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AN ENVIRONMENTAL SOURCE BOOK ON THE PHOTOVOLTAICS INDUSTRY

P.D. Moskowitz, P.D. Kalb, J.C. Lee,
and V.M. Fthenakis

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Abstract

This report presents background information on the photovoltaics industry to assist the U.S. Environmental Protection Agency (EPA) evaluate premanufacture notice and significant new use submittals from the industry. It also provides information for the photovoltaics industry on the Toxic Substances Control Act compliance requirements. In this industry, a large diversity of toxic and hazardous chemicals are used. Attention is currently focused on such gases as silane, phosphine, arsine, diborane, and hydrogen selenide which may be used in large quantities and for which there is limited industrial experience. Most materials used by the industy are already listed in the Toxic Substances Control Act Inventory List. Unlisted compounds are used as feedstocks or are the actual products themselves. Manufacturers using or producing unlisted materials must apply to EPA for a Premanufacture Notification. Some materials - especially those defined to be acutely toxic - contained in the Inventory Listing may be used in larger quantity or in applications which differ from current industrial use; these are potential candidates for Significant New Use Rules.

Acknowledgments

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ACRONYMS AND ABBREVIATIONS

ALARA	As low as reasonably achievable
BNL	Brookhaven National Laboratory
CSVT	Close-spaced vapor transport
CDV	Chemical vapor deposition
EPA	Environmental Protection Agency
EVA	Ethylene vinyl acetate
FPUP	Federal Photovoltaic Utilization Program
IDLH	Immediately dangerous to life or health
ILO	International Labour Office (United Nations)
kW	Kilowatts (subscript "p" refers to maximum power capability)
MBE	Molecular beam epitaxy
MOCVD	Metal organic chemical vapor deposition
MW	Megawatts (subscript "p" refers to maximum power capability)
OSHA	Occupational Safety and Health Administration
PMN	Premanufacture Notice
SNUR	Significant New Use Regulations
TLV	Threshold limit value
Torr	Millimeters of mercury at 0^0 celsius
TSCA	Toxic Substances Control Act
W	Watts (subscript "p" refers to maximum power capability)

1. INTRODUCTION

Photovoltaic cells are solid state devices that convert sunlight into electricity. Although the photovoltaic effect was first observed in the 19th century, the first practical solar cell was constructed only in 1954. Since 1958, photovoltaic devices have been used to provide electric power for many space systems. Solar devices have also been used to operate irrigation pumps, navigation systems, and other remote installations. Recently, these devices have been used in grid-connected residential, commercial, and large central-station applications. Although their costs are still high, they are expected to be substantially reduced during the next ten years by research and development already in progress. These factors are expected to result in large growth in the photovoltaics industry.

This report presents background information on the photovoltaic industry to assist the U.S. Environmental Protection Agency - Office of Toxic Substances evaluate future Premanufacture Notice (PMN) submittals and the need for Significant New Use Regulations (SNUR), implemented under authority granted by the Toxic Substances Control Act (TSCA).[1]

In this context, this report:

(i) Gives an overview of the structure and nature of the past, present and future photovoltaics industry;

(ii) Provides descriptions of the steps involved in synthesizing and assembling photovoltaic cells, modules and arrays;

(iii) Identifies chemicals used in these processes;

(iv) Describes potential chemical and physical hazards to workers in manufacturing facilities;

(v) Describes potential hazards to public health and the environment from routine and accidental releases from manufacturing facilities;

(vi) Describes occupational and environmental control technology options;

(vii) Discusses applicability of current rules and regulations promulgated under the authority of the Toxic Substances Control Act to potential chemical hazards in photovoltaic cell manufacturing facilities.

2. THE PHOTOVOLTAICS INDUSTRY

2.1 History

The physical phenomenon responsible for converting sunlight to electricity - the photovoltaic effect - was first observed in 1839 by a French physicist, Edmund Becquerel. He noted that a voltage appeared when one of two identical electrodes in a weakly conducting solution was illuminated. The photovoltaic effect was first studied in solids such as selenium in the late 19th century. In the 1880s selenium photovoltaic cells were built that converted light to electricity with 1 to 2% efficiencies. Selenium photovoltaic cells never became practical energy systems, however, because their cost was too high relative to the amount of power they produced.[2]

Over the years, knowledge of the underlying physics of the photovoltaic phenomenon expanded. In the 1920s and 1930s, quantum mechanics provided the theoretical foundation for the present understanding of the photovoltaic effect. A major step forward in solar-cell technology was the development in the early 1950s of a method for producing highly pure crystalline silicon, which was used by Bell Telephone Laboratories in 1954 to produce a silicon photovoltaic cell with 4% efficiency. Bell Laboratories soon produced cells with 11% efficiency, heralding an entirely new era of power-producing cells.[3]

In the 1950s a few schemes for commercial application of silicon photovoltaic cells were tried, mostly in regions geographically isolated from electric utility lines. These schemes were not very successful, but an unexpected boom arose from a different quarter in 1958, when the U.S. Vanguard space satellite was launched. This satellite used a small array of photovoltaic cells to power its radio. The cells worked so well that space scientists soon realized that they could provide an effective power source for many space missions. Photovoltaic energy systems have been an integral part of the space program ever since.[2,3]

Photovoltaic cells have also been used in terrestrial applications since the late 1950s, but only since 1975 has the market for earth-based systems outstripped that for space systems. Currently photovoltaic systems are penetrating, stepwise, three different domestic and international markets: (i) very small applications in electronic equipment and novelty items such as calculators; (ii) small remote non-grid-connected applications such as mountain-top radio repeaters; and (iii) electric power systems comprising small (10 kW_p), intermediate (500 kW_p) and large (1-100 MW_p), installations serving single residences, commercial and industrial settings, and central-station generators, respectively.[4] The high cost of these systems has been the main hindrance to more extensive use in these applications, but the rising costs of alternative energy supplies along with the decreasing costs of photovoltaic devices are now resulting in rapid expansions into these markets.

2.2 Government Programs

In the early 1970s, initial support for the development of earth-based photovoltaic energy systems was provided by the National Science Foundation. The work was transferred in 1974 to the newly established Energy Research and Development Administration. Since 1975, the federal government and the U.S. photovoltaic industry have worked together in pursuit of low cost, high performance photovoltaic energy systems. Over this period the government has spent more than $700 million on programs to develop commercially viable photovoltaic devices.[5]

Despite significant progress in reducing photovoltaic electricity costs, commercially available systems and designs are still cost-competitive only for remote and special purpose applications. Consequently, the U.S. Department of Energy - National Photovoltaics Program is currently supporting research, under the Solar Photovoltaic Energy Research, Development and Demonstration Act of 1978, to improve cell conversion efficiency, life expectancy, and reliability of photovoltaic cells, modules, arrays, power conditioning units, and systems and to reduce overall costs, in order to help the technology become cost-competitive in the large bulk power markets.[5]

Recently federally supported research has been directed toward three different types of photovoltaic cells: (i) thin films, (ii) high efficiency multi-junction cells, and (iii) advanced silicon sheet cells. Although still in the early stages of development, thin films offer the potential for very low cost cells because they require less material and offer the potential for more highly automated production techniques. High efficiency multi-junction cells, a longer-term option, may yield conversion efficiencies twice those of conventional cells, so that higher production costs could be offset by higher output of electricity. The objective of the silicon sheet research is to overcome generic impediments to improving crystalline ribbon quality and growth rate, in order to reduce costs of crystalline silicon cells through increased automation and decreased loss of expensive materials.

In addition to supporting basic research, the federal government has encouraged the technologies' development through four successive "block buys" under the Federal Photovoltaic Utilization Program (FPUP) authorized by the Federal Photovoltaic Utilization Act of 1978. Through this program, the federal government purchased a large number of photovoltaic devices for distribution to federal agencies for applications such as lighthouses, military housing, and park lighting. The purpose of these block buys was to boost private sector production and to lower unit costs, while at the same time providing equipment for test applications and demonstrations. The program was quite successful; array prices dropped from $30/Wp to about $9/Wp within three years, showing how quickly the cost of supplying photovoltaic devices can come down with innovation and volume production.[6] An incentive for purchasing these devices also was provided by including them within the class of solar equipment for which a tax credit was allowed; consumers could deduct 40% of the first $10,000 spent for their purchase and installation. Under the new tax laws, this tax credit was not renewed.

2.3 Industry Programs

The photovoltaics industry has grown rapidly both within and outside the U.S. Of the approximately 40 solar module manufacturers, seven are located in the U.S. (Table 1), twelve in Europe, and fourteen in Japan. About ten companies are producing photovoltaics on a small scale in developing countries.[3]

TABLE 1. U.S. PRODUCTION OF PHOTOVOLTAIC CELLS (MW) 1984 - 1985

Company	1984	1985	Type
ARCO Solar	5.5	4.7	Single crystal-Si
	0.0	0.2	Amorphous-Si
United Energy Corporation	3.0	0.0	Concentrator
Solarex	1.5	1.9	Polycrystal-Si
	0.5	0.2	Single Crystal-Si
	0.1	0.1	Amorphous-Si
Solec International	0.4	0.4	Single Crystal-Si
Motorola	0.3	0.5	Polycrystal-Si
Solenergy	0.1		Single Crystal-Si
Mobile Solar	0.1	0.1	Ribbon-Si
Other	0.2	0.5	*
Total	11.7	8.6	

*80% was made of single crystal-Si in 1984 and 60% was made of amorphous-Si in 1985.

Source: References 7, 8, and 9.

In recent years, international joint ventures and licensing arrangements have become popular, allowing companies to enter foreign markets and boost sales. American and European companies have formed many partnerships and both are now forging links with their competitors in Japan. Several companies have signed contracts to build photovoltaics manufacturing plants abroad. This has helped other countries to move forward while providing the U.S. firms with needed revenue.

2.4 Technology

A typical flat-plate solar cell of present design (Figure 1) is about 100 cm^2 in size and contains a flat layer of semiconductor material. When sunlight strikes the cell, electrons are freed in the semiconductor material, and an electric current is generated. The electricity is collected and transported by metallic contacts placed in a grid-like fashion on the surface of the cell. Groups of cells are mounted together on a rigid plate and are electrically interconnected to form photovoltaic modules. A typical module can convert about 11% of the incoming sunlight to electricity and has a generating capacity of 50 W_p. Some modules are designed to concentrate sunlight before conversion. These contain lenses that focus sunlight onto smaller cells, 1 cm^2 or less in area, and can convert about 14% of the incoming sunlight to electricity. In either case, groups of modules are usually mounted together on a permanently attached frame and are interconnected to form photovoltaic arrays (Figure 2).

2.5 System Designs

Solar cells can be made from a number of materials and formed in a variety of designs; for discussion purposes, they can be classified by material and by type of fabrication process.

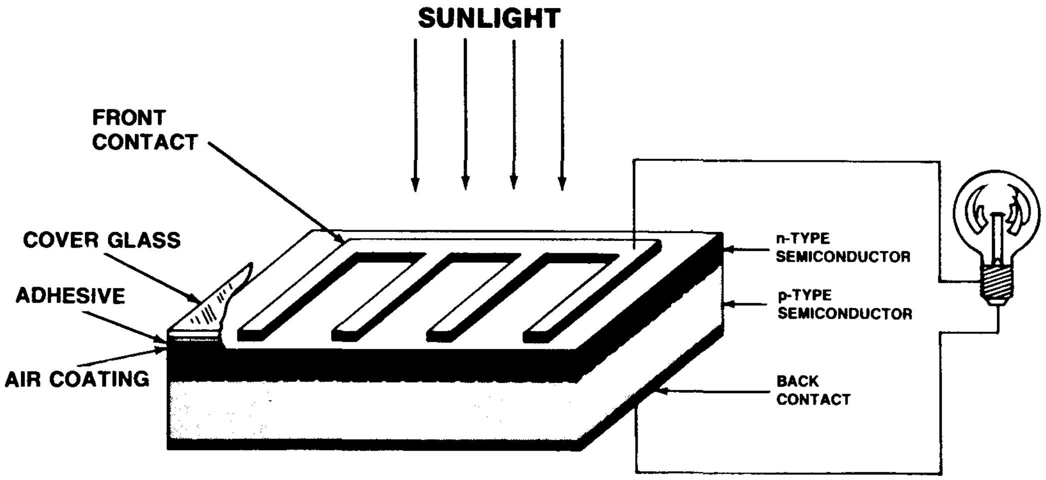

Figure 1. Basic photovoltaic (solar cell).

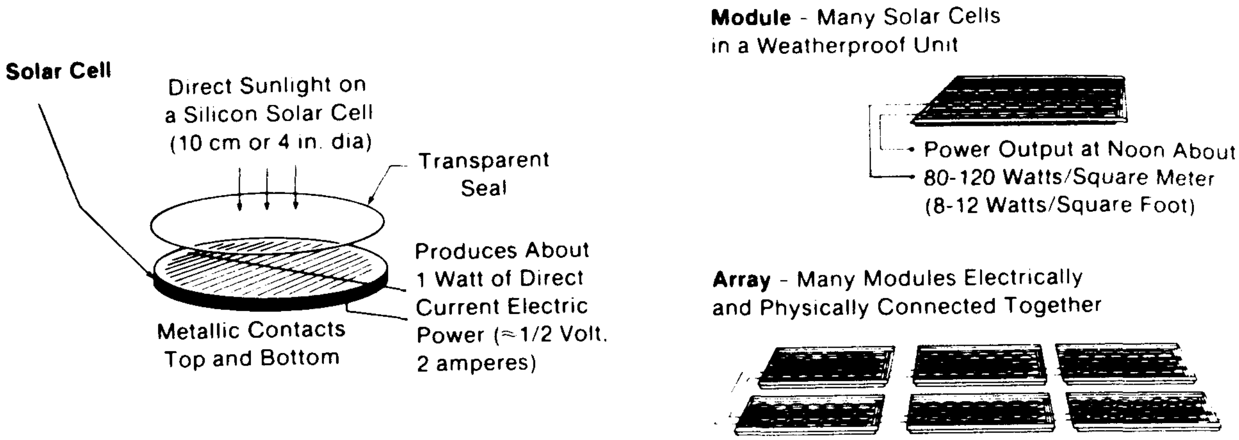

Figure 2. Cell, modules, and array configurations.

Single-crystal silicon is the most frequently used and best understood semiconductor material for photovoltaic cells. In cell fabrication, a Czochralski or a floating-zone process is used to obtain single-crystal silicon from polycrystalline silicon. These processes, particularly the Czochralski, have been the dominant ones in photovoltaics manufacture since their rediscovery in 1954; in 1982, they were used for more than 60% of all photovoltaic cells produced worldwide (Table 2). These processes, however, are both expensive and wasteful, therefore new material and process options have been developed; some are now being used commercially, and others are still being studied.

One way to reduce costs is to fabricate the single-crystal cells less expensively by using less-refined silicon and by reducing excessive material losses due to cutting. Edge-defined film-fed growth, ribbon-to-ribbon growth, and dendritic web growth are among the processes for making cheaper silicon cells. Some of these options are now just beginning to be used commercially. In 1982, their share of the market was about 19% (Table 2); in the near-term, they will continue to grow.

In a continuing effort to reduce system costs further, federally sponsored research has recently been directed towards two different approaches to cell fabrication: thin films and high-efficiency multi-junction cells. Although still in the early stages of development, thin films offer the potential for making very inexpensive cells because they require less material and allow more highly automated production. Amorphous silicon alloys and several polycrystalline compound semiconductors (e.g., gallium arsenide, copper indium diselenide, cadmium telluride, zinc phosphide) show promise as materials for cost-competitive single-junction thin-film cells and some of them may be used also in multi-junction cells.

TABLE 2. PHOTOVOLTAICS MARKET SHARE BY TECHNOLOGY

	1981[a]		1982[a]		1983[b]		1984[c]		1985[d]	
Technology	MW	%	MW	%	MW	%	MW	%	MW	%
Single crystal	4.1	69	5.6	62	10.9	50	9.9	41	10.9	45
Concentrator	1.0	17	1.0	11	4.5	21	3.1	13	0	0
Polycrystal[e]	0.7	11	1.6	18	3.1	14	3.9	16	20.1	20
Ribbon[e]	0	0	0.1	1	0.1	0.5	0.2	1	0.2	1
Amorphous[e]	0.2	3	0.8	9	3.1	14.3	6.9	29	8.5	35
Total	6.0		9.1		21.7		24.0		39.7	

[a] Percent market share from Reference 10. Megawatt production approximated based on world-wide sales data from Reference 11.

[b] Megawatt production and market share data from Reference 11.

[c] Megawatt production data from Reference 12.

[d] Megawatt production data from Reference 13.

[e] Semicrystalline or polycrystalline devices.

So far these materials have shown relatively low efficiency, and in some cases they are unstable. The maximum efficiencies achieved for small, laboratory-scale (1 cm^2) thin films are 11 to 12% and for larger cells (100 cm^2), 7.5%. These are much higher than those previously achieved but still not as high as those of cells now made by more conventional means, e.g. laboratory-scale cells made by the Czochralski process now approach 20% efficiency, and production-scale single crystals are available with 10 to 13% efficiencies. Long-term research may yield small-cell efficiencies as high as 18% with use of selected materials -- possibly as high as 25% with some films. As shown in Table 2, thin films based on amorphous silicon are now appearing in the market-place. Ultimately, these types of materials and fabrication processes will replace those currently used.

Multi-junction cells are capable of conversion efficiencies as high as 20 to 35%.[5] The primary concept under development entails layering different semiconductor materials so that each layer converts a different portion of the solar spectrum into electricity, thus increasing the percentage of protons that can be converted. Initial research has focused on two areas: crystalline multi-junction concentrator cells and amorphous thin-film multi-junction cells. These concepts are still under investigation and have not yet been commercially used.

2.6 Production

In 1982, worldwide production of photovoltaic devices was 8.4 to 9.0 MW_p (This refers to the maximum amount of power the devices are capable of producing); of this, 4.9 to 5.5 MW_p were produced by U.S. manufacturers (Table 2). This contrasts sharply with U.S. module shipments in 1975, estimated at 300 kW_p (Figure 3). Corresponding increases have been realized

TABLE 3. U.S. PHOTOVOLTAIC MODULE SHIPMENTS BY APPLICAITON, 1983 to 1984

Application	1983	1984
Third-party-financed central station	4.5	2.1
Third-party-financed distributed uses (<5 kW)	4.5	3.0
Exports	2.0	2.9
Off-the-grid residential	0.8	1.5
Off-the-grid industrial/commercial	0.6	1.0
Government projects	0.7	1.2
Total	13.1	11.7

Source: Reference 9.

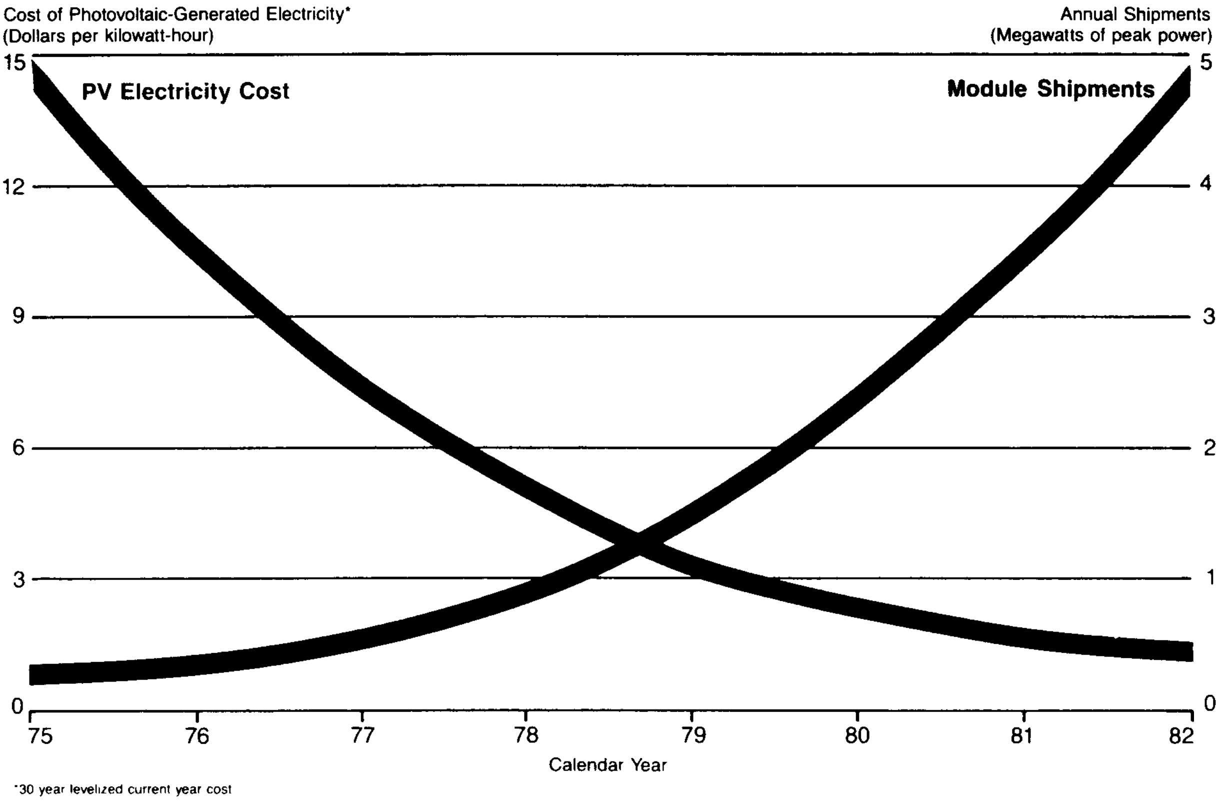

Figure 3. U.S. photovoltaic costs and shipments as estimated by the U.S. Department of Energy. Source: Reference 5.

also in the installed annual production capacity currently estimated to be 13.1 MW_p.

After a dramatic increase in production from 5.7 MWp to 13.1 MWp between 1982 and 1983, total U.S. photovoltaic module shipments has declined to 11.7 MWp and 8.6 MWp in 1984 and 1985, respectively. During the same period, however, worldwide production has steadily increased from 9.3 MWp in 1982 to 25 MWp in 1985.

The projection of future production of photovoltaic cells depends on a variety of factors, with the unit production cost being the most significant one. Other important factors that affect the demand of photovoltaic cells are government tax credits and the price of competitive energy sources. Since future values of these factors are highly uncertain, any forecast of future photovoltaic industry's output has to be highly speculative in nature. A 1984 projection made by Photovoltaic News put the worldwide sales at 500 MWp in 1990 at an assumed unit cost of \$3/Wp.[9] In the same projection, however, 1985 sales are estimated at 60 MWp or 2.5 times higher than the actual production during that year.

Assuming that the share of U.S. production in 1990 stays at 35% of the world market as in 1985, total U.S. photovoltaic cells output is estimated to be 70 MWp. The 70 MWp figure should be considered a high case as the U.S. share in the world market is expected to decrease as the current trends show. Moreover, this projection calls for an added production capacity of more than 50 MWp between now and 1990. Since a lead time of several years is generally required for planning and construction of a major photovoltaic production facility, this would mean immediate commitment of large investment in U.S. photovoltaic industries. Although several photovoltaic facilities are either under planning or construction, their combined capacity does not seem to come close to the 50 MWp level. A "guesstimate", is that by 1990 U.S. photovoltaic cells production will lie between 20 MWp and 70 MWp. Again, the key factor that determines future production level of photovoltaic cells is how fast the technology can become a fully cost-effective energy option.

2.7 Markets

The future role of photovoltaic devices ultimately will be determined by their costs in comparison with those of competing alternatives. The average price of photovoltaic modules has dropped from $20/Wp in the late 1970s to less than $6/Wp in 1984 (Figure 3). Today, photovoltaic power generation typically costs between $0.50 and $1/kWh, depending on the size of the system, the location, and the method of financing.[5] In its Five Year Research Plan for 1984 - 1988,[5] the U.S. Department of Energy established the goal of a levelized current dollar cost of $0.15/kWh, or $2/Wp. Although this goal has not yet been met, it now appears that commercial technologies which can drive costs below that level will be available soon, possibly by the late 1980s. As prices fall, new markets will open. The first real market competition in photovoltaics is likely to occur in the developing countries in the late 1980s. In these countries the common source of electricity in most villages today is diesel generators, but they are unreliable and expensive, the power costing $0.2 to $1/kWh. If photovoltaics prices fall by 50% or more, solar power will become economical in these areas. The long-range target of most photovoltaic programs, however, is to produce electricity that is economical compared with power from conventional centralized systems in developed countries. The steadily rising cost of these systems in recent years works in favor of photovoltaics. Average electricity prices in the U.S. are below $0.06/kWh, but new plants being completed will have prices ranging from $0.08 to more than $0.20/kWh; prices in Japan, which relies on oil for power generation, already average $0.12 to $0.15/kWh. The long-range target for photovoltaics is ambitious, but is thought to be achievable by the 1990s.[3]

Based on the current market trend (Table 2) and research and development (R&D) emphasis in photovoltaics,[14] the world-wide market share of single crystal silicon cells is expected to decline from 45% to around 30% by 1990. Amorphous silicon which increased its market share from 29% to 35% between 1984 and 1985, is expected to pass single crystal silicon as the dominating technology by 1990. Polycrystalline and ribbon silicon will fill in the rest of the market. New thin films and multijunction technologies will only have a very limited market by 1990, although they are likely to gradually dominate the market over the coming decade.

Power generation demonstration projects account for the largest consumption of photovoltaic cells produced in the U.S. Exports, which have been growing rapidly in the last few years, are the second largest end-use at present. The remaining photovoltaic module shipments are primarily used in cost-effective specialty markets such as off-grid (terrestrial) power and defense projects. Table 3 provides a breakdown of U.S. photovoltaic module shipments by application for 1983 and 1984. For future markets, the greatest potential of photovoltaic applications lies in power generation. The rate at which this potential can be realized, however, depends entirely on the technology's future economic competitiveness. Overseas markets, cost-effective specialty markets, and consumer product markets are expected to grow steadily as photovoltaic production technology and cell designs continue to improve.

2.8 Employment

Current employment statistics on U.S. photovoltaic industries are not available. Neither the U.S. Department of Labor nor the Census of Manufacturers published by the Commerce Department keep separate data for the number of employees directly or indirectly involved in the manufacturing of photovoltaic cells. Most individual manufacturers also consider their employment information proprietary. However, based on an estimated value of $70 million in the industries total product shipments in 1985,[9] and assuming 20% of that value is attributable to the value added from labor [the share of value added from production workers and all employees in semiconductor industries (SIC 3674) was about 9% and 28%, respectively in 1982], total employment in current U.S. photovoltaic industries can be roughly estimated to be in the range of 200 to 400 persons. Assembly line operators should account for the largest fraction of this labor force, followed by maintenance workers, engineers, and administrative staff. It should be emphasized here that this estimation is only indicative and is intended to provide an order of magnitude estimate of the employment figure in the photovoltaic industry.

Future employment profiles in the industry depend on total projected output, the mix of production technology, and the degree of automation within the industry. A higher projected output would require a larger labor force in the industry. Also, different cell designs and production technologies have different labor requirements. Table 4 summarizes the labor requirements of two hypothetical 10 MW_p production plants established in a previous BNL study.[16]

Assuming that total output of photovoltaic cells in the U.S. will reach 70 MWp in 1990, and if the average of the labor requirements of the two technologies in Table 4 is used for extrapolation, a rough employment profile of the industry can be established for 1990 (Table 5). The profile will consist of about 200 to 220 assembly line operators, 50 to 60 maintenance workers, 25 to 30 engineers and technicians, and 30 to 35 administrative personnel. The employment profile of a lower projected output can be linearly scaled down from these figures as shown in Table 5. Note that the projected employment figure for 70 MWp output in 1990 is close to the estimated employment in 1985 when total output of photovoltaic cells was under 10 MWp. The reason for this is that future large scale production facilities with high automation have much lower labor intensity as compared to existing small, disaggregated batch production units.

In addition to the industrial employment in photovoltaic cell production, there is a sizable team of scientists, engineers, and technicians engaged in the R&D of photovoltaic technologies (See Appendices A and B). Again, there are no employment data on R&D personnel in either the industries or in research institutions, including universities. However, based on the current R&D budget of $55 million under the U.S. Department of Energy - National Photovoltaics Program,[17] we estimate that about 500 persons are presently working on photovoltaics R&D projects sponsored by the government. There is no information on private-sector funds allocated for photovoltaic R&D, although we believe that its value is likely to be no less than the government funding. Since the funding of R&D projects is in part, a policy decision, there is no good basis for us to project future employment in photovoltaics R&D. It is reasonable to assume, however, that employment in this activity will gradually increase as the photovoltaic industry expands.

TABLE 4. LABOR REQUIREMENTS FOR PHOTOVOLTAIC PRODUCTION FACILITIES (10 MWp/yr) (IN NUMBER OF EMPLOYEES)

Technology	Operators	Maintenance workers	Engineers/ technicians	Administrative personnel
Single crystal Si	42	13	5	6
Ribbon Si	21	3	2	4

Source: Reference 16.

TABLE 5. PROJECTED EMPLOYMENT PROFILES BY OUTPUT IN U.S. PHOTOVOLTAIC INDUSTRY - 1990 (NUMBER OF PERSONS)

Output (MWp)	Operators	Maintenance workers	Engineers/ technicians	Administration personnel
20	57 - 62	14 - 17	7 - 9	9 - 10
30	85 - 93	21 - 26	11 - 14	13 - 15
40	114 - 124	28 - 34	14 - 17	17 - 20
50	143 - 155	35 - 43	18 - 22	22 - 25
60	171 - 186	42 - 51	21 - 26	26 - 30
70	200 - 220	50 - 60	25 - 30	30 - 35

Source: Extrapolated from Reference 16.

3. MANUFACTURING PROCESSES

The fabrication of photovoltaic cells generally involves a series of discrete production processes, with each process requiring several operations. In this section, a sequence of process steps are described which are currently used in industry and laboratories. For each of these process steps, some commonly used process options in either commercial production or in research activities are also identified (Table 6). Note that the exact specification of a process sequence depends on the technology and cell design, which does not necessarily require every process step or follow its order of flow as shown in Table 6. Also, certain process steps (e.g., scribing) may have to be applied repeatedly in some process sequences. Technologically, all of the processes listed in Table 6 can be carried out with a high degree of automation, although some are still performed manually because of capital considerations. Figure 4 shows sample manufacturing sequences in production of several different photovoltaic cell types. Brief descriptions of these process steps are presented below.

3.1 Substrate Preparation[16,20,22]

In a photovoltaic cell, the active layer is deposited on a substrate. The substrates (e.g., glass, stainless steel, silicon) are usually washed in weak detergent and rinsed with deionized water before further processing. In some cases, impurities, saw damage, or surface oxidation on the substrates must be removed by etching. This may be accomplished by using concentrated acid or alkali solutions, or "dry etching" with gaseous plasma. In a wet etching operation, the substrates are automatically loaded into an etch tank containing strong acid or alkali solutions. Commonly used etch solutions are hydrofluoric acid or hydrofluoric/nitric acid mixtures. Other

TABLE 6. PROCESS STEPS AND OPTIONS IN FABRICATING PHOTOVOLTAIC CELLS

Process step	Process option	Technical status
Substrate preparation	Detergent wash	Commercialized
	Methanol wash	"
	Acid etch	"
	Alkali etch	"
	Plasma etch	"
Metallization	Chemical vapor deposition (CVD)	Commercialized
	Evaporation	"
	Electroplating	"
	Sputtering	"
Transparent contact deposition	Chemical vapor deposition (CVD)	Commercialized
	Evaporation	"
	Chemical spraying	"
	Sputtering	"
Junction formation	Chemical vapor deposition (CVD)	Commercialized
	Glow discharge	"
	Evaporation	"
	Reactive sputtering	"
	Ion implantation	"
	Diffusion	"
	Metal organic chemical vapor deposition (MOCVD)	"
	Close-spaced vapor transport (CSVT)	R&D
	Molecular beam epitaxy (MBE)	"
Passivation	Anodic oxidation	R&D
	Heat treatment	"
	Chemisorption	"
Scribing	Mechanical	Commercialized
	Laser	"
Anti-reflective	Chemical vapor deposition	Commercialized
	Evaporation	"
Cell interconnection	Soldering	Commercialized
Encapsulation	Vacuum bonding	Commercialized
Module testing	Simulated sunlight	Commercialized

Source: See text for specific references.

Silicon Czochralski Ingot Process	Silicon Ribbon Process	Silicon Dendritic Web Process	Silicon Cast Ingot Process	Amorphous Silicon p-i-n on Glass	Gallium Arsenide $p/n/n^+$ Homojunction on Metal
Single-Crystal Growth	Ribbon Growth	Sheet Growth	Ingot Casting	Substrate Cleaning	Substrate Preparation
Ingot Processing	Aluminum (p^+) Application	Cleaning and Prediffusion Etch	Ingot Processing	Transparent Contact Deposition	Back Metallization
Junction Formation	Plasma Etching	Back Junction Formation	Surface Preparation	Division in Strips	Division in Strips
Perimeter Grinding	Ion Implantation	Front Junction Formation	Junction Formation	α-Si:H Deposition p-i-n Layers	GaAs Deposition $p/n/n^+$ Layers
Wafer Etching	Metallization	Anti-reflective Coating	Anti-reflective Coating	Division in Strips	Passivation
Metallization	Anti-reflective Coating	Print and Etch Grind Pattern	Print and Etch Grind Pattern	Back Metallization	Division in Strips
Anti-reflective Coating	Cell Interconnection	Metallization	Solder Applicn. Wafer Etching	Division in Strips	Grid Formation
Cell Testing	Encapsulation	Cu Plate Cell Separation	Cell Testing	Module Testing	Module Testing
Cell Interconnection	Module Testing	Cell Interconnection	Cell Interconnection	Protective Lamination	Anti-reflective Coating
Encapsulation		Encapsulation	Encapsulation	Power Connector Application	Power Connector Application
Module Testing		Module Testing	Module Testing	Module Testing	Module Testing

Figure 4. Process operations associated with alternative photovoltaic fabrication industries. Source: References 16, 18-21.

acids such as sulfuric or hydrogen peroxide/sodium hydroxide mixtures may also be used depending on the substrate and the volume of material to be removed.

The etching process is usually followed by rinses with deionized water and a final drying step. This is accomplished by placing the etched substrates into a deionized water bath. The substrates are then either spin-dried or blow dried with nitrogen.

In plasma etch, the substrates are placed into a vacuum chamber to react with the plasma (usually of carbon tetrafluoride in oxygen if oxidized silicon is to be removed from silicon substrate) generated by a radio-frequency source. The plasma contains ions, free radicals and electrons which react with the layer to be etched. The volatile reaction products formed are removed by vacuum pumping.

3.2 Metallization[16,22]

Substrates or wafers are metallized to form a back-surface field and back contact and a front-surface current-carrying grid. In general, the back and front metallization processes are accomplished separately, with intermediate processes (e.g., junction formation) carried out in between. Evaporation and electroplating are the most frequently used process options in this step. Metal evaporation is conducted in a vacuum chamber at a pressure of 10^{-7} to 10^{-6} torr. The source metal placed in the chamber is heated to a high temperature so that it evaporates and deposits as a fine mist onto a heated substrate. Aluminum, copper, titanium, nickel, and silver are commonly used evaporants. In electroplating, wafers are first covered with a photoresist through a mask that defines the metallization pattern. They are then exposed to a light source to polymerize the resist before they are dipped into a tank of plating solution (e.g., nickel hypophosphite). After plating, acetone is normally used to remove the resist on the wafers before they are rinsed and dried.

3.3 Transparent Contact Deposition[19,23,24]

The purpose of this process is similar to metallization. When a glass substrate is used, a transparent conducting layer is required so that the sunlight can pass through to the active layers. Commonly used process options for transparent contact deposition are chemical vapor deposition (CVD) and sputtering. In the CVD process, gaseous feedstocks are brought into a silica reactor by a carrier gas (e.g., hydrogen) where they undergo a chemical reaction on decomposition at a high temperature (500° to 600° C) resulting in the deposition of a stable compound on the substrate surface. In the CVD of indium-tin oxide, a frequently used transparent contact material, indium oxide and tin oxide gases are used as feedstocks. In sputtering, the solid feedstocks are sputtered by either a high energy ion beam, a magnetron sputtering source, or a radio-frequency source in a vacuum chamber. The atoms released from the solids are subsequently deposited on a heated substrate. In some cases, the injection of a gaseous feedstock into the chamber is required to react with the solid particles and form the desired compound (layer) on the substrate.

3.4 Junction Formation[16,19,21,24,25,26]

This is the key and often the most complex process in fabricating a photovoltaic cell. It involves the formation of a p-n junction by either introducing dopants in the structure of intrinsic solid materials (single crystal, polycrystalline), or depositing layers of dopants on top of intrinsic layers (thin films). The active layers that form the p-n junction enable the cell to produce electricity. Therefore, the efficiency of the finished cell depends critically on the quality of the active layers formed in this step. A large variety of process options can be used for junction formation; the selection of a particular process option depends on the materials used and the junction design. For example, CVD and close-spaced vapor transport (CSVT) are particularly suitable for epitaxial thin-film deposition, while ion implantation and diffusion are usually used for doping thicker layers. Metal organic chemical vapor deposition (MOCVD) is used when the required layers can be derived from metal organic compounds (e.g., trimethyl gallium for gallium arsenide deposition). In ion implantation, ions from a gaseous compound (e.g., phosphine) or a solid element (phosphorus) are implanted into the wafers in a closed vacuum chamber. The ions are first accelerated to pass through a mass spectrometer for removing unwanted species, then they are focused into a narrow beam to bombard the surface of the wafers for implantation. Following implant, the wafers must be annealed by either pulse electron or laser pulse to repair the damage to the crystal structure caused by ion implantation. Diffusion usually takes place in a high temperature furnace where a dopant is passed over a heated substrate to form the p-n junction on its surface. The dopant source may be solid (e.g., arsenic), liquid (e.g., boron trichloride) or gaseous (e.g., arsine, diborane, phosphine). Liquid and gaseous dopants along with carrier gases are usually piped into the furnace directly from the supply (often pressurized bottles for gases or bubblers for liquids). Solid dopants may be manually loaded into the furnace on a paddle. The CSVT process involves the evaporation of a high purity source material (e.g., cadmium telluride) in a vacuum reactor, where the substrate is kept at an extremely close distance (usually less than one mm) from the source material. The deposition normally takes place in a hydrogen environment which serves as a transporting agent. Molecular beam epitaxy (MBE) employs an ultra-high vacuum chamber (base pressure in the low 10^{-10} torr range) in which the source material is bombarded by a high energy ion gun at high temperatures. The solid particles released from the sources form a thin layer on the appropriately positioned substrate. Like the CSVT process, MBE is still under research and is used only to make experimental photovoltaic cells.

3.5 Passivation[19]

This process is intended to grow an insulating barrier over the grain boundaries of the active layers in order to cut down the carrier recombination rate and thus improve the open circuit voltage and the fill factor of the cell. Although the techniques employed in passivation are well developed, the selection of an effective passivation process of specific active layers is often difficult and requires further research effort. Frequently applied passivation techniques in laboratories include anodic oxidation, heat treatment, and chemisorption. In anodic oxidation, the wafers are dipped in an electrolytic bath filled with an electrolyte usually composed of a weak acid and glycol mixture. An effective oxide film is grown on the active layer with appropriate voltage, current density, and temperature. In heat treatment, the wafers are simply put into an oven and heated to a high temperature (usually between 350° C to 500° C, depending on the material). In laboratories, ruthenium treatment is often used in promoting chemisorption. The wafers are dipped in a solution containing ruthenium ions which are chemisorbed into the grain boundaries of the active layer to form an insulating barrier.

3.6 Scribing[20,27]

Scribing, sometimes required more than once during the manufacturing process, is mainly used to divide the large area thin-film deposited on substrates into narrow strips, forming the individual solar cells. The scribing can be performed mechanically or by lasers. The most commonly used lasers in photovoltaic industries are high-power units classified as Class IV lasers by the American National Standards Institute and by the Bureau of Radiological Health of the U.S. Food and Drug Administration.

3.7 Anti-reflective Coating[19,25]

This process deposits an anti-reflective coating on wafers to decrease the loss of sunlight due to reflection. An anti-reflective coating is typically applied through chemical vapor deposition or evaporation. Silicon monoxide and antimony trioxide are typical materials deposited on the cell for antireflective purposes.

3.8 Cell Interconnection[20,22]

The finished cells are assembled in this process to form operative modules. The cells are bonded together by interconnect buses and tabs soldered on the front and back of each cell. This is achieved in several operations including cell alignment, interconnect placement, string assembly, solder reflow, and final module interconnect. Thin-film cells are produced in sheets and therefore do not need mechanical interconnection.

3.9 Encapsulation[20,22]

In a typical encapsulation process, the modules are placed on top of ethylene vinyl acetate (EVA) sheets backed by glass substrates. Another sheet of EVA is placed on top of the assembly, followed by a sheet of tedlar. The sandwiched assembly is then baked in a vacuum laminator for sealing.

3.10 Module Testing[20,22,25]

Before shipping, the modules are tested to demonstrate function and to rate their performance by exposure to simulated sunlight.

4. CHEMICAL USE

Many different cell materials and production processes are being used to fabricate photovoltaic cells in commercial production facilities and in research laboratories. These activities require a great variety of chemicals used mainly as feedstocks, dopants, solvents, or transport agents in the manufacturing process. Because of the limited efficiencies of these processes, significant quantities of various chemical products are also being produced as residuals. Table 7 provides a long listing of chemicals used or generated in the manufacture of photovoltaic cells. The list is compiled, in part, from material requirements in current production facilities and research laboratories. Most of the residuals were identified from previous studies conducted at Brookhaven National Laboratory.[18-21,23,25,32] Although fairly comprehensive, Table 7 is intended to be representative rather than exhaustive - for example, some of the materials currently used, which are proprietary and consequently not reported in the open literature, are not included in this accounting.

To quantify the use of chemicals and the residual products listed in Table 7 requires a broad information base covering at least projections in future photovoltaic cell demand, the market share of individual cell types, process options, and engineering specifications. This is beyond the scope of this effort. In Table 8, however, some feedstock requirements for a

TABLE 7. MATERIALS USED OR GENERATED IN THE MANUFACTURE OF PHOTOVOLTAIC CELLS[a]

Material	CAS registry number	Process application and/or operation
Abietic acid	00514-10-3	Solder flux component
Acetic acid	00064-19-7	Metal and semiconductor etch component
Acetone	00067-64-1	Wafer cleaner, solvent
Acetylene	00074-86-2	Welding gas
Aluminum	07429-90-5	Metallization
Aluminum acetate	08006-13-1	Etch component
Aluminum oxide	01344-28-1	Packaging material; abrasive - wafer polish
Ammonia	07664-41-7	Carrier gas - expitaxial deposition; plasma etch component
Ammonium bifluoride	01341-49-7	Etch component
Ammonium chloride	12125-02-9	Etch component
Ammonium fluoride	12125-01-8	Oxide etch component
Ammonium hydroxide	01336-21-6	Wafer cleaner, etch component
Ammonium persulfate	07727-54-0	Wafer cleaner, etch component
Amorphous silicon		Semiconductor material
Aniline	00062-53-3	Solvent
Antimony	07440-36-0	Dopant (P-type) - diffusion, ion implantation crystal growth
Antimony trioxide	01309-64-4	Dopant (P-type) - diffusion, crystal growth; anti-reflective coating
Argon	07440-37-1	Carrier gas - ion implantation
Arsenic	07440-38-2	Dopant (N-type) - diffusion, ion implantation, crystal growth
Arsenic trichloride	07784-34-1	Dopant (N-type) source - expitaxial deposition
Arsenic trioxide	01327-53-3	Dopant (N-type) source - diffusion

(continued)

TABLE 7. (continued)

Arsine	07784-42-1	Dopant (N-type) source - diffusion, epitaxial deposition, ion implantation
Asbestos	01332-21-4	Insulator, packaging material
Beryllium	07440-41-7	Metallization
Beryllion oxide	01340-56-9	Insulator, packaging material
Boric acid	11113-50-1	Dopant (P-type) source - diffusion, epitaxial deposition, ion implantation, crystal growth
Boron	07440-42-8	Dopant (P-type) - diffusion, epitaxial deposition, ion implantation, crystal growth
Boron carbide	12069-32-8	Abrasive - wafer dicing, lapping, and polishing
Boron hydride	19287-45-7	Dopant (p-type) source - epitaxial deposition
Boron nitride	10043-11-5	Dopant (P-type) source - diffusion, epitaxial deposition, ion implantation
Boron tribromide	10294-33-4	Dopant (P-type) source - diffusion, epitaxial deposition, ion implantation
Boron trichloride	10294-34-5	Dopant (P-type) source - diffusion, epitaxial deposition, ion implantation
Boron trifluoride	07637-07-2	Dopant (P-type) source - diffusion, epitaxial deposition, ion implantation
n-Butyl acetate	00123-86-4	Photoresist developer
Cadmium	07440-43-9	Dopant (P-type) - epitaxial deposition, ion implantation; solder component
Cadmium chloride	10108-64-2	Feedstock - epitaxial deposition
Cadmium sulfide	01306-23-6	Feedstock - epitaxial deposition
Cadmium telluride	01306-25-8	Semiconductor material
Calcium hydroxide	01305-62-0	Wastewater treatment
Calcium hypochloride	07778-54-3	Etch component, oxidizer

(continued)

TABLE 7. (continued)

Carbon dioxide	00124-38-9	Testing gas, coolant
Carbon monoxide	00630-08-0	Reducing gas - metallization, epitaxial deposition
Carbon tetrafluoride	0075-73-0	Nitride etch component
Ceric ammonium nitrate	16774-21-3	Etch component, oxidizer
Chlorobenzene	00108-90-7	Solvent, degreaser
Chloroform	00067-66-3	Solvent, degreaser
Chloroformate compounds	(b)	Solvent, degreaser
Chloromethane	00074-87-3	Solvent, degreaser
Chlorosilane	13465-78-6	Epitaxial deposition, passivation, ion implantation, crystal growth
Chromic acid	54991-58-1	Etch component, cleaning solution, photoresist stripper solution component
Chromic oxide	01308-38-9	Abrasive - wafer polishing
Chromium	07440-47-3	Metallization, plating operation
Chromium trioxide	01333-82-0	Crystal growth
Citric acid	00077-92-9	Etch component
Cobalt	07440-48-4	Conductor metal, packaging material
Cobalt sulfate	10124-43-3	Feedstock - electrode
Cobalt sulfide	01317-42-6	Feedstock - electrode
Copper	07440-50-8	Conductor metal, metallization, packaging material
Copper chloride	01344-67-8	Feedstock
Copper indium diselenide	12018-95-0	Semiconductor material
Copper nitrate	03251-23-8	Etch component, oxidizer
Copper sulfide	01317-40-4	Feedstock

(continued)

TABLE 7. (continued)

Diamond	07782-40-3	Abrasive - wafer dicing, lapping, and polishing
Diborane	19287-45-7	Dopant (P-type) source - diffusion, epitaxial deposition, ion implantation
Dichlorosilane	04109-96-0	Epitaxial deposition, passivation, ion implantation, crystal growth
Diethyl telluride	00627-54-3	Dopant (N-type) source - epitaxial deposition
Dimethyl formamide	00068-12-2	Solvent
Dimethyl zinc	00544-97-8	Dopant - epitaxial deposition
Epichlorohydrin	00106-89-8	Epoxy resin component
Ethanol	00064-17-5	Wafer cleaner
Ethanol amine	00141-43-5	Photoresist stripper component
2-Ethoxy ethanol	00110-80-5	Wafer cleaner, degreaser, solvent, photoresist component
Ethyl acetate	00141-78-6	Solvent, degreaser
Ethylene glycol	00107-21-1	Photoresist remover
Ferric chloride	07705-08-0	Etch component, oxidizer
Fluoride	07782-41-4	Solder flux component
Fluoroboric acid	16872-11-0	Dopant (P-type) source - epitaxial deposition, crystal growth
Formaldehyde	00050-00-0	Solder by-product gas
Gallium	07440-55-3	Dopant (P-type) - epitaxial deposition, ion implantation, crystal growth; solder component
Gallium arsenic phosphide		Semiconductor material
Gallium arsenide	01303-00-0	Semiconductor material
Gallium chloride	13450-90-3	Dopant (P-type) source - epitaxial deposition

(continued)

TABLE 7. (continued)

Gallium oxide	120-24-21-4	Dopant (P-type) source - diffusion, crystal growth
Gallium phosphide	12063-98-8	Semiconductor material
Garnet	68553-01-5	Abrasive - wafer dicing, lapping and polishing
Germane	07782-65-2	Epitaxial deposition, crystal growth
Germanium	07440-56-4	Semiconductor material, metallization, solder component
Glycerine	00056-81-5	Etch component
Gold	07440-57-5	Conductor metal, lead attachment, metallization, solder component
Graphite	07782-42-5	High-temperature material - epitaxial deposition, metallization, crystal growth
Helium	07440-59-7	Process and carrier gas, leak detector
Hexamethyldisilizane (HMDS)	00999-97-3	Patterning, wafer surfactant
Hexane	00110-54-3	Solvent
Hydrobromic acid	10035-10-6	Etch component
Hydrochloric acid	07647-01-0	Etch component
Hydrofluoric acid	07664-39-3	Oxide and semiconductor etch component
Hydrogen	01333-74-0	Carrier gas - epitaxial deposition, annealing, ion implantation
Hydrogen bromide	10035-10-6	
Hydrogen chloride	07647-01-0	Gas phase etch, epitaxial deposition
Hydrogen peroxide	07722-84-1	Etch component, wafer cleaner, oxidizer
Hydrogen selenide	07783-07-5	Feedstock - reactive sputtering deposition of $CuInSe_2$
Hydrogen sulfide	07783-06-4	Feedstock - reactive sputtering deposition of CdS
Indium	07440-74-6	Dopant (P-type) - metallization; solder component; feedstock epitaxial deposition

(continued)

TABLE 7. (continued)

Indium chloride	13465-10-6	Feedstock - transport contact layer
Indium antimonide	01312-41-0	Semiconductor material
Iodine	07553-56-2	Etch component, oxidizer
Isodecane	27136-79-4	Photoresist component
Isopropanol	00067-63-0	Etch component
Krypton 85	07439-90-0	Leak testing
Lead	07439-92-1	Solder component
Liquid nitrogen	07727-37-9	Coolant
Magnesium	07439-95-4	Packaging material
Manganese	07439-86-5	Packaging material
Mercury	07439-97-6	Epitaxial deposition
Methane	00074-82-8	By-product gas; fuel
Methanol	00067-56-1	Wafer cleaner, solvent
2-Methoxyethyl acetate	000110-49-6	Solvent, degreaser
Methylene chloride	00075-09-2	Solvent
Methyl ethyl ketone	00078-93-3	Solvent
Methyl isobutyl ketone	00108-10-1	Solvent
Molybdenum	07439-98-7	Packaging material, metallization
Nickel	07440-02-0	Packaging material, metallization
Nickel chloride	07718-54-9	Feedstock
Nitric acid	07697-37-2	Metal and semiconductor etch component, photoresist stripper component
Nitric oxide	10102-43-9	By-product gas from etch tanks
Nitrogen	07727-37-9	Carrier gas - diffusion, epitaxial deposition; bonding gas

(continued)

TABLE 7. (continued)

Nitrogen dioxide	10102-44-0	By-product gas from etch tanks
Nitrous oxide	10024-97-2	By-product gas from etch tanks, epitaxial deposition passivation
Oxygen	07782-44-7	Oxidization, passivation, bonding gas
Ozone	10028-15-6	Oxidation, by-product gas from ultra-violet photoresist exposure step
Palladium	07440-05-3	Metallization
Perchloric acid	07601-90-3	Etch component
Phenol	00108-95-2	J-100 component
Phosphine	07803-51-2	Dopant (P-type) source - diffusion, epitaxial deposition, ion implantation, passivation
Phosphoric acid	07664-38-2	Aluminum and semiconductor etch
Phosphorus	07723-14-0	Dopant (N-type) source - diffusion, epitaxial deposition, ion implantation
Phosphorus oxychloride	10025-87-3	Dopant (N-type) source - diffusion, epitaxial deposition, ion implantation
Phosphorus pentoxide	01314-56-3	Dopant (N-type) source - diffusion, epitaxial deposition, ion implantation
Phosphoric tribromide	07789-60=8	Dopant (N-type) source - diffusion, epitaxial deposition, ion implantation
Platinum	07440-06-4	Metallization
Polyethylene	09002-88-4	Lamination
Polyisoprene	09003-31-0	Encapsulation material
Potassium dichromate	07778-50-9	Etch, oxidizer
Potassium hydroxide	01310-58-3	Etch component
Potassium iodide	12298-68-9	Photolithography
Propane	00074-98-6	Fuel gas
Propanol	00071-23-8	Wafer cleaner, etch additive

(continued)

TABLE 7. (continued)

Rhodium	07440-16-6	Conduction metal, plating, packaging material
Selenium	07782-49-2	Dopant (N-type) - epitaxial deposition
Selenium dioxide	07446-08-4	Feedstock - epitaxial deposition
Silane	07803-62-5	Feedstock - a-Si deposition, glow discharge, CVD
Silica (crystalline)	60676-86-0	Glass, ceramic packages
Silicon	07440-21-3	Semiconductor material
Silicon carbide	00409-21-2	Abrasive - wafer dicing, lapping, and polishing
Silicon dioxide	06731-86-9	Passivation coat and packaging material
Silicon hydride	13774-94-2	Feedstock (see silane)
Silicon monoxide	10097-28-6	AR coat
Silicon nitride	12003-60-2	Passivation coat and packaging material
Silicon tetrachloride	10026-04-7	Feedstock - a-Si deposition, glow discharge, CVD
Silicon tetrafluoride	07783-61-1	Feedstock - a-Si deposition, glow discharge, CVD
Silver	07440-22-4	Conductor metal, metallization, solder component
Sodium hydroxide	01310-73-2	Etch component, wastewater treatment
Sodium hypophosphite	13721-43-2	
Stoddard solvent	08052-41-3	Wafer cleaner, degreaser
Sulfur	07704-34-9	
Sulfur hexafluoride	02551-62-4	Gas phase etch component
Sulfuric acid	07664-93-9	Etch component, wafer cleaner, photoresist stripper component
Tantalum	07440-25-7	Feedstock - AR coating
Tantalum pentoxide	01314-61-0	AR coat

(continued)

TABLE 7. (continued)

Tellurium	13494-80-9	Metallization
Terpineol	08000-41-7	
Tetrachloroethylene	00127-18-4	Solvent
Tetrachlorosilane	10026-04-7	Epitaxial deposition, passivation, ion implantation, crystal growth
Tetramethyl ammonium hydroxide	0075-59-2	Etch component
Thiourea	00062-56-6	Spray pyrolysis
Tin	07440-31-5	Solder component
Tin chloride	01344-13-4	Feedstock - transport contact layer
Tin oxide	01322-29-2	Feedstock - transport contact layer
Titanium	07440-32-6	Metallization
Titanium dioxide	13463-67-7	Metal contact
Toluene	00108-88-3	Photoresist component, wafer cleaner, solvent, varnish component
Toluene diisocyanate (TDI)	00584-84-9	Flux component
Tributyl phosphate	00126-73-8	Encapsulation material
1,2,4-Trichlorobenzene	00120-82-1	Solvent
1,1,1-Trichlorethane	00071-55-6	Solvent, degreaser
Trichlorethylene	00079-01-6	Wafer cleaner, degreaser, dewaxing, J-100 component
Trichlorosilane	10025-78-2	Epitaxial deposition, passivation, ion implantation, crystal growth
Trifluoroethylene	00359-11-5	Degreaser, wafer cleaner
Trimethyl aluminum	00075-24-1	Feedstock - epitaxial deposition
Trimethyl gallium	01445-79-0	Dopant (P-type) source - epitaxial deposition
Trimethyl indium	03385-78-2	Feedstock - epitaxial deposition

(continued)

TABLE 7. (continued)

Trimethyl zinc		Feedstock - epitaxial deposition
Tungsten	07440-33-7	Metallization
Urethane	00051-79-6	
Vanadium	07440-62-2	Metallization
Vinyl acetate	00108-05-4	Encapsulation material
Xylene	01330-20-7	Photoresist component, wafer cleaner, solvent
Zinc	07440-66-6	Dopant (P-type) - diffusion, epitaxial deposition; solder component; metallization
Zinc chloride	07646-85-7	Feedstock - epitaxial deposition
Zinc fluoroborate	13826-88-5	Electroplating agent
Zinc phosphide	12037-79-5	Semiconductor material
Zirconium	07440-67-7	Metallization
Zirconium oxide	01314-23-14	Abrasive - wafer polishing

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[a] Information derived from References 16, 28, 29, 30, 31.
[b] Generic compound; no CAS registry number.

TABLE 8. PROCESS SEQUENCE AND PRINCIPAL POLLUTANTS IN a-Si P-I-N PHOTOVOLTAIC CELL PRODUCTION

Activity	Process step	Principal pollutant	Quantity*	Environmental controls
Substrate cleaning	Detergent wash and deionized water rinse	Weak alkaline solution	700 m^3	Liquid waste treatment plant
Transparent contact deposition	Sputtering	ITO (solid)	208 kg	Secure landfill (possible recycle)
Division in strips	Laser scribing	ITO dust	Neg	Secure landfill
Active layer deposition	rf glow discharge	SiH_4 gas B_2H_6 gas PH_3 gas	1243 kg 0.3 kg 0.5 kg	KOH-KMn04 scrubbers Liquid waste treatment plant
Division in strips	Laser scribing	Si dust In_2O_3 dust	Neg Neg	Secure landfill
Back metallization	Evaporation	Al (solid)	112 kg	Recovery
Division in strips	Laser scribing	Si and Al fumes SnO_2 and In_2O_3 dusts	Neg Neg	Secure landfill
Module testing	Electrical	Defective cells	Neg	Secure landfill
Power interconnection	Seam bonding to Al interconnectors	Al strips	200 kg	Recovery
Protective lamination	Vacuum encapsulation	EVA fumes EVA and Tedlar materials	Neg 345 kg	Municipal landfill

*Per output of cells generating 10 MWp. Neg = negligible.
**Includes sludge disposal to secure landfills.
Source: Reference 33.

hypothetical 10 MW_p a-Si cell manufacturing facility are presented for illustrative purposes. Quantitative estimates for some other materials are discussed later in this text.

Table 9 identifies toxic or hazardous materials which may be used at hypothetical production facilities. The compounds included in this list have recently been identified by the EPA as "Acutely Toxic Chemicals." These materials are capable of producing serious health effects that are manifested either immediately or shortly after an acute exposure such as an accidental air release. Other materials not contained on this list which can also present acute or chronic risks to health and safety may also require close scrutiny (see Table 10); some of these are highlighted below.

5. OCCUPATIONAL HEALTH HAZARDS

A large diversity of chemical and physical agents which can present health hazards to workers may be associated with photovoltaic cell manufacturing processes. In order to provide focus to the identification of these potential hazards, the discussions presented below are broken down into four categories (i.e., explosives and flammables, corrosives and oxidizers, poisons, and miscellaneous). Although this classification scheme, like all others is somewhat arbitrary and at times overlapping (e.g., a material may be both corrosive and poisonous), it provides a useful approach for condensing a large volume of information. The discussions do not attempt to cover all materials and all hazards. Rather, they attempt to focus on those materials and hazards which are thought to present potential threats to health and the environment because of the volumes involved or because of the inherent toxicologic or physical properties of the individual compounds. Although hazard is a function of both exposure and toxicity, only toxicologic issues are discussed because monitoring data from the

TABLE 9. MATERIALS USED IN PHOTOVOLTAIC CELL MANUFACTURE AND LISTED BY EPA AS ACUTELY TOXIC

Material	CAS Registry Number
Arsenic trichloride	07784-34-1
Arsenic trioxide	01327-53-3
Arsine	07784-42-1
Boron hydride	19287-45-7
Boron trichloride	10294-34-5
Boron trifluoride	07637-07-2
Cobalt	07440-48-4
Diborane	19287-45-7
Fluoride	07782-41-4
Gallium chloride	13450-90-3
Hydrofluoric acid	07664-39-3
Hydrogen selenide	07783-07-5
Nickel	07440-02-0
Nitric acid	07697-37-2
Nitric oxide	10102-43-9
Nitrogen dioxide	10102-44-0
Ozone	10028-15-6
Phenol	00108-95-2
Phosphine	07803-51-2
Phosphoric tribromide	07789-60-8
Phosphorous	07723-14-0
Phosphorous oxychloride	10025-87-3
Phosphorous pentoxide	01314-56-3
Sulfuric acid	07664-93-9
Tellurium	13494-80-9
Toluene diisocyanate	00584-84-9

Source: Reference 34 cross referenced to Table 7 in this report.

TABLE 10. TOXICOLOGIC PROPERTIES OF MATERIALS USED OR GENERATED IN THE MANUFACTURE OF PHOTOVOLTAIC CELLS

Material	Expl.	Flam.	Oxid.	Cor.	Poison	TLV*	IDLH*	Remark**
Abietic acid	Low	Low	-	-	Mod.	NA	NA	b
Acetic acid	Mod.	Mod.	-	-	Mod.	10	1,000	a,b,c
Acetone	Mod.	High	-	-	Mod.	750	20,000	a,b,d
Acetylene	Mod.	High	-	-	Low	NA	10	a
Aluminum	Mod.	Mod.	-	-	-	10^*	NA	
Aluminum acetate	-	-	-	-	-	NA	NA	
Aluminum oxide	-	-	-	-	-	10^*	NA	
Ammonia	Mod.	Low	-	-	High	25	500	a
Ammonium bifluoride	-	-	-	-	High	NA	NA	a,b,c,d
Ammonium chloride	-	-	-	-	High	10^*	NA	e
Ammonium fluoride	-	-	-	-	High	NA	NA	b,d
Ammonium hydroxide	-	Low	-	-	High	NA	NA	a,b
Ammonium persulfate	Mod.	Mod.	High	-	Mod.	NA	NA	b
Amorphous silicon	-	Mod.	-	-	NA	NA	NA	
Aniline	-	Mod.	-	-	High	2	100	a,b,f
Antimony	Mod.	Mod.	-	-	High	0.5^*	80*	b,d,j
Antimony trioxide	-	-	-	-	High	NA	80*	a,b,d,i
Argon	-	-	-	-	-	NA	NA	
Arsenic	Low	Mod.	-	-	High	0.2	NA	e,g,i
Arsenic trichloride	-	-	-	-	High	NA	NA	a,b
Arsenic trioxide	-	-	-	-	High	NA	NA	b,g,i
Arsine	Mod.	Mod.	-	-	High	0.05	6	a
Asbestos	-	-	-	-	Mod.	0.06	NA	a,h
Beryllium	Low	Mod.	-	-	High	0.002	NA	a,i
Beryllium oxide	-	-	-	-	High	0.002	NA	a,i
Boric acid	-	-	-	-	High	NA	NA	b
Boron	High	Mod.	-	-	Mod.	NA	NA	b
Boron carbide	-	-	-	-	High	NA	NA	b
Boron hydride	High	High	-	-	High	NA	NA	b,c
Boron nitride	-	-	-	-	High	NA	NA	b
Boron tribromide	High	Mod.	-	-	High	1	NA	b
Boron trichloride	-	-	-	Mod.	High	NA	NA	b

(continued)

TABLE 10. (continued)

Boron trifluoride	-	-	-	Mod.	High	1	100	a
n-Butyl acetate	Mod.	High	-	-	Mod.	200	NA	a
Cadmium	Mod.	Mod.	-	-	High	0.05*	40*	b,i
Cadmium chloride	Mod.	Mod.	-	-	High	0.05*	NA	a,b,c,i
Cadmium sulfide	Mod.	Mod.	-	-	High	0.05*	NA	b,i
Cadmium telluride	Mod.	Mod.	-	-	High	0.05*	NA	b,i
Calcium hydroxide	-	-	-	-	Low	5*	NA	b
Calcium hypochloride	Mod.	Mod.	High	-	High	NA	NA	a,b
Carbon dioxide	-	-	-	-		5,000	50,000	
Carbon monoxide	High	High	-	-	High	50	1,500	a
Carbon tetrafluoride	-	-	-	-	Low	NA	NA	a
Ceric ammonium nitrate	Mod.	Mod.	-	-	Low	NA	NA	b
Chlorobenzene	Mod.	High	-	-	Mod.	75	2,400	a,b,g
Chloroform	-	Low	-	-	Mod.	NA	1,000	a,b,i
Chloroformate	NA	NA	NA	NA	NA	NA	NA	
Chloromethane	Low	High	-	-	Low	NA	NA	a
Chlorosilane	Low	High	-	-	High	NA	NA	a,b,c
Chromic acid	High	High	High	-	High	0.05*	30*	a,i
Chromic oxide	NA	NA	-	-	High	0.05*	500*	a,i
Chromium	-	Mod.	-	-	High	0.5*	500*	a,i
Chromium trioxide	High	High	High	-	High	0.05*	500*	a,i
Citric acid	-	Low	-	-	Mod.	NA	NA	a,b,i
Cobalt	-	Mod.	-	-	Low	NA	20*	b,i,j
Cobalt sulfate	-	Mod.	-	-	Low	NA	NA	b,i
Cobalt sulfide	-	Mod.	-	-	Low	NA	NA	b,i
Copper	-	-	-	-	High	1*	NA	d
Copper chloride	-	-	-	-	High	NA	NA	a,b
Copper indium diselenide	NA	NA	NA	NA	NA	NA	NA	
Copper nitrate	-	-	-	-	Mod.	NA	NA	b
Copper sulfide	-	-	--	-	Mod.	NA	NA	b
Diamond	NA	NA	NA	NA	NA	NA	NA	
Diborane	Mod.	High	-	-	High	0.1	40	a
Dichlorosilane	Na	NA	NA	NA	NA	NA	NA	
Diethyl telluride	-	High	-	-	Low	NA	NA	b
Dimethyl formamide	Mod.	Mod.	-	-	High	NA	3,500	a,d
Dimethyl zinc	Mod.	High	-	-	Low	NA	NA	b

(continued)

TABLE 10. (continued)

Epichlorohydrin	Low	High	-	-	High	2	100	b
Ethanol	Low	High	-	-	Mod.	1,000	NA	b,c,f
Ethanol amine	-	Mod.	-	-	Mod.	NA	1,000	b,c,d,g
2-Ethoxy ethanol	Mod.	Low	-	-	Mod.	NA	6,000	b,c
Ethyl acetate	Mod.	High	-	-	Mod.	400	10,000	a,d
Ethylene glycol	Mod.	Low	-	-	Mod.	50	NA	b,c,d,f
Ferric chloride	-	-	-	-	High	1*	NA	b,d
Fluorides	-	-	-	-	High	2.5*	500*	b
Fluoroboric acid	NA	NA	NA	NA	NA	NA	NA	
Formaldehyde	Low	High	-	-	High	2	100	c,i
Gallium	-	-	-	-	High	NA	NA	g,j
Gallium arsenic phosphide	NA	NA	NA	NA	NA	NA	NA	
Gallium arsenide	-	-	-	-	Mod.	NA	NA	b
Gallium chloride	-	-	-	-	High	NA	NA	a
Gallium oxide	-	-	-	-	Low	NA	NA	b
Gallium phosphide	-	-	-	-	High	NA	NA	a
Garnet	NA	NA	NA	NA	NA	NA	NA	
Germane	NA	NA	NA	NA	NA	NA	NA	
Germanium	-	Mod.	-	-	Mod.	NA	NA	g,j
Glycerine	-	Low	-	-	Mod.	NA	NA	b,f,g
Gold	-	-	-	-	-	NA	NA	
Graphite	-	-	-	-	Low	NA	NA	a
Helium	-	-	-	-	-	NA	NA	
Hexamethyldisilizane (HMDS)	NA	NA	NA	NA	NA	NA	NA	
Hexane	Mod.	High	-	-	Low	50	5,000	b
Hydrobromic acid	-	-	-	-	High	NA	NA	a,b
Hydrochloric acid	-	-	-	-	Mod.	NA	100	a,b,c
Hydrofluoric acid	-	-	-	High	High	NA	NA	a,b,c
Hydrogen	High	High	-	-		NA	NA	
Hydrogen bromide	-	-	-	-	High	3	50	a,b
Hydrogen chloride	-	-	-	-	Mod.	5	100	a,b,c
Hydrogen peroxide	High	High	High	-	High	1	75	a,b,c
Hydrogen selenide	High	High	-	-	High	0.05	2	a,c
Hydrogen sulfide	Mod.	High	-	-	High	10	300	a
Indium	-	Mod.	-	-	High	0.1*	NA	g
Indium chloride	-	-	-	-	Mod.	NA	NA	b

(continued)

TABLE 10. (continued)

Indium antimonide	-	-	-	-	Mod.	NA	NA	d
Iodine	-	-	-	-	High	0.1	10	c
Isodecane	Mod.	Mod.	-	-	Low	NA	NA	a
Isopropanol	Mod.	Hifh	-	-	Mod.	400	NA	b,d
Krypton 85	-	-	-	-	-	NA	NA	
Lead	Mod.	Mod.	-	-	High	0.15*	0.05*	a,b,c,h
Liquid nitrogen	-	-	-	-	-	NA	NA	
Magnesium	Mod.	High	-	-	Mod.	NA	NA	b
Manganese	Mod.	Mod.	-	-	High	5*	10,000	a,d
Mercury	-	-	-	-	High	0.01*	28*	b,c
Methane	High	High	-	-		NA	NA	
Methanol	Mod.	High	-	-	Mod.	200	NA	a
2-Methoxyethyl acetate	NA	NA	NA	NA	NA	NA	NA	
Methylene chloride	-	-	-	-	Mod.	100	NA	a,b,d,g
Methyl ethyl ketone	Mod.	High	-	-	Mod.	200	NA	b
Methyl isobutyl ketone	Mod.	High	-	-	Mod.	50	NA	a,b
Molybdenum	Low	Mod.	-	-	High	10*	NA	d,g
Nickel	-	-	-	-	Low	1*	NA	b,i
Nickel chloride	-	-	-	-	High	0.1*	NA	e,f
Nitric acid	Mod.	Mod.	High	-	High	2	100	c
Nitric oxide	-	-	-	-	High	25	100	a,c
Nitrogen	-	-	-	-		NA	NA	
Nitrogen dioxide	Mod.	Mod.	-	-	High	3	50	a
Nitrous oxide	Mod.	Mod.	-	-	Mod.	NA	NA	a
Oxygen	Low	Low	-	-	-	NA	NA	
Ozone	High	High	-	-	High	0.1	10	a,c
Palladium	-	Low	-	-	Low	NA	NA	b
Perchloric acid	Mod.	Mod.	-	-	High	NA	NA	a,b
Phenol	-	Mod.	-	-	High	5	100	b,c,d,g
Phosphine	Mod.	Hifh	-	-	High	0.3	200	a
Phosphoric acid	-	-	-	-	Mod.	1*	NA	b,c
Phosphorus	Mod.	High	-	-	-	0.1*	NA	
Phosphorus oxychloride	-	-	-	-	Hig	0.1	NA	a,b,c
Phosphorus pentoxide	-	High	-	-	Low	NA	NA	b,c
Phosphoric tribromide	-	-	-	High	High	NA	NA	b
Platinum	-	-	-	-	Low	1*	NA	b,c

(continued)

TABLE 10. (continued)

Polyethylene	-	-	-	-	Low	NA	NA	
Polyisoprene	NA	NA	NA	NA	NA	NA	NA	
Potassium dichromate	-	Mod.	-	-	High	NA	NA	a,b,g
Potassium hydroxide	-	Mod.	-	-	High	2*	NA	b,c
Potassium iodide	-	-	-	-	High	NA	NA	f
Propane	High	High	-	-	-	NA	20,000	
Propanol	Mod.	High	-	0	Mod.	200	NA	a,b,c
Rhodium	-	Mod.	-	-	NA	1*	NA	j
Selenium	-	-	-	-	Low	0.2*	100*	b,i
Selenium dioxide	-	-	-	-	High	0.2*	100*	g
Silane	Mod.	High	-	-	Mod.	5	100*	a,c
Silica (crystalline)	-	-	-	-	Mod.	3*	NA	a
Silicon	-	Mod.	-	-	-	10*	NA	
Silicon carbide	-	-	-	-	Low	5*	NA	a
Silicon dioxide	-	-	-	-	Mod.	3*	NA	a
Silicon hydride	Mod.	High	-	-	Mod.	NA	NA	a,c
Silicon monoxide	-	Mod.	-	-	-	NA	NA	
Silicon nitride	-	Mod.	-	-	-	NA	NA	
Silicon tetrachloride	-	-	-	-	Mod.	NA	NA	a
Silicon tetrafluoride	-	-	-	-	High	NA	NA	
Silver	-	Mod.	-	-	-	0.1*	NA	
Sodium hydroxide	-	-	-	High	High	2*	200*	b,d
Sodium hypophosphite	Low	Mod.	-	-	Mod.	NA	NA	d
Stoddard solvent	Mod.	Mod.	-	-	Mod.	NA	NA	a,b
Sulfur	Mod.	Low	-	-	Low	NA	NA	a
Sulfur hexafluoride	-	-	-	High	-	1,000	NA	
Sulfuric acid	-	High	-	High	Mod.	1*	80*	b
Tantalum	-	Mod.	-	-	NA	5*	NA	
Tantalum pentoxide	-	-	-	-	NA	NA	NA	
Tellurium	-	Mod.	-	-	High	0.1*	NA	g
Terpineol	NA	NA	NA	NA	NA	NA	NA	
Tetrachloroethylene	-	-	-	-	Mod.	50	500	a,b,c,d,g
Tetrachlorosilane	-	-	-	-	Mod.	NA	NA	a
Tetramethyl ammonium hydroxide	-	-	-	-	High	NA	NA	a,b,c
Thiourea NA	-	-	-	-	High	NA	NA	d,i
Tin	-	Low	-	-	-	2*	400*	

(continued)

TABLE 10. (continued)

Tin chloride	-	Low	-	Mod.	High	2*	400*	d
Tin oxide	-	-	-	-	-	2*	400*	
Titanium	Mod.	Mod.	-	-	-	NA	NA	
Titanium dioxide	-	-	-	-	-	10*	NA	
Toluene	Mod.	Low	-	-	Mod.	100	2,000	a,b,d
Toluene diisocyanate (TDI)	-	Low	-	-	High	NA	10	a
Tributyl phosphate	-	Low	-	-	High	NA	1,300*	d
1,2,4-Trichlorobenzene	-	Low	-	-	Mod.	5	NA	b,d
1,1,1-Trichlorethane	-	-	-	-	Mod.	10	NA	b,d
Trichlorethylene	-	Low	-	-	High	50	1,000	f
Trichlorosilane	NA	High	-	-	Mod.	NA	NA	a,b
Trifluoroethylene	NA	NA	NA	NA	NA	NA	NA	
Trimethyl aluminum	Mod.	High	-	-	High	NA	NA	
Trimethyl gallium	-	High	-	-	High	NA	NA	g
Trimethyl indium	NA	NA	NA	NA	NA	NA	NA	
Trimethyl zinc	NA	NA	NA	NA	NA	NA	NA	
Tungsten	-	Mod.	-	-	Mod.	5*	NA	d
Urethane	-	-	-	-	Mod.	NA	NA	b,d,g,i
Vanadium	-	Mod.	-	-	Mod.	0.05*	NA	a
Vinyl acetate	-	High	-	-	Mod.	10	NA	a,d
Xylene	Mod.	High	-	-	Mod.	100	10,000	a,b
Zinc	-	Mod.	-	-	High	NA	NA	d
Zinc chloride	-	-	-	-	High	1*	2,000*	a,d,f,h
Zinc fluoroborate	NA	NA	NA	NA	NA	NA	NA	
Zinc phosphide	-	-	-	-	High	NA	NA	b
Zirconium	High	High	-	-	Low	5*	NA	a,j
Zirconium oxide	NA	NA	-	-	Low	NA	NA	a

Abbreviations: Mod. = moderate; "-" = none; NA = not available; TLV = threshold limit value as given by American Conference of Governmental Industrial Hygienists (Reference 35).

*TLV in mg/m^3, otherwise in ppm.

**Toxic routes: a = inhalation; b = oral; c = dermal; d = intraperitoneal; e = intramuscular; f = intravnous; g = subcutaneous; h = recognized carcinogen; i = experimental carcinogen; j = radioactive.

Source: References 34, 35, 37.

photovoltaics industry are not yet available. Similarly, discussions focus on hazards to health and the environment rather than risks, because the probability of an individual being exposed to these hazardous agents is not currently known. Such exposures could arise from the routine operation of the facility or from an accidental event (e.g., cylinder rupture, cylinder puncture, regulator failure, leak in lines between cylinders and process equipment, or failure of manufacturing equipment).

Considering the level of consequences associated with these hazards, appropriate control strategies are required in both the design and operation of commercial-scale photovoltaic manufacturing facilities. Occupational and environmental control options are discussed in Section 7.

5.1 Explosive and Flammable

Explosive compounds are those which can undergo and sustain chain reactions during oxidation. Of the various compounds used in photovoltaic cell manufacture, silane and hydrogen present the greatest potential explosive hazards. Flammable materials can be ignited and sustain a flame over a range of conditions (e.g., temperature and pressure). In photovoltaics cell manufacture, materials used in relatively large quantity that present flammability hazards include hydrogen and methane. Of these materials, most interest focuses on the silanes because of the pyrophoric nature of these materials and their relatively large scale applications.

Pure gaseous monosilane (SiH_4) and dislane (Si_2H_6) are extremely reactive gases. Both are considered self ignitable or pyrophoric and can ignite spontaneously and burn or explode when released into air (depending on concentration and flow rate). Even gas concentrations below explosion limits may explode in the event that ignition is delayed and pocketing occurs. Because of the reactive and pyrophoric properties of these gases, conventional measurement techniques to find explosion limits, rates of pressure increase, and maximum pressure for combustion explosion in closed vessels or vessels with vents are difficult to obtain. Consequently, explosion limits in air, either with silane mixed with inert or reactive diluent gases (e.g., hydrogen) or as pure gases are generally reported as unknown.[38,39]

The potential damage from explosion depends on many factors including: the energy content of the explosive mixture, distance to sensitive targets, and the nature of the target (e.g., people and equipment). Because of the likely ignition of these materials in close proximity to the source, the potential hazard to occupational health from an accidental leak is relatively large, while the potential hazard to public health is relatively small.[40]

5.2 Corrosives and Oxidizers

A corrosive agent of principal concern in the photovoltaics industry is hydrofluoric acid. It is used in the etching of thick film silicon photovoltaic cells to remove oxidized silicon, to remove saw damage (for ingot wafers), and to prepare the wafer for further processing. In this process operation, workers dip wafers into a hot, concentrated, hydrofluoric or hydrofluoric/nitric acid bath to remove surface imperfections. In the course of this activity, they may be exposed to hydrofluoric fumes and drippings. Hydrofluoric acid is extremely corrosive and is not easily washed off the skin. It continues to corrode until diluted within the exposed tissues or neutralized by calcium in the bone. The large number of hydrofluoric acid burns witnessed in the semiconductor industry created the first awareness that micorelectronics shared with other industries a measurable level of risk to the health and safety of workers.[41]

Both the semiconductor and photovoltaics industries are now beginning to replace "wet etching" using hydrofluoric and other acids, by a process called plasma etching. This process presents different hazards to workers[27,41] (i.e., radiofrequency radiation) which are discussed below in Section 5.4.

Oxidizing materials are those which spontaneously react with oxygen; explosives react spontaneously and violently. In this context, some materials could be classified as explosives, flammables and oxidizers. Hydrogen peroxide is a strong oxidizing agent which may be used as a cleaner in photovoltaic cell manufacturing. Like other strong oxidizers, hydrogen peroxide in sufficient concentrations will chemically erode skin on contact.

5.3 Poisons

The health effects of poisonous materials may be divided into two classes for discussion purposes: acute poisonings arising from short-term exposures to relatively large concentrations of materials which may cause shock, or collapse, severe inflammation of the lungs, or even death; and, a wide range of effects arising from low-level sublethal exposures which may continue over periods of months or years.

In photovoltaic cell manufacture there are a variety of toxic gases, liquids and solids that can present acute hazards to workers who are accidently exposed to these agents.[28,32,41] Attention has focused on toxic gases (e.g., arsine, diborane, hydrogen selenide, and phosphine) because of their potential large scale use in the photovoltaic industry and because of their potential to expose workers in short periods of time to high doses. These gases are often diluted to relatively low concentrations (but still higher than Threshold Limit Values [TLV][35]) before application. Some process applications, however, require higher concentrations which increase the hazard to health. The use of 100% phosphine, for example, is increasing.[41] Although many of these gases are already being used in industry, the quantities and application modes differ from photovoltaic cell manufacturing. In some cases there is only limited experience in the handling of a gas (e.g., hydrogen selenide). The volumes of some gases (e.g., phosphine in Zn_3P_2 production) could be larger than all other current applications.[18] Lack of experience in the handling and control of these materials can increase the risk to workers.

In production facilities, workers may also be exposed to many compounds at sublethal doses over long periods. These can result in a potpourri of health effects ranging from dermatitis to cancer.[28,32,41,42] Interest now focuses on those materials thought to present cancer risks to the workforce. Known or suspected human carcinogens which may be used by the industry include arsenic compounds, cadmium compounds, thiourea, methylene chloride. Unlike "nonthreshold" based pollutants where a limiting exposure is tolerated in both a regulatory and practical sense, it is now recognized that exposures to carcinogens result in incremental risks to worker health. OSHA and industry efforts are underway to eliminate the use of these materials, or to limit worker exposures to these compounds to levels as low as reasonably achievable (i.e., ALARA).[43]

In some cases, materials are used or generated during photovoltaic cell production for which even the most basic toxicologic information is lacking (e.g., gallium arsenide and copper indium diselenide). Although there is little or no knowledge about the hazards presented by these materials, their production depends on the use of materials which are quite toxic or hazardous (i.e., hydrogen selenide in copper indium diselenide and arsenic in gallium arsenide).[18,21]

5.4 Miscellaneous

In the manufacture of thin-film photovoltaic cells, electrical and electromagnetic fields generated from process equipment may present occupational hazards. Radio-frequency (rf), plasma etching, plasma deposition and sputtering equipment, if not designed and maintained properly, may emit nonionizing radiation into the occupational workspace. Laser scribing equipment may also present electrical shock and laser beam hazards to employees.[27]

In this industry, electrocution is a hazard of principal concern because of the large capacitor banks and very high-voltage power supplies used. In the semiconductor industry, it is a major cause of fatalities.[41]

Recently, the National Institute of Health/Occupational Safety and Health Administration conducted a survey to determine rf emissions around plasma etching units (comparable to rf plasma deposition units) in semiconductor facilities.[44] These studies showed that most of the units examined were emitting rf radiation levels below the levels set by the American National Standards Institute or the American Conference of Governmental and Industrial Hygienists. Rf emissions at ~10% of the units, however, were high enough to arouse concern about potentially hazardous emissions.[27]

Eye exposure to laser beams may result in serious injury. Skin exposures are not so dangerous since more energy is required to cause injury, and exposures can be felt and avoided. Reflective materials in the environment in which lasers operate can increase potential hazards. Also, flammable materials in the beam's route can be ignited as the beam scatters them.[27]

6. ENVIRONMENTAL RELEASES

The quantity and type of materials released to the environment from a manufacturing facility depend on the production and control technology alternatives used. Specific emission standards for the photovoltaics industry have not yet been set. Emission control standards developed for related industries (e.g., the semiconductor industry),[45] however, may provide guidelines for control technology requirements in the photovoltaics industry.

In these manufacturing facilities, a large variety of materials may be used; some may be released as by-products of normal or abnormal plant operations. Although manufacturing facilities may produce liquid, solid, and gaseous effluents, only gaseous effluents are likely to present acute hazards to public health. Liquid and solid wastes may also present hazards, but these can only expose the public through indirect pathways (i.e., drinking water and foodchains) and over longer time periods. Exposures via these pathways can also be more easily monitored and controlled. Hence liquid and solid wastes may present chronic, but not acute risks to public health.

6.1 Air Emissions

At present EPA has not established emissions standards for the routine or accidental discharge of atmospheric pollutants from the photovoltaics industry. National Emission Standards for Hazardous Air Pollutants for arsenic[46] and cadmium[47] might provide guidance to regulators on photovoltaic industry use of these materials. Although state and local regulations aimed at controlling routine and accident-related emissions from various industries have not been catalogued, they generally require prudent control engineering practices. State agencies are especially concerned with waste streams (air, water and solid) containing toxic or hazardous materials; such waste streams from photovoltaic manufacturers will certainly come under close scrutiny by these agencies. In New York State, for example, sources emitting air contaminants that are suspected of being human carcinogens or are known to be highly toxic must apply the "Best Available Control Technology" to the effluent stream.[48] Furthermore, applicants for emissions discharge permits must demonstrate that the projected emissions levels will comply with specific "Acceptable Ambient Levels" approved by the state agency.

In Table 11 some toxic or hazardous pollutants which might be emitted from hypothetical facilities are shown. The actual hazards to health from these materials depend on the inherent toxicologic properties of the materials, and the intensity, frequency, and duration of human exposures to such agents from normal or abnormal plant operations. In turn, actual exposures to the public will be influenced by several factors including: (i) availability and efficiency of safety and pollution control systems and emergency response plans; (ii) media into which the pollutants are emitted; and (iii) size, location and type of populations living adjacent to production facilities.

Potential effects on air quality from some routine emissions from a hypothetical 10 MWp a-Si photovoltaic cell manufacturing facility were evaluated using an impact screening method[48] adopted by the New York State Department of Environmental Conservation. Maximum annual ambient concentrations are estimated based on a number of assumptions including: (i) point source release, (ii) negligible building wake effects, (iii) negligible thermal and momentum plume rise, (iv) effective stack height of 25 feet, and (v) typical annual average meteorological conditions. Criteria

TABLE 11. TOXIC OR HAZARDOUS ATMOSPHERIC POLLUTANTS FROM PHOTOVOLTAIC CELL MANUFACTURING FACILITIES

Compound	Source	Pollutants released (kg/yr)[a] Uncontrolled	Controlled
Arsine	GaAs-halide CVD	14,670	770
Cadmium telluride	CdTe-CSVT	40	*
	CdTe-CVD	200	10
Diborane	a-Si-glow discharge	0.5	0
	a-Si-reactive sputtering	0.3	0
	a-Si-CVD	0.9	0
Hydrogen	CdTe-ED	*	*
	CdTe-CSVT	8,900	*
	CdTe-CVD	8,900	*
	Zn_3P_2-MOCVD	8,900	*
	GaAs-halide CVD	1,170	130
Hydrogen chloride	GaAs-halide CVD	1,640	200
Hydrogen selenide	$CuInSe_2$-sputtering	952	10
Hydrogen sulphide	$CuInSe_2$-sputtering	366	4
Metal vapors	$CuInSe_2$-All	*	*
Methane	Zn_3P_2-MOCVD	960	*
	GaAs-MOCVD	3,590	400
Phosphine	Zn_3P_2-MOCVD	3,050	80
	a-Si-glow discharge	0.5	0
	a-Si-reactive sputtering	0.5	0
	a-Si-CVD	1.4	0
Silane	a-Si-glow discharge	1,423	7
	a-Si-CVD	396	3
Silicon tetrafluoride	a-Si-glow discharge	4,620	25
Trimethyl gallium	GaAs-MOCVD	500	*
Zinc phosphide	Zn_3P_2-CSVT	*	*

Abbreviations: see Table 6.
*Insignificant quantity.
[a] Assuming hypothetical 10 MWp/yr production facilities.
Source: References 18, 19.

for assessing acceptable ambient levels are based on established federal and state standards where available, or (as in this case) on threshold limit values (TLVs)[35] given by the American Conference of Governmental Industrial Hygienists. Results of this analysis presented in Table 12 indicate that routine emissions of toxic gases from photovoltaic manufacturing facilities are orders of magnitude lower than threshold limit values. Consequently, these routine releases should not endanger public health.

At manufacturing facilities, gases may also be accidentally released from leaking process, storage and control systems during abnormal or transient conditions (e.g., fire, power failure, start-up and shut-down). Because of the highly toxic and hazardous nature of many feedstock gases, large volumes in stock, and the uncontrolled nature of such releases, health hazards can be significant. Such accidental releases are now receiving great attention because of the recent tragedy in Bhopal, India. As a result of this incident, strategies are being developed by the EPA/Chemical Emergency Preparedness Program[46] to identify acutely toxic chemicals for which communities may need to develop voluntary emergency preparedness programs. As a first step in this process, they have prepared an interim list of 403 acutely toxic chemicals which could present significant hazards to public health. Similar efforts are being organized by the United Nations-International Labour Office (ILO) in Geneva, Switzerland.[49] The ILO has prepared a list of dangerous substances which can cause extensive damage to property or kill or injure persons within or outside the site boundary.

Table 13 compares some projected gas inventories at photovoltaic cell fabrication facilities with these guidelines. As shown, many compounds used in photovoltaic cell manufacture are included in these lists. Furthermore, some projected inventories may exceed the ILO and EPA guidelines.

TABLE 12. ESTIMATED GROUND-LEVEL CONCENTRATIONS OF SOME ATMOSPHERIC POLLUTANTS DURING NORMAL OPERATION OF A 10 MWP A-SI PHOTOVOLTAIC CELL PLANT[a]

Pollutant	TLV[b] mg/m^3	Emission rate (lb/hr)[c]	Maximum annual concentration (mg/m^3)[d]
SiH_4	7.	$7x10^{-3}$	$3x10^{-5}$
SiF_4	2.5[e]	$2x10^{-3}$	$8x10^{-6}$
B_2H_6	0.1	$1x10^{-4}$	$4x10^{-7}$
PH_3	0.4	$2x10^{-4}$	$8x10^{-7}$

[a] Methodology provides conservative estimates of maximum annual ambient levels for typical emissions and meteorology, as described in text.

[b] TLV = threshold limit value as defined by the American Conference of Governmental Industrial Hygienists.

[c] Assuming scrubber efficiency of 98% for SiH_4 and SiF_4; 50% for B_2H_6 and PH_3.

[d] Estimated concentration, mg/m^3 = 4.218 * emission rate, lb/hr / (effective emission height)$^{2.16}$ where effective emission height is assumed to be 25 feet above ground.

[e] No TLV established for SiF_4; since SiF_4 is highly toxic and can form HF in contact with air, the TLV for HF is assumed.

TABLE 13. A COMPARISON OF ON-SITE INVENTORIES WITH ILO GUIDELINES

Gas	Source	Annual feedstock (kg)	Average weekly stock (kg)	Threshold quantity ILO (kg)[a]	Ratio (weekly stock/ threshold quantity)
Arsine	GaAs halide CVD	23,660	480	10	48
	MOCVD	6,520	130	10	13
Chlorosilanes	a-Si glow discharge	4,754	95	NA	-
Diborane	a-Si glow discharge, CVD, and RS	<1	0.02	NA	-
Hydrochloric acid	GaAs Halide CVD	3,850	80	250,000	<<1
Hydrogen	Zn_3P_2-MOCVD[b]	10,000	200	50,000	<<1
Hydrogen selenide	$CuInSe_2$-RS	1,600	32	10	3.2
Hydrogen sulfide	CdS-RS	600	12	50,000	<<1
Phosphine	Zn_3P_2-MOCVD	4,000	80	100	0.8
	a-Si CVD	2	0.04	100	<<1
Silane	a-Si glow discharge	1,500	30	NA	-
	CVD	600	12	NA	-

Abbreviations: CSVT, close spaced vapor transport; CVD, chemical vaopr deposition; ED, electrodeposition; MOCVD, metallorganic chemical vapor deposition; RS, reactive sputtering; NA, not available; -, not applicable.

[a] Quantity beyond which major-accident hazard may be created as defined by ILO.

[b] Smaller quantities of hydrogen may be required for other process alternatives, for example, a-Si glow discharge, CdTe-CSVT, CdTe-CVD, CdTe-ED, and CVD.

Source: References 18-21, 23, 46, 49.

6.2 Solid Wastes

Solid wastes produced in some manufacturing processes studied and their potential sources are shown in Table 14. In most cases, these are residuals from the deposition or environmental control systems. Some of these wastes may be classified as hazardous under the Hazardous and Solid Waste Amendment Act of 1984.[50]

6.3 Liquid Effluents

Liquid wastes may arise from wet etching operations or from solvents used in cleaning processes. Efforts are now underway to eliminate wet etching operations. Consequently, attention is now focused on the control of leaking solvents from storage tanks (often trichloroethane). In the semiconductor industry, underground storage tanks have leaked cleaning solvents into the groundwater and contaminated public water supply wells in Silicon Valley. This problem appears to be endemic to many semiconductor manufacturing facilities in that region. As a result of these leaks, many lawsuits have been filed against some large semiconductor manufacturers in the industry.[41,51]

7. OCCUPATIONAL AND ENVIRONMENTAL CONTROL OPTIONS

Materials used and contaminants generated in the production of photovoltaic devices may present hazards to workers and to the public. These will need to be managed by applying a wide range of administrative and engineering control options. The specific options will depend on the materials, their applications, and the nature and quantities of waste produced. A material by material analysis of such options is beyond the scope of this effort. Consequently, only general guidelines are presented. Some specific details on toxic and hazardous gases are presented, however,

TABLE 14. TOXIC OR HAZARDOUS SOLID WASTES FROM PHOTOVOLTAIC CELL MANUFACTURING FACILITIES

Compound	Source	Residuals (per year)[a]
$CuInSe_2$ compounds	$CuInSe_2$-TE	3,430 kg
	$CuInSe_x$-Sputtering	2,770 kg
CdS	CdS-TE	2,060 kg
	CdS-Sputtering	1,660 kg
CdZns	CdZnS-TE	1,820 kg
CdTe	CdTe-CSVT	410 kg
	CdTe-CVD	1,980 kg
	CdTe-HWVE	1,970 kg
Si compounds	Si-RS	205 kg
GaAs compounds	GaAs-CVD	9,900 kg
	GaAs-MOCVD	8,830 kg
Zn_3P_2	Zn_3P_2-CSVT	1,140 kg
	Zn_3P_2-MOCVD	653 kg

Abbreviations: TE = thermal evaporation; CSVT = close spaced vapor transport; CVD = chemical vapor deposition; HWVE = hot-wall vacuum evaporation; RS = reactive sputtering; MOCVD = metal-organic chemical vapor deposition.

[a] Assuming hypothetical 10 MWp/yr production facilities.

Source: References 18, 19.

because of the wide concern about the use and risk from these materials in this industry.

7.1 Occupational

In general, safe management of materials used in photovoltaic cell production is possible if basic industrial hygiene practices are followed. Because of the early maturity of this industry, occupational hazard management approaches employed have not been catalogued. Thus, the following discussion focuses on theory rather than practice.

As outlined by Feiner, the purpose of industrial hygiene programs is to prevent or minimize worker exposures' to dangerous materials.[52] While ventilation control is the most widely used method for achieving this protection, other procedures are available:

(i) Plant, Process and Equipment Design - Incorporation of industrial hygiene control principles into the design of new process equipment and facilities. Automation and automatic operations which require few if any workers are examples of this principle. Other examples include enclosed chemical processes, and grouping of hazardous operations to localize control.

(ii) Process Change - Often a simple change in a process can reduce contaminant dispersion; for example, batch charging of materials that are slightly wetted or contained in paper bags rather than in a dry bulk state may eliminate or reduce the need for control in storage bins and batch mixers.

(iii) Substitution - The most efficient strategy to reduce hazards is to simply choose technologies which do not require use of large quantities of toxic or hazardous materials. In the photovoltaics industry, for example, this might result in the selection of a-Si thin film alternatives, instead of GaAs or Zn_3P_2, because of the inherent toxicity of cadmium and phosphorus compounds, and the large volumes of feedstock materials required.

(iv) Isolation in Time or Space - Isolate workers in time and space from operations which may generate contaminants in such quantities that could present hazards to health. Enclosing dangerous operations together in separate rooms or buildings not only sharply reduces the number of workers exposed but may also simplify control procedures. An opposite approach to this, is to isolate the personnel in closed ventilated work spaces under positive pressure, to reduce worker exposures to contaminants.

(v) Housekeeping and Maintenance - Good industrial housekeeping and maintenance assists in contaminant control. Dust or other contaminants may be resuspended by plant activities. Good housekeeping can reduce this exposure pathway.

(vi) Decontamination and Emergency Procedures - In the event of an accident (e.g., the breaching of a high pressure gas line containing a toxic gas) facility safety managers should implement pre-developed emergency response efforts. These may include but not be limited to such activities as liaison with outside authorities, appointment and definition of the roles and responsibilities of emergency response personnel, development of site action plans including fire-fighting procedures and rescue systems, and plant shut-down procedures. After the situation is brought under control, procedures to decontaminate work areas, equipment, and clean-up workers should be implemented.

A previous BNL study reviewed gas hazards associated with the manufacture of a-Si photovoltaic cells and identified a series of control options available to reduce health and safety risks.[23] In Tables 15-17, specific administrative and engineering controls for explosive (i.e., silane), flammable (e.g., methane), and toxic (e.g., arsine and phosphine) gases used in photovoltaic cell production[11,53] are presented.

In general, the photovoltaics industry has implemented many of these suggestions because of the recognized hazards presented by these materials. Actual approaches adopted are, however, at the discretion of the specific manufacturers because of the lack of regulatory or industry-wide voluntary compliance requirements.

7.2 Environmental

Photovoltaic plants may produce liquid, solid, and gaseous pollutants. The mix of options available for the control of these materials depends on many factors including the nature and quantity of waste produced and the regulatory standards imposed by federal, state, and local environmental agencies.

7.2.1 Gaseous Pollutants

In the photovoltaics industry the major gas streams of interest may contain such materials as silane, phosphine, diborane and arsine. For air pollutant control, wet scrubbing is most commonly used for these types of pollutants. A wet scrubber is a device that enhances gas-liquid contact, promotes reaction between the liquid and the gas, and produces liquid or solid residuals which are less toxic and relatively easy to handle. A common type of scrubber, the packed-bed scrubber, contains an inert packing media which when irrigated with scrubbing liquid breaks the liquid streams

TABLE 15. SILANE OCCUPATIONAL SAFETY OPTIONS

A. Administrative Controls

1. Silane cylinders to be stored separately from toxic, corrosive, flammable, oxidizing, and water reactive materials.

2. Stored volumes to be the minimum possible.

3. Scrubber for $SiH_4$to be located outdoors or in a very well ventilated area.

B. Engineering Controls

4. Storage cabinet to be continuously purged with high velocity air flow, probably through several ports, to assure mixing of air with SiH_4.

5. Continuous N_2 purging of storage cabinets.

6. Excess flow limiter (typically a 6-mil orifice) in the cylinder valve.

7. Exposure-resistant cabinet construction with pads, roof, double fences, and fire protection sprinklers.

8. Gas monitors with automatic shutoff valve at the cylinder.

9. SiH_4/H_2 effluent from the process or the scrubber to be diluted with N_2 to lower the SiH_4 concentration below 0.5% before it mixes with air.

10. All exhaust lines to be made of noncombustible material.

11. Adequate N_2 purging of the oil reservoir chamber of vacuum pumps to prevent pyrophoric gas accumulation (e.g., SiH_4).

12. Separate vent and reactor exhaust lines to prevent SiH_4 from mixing with air.

13. Emergency scrubber to control accidental release of stored gas.

Source: Reference 23.

TABLE 16. FLAMMABLE GASES OCCUPATIONAL SAFETY OPTIONS

A. Administrative Controls

1. Safety education and training of employees when they are hired and at frequent intervals after.

2. Cylinder valves to be plugged and capped during transport.

3. Cylinders (even those with a zero pressure indication) to be kept away from heat.

4. Frequent inspection of all electrical systems from damage that may produce a spark.

5. Cylinder valves not to be opened into a dead-end pipe. A jet stream colliding with a wall can, by adiabatic compression, produce temperatures so high that even copper tubing will melt.

6. Valves of cylinders containing flammable gas (e.g., H_2) to be opened slowly since fast ejection of these gases may create an electrostatic potential high enough to ignite them.

7. Vacuum pumps to be inspected frequently for damage, leaks, and corrosion.

B. Engineering Controls

8. Automatic sprinkler systems in storage cabinets and above heated pipes.

9. Grounding of all metal parts in contact with flammable gases to suppress static electricity.

10. Floor and workers' shoes to be conductive so that electrostatic charges can be dissipated.

11. Liquid N_2 traps not to be used in vacuum system lines, because if O_2 (or air) enters the system it may condense in the trap and create a highly explosive mixture with the flammable gas.

12. Vacuum pumps can leak through junctions and allow O_2 to contact the flammable gas. Unnecessary valves to be eliminated and a dry N_2 line connected to purge pump intake compartments.

13. Pump exhaust to be designed to prevent condensation (see Section 4.3).

14. Automatic shutdown of process in the event of vacuum leak (pressure increase).

Source: Reference 23.

TABLE 17. TOXIC GASES OCCUPATIONAL SAFETY SUMMARY

A. Administrative Controls

1. Compressed gas cylinders to be stored in well vented cabinets or in outside secured storage areas.

2. Proper respiratory equipment provided and personnel to be instructed in its operation and limitations.

3. Stored gases kept at a minimum.

4. Scrubber to be located outdoors.

B. Engineering Controls

5. Leak detection systems to be installed in gas cabinets and other spaces where a leak of toxic gas may occur. Automatic valve shutoff provided if concentrations exceed threshold limit value.

6. High ventilation of the occupational space to keep toxic gas concentration below TLV if small plumbing system leak exists. Absence of this air flow should sound an alarm and preferably suspend gas supply to the reactor system.

7. Well designed and ventilated reactor chambers to prevent accumulation of reactive gases.

8. Free of mechanical joints supply lines, except in well ventilated areas. No fittings in unventilated space. All lines He pressure drop tested to show <1-psi pressure drop in 30 psi, in 24-hr periods.

9. Emergency scrubber to control accidental release of stored SiF_4.

Source: Reference 23.

into surface films. Gas then flows across these films creating close gas/liquid contact. In the most basic spray-type scrubber, gas enters an expansion space where its velocity is reduced and it passes slowly through liquid sprays in which the large liquid surface area provides the desirable gas/liquid interface of reaction. A venturi scrubber is recommended when particulates exist in the gas stream and when hazardous gases are in high concentration. The gas is accelerated by passing through a small opening into a converging nozzle. The high velocity of the gas and the injection of liquid into the nozzle create high turbulence which results in excellent mixing between liquid and gas. Furthermore, shear forces between liquid droplets and high-velocity gas atomize the droplets to create a larger liquid/gas contact area.

Scrubbing methods may be combined for higher removal efficiencies. Venturi and packed bed scrubbers are used in sequence in the same or separate equipment to control silane or silicon tetrafluoride, phosphine and diborane emissions from photovoltaic cell facilities. Scrubber liquids used are potassium hydroxide solution for silane and silicon tetrafluoride, and potassium permanganate or sodium hypochlorite for phosphine and diborane.

Some scrubber liquids used to deactivate certain toxic compounds may react violently with other compounds present; e.g., potassium permanganate used to deactivate phosphine may produce fire when hydrogen is present. Scrubbing with potassium hydroxide and sodium hypochlorite is an alternative not likely to create any fire hazards.

Combustion, oxidation and carbon adsorption may also be used for control purposes.[54] Controlled combustion and oxidation are used to reduce hazards associated with flammable and toxic gases including silane, diborane and phosphine. In these systems, process exhaust gases enter through the unit's flame check and are mixed with controlled amounts of oxygen/air in an oxygenator section. This section is maintained at about 800 - 1000°C. Controlled oxygen enrichment produces a mixture that can be effectively combusted and heat from the high temperature elements enhances the chemical reaction of the combustible gases and vapors. Safety and insurance regulations generally limit the maximum concentration of a controlled gas to 25% of the low explosion limit. This concentration will supply only part of the heat required to sustain combustion so that auxiliary fuel may be needed. In such units, the expected reactions for silane, phosphine and diborane are as follows:

$$SiH_4 + 2O_2 \longrightarrow SiO_2 + 2H_2O$$

$$2PH_3 + 3O_2 \longrightarrow P_2O_3 + 3H_2O$$

$$2PH_3 + 4O_2 \longrightarrow P_2O_5 + 3H_2O$$

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$$

The controlled combustion and oxidation approach has been shown to be highly efficient in the combustion of silane - results suggesting performance efficiencies approaching 100%. The system under defined operating conditions for phosphine, however, appears to be inefficient. It is possible that higher temperature conditions (above 1000°C) or higher residence time of the effluent in the hot zone may be more effective in reducing phosphine emissions.[55]

Carbon adsorption is very effective in removing several toxic gases (e.g., phosphine, arsine, hydrogen selenide and hydrogen sulfide) from effluent streams of moderate flow rates and low concentrations.[56,57] Porous carbon adsorbs gas molecules by mechanisms involving Van der Waals surface attraction and capillary condensation. Its capacity depends on its properties and the operating conditions. Typical efficiencies range from 5 to 30%. This suggests that carbon adsorption may be very effective in controlling dopant gases at the very low flow rates used in the industry, but not for feedstock gases which have very high flow rates. For these gases, carbon adsorption may be used as a final "polishing" stage.[54] In some cases, carbon adsorption may also provide an economically feasible method for the recovery of some gases. Phosphine, for example, can be regenerated from carbon by heating with steam or hot air, either internally with a fixed bed or externally with a moving bed. Phosphine regeneration, however, is not currently practiced for small applications.

7.2.2 Solids and Liquids

Solids and liquids produced during photovoltaic cell production are principally residuals arising from deposition processes or from wet operations such as acid etching, scrubber by-products, solvents, or from vacuum pump oils contaminated with dopant gases. These wastes, by definition, may often be classified as hazardous under the Resource Conservation and Recovery Act. Once these wastes are classified as hazardous and if they are produced in quantities greater than 100 kg/month, manufacturers will need to respond to many different regulations including implementation of manifest systems to track shipments of hazardous wastes, development of emergency preparedness plans for prevention of hazards and disposal of these wastes in controlled landfills.[58]

Leaks from underground storage tanks are now being addressed by EPA through the development of model ordinances that will require some form of double vaulting of underground storage tanks. Application of this approach by the photovoltaics industry should reduce the risk from these materials.

Liquid wastes to be discharged to surface waters or to publicly owned treatment works will need to adhere to various regulatory standards imposed by EPA under the Clean Water Act.[59] For the semiconductor industry (which by definition includes the photovoltaics industry - "semiconductor means solid state device...and interconversion between light energy and electrical energy"), EPA has defined effluent limitations for best practicable technology (BPT), best available technology (BAT), and best conventional technology (BCT) for existing facilities, and new source performance standards (NSPS) for new plants to include specific effluent limitations for arsenic, fluoride, pH, total suspended solids, and "total toxic organics". Approaches for meeting these standards are described elsewhere.[45]

8. TOXIC SUBSTANCES CONTROL ACT

Prior to enactment of TSCA, existing environmental legislation e.g., Clean Air Act, Federal Water Pollution Control Act, etc., provided for regulatory control of potentially toxic materials only after their discharge into the environment. As awareness of the scope and severity of hazards associated with toxic pollutants increased, the need for screening and/or testing of chemicals before they are used on a production scale was realized by Congress and became the major motivation for passage of TSCA. The Toxic Substances Act empowered EPA with two major regulatory obligations: (i) acquisition of information on existing chemical substances to identify and evaluate potential hazards; and (ii) regulate production, use, distribution, and disposal of such substances, where necessary.[60] These objectives are met through implementation of TSCA provisions including: an inventory list, pre-manufacturing notice, significant new use, reporting/record-keeping requirements, and testing criteria. The following sections review highlights of TSCA and provide a discussion of its major impacts on the photovoltaics industry.

8.1 Inventory List

Under the regulatory powers granted by TSCA, EPA issued a one-time reporting requirement to chemical manufacturers, processors and importers to develop an inventory list of pre-existing chemicals. The initial inventory reporting obligations were limited to those companies where:

(i) >30 wt % of their products were classified under Standard Industrial Classification (SIC) code categories 28 or 2911; or

(ii) the total chemical production/importation exceeded one million pounds; or

(iii) any chemical was manufactured/imported in quantities ≥100,000 pounds.

Small manufacturers (defined as those with total sales <$5 million) were exempted from some of the one-time reporting requirements.

The original inventory is updated periodically based on premanufacture notification entries, and currently contains over 58,000 substances. Substances not included in the inventory are subject to the premanufacture notification process (see Section 8.2). Those substances that are listed in the inventory may still be subject to significant new use rules (see discussion in Section 8.3).

8.2 Premanufacture Notification

The major regulatory emphasis of TSCA is the ongoing requirement for premanufacture notification (PMN) included under Section 5(a). This section requires that EPA be notified ninety days prior to manufacture or import of new chemical substances, i.e., those not included on the inventory list. The intent of the PMN regulation is to provide EPA with enough information on new chemical substances to be able to estimate potential impacts on public health and safety.

General Premanufacture Notice procedural requirements embodied in 40 CFR 720[61] are reviewed below. Section 8.4 contains a discussion on PMN requirements for the photovoltaics industry.

The PMN process begins by identifying chemical substances to be manufactured, imported, distributed in commerce, processed or disposed of. TSCA defines a chemical substance as any organic or inorganic substance of a particular molecular identity, including any combination of such substances occurring in whole or in part as a result of a chemical reaction occurring in nature and any element or uncombined radical. Specifically exempted are mixtures, pesticides (regulated under the Federal Insecticide, Fungicide and Rodenticide Act, or FIFRA), nuclear materials (as regulated under the Atomic Energy Act of 1954), articles subject to the Internal Revenue Code of 1954, and food, additives, cosmetics and drugs (regulated under the Federal Food, Drug and Cosmetic Act).

Several additional exemptions have been granted by EPA through issuance of TSCA regulation, 40 CFR 720, including the use of small quantities for research and development (defined as quantities not greater than reasonably necessary for such purposes),[62] chemical substances to be test marketed,[63] and those which will be exported only.[64] A complete list of PMN exemptions is included in Table 18.

If a substance is not exempt from PMN requirements the next step is to search the Toxic Substances Inventory Data Base to determine if: (i) it was included in EPA's original inventory, i.e., it was "grandfathered - in", or (ii) a PMN has already been filed with EPA. If either of the above are affirmed, the substance may be subject to a Significant New Use Rule (see Sec. 8.3). Some substances are included in a Confidential Inventory to protect companies from having to disclose sensitive process information.

Specific action can be taken to search the Confidential Inventory if necessary.

Submitting a PMN form is not a trivial effort, as EPA requires a substantial amount of data and supporting documentation in three major categories: (i) physical and chemical properties/environmental fate data (e.g., such as density, solubility, volatility, and explosiveness); (ii) health effects data (e.g., mutagenicity, mammalian adsorption); and, (iii) environmental effects data (e.g., plant uptake, bioaccumulation and bioconcentration). TSCA does not require development of test data; only data in one's possession or control, and descriptions of known or ascertainable data. In some critical areas, e.g., toxicity and carcinogenicity, it may be in the interest of the PMN submitter to perform tests where lacking, so that EPA could make a more informed ruling. Specific data requirements are detailed in the Instructions Manual for Premanufacture Notification of New Chemical Substances.

When EPA receives a PMN it first reviews it to confirm that the substance is indeed subject to notification requirements; the submitter is notified to acknowledge receipt; a PMN number is assigned; and the 90 day review period begins. If errors or incomplete submissions are found the PMN is returned for correction/completion. Objections to EPA ruling of incomplete submission can be appealed. Upon completion of EPA review a notice is published in the Federal Register summarizing PMN information. In the absence of regulatory action and after a notice of commencement of manufacture or import has been filed by the PMN submitter, manufacture/import of the substance may begin.

8.3 Significant New Use Regulations

In addition to regulatory authority over new chemical substances, EPA is mandated with the responsibility (through TSCA Section 5(a)(2)) to monitor significant new uses of existing chemicals for potential hazards. Determination of a significant new use is made by EPA based on consideration of:

(i) the projected volume of manufacturing and processing of a chemical substance;

(ii) the extent to which a use changes the type or form of exposure of human beings or the environment to a chemical substance;

(iii) the extent to which a use increases the magnitude and duration of exposure of human beings or the environment to a chemical substance; and

(iv) the reasonably anticipated manner and methods of manufacturing, processing, distribution in commerce, and disposal of a chemical substance.

If EPA decides any of the above criteria are satisfied, it can issue a significant new use regulation (SNUR) for that substance. SNUR notices are published in the TSCA Chemical Substances Inventory (as footnotes). Federal Register/Code of Federal Regulations, and the TSCA <u>Chemical in Progress Bulletin</u>. General applicability provisions for a significant new use regulation are spelled out in the first SNUR, issued in September 1984.[65] Documentation requirements for compliance with a SNUR are similar to those for a PMN. EPA has used this authority sparingly, as only several SNURs have been issued to date.

8.4 Premanufacture Notice Requirements for the Photovoltaics Industry

As noted, a wide variety of both hazardous and non-hazardous chemical substances are required in the manufacture of photovoltaic cells. In order to review the PMN compliance requirements for the photovoltaics industry as a whole, a search of the EPA Toxic Substances Inventory Data Base was conducted; materials listed in Table 7 were input by name and by CAS registry number. The latter approach proved more useful since searching by name yielded many multiple outputs reflecting overlapping of compound names.

Results of this effort showed that the overwhelming majority of photovoltaic materials searched are included in the Inventory. This reflects the many similarities between processing of semiconductors in general and photovoltaic cells.

8.5 Significant New Use Requirements for the Photovoltaics Industry

Although most of the feedstock and supporting materials required in the manufacture of photovoltaic cells are used in making semiconductors and other products, quantities of specific substances used and the nature of their application may change, thus making them susceptible to review under the SNUR program. As discussed above, EPA has to date infrequently exercised its option to issue SNURs. However, based on the known toxic hazards of some of these materials and projected increases in their volumes needed for photovoltaic manufacturing, TSCA criteria for significant new use may be met. Determination of specific SNUR candidates will depend on factors such as photovoltaic cell types and manufacturing processes selected, and consumer demand.

9. DISCUSSION AND CONCLUSIONS

The photovoltaics industry has grown rapidly in size and in diversity over the past ten years. With continued growth and the introduction of new process and material alternatives, a range of possible hazards to health and the environment may arise if adequate concern is not focused on these issues. Based on the analyses presented in this report, several key issues areas may be identified where hazards may exist or where more information is needed. These may be divided into the following categories for discussion purposes: Toxicology, occupational hazards and control options, environmental hazards and control options, and TSCA.

Toxicology - A large diversity of materials are used in photovoltaic cell production. Many are hazardous or toxic. Principal interest in the industry now focuses on several gases which will be widely used (i.e., arsine, phosphine, diborane, and silane). The acute and chronic health effects of these materials are reasonably well understood. The conditions under which silane burns and explodes, the stoichiometry and the potential damage arising from such explosions, however, is not well understood. In some cases, materials (i.e., gallium arsenide and copper indium diselenide) are used or generated for which even the most basic toxicological information is lacking (e.g., animal studies). These require further study. In addition, there are a class of compounds known as metallorganics which will likely be used in larger quantities in the future. The toxicology and chemical reactivity of these materials (e.g., trimethyl gallium, tetramethyl tin) need to be better understood.

Occupational Hazards and Control Technology Options - Toxic and hazardous materials for which only limited industrial experience exists may receive wide scale use in the industry. As a result, prescribed methods for the safe handling and disposal of some of these materials are not available. Although this provides the manufacturers with flexibility in the design and operation of their facilities, it also presents uncertainties to the extent that they can be assured of the effectiveness of the control strategies applied. In this regard, such strategies need to be identified and evaluated to assure their effectiveness. In evaluating these control options, baseline data describing current practices and exposure patterns are needed, but not available. Consequently, efforts to collect baseline monitoring information for routine and accidental conditions in plant settings should be initiated. Similarly, engineering and administrative control options need to be more thoroughly described and evaluated. In these evaluations, special attention should focus on safety systems required to prevent catastrophic exposures during both accidental and normal operating conditions. The implementation of event and fault tree analyses as currently used in the nuclear and aerospace industries may be helpful in these applications.

Environmental Hazards and Control Technology Options - Methods for controlling routine and accidental releases of the gases to be used by this industry have not yet received close scrutiny by federal and state agencies. Although a range of such options exists (e.g., scrubbing, incineration, carbon adsorption) their operability has yet to be adequately demonstrated. Furthermore, their potential use in an accident is questionable. Hence, mechanisms for controlling accidental releases which present the largest hazards to public health require closer examination. Hazardous liquid and solid wastes may also be produced. In general, these do not present acute risks to health. Furthermore, control options for these materials are in use in related industries.

10. REFERENCES

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APPENDIX A

PHOTOVOLTAIC R&D ACTIVITIES - U.S. INDUSTRIES AND INSTITUTIONS

				Misc. cell fabrication process development			
Firm/Institution	Cell type	Junction design/ formation	Deposition process development/ active layers	Metallization	AR coating	Passivation	Encapsulation
Ametek Inc., Paoli, PA	CdTe thin film	x	x				
ARCO Solar, Inc. Chatsworth, CA	$CuInSe_2$ thin film;	x	x	x			
	CdTe - thin film	x	x	x			
	a-Si	x	x	x			
Bell Laboratories Murray Hill, NJ	InP - liquid junction	x					
Coronar Corporation Princeton, NJ	a-Si	x	x				
Applied Solar Energy Corp., City of Industry, CA	GaAs thin film - concentrator	x	x				
	AlGaAs/GaAs thin film	x	x				
Minnesota Mining and Manufacturing, St. Paul, MN	a-Si	x	x				
Boeing Company Seattle, WA	$CuInSe_2/(CdZn)S$ thin film	x	x				
Chevron San Francisco, CA	GaAs alloys - conentrator	x	x				
Entech, Inc. Dallas, TX	GaAs thin film - concentrator	x	x				

(continued)

APPENDIX A (continued)

Solorex Corporation Rockville, MD	Polycrystalline - Si	x			
Sovonics Solar Sys. Cleveland, OH	a-Si	x	x		
Solavolt Internat. Phoenix, AZ	Polycrystalline-Si	x	x		x
Solenergy Corp. Wuburn, MA	GaAs alloys - multijunction	x	x		
Spire Company Bedford, MA	GaAs thin film		x		
	a-Si alloys - multijunction	x			
Energy Conversion Devices, Troy, MI	a-Si alloys - multijunction	x	x		
Westinghouse Corp. Pittsburgh, PA	Single Crystal Si - float zone	x		x	
	Ribbon Si	x	x	x	
Photo Power, Inc. El Paso, TX	CdS/Cd_xS - thin film	x	x		
International Solar Electric Technology Inglewood, CA	$CuInSe_2/CdS$ - thin film	x	x		
Electronic and Information Sector Lab, St. Paul, MN	a-Si		x		
Hughes Research Lab Malibu, CA	GaAs/Si - multijunction	x	x		

(continued)

APPENDIX A (continued)

Research Triangle Institute, Research Triangle Park, NC	Ge-tunnel junction	x			
Varian Associates	GaAs alloys - multijunction	x	x		
Univ. of Delaware Newark, DE	GaAsP/Si - multijunction	x	x		
Princeton Univ. Princeton, NJ	a-Si : H	x	x		
Stanford Univ. Stanford, CA	Single crystal Si-float zone	x			
MIT Cambridge, MA	GaAs Alloys - two junction	x	x		
	a-Si : H		x		
Southern Methodist Univ., Dallas, TX	a-Si : H		x		
Brookhaven Nat. Lab. Upton, NY	a-SiH		x		
NASA, Lewis Research Center, Cleveland, OH	GaAs thin film	x			
JPL Pasadena, CA	a-Si	x	x		
Sandia National Lab Albuquerque, NM	Si-concentrator	x	x	x	x
	GaAs thin film - concentrator	x	x		

(continued)

APPENDIX A (continued)

SERI Golden, CO	GaAsP thin film	x	x		
	a-Si alloys multijunction	x	x		
	a-Si : H				x
	Single Crystal - Si		x	x	

Source: References 14, 17.

APPENDIX B

COMMERCIAL PRODUCTION OF PHOTOVOLTAIC CELLS IN THE U.S.

Firm/Location	Cell Type	Production (MW) 1984	Production (MW) 1985
Applied Solar Energy Corporation 15251 East Don Julian Street City of Industry, California 91746	GaAs thin film	*	*
ARCO Solar, Inc. P. O. Box 2105 Chatsworth, California 91313	Single crystal-Si a-Si	5.5 *	4.7 0.2
Chronar Corporation P. O. Box 177 Princeton, New Jersey 08542	a-Si	*	0.2
General Electric 6901 Elmwood Avenue Philadelphia, Pennsylvania 19142	Single Crystal-Si	*	*
Mobile Solar Energy Corporation 16 Hickory Drive Waltham, Massachusetts 02254	Ribbon Si	0.1	0.1
Intersol Power Corporation 1700 Pennsylvania Avenue, NW Suite 300 Washington, D.C. 20007	GaAs thin film	*	*
Motorola 1301 Algonquin Road Schaumburg, Illinois 60196	Polycrystalline-Si	0.3	0.5
Solec International, Inc. 12533 Chadron Avenue Hawthorne, California 90250	Single crystal-Si Polycrystalline-Si a-Si	0.4 * *	0.4 * *
Solarex Croporation 1335 Piccard Drive Rockville, Maryland 20850	Single crystal-Si Polycrystalline-Si a-Si	0.5 1.5 0.1	0.2 1.9 0.1
Spire Corporation Patriots Park Bedford, Maryland 01730	GaAs thin film	*	*

(continued)

APPENDIX B (continued)

Silicon Sensors, Inc. Old Highway 18 E. Dogeville, Wisconsin 53533	Selenium Single crystal-Si	* *	* *
Spectrolab, Inc. 12500 Gradstone Avenue Sylmar, California 91342	AlGaAs/GaAs thin film	*	*
Sovonics Solar Systems** Cleveland, Ohio	a-SI	*	0.1
Westinghouse Corp. P. O. Box 10864 Pittsburgh, Pennsylvania 15222	Ribbon Si	*	0.1
United Energy Corp. 420 Lincoln Center Drive Foster City, California 94404	Single crystal Si - concentrator	3.0	0.0
Total		11.7	8.6

*Precise production data not available, but are known to be less than 0.1 MW.
**No longer in production as of 1986.
Source: References 8, 9.