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Toxic Materials Used in Thin Film Photovoltaics and Their Impacts on Environment

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Abstract

Photovoltaic industry has proved to be a growing and advantageous source of energy as it can be renewable, sustainable, reliable and clean. Significant improvements have been made in materials used and the production processes to reduce the costs, and to avoid possible issues induced by some hazardous materials. However, some health and environment challenges last, which must be overcome to make this technology a source of truly clean energy. This chapter provides an overview on the major environmental impacts of thin film technology associated with the use of toxic materials and the chemicals in the manufacturing processes. A summary of Environmental, Health and Safety issues associated with some thin film technologies like copper indium gallium diselenide (CIS/CIGS), cadmium telluride (CdTe) and amorphous silicon (a-Si) is done, in order to investigate potential infections induced by the environmental release of trace elements, usually coming from chemical vapor inhalation and eventually accidental spills during the manufacturing processes, on the health of humans and animals. Potential solutions will be provided to prevent some environmental issues.

Keywords: hazardous materials, toxic chemicals, manufacturing processes, environmental impacts, thin film technology, recycling, waste minimization

1. Introduction

The sun undoubtedly is known to be an incredible and inexhaustible source of energy, allowing the generation of electricity and showing distinct environmental advantages over conventional source. Once took out from the manufactory, photovoltaic (PV) systems do not produce any toxic gas emissions, any noise or greenhouse gases. However, as with any industrial product, there are health and environmental impacts associated with the manufacture of solar cells and solar panels. The PV industry uses harmful and flammable substances, although in small amounts, which can involve environmental and occupational risks. The main environmental impacts of solar panels are associated with the use of land, water, natural resources, hazardous materials, life-cycle global warming emissions etc.

The solar cell manufacturing process involves a number of harmful chemicals. These substances, similar to those used in the general semiconductor industry, include sulfuric acid, hydrogen fluoride, hydrochloric acid, nitric acid, 1,1,1-trichloroethane, and acetone. The amount and type of chemicals used depends on the

type of cell and the technology used [1]. Thin film PV (TFPV) technology contains a higher number of toxic materials than those used in traditional silicon PV technology, including indium, gallium, arsenic, selenium, cadmium, telluride [2]. These materials must be handled and disposed of properly, to avoid with time serious environmental and human health problems.

The current idea of the industry is to ensure that these highly valuable and often rare materials are recycled, to foresee the pollution hazards. This chapter deals with the possibility of chemicals used in PV cell manufacturing process to be released to air, water surface and the environment. An overview on the TFPV industry will be done to understand how TFPV cells and modules are designed and fabricated. Some hazardous materials and chemicals used in the manufacture of TFPV technology and their relative toxicity to human health and environment will be produced. Finally, some solutions to anticipate long term harmful impacts of these products will be proposed.

2. Overview of the thin film photovoltaic industry

2.1 Development of thin film solar cells

The ultimate goal in the manufacturing of a PV module is widely determined by the cost per unit power output. The development of new PV technologies based on thin film materials has been led by the need for cheaper and more efficient semiconductor materials. Thin film solar cells (TFSCs) have the potential for rapid growth and low cost production. They have several advantages in manufacturing processes compared to conventional silicon solar cells such as [3]:

- Cheaper to produce
- Lower consumption of materials
- Fewer processing steps
- Availability of materials
- Simplified materials handling
- Can be deposited on many different substrates
- A variety of deposition technique
- Process lends itself to automation
- Integrated, monolithic circuit design instead of assembly of individual solar cells into final products

TFSCs are typically made up of thin layers of semiconductor materials, for instance cadmium or zinc sulfide, glass, and a contact material. The materials used in the design of TFSCs include polycrystalline silicon, amorphous silicon (a-Si), and semiconductor compounds. Semiconductor compounds include cadmium sulfide (CdS), cadmium telluride (CdTe), copper sulfide (CuS₂), copper indium diselenide (CIS), copper indium gallium diselenide (CIGS), copper gallium diselenide (CGS), germanium (Ge), and gallium arsenide (GaAs) [4]. Other semiconductor compounds like copper zinc tin sulfide (CZTS), copper zinc tin selenide (CZTSe)

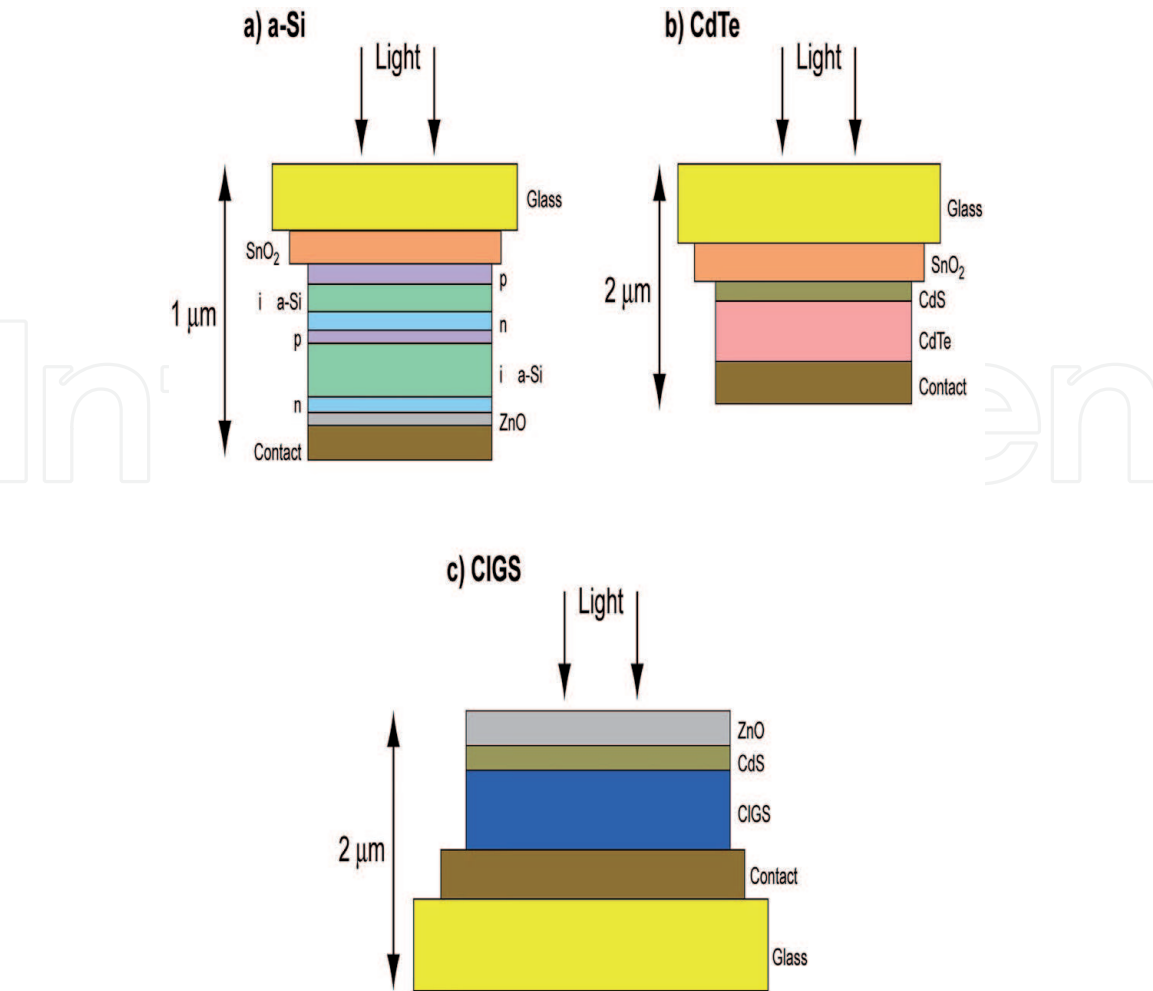


Figure 1.
Examples of thin-film solar cells structures: (a) amorphous silicon, (b) cadmium telluride, and (c) copper indium gallium diselenide [5].

and copper iron tin sulfide (CFTS) have proved over recent years their potential to convert the solar radiation into electricity and are being developing in laboratories. In these solar cells, the n material can be made of CdS or ZnS, while the p material can be made of CuInSe₂ (CIS) or Cu₂ZnSnS₄ (CZTS). Gallium arsenide (GaAs) solar cells can use aluminum, indium, or phosphorous as p or n-type materials. In **Figure 1**, are shown typical traditional structures of a-Si, CdTe and CIGS thin film solar cells.

To achieve better conversion efficiency, the active layer of the cell should have its band gap energy within the optimum range of 1.1–1.8 eV [5, 6]. Amorphous silicon is just at the rear end of the optimum band gap range at 1.8 eV [6]. Ge (0.66 eV) and CdS (2.45 eV) for example, have band gap energies outside of the optimum range, which means that those materials show limited conversion efficiencies. Ge is usually used to improve conversion efficiency of amorphous silicon cells [7], whereas, CdS is used to improve conversion efficiency in CIS and CdTe cells [8]. In general, on the basis of the band gap, materials used in TFSCs such as GaAs and CdTe have higher theoretical conversion efficiency than crystalline silicon, as they show band gap energies close to the optimum value of approximately 1.5 eV [8].

Thin film materials have higher light absorption capabilities than crystalline silicon as they have a direct absorption profile. Therefore, they can be shaped thinner than conventional silicon which must cut on wafers. For example, $1\ \mu\text{m}$ of a GaAs direct semiconductor is sufficient to absorb the same quantity of the photons light than $100\ \mu\text{m}$ of an indirect silicon semiconductor. CIS or CIGS are direct band gap polycrystalline materials with high absorption coefficients in the order of $10^5\ \text{cm}^{-1}$, allowing the active layer only to be about $2\ \mu\text{m}$ [9]. Some CIGS-based solar cells

usually introduce a thin film of CdS on the top of the CIGS layer as a buffer layer, in order to ensure the electrical transition between the CIGS layer and the window layer (the front of the cell). Zinc, molybdenum, tin, and aluminum are used in these cells as front and back contacts or components of the layers.

The efficiency of the energy conversion process is determined by the materials parameters and technical design of the solar cell. Theoretical research on TFSCs indicates that, devices could achieve conversion efficiencies up to 25% under lab conditions [10]. In addition, efficiencies of cells can substantially increase by stacking interconnected cells, which could achieve up to 41.9% for tandem (two cells) and 50% for multi cells [11]. Concentrator systems and devices used to track the sun can be another way to improve efficiency of PV systems. For example, the use of terrestrial concentrator GaAs/Ge solar cells achieved conversion efficiency up to 36.9% [12]. The first TFSCs had conversion efficiencies of 8–12% [4]. **Table 1** presents the record lab efficiencies for cells and modules of different technology. Note that these are just record lab efficiencies, not commercially guaranteed efficiencies.

Crystalline silicon-based technologies continue to dominate the world market share with about 95% of the total production in 2017 [26]. The share of multi crystalline technology is now about 62% of total production [26]. In 2017, the market share of all thin film technologies counted for about 5% [26]. Amorphous silicon holds 4% of this part followed by cadmium telluride with 1%. The others, especially CIGS and thin film silicon, although already available at the commercial stage still represent a negligible part of the market.

Thin film materials such GaAs, GaInP₂, and CIGS have been investigated for the development of concentrator cells. Concentrator cells have been designed to increase the intensity of the solar radiation on PV cells through the use of optical lenses. They consist of optical lenses, a cell assembly, a housing element, a secondary concentrator to reflect off-center light rays onto the cell, a mechanism to dissipate excess heat produced by concentrated sunlight, and various adhesives and contacts [27]. The main advantages of concentrator cells are: they reduce the number or size of solar cells used, enhance the power output, and enhance the solar cell efficiency under concentrated sunlight [8]. A conversion efficiency of 32% has been reported for concentrator cells [28]. This other way to increase the cells efficiency nevertheless presents some drawbacks: they involve expensive tracking systems and

| Technology | Cell efficiency (%) | Module efficiency (%) | Description cell/module |
|---------------------------|---------------------|-----------------------|--|
| Crystalline silicon | 26.7 ± 0.5 | 24.4 ± 0.5 | Kaneka [14]/Kaneka (10 ⁸ cells) [14] |
| Multi crystalline silicon | 22.3 ± 0.4 | 19.9 ± 0.4 | FhG-ISE [15]/Trina solar (120 cells) [16] |
| CIGS | 21.7 ± 0.5 | 19.2 ± 0.5 | Solar Frontier [17]/Solar Frontier (70 cells) [18] |
| CdTe | 21.0 ± 0.4 | 18.6 ± 0.5 | First Solar [19]/First Solar [20] |
| Thin film silicon | 10.5 ± 0.3 | – | CSG solar [21]/ |
| Amorphous silicon | 10.2 ± 0.3 | 9.1 | AIST [22] |
| GaAs | 28.8 ± 0.9 | 25.1 ± 0.8 | Alta devices [23]/Alta devices [24] |
| CZTS | 10.0 ± 0.2 | – | UNSW [25] |

Table 1.
Confirmed terrestrial record cell and module efficiencies measured under the global AM 1.5 spectrum (1000 W/m²) at a cell temperature of 25°C (IEC 60904-3: 2008, ASTM G-173-03 global) [13].

more precise controls than the traditional flat plate systems, they generate higher operating temperatures, which can decrease the long-term stability and lifetime of the PV cells. Concentrator cells were first designed for space applications, but modules for terrestrial applications are already commercially available [8].

2.2 The manufacturing processes

It is known that the complexity of solar cells and modules manufacturing strongly raises their costs. Conventional silicon is handled in different many ways, complicating therefore fabrication processes. First, silicon raw material is melted at very high temperatures and grown into a silicon ingot. Then, the ingot is molded and sawn into individual wafers for cell processing [3]. After testing, individual cells are connected together in a suitable electrical configuration. Finally, the connection circuit is hermetically packaged in a weatherproof flat container, typically with an aluminum frame. **Figure 2** shows the flowchart describing the complete process to manufacture a conventional crystalline silicon-based module. The process requires more than 20 separate steps before a module is complete.

In contrast to crystalline silicon, thin film manufacturing steps are very simple. For example, the connection of the circuit from individual cells is removed. Instead of processing and handling ingots, wafers and cells, the final circuit is directly fabricated on a single large substrate, usually glass [3]. Thin film circuits require

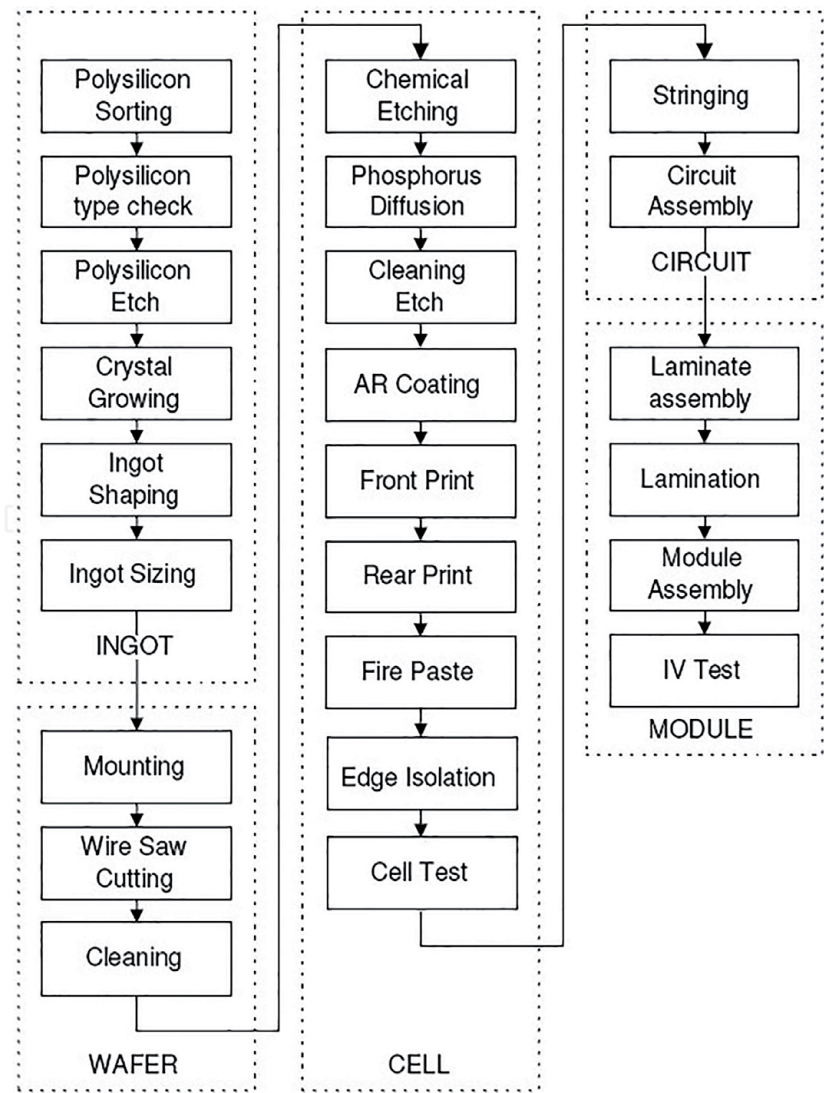


Figure 2.
Different process steps for fabrication of crystalline silicon modules [3].

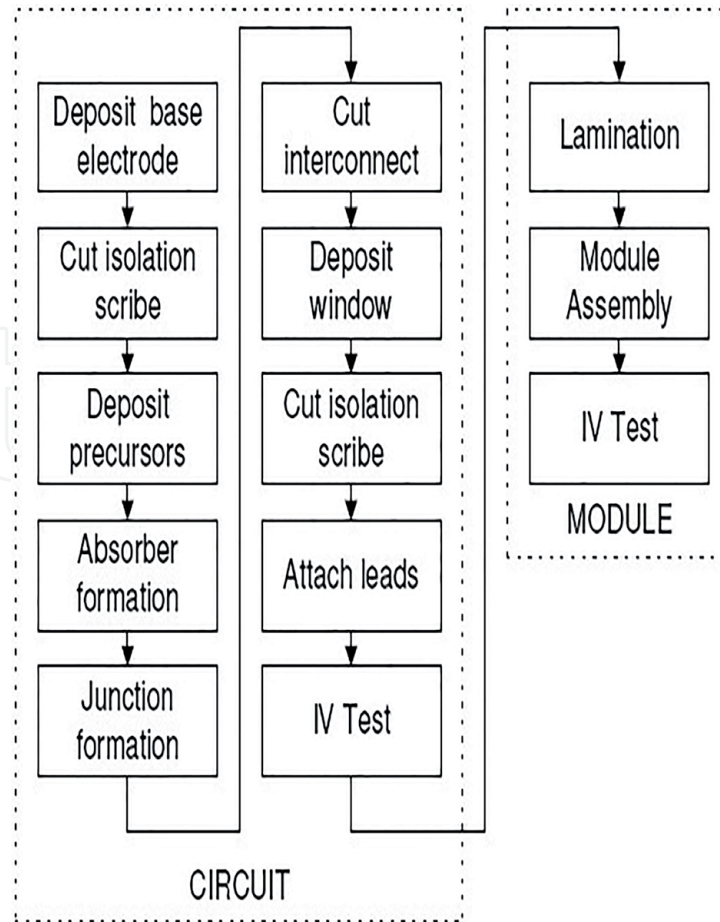


Figure 3.
Different process steps for fabrication of thin film modules [3].

the deposition of three main layers namely a back contact or a base electrode layer usually deposited on glass, a semiconductor layer and a transparent window layer also acting like a conductor front contact as it is typically seen in **Figure 1(c)**. The semiconductor layer is divided into the absorber and buffer layers. The stack of the absorber layer in one side and the buffer and window layers in another side creates an efficient n-p PV heterojunction. In TFSCs, the crucial phenomena of charge carriers generation and separation occur within the absorber; this layer therefore plays an important role in defining the electrical output parameters of the solar cell and usually confers its name to the technology. We have for instance CdTe for cadmium telluride based PV technology, CIGS for a range of chalcopyrite based PV technology and CZTS for a range of kesterite-based PV technology [3, 29].

An important advantage of thin film PV module manufacturing is found in the monolithic series interconnection of individual cells. Thin film cells are interconnected through simple patterning steps integrated into the processing line. The patterning steps achieve the integrated series interconnection from cell to cell on the circuit as shown in **Figure 3**. Three scribes between deposition steps complete the cell definition, separation and interconnection. A transparent conductive oxide (TCO) can also be integrated to the system for photon absorption optimization [29].

3. Chemicals and materials used in the fabrication of thin film cells and modules

To produce thin film PV devices, a variety of chemicals and materials is used. The types and quantities of chemicals used will depend on the type of the

| CIS | CIGS | CZTS | GaAs | CdTe | Cu ₂ S | a-Si |
|-------------------|------------|-------------------|-------------------|------------------|-----------------------|-----------------------|
| Cadmium | Cadmium | Cadmium | Arsenic | Cadmium chloride | Ammonium chloride | Acetone |
| Copper | Copper | Copper | Arsine | Cadmium | Ammonium fluoroborate | Aluminum |
| Hydride gas | Gallium | Hydrogen selenide | Gallium | Molybdenum | Cadmium sulfide | Chloro-silanes |
| Hydrogen sulfide | Indium | Hydrogen sulfide | Hydrochloric acid | Nickel | Chromate coating | Diborane |
| Hydrogen selenide | Molybdenum | Molybdenum | Methane | Sulfur | Copper | Hydrochloric acid |
| Indium | Selenium | Selenium | Phosphine | Tellurium | Cuprous chloride | Hydrofluoric acid |
| Molybdenum | Zinc | Thiourea | Trichloroethylene | Thiourea | Gold | Hydrogen |
| Selenium | | Tin | Triethyl gallium | Tin | Hydrochloric acid | Isopropanol |
| Zinc | | Zinc | Trimethyl gallium | | Hydrogen sulfide | Nitrogen |
| | | | | | Methanol | Phosphine |
| | | | | | Nickel | Phosphoric acid |
| | | | | | Nitrogen | Silane |
| | | | | | Polyvinyl butyral | Silicon tetrafluoride |
| | | | | | Silicon monoxide | Silicon |
| | | | | | Sodium chloride | Sodium hydroxide |
| | | | | | Tantalum pentoxide | Tin |
| | | | | | Zinc | |
| | | | | | Zinc fluoroborate | |

Table 2.
Chemicals and materials involved in the manufacturing process of different thin film PV technology [8].

technology and the type of cell being produced. One can found also some variability in the use of chemicals for producing the same type of PV solar cells by different PV manufacturers. This means that each manufacturer has its own recipe to produce a type of solar cell. **Table 2** gives a general list, but non-exhaustive of chemicals and materials used in the manufacturing of some TFSCs and modules.

In TFPV technology, only few amounts of semiconductor materials are necessary to produce thin or ultra-thin layers of a solar cell. The amounts of chemicals and materials used in the manufacturing of TFPV devices vary depending on the type of cell being produced. For example, the quantity of cadmium in a CIS PV module is evaluated at 0.04 g/m² and in a CdTe PV module at 5 g/m² [30]. Research allowed reducing significantly the amount of cadmium in PV devices by using light-trapping methods [8]. These methods have led to reduce the thickness of CdTe layers from 2 to 0.5 µm, corresponding to 5.5 and 0.55 g/m² amount of cadmium, respectively [8]. A diversified number of acids and corrosive liquids are used sensibly in large quantities during the manufacturing processes. These chemicals, similar to those used in the general semiconductor industry, and including sulfuric acid, hydrochloric acid, hydrogen fluoride and nitric acid are primarily used for cleaning wafers in the case of crystalline silicon or for removing impurities from raw

| Material | Source | DOT hazard classification | Critical effects |
|-------------------------|-----------------------------------|---------------------------------|----------------------------------|
| Arsenic | GaAs | Poison | Cancer, lung |
| Arsine | GaAs (CVD) | Highly toxic gas | Blood, kidney |
| Cadmium | CdTe, CdS, CdCl ₂ | Poison | Cancer, kidney, bone |
| Diborane | a-Si dopant | Flammable gas | Pulmonary |
| Diethyl silane | a-Si deposition | Flammable liquid | |
| Diethyl zinc | | Pyrophoric liquid | |
| Dimethyl zinc | | Spontaneously combustible | |
| Hydrochloric acid | a-Si, GaAs, Cu ₂ S/CdS | Corrosive material | |
| Hydrofluoric acid | a-Si | Corrosive material | |
| Hydrogen | a-Si | Flammable gas | Fire hazard |
| Hydrogen selenide | CIS | Highly toxic gas | Irritant |
| Hydrogen sulfide | CIS, Cu ₂ S/CdS | Flammable gas | Irritant, Fire hazard |
| Indium | CIS, CIGS | Not regulated | Pulmonary, bone |
| Methane | GaAs | Flammable gas | Fire hazard |
| Molybdenum hexafluoride | | Toxic and corrosive gas | |
| Oxygen | x-Si | Gaseous oxidizer | |
| Phosphine | a-Si dopant | Highly toxic and pyrophoric gas | Irritant, fire hazard |
| Phosphorus oxychloride | x-Si | Corrosive material | Irritant, kidney |
| Selenium | CIS, CZTS | Poison | Irritant |
| Silane | a-Si deposition | Pyrophoric gas | Irritant, fire, explosion hazard |
| Silicon tetrafluoride | a-Si deposition | Toxic and corrosive gas | |

| Material | Source | DOT hazard classification | Critical effects |
|-------------------------|--------|------------------------------------|------------------|
| Tellurium | CdTe | Not regulated | Cyanosis, liver |
| Tertiarybutyl arsine | | Pyrophoric and highly toxic liquid | |
| Tertiarybutyl phosphine | | Pyrophoric liquid | |
| Trimethyl aluminum | | Pyrophoric liquid | |
| Trimethyl gallium | GaAs | Pyrophoric liquid | |
| Tungsten hexafluoride | | Toxic and corrosive gas | |

Table 3.
Hazard classification of chemicals typically used in PV module manufacturing [31, 32].

semiconductor materials. Solvents like acetone, ethanol and 1,1,1-trichloroethane are also used for cleaning in different steps of the fabrication processes.

Many hazardous materials as well as explosive and toxic gases are involved in the manufacturing processes of thin film PV cells and modules. **Table 3** presents a general list of some materials and chemicals and their description, classified as hazardous by the Department of Transportation (DOT) in USA and used in the whole PV industry. But the amounts and recipes vary from one manufacturer to another. Moreover, it is possible that some of these chemicals may no longer be used for PV devices production as the fabrication processes are constantly changing and evolving [8].

The wastes generated by the semiconductors materials used in TFPV industry are in general non-negligible. Acids and solvents each represented about one-third of the total wastes by weight (about 7000 tons) [33]. About 35% of the semiconductor wastes were evacuated as diluted acid solutions to sewage treatment plants and 37% were sent to offsite treatment facilities. About 27% of the total wastes were released to the atmosphere. Only 0.8% of the total wastes were discharged directly to the surface water and 0.015% to the landfills [33].

4. Potential health and environmental hazards

The manufacturing of PV devices includes some chemicals which can be toxic or harmful to the humankind. The potential for health concerns is not only depend on the material harmful characteristics, but also on certain conditions which must be taken into account. For example, in addition to harmful characteristics of the chemicals, their concentration must be high enough to constitute a real problem in a given environment: a human or an animal must be in the surroundings of where the device or compound is used; there must be a total exposition process from the compound to the environment. Most often, the primary persons exposed to the PV manufacturing residues are the plant workers. The easiest exposure route for workers is inhalation of vapors or dusts and also via direct contact if spills occur [8]. Another route for workers to be infected by chemicals resulting from manufacturing processes could be accidental ingestion. The ones outside a manufacturing environment could be infected by chemicals via inhalation from stack emissions, elusive air emissions or from accidental release after fire or explosion [8]. But the exposure of nearby residents or other workers would be less than the plan workers because the chemicals would be dispersed in the ambient air after their emission. There are possibilities for lands containing spent PV modules to pollute the environment. For example, at the surroundings of spent PV modules, groundwater seepage could reach a drinking water source or river; but in both cases, there would be dilution

(not totally) of the waste before the water was used. In short, any vapor emissions or groundwater seepage would be diluted by the ambient air or by the water before reaching nearby residents.

It is well known that the fabrication of PV cells and modules needs the use of more or less large quantities of solvents and acids for synthesis and cleaning, gases for depositing ultra-thin film of semiconductors materials and metals according to the type of PV cell or module being fabricated. Most of these chemicals are highly toxic and harmful for humans and environment. Here are discussed some health and environment issues caused by chemicals hazards related to materials' toxicity, flammability, explosiveness, and carcinogen nature. Below is a summary of potential health and environmental issues concerning the manufacture and the use of some thin film technologies such as CdTe, a-Si and CI(G)S.

4.1 Cadmium telluride (CdTe)

The manufacturing of CdTe solar cells can cause occupational health risks associated with the toxicity of the main constitutive materials such as CdTe, CdS, and cadmium chloride (CdCl_2). Since cadmium compounds are usually used in powder and in liquid form, the primary route of exposure in manufactory settings is inhalation of cadmium-containing vapors or dust or ingestion of spills if this occurs. Processes in which cadmium compounds are used or produced in the form of fine fumes or particles present more risks to health, because they promote the absorption of these fine particles by the lung and thus can cause lung cancer. A long-term exposure can also have harmful effects on bone and kidney [32]. In addition, the inhalation of cadmium-containing vapors or dusts can result in metal vapor fever, pneumonitis, pulmonary edema, and finally death [32]. Since cadmium is produced primarily as a by-product of zinc mining, the levels of Cd production is fixed by the levels of zinc production. Because Zn is produced in large amounts, considerable amounts of Cd are also generated as by-product, without taking into account the amount used or required in PV technology. If the amount of Cd generated as a by-product of zinc is not totally absorbed by the whole market, it is discharged to the environment as hazardous waste. Thus, encapsulating Cd in CdTe for PV modules fabrication could be a trusty way to preserve the environment of hazards that can cause free elemental Cd. CdTe is more stable and insoluble to water; as such, it may be less toxic or harmful than free elemental Cd.

CdTe and CdS thin films are solid and are packaged into thick layers of glass or a waterproof container. At ambient conditions, the vapor pressure of CdTe is zero. Therefore, it is impossible for any vapors or dust to be released when using CdTe PV modules. The only or the more plausible way for cadmium to be released and absorbed by residents is via consumed modules in residential fires. Even in this way, flame temperatures in residential fires typically 800–1000°C, are not sufficient to vaporize CdTe [34]. The melting point of CdTe is 1041°C, and evaporation starts at 1050°C. The melting point of CdS is 1750°C [34]. Previous studies showed that CdTe releases are not probable to happen during residential fires or accidental breaks [35–37]. The potential for CdTe emissions could occur only in the case of industrial fires or from incinerating spent PV modules. In the first case, the fire itself probably would cause much greater risk than any potential Cd emissions [38]. The second case can happen only if CdTe modules end in waste-incineration streams [32].

4.2 Amorphous silicon (a-Si)

Amorphous silicon based solar cells are usually fabricated using the plasma enhanced chemical vapor deposition (PECVD) technique. Silane gas (SiH_4), mainly

used as precursor, is extremely pyrophoric and represents the main safety hazard of this technology. It can spontaneously ignite for lower concentrations ranging from 2 to 3%, depending on the carrier gas. Due to the high pyrophoric nature of silane and even for concentrations lower than 2% in the carrier gas, pyrophoric footprints can be found locally if mixtures are not complete. Mixtures could be metastable and ignited after a certain time, for silane concentrations greater than 4.5% [32].

Amorphous silicon solar cells contain a large concentration of hydrogen atoms about 10%, as they are crucial for the material electronic properties [3]. But, the technology usually refers to use the words “amorphous silicon” instead of “hydrogenated amorphous silicon (a-Si:H),” because “unhydrogenated amorphous silicon” is of no use in electronic devices [3]. Hydrogen used in amorphous silicon manufacturing is explosive and flammable [32]; therefore, it is necessary for PV manufacturers to use highly sophisticated gas handling systems to minimize and even avoid the risks of fire and explosions. One efficient way to overcome these hazards is to store silane and hydrogen gases in bulk from tube trailers to avoid changing gas cylinders. Others toxic gases such as arsine (AsH_3), phosphine (PH_3) and germane (GeH_4), used as doping-gases in the amorphous silicon manufacturing cannot pose any serious hazards to the public health or the environment if they are used in very small amounts. However, leakage of these gases should be avoided because it could cause significant occupational risks.

4.3 Copper indium (gallium) diselenide (CI(G)S)

CIGS thin films can either be deposited by the thermal co-evaporation of the constitutive elements, or by the fast deposition of metal precursor layers which then react in a subsequent processing step to form the final compound [3]. In CIGS TFSCs, a very thin film of cadmium sulfide (CdS) is deposited by chemical bath method and acting as a buffer layer. However, CIGS solar cells freed of toxic cadmium have already been successfully produced [39]. The toxicity of copper, indium, gallium, and selenium is considered benign. In addition, elemental selenium is capital in the human nutrition; daily absorptions of 500–860 μg of selenium are acceptable for long periods [40]. Although elemental selenium has only a moderated toxicity associated with it, hydrogen selenide (H_2Se) used in the manufacture of CIGS TFSCs is highly toxic and is dangerous to life and health [32]. Hydrogen selenide acts like arsine gas on human body even though its vapor pressure is lower than that of arsine. Moreover, it can oxidize to the less toxic selenium on the mucous membranes of the breathing system. The manufacturing system should be enclosed under negative pressure, and should be exhausted through an essential control scrubber to prevent hazards from highly toxic H_2Se gas. Associated hazardous chemicals can be minimized by using safer alternatives methods like flow restricting valves and other safety options presented in detail by Fthenakis [41]. Some studies have shown that CIS and CGS have mild systemic toxicity and have shown no effects on ovulation, reproduction, liver and kidney [8]. But CIS was found to be less toxic than CGS and CdTe [8].

5. Methods to prevent environmental concerns

The releases of chemicals in form of vapors or spills from the PV industry constitute the real hazards to the public health and to the environment. A variety of treatment methods or ways have been developed to manage or to minimize wastes produced by PV industries. These methods include waste minimization and recycling of PV modules at the end of their life.

5.1 Waste minimization

Waste minimization is usually employed in the semiconductor industry, and is also appropriate to the PV sector. It includes reuse of rinse water after treatment, shifting toward less toxic chemicals as possible, control of spills and leaks, reduction of vapor losses, and selection of process that use fewer hazardous chemicals [8]. Some of these methods are not broadly used in the semiconductor sector due to the requirement of highly purified materials. The main goal to reuse processed chemicals in the semiconductor sector is to limit amounts of some harmful solvents and acids. A lot of changes have been successfully made in the manufacturing processes such as using less toxic materials instead of hazardous and replacing acid bath processing by acid spray in cleanings [33]. Splitting of spent solvents by type like chlorinated and non-chlorinated solvents can help increasing the volume of solvents that can be easily recycled [8].

Another way to minimize wastes generated during the fabrication of thin film solar cells and modules is reducing the amounts of toxic elements. For example, the possibility of reducing the quantity of toxic cadmium in the synthesis of CdS thin films, which plays the role of the buffer layer in CdTe and CIS solar cells has been investigated. It was found that by varying the solution concentration and temperature in the chemical bath deposition process for instance, the typical concentration of cadmium can be reduced up to 10 times [42]. These different ways to operate can help reducing substantially the amount of wastes generated during the PV manufacturing processes.

5.2 Recycling

It will be many years before most PV panels come to the end of their life (about 30 years), so it is needed to put in place some recycling schemes to prevent in time the harmful effects of spent panels on the environment. Some major PV manufacturers have experienced a promising approach called “cradle to cradle” [8]. The concept of this approach is to recycle the toxic materials of the process into new products, which are less or not at all toxic. This approach has enabled reducing the potential for release wastes into the environment, and enhancing the amount of new resources that must be obtained.

There are different ways or models of recycling PV modules implemented by PV manufacturers. Deficient PV systems from manufacturing plants and spent PV modules are collected by manufacturers for being recycled. The first intent was to apply the electronics model of recycling, which involves an intermediate company that would gather the spent PV modules, dismount them, and deal the usable parts. Unfortunately, this model is less suitable to the PV sector, because usable materials are very thin, and therefore, the modules are difficult to dismantle. An efficient way for recycling PV modules is to use large metal smelters to melt scrap PV modules. For example, save cadmium from CIS modules would need the use of a copper and zinc smelter, whereas CdTe cannot be melted in a zinc smelter as cadmium is a by-product of zinc mining. A method of recycling CdTe modules and developed by Solar Cells Inc. involves dismantling of the module, followed by glass milling and separation of the metals following a combination of physical and chemical methods such as chemical dissolution, mechanical separation, precipitation, and electrodeposition [43]. By this way, about 80% of the original tellurium was saved. Another method for recycling CIS and CdTe modules, and developed by Drinkaard Metalox Inc. uses chemical stripping, electrodeposition, precipitation, and evaporation. About 95% of tellurium and 96% of the lead for cells connection were saved by combining these different methods. This method allows the potential reuse of

the substrate, because the metal conducting layer remains connected to the glass substrate after the separation of the elements [44]. A method of recycling CIS and CdTe modules based on electrochemical reactions in a closed loop system has been experienced at the early of years 2000 By Menezes et al. [45]. This approach could also lead to improve efficiency in the original CIS solar cells.

In addition to the environment safety, another major reason for developing relevant and cost-effective methods for recycling PV modules is the scarcity of some of the exotic elements used in PV industry. Reserves of some elements like germanium, indium and tellurium are low and continue to decrease with time [8]. Considering that the TFPV technology is still growing, it is needed to develop more feasible ways to recycle PV materials in order to preserve their reserves in the earth crust.

6. Conclusions

This chapter has shown the potential of some materials and chemicals used in the manufacture of thin film PV solar cells and modules to be hazardous. These hazardous chemicals can pose serious health and environment concerns, if proper cautions are not taken. Hazards could arise first from the toxicity and explosiveness of specific gases, then could affect occupational health and, in some cases, public health through accidents or elusive air emissions. Accidental releases of toxic gases and vapors can be prevented by minimizing wastes produced during the processes through choosing safer technologies, processes and less toxic materials. Recycling is expected to be the preferred disposal option for spent PV modules in the future, in order to minimize the potential environmental impacts and recover source of metals. Research is ongoing to build feasible methods of recycling spent modules for environmental safety.

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Conflict of interest

The authors declare that they have no conflict of interest.

Notes/thanks/other declarations

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