

ENVIRONMENTAL HEALTH AND SAFETY (EHS) ISSUES IN III-V SOLAR CELL MANUFACTURING

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ABSTRACT

Large-scale manufacturing of III-V high-performance photovoltaics will require close attention to environmental, health and safety (EHS) issues. This paper reviews such issues and highlights challenges resulting from using large quantities of arsine, phosphine, and hydrogen in current MOCVD. These gases can be used safely when multi-layers of protection are implemented; these are discussed herein. The cost related to risk management must be considered in deciding upon new and larger manufacturing facilities. The best way to minimize both the risks associated with hazardous chemicals and the costs of managing risk is to consider safer delivery and/or alternative sources. Alternatives are outlined for scaling up production in the short-term and in the future.

1. INTRODUCTION

As III-V multi-junction photovoltaics (PV) reach new efficiency records, they raise interest for high-volume terrestrial applications, expanding their use well beyond current satellite applications. This paper reviews recent advances in the management of EHS issues associated with manufacturing III-V based solar cells, highlights some EHS challenges posed by scaling-up of these technologies, and suggests methods to mitigate EH&S hazards. A proactive EHS approach serves the industry well, as it promotes the early development of safer alternatives and the minimization of EHS costs. Voluntarily and effectively managing EHS risks before large-scale commercialization maintains the safe and environmentally friendly characteristics of PV.

2. ESTIMATES OF FEEDSTOCK MATERIALS

Material-utilization rates (defined as the fraction of the chemical precursor incorporated into the PV product) for hydride gases in metal-organic chemical vapor deposition (MOCVD, also referred to as metal organic vapor-phase epitaxy, or MOVPE) are very low (e.g., 1 to 5 mol%). These rates for metal-organics gases in MOCVD are about 20 to 50 mol %. Thus, the hydrides currently used in MOCVD are about 10 to 50 times in excess of the amount deposited on the PV pattern, and the metal-organics are at about 1 to 2 times (100% to 200%) excess. A fraction of the unused materials will be deposited on the reactor's walls, shields, and ducts, and the remainder, in gaseous form, can be collected by cold traps or similar devices. The carrier gas (currently H₂) is used at flow rates 20 to 60 times greater than those of the other process gases/vapors. In contrast, material utilization rates for molecular beam

epitaxy (MBE) deposition process are 40 to 70% mol% for Ga and 10 to 20 mol% for As.

Table 1 shows the estimated quantities of feedstock materials required for a 10 MW/yr production using MOCVD. They are based on today's material- utilization ratios and the cell's conversion efficiency and thickness. The underlying assumptions are: Electric conversion efficiency of 25 % for flat panels and 30% for 500x concentrators; 1 KW/m² solar insolation; 10% module loss; 5% material-utilization ratio for hydrides; 30% material-utilization ratio for metal-organics; cell thickness of 6 μm (total) for GaAs, and 1.5 μm (total) for GaInP₂. Material estimates for fabricating substrates are not included. As this table shows, the estimated requirements for 500x concentrators are lower than those of flat panels by a factor of about 600.

3. IDENTIFICATION AND CHARACTERIZATION OF HAZARDS IN MANUFACTURING III-V SOLAR CELLS

The manufacture of III-V photovoltaic cells involves hazards primarily associated with the raw materials used. The MOVPE process, particularly, utilizes metal-alkyl materials, such as trimethyl gallium, trimethyl aluminum, and trimethyl indium, or their triethyl derivatives. These precursors are pyrophoric liquids at ambient temperature, and storing and handling them are significant issues. MOVPE also uses hydride gases to lay down major constituents of the layers (arsine, and phosphine), and for dopants (hydrogen selenide, hydrazine, ammonia, dimethylhydrazine, silane, or disilane). These gases are toxic, flammable, or both. During processing, these gases may be accidentally released directly from leaking gas lines or reactors, or as reaction by-products. Because of their extreme toxicity, even small releases may adversely affect a worker's health. Details on the physical properties and regulatory exposure limits are summarized elsewhere [1]. These hydrides may be replaced in the future by the use of tertiary butyl arsine (TBAs) and tertiary butyl phosphine (TBP). We examined the advantages and difficulties of this substitution [1]. It appears that there are no intrinsic technical barriers to growing PV-quality GaAs with TBAs and GaAsP, or GaInP₂ with TBP. In the short-term, toxic hydrides could be supplied at reduced or internally regulated pressures.

Materials used for MBE generally are elemental solids that are not especially reactive under ambient conditions. However, precautions are required for handling arsenic, beryllium, and phosphorus. Arsenic and beryllium present toxic exposure hazards if powders or particulates containing them become airborne, while phosphorus is a fire hazard. Of the various hazardous materials used in

both MOVPE and MBE, arsenic stands alone as a chronic concern because it is a human carcinogen.

With the advent of nitrogen-doped systems and the consequent use of hydrazine and dimethylhydrazine, there are additional issues to consider. Both chemicals are strong reducing agents and flammable. Hydrazine also is

a potential carcinogen. In MOVPE systems, dimethylhydrazine is preferred as a source of nitrogen because it has a high vapor pressure and is easily incorporated into MOVPE systems [2].

Table I. Material Estimates for a 10 MW/yr MOCVD Facility

				Flat Plate	Concentrator (500x)
				44,444	37,037*
				Mass	Mass
Layer	Feedstock	Element	Ratio Layer	(kg/yr)	(kg/yr)
GaAs	Ga(CH ₃) ₃	Ga	0.48	4,160	6.9
(alternative)	Ga(CH ₂ CH ₃) ₃	Ga	0.48	5,682	9.5
GaAs	AsH ₃	As	0.52	16,463	27.4
GaInP ₂	Ga(CH ₃) ₃	Ga	0.28	610	1.0
GaInP ₂	In(CH ₃) ₃	In	0.47	1,052	1.8
GaInP ₂	PH ₃	P	0.25	669	1.1
AlGaInP	Al(CH ₃) ₃	Al	0.11	1	0.002
AlGaInP	Ga(CH ₃) ₃	Ga	0.29	4	0.007
AlGaInP	In(CH ₃) ₃	In	0.47	7	0.012
AlGaInP	PH ₃	P	0.13	2	0.004
In _{0.08} Ga _{0.92} As _{0.97} N _{0.03}	Ga(CH ₃) ₃	Ga	0.438	1,260	2.1
In _{0.08} Ga _{0.92} As _{0.97} N _{0.04}	In(CH ₃) ₃	In	0.063	189	0.3
In _{0.08} Ga _{0.92} As _{0.97} N _{0.03}	AsH ₃	As	0.496	6,699	11.2
In _{0.08} Ga _{0.92} As _{0.97} N _{0.04}	(CH ₃) ₂ NNH ₂	N	0.003	197	0.3
Hydrogen (50x dilution)				2,723,721	4,539.

* This is the total module area; the corresponding cell is 66.7 m²

4. HAZARD MANAGEMENT

GaAs semiconductor and PV manufacturers currently employ sophisticated engineered systems to isolate hazardous materials from the workplace and to monitor for potential employee exposures. These include secondary enclosures, ventilation systems, chemical detection, and neutralization systems, and automating delivery and process systems as much as possible. Administrative control options include limiting chemical inventories, training employees, and establishing safe operating procedures and emergency preparedness and response plans. For MOVPE and MOMB E manufacturers, three areas of major concern are storing and handling hydride gases and metal-organic liquids, managing liquid- and gas-effluents, and maintaining equipment. Management of hazards in manufacturing requires a combination of administrative, engineering, and personal hazard-control options. A checklist of such options that can be used in internal audits can be found elsewhere [1]. Below we discuss layers of protection that can minimize or reduce the hazards associated with these operations [3].

1. *Limiting inventories* to the minimum practical quantities proportionally reduces the inherent hazards associated with these materials.

2. *Prevention and minimization of releases* – Safety options to suppress a hazard when an accident-initiating event occurs include the following: inherently safer process designs, gas distribution and storage systems, early leak-detection, flow restricting- and isolation-valves, cooling systems and double-containment.

3. *Remotely operated cylinder valves* – These valves enhance safety by separating workers from hazards and allowing remote shutdown in an emergency; the valves can be integrated into a purge cycle.

4. *Toxic gas monitoring systems* – These systems can give an early warning and allow the process or source to be shut down before dangerous exposures occur.

5. *Flow restrictors* – Fail-safe equipment and valves, warning systems, and safety controls can reduce and interrupt gas leakage. Flow-restricting orifices in cylinder valves have become a common option in pressurized cylinders with highly toxic gases and pyrophoric gases (e.g., AsH₃, PH₃, SiH₄). These orifices can reduce the flow out of an open cylinder-valve by up to two orders of magnitude; therefore, they offer superb passive-flow reduction.

6. *Double containment in the form of double co-axial distribution lines and raceways*, is an important measure against leaks of toxic gases. In addition, secondary enclosures should be used for processes, and pollution-

control stations handling toxic vapors, to contain any fugitive emissions and divert them to pollution-control equipment. In small commercial and R&D facilities, process equipment often will be situated in negative pressure enclosures. Such a degree of isolation in future large production facilities will require complete automation of the deposition process. Isolating workers from the process in large-scale operations will require load locks between reaction chambers

7. *Redundancy of critical systems* – If a hazard analysis identifies accidents that can be caused by the failure of a single component, redundant components may have to be installed. Such critical components may include, but are not limited to, flow regulators, valves, exhaust fans, pumps, and compressors. For example, reactor rooms and hazardous-gas rooms and cabinets must be equipped with a dedicated exhaust ventilation system with a redundant fan. Both fans should be connected to an emergency power supply and designed so that the auxiliary fan is automatically switched on if the primary one fails.

8. *Safe Operating procedures* - The importance of administrative options and procedures cannot be overemphasized. In the chemical industry, many accidents have happened not because safety-engineering systems were lacking, but because safe procedures and preventive strategies were not followed. Training personnel is extremely important in all facilities. Written operating- and maintenance-procedures should always be in place, and strictly adhered to at all times. An operator who does not follow a standard written procedure and does not go through a checklist can become complacent. Also, periodic internal audits or third-party audits of operations are recommended.

5. CHALLENGES AND OPPORTUNITIES

1. Use of arsine and phosphine in high volumes

In current manufacturing of III-V photovoltaics by MOCVD, relatively high quantities of arsine are used. A facility with a 10 MW/yr production of flat-panel III-V modules will consume about 23 tons of arsine a year, while a 10 MW/yr production of 500x concentrators will require only 38 kg of arsine per year. The quantities required in flat-panel designs could present terrible risks. We note that arsine is almost as toxic as methyl isocyanate (MIC), based on their TLV-TWA, and that a release of 40 tons of the latter in Bhopal killed 3,000 people and injured 200,000 more.

Like many other highly toxic or explosive gases used in the chemical industry, arsine can be used safely if appropriate hazard control and risk management- options are implemented. However, the cost related to risk management has to be considered in deciding upon new technologies and facilities. 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 .

Opportunity: These hydrides may be replaced in the future by the use of tertiary butyl arsine (TBAs) and tertiary butyl phosphine (TBP). It appears that there are no intrinsic technical barriers to growing PV-quality GaAs

with TBAs and GaAsP, or GaInP₂ with TBP [4,5,6]. In addition to being liquid and much less toxic than the hydrides, TBAs and TBP are likely to be used at lower flow-rates than arsine and phosphine, thereby reducing storage and delivery requirements, process effluents, and waste. These benefits also translate to reductions in capital- and operating-costs in future facilities. A drawback is that TBAs and TBP are more expensive than the hydrides they replace, to the extent that using less material still results in higher operating cost. In addition, re-optimization of the process may be needed since doping efficiency and growth rate as a function of temperature may differ. These drawbacks that inhibit changes in current facilities could easily be implemented in future, large-scale commercial applications. Consequently, the cost of the more expensive materials would likely fall with increasing production volumes.

Until substitutes are tested and implemented, however, it would be prudent to use arsine and phosphine from reduced-pressure containers, which are commercially available.

In-situ generation of arsine is another option that would reduce transportation and storage risks; such generation has been the subject of investigation and small systems are commercially available [7].

2. Use of large volumes of hydrogen gas

Large volumes of hydrogen are required in today's III-V manufacturing. At the considered reference production level of 10 MW/yr, the quantities required are 1,500 ton/yr for flat-panels and 2.5 ton/yr for 500x concentrators.

Hydrogen is flammable and potentially explosive in concentrations of 4 % to 75% in air. If hydrogen is mixed with small amounts of silane, which is used as a dopant, its upper flammability limit increases to 98%, and the pyrophoric silane can act as a source of ignition for the mixture.

Hydrogen is used widely and safely in the chemical, semiconductor and other industries. However, its potential for flammability/explosiveness has to be considered in conjunction with the toxicity of the metal hydrides discussed earlier. Large separation zones and expensive delivery systems will be required to effectively keep these gases apart. The capital costs in ensuring safety in large III-V facilities, and potential losses in production, could be significant. For example, hydrogen sensors and automatic shut-offs would be required to immediately interrupt the process and disconnect all ignition sources in case of an alarm. Considering the corresponding high costs of management and of potential liability, the search for alternatives is wise.

Opportunity: Research efforts are being made in Europe [8] 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. This challenge is well worth taking. In addition to its safety advantage, nitrogen is 14 times heavier than hydrogen, a feature that is positively reflected in the decomposition of the source materials [8]. Bonds break more easily upon collision with heavy nitrogen. Other physical properties lead to a more

homogeneous distribution of heat in the region of the substrate or of the starting materials, both of which significantly improve the quality of the epitaxial layers [8].

6. CONCLUSION

Large-scale manufacturing of III-V high-performance photovoltaics will require close attention to environmental, health and safety (EHS) issues. The main issues arise from using large quantities of arsine, phosphine, and hydrogen in current MOCVD processes. These gases can be used safely when appropriate options for hazard control and risk management are established. However, multi-layers of protection are needed, and the cost related to risk management must be considered in deciding upon new and larger manufacturing facilities. The best way to minimize both the risks associated with hazardous chemicals and the costs of managing risk is to consider safer delivery and/or alternative sources.

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