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OVERVIEW OF POTENTIAL HAZARDS

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1. INTRODUCTION

Photovoltaic (PV) technologies have distinct environmental advantages for generating electricity over conventional technologies. The operation of photovoltaic systems does not produce any noise, toxic-gas emissions, or greenhouse gases. Photovoltaic electricity generation, regardless of which technology is used, is a zero-emissions process.

However, as with any energy source or product, there are environmental, health and safety (EHS) hazards associated with the manufacture of solar cells. The PV industry uses toxic and flammable-substances, although in smaller amounts than many other industries, and use of hazardous chemicals can involve occupational and environmental hazards. Addressing EHS concerns is the focus of numerous studies of the National Photovoltaic EHS Assistance Center at Brookhaven National Laboratory, which operates under the auspices of the US Department of Energy (DOE). More than 150 articles highlighting these studies are posted in the Center's website (www.pv.bnl.gov). This work has been done in cooperation with the US DOE PV Program and the US PV industry, which takes EHS issues very seriously and reacts proactively to concerns. Below is a summary of EHS issues pertaining to the manufacture of crystalline-Si (α -Si), amorphous-silicon (α -Si), copper indium diselenide (CIS), copper indium gallium diselenide (CGS), gallium arsenide (GaAs) and cadmium telluride (CdTe), which are currently commercially available.

2. OVERVIEW OF HAZARDS IN PV MANUFACTURE

In manufacturing photovoltaic cells, health may be adversely affected by different classes of chemical and physical hazards. In this chapter, discussion focuses on chemical hazards related to the materials' toxicity, corrosivity, flammability, and explosiveness. These hazards differ for different thin-film technologies and deposition processes. The main hazards associated with specific technologies are shown in Table 1. A listing of hazardous materials used in manufacturing is shown in Table 2.

Table 1. Major Hazards in PV Manufacturing

Module Type	Types of Potential Hazards
x-Si	HF acid burns SiH ₄ fires/explosions Pb solder / module disposal
a-Si	SiH ₄ fires/explosions
CdTe	Cd toxicity, carcinogenicity, module disposal
CIS, CGS	H ₂ Se toxicity, module disposal
GaAs	AsH ₃ toxicity, As carcinogenicity, H ₂ flammability, module disposal

Table 2. Some Hazardous Materials used in Current PV Manufacturing

Material	Source	TLV-TWA ¹ (ppm)	STEL ² (ppm)	IDLH ³ (ppm)	ERPG2 ⁴ (ppm)	Critical Effects
Arsine	GaAs CVD	0.05	-	3	0.5	Blood, kidney
Arsenic compounds	GaAs	0.01 mg/m ³	-	-	-	Cancer, lung
Cadmium compounds	CdTe and CdS deposition CdCl ₂ treatment	0.01 mg/m ³ (dust) 0.002 mg/m ³ (fumes)	-	-	NA	Cancer, kidney
Carbon tetrachloride	Etchant	5	10		100	Liver, cancer, greenhouse gas
Chloro-silanes	a-Si and x-Si deposition	5	-	800	-	Irritant
Copper	CIS deposition	1 mg/m ³ (dust) 0.2 mg/m ³ (fumes)	-	100 mg/m ³	-	
Diborane	a-Si dopant	0.1	-	40	1	CNS, pulmonary
Germane	a-Si dopant	0.2	-	-	-	Blood, CNS, kidney
Hydrogen	a-Si deposition	-	-	-	-	Fire hazard
Hydrogen fluoride	Etchant	-	C ⁵ 3	30	20	Irritant, burns, bone, teeth
Hydrogen selenide	CIS sputtering	0.05	-	1	-	Irritant, GI, flammable
Hydrogen sulfide	CIS sputtering	10	15	100	30	Irritant, CNS, flammable
Indium compounds	CIS deposition	0.1 mg/m ³	-	-	-	Pulmonary, bone, GI
Lead	Soldering	0.05 mg/m ³	-	-	-	CNS, GI, blood, kidney, reproductive
Nitric acid	Wafer cleaning	2	4	25	-	Irritant, Corrosive
Phosphine	a-Si dopant	0.3	1	50	0.5	Irritant, CNS, GI, flammable
Phosphorous oxychloride	x-Si dopant	0.1				Irritant, kidney
Selenium compounds	CIS deposition	0.2 mg/m ³		1 mg/m ³		Irritant
Sodium hydroxide	Wafer cleaning		C ⁵ 2 mg/m ³	10 mg/m ³	5 mg/m ³	Irritant
Silane	a-Si deposition	5	-	-	-	Irritant, fire & explosion hazard
Silicon tetrafluoride	a-Si deposition	-				
Tellurium compounds	CIS deposition	0.1 mg/m ³				CNS, cyanosis, liver

- ¹ TLV-TWA: The Threshold Limit Value, Time Weighted Average is defined by the American Conference of Governmental Industrial Hygienists (ACGIH) as the time-weighted average threshold concentration above which workers must not be exposed during work-shifts (8 hr/day, 40 hr/week)
- ² STEL: The Threshold Limit Value, Short Term Exposure Level, is defined by the American Conference of Governmental Industrial Hygienists (ACGIH) as the maximum concentration to which workers can be exposed for a period up to 15 minutes, provided not more than four excursions per day are permitted with at least 60 minutes between exposure periods and provided that daily PEL is not also exceeded.
- ³ IDLH: The Immediately Dangerous to Life or Health Concentration is defined by the National Institute for Occupational Safety and Health (NIOSH) as the maximum concentration from which one could escape within 30 minutes without any escape-impairing symptoms or any irreversible health effects.
- ⁴ ERPG-2: The Emergency Response Planning Guideline-2, is defined by the American Industrial Hygiene Association (AIHA) as the concentration below which nearly all people could be exposed for up to one hour without irreversible or other serious health effects or symptoms that would impair their ability to take protective action.
- ⁵ C Threshold Limit Value-Ceiling -defined by ACGIH as the concentration that should not be exceeded during any part of the working exposure.
- Not available

3. CRYSTALLINE SILICON (x-Si) SOLAR CELLS

Occupational Health Issues

In the manufacture of wafer-based crystalline silicon solar cells, occupational health issues are related to potential chemical burns and the inhalation of fumes from hydrofluoric acid (HF), nitric acid (e.g., HNO₃) and alkalis (e.g., NaOH) used for wafer cleaning, removing dopant oxides, and reactor cleaning. Dopant gases and vapors (e.g., POCl₃, B₂H₃), also are hazardous if inhaled. POCl₃ is a liquid, but in a deposition chamber it can generate toxic P₂O₅ and Cl₂ gaseous effluents. Inhalation hazards are controlled with properly designed ventilation systems in the process stations. Other occupational hazards are related to the flammability of silane (SiH₄) and its byproducts used in silicon nitride deposition; these hazards are discussed in the a-Si section below.

Public Health and Environmental Issues

No public health issues were identified with this technology. The environmental issues are related to the generation of liquid- and solid-wastes during wafer slicing, cleaning, and etching, and during processing and assembling of solar cells.

The x-Si PV industry has embarked upon programs of waste minimization and examines environmentally friendlier alternatives for solders, slurries and solvents. Successful efforts were reported in laboratory and manufacturing scales in reducing the caustic waste generated by etching. Other efforts for waste minimization include recycling stainless-steel cutting wires, recovering the SiC in the slurry, and in-house neutralization of acid and alkali solutions.

Finally, the content of Pb in solder in many of today's modules creates concerns about the disposal of modules at the end of their useful life. One x-Si manufacturer has developed and is using Pb-free solders, and has offered the technology know-how to others who are considering such a change (Fthenakis and Gonsiorawski, 1999).

4. AMORPHOUS SILICON (α -Si) SOLAR CELLS

Amorphous silicon, cadmium telluride, copper indium selenide and gallium arsenide are thin-film technologies that use about 1/100 of the photovoltaic material used on x-Si.

Occupational Safety Issues

The main safety hazard of this technology is the use of SiH₄ gas, which is extremely pyrophoric. The lower limit for its spontaneous ignition in air ranges from 2% to 3%, depending on the carrier gas. If mixing is incomplete, a pyrophoric concentration may exist locally, even if the concentration of SiH₄ in the carrier gas is less than 2%. At silane concentrations equal to or greater than 4.5%, the mixtures were found to be metastable and ignited after a certain delay. In an accident, this event could be extremely destructive as protection provided by venting would be ineffective. Silane safety is discussed in detail elsewhere (Fthenakis and Moskowitz 1990; Britton, 1991; Tamanini et al, 1998). In addition to SiH₄, hydrogen used in a-Si manufacturing, also is flammable and explosive. Most PV manufacturers use sophisticated gas-handling systems with sufficient safety features to minimize the risks of fire and explosion. Some facilities store silane and hydrogen in bulk from tube trailers to avoid frequently changing gas

cylinders. A bulk ISO module typically contains eight cylindrical tubes that are mounted onto a trailer suitable for over the road and ocean transport. These modules carry up to 3000 kg of silane. Another option is a single, 450 liter cylinder, mounted on a skid, which contains up to 150 kg of silane (mini-bulk). These storage systems are equipped with isolation and flow restricting valves.

Bulk storage decreases the probability of an accident, since trailer changes are infrequent, well-scheduled special events that are treated in a precise well-controlled manner, under the attention of the plant's management, safety officials, the gas supplier, and local fire-department officials. On the other hand, if an accident occurs, the consequences can be much greater than one involving gas cylinders. Currently, silane is used mainly in glow discharge deposition at very low utilization rates (e.g., 10%). To the extent that the material utilization rate increases in the future, the potential worst consequences of an accident will be reduced.

Toxic doping-gases (e.g., AsH_3 , PH_3 , GeH_4) are used in quantities too small to pose any significant hazards to public health or the environment. However, leakage of these gases can cause significant occupational risks, and management must show continuous vigilance to safeguard personnel. Applicable prevention options are discussed elsewhere (Moskowitz and Fthenakis, 1991); many of these are already implemented by the US industry.

Public Health and Environmental Issues

Silane used in bulk quantities in a-Si facilities may pose hazards to the surrounding community if adequate separation zones do not exist. In the United States, the Compressed Gas Association (CGA) Guidelines specify minimum distances to places of public assembly that range from 80 ft to 450 ft depending on the quantity and pressure of silane in containers in use (CGA P-32, 2000). The corresponding minimum distances to the plant property lines are 50 ft to 300 ft. Prescribed separation distances are considered sufficient to protect the public under worst-condition accidents.

No environmental issues have been identified with this technology.

5. CADMIUM TELLURIDE (CdTe) SOLAR CELLS

Occupational Health Issues

In CdTe manufacturing, the main concerns are associated with the toxicity of the feedstock materials (e.g., CdTe, CdS, CdCl₂). The occupational health hazards presented by Cd and Te compounds in various processing steps vary as a function of the compound specific toxicity, its physical state, and the mode of exposure. No clinical data are available on human health effects associated with exposure to CdTe. Limited animal data comparing the acute toxicity of CdTe, CIS and CGS, showed that from the three compounds, CdTe has the highest toxicity and CGS the lowest (Fthenakis et al, 1999) No comparisons with the parent Cd and Te compounds have been made. Cadmium, one of CdTe precursors, is a highly hazardous material. The acute health effects from inhalation of Cd include pneumonitis, pulmonary edema, and death. However, CdTe is insoluble to water and, as such, it may be less toxic than CdTe. This issue needs further investigation.

In production facilities, workers may be exposed to Cd compounds through the air they breathe, as well as by ingestion from hand-to-mouth contact. Inhalation is probably the most important pathway, because of the larger potential for exposure, and higher absorption efficiency of Cd compounds through the lung than through the gastrointestinal tract. The physical state in which the Cd compound is used and/or released to the environment is another determinant of risk. Processes in which Cd compounds are used or produced in the form of fine fumes or particles present larger hazards to health. Similarly, those involving volatile or soluble Cd compounds (e.g., CdCl₂) also must be more closely scrutinized. Hazards to workers may arise from feedstock preparation, fume/vapor leaks, etching of excess materials from panels, maintenance operations (e.g., scraping and cleaning), and during waste handling. Caution must be exercised when working with this material, and several layers of control must be implemented to prevent exposure of the employees. In general, the hierarchy of controls includes engineering controls, personal protective equipment, and work practices. Area and personal monitoring would provide information on the type and extent of employees' exposure, assist in identifying potential sources of exposure, and gather data on the effectiveness of the controls. The US industry is vigilant in preventing health risks, and has established proactive programs in industrial hygiene and environmental control. Workers' exposure to cadmium in PV

manufacturing facilities is controlled by rigorous industrial hygiene practices, and is continuously monitored by medical tests, thus preventing health risks (Bohland and Smigielski, 2000).

Public Health and Environmental Issues

No public health issues have been identified with this technology. Environmental issues are related to the disposal of manufacturing waste and end-of-life modules; these are discussed in section 9 below.

6. COPPER INDIUM SELENIDE (CIS) SOLAR CELLS

Occupational Health and Safety

The main processes for forming copper indium diselenide solar cells are co-evaporation of Cu, In and Se and selenization of Cu and In layers in H₂Se atmosphere. The toxicity of Cu, In and Se is considered mild. Little information exists on the toxicity of CIS. Animal studies have shown that CIS has mild to moderate respiratory track toxicity; in comparing CIS, CGS and CdTe, CIS was found to be less toxic than CdTe and somewhat more toxic than CGS.

The selenium TLV-TWA of 0.2 mg/m³ as selenium were set to prevent systemic toxicity, and to minimize the potential of ocular and upper-respiratory tract irritation. Interestingly, selenium is an essential element in the human diet and daily intakes of 500-860 µg of selenium are tolerated for long periods (Piscator, 1989).

Although elemental selenium has only a mild toxicity associated with it, hydrogen selenide is highly toxic. It has an Immediately Dangerous to Life and Health (IDLH) concentration of only 1 ppm. Hydrogen selenide resembles arsine physiologically; however, its vapor pressure is lower than that of arsine and it is oxidized to the less toxic selenium on the mucous membranes of the respiratory system. Hydrogen selenide has a TLV-TWA of 0.05 ppm to prevent irritation, and prevent the onset of chronic hydrogen selenide-related disease. To prevent hazards from

H₂Se, the deposition system should be enclosed under negative pressure and be exhausted through an emergency control scrubber. The same applies to the gas cabinets containing H₂Se cylinders in use.

The options for substitution, isolation, work practices, and personnel monitoring discussed for CdTe are applicable to CIS manufacturing as well. In addition, the presence of hydrogen selenide in some CIS fabrication processes requires engineering and administrative controls to safeguard workers and the public against exposure to this highly toxic gas.

Public Health and Environmental Issues

Potential public health issues are related to the use of hydrogen selenide in facilities that use hydrogen selenide as a major feedstock material. Associated hazards can be minimized by using safer alternatives, limiting inventories, using flow restricting valves and other safety options discussed in detail elsewhere (Fthenakis, 2001). Emissions of hydrogen selenide from process tools are controlled with either wet or dry scrubbing. Also, scrubbers that can control accidental releases of this gas are in place in some facilities. Environmental issues are related to the disposal of manufacturing waste and end-of-life modules; these are discussed in section 9 below.

7. GALLIUM ARSENIDE (GaAs) HIGH EFFICIENCY SOLAR CELLS

Occupational Health and Safety

MOCVD is today's most common process for fabricating III/V PV cells; it employs the highly toxic hydride gases, arsine and phosphine, as feedstocks. Similarly to silane and hydrogen selenide handling, the safe use of these hydrides requires several layers of engineering- and administrative-controls to safeguard workers and the public against accidental exposure. Such requirements pose financial demands and risks that could create difficulties in scaling-up the technology to multimegawatt levels. One part of the problem is that today's use of the hydrides in MOCVD is highly ineffective. Only about 2% to 10% are deposited on the PV panels, as a 10-50 times excess of V to III (As to Ga) is required. Metal-organic compounds are used more effectively, with their material utilization ranging from 20- 50%. In scaling up to 10 MW/yr production using MOCVD, the current designs of flat-plate III-V modules will require

approximately 23 metric tons of AsH₃, 0.7 tons of PH₃, 7 tons of metal organics, and 1,500 tons of hydrogen.¹ These quantities can be effectively delivered only with tube trailers, each carrying 2-3 tons of gases. The potential consequences of a worst-case failure in one of these tube trailers could be catastrophic. On a positive note, however, it is more likely that terrestrial systems will be concentrators, not flat-plates, because the former would be less expensive to manufacture. PV cells were shown to concentrate light between 100 and 2000 times. A possible practical strength is 500x concentrators; the material requirements for producing such concentrators are 600 times less than those needed for flat-plates.

The best way to minimize both the risks associated with certain chemicals and the costs of managing risk is to assess all alternatives during the first steps of developing the technology and designing the facility. These hydrides may be replaced in the future by the use of tertiary butyl arsine (TBAs) and tertiary butyl phosphine (TBP) (Komeno, 1994); it appears that there are no intrinsic technical barriers to growing PV-quality GaAs with TBAs and GaAsP, or GaInP₂ with TBP. Until substitutes are tested and implemented, however, it might be prudent to use arsine and phosphine from reduced-pressure containers, which are commercially available. Research efforts are being made in Europe (Juelich, 2001) to replace hydrogen by inert nitrogen. Apparently, there is no inherent reason to prohibit such a substitution. However, since molecular hydrogen decomposes to some extent, and atoms participate in the gas-phase chemistry, the PV research community is challenged with learning how to optimize III-V growth conditions with nitrogen.

8. OPERATION OF PV MODULES

The operation of PV systems does not produce any emissions. Although tiny amounts of semiconductor materials (e.g., 5 g per m²) are imbedded in the module, toxic compounds cannot cause any adverse health effects unless they enter the human body in harmful doses. The only

¹ These estimates are based on generic data applicable to the largest current MOCVD reactors (e.g., EMCORE Enterprise E400 and Aixtron AIX3000), and carry some unquantified uncertainty. Production for 24 hours a day by one of these reactors could provide about 100 kWp/year, so 100 such reactors will be needed for the 10 MW production-basis we are considering herein. Therefore, larger reactors will be needed at this scale, thereby introducing more uncertainty in our estimates.

pathways by which people might be exposed to PV compounds from a finished module are by accidentally ingesting flakes or dust particles, or inhaling dust and fumes. The photovoltaic material layers are stable and solid, and are encapsulated between thick layers of glass or plastic. Unless the module is ground to a fine dust, dust particles cannot be generated. All the photovoltaic materials examined herein have a zero vapor pressure at ambient conditions. Therefore, it is impossible for any vapors or dust to be generated during normal use of PV modules.

The potential exists for exposure to toxic vapors via inhalation if the modules are consumed in residential fires and people breath the smoke from the fire (Moskowitz and Fthenakis, 1990). However, common US residential fires are not likely to vaporize CdTe and GaAs layers; flame temperatures in roof fires are in the 800-900 °C range. The melting point of CdTe is 1041 °C, and evaporation occurs at 1050 °C in open air and at about 900 C under non-oxidizing conditions. The melting point of CdS is 1750 °C and of GaAs is 1238 °C. CIS started evaporating at 600 °C, but only a 20% weight loss was measured at 1000 °C (Steinberger, 1997).

The potential for significant photovoltaic material emissions may exist only in large externally fed industrial fires. In any case, the fire itself probably would pose a much greater hazard than any potential emissions of photovoltaic materials.

9. PHOTOVOLTAIC MODULE DECOMMISSIONING

PV modules will have to be decommissioned at the end of their useful life, 20 to 30 years after their initial installation. In decommissioning these devices, the principal concern will be associated with the presence of Cd in CdTe and CdS solar films and the presence of Pb in x-Si modules if they contain Pb-based solder. If these modules end in a municipal waste incinerator (MWI), the heavy metals will gasify and a fraction of those will be released in the atmosphere. If the MWI is equipped with ESP this fraction can be as small as 0.5% with the balance of the heavy metals remaining in the ash. The ash itself will have to be disposed of in controlled landfills.

If the modules end in municipal landfills, then the potential for the heavy metals to leach out in the soil exist. The leachability of metals in landfills, is currently characterized by two elution tests: the US-EPA Toxicity Characterization Leachate Profile (TCLP), and the German DEV S4 (Deutsches Einheitsverfahren). In these tests, small pieces ($<1 \text{ cm}^2$) of broken modules are suspended and rotated in an eluent for 24 hours. The metals present in the eluent are then measured and compared with limits prescribed by each testing protocol. If the metal concentration exceeds the limits, the modules are demonstrating the metal's leachability and may need to be recycled or disposed of in a hazardous waste landfill; if the metals are not leaching in excessive quantities the modules can be disposed of in a commercial landfill. Some early CdTe modules have failed the TCLP and the DEV tests (Fthenakis et al., 1995; 1996). Current CdTe modules produced by BP Solar and by First Solar are reportedly passing the TCLP. The same experience happened with x-Si; in exploratory tests with a small number of commercial x-Si modules, some modules fail the TCLP limit for Pb by about 30% (Eberspacher, 1998). Currently (October 2002), Astropower reports that their modules pass the TCLP test. Exploratory tests on CIS modules showed that they pass the test for Se. No tests are reported for GaAs modules. The a-Si modules contain very little hazardous material and easily pass the test. It should be noted that the TCLP test is conservative, as it requires breakage of the whole module to very small pieces, whereas the photovoltaic layer will be sandwiched between two layers of glass and reasonably isolated from the environment.

The ultimate solution to the PV waste and end-of-life management is recycling of useful materials. Recent studies showed that recycling, based on current collection/recycling infrastructure and on emerging recycling technologies, is technologically and economically feasible (Fthenakis, 2002). Reclaiming metals from used solar panels in large centralized applications can be done in metal smelting/refining facilities which use the glass as a fluxing agent and recover most of the metals by incorporating them in their product streams. In dispersed operations, small quantities and high transportation costs make this option relatively expensive. Research supported by the US DOE developed technologies for hydro-metallurgical separation that may be used in both small-scale (in-house) and large-scale recycling. These

options are being investigated by the photovoltaic industry as part of their pro-active long-term environmental strategy to preserve the environmental friendliness of solar cells.

10. CONCLUSION

The manufacture of photovoltaic modules uses some hazardous materials which can present health and safety hazards, if adequate precautions are not taken. Routine conditions in manufacturing facilities should not pose any threats to health and the environment. Hazardous materials could adversely affect occupational health and, in some instances, public health during accidents. Such hazards arise primarily from the toxicity and explosiveness of specific gases. Accidental releases of hazardous gases and vapors can be prevented through choosing safer technologies, processes, and materials, better use of materials, and by employee training and safety procedures. As the PV industry vigilantly and systematically approaches these issues and mitigation strategies, the risk to the industry, the workers, and the public will be minimized.

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