V. Fthenakis (BNL): Environmental, Health, and Safety Issues in Photovoltaic Technologies: A Summary (draft)

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 energy not only can help meet the growing worldwide demand for electricity, but it can do so without incurring the high economic and environmental costs of burning fossil fuels and installing power lines. Compared to burning coal, every gigawatt-hour of electricity generated by photovoltaics would prevent the emission of about 10 tons of sulfur dioxide, 4 tons of nitrogen oxides, 0.7 tons of particulates, and up to 1000 tons of carbon dioxide.

As with any energy source or product, there are environmental, health and safety (EHS) hazards associated with the manufacture, use, and disposal of solar cells. Although the PV industry uses far smaller amounts of toxic- and flammable-substances than many other industries, its use of hazardous chemicals can entail occupational and environmental hazards. Addressing EHS concerns is the focus of numerous studies at Brookhaven National Laboratory, under the auspices of the US Department of Energy's National Photovoltaic Program. More than 150 articles highlighting these studies are posted in our bibliography. Below is a summary of EHS issues pertaining to the manufacture of crystalline-Si, amorphous silicon, $CuInSe_2$ and CdTe solar cells. We will promptly send the full articles to the reader who wants more details.

Crystalline Silicon Solar Cells

Occupational Health Issues

The occupational health issues are related to chemical burns and the inhalation of fumes from hydrofluoric acid (HF) and other solutions of acids (e.g., HNO_3) and alkalis (e.g., NaOH) used for cleaning wafers, removing dopant oxide, and cleaning the reactor. Dopant gases and vapors (e.g., $POCl_3$, B_2H_3), also are hazardous when inhaled. $POCl_3$ is a liquid, but in a deposition chamber it can generate toxic P_2O_5 and Cl_2 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 (SiH_4) and its byproducts from silicon nitride deposition; these hazards are discussed in the a-Si section below.

Environmental Issues and Waste Minimization

The environmental issues are related to the generation of liquid- and solid-wastes during wafer slicing, cleaning, and etching, and processing and assembling of solar cells.

The PV industry has embarked upon programs of waste minimization and examines environmentally friendlier alternatives for solders, slurries and solvents. Waste minimization can be effective in crystalline Si-cell manufacturing, as demonstrated by successful programs in the laboratory and in manufacturing plants. For example, the Photovoltaic Device Fabrication Laboratory at Sandia National Laboratories reduced waste generation by 75% since 1990 by substituting re-using and recycling materials. By switching from ID saws to multiple-wire saws, Siemens Solar Corporation reduced by about 20% the caustic waste generated by etching that removes saw-damage after wafer slicing. Wire-sawn wafers require less etching to remove saw damage, and simultaneously, increase productivity as more wafers per inch of Si ingot are obtained. Additional options for waste minimization under investigation include recycling stainless-steel cutting wires, recovering the SiC in the slurry, and in-house neutralization of acid and alkali solutions.

Amorphous Silicon Solar Cells

Occupational Safety Issues

Amorphous silicon cells are currently by glow discharge deposition from mixtures of SiH_4/H_2, or $SiH_4/GeH_4/H_2$. Because of the low material utilization of deposition process (e.g., 10%), a relatively large volume of these gases is used. The main safety hazard of this technology is the use of SiH_4 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 %. If SiH_4 escapes in a partially confined space at flow rates above 300 lpm, an explosion is likely. Releases in open air usually ignite and burn smoothly; under appropriate circumstances, burning or flaring can be a mechanism for preventing an explosion. In addition to SiH_4, hydrogen used in a-Si manufacturing and in producing small quantities of crystalline-Si also is explosive. Earlier publications discussed SiH_4 and H_2 safety in detail. 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 in tube trailers to avoid frequently changing gas cylinders. 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.

Toxic doping-gases (e.g., AsH_3, PH_3) 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 were presented in previous publications.

Public Health and Environmental Issues

For a-Si facilities that use bulk silane, the potential consequences from a catastrophic release need to be assessed on a facility-specific basis. No significant environmental issues have been identified with this technology.

Cadmium Telluride Solar Cells

CdTe solar cells can be manufactured by several deposition techniques, such as close-spaced sublimation, electrodeposition, and spraying. The CdS films needed for heterojunction formation usually are formed by spray pyrolysis or solution growth. The efficiency of material utilization in these processes ranges from a high of 90% for electrodeposition, to a low of 5% to 10% for spray pyrolysis.

Occupational Health Issues

The occupational health hazards from Cd- and Te-compounds in various processing steps vary with the compounds' toxicities, their physical state, and the mode of exposure. No clinical data are available on human health effects associated with exposure to CdTe. Research at the National Institute of Environmental Health Sciences (NIEHS), compared the toxicity of CdTe, CIS, and CGS in animal experiments simulating ingestion and inhalation; CdTe had the highest toxicity and CGS the lowest. In the United States, the Occupational Safety and Health Administration (OSHA) regulate one of the parent compounds, Cd, that is considered both toxic and a lung carcinogen OSHA considers all Cd compounds (including CdTe) to be toxic.

In production facilities, workers could be accidentally exposed to Cd compounds through inhalation or ingestion from hand-to-mouth contact. Processes in which Cd compounds are used or produced as fine particles or fumes present larger risks. Spray pyrolysis with its very low utilization efficiency generates a large quantity of by-products and fine particles. Some of these materials will be deposited on the reactor's wall, requiring periodic scraping or chemical removal and cleaning. The large fraction remaining will be contained in the exhaust gas. In this type of process, hazards to workers may arise from preparing the feedstock, from fume and vapor leaks, and such maintenance operations. Since feedstocks in less fine form are inherently safer

Hazard management options include the use of CdTe and CdS in coarse particle or pellet sizes, process automation, isolation and local ventilation, air monitoring, personal protective equipment, and prudent work practices. These were presented in earlier articles. CdTe PV manufacturing facilities implement industrial-hygiene programs that include biomonitoring. In today's CdTe facilities, no detectable levels of cadmium have been reported from monitoring people during manufacturing and maintenance operations.

Public Health and Environmental Issues

The health of the public may be affected from chronic exposure to Cd compounds released to the environment as a by-product of different manufacturing steps, or as a waste from the uncontrolled disposal of spent photovoltaic modules. The magnitude of potential releases from manufacturing depends on the methods and controls implemented in each facility. For example, a 10 MWp PV fabrication plant, using electrodeposition with an efficiency of 90% in forming a 2 μm CdTe layer, would generate only 11 kg/yr of Cd and 12 kg/yr of Te, mostly as ions in solution. Therefore, electrodeposition poses minimal public-health hazards during routine operations. Only if accidentally the electrodeposition batch becomes contaminated, or a spill occurs, may additional material need treatment.

A less efficient deposition process (e.g., spray pyrolysis with an estimated efficiency of 10%), would generate about 950 kg of $CdCl_2$, CdO, HCl, H_2S and thiourea byproducts. Some of this material will be deposited on the reactor's walls, but most will be in a gaseous form in the exhaust stream. Under these assumptions, a 10 MW_p plant may generate emission flow rates of about 0.45 kg/hr during an 8 hr/day, for 250 days-per-year. These can be removed by 99+% efficiency by using HEPA filters or other pollution control equipment.

Copper Indium Selenide Solar Cells

Copper Indium Selenide ($CuInSe_2$, CIS) thin-films can be formed by several processes, including co-evaporation (i.e., physical vapor deposition) of Cu, In, and Se, and selenization of Cu and In layers in a H_2Se atmosphere. In the second method, Cu and In are deposited by electron-beam evaporation and sputtering techniques. Other options involve gallium sources and the formation of copper gallium selenide layers (CGS). Heterojunctions typically are formed with CdS film. The health and safety issues related to CdS were discussed in the context of CdS/CdTe solar cells, above.

Occupational Health and Safety Issues

There is limited information on the toxicity of CIS and CGS. As discussed earlier, limited animal testing comparing CdTe, CIS, and CGS showed that CGS has the lowest toxicity, and that CIS is somewhat more toxic than CGS but less so than CdTe. Measurements of airborne concentrations of copper, indium, and cadmium from mechanical scribing and deposition operations on CIS/CdS modules demonstrated that they were well below their threshold levels. .

The main safety issue in producing CIS cells is related to the highly toxic gas hydrogen selenide used as feedstock in some processes. Accident-prevention options were described in earlier articles.

Hazard Management and Environmental Issues

The options for substitution, isolation, work practices, and personnel monitoring outlined for CdTe are applicable to CIS manufacturing too. In addition, using hydrogen selenide in some CIS fabrication processes requires engineering and administrative controls to safeguard workers and the public from exposure to this highly toxic gas; these may include limited inventories, and flow-restricting valves. Routine and accidental emissions of hydrogen selenide from process tools can be controlled with wet or dry scrubbing. Such systems were discussed in earlier articles.

CONCLUSION

The manufacture of photovoltaic modules uses some toxic- and explosive-gases, corrosive liquids, and suspected carcinogens in solid form. Routine conditions in manufacturing facilities should not pose any threats to health and the environment. Quality control in these facilities demands especially clean conditions, with air concentrations of contaminants in occupational space much below the threshold exposure limits. However, as general guidance, all facilities working with hazardous materials should continue to control exposures by monitoring, employing engineering controls and personal protective equipment, and instituting good work practices.

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. This effort is especially important in view of the anticipated multi-hundred MW production facilities to meet the increased demand for PV.