the semiconductor industry is the single largest industry in the electronic components category, accounting for 43 percent of the employment (CEDD, 1980).

The major drawback associated with this method is the lack of an established scheme for cross-referencing between CEDD's employment figures (CEDD, 1980) and occupational statistics from other state agencies. Occupational classes of injury and illness statistics compiled by the California Department of Industrial Relations (CDIR, 1980) cannot be uniequivocally correlated with CEDD's occupational employment figures. Because of this deficiency, comparison of occupational injury and illness statistics with occupational employment is limited to an interpretation of the occupational class descriptions. The descriptive interpretation performed for this report is presented in Table 3.1-1. Total employment for the semiconductor industry is apportioned into individual occupations by use of the following equation.

$$E_{c} = \sum_{i=1}^{n} (e_{i}/t)T \qquad (Eq. 1)$$

where:

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- t = total employment for the electronic components and accessories industry
- T = total employment for the semiconductor industry

The results of this apportionment provide an estimate of employment for occupations in the semiconductor industry for which injury and illness statistics exist.

Table 3.1-1 indicates the occupations considered, the occupational ratios (e_i/t) determined from the California Occupational Employment statistics, the estimated employment by occupation for the semiconductor industry, $(e_i/t)T$, and the estimated employment by occupational category (E_c) . The employment figures determined for each occupational category (E_c) are then used to estimate annual employee-hours within the semiconductor industry.

3.1.2 Annual Employee-Hours

Annual employee-hours for each occupational category are used in calculation of occupational injury, illness, and fatality rates. The total annual employee-hours for each occupational category are determined from the figures on occupational employment (E_c) in Table 3.1-1. An annual average for total hours worked is applied to each estimated employment figure to calculate annual employee-hours by occupational category according to the following equation:

$$H_{c} = E_{c} (2000)$$
 (Eq. 2)

where:

 H_{C} = annual employee-hours by occupational category E_{C} = employment by occupational category, Table 3.1-1 2000 = annual average hours worked per employee

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Dccupational category	California Department of Industrial Relations, cccupational classes (code)	California Employment Development Department occupational descriptions ^b	Occupation ratio e _i /t	Estimated employment by occupation (e _i /t)T	Estimated total employment by occupational category Ec
Material handling	Shipping and receiving clerks	Shipping and receiving clerks	0.0101	423	641
occupations	(374) Freight and material handlers (753)	Shipping packers Production packers Order fillers	0.0025 0.0020 0.0007	105 84 29	
Metal plating occupations	Metal platers (635)	Dip platers Electroplaters	0.0052 0.0095	218 398	616
Material abrading	Filers, polishers, sanders	Filers, grinders, buffers	0.0045	187	317
occupations	Grinding machine operatives	machine operators	0.0029	122	
		machine operators	0.0002	8	
Assembling occupa- tions	Assemblers (602)	Electrical and electronic assemblers - Class A - Class B Electro-mechanical assemblers - Class A - Class B Encapsulators Instrument makers - Class A - Class B All other assemblers - Class B - Class C	0.0366 0.0734 0.0072 0.0046 0.0045 0.0010 0.0037 0.0419 0.1011	1,534 3,076 302 193 189 42 155 1,756 4,237	11,484
Inspecting occupa- ticns	Checkers, examiners and inspectors (610)	Inspectors Supervisors Testers	0.0294 0.0239 0.0182	1,232 1,002 763	2,997

TABLE 3.1-1. OCCUPATIONAL DESCRIPTIONS, RATIOS, AND ESTIMATED EMPLOYMENT FOR THE CALIFORNIA SEMICONDUCTOR INDUSTRY

(Continued)

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TABLE 3.1-1 (Continued)

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Occupational category	California Department of Industrial Relations, occupational classes (code) ^a	California Employment Development Department occupational descriptions	Occupation ratio e _i /t	Estimated employment by occupation (e _i /t)T	Estimated total employment by occupational category Ec
Maintenance occupa- tions	Electricians and electrician apprentices (430, 431) Sheet metal workers, tinsmiths and apprentices (535, 536) Plumbers and pipefitters	Electricians Helpers Instrument mechanics Maintenance repairmen	0.0009 0.0005 0.0004	38 21 17	754
	and apprentices (522, 523) Air conditioning. heating, and refrigeration mechanics, and repairmen (470)	and general utility Mechanic, maintenance Sheet metal workers	0.0060 0.0051	251 214 67	
	Hiscellaneous mechanics and repairmen (492) Mechanics and repairmen not specified elsewhere (495)	Millwrights All other mechanics and repairmen	0.0002	8	
Technical occupations	Electrical and electronic technicians (153) dechanical engineering	Electrical and electronic technicians Mechanical engineering	0.0477	1,999	3,134
	technicians (155) Engineering and scientific technicians (162)	technicians Scientific technicians All other engineering	0.0017 0.0010	71 42	
	Chemical technicians (151) Fechnicians not specified eisewhere (173)	technicians All other technicians	0.0232 0.0012	972 50	
Occupations not specified	-	-	0.5242	21,970	21,970
All occupations	םוו workers	All occupations	· 1.0000	41,913	41,913

^aCDIR, ≩980. ^bCEDD, ⁻080.

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The annual average hours worked by each employee is an assumed value based on assumption of a 40-hour work week and a 50-week year for each employee. The value includes a 2-week vacation period but not national or religious holidays. It is assumed that any time lost to holidays is roughly offset by occasional periods of overtime work and vice versa. Results of the annual employee-hour calculations are presented in Table 3.1-2.

3.1.3 Lost Workday Cases for Injuries, Illnesses and Fatalities

Total lost workday cases for the California semiconductor industry are available through the California Department of Industrial Relations (CDIR, 1980). These statistics are part of a Federal-state cooperative program that provides the public with occupational injury and illness data derived from each state's Worker's Compensation records. The program, known as the Supplementary Data System (SDS), is sponsored by the Bureau of Labor Statistics (U.S. Dept. of Labor, 1980). To date, 24 states and the Virgin Islands have made data on occupational injury and illness available through SDS.

In addition to the information required for input to SDS, the State of California has a unique ability to perform computer-assisted retrieval and arrangement of the occupational statistics data base. Using the California retrieval system, we have compiled the lost workday cases reported for the semiconductor industry for each occupation by the "nature of injury." Data on lost workday cases are available for 27 occupations within the semiconductor industry. The cases in each occupation are further grouped according to 42 "nature of injury" categories, which include both occupational injuries and illnesses.

So as to arrange the California data into a more useful form, we have grouped each occupation reporting lost-workday cases into an Occupational Category (E_c) . The occupational descriptions presented by the California retrieval system are arranged into occupational categories in Table 3.1-1. Again, because of the lack of an established cross-reference between

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Uccupational category	Estimated total employment ^b	Estimated annual employee-hours (10 ⁶)
Material handling	641	1.282
Metal plating	616	1.232
Material abrading and polishing	317	0.634
Assembling	11,484	22.968
Inspecting	2,997	5.994
Maintenance	754	1.508
Technical	3,134	6.268
Occupations not specified	21,970	43.940
All occupations (total)	41,913	83.826

TABLE 3.1-2. ESTIMATED ANNUAL EMPLOYEE-HOURS BY OCCUPATIONAL CATEGORY^a

 $^{a}\mbox{Equivalent}$ to \mbox{H}_{C} of Equation 2.

^bEstimated total employment by occupational category within the California semiconductor industry, Table 3.1-1.

occupational statistics and employment records, the occupations are arranged on the basis of an interpretation of the occupational descriptors.

The "nature of injury" data, which include all events causing 1 or more lost workdays, also are arranged in a useful form. The Bureau of Labor Statistics and the California Department of Industrial Relations use a single set of injury and illness category descriptors (U.S. Dept. of Labor, 1979a; CDIR, 1979) which are also used in this study:

- Injury--Any event resulting in cut, fracture, sprain, amputation, etc., which results from a work accident or from exposure in the work environment.
- 2) Illness--Any abnormal condition or disorder, other than one resulting from an occupational injury, caused by exposure to environmental factors associated with employment. It includes acute and chronic illnesses or diseases which may be caused by inhalation, absorption, ingestion, or direct contact, and which can be included in the categories listed below. The following categories are used to classify occupational illnesses.
 - Occupational skin diseases or disorders Examples: Contact dermatitis, eczema, or rash caused by primary irritants and sensitizers or poisonous plants; oil acne; chrome ulcers; chemical burns or inflammations; etc.
 - Dust diseases of the lungs (pneumoconioses) Examples: Silicosis, asbestosis, coal worker's pneumoconiosis, byssinosis, and other pneumoconioses.
 - Respiratory conditions due to toxic agents Examples: Pneumonitis, pharyngitis, rhinitis or acute congestion due to chemicals, dusts, gases or fumes; farmer's lung, etc.
 - Poisoning (systemic effects of toxic materials) Examples: Poisoning by lead, mercury, cadmium, arsenic, or other metals; poisoning by carbon monoxide, hydrogen sulfide or other gases; poisoning by insecticide sprays such as parathion, lead arsenate; poisoning by other chemicals such as formaldehyde, plastics, and resins; etc.

Disorders due to physical agents (other than toxic materials) Examples: Heatstroke, sunstroke, heat exhaustion and other effects of environmental heat; freezing, frostbite and effects of exposure to low temperatures; caisson disease; effects of ionizing radiation (isotopes, X-rays, radium); effects of nonionizing radiation (welding flash, ultraviolet rays, microwaves, sunburn); etc.

Disorders due to repeated trauma. Examples: Noise-induced hearing loss; synovitis, tenosynovitis, and bursitis; Raynaud's phenomena; and other conditions due to repeated motion, vibration, or pressure.

All other occupational illnesses Examples: Anthrax, brucellosis, infectious hepatitis, malignant and benign tumors, food poisoning, histoplasmosis, coccidioidomycosis, etc.

In addition to the categories defined in these descriptions, we have, established an "all unclassified illnesses" category, which does not refer to specific illnesses but rather indicates an "average occupational illness." The importance and application of this category will become evident in the section on Injury, Illness, and Fatality Statistics.

Lost-workday cases by specific occupational injury or illness are grouped according to the appropriate "injury or illness category." The results of this arrangement are presented as total workday cases (C) in the first columns of Tables 3.1-3 through 3.1-11.

Calculation of Lost-Workday Fatality Cases (c1)--

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The occupational injury and illness survey performed by CDIR includes both the lost-workday cases and the number of fatalities. The fatalities are reported regardless of the length of illness or the interval between injury and death. The cases of lost workdays are reported for any event that results in lost workdays or any nonfatal case that requires medical restriction of work or motion (U.S. Dept. of Labor, 1978). TABLE 3.1-3. LOST WORKDAY CASES AND TOTAL LOST WORKDAYS FOR THE MATERIAL HANDLING OCCUPATIONS

			•	Fatality	statistics	Injury and il i	ness statistics	Total lest
Injury or illness category	Total lost workcay cas∈s C	Lost workday fatality cases ^C l	Lost workday injury and illness cases ^C 2	Frequency rate, cases per 10 ⁶ employee-hours f ₁	Fatality rate, total days lost per 10 ⁵ , employee-hours F	Frequency rate, cases per 10 ⁶ employee-hours f ₂	Severity rate, total days lost per 10 employee-hours ^S 1	workdays, total days lost per 103 employee-hours W
Injuries	1							
All injuries	48	0.05	47.95	0.039	0.234	37.4	0.449	0.683
Ellnesses								
Occupational skin disease or skin disorder	4	Neg.	4			3.1	0.028	0.028
Dust diseases of the lungs								
Respiratory conditions due to toxic agents								- - - -
Poisoning	1							
Disorders due to physical agents						4 4 4		
Disorders associated with repeated trauma								
All other occupational illnesses								
All unclassified illnesses	6	0.01	5.99	0.008	0.048	4.7	0.089	0.137
Total	58			0.047	0.282		0.566	0.848

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TABLE 3.1-4. LOST WORKDAY CASES AND TOTAL LOST WORKDAYS FOR THE METAL PLATING OCCUPATIONS

				Fatality	statistics	Injury and illn	ess statistics	
Injury or illness category	⁻ otal lost workday cases C	Lost workday fatality cases ^C l	Lost wcrkday injury and illness cases ^C 2	Frequency rate, cases per 10 ⁶ employee-hours f ₁	Fatality rate, total days,lost per 10 employee-hours F	Frequency rate, cases per 10 ⁶ employee-hours f ₂	Severity rate, total days lost per 10 employee-hours ^S 1	workdays, total days lost per 10 ³ employee-hours W
Injuries						•		
All injuries	.3	0.01	7.99	0.008	0.0448	6.5	0.078	0.126
lllnesses								
Occupational skin diseas≘ or skin disord⊵r	10	0.01	9.99	0.008	0.043	8.1	0.073	0.121
Dust diseases of the lungs	2	Neg.	2			1.6	0.034	0.034
Respiratory conditions due to toxic agents							1	
Poisoning	2	0.01	1.99	0.008	0.048	1.E /	0.019	0.067
Disorders due to physical agents								
Disorders associated with repeated trauma	•							
All other occupational illnesses								
All unclassified illnesses								
Total	22			0.024	0.144		0.204	0.348

TABLE 3.1-5. LOST WORKDAY CASES AND TOTAL LOST WORKDAYS FOR THE MATERIAL ABRADING AND POLISHING OCCUPATIONS

				Fatality	statistics	Injury and illn	ess statistics	
Injury or illness category	Total lost workday cases C	Lost workday fatality cases ^C l	Lost workday injury and illness cases ^C 2	Frequency rate, cases per 106 employee-hours f ₁	Fatality rate, total days lost per 10 ³ employee-hours F	Frequency rate, cases per 10 ⁶ employee-hours f ₂	Severity rate, total days ₃ lost per 10 employee-hours ^S 1	Workdays, total days lost per 103 employee-hours W
Injuries								
All injuries	4	Neg.	4			6.3	0.076	0.076
Illnesses								
Occupational skin disease or skin disorder	2	Neg.	2			3.2	0.029	0.029
Dust diseases of the lungs								
Respiratory conditions due to toxic agents								
Poisoning								
Disorders due to physical agents	2.	Neg.	2			3.2	0.032	0.032
Disorders associated with repeated trauma								
All other occupational illnesses								
All unclassified illnesses	2	Neg.	2			3.2	0.06	0.061
Total .	10						0.198	0.198

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TABLE 3.1-6. LOST WORKDAY CASES AND TOTAL LOST WORKDAYS FOR THE ASSEMBLING OCCUPATIONS

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La				Fatality	statistics	Injury and illr	ness statistics	
Injury or illness category	Total los- workday cases	Lost workday fatality cases ^C l	Lost workday injury and il ness cases ^C 2	Frequency rate, cases per 106 empioyee-hours f ₁	Fatality rate, total days isst per 103 employee-hours F	Frequency rate, cases per 10 ⁶ employee-hours ^f 2	Severity rate, total days ₃ lost per 10 employee-hours ^S 1	lotal lost workdays, total days lost per 10 employee-hours W
Injuries								,
All injurtes	134	0.18	183.82	0.008	0.048	8.0	0.096	0.144
Illnesses								
Occupational skin disease o≕ skin disorder	70	Neg.	70			3.0	0.027	0.027
Dust diseases of the lungs	21	0.02	20.98			0.3	0.006	0.006
Respiratory conditions due to toxic agents	2	Neg.	2			0.1	0.001	0.001
Poisoning	18	0.07	17.93	0.003	0.018	0.8	0.010	0.028
Disorders due to physical agents	6	Neg.	6		- - - -	0.3	0.003	0.003
Disorders associated with repeated trauma								
All other occupational illnesses		-						
All unclassified illnesses	24	0.02	23.98	0.001	0.005	1.0	0.019	0.019
Total	31 2			0.012	0.071		0.162	0.228

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TABLE 3.1-7. LOST WORKDAY CASES AND TOTAL LOST WORKDAYS FOR THE INSPECTING OCCUPATIONS

£				Fatality	statistics	Injury and fll	ness statistics	
Injury or illness category	Total lost workday cases C	Lost workday fatality cases ^C l	Lost workday injury and illness cases ^C 2	Frequency rate, cases per 10 ⁶ employee-hours ^f 1	Fatality rate, total days lost per 10 ³ employee-hours F	Frequency rate, cases per 10 ⁶ employee-hours ^f 2	Severity rate, total days lost per 10 ³ employee-hours ^S 1	Total lost workdays, total days lost per 103 employee-hours W
Injuries					1			
All injuries	62	0.06	61.94	0.010	0.060	10.3	0.124	0.184
Illnesses					1			
Occupational skin disease or skin disorder Dust diseases of	10	Neg.	10			1.7	0.015	0.015
Respiratory conditions due to toxic agents		2 						
Poisoning	2	0.01	` 1.99	0.002	0.012	0.3	0.004	0.016
Disorders due to physical agents	. 2	Neg.	2			0.3	0.003	0.003
Disorders associated with repeated trauma						•		
All other occupational illnesses							- -	
All unclassified illnesses	8	0.01	7.99	0.002	0.012	1.3	0.025	0.037
Total	34			0.014	0.084		0.171	0.255

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TABLE 3.1-8. _OST WORKDAY CASES AND TOTAL LOST WORKDAYS FOR THE MAINTENANCE OCCUPATIONS

<u></u>				Fatality	statistics	Injury and ill	ness statistics	Total lost
Injur, or illness category	Total lost workday cases C	Lost workday fatality cases ^C l	Lost workday injury and illness cases [.] C ₂	Frequency rate, cases per 106 employee-hours f ₁	Fatality rate, total days lost per 10 ³ employee-hours F	Frequency rate, cases per 10 ⁶ employee-hours f ₂	Severity rate, total days ₃ lost per 10 ³ employee-hours ^S 1	workdays, total days lost per 10 ³ employee-hours W.
Injuries								
All irjuries	24	0.02	23.98	0.013	0.080	15.9	0.191	<u>,</u> 0.271
Illnesses								
Occupational skin disease or skin disorder								
Dust ciseases of the lungs	2	Neg.	2			1.3	0.027	0.027
Respiratory cond tions due to toxic agents								
Poiscning								
Disorders due to physical agents								
Disorders associated with repeated trauna								*
All other occupational illnesses					,			
All unclassifiec illnesses	2	Neg.	2			⁻ .3	0.025	0.025
Total	28			0.013	0.080		0.243	0.323

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				Fatality	statistics	'Injury and illn	less statistics	Tetal
Injury or illness category	Total lost workday cases C	Lost workday fatality cases ^C l	Lost workday injury and illness cases ^C 2	Frequency rate, cases per 106 employee-hours f1	Fatality rate, total days lost per 10 ³ employee-hours F	Frequency rate, cases per 106 employee-hours f ₂	Severity rate, total days lost per 10 employee-hours ^S 1	workdays, total days lost per 10 ³ employee-hours W
Injuries								
All injuries	. 32	0.03	31.97	0.005	0.029	5.1	0.061	0.090
Illnesses								
Occupational skin disease or skin disorder	34	Neg.	34			5.4	0.049	0.049
Dust diseases of the lungs								
Respiratory conditions due to toxic agents								
Poisoning	• 6	0.02	5.98	0.003	0.019	0.9	0.011	0.030
Disorders due to physical agents	4	Neg.	4			0.6	0.006	0.006
Disorders associated with repeated trauma								
All other occupational illnesses								
All unclassified illnesses	8	0.01	7.99	0.002	0.012	1.3	0.025	0.037
Total	84			0.010	6.060		0.152	0.212

TABLE 3.1-9. LOST WORKDAY CASES AND TOTAL LOST WORKDAYS FOR THE TECHNICAL OCCUPATIONS

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Injury or illness category	Tctël lost workday cëses C	Lost workcay fatality cases ^C l	Lost workday injury and illness cases ^C 2	Frequency rate, cases per 106 employee-hours ^f 1	Fatality rate, total days lost per 103 employee-hours F	Frequency rate, cases per 106 emplcyee-hours f ₂	Severity rate, total days ₃ lost per 10 employee-hours ^S 1	workdays, total days lost per 10 ³ employee-hours W
Injuries								
All injuries	4 04	0.40	403.60	0.009	0.054	9.2	0.110	0.164
Illnesses								
Occupational skin disease or skin diserder	66	Neg.	66			Ţ.\$	0.014	0.014
Dust diseases of the lungs	4	Neg.	4			0.1	0.002	0.002
Respiratory conditions due to floxic agents	4	0.01	3, 99	Neg.		0.1	0.001	0.001
Poisoning	22	0.09	21.91	0.002	0.012	0.5	0.006	0.018
Disorders due to physical agents	10	Neg.	10			0.2	0.002	0.002
Disorders associated with repeated trauma								
All other occupational illmesses	4	0.03	3.97	0.001	0 006	0.1	0.003	0.009
All unclassified illuesses	42	0.04	41.96	0.001	0.006	3.0	0.019	0.025
Total	556			0.013	0 078		0.157	0.235

TABLE 3.1-10. LOST WORKDAY CASES AND TOTAL LOST WORKDAYS FOR UNSPECIFIED OCCUPATIONS

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TABLE 3.1-11. LOST WORKDAY CASES AND TOTAL LOST WORKDAYS FOR ALL OCCUPATIONS

				Fatality	statistics	Injury and illn	ess statistics	Total loss
Injury or illness category	Total lost workday cases C	Lost workday fatality cases ^C 1	Lost workday injury and illness cases ^C 2	Frequency rate, cases per 10 ⁶ employee-hours ^f 1	Fatality rate, total days lost per 10 ³ employee-hours F	Frequency rate, cases per 106 employee-hours f ₂	Severity rate, total days ₃ lost per 10 ³ employee-hours ^S 1	vorkdays, total days, lost per 10 employee-hours W
Injuries								······································
All injuries	766	0.77	765.23	0.009	0.054	9.1 .	0.109	0.153
Illnesses		*						
Occupational skin disease or skin disorder	196	Neg.	196			2.3	0.021	0.021
Dust diseases of the lungs	16	0.02	15.98	0.002	0.012	0.2	0.004	0.016
Respiratory conditions due to toxic agents	6	0.01	5.99	Neg.		0.1	0.008	0.008
Poisoning	50	0.20	49.80	0.002	0.012	0.6	0.007	0.019
Disorders due to physical agents	24	Neg.	24			0.3	0.003	0.003
Disorders associated with repeated trauma	· · ·							
All other occupational illnesses	4	0.03	3.97	Neg.		0.1	0.001	0.001
All unclassified illnesses	92	0.09	91.91	0.001	0.006	1.1	0.021	0.027
Total	1154			0.014	0.084		0.174	0.258

In categorizing the total lost-workday cases (C) into fatal and nonfatal events, it is necessary to identify those cases that resulted in a fatality. Fatality rates (r) for individual injury and illness categories are presented in Table 3.1-12. These rates are based upon the most recent nationwide figures for injury- and illness-related fatalities (U.S. Dept. of Labor, 1979a,). The fatality rates are used in the following equation to calculate lost-workday fatality cases (c_1) :

$$c_1 = rC \tag{Eq. 3}$$

where:

- c1 lost-workday fatality cases
- r = fatality rate for a specific injury or illness category (Table 3.1-12)
- C = total lost-workday cases, by injury and illness category (Tables 3.1-3 through 3.1-11)

In calculation of lost-workday fatality cases, we noted that in a few injury or illness categories the fatality rate is less than 0.05 percent. A fatality rate of approximately 1 in 2000 cases cannot be considered insignificant from an occupational health standpoint; however, a rate less than 0.05 percent is considered negligible for the purpose of estimating fatalities in a single industry, i.e., the semiconductor industry with a relatively small employment figure. The lost-workday fatality cases (c_1) calculated with Equation 3 are given in Tables 3.1-3 through 3.1-11 for each injury and illness category by occupation.

Calculation of Lost-Workday Injury and Illness Cases (c2)--

The occupational statistics collected in California include both fatal and nonfatal lost-workday cases. As presented above the number of lost-workday fatality cases (c_1) can be determined for each occupational category by use of a set of national industry-wide fatality rates. The lost-workday injury and illness cases (c_2) can be calculated by subtracting the fatality-

TABLE 3.1-12.	FATALITY RATES	AND AVERAGE	LOST WORKDAYS PER
LOST-WORKDAY	CASE FOR INJURY	AND ILLNESS	CATEGORIES

Injury or illness category	Fatality rate ^a (percentage) r	Average lost workdays per lost-workday case ^b (w _l)
Injuries ·		
All injuries	0.1	12
Illnesses		
Occupational skin disease or skin disorder	c	9
Dust diseases of the lungs	0.1	21
Respiratory conditions due to to toxic agents	0.2	12
Poisoning	0.4	12
Disorders due to physical agents	c	10
Disorders associated with repeated trauma	с	28
All other occupational illnesses	0.7	28
All unclassified illnesses (average)	0.1	19
Fatality		
All deaths		6000

^aFatality rate taken from national industry-wide Occupational Injuries and Illnesses Statistics (U.S. Department of Labor, 1979a).

^bAverage lost workdays per lost workday case taken from California industrywide Occupational Illness Statistics (CDIR, 1979).

^CIndicates a percentage of less than 0.05.

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related cases (c_1) from the total lost workday cases (C). This simple operation provides an estimate of all nonfatal injuries and illnesses attributed to each occupational category in the semiconductor industry. The operation is expressed in Equation 4.

$$c_2 = C - c_1$$
 (Eq. 4)

where:

 $c_2 = lost-workday$ injury and illness cases

C = total lost-workday cases, by injury and illness category (Tables 3.1-3 through 3.1-11)

c₁ = lost-workday fatality cases

The purpose of breaking out fatal and nonfatal lost-workday cases is to facilitate the application of "average number of lost workdays (w_1) " to specific injuries, illnesses, and death. The number of lost workdays associated with a given injury or illness varies with the severity of the resulting debilitation.

The number of lost workdays attributed to a worker's death has been assigned a standard value. Concerning specific injuries or illnesses, average lost-workday values are assigned to each category. These lost-workday values, presented in Table 3.1-12, are used to estimate severity and fatality rates in a later subsection on the calculation of severity rates (s₁).

3.1.4 Statistics On Injury, Illness, and Fatality

Comparison of industry-wide (semiconductor) data with specific industrial operations (production of photovoltaics) requires the use of some form of standardized statistics. The standardized statistics we have selected for use are taken from those recommended by the American National Standard Institute (ANSI, 1969).

The standard procedure for dealing with injury or illness data is to calculate a frequency and severity rate that relates disabling lost-workday cases, and days charged as a result of them, to the number of employee-hours worked. These rates are then adjusted for differences in the hours of exposure.

In addition to the established procedures, a frequency rate and fatality rate can be calculated to estimate the lost time associated with worker deaths. No variation in severity is assigned to any specific fatality; the severity of death is taken to be an absolute nonvarying value resulting in 6000 lost workdays per fatality (National Safety Council, 1978).

Calculation of Frequency Rates for Injuries, Illnesses, and Fatalities--

Frequency rates are used to relate the cases of injury and illness to the hours of exposure (hours worked). The rate is expressed in terms of the number of cases per million employee hours. Frequency rates are based on the total number of disabling injuries or illnesses occurring within a given calendar year.

Two types of frequency rates are calculated for occupations in the California semiconductor industry. A rate was first calculated for the fatal injuries and illnesses using the standard procedure for developing descriptive statistics from occupational data. The following equation is used to calculate the frequency rate of fatal injury and illness:

$$f_1 = c_1 / H_c$$
 (Eq. 5)

where:

 f_1 = frequency rate of fatal injury and illness

 $c_1 = lost-workday$ fatality cases

H_c = annual employee-hours by occupational category
 (Table 3.1-2)

The frequency rates for fatal injury and illness determined from this calculation are given in Tables 3.1-3 through 3.1-11. Calculation of Severity and Fatality Rates-- Severity rates relate the days charged for a given injury or illness to the hours of exposure (hours worked). The severity rate is expressed in days lost per million employee hours. The rate is based on all days lost because of disabling injuries or illnesses within a given calendar year.

The severity rates calculated for occupations within the California semiconductor industry are based on average days lost in specific injury or illness categories. The average lost-workdays per lost-workday case for each injury or illness category are given in Table 3.1-12. Severity rates are calculated according to Equation 7.

$$s_1 = f_2 w_1 / 1000$$
 (Eq. 7)

where:

- f₂ = frequency rate, lost-workday cases per million employee-hours (Tables 3.1-3 through 3.1-11)
- w₁ = average lost workdays per lost-workday case
 (Table 3.1-12)

A similar fatality rate can be derived from the frequency rate for fatalities and the fixed severity value of 6000 days, according to Equation 8.

$$\mathbf{F} = \mathbf{f}_1 \mathbf{s}_1 \tag{Eq. 8}$$

where:

- F = fatality rate, lost workdays per million employeehours
- f₁ = frequency rate, lost-workday cases per million employee-hours (Tables 3.1-3 through 3.1-11)
- s₁ = 6000 lost workdays per fatality (National Safety Council, 1978)

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3.1.5 Total Lost Workdays and Fatality Rates by Occupation

Total lost workdays per thousand employee-hours can be determined for each occupation by summing the lost-workday values (W) determined for each injury or illness category within a given occupation. The total lost-workday rates for each occupation are given in Table 3.1-13. The occupational lostworkday rates are also expressed in terms of hundreds of employee-years.

A fatality rate per million employee-hours is determined for each occupation by summing the injury or illness fatality rates within each occupation. The total fatality rates for each occupation are given in Table 3.1-13. The occupational fatality rates are also expressed in terms of hundreds of employee-years. Figure 3.1-1 represents the lost-workday and fatality rates listed in Table 3.1-13.

Occupational injury, illness, and fatality statistics for the base material industries are also presented in Table 3.1-13. The base material industries are represented by five industrial categories. The statistics for each industrial category represent an average for all occupations. The statistical information for the metal mining industry (SIC 10), primary aluminum smelting and processing industry (SIC 3334), primary nonferrous metals smelting and processing industry (SIC 3339), and inorganic chemical manufacturing industry (SIC 2819) were obtained from the Bureau of Labor Statistics', Occupational Injuries and Illnesses in 1977: Summary (U.S. Dept. of Labor, 1979b). The statistical information for the sandstone mining and processing industry (subset of SIC 14) was obtained from Mine Safety and Health Administration's, Injury Experience in Stone Mining, 1978 (U.S. Dept. of Labor, 1979c). These information sources present the occupational data needed for a risk assessment of each industry.

TABLE 3.1-13. TOTAL LOST WORK DAYS AND FATALITY RATES BY OCCUPATION

	Total lost workdays per		Fatalities per		
Industrial and occupational category	Thousand employee- hours	Hundred employee- years ^a	Million employee- hours	Hundred employee- years ^a	
Semiconductor industry ^b					
Material handling	0.848	170	4.7×10^{-2}	9.4×10^{-3}	
Metal plating	0.348	70	.2.4 x 10 ⁻²	4.8×10^{-3}	
Material abrading and polishing	0.198	40	Neg.	Neg.	
Assembling	U. 228	46	1.2 × 10 ^{-?}	2.4 x 10 ⁻³	
Inspecting	0.255	51	1.4 x 10 ⁻²	2.8×10^{-3}	
Maintenance	0.323	65	1.3×10^{-2}	2.6×10^{-3}	
Technical	0.212	- 42	1.0×10^{-2}	2.0×10^{-3}	
Occupations not specified	0.235	47	1.3 × 10 ⁻²	2.6×10^{-3}	
All occupations (industry-wide values)	0.258	52	1.4 x 10 ⁻²	2.8 x 10 ⁻³	
Metal mining industry ^c					
All occupations	0.420	84	3.7×10^{-2}	7.4×10^{-3}	
Sandstone mining and processing industry ^d				·	
All occupations	1.055	211	1.0×10^{-1}	2.0×10^{-2}	
Primary aluminum Smeiting and processing industry ^C					
All occupations	0.480	96	6.0×10^{-2}	1.2×10^{-2}	
Primary nonferrous metals smelting and processing industry ^C					
All occupations	0.399	80	7.0 × 10 ⁻²	1.4×10^{-2}	
Inorganic chemicals industry ^c					
All occupations	0.234	47	3.2×10^{-2}	6.3×10^{-3}	

^aThe conversion from employee-hours to employee-years format was performed to facilitate the comparison of these statistics with other published values.

^bValues calculated from information available from CDIR, 1980; CEDD, 1980; CEDD, 1979; U.S. Department of Labor, 1980.

^CValues taken from U.S. Dept. of Labor, 1979, b.

d_{Values} taken from U.S. Dept. of Labor, 1979, c.

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The occupational statistics in Table 3.1-13 and Figure 3.1-1 can be used to estimate the number of total lost workdays and fatalities associated with a semiconductor (or photovoltaic) process. Three potential sources of error could significantly affect the magnitude of a lost-workday or fatality rate. One is the inaccurate reporting of lost-workday cases. The only cases legally recognized as recordable events are those that cause illness or death, require medical treatment, produce loss of consciousness, restrict work or motion, cause transfer of the employee to another job, or cause termination of employment (U.S. Dept. of Labor, 1978). The greatest cause of inaccuracy results from the ambiguity involved in designating medical treatment. Reporting requirements of the Workman's Compensation programs and the Occupational Health and Safety Administration (OSHA) distinguish between recordable medical treatment and nonrecordable first-aid treatment. Company health and safety officials responsible for reporting recordable events often confuse or ignore many of the distinctions designed to exclude first-aid treatment from the body of recorded events. This problem arises mostly in cases where the severity of the injury and the required degree of treatment are highly variable. In occupations that require extensive handling of tools or materials the frequency of minor injuries is often high, and as a result a larger number of inaccurate recordings are reported for these occupations. This type of error may account for a portion of the very high lost-workday rate calculated for material-handling occupations in the semiconductor industry (Table 3.1-12 and Figure 3.1-1).

Another source of error arises from the method by which the number of lost workdays is assigned to various injuries or illnesses. The procedure for reporting days lost to the Workman's Compensation program includes both actual days lost and scheduled days lost. The difference is that actual days lost are the number of days "actually" lost for each illness or injury; the scheduled days lost reflects a standard set of



Figure 3.1-1. Total lost workdays and fatality rates by occupations within the semiconductor industry.

"scheduled" charges. A scheduled charge is an assumed, after an average, value for the number of lost days for a specific injury or illness.

The last source of potentially significant error is the method we have used to estimate the number of employees associated with each occupation. Because the apportioning of employment from industry totals to specific occupations is based on an interpretation of occupational category descriptors, the employment figures for each occupation may be underestimated.*

An underestimation of occupational employment could also contribute to the high rates of occupational injury, illness, and fatalities in the material-handling occupation (Table 3.1-13, Figure 3.1-1).

3.2 EVALUATION OF CHEMICAL TOXICITY

To determine the degree of chemical hazard associated with processes and occupations in the photovoltaics industry, it is necessary to characterize the toxic nature of each chemical substance for which an exposure potential exists. The characterization of a chemical's toxicity is achieved through the association of a particular dose to a given effect. Because this study is concerned with estimating the frequency and level of human morbidity and mortality the effects considered will be those which produce a lethal or disabling non-lethal response in the worker.

^{*} It is doubtful that the employment figures are overestimated. In the apportioning, great care was taken to include those occupational employment categories whose descriptors could be associated with only one class of occupational health statistics and thus excludes employment figures with more ambiguous descriptions. This procedure is belived to produce either a reasonably accurate estimation of occupational employment or one that is underestimated. It is believed that an underestimate (which yields more severe or "worst case" injury rates) is preferrable to an overestimate, which could mask the potential risks.

The four photovoltaic cell production processes considered in this document use a large number of both common and exotic chemical substances. Of all the substances involved in the production operations, sixty-two have been identified as conceivably having the potential to present some degree of hazard This hazard potential was established on the to the worker. relative capacity of each substance to be emitted to the work environment either as a process emission during normal operation and maintenance, or as an accidental emission resulting from equipment failure or breakdown. The large number and the exotic nature of many of these substances prevents an extensive individual examination of each chemical. However, to provide both a comprehensive review of chemical toxicity, and an in-depth analysis of substances with the greatest hazard potential, a screening procedure will be used to assess the available toxicity, carcinogenicity, mutagenicity, and teratogenicity data on each chemical substance. The screening process will identify those substances with the greatest potential for producing harm. The result of this screening process will be to focus the hazard evaluation procedures on the most potent chemicals.

3.2.1 <u>Toxicity Screening</u>

The objective of screening is to identify the most toxic substances workers are exposed to during the production of photovoltaic cells. To make this identification it is necessary to order the chemicals based upon their relative toxicity. To perform such a toxicity ranking it is necessary that an index be selected for comparison.

A large number of indices are available for defining a substance's toxicity. These indices, although covering a broad range of toxic effects, can be grouped into one or two categories depending upon whether the indicated response is lethal or non-lethal. Lethality is most often chosen as an index of a substance's toxic potential because of its unequivocal nature and long extensive use. Lethality in the form of acute median

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lethal doses (LD_{50}) are available for a large number of substances. Because of the exotic nature of the chemical substances used in the production of photovoltaics, measurements of median lethality were chosen over other indices of lethality in hopes of aquiring information on the largest number of substances.

The comparison of chemical toxicity based upon indices of median lethality has one major drawback. It should be recognized that although two chemical substances may be ranked in a particular order based on median lethality, the relationship between other points on the dose-response curves may not reflect the same order. Two chemical substances with identical values of median lethality may have widely different slopes associated with their individual dose-response curves. The result of this difference is that at higher (LD_{99}) or lower (LD_{10}) positions of lethality the two curves may differ widely on the amount of chemical required to produce the given response. With this limitation in mind it is still felt that for purposes of screening, an index based on median values is an acceptable measure of lethality.

In addition to the use of median lethality (an index which is determined from and most applicable too acute exposures) some less acute and more subtle responses should be considered as indices. Sub-acute and chronic exposures to chemical substances can result in carcinogenic or teratogenic death. The indices chosen to identify substances producing these forms of death are: the lowest total dose administered over the shortest time period (LD_{low}) , and the lowest concentration (LC_{low}) . The result of the screening procedure which deals with an index of lethality as an expression of toxicity will be the ranking of chemical substances relative to each other.

Non-lethal expressions of toxicity e.g., burns, dermatitis, pneumonitis, etc., can not be adequately treated through a ranking based solely upon lethality. It is recognized that such an approach would overlook substances which at some level of exposure can cause severe and debilitating illness without ever resulting in death. To account for such possibilities nonlethal effects will be screened and identified using a debility ranking scheme.

3.2.2 <u>Toxicity Classification--Median Lethality, Carcinogenicity</u> and Teratogenicity

In an effort to develop realistic guidelines for the safe use of chemical agents Hodge and Sterner (1949) were the first to suggest a scheme for expressing relative chemical toxicity. Using median lethality as an index, a system of classification was developed which associated known human experience with animal exposure data. The use of this scheme resulted in estimates of "probable lethal doses in man". Gleason (1969) expanded on this orginal idea producing a classification guide for placing chemical agents into categories based on their relative toxicity.

The toxicity classification method as it has evolved from the work of Hodge, Sterner, and Gleason is presented in Table 3.2-1. A few modifications have been made to the classification method for the purposes of this study.

The first modification made was a clarification of the scheme's format. A number of sources (Casarette, 1975; Loomis, 1978; National Safety Council, 1978) present partial or conflicting versions of the classification scheme. The numerical toxicity ranking shown in the first column on Table 3.2-1 has been presented in the literature in both ascending (1 to 6) and descending (6 to 1) order. It is felt that the descending order presents the clearest numerical representation, and for this reason has been chosen for use in the study. In addition to the numerical ranking, discrepancies have arisen in the use of descriptive terms. The majority of the authors reviewed (Hodge, 1949; Gleason, 1969; Loomis, 1978; National Safety Council, 1978) use the descriptive terms presented in the second column

		LD ₅₀	LC50 4 hour	LD50	Probable lethality in man	
Toxicity rating	Commonly used term	single oral dose for rats (mg/kg)	inhalation exposure in rats (ppm)	skin for rabbits (mg/kg)	Oral (mg/kg)	Inhalation ^a (ppm)
6	Extremely toxic ^b	<]	<10	<5	<5	<1
5	Highly toxic	1-50	10-100	5-39	5-50	1-10
4	Mcderately toxic	50-500	100-1,000	44-349	50-500	10-100
3	Slightly toxic	500-5,000	1,000-10,000	350-2,819	500-5,000	100-1,000
2	Practically nontoxic	5,000-15,000	10,000-100,000	2,800-22,600	5,000-15,000	1,000-10,000
1	Relatively harmless	>15,000	>100,000	>22,600	>15,000	>10,000

TABLE 3.2-1. MODÌFIED TOXICITY CLASSIFICATION SCHEME^a

^a Hodge, 1949 and Gleason, 1969.

 $^{\rm b}$ Probable lethal concentrations in man were estimated as one tenth the ${\rm LC}_{50}$ in rats.

^C The "extremely toxic" expression will also be applied to any agent causing carcinogenic, neoplastic, mutagenic, or teratogenic effects in one or more animal species.

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of Table 3.2-1. Casarette and Doull (1975) have on the other hand employed a different set of six terms; supertoxic, extremely toxic, very toxic, moderately toxic, slightly toxic, and practically non-toxic. These alternate terms are associated with the same exposure concentrations found in Table 3.2-1, and can be interchanged. The descriptive terms used in this study were chosen because of their more frequent occurrence in the literature.

The second modification made to the classification scheme was an expansion of the "probable lethal dose in man" column. The initial classification scheme related median lethal doses in test animals to acute oral exposures in man. The classification scheme relates probable lethal dose in man to the oral LD₅₀ of rats using a 1:1 ratio. The human dosage is also related on a 1:2 ratio with the LD_{50} dose for skin exposure in rabbits. In attempting to expand on the utility of this classification, probable lethal concentrations were estimated for acute inhalation exposures in man. The inhalation exposures were determined using a 1:10 ratio between $LC_{5,0}$ four-hour inhalation exposures in rats and probable lethal concentrations in man. The 1:10 ratio was selected because it represents the minimum limit of the traditional "safety factor" range (1:10 through 1:5000) used to predict toxicity in man from animal test data on industrial chemicals (Patty, 1979). In using this ratio it was assumed that its application to an animal LC_{50} value was as appropriate as its traditional application to an animal "no-adverse-effect" level.

The modified toxicity classification scheme only assesses the lethality of chemicals based upon single doses or concentrations administered for very short periods of time. It is recognized that the principal lethal effect of some substances will only result from exposures over prolonged periods. To account for the action of these substances carcinogenic, neoplastic, mutagenic, and teratogenic effects on animals will be identified. The treatment of this type of chronic exposure data will be based on an all-or-none approach. Substances which have been identified as positive animal carcinogens, or have produced cancer in one or more species, are mutagens, or have produced neoplasts in one or more species, will be designated as extremely harmful agents. Substances which have produced teratogenic effects in one or more species will also be designated as extremely harmful agents. After this initial identification no attempt will be made to rank these carcinogenic or teratogenic substances relative to each other. Each substance will be treated as an "extremely toxic" agent under the modified toxicity classification scheme.

The Registry of Toxic Effects of Chemical Substances (NIOSH, 1979) was the primary source document used to inventory the measured levels of median lethality. The median lethality data reviewed was limited to rat and rabbit species only. However, in addition to recording median lethal concentrations in rats, the lowest lethal concentration (LC_{low}) was also This LC value was used when a source of median recorded. lethality data was unavailable. Indices of mutagenicity, neoplasticity, carcinogenicity, and teratogenicity were recorded regardless of the animal species in which the effect was observed. Human exposúre data (when it was available) was also recorded. The majority of the human data was expressed in terms of the lowest dose (LD_{low}) or concentration (LC_{low}) at which a death had occurred.

Both the animal and human exposure data were used to assess the relative toxicity of each chemical substances. When human data was available it was given precedence over animal data in the determination of toxicity. The results of the review of animal lethality data is presented in Table 3.2-2. The human lethality data is presented in Table 3.2-3.

The results of the toxicity screening and evaluation procedure using the classification scheme, and lethality data from both humans and animals are presented in Table 3.2-4. The chemical substances are ranked according to the route of entry,

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TABLE 3.2-2. ANIMAL LETHALITY DATA^a

Chemical substance	LD50 Single oral dose for rats img/kg)	LC50 4 hour inhalation exposure in rats (ppm)	LD ₅₀ Skin exposure in rabbits (mg/kg)	Indicies of carcinogenicity or teratogenicity
Acetic acid	3,100	(16,000 LC _{10w}) ^b	1,060	_
Acetone	9,750 ^b	(54,000 LC) ^b	20,000	-
Aluminum (metal)	_	-	-	-
Ammonia	350	(2,000 LC ₁₀₁₁) ^b	. -	-
Ammonium hydroxide	350	b	-	
Arsenic troxide	20 ^b	с	-	Suspect human carcinogen ^b
Beryllium (metal)	-	с	-	Positive animal carcinogen
Boron hydride	- `	50	-	-
Boron trichloride	-	(20 LC ₁₀₀ /7 h)	-	-
Boron trifluoride	-	(750 LC ₁₀₁ /5.5 h)	-	-
Cadmium (metal)	-	C	· -	Positive animal carcinogen Teratogenic in mice
Cadmium chloride	83	-	c	Positive animal carcinogen Teratogenic in rats and mice
Cadmium sulfide	-	· _	c	Positive animal carcinogen
Carbon monoxide	-	1807	-	-
Carbon tetraflupride	-	(895,000 LC ₁₀₁ /15 min)	-	-
Ch r omium	-	-	· _	-
Copper (metal)	-	- -	-	-
Copper (II) chloride	-	-	-	-
Ethyl alcohol	1.4×10^4	-	0 ·	Carcinogenic in mice Teratogenic in mice
Gallium arsenide	d	d	d	đ
Gold (metal)	· -	-	-	Carcinogenic in both rats and mice

(Continued)

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TABLE 3.2-2 (continued)

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Chemical substance	LD ₅₀ Single oral dose for rats (mg/kg)	LC ₅₀ 4 hour inhalation exposure in rats (ppm)	LD50 Skin exposure in rabbits (mg/kg)	Indicies of carcinogenicity or teratogenicity
Hydrogen (gas)	-	-	-	· –
Hydrogen bromide	-	(2,858 LC ₅₀ /1 h)	-	-
Hydrogen chloride (anhydrous vapor) (aqueous aerosol)	-	(4,701 LC ₅₀ /30 min) (5,666 LC ₅₀ /30 min)	-	-
Hydrogen fluoride (anhydrous vapor) (aqueous aerosol)	-	(1,276 LC ₅₀ /1 h) ^b	-	 -
Hydrogen peroxide	-	-	-	-
Iron (metal)	-	-	-	-
Isopropanol	5,840 ^b	-	1.3×10^4	-
Lead (metal)	b	-	-	-
Magnesium (metal)	ь	-	-	-
Methanol	$1.3 \times 10^{4^{\circ}}$	-	2.0×10^4	-
Nickel (metal)	-	с	-	Positive animal carcinogen
Nitric acid	b	65	-	-
Nitrogen dioxide	-	88	-	-
Nitrogen (gas)	-	-	-	-
Nitrogen monoxide	-	-	-	-
Ozone .	-	4.8	-	-
Phosphorous oxychloride	280	48	-	-
Phosphine	-	11	-	-
Silicon	d	d	d d	đ
Silicon carbide	d	d	d	d
Silicon dioxide (amorphorous)	-	_	-	-

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(Continucd)

TABLE 3.2-2 (continued)

Chemical substance	LD50 Single oral dose for rats (mg/kg)	LC50 4 hour inhalation exposure in rats (ppm)	LD59 Skin exposure in rabbits (mg/kg)	Indicies of carcinogenicity or teratogenicity
Silicon dioxide (crystalline)	-	Ь	-	-
Silicon hydride	-	9,600	-	-
Silicon nitride	đ	d	d	d ·
Silicon tetrachloride	-	8,000	-	-
Silicon tetrafluoride	-	-	-	-
Silver (metal)	-	-	b	Carcinogenic in rats
Sodium hydroxide	- · .	-	-	-
Sodium hypophosphite	-	-	-	-
Sulfuric acid (amhydrous vapor) (aqueous aerosol)	2,140	(178 LC 1/0 H)		Ξ
Thiourea	125 ^C	-	-	Positive animal carcinogen
Tin⊨(metal)	-	-	i –	Carcinogenic in rats
Tin (II) chloride	700	-	-	-
Tin (II) oxide	d	d	d	d
Titanium dioxide	-	-	b	Carcinogenic in rats
Trichloroethylene	4,920 ^C	8,000	-	Positive animal carcinogen
Hydrogen cyanide	10 ^E	(484 LC ₅₀ /1 h) ^D	-	-
Polyethylene	-	-	-	Neoplastic in rats and mice
Urethane	-	-	-	-
Vinyl acetate	2,920	(4,000 LC _{10w})	-	' -
Zinc chloride	350	-	-	. -

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^aNIOSH, 1979.

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 $^{\mathrm{b}}$ Demotes availability of human exposure data for this substance see Table 3.2-3.

^CIndicates route of carcinogenic, neoplastic or teratogenic agent.

d_{Data not reported.}

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TABLE 3.2-3. HUMAN LETHALITY DATA^a

Chemical substance	Route	Description of exposure	Dose or concentration
Acetone	Oral	LD	50 mg/kg
Ammonia	Inhalation		30,000 ppm/5 min
Ammonium hydroxide	Inhalation		5,000 ppm
Arsenic trioxide	Oral Inhalation	LD ₅₀	1,430 µg/kg Carcinogenic
Cadmium	Inhalation	LClow	39 mg/m ³ /20 min
Carbon monoxide	Inhalation		4,000 ppm/30 min
Hydrogen fluoride (anhydrous vapor)	Inhalation		50 ppm/30 min
Isopropanol	Oral	LD	8,600 mg/kg
Lead (metal)	Oral		450 mg/kg/GY*
Methanol	Oral		340 mg/kg
Nitric acid	Oral		340 µg∕kg
Nitrogen dioxide	Inhalation		200 ppm/1 min
Phosphine	Oral Inhalation	LD LClow	5 mg/kg 1,000 ppm
Silicon dioxide	Inhalation		300 mg/m ³ /10 y
Hydrogen cyanide	Oral Inhalation	LD LC low	570 µg/kg 120 mg/m ³ /1 h 200 mg/m ³ /10 h
Zinc chloride	Oral Inhalation	LD LC low	50 mg/kg 4,800 mg/m ³ /30 min

^aNIOSH, 1979.

*Data for women.

toxicity classification, and whether the original data used to assess toxicity was from human or animal exposures. The table also designates which substances were considered "extremely toxic" by virtue of the chemicals ability to produce mutagenic, neoplasic, carcinogenic or teratogenic effects.

3.2.3 <u>Toxicity Classification--Nonlethal Disease States and</u> <u>Irritants</u>

The chemical substances used in the production of photovoltaic devices have produced, in addition to acute lethal effects, a variety of chronic non-lethal debilitating diseases. Unlike lethality these chronic non-lethal diseases cannot be related to a single toxicological end-point. Even if such a universal index of non-lethal toxicity could be found its use would undoubtably result in an oversimplified view of some very complex and hazardous illnesses. The lack of a single index prevents the development of any meaningful screening procedure or classification scheme for determining a substance's relative nonlethal toxicity.

In lieu of a useful index, chemical substances can be classified according to their nature as a disease producing agent. This classification procedure is accomplished by relating each chemical substance to the occupational disease it most frequently produces. The diseases are then ranked according to the resulting level of debilitation.

The chemical substances used in the photovoltaic production processes are presented in Table 3.2-5 according to the occupational disease states they are known to produce.

Chemical substances known to act at the sight of contact with biological tissue are classified as local toxic agents. This class includes skin irritants, corrosive agents, sensitizing agents, and mucuous membrane irritants. Also included in the class of local toxic agents are chemicals known to produce severe pulmonary disorders; i.e., severe pulmonary irritants, pulmonary sensitizers, fibrogenic agents, asphyxiants, and benign pneumoconioses.

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Route	Extremely toxic	Highly toxic	Moderately toxic	Slightly toxic	Practically nontoxic	Relatively harmless
Oral	Arsenic troxide ^a	Acetone	Ammonia	Acetic acid	Ethyl alochol	
H	Nitric acid ^a	Phosphine ^a	Ammonium hydroxide	Sulfuric acid (anhyd.)	Isopropanol ^a	
	Hydrogen ^a cyanide		Cadmium chloride	Tin (II) chloride		
	Ethyl alcohol ^{b,c}		Lead ⁰	Vinyl acetate		
	Thiourea ^b		Methanol ^a	Trichloro- ethylene		
	Trichloro- ethylene ^a		Phosphorus oxychloride			
	Zinc chloride ^a		Thiourea			
Inhalation	Arsenic troxide ^b	Boron hydride	Boron trifluoride	Silicon dioxide ^a	Acetic acid	
	Nickel (metal) ^b	Boron trichloride	Carbon monoxide ^a	Silicon• hydride	Acetone	
	Cadmium (metal) ^{a,b,c}	Hydrogen fluoride ^a (anhyd.)	Hydrogen bromide	Silicon tetrachloride	Ammonia ^a	
	Ozone	Nitric acid	Hydrogen chloride (anhyd.)	Trichloro- ethylene	Ammonium hydroxide ^a	
	Hydrogen cyanide	Nitrogen dioxide ^a	Hydrogen chloride (aq.)	Vinyl acetate	Carbon tetrafluoride	
	Zinc chloride ^a	Phosphorus oxychloride	Sulfuric acid (aq.)			
		Phosphine	Hydrogen cyanide ^a			
Dermal	Cadmium ^{b,c} chloride			Acetic acid	Acetone	
	Cadmium ^b sulfidc				Isopropanol	
	Titanium dioxide ^b				Methano]	
Other ^d	Beryllium ^b (metal)					·
	Gold (metal) ^b					
	Silver (metal) ^b					
	Tin (metal) ^b					
	Polyethylene ^b			[

TABLE 3.2-4. RELATIVE TOXICITY OF CHEMICAL SUBSTANCES IN THE PHOTOVOLTAICS INDUSTRY-LETHALITY

^aToxicity ranking based upon human exposure data, Table 3-2.3.

^bExtreme toxicity ranking by virtue of the chemicals mutagenic, neoplastic, or carcinogenic behavior, Table 3.2-2.

 $^{\rm C}$ Extreme toxicity ranking by virtue of the chemicals teratogenic behavior, Table 3.2.2.

 $^{\mathsf{d}}$ Other routes of administration; intermuscular, implantation, and intavenous.

TABLE 3.2-5. CHEMICAL SUBSTANCES PRODUCING NON-LETHAL DISEASE STATES, IRRITATION, AND CORROSION^a

Local toxic agents Skin disorders

Primary irritants

Corrosive agents Acetic acid Hydrogen bromide Hydrogen chloride Hydrogen fluoride Hydrogen peroxide Nitric acid Sodium hydroxide Sulfuric acid Irritants Ammonium hydroxide Acetone Ammonia Arsenic Beryllium Boron trifluoride Copper (metal dust) Cyanides (alkali) Methanol Nickel (metal) Silver (metal) Tin compounds Trichloroethylene

Sensitizing agents

Acetic acid Beryllium Copper dust Nickel (metal)

Mucous membrain disorders (mild irritants)

Acetic acid	Isopropanol
Acetone	Silver compounds
Arsenic trioxide	Sodium hydroxide
Copper compounds	Tin compounds
Hydrogen bromide	Trichloroethylene
Hydrogen peroxide (90%)	Trichloroethylene

(continued)
TABLE 3.2-5 (continued)

Pulmonary disorders

Severe pulmonary irritants

Ammonia Beryllium Boron trifluoride Cadmium Hydrogen chloride Hydrogen fluoride Nitric acid Silicon tetrafluoride Sulfuric acid

Pulmonary sensitizers

Nickel (metal)

Fibrogenic agents

Aluminum (metal powder) Silicon dioxide (amorphous and crystalline)

Benign pneumoconiosis producing agents

Aluminum (metal powder) Silicon dioxide (amorphous) Tin (II) oxide

Asphyxiants

Simple asphyxiants Hydrogen Nitrogen Chemical asphyxiants Hydrogen cyanide

Systemic agents Nervous system disorders

CNS depressants

Acetone Ethyl alcohol Isopropanol Trichloroethylene

Peripheral neuropathogenic agents

Arsenic trioxide Lead

^aProctor, 1978.

Chemical substances known to act at sights distant to the initial point of contact are classified as systemic toxins. These agents include central nervous systems depressants and peripheral neuropathogens.

The debility ranking described previously is based upon a subjective interpretation of disease severity. The diseaseproducing agents listed in Table 3.2-6 can be further classified into more general occupational illness categories (U.S. Dept. of Labor, 1979a; CDIR, 1979). The occupational illness categories can then be ordered based upon the average severity accociated with each category's component diseases. Severity is measured as the average number of lost workdays per lost-workday case (see Table 3.1-12). The severity ranking can be used to indicate the degree of debility associated with exposure to specific disease producing agents. Table 3.2-5 presents the relative debility ranking for occupational illness categories.

The application of the debility ranking scheme to specific chemical substances; i.e., potential disease producing agents, is accomplished in Table 3.2-7. A debility ranking is assigned to each chemical substance that is known to produce one or more disease states in humans. The summation of all numerical values gives an indication of the potential debility producing nature of each chemical substance.

This method of interpretation is not meant to imply that one disease is more acceptable than another, or that any disease listed in Table 3.2-4 is considered tolerable in a work environment. The ranking assumed that all disease states listed are undesirable, and substances producing these disease states are hazardous to worker's health. It is within a given group of hazardous chemical agents that the risk to worker health is compared. A statement resulting from the use of this debility ranking might read; "the existence of a pulmonary sensitizer in the work environment presents a greater risk to worker health than does the presence of a primary irritant."

Occupational illness categories and associated disease producing agents	Debility ranking ^a
Occupational skin disease or skin disorder	1
Primary irritants Sensitizing agents Corrosive agents	
Dust diseases of the lung	4
Benign pneumoconious producing agents Fibrogenic agents	
Respiratory conditions due to toxic agents	3
Mucuous membrain irritants Severe pulmonary irritants Pulmonary sensitizers	
Poisoning	2
Asphyxiants (chemical) Central nervous system depressant Peripheral neuropathogenic agents	
All unclassified illnesses	
Asphyxiants (physical)	

TABLE 3.2-6. DEBILITY RANKING

^aThe severity of debilitation decreases with a decrease in the numerical value of the ranking; i.e., 4>3>2>1.

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Substance	Cccupational skin disease or skin disorder	Dust diseases cf the lungs	Respiratory conditions due to toxic agents	Poisoning	Total debility ranking
Acetic acid	1		3		4
Acetone			3	2	6
Aluminum (metal)		4	2		4
Ammonia Ammonia			3		4
Ammonium nyaroxide			2	2	-
Arsenic trioxide Boryllium (motal)	1		່ <u>.</u>	۷	Δ.
Boron hydride			5		-
Boron trichloride					-
Boron trifluoride]		3		4
Cadmium (metal)			3		3
Cadmium chloride			3		3
Cadmium sulfide					-
Carbon monoxide				2	2
Carbon tetrafluoride			3	2	5
Chromium (metal)			3		3
Copper (metal)			3		4
Copper (11) chloride			3	2	4
Ethyl alconol Callium angonido				۷	2
Gold (motal)	· 1				1
Hydrogen (gas)					_
Hydrogen bromide	1		3		4
Hydrogen chloride			3		4
Hydrogen cyanide				2	2
Hydrogen fluoride	1		3 .		4
Hydrogen peroxide	1.		3		4

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TABLE 3.2-7. DETERMINATION OF POTENTIAL DEBILITY

(continued)

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TABLE 3.2-7 (continued)

Substance	Occupational skin disease or skin disorder	Dust diseases of the lungs	Respiratory conditions due to toxic agents	Poisoning	Total debility ranking
Iron (metal)			3		3
(Isopropano)			3	2	5
Magnesium (metal)				2	;2
Methanol	1				-
Nickel (metal)	i		3		. I Д
Nitric acid	1		3		4
Nitrogen (gas)					-
Nitrogen dioxide (gas)			3		3
Nitrogen monoxide (gas)					· -
Uzone (gas) Dhosphonus ovuchlanida			3		3
Phosphine Phosphine			3		3
Polvethvlene			3		3.
Silicon					-
Silicon carbide					-
Silicon dioxide (amorphous)		4			4
Silicon dioxide (crystallin	ie)	4			4
Silicon hydride			3		3
Silicon nitride					-
Silicon tetrachioride			4		-
Silver (metal)	1 1		3		
Sodium hydroxide			3		4
Sodium hypophosphite	• •		5		-
Sulfuricacid	1		3		4
Thiourea					_
Tin (metal)	1		3		4
Tin (II) chloride	1		3		4
lin (11) oxide		4	3		8
litanium dioxide					-
In ichioroethylene			2	0	3
Vinvl acetate	1			Z	
7inc chloride			3		

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SECTION 4

SILICON-I PROCESS

The following sections discuss processes that encompass the fabrication of silicon n/p homojunction cells, from mining of the raw materials to completion of the solar module. The discussion includes estimates of materials and manpower needed for the manufacture of 100 MW_{peak(pk)} of these silicon cells. Potential emissions, wastes, and controls are discussed when applicable and when information is available.

A few basic assumptions were made in an effort to simplify the calculations of material usage and manpower requirements:

- The finished silicon wafer is 200 µm thick.
- ^o The wafer is 10.16 cm (4 in.) in diameter, with a surface area of 81.07 cm² (12.56 in.²).
- The completed solar cell is 15 percent efficient.
- Each completed cell generates 1.216 W of power at AMl conditions.
- All calculations are based upon production of 100 MW pk of cells per year.
- A plant operates 5 days/wk, 24 h/day, 50 wk/yr (6000 h/yr).
- Process throughput efficiencies are 100 percent.

Calculations based on these assumptions show that 82,236,842 cells would be required for production of 100 MW_{pk} per year. All material requirements for operations preceding completion of the finished silicon wafer were back-calculated on the basis of the total amount of silicon required for the finished wafers.

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Estimates of manpower requirements are based primarily on information obtained from reports submitted under Jet Propulsion Laboratories (JPL) Low-Cost Silicon Array Project (LSA). Because of variations in the throughput rates for a particular operation or manpower required per machine, an average was calculated or an estimate was made on the basis of the information available.

4.1 MINING AND REFINING OF QUARTZ - SILICON I

4.1.1 Process Description

Most sand deposits can be handled by means of a dredge and the sand pumped to the treatment plant in a slurry. Where the sand is mined from deposits above the water table, however, truck transport to the treatment plant may be required. The following process steps would most likely produce the quality of quartz required for production of metallurgical-grade silicon (MG-Si).

- Primary classification and dewatering under 20-mesh size is treated.
- Attrition scrubbing removal of surface stain.
- Secondary classification removal of slimes generated by attrition scrubbing.
- ° Conditioning reagents such as H_2SO_4 and iron promoting reagents are added to clean to specifications.
- ^o Flotation reagents such as fuel oil, H_2SO_4 , pine oil, petroleum sulfonate, and a xanthate reagent are added to activate and float impurities; H_2SO_4 is used to keep the pH level around 2.5 to 3.0. The froth containing the impurities is separated from the sand in a flotation machine.
- Final desliming the clean sand is dewatered to 15 to 20 percent moisture content and conveyed to stock pile or drainage bins.

It should be noted that some quartz deposits in the western United States are of very high purity (95 to 99 percent) and may require less vigorous purification steps.

4.1.2 Material Requirements

The total amount of sand and gravel required for production of 100 MW_{pk} of solar cells was back-calculated from the total amount of single-crystal silicon required for production of this quantity of cells. The quantity of single-crystal silicon was calculated in accordance with the assumptions listed earlier. The calculation for sand and gravel requirements was based on findings of Battelle (Watts, et al, 1979). It was approximated on the basis of the Battelle findings that 0.66 percent of the total sand and gravel quarried resulted in silicon in the active layers of the n/p homojunction silicon cell.

The total sand and gravel required to produce 3.11 Mg/MW of single-crystal silicon cells is therefore 471.2 Mg/MW or 47,120 Mg/yr for a 100 MW/yr plant. On the assumption that this plant is to be constructed in 1985, the projected quantity of sand and gravel mined in 1985 is 1.06 billion tons (U.S. Dept. of Interior, 1980a). The percentage of the total used for the 100 MW/yr plant would therefore be 0.0049 percent.

4.1.3 Manpower Estimates

It is estimated that 0.08 employee-hour is needed to produce 1 Mg of sand and gravel (U.S. Dept. of Interior, 1980a). Total manpower needed to produce the sand required for the hypothetical 100-MW plant would be 3769.6 employee-hours per year.

4.1.4 Emissions, Wastes, and Controls

Reported fugitive emissions from drilling, blasting, loading and transport on unpaved roads, washing, crushing, screening, conveying, and stockpiling sand and gravel are 34.7 g/Mg total and 3.6 g/Mg respirable dust (Chalekode, P.K. et al, 1978). Another study reports emissions of 0.05 kg/Mg for sand and gravel quarrying operations (U.S. Environmental Protection Agency, 1977). On the basis of these values, total dust emissions from mining of quartz for the 100-MW/yr facility may range from 1.64 to 2.36 Mg/yr, and emissions of respirable dust, 0.17 Mg/yr. It is also reported that of the 3.6 g/Mg of respirable dust an average of 17 percent was free silica (Chalekode, P.K. et al, 1978). This means that approximately 0.029 Mg/yr of free silica would be respirable.

Fugitive emissions can be controlled by wetting roads with water, a chemical agent, or oil, or by paving the roads. Emissions from storage piles can be reduced by wetting or enclosure. Use of an enclosed conveyer with baghouse and use of filters on crushers may also be helpful in controlling dust.

4.1.5 Occupational Hazards

Many types of physical injuries are sustained by workers involved in stone mining. Table 4.1-1 gives the types and numbers of injuries to workers at open pit surface mines, dredging operations, and processing plants in 1978 (Injury Experience in Stone Mining, U.S. Dept. of Labor, 1979c). Table 4.1-2 classifies and enumerates the injuries that occurred in all sandstone mining and processing operations in 1978.

Another major hazard to workers mining quartz is exposure to crystalline silica and the potential for development of silicosis. Dust control and personnel protection (i.e. particulate-filtering masks) can help to reduce worker exposure to crystalline silica.

4.1.6 Risk Determination

The total labor requirement necessary to produce enough silica cand for the hypothetical 100 MW plant would be 3769.6 employee-hours, or approximately 1.88 full time employees. Using the occupational statistics presented in Table 3.1-13 this would result in approximately 4.0 lost workdays including approximately 3.8 x 10^{-4} fatalities.

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TABLE 4.1-1. INJURIES AND FATALITIES AT SURFACE MINES IN 1978

.

Work location and nature of injury	Fatal injuries	Total injuries
Surface Mines:		
Open pit:		
amputation/enculeation		34
asphyxiation/drowning	2	5
burn/scald (not chemical)	1	84
chemical Durn		15
concussion (cerebral)	7	5
cut or puncture	,	500
dermatitis		500
dislocation		18
dust in eye		104
electric shock	1	7
electric burn (contact)		7
fracture	1	346
heat/sunstroke		2
nernia (not disc)		38
radiation/ultra violet		26
scratch/abrasion		20
strain/sprain		629
multiple injuries	4	166
other injury, nec		68
unclassified (no data)	7	185
Total or Average	23	2,778
Dredge:		
burns/scald (not chemical)		1
contusion or bruise		3
cut or puncture		3
fracture fraczing/frastbita		2
strain/sprain		ן ק
unclassified (no data)		i i
Total or Average		16
Processing Plants		
amputation/enculeation		42
asphyxiation/drowning	4	
burn/scald (not chemical)	1	153
chemical burn		103
concussion (cérébral)	1	6
contusion or bruise	4	546
cut or puncture		565
dermatitis ·		15
distocation dust in ove		19
electric shock	2	8
electric burn (contact)	2	9
fracture	4	425
hearing impairment	i i	2
heat/sunstroke] <u>ī</u>
hernia (not disc)		37
poisoning (systemic)		11
radiation/ultra violet	1	54
scratch/abrasion		48
strain/sprain		1,011
multiple injuries	2	203
other injury, nec.		/0
UNCLASSITIED (NO DATA)	5	199
Total or Average	23	3,732

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TABLE 4.1-2. NUMBER OF INJURIES BY ACCIDENT CLASSIFICATION FOR SANDSTONE MINING AND PROCESSING OPERATIONS

	Sandstone Mining		Processing		
٠	Fatalities	Total injuries	Fatalities	Total injuries	
Electrical	0	2	0	2	
Entrapment	0	0	0	0	
Exploding vessels under pressure	0	3	0	2	
Explosives and breaking agents	0	1	n	'n	
Falling, rolling or sliding material	0	· 7	0	3	
Fall of face rib, side or highwall	0	4	0	0	
Fall of roof (underground mines only)	0	0	0	0	
Fire	0	3	0	0	
Handling material	0	68	0	87	
Handtools	0	32	0	21	
Nonpowered haulage	0	0	0	7	
Powered haulage	1	25	0	8	
Hoisting	⁻ 0	2	0	3	
Ignition or explosion of gas or dust	0	0	0	1	
Impoundment	0	0	0	0	
Inundation	0	0	0	0	
Machinery	0	31	0	21	
Slips or falls of persons	0	41	0	. 43	
Stepping or kneeling on object	0	5	0	1	
Striking or bumping	Q	1	0	4	
Other	0	15	0	11	
Total	1	240	0	214	

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4.2 METALLURGICAL SILICON PRODUCTION

4.2.1 Process Description

Production of metallurgical-grade silicon (MG-Si) involves the reduction of SiO_2 in an electric-arc furnace with coke. The silicon slag is drained from the bottom of the furnace and allowed to crystallize before being milled to a chunk form. It is then transferred by enclosed rail or truck to a silicon purification facility.

4.2.2 Material Requirements

The quantity of quartz (SiO_2) required as feed to the electric-arc furnace for production of 100 MW of cells was backcalculated from the total quantity of silicon required for the finished cells. Calculations for feed to the furnace were based on a process flow diagram by Gandel (Gandel et al, 1977).

It is assumed that the yield of MG-Si is about 36.3 percent of the 98 percent-SiO₂ feed. This includes an estimated 2 percent loss during the milling operation.

The quantity of 98 percent SiO_2 required for production of 100 MW of cells is calculated to be 245.4 Mg/MW. The amount of coke required is also based on estimates by Gandel et al. For the 100-MW plant in this study the requirement is 94.2 Mg/MW of coke.

The total amount of MG-Si produced for the 100-MW plant is 89.9 Mg/MW. This total of 8900 Mg is about 7.95 percent of the total metallurgical silicon produced in 1977.

4.2.3 Manpower Requirements

According to one estimate, about 12.7 employee-hours was required to produce 1 ton of MG-Si in 1979 (U.S. Dept. of Interior, 1980a). On this basis, the production of 8900 Mg of MG-Si would require 11.5 employee-hours per Mg of MG-Si or a total of 102,350 employee-hours.

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4.2.4 Emissions, Wastes, and Controls

It is reported that 0.002 kg of particulate was emitted for every kilogram of coke produced (Neff, T.L., 1979). Production of the 9420 Mg of coke (9,420,000 kg) required for the hypothetical 100-MW facility would then cause emission of 18.84 Mg/yr of particulates.

Gandel et al. (1977) estimate that about 14.87 percent of the feed quartz is lost as SiO and ash. Of this 14.87 percent, 14.4 percent is SiO. Therefore, 35.33 Mg/MW of SiO and 1.15 Mg/MW of ash are emitted. These particulates are collected in a series of chambers and filters and disposed of as waste.

Another estimate of emissions from silicon electric-arc furnace operations is 625 lb/ton (312.6 kg/Mg) (Crossman, L., 1974 in Solar Program Assessment: Environmental Factors). On the basis of this emission factor, the total fugitive emissions from producing the 89.9 Mg/MW of MG-Si would be 28.1 Mg/MW, primarily as submicrometer-sized particulates.

For the hypothetical 100-MW plant MG-Si is milled into chunk form and shipped to the purification plant. A 2 percent loss or 1.8 Mg/MW is assumed for this milling operation (Gandel, et al, 1977). Shipment to the purification facility is assumed to be in enclosed truck or rail car; thus losses during transport are negligible and the amount of MG-Si reaching the plant is 88.1 Mg/MW.

4.2.5 Occupational Hazards

One potential hazard for workers in MG-Si production is exposure to silica in either crystalline, fused, or amorphous form. Because many of the particulates emitted are of submicrometer size, capturing all of them in the exhaust system may be difficult. It is possible that significant quantities of silica may fall back into the workplace. One estimate is that 12 to 14 tons/day of vaporized silica (which cools to form a fine powder of primarily amorphous silica) was emitted through the stacks and into the workplace (Vitrums et al, 1977). Exposure to crystalline silica may also occur during handling of raw materials such as in transfer from shipping vehicles to storage bins and in loading of quartz into furnaces.

There are numerous potential safety hazards because workers are actively involved in these operations. Although no published data were found on injuries in this industry, the predominant types of potential injury would be burns, eye injuries, electric shock, cuts, abrasions, and similar injuries.

4.2.6 <u>Risk Determination</u>

The labor to refine enough MG-Si from silica sand for a 100 MW/yr plant is estimated to be 102,350 employee-hours, or approximately 51.18 full time employees. Using the occupational statistics associated with the production of industrial inorganic chemicals (SIC 281), given in Table 3.1-13, this level of activity will result in 23.9 lost workdays including an estimated 3.3 $\times 10^{-3}$ fatalities.

4.3 SILICON PURIFICATION

4.3.1 Process Description

In the purification process MG-Si is introduced into a chlorination reactor with hydrochloric acid (HCl) and a catalyst. The resultant mixture of chlorosilanes [monochlorosilane (SiH₃Cl), dichlorosilane (SiH₂Cl₂), trichlorosilane (SiHCl₃), silicon tetrachloride (SiCl₄)] proceeds through a series of separations by condensation and distillation to produce primarily SiHCl₃. The SiHCl₃ is saturated with hydrogen and fed to a deposition chamber that contains a U-shaped seed rod of single-crystal silicon electrically heated to approximately $1100\frac{1}{4}$ C. The H₂-saturated SiHCl₃ decomposes on the seed rod, depositing polycrystalline silicon.

4.3.2 Material Requirements

It is assumed that the silicon is unloaded at the purification plant from an enclosed rail car or truck via an enclosed conveyer system vented to a baghouse. At this plant, the chunk MG-Si is milled once again, this time to <20 mesh (Briggs et al, 1979) for feed to the chlorination reactor. Under the assumption of a 2 percent loss during this milling operation, the total MG-Si feed to the chlorination reactor is 86.3 Mg/MW. Based on material flows by Gandel et al., the quantity of HCl required to react with this amount of MG-Si is approximately 375 After separations and distillations the quantity of Mg/MW. trichlorosilane (SiHCl₃) fed to the polycrystalline silicon deposition chambers is about 522.1 Mg/MW. About 28.95 percent of this is recycle. Feeding of this amount along with 96.4 Mg/MW hydrogen (H₂) results in the production of 12.87 Mg/MW polycrystalline silicon (hereafter called poly-Si).

4.3.3 Manpower Requirements

A plant producing 1000 Mg/yr of poly-Si by the Siemans process would require about 58 operators per shift (Personal communication with Dr. Carl Yaws, LeMarr University, Beaumont, Texas, 1980). Three-shift operation and 7533 h/yr operating time (as is estimated for the new Union Carbide Process) would require 436,914 employee-hours per year for operation. The same study estimates manpower requirements for supervision and maintenance to be about 15 and 43 percent of the operator requirements, respectively, or 65,537 employee-hours per year for supervisory (foremen) labor and 187,873 employee-hours per year for maintenance.

An estimate of 1287 Mg/yr of poly-Si was derived for the 100-MW plant. For production of this quantity of poly-Si, the manpower requirements for operation, maintenance, and supervision would be 562,308, 241,793, and 84,346 employee-hours per year respectively.

4.3.4 Emissions, Wastes, and Controls

As mentioned above, silicon emissions occur during milling of the MG-Si at the purification plant to a \leq 20-mesh size. Assuming a 2 percent loss, 1.8 Mg/MW of MG-Si dust is emitted during this operation. It is assumed that a filter is used to capture emissions from this operation.

Some emissions of chlorosilanes probably occur during silicon purification. Since the chlorosilanes react with moisture in the air to form HCl, the emissions would occur primarily as HCl. Potential fugitive emissions from this purification process have not been quantified. Measurements with tube detectors have indicated levels below 1 ppm in the workplace (Briggs et There is also potential for emissions from the al, 1980). deposition chambers, especially if a cracked or burst reactor causes the release of chlorosilanes. Deposits on the reactor walls, on the outside of a cracked reactor, and on the walls and roof of the building were reported at one plant (Briggs et al, These were described as being polysiloxanes and amor-1980). phous silica. Leakage and accumulation of H₂ also could create Detectors with alarms can be a potential explosion hazard. installed in these areas to warn when a designated percentage of the lower explosive limit (LEL) for H₂ is reached. The liquid and/or solid waste from distillation bottoms probably will require disposal.

4.3.5 Occupational Hazards

Potential occupational hazards in silicon purification are: exposure to silicon during milling; low-level exposure to HCl or chlorosilanes from leaking pipes, valves, or pumps; inhalation of silicon dust while removing the poly-Si rods from the deposition chamber; exposure to polysiloxanes or silica dust from cracked reactors; and exposure to solvents while cleaning the insides of reactors between runs. Table 4.3-1 showing results

Sample description	Sampling time (h)	Concentration mg/m ^{.3}
Personal sample: during cleaning of a unit	1.12	0.07
Area sample: 10 ft from battery of Sieman's units	6.47	<0.02
Area sample: between units	8.07	0.03
Area sample: in control room	8.03	· 0.11

TABLE 4.3-1. RESULTS OF SAMPLING FOR PARTICULATES IN SIEMAN'S PROCESS AREA

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of a sampling survey at one plant (Briggs et al, 1980), indicates that the purification area is almost devoid of particulates. Another potential hazard is explosions from H_2 ignition.

Maintenance personnel may also be exposed to residual compounds in servicing or repair of piping, tanks, reactors, or other components. It is likely that such exposures would be low level unless there were an accidental release caused by rupture of a pipe, tank, reactor or a release through a rupture disc vented to the workplace. The results in Table 4.3-1 help to confirm this.

Because most of the purification processes are relatively automated, actual physical labor and interaction of workers and equipment are minimized except possibly for the maintenance of equipment and handling of finished poly-Si ingots. The most likely injuries would seem to be burns and eye injuries from exposure to acid or chlorosilanes, and cuts, bruises, and possibly broken bones from handling of the finished ingots.

4.3.6 Risk Determination

The production of enough polycrystalline silicon (by the Sieman's process) to supply a 100 MW production operation will require a total of 888,447 employee-hours or approximately 444 full time employees. Using the occupational statistics associated with the production of industrial inorganic chemicals (SIC 281), given in Table 3.1-13, this level of employment will result in 207.9 lost workdays including an estimated 2.8 x 10^{-2} fatalities.

4.4 SINGLE=CRYSTAL SILICON GROWTH

4.4.1 Process Description

Following poly-Si rod deposition the rods are crushed into chunks. The poly-Si is then deposited in a quartz crucible for single-crystal growth.

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Crystal growth is accomplished by the multiple-pull Czochralski method, a process in which polycrystalline semiconductor-grade silicon (SeG-Si) is broken into small chunks and a dopant, commonly boron, are melted in a quartz crucible and a seed silicon crystal is introduced. Given an argon or helium atmosphere with controlled temperature and controlled rotation of the crucible, the crystal is slowly withdrawn at a controlled rate to pull the cylindrical single-cell silicon into the crucible. In the muliple-pull method, four crystals can be pulled before the crucible must be cooled down and disposed of.

4.4.2 Material Requirements

With consideration of losses from poly-Si rod crushing, it is estimated that 12.81 Mg/MW enters the melt for single-crystal growth.

Also introduced into the crucible at this time are chunks of silicon that have been doped with boron. If the desired density of boron in the crystal is 1.2×10^{17} atoms/cm³, a total of 2.69 g/MW of boron is required for doping. If boron trichloride (BCl₃) is used as the source, 31.1 g/MW of BCl₃ is required for 100 MW of cells.

When crystal growth is complete, the ingots are removed from the crucibles. Estimated crucible waste losses are 7 percent (Gandel et al, 1977). Assumption of 7 percent results in a loss of 0.9 Mg/MW. Net silicon production from the single-crystal pulling is therefore 11.91 Mg/MW.

4.4.3 Manpower Requirements

Manpower requirements for the crystal pulling operation are based on a growth rate of 1.4 kg/h (D'Aiello, et al 1977), operation of 6000 h/yr in three shifts per day, and three pullers per operator (Coleman, et al 1979).

A total of 39 direct workers per shift or 234,000 employeehours per year would be required for the crystal pulling section for production of 100 MW of cells. Other direct labor requirements are for support engineers, technicians, quality control personnel, and foremen. If it is assumed that manpower requirements for these positions are 0.06, 0.18, 0.03,* and 0.05* worker per shift per crystal puller, respectively, the requirements for these positions are 42,120, 126,360, 21,060, and 35,100 employee-hours respectively. Maintenance requirements are assumed to be 0.075 worker per machine per shift* or 52,500 employee-hours per year. In summary, a total of 511,140 employee-hours per year is needed, including maintenance requirements.

4.4.4 Emissions, Wastes, and Controls

Based upon material flow diagrams, a 0.5 percent loss is assumed for poly-Si crushing (Gandel et al, 1977). The 0.5 percent loss from the crushing operation (0.06 Mg/MW) is routed to a filter having a control efficiency of about 97.5 percent (Gandel et al, 1977). A loss of 7 percent or 0.9 Mg/MW is calculated for crucible waste.

4.4.5 Occupational Hazards

Potential for occupational illness in this area is virtually nonexistent. The potential exposure to silicon in milling operations, removal of crystals, maintenance of growers, and melt pots, would most likely be minor. The most likely injuries would be cuts and bruises, burns, broken bones, sprains, and similar injuries during materials handling and maintenance.

A personal sampling survey of ingot growing operators performed at one plant during normal operation showed total particulate levels of 0.13 to 0.15 mg/m^3 (Briggs et al, 1980).

^{*} In the manpower estimates on which these values are based, the requirements for crystal pulling, cropping, and ingot grinding were lumped together. We have divided the manpower requirements evenly between crystal pulling and cropping/ ingot grinding.

During cleaning operations <0.06 to 0.15 mg/m³ total particulate was found (note: samplers were worn only half the time). Concentrations of respirable dust during cleaning operations were less than 0.07 mg/m³. Area samples taken near growers during cleaning showed total particulate levels from 0.14 to 0.18 mg/m³. Table 4.4-1 gives results of sampling surveys performed.

In the same plant where the survey was performed, solvents were used to clean the ingot growers. The solvent contained trichlorotrifluoroethane (TCF) and 1,1,1-trichloroethane (TCE). Personal samples taken during cleaning showed 1000 ppm TCF and 1.5 ppm TCE over a sampling period of about 42 minutes. Area samples taken during this cleaning showed 33 and 1.2 ppm of TCF and TCE, respectively. Workers performing this operation should be adequately protected from inhalation and dermal contact with the solvents.

4.4.6 Risk Determination

Production of the amount of single crystal silicon necessary for a 100 MW plant will require 511,140 employee-hours. Using the occupational injury, illness, and fatality statistics in Table 3.1-13 lost workdays and the number of fatalities can be determined for this operation. Approximately 402,480 hours will be contributed by technical occupations i.e., line operators, engineers, and technician; this effort will result in 85.3 lost workdays and approximately 4.0 x 10^{-3} fatalities. Another 56,160 hours will be contributed by inspecting occupations i.e., foreman and quality control engineers; this will result in 14.3 lost workdays and 7.9 x 10^{-4} fatalities. Maintenance activities associated with this process will contribute 52,500 hours of labor resulting in an estimated 17.0 lost workdays and 6.8 x 10^{-4} fatalities.

The single crystal silicon process will result in a total of 116.6 lost workdays including 5.47×10^{-3} fatalities for every 100 MW of crystalline silicon produced.

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		Conc	entration
Sample description	Sampling time (h)	mg/m ³	Estimated TWA, mg/m ³
Personal sample: Cz operator	6.37	0.26	-
Tulal SiO2 Crystalline α-quartz		0.06 <0.01	
Cz growing area: location near operator of sample No. 3	6.33	0.13	
Personal sample: Cz operator	7.0	0.25	
Cz growing area: location near operator in sample 18	7.0	0.15	
Personal sample: Cz operator during grower cleaning	0.45	<0.19	
Cz unit area sample: location near operator in sample 36	0.48	0.19	
Ingot growing operator; normal operation	6.45	0.15	
Wafer slicing operator; very little operation	2.23	0.06	
Wafer slicing operator; normal operation	3.08	0.74	0.45
Total SiO2 Crystalline α-quartz		0.22 <0.03	
Ingot growing operator; cleaning grower	1.45	0.15	
Same operator as at sample 10; respirable particulates	1.45	<0.07	
Area sample near crystal grower during cleaning	1.43	0.16	
Ingot growing operator; normal operation	7.58	0.13	
Total SiO ₂ Crystalline α-quartz		0.04 <0.01	

TABLE 4.4-1. PARTICULATES AND SILICA LEVELS IN CRYSTAL-GROWING AREA (Briggs et al, 1979)

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4.5 INGOT PROCESSING

4.5.1 Process Description

Ingot processing involves removing the tapered ends from the single-crystal silicon ingot, grinding the ingot to the desired diameter, slicing the ingot into wafers, and etching the wafers to remove saw damage.

4.5.2 Material Requirements

After the crystals are removed from the pullers, the tapered ends are cropped with an O.D. diamond saw, which results in a loss of about 21 percent or 2.5 Mg/MW. The quantity of waferable ingot left is 9.41 Mg/MW. Grinding this quantity to the diameter desired results in a loss of about 3 percent (D'Aiello, R.V., 1977) or 0.28 Mg/MW. Thus 9.13 Mg/MW of silicon is left for wafer sawing.

After grinding, the ingots are sliced into wafers with a multiwire slurry saw having 900 blades (Bickler et al, 1978). An assumed kerf loss of 45 percent from this operation is based on estimates by Gandel et al, RCA (D'Aiello, R.V., 1977), and Motorola (Coleman, et al, 1979); thus 5.02 Mg/MW of silicon wafers is produced, with 4.11 Mg/MW loss as kerf. The total amount of slurry required is estimated at 8.3 kg/kg of poly-Si produced; the slurry consists of equal parts of oil, clay, and SiC grit (Gandel, et al, 1977). Production of an estimated 12.87 Mg/MW of poly-Si would use 106.8 Mg/MW of slurry (35.6 Mg/MW each of oil, SiC grit, and clay).

After the sawing operation the wafers are etched to remove saw damage in a mixture of hot nitric (HNO_3) , hydrofluoric (HF), and acetic acids. According to one estimate about 0.003 inch is etched from each side of the wafer, resulting in a loss of about 38 percent by weight (D'Aiello, R.V., 1977). The quantity of silicon wafers after this etch is 3.11 Mg/MW, and 1.91 Mg/MW contaminates the acid mix.

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The proportions of the acid mix constituents are assumed to be about 3/1/1.5 of HNO_3 , HE, and acetic acid, respectively. If 0.7 gal of this mix is used to etch 50 wafers (D'Aiello et al, 1977), the total volume required to etch 1 MW of cells would be 11,513 gallons. The acid requirements therefore are 35.7 Mg/MW of HNO_3 , 7.8 Mg/MW of HF, and 12.5 Mg/MW of acetic acid.

4.5.3 Manpower Requirements

Manpower requirements for cropping and grinding are estimated to be 0.25 person per shift per crystal puller (D'Aiello, R.V., 1977). The operating requirements based on this estimate is about 88 persons, or 175,500 employee-hours per year. Requirements for maintenance, quality control, and supervision are estimated to be 0.075, 0.03, and 0.05 worker per shift per crystal puller,* respectively. The manpower requirements then are 52,650 employee-hours per year for maintenance, 21,060 employeehours per year for quality control, and 35,100 employee-hours per year for supervision. Total manpower requirements excluding maintenance would be about 231,660 employee-hours per year.

Manpower estimates for the sawing operation are based on assumptions that each saw slices 90 wafers/h (Bickler et al, 1978) and that one direct laborer could operate 15 saws (this is an average based on estimates from D'Aiello, 1977, and Coleman et al, 1979). Also, one maintenance worker was assigned to every 15 saws. Based on the above assumptions, a 6000-h/yr operating schedule, and three shifts/day, the manpower requirements are 11 saw operators/shift, or 66,000 employee-hours per year and 10.6 maintenance personnel per shift, or 63,600 employee-hours per year.

The etching operation is relatively automated. An operator loads the plastic cassette with wafers and the cassette is then automatically dipped into the etch tank. Etching is followed by sequential rinses and a final drying step. With a 7500 cell per hour throughput and with 0.5 direct operator per system, the

^{*} See Section 4.4.3.

manpower requirements are 6000 employee-hours per year. Maintenance requirements are estimated at 0.05 worker per station per shift, or about 600 employee-hours per year.

4.5.4 Emissions, Wastes, and Controls

Silicon is lost in several of the processes. About 2.5 Mg/MW is lost in cropping, 0.28 Mg/MW in grinding, 4.11 Mg/MW in wafer slicing, and 1.91 Mg/MW in wafer etching. Part of these losses can be reclaimed, and the rest can be sold to an industry requiring silicon of a lesser quality. An estimated 99 percent of the slurry used for the saws is recirculated, with 1 percent potential airborne emissions (Gandel et al, 1977). If 1 percent does become airborne, slurry emissions would be 1.07 Mg/MW for the hypothetical 100-MW plant. Acid wastes will require neutral-ization and disposal or recycling.

4.5.5 Occupational Hazards

Major hazards in this area are potential injuries such as cuts, sprains, back injuries, and eye injuries from handling of ingots, sawing, and grinding. Operators and maintenance personnel could be subject to chemical burns from acid exposure unless proper precautions are taken. Though there is some potential for inhalation of silicon dust in this area and from slurry emissions during wire sawing, these should not pose significant dangers. Inhalation of acid vapors from the hot acid etch tank is another potential hazard, but this is controllable with proper ventilation. Table 4.5-1 shows results of a sampling survey of workers involved with the cropping, rounding, grinding, etching, and wafering of ingots, and with etching of wafers (Briggs ct al, 1980). These data indicate that particulate and fume emissions from acid etch tanks should not pose great health threats.

4.5.6 Risk Determination

Ingot processing operations including the three distinct process steps i.e., cropping and grinding, sawing, and etching

		Conce	ntration
Sample description	Sampling time (h)	mg/m ³ (ppm)	Estimated TWA, mg/m ³ (ppm)
Personal sample: ingot-cropping operator	5.98	0.24	
Total SiO2 Crystalline α-quartz		0.06 <0.02	
Personal sample: ingot-cropping operator	7.25	0.34	
Personal sample: ingot-rounding operator	6.87	0.24	
Total SiO ₂ Crystalline α -quartz		0.05 <0.01	
Personal sample: ingot-grinding (flat operator)	7.02	0.22	
Total SiO ₂ Crystalline α-quartz		<0.01 <0.01	
Personal sample: ingot-etching operator	4.32	0.56 (0.81)	
Ingot etching area sample near above operator	1.63	3.45 (5.00)	
Personal sample: ingot-etching operator	3.65	0.58 (0.84)	
Same operator as above sample	3.57	0.68 (0.99)	0.63 (0.91)
Ingot etching area sample near Unit 63 - 5 ft high	3.35	0.86	
Area sample at same location as above sample	3.95	0.86 (1.25)	0.86 (1.25)
Personal sample: ingot-slicing operator	6.82	0.34	
Total SiO2 Crystalline α-quartz		<0.01 <0.01	
Personal sample: ingot-slicing operator	4.50	0.52	
Total SiO2 Crystalline α-quartz (continued)		0.11 <0.02	

TABLE 4.5-1. SUMMARY OF SAMPLING SURVEY IN INGOT PROCESSING AREA

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TABLE 4.5-1 (continued)

Sampling time mg/m	Estimated TWA, mg/m ³ (ppm)
Sample description (h) (ppm	
Ingot slicing area sample near above operator 6.92 0.36	
Wafer slicing operator; light operation 3.17 0.11	
Wafer slicing operator; normal operation 4.5 0.44	0.31
Total SiO2 0.10 Crystalline α-quartz <0.02	
Ingot growing operator during cleaning; sample worn half of time 1.33 <0.06	
Same operator as above sample; respirable particulates 1.32 <0.07	
Area sample near ingot grower during cleaning 1.37 0.14	
Grab samples of particulate coating in ingot grower walls -	
Total SiO ₂ a Crystalline α-quartz b	
Wafer-etching: area beside sample 40, HF bubbler 1.45 0.03 (0.04)
Personal sample: wafer-etching operator, HF filter 4.92 0.60 (0.87)
Wafer-etching area: midroom, HF filter 5.6 0.01 (0.01)
Wafer-etching area: beside above sample, Area 1, HF bubbler 1.0 0.07 (0.11)
Personal sample: wafer-etching operator, Area 2, HF filter 4.15 0.01 (0.01)
Wafer-etching area: between booths, Area 2, HF filter 5.37 <0.01 (<0.01	ý .
Wafer-etching area: beside above sample, Area 2, HF bubbler 1.98 <0.01 (continued))

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TABLE 4.5-1 (continued)

		Concentra	
Sample description	Sampling time (h)	mg/m ³ (ppm)	Estimated TWA, mg/m ³ (ppm)
Wafer-etching area: between booths, Area 2, HF bubbler	3.17	0.01 (0.02)	
Wafer-etching area: midroom, Area 1, HF bubbler	4.18	0.01 (0.01)	
Personal sample: wafer-etching operator, HF filter	6.12	0.03 (0.04)	
Personal sample: wafer-etching operator, HF filter	2.18	0.03 (0.04)	
Personal sample: remainder of shift for operator in above sample	3.98	0.35 (0.51)	0.24 (0.35)
Wafer-etching area: midroom HF filter	3.05	0.02 (0.03) ⁻	
Wafer-etching area: continuation of above sample	3.95	0.01 (0.02)	0.01 (0.02)
Wafer-etching area sample: midroom - NO NO2	2.0	0.16 (0.13) 0.15 (0.09)	
Personal sample: wafer-etching operator - NO NO2	6.85	0.10 (0.08) 0.09 (0.05)	
Personal sample: wafer-etching operator - NO NO ₂	5.1	0.17 (0.14) 0.11 (0.06)	
Wafer-etching area sample: midroom - NO NO ₂	5.0	0.10 (0.08) 0.10 (0.05)	

^a Concentration equivalent to 16 percent of sample.

 $^{\rm b}$ Concentration equivalent to <1 percent of sample.

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requires a total of 420,510 employee hours. Using the occupational injury, illness, and fatality statistics in Table 3.1-13 lost workdays and the number of fatalities can be determined for this operation. The total labor figure has been estimated to include 241,500 hours contributed by material abrading and polishing occupations i.e., line operators. This level of effort should result in approximately 47.8 lost workdays. Virtually no fatalities are expected to result from this activities. Inspecting occupations i.e., supervisors and quality control engineers, will contribute 56,160 hours resulting in 14.3 lost workdays and 7.9 x 10^{-4} fatalities. Metal plating occupations i.e., etching, will perform 6000 hours of labor resulting in 2.1 lost workdays and 1.4×10^{-4} fatalities. Maintenance occupations are expected to contribute 116,850 hours resulting in 37.7 lost workdays and 1.5×10^{-3} fatalities.

The ingot processing activities associated with the production of a 100 MW/yr plant are expected to result in a total of 101.9 lost workdays including 2.43 x 10^{-3} fatalities.

4.6 JUNCTION FORMATION

4.6.1 Process Description

Junction formation is accomplished in a four-tube diffusion furnace. Incoming wafers are manually loaded into silicon boats and automatically loaded into the furnace. After the diffusion cycle is complete, the boats are automatically unloaded from the furnace and the wafers transferred to another cassette by means of a clamshell unloader and cassette stacker. The cassettes are transferred to the next step. A throughput rate of 2000 wafers/h is assumed in calculations for this process (D'Aiello, R.V., 1977).

4.6.2 Materials Requirements

The calculations presented here are based on the use of phosphorous in the form of phosphorous oxychloride $(POCl_3)$ as

the diffusion gas. At a doping density of 15 x 10^{16} atoms/cm³, the quantity of phosphorous required is 10.3 g/MW for 100 MW of cells. The amount of phosphorous oxychloride (POCl₃) required to achieve this doping density would be 50.94 g/MW.

4.6.3 Manpower Requirements

With 0.25 operator per furnace, it is calculated that two direct laborers per shift or 12,000 employee-hours would be needed to process 100 MW of cells. With a requirement of 0.15 maintenance person per furnace, a total of 1.05 maintenance persons per shift, or 6300 employee-hours per year is required to maintain the furnaces. Other direct labor requirements are 0.025, 0.1, and 0.05 worker per shift per furnace for support engineers, machine attendants, and foremen, respectively (D'Aiello, et al 1977). On this basis it is calculated that 1050 employee-hours per year would be required for support engineers, 4200 for machine attendants, and 2100 for supervisors. A total of 19,350 employee-hours per year would be required, excluding maintenance.

4.6.4 Emissions, Wastes, and Controls

Potential exhaust emissions from use of phosphorous oxychloride (POCl₃) include HCl, P_2O_5 , and Cl_2 . A scrubber may be used to remove any corrosive gases formed. The chances of exhaust system defects are increased by the formation of the corrosive gases. An automatic shutoff of dopant gas to the furnace should be incorporated into the system in the event that ventilation fails. An alarm could also be installed to warn of high levels of dopant gas in the workplace. If the gas tanks are kept isolated in a well-ventilated room, this should not be a problem.

4.6.5 Occupational Hazards

Chronic or acute exposure to $POCl_3$ and breakdown products is the major hazard to workers in this operation. Because of the small amounts used it is unlikely that emissions into the workplace would be significant. Isolation of the gases in a well-ventilated room should also prevent a major accidential exposure. Leaks from piping could still be a problem, however.

Although some residual deposits may occur inside furnaces, piping, etc., these should not pose significant health threats to maintenance personnel.

Other potential hazards may be burns from the furnace or from heated wafers, and injuries caused in material handling.

4.6.6 Risk Determination

Junction formation requires a total of 25,650 employeehours of work effort. Using the occupational injury, illness, and fatality statistics in Table 3.1-13 lost workdays and the number of fatalities can be determined for this operation. The technical occupations i.e., line operators, machine attendants, and engineers contribute 17,250 hours to this operation. This activity will result in 3.6 lost workdays and approximately 1.7 $x 10^{-4}$ fatalities. The inspecting occupations, primarily supervisors, contribute 2,100 hours, resulting in 0.5 lost workdays and approximately 2.9×10^{-5} fatalities. The maintenance required for this operation is 6,300 hours which should result in 2.0 lost workdays and 8.2 x 10^{-5} fatalities. The entire operation will result in a total of 6.1 lost workdays including 2.81 x 10^{-4} fatalities.

4.7 PERIMETER GRIND

4.7.1 Process Description

A semi-automatic wafer edge grinder is used in this process. The contour grinder described is a five-track machine that automatically extracts 5 wafers from a 25-wafer cassette initially loaded by the operator (Headway Research, Inc., Product Information). The machine automatically centers, grinds, rinses, and spins dry the wafers and then loads them into a cassette for transfer to the next operation. Grinding is accomplished with a flexible, plastic, diamond-impregnated disc. Water is automatically dispensed during contouring for lubrication and after contouring to rinse silicon particles from the wafers. Water and particulates exit through a waste drain.

4.7.2 Material Requirements

The only material requirements are for replacement of grinding discs.

4.7.3 Manpower Requirements

At a labor rate of 0.25 direct laborer per machine, it is calculated that 2 operators/shift would be required, or 12,000 employee-hours per year, for processing 100 MW of cells.

Other direct labor requirements are 0.01 workers per shift per grinder for support engineers, 0.05 for machine attendants, and 0.05 for foremen (D'Aiello, R.V., 1977). No maintenance requirements are given, however, an estimate of 720 man-hours will be used. On the basis of the above estimates, manpower requirements for support engineers, machine attendants, and foremen are 360, 1800, and 1800 employee-hours per year, respectively.

4.7.4 Emissions, Wastes, and Controls

The only waste generated is the silicon dust, with minute amounts of phosphorous and boron. This waste is removed with water sprays. On the assumption that 5μ m is removed from each wafer, a total of 0.61 kg/MW or 61 kg/yr of dust would be generated. No special treatment would be needed for this small quantity.

Silicon dust in the workplace is minimized by the water sprays and the cover. Periodic cleaning of the grinders should not require special precautions.

4.7.5 Occupational Hazards

Because this operation is almost totally automated and is treated with water sprays to remove dust, hazards to the worker

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are minimal. Only minor injuries from material handling (loading and unloading machines) or maintenance would be expected to occur.

Several safety features are applied in the contour grinding process. Explosion-proof motors are used. A cover over the holding chucks protects against flying particles in case a wafer should break during grinding. Wafers are held to the chuck by vacuum, and a fail-safe vacuum interlock system is used to shutdown the motor if a substrate is not on the chuck (Headway Research, Inc., Product Information).

4.7.6 Risk Determination

Perimeter grinding requires an effort of 16,680 employee-Using the occupational injury, illness, and fatality hours. statistics in Table 3.1-13 lost workdays and the number of fatalities can be determined for this operation. Material abrading and polishing occupations i.e., line operators and machine attendants, contribute 13,800 hours to the labor total resulting in 2.7 lost workdays. No fatalities should result from these activities. Technical occupations, primarily engineers, contribute 360 hours resulting in 0.1 lost workdays and 3.6 x 10^{-6} fatalities. Perimeter grinding requires 1,800 hours of foreman supervision thus inspecting occupations will experience 0.5 lost workdays and approximately 2.5 x 10^{-5} fatalities. Maintenance for the grinding operations require 720 hours of This activity will result in an estimated 0.2 lost effort. workdays and 9.4 x 10^{-6} fatalities. The entire operation will result in a total of 3.5 lost workdays including 3.8 x 10^{-5} fatalities.

4.8 ETCHING

4.8.1 Process Description

In this process HF or HF/HNO_3 acids are used to remove the SiO_2 layer formed during the diffusion process. A plastic cassette containing the wafers is manually loaded into the etch

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tank. The cassette is automatically transferred to three successive rinse tanks and a hot air dryer (D'Aiello, R.V., 1977). The cassette is then ready for transfer to the next station. Throughput of this operation is 6000 wafers per hour (D'Aiello, R.V., 1977 and JPL SAMICS Model Output Data, 1980).

4.8.2 Material Requirements

Acid requirements are estimated for HF acid and for a HF/HNO_3 mixture. When it is assumed that 0.098 liter of HF is needed to etch the oxide layer from 1000 wafers (D'Aiello, R.V., 1977), the acid requirement is 80.6 liters/MW or 79.6 kg/MW for 100 MW of cells.

When it is assumed that 6.33 gm HF and 4.2 gm HNO_3 are needed for every kilogram of poly-Si produced (Gandel et al, 1977) the acid requirements are 81.1 kg HF/MW (82.17 liter/MW), and 53.8 kg HNO_3/MW (35.8 liter/MW).

4.8.3 Manpower Requirements

At a labor rate of 0.5 operator per station, a total of 2 operators/shift or 12,000 employee-hours per year would be required to process 100 MW of cells. At a maintenance labor rate of 0.15 worker per station per shift the maintenance requirement is 2700 employee-hours per year. At a labor rate of 0.05 worker per station per shift foremen requirements are 900 employeehours per year. Excluding maintenance, the direct labor requirements are 12,900 employee-hours per year.

4.8.4 Emissions, Wastes, and Controls

According to material estimates, recycling or disposal will be required for 8060 liters of HF or 8217 liters of HF and 3580 liters of HNO_3 . Also during the etching process silicon tetrafluoride (SiF₄) gas is released at a rate of 0.11 kg/kg of poly-Si (Gandel et al, 1977). Processing of 12.87 MT/MW of poly-Si would release about 1.42 MT/MW or 141,570 kg/yr of SiF₄. A ventilation hood located over the tank removes the vapors to a lime (Ca(OH)₂) scrubber where calcium fluoride (CaF) and various

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other waste products are formed and routed to a neutralization pond (Gandel, et al, 1977). Because the vapors are corrosive, it is essential to use the proper materials for construction of the ventilation system. A breach in the integrity of the system could result in vapor emissions into the workplace air.

4.8.5 Occupational Hazards

Leakage of SiF_4 into the workplace could occur if ventilation is inadequate or if there are leaks in the system. Because SiF_4 has a pungent odor, large leaks would be detected quickly so that workers are unlikely to be exposed for any great duration. Continuous low-level exposures could possibly go unnoticed, however.

Another potential hazard is inhalation of fumes generated by the hot acid etch tanks. If the survey results in Table 4.5-1 are indicative of most other etching operations, such exposures should be minimal.

Acid burns would most likely account for many injuries occurring in this operation. These may be minimized by use of tank shields and protective clothing such as aprons, gloves, and full-shield face masks.

4.8.6 Risk Determination

Etching operations require a total of 15,600 employee-hours of labor. Using the occupation injury, illness, and fatality statistics in Table 3.1-13 lost workdays and the number of fatalities can be determined for this operation. The metal plating occupations i.e, the line operators, contribute 12,000 hours which are estimated to result in 4.2 lost workdays and 2.9 x 10^{-4} fatalities. Inspecting occupation in the person of foremen will contribute 900 hours, resulting in 0.2 lost workdays and approximately 1.3 x 10^{-5} fatalities. The maintenance effort for the etching operations will constitute 2,700 employee-hours resulting in 0.9 lost workdays and 3.5 x 10^{-5} fatalities. A total of 5.3 lost workdays including 3.4 x 10^{-4} fatalities will result from the etching operation.

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4.9 METALLIZATION

4.9.1 Process Description The first step in metallization by electroless plating is to apply a resist through a mask that defines the metallization pattern. The wafers are automatically loaded into the printer, where a squeegee containing the photoresist is passed over the stainless steel or synthetic fiber screen to print the pattern. The wafer is then exposed to a light source to fix the resist. The wafers are automatically loaded into a cassette and transferred to the plating station. There the cassettes are manually loaded onto a walking beam mechanism that automatically dips the wafers sequentially into tanks of plating solution, acetone to remove the resist, and a water rinse; they are finally conveyed to a dryer (Wihl, M., 1978 and Coleman et al, 1979). The wafers are then conveyed through multiple-tube furnaces, where they are sintered at about $500\frac{1}{4}$ C in a nitrogen atmosphere (Coleman, et al, 1979). The cells are then transferred to the solder coating operation, where they are automatically dipped in a flux, preheated in an oven to prevent temperature shock and breakage, dipped in the solder, cleaned (aqueous), rinsed, and dried.

4.9.2 Materials Requirements

The primary constituents of the nickel plating solution are nickel, sodium hypophosphite, and ammonium hydroxide (Wihl, M., 1978). According to one estimate, 1 liter of nickel plating solution could plate 500 4-inch wafers (Wihl, M., 1978). About 1645 liters/MW of plating solution would be needed for 100 MW of cells. If the largest portion of the plating solution is assumed to be nickel hypophosphite, and the density is 1.82 g/cm^3 , about 2.99 Mg/MW of plating solution would be required.

If it is assumed that the cost of acetone per wafer is 0.001 (Wihl, M., 1978) and the cost per gallon is about 1.15, about 8.7×10^{-4} gal or 3.3×10^{-3} liter would be required to remove the photoresist from each wafer. This would come to about 2714 liters/MW or 2.14 Mg/MW.

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The flux to be used is zinc chloride. No material estimates were made for the flux.

The solder is a 60/40 lead/tin mixture. An estimate by Solarex (Wihl, M., 1978) is that 1 cm³ of solder can coat six cells. Based on this assumption the solder requirement is 137.1 l/MW. At a density of about 9.72 g/cm³ for the solder, 1.3 Mg/MW is needed to coat 100 MW of cells.

A urethane varnish made thixotropic (i.e., it liquefies) under pressure and becomes firm when not) with titanium dioxide (TiO₂) is used as the resist (Wihl, M., 1978). At an estimated rate of 100 wafers per liter, about 822.4 1/MW is needed for production of 100 MW of cells.

4.9.3 Manpower Requirements

Manpower estimates are based on throughputs of 7200 wafers/h for the electroless nickel station, and for the solder coat solution and on one operator each per electroless nickel station and solder coating station (Wihl, M., 1978 and Coleman et al, 1979). A total of 2 workers/shift or 12,000 employeehours per year each for the electroless plate and solder coat operations would be required for production of 100 MW of cells. With allocation of 6 and 1 percent for maintenance personnel and foremen, the respective requirements would be 720 and 120 employee-hours per year.

4.9.4 Emissions, Wastes, and Controls

Estimates show that about 822.4 liters/MW of the masking ink (urethane varnish/TiO₂) will be used. If masking is done by a negative silkscreening technique, approximately 90 percent of the cell area will be masked, leaving 10 percent for metallization. Therefore, about 740.2 liters/MW will be removed with the 2714 liters/MW of acetone and must be disposed of. It has been suggested that a recoverable solvent might be substituted for acetone to reduce material consumption. Electroless plating is a very efficient operation [>90 percent (Watts et al, 1979)]. Losses would occur only through dripping or changing of the bath. In an ammoniacal solution, however, ammonia (NH_3) may be liberated from the heated bath. Therefore a ventilation hood will be required to remove any NH_3 that evolves and prevent contamination of the workplace air. Ventilation will also be required over the acetone tank to prevent the escape of fumes into the workplace.

Like electroless plating, solder dipping is ≥ 90 percent efficient (Watts et al, 1979). Because the solder adheres only to the metal surfaces, losses occur only from dripping or replacement of solder. The solder pot must be ventilated to remove any fumes generated. The acid flux bath also must be ventilated because hazardous chloride or formaldehyde fumes may be released.

4.9.5 Occupational Hazards

One hazard associated with this operation is potential exposure to nickel and/or nickel compounds (i.e. nickel hypophosphite). This would probably be dermal exposure, since it is unlikely that a significant amount of nickel fumes would be released at the plating bath temperature (93-95°C).

Periodic cleaning and maintenance of plating tanks may be especially hazardous unless precautions are taken. The use of proper protective clothing should, however, prevent significant exposures. Covering of plating tanks will also significantly reduce potential for accidental exposures.

Other potential hazards in the nickel plating operation are volatile components of the masking ink and the cleaning agent, which in this example is acetone. Fumes from these materials would be easily controlled with proper ventilation. Proper protective clothing should prevent dermal exposure to these materials.

A cover on the plating tank causes condensation and can reduce emissions of NH_3 significantly; in addition, local ventilation should be installed in this area to remove any NH_3 escaping.

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Because the solder is 60 percent lead, precautions must be taken to protect workers from lead oxide and suboxide fumes. Maintenance workers repairing or cleaning the solder pot must be especially cautious.

The flux may emit fumes that can be irritating to the eyes and mucous membranes. Zinc chloride is a severe pulmonary irritant and is corrosive to the skin. Adequate ventilation and protective clothing will also be required for this operation.

4.9.6 Risk Determination

Based upon the number of wafers to be produced by a 100 MW/yr plant the total labor requirement for metallization was determined to be 25,680 employee-hours. Using the occupation injury, illness, and fatality statistics in Table 3.1-13 lost workdays and the number of fatalities can be determined for this operation. The electroless plating, photoresisting, and solder coating operations will require 24,000 hours of labor. These employee-hours will be contributed by individuals in the metal plating occupations. This active will result in 8.4 lost workdays and 5.8 x 10^{-4} fatalities. The inspecting occupations i.e., foremen will contribute 240 hours resulting in 0.1 lost workdays and 3.4 x 10^{-6} fatalities. Maintenance for the metallization processes will require 1440 hours of labor, resulting in 0.5 lost workdays and 1.9 x 10^{-5} fatalities. A total of 9.0 lost workdays including 6.0 x 10^{-4} fatalities are expected to occur during the metallization process.

4.10 ANTIREFLECTIVE COATING

4.10.1 Process Description

In this process an eight-tube diffusion module is used for the chemical vapor deposition (CVD) of silicon nitride (Si_3N_4) using SiH_2Cl_2 and NH_3 as the deposition gases (Coleman et al, 1979). The process is fairly automated, and the module needs 1 operator. A throughput of 2000 wafers/h has been projected for this operation (Coleman et al, 1979).

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4.10.2 Material Requirements

At flow rates of 10 cm³/min for SiH₂Cl₂ and 15 cm³/min for NH₃, the deposited coating of Si₃N₄ is 700 Å thick (Coleman et al, 1979). Total SiH₂Cl₂ required is 1.27 ft³/MW per diffusion tube or 71.12 ft³/MW, and for NH₃ 1.91 ft³/MW per diffusion tube or 106.96 ft³/MW. The total quantity of Si₃N₄ deposited would be 1.6 kg/MW. Since the CVD process is reported to be a nominal 65 percent efficient (Watts et al, 1979), a theoretical total of 2.5 kg/MW would be formed. Of the total unused portion of the materials about 50 percent is reported to deposit on the reactor walls and 50 percent is lost to the exhaust (Watts et al, 1977). On the basis of these estimates, about 12.80 ft³/MW of SiH₂Cl₂ and 19.25 ft³/MW of NH₃ would be exhausted and about 0.45 kg/MT of Si₃N₄ would be deposited on the reactor walls. Therefore a total of 2.05 kg/MW Si₃N₄ is formed, and the remaining 0.45 kg/MW of the theoretical amount is lost as SiH₂Cl₂ and NH₃.

4.10.3 Manpower Requirements

Processing the number of cells needed to generate 100 MW of power requires a total of seven diffusion tube modules (eight tubes for each module). With 1 operator/machine/shift, a total of 21 operators per day or 42,000 employee-hours per year would be required. With maintenance and supervisory requirements of 6 percent and 1 percent of this total, the annual requirements for foremen and maintenance personnel are 2520 and 420 employeehours, respectively.

4.10.4 Emissions, Wastes, and Controls

A small scrubber may be required to treat the gases evolved (about 12.44 CF/MW SiH_2Cl_2 and 18.72 CF/MW NH_3) before they are discharged into the atmosphere. Also formation and condensation of HCl in the ventilation system should be prevented, to eliminate leaks that may cause discharge of exhaust into the workplace air.

4.10.5 Occupational Hazards

Periodic cleaning of the reactor walls may be required to remove accumulated Si_3N_4 deposits. Though Si_3N_4 is reportedly stable and relatively innocuous, details on its toxicity are scarce and precautions should be taken to protect workers. Since this operation takes place under vacuum, emissions of SiH_2Cl_2 (as HCl), and NH_3 into the workplace should be minimal. Because this operation requires minimal operator interaction, injuries should not be a significant factor.

4.10.6 Risk Determination

Antireflective coating requires 44,940 employee-hours of labor. Using the occupational injury, illness, and fatality statistics in Table 3.1-13 lost workdays and the number of fatalities can be determined for this operation. Technical occupations in the form of line operators contribute 42,000 hours to the total labor requirement resulting in 8.9 lost workdays and 4.2 x 10^{-4} fatalities. Inspecting occupations i.e., foremen, contribute 420 hours of labor resulting in 0.1 lost workdays and 5.9 x 10^{-6} fatalities. Maintenance for the antireflective coating constitutes 2,520 hours resulting in 0.8 lost workdays and 3.3 x 10^{-5} fatalities. The antireflective coating operations will result in a total of 9.8 lost workdays including 4.6 x 10^{-4} fatalities.

4.11 CELL TESTING

4.11.1 Process Description

Cassettes are manually loaded into the machine. Wafers are then automatically aligned and fed to the illumination source, which simulates sunlight for cell testing. Cells are then sorted into cassettes according to performance. Cassettes are removed by an operator and transferred to the next operation. A throughput of 720 cells/hr is estimated for this process.

4.11.2 Material Requirements

No materials are used during this process step.

4.11.3 Manpower Requirements

At a manpower rate of 1 operator/station/shift (Coleman et al, 1979), a total of 57 operators would be required, or 114,000 employee-hours per year. Allocations of 6 and 1 percent of this total give requirements of 6840 employee-hours per year for maintenance personnel and 1140 for a foreman.

4.11.4 Emissions, Wastes, and Controls

The only potential emissions from this operation would be generation of ozone and nitrogen oxides from the light source. This is expected to be minimal and would not result in significant accumulation as long as room ventilation is adequate.

4.11.5 Occupational Hazards

The only potentially hazardous exposure would be to small amounts of ozone and/or nitrogen oxides that could be generated during the sun simulation test. This exposure should be minor and easily controlled.

Minor injuries may occur during handling of cassettes and wafers while the operator loads and unloads test machines.

4.11.6 Risk Determination

Cell testing requires 121,980 employee-hours of labor. Using the occupation injury, illness, and fatality statistics in Table 3.1-13 lost workdays and the number of fatalities can be determined for this operation. The majority of these hours will be contributed by the assembling occupations i.e., line testers. The total labor requirement has been estimated to be approximately 114,000 hours. This level of activity is expected to produce 26.0 lost workdays and 1.4 x 10^{-3} fatalities. Inspecting occupations i.e., foremen, will contribute 1,140 hours of labor resulting in 0.3 lost workdays and 1.6 x 10^{-5} fatalities. Maintenance requirements for cell testing operations constitute 6,840 hours. This level of activity will result in 2.2 lost workdays and 8.9 x 10^{-5} fatalities. Cell testing activities will result in a total of 28.5 lost workdays including 1.5 x 10^{-3} fatalities.

4.12 INTERCONNECTION

4.12.1 Process Description

Interconnection will consist of several process steps including cell alignment, interconnect placement, string assembly, solder reflow, and array or module interconnect. In the first step interconnect tabs are soldered onto the back of the cells and cut to length. The cells are then automatically flipped over with a vacuum chuck, and a solder paste dot is applied to the front of each cell. The cells are then aligned, the interconnect tab is positioned on the front contact pad, and the assembly consisting of 12 cells in series is fed to the solder reflow oven. All of these processes are done automatically. The string assemblies are then tested and transferred to the array assembly area, where twelve, 12-cell strings are positioned into an array tray. Interconnect tabs are placed on interconnect buses and soldered. The throughput for interconnect tab placement and alignment into strings is 1200 cells/h; for solder reflow, 2400 cells/h; and for array assembly, 3600 cells/h (D'Aiello, R.V., 1977).

4.12.2 Materials Requirements

If it is assumed that 2-ounce copper interconnects are used (Lockhead Missles and Space Company, Inc., 1978) and 144 interconnect tabs are needed per module, a total of 46.6 Mg/MW of copper is required for the interconnects.

Although the amount of solder used has not been estimated, a 60/40 lead/tin solder will be applied to the interconnects prior to reflow soldering.

4.12.3 Manpower Requirements

For interconnect tab application and cell alignment 1200 cells are processed per hour, by 0.167 worker and 0.1 maintenance worker/station/shift. On this basis requirements are 2 operators/ shift or 12,000 employee-hours per year, plus 1.2 maintenance workers/shift or 7200 employee-hours per year. Also 0.333 rework operator/station/shift is required for these first operations. These requirements total about 23,220 employeehours per year.

For the solder reflow station assumptions include a throughput of 2400 cells/h processed by, 1 operator and 0.1 maintenance worker/station/shift. Total manpower requirements for this station would be 6 operators/shift or 36,000 employee-hours per year and 0.6 maintenance worker/shift or 3600 employee-hours per year.

For the panel interconnect the assumptions are a throughput of 3600 cells/h, and a maintenance requirement of 0.1 worker/ station/shift. No direct labor is required. A total of 0.4 maintenance worker/shift or 2400 employee-hours per year is required. About 7200 employee-hours per year is required for foremen in this entire area.

4.12.4 Emissions, Wastes, and Controls

The major potential emission from this process will be in solder reflow operation, where fumes from the lead-tin solder might be released. Adequate ventilation will be required to remove any fumes generated from the reflow oven.

4.12.5 Occupational Hazards

The primary occupational hazard in this process is exposure to lead fumes. It is doubtful that emissions from the reflow ovens will be significant, however, since oven temperatures are only high enough to remelt the solder, not to vaporize it to any significant degree. Table 4.12-1 shows results of a sampling survey for lead in a cell interconnection process (Briggs et al,

· · · · · · · · · · · · · · · · · · ·	Sampling ' time (h)	Concentration .	
Sample description		µ g∕ m ³	Estimated TWA, $\mu g/m^3$
 Soldering operator; normal operation 	5.87	<1.3	
Area sample in interconnection central work area	3.17	10	
Soldering operator; normal operation	3.10	7.4	
Area sample in interconnection central work area	7.67	1.1	

TABLE 4.12-1. SAMPLING FOR LEAD FROM CELL INTERCONNECTION SOLDERING

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1980). The operations summarized in the table were done manually with soldering irons. Although the potential for worker exposure probably would be greater in the manual operation than in solder reflow, all exposures in this survey were well below the 50 μ g/m³ level set by NIOSH.

Material handling by workers is minimal for the interconnection sequence described, and physical injuries would be fewer than in a more manually oriented operation. The most likely injury during this operation would be burns from accidental contact with ovens, hot cassettes, or wafers.

4.12.6 <u>Risk Determination</u>

The interconnection procedure comprises three separate operations: tab application and cell alignment, solder reflow, and panel interconnection. The total labor requirements for the interconnection procedure is estimated to be 72,420 employee-Using the occupational injury, illness, and fatality hours. statistics in Table 3.1-13 lost workdays and the number of fatalities can be determined for this operation. The assembling operations i.e., line operators, and rework operators account for 52,020 hours of labor resulting in 11.9 lost workdays including 6.2 x 10⁻⁴ fatalities. Inspecting occupations i.e., foremen, account for 7,200 hours of labor resulting in 1.8 lost workdays including 1.0 x 10^{-4} fatalities. Maintenance activities for the interconnection procedures requires 13,200 hours of labor, resulting in 4.3 lost workdays and 1.7 x 10^{-4} fatalities. The interconnection procedures will cause a total of 18.0 lost workdays including 8.9 x 10^{-4} fatalities.

4.13 ENCAPSULATION

4.13.1 Process Description

Washed and dried glass sheets are conveyed to an air table, where a sheet of ethylene vinyl acetate (EVA) is applied. With the EVA side up, the cell array, held by a vacuum, is aligned with the EVA/glass sheets and the assembly placed on the EVA. A second sheet of EVA and a sheet of Mylar are then placed on top of the array and transferred to an autoclave, where heat under a vacuum is applied to bond the assembly together. The assembly is then transferred to a framing operation. An aluminum frame is used. A throughput of 7200 cells/h is assumed for the glass/ EVA/Mylar assembly and final assembly. A throughput of 21,600 cells/h is assumed for the frame assembly station (D'Aiello, R.V., 1977).

4.13.2 Materials Requirements

It is assumed that the module contains 144 cells and measures 50 inches square. Other assumptions are that the EVA layer is 0.02 inch thick and weighs 0.048 g/cm²; the Mylar is 0.008 inch thick, and the glass weighs 2.51 lb/ft² (Watts, et al, 1979, and, Lockhead Missles and Space Company, Inc., 1978). Material requirements based on these figures are 4.42 Mg/MW of EVA, 1.87 m³/MW of Mylar, and 112.85 Mg/MW of glass.

4.13.3 Manpower Requirements

At throughputs of 7200 cells/h for the glass/EVA/Mylar operation and final assembly stations, and 21,600 cells/h for the frame assembly operation, it is estimated that 4 workers are required per glass/EVA/Mylar station per shift, 1 worker/frame system/shift, 4 workers/final assembly station, and 0.1 maintenance worker/shift for each of these stations. Calculations indicate that 8 workers/shift or 48,000 employee-hours per year direct labor and 0.2 maintenance worker/shift or 1200 employeehours per year are needed for each the glass/EVA/Mylar and final frame assembly operations, and 1 worker/shift or 6000 employeehours per year direct labor and 0.3 maintenance worker or 600 employee-hours per year for the framing operation. Foreman requirements are 0.1 persons/shift/maintenance or 1200 employeehours per year. In summary, 102,000 employee-hours per year are required for operation, 3000 for maintenance, and 1200 for supervision.

4.13.4 Emissions, Wastes, and Controls

The only potentially major emission from these operations are fumes generated during the autoclave operation in which the EVA is heated to seal the module. Potential emissions from heating are acetic acid, CO_2 , CO, and monomer constituents. If significant amounts of fumes are generated, an organics filter of some kind may be needed to treat the gas before discharge to the atmosphere.

4.13.5 Occupational Hazards

The primary hazards for workers in this area would be inhalation of fumes that could be given off in the sandwiching operation. Since this operation will be under a slight vacuum, emissions to the work environment should be minimal. Burns from contact with equipment are a more prominent hazard. Precautions such as safety barriers isolating workers from these hot surfaces should suffice to prevent worker contact.

Note also that EVA is a copolymer of polyethylene and vinyl chloride. Very little information is available on EVA, but vinyl chloride is a known human carcinogen and is a fire and explosion hazard. Though the polymer is probably more stable, vinyl chloride fumes could be a potential hazard.

4.13.6 Risk Determination

Encapsulation requires 106,200 hours of labor. Using the occupational injury, illness, and fatality statistics in Table 3.1-13 lost workdays and the number of fatalities can be determined for this operation. The assembling occupations in the form of line operators contribute 102,000 hours resulting in 23.2 lost workdays and 1.2 x 10^{-3} fatalities. Inspecting occupations i.e., foremen account for 1,200 hours of labor resulting in 0.3 lost workdays and 1.7 x 10^{-5} fatalities. Maintenance requires 3,000 hours resulting in 1.0 lost workdays and 3.9 x 10^{-5} fatalities. The entire encapsulation procedure is expected to result in 24.5 lost workdays including 1.3 x 10^{-3} fatalities.

4.14 MODULE TEST

4.14.1 Process Description

Modules are automatically indexed into the test area where a pulsed lamp system which simulates sunlight is used to test the modules.

4.14.2 Material Requirements

No materials will be required for this process.

4.14.3 Manpower Requirements

Based on throughput rates of 240 modules/hour and one operator per test station it was calculated that one test station, and therefore one operator per shift or 6000 employeehours per year would be needed. If maintenance and foreman requirements are assumed to be 6 and 1 percent, respectively of operator requirements, then maintenance requirements are 360 employee-hours per year and foreman requirements are 60 employee-hours per year.

4.14.4 Emissions, Wastes, and Controls

Except for potential generation of a small amount of nitrogen oxides and ozones this process will be clean. The small amount of these gases generated should have no environmental impact.

4.14.5 Occupational Hazards

As mentioned above small amounts of nitrogen oxides and ozone could be generated from the sun simulation lamp used. These should be easily removed by adequate room ventilation, thus preventing or minimizing any worker exposure.

4.14.6 Risk Determination

The module testing procedure will require a total of 6,420 hours of labor. The inspecting occupations will contribute 6,060 employee-hours resulting in 1.5 lost workdays and 7.6 x 10^{-5} fatalities. Maintenance activities for the module testing

operation requires 360 employee-hours resulting in 0.1 lost workdays and 4.7 x 10^{-6} fatalities. The module testing procedure will cause a total of 1.6 lost workdays and 8.0 x 10^{-5} fatalities.

4.15 DATA SUMMARY

Presented in Table 4.15-1 is a summary of materials, emissions, and wastes for the hypothetical 100 MW/yr manufacturing plant. The manpower and risk data for the Si-I process are presented in Section 8.

Process type	Material	Material requirements	Emissions and wastes
<u>Mining and refining of</u> <u>quartz</u>	Sand and gravel to produce 3.11 Mg/MW of single-crystal sili- con cells Sand and gravel mined in 1985 Total dust Respirable dust Respirable free silica	471.2 Mg/M₩ 1.06 5illion tons	16.34 to 23.5 kg/MW 1.70 kg/MW 0.289 kg/MW
<u>Metallurgical silicon</u> production	98% SiO ₂ Coke MG-Si Coke particulate SiO particulate Ash particulate Fugitive particulates (Estimate 2) MG-Si milling loss	245.4 Mg/MW 94.2 Mg/MW 89.0 Mg/MW 1)	0.188 Mg/MW 35.33 Mg/MW 1.15 Mg/MW 28.1 Mg/MW 1.8 Mg/MW
Silicon purification	MG-Si feed to chlorinator HCl for reaction SiHCl3 feed to poly- crystalline silicon deposition chamber H2 to chamber Poly-Si produced Loss due to crushing	86.3 Mg/MW 375 Mg/MW 522.1 Mg/MW 96.4 Mg/MW 12.87 Mg/MW	0.06 Mg/MW

TABLE 4.15-1. MATERIAL AND WASTE SUMMARY FOR SILICON-I PROCESS

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TABLE 4.15-1. (continued)

Process type	Material	Material requirements	Emissions and wastes
Single crystal pulling	Boron for doping BCl ₃ for doping Poly-Si Crucible waste	2.69 g/MW 31.1 g/MW	0.9 Mg/MW
<u>Ingot processing</u>	Loss due to tapering Loss due to grinding Silicon for wafer sawing Kerf loss Slurry Contamination in acid mix (Silicon) Acid for etching ° Nitric ° Hydrofluoric ° Acetic Slurry (air emission losses)	9.31 Mg/MW 106.8 Mg/MW 35.7 Mg/MW 7.8 Mg/MW 12.5 Mg/MW	2.5 Mg/MW 0.28 Mg/MW 4.11 Mg/MW 105.7 Mg/MW 1.91 Mg/MW 35.7 Mg/MW 35.7 Mg/MW 7.8 Mg/MW 12.5 Mg/MW 1.07 Mg/MW
Junction formation	Phosphorous for doping POCl ₃ for doping	10.3 g/MW 50.94 g/MW	
Perimeter grind	Silicon dust		0.61 kg/MW
<u>Etching</u>	Acid when HF is used Acid when HF/HNO ₃ mixture is used ° HF ° HNO ₃ SiF4	79.6 kg/MW 81.1 kg/MW 53.8 kg/MW	79.6 kg/MW 81.1 kg/MW 53.8 kg/MW 1.42 Mg/MW
<u>Metallization</u>	Plating solution Acetone Solder Urethane varnish	2.99 Mg/MW 2.14 Mg/MW 1.3 Mg/MW 822.4 1/MW	2.99 Mg/MW 2.14 Mg/MW

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(continued)

Process type	Material	. Material requirements	Emissions and wastes
Antireflective coating	SiH ₂ Cl ₂ NH ₃	71.12 ft ³ /MW 106.96 ft ³ /MW	
Interconnection	Copper	46.6 Mg/MW	
Encapulation	EVA Mylar Glass	~ 4.42 Mg/MW 1.87 m ³ /MW 112.85 Mg/MW	

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TABLE 4.15-1 (continued)

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SECTION 5

SILICON II PROCESS

This section deals with a somewhat more advanced cell processing sequence for silicon n/p homojunction cells. As with the Silicon-I processes, a process description for each step, material requirements, manpower requirements, potential emissions and wastes, controls and fail-safe systems, occupational hazards, and risk determination.

The basic assumptions used in material calculations are as follows:

- The finished wafer thickness is 0.008 inch (0.020 cm).
- ° The cell dimensions are 7.5 cm by 10 cm (75 cm^2).
- The completed cell is 15 percent efficient.

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 Each completed cell generates 1.125 watts of power at AM 1 conditions.

 All calculations are based upon production of 100 MW of cells per year.

Plant operating time is 5 days/wk, 24 h/day, 50 wk/yr (6000 h/yr).

On this basis it is calculated that 88,888,889 cells must be produced for 100 MW of cells per year. As with the Silicon-I process, the material requirements for operations preceding completion of the finished wafer were back-calculated from the total amount of silicon required for the finished wafers.

Manpower requirements are based primarily on information obtained from the LSA Project Technology Development Update (Goldsmith, Bickler, 1978). Using the total direct labor required and total labor costs for the 250 MW/year plant described, manpower requirements for each process were calculated on a proportionality basis using the labor costs for each process given in the report.

5.1 MINING AND REFINING OF QUARTZ

5.1.1 Process Description

The process described in Section 4.1.1 for the Silicon-I process would be applicable to the Si-II process as well.

5.1.2 Material Requirements

The total amount of sand and gravel required was backcalculated from the total amount of MG-Si and the ratio of MG-Si to sand and gravel, as was done regarding the Silicon-I process. On this basis, about 19.1 percent of the raw sand and gravel is converted to MG-Si. By this estimate, about 27.25 Mg/MW of sand and gravel would be required.

With an estimated 1.06 billion tons of sand and gravel to be quarried in 1985 (U.S. Dept. of Interior, 1980a), the quantity required for the solar cells would be only 0.0003 percent of the total mined. Based on the ratio of raw sand and gravel and the quantity of 98 percent quartz needed for MG-Si production in the Si-I process, production of the required 5.20 Mg/MW MG-Si would require 14.20 Mg/MW of 98 percent SiO₂.

5.1.3 Manpower Requirements

On the assumption that 0.09 employee-hour is needed to produce 1 Mg of sand and gravel (U.S. Dept. of Interior, 1980a), the total manpower required to produce the sand and gravel for production of 100 MW_{pk} of cells would be 245.2 employeehours/yr.

5.1.4 Emissions, Wastes, and Controls

As discussed earlier, the estimates of fugitive emissions from sand and gravel quarrying operations range from 34.7 to 50 g/Mg of sand and gravel processed (Chalekode, P.K. et al 1978 and U.S. Environmental Protection Agency, 1977). With these emission factors, the estimated emissions from this mining operation that could be attributed to solar cell production would range from 94.6 to 136.3 kg/yr. Generation of respirable dust generated was reportedly 3.6 g/Mg (Chalekode, P.K. et al, 1978), of which a total of 9.8 kg/yr is attributable to solar cell production. Of the 3.6 g/Mg respirable dust, an average of 17 percent is free silica (Chalekode, P.K. et al, 1978) according to these estimates, about 1.7 kg/yr of free silica would be respirable.

5.1.5 Occupational Hazards

The hazards described in Section 4.1.5 for the silicon-I process will be applicable for the silicon-II process.

5.1.6 Risk Determination

The total labor requirement necessary to produce enough silica sand for the hypothetical 100 MW/yr plant is 245.2 employee-hours. Using the occupational injury, illness, and fatality statistics in Table 3.1-13, the total lost workdays and the number of fatalities can be determined for this operation. The activity of non-metallic mineral mining occupations will result in approximately 0.2 lost workdays including 4.9 x 10^{-6} fatalities.

5.2 METALLURGICAL SILICON PRODUCTION

5.2.1 Process Description

Metallurgical silicon is produced in the manner described in Section 4.2.1.

5.2.2 Material Requirements

Material requirements for all processes preceding the finished silicon wafer were back-calculated on the basis of the total amount of single-crystal silicon required. With consideration of the losses incurred from polycrystalline silicon production to the finished wafer, the calculated requirement for polycrystalline silicon is 4.33 Mg/MW or 433 Mg/yr. Because the material requirements for the Union Carbide silane production and pyrolysis plants are for a 1000 Mg/yr plant (Union Carbide Corp., 1979), all throughputs in these calculations are scaled down by use of a direct multiplier of 0.433. On this basis it is calculated that 4.99 Mg/MW of MG-Si would be needed to produce the high-purity polycrystalline silicon required. Assuming a 4 percent loss in milling to chunk form and in final milling to the desired particle size, a total of 5.20 Mg/MW of MG-Si is produced initially. Based on estimates of Gandel et al. (1977), the coke requirment for production of the 5.20 Mg/MW MG-Si is 5.45 Mg/MW.

5.2.3 Manpower Requirements

As noted in Section 4.2.3, the production of 1 Mg of MG-Si takes 11.5 employee-hours. A total of 5773 employee-hours would be needed to produce the required quantity of MG-Si.

5.2.4 Emissions, Wastes, and Controls

Based on estimates of Gandel et al. (1977), the particulate emissions from coke production are 0.002 kg/kg of coke produced. Emissions resulting from production of coke required for MG-Si production would be about 1.09 Mg/yr.

By use of emission estimates by Gandel et al. (1977), it is calculated that the electric arc furnace operation emits about 2.03 Mg/MW of SiO and ash, of which 1.97 Mg/MW is SiO. Most of these particulates are collected by filters.

Another estimate of particulate emissions during electric arc furnace operation is 6.25 lb/ton of silicon produced (U.S.

Department of Energy, 1977); on this basis the total particulate emission would be 1.62 Mg/MW.

The assumption of a 2 percent loss during milling of the MG-Si into chunk form results in a loss of 0.1 Mg/MW. It is assumed that a filter services the mill. A 2 percent loss is also assumed for milling of the chunk MG-Si into a finer mesh material for feeding to the reactor; this assumption also results in a loss of 0.1 Mg/MW. Again, a filter services this mill.

5.2.5 Occupational Hazards

Potential exposure of workers could occur during maintenance of the filters, during charging of the furnaces with coke and quartz, and during normal operation of the electric arc furnace when the exhaust ventilation system might not capture the submicron-sized silicon particles and coke emissions. Emissions may also occur during conveying of coke, quartz, and MG-Si. Numerous types of injuries could occur during these operations because of the high interaction of workers with the process. The most likely injuries are cuts, bruises, sprains, bone fractures, and burns.

5.2.6 Risk Determination

The labor to refine enough MG-Si from silica sand for a 100 MW/yr plant is estimated to be 5773 employee-hours. Using the occupational injury, illness, and fatality statistics associated with the production of industrial inorganic chemicals (SIC 281) given in Table 3.1-13, this level of activity will result in 1.4 lost workdays including 1.8×10^{-4} fatalities.

5.3 SILICON PURIFICATION

5.3.1 Process Description

From a number of viable processes being developed for low-cost production of semiconductor-grade (Se-G-Si) poly-Si,

the Union Carbide process involving the production and subsequent pyrolysis of silane was selected as the model for this study.

The process designed by Union Carbide converts 98 percent pure, commercial, metallurgical-grade silicon into ultra-highpurity silicon metal suitable for solar-cell applications. The feed metallurgical silicon is converted to gaseous trichlorosilane (TCS) in a hot, copper-catalyzed, fluid-bed reactor. Nonvolatile metal-chloride contaminants are separated from the reactor product stream by removal of a small, liquid fraction at its dewpoint, and hydrogen is subsequently separated as a noncondensable gas from the condensed crude TCS liquid (Union Carbide Corp., 1979). The crude TCS liquid is stripped free of dissolved volatile impurities in a stripping column. The material is then processed through a series of three conventional distillation columns and two redistribution reactors by use of an amine-based ion exchange resin. This equipment progressively replaces chlorine in the chlorosilane molecules with hydrogen, pushing the heavily chlorinated compounds back to the start of the process and the hydrogen-rich molecules forward. Ultimately, silane is produced and subjected to a final distillation in the fourth column, which yields an ultra-high-purity, liquid silane product (Union Carbide Corp., 1979).

The pure silane is pyrolyzed to form hydrogen gas and high-purity silicon metal in powder form. The powder is consolidated by melting and removed from the process (Union Carbide Corp., 1979).

5.3.2 <u>Materials Requirements</u>

Along with some makeup H_2 , the feed materials to the fluid bed reactor are copper catalyst, MG-Si, and recycled chlorosilane streams. All calculations are based on a plant operating time of 7533 h/yr.* For production of 4.33 Mg/MW Se-G-Si, the

^{*} A final product rate of 132.75 kg/h produces 1000 Mg/yr; 1000 Mg/yr ÷ 132.75 kg/h = 7533 h/yr.

following are the calculated feed rates to the hydrogenation reactor (in Mg/MW):

MG-Si - 4.98 (small amount lost to storage bin vent) HCl - 6.13 Dichlorosilane (DCS) - 0.41 Trichlorosilane (TCS) - 37.87 Silicon Tetrachloride (STC) - 526.86 Copper catalyst - 1.41 kg/hr

The effluent stream consists of:

 $\begin{array}{rrrr} HC1 & - & 0.19 \\ DCS & - & 2.32 \\ TCS & - & 128.86 \\ SCS & - & 439.79 \\ H_2 & - & 5.53 \end{array}$

The materials are then processed through a series of distillation and redistribution reactors until an ultrapure silane (SiH_4) product is obtained. Production of the 4.33 Mg/MW Se-G-Si requires 5.62 Mg/MW of silane. The amount of poly-Si powder formed in the pyrolysis reactor is 4.9 Mg/MW. This is transferred to a powder storage hopper, from which an estimated loss of 11.6 percent results (Union Carbide Corp., 1979) in the final quantity of 4.33 Mg/MW.

5.3.3 Manpower Requirements

Union Carbide personnel* indicate that 36 workers are needed on all shifts to operate the 1000 Mg/yr facility. It is calculated from process flow diagrams that about 7533 h/yr is needed to produce this quantity of silicon. With this assumed plant operating time and 3 shifts per day, an average employeeyear would be 2511 hours. Because only 433 Mg/yr of solar-grade silicon is needed for production of 100 MW of cells, a scaledown factor of 0.433 is used in all calculations.

Labor categories for the 36 total workers required are as follows: 9 for direct operation of the silane plant; 5 operators and 1 mechanic for the pyrolysis plant; and 4 lab

^{*} Telephone conversation, Dr. H. Morihara Linde Div., Union Carbide and T. Owens, PEDCo Environmental, Inc., May 12, 1980.

technicians, 6 maintenance workers, 8 shift supervisors, 1 chemist, and 2 secretaries for over-all operation. On this basis the requirements for production of 433 Mg/yr silicon would be as follows (in employee-hours/yr):

silane plant operators - 9785.4 pyrolysis plant operators - 5436.3 pyrolysis plant maintenance - 1087.3 laboratory technicians - 4349 plant maintenance - 6523.6 supervisors - 8698.1 chemist - 1087.3

5.3.4 Emissions, Controls, and Wastes

Gaseous process wastes are routed into four collection headers: noncombustible gas containing no silane or chlorosilanes, combustible gas containing no silane or chlorosilanes, chlorosilane gases, and silane-hydrogen gases (Union Carbide Corp., 1979).

The noncombustible and the combustible gases containing no silane or chlorosilanes are passed separately through bag filters before being discharged to the atmosphere. Another bag filter located over the MG-Si storage bin processes estimated emissions of 0.003 Mg/MW. The fines from these filters are reused by dumping them back into the MG-Si storage bin (Union Carbide Corp., 1979).

Chlorosilane gases from the melter apparatus, the STC storage tank, the MG-Si lock hopper, the crude TCS storage tank, and rupture disc vents are combusted in an atomizing pre-mix burner. Silane-hydrogen gases from the crude TCS stripper column are combusted in a nozzle-mix burner (Union Carbide Corp., 1979).

Liquid wastes from the waste chlorides tank bottoms and crude TCS storage tank bottoms are combusted in an atomizing, pre-mix burner (Union Carbide Corp., 1979). All burners discharge into a vacuum collection system with enough excess air to quench any flames. As a means of converting all chlorinated material to hydrogen chloride, hydrogen functionality is added, where necessary, in the form of natural gas. To minimize atmospheric venting of chlorosilanes as a result of process upsets, overpressure relief lines are manifolded to a pressure-relief catch tank, which phase-separates and feeds material to appropriate burners for disposal (Union Carbide Corp., 1979).

Combustion gases from the burners are collected in a silica agglomerator, and allowed to cool to about 150 to 200°C. Silica particles formed in the combustion process agglomerate when cooled in this fashion to form larger, more easily controlled particles. The fumed silica, along with metal oxides formed in the flames, is collected by bag filters. The solids collected by the bag filters, primarily fumed silica, are discharged through a cyclone and an airlock to the silica dust bin. The silica dust is packed into 55-gallon drums and subjected to a vibrating table to densify the dust. Trace quantities of submicrometer-sized solids remaining in the combustion gases are removed by a high-energy venturi driven by a medium-strength, muriatic solution. As the combustion gases pass through the venturi, they are cooled to near dew point by humidification. The high-energy venturi is purged of collected solids whenever the solids concentration reaches about 2 percent. Approximately 100 gallons of liquid is purged into a neutralizing tank, where it is neutralized with lime to precipitate solids. Leachable calcium chloride is filtered from the solids by gravity percolation through a sand filter to a sewer. The gases, cleaned of solids, are then scrubbed free of hydrogen chloride with a two-stage venturi ejector to produce a nominal 20 percent muriatic acid solution. The scrubbed gases, cleaned of hydrogen chloride to parts-per-million levels, then pass through the muriatic tailing column, which has been packed with a sacrifical metal surface. The gas that is exhausted to the atmosphere by a

waste gas induction blower has concentrations of solid particulate and hydrogen chloride that are well below regulated limits (Union Carbide Corp., 1979).

The fumed silica byproduct from the bag filters is marketable as a low-performance filler for tires and other rubber products. The medium-strength, muriatic acid is marketable for such applications as pickling metals.

5.3.5 Occupational Hazards

Exposure of maintenance personnel to silicon dust could occur during changing or servicing the various bag filters and dust collection systems and also during packing of the waste dust into 55-gallon drums. Proper protective equipment during these operations should minimize exposure. Exposure to hydrogen chloride via hydrolysis of the chlorosilanes is another potential hazard. Small leaks in piping, valves, or pumps could result in chronic exposure. Unless a major accident occurrs (e.g. pipe rupture, tank rupture, explosion) acute exposure to chlorosilanes is unlikely. It appears that rupture disc vents are vented to a pressure-relief catch tank to prevent discharge into the workplace or atmosphere in the event of upset conditions.

Hydrogen leaks must be controlled to minimize explosion hazards. Most hydrogen in this process is recycled, but some is burned.

Maintenance personnel servicing tanks and reactors may come into contact with various residual wastes, such as acids, dusts, and fumes.

5.3.6 Risk Determination

The silicon purification step in the silicon II process requires 36,967 employee-hours of labor to produce the needed 433 Mg/yr of silicon. Using the occupational injury, illness, and fatality statistics associated with the production of industrial inorganic chemicals (SIC 281) given in Table 3.1-13, this level of production will result in 8.6 lost workdays including 1.2×10^{-3} fatalities.

5.4 RIBBON GROWTH

5.4.1 Process Description

The edge-defined film-fed growth (EFG) process is used for silicon sheet processing. In the EFG process capillary action causes molten Se-G silicon to rise inside a graphite die. A silicon ribbon seed is then brought into contact with the liquid at the top of the die, and the temperature is adjusted so that liquid from within the die begins to solidify on the seed ribbon. As the seed is pulled upward, a crystalline ribbon grows downward so that the interface between the melt and the crystal stays just above the die. The dimensions of the top of the die determine the shape of the ribbon (Mobil Tyco, 1978).

For the sheet growth area in the hypothetical 100-MW production plant, pairs of ribbon-growing machines will be supplied molten silica from a melt replenish vat located between the two machines. Each ribbon-growing machine can grow five ribbons. The ribbons are scribed and cut at the machines (Goldsmith and Bickler 1978).

5.4.2 Material Requirements

The SeG-Si is the only material required for this process. Total throughput of SeG-Si is 4.33 Mg/MW.

5.4.3 Manpower Requirements

Out of the 1152 direct workers required for the 250-MW plant, 692 are required for the EFG growth, scribe and cut area. By application of a factor of 100/250, the estimated manpower requirements are 277 workers/yr or 554,000 employee hours/yr. If 1 maintenance worker is required for each 10 growers, the maintenance requirement is 15.6 workers or 31,200 employee-hours/yr.

5.4.4 Emissions, Wastes, and Controls

Process emissions in this area will be minimal. The only potential emissions would occur when dust is generated in the scribe and cut operation.

5.4.5 Occupational Hazards

If a laser is used to cut or scribe the sheets into individual cells, precautions must be taken to protect workers from vaporized materials, radiation (ultraviolet, X-ray, and highluminance visible), electrical hazards, flying particles, and cryogenic coolants (Briggs et al, 1980).

5.4.6 Risk Determination

The labor effort required for enough silicon ribbon growth to supply a 100 MW/yr plant is estimated at 585,200 employeehours. Using the occupational injury, illness, and fatality statistics in Table 3.1-13 the total lost workdays and the number of fatalities can be determined for this process. The technical occupations, i.e. line operators, contribute the major of hours to this process, approximately 554,000. This level of activity will result in 117.4 lost workdays and 5.5 x 10^{-3} fatalities. Maintenance for this process will require 31,200 employee-hours resulting in 10.1 workdays and 4.0 x 10^{-4} fatalities. The ribbon growth process will result in a total of 127.5 lost workdays including 5.9 x 10^{-3} fatalities.

5.5 p⁺ ALUMINUM - BACK CONTACT APPLICATION

5.5.1 Process Description

Process subconveyers are used to deliver the cut sheet wafers to each of the p^+ aluminum spray machines. In the spraying operation, a shaft containing the spray gun moves from front to rear in the coating compartment at a precisely controlled rate and deposits an aluminum powder/ethanol mixture on the passing substrates (Wihl, M., 1978). The wafers then pass through ovens, where they are dried and fired.

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5.5.2 Material Requirements

It is calculated that approximately 0.002467 g of aluminum powder and 0.049338 g of ethanol are needed to cover 1 cm² of wafer (Wihl, M., 1978). The calculations based on these estimates indicate that 0.164 Mg/MW of Al powder and 3.29 Mg/MW (4168 liters/MW) of ethanol would be required. With a process efficiency of 30 percent for chemical spraying operations (Watts, et al, 1979), total material requirements would be 0.547 Mg/MW Al powder and 10.97 Mg/MW (13,893 liters/MW) of ethanol.

5.5.3 Manpower Requirements

Manpower for the 250-MW plant is calculated to be 29.2 workers. For the 100-MW plant, 11.7 workers or 23,400 employeehours/yr would be required. Maintenance requirements for this equipment are estimated to be 20 percent of operator requirements (D'Aiello, 1977). Thus 3900 employee-hours/yr would be required for maintenance and 19,500 employee-hours/yr for operation.

5.5.4 Emissions, Wastes, and Controls

The primary emissions will be fumes and mists generated during the drying and firing operations. In one system the conveyer passes through a heated cleaning chamber, where it is sprayed prior to exiting to eliminate buildup (Zicon Corp., Product Information). The cleaning agent would most likely be a solvent, possibly ethanol. Emissions would also occur during line flushing and nozzle cleaning.

A class 100 vertical downdraft exhaust system is used in one system described for the spray chamber (Zicon Corp., Product Information). Air entering the chamber passes through prefilters and HEPA filters before passing over the coating area to remove any mist or vapor emitted during spraying. The air then passes through an exhaust filter and is discharged through a stack into the atmosphere (Zicon Corp., Product Information). The spray chamber and attached ovens are completely enclosed to help prevent escape of materials into the workplace air.

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Assuming a 30 percent process efficiency, for chemical spraying (Watts et al, 1979) losses of aluminum powder and ethanol during the spraying would be 0.383 and 7.68 Mg/MW, respectively. It is safe to assume that the remainder of the ethanol, 3.29 Mg/MW would be vaporized and lost during drying and firing operations.

Safety features on this equipment include complete shielding of all electrical wiring that comes into contact with the coating material and an exhaust interlock that prevents spraying if the exhaust flow rate becomes inadequate (Zicon Corp., Product Information). The exhaust flow rate of the equipment described is about 500 cfm.

An infrared processing oven is used with one system. Since this is enclosed and automated, the exposure of workers to infrared radiation should be minimal.

5.5.6 Risk Determination

The labor requirement for p^+ aluminum-back control application was determined to be 23,400 employee-hours. Using the occupational injury, illness, and fatality statistics in Table 3.1-13, the total lost workdays and the number of fatalities can be determined for this process. The technical occupations, i.e. line operators, contribute 19,500 hours to the total labor effort. This activity results in 4.1 lost workdays and 2.0 x 10^{-4} fatalities. The necessary maintenance for this process requires 3,900 hours resulting in 1.3 lost workdays and 5.1 x 10^{-5} fatalities. The entire process activities will result in a total of 5.4 lost workdays and 2.5 x 10^{-4} fatalities.

5.6 PLASMA ETCH

5.6.1 Process Description

From the aluminum back spray operation the wafers go directly to a plasma etch process, which removes the silicon oxide film formed on the surface. In this process, carbon tetraflouride (CF_4) in oxygen is used as the etchant gas. The

composition of the gas is 8.5 percent oxygen and 91.5 percent CF_4 (LFE Corp., Product Information). When the cells enter the reaction chamber, a slight vacuum is pulled in the chamber and the etching gas (CF_4 + O_2) is introduced at a controlled rate; radio-frequency energy is applied to generate active gas species.

The active species react with the SiO_2 film and form volatile reaction products that are removed by a vacuum pump. The volatile reaction products may include silicon tetrafluoride (SiF₄), silicon oxyfluoride species (SiOF₂, Si₂OF₆), oxygen (O₂), fluorine (F₂), and CO₂ (LFE Corp., Product Information).

After the plasma etch process, wafers are automatically replaced on the conveyer system and transferred to the next process.

5.6.2 Materials Requirements

The etchant materials are CF_4 and oxygen. A flow rate of 50 cm³/min is assumed. Based on this flow rate and an operating time of 6000 h/yr, the total materials requirement is 0.18 m³/MW of CF_4 and O_2 .

5.6.3 Manpower Requirements

For a 250-MW/yr plant, the manpower requirement is 40.4 direct laborers. For a 100-MW/yr plant, the requirment is 16.2 direct laborers or 32,400 employee-hours/yr. Of the total 16.2 workers, maintenance requirements are estimated to be 0.1 workers/machine/shift. Therefore, the total maintenance labor will be 1.6 persons or 3200 employee-hours/yr.

5.6.4 Emission, Wastes, and Controls

Primary emissions from this process will be SiF_4 , $SiOF_2$, Si_2OF_6 , O_2 , F_2 , and CO_2 which will be removed by a vacuum pump. Since the quantities discharged will be relatively small, it is doubtful that treatment or control of these emissions will be required. A molecular sieve may be used on the vacuum pump discharge side to prevent oil emissions from the vacuum pump.

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5.6.5 Occupational Hazards

Hazards to workers operating the plasma etchers will be few. Since a vacuum is pulled before any gases are released into the reaction chamber, the chances that the gas will be released into the workplace are low. The gas used $(CF_4 + O_2)$ is relatively nontoxic, nonflammable and noncorrosive. Because small quantities are used, the exposures would be minor unless the contents of a cylinder were released accidentally.

Since the plasma is generated with a radiofrequency power source, there is potential exposure to radiofrequency radiation. The power source used for plasma etching, however, is said to be typically at a frequency of 13.5 MH_2 , which is well below the standard for occupational exposure set by the Occupational Safety and Health Administration (OSHA). The OSHA regulation applies only to sources operating with frequencies from 10 to 10,000 MH_2 (NIOSH/OSHA Current Intelligence Bulletin 33, 1979).

5.6.6 Risk Determination

The plasma etching operation requires 35,600 employee-hours of labor. Using the occupational injury, illness, and fatality statistics in Table 3.1-13, the total lost workdays and the number of fatalities can be determined for this process. The technical occupations, in the form of skilled line operators, contributes 32,400 hours to the total labor requirement. This level of activity will result in 6.9 lost workdays and 3.2 x 10^{-4} fatalities. The maintenance effort necessary to keep the plasma etching process operational is expected to be 3,200 employee-hours. This level of exposure will result in 1.0 lost workdays and 4.2 x 10^{-5} fatalities. The entire process will result in 7.9 lost workdays and 3.6 x 10^{-4} fatalities.

5.7 ION IMPLANTATION

5.7.1 Process Description

Wafers are carried from the plasma etching operation to the ion implanters on a conveyer. It is assumed that about four wafers can be implanted simultaneously in each system, and implant time is about 3.8 seconds at a dose of 1 x 10^{15} ions/ cm². About four implantation stations will be required to achieve the desired throughput. The cassettes containing the wafers are loaded onto the implanter; they are gravity fed to the input vacuum-lock, then gravity fed to the implant chamber, where they are positioned in platens for ion implanation. Upon completion of the implant the platens rotate to the exit position. The wafers enter the exit vacuum lock, which is brought to atmospheric pressure, and then are fed into a waiting cassette (Varian/Extrion Div., Product Information, 1979).

After implantation a laser pulse anneal will be required to restore crystallinity to the implanted silicon surface. Two types of lasers for pulse anneal have been identified, a ruby laser and a YAG laser. Energy levels in excess of 15 joules will be produced in a 10 to 50 ns pulse (Lockheed Missles and Space Co., Inc. 1978).

5.7.2 <u>Materials Requirements</u>

The chief material requirement is for phosphorous, the source being phosphine (PH_3) . To achieve a doping density of 1 x 10^{15} P⁺ 31 ions/cm², the total amount of phosphine required would be 3.76 g PH₃/MW or about 2.46 liters/MW. The PH₃ is supplied in bottles as a mixture of 15 percent PH₃ in H₂. Pump oils or cryogenic liquids and freon will be needed for the platen cooling system.

5.7.3 Manpower Requirements

Calculations developed for a 250-MW plant (Goldsmith and Bicker 1978), indicate that manpower requirements at the 100-MW

plant would be approximately 16.2 workers. Based on an operator/maintenance/foreman ratio of 100:6:1, the requirments are 30,280 employee-hours/yr for operation, 1816.8 for maintenance, and 302.8 for a foreman.

5.7.4 Emissions, Wastes, and Controls

One published estimate of emissions from ion implanation of phosphorous is 50 percent of the input (Coleman et al, 1979). On the basis of this estimate, about 1.88 g/MW PH_3 would be exhausted.

Emissions could result from leaks or malfunctions in the vacuum system. In one system this possibility is minimized by backing all primary vacuum pumps (oil diffusion or cryopumps) with mechanical roughing pumps and providing fail-safe precautions for shutdown of the system in the event of a vacuum leak, system malfunction, or facilities failure (water, power, compressed air) (Varian/Extrion, Product Information, 1979).

Since the doping gas is 85 percent H_2 , at least 25.07 g/MW H_2 will be released. At the exhaust ventilation rate for the system, which is about 600 cfm, the H_2 should be diluted sufficiently to prevent any fire or explosion hazards.

5.7.5 Occupational Hazards

Primary hazards to workers would be exposure to PH_3 , electrical shock, and radiation. Exposure to PH_3 is very unlikely since the system is under vacuum and includes backup vacuum pumps in case of primary pump failure. In addition, the system is automatically shutdown in case of vacuum leaks, system malfunctions, or facilities failure (Varian/Extrion, Product Information, 1979).

Electrical hazards are minimized during normal operation by elimination of exposed high-voltage areas. Access points are interlocked so that high voltage is removed wherever they are not in place. Radiation shields are provided; levels around the accelerater at maximum rated energy and current are ≤ 0.25 mR/h on all external surfaces (Varian/Extrion, Product Information, 1979).
5.7.6 Risk Determination

The ion implantation process requires a total of 32,400 employee-hours. Using the occupational injury, illness, and fatality statistics in Table 3.1-13, the total lost workdays and the number of fatalities can be determined for this process. The technical occupations, i.e. line operators, contribute 30,280 hours to the labor total resulting in 6.4 lost workdays and 3.0 x 10^{-4} fatalities. The inspecting occupations i.e. foreman, contribute 303 hours resulting in 0.1 lost workdays and 4.2 x 10^{-6} fatalities. Maintenance for the process will require 1,817 employee-hours, which will result in 0.6 lost workdays and 2.4 x 10^{-4} fatalities. Total entire process operations should produce a total of 7.1 lost workdays and 3.3 x 10^{-4} fatalities.

5.8 BACK AND FRONT METALLIZATION

5.8.1 Process Description

The wafers are thick-film printed with a silver-based ink. They arrive by conveyor in cassettes, which are loaded by the operator into an automatic loader (D'Aiello 1977). Each wafer is inserted into the printer, where a mesh screen is placed over it, and a squeegee carrying the silver ink is rolled over the screen to print the pattern. Wafers are then collated into parallel rows and enter a dryer. In the back metallization process, the wafers enter a furnace and are sintered at $550\frac{1}{3}$ C immediately after drying. They are then automatically reloaded into cassettes and transferred to the front metallization process.

In front metallization, the wafers are automatically loaded into cassettes following drying. These cassettes are again loaded by the operator into a loader, where the wafers are inserted into the printer and a bus bar pattern printed. The wafers are again collated, dried, then fired at 550°C and reloaded into cassettes (D'Aiello 1977).

5.8.2 Material Requirements

Back Metallization--

Calculation of the silver-based ink requirements for the back grid are based on the following assumptions; the density of the Ag-ink is 3.75 g/cm^3 ; the grid pattern covers 25 percent of the back cell area; and $2.6974 \times 10^{-3} \text{ cm}^3$ of silver ink per cm² of cell surface is required (D'Aiello 1977). On this basis it is calculated that 0.68 Mg/MW of silver ink is needed for back metallization. This is the total amount required; the amount covering the cell is 25 percent of this or 0.17 Mg/MW, leaving 0.51 Mg/MW deposited on the screen.

Front Metallization --

For front metallization, the silver ink is used for the grid and bus bar applications. Again it is assumed that the ink density is 3.75 g/cm^3 and the ink needed to cover 1 cm² of cell area is $2.6974 \times 10^{-3} \text{ cm}^3$. The fine grid is assumed to cover 4 percent of the front cell area and the bus bars about 1 percent (D'Aiello 1977). Total ink requirements are estimated to be 1.35 Mg/MW. Since only 5 percent or 0.067 Mg/MW covers the cell proper, 1.283 Mg/MW is wasted on the screen.

5.8.3 Manpower Requirements

From estimates of manpower requirements for a 250 MW production facility (Goldsmith and Bickler 1978) it is calculated that that 100-MW plant will require 11.7 direct laborers or 23,400 employee-hours/yr for back metallization and the same number for front metallization. On the basis of estimates reported elsewhere (D'Aiello 1977) about 54.8 percent of the manpower requirements are for operation, 4.1 percent for engineering support, 32.9 percent for maintenance, and 8.2 percent for foremen in the front metallization process. Allocation of the total 23,400 employee-hours/yr is 12,823.2 for operation; 959.5 for engineering support; 7698.6 for maintenance; and 1918.8 for supervision. For back metallization the estimates from the same source are 50.6 percent for operators, 3.8 percent for engineering support, 30.4 percent for maintenance, and 15.2 percent for a foreman. Allocation of the total 23,400 employee-hours/yr is 11,840.4 for operators; 889.2 for engineering support; 7113.6 for maintenance and 3556.8 for foremen.

5.8.4 Emissions, Wastes, and Controls

The primary source of waste from the process will be the disposal of used screens with wasted ink material. It is not known how many printings can be made before the screen must be disposed of, since this will vary with the type of screen. It is also possible that the screen can be cleaned several or many times and reused before disposal is required. In this case, the solvent or cleaning agent containing the stripped silver ink would have to be disposed of or recycled.

Another potential source of emissions would be the drying and firing operations. Although it is doubtful that significant metal vapor emissions would occur at the designated process temperatures, carrier agents used to formulate the silver pastes or inks could be vaporized during these operations; thus adequate ventilation would be required to remove the vapors and prevent contamination of the workplace air.

5.8.5 Occupational Hazards

Analyses of several silver inks have shown significant levels of toxic metals besides silver (e.g. lead, nickel, antimony)(D'Aiello, R.V., 1977).

Workers should be aware of the potential danger when handling the inks and when cleaning or disposing of screens, squeegees, or process wastes. Depending on the type of carrier used to formulate the inks, dermal absorption is possible. Also as mentioned above, vapors given off during drying and firing operations could result in worker exposure if ventilation is inadequate. A sampling survey of one plant showed that operators were exposed to silver levels from 10.4 to 60 μ g/m³ of silver. All of these are above the recommended TLV of 0.01 mg/m³ established by the ACGIH. Efforts should be taken to keep silver levels below this level. Table 5.8-1 gives results of the sampling survey.

5.8.6 Risk Determination

The back and front metallization process requires a total labor effort of 46,800 employee-hours. Using the occupational injury, illness, and fatality statistics in Table 3.1-13, the total lost workdays and the number of fatalities can be determined for this process. The technical occupations, i.e., line operators and engineers, contribute a total of 26,512 hours toward the total labor requirement. This level of activity produces a worker exposure which is expected to result in 5.6 lost workdays and 2.6 x 10⁻⁴ fatalities. The inspecting occupations, both foremen and supervisors, contribute a total of 5475 hours of labor, resulting in 1.4 lost workdays and 7.7 x 10^{-5} fatalities. Maintenance for this process requires an effort of 14,812 employee-hours which is expected to result in 4.8 lost workdays and 1.9×10^{-4} fatalities. The entire process is expected to cause a total of 11.8 lost workdays including 5.3 x 10^{-4} fatalities.

5.9 ANTIREFLECTIVE COATING

5.9.1 Process Description

Wafers are loaded onto a conveyer belt that moves them through the antireflective coating stations. The wafers are next sprayed with a titanium dioxide (TiO_2) antireflective coating, followed by an air-flash to remove any bubbles that may have formed and to settle the coating material. The wafers are next transferred to an infrared drying zone, then reloaded into a cassette, in which they undergo a 15-minute bake at about 200°C (D'Aiello 1977).

Sample description	Sampling Time (h)	Sample volume, liters,	Total sample weight, µg	Concent ug/n ³	Estimated TWA,
Operator; silver paste application	2.87 3.22	760	7.9	10.4	·
Operator; silver paste application	3.12 0.33	396	8.7	22.0	
Operator; silver paste application at larger machine	2.76	315	14.0	20.6	21.4
Operator; silver paste	2.74	317	19.0	60.0	

TABLE 5.8-1. SAMPLING SUMMARY FOR SILVER FROM METALLIZATION SILVER PASTE APPLICATION

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5.9.2 Material Requirements

On the basis of earlier estimates (D'Aiello 1977), it is calculated that 0.00268 cm^3 of TiO_2 antireflective coating is required for each cm² of cell surface area. Based on a 30 percent process efficiency for chemical spraying (Watts et al. 1979), the estimated reuirement for 100 MW of cells is 178.67 liters/MW. The total quantity that would be deposited on the cells is 53.6 liters/MW.

5.9.3 Manpower Requirements

Based on manpower estimates for a 250-MW production facility, the requirement for this process in a 100-MW facility is 16.2 direct laborers or 32.400 employee-hours/yr. Operator requirements are assumed to be 58.8 percent of the total; maintenance requirements, 11.8 percent; and engineering support, 29.4 percent. The resultant allocations are 19,051.2 employeehours/yr for operation, 3823.2 for maintenance, and 9525.6 for engineering support.

5.9.4 Emissions, Wastes, and Controls

The major potential emissions from the antireflective coating operation will be fumes or vapors generated during spraying, drying, and firing. One commercial spray system has a heated cleaning chamber that is sprayed to clean the conveyer before it exits to eliminate buildup (Zicon Corp., Product Information). Though the cleaning agent is not known, this is another potential source of emissions. Periodic flushing of the lines and nozzles could result in additional emissions. The liquid cleaning agent would also require disposal.

On the assumptions that estimates by D'Aiello (1977) are for the total quantity of material needed to cover the cell, including losses, and that process efficiency for chemical spraying is 30 percent (Watts et al. 1979) it is calculated that 125.1 liters/MW would be lost on the conveyer, chamber walls, or other surfaces, or to the exhaust. It is also assumed that the carrier used to formulate the spray coating would be completely lost during drying and firing operations.

The ventilation system described for the commercial spray system mentioned above is said to be a class-100 vertical downdraft exhaust system, consisting of prefilters and HEPA filters for incoming air, which sweeps over the coating area to remove some of the material not adhering to the cells. The exhaust air passes through a filter and is discharged through a stack (Zicon Corp., Product Information). Spray chambers and ovens are completely enclosed to prevent escape of materials.

Electrical wiring in the system is completely shielded from all spray materials, and an exhaust interlock is used to prevent spraying if the exhaust ventilation flow rate should become inadequate (Zicon Corp., Product Information).

5.9.5 Occupational Hazards

Potential hazards to workers include exposure to fumes and mists not captured by the ventilation system and exposure in handling of coating materials. These exposures should be minor, however. In the event ventilation falls below design levels, the system is automatically shutoff to prevent the diffusion of vapors into the workplace.

Maintenance cleaning is reduced or eliminated because cleaning of the system described is automated. Exposure could occur during repairs, but this possibility is reduced by the automatic cleaning of the conveyer, which reduces worker contact with dirty machine surfaces.

Electrical and fire hazards are reduced by eliminating exposure of wiring to spray materials. Although infrared ovens are used, exposure to infrared radiation should not be a problem because the system is enclosed. There is a possibility of burns from contact with hot surfaces.

5.9.6 Risk Determination

The antireflective coating operation requires a labor effort of 32,400 employee-hours. Using the occupational injury, illness, and fatality statistics in Table 3.1-13, the total lost workdays and the number of fatalities can be determined for this process. The technical occupations i.e. line operators and engineers, contribute 28,577 hours to the work effort resulting in 6.0 lost workdays and 2.8 x 10^{-4} fatalities. Maintenance for this process requires a total of 3,823 employee-hours resulting in exposures that are expected to produce 1.2 lost workdays and 5.0 x 10^{-5} fatalities. The total process operations are expected to cause 7.2 lost workdays including 3.3 x 10^{-4} fatalities.

5.10 INTERCONNECTION

5.10.1 Process Description

The process used for interconnection is very similar to the one discussed in Section 1.12.1. By use of industrial robots, the cells are aligned into strips of 12 parallel cells and an aluminum interconnect is ultrasonically bonded to the back of the cells. These are fed to an assembly machine which puts them into module fixtures for solder reflow. A module consists of 16 rows of 12 parallel connected cells. This assembly is conveyed to a vapor-phase solder reflow oven where the interconnect strips are connected to the front contacts (Goldsmith and Bickler, 1978). It is assumed that each module contains 192 cells, that each station can process 40 modules/h, and that 77.16 modules/h are required to manufacture 100 MW of cells per year.

5.10.2 Material Requirements

The major material requirement for this process is the presoldered interconnect strips. If is assumed that each interconnect is about 0.6 ounce (17 gm), and one interconnect is required for each cell, approximately 15.1 Mg/MW of aluminum would be required for production of 100 MW/yr of cells. Because it is not known how much solder will be applied to each interconnect, no estimate is given for this material requirement. The solder is 60/40 lead-tin.

5.10.3 Manpower Requirements

Based on estimates for a 250-MW/yr facility, the total manpower requirements for a 100-MW/yr facility are about 47.6 direct laborers or 95,200 employee-hours/yr. Manpower estimates for these operations are 61.4 percent for hourly operators, 17.5 percent for a rework operator, 15.8 percent for maintenance, and 5.3 percent for a foreman. The resultant requirements in employee-hours/yr are 58,452.8 for hourly operators, 16,660 for a rework operator, 15,041.6 for maintenance, and 5045.6 for a foreman.

5.10.4 Emissions, Wastes, and Controls

The major potential emissions would be lead fumes generated during the solder reflow operation. It is doubtful that these will be significant because the reflow ovens are enclosed and will no doubt be ventilated. If a flux is used, there will also be potential emissions from the flux. If a zinc chloride $(ZnCl_2)$ flux is used, HCl or zinc oxychloride fumes [Zn(OH)Cl]could be generated. A flux removal spray system would also be required; water spray would be sufficient for a zinc chloride flux. The mildly acidic spray effluent would have to be neutralized. Use of a flux may not be required, however, because a fluxless vapor-phase solder reflow process has been operated successfully (Lockheed Missles and Space Co., Inc., 1978).

Interlock logic should be incorporated into the design of the reflow oven system to shut down the system in the event that the ventilation system fails.

5.10.5 Occupational Hazards

Exposure of workers to lead oxide fumes appears to be the major potential hazard in this operation. Maintenance personnel could also be exposed to residual deposits on equipment during servicing, although this should be easily controlled by use of proper protective clothing. Because this operation involves hot surfaces, burns may be an eminent hazard unless protective barriers are used to isolate workers from such surfaces.

5.10.6 Risk Determination

The total labor requirement for interconnection has been determined to be 95,200 employee-hours. Using the occupational injury, illness, and fatality statistics in Table 3.1-13, the total lost workdays and the number of fatalities can be determined for this process. The assembling occupations i.e. line operators and rework operators, contribute 75,112.8 hours, resulting in an expected 17.1 lost workdays and 9.0 x 10^{-4} fatalities. Inspecting occupations i.e. foremen, contribute 5,045.6 hours of labor resulting in 1.3 lost workdays and 7.1 x 10^{-5} fatalities. Maintenance requirements for this process will total 15,041.6 employee-hours, producing an exposure which is expected to result in 4.9 lost workdays and 2.0 x 10^{-4} fatali-The interconnection process will cause a total of 23.3 ties. lost workdays including 1.17 x 10^{-3} fatalities.

5.11 ENCAPSULATION

5.11.1 Process Description

The process described in Section 4.13.1 will be applicable here also.

5.11.2 Materials Requirements

The following assumptions were made in calculating material requirements for this process:

Soda lime glass - 2.51 lb/ft² EVA pottant - 0.02 in. thick (0.048 g/cm² or 0.94 g/cm³) Mylar back - 0.008 in. thick Module dimensions - 4 ft by 4 ft

On this basis it is calculated that production of 100 MW of cells per year would require approximately 84.3 Mg/MW of glass, 3.5 Mg/MW of EVA, and 1.49 m³/MW of Mylar.

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5.11.3 Manpower Requirements

From the estimates for a 250-MW/yr facility, it is calculated the 100 MW/yr facility would require a total of 54.8 workers or 109,600 employee-hours/yr. Operator requirements would be 95.7 percent of the total, maintenance 3.2 percent, and foreman 1.1 percent giving, in employee-hours/yr, 104,887.2 for operation, 3507.2 for maintenance, and 1205.6 for supervision.

5.11.4 Emissions, Wastes, and Controls

Those described in Section 4.13.4 would also apply here.

5.11.5 Occupation Hazards

Those described in Section 4.13.5 would also apply here.

5.11.6 Risk Determination

Encapsulation requires a total labor effort of 109,600 employee-hours. Using the occupational injury, illness, and fatality statistics in Table 3.1-13, the total lost workdays and the number of fatalities can be determined for this process. The assembling occupations i.e. line operators will contribute 104,887.2 employee-hours to the labor total. This activity is expected to cause 23.9 lost workdays and 1.26 x 10^{-3} fatalities. Inspecting of the process will require 1,205.6 employee-hours from supervisory personnel. This activity will result in 0.3 lost workdays and 1.7 x 10^{-5} fatalities. Maintenance for this process will require 3,507.2 employee-hours, resulting in an expected 1.1 lost workdays and 4.6 x 10^{-5} fatalities. The entire process will cause a total of 25.3 lost workdays including 1.32 x 10^{-3} fatalities.

5.12 MODULE TEST

5.12.1 Process Description

The description discussed in Section 4.14.1 also apply here.

5.12.2 Material Requirements

No materials will be used here.

5.12.3 Manpower Requirements

It was calculated that a total of 4.5 employees would be required for this operation in a 250 MW/yr plant. For a 100 MW plant it was calculated that a total of 1.8 employees or 3600 employee-hrs per year would be required. If maintenance and foreman requirements are assumed to be 6 and 1 percent of operator requirements respectively then 3364.5 cmployee-hrs per year would be required for operation. 33.6 employee-hours per year for a foreman, and 201.9 employee-hrs per year for maintenance.

5.12.4 Emission, Wastes, and Controls

Some nitrogen oxides and ozone may be generated by the U.V. lamp but these should be of little environmental concern.

5.12.5 Occupational Hazards

Though some ozone and nitrous oxides may be generated, adequate air exchange in this area should prevent any significant concentrations from accumulating.

5.12.6 Risk Determination

The module testing procedure will require a total of 3,600 hours of labor. The inspecting occupations will contribute 3,398 employee-hours resulting in 0.9 lost workdays and 4.8 x 10^{-5} fatalities. Maintenance activities for the module testing operation requires 202 employee-hours resulting in 0.1 lost workdays and 2.6 x 10^{-6} fatalities. The module testing procedure will cause a total of 1.0 lost workdays and 5.1 x 10^{-5} fatalities.

5.13 DATA SUMMARY

Presented in Tables 5.13-1 are summaries of materials, emissions, and wastes. Manpower and risk data for the Si-II process is presented in Section 8.

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Process step	Material	Material requirements	Emissions and wastes
<u>Mining and refininc of guartz</u> .	Sand and gravel 90% quartz Total dust Respirable dust Respirable free silica	27.25 Mg/MW 14.2 Mg/MW	0.944 to 1.36 kg/MW (5.26 to 7.59 kg/yr) 96.9 g/MW 17.1 g/MW
<u>Metallurgical silicon</u> production	MG-Si Polycrystalline silicon Coke Coke particulate SiO particulate Ash particulate Mg-Si milling loss	5.20 Mg/MW 4.33 Mg/MW 5.45 Mg/MW	10.7 kg/yr 1.97 Mg/MW 0.06 Mg/MW 0.1 Mg/MW
<u>Silicon purification</u>	Reactor feed ° Mg-Si ° HCl Dichlorosilane Trichlorosilane Silicon tetrachloride Copper catalyst	4.98 Mg/MW 6.13 Mg/MW 0.41 Mg/MW 37.87 Mg/MW 526.86 Mg/MW 1.41 kg/hr	· · ·
<u>Ribbon growth</u>	SeG-Si	4.33 Mg/MW	
<u>Aluminum - back contact</u> <u>application</u>	Al powder Ethanol	0.547 Mg/MW 10.97 Mg/MW	
Plasma etch	CF ₄ and O ₂	0.18 m ³ /MW	
(continued)		1	I

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TABLE 5.13-1. MATERIAL AND WASTE SUMMARY FOR SILICON-II PROCESS

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TABLE 5.13-1 (continued)

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Process step	Material	Material requirements	Emissions and wastes
<u>Ion implantation</u>	Phosphine PH ₃ H ₂	3.76 g/MW	1.88 g/MW 25:07 g/MW
Back and front metallization	Silver ink for back Silver ink for front	0.68 Mg/MW 1.35 Mg/MW	-
Antireflective coating	TiO2 antireflective coating	53.6 1/MW	
Interconnection	Aluminum	15.1 Mg/MW	
Encapsulation	Glass EVA Mylar	84.3 Mg/MW 3.5 Mg/MW 1.49 m ³ /MW	

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SECTION 6

CADMIUM SULFIDE BACKWALL SPRAY PROCESS

6.1 INTRODUCTION

This section describes the production of cadmium sulfide/ copper sulfide (CdS/Cu_xS) backwall cells by a spray process. As with the silicon and other production processes, where possible this discussion presents for each step a brief process description, material requirements, manpower requirements, potential emissions, wastes and controls, occupational hazards, and risk determination.

Only one company, Photon Power, Inc., of El Paso, Texas, is currently a major U.S. producer of CdS/Cu_xS cells by the spray method. Because of the many proprietary aspects of this process, material and manpower information obtained from Photon Power is not presented directly but is used to develop qualitative and quantitative risk information. The material estimates are based on information available in the literature. Where available, applicable information in the literature is used to supplement information on materials and manpower requirements. Estimates of materials requirements are based on the following assumptions:

- C^o Each panel has a 5 percent conversion efficiency
 - ^o Each panel is 50 cm by 61 cm (3050 cm²) and generates 15.25 W of power.
- About 6,557,377 panels are required to produce 100 MW_{pk} of power.
- All calculations are based on production of 100 MW pk of cells.
- Manpower estimates are based on an operating schedule of 24 h/day, 250 day/yr (6000 h/yr).

Manpower information obtained from Photon Power, Inc., was for a 5 MW/yr plant. Taking into account economics of scale-up to a 100 MW facility a worst-case manpower estimate of 5 times that required for the 5 MW/yr plant was used for calculations. (Personal communication with Peter Locke, Photon Power, Inc., 8/80).

6.2 CADMIUM REFINING

6.2.1 Process Description

Cadmium can be produced from the following byproducts of tour basic operations, all involving zinc:

- 1. Fumes and dusts from roasting and sintering of zinc concentrates.
- Dusts from smelting of lead-zinc or copper-lead-zinc ores.
- 3. Recycled zinc metal containing cadmium.
- 4. Purification sludge from electrolytic zinc plants.

The first two byproducts are the primary source of cadmium and are discussed in more detail below.

Various cadmium-bearing dusts, fumes, and sludges from primary zinc plants first undergo a leaching process, which selectively dissolves as much cadmium as possible. Leaching precipitates lead and other impurities without precipitating any of the dissolved cadmium. The fumes and dusts are leached with dilute sulfuric acid and sodium chlorate to ensure complete dissolution of cadmium sulfide. Cadmium goes into solution by the following reaction:

$$CdO + H_2SO_4 \rightarrow CdSO_4 + H_2O$$

Sodium chlorate is a strong oxidizing agent, added to prevent reduction of any sulfur to sulfide and to prevent precipitation of cadmium or thallium as sulfides. The cadmium and lead are converted to sulfates and chlorides. The cadmium compounds remain in solution, but lead is almost completely converted to insoluble lead sulfate.

Instead of a direct leach with sulfuric acid, in at least one plant the dust is first roasted and then water-leached. The sinter fume is heat-treated in a four-hearth roaster, which selectively sulfates the cadmium and makes about 90 percent of it water-soluble. The water leach that follows produces relatively pure cadmium solutions containing about 40 g/liter (0.3 lb/gal) of cadmium and 10 g/liter (0.08 lb/gal) of zinc. Addition of sodium bichromate to this solution removes about 90 percent of the soluble lead. The residual solids are batchtreated with scrubber liquor and concentrated acid.

The cadmium-zinc sulfate solution is then treated with zinc dust to precipitate cadmium as a metallic sponge and then to separate it from most of the zinc dust while the solution is agitated. To avoid excess zinc contamination, usually only 90 to 95 percent of the cadmium in solution is precipitated. The initial precipitation with zinc dust may yield a liquor containing a residual 0.2 g/liter (1.7×10^{-3} lb/gal) of cadmium and 30 to 40 g/liter (0.25 to 0.3 lb/gal) of zinc. To further decrease overall cadmium discharge, the stripped liquor is heated to $40\frac{1}{4}$ C ($104\frac{1}{4}$ F) and precipitated again with 1.6 times the stoichiometric amount of zinc to reduce the liquor to 0.04 g/liter (3.3×10^{-4} lb/gal) of cadmium and 30 to 40 g/liter (0.25 to 0.3 lb/gal) of zinc.

The cadmium sponge (a porous precipitate) is then filterpressed. It contains about 69 percent cadmium, 30 percent moisture, and small amount of lead and zinc. It is steam-dried or dewatered in a centrifuge. The solution from filtration, containing practically all of the zinc added and about 10 percent of the cadmium as chlorides and sulfates, is returned to the sintering operation.

The sponge is then processed either by electrolytic or pyrometallurgical methods.

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The flue dusts generated by lead smelting are also processed to recover cadmium. Since dust from the blast furnace exhaust gases is recycled to the sintering machine, sinter dust becomes enriched in cadmium, thallium, and zinc.

When cadmium content in the dust reaches 12 percent by weight or greater, the dust is subjected to a separate roasting operation for cadmium separation and recovery.

The spray process for cadmium sulfide cell production uses cadmium chloride $(CdCl_2)$ as one of the chemicals for deposition of the CdS layer. One method for preparation of the anhydrous salt of CdCl₂ is reaction of cadmium metal with hydrochloric acid or chlorine gas. Under normal conditions of temperature and humidity, dicadmium chloride pentahydrate (2 CdCl₂ · 5H₂O) is the stable compound forming colorless, monoclinic crystals from the anhydrous salt and water. Cadmium chloride is usually sold in the pentahydrate form (Kirk-Othmer, 1979).

6.2.2 Material Requirements

In calculation of cadmium and CdCl₂ requirements, the thickness of the CdS layer is assumed to be 4 μ m. On this basis, the amount of CdS deposited is 0.38 Mg/MW. If it takes 1 mole or 112.40 grams of cadmium and 1 mole or 32.064 grams of sulfur to produce 1 mole of CdS, then the total amount of cadmium deposited is 0.30 Mg/MW. With a theoretical ratio of 0.6032 for deposition of cadmium from CdCl₂, then 0.50 Mg/MW of $CdCl_2$ is required to deposit the cadmium on the cells. Process efficiency for chemical spraying has been estimated to be about 30 percent (Watts et al. 1979).* At 30 percent process efficiency a total of 1.67 Mg/MW of cadmium chloride would be By back-calculation, the total amount of cadmium required. required would be 1.01 Mg/MW or 101 Mg/yr. This would be about 6.4 percent of the estimated total cadmium produced in 1979 (Mineral Commodity Summaries, 1980).

^{*} Efficiency for this spray process has been increased to about 50 percent (personal communication with P. Locke, Photon Power, Inc.).

6.2.3 Manpower Requirements

Information obtained from the U.S. Department of the Interior (Mineral Commodity Summaries, 1980) indicates that 491 employee-hours are needed to produce 1 ton of cadmium. On this basis, it is calculated that 54,674 employee-hours/yr would be required to produce the 101 Mg/yr of cadmium needed for a 100 MW production plant. No information is available in the literature on the manpower requirements for producing CdCl₂.

6.2.4 Emissions, Wastes, and Controls

In production of metallic zinc, most of the cadmium is emitted in the roasting and sintering process, and particulates are usually collected in baghouses and/or electrostatic precipitators. Cadmium compounds emitted are $CdCl_2$ during roasting and cadmium oxide (CdO) during sintering and smelting.

If all the cadmium used for production of the solar cells is obtained from zinc smelting operations, the emission factor for cadmium would be 1.0 kg/10³ kg of zinc produced (Anderson, 1973). If it is assumed that the ratio of cadmium to zinc in the ores is 0.5 percent, then 20,200 Mg/yr of zinc would be produced and thus 20.2 Mg/yr of cadmium fugitive emissions would be released. An emission factor of 13 kg/10³ kg is reported (Anderson, 1973) for cadmium refining, from which 1313 kg/yr of cadmium fugitive emissions would be released.

6.2.5 <u>Occupational</u> Hazards

Exposure to cadmium at smelters and refineries can be serious. At one secondary smelter producing primarily cadmium, environmental sampling indicated that 50 percent of 51 samples from cadmium breathing zones exceeded the OSHA standard of 0.1 mg/m^3 and 60 percent exceeded both the National Institute of Occupational Safety and Health (NIOSH) recommended standard of 0.04 mg/m³ and the ACGIH TLV of 0.005 mg/m³ (Gunter et al., 1977 and ACGIH, 1980). Levels of cadmium ranged from 0.01 to 1.91 mg/m^3 . Job classifications that exhibited the highest levels of cadmium exposure included solution chargers, mixer operators in the calcining area, a retort operator, furnace operators in the calcine area, and a shop mechanic (Gunter et al. 1977). Because of worker mobility among jobs in the plant, identification of higher versus lower exposure groups on the basis of breathingzone samples is limited.

Workers at plants producing $CdCl_2$ may also be exposed to cadmium in the metallic or chloride form. No information on exposure levels in this industry was found in the literature. Hydrochloric acid used to manufacture the $CdCl_2$ also creates an acute and chronic hazard to workers.

6.2.6 Risk Determination

The cadmium refining operations require a total labor effort of 54,674 employee-hours to produce enough metal for a 100 MW/yr production plant. Using the occupational injury, illness, and fatality statistics for primary nonferrous metals production given in Table 3.1-13, it is possible to estimate total lost workdays and fatalities for these process operations. The activity associated with this process is expected to result in 21.0 lost workdays and 3.8 x 10^{-3} fatalities.

6.3 SUBSTRATE PROCESSING

6.3.1 Process Description

Processing includes washing and drying of precut glass substrates followed by metallization with a tin chloride $(SnCI_2)$ spray. The operator first places the untreated glass on the inlet to the glass washer, through which it is conveyed and washed with rotary brushes, then air dried. The operator then removes the glass from the outlet.

The cleaned glass is conveyed to a radiant oven with automatic load and unload capabilities. The glass is heated and sprayed with a solution of $SnCl_2$ in methanol. Upon contact with the glass the $SnCl_2$ oxidizes to form a layer of tin oxide (SnO_2) .

6.3.2 Material Requirements

Under the assumption that the density of the glass is 12.25 kg/m² (2.51 lbs/ft²), the amount of glass required for the substrate would be 211.5 Mg/MW. The required quantity of tin chloride/methanol solution is proprietary information.

6.3.3. Manpower Requirements

Operator requirements are considered proprietary. It is reported, however, that 20 employee-hours/wk or about 1000 employee-hours/yr are needed for preventive maintenance and about 160 employee-hours/yr for scheduled maintenance on the glass washer.

Requirements for the SnCl₂ ovens are about 7500 employeehours/yr for preventive maintenance and 240 employee-hours/yr for scheduled maintenance. Also, about 120 employee-hours/yr are required for collection of the tin dust for recovery from the fabric filters and about 80 employee-hours/yr for replacement of filter bags.

6.3.4 Emissions, Wastes, and Controls

When the SnCl₂/methanol solution is sprayed on the hot glass, a number of waste products are formed and exhausted to a baghouse. The emissions include a tin chloride of unknown form, tin oxide and formic acid. The tin chloride is the major emission and is described as a hydroscopic fine white powder. Control efficiency of the baghouse that treats the exhaust is reported to be greater than 97 percent. There are two baghouses, one used as backup when the other is off-line for maintenance or cleaning. The dust collected from the fabric filters is stored and shipped to a chemical supplier for recovery of the tin.

6.3.5 Occupational Hazards

Workers around the SnO_2 spray process are potentially exposed to $SnCl_2$, methanol, and breakdown products such as formic

acid, tin oxide, and an unidentified form of tin chloride. Table 6.3-l summarizes a sampling survey of workers in the tin oxide area (Briggs et al., 1980).

The tin occurs primarily as tin oxide or tin chloride. Tin oxides are considered a nuisance dust with a particulate TLV of 10 mg/m^3 ; inorganic tin compounds other than the oxide have a time-weighted average (TWA) exposure limit of 2 mg/m³ and a short-term exposure limit (STEL) of 4 mg/m³. The survey results show that all concentrations are well below these levels; thus, this operation should not pose a significant hazard to workers from exposures to tin. The only other serious exposure potential would occur when the baghouse filters are cleaned or replaced and the dusts are collected for tin recovery.

For methyl alcohol the TWA is 260 mg/m³ and the STEL is 310 mg/m³. Samples taken in the survey show levels far below these standards. No samples were taken for formic acid; if methyl alcohol levels are indicative, however, the levels of formic acid should also be well below the TWA of 9 mg/m³. Thus the survey indicates that worker exposure on the tin oxide spray line should be easily controlled.

Possible physical injuries in these processes would be cuts from glass handling and burns from the ovens.

6.3.6 <u>Risk Determination</u>

Employment figures and labor requirements for the remainder of the cadmium sulfide cell production are considered proprietary information. Due to the sensitive nature of the labor requirements the calculations performed for each process risk assessment will not be presented. Lost workdays and totality values will not be displayed by individual process. The total lost workdays and fatality values are presented in Section 8, Hazard Analysis and Risk Assessment.

	· · · · · · · · · · · · · · · · · · ·	· · · · · · · · · · · · · · · · · · ·	Conc	entration
Sample description	Substance sampled	Time sampled, h	. µg∕m ³	Estimated TWA (µg/m ³)
Tin oxide spray operator, normal operation	Tin	3.92	5.5	
Supervisorthroughout plant	Tin	3.85	0.5	
Tin oxide spray operator, normal operation	Tin	6.58	019.7	
Tin oxide spray operator, cleanup	Tin	1.47	28.9	
Operator (for sample II), cleanup of tin oxide, at Cd ₂ S No. 1 spray line	Tin	3.52	0.6	0.9
Tin oxide spray operator, cleanup	Tin	2.18	45.3	
Tin oxide spray operator	Methyl alcohol	3.03	*3.21 (2.5)	
Tin oxide spray operator	Methyl alcohol	3.93	12.10 (9.3)	

TABLE 6.3-1. SUMMARY OF SAMPLES TAKEN IN TIN OXIDE SPRAY OPERATION

*For methyl alcohol concentration is expressed in mg/m^3 and (ppm).

6.4 CADMIUM SULFIDE APPLICATION

6.4.1 Process Description

The cadmium sulfide (CdS) layer is applied in essentially the same manner as the SnO_2 layer. The metallized glass sheets are automatically loaded into radiant ovens, wherein solutions of CdCl₂ and thiourea (H₂NCSNH₂) are sprayed onto the heated substrate, forming a layer of CdS. This operation is performed a second time in another battery of ovens to obtain the desired CdS thickness.

6.4.2 Material Requirements

It was calculated in Section 6.2.2 that the manufacture of 100 MW of cells would require about 1.01 Mg/MW of $CdCl_2$.

If the CdS layer is assumed to be 4 μ m thick (Watts et al. 1979), then the amount of sulfur deposited on the cells would be 0.086 Mg/MW. If a theoretical deposition ratio of sulfur to thiourea is 0.4212, then 0.204 Mg/MW of thiourea would be needed for deposition of the required amount of sulfur. If 30 percent efficiency is assumed for chemical spraying (Watts et al. 1979), then a total of 1.69 Mg/MW of thiourea would be required for deposition of the sulfur.*

6.4.3 Manpower Requirements

Operator requirements are considered proprietary information.

It is estimated that about 30,000 employee-hours/yr are required for preventive maintenance and 720 employee-hours/yr for general scheduled maintenance. Also about 120 employeehours are required annually for collection of cadmium dusts from fabric filters for cadmium recovery and 80 for replacement of filter bags.

^{*} As noted above the efficiency for this spray process has been increased to about 50 percent. Therefore, only 0.41 Mg/MW of thiourea would be required.

6.4.4 Emissions, Wastes, and Controls

Emissions from this process will include unreacted $CdCl_2$, CdS and other cadmium complexes, in addition to degradation products of thiourea. These emissions are ducted to a baghouse system separate from, but similar to, that used to treat emissions from the SnO_2 spray process. Thus with a 50 percent process efficiency about 0.204 Mg/MW will be ducted to the baghouse system. It is hoped that this can be recovered for recycle. The dust will be collected periodically for cadmium recovery.

6.4.5 Occupational Hazards

The major hazard is, of course, exposure to cadmium and cadmium compounds. Results of a sampling survey performed on workers at a pilot line facility are presented in Tables 6.4-1 and 6.4-2 (Briggs, et al., 1980). Some samples showed concentrations above the TWA of 0.05 mg/m³. Several of these were taken during cleaning operations and thus represent a relatively short-term exposure. Only one of the samples taken during cleaning operations was above the STEL of 0.2 mg/m³. Two samples taken during normal operations showed cadmium levels above the 0.05 mg/m³ TWA limit.

These data indicate a potentially hazardous situation for workers involved with the cadmium spray lines. The pilot line operation that was sampled, however, would be expected to have fewer controls than a full-scale production line.

Data on thiourea samples taken in the same survey are presented in Table 6.4-3. Because no threshold limit has been established for thiourea, it is difficult to interpret these data. Because it has been reported to be an animal carcinogen, appropriate precautions should be taken.

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			Concentration	
Sample No.	Sample description	Sampling time, h	μ g/m 3	TWA (µg/m ³)
2	CdS No. 1 spray operator	3.95	16.4	
3	CdS No. 2 spray operator	5.25	28.2	
1	*Tin oxide spray operator	3.82	29.8	
4	Area sampling-'between CdS No. 1 and No. 2 spray lines	5.10	12.9	
7.	Supervisor (throughout plant)	3.85	9.8	
31	CdS No. 1 spray operator	4.17	13.8	
34	CdS No. 2 spray operator	6.37	24.9	
30	*Tin oxide spray operator	3.97	18,9	
33	Operator (throughout spray line)	2.22	59,3	-
37	Area samplespray area about	7.53	9.0	
29	Supervisor (throughout plant)	2.92	58.5	

TABLE 6.4-1. SUMMARY OF SAMPLING SURVEY FOR CADMIUM EXPOSURE DURING NORMAL OPERATION

*Tin oxide spray operators helped to clean cadmium spray lines after they had completed cleaning the tin spray lines.

Samplo		C	Concentration		
No.	Sample description	time, h	µg/m ³	TWA (µg/m ³)	
10	CdS No. 2 spray operator ćleanup	2.35	17.7		
27	Operator (for sample 10), cleanup	3.53	15.6	16.4	
22	*Tin oxide spray operator cleanup	2.18	45.3		
28	Operator (for sample 22), cleanup on CdS No. 2	3.48	34.5	38.5	
11	*Tin oxide spray operator cleanup	1.47	48.7		
19	Operator (for sample 11) CdS No. 2 cleanup	1.90	15.9		
26	Operator (for sample 11), tin oxide cleanup, Cd ₂ S No. 1 spray operation	3.52	11.9	21.4	
12	Operator for solution preparation and CdS No. 1 spray setup	1.23	10.9	· · ·	
20	Operator (for sample 12), Cd ₂ S No. 2 cleanup	2.07	821.0	506,0	
13	CdS No. 1 spray operator, normal operation	2.42	10.5		
23	Operator (for sample 13), normal operation	4.52	18.4	15.9	
17	Supervisorthroughout plant	2.08	8.0		
24	Supervisorthroughout plant	4.53	4.4	5.5	

TABLE 6.4-2. SUMMARY OF SAMPLING SURVEY FOR CADMIUM EXPOSURE DURING CLEANING OPEATIONS

*Tin oxide spray operators helped clean cadmium spray lines after they had completed cleaning the tin spray lines.

TABLE 6.4-3. SAMPLE RESULTS FOR THIOUREA AT CdS SPRAY LINE

			Concentration	
Sample No.	Sample description	Sampling time, h	Thiourca, µg/m ³	Estimated TWA (µg/m3)
14	Operator preparation of CdS No. 1 spray solution	1.15	44.5	
21	Operator (for sample 14), CDS No. 2 cleanup	1.98	22.8	30.8
15	CdS No. 1 spray operator, normal operation	2.28	21.2	
25	Operator (for sample 15), normal operation	4.58	20.6	20.8
36	CdS No. 1 spray operator, normal operation	7.78	3.0	

6.5 METALLIZATION GRID PATTERN

6.5.1 Process Description

In this patented process panels are positioned on an automated X-Y motion table where a grid is patterned by scraping lines across the panel down to the tin layer. The tin layer is removed by a laser. As the lines are scraped, one needle applies a strip of permanent resist while a second needle applies a temporary resist. Dust created by the scraping operation is removed with a vacuum.

6.5.2 Material Requirements

Except for the resists, no materials are required for this process.

6.5.3 Manpower Requirements

Operator requirements are proprietary. Annual requirements for preventative maintenance are estimated at 1250 employeehours; for general scheduled maintenance, about 1000 employeehours; and for changing of the vacuum bags in the vacuum removal system, about 1250 employee-hours.

6.5.4 Emissions, Wastes, and Controls

Cadmium sulfide dust from the scraping operation will be the primary waste product. It is estimated that the vacuum system will remove approximately 400 pounds of CdS dust annually. The dust will be placed in containers for recovery or for disposal in an approved landfill.

6.5.5 Occupational Hazards

Worker exposure to the CdS dust will be the major hazard. Table 6.5-1 gives data from a sampling survey of the grid patterning area of a pilot operation. The survey showed one elevated exposure level for a worker primarily involved in cleanup operations. This could indicate that better control of dust is required during cleanup. Protective clothing is reported to be

Sample No.	Sample description	Sampling time, h	Concentration $(\mu g/m^3)$
5	Cell division operatior, primary cleanup operations	3.35	65.7
16	Cell division operator, cell division and cleanup	7.88	5.6
6	Area sampleoutside workshop 18 in. from discharge of vacuum blower from cell division area	4.38	9.8
18	Area samplesame area as sample 6	5.10	14.8

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TABLE 6.5-1. SAMPLING RESULTS FOR CADMIUM IN GRID PATTERN OPERATION

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mandatory in this area. Another source of potential exposure is changing of vacuum bags. Collecting the dust and placing it in containers also involves potential exposure. Use of proper protective clothing and respirators during these operations should minimize exposure.

6.5.6 Risk Determination

Employment figures and labor requirements for the remainder of the cadmium sulfide cell production are considered proprietary information. Due to the sensitive nature of the labor requirements the calculations performed for each process risk assessment will not be presented. Lost workdays and totality values will not be displayed by individual process. The total lost workdays and fatality values are presented in Section 8, Hazard Analysis and Risk Assessment.

6.6 COPPER DIP

6.6.1 Process Description

The glass panels, now with a CdS layer, are transferred through a series of process tanks, two of which contain proprietary copper chloride solutions. Other tanks are rinse tanks containing deionized water. Panels are manually loaded onto a conveyor, which takes the panels through the process steps, then manually unloaded. Dipping the CdS-coated panels into the copper chloride solutions results in a topotaxial ion exchange wherein two copper ions replace one cadmium ion in the CdS lattice structure while the sulfur position in the lattice remains the same. This results in the formation of the CdS/Cu₂S layer.

6.6.2 Material Requirements

For material estimates it is assumed that the Cu_2S layer is 1 µm thick. For 100 MW of CdS/Cu₂S panels, a total of 2 million cm³ of Cu₂S is deposited. At a density of 5.6 g/cm³, the Cu₂S requirement is 0.112 Mg/MW. If theoretically 79.85 percent of

this is copper, then the total copper requirement is 0.089 Mg/MW. At an assumed ratio of 0.642 for deposition of copper from copper chloride, 138.63 kg/MW of CuCl is required. One source estimates that the efficiency of the process is about 50 percent if no chemicals are recycled (Watts et al. 1979). On the basis of a 50 percent efficiency, 277.26 kg/MW of CuCl would be required.

6.6.3 Manpower Requirements

Operator manpower information is proprietary. The annual manpower needs for preventive maintenance are 500 employee=hours and for general maintenance, about 2000 employee-hours. Also, for the liquid waste treatment system that treats the copper dip wastes, the estimated annual requirements are 1500 employeehours for preventive maintenance and about 160 employee-hours general scheduled maintenance.

6.6.4 Emissions, Wastes and Controls

The primary waste will be the copper dip solutions, which when spent will be discharged to a liquid waste treatment system and treated with a flocculating agent to remove process chemicals. Collected sludge will be pumped to solar dryers, then manually put into containers. The sludge will either be sent for copper recovery or be disposed of in an approved landfill.

6.6.5 Occupational Hazards

The only potential occupational exposure hazards are inhalation of copper fumes or mists around the dipping tank area and inhalation of dusts containing copper when dried sludge from the solar drying beds is placed in containers. The TWA for copper fumes, mists, and dusts is 0.2 mg/m³. Exposure to workers should be easily kept below this level with adequate ventilation and proper protective equipment.

Dermal exposure to copper chloride may cause skin and eye irritation. Hot solutions could also cause burns.

6.6.6 Risk Determination

Employment figures and labor requirements for the remainder of the cadmium sulfide cell production are considered proprietary information. Due to the sensitive nature of the labor requirements the calculations performed for each process risk assessment will not be presented. Lost workdays and totality values will not be displayed by individual process. The total lost workdays and fatality values are presented in Section 8, Hazard Analycic and Risk Assessment.

6.7 METALLIZATION AND HEAT TREATMENT

6.7.1 Process Description

Deposition of the metal collection grid is accomplished by vacuum evaporation. Panels are manually loaded into the vacuum chamber, where three metals prepared in pellet form are sequentially evaporated onto the panel surfaces. The vacuum is then broken, and the groups of panels are manually unloaded from the evaporator and loaded into an oven for heat treatment. The grid metals include copper, lead, and a proprietary metal.

6.7.2 Material Requirements

In calculation of material requirements the following assumptions were made:

- The top copper electrode is 0.7 µm thick and covers about 90 percent of the cell surface area. Evaporation for this step is 35 percent efficient (Watts et al. 1979).
- ^o The top lead (Pb) electrode is 2 µm thick and covers 90 percent of the cell surface area. The evaporative process for this step is 35 percent efficient (Watts et al. 1979).

On the basis of these assumptions it was determined that 0.31 Mg/MW of copper and 1.17 Mg/MW of lead would be required for the top electrodes.

6.7.3 Manpower Requirements

Operator requirements are considered proprietary. Estimated annual requirements for preventative maintenance and for scheduled maintenance are 150 and 200 employee-hours, respectively.

6.7.4 Emissions, Wastes, and Controls

The efficiencies for deposition are relatively low; only 35 percent for the top copper and lead electrodes. On the basis of these estimates, 0.20 Mg/MW of copper and, 0.76 Mg/MW of lead, would be either exhausted, deposited on the vacuum chamber walls, or deposited on the substrate holder. Materials not deposited on the substrate may be partially recovered by collection on strategically located chickding within the vacuum chamber, followed by recovery of the collected materials (Watts et al. 1979).

An operation performed in the pilot plant consisted of cutting of lead sheet, melting the lead, and pouring it into molds to form the bullets used to load the metallization boats. If this operation were performed on a large-scale, emissions would be of no significance environmentally, but ventilation would be needed to remove fumes from the workplace.

6.7.5 Occupational Hazards

Although the potential exists for exposure to metal fumes, exposure levels are likely to be low since the process takes place under vacuum. If lead bullets are produced in-plant, this would be the most potentially serious hazard in the metallization area. Samples taken on an operator performing this function showed lead exposure levels of 17.1 and 5.0 μ g/m³ in sampling periods of 2.95 and 2.67 hours, respectively. An estimated TWA of 11.5 μ g/m³ was calculated for these samples. Although this is well below the AGCIH TWA of 0.15 mg/m³, it should be recognized that this operation would process significantly more lead at a 100 MW/yr production level and thereby increase the exposure potential.

6.7.6 Risk Determination

Employment figures and labor requirements for the remainder of the cadmium sulfide cell production are considered proprietary information. Due to the sensitive nature of the labor requirements the calculations performed for each process risk assessment will not be presented. Lost workdays and totality values will not be displayed by individual process. The total lost workdays and fatality values are presented in Section 8, Hazard Analysis and Risk Assessment.

6.8 ELECTRICAL CONNECTIONS

6.8.1 Process Description

This process involves simply the application of bus bars and electrical leads to the panels. It will be performed manually, most likely by soldering.

6.8.2 Material Requirements

No material estimates are available. The only materials used are the metal bus bars, the wire leads, and the solder.

6.8.3 Manpower Requirements

Operator requirements are considered confidential. No maintenance requirements are reported.

6.8.4 Emissions, Wastes, and Controls

Emissions and wastes from the soldering operation would be minimal and of little environmental significance.

6.8.5 Occupational Hazards

The only potential occupational exposure would be to fumes from soldering, which should be easily controlled with local ventilation. Since this operation is manual, injuries from materials handling would be of concern also. These would most likely be minor cuts, abrasions, and burns.

6.8.6 Risk Determinations

Employment figures and labor requirements for the remainder of the cadmium sulfide cell production are considered proprietary information. Due to the sensitive nature of the labor requirements the calculations performed for each process risk assessment will not be presented. Lost workdays and totality values will not be displayed by individual process. The total lost workdays and fatality values are presented in Section 8, Hazard Analysis and Risk Assessment.

6.9 ENCAPSULATION

6.9.1 Process Description

This process is still under development. Materials being considered are glass and various plastics.

6.9.2 Material Requirements

Since the material to be used is unknown, requirements on a weight basis could not be calculated. For production of 100 MW of cells it is estimated that 2 million m^2 of the material will be required.

6.9.3 Manpower Requirements

Operator requirements are considered proprietary and therefore not presented. No maintenance estimates were available since the process is not yet fully developed.

6.9.4 Emissions, Wastes, and Controls

Emissons should be minimal. Depending on the material used for encapsulation and how it is applied, some fumes may be generated, but these should be of little consequence environmentally.

6.9.5 Occupational Hazards

Any fumes that might be generated should be easily controlled. It is difficult to speculate on physical hazards because the process has not been defined.
6.9.6 Risk Determination

Employment figures and labor requirements for the remainder of the cadmium sulfide cell production are considered proprietary information. Due to the sensitive nature of the labor requirements the calculations performed for each process risk assessment will not be presented. Lost workdays and totality values will not be displayed by individual process. The total lost workdays and fatality values are presented in Section 8, Hazard Analysis and Risk Assessment.

6.10 TEST AND FRAME ASSEMBLY

6.10.1 Process Description

The encapsulated panel is tested by use of simulated sunlight. An operator manually loads and unloads the panel onto a test table. If the panel passes the test, it is manually arranged into a frame.

6.10.2 Manpower Requirements

Operator requirements are considered proprietary. It is reported that about 120 employee-hours/yr will be required for preventative maintenance and 40 employee-hrs/yr for scheduled maintenance for the test station.

For frame assembly, an estimated 500 employee-hours/yr will be required for preventative maintenance and 160 employeehours/yr for general scheduled maintenance.

6.10.3 Material Requirements

Material estimates for the frames are not available.

6.10.4 Emissions, Wastes, and Controls

No emissions or wastes are expected for this process.

6.10.5 Occupational Hazards

Physical injuries can occur in this area because of the manual involvement in the process. Minor cuts and abrasions will most likely be the predominant injuries.

6.10.6 Risk Determination

Employment figures and labor requirements for the remainder of the cadmium sulfide cell production are considered proprietary information. Due to the sensitive nature of the labor requirements the calculations performed for each process risk assessment will not be presented. Lost workdays and totality values will not be displayed by individual process. The total lost workdays and fatality values are presented in Section 8, Hazard Analysis and Risk Assessment.

6.11 DATA SUMMARY

Presented in Table 6.11-1 is a summary of materials, emissions, and Wastes. Manpower and risk data for the cadmium sulfide are presented in Section 8.

<u> </u>		<u>``</u>	
Prócess step	Material	Material requirements	Emissions and wastes
<u>Cadmium refining</u>	Cadmium chloride Cadmium ° Cadmium refining fugitive emissions ° Cadmium processing fugitive emissions	4.13 Mg/MW 2.49 Mg/MW	32.3 kg/MW 49.7 kg/MW
Substate processing	Glass	211.5 Mg/MW	
Cadmium sulfide application	Thiourea	1.69 Mg/MW	
Metallization grid pattern	CdS		1.81 kg/MW
<u>Copper dip</u>	CuC1	277.26 Mg/MW	
<u>Metallization and post heat</u> <u>treatment</u>	Copper for top elec- trode Lead for top electrode Nickel Chromium Iron Copper for grid contact Copper Lead Nickel Chromium Iron	0.31 Mg/MW 1.17 Mg/MW 39.7 kg/MW 6.29 kg/MW 3.14 kg/MW 2.55 Mg/MW	2.66 Mg/MW 0.76 Mg/MW 38.3 kg/MW 6.07 kg/MW 3.03 kg/MW
Encapsulation	Unknown material	111,400 m ²	

TABLE 6.10-1. MATERIAL AND WASTE SUMMARY FOR CADMIUM SULFIDE PROCESS

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SECTION 7

GALLIUM ARSENIDE

This section deals with the production of single-crystal gallium arsenide concentrator cells, presenting the same topics discussed in connection with the cell production processes described earlier: process description, materials requirements, manpower requirements, process emissions, wastes, and controls, potential occupational hazards, and risk determination.

A major problem in developing data on manpower and materials for a GaAs production facility is that the major effort is still in research and development programs. One company has published information on a pilot-scale production facility, much of which provides the basis for manpower and material projections in this section. Where applicable, comparisons are drawn between processes for production of silicon and of GaAs, since several of them are very similar.

The following assumptions were made to simplify calculations of manpower and material requirements for the GaAs process:

- The active cell diameter is 1.245 cm (0.490 in.) (cell area is 1.217 cm²).
- The final GaAs substrate wafer is 125 µm thick.
- Cell efficiency is 18 percent at 400 suns concentration.
- At 400 suns each cell generates 8.7624 watts of power.
 The density of GaAs is 5.316 g/cm³.

- The work schedule is 24 h/day, 5 days/wk, 50 wks/yr or 6000 h/yr.
- All throughput efficiencies are 100 percent.

On the basis of assumption No. 5, it is calculated that 11,412,398 cells would be produced in a 100-MW_{nk} plant.

All material requirements for processes prior to and including wafer slicing are back-calculated from the amount of single-crystal GaAs in the finished wafer substrates.

7.1 GALLIUM REFINING

7.1.1 Process Description

According to one report, two companies in the United States produced gallium in 1979, one as a byproduct of alumina production and one as a byproduct of zine production (U.S. Dept. of Interior, 1979a). Gallium production from aluminum and zine refining is discussed briefly.

After zinc is reduced and distilled in retorts, the residues in the retorts are treated, along with iron muds produced as a result of purifying zinc sulfate solutions, to remove the gallium. The residues are first dissolved in caustic soda. The resulting solutions, containing gallium and aluminum, may then be treated by various methods. Extraction of gallium is usually done with an organic solvent to obtain gallium chloride. In this process the solution is neutralized, precipitating a mixture of hydroxides containing gallium. This mixture is dissolved in hydrochloric acid to give a 5-6N solution. The acid mixture is then extracted several times with an organic solvent (usually ether), which dissolves gallium preferentially. After distillation of the solvent, the gallium chloride is neutralized with an excess of soda, giving sodium gallate (III). Metallic gallium is then produced by electrolysis. Many variations of this method are probably used, depending on the nature of the impurities (Kirk and Othmer, 1966).

The estimated ratio of gallium to aluminum in bauxite is about 1:3000 to 1:8000 (Kirk and Othmer, 1966). In the extraction of sodium aluminate from bauxite, caustic is used. The aluminate is precipitated by bubbling CO₂ through the caustic The caustic solution is recirculated and reused for solution. extraction of aluminate from bauxite. Recirculation of the caustic solution eventually causes a buildup of gallium. After the ratio of aluminum to gallium in the caustic solution reaches approximately 500:1, the aluminate is precipitated with CO_2 . The filtrate is then treated with additional CO_2 to precipitate the gallate and remaining aluminate. The precipitate is subjected to a leaching with sodium hydroxide to yield a gallate-rich leachate, from which the gallium is deposited electrolytically. The gallium is 99.5 percent pure. It is further refined to attain purity as high as 99.999 percent (Gandel et al, 1977).

One of the two producers of gallium uses a variation of this process, in which the sodium aluminate solution is treated with lime to precipitate most of the alumina as calcium aluminate. Carbon dioxide is then used as in the process described above (Kirk and Othmer, 1966).

Purification of gallium to semiconductor-grade quality can be accomplished by several physical and chemical processes. Commercially applicable purification methods fall into three categories (Kirk and Othmer, 1966).

1. Chemical treatments, as with acids or with gases, such as oxygen, at high temperatures.

 Physicochemical methods, such as filtration of the fused metal, heating in vacuum, repeated solution, and electrolysis.

3. Physical methods, principally by crystallization as monocrystals. It has also been proposed to convert the gallium into a compound, such as the chloride, purify that, and then reconvert it to the metal.

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7.1.2 Material Requirements

The gallium requirements for the substrate wafers for a 100- MW production facility are back-calculated from the quantity of GaAs in the single-crystal wafers. Calculations of the gallium for all other GaAs or GaAlAs layers are based on their thickness. On the basis of total gallium requirements and the assumption that the gallium content of the bauxite mined is 0.005 percent (Gandel et al, 1977), it is estimated that the mining of about 287.2 Mg/MW of bauxite would be required to produce the 1436 kg of gallium needed for a 100-MW production plant. No estimates for gallium content in zinc blends were found.

Although no information is available on domestic production of gallium metal, the U.S. production can be estimated from imports for consumption and total domestic consumption. On this basis the estimate is 2500 kg/yr for domestic production (U.S. Dept. of Interior, 1980a). If 1436 kg is required to produce 100 MW of cells, this requirement represents 57.4 percent of the estimated gallium produced in the United States in 1979.

The total amount of bauxite mined in 1979 is estimated to be about 1.7 x 10^6 Mg. Production of the gallium needed for a 100-MW plant would require an estimated 28,720 Mg of bauxite, or only about 1.69 percent the total mined in 1979.

7.1.3 Manpower Requirements

Manpower requirements for gallium production are estimated to be 16 employee-hours per kilogram produced (U.S. Dept. of Interior, 1980a). On the basis of this estimate 22,976 employee-hours per year are required for gallium refining. It was also estimated that 0.35 employee-hour is required to mine 1 ton of bauxite. Since 28,720 Mg (31,663.8 short tons) of ore is needed to produce the gallium required, 11,082.3 employee-hours/ yr would be necessary to mine the bauxite.

7.1.4 Emissions, Wastes, and Controls

It should be noted that even though bauxite mining and aluminum refining are steps leading to gallium recovery, the aluminum demand will most likely always be the controlling factor in the quantity of bauxite mined. If the gallium content of bauxite is 0.005 percent, about 85 Mg of gallium was recoverable from the bauxite mined in 1979. Only an estimated 6.9 percent (5905 kg/85 Mg) of the theoretical quantity of gallium was recovered in 1979, which would indicate that even a significant increase in gallium demand would not affect the mining of bauxite.

One can therefore assume that no emissions or wastes from mining of bauxite or aluminum refining can be attributed to gallium production, since these processes will not likely be affected by an increase in demand for gallium.

No information was found in the literature on emissions and wastes from gallium refining. Waste slurries and sludges no doubt remain after extraction. Although caustic wastes are reduced by recirculation and reuse, they eventually must be disposed of, as must the acid wastes (HCl) and organic solvents.

7.1.5 Occupational Hazards

Because of the lack of specific information, hazards involved in the refinement of gallium, the following is a general discussion of potential hazards.

The caustic and HCl used for extraction in the process could be the source of chemical burns, including eye injuries, to workers involved in handling these chemicals or working near tanks or reactors that contain them. Use of ether as a solvent in the process presents an explosion hazard as well as a health hazard to workers.

Numerous types of physical hazards are probable. According to statistics of the U.S. Department of Labor, Mine Safety and Health Administration for Metallic Mineral Mining (1979d), a total of 499 injuries occurred in 1979 in mining and processing of alumina, and 24 in mining and processing of aluminum. In mining and processing of alumina, the major causes of injuries were electrical equipment; exploding vessels under pressure; falling, rolling, or sliding material; handtools; powered haulage (vehicular accidents); machinery; slips and falls; and materials handling. In aluminum mining and processing the major causes were materials handling, powered haulage, machinery, and slips or falls.

7.1.6 Risk Assessment

The labor requirement necessary to produce enough gallium for a 100 MW/yr plant would be approximately 11,082 employeehours for extraction and 22,976 employee-hours for refinement. Using the occupational injury, illness, and fatality statistics presented in Table 1.3-13, total lost workdays and fatalities can be determined for these processes. The occupational health and fatality values were determined using statistics from the metal mining occupations for extraction, and primary aluminum smelting and processing occupations for refinement. The extraction of gallium metal will result in 4.6 lost workdays and 4.1×10^{-4} fatalities. The refining will result in 11.0 lost workdays and 1.4×10^{-3} fatalities. The entire operation is expected to result in a total of 15.6 lost workdays and 1.8×10^{-3} fatalities.

7.2 ARSENIC REFINING

7.2.1 Process Description

Arsenic is produced in a trioxide form as a byproduct of copper and lead smelting and is contained in the flue dusts from these operations. The flue dusts, containing 10 to 30 percent arsenic, are roasted at 400°C (752°F), at which temperature the arsenic vaporizes. The vapor then condenses to produce arsenic trioxide of 90 to 95 percent purity. This crude arsenic trioxide is resublimed in a reverberatory furnace at 550°C (1022°F)

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and then passed through a series of condensing chambers of gradually decreasing temperature. The purity of the arsenic trioxide obtained may range from 94.9 to greater than 99 percent. Arsenic metal may also be produced from the trioxide by reduction with charcoal, followed by condensation of the metal vapor (Gandel et al, 1977 and PEDCo Environmental, Inc., 1976b).

7.2.2 Material Requirements

As with gallium, the total quantity of arsenic needed for production of the GaAs required for 100 MW of cells is backcalculated from the amount of GaAs in the final single-crystal substrate layer and the other LPE-deposited layers. Based on estimates and assumptions presented later, a total of 18.48 kg/MW, or about 1.85 Mg, of arsenic will be needed to produce 100 MW of cells.

No data are available in the literature on production of arsenic in the United States as this is considered proprietary.

7.2.3 Manpower Requirements

Assuming that 75 percent of the domestic arsenic used is imported, it was estimated that about 4000 tons of arsenic is produced in the United States. Assuming that 76,800 employeehours per year is needed for production, (8 workers/shift, plus 20 percent additional for maintenance) 19.2 employee-hours are required to produce 1 ton of arsenic. Therefore for production of 1.85 Mg of arsenic for the 100 MW plant, about 39 employcehours per year are required.

7.2.4 Emissions, Wastes, and Controls

It has been estimated that about 49 percent of arsenic emitted at copper smelters is retained in cyclones and bag filters while about 51 percent escapes to the atmosphere (PEDCo Environmental, Inc., 1976a). The collected dusts may be used to recover arsenic trioxide (As_2O_3) , recycled to the smelting furnace, deposited on land, or stored for future processing. It is estimated that about 17 kilograms of flue dust per Mg of copper is are disposed of on land. Disposal in typical land-fills is a problem because of the high toxicity and low solubility of the wastes. The waste streams of As_2O_3 from all metallurgical smelters total 9100 Mg/yr.

Control of flue gas wastes is accomplished primarily with electrostatic precipitators and baghouses. Some high-pressuredrop venturi scrubbers are also used.

Other wastes are the slag from furnaces, which is either disposed of on land or granulated in water, and sulfur oxides from converters, roasters, and reverberatory furnaces. If the slag is granulated, the water may also require disposal or recycling since it usually contains arsenic.

7.2.5 Occupational Hazards

Information from the Department of Labor and Industries indicates that, as expected, the primary hazard is exposure to arsenic above recommended levels. The plant cited produced lead and selenium as well as arsenic. Arsenic was a problem in the lead and selenium operations in addition to the arsenic operations. Workers overexposed to arsenic in the arsenic plant included hoistmen, hoistman helpers, hopper men, furnacemen, blender operators, and millmen/car loaders. These same workers were also overexposed to antimony. Several of the workers in the arsenic plant were also found to be overexposed to lead.

Other hazards cited include potential overexposure to noise, SO_2 , acids, and copper; various electrical hazards; and working of welders in confined spaces without proper ventilation. Protective clothing and respiratory protection gear were worn improperly or not at all. It was recommended that a more thorough safety training program be initiated for workers and that supervisory control of all personal protection programs be improved.

7.2.6 <u>Risk Determination</u>

The labor requirement for refinement of enough arsenic to supply a 100 MW/yr plant is estimated at approximately 39 employee-hours. This level of activity is not expected to result in any significant amount of lost workdays or fatalities.

7.3 GALLIUM ARSENIDE PRODUCTION

7.3.1 Process Description

The first step in fabrication of single-crystal GaAs cells is the synthesis of polycrystalline GaAs. Gallium in chunk form is loaded in a quartz boat and placed at one end of a long glass tube. Crushed metallic arsenic is loaded into the other end of the tube, and both ends are sealed in vacuum. The tube on a roller assembly enters a two-zone tube furnace. The arsenic end is maintained at 610° to 620°C (1130° to 1148°F), while the gallium end is kept at 1250°C (2282°F) [melting point of GaAs is 1238°C (2260°F)]. The arsenic vaporizes and reacts stoichiometrically with molten gallium to form GaAs. At GaAs melt temperatures, gallium may react with the quartz (SiO₂) boat to form The large temperagallium oxide (Ga₂O) (Gandel et al, 1977). ture gradient maintained over the glass tube prevents transport of the Ga_2O , and a high vapor pressure of Ga_2O is maintained to prevent it from contaminating the GaAs. Residual arsenic in the bottle is held to a minimum by adding less than the stoichiometric amount of arsenic.

7.3.2 <u>Material Requirements</u>

The quantity of GaAs required for the single-crystal substrate is calculated by assuming certain losses for wafer polishing, wafer slicing, and losses from the single-crystal growth process. The required amount of polycrystalline GaAs is calculated to be 32.9 kg/MW. Since 1 mole of Ga and 1 mole of As are needed to form 1 mole of GaAs, 69.72 g of Ga and 74.9216 g of As are needed to form 1 mole of GaAs. At this ratio of 74.9216/69.72 (1.075), the required quantities for production of 32.9 kg/MW of polycrystalline GaAs are 15.9 kg/MW of Ga and 17.0 kg/MW As.

7.3.3 Manpower Requirements

With the assumptions that each poly-reactor can synthesize 3 kg of GaAs per day and that one operator can operate 2.5 reactors (Bell, 1980), the calculated manpower requirements are 2 operators per shift or 12,000 employee-hours/yr. No data are available on supervisory or maintenance requirements; therefore, a ratio of foremen to maintenance to operators of 1:6:100 used to estimate manpower for a hypothetical silicon production plant (Coleman et al, 1977) is also used for these manpower estimates. On this basis, about 720 employee-hours/yr would be required for maintenance and 120 employee-hours/yr for a foreman.

7.3.4 Emissions, Wastes, and Controls

The most hazardous potential emission from the compounding of GaAs is accidental release of arsenic trioxide (As_2O_3) . Ιt has been reported that the quartz boats sometimes explode releasing As₂O₃ (Briggs et al, 1980). An alarm system was incorporated into the compounding system to detect upset conditions. When the alarm sounded, a crew equipped with self-contained breathing apparatus and protective clothing entered the reactor room after a specified waiting period to clean up any arsenic or arsenic trioxide that may have been released. Another potential hazard arises because one section of the quartz reaction bottle is etched with HF-HNO3 to remove the residual arsenic after the reaction so it can be reused (Gandel et al, 1977). Therefore, the arsenic contaminated HF-HNO3 constitutes another potential waste. It is not known how much of the acid mix would be required in production.

7.3.5 Occupational Hazards

The major occupational exposure hazard would of course be from As or As_2O_3 . Results of one sampling survey for arsenic in the compounding area and related operations are given in Table 7.3-1 (Briggs et al, 1980).

	Arsenic concentration,	
Breakout of GaAs quartz cylinder	<1.8 µg/m ³	
GaAs preparation area: personal sample	87.3 μg/m ³	
Wipe samples		
GaAs crucible assembly, weighing: top of system	1.29 mg/m ³	
As weighing: hood top	13.0 mg/m ³	
Crucible welding operation: tabletop	13.3 mg/m ³	

TABLE 7.3-1. SAMPLING SURVEY FOR ARSENIC IN GaAs COMPOUNDING AREA AND RELATED OPERATIONS

Even the small quantity of data in Table 7.3-1 indicates a potential problem of arsenic exposure. The one personal sample of 87.3 μ g/m³ exceeds the recommended TLV of 50 μ g/m³. The wipe samples indicate that significant amounts of arsenic could accumulate on surfaces. Thorough housekeeping practices are needed to prevent this. Although exposure to GaAs could also occur, this does not appear to be as hazardous as exposure to arsenic in the elemental or trioxide form. More information is needed on the toxicity of GaAs.

7.3.6 Risk Determination

The total labor requirement for the production of gallium arsenide is estimated to be 12,840 employee-hours. Using the occupational injury, illness, and fatality statistics presented in Table 3.1-13, the total lost workdays and fatalities can be determined for this process. The technical occupations contribute 12,000 hours to the proposed work effort resulting in an expected 2.5 lost workdays and 1.2 x 10^{-4} fatalities. The supervisor of the production process is performed by foremen,

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this inspecting occupation contributes 120 hours to the work effort resulting in 0.1 lost workdays and 1.7 x 10^{-6} fatalities. Maintenance of the process will require 720 employee-hours resulting in 0.2 lost workdays and 9.4 x 10^{-6} fatalities. The entire process activity is expected to result in a total of 2.8 lost workdays and 1.3 x 10^{-4} fatalities.

7.4 LIQUID-ENCAPSULATION CZOCHRALSKI SINGLE-CRYSTAL GROWTH7.4.1 Process Description

This process is almost identical to that described in Section 4.6.1 for single-crystal growth of silicon. In singlecrystal growth of GaAs, the chunk polycrystalline GaAs is loaded into a quartz ampule with an outer graphite receptor. It is then melted at about 1238°C (2260°F), and the crystal is pulled in a pressurized atmosphere of about 90 MPa (100 atm)* (Briggs et al, 1980). The GaAs melt is covered with a liquid blanket of boric oxide (B_2O_3) to prevent arsenic loss (Harrison, 1973). Tin is added to the melt as a dopant to make the crystal n-type.

7.4.2 Materials Requirements

The estimated quantity of polycrystalline GaAs entering the melt is 27.4 kg/MW. On the basis of estimates of crucible losses in single-crystal growth of silicon, a 7 percent loss is assumed to occur in Czochralski growth of GaAs crystals. The amount of single-crystal GaAs leaving the process is therefore 25.5 kg/MW.

The quantity of tin added is 10^{18} atoms/cm³ (Magot, 1979 and James et al, 1977). It is calculated that approximately 0.34 g/MW of tin is needed to produce 100 MW of cells.

7.4.3 Manpower Requirements

Assuming that one crystal puller can grow about 2 kg of single-crystal GaAs per 24-hour day (Bell, 1980), each grower

^{*} In some systems the pressures are only slightly above 1 atmosphere.

would be capable of growing 500 kg of single-crystal GaAs per year.

Since 2550 kg of single-crystal GaAs is required for 100 MW of cells, about 6 growers would be needed. If 1 operator can attend 3 growers, 2 operators, or 12,000 employee-hours/yr, would be needed. On the basis of the manpower estimates given for silicon cells in Section 4.4.3, the requirements for support engineers, technicians, quality control personnel, foremen, and maintenance workers for single-crystal growth of GaAs are 2160, 6480, 1080, 1800, and 2700 employee-hours/yr, respectively.

In one R&D facility, crystal growth was monitored outside the growth area by use of television cameras and other electronic instruments (Briggs et al, 1980). It is not known whether this method of surveillance would affect manpower requirements significantly.

7.4.4 Emissions, Wastes, and Controls

Emissions during this process will be minimal, although some As_2O_3 may be released during the growth process. It is estimated that about 1.9 kg/MW or 190 kg of GaAs is lost in the process. This material is assumed to be lost in the graphite, quartz, or alumina crucible and to be either recyled or disposed of. Crucibles also must be recycled or disposed of eventually. Another potential waste product is boron oxide (B_2O_3) . It is doubtful that the quantity will be significant because the B_2O_3 adheres to the surface of the GaAs crystal as it is withdrawn and is eventually depleted (Harrison, 1973).

7.4.5 Occupational Hazards

Potential exposures in the crystal growth area are to GaAs, As₂O₃, B₂O₃, and to the ammonium-hydroxide (NH₄OH) and hydrogen peroxide (H₂O₂) used to clean equipment surfaces. Toxicity of GaAs and B₂O₃ appears to be low (Briggs et al, 1980); little information is available on these compounds, however, and the potential for hazardous exposure must be considered. Small amounts of As_2O_3 may be deposited outside the melt. Precautions should be taken to eliminate these emissions. If pullers are isolated and operated outside the growing area, worker exposure should be eliminated except during removal of the boule, cleanup of the equipment, and charging of the melt with additional poly-GaAs. Workers should wear appropriate protective clothing and respirators to minimize exposure to As_2O_3 , NH_4OH , and H_2O_2 during these cleanup and preparation operations. Workers should take the same precautions during cleanup operations following an accidental release.

7.4.6 Risk Determination

The total labor requirement for the liquid-encapsulation Czochralski single crystal growth process is estimated to be 24,420 employee-hours. Using the occupational injury, illness, and fatality statisites presented in Table 3.1-13, the total lost workdays and fatalities can be determined for this process. The technical occupations are expected to contribute 20,640 employee-hours including line operators, engineers, and techni-This activity is expected to result in 4.4 lost workdays cian. and 2.1 x 10^{-4} fatalities. The inspecting occupations will contribute 1,080 employee-hours to the total labor requirement. This effort is expected to result in 0.3 lost workdays and 1.5 x 10⁻⁵ fatalities. Maintenance necessary to sustain this operation will contribute 2,700 employee-hours, resulting in 0.9 lost workdays and 3.5×10^{-5} fatalities. The entire process will result in 5.6 lost workdays and 2.6 x 10^{-4} fatalities.

7.5 INGOT PROCESSING

7.5.1 Process Description

As with silicon ingots, the processing of GaAs ingots involves cropping the tapered ends, slicing the ingots into wafers, and lapping and polishing the wafers to remove saw damage.

7.5.2 Material Requirements

Cropping losses are estimated at 20 percent, so that the quantity of waferable ingot remaining after the crop is 20.4 kg/MW. After the ingot is cropped, a multiwire saw is used to produce the substrate wafers. An estimated kerf loss of 50 percent is assumed, slightly higher than for silicon because GaAs is more fragile. After kerf losses the quantity of GaAs The estimated quantity of wire saw remaining is 10.2 kg/MW. slurry for sawing GaAs crystals is the same as that for silicon crystals (8.3 kg slurry/kg polycrystalline GaAs). On this basis, about 22,742 kg of slurry will be required. This estimate is assumed to include the recycle and make-up slurry. If the slurry consists of equal parts of mineral oil, clay, and SiC grit, about 7580.7 kg of each component will be required.

After the wafer sawing, the wafers are lapped and polished to remove saw damage. If a 10 percent loss is assumed, then 9.2 kg/MW of finished GaAs wafers remains after this process step. The polishing agent is a hypochlorite (bleach) solution. The quantity of hypochlorite used is not available.

It should be noted that the total losses of GaAs from ingot processing are estimated here at about 33.6 percent. Losses of 29 percent are reported elsewhere (Gandel et al, 1977).

7.5.3 Manpower Requirements.

Estimates of manpower requirements for the cropping, slicing and polishing processes are the same as those in Section 4.5.3 for the Silicon I process, since the processes are very similar. For cropping the ingot the estimate is 0.75 operator/ shift/puller. Based on this estimate, about 27,000 employeehours/yr would be required for cropping. Requirements for maintenance, quality control, and supervision are estimated to be 0.075, 0.03, and 0.05 operators/shift/puller, respectively. On this basis, the requirement for maintenance, quality control, and supervisory personnel would be 2790, 1080, and 1800 employee-hours/yr. Manpower estimates for wafer slicing are based on a throughput rate of 200 wafers/day/saw (Maget, 1979) (or 500 cells/day/ saw, since there are 4 cells/wafer) and 15 saws/operator (see Section 4.5.3). On the basis of these assumptions it is calculated that 4 operators or about 24,000 employee-hours/yr would be required for operation. If maintenance requirements are also assumed to be 1 person per 15 saws, then 3.8 maintenance workers or 22,800 employee-hours/yr are needed.

Estimates for wafer polishing are based on a semi-automated tank system in which a cassette holding the wafer is sequentially dipped in the hypochlorite solution, rinsed, and dried. For this system in the silicon I process a throughput of 7500 cells/h is assumed. With this same estimate and the assumption of 0.5 operators/station/shift, the wafer polishing requirement is 1 operator or 6000 employee-hours/yr. If maintenance requirements are 0.05/station/shift, only 300 employee-hours/yr would be required.

7.5.4 Emissions, Wastes, and Controls

Gallium arsenide wastes will be generated from cropping and sawing primarily. The quantity of GaAs lost from cropping will be about 5.1 kg/MW, and from wafering, about 10.2 kg/MW. It is assumed that a large-scale production facility would find it cost-effective to recover the GaAs kerf losses from the cutting The estimated quantity of cutting grit is based on rearit. cycling of the grit until it is no longer satisfactory. Additional slurry is added, and the used slurry disposed of. Under these circumstances, 22,742 kg (22.7 Mg) of the mineral oil/ clay/SiC grit slurry must be disposed of or recycled. During the cutting of wafers, approximately 1 percent of the slurry (a total of 227.4 kg in this case) may be emitted into the workplace (Gandel et al, 1977). Local ventilation for each saw It is not known what should remove most of these emissions. quantity of hypochlorite solution is used to polish the wafers, but a significant quantity probably must be disposed of.

7.5.5 Occupational Hazards

Potential occupational exposures in ingot cropping would be primarily to GaAs particulates by inhalation during cropping and sawing; to the sawing slurry by inhalation, and to the hypochlorite solution by dermal or inhalation exposure during wafer polishing. As noted previously, both gallium and arsenic are hazardous in pure form but the toxicity of GaAs is relatively unknown.

Table 7.5-1 shows results of personal and area samples taken in the ingot wafering area (Briggs et al, 1980). Arsenic concentrations given are as elemental arsenic and not as arsenic in GaAs. Although these levels are below the established TLV of 50 μ g/m³, precautions in this area are still required. Dermal exposure to hypochlorite can cause chemical burns, and inhalation may result in dyspnea, pulmonary edema, nausea, and possibly perforation of the esophagus and stomach if exposure is severe. Fumes can also cause eye irritation.

Potential injuries would be primarily cuts from materials handling and eye injuries from flying particles during cropping or sawing.

	Arsenic concentration, ^a µg/m ³
Personal sample	14.9
Area sample near above operator	15.0
Personal sample	-11.3
Area sample near operator in above sample	

TABLE 7.5-1. SAMPLING SURVEY FOR ARSENIC IN GaAs WAFERING AREA

^a As elemental arsenic.

7.5.6 Risk Determination

Ingot processing include cropping, slicing, and polishing operations will result in a total labor requirement of 85,770 employee-hours. Using the occupational injury, illness, and fatality statistics presented in Table 3.1-13, the total lost workdays and fatalities can be determined for this process. The material abrading and polishing occupations are expected to contribute 57,000 employee-hours toward the work effort. This activity is expected to result in 11.3 lost workdays, no fatalities are expected to occur. The inspecting occupations will contribute 2,880 employee-hours toward supervision of the entire process. This level of activity is expected to result in 0.7 lost workdays and 4.0 x 10^{-5} fatalities. Maintenance requireingot processing equipment will require 25,890 ments for employee-hours, resulting in 8.4 lost workdays and 3.4 x 10^{-4} fatalities. The entire operation is expected to result in a total of 20.4 lost workdays and 3.8 x 10^{-4} fatalities.

7.6 LIQUID-PHASE EPITAXIAL (LPE) DEPOSITION

7.6.1 Process Description

This process, referred to as pulse-heated LPE, was developed by Varian to increase throughput over that of conventional LPE processes (Maget, 1979). The apparatus, a pulseheated boat assembly, consists of a heater, a solution well, and a wafer carrier. A schematic of the assembly is shown in Figure 7.6-1. A complete reactor system also includes a furnace, a quartz reactor tube connected to an interlock chamber, and a magnetically coupled push-rod.

In this process wafers are placed into carriers, which are then stacked into a cartridge. The cartridge passes through a vacuum interlock into a chamber area, from which the carriers have access to a track leading to the pulse-heated boats. Each



Figure 7.6-1 Pulse-heated boat assembly for pulse LPE process (Maget, 1979).

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carrier travels down the track to the pulse-heated boat, deposition is performed, and the carrier returns to the cartridge. This is repeated until all carriers have returned to the cartridge. The cartridge then returns through the vacuum interlock, and the wafers are sent to the next process.

The pulse LPE process uses a saturation GaAs wafer which is locally heated and positioned over a solution well in contact with liquid gallium in the well. The wafer is then heated driving arsenic from the wafer into the gallium solution. After the desired amount of arsenic is attained in the gallium solution, the heat is turned off and a substrate positioned under the solution well. Deposition takes place as the excess nutrient concentration is relieved causing growth on the wafer.

For each cell produced, three different layers are deposited by pulse-heated LPE; an n-type GaAs buffer layer on the substrate; a p-type $Al_{0.93}$ $Ga_{0.07}$ As window layer, and a lattice matching p GaAs layer.

7.6.2 Materials Requirements

The n-type GaAs buffer layer is assumed to be 30 µm thick. It is calculated that 2.2 kg/MW of GaAs would be required. If the process is 95 percent efficient (Watts, et al, 1979), 2.3 kg/MW would be needed; 1.1 kg/MW of gallium and 1.2 kg/MW of arsenic.

Tin is the dopant in this process (Maget, 1979 and James et al, 1977). Based on a doping concentration of 7 x 10^{17} atoms/ cm³, an estimated 57.5 mg/MW of tin would be needed.

The next layer deposited by LFE is the p Al_{0.93} $Ga_{0.07}$ As window layer. Since no density value is available for AlGaAs and about 95 percent by weight of the AlGaAs is AlAs, the density of AlAs (3.81 g/cm³) is used in estimating this material requirement. At this density the requirement for a 0.6-µm-thick layer is 334.2 g/MW of AlGaAs. The proportions are about 80 g/MW Al, 15.5 g/MW Ga, and 238.2 g/MW As.

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The dopant for this window layer is magnesium (Maget, 1979 and James et al, 1977). At a doping concentration of 5 x 10^{17} atoms/cm³ about 1.7 mg/MW of magnesium would be required.

The final GaAs layer is a lattice matching layer that facilitates contact with the AlGaAs layer (James et al, 1977). The lattice matching layer is 2 μ m thick and would therefore require 82.1 g/MW GaAs, or 39.6 g/MW Ga and 42.5 g/MW As.

It is also assumed that magnesium is used for the p-type dopant in this layer at a concentration of 10¹⁸ atoms/cm³. At this concentration, 0.56 Mg/MW of magnesium would be needed for the lattice matching GaAs layer.

7.6.3 Manpower Requirements

Calculation of manpower requirements for deposition of the n-GaAs, p-AlGaAs, and p-GaAs layers, is based on a throughput rate of 10 cells/h/furnace (80 cells/shift/furnace), operator requirements of 0.5 worker/machine/shift (Maget, 1979 and Bell, 1980), maintenance requirements of 0.1 worker/machine/shift,* and foremen requirements of 0.05 worker/machine/shift. At the specified throughput rate, 191 LPE reactors would be needed to produce the required number of cells/yr. Therefore, the requirements are for about 96 operators or 576,000 employeehours/yr along with 114,600 employee-hours/yr for maintenance personnel, and 57,300 employee-hours/yr for foremen. Note that the specified throughput rate is for a laboratory pilot-scale plant; significantly higher throughput rates should be achieved in a large-scale production facility. The estimates should therefore be viewed as manpower requirements for a worst-case production rate.

7.6.4 <u>Emissions, Wastes, and Controls</u>

Since the LPE process is under vacuum, emissions into the workplace during normal operation should be minimal. Hydrogen

^{*} Maintenance for this operation is assumed to be slightly higher than the 0.075 worker/machine/shift for Czochralski crystal growth because the LPE reactors must be disassembled and cleaned periodically.

is used to purge the vacuum tube and prevent arsenic emissions. The hydrogen may be exhausted through an oil bubbler to remove any arsenic formed and then vented to an exhaust duct. Some arsenic vapor escaping into the hydrogen may be deposited on the quartz reactor walls. Wastes would be generated in cleaning out the solution wells, furnaces, quartz reactor tubes, oil bubbler, and vacuum pumps.

7.6.5 Occupational Hazards

The major potential occupational exposure would again be to arsenic and GaAs when workers load the boats, replenish the solution wells, and especially when they maintain and clean the LPE furnaces, reactors, and boat assemblies. Exposure could also occur during maintenance of vacuum pumps and exhaust piping. These hazards should be easily controlled by proper use of protective clothing and respirators.

Use of hydrogen for purging the reactor tubes creates a potential fire and explosion hazard. Use of hydrogen monitors to detect possible buildup to dangerous levels should alleviate this hazard.

Worker interaction with process equipment should be limited except during maintenance, so as to minimize such injuries as cuts and burns.

7.6.6 <u>Risk Determination</u>

The labor requirement for the liquid phase epitaxial (LPE) deposition process is 747,900 employee-hours. Using the occupational injury, illness, and fatality statistics presented in Table 3.1-13, the total lost workdays and fatalities can be determined for this process. The technical occupations, represented by line operators, will contribute 576,000 hours towards the total labor effort. This activity is expected to result in 122.1 lost workdays and 5.8 x 10^{-3} fatalities. Inspecting occupations will contribute 57,300 employee-hours toward the supervision of the LPE deposition process. This effort will

result in an estimated 14.6 lost workdays and 8.0 x 10^{-4} fatalities. Maintenance occupations will contribute 114,600 employee-hours resulting in 37.0 lost workdays and 1.5 x 10^{-3} fatalities. The entire process is expected to result in a total of 173.7 lost workdays and 8.1 x 10^{-3} fatalities.

7.7 DEPOSITION OF SIO₂ LAYER

7.7.1 Process Description

In this process an amorphous SiO_2 layer is deposited as a protective coating by use of a plasma CVD reactor. The SiO_2 layer serves as a plating mask for metallization and prevents contamination of the GaAs layer (Maget et al. 1979). Deposition is accomplished by use of a 1.5 percent silane (SiH₄) argon gas mixture and nitrous oxide (N₂O) gas. Considering the performance of state-of-the-art plasma deposition systems, we assume that 40 cells/h can be processed and that process efficiency is 65 percent.

7.7.2 Materials Requirements

No published values were found for the flow rates of SiH₄/ argon and N₂O required for deposition. Therefore the estimates of the final quantity of SiO₂ deposited on the cell is based on a thickness of 1000/Å and a density of 2.19 g/cm³. The amount of SiO₂ actually deposited on the cells is calculated to be 3.0 g/MW. Since the process is assumed to be only 65 percent efficient, a total of 4.6 g/MW SiO₂ is formed, with 1.6 g/MW lost as waste. The required quantity of SiH₄ is based on a deposition rate of 0.874 Si/SiH₄ (Watt et al. 1979). On the basis of this estimate 2.46 g/MW of SiH₄ would be required. At a density of 1.44 g/l it would require 1.71 l/MW SiH₄. Since the SiH₄ content of the gas mixture is 1.5 percent it would require 164 g/MW or 114 l/MW. The other 98.5 percent is argon.

The quantity of N_2O required using a theoretical deposition rate of 0.3635 for N_2O was calculated to be 6.74 g/MW or 3.41 ℓ/MW .

7.7.3 Manpower Requirements

Manpower calculations are based on a throughput rate of 40 cells/h and 0.25 worker/machine/shift (Maget, 1979 and LFE Product Information). On this basis the requirements are for 48 plasma CVD machines, and thus for 12 operators/shift or 72,000 employee-hours/yr. In the absence of published estimates, the maintenance and supervisory requirements are based on a ratio of 100:6:1 (operators:maintenance:foreman). Thus, 4320 employee-hours/yr are needed for maintenance personnel and 720 for a foreman.

7.7.4 Emissions, Wastes and Controls

Emissions and wastes from this process will be minimal. Total waste is calculated to be about 160 g/yr as SiO_2 . Some of this is probably emitted SiH_4 and N_2O , plus some SiO_2 deposited on reactor walls and substrate carriers. Vacuum pump oil is another waste that must be disposed of; the quantities should be small. In one commercial plasma system a molecular sieve may be used on the discharge side of the vacuum pump to prevent emissions of pump oil (LFE Corp., product information).

7.7.5 Occupational Hazards

Worker hazards will be slight. The process is almost entirely automated, and little worker interaction with equipment is required. The process is also under vacuum, so that emissions into the workplace should be minimal. The SiO_2 is produced in an amorphous form and therefore is of little concern, especially at the levels present here.

There is some potential for exposure to SiH_4 and N_2O , but the quantities are so small and flow rates so low that significant levels would be emitted only by an accidental release during handling of the source tanks.

None of the substances are major health hazards; only a large release would pose any serious health problems. One potentially serious hazard, however, is silane, which may ignite

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spontaneously upon exposure to moisture in the air and lead to a fire or explosion. Use of an inert gas to purge the plasma system should prevent this problem in the machine area.

7.7.6 <u>Risk Determination</u>

Deposition of the SiO₂ layer will require a total of 77,040 employee-hours. Using the occupational injury, illness, and fatality statistics presented in Table 3.1-13, the total lost workdays and fatalities can be determined for this process. The technical occupations, in the form of line operators, will contribute 72,000 hours resulting in 15.3 lost workdays and 7.2 x 10⁻⁴ fatalities. The inspecting occupations in the capacity of foremen will contribute 720 hours toward the total work effort resulting in 0.2 lost workdays and 1.0 x 10^{-5} fatalities. The maintenance occupations will provide 4,320 hours for maintaining and repairing equipment, this is expected to result in 1.4 lost workdays and 5.6 x 10^{-5} fatalities. The total activity required for the deposition of SiO₂ will result in 16.9 lost workdays and 7.8 x 10^{-4} fatalities.

7.8 FRONT METALLIZATION

7.8.1 Process Description

Front metallization basically involves the following steps:

- * Application and development of photoresist
- Etching of the contact pattern through the SiO2 and GaAs to the AlGaAs layer.
- * Application of a metal grid by evaporation
- Removal of excess metal and photoresist.

Automated photolithography equipment has been developed. The etch process could also be easily automated by use of a walking beam to transport the wafers in cassettes through the tanks. Metallization is presently done by vacuum evaporation, with gold and tin as the front contact metals. The photoresist and excess metal are then removed with acetone.

7.8.2 Material Requirements

In calculation of the needed quantity of photoresist, it is assumed that the application is 5 μ m thick and covers 90 percent of the cell area. On this basis the total amount required is 69.4 ml/MW or 6.94 liters/yr. Of this quantity 62.5 ml/MW would be deposited directly on the cell and 6.9 ml/MW on the mask.

The next step involves etching the contact pattern with an HBr/Br solution (Briggs, et al., 1980) or a proprietary buffered oxide etch (Bell, 1980). No information is available on material requirements for the etching solution. The quantities of SiO_2 and GaAs removed in this step would be 0.3 and 7.8 g/MW, respectively.

Assumptions used in calculating metal requirements are that the grid covers 10 percent of the cell area, the metal layer is 5 μ m thick, the contact is 80 percent Au and 20 percent Mg, and deposition by evaporation is 50 percent efficient. On this basis a total of 188.8 g/MW of Au and 4.8 g/MW of Mg would be required. Since the process is assumed to be 50 percent efficient, half would be deposited on the cell and half deposited on the substrate holder reactor walls or exhausted.

Based on an estimated value of 0.041 ml/cm_2 of acetone, the requirement for 100 MW of cells would be about 5.7 l/MW or 4.5 kg/MW of acetone.

7.8.3 Manpower Requirements

At a throughput rate of 50 cells/h and 0.5 worker/shift/ machine, the operating requirements are 19.5 operators/shift or 117,000 cmploycc-hours/yr. At a ratio of 100:6:1 (operators: maintenance:foremen) the additional labor requirements are 7020 employee-hours/yr for maintenance workers and 1170 for foremen.

For etching and photoresist removal it is estimated that only one station is required for each of these operations and that manpower needs are 0.5 operator/station/shift or 3000 employee-hours/yr. For the photoresist application a throughput rate of 3600 cells/h is assumed; this is less than half the proposed rate for processing of silicon wafers (Wihl 1978). At this rate only one station would be required. At 1 operator per station, the annual requirement is for 1 operator or 6000 employee-hours. At 6 percent of operator requirements, the annual maintenance requirement is 360 employee-hours; at 1 percent of operator requirements, the annual foreman requirement is 60 employee-hours.

7.8.4 Emissions, Wastes and Controls

The major potential emissions and wastes from these processes would be from the etching solution and the acetone. Although requirements for the etching solution are not known, it is most likely that some of the solution will be wasted and must be neutralized with lime and soda ash. Proper ventilation over the etch tank should easily prevent emissions into the workplace.

If acetone is used for removal of the photoresist, it must be desposed of or recycled. Since such a small amount is used, it could be incinerated. As with the etch solution, local ventilation will be needed over the acetone tank to prevent emissions into the workplace.

Metal emissions from the vacuum evaporation process should be minimal.

7.8.5 Occupational Hazards

The primary occupational hazard is exposure to the HBr/Br or other etching solution. Protective clothing is essential in this area because of the corrosive action of these substances on the eyes, skin, and mucous membranes. Continued exposures to low concentrations of bromine may cause acne-like skin lesions, whereas long-term exposures to hydrobromic acid may cause chronic nasal and bronchial discharge and dyspepsia. Some protective clothing may also be required for workers in the photoresist removal area to prevent exposure to acetone which may cause dermatitis by dermal exposure and headaches and nausea from inhalation. The primary danger from acetone is the potential for fires. Every precaution should be taken to eliminate fire hazards. Additionally, a fire extinguisher containing dry chemcials, CO_2 , or alcohol foam should be kept in the area.

Since the quantities of metals used are so small and the process is under vacuum, significant exposures to metals are unlikely.

7.8.6 Risk Determination

The front metallization process requires a total labor effort of 137,610 employee-hours. Using the occupational injury, illness, and fatality statistics presented in Table 3.1-13, the total lost workdays and fatalities can be determined for this process. The metal plating occupations associated with this process are expected to contribute 129,000 hours toward the This level of activity is expected to total labor requirement. lost workdays and 3.1 x 10^{-3} fatalities. result in 44.9 Inspecting occupations will contribute 1,230 employee-hours of labor, resulting in 0.3 lost workdays and 1.6 x 10^{-5} fatalities. The maintenance of this process will require 7,380 employeehours of labor. The maintenance activity is expected to result in 2.4 lost workdays and 9.6 x 10^{-5} fatalities. Activity associated with the metallization process is expected to result in a total of 47.6 lost workdays and 3.2 x 10^{-3} fatalities.

7.9 BACK METALLIZATION

7.9.1 Process Description

This process is the same as front metallization except that it entails no photoresist application or removal and no etching step. The back contact, consisting of gold (Au) and tin (Sn), is deposited by vacuum evaporation.

7.9.2 Material Requirement

It is assumed that the back layer is 5 μ m thick and covers the entire back of the cell, and that the deposition process is 50 percent efficient (Watts et al., 1979). No information was found on the proportion of gold to tin. It is estimated that a total of 138.8 cm³/MW of Au-Sn would be required, with half deposited on the cell and half lost on the substrate holders or reactor walls or discharged through the exhaust. Much of this would most likely be recovered for the gold.

7.9.3 Manpower Requirements

It is assumed that the throughput rate is 50 cells/h and that 1 operator can operate two metallization stations (Maget, 1979 and Bell, 1980). On this basis, 39 vacuum evaporation stations would be required, with a total of 19.5 operators or 117,000 employee-hours/yr. At rates of 6 and 1 percent, respectively, of operator requirements, the annual requirements for maintenance and foreman personnel would be 7020 and 1770 employee-hours.

7.9.4 Emissions, Wastes, and Controls

This operation should cause no major emission or waste problems. The quantities of metals are relatively small, and the metals used pose no significant environmental threat. Disposal of vacuum pump oil will be a minor concern.

7.9.5 Occupational Hazards

Hazardous exposures should be minimal, limited primarily to maintenance personnel performing routine cleaning or maintenance of vacuum evaporation apparatus and vacuum pumps and to repair and replacement of plumbing equipment. Gold and tin are not particularly hazardous, especially at the levels one can expect in this operation. Since the metal must be vaporized by some means to effect deposition, there is potential for workers to sustain burns from equipment.

7.9.6 Risk Determination

The back metallization process requires 125,790 employeehours of labor. Using the occupational injury, illness, and fatality statistics presented in Table 3.1-13, the total lost workdays and fatalities can be determined for this process. The metal plating occupations contribute 117,000 employee-hours toward fulfillment of the labor requirement. This activity is expected to result in 40.7 lost workdays and 2.8 x 10^{-3} fatalities. The inspecting occupations will contribute 1,770 employee-hours resulting in 0.6 lost workdays and 2.5 x 10^{-5} fatalities. Maintenance for the back metallization process will require 7,020 employee-hours resulting in 2.3 lost workdays and 9.1 x 10^{-5} fatalities. The entire process operation is expected to result in 43.6 lost workdays and 2.9 x 10^{-3} fatalities.

7.10 PLATE FRONT CONTACTS

7.10.1 Process Description

The front Au-Mg contact is plated with an additional gold layer by an electrolytic process. This process will most likely be semi-automated with a walking-beam arrangement to transfer the wafers through the various steps.

7.10.2 Material Requirements

A layer 5 μ mm thick is assumed. Since the front metal grid covers only 10 percent of the cell surface, the amount of gold deposited on the cell is 134.36 g/Mw. At an efficiency of 80 percent for electroplating operations (Watts et al., 1979), the total amount of gold required would be 167.95 g/Mw. It is assumed that a gold cyanide solution consisting of potassium gold cyanide, potassium carbonate, and potassium cyanide in an acid solution is used (Amer. Society for Testing Materials, 1972). If the concentration of potassium gold cyanide in the solution is 3.8 g/liter, the quantity of gold would be approximately 2.6 g/liter. The amount of plating solution required for deposition would therefore be 64.6 liters/Mw.

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7.10.3 Manpower Requirements

It is assumed that a throughput rate of 400 cells/h can be achieved in each plating system and that each system requires 0.5 direct labor operators/shift. On this basis five plating systems are required, and 2.5 direct operators or 15,000 employee -hours/yr. At the labor ratio of 100:6:1 (operators: maintenance: foreman) about 900 employee -hours/yr are required for maintenance and 150 for supervision.

7.10.4 Emissions, Wastes, and Controls

Some acid fume emissions from the plating tank should be easily controlled with an acid scrubber. The high cost of gold is likely to necessitate recovery of the remaining gold from the electrolytic solution. The gold may be recovered by evaporation, ion exchange, or reverse osmosis techniques. The remainder of the electrolytic solution must then be disposed of. Cyanides are usually treated by alkaline chlorination, accomplished by the addition of lime or sodium hydroxide and subsequent addition of chlorine gas (Nemerow, 1978).

7.10.5 Occupational Hazards

The major potential for hazard to workers is dermal, or inhalation exposure to the plating solution. Fumes from the plating tank should be easily controlled with local ventilation.

Workers who handle or mix these solutions should be attired with protective clothing and respirators. Maintenance personnel who clean or repair the tanks should follow the same precautions.

7.10.6 Risk Determination

The front contact plating process requires a total of 16,050 employee-hours of labor. Using the occupational injury, illness, and fatality statistics presented in Table 3.1-13, the total lost workdays and fatalities can be determined for this process. The metal plating occupations contribute 15,000

employee-hours, in the form of line operators, toward the total labor requirement. This activity is expected to result in 5.2 lost workdays and 3.6 x 10^{-4} fatalities. The inspecting occupations contribute 150 employee-hours resulting in 0.1 lost workdays and 2.1 x 10^{-6} fatalities. Maintenance efforts to sustain this operation will require 900 employee-hours resulting in 0.3 lost workdays and 1.2 x 10^{-5} fatalities. The entire operation is expected to result in a total of 5.6 lost workdays and 3.7 x 10^{-4} fatalities.

7.11 REMOVAL OF THE LATTICE-MATCHING GAAS LAYER

7.11.1 Process Description

This layer is added initially to facilitate contact with the AlGaAs layer. After metallization this layer is removed with a solution of ammonium hydroxide (NH_4OH), hydrogen peroxide (H_2O_2), and water. This operation requires a dip in the etch solution for a specified time, followed by a dip in a rinse tank and a final drying step.

7.11.2 Material Requirements

No estimates are available regarding the quantities of etch solution. The solution is mixed in proportions of 4:1:1 for MH_4OH , H_2O_2 , and H_2O , respectively (Bell 1980).

7.11.3 Manpower Requirements

For this operation, a throughput rate half of that feasible for silicon cell etching (3600 cells per hour) is assumed to be a reasonable and conservative estimate. Direct operator requirements are 0.5 per shift per etch station. On this basis, 3000 employee-hours/yr would be required. If requirements are the same as in the silicon etching processes, 900 and 300 employee-hours/yr are needed for maintenance and foreman personnel, respectively.
7.11.4 Emissions, Wastes, and Controls

The process will obviously generate etching solution wastes, in unknown quantities. The total amount of GaAs in the waste will be about 70.2 g/MW or 7.02 kg/yr. The $NH_4OH:H_2O_2:H_2O$ solution can be disposed of by simply diluting with water, then neutralizing with an acid such as HCl (ITII, 1979).

Some ammonia fumes may be generated from the etch solution and exhausted. These should be easily controlled by use of a scrubber utilizing an acidic spray.

7.11.5 Occupational Hazards

Dermal and ocular exposure to the etching solution is the major hazard. Both NH_4OH and H_2O_2 are irritants to the skin, mucous membranes, and eyes and may cause burns. If the etching solution is mixed in the plant, both chemicals must be handled with extreme care in concentrated form. Inhalation of H_2O_2 may cause fatal pulmonary edema in a short time because it is such a powerful oxidant. Solutions of high concentration can ignite combustible materials and explosively decompose in contact with such metals as Pt, Ag, Cu, Cr, and Mn.

Potential exposure of workers to NH_3 vapors should be a minor hazard with proper ventilation.

7.11.6 <u>Risk Determination</u>

The total labor requirement for this process is estimated to be 4,200 employee-hours. Using the occupational injury, illness, and fatality statistics presented in Table 3.1-13, the total lost workdays and fatalities can be determined for this process. The metal plating occupations, represented by line operators, will contribute 3,000 hours to the total. This activity is expected to result in 1.0 lost workdays and 7.2 x 10^{-5} fatalities. The inspecting occupations, represented primarily by supervisors, will contribute 300 hours resulting in 0.1 lost workdays and 4.2 x 10^{-6} fatalities. Maintenance of this process will contribute 900 employee-hours, resulting in 0.3 lost workdays and 1.2 x 10^{-5} fatalities. The entire process operations is expected to result in 1.4 lost workdays and 8.8 x 10^{-5} fatalities.

7.12 ANTIREFLECTIVE COATING - PLASMA DEPOSITION

7.12.1 Process Description

The antireflective coating is deposited by bleeding 1.5 percent $SiH_4/argon$ mixture and N_2 gases into a plasma reactor, where they react to form a silicon nitride (Si_3N_4) layer. This process is controlled by a microprocessor and requires an operator only to load and unload the cassettes.

7.12.2 Material Requirements

If the Si₃N₄ layer is 700 Å thick, the total amount deposited on the cells will be 2.67 g/MW. At a deposition efficiency of 65 percent, a total of 4.11 g/MW will be generated. Of the 4.11 g/MW of Si₃N₄, about 60.1 percent, or 2.47 g/MW, is silicon. If 0.874 of the SiH₄ is deposited as silicon, then 2.83 g/MW or 1.96 liters/MW of SiH₄ is needed theoretically. The quantity of SiH₄ actually required is probably higher, because it is unlikely that all of the silicon in silane is deposited. Since the silane content of the gas is only 1.5 percent, then 130.7 liters/MW of the SiH₄/argon gas mixture is required.

Since nitrogen is theoretically 39.9 percent of the Si_3N_4 then 1.64 g/MW or 1.31 liters/MW is needed, if it is assumed that 100 percent is utilized for deposition.

7.12.3 Manpower Requirements

Assumptions are that 50 cells per hour can be processed with state-of-the-art equipment, and that 0.25 direct operator/ shift is required for operation of each plasma system. The manpower requirement is then 9.75 direct operators/shift, or 58,500 employee-hours/yr. The maintenance and foreman personnel requirements, calculated at 6 and 1 percent, respectively, are 3510 and 585 employee-hours/yr.

7.12.4 Emissions, Wastes, and Controls

Emissions from this process will be minimal. Some gases, primarily H_2 , will be exhausted. For every 140.3 g of Si_3N_4 formed, about 12.1 g of H_2 will be exhausted. This is equal to about 394 liters of H_2 per year. This is not a major amount and should be easily controlled.

Since this process is under a slight vacuum, there will be vacuum pump oil wastes and some oil fume exhaust but these should be minor also.

7.12.5 Occupational Hazards

Since the process is under vacuum and such minor quantities of the gases are used, occupational exposure potential will be low. None of the gases used are extremely hazardous, and a major release would be required to create a potentially hazardous situation. This is unlikely to occur unless by a major accident in the handling of raw materials. Though H_2 and SiH_4 present fire and explosion hazards, the quantities released at any one time are small and potential for hazard should be slight. The argon and N_2 being emitted at the same time will dilute the H_2 and provide an inert environment to reduce even further the potential of a fire or explosion.

7.12.6 Risk Determination

The antireflective coating-plasma deposition process requires a total of 62,595 employee-hours to operate a 100 MW/yr production plant. Using the occupational injury, illness, and fatality statistics presented in Table 3.1-13, the total lost workdays and fatalities can be determined for this process. The primary labor effort, approximately 58,500 employee-hours, is expected to come from line operators. This labor effort is expected to result in 12.4 lost workdays and 8.2 x 10^{-4} fatalities. These values were calculated using occupational statistics that characterize all occupations within the semi-conductor industry. The inspecting occupations will contribute 585 employee-hours to the total labor requirement, resulting in 0.1 lost workdays and 8.2 x 10^{-6} fatalities. Maintenance for this process will require 3,510 employee-hours. The maintenance activity is expected to result in 1.1 lost workdays and 4.6 x 10^{-5} fatalities. The entire process operations will result in 13.6 lost workdays and 8.7 x 10^{-4} fatalities.

7.13 FINAL CELL PROCESSING

7.13.1 Process Description

Final cell processing includes the following operations:

- Soldering of the cell to a ceramic substrate
- Attachment of the leads to the cell assembly
- Encapsulation of the cells
- ° Testing on a pulse simulator at 400 suns
- Mounting of cell assemblies on a polysulfone holder.

At the present time these operations are highly dependent on manual labor. They could, however, be automated to a greater degree. An Au-Sn solder is used to solder the cell to the ceramic substrate. This is accomplished by use of a solder fixture that holds and aligns the ceramic, the cell, the leadframe and solder. This assembly makes a single pass through a belt furnace. The back and front connections are made simultaneously.

After attachment to the ceramic substrate, the cells may be encapsulated to provide protection from the environment. The encapsulation process is not yet developed fully. One coating used for the cell was a transparent epoxy.

After encapsulation the cells are tested at 400 suns on a pulse simulator. This process should be easily automated, since it is similar to the testing of silicon cells.

Following the test, the cell and ceramic heatsink are clamped to a plastic polysulfone holder, which is designed with provisions for jet cooling the back of the ceramic.

7.13.2 Material Requirements

For the ceramic substrate (Al_2O_3) a diameter of 2.49 cm (0.98 in.) and thickness of 0.13 cm (0.05 in.) are used in calculating the required amount. This quantity is calculated to be 144.8 kg/MW (1.52 cm).

The copper leads were estimated to be about 0.6 in. (1.52 cm) in diameter. As shown in Figure 7.13-1, the lead encircles the cell. The positive and negative prongs are estimated to be about 0.5 in.² (3.2 cm²) each. Area of the main body of the lead is about 0.6 cm². Thus with the prongs the total area is about 7 cm². At a thickness of 0.007 in. (0.018 cm), the total amount of copper required is about 0.13 Mg/MW.

No estimates of the amount of Au-Sn solder used to mount the cells were found in the literature.

The encapsulate layer, if applied, is assumed to be 0.01 in. (0.0254 cm) thick. Density values cannot be used in the estimates because specifics are not available on the kind of epoxy to be used. At a thickness of 0.01 in., 3.54 liters/MW of encapsulate would be needed.

Finally, the cell assembly is mounted to the polysulfone cooler holder. No material estimates are available.

7.13.3 Manpower Requirements

On the basis of a throughput of 480 cells/shift (60/h) and 1 worker/shift per assembly and furnace station, it is calculated that 32 stations and thus 32 workers/shift would be required for the ceramic solder operation. This is 192,000 employee -hours/yr. At ratios of 6 and 1 percent of operator requirements, respectively, 11,520 employee -hours/yr would be required for maintenance personnel and 1920 for foremen.

It is not known whether or not an encapsulant will be necessary since the Si_3N_4 antireflective layer may also be used



Figure 7.13-". GaAs concentrator cell (Maget, 1979).

as a protective coating. Since no details were available on the encapsulation process manpower requirements were not calculated.

7.13.4 Emissions, Wastes, and Controls

The only potential emissions from this process are fumes from the solder paste generated during furnace heating, and possibly some epoxy fumes from the encapsulation process. These should be minimal and easily controlled.

7.13.5 Occupational Hazards

Occupational exposures should be minimal. Use of an epoxy for encapsulation could be a potential hazard, although one that is difficult to determine when the type of epoxy is unknown. Epoxies in general may cause dermititis, burns, erythema, and sensitization upon dermal contact and irritation of mucous membranes upon inhalation.

Since some manual labor will be involved in loading of the solder fixtures, physical injuries such as cuts may be prominent. Burns may also be a common injury because of the furnaces.

7.13.6 Risk Determination

The labor requirement for final cell processing is estimated to be 205,440 employee-hours. Using the occupational injury, illness, and fatality statistics presented in Table 3.1-13, the total lost workdays and fatalities can be determined for this process. The assembling occupations are expected to contribute 192,000 employee-hours toward the total labor effort, this will result in 43.8 lost workdays and 2.3 x 10^{-3} fatalities. Inspecting occupations will contribute 1,920 employeehours resulting in 0.5 lost workdays and 2.7 x 10^{-5} fatalities. Maintenance occupations will contribute 11,520 employee-hours of labor resulting in 3.7 lost workdays and 1.5 x 10^{-4} fatalities. The activity associated with the entire process is expected to result in a total of 48.0 lost workdays and 2.5 x 10^{-3} fatalities.

7.14 MODULE ASSEMBLY

7.14.1 Process Description

The first step in module assembly is attachment of the cell assembly to the base of the lens mounting cone. In this assembly the flange of the cell cooler is bolted to the base of lens mounting cone with the cell protruding into the the interior of the cone (Maget 1979). This subassembly is then bolted to a U-shaped aluminum channel with flanges by use of four studs protruding from the base of the cone. Three -inch holes are punched in the back of the channel to allow access to the back of the cells for cell replacement and alignment and for electrical and coolant connections (Maget 1979). Ten of the cell/lens subassembles are attached to the channel in series to form a module.

7.14.2 Material Requirements

The extruded aluminum channel is 4 by 5.75 by 0.063 in. Since the base of the lens support cone is calculated to be about 13.86 in. in diameter and ten subassemblies are mounted per module, the channel for each module is at least 138.6 inches long. Based on these estimates the aluminum requirement is about 60.67 Mg/MW.

The hexagonal Fresnel lenses are about 0.25 in. thick and 10.13 in. (25.73 cm) across the flat face. It is calculated that each lens weighs about 0.31 kg, on the assumption that the lens is made from methyl methacrylate with a density of 0.936 g/cm^3 . A total of 35.4 Mg/MW of methyl methacrylate is required for production of the lens. It is also assumed that the lens support cone is methyl methacrylate. The cone is 12.5 in. long, 10.13 in. at the top of each side, and 8 in. at the bottom of each side. The area of each side is about 114 in.², and the total area for one support cone would be approximately 684 in.² or 4412.9 cm². At a thickness of 0.25 in. (0.635 cm) the total amount of plastic required would be 299.33 Mg/MW.

7.14.3 Manpower Requirements

It is assumed that the module fabrication is manual and that 1 worker could assemble 2 modules per hour. On this basis a total of 95.2 workers, or 571,200 employee-hours/yr would be needed to produce the required quantity of modules. Foreman requirements, at 1 percent of direct worker requirements, are 5712 employee-hours/yr.

7.14.4 Emissions, Wastes, and Controls

There should be no emissions from module assembly operations. The only wastes should be scrap material.

7.14.5 Occupational Hazards

Except for some potential exposure to fumes in the brazing or soldering of cell interconnects, occupational exposures should be nonexistent. Since the assembly is primarily manual, most injuries will be physical, such as cuts, punctures, and scratches.

7.14.6 Risk Determination

The module assembling will require 576,912 hours of labor. Using the occupational injury, illness, and fatality statistics presented in Table 3.1-13, the total lost workdays and fatalities can be determined for this process. The assembling occupations are expected to contribute 571,200 hours toward this effort, resulting in 130.2 lost workdays and 6.8 x 10^{-3} fatalities. Inspecting occupations will contribute another 5,712 employee-hours resulting in 1.5 lost workdays and 8.0 x 10^{-5} fatalities. Minimal maintenance is required for this process. The entire operation is expected to produce 131.7 lost workdays and 6.8 x 10^{-3} fatalities.

7.15 DATA SUMMARY

Presented in Table 7.15-1 are summaries of materials, emissions and wastes. Manpower and risk data for the GaAs process are presented in Section 8.

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Process step	Material	Material requirements	Emissions and wastes
Gallium refining	Bauxite	287.2 Mg/MW	
Arsenic refining	Arsenic	13.48 kg/MW	
<u>Gallium arsenide production</u>	Gallium Arsenic	15.9 kg/MW 17.0 kg/MW	
<u>Liquid-encapsulation</u> <u>Czechralski single crystal</u> growth	Polycrystalline ° GaAs ° Tin	27.4 kg/MW 0.34 g/MW	1.9 kg/MW
Ingot processing	GaAs Mineral oil (clay) ° SiC grit slurry		15.3 kg/MW 0.226 Mg/M
Liquid phase epitaxial (LPE) deposition	Tin AlGaAs Mg GaAs	57.5 mg/MW 334.2 g/MW 2.26 mg/MW 2.38 kg/MW	
Deposition of SiO ₂ layer	SiO ₂ SiH4 SiH4/Argon N ₂ 0	4.6 g/MW .71 1/MW .14 1/MW 3.41 1/MW	1.60 g/MW
Front metallization	Photoresist Au Mg Acetone	69.4 m1/MW 188.8 g/MW 4.8 g/MW 5.7 1/MW	
Back metallization	A u -Su	138.8 cm ³ /MW	

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TABLE 7-15.1. MATERIAL AND WASTE SUMMARY FOR GALLIUM ARSENIDE PROCESS

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TABLE /- 19.1 (CONTINUED	TABLE	7-15.1	(continued
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Process type	Material	Material requirements	Emissions and wastes
<u>Plate front contacts</u>	Gold Plating solution	167,95 g/MW 64.6 l/MW	
Removal of the lattice- matching GaAs layer	GaAs		70.2 g/MW
Antireflective coating- plasma deposition	Si ₃ N4 SiH4 SiH4/argon gas Mixture Nitrogen H ₂ gas	4.11 g/MW 2.83 g/MW 130.7 1/MW 1.31 1/MW	0.354 g/MW
Final cell processing	Copper 🦟 Encapsulate 👋	0.13 Mg/MW 3.54 1/MW	
Module assembly	Aluminum Methyl methacrylate	60.67 Mg/MW 299.33 Mg/MW	

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SECTION 8

ANALYSIS AND RISK ASSESSMENT

8.1 STATISTICAL RISK ASSESSMENT

The risk assessment that follows is an attempt to define the types and levels of health problems that will confront a labor force involved in production of photovoltaic devices. Lowrence (1976) has defined risk as a measure of the probability and severity of harm to human health. In this report we direct attention to defining both the probability of specific disease states and the magnitude of their severity. The data used to construct these probabilities and severity rates were not derived directly from photovoltaic processes but were taken from analogous processes within the semiconductor industry. А detailed description of the data sources and their limitations is presented in Section 3.1. Notwithstanding the problems associated with a risk assessment performed by analogy, it is believed that this technique constitutes the best available procedure.

The risk assessment required the determination of both employment levels and occupational health statistics. Next, the types of occupations associated with each process and their anticipated levels of employment were estimated for each photovoltaic production process. Lost workdays and fatality rates were then applied to these employment levels to estimate the risk associated with occupations in each process.

The occupational health statistics were applied by first identifying the occupations in the photovoltaic processes that

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are analogous to occupations in the occupational categories developed for this report (see Table 3.1-1).*

When an analogous occupation was identified, the associated health statistics were applied to the anticipated employment levels to produce an estimate of lost workdays and fatalities for each occupation. The values for occupational injury, illness, and fatality were then grouped according to specific process steps. The individual process steps were collected into a single production process, permitting the calculation of total lost workdays and fatalities for each photovoltaic cell production technology.

Table 8.1-1 presents the lost workday and fatality values associated with each process step in the silicon I photovoltaic production process. Subtotals are presented for production of both base materials and photovoltaic cells. Production process totals represent the entire silicon I photovoltaic production Similar summaries of lost workday and fatality technology. values are presented for silicon II and gallium arsenide technologies in Tables 8.1-2 and 8.1-3, respectively. Proprietary claims to information used in the estimation of labor requirements for the cadmium sulfide process preclude the breakdown of lost workday and fatality values into process steps. The base material and photovoltaic cell production subtotals and the production totals for the cadmium sulfide process are presented in Table 8.1-4.

The selection of base-material industries is not all-inclusive; therefore, it is not appropriate to compare the basematerial portions of these summaries.

^{*} When it was not possible to assign a specific occupation to one of the occupational categories, the "technician" category was used as a source of default statistics. When the occupation was not recognized as technical, the "all unclassified illnesses" or "all other occupational illnesses" categories were used as sources of default statistics.

TABLE 8.1-1. LABOR REQUIREMENTS, TOTAL LOST WORKDAYS, AND FATALITIES ASSOCIATED WITH 100-MW/YR SILICON I PRODUCTION PROCESS

Process step	Labor employee-hours	Total lost workdays	Fatalities
Mining and refining of quartz Metallurgical silicon production Silicon purification and polyconysta	3,770 102,350	4.0 23.9	$\begin{array}{c} 3.8 \times 10^{-4} \\ 3.3 \times 10^{-3} \end{array}$
line silicon production	888,447	207.9	2.8×10^{-2}
Subtotal	994,567	235.8	3.17×10^{-2}
Single crystal silicon growth Ingot processing Junction formation Perimeter grind Etching Metallization Antireflective coating Cell testing Interconnection Encapsulation Module testing	511,140 420,510 25,650 16,680 15,600 25,680 44,940 121,980 72,420 106,200 6,420	116.6 101.9 6.1 3.5 5.3 9.0 9.8 28.5 18.0 24.5 1.6	5.47×10^{-3} 2.43×10^{-4} 2.81×10^{-4} 3.8×10^{-4} 3.4×10^{-4} 4.6×10^{-4} 4.6×10^{-3} 1.5×10^{-3} 8.9×10^{-3} 1.3×10^{-5} 8.0×10^{-5}
Subtotal	1,367,220	324.8	1.3 x 10 ⁻²
Total	2,361,787	560.6	4.5 x 10^{-2}

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TABLE 8.1-2.	LABOR REC	UIREMENTS,	TOTAL	lost	WORKDAYS,	AND FATALITIES
ASSOCI	ATED WITH	100-MW/YR	SILICON	ΙI	PRODUCTION	PROCESS

Process step	Labor employee-hours	Total lost workdays	Fatalities
Mining and refining of quartz Metallurgical silicon production Silicon purification	245 5,773 36,967	0.2 1.4 8.6	4.9 x 10 ⁻⁶ 1.8 x 10 ⁻⁴ 1.2 x 10 ⁻³
Subtotal	42,985	10.2	1.38×10^{-3}
Ribbon growth p+ Aluminum-back contact	585,200	127.5	5.9×10^{-3}
Application Plasma etching Ion implantation Back and front metallization Antireflective coating Interconnection Encapsulation Module testing	23,400 35,600 32,400 46,800 32,400 95,200 109,600 3,600	5.4 7.9 7.1 11.8 7.2 23.3 25.3 1.0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
Subtotal	964,200	216.5	1.0×10^{-2}
Total	1,007,185	226.7	1.1 x 10 ⁻²

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TABLE 8.1-3. LABOR REQUIREMENTS, TOTAL LOST WORKDAYS, AND FATALITIES ASSOCIATED WITH 100-MW/YR GALLIUM ARSENIDE PRODUCTION PROCESS

Process step	Labor employee-hours	Total lost workdays	Fatalities		
Mining and refining of gallium Refining of arsenic Gallium arsenide production	34,058 39 12,840	15.6 Neg. 2.8	1.8 x 10 ⁻³ Neg. 1.3 x 10 ⁻⁴		
Subtotal	. 46,937	18.4	1.93×10^{-3}		
Liquid-encapsulation Czochrolski single crystal growth Ingot processing Liquid phase epitaxial (LPE) deposition Deposition of SiO ₂ layer Front metallization Back metallization Plate front contacts Removal of the lattice-matching GaAs layer Antireflective coating-plasma deposition Final cell processing Module assembly	24,420 85,770 747,900 77,040 137,610 125,790 16,050 4,200 62,595 205,440 576,912	5.6 20.4 173.7 16.9 47.6 43.6 5.6 1.4 13.6 48.0 131.7	$\begin{array}{ccccccc} 2.6 & \times & 10^{-4} \\ 3.8 & \times & 10^{-4} \\ \hline 3.8 & \times & 10^{-3} \\ 8.1 & \times & 10^{-3} \\ 7.8 & \times & 10^{-3} \\ 3.2 & \times & 10^{-3} \\ 2.9 & \times & 10^{-3} \\ 3.7 & \times & 10^{-4} \\ \hline 3.7 & \times & 10^{-5} \\ \hline 8.8 & \times & 10^{-5} \\ \hline 8.7 & \times & 10^{-3} \\ 2.5 & \times & 10^{-3} \\ 6.8 & \times & 10^{-3} \end{array}$		
Subtotal	2,063,727	508.1	2.6×10^{-2}		
Total	2,110,664	526.5	2.79×10^{-2}		

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Process step	Labor employee-hours	lotal lost workdays	Fatalities
Cadmium refining	54,674		
Subtotal	54,674	21.8	3.8×10^{-3}
Cadmium śulfide photovaltaic cell and array production	619,450		
Subtotal	619,450	142.0	6.4×10^{-3}
Total	674,124	163.8	1.0×10^{-2}

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TABLE 8.1-4. LABOR REQUIREMENTS, TOTAL LOST WORKDAYS, AND FATALITIES ASSOCIATED WITH 100-MW/YR CADMIUM SULFIDE PRODUCTION PROCESS

Values for total lost workdays and fatalities for each process are presented as bar graphs in Figure 8.1-1 and 8.1-2. The unshaded portions of each graph represent the lost workdays and fatalities associated with the actual photovoltaic production process. Although the labor requirement of each process exerts the greatest single influence on risk, the photovoltaic production processes can be compared, since each process deals with essentially the same task; manufacturing of a photovoltaic device to meet a 100-MW/yr demand.

The shaded area of each bar represents that portion of the lost workdays or fatalities attributable to basematerial pro-The base-material industries of each process influence duction. the lost workday and fatality totals to varying degrees. The selection of base-material operations to be included in process labor requirements was not arbitrary, yet the resultant values are not amenable to direct comparisons among the four photovoltaic technologies. A base substance is defined in this report as the material comprising the active portion of the photovoltaic cell. Although these substances are critical to the operation of the device, they do not necessarily constitute the major quantity of material used in the final product. In some cases production of a substance that is not part of the active portion of a photovoltaic device, e.g., a structural or protective material, may require a substantial labor force. Inclusion of all industries manufacturing major materials; i.e., active, structural, and protective, would undoubtedly have altered the structure of the bar graphs in Figures 8.1-1 and It was not within the scope of this project to consider 8.1-2. all base-material industries.

The lost workday and fatality rates per 100 employee-years associated with each process are presented in Figures 8.1-3 and 8.1-4. These graphs indicate the relative risk to workers in each photovaltaic cell production process. Although these



PRODUCTION PROCESS





PRODUCTION PROCESS

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Figure 8.1-2. Total number of fatalities for four 100-MW per year photovoltaic cell production processes.







Figure 8.1-4. Fatalities per 100 employee-years for the photovoltaic cell production processes.

graphs can be used to interpret the data from each of the four processes, conclusions about the hazards associated with each process should not be based upon the graphs alone.

8.2 CHEMICAL HAZARD ANALYSIS

A qualitative hazards assessment scheme was developed to put into perspective the potential chemical hazards involved with materials usage in the four photovoltaic manufacturing processes. The results are presented in Tables 8.2-1 to 8.2-4. The hazard analysis scheme involves assignment of a toxicity ranking number and an exposure potential ranking number to the acute and chronic toxicity characteristics of each process material. The acute toxicity ranking is based on short-term exposure level (STEL) (ACGIH, 1980) for the substance and/or the severity of the resulting injury or disease. Although this technique is recognized as being highly subjective, it is considered sufficient for the purposes of a qualitative analysis.

The chronic toxicity ranking for each substance was assigned by use of published time-weighted averages (TWA) (ACGIH, 1980) arranged according to the following scheme:

Chronic toxicity ranking	TWA, <u>mg/m³</u>			
. 1	1000+			
2	10 - 1000			
3	7 - 10			
4	2 - 7			
5	0.1 - 2			
6	< 0.1			

The relative hazard of a substance is estimated by multiplying the toxicity and exposure rankings; the resulting product is designated as the hazard potential ranking, which may range from a minimum of 1 to a maximum of 24. Materials with a ranking from 1 to 9 are considered to pose a low hazard to the worker; from 10 to 14, a moderate hazard; from 15 to 19, a high hazard, and from 20 to 24, an extremely high hazard.

LEGEND FOR TABLES 8.2-1 THROUGH 8.2-4

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Toxicity Ranking (1-6)

- 6 Extremely toxic
- 5 Highly toxic
- 4 Moderately toxic
- 3 Slightly toxic
- 2 Practically nontoxic
- 1 Relatively harmless

Exposure Potential Ranking (1-4)

- 4 High potential
- 3 Moderate potential
- 2 Low potential
- 1 Practically no potential
- unk Unknown

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- I Inhalation
- D Dermal
- A Animal
- H Human

Basis of Exposure Potential Ranking

TLV - Based on TLV and available sampling data EE - Based on TLV and engineering judgement

TABLE 8.2-1. HAZARD RATING FOR SI_ICON-I PROCESS

		1					<u></u>	· · · · · · · · · · · · · · · · · · ·	r				
	ļ	Probable route(s)	Source of		Acute	Acute	Acute hazard		Chronic	Chronic exposure	Chronic hazard	Basis for	
		of	toxicity		toxicity	potential	potential		toxicity	potential	potential	potential	
Process	Chemical	exposure	data	STEL	ranking	ranking	ranking	TWA	ranking	ranking	ranking	ranking	Teratogen Carcinogen
Sand and gravel mining	Silica (crystalline)	1	н		1	1	1	0.32 mg/m ^{3a}	5	4	20	EE	
MG-Si production	Silica (amorphous)	1	н		- 1	1	1	0.32 mg/m ³⁴	5	2	10	EE	
	Silicon	1	A	20 mg/m ³	- 1	unk	low	l0 mg/m ^{3b}	unk	2	low	EE	
	co	1	A	15,000 ppm	3	unk	Tow	5000 ppm	ī	2	2	EE	
	SiO _x waste	1			1.	unk	low	c	usk	unk	unk		
	SIC	Ľ	A	20 mg/m ³	1	unk	low	10 mg/m ^{3b}	3	2	6	EE	
Silicon purification	Chlorosilanes	·I	A		3	2	6	7 mg/m ^{3d}	₽d	2	8	EE	
		D			4	3	12	(5 ppm) ^d				EE	
	нст	1	н		4	2	8	7 mg/m ³	4	2	8	EE	
		D			4	3	12	(5 ppm) +				EE	
	H ₂	I		Asphyxiant	, 1	1	1	- ·	2	1	2	EE	o
	Silicon	t	A	20 mg/m ³	1	2	2	1C mg/m ³	3	2	6	EE	
Sieman's process	Silicon	l l	A	20 mg/m ³	1	ז	1	1C mg/m ³	3	2	6	TLV	
	Solvent	ſ	н	1225 mg/m ³	3	1	3	980 mg/m ³	2	2	4	EE	
	,	٥	н	(500 ppm)		}		(400 ppm)					
Czochraliski	Silicon	I	A	20 mg/m ³	1	1	1	1C mg/m ³	unk	2	low	TLV	
	Solvent ^e	1	н	1225 mg/m ³	3	1	3	960 mg/m ³	2	2	4	EE	
		D	н	(500 ppm)				(400 ppm)				EE	
	8C13	I	A	f	5	2	10	f	4	1	4	EE	
Ingot processing	Silicon	I	A	20 mg/m ³	1	1	1	10 mg/m ³	3	2	6	TLV	
	HF9	I	А,Н		5	2	10	2 mg/m ³	5	2	10	TLV	
		D	А,Н		6	3	18	(∶ppm)				EE	

(continued)

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TABLE 8.2-1 (continued)

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-		T	r								r			
-	Process	Chemica 1	Probable route(s) of exposure	Source of toxicity data	STEL	Acute toxicity ranking	Acute exposure potential ranking	Acute hazard potential ranking	TWA	Chronic toxicity ranking	Chron:c exposure potent:al ranking	Chronic hazard potential ranking	Basis for exposure potential ranking	Teratogen Carcinogen
		HN03 ⁹	I	А,Н	10 mg/m ³	5	2	10	5 mg/m ³	4	2	8	EE	
			D	н	(4 ppm)	4	· 3	12	(2 ppm)				EE	
		Acetic ^g	I	А,Н	37 mg/m ³	3	2	6	25 mg/m ³	2	2	4	EE	
			D	A,H	(15 ppm)	3	3	9	(10 ppm)				EE	
		Slurryh	· · I			۱.	unk	low		unk	unk	unk		
		NO2	I	A,H		3	1	3	9 mg/m ³	3	2	6	TLV	
		NO	I	A	45 mg/m ³	3	1	3.	30 mg/m ³	2	2	4	TLV	
	Junction formation	POCI3	I	A		5	2	10		3	2	6	EE	
	Perimeter grind	Silicon	I	A	20 mg/m ³	۱	ר	1	10 mg/m ³	3	1	3	EE	
l N	Oxide etch	HF	I	A,H		5	2	10	2 mg/m ³	5	2	10	TLV	
29			D	A,E		6	3	18	(3 ppm)				EE	
I		HNO3	I	A,H	10 mg/m ³	5	2	10	5·mg/m ³	4	· 2	8	EE	-
			D	н	(4 ppm)	4	3 .	12	(2 ppm)				EE	
	Metallization	Nickel	. D,I	A,H		4	3	12	1 mg/m ³	5	3	15	TLV	×
		Sodium hypophosphite	D,1			2	3	6		unk	unk	unk	EE	
		Solder Pb	I	A,H	0.45 mg/m ³	4	2	8	0.15 mg/m ³	5	3	15	TLV	
		Solder Sn	I	Å	4 mg/m ³	3	2	6	2 mg/m ³	5	2	10	EE	×
		Photoresist ⁱ (urethane/Ti0 ₂)	D,I .	A		unk	1	low	10 mg/m ^{3j}	2	2	4	EE	x x
		ZnCl ₂ flux	D,I	A,H	2 mg/m ³	6	3	18	1 mg/m ³	5	3	15	EE	
	Antireflection coating	SIH2C12	I	A		4	2	8	7 mg/m ^{3d}	4 ^d	2	8	EE	
		NH3	I	A,H	35 ppm –	4	2	8	25 mg/m ³	2	2	4	EE	
	•	si ₃ N ₄	I			unk	unk	unk		unk	unk	unk	unk	

.

(continued)

TABLE 8.2-1 (continued)

Process	Chemica I	Probable route(s) of exposure	Source of toxicity data	STEL	Acute toricity ramking	Acute exposure potential ranking	Acute hazard potential ranking	TriA.	Chronic toxicit/ ranking	Chronic exposure potential ranking	Chronic hazard potential ranking	Basis for exposure potential ranking	Teratogen Carcinogen
Cell test	UV light	C	A,H	j		2	Jow	j.				EE	
	Ozone	I	А,Н	0.5 ррт	6	1	6	0.1 ppm	3	2	6	EE	
Interconnection	Solder (Pb)	1	A,H	0.45 mg/m ³	4	1	+	0.15 mg/m ³	5	2	10	TLV	
	Sn (Sn)	1	A	4 nag∕an ³	3	1	3	2 mg∕m ³	5	2	10	EE	×
Encapsulation	EVA polyethy72ne ^k	1	A		nk	unk	unk	}	unk	unk	unk		
	EVA vinyl acetate	1			Jink	unk	unk		1	unk	unk		
	Mylar	i.			unk	unk	unk		unk	unk	unk		
	[sopropy] alcohol	I "D	A,H	500 ppm	2	2	4	400 ppm	2	2	4	TLV	

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^a TLV for total dust assuming the quartz content is 90 percent.

^b Recommended TLV for total dust.

^c This SiO_x waste has yet to be completely defined. It is believed to consist of amorphous and fused silica.

^d Same as hydrogen chloride.

^e The solvent for cleaning the reactors may vary but isopropanol was used for this analysis.

f No STEL or TWA has been adopted for BC13; for boron tribromide (BEr3), a STEL of 3 ppm and a TWA of 1 ppm have been recommended. These would be appropriate values for BC13 also though the Br ion may be considered slightly more toxic.

⁹ These are present in a mixture for this process so the effects may be different than from each individually.

^h Composed of SiC, mineral oil, and clay grit.

¹ The photoresist used for this example was a urethane/TiO2 mixture. Poss bilities for photoresist are numerous.

^j See ACGIH TLV's for Chemical Substances and Physical Agents in the Work Environment with Intemded Changes, 1978. ^kExperimentally neoplastic.

TABLE 8.2-2. HAZARD RATING FOR SILICON-II PROCESS

													· · · · · · · · · · · · · · · · · · ·		
·	Process	~ Chemical	Probable route(s) of exposure	Source of toxicity data	STEL	Acute toxicity ranking	Acute exposure potential ranking	Acute hazard potential ranking	TWA	Chronic toxicity ranking	Chronic exposure potential ranking	Chronic 'hazard potential ranking	Basis for exposure potential ranking	Teratogen Car	rcinogen
	Sand and gravel mining	Silica (crystalline)	I	H		1	1	1	0.32 mg/m ^{3a}	5	4	20	EE		
	MG-Si production	Silica (crystalline)	I.	H		1	1	١	0.32 mg/m ^{3a}	5	2	10	EE		
		Silica (amorphous)	I	H	•	۱	1	١	5 mg/m ^{3b}	3	3	9 .	. EE		
		Silicon	I	A	20 mg/m ³	1	unk	low	10 mg/m ^{3b}	3	2	6	EE		
		co	I	A	400 ppm	3	unk	1ow	50 ppm	1	2	2	EE		
		SiO _k waste	I			1	unk	low	c	unk	2	low	EE		
		SIC	I	A	20 mg/m ³	្រា	unk	low	10 mg/m ^{3b}	3	2	6	EE		
1	Silicon purification	Chlorosilames	1	Ą.		3	2	6	7 mg/m ^{3a}	4	. 2	8	EE	-	
23			D			4	2	8	(5 ppm)						
1	•	нст	1	н		4	2	8	7 mg/m ³	4	2	8	EE		
·			D			4	2	8	(5 ppm)						
		Silicon _	1	A	20 mg/m ³	1	2	2	10 mg/m ³	3	2	6	EE		
		Silane	I	A	2 mg/m ³	3	unk	mod.	0.7 mg/m ³	5	3	15	· EE	l	
		H ₂	I.	A	Asphyxiant	1	1	1		2	1	2	EE		
		Silica	I	A ,H		. 1	1	1	0.32 mg/m ^{3b}	5	ľ	5	EE .		
	Ribbon growth	Silicon	1	A	20 mg/m ³	1	1	1	10 mg/m ³	3	2	6	EE		
	Back contact application	Aluminum	1,D	A		2	1	2		unk	, I	low	EE		
		Ethanol	I,D	A,H		2	2	4	1900 mg/m ³	1	2	2	EE	c	c
	Plasma etch	CF4	1	A		2	2	4		unk	unk	unk			
		SIF4	I			4	2	8		unk	unk	unk			
		Other rxn species		Needs fur	ther characteri	zation	} .								
	ion implantation	PH3	I	А,Н	1 mg/m ³	5	2	10	0.4 mg/m ³	5	2	10	EE		
	Annea 1	Laser	D		d	5	2	10	d						

(continued)

TABLE 8.2-2 (continued)

	Process	Chemical	Probable route(s; of exposure	Source of toxicity data	STEL	Acute toxicity ranking	Acute exposure potential ranking	Acute hazard potential rankińg	TWA	Chronic toxicity ranking	Chronic exposure potential ranking	Chronic hazard potential ranking	Basis for exposure potential ranking	Teratogen Carcinogen
	Metallization	Silver	I	h		2	1	2	0.1 mg/m ³	6	2	8	EE	×
		Solvent	i D	Needs	to be identi	fied								
	Antireflective coating	Ti0 ₂	i	Ι , Α	20 mg./m ³	1	1	1	10 mg/m ³	3	2	6	EG	
י גרנ		Solvent) D	Needs	 to be identi 	fied I								
	Interconnection	Solder Pb	I	А,Н	0.45 mg/m ³	4	1	4	0.15 mg/m ³	5	2	10	TLV	
		Solder Sn	I	A	4 mg/m ³	3	1	3	2 mg/m ³	5	: 2	10	EE	x
	Encapulation	EVA (polyethy:ene ^e)	I	A		unk	unk	urk		unk	unk	unk		
		EVA (vinyl acetate)	Т			unk	unk	urik		unk	unk	unk		
		Mylar	1			unk				unk				
		Isopropyl alcohol	I,D	A,H	1225 mg/m ³	2	2		980 mg/m ³ (400 ppm)	2	2	4	TLV	

^a Same as for hydrogen chloride.

^b TLV for total dust assuming the quartz content is 90 percent.

^C Ethyl alcohol has been shown to be carcinogenic and teratogenic in mice by an oral route of administration. It is highly unlikely that exposure will occur by this route in this process.

^d See the ACGIH TLV's for Chemical Substances and Physical Agents in the Workroom Environment, 1978.

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^eExperimentally neoplastic.

TABLE 8.2-3. HAZARD RATING FOR CADMIUM SULFIDE SPRAY PROCESS

····														
Process	Chemical	Probable route(s) of exposure	Source of toxicity data		Acute toxicity ranking	Acute exposure potential ranking	Acute hazard potential ranking	TWA	Chronic toxicity ranking	Chronic exposure potential ranking	Chronic hazard potential ranking	Basis for exposure potential ranking	Teratogen	Carcinogen
Cadmium refining	Cadmium dusts	I	A,H	0.2 mg/m ³	5	3	15	0.05 mg/m ³	6	4	24	TLV	x	x
	Cadmium oxide	I	A,H											
Cadmium chloride formulation	cdc12	I	A,H	0.2 mg/m ^{3a}	5	3	15	0.05 mg/m ^{3a}	6	3	18	EE	×	x
		D	А,Н		5									
Substrate processing	SnC12	1,0	A	4 mg/m ^{3b}	4	2	8	2 mg/m ^{3b}	5	2	10	TLV		
	Methano]	I	А,Н	310 mg/m ³	3	2	6	260 mg/m ³	2	2	4	EE		
		D	н	(250 ppm)			1	(200 ppm)						
	Other rxn products ^C	I	These need	further charac	terization									
Cadmium spray	CdC12	г	A	2 mg/m ^{3a}	5	2	10	0.05 mg/m ^{3a}	6	2	12	TLV	×	x ·
1	CdS	I	A	2 mg/m ^{3a}	5	2	10	0.05 mg/m ³ ·	6	2	12	TLV	x	x
	Thiourea	I	A		5	unk	Moderate		unk	unk	unk			d
	Other rxn products ^e	I	Needs fu	rther character	ization									
I Metailization grid pattern	CdS dust	I	A	2 mg/m ^{3a}	5	2	10	0.05 mg/m ³	6	3	18	ŢĻV	x	x
Copper dip	CuCl	l I	А,Н	i	4	3	12	0.2 mg/m ^{3f}	5	2	10	EE		
		D			unk	unk	unk							
Metallization	Copper	I	A,H		3	2	6	0.2 mg/m ³	5	2	10	EE		
	Lead	I	А,Н	0.45 mg/m ³	4	2	8	0.15 mg/m ³	5	3	15	TLV		
	Nickel ^g	Ι.	А,Н		3	2	6	1 mg∕m ³	5	2	10	EE		x
	Chromium ⁹	I	А,Н		2	1	2	0.5 mg/m ³	5	2	10	EE		h
	Iron ⁹	I.		10 mg/m ³¹	2	1	2	5 mg/m ³	3	2	6	EE	l.	

^a As a cadmium salt.

 $^{\rm c}$ For all inorganic tin compounds except SnH₄ and SnO₂. C Unidentified species resulting from the spraying of SnCl₂/methanol on hot glass substrate.

^d Is an experimental carcinogen via oral administration to animals. Effects from inhalation are not reported in the literature.

^e Unidentified reaction products from CdCl₂ and Th⁻ourea.
 ^f TWA is for copper fume, dusts, and mists.

⁹ These are applied as an alloy.

h Many chromate salts are suspect carcinogens. Chromium oxides, which would be likely emission following heat treatment, are experimental carcinogens via inhalation.

¹ TLV's for iron oxide fumes which may be formed upon heat treatment.

TABLE 8.2-4. HAZARD RATING FOR SINGLE CRYSTAL GALLIUM ARSENIDE PROCESS

Process	Chemical	Probabie route(s) of exposure	Source of toxicity data	STEL	Acut≘ toxicity ranking	Acute exposure potential ranking	Acute hazard potential ranking	TWA	Chronic toxicity ranking	Chronic exposure potential ranking	Chronic hazard potential ranking	Basis for exposure potential ranking	Teratogen Carcinogen
Bauxite mining	Alumina	I	A	20 mg≠m ³	· 1	3.	3	10 mg/m ³	3	unk	low	EE	
	NaOH	D	A,H		4	unk	unk	2 mg/m ³	5	unk	unk		
	нст	I	А,Н		4	unk	unk	7 mç/m ³	4	unk	unk		
		D	н		4	unk	unk	(5 ppm)					
	Ether	I		1500 ng/m ³ .	3	unk	low	1200 mg/m ³	1	unk	low	EE	
	Gallium	1	A		4 ^a	unk	low		enk	unk	unk		
	Gallium chloride	1	A		4	unk	low		unk	unk	unk	2	
Arsenic refining	Arsenic trioxide	I	н		5	3	15	0.05 mg/m ³	6	4	24	TLV	x
Gallium arsenide production	Gallium	I	A		4 ^a	2 [·]	8		enk	unk j	unk	-	
ა ა	Arsenic	I	н		5	2	10	0.5 mg/m ³	5	2	10	EE	×
ζ.	Gallium arsenide	I	A		2 ^b	1	2		wnk	unk	unk		
Single crystal growth	GaAs	I	A		2 ^b	1	2	- •	ank	unk	unk ·		
	8 ₂ 0 ₃	I	· A	20 mg⊮m ³	2	2	4	10 mg/m ²	3	2	6	EE	
	As 203	I	н́		5	2	10	0.05 mg/m ³	6	2	12	EE	
	кн ₄ он	I	А,Н		3	unk	low		unk	unk	unk		
		D			3	unk	low						
	H ₂ 0 ₂ (90%) ^C	1	A	3 mg/m ³	4	2	8	1.5 mg/m ³	5	2	10	EE	
		D	H ·		4	3	12						
Ingot processing	GaAs	I	A		2p	1	2		ank	unk	unk		
	Slurry	I			ז	unk	low		unk	unk	unk		
	Hypochlorite solution	I	н		3	2	6		3	2	6	EE	
		D	н		3	2	6		3	3	9	EE	

(continued)

TABLE 8.2-4 (continued)

Process	Chemical	Probable route(s) of exposure	Source of toxicity data	STEL	Acute toxicity ranking	Acute exposure potential ranking	Acute hazard potential ranking	TWA	Chronic toxicity ranking	Chronic exposure potential ranking	Chronic hazard potential ranking	Basis for exposure potential ranking	Teratogen Carcinogen
LPE deposition	GaAs	I	A		2 ^b	1	2		unk	unk	unk	•	
	AlGaAs	I	E I		2	1	2		unk	unk	unk		
	Tin	T	A,H	4 mg/m ³	3	1	3	2 mg/m ³	5	1	5	EE	x
	Magnesium	I	А,Н		2	1	2	10 mg/m ^{3e}	3	1	3	EE	
- *	As	Ĭ	н		5	2	10	0.5 mg/m ³	5	1	5	EE	×
	H ₂	I		Asphyxiant	1	ו	1		2	1	2	EE	
SHO ₂ deposition	Silane (Sila ₄)	I	A	2 mg/m ³	3	2	6	0.7 mg/m ³	5	2	10	EE	
	Nitrous oxide (N ₂ 0)	I		Asphyxiant	1	1	1		2	2	4	EE	x
Metallization	Photoresist	I,D				W111	depend on	the type of	photoresi	st used			
I	HBr	I			4	Z	8	10 mg/m ³	3	2	6	EE	
ິ		D			4	3	12						
л	Br .	I		2 mg/m ³	5	2	10	0.7 mg/m ³	5	ĩ	10	EE	
	Buffered oxide	·	Needs fu	l rther character	ization								
	Acetone	I		3000 mg/m ³	2	2	4	2400 mg/m ³	1	2	2	EE	
	•	D		(1250 ppm)	2	3	6	(1000 ppm)				EE	×
	Gold	I		1	2	1	2		1	1	1	EE	-
	Magnesium	I	А,Н		2	1	2	10 mg/m ^{3e}	3		3	EE	
	Tin	• I	΄A,Η	4 mg/m ³	3	1	3	2 mg/m ³	5	2	10	EE	
Plating front contacts	Gold cyanide ^f	1,0	н	16 mg/m ³	6	3	18	10 mg/m ³	3	2	6	EE	
	Potassium carbonate	D	A	-	3	2	6		unk	umk	unk		
Removal of GaAs layer	ин _а он	I	A,H		3	2	6		unk	unk	unk	EE	
		D			3	3	9		unk	unk	unk	EE	
	H ₂ D ₂ ^C	t	A	3 mg/m ³	4	2	8	1.5 mg/m ³	5	2	10	EE	
		D	н		4	3	12					EE	

(continued)

TABLE 8.2-4 (continued)

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_	Process	Chemical	Probatie route(s) of exposure	Source of towicity Jata	STEL	Acute toxicity manking	Acute exposure potential ranking	Acute hazard potential ranking	IWA	©hroni: ⊐xicity ranking	Chronic exposure potential ranking	Chronic hazard potential ranking	Basis for exposure potential ranking	Teratogen Carcinogen
_	Antireflective coating	SiH ₄ N ₂ Si ₂ N ₄	I I . I	A	2 mg/m ³ Asphyxiant	3 1 unk	2 1 unk	6 1 unk	0.7 гg/m ³	5 2 unk	2 1 unk	10 2 unk	EE · EE	
- 236 -	Final cell processing	H ₂ Alumina	I	A	Asphyxiant 20 mg/m ³	1	1	1	10 mg/m ³	3	1.	3	EE	
•		Copper Gold	I	д ,Н	4. mo./m ³ⁱ	3	1 2 2	3	0.2 mg/m ³	5	1	5 1	EE EE	x x
		Encapsulant	•	Needs fu	rther characteri	zation	2	D	2 mg/m ³	5	2	10	EE	

^a This acute toxicity ranking is based on subcutaneous administration of 110 mg/kg for rats.

b Based on oral route of administration.

^C TWA and STEL is for a 90 percent H₂O₂ concentration

^d Based on toxicity of GaAs.

^e For magnesium oxide fume.

^f Based on toxicity of hydrogen cyanide.

The assessment of chronic hazards presented a complex problem. Several of the materials involved in each process are suspect carcinogens or teratogens, and from this standpoint no safe exposure level is associated with their use. Yet, for several of these compounds a TWA is cited as a guideline to indicate safe exposure. As a means of addressing this problem, therefore, the chronic hazard potential of a substance is based on those effects of the material other than carcinogencity or teratogenicity, which are treated separately.

A second problem was that no published TWA values were available for some materials used in the processes. Materials lacking published TWAs are ranked according to the level of debility they produce (Section 3.2.3). The materials are classified as primary skin irritants, skin sensitizers, eye or mucous membrane irritants, pulmonary sensitizers, fibrogenic dusts, benign pneumoconiosis producers, asphyxiants, CNS depressants, or peripheral neuropathogenic agents. On the basis of the debility associated with each of these disease states, а debility ranking from 1 to 4 (Table 3.2-6) was used in place of the TWA chronic toxicity ranking. The relative level of debility is based on the total lost workdays per incident for that particular disease state (CDIR 1979). Theoretically, a specific material could have a maximum chronic toxicity ranking of 25 if it is associated with manifestations of all eight disease states. A high ranking in this system does not necessarily establish that a substance is inherently more dangerous than one with a lower ranking. One substance may cause a single serious disease state, whereas another may cause several minor The debility ranking of the latter will be disease states. higher because it can be expected to result in more and different diseases, leading to more lost workdays. The same is true of the hazard ratings. A higher hazard rating indicates the potential of a substance to cause a greater number of lost workdays. The final hazard ranking is based on two factors:

the material's toxicity, and the potential for exposure to that material in a particular solar cell processing step.

The exposure potential ranking used to derive an acute or chronic hazard rating has a range from 1 to 4, with 1 indicating practically no exposure and 4 indicating a high exposure potential. The assessments of most exposures are based on the quantity of material used in the process; the degree of worker interaction with the process (i.e., degree of automation); how easily the process feed, reactants, and wastes can be controlled; and finally, the likelihood that the STEL (for acute exposures) or the TWA (for chronic exposures) might be exceeded. Chronic exposures established by this method are assigned an engineering estimate (EE) designation in the exposure potential Some chronic exposures are based on actual ranking column. worker exposure data from the literature (Briggs et al. 1980), these are indicated with a threshold limit value (TLV) designa-Where information concerning toxicity was scarce or tion. information concerning the process or operation was lacking, the designation is "unknown" (unk).

Tables 8.2-5 and 8.2-6 the cell processing materials that by virtue of their acute and/or chronic hazard potential ranking appear to pose the greatest problems. Mining and refining materials are not included.

For the silicon-I process only dermal exposure to HF acid and $2nCl_2$ shows a high range of acute hazard potential. The other rankings for the silicon-I process are in the moderate range. For the silicon-II process no materials show a high ranking. In the cadmium sulfide process the only material showing a high ranking for acute hazard potential is cadmium chloride during formulation; in the gallium arsenide process only gold cyanide shows a high ranking.

A comparison of the silicon-I and silicon-II processes indicates that one major difference is wet etching versus plasma etching; plasma etching appears to be a much safer process.
TABLE 8.2-5. MAJOR ACUTE HAZARDS

Material	Process step	Acute hazard potential rating
Silicon I	-	
Chlorosilanes HCl BCl ₃ HF HNO3 HNO3 POCl3 Nickel ZnCl2	Purification Purification Doping Etching Etching Etching Etching Doping Metallization Metallization	12 (dermal) 12 (dermal) 10 10 (inhalation) 18 (dermal) 10 (inhalation) 12 (dermal) 10 12 18
Silicon II		
PH3 Laser	Doping Anneal	10 10
Cadmium sulfide		
CdCl2 CdCl2 CdS Thiourea CdS CuCl	Formulation Cadmium spray Cadmium spray Cadmium spray Metallization grid pattern Copper dip	15 10 10 moderate 10 12
Gallium arsenide		
Arsenic Arsenic trioxide H ₂ O ₂ Arsenic HBr Bromine Gold cyanide H ₂ O ₂	GaAs production Single crystal growth Single crystal growth LPE deposition Etch Etch Plating GaAs removal	10 10 12 (dermal) 10 12 (dermal) 10 18 12 (dermal)

TABLE 8.2-6. MAJOR CHRONIC HAZARDS

Material	Process step	Chronic risk potential rating
Silicon I		
HF Nickel Lead Tin ZnCl ₂ Lead Tin	Etching Metallization Metallization Metallization Metallization Interconnection Interconnection	10 15 15 10 15 10 10 10
Silicon II	· ·	
Silane Phosphine Lead Tin	Silicon purification Ion implanation Interconnection Interconnection	15 10 10 10
Cadmium sulfide		
CdCl2 SnCl2 CdCl2 CdS CdS Copper chloride Copper Lead Nickel Chromium	Formulation Substrate processing Cadmium spray Cadmium spray Metallization grid pattern Copper dip Metallization Metallization Metallization Metallization	18 10 12 12 18 10 10 15 10 10
Gallium arsenide	· · ·	· · ·
Arsenic Arsenic trioxide Hydrogen peroxide Silane Bromine Tin Hydrogen peroxide Silane Tin	GaAs production Single crystal growth Single crystal growth SiO ₂ reposition Etching Metallization GaAs removal Antireflective coating Soldering	10 12 10 10 10 10 10 10 10 10

Also, electroless plating, used in the silicon-I, process appears to create a more hazardous situation that does metallization by screen printing. It is noted also that chlorosilane and HCl in the silicon-I process have moderate rankings, whereas in the silicon-II process they have a low ranking. The reasons for this difference are that fewer people would be involved in the new Union Carbide process, and the potential for an acute exposure would be lower. Secondly it is believed that the new process would incorporate better safety controls.

In the cadmium sulfide process only CdCl2 during formulation of the aqueous mixture is given a high hazard rating. This is primarily due to the large quantities of material that are used and handled by workers during the formulation step. Determining a hazard rating for thiourea was somewhat difficult because of a scarcity of toxicity data. Thiourea is reported to have high acute toxicity via intraperitoneal injection in rats (Sax, 1979). No value for toxicity by inhalation was found in the literature. Scarcity of data makes it difficult to project what would constitute an acute exposure. Thus, on the basis of available toxicity data alone, a moderate hazard ranking was assigned, indicating a moderate likelihood of exposure to concentrations that would constitute an acute exposure leading to worker injury.

The remainder of the materials listed under the cadmium sulfide process have moderate hazard potential rankings. Except for copper chloride, most of these substances have a moderate ranking because of their high acute toxicity, meaning that there is little likelihood of an acute exposure episode in processes where the chemicals are used. Copper chloride, though of moderate toxicity, has a moderate acute exposure potential owing to the nature of the process and thus is rated a moderate acute hazard.

In the gallium arsenide process only gold cyanide received a high acute hazard ranking, which is based on the toxicity of hydrogen cyanide (HCN). Because HCN has a relatively low STEL and exposure can occur via inhalation and dermal routes, it is given a moderate ranking for acute exposure potential.

Table 8.2-6 lists what appear to be the major chronic hazards among the substances with published TWA's (when teratogenic and/or carcinogenic potential is not considered). Though teratogenic and carcinogenic potential are not used as criteria in the chronic hazard rating system, it is emphasized that any material with teratogenic or carcinogenic potential must be considered to be a high chronic hazard risk.

noted above, the alternative chronic hazard rating As system does not necessarily indicate the seriousness of the disease states a particular material may cause, but does indicate the potential of the material to result in lost time due to the disease state(s) it causes. Of course, the more serious disease states would be expected to lead to more lost workdays per incident, but use of material causing several disease states may result in more total lost workdays than use of a material causing only one disease state of a more serious nature. Within the constraints of this chronic hazard rating system, it is unrealistic to try to categorize materials as constituting a high or low chronic hazard; rather, one should be able to judge by the relative magnitude of the chronic hazard rating the potential of a substance to cause disease that results in lost workdays.

The tables show many "unknowns" because of a lack of information on the toxicity of the materials, on the complexities of the processes in which the materials are used, or both. Also, in some instances complex chemical reactions cause the formation byproducts that have not yet been entirely identified. of Finally, it is stressed that these tables by no means list all of the materials that might be used in the four solar cell manufacturing processes. Materials such as photoresists, plating baths, and etching solution, are often proprietary and vary among manufacturers. Process designs and the use and application of materials may vary significantly. In light of

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these factors, the information presented is considered valuable in indicating areas of major concern and areas in which more information is needed; thus it can be used as a starting point for more detailed investigations.

8.3 DATA SUMMARY FOR 1 MILLION BTU (5.57 Mg/yr) GENERATING FACILITIES

So that the results of this study may be compared with data from similar studies concerning other energy technologies, the data are converted to correspond to a 1 million Btu/yr photovoltaic electric plant. Tables 8.3-1 to 8.3-4 summarize the manpower and risk data; Tables 8.3-5 to 8.3-8 summarize the material and wastes.

Process step	Labor employee-hours	Total lost workdays	Fatalities
Mining and refining of quartz Metallurgical silicon production	12 321	0.2 1.3	$\begin{array}{ccc} 2.1 & \times & 10^{-5} \\ 1.8 & \times & 10^{-4} \end{array}$
line silicon production	49,486	11.6	1.6×10^{-3}
Subtotal	49,819	13.1	1.8×10^{-3}
Single crystal silicon growth Ingot processing Junction formation Perimeter grind Etching Metallization Antireflective coating Cell testing Interconnection Encapsulation Module testing	28,470 23,395 1,429 929 869 1,430 2,503 6,794 4,034 5,915 358	6.5 5.7 0.3 0.2 0.3 0.5 0.5 1.6 1.0 1.4 0.1	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
Subtotal	72,126	18.1	7.4 $\times 10^{-4}$
Total	79,215	31.2	2.5×10^{-3}

TABLE 8.3-1.LABOR REQUIREMENTS, TOTAL LOST WORKDAYS, AND FATALITIES
ASSOCIATED WITH A 5.57-MW/YR SILICON I PRODUCTION PROCESS

TABLE 8.3-2. LABOR REQUIREMENTS, TOTAL LOST WORKDAYS, AND FATALITIES ASSOCIATED WITH A 5.57-MW/YR SILICON II PRODUCTION PROCESS

Process step	Labor employee-hours	Total lost workdays	Fatalities
Mining and refining of quartz Metallurgical silicon production Silicon purification	14 322 2,059	Neg. 0.1 0.5	2.7×10^{-7} 1.0 x 10 ⁻⁵ 6.7 x 10 ⁻⁵
Subtotal	2,395	0.6	7.7 x 10 ⁻⁵
Ribbon growth p+ Aluminum-back contact application Plasma etching Ion implantation Back and front metallization Antireflective coating Interconnection Encapsulation Module testing	32,596 1,303 1,983 1,805 2,607 1,805 5,303 6,105 201	7.1 0.3 0.4 0.4 0.6 0.4 1.3 1.4 0.1	3.3×10^{-4} 1.4×10^{-5} 2.0×10^{-5} 1.8×10^{-5} 3.0×10^{-5} 1.8×10^{-5} 1.8×10^{-5} 6.5×10^{-5} 7.4×10^{-6} 2.8×10^{-6}
Subtotal	53,708	12.1	5.7×10^{-4}
Total	56,103	12.7	6.5×10^{-4}

Process step	Labor employee-hours	Total lost workdays	Fatalities
Mining and refining of gallium Refining of arsenic Gallium arsenide production	1,897 2 715	0.9 Neg. 0.2	1.0 x 10 ⁻⁵ Neg. 7.2 x 10 ⁻⁶
Subtotal	2,614	1.1	1.1 x 10 ⁻⁴
Liquid-encapsulation Czochrolski single crystal growth Ingot processing Liquid phase epitaxial (LPE) deposition Deposition of SiO ₂ layer Front metallization Back metallization Plate front contacts Removal of the lattice-matching GaAs layer Antireflective coating-plasma deposition Final cell processing Module assembly	1,360 4,777 41,658 4,291 7,665 7,006 894 234 3,487 11,443 32,134	0.3 1.1 9.7 0.9 2.1 2.4 0.3 0.1 0.8 2.7 7.3	1.4×10^{-5} 2.1×10^{-5} 4.5×10^{-4} 4.5×10^{-4} 1.8×10^{-4} 1.6×10^{-4} 1.6×10^{-5} 4.9×10^{-6} 4.8×10^{-5} 1.4×10^{-4} 3.8×10^{-4}
Subtotal	114,949	28.3	1.5×10^{-3}
Total	117,563	29.4	1.6×10^{-3}

TABLE 8.3-3. LABOR REQUIREMENTS, TOTAL LOST WORKDAYS, AND FATALITIES ASSOCIATED WITH A 5.57-MW/YR GALLIUM ARSENIDE PRODUCTION PROCESS

TABLE 8.3-4.	LABOR REQUIREMENTS,	TOTAL LOST WOR	RKDAYS, AND	FATALITIES
ASSOCIATED	WITH A 5.57-MW/YR CA	ADMIUM SULFIDE	PRODUCTION	PROCESS

Process step	Labor employee-hours	Total lost workdays	Fatalities
Cadmium refining	3,045		
Subtotal	3,945	1.2	2.1×10^{-4}
Cadmium sulfide photovaltaic cell and array production	34,503		
Subtotal		7.9	3.6×10^{-4}
Total	34,503	9.1	5.7×10^{-4}

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Process step	Material	Material requirements	Emissions and wastes
<u>Mining and refining of</u> <u>quartz</u>	Sand and gravel to produce 3.11 Mg/MW of single-crystal sili- con cells Sand and gravel mined in 1985 Total dust Respirable dust Respirable free silica	2624 Mg/yr 59 million tons	91.01 to 131.2 kg/yr 9.47 kg/yr 1.61 kg/yr
<u>Metallurgical silicon</u> production	98% SiO2 Coke NG-Si Particulate SiO particulate Ash particulate Fugitive NG-Si milling loss	1367 Mg/yr 524.7 Mg/yr 495.7 Mg/yr	1.05 Mg/yr 197 Mg/yr 6.40 Mg/yr 156 Mg/yr 10 Mg/yr
<u>Silicon purification</u>	MG-Si feec to chlorinator FCl for reaction SiHCl ₃ feed to poly- crystalline silicon depositicn chamber F2 to chamber Foly-Si produced Loss due to crushing	481 Mg/yr 2090 Mg/yr 2908 Mg/yr 537 Mg/yr 71.68 Mg/yr	0.3 Mg/yr

TABLE 8.3-5. MATERIAL AND WASTE SUMMARY FOR SILICON-I PROCESS

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TABLE 8.3-5 (continued)

Process step	Material	Material requirements	Emissions and wastes
Single crystal pulling	Boron for doping BCl ₃ for doping Poly-Si Crucible waste	150.g/yr 173 g/yr 5 Mg/yr	
<u>Ingot processing</u>	Loss due to tapering Loss due to grinding Silicon for water sawing Kerf loss Slurry Contamination in acid mix Acid for etching ° Nitric ° Hydrofluoric ° Acetic Slurry	14 Mg/yr 1.6 Mg/yr 51.8 Mg/yr 22.9 Mg/yr 594.9 Mg/yr 10.6 Mg/yr 199 Mg/yr 43 Mg/yr 69.6 Mg/yr	5.96 Mg/yr
Junction formation	Phosphorous for doping POC1 ₃ for doping	57.4 g/yr 283.7 g/yr	
Perimeter grind	Silicon dust		'3.4 kg/yr
<u>Etching</u>	Acid when HF is used Acid when HF/HNO3 mixture is used ° HF ° HNO3 SiF4	443 kg/yr 452 kg/yr 300 kg/yr	7.91 Mg/yr
<u>Metallization</u>	Plating solution Acetone Solder Urethane varnish	16.6 Mg/yr 11.9 Mg/yr 7.2 Mg/yr 4581 1/yr	

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Process step	Material	Material requi∽ements	Emissions and wastes
Antireflective coating	SiH2Cl2 NH3	396 ft ³ /yr 596 ft ³ /yr	
Interconnection	Copper	260 Mg/yr	
<u>Encapulation</u>	EVA Mylar Glass	24.6 Mg/yr 10.4 m ³ /yr 628 Mg/yr	

TABLE 8.3-5 (continued)

Process step	Material	Material requirements	Emissions and wastes
<u>Mining and refining of</u> <u>quartz</u>	Sand and gravel 90% quartz Total dust Respirable dust Respirable free silica	151.8 Mg/yr 79.1 Mg/yr	5.26 to 7.59 kg/yr 540 g/yr 95 g/yr
<u>Metallurgical silicon</u> production	MG-Si Polycrystalline silicon Coke Coke particulate SiO particulate Ash particulate Mg-Si milling loss	29.0 Mg/yr 24.1 Mg/yr 30.4 Mg/yr	0.06 Mg/yr 11.0 Mg/yr 0.33 Mg/yr 0.56 Mg/yr
<u>Silicon purification</u>	Reactor feed ° Mg-Si ° HCl Dichlorosilane Trichlorosilane Silicon tetrachloride Copper catalyst	27.7 Mg/yr 34.1 Mg/yr 2.3 Mg/yr 210.9 Mg/yr 2935 Mg/yr 1.41 kg/hr	
Ribbon growth	SeG-Si	24.1 Mg/yr	
P ⁺ aluminum - back contact application	Al powder Ethanol	3.05 Mg/yr 61.1 Mg/yr	2.13 Mg/yr 61.1 Mg/yr
<u>Plasma etch</u>	CF ₄ and O ₂	1.00 m ³ /yr	
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TABLE 8.3-6. MATERIAL AND WASTE SUMMARY FOR SILICON-II PROCESS

TABLE 8.3-6 (continued)

Process step	Material	Material requirements	Emissions and wastes
Ion implantation	Phosphine PH ₃ H ₂	20.⊊ g/yr	10.5 g/yr 140 g/yr
Back and front metallization	Silver ink for back Silver ink for front	3.79 Mg/yr 7.52 Mg/yr	
Antireflective coating	TiO ₂ antireflective coating	298 1/yr	
Interconnection	Aluminum	84.1 Mg/yr	
<u>Encapsulatior</u>	Glass EVA Mylar	470 Mg/yr 19.5 Mg/yr 8.30 m ³ /MW	

Process step	Material	Material requirements	Emissions and wastes
Cadmium refining	Cadmium chloride Cadmium Cadmium refining	23.0 Mg/yr 13.9 Mg/yr	
	fugitive emissions Cadmium processing fugitive emissions		180 kg/yr 0.277 Mg/yr
Substate processing	Glass	1178 Mg/yr	
Cadmium sulfide application	Thiourea	9.41 Mg/yr	
Metallization grid pattern	CdS		10.1 kg/yr
Copper dip	CuC1	1544 Mg/MW	
Metallization and post heat treatment	Copper for top elec- trode	1.73 Ma/vr	
	Lead for top electrode Nickel Chromium	6.52 Mg/yr 221 kg/yr 35.0 kg/yr	
	Copper for grid contact	17.5 kg/yr 14.2 Mg/yr	14.0.14
• • • • • • • • • • • • • • • • • • •	Lead Nickel Chromium Iron		14.8 Mg/yr 4.23 Mg/yr 213 kg/yr 33.8 kg/yr 16.9 kg/yr
Encapsulation	Unknown material	111,400 m ²	- · · · · · · · · · · · · · · · · · · ·

TABLE 8.3-7. MATERIAL AND WASTE SUMMARY FOR CADMIUM SULFIDE PROCESS · · .

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TABLE 8.3-8	. MATERIAL	AND	WASTE	SUMMARY	FOR	GALLIUM	ARSENIDE	PROCESS
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Process step	Material	Material requirements	Emissions and wastes
Gallium refining	Bauxite	1600 Mg/yr	
Arsenic refining	Arsenic	102.9 kg/yr	÷ .
Gallium arsenide production	Gallium Arsenic	88.6 kg/yr 94.7 kg/yr	
<u>Liquid-encapsulation</u> <u>Czochralski single crystal</u> growth Ingot processing	Polycrystalline ° GaAs ° Tin GaAs Mineral oil (clay) ° SiC grit slurry	153 kg/yr 1.9 g/yr	(10.6 kg/yr) 85.2 kg/yr 1.26 Mg/yr
<u>Liquid phase epitaxial (LPE)</u> deposition	Tin AlGaAs Mg GaAs	320 mg/yr 1861 g/yr 12.6 mg/yr 13.3 kg/yr	
Deposition of SiO ₂ layer	SiO2 SiH4	25.6 g/yr 0.44 g/yr	9 g/yr
Front metallization	Photoresist Au Mg Acetone	386 ml/yr 1052 g/yr 26.7 g/yr 31.7 l/yr	
Back metallization	Au-Su	773 cm ³ /yr	
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TABLE 8.3-8 (continued)

Process step	Material	Material requirements	Emissions and wastes
Plate front contacts	Gold Plating solution	935 g/yr 360 1/yr	
Removal of the lattice- matching GaAs layer	GaAs		391 g/yr
<u>Artireflective coating-</u> <u>plasma deposition</u>	Si ₃ N4 SiH4 SiH4/argon gas ° Mixture ° Nitrogen H2 gas	22.9 g/yr 15.8 g/yr 728 l/yr 7.30 g/yr	1.97 g/yr
Final cell processing	Copper Encapsulate	0.72 Mg/yr 19.7 l/yr	
Module assembly	Aluminum Methyl methacrylate	Mg/yr 1667 Mg/yr	· \

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APPENDIX A

Material Calculations for Si-I Process

The following assumptions are made:

- The cell is 4 inches in diameter (81.07 cm^2)
- The finished wafer is 200 µm thick
- The cell is 15 percent efficient under AM 1 conditions
- Each finished cell generates 1.216 watts of power.
 For a 100 MW/yr production facility, 82,236,842 cells will be produced
- Calculations are based on a 100 MW/yr production rate.
 Amount of silicon in the finished wafers:

 $\frac{82,236,842 \text{ wafers}}{100 \text{ MW}} \times \frac{1.6214 \text{ cm}^3}{\text{cell}} \times \frac{2.33 \text{ g}}{\text{cm}^3} \times \frac{1 \text{ Mg}}{106 \text{g}} = 3.11 \text{ Mg/MW}$ A saw damage etch results in a 38 percent loss (D'Aiello, 1977).

(1-0.38) = 3.11 Mg/MWx = 5.02 Mg/MW where x = the quantity of silicon prior to the etch.

Multiple wire sawing results in a 45 percent kerf loss (based on estimates from D'Aiello, 1977, Coleman, et al., 1979, Gandel, et al., 1977).

(1-0.45) = 5.02 Mg/MWx = 9.13 Mg/MW where x = quantity of silicon prior to sawing.

Grinding the ingot results in a 3 percent loss (D'Aiello, 1977).

(1-0.03) = 9.13 Mg/MWx = 9.41 Mg/MW where x = the quantity of silicon prior to grinding

Cropping results in a loss of approximately 21 percent (estimate based on data presented in Gandel, et al., 1977, Coleman, et al., 1979 and D'Aiello, 1977).

(0-0.21) x = 9.41 Mg/MW x = 11.91 Mg/MW where x = quantity of silicon prior to cropping

Crucible wastes result in a 7 percent loss (Gandel, et al., 1977).

An 0.5 percent loss is estimated for crushing of poly-Si rods before introduction to the single crystal pullers (Gandel, et al., 1977).

(1-0.005) x = 12.81 Mg/MW
x = 12.87 Mg/MW where x = quantity of poly-Si prior
to crushing.

To produce the required 12.87 Mg/MW poly-Si, the following quantity of materials are required:

Hydrogen (H₂) - 96.4 Mg/MW
Trichlorosilane (SiHCL₃) - 522.1 Mg/MW of this total, about
28.95 percent is recycle, so
371 Mg/MW is new feed. (These
calculations are based on a material flow diagram presented by
Gandel, et al., 1977 for production of 100 MW of cells.)

To produce the required quantity of SiHCL₃ needed, the following is needed to feed the fluid bed reactor: (Based on estimates by Gandel, et al., 1977.)

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HCL - 375 Mg/MW

Metallurgical grade silicon (MG-Si) - 86.3 Mg/MW

Feed to the electric arc furnace was based on material balances by Gandel, et al. 1977. Using proportions of 0.3665 for the amount of raw quartz (SiO₂) to MG-si produced and 1.048, for the amount of coke used to the amount of MG-Si produced, raw quartz and coke requirements were estimated at 245.4 Mg/MW and 94.2 Mg/MW respectively.

Emissions

Particulate emissions = 0.002 kg/kg coke produced (Neff, T.L. 1979); therefore, emissions resulting from coke produced for this process are:

9,420,000 $\frac{\text{kg coke}}{\text{yr}} \propto \frac{0.002 \text{ kg}}{\text{kg coke}} = 18.84 \text{ Mg/yr}$ SiO emissions = 0.144 x raw quartz = (0.144)(245.4) = 35.3 Mg/MW Ash emissions = 0.0047 x raw quartz = (0.0047)(245.4) = 1.15 Mg/MW (Estimates based on material flow by Gandel, et al., 1977)

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Emission factor for silicon electric arc furnace = 625 lb/ton of MG-Si

(From Crossman, L. 1974 - In: Solar Program Assessment: Environmental Factors)

Emissions = $\frac{24540 \text{ Mg}}{\text{yr}} \times \frac{312.6 \text{ kg}}{\text{Mg}} = 28.1 \text{ Mg/MW}$

Sand requirements (Watts, et al., 1979)

It was estimated from data presented that approximately 0.66 percent of the total sand and gravel needed for solar cell manufacture resulted in silicon in the active layers of the n/p homojunction cell. Total sand and gravel needed:

3.11 Mg/MW/0.0066 = 471.2 Mg/MW

Cell Processing

In the etch to remove saw damage a 3:1:1.5, HNO₃/HF/acetic acid mixture is used. An acid used rate of 0.7 gal/50 wafers (D'Aiello, 1977) is used:

 $\frac{82,236,842 \text{ cells}}{100 \text{ MW}} \times \frac{0.7 \text{ gal acid}}{50 \text{ cells}} = 11,513 \text{ gal/MW}$ If the amount of HF = x, then HNO = 3x, acetic = 1.5x x + 3x + 1.5x³ = 11,513 gal.

> HF = 2,093 gal/MW or 7.0 Mg/MW HNO3 = 6,280 gal/MW or 35.7 Mg/MW Acetic = 3,140 gal/MW or 12.5 Mg/MW

This etch removes a total of 0.003 inches from both sides of the wafer (D'Aiello, 1977) so the quantity of Si waste is:

 $\frac{0.003 \text{ in.}}{\text{wafer}} \times \frac{2.54 \text{ cm}}{\text{in.}} \times \frac{81.07 \text{ cm}^3}{\text{wafer}} \times \frac{2.339}{\text{cm}^3} \times \frac{82,236,842 \text{ wafers}}{100 \text{ MW}}$ $\times \frac{1 \text{ kg}}{1000 \text{ gm}} = 1183.7 \text{ kg/MW}$ silicon waste

Junction Formation

For boron doping boron trichloride (BCl₃) is used at a rate of 1.2×10^{17} atoms/cm³ (Gandel, et al., 1977).

$$\frac{1.2 \times 10^{17} \text{ atoms}}{\text{cm}^3} \times \frac{133,338,820 \text{ cm}^3}{100 \text{ MW}} \times \frac{117.17 \text{ g BCl}^3}{\text{mole}}$$
$$\times \frac{1 \text{ mole}}{6.02 \times 10^{23} \text{ atoms}} = 31.1 \text{ g/MW BCl}_3$$

For phosphorous doping phosphorous oxychloride (POCl₃) is used at a rate of 15 x 10^{16} atoms/cm³ (Gandel, et al., 1977).

$$\frac{15 \times 10^{16} \text{ atoms}}{\text{cm}^3} \times \frac{133,338,820 \text{ cm}^3}{100 \text{ MW}} \times \frac{153,339 \text{ POC1}}{\text{mole}}_{3}$$
$$\times \frac{1 \text{ mole}}{6.02 \times 10^{23} \text{ atoms}} = 50.94 \text{ g/MW POC1}_{3}$$

A wafer perimeter grind results in a 5 μ loss: (D'Aiello, 1977).

5.0 x 10^{-6} M x 0.32M x 0.0002M = 3.2 x 10^{-10} M³ lost per wafer or 3.2 x 10^{-4} cm³ lost per wafer

$$\frac{3.2 \times 10^{-4} \text{ cm}^3}{\text{wafer}} \times \frac{82,236,842 \text{ wafers}}{100 \text{ MW}} \times \frac{2.33 \text{ gm}}{\text{cm}^3} \times \frac{1 \text{ kg}}{1000 \text{ gm}} = 0.61 \text{ kg/MW}$$

Acid etch to remove oxide layer Estimate 1 (D'Aiello, 1977) 0.0981 HF/1000 wafers

 $\frac{82,236,842 \text{ wafers}}{100 \text{ MW}} \times \frac{0.098 \text{l}}{1000 \text{ wafers}} = 80.6 \text{ 1/MW HF}$ or 79.6 kg/MW

Estimate 2 (Gandel, et al., 1977) 6.33g HF/kg poly-Si 4.2g HNO₃/kg poly-Si

 $\frac{12.81 \text{ kg poly-Si}}{MW} \times \frac{6.33 \text{g HF}}{\text{kg poly-Si}} = 81.1 \text{ kg HF/MW}$

 $\frac{12.81 \text{ kg poly-Si}}{MW} \times \frac{4.2 \text{g HNO}_3}{\text{kg poly-Si}} = 53.8 \text{ kg HNO}_3/MW$

SiF₄ released - 0.11 kg/kg of poly-Si (Gandel, et al., 1977)

(12.84 MT/MW) = 1,284,000 kg/yr

1,284,000 yr x 0.11 kg $\text{SiF}_4 = 141,570 \text{ kg/yr SiF}_4$ released A urethane varnish is used for the photoresist. It is esestimated that 100 wafers can be coated per liter of photoresist solution (Wihl, 1978). The quantity of photoresist needed is:

 $\frac{82,236,842 \text{ wafers}}{100 \text{ MW}} \times \frac{1\ell}{100 \text{ wafers}} = 822.4 \text{ }\ell/\text{MW}$

Antireflection Coating

SiH₂Cl₂ flow rate = 10 cm³/min NH₃ flow rate = 15 cm³/min layer thickness - 700A^o (Coleman, et al., 1979) SiH₂Cl₂ = $\frac{10 \text{ cm}^3}{\text{min}} \times \frac{60 \text{ min}}{\text{h}} \times \frac{6000 \text{ h}}{100 \text{ MW}} \times \frac{3.53 \times 10^5 \text{ ft}^3}{\text{cm}^3}$ = 1.27 ft³/MW/tube or 8.89 ft³/MW/7-tube diffusion module NH₃ = $\frac{15 \text{ cm}^3}{\text{min}} \times \frac{60 \text{ min}}{\text{h}} \times \frac{6000 \text{ h}}{100 \text{ MW}} \times \frac{3.53 \times 10^5 \text{ CP}}{\text{cm}^3}$ = 1.9 ft³/MW/tube or 13.37 ft³/MW/ 7-tube diffusion module

It was estimated that for the throughput required, 8, 7-tube diffusion modules would be required. Therefore:

Total SiH₂Cl₂ needed = (8.89 ft³/MW) (8) = 71.12 ft³/MW Total NH₃ needed = (13.37 ft³/MW) (8) = 106.96 ft³ MW Total Si₃N₄ deposited: $\frac{5.675 \times 10^{-4} \text{ cm}^3}{\text{Cell X}} \times \frac{82,236,842}{100 \text{ MW}} \text{ cells} \times \frac{3.44\text{ q}}{\text{cm}^3} = 1.6 \text{ kg/MW}$

Total $\text{Si}_{3}^{N}_{4}$ formed theoretically assuming CVD is 65 percent efficient:

$$\frac{1.6 \text{ kg/MW}}{0.65} = 2.5 \text{ kg/MW}$$

Of the unused portion (2.5-1.6 or 0.9 kg/MW) 50 percent is deposited on the reactor walls and 50 percent is exhausted according to one estimate (Watts, et al., 1979).

$$\frac{2.5 \text{ kg/MW}}{0.45 \text{ kg/MW}} = \frac{71.12 \text{ ft}^3/\text{MW SiH}_2\text{Cl}_2}{\chi}$$

 $x = 12.80 \text{ ft}^3/\text{MW}$ where x is the volume of SiH_2Cl_2 that would be exhausted.

$$\frac{2.5 \text{ kg/MW}}{0.45 \text{ kg/MW}} = \frac{106.96 \text{ ft}^3/\text{MW NH}}{\text{X}}$$

$$X = 19.25 \text{ ft}^3/\text{MW} \text{ where X is the volume of NH}_3 \text{ that would}$$
be exhausted.

Interconnection

For interconnects it was assumed that they were 2 ounce copper tabs (Lockheed, 1977). It was assumed to connect the 144 cells of the module in series would require a minimum of 144 tabs. Therefore:

$$\frac{82,236,842 \text{ cells}}{100 \text{ MW}} \times \frac{\text{module}}{144 \text{ cells}} \times \frac{144 \text{ tabs}}{\text{module}} \times \frac{202}{\text{tab}} \times \frac{1 \text{ kg}}{35.27 \text{ oz}}$$
$$= \frac{46.63 \text{ Mg}}{\text{MW}}$$

The tabs will be pre-tinned with a 60/40 lead/tin solder. No material estimates were made for the solder.

Encapsulation - Assume panel is 50 inches square and has 144 cells,

For the glass:

Wgt of glass = 2.51 lbs/ft² (Carbajal, 1977) $\frac{82,236,842 \text{ cells}}{100 \text{ MW}} \times \frac{1 \text{ module}}{144 \text{ cells}} \times \frac{17.36}{\text{module}} \times \frac{2.51 \text{ lbs}}{\text{ft}^2}$ = 112.85 Mg/MW For the EVA:

Layer is 0.02 inches thick and weighs 0.048 g/cm^2 (Watts, et al., 1979)

 $\frac{82,236,842 \text{ cells}}{100 \text{ MW}} \times \frac{1 \text{ module}}{144 \text{ cells}} \times \frac{1612.9}{\text{module}} \times \frac{0.048\text{g}}{\text{cm}^2}$ = 4.42 Mg/MW EVA

For the Mylar:

Mylar layer is assumed to be 0.008 inches thick (Watts, et al., 1979).

 $\frac{82,236,842 \text{ cells}}{100 \text{ MW}} \times \frac{1 \text{ module}}{144 \text{ cells}} \times \frac{327.74 \text{ cm}^3}{\text{module}} = 1.87 \text{ m}^3/\text{MW}$

Materials Requirements for Si-II Process

The following assumptions will be made for materials calculations:

- 1. Cell manufactured is 15 percent efficient.
- 2. Cell area is 75 cm^2 .
- 3. Cell thickness is 0.008 inches (0.020 cm) final.
- 4. Calculations are based on a 100 MW/yr facility. For this study a 100 percent yield was assumed for all processes for simplification.
- 5. Each finished cell generates 1.125 watts of power; therefore a total of 88,888,889 cells must be produced for 100 MW.
- 6. Work schedule is 5 days/week, 24 hours/day, 50 week/yr. (6000 hours).
- A. 1. Total amount of silicon in cells produced is:

 $\frac{88,888,889 \text{ cells}}{100 \text{ MW}} \times \frac{1.5 \text{ cm}^3}{\text{cell}} \times \frac{2.33 \text{ gmSi}}{\text{cm}^3} \times \frac{1 \text{ Mg}}{106 \text{ gms}}$

= 3.11 Mg/MW

2. Assuming a ribbon etch following EFG growth removes 20 μ m (0.002 cm) this means of 10 percent loss from this ,step. Therefore, silicon prior to etch is:

(1-0.1)(x) = 3.11X = 3.46 Mg/MW

3. Assuming yield (mass ribbon wafers/mass polycrystalline silicon used) is 0.8. The amount of polycrystalline silicon required is:

$$\frac{3.46 \text{ Mg/MW}}{X} = 0.8$$

x = 4.33 Mg/MW polycrystalline silicon required.

	4.	No l	oss is assumed from the laser scribe operation.			
в.	Poly	cryst	alline Silicon Production (Union Carbide, 1979)			
	This mate requ to p mult puts 7533	is n rial ired roduc iplie . Pl h/yr	ot a complete materials balance but gives major flows. Total amount of polycrystalline silicon is 4.33 Mg/MW. Since the U.C. plant is designed e 1000 Mg/yr and only 433 Mg/yr are required, a r of 0.433 will be used to scale down all through- ant operating time was calculated to be about			
	1.	MG-S	i (98 percent) to storage bin - 66.20 kg/h			
		Bin	= 4.99 Mg/MW is vented to a filter. Amount to filter = 0.04 kg/h = 0.003 Mg/MW			
•	2.	Copper catalyst - 1.41 kg/h				
	3.	Materials to hydrogenation reactor				
		a. b. c. d. e. f.	HCL - 1.70 kg/h = 0.13 Mg/MW DCS - 5.43 kg/h = 0.41 Mg/MW TCS - 502.7 kg/h = 37.87 Mg/MW STC - 6994 kg/h = 526.86 Mg/MW Mg-Si - 66016 kg/h = 4.98 Mg/MW H ₂ - 41.48 kg/h = 3.12 Mg/MW			
	 Materials from hydrogenation reactor to waste settlin tank 					
-		a. b. c. d. e.	HCl - 2.49 kg/h = 0.19 Mg/MW DCS - 30.79 kg/h = 2.32 Mg/MW TCS - 1710 kg/h = 128.86 Mg/MW SCS - 5836 kg/h = 439.79 Mg/MW H_2 - 73.5 kg/h = 5.53 Mg/MW			
	5.	Materials from waste settling tank to waste chlorides tank				
		a. b.	TCS - 8.75 kg/h STC - 45.9 kg/h			
			This waste stream also contains dissolved metal salts (Al, Fe), copper catalyst dust, silicon powder dust, complexed metal salts. This is burned in a liquid waste burner.			
	6.	Mate: tank	rials from waste settling tank to crude TCS storage . These materials first pass through a condensor.			

a. HCl - 6.78 kg/h = 0.06 Mg/MW
b. DCS - 25.6 kg/h = 1.93 Mg/MW
c. TCS - 1471 kg/h = 110.81 Mg/MW bottoms from the crude TCS tank well
d. STC - 5342 kg/h = 402.41 Mg/MW require waste disposal

Chlorosilane gases given off are combusted in a nozzle-mix burner.

- 7. The same amount of materials go from TCS storage tank to the stripper column.
- 8. Gases from the stripper column go to a condensor, then to a silane storage tank. Part of the condensate is recycled to the stripper column and part is burned in a mix nozzle gas burner. The amount burned is:

a. HCl - 0.79 kg/h = 0.06 Mg/MWb. $SiH_4 - 0.74 \text{ kg/h} = 0.06 \text{ Mg/MW}$ c. MCS - 0.10 kg/h = 0.01 Mg/MWd. DCS - 1.95 kg/h = 0.15 Mg/MWe. TCS - 0.50 kg/h = 0.04 Mg/MW

Emissions from the condensor receiver (silanes and H_2) are combusted in a nozzle mix burner feed.

9. The bottoms from the stripper column go to a reboiler. From the reboiler some is recycled back to the column. The rest goes to a TCS distillation column. The amount going to distillation is:

a. DCS - 23.6 kg/h = 1.78 Mg/MW
b. TCS - 1470.5 kg/h = 110.74 Mg/MW
c. STC - 5342 kg/h = 402.41 Mg/MW

 Also entering into the TCS distillation column is the following components from the TCS redistribution reactor: (contains amberlyst A-21 amine based ion exchange resin)

a. MCS - 18.3 kg/h = 1.38 Mg/MW b. DCS - 658 kg/h = 49.57 Mg/MW c. TCS - 7361 kg/h = 555.50 Mg/MW d. STC - 1345 kg/h = 101.32 Mg/MW

11. Top cut from the TCS distillation column goes through a condensor to the DCS distillation column. Amounts entering the DCS column are:

a.	SiH4 - 0.61 kg/h = 0.04 Mg/MW	After the condensor
b.	MCS - 18.3 kg/h = 1.38 Mg/MW	the stream is divided
c.	TCS - $8566 \text{ kg/h} = 645.28 \text{ Mg/MW}$	so some is recycled
d.	STC = 0.40 kg/h = 0103 Mg/MW	to the TCS dis-
		tillation column

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12. Bottom cut from the TCS distillation column goes to a reboiler where a portion is recycled to the TCS distillation column and the remainder is returned to the STC storage tank. Amounts to STC tank

a. TCS -]54 kg/h = 19.96 Mg/MW b. STC - 6487 kg/h = 488.66 Mg/MW

13. Top cut from DCS distillation column goes through a condensor. After the condensor the stream is split. Some is recycled back to the DCS distillation column, and some is routed to the DCS redistribution column (contains A-21 ion exchange resin). Amount into DCS redistribution column is:

a. Silane - 2.9 kg/h = 0.22 Mg/MW
b. MCS - 250 kg/h = 18.83 Mg/MW
c. DCS - 1421 kg/h = 107.04 Mg/MW
d. TCS - 604 kg/h = 45.50 Mg/MW
e. STC - 0.13 kg/h = 0.01 Mg/MW

14. Bottom cut from DCS distillation column goes through a reboiler through a condensor, then to the TCS redistribution reactor. Amounts entering the redistribution reactor are:

a.	MCS -	0.11 kg/h = 0.01 Mg/MW	The top cut from
b.	DCS -	46.4 kg/h = 3.50 Mg/MW	the reboiler is
ç,	TÇS -	9125 kg/h = 687.39 Mg/MW	returned to the
d.	STC -	213.6 kg/h = 16.09 Mg/MS	DCS distillation
			column

15. The top cut from the DCS redistribution column goes to the silane distillation column. The top cut from the silane distillation column goes through a condensor, then through a silane shift tank, through a filter and to the pyrolysis reactor. Silane entering the pyrolysis reactor is:

74.6 kg/h = 5.62 Mg/MW

- 16. The bottom cut from the silane distillation column goes to a reboiler. Here the stream is split with some recycled to the silane distillation column and some to the DCS distillation column.
- 17. Materials from the pyrolysis reactor to the Si powder storage are:

a. Silicon - 65 kg/h = 4.90 Mg/MW

- b. Silane 0.39 kg/h = 0.03 Mg/MW
- c. Hydrogen 9.3 kg/h = 0.70 Mg/MW
18. Material from the Si powder storage to melter-consolidation. a. Silicon - 57.5 kg/h = 4.33 Mg/MW Si loss from powder storage - 7.4 kg/h b. = 0.57 Mg/MWChlorosilane gases emitted and go to pre-mix burner feed. 19. Final product - 57.5 kg/h = 4.33 Mg/MW с. Application of Aluminum Back Contact - Spray 1. Aluminum powder and ethanol Al powder - 0.002467 gm/cm^2 (based on data from Wihl, 1978) $\frac{0.002467 \text{ gm}}{\text{cm}^2} \times \frac{75 \text{ cm}^2}{\text{wafer}} \times \frac{88,888,889 \text{ wafers}}{100 \text{ MW}} \times \frac{1 \text{ Mg}}{106 \text{ gm}}$ = 0.164 Mg/MW Ethanol - 0.049338 gm/cm^2 (based on data form from 2. Wihl, 1978) $\frac{0.049338 \text{ gm}}{\text{cm}^2} \times \frac{75 \text{ cm}^2}{\text{wafer}} \times \frac{88,888,889 \text{ wafers}}{100 \text{ MW}} \times \frac{1 \text{ Mg}}{106 \text{ gm}}$ = 3.29 Mg/MWDensity of ethanol 0.7893 gm/cm³ $\frac{3.29 \times 10^6 \text{ gms}}{MW} \times \frac{1 \text{ lit}}{789.3} = \frac{4168.25 \text{ lit}}{MW}$ Since the wafers are dried and fired after this step, it can be assumed that all of the ethanol is driven off. Plasma Etch - SiO₂ Removal D. Flow rate of CF_4/O_2 gas = 50 cm³/min (LFE Corp., 1980).

Plant operating time is 6000 h/yr.

$$CF_4/O_2 = \frac{6000}{\text{yr}} \text{ h} \times \frac{60 \text{ min}}{\text{h}} \times \frac{50 \text{ cm}^3}{\text{min}} \times \frac{1 \text{ m}^3}{1 \times 106 \text{ cm}^3}$$

= 18 m³/yr or 0.18 m³/MW

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E. Ion Implantation

F.

PH₃ used (Extrion/Varian, 1980) Assume dose of 1×10^{15} atoms/cm² (Lockheed, 1978) $PH_{3} = \frac{1 \times 10^{15} \text{ atoms}}{\text{cm}^{2}} \times \frac{75 \text{ cm}^{2}}{\text{cell}} \times \frac{33.9977/\text{g}}{\text{mole}} \times \frac{1 \text{ mole}}{6.02 \times 10^{23} \text{ atoms}}$ $x \frac{88,888,889 \text{ cells}}{100 \text{ MW}} = 3.76 \text{ g/MW}$ $PH_3 = \frac{3.76 \text{ g/MW}}{1.529 \text{ g/l}} = 2.46 \text{ l/MW PH}_3$ Metallization - Back Pattern (RCA) 1. Assumptions: Ag-Paste is 3.75 g/cm³ (D'Aiello, 1977) 1) 2) Back grid covers 25 percent of cell (D'Aiello, 1977) 0.158 cm³ Ag-Paste/wafer (D'Aiello, 1977) 3) Amount of paste/wafer = $(3.75 \text{ g/cm}^3) \left(\frac{0.202 \text{ cm}^3}{\text{wafer}}\right)$ = 0.76 gm/waferTotal required = $\frac{0.76 \text{ gm}}{\text{wafer}} \times \frac{88,888,889 \text{ wafers}}{100 \text{ MW}} = 0.68 \text{ Mg/MW}$ If 25 percent of cell is covered, 75 percent is wasted on the mesh grid. Front Pattern and Bus Bars 2. Assume Ag-Paste is 3.75 g/cm^3 , front fine grid covers 4 percent of area (D'Aiell, 1977). Bus bar covers 1 percent. Assume 0.158 cm³ Ag-Paste/wafer (D'Aiello, 1977). <u>Paste/Wafer</u> - $(3.75 \text{ g/cm}^3)(\frac{0.202 \text{ cm}^3}{\text{wafer}}) = 0.76 \text{ gm/wafer}$ each for fine grid and bus bar or 1.52 gm/wafer total. Total required = $\frac{1.52 \text{ gm}}{\text{wafer}} \times \frac{88,888,889 \text{ wafers}}{100 \text{ MW}}$ = 1.35 Mg/MW

If only 5 percent of cell is covered, 95 percent is wasted on mesh grid.

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G. Antireflective Coating

Assume: Titanium dioxide (TiO₂) spray coating

0.157 cm³/cell - 0.00268 cm³/cm² cell area (based on information from D'Aiello, 1977)

Total =
$$\frac{88,888,889 \text{ cells}}{100 \text{ MW}} \times \frac{0.201 \text{ cm}^3}{\text{cell}}$$

= $\frac{178667 \text{ cm}^3}{\text{MW}} = \frac{178.67 \text{ lit/MW}}{\text{lit/MW}}$

H. Interconnection - Solder Reflow

Since copper interconnects were 2 ounces, the aluminum interconnects were assumed to have the same dimensions so that the density of the materials was the only difference; thus, the aluminum interconnects were: $\frac{2.702 \text{ g/cm}^3}{8.92 \text{ g/cm}^3} \times 2 \text{ oz or } 0.6 \text{ ounces}$ each (17 gm). If each module contains 192 cells and it is assumed that 1 interconnect strip is used for each cell, aluminum requirements are:

 $\frac{88,888,889 \text{ cells}}{100 \text{ MW}} \times \frac{17 \text{ gm}}{\text{cell}} = 15.1 \text{ Mg/MW} \text{ aluminum}$

I. Encapsulation

Assumptions -

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Total glass =
$$\frac{2.51 \text{ lbs}}{\text{module}} \times \frac{16}{100 \text{ MW}} \times \frac{462,963}{100 \text{ MW}} = \frac{84.3 \text{ Mg/MW}}{100 \text{ MW}}$$

EVA Pottant - $\frac{0.02 \text{ inches}}{\text{module}} \times \frac{2304 \text{ in.}^2}{\text{module}} \times \frac{492,963 \text{ modules}}{100 \text{ MW}}$
= 227157.35 in.³/MW

EVA Pottant - $\frac{0.048g}{cm^2} \times \frac{14864.486 cm^2}{module} \times \frac{492,963 module}{100 MW}$

= 3.5 Mg/MW EVA

,

Mylar - 0.008 in. x
$$\frac{2304 \text{ in.}^2}{\text{module}}$$
 x $\frac{492,963}{100 \text{ MW}} = \frac{90862.9 \text{ in.}^3}{\text{MW}}$
= $\frac{1.49 \text{ M}^3}{\text{MW}}$

Material Requirements for GaAs Concentrator Cells

Assumptions

- 1. Active cell diameter is 0.490 in. (l.245 cm), cell area = 1.217 cm^2 .
- Cell efficiency is 18 percent at AM 1 conditions and 400 suns.

3. Each cell generates 8.7624 watts of power:

$$0.18 \times \frac{1000 \text{ watts}}{M^2} \times \frac{0.0001217 \text{ M}^2}{\text{cell}} \times 400 = 8.7624$$

- 4. Therefore for 100 MW of cells, 11,412,398 of these cells are required.
- 5. Final wafer thickness is 0.125 mm.
- 6. Density of GaAs is assumed to be 5.316 g/cm^3 .
- 7. Cell fabrication efficiencies for all production processes are 100 percent.
- Work schedule is 24 h/day, 5 days/wk, 50 wks/yr or 6000 h/yr.

Calculations

A. Single Crystal GaAs in Final Wafer

1.
$$\frac{11,412,398 \text{ cells}}{100 \text{ MW}} \times \frac{1.217 \text{ cm}^2}{\text{cell}} \times \frac{6.0125 \text{ cm}}{\text{cell}} \times \frac{5.316 \text{ g}}{\text{cm}^3}$$
$$\times \frac{1 \text{ kg}}{1000 \text{ g}} = 9.2 \text{ kg/MW}$$

2. Assume 10 percent loss during wafer polish (based on estimates for silicon)

(1-0.1) $\chi = 9.2 \text{ kg/MW}$ X = 10.2 kg/MW

3. Assume 50 percent kerf loss during multi-wire wafer slicing (based on estimates for silicon)

$$(1-0.5)$$
 X = 10.2 kg/MW
X = 20.4 kg/MW

4. Assume a 20 percent cropping loss (based on estimates from silicon)

(1-0.2)(X) = 20.4 kg/MWX = 25.5 kg/MW

5. Assume a 7 percent loss from LEC crystal growth (based on estimates from silicon)

 $(1-0.07)(\chi) = 25.5 \text{ kg/MW}$ X = 27.4 kg/MW polycrystalline GaAs entering single crystal growth

÷ ...

6. The substrate layer is tin doped at a concentration of 1018 atoms/cm3 (James, et al., 1977). Therefore:

$$\frac{11,412,398 \text{ cells}}{100 \text{ MW}} \times \frac{0.0152 \text{ cm}^3}{\text{cell}} \times \frac{10^{18} \text{ atoms}}{\text{cm}^3}$$
$$\times \frac{1 \text{ mole}}{6.02 \times 10^{23} \text{ atoms}} \times \frac{118.69 \text{ g}}{\text{mole}} \text{ or}$$
$$0.34 \text{ g/MW of Sn are required.}$$

B. Quantity of Gallium and Arsenic

Assume 1 mole of Ga, and 1 mole of As are required to produce 1 mole of GaAs.

This would be 69.72 g Ga and 74.9216 g of As per mole of GaAs.

Therefore As/Ga = 1.075 g As/g Ga

For 27.4 kg/MW poly-GaAs: Ga = χ , As = 1.075X

 $1.075 \text{ X} + \chi = 27.4 \text{ kg/MW}$

2.075X = 27.4 kg/MW X = 13.2 kg/MW Ga 1.075X = 14.2 kg/MW As

C. Bauxite Requirements

Assume that 0.005 percent of bauxite ore is Ga (Gandel, et al., 1977). The total amount of Ga for all layers is 14.3551 kg/MW or 1435.5 kg total. Therefore, the total amount of bauxite

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required would be 1435.5/0.00005 or 28,710 Mg or 287.1 Mg/MW.

D. Copper Ore Requirements for Arsenic

Assume ore contains about 2 percent As (Kirk and Othmer, 1978):

Total As for all layers = 15.6807 kg/MW As = 1568.07 kg/0.02 = 78,403.5 kg = 78.4 MT or 0.784 MT/MW

Cell Fabrication

E. n-type GaAs Buffer Layer

1. Layer is 30μ thick (James, et al., 1977, and Maget, 1979) $GaAs = \frac{11,412,398 \text{ cells}}{100 \text{ MW}} \times 0.003 \text{ cm x} \frac{1.217 \text{ cm}^2}{\text{cell}}$ $\times \frac{5.316 \text{ g}}{\text{cm}^3} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 2.2 \text{ kg/MW}$

Assuming LPE process is 95 percent efficient (Watts, et al., 1979):

 $GaAs = \frac{2.2 \text{ kg/MW}}{0.95} = 2.3 \text{ kg/MW} GaAs$ Ga = 1.1 kg/MW

As = 1.2 kg/MW

 Layer is Sn doped at 7x10¹⁷ atoms/cm³ (James, et al., 1977, and Maget, 1979)

 $Sn = \frac{11,412,398 \text{ cells}}{100 \text{ MW}} \times \frac{0.003651 \text{ cm}^3}{\text{cell}} \times \frac{7\times10^{17} \text{ atoms}}{\text{cm}^3}$ $\times \frac{118.69 \text{ g}}{\text{mole}} \times \frac{1 \text{ mole}}{6.02 \times 10^{23} \text{ atoms}}$

= 57.5 mg Sn/MW

F. p-type Al_{0.93} Ga_{0.07} As Window Layer

1. Layer is 0.6 μ thick (Maget, 1979) For 1 mole of Al_{0.93} Ga_{0.07} As:

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25.093 g of Al 4.88 g of Ga 74.9216 g of As

are required.

Since no density could be found for AlGaAs and about 95 percent by weight of the AlGaAs is AlAs, the density of AlAs (3.81 gm/cm^3) was used for this calculation.

AlGaAs = $\frac{11,412,398 \text{ cells}}{100 \text{ MW}} \times \frac{7.302 \times 10^{-4} \text{ cm}^3}{\text{cell}} \times \frac{3.81 \text{ g}}{\text{cm}^3}$ = 317.5 g/MW

Assuming a 95 percent efficiency for the LPE process: Λ IGaAs = $\frac{317.5g/MW}{0.95}$ - 334.2 g/MW

Al = 80.0 g/MW Ca - 15.5 g/MW As = 238.2 g/MW

2. This layer is doped with magnesium at a concentration of 5x1017 atoms/cm3 (James et al., 1979)

$$Mg = \frac{11,412,398 \text{ cells}}{100 \text{ MW}} \times \frac{7.302 \times 10^{-4} \text{ cm}^3}{\text{cell}} \times \frac{5 \times 10^{17} \text{ atoms}}{\text{cm}^3}$$
$$\times \frac{24.312 \text{ gms}}{\text{mole}} \times \frac{1 \text{ mole}}{6.02 \times 10^{23} \text{ atoms}} = 1.7 \text{ mg/MW}$$

G. pGaAs Lattice Matching Layer

1. Layer is lµ thick (James, et al., 1977, and Maget, 1979)

$$GaAs = \frac{11,412,398 \text{ cells}}{100 \text{ MW}} \times \frac{1.217 \times 10^{-4} \text{ cm}^3}{\text{cells}} \times \frac{5.316 \text{ g}}{\text{cm}^3}$$

= 78g/MW deposited on cells

Assuming a 95 percent efficiency for LPE deposition: (Watts, et al, 1979)

 $GaAs = \frac{78g/MW}{0.95} = 82.1 g/MW$ Ga = 39.6 g/MWAs = 42.5 g/MW The dopant is Mg and is applied at a concentration of 10¹⁸ atoms/cm³ (James, et al., 1977).

$$Mg = \frac{11,412,398 \text{ cells}}{100 \text{ MW}} \times \frac{1.217 \times 10^{-4} \text{ cm}^3}{\text{cell}} \times \frac{10^{18} \text{ atoms}}{\text{cm}^3}$$
$$\times \frac{24.312g}{\text{mole}} \times \frac{1 \text{ mole}}{6.02 \times 10^{23} \text{ atoms}}$$
$$= 0.56 \text{ mg/MW}$$

H. Plasma deposition of SiO₂ layer by (Maget, 1979)

- 1. SiO₂ layer is 1000 Å thick (0.1μ)
- 2. Density of amorphous SiO₂ is 2.19 g/cm³
- CVD process is assumed to be 65 percent efficient (Watts, et al., 1979)

 $SiO_{2} = \frac{11,412,398 \text{ cells}}{100 \text{ MW}} \times \frac{1.217 \times 10^{-5} \text{ cm}^{3}}{\text{cell}} \times \frac{2.199}{\text{cm}^{3}}$ = 3.0 g/MW $= \frac{3.09/\text{MW}}{0.65} = 4.6 \text{ g/MW total used}$ 3.0 g/MW actually deposited1.6 g/MW waste

For 1 mole of SiO_2 28.086 g Si and 31.9988g O_2 are required. Therefore 1 mole of SiO_2 contains 46.74 percent Si and 53.26 percent O_2 by weight. Of the total 4.6 g/MW SiO_2 , 2.15 g/MW is Si and 2.45 g/MW is O_2 .

Assuming a theoretical deposition rate of 0.874 of Si from SiH_A it would require:

 $\frac{2.15g}{MW} \text{ Si x } \frac{g \text{ SiH}_4}{0.874g} \text{ Si} = 2.46g/MW \text{ SiH}_4$

At a density of $1.44g/\ell$ it would require:

$$\frac{2.46g/MW}{1.44g/l} = 1.71 l/MW$$

Since the SiH₄/Argon gas mixture contains only 1.5 percent silane it would require:

$$\frac{1.71 \ l/WM}{0.012} = 114 \ l/MW \text{ of the gas mixture}$$

or

 $\frac{2.46g/MW}{0.015} = 164g/MW \text{ of the gas mixture.}$

For the nitrous oxide a theoretical deposition rate of 0.3635 oxygen from N₂O was assumed. Therefore:

$$2.45 \text{g/MW} \times \frac{1 \text{g N}_2 \text{O}}{0.3635 \text{gO}} = \frac{6.74 \text{g N}_2 \text{O}}{\text{MW}}$$

At a density of 1.977g/l, 3.41 l/MW would be required.

I. Photoresist Application

 Assume photoresist is 5µ thick and pattern covers 90 percent of cell area (Watts, et al., 1979)

Photoresist = $\frac{11,412,398 \text{ cells}}{100 \text{ MW}} \times \frac{6.085 \times 10^{-4}}{69.4 \text{ ml/MW}} \times \frac{1 \text{ ml}}{100 \text{ sed}}$

 $69.4 \text{ ml/MW} \times 0.9 = 62.5 \text{ ml/MW} \text{ on the cell} \\ 6.9 \text{ ml/MW} \text{ on mask}$

- J. Remove SiO₂ and GaAs where photoresist is not applied.
 - 1. SiO₂ and GaAs removed is 10 percent of total deposited on the cell since the photoresist covers 90 percent of the cell area.

 SiO_2 removed = (3.0 g/MW)(0.1) = 0.3 g/MWGaAs removed = (78 g/MW)(0.1) = 7.8 g/MW

K. Front Metallization

- Metal covers 10 percent of cell area (Watts, et al., 1979)
- Layer is 5µ thick (Watts, et al., 1979)
- Au-Mg contact, 80 percent Au and 20 percent Mg (Watts, et al., 1979)
- 4. Deposition is by evaporation and is assumed to be 50 percent efficient, with 80 percent packing density of cells on holders (Watts, et al., 1979).

Au-Mg = $\frac{11,412,398 \text{ cells}}{100 \text{ MW}} \times \frac{6.085 \times 10^{-4} \text{ cm}^3}{\text{cell}} \times 0.1$

$$\frac{6.94}{\text{cell}}$$
 cm³/MW deposited on

Since the process is 50 percent efficient: Total Au-Mg = $\frac{6.94 \text{ cm}^3/\text{MW}}{0.5} = \frac{13.88 \text{ cm}^3}{\text{MW}}$

Therefore about 6.94 cm^3/MW is lost on the substrate holder, the vacuum chamber walls and the mask.

Total amount of Au = $\frac{13.88 \text{ cm}^3}{\text{MW}} \times \frac{17 \text{ g}}{\text{cm}^3} \times 0.8 = 188.8 \text{ g/MW}$ Total amount of Mg = $\frac{13.88 \text{ cm}^3}{\text{MW}} \times \frac{1.74\text{g}}{\text{cm}^3} \times 0.2 = 4.8 \text{ g/MW}$

L. Back Metallization

- 1. Back contact is Au-Sn (James, et al., 1977)
- 2. Contact is 5µ thick (Watts, et al, 1979)
- Deposition by evaporation is 50 percent efficient (Watts, et al., 1979)

Au-Sn = $\frac{11,412,398 \text{ cells}}{100 \text{ MW}} \times \frac{6.085 \times 10^{-4} \text{ cm}^3}{\text{cell}}$

= 69.4 cm³/MW deposited on cells

Total Au-Sn = $\frac{69.4 \text{ cm}^3/\text{MW}}{0.5}$ = 138.8 cm³/MW Therefore 69.4 cm³/MW is lost

M. Photoresist Removal

- 1. Acetone is used to remove the photoresist
- Based on estimates presented above in Section 4.11, it requires about 0.04 ml/cm² for photoresist removal (Wihl, 1978). Therefore for each cell about 0.05 ml of acetone is needed.

Total acetone - $\frac{11,412,398 \text{ cells}}{100 \text{ MW}} \times \frac{0.05 \text{ ml}}{\text{cell}} \times \frac{1\ell}{1000 \text{ ml}}$

 $= 5.7 \ \ell/MW$

- N. Removal of Remaining SiO, Protective Layer
 - 1. A buffered oxide etch is used for removal. Amount required is unknown.
- O. Removal of Top p-GaAs Layer
 - NH₄OH:H₂O₂:H₂O in a 4:1:1 solution is used (personal communication, R. Bell of Varian with T. Owens, PEDCo, May, 1980). Quantity of etchant is unknown.
 - 2. Quantity of GaAs removed:

78 g/MW initially deposited, and 10 percent removed during front contact metallization; therefore, 70.2 g/MW or a total of 7.02 kg per year is removed as waste.

- P. Antireflective Coating Plasma Deposition
 - 1. Coating is Si₃N₄ (Maget, 1979)
 - 2. Layer is 700 A thick
 - 3. SiH4/argon and N₂ are used to make layer (LFE Corp., 1979)
 - 4. The SiH4 is 1.5 percent of the mixture (LFE Corp., 1979)
 - 5. Assume 330 CF of SiH4/argon will provide 80 hours of deposition at a flow rate of 1947 cc/min, and this flow rate is required for deposition of the 700Å layer.

Total Si₃N₄ deposited = $\frac{11,412,398 \text{ cells}}{100 \text{ MW}} \times \frac{8.519 \times 10^{-6} \text{ cm}^3}{\text{ cell}}$ $x \frac{3.44 \text{ g}}{\text{cm}} = 2.67 \text{ g/MW}$ Total amount of GAS = $\frac{6000 \text{ h}}{\text{yr}} \times \frac{330 \text{ CF}}{80 \text{ h}} = 24,750 \text{ CF/yr}$ = 247.5 CF/MWAmount of $SiH_4 = \frac{247.5 \text{ CF}}{MW} \times 0.015 = 3.7 \text{ CF/MW}$ at 1.44 g/l this is 150.9 g/MW Ceramic Substrate (Al₂O₃) Assume substrate is approximately 2 x diameter of cell 1. or 0.98 inch. 2. Assume substrate is about 0.05 inches thick. Density of Al_2O_3 is assumed to be 3.965 g/cm³. 3. Amount alumina substrate = $\frac{11,412,398 \text{ substrate}}{100 \text{ MW}}$ $x \frac{0.32 \text{ cm}^3}{\text{substrate}} \times \frac{0.32 \text{ cm}^3}{\text{substrate}} \times \frac{3.965 \text{ g}}{\text{cm}^3} = 144.8 \text{ kg/MW}$ Lead Frames 1. Assume a diameter of about 0.6 inches (1.52 cm) 2. Assume they are copper with silver plating and are 0.007 inches thick (0.02 cm) Approximate area for each lead is 0.6 cm² $[0.76 \text{ cm}]^2(\pi)$ - 1.217 cm²] = 0.6 cm². 3. Total = $\frac{11,412,398 \text{ leads}}{100 \text{ MW}} \times 0.6 \text{ cm}^2 \times 0.02 \text{ cm} \times \frac{8.92 \text{ g}}{\text{cm}^3}$

$$= 12.22 \text{ kg/MW}$$

S. Cell Mounting to Substrate

Q.

.R.

1. Au-Sn solder used. Amount per cell unknown.

T. Encapsulate

- 1. A transparent opto-electronic epoxy is used (Maget, 1979)
- 2. Assume a coating 0.01 inches thick.

Amount of epoxy = $\frac{11,412,398}{100 \text{ MW}} \times \frac{0.031 \text{ cm}^3}{3.54 \text{ }\ell/\text{MW}} = 3.54 \text{ }\ell/\text{MW}$

U. Cells Mounted on Polysulfone Holder (Maget, 1979)

- 1. Quantity used unknown
- V. Module Assembly
 - Module is a 4" x 5.75" U-shaped aluminum box channel (Maget, 1979)
 - 2. Channel is 0.063 in. thick. Aluminum needed = $\frac{11,412,398 \text{ cells/100 MW}}{10 \text{ cells/module}} \times \frac{23.74}{\text{module}}$

x 2.702 g = 0.73 Mg/MW13.75 in. x 138.6 x 0.063 in. = 120.06 in.³ $\frac{1967.43 \text{ cm}^3}{\text{module}} \times \frac{2.702 \text{ g}}{\text{cm}^3} \times \frac{11,412,398 \text{ cells}}{100 \text{ MW}} \times \frac{1 \text{ module}}{10 \text{ cells}}$

W. Fresnel Lens and Housing

1/4" = thickness; lens is hexagonal, 25.74 cm across flat
 face.

It is assumed the lens are methyl mathacrylate plastic with a density of 0.936g/cm³. There are 10 cell-lens assemblies per module with 1 Fresnel lens and support cone per cell.

Wgt/Fresnel lens = $(0.635 \text{ cm})(573.74 \text{ cm}^2)(0.936 \text{ g/cm}^3)$ = 0.341 kgTotal needed for 100 MW of cells = $\frac{0.341 \text{ kg}}{\text{lens}} \times \frac{11,412,398 \text{ cells}}{100 \text{ MW}}$ $\times \frac{1 \text{ lens}}{\text{CEH}} = 38.92 \text{ Mg/MW}$ For lens housing:

Sides were calculated to be 14.86 cm wide. A length of 1.5 times the width or 27.29 cm was assumed. It was also assumed that the plastic for the housing had the same density as the lens.

Plastic for housing =

 $\frac{14.86 \text{ cm x } 22.29 \text{ cm x } 0.635 \text{ cm}}{\text{cell}} \times 6 \text{ sides x } \frac{0.9369}{\text{cm}^3}$ $\times \frac{11,412,398 \text{ cclls}}{100 \text{ MW}} = 134.8 \text{ Mg/MW}$

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