



Toward a Just and Sustainable Solar Energy Industry

A Silicon Valley Toxics Coalition
White Paper
January 14, 2009





About Silicon Valley Toxics Coalition:

- Silicon Valley Toxics Coalition (SVTC) is a diverse organization that promotes human health and environmental justice in the high-tech industry through research, advocacy, and grassroots organizing.
- Our goal is environmental sustainability and clean production for industry and improved health and democratic decision making for the communities and workers most affected by the high-tech revolution.
- We envision a toxic-free future in which each new generation of technical advances includes parallel and proportionate advances in social and environmental justice.

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Executive Summary

Every hour, enough solar energy reaches the Earth to meet human energy needs for an entire year. Solar photovoltaic (PV) technology is widely seen as a “win-win” solution that can harness this “free energy” to address global warming, reduce U.S. dependence on energy imports, create “green jobs,” and help revitalize the U.S. economy.

Solar energy will play an essential role in meeting these challenges, but as the solar PV sector expands, little attention is being paid to the potential environmental and health costs of that rapid expansion. The most widely used solar PV panels are based on materials and processes from the microelectronics industry and have the potential to create a huge new wave of electronic waste (e-waste) at the end of their useful lives, which is estimated to be 20 to 25 years. New solar PV technologies are increasing cell efficiency and lowering costs, but many of these use extremely toxic materials or materials with unknown health and environmental risks (including new nanomaterials and processes).

With the solar PV sector still emerging, we have a limited window of opportunity to ensure that this extremely important industry is truly “clean and green,” from its supply chains through product manufacturing, use, and end-of-life disposal. The solar industry has taken a leadership role in addressing the world’s pressing energy and environmental challenges and will serve as a model for how other innovative “green” industries address the lifecycle impacts of their products.

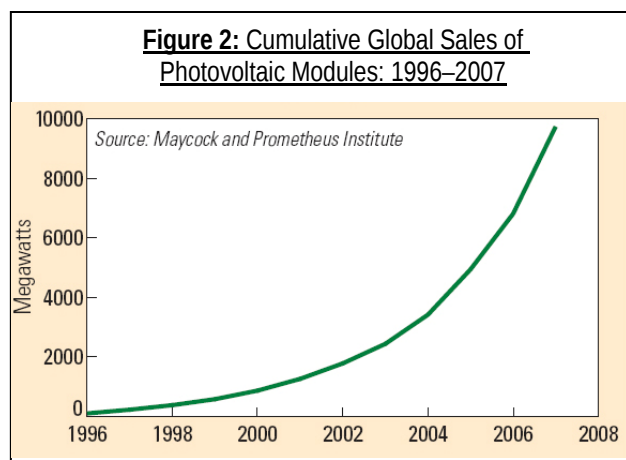
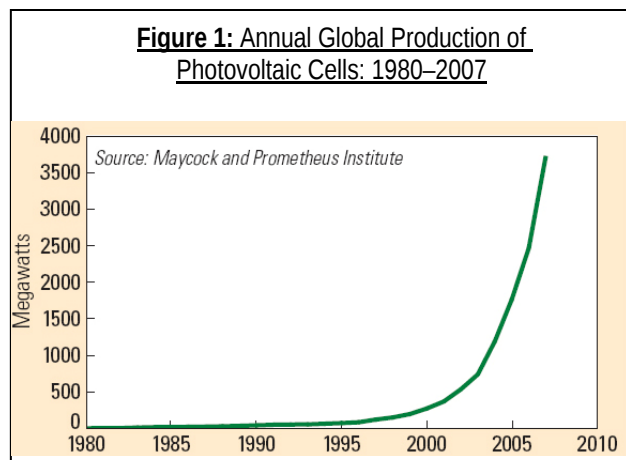
In this white paper, the Silicon Valley Toxics Coalition (SVTC) provides an overview of the health and safety issues faced by the solar PV industry, including the toxic materials used in manufacturing and the potential end-of-life disposal hazards of solar PV products. The report also lays out recommendations to immediately address these problems to build a safe, sustainable, and just solar energy industry. These recommendations include:

- Reduce and eventually eliminate the use of toxic materials and develop environmentally sustainable practices.
- Ensure that solar PV manufacturers are responsible for the lifecycle impacts of their products through Extended Producer Responsibility (EPR).
- Ensure proper testing of new and emerging materials and processes based on a precautionary approach.
- Expand recycling technology and design products for easy recycling.
- Promote high-quality “green jobs” that protect worker health and safety and provide a living wage throughout the global PV industry, including supply chains and end-of-life recycling.
- Protect community health and safety throughout the global PV industry, including supply chains and recycling.

I. Introduction

The solar photovoltaic (PV) industry is at the forefront of a multibillion dollar “clean and green” technology sector that is seeking solutions to the critical environmental issues that threaten the planet. The solar PV industry has seen tremendous growth in the past decade and continues to expand even as credit markets contract. In 2007, the industry grew by 62 percent and earned \$17.2 billion in global revenues.¹ The number of solar cells produced globally has increased sevenfold in the past five years, and cumulative installations have increased fivefold over that time.²

Although solar power now provides just 1/10th of 1 percent of U.S. energy consumption, that share is rapidly expanding as costs become more competitive with conventional energy sources. By some estimates, each time the volume of solar PV cell shipments doubles, the price falls by about 20 percent.³ The sector forecasts sustained growth, as calls for carbon-free energy and green jobs translate into increased investment in renewable energy, tax incentives for solar PV systems, and subsidies for solar PV research.[†]



Solar energy is an essential part of the global move toward clean, renewable energy, and it is critical that the growing solar PV industry is itself truly safe and sustainable. Little attention is currently being paid to the potential risks and consequences of scaling up solar PV cell production. The solar PV industry must address these issues immediately, or risk repeating the mistakes made by the microelectronics industry.⁴ The electronics industry's lack of environmental planning and oversight resulted in widespread toxic chemical pollution that caused death and injury to workers and people living in nearby communities. The high-tech industry's legacy now includes the growing global tide of toxic electronic waste, or e-waste.⁵

Figure 1 and 2 used courtesy of Worldwatch Institute, *Vital Signs Online*, www.worldwatch.org

[†] The federal budget for solar PV research was \$106 million in 2007. Department of Energy, “Budget.” <http://www1.eere.energy.gov/solar/budget.html> (accessed July 13, 2008).

Extended Producer Responsibility

Extended Producer Responsibility (EPR) requires companies to take responsibility for the impacts of their products: from the materials used in manufacturing to product recycling. One well-known form of EPR is producer take back, which requires companies to take back their products when users are done with them and ensure that they are recycled safely and responsibly.

EPR policies provide incentives for companies to design and produce cleaner and more easily recyclable products, and discourage the practice of “planned obsolescence” (intentionally making products that quickly become out of date or useless).

Although all electronics companies take back their products in the European Union, some companies (including Dell, HP, and Sony) have already adopted voluntary take-back policies in the U.S., setting the pace for the rest of the industry. In the U.S., 15 states have passed legislation mandating some type of EPR.[†]

[†]Electronics TakeBack Coalition,
<http://www.computertakeback.com>

Although the solar PV boom is still in its early stages, disturbing global trends are beginning to emerge. For example, much of the polysilicon feedstock material (the highly refined silicon used as the basic material for crystalline silicon PV cells) is produced in countries like China, where manufacturing costs and environmental regulatory enforcement are low.⁶ In March 2008, the *Washington Post* reported that at least one plant in China's Henan province is regularly dumping extremely toxic silicon tetrachloride (a corrosive and toxic waste product of polysilicon manufacturing) on nearby farmland. According to Li Xiaoping, deputy director of the Shanghai Academy of Environmental Sciences, “Crops cannot grow on this, and it is not suitable for people to live nearby.”⁷ Silicon tetrachloride makes the soil too acidic for plants, causes severe irritation to living tissues, and is highly toxic when ingested or inhaled.⁸

For more than 25 years, the Silicon Valley Toxics Coalition (SVTC) has been a leading advocate for safety and manufacturer responsibility in the electronics industry. SVTC is now applying that long experience to the solar PV industry with its **Clean and Just Solar Industry** initiative. The initiative's goal is to ensure that this promising new technology is as safe and sustainable as possible by promoting “cradle to cradle” product stewardship and “lifecycle thinking” throughout the solar PV supply chain.

SVTC is urging the adoption of policies that:

- **Reduce and eventually eliminate the use of toxic materials and develop environmentally sustainable practices.** This includes proper testing of new and emerging materials based on a precautionary approach. This approach requires that materials be proven safe before use, rather than waiting until they cause harm.
- **Ensure that solar PV manufacturers are responsible for the lifecycle impacts of their products through Extended Producer Responsibility (EPR) (see sidebar, page 3).** Solar PV companies should take back decommissioned solar panels and recycle them responsibly. Responsible recycling does not export waste overseas or use U.S. prison labor.

- **Ensure proper testing of new and emerging materials and processes based on a precautionary approach.**

Those advocating the use of new chemicals or processes must prove their safety (rather than requiring communities or workers to prove their dangers).

- **Expand recycling technology and design**

products for easy recycling: Current solar PV products contain many toxic materials that should not enter the waste stream when products are decommissioned. Requiring manufacturer responsibility will provide an incentive to design less-toxic solar PV products that are easier to recycle. It will also spur development of safe recycling technologies.

- **Promote high-quality “green jobs” that protect worker health and safety and provide a living wage throughout the global PV industry,**

including supply chains, production, and recycling. Manufacturers must monitor supply chains to ensure safe and just conditions for workers. (See Green Jobs sidebar).

- **Protect community health and safety throughout the global PV industry, including supply chains and end-of-life recycling.** People have the right to know what toxic materials are being used in their communities.

Green Jobs

The emerging environmental sector has the potential to create millions of “green jobs” at all levels and help revitalize the U.S. industrial economy. A broad spectrum of U.S. labor unions, environmentalists, community groups, and businesses is calling for major nationwide investments in a new clean energy economy that addresses climate stability, energy security, and economic prosperity.

The accepted definition of “green-collar jobs” closely follows that developed by Raquel Pinderhughes, professor of urban studies at San Francisco State University.[†] Green-collar jobs improve environmental quality while offering a living wage, health and other benefits, job satisfaction, access for entry-level workers, and opportunities for career advancement.

Major national organizations, including the Apollo Alliance and Green for All, are proposing concrete programs for the large-scale creation of green-collar jobs. The Apollo Alliance’s New Apollo Program, for example, proposes a comprehensive investment strategy of \$500 billion over the next ten years that would create five million high-quality green-collar jobs and transform the U.S. energy infrastructure.

The solar sector has the potential to open up hundreds of thousands of jobs in fields including manufacturing, construction, installation, and maintenance. However, without careful attention to job quality, this industry that seeks to be environmentally sustainable could end up producing unsustainable jobs—jobs that keep workers and their families in poverty, add to the nation’s health insurance crisis, or put workers’ health and safety at risk through toxic exposure. As Green for All puts it, “We must say ‘No’ to solar sweatshops and Wal-Mart wind farms.” As the solar PV industry grows, we must ensure that the resources invested in the industry are used to create high-quality jobs that are accessible to all workers and communities.

[†] Raquel Pinderhughes, *Green Collar Jobs*, Berkeley Office of Energy and Sustainable Development, 2007.

II. Overview of Solar Photovoltaic (PV) Technology

A. Solar PV Basics

Solar energy technology uses the “**photovoltaic (PV) effect**” to capture sunlight and convert it into electricity. Typically, solar PV cells are made by sandwiching together two thin layers of semiconductor material. The two layers have slightly different chemical compositions that facilitate electron transfer between them. When sunlight energy is absorbed by a solar cell,[†] it causes electrons to “escape” from molecules in one layer of material and move to those in the other. This creates an electrical field that can be converted into electricity (see Figure 3).

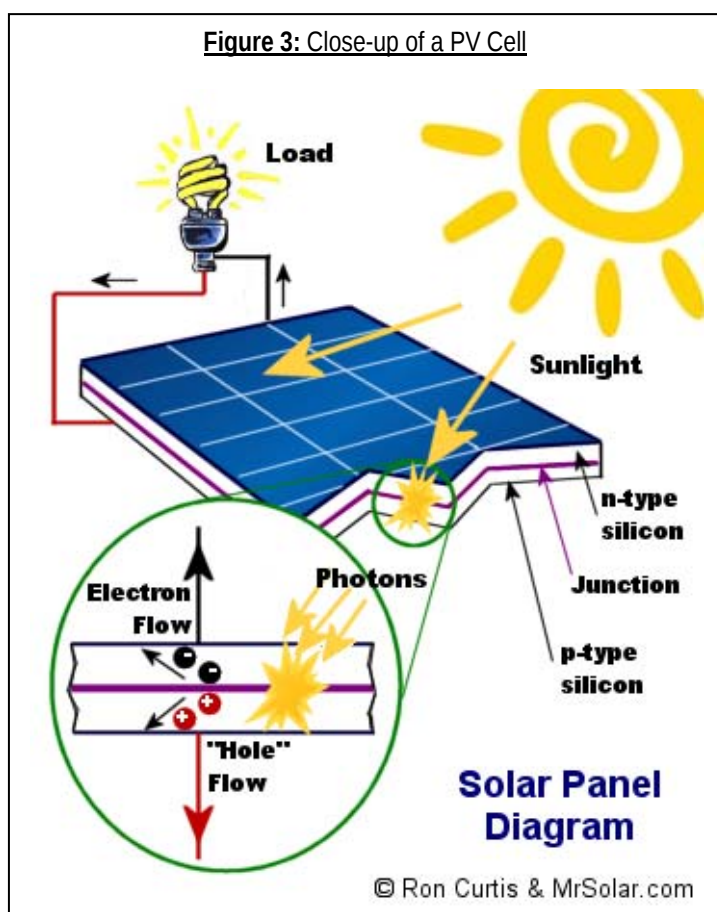


Figure 3 used courtesy of Online Solar Inc., <https://www.mrsolar.com>

Today's most common solar PV technology is based on silicon semiconductors and uses manufacturing processes and materials similar to those of the microelectronics industry. In addition, the solar PV industry is rapidly developing novel materials and processes to increase cell efficiency (the amount of solar energy converted into electricity per area of semiconductor). New technologies are also lowering costs by using less semiconductor material and streamlining production. At the leading edge of today's PV industry are “thin-film” cells. These use very small amounts of semiconductor materials, which are applied in thin layers to inexpensive glass, metal, and plastic surfaces. Potential thin-film applications also include construction materials, such as roof tiles and siding, and even clothing, for “wearable” PV.

Unfortunately, many of these new technologies use toxic, explosive, corrosive, or potentially carcinogenic materials, such as cadmium and selenium. Other processes rely on newly developed materials that have not been sufficiently tested for

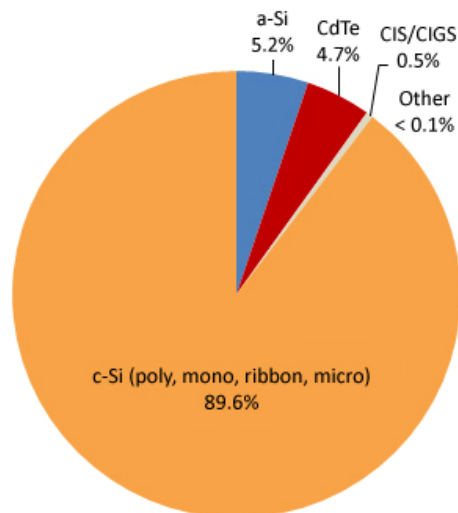
[†] The terms solar photovoltaic (PV) “cells,” “modules,” and “panels” will be used interchangeably throughout this report. The solar cell is the manufactured unit of PV technology, typically ranging from less than one inch to several inches across, and it includes semiconductor material, a substrate, a protective layer, and wiring to conduct electricity. Cells are assembled into modules, and modules are assembled into larger collections of panels and arrays.

toxicity. Increasingly, these materials are the products of nanotechnology (nanotech), which relies on the distinctive chemical, physical, and electrical properties of materials at the molecular scale. Nanotech could potentially provide new and useful materials for a wide range of industries, but the novel properties of these materials present significant challenges to safeguarding workers, consumers, and the environment.^{9,10}

B. Crystalline Silicon (c-Si) Solar Cells

Silicon-based solar cells were first used in the 1950s, and they remain the backbone of the solar industry. **Crystalline silicon (c-Si)** cells—those typically used in rooftop panels and large utility company arrays—dominate the solar PV industry and will continue to do so in the near future.¹¹ However, the dominance of c-Si is waning somewhat. In 2004, approximately 88 percent of the solar PV panels produced in the U.S. were c-Si, but by 2006 that percentage had fallen to 69 percent.¹²

Figure 4: Global Market Share of Solar PV Semiconductors in 2007†



*Other includes gallium arsenide, zinc manganese tellurium, indium gallium phosphide/germanium, and indium gallium nitride

Legend:

c-Si - Crystalline silicon
a-Si - Amorphous silicon
CIS - Copper indium selenide
CIGS - Copper indium gallium selenide
CdTe - Cadmium telluride

Individual c-Si cells are assembled from thin wafers of silicon that are cut from **monocrystalline silicon** cylinders (called “rods” or “ingots”) or from blocks of cast **multicrystalline silicon**. Two wafers are slightly altered (or “doped”) with small

Figure 5: Polycrystalline Panel



amounts of different impurities to facilitate electron transfer, for example phosphorous in one wafer and boron in another. The wafers are sandwiched together between glass or layers of ethyl vinyl acetate and a polymer laminate to protect the cells. Metal grids and contacts conduct the electrical energy produced, and inverters change the direct current (DC) produced by solar cells to the alternating current (AC) used in power lines (see Figure 3, page 5).

Solar PV cells are combined into modules (typically several square feet), then into panels or arrays. One significant problem for c-Si production is the loss of material in sawing—as much as 50 percent of the highly refined and increasingly expensive silicon is lost in the process.¹³

† Source: Daniel Ruoss, *Market Overview of Silicon and Non-Silicon Technologies and a Perspective of the PV Market and Technologies Development*, Envision,

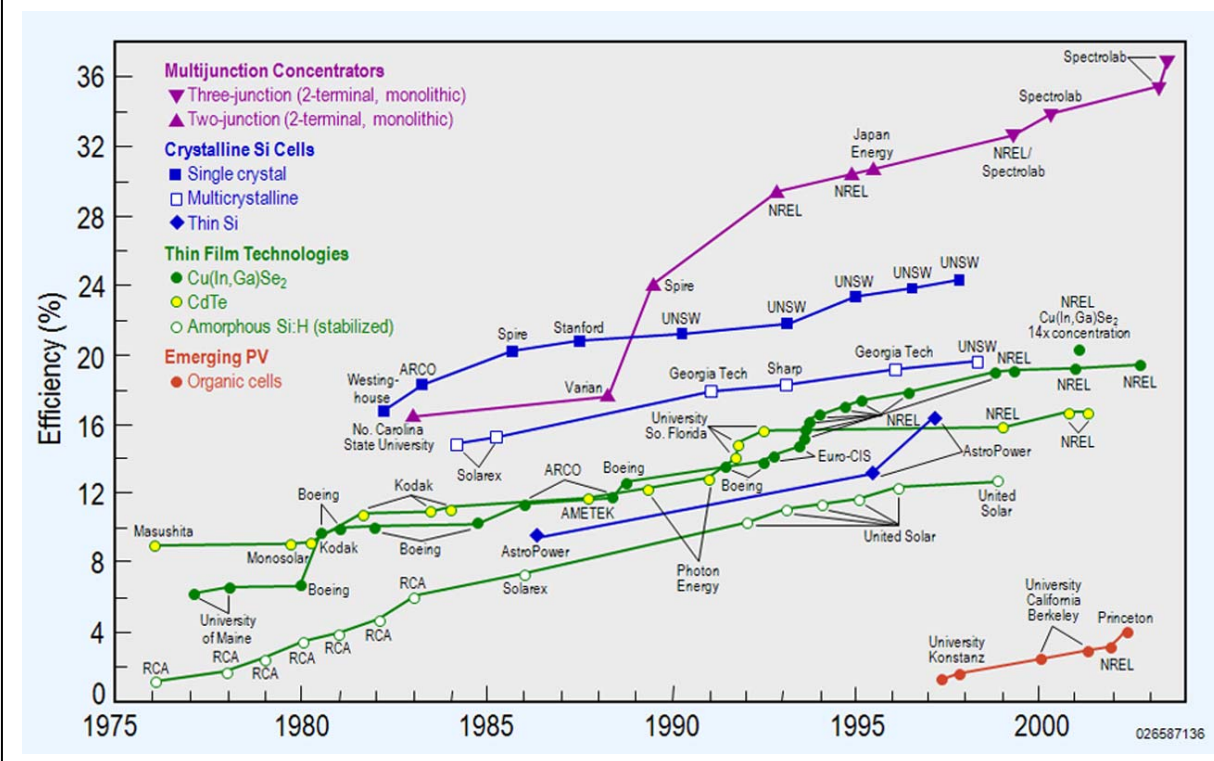
Figure 6: Best Research-Cell Efficiencies

Image used courtesy of National Renewable Energy Laboratory

Other silicon-based processes include “**ribbon c-Si**,” in which molten silicon is cast into thin ribbons, eliminating the need for sawing. Also under development for potential use in multijunction PV cells (see below) is **crystalline thin-film silicon**, not to be confused with the amorphous silicon (a-Si) thin film below.¹⁴

C. Thin-Film Solar Technologies

By using very thin layers of semiconductor material, thin-film solar PV cells reduce costs and increase manufacturing efficiency. A wide variety of thin-film materials are being developed for use on an equally wide range of surfaces. These materials and the methods used to apply them are increasingly complex, and many employ untested nanomaterials and processes. Among the thin-film solar PV cells in use and development are the following:

- **Cadmium telluride (CdTe)** is the fastest growing commercial thin-film technology both because it is less expensive to manufacture than other solar PV and because it is one of the most efficient at converting sunlight into electricity.¹⁵ The first cadmium telluride solar PV cells were made commercially available in 2001. Other emerging applications for this

material include the use of quantum dots,[†] which are also being investigated for use in applications such as LEDs and medical imaging.¹⁶

- **Copper Indium Selenide (CIS) and Copper Indium Gallium Selenide (CIGS)**

Although CIS and CIGS thin-film technologies have only been recently commercialized, they are producing impressive efficiency rates (approaching 20 percent) in laboratory tests (see Figure 6, page 7). These new technologies have the potential to revolutionize the solar industry with cheap, efficient PV cells. They use a process very similar to ink printing or lithography to apply semiconductor material to a wide range of lightweight backings. Some companies are using nanotechnology to increase CIGS efficiencies.¹⁷

- **Amorphous silicon (a-Si)** solar PV cells are widely used to power small, low-power consumer devices like watches, calculators, and outdoor lighting. This non-crystalline form of silicon is applied as a thin film to various surfaces. Amorphous silicon cells have been commercially available since the 1970s, and they are relatively inefficient at converting sunlight to electricity (reaching a maximum of about 12 percent).¹⁸ However, because they are a thousand times thinner than c-Si cells, they use less silicon and are much cheaper to produce. They can also be made more efficient by stacking with other thin-film semiconductors.¹⁹

D. Gallium Arsenide (GaAs) and Multijunction Cells

Multijunction solar PV panels use two or more types of semiconductor cells that absorb different parts of the solar spectrum. The ability to capture light from this broader spectrum makes multijunction cells more efficient. The maximum efficiency of a single solar cell based on one material is about 30 percent, but multijunction cells are already approaching 40 percent in laboratory tests.²⁰ Because of their complexity, multijunction PV cells are expensive to manufacture, limiting current commercial availability to military and communications satellites.

Current multijunction PV cells use gallium arsenide (GaAs) combined with thin-film materials such as cadmium telluride (CdTe) and amorphous silicon (a-Si). Additional materials under development for multijunction cells include zinc manganese tellurium, indium gallium phosphide/germanium, and indium gallium nitride.

[†] Quantum dots are semiconductor crystals fabricated from the bottom up. Rather than being cut from larger crystals, quantum dots are precipitated onto a surface, creating less waste in the process. These are nanometer-scale particles, so they exhibit quantum properties that come with advantages (such as potential to produce dots of different sizes to absorb different parts of the solar spectrum); but they also present potential risks and uncertain hazards. Quantum dots are made from materials such as carbon, silicon, gallium arsenide, cadmium telluride, and cadmium selenide.

III. Hazardous Materials Used in Solar PV Cell Production

Silicon-based solar PV production involves many of the same materials as the microelectronics industry and therefore presents many of the same hazards. At the same time, emerging thin-film and nanotech-based cells pose unknown health and environmental dangers. This section provides an overview of the hazards posed by current and emerging solar PV production technologies.

A. Crystalline Silicon (c-Si)

As with the production of silicon chips, production of c-Si wafers begins with the mining of silica (SiO_2), found in the environment as sand or quartz.[†] Silica is refined at high temperatures to remove the O_2 and produce metallurgical grade silicon, which is approximately 99.6 percent pure. However, silicon for semiconductor use must be much purer. Higher purities are achieved through a chemical process that exposes metallurgical grade silicon to hydrochloric acid and copper to produce a gas called trichlorosilane (HSiCl_3). The trichlorosilane is then distilled to remove remaining impurities, which typically include chlorinated metals of aluminum, iron, and carbon. It is finally heated or “reduced” with hydrogen to produce silane (SiH_4) gas. The silane gas is either heated again to make molten silicon, used to grow monocrystalline silicon crystals, or used as an input for amorphous silicon (see next section).

The next step is to produce crystals of either monocrystalline or multicrystalline silicon. **Monocrystalline silicon** rods are pulled from molten silicon, cooled, and suspended in a reactor at high temperature and high pressure. Silane gas is then introduced into the reactor to deposit additional silicon onto the rods until they “grow” to a specified diameter. To produce **multicrystalline silicon**, molten silicon is poured into crucibles and cooled into blocks or ingots. Both processes produce silicon crystals that are extremely pure (from 99.99999 to 99.9999999 percent), which is ideal for microchips, but far more than required by the PV industry. The high temperatures required for c-Si production make it an extremely energy intensive and expensive process, and also produces large amounts of waste. As much as 80 percent of the initial metallurgical grade silicon is lost in the process.²¹

Sawing c-Si wafers creates a significant amount of **waste silicon dust called kerf**, and up to 50 percent of the material is lost in air and water used to rinse wafers.²² This process may generate silicon particulate matter that will pose inhalation problems for production workers and those who clean and maintain equipment. The U.S. Occupational Safety and Health Administration (OSHA) has set exposure limits to keep ambient dust levels low and recommends the use of respiratory masks, but it has been suggested that, despite the use of respiratory masks, workers remain overexposed to silicon dust.²³

[†] The mining of metallurgical grade silica can produce silica dust that has been associated with silicosis, a severe lung disease. Only a fraction of silica goes to the semiconductor industries, with most being mined for the steel industry.

The use of **silane gas** is the most significant hazard in the production of c-Si because it is extremely explosive and presents a potential danger to workers and communities.²⁴ Accidental releases of silane have been known to spontaneously explode, and the semiconductor industry reports several silane incidents every year.²⁵

Further back in the silicon supply chain, the production of silane and trichlorosilane results in waste **silicon tetrachloride (SiCl₄)**, an extremely toxic substance that reacts violently with water, causes skin burns, and is a respiratory, skin, and eye irritant.²⁶ Although it is easily recovered and reused as an input for silane production, in places with little or no environmental regulation, silicon tetrachloride can constitute an extreme environmental hazard. As the *Washington Post* reported in March 2008 (see above), polysilicon manufacturing is expanding rapidly in China, but facilities to recycle silicon tetrachloride and other toxic outputs are not keeping pace.²⁷

The extremely potent greenhouse gas **sulfur hexafluoride (SF₆)** is used to clean the reactors used in silicon production. The Intergovernmental Panel of Climate Change (IPCC) considers sulfur hexafluoride to be the most potent greenhouse gas per molecule; one ton of sulfur hexafluoride has a greenhouse effect equivalent to that of 25,000 tons of CO₂.²⁸ It can react with silicon to make **silicon tetrafluoride (SiF₄)** and **sulfur difluoride (SF₂)**, or be reduced to **tetrafluorosilane (SiF₄)** and **sulfur dioxide (SO₂)**. SO₂ releases can cause acid rain, so scrubbers are required to limit air emissions in facilities that use it.

It is imperative that a replacement for sulfur hexafluoride be found, because accidental or fugitive emissions[†] will greatly undermine the reductions in greenhouse gas emissions gained by using solar power.

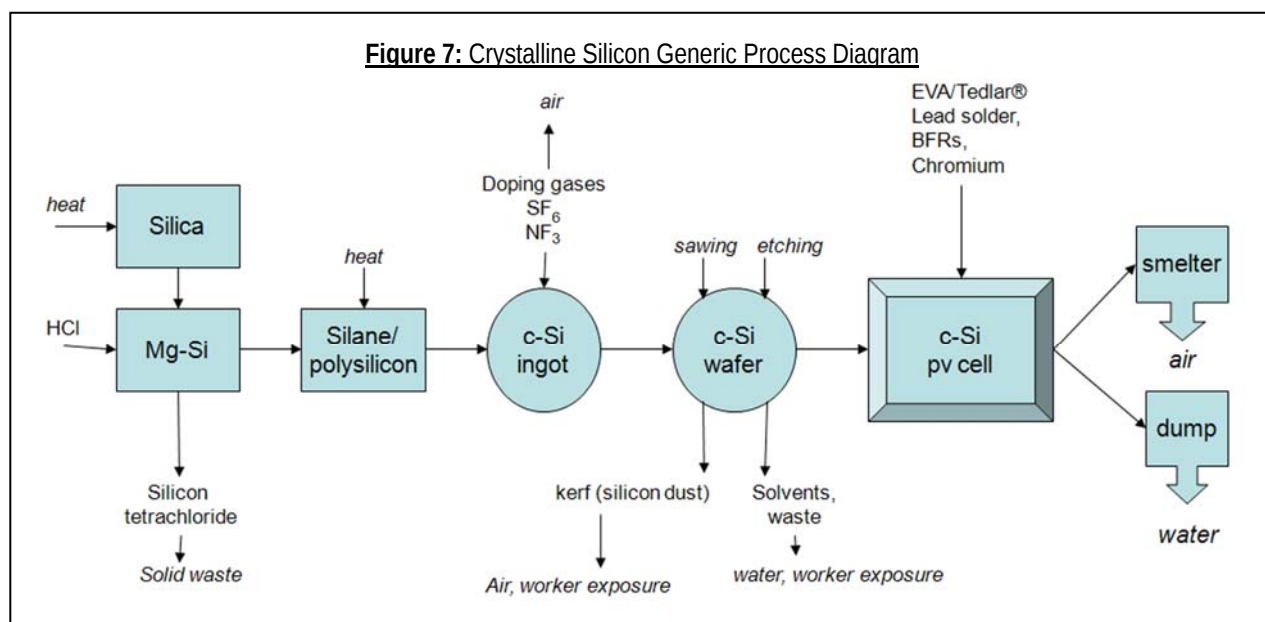
Other chemicals used in the production of crystalline silicon that require special handling and disposal procedures include the following:

- Large quantities of **sodium hydroxide (NaOH)** are used to remove the sawing damage on the silicon wafer surfaces. In some cases, **potassium hydroxide (KOH)** is used instead. These caustic chemicals are dangerous to the eyes, lungs, and skin.
- Corrosive chemicals like **hydrochloric acid**, **sulfuric acid**, **nitric acid**, and **hydrogen fluoride** are used to remove impurities from and clean semiconductor materials.
- Toxic **phosphine (PH₃)** or **arsine (AsH₃)** gas is used in the doping of the semiconductor material. Though these are used in small quantities, inadequate containment or accidental release poses occupational risks.²⁹ Other chemicals used or produced in the doping process include **phosphorous oxychloride**, **phosphorous trichloride**, **boron bromide**, and **boron trichloride**.
- **Isopropyl alcohol** is used to clean c-Si wafers. The surface of the wafer is oxidized to silicon dioxide to protect the solar cell.

[†] Fugitive air emissions are air pollutants that are not caught by a capture system. These may be due to equipment leaks, evaporative processes, and windblown disturbances.

- **Lead** is often used in solar PV electronic circuits for wiring, solder-coated copper strips, and some lead-based printing pastes.
- Small quantities of **silver** and **aluminum** are used to make the electrical contacts on the cell.

Chemicals released in fugitive air emissions by known manufacturing facilities include **trichloroethane**, **acetone**, **ammonia**, and **isopropyl alcohol**.³⁰



For further explanation of the above process diagram refer to Figure 7 in Appendix B, page 39.

A1. Monocrystalline Silicon Production Hazards

Monocrystalline silicon (mono c-Si) is formed when the one single crystal cools into a cylinder (called a rod or ingot). Thin wafers are then cut from the cylinder.

Mono c-Si is produced in large quantities for the computer industry. Because the purity of silicon needed for solar PV is less than that required for silicon chips, the PV industry has historically relied on purchasing (at reduced cost) silicon wafers and polysilicon feedstock rejected by the chip makers.³¹ The production of solar grade silicon is growing as demand in the PV industry is outstripping the available computer industry castoffs.

In addition to the chemicals used by all crystalline silicon cell production (see above), additional chemicals used to manufacture mono c-Si solar cells include **ammonium fluoride**, **nitrogen**, **oxygen**, **phosphorous**, **phosphorous oxychloride**, and **tin**.³² Like most industrial chemicals, these materials require special handling and operating standards to prevent workplace hazards or exposure to toxics.

A2. Multicrystalline Silicon Production Hazards

To make multicrystalline silicon (multi c-Si) wafers, molten silicon is poured into crucibles under an inert atmosphere of argon gas and slowly cooled to form thin squares. These cells are typically less pure than mono c-Si, particularly around the edges due to contact with the crucible during crystallization. They are less efficient but are also less expensive and less energy-intensive to make. Multi c-Si has a significant share of the c-Si market at about 67 percent in 2004.³³ Overall, the lifecycle impacts of mono c-Si and multi c-Si have a similar profile, although the energy used in production is higher for mono c-Si.³⁴

Other materials used or produced in the manufacturing of multi c-Si that require special handling and operating procedures include **ammonia, copper catalyst, diborane, ethyl acetate, ethyl vinyl acetate, hydrogen, hydrogen peroxide, ion amine catalyst, nitrogen, silicon trioxide, stannic chloride, tantalum pentoxide, titanium, and titanium dioxide.**³⁵

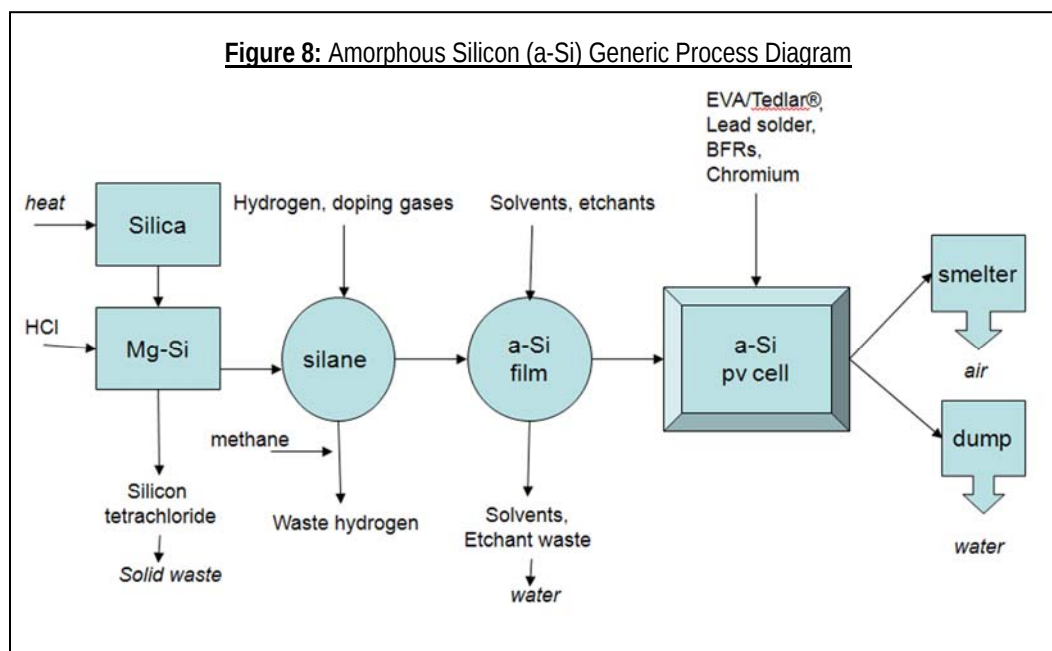
New production practices are on the c-Si manufacturing horizon, and new technologies are being developed to significantly reduce energy consumption.³⁶ Efforts are being made to make thinner wafers—microcrystalline Si and nanocrystalline Si—that use less silicon, but these require manufacturing techniques from nanotechnology that may pose new kinds of occupational risks.

B. Amorphous Silicon (a-Si) Thin Film

The chemical composition of amorphous silicon (a-Si) allows it to be deposited in a thin layer on materials such as plastics, glass, and metal. To make a-Si cells, **silane** or **chlorosilane** gas is heated and mixed with **hydrogen**, then deposited as a thin film of a-Si (an alloy of silicon and hydrogen) on these materials. As mentioned previously, silane (SiH_4) gas is extremely explosive and poses a potential hazard to production workers and nearby communities.³⁷ The semiconductor industry has a history of silane gas explosions and occupational injuries.³⁸ Chlorosilane gases are also very toxic and highly flammable.³⁹ However, because the amount of silicon used is much smaller than in crystalline silicon production, less silane is needed to produce a-Si.

Hydrogen is also an explosive gas, and therefore poses an occupational hazard for workers.⁴⁰ In addition, **methane** gas is often mixed with the waste streams from the deposition process to literally burn off additional hydrogen. Methane is another highly flammable gas that poses a greenhouse gas threat if released into the atmosphere. Germane gas, often used to dope a-Si, is also explosive and considered toxic to the blood and kidneys.⁴¹

Chemicals used to etch and clean wafers—such as **hydrochloric acid, hydrofluoric acid, phosphoric acid, and sodium hydroxide**—require special handling to avoid occupational injury. Other dangerous chemicals used in the manufacture of a-Si include **acetone, aluminum, chlorosilanes, diborane, phosphine, isopropanol, nitrogen, silicon tetrafluoride, tin**, and, where germane is used, **germanium** and **germanium tetrafluoride.**⁴² The tetrafluoride compounds above can emit toxic fumes if heated.



For further explanation of the above process diagram refer to Figure 8 in Appendix B, page 39.

C. Cadmium Telluride (CdTe) Thin Film

Cadmium telluride (CdTe) thin-film solar PV panels use layers of CdTe and cadmium sulfide (CdS). **Cadmium (Cd)** is a by-product of zinc mining, and batteries and solar cells are major end uses. The rare metal **tellurium (Te)** is a by-product of copper, lead, and gold mining, and its scarcity may eventually prove to be a bottleneck for CdTe cell production. This will make the recovery of Te through recycling essential for the success of this rapidly growing technology.

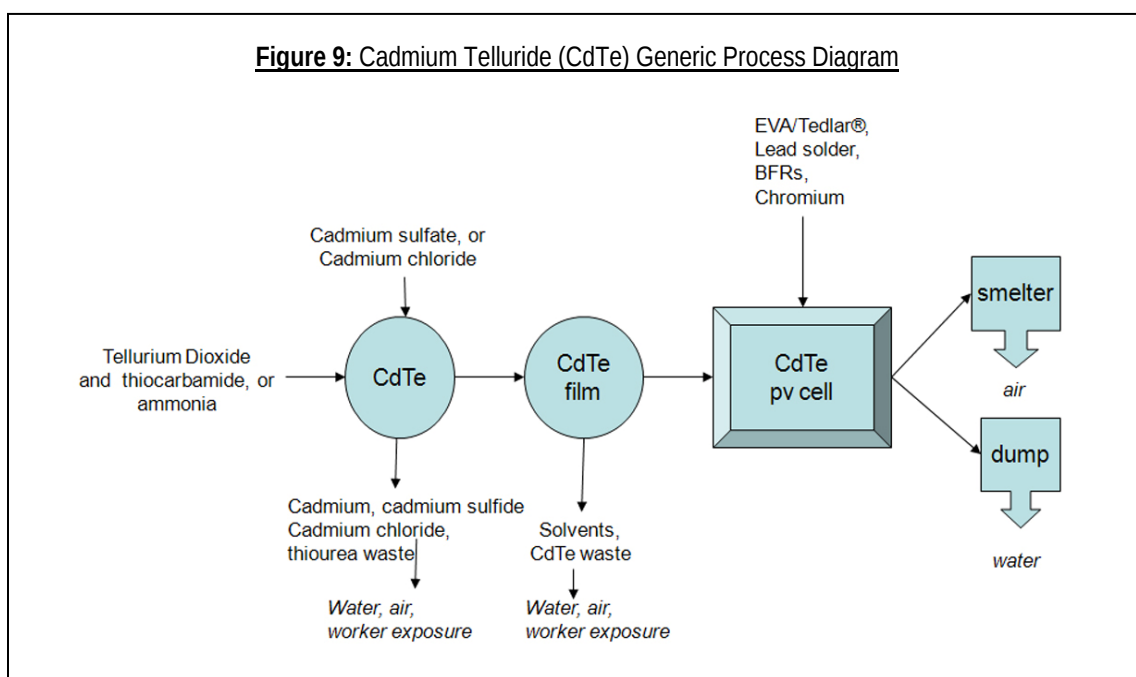
Cadmium telluride PV cells are produced by a process called electrodeposition, which efficiently applies a thin film of semiconductor material to glass or plastic, with less raw material waste than amorphous silicon thin-film production. CdTe thin films are deposited via electrical charge onto a surface using a solution of **cadmium sulfate (CdSO₄)** or **cadmium chloride (CdCl₂)**, mixed with **tellurium dioxide (TeO₂)**. Cadmium in wastewater used to rinse CdTe films presents potential water pollution issues, but it can be reclaimed and reused in the deposition of the cadmium sulfide (CdS) layer.⁴³

There are several ways of producing the CdS layer. One method deposits the layer by heating the surface and directly applying a mixture of cadmium sulfate (CdSO₄), thiourea (also called thiocarbamide, CS(NH₂)₂), and ammonia (NH₃); only 1 percent of the cadmium used as an input is disposed of as solid waste.⁴⁴

Another method uses the same chemicals and dips the surface into a chemical bath, but this method is less efficient in terms of raw material use. A third method deposits a solid CdS powder directly onto the surface after vaporizing the chemicals. In each of these methods the cadmium compounds are recycled, albeit not at 100 percent, as some

material is released in air exhaust and water effluent. For the latter two methods mentioned above, 10 to 30 percent of cadmium input is disposed of as solid waste.⁴⁵

The major health and safety hazards associated with the manufacture of CdTe cells relate to the use of **cadmium**, **cadmium sulfide**, **cadmium chloride**, and **thiourea**. Cadmium is a known carcinogen⁴⁶ and is considered “extremely toxic” by the U.S. Environmental Protection Agency (EPA)⁴⁷ and Occupational Safety and Health Administration (OSHA).⁴⁸ It has the potential to cause kidney, liver, bone, and blood damage from ingestion and lung cancer from inhalation, and workers may be exposed to cadmium compounds during the manufacturing process. The European Economic Community (EEC) has prohibited the sale of most products containing cadmium for health and safety reasons. While the toxicity of cadmium is well known, there is limited information on cadmium telluride (CdTe) toxicology.⁴⁹ It is not clear whether or not the EEC will grant CdTe manufacturers the exemptions necessary to allow sales of these modules in the European Union (E.U.). It is believed to be less toxic than cadmium compounds found in nickel cadmium (NiCd) batteries.⁵⁰ The Pesticide Action Network recognizes thiourea as a “Bad Actor Chemical” because it is a known carcinogen and can be toxic.⁵¹



For further explanation of the above process diagram refer to Figure 9 in Appendix B, page 40.

The potential for dust and fumes creates potential hazards for workers during the preparation of materials, from scraping and cleaning CdTe products, and from fugitive emissions. Other hazardous inputs in the production of CdTe panels include **molybdenum, nickel, sulfur, tellurium, and tin**.⁵²

As noted previously, the emerging use of nanoscale CdTe, also known as CdTe quantum dots, raises unknown safety issues that must be identified and addressed.⁵³ Properties of materials at the nanoscale may differ significantly from those of larger particles of the same material, including increased toxicity, potential for bioaccumulation, and nanoparticle mobility in the body.

Another safety concern regarding materials used in CdTe (and also in CIS/CIGS cells, discussed below), is the **risk of toxic releases during** fires in residential and commercial structures where these cells are installed. The compounds that would be released during fires pose a potential risk of toxic exposure, although the short-term nature of fires and the fact that cadmium vaporizes at temperatures higher than typical household fires, suggest that the risk is minimal.⁵⁴ However, the release of toxics from commercial buildings and industrial facilities during fires remains a concern, as fire temperatures can be higher in these kinds of structures.

D. Copper Indium Selenide (CIS) and Copper Indium Gallium Selenide (CIGS)

This rapidly emerging solar PV semiconductor technology has the potential to revolutionize the industry with its ability to print thin layers of semiconductor material on a wide range of materials. CIS and CIGS are also some of the best-absorbing semiconductor materials.

Depositing the CIS/CIGS layers onto a surface requires the mixing of **copper** and **indium** (and **gallium** in CIGS) with **hydrogen selenide** and the use of various industrial techniques.⁵⁵ One new process using nano-sized particles in an ink suspension is able to utilize 100 percent of gallium and indium inputs, which is important because these are globally rare metals.⁵⁶

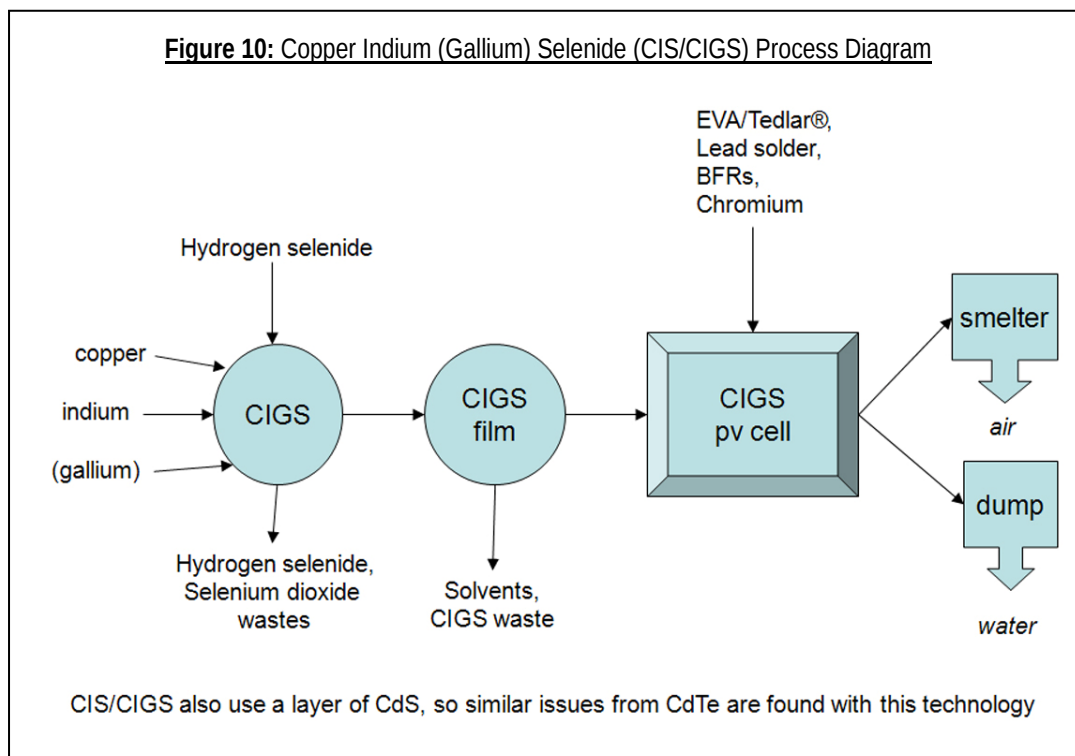
There is little information available about the toxicity of CIS or CIGS crystals, but numerous chemicals are used in the production of CIS and CIGS panels, many of them very toxic. These include **hydrogen selenide (or selenium hydride, H₂Se)**, which is considered highly toxic and dangerous at concentrations as low as 1 part per million in the air. It is used as the primary source of selenium and is consumed in the step called selenization, in which hydrogen selenide is introduced into the atmosphere of a reactor to provide excess selenium to react with the other metals. Hydrogen selenide will present potential occupational health and safety issues. New processes that avoid using hydrogen selenide have been developed, but these are more expensive and are not currently used to manufacture CIS/CIGS.⁵⁷

Another concern with the use of selenium is the potential formation of **selenium dioxide (SeO₂)** at high temperatures. Selenium dioxide is a tissue poison like arsenic, and great care must be taken to ensure that workers are not exposed to this occupational air pollutant.⁵⁸ Reactions at high temperatures facilitate the uniformity of CIGS and CIS crystals,

which is important for scaling up solar cell production. Selenium dioxide is vented into a water solution, where it forms elemental selenium. The recovery of selenium in this step is very high, but not 100 percent, and fugitive emissions do occur.⁵⁹

CIS/CIGS panels often use a layer of **cadmium sulfide (CdS)**. Salts of cadmium are released into the water as CIS cells are rinsed, which means that the concerns above about cadmium apply. The CdS layer can be replaced with an alternative material, such as zinc sulfide (ZnS) or indium sulfate (In_2SO_4), but CdS is more efficient.⁶⁰

Copper, indium, and selenium are considered to have a mild toxicity, while gallium (only used in CIGS) has a low toxicity. Dust from copper, indium, gallium, and selenium accumulate in the equipment used for production, presenting potential inhalation risks to workers.⁶¹ Other materials used in CIS and CIGS production include **hydrogen sulfide** (a gas used in CIS cell production), **molybdenum**, and **zinc oxide**. Molybdenum and zinc oxide are used as the back and front contacts that carry the electricity and are considered non-toxic.⁶²



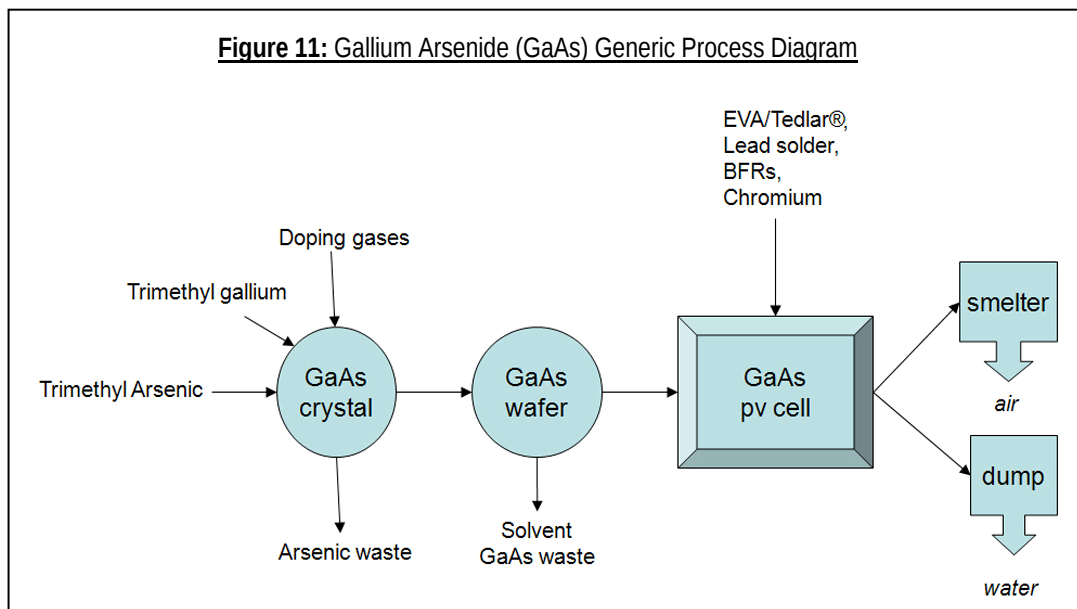
For further explanation of the above process diagram refer to Figure 10 in Appendix B, page 40.

E. Gallium Arsenide (GaAs) and Multijunction Cells

Gallium arsenide (GaAs) is currently used in multijunction solar PV cells, combined with thin-film materials such as **cadmium telluride (CdTe)**, **amorphous silicon (a-Si)**, **aluminum indium phosphide (AlInP)**, **aluminum gallium indium phosphide (AlGaInP)**, or **gallium indium phosphide (GaInP)**. GaAs technology is also used in concentrator cells, which focus incoming sunlight to increase its intensity. Because of the high cost of inputs and the manufacturing process, GaAs cell adoption has been limited to communication and military satellite applications.

The production of GaAs crystals starts with **gallium** and **arsenic** in pure form. The materials are combined and GaAs crystals grow on a surface made of **germanium** or **silicon**. Newer methods use **trimethyl gallium ((CH₃)₃Ga)** and **trimethyl arsenic ((CH₃)₃As)** gases. There is a debate in the scientific community about whether trimethyl arsenic detoxifies arsenic or transforms it into a carcinogen.⁶³ These gases are exposed to a heated surface where the GaAs crystals are grown. Different layers of these crystals are doped with different gases to make each layer sensitive to different parts of the solar spectrum.

The limited toxicological data on gallium arsenide suggest that it could have profound effects on lung, liver, immune, and blood systems if workers are exposed for extensive periods during manufacturing or if chemicals are accidentally released.⁶⁴ There is little toxicological data on gallium, but it is widely used as a marker/tag in MRI tests, and believed to be safe in small doses.



For further explanation of the above process diagram refer to Figure 11 in Appendix B, page 41.

Additional toxic materials used to produce GaAs PV cells include the following:

- **Arsenic** is a metalloid used to produce gallium arsenide crystals. Arsenic is highly toxic and carcinogenic,⁶⁵ and extreme caution will be required to avoid occupational hazards as the use of this technology expands.
- **Phosphine** and **arsine** are highly toxic gases used to dope GaAs crystals, but they are not found in the final PV cells. Less toxic alternatives are being developed (including tertiary butyl arsine and tertiary butyl phosphine),⁶⁶ and researchers are looking into substituting hydrogen with non-explosive (inert) nitrogen.
- **Trichloroethylene**, a known carcinogen, is a solvent used for cleaning. Other chemicals used or produced in the manufacturing process include **hydrochloric acid**, **methane**, **triethyl gallium**, and **trimethyl gallium**,⁶⁷

F. Emerging Solar PV Technologies

It is difficult to speculate about the production hazards presented by the next generation of solar PV technology as most are still in the theoretical or laboratory stages of development. Future applications for solar PV include new configurations of **multijunction cells**, as well as the following:

- **Dye-sensitized solar cells** release electrons from (in one particular case) titanium dioxide covered in a pigment that effectively absorbs sunlight.
- **Organic (living or dead carbon-based) solar cells** are made of biodegradable materials. At this point, many of these organic technologies degrade during operation, making them very unstable and far from commercial viability.
- **Hybrid cells** that combine various technologies and therefore present all the production hazards associated with their constituent semiconductors.

Emerging solar cell technologies are also rapidly incorporating advanced techniques in nanotechnology, such as the deposition of nanocrystals. Nanotechnology applications to solar cell manufacturing include nanoparticles suspended in ink, quantum dots, nanowires, and silver cells. Nanotech is also being used to produce very stable laminate layers to protect solar cells. These emerging uses merit considerable attention and the development of proactive labor standards to safeguard against unknown hazards.

IV. Potential End-of-Life Hazards for Solar PV Products

What will happen to today's solar panels at the end of their usefulness, which is estimated at 25 years or more? Not only do solar PV products contain many of the same materials as electronic waste (e-waste), but they also contain a growing number of new and emerging materials that present complex recycling challenges. These challenges include finding ways to recycle the small amounts of valuable materials on which many of the new solar PV technologies are based.

Much like e-waste, solar panels will leave a toxic legacy if they end up in landfills (where the materials they contain can leach into groundwater) or incinerators (where burning can release toxic materials into the air).⁶⁸ To avoid a repeat of the e-waste crisis, we need to ensure that decommissioned solar PV products are recycled responsibly and do not enter the waste stream at all. Responsible recycling means that waste is not shipped to developing countries for dismantling or recycled using U.S. prison labor.

One option could be to recycle solar PV panels that contain toxic metals at existing responsible e-waste recycling facilities[†] or at facilities that recycle batteries containing lead and cadmium, thereby keeping toxics out of the municipal incinerators and landfills.⁶⁹ However, the latter hazardous waste recovery facilities are often low-tech and in need of substantial research and development to improve their environmental footprint. For example, most recycling facilities reclaim metals using smelters, which are known to increase the risk of lung cancer from cadmium exposure in recycling workers and residents in nearby communities.⁷⁰

Extended Producer Responsibility (EPR), such as manufacturer take-back requirements (see sidebar, page 3), will be the key to ensuring that these complex and diverse solar PV products can be safely recycled. Making manufacturers responsible for the lifecycle impacts of their products will provide incentives for the development of safe and effective recycling technologies and for the design of products that are easier to recycle. Plans for recovering and recycling materials at the end of product life should be standard practice for any product identified as a “renewable” energy source.

A. Solar PV Toxic Waste is Also E-Waste

Because solar PV semiconductor manufacturing processes have roots in the microelectronics industry, many of the chemicals found in e-waste are also found in solar PV, including lead, brominated flame retardants, cadmium, and chromium. Each of these is described in more detail below. Many of the toxic materials currently used in the PV sector are being phased out of electronic products in the E.U., but are still currently used in most of the U.S.

[†] Recyclers that have signed the landmark “Electronic Recyclers Pledge of True Stewardship.” For additional information, see: http://www.computertakeback.com/the_solutions/recycler_s_pledge.cfm

Lead is often used in electronic circuits, including solar PV circuits, for wiring, solder-coated copper strips, and some lead-based printing pastes.⁷¹ Lead is highly toxic to the central nervous system, endocrine system, cardiovascular system, and kidneys.⁷² Because lead accumulates in landfills, discarded solar PV panels have the potential to leach into drinking water. In one study, solar PV modules using lead solder exceeded by 30 percent the maximum allowable concentrations for lead in the Toxicity Characteristic Leaching Procedure (TCLP) standards set by the U.S. EPA.⁷³ This can be easily resolved by using lead-free solders (such as those containing tin, silver, or copper), but current U.S. regulations do not require lead-free solder in the manufacture of solar panels or any electronic devices.⁷⁴ The E.U. has been more proactive, restricting the sale of electronics with lead-based solders.

Brominated flame retardants (BFRs), polybrominated biphenyls (PBBs), and polybrominated diphenylethers (PBDEs)

are added to plastics to make them less flammable. They are used in circuit boards

and solar panel invertors (which convert DC to usable AC power). BFRs contain bromine atoms, which are released as the plastic heats. Combustion is slowed as the additional bromine in the air interferes with the supply of oxygen needed to sustain fire.

Brominated flame retardants have become ubiquitous in the environment; they are found at high levels in a wide range of living organisms, from harbor seals in San Francisco Bay, to Arctic polar bears, to the breast milk of humans in the United States.⁷⁵ PBDEs bioaccumulate in fatty tissues; they are recognized as toxic and carcinogenic and are described as endocrine disrupters.⁷⁶ The E.U. and the states of Washington and California have banned the manufacture, distribution, or processing of goods with PBDEs.

The Global E-Waste Crisis

The global tide of toxic electronic waste (e-waste) is an escalating environmental and health disaster, especially for countries in Asia, West Africa, and Latin America where e-waste is often shipped for cheap recycling.

According to EPA estimates, in 2005 more than 2.6 million tons of e-waste were generated in the U.S., and that flood of waste is expected to increase dramatically with the nationwide switch from analog to digital TV in February 2009.

In 2005, only 12.5 percent of that 2.6 million tons was collected for recycling. The remainder—more than 87 percent—was disposed of, largely in U.S. landfills or incinerators. The hazardous materials in e-waste, which include lead and other toxic heavy metals like mercury, chromium, and cadmium, can leach out of the landfills into groundwater and streams, and the burning of plastics can emit dioxins into the air. As of March 2008, at least ten states had passed laws banning disposal of some electronics in landfills.[†]

Some of that 12.5 percent of e-waste collected for recycling is recycled responsibly, but an estimated 50 to 80 percent of it is exported to developing countries where it is dismantled or disposed of using very rudimentary and toxic technologies.^{††} The imprecision of that estimate reflects the fact that it is almost impossible to track the amount of U.S. e-waste that is shipped overseas. The U.S. is one of only three nations (the others are Afghanistan and Haiti) that have not ratified the Basel Convention, an international treaty designed to stop free trade in hazardous wastes. In addition, a significant amount of U.S. e-waste is recycled using prison labor in this country.^{†††}

[†] Electronics TakeBack Coalition, "E-Waste: The Exploding Global Electronic Waste Crisis," October 10, 2008 (Issue briefing book), p. 8, available at <http://www.computertakeback.com>

^{††} Ibid., p. 4.

^{†††} Ibid., p. 6.

Hexavalent chromium (Cr(VI)) is used in many solar panels as a coating to absorb solar radiation, and it is also found in screws and circuit board chassis. It is considered carcinogenic.⁷⁷ Several companies have phased out the use of hexavalent chromium in solar modules.

Solar PV, like most electronics equipment, contains recoverable metals. Copper wiring, nickel, silver, and aluminum contacts, and aluminum frames can be recycled like other scrap metals.

The sections below outline the end-of-life recycling challenges for specific solar PV technologies.

B. Crystalline Silicon (c-Si)

End-of-life hazardous waste issues: As outlined above, c-Si circuitry and inverters contain hazardous materials such as **lead, brominated flame retardants, and hexavalent chromium**. Toxic materials contained in the actual c-Si semiconductor materials are below levels regulated by the EPA.

Recycling options: Used silicon wafers can be melted into new silicon ingots and cut into new wafers. It takes far less energy (estimates range from 30 to 90 percent less) to process c-Si feedstock from recycled silicon than it does to process raw silica.⁷⁸ Furthermore, in recent years a silicon shortage has made recycling silicon PV an even more attractive option. A company located in Freiburg, Germany, is one of the few in the world that operates a c-Si recycling plant to reuse defective and used c-Si for new panels.⁷⁹

C. Amorphous Silicon (a-Si)

End-of-life hazardous waste issues: Amorphous silicon PV panels contain no EPA-regulated toxic materials, aside from those contained in the circuit boards (as noted above).

Recycling options: Since most a-Si PV panels are currently found in consumer products, they are typically disposed of in household waste streams. As with other small electronic devices, these products contribute to the overall e-waste load on local landfills. Amorphous silicon cells are also being used in combination with other materials to make multijunction panels (see below). The a-Si panels on these consumer products can be recycled through standard glass recovery/recycling processes, but they rarely are because they are attached to consumer products that are typically just thrown in the trash.

D. Cadmium Telluride (CdTe)

End-of-life hazardous waste issues: While the hazards of cadmium are well known, the toxicity of cadmium telluride (CdTe) is not as clear. It is believed to be less toxic than cadmium compounds (cadmium hydroxide) found in nickel cadmium (NiCd) batteries because it does not dissolve in water as readily.⁸⁰ However, tests to date are inconclusive.

Early studies of how metals may leach into groundwater show that CdTe modules failed both the TCLP and DEV[†] tests.^{81,82,83,84} More recent studies indicate that CdTe panels marginally pass TCLP standards,^{85,86} and one manufacturer reports that its panels currently pass TCLP and DEV tests.^{87,88} Potential future applications include CdTe quantum dots, shown to cause damage to cell biology and cell death.⁸⁹

Recycling options: Even though recycling technologies and processes are being developed, no company is yet reusing discarded CdTe panels as a manufacturing input for new ones. CdTe panels will go to the smelters that treat television cathode ray tubes (CRTs), fluorescent lights, and Ni-Cad and lead-acid batteries. There are several recycling methods in development by private industry and government labs to recover the metals in CdTe panels instead of burning them, but these are limited to pilot projects.^{90, 91} These methods include the use of strong acids (such as sulfuric acid) to strip off metals from crushed PV modules, providing a solution rich in metals that is further processed with sodium hydroxide, sodium carbonate, sodium metabisulfite, zinc, or iron to recover cadmium and tellurium.⁹²

Some of the intermediate compounds that could enter the waste stream from the recycling process above include **sodium sulfide** and **tellurium sulfide**. Potential waste products include **tellurium dioxide**, **sulfur dioxide**, and potential emissions from the **polymer laminate** and casing. Since these recycling efforts are still at the pilot scale, it is unclear what kinds of tasks will be automated and which will put workers at risk. It is also unclear if recovered cadmium will be economically competitive for reuse, or simply treated as hazardous waste. Recovery of tellurium, however, is very important because of low global availability.

E. Copper Indium Selenide (CIS) and Copper Indium Gallium Selenide (CIGS)

End-of-life hazardous waste issues: **Selenium** is a regulated substance that bioaccumulates in food webs and forms compounds such as **hydrogen selenide**, which is considered highly toxic and carcinogenic by the EPA.⁹³ CIGS has toxicity levels similar to CIS with the addition of **gallium**, which is associated with low toxicity. CIS and CIGS semiconductors also use **cadmium sulfide (CdS)** as a buffer layer, so cadmium is also a potential hazard. In addition, **cadmium telluride (CdTe)** is often used as a buffer material in these modules, which introduces the CdTe toxicity issues discussed above. In an acute toxicity comparison of CdTe, CIS, and CIGS, researchers found CIGS to have the lowest toxicity, and CdTe to have the highest.⁹⁴

Recycling options: No recycling processes to recover elements for reuse have been explored beyond the pilot scale.⁹⁵ Indium, a by-product of zinc mining, is extremely rare, and it has competing uses in the flat screen television industry. The high value of this metal will make recycling important for the success of CIS/CIGS PV technologies.

[†] The German “DEV S4” (Deutsches Einheitsverfahren) test, similar to the U.S. TCLP, is used by the E.U. to ensure that potentially toxic materials do not leach into the groundwater near waste disposal sites.

F. Gallium Arsenide (GaAs) and Multijunction Panels

End-of-life hazardous waste issues: The limited toxicological data on **gallium arsenide (GaAs)** suggest that it could have profound effects on lung, liver, immune, and blood systems.⁹⁶ It is also considered likely that these crystals would release arsine or arsenic if deposited in landfills; arsenic is highly toxic and carcinogenic.⁹⁷ As noted above, there is little toxicological data on gallium, but it is believed to be safe in small doses.

Recycling options: There are no pilot-scale recycling facilities for GaAs and multijunction PV (which also incorporates materials such as cadmium telluride and amorphous silicon). Other potentially toxic materials under development for use in multijunction PV include **zinc manganese tellurium, indium gallium phosphide/germanium, and indium gallium nitride**. As noted previously, the global rarity of metals such as indium and tellurium will make recycling essential to the success of solar PV based on these materials.

G. Emerging Solar PV Technologies

End-of-life hazardous waste issues: Most of the end-of-life hazards for emerging solar PV technologies have not been analyzed. In some cases, emerging products simply combine existing semiconductors (or advanced forms of existing semiconductors), and they will therefore carry the hazardous waste issues of all the technologies employed. For example, a multijunction cell of amorphous silicon and gallium arsenide will entail hazards posed by all of the materials and processes used.

Even less is known about the hazards of newer PV technologies. Dye-sensitized solar cells are based on a combination of a dye and titanium dioxide (which is not considered toxic), so the hazards of these technologies will be based on the toxicities of the dyes used, which at this point are not clear. Silver cells will pose hazards related to the mild toxicity of silver, as well as any new hazards presented by the use of silver nanocrystals.

Recycling options: Because of the diversity of materials used, recovery of semiconductor materials in multijunction cells will be complicated unless the different crystals are mechanically or manually disassembled, at which point their recovery processes will be similar to those described above. It is too early to say how dye-sensitive cells are going to be recycled. Organic, carbon-based, solar PV will pose little if any risk since it would be biodegradable. Understanding the end-of-life impacts of hybrid cells will depend on knowing which technology is being utilized.

Of particular concern for emerging solar cell technologies' end-of-life are the uncertain hazards associated with the use of nanomaterials and technologies. As previously noted, the fate of nano-sized particles can be much different than that of larger sized particles of the same materials. Materials not considered hazardous may, in fact, become hazardous if their bioaccumulative or toxicity characteristics change at the nanoscale. It is also unclear how nanoparticles found in ink suspensions or nanoparticles (such as quantum dots) sprayed onto surfaces will degrade when exposed to cracks in the solar cells' protective layers.

V. Current Regulatory Framework for Solar PV Products

As with any rapidly developing industry, regulatory agencies around the world are struggling to keep current with new technologies and materials. This section provides an overview of the status of environmental and health regulation for solar PV products.

A. Overview of U.S. Regulations Relating to Solar PV

A1. Manufacturing Chemicals and Materials

In 1986, SVTC campaigned with other environmentalists nationwide to persuade Congress to pass the national Emergency Planning and Community Right-to-Know Act, which established toxic chemical reporting requirements for states, local governments, and industry.

The requirements of the act include the Toxics Release Inventory (TRI)—an inventory of routine toxic chemicals emissions required of facilities with 10 or more employees that use 10,000 pounds or more of EPA-listed hazardous chemicals. In addition, companies are required to prepare Materials Safety Data Sheets (MSDSs) that list each chemical's common name and health impacts. These are used to inform workers and emergency response teams of potential risks.

Solar PV manufacturing is subject to the requirements above if the materials used are EPA-listed. However, there is concern that new nanomaterials used in solar panels will not be adequately covered by these regulations because existing reporting requirements and regulations are based on the volume of materials in use. Although nanomaterials often exhibit very different properties than larger sized particles of the materials, they are considered the same for regulatory purposes. For example, some nanomaterials have the potential to be extremely toxic in very small amounts, but current regulations do not reflect this danger. Therefore, current MSDSs for bulk materials may not adequately address the potential hazards of nanomaterials.

A2. PV Product Disposal and End-of-Life Regulation

U.S. regulation of solar PV products' end-of-life disposal is based on the federal Resource Conservation and Recovery Act (RCRA) and on state policies like California's Hazardous Waste Control Law (HWCL). If solar panels are determined to be hazardous waste, RCRA (and HWCL in California) could be used to regulate their handling, recycling, reuse, storage, treatment, and disposal.

Decommissioned or defective solar panels are currently considered hazardous waste by regulators if they do not meet the U.S. Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP) standards (and this determination varies depending on the technology used). TCLP is intended to ensure that potentially toxic

materials do not leach into the groundwater near waste disposal sites. The E.U. relies on the similar German “DEV S4” (Deutsches Einheitsverfahren) test. The TCLP test is required for all new solar panels that enter the U.S. market.

California’s Hazardous Waste Control Law (HWCL) has even stricter hazardous waste designations than the federal government, requiring that materials pass an additional toxicity test. California is the only U.S. state with a toxics policy similar to the E.U. (see below). For example, California prohibits the manufacture, distribution, and processing of brominated diphenylethers (PBDEs) and also requires that substitutes for **brominated flame retardants** (BFRs) not be persistent, bioaccumulative, or toxic.

B. Regulation in the European Union and Other Countries

In February 2003, the E.U. established the WEEE (Waste Electrical and Electronic Equipment) and RoHS (Restriction of Hazardous Substances) directives. Both policies seek to minimize the amount of electronic waste headed for landfills and incineration. WEEE sets minimum recycling targets with which member states must comply. No explicit ruling has been made on whether WEEE applies to PV systems, but Article 13 of WEEE mentions the possible incorporation of solar PV products.⁹⁸ In anticipation of the inclusion of PV systems in WEEE, the European Photovoltaic Industry Association and German Business Association have launched the “PV Cycle” program to develop “a European-wide collection, recycling, and recovery system.”⁹⁹ This effort by industry (although only voluntary) is an excellent first step in minimizing the end-of-life impacts of PV systems, but should not preclude the specific inclusion of solar PV systems in the WEEE.

Beginning in July 2006, the RoHS required that electronics sold on the E.U. market contain only minimal amounts of lead, mercury, cadmium, chromium, polybrominated biphenyls (PBBs), or brominated diphenylethers (PBDEs). The maximum threshold is 1,000 parts per million (0.1 percent) of each of the above, with the exception of cadmium which is more restrictive, at 10 parts per million (0.01 percent). U.S. policies are less restrictive, although PBBs have now been banned in the U.S. Manufacturers in the U.S. must comply with RoHS for products sold in the E.U., but not for products sold domestically.

In Japan, the leading PV manufacturing country for most of the past decade, laws require the collection of electrical appliances (such as refrigerators and washing machines) for recycling, but computers and other electronics products are not specifically included.¹⁰⁰ A fee is assessed on electrical appliance retailers, with retailers required to take back products and transport them to collection sites.

C. The Toxic Waste Burden on U.S. State and Local Governments

The solar PV industry has the potential to provide enormous environmental benefits, but the toxic materials contained in solar panels will present a serious danger to public health and the environment if they are not disposed of properly when they reach the end of their useful lives.

Of the 73 bills related to the solar PV industry that were introduced in the California Legislature during 2007 and 2008, none addressed the manufacturing or end-of-life hazards discussed in this report. Most of the bills focused on installation targets and tax incentives/rebates for photovoltaic adoption. Lawmakers must expand their support for solar energy to encompass a comprehensive lifecycle approach and build a solar sector that is truly sustainable and just.

The problem of solar PV waste is part of the larger issue of how to deal with dangerous or toxic consumer waste in general, a responsibility that currently falls mostly on the local and regional governments that operate public landfills. This waste includes a wide range of toxic consumer products, such as arsenic-treated lumber, hypodermic needles, electronic waste, batteries, and fluorescent light bulbs.

While state policies around the nation are being enacted to address these problems, much of this legislation consists simply of bans on the disposal of hazardous waste in landfills. Such bans do nothing to reduce product toxicity or the total volume of consumer waste—they simply shift the burden of toxic waste collection and management to already under-funded local and regional governments. In California, for example, local governments spend a total of more than \$100 million a year collecting and properly managing household hazardous products alone.

To address this growing problem, local governments throughout the country are beginning to take collective action to demand policies that put the responsibility for consumer waste back on product manufacturers. In California, local governments are working with the California Product Stewardship Council (<http://www.calpsc.org/>) to help move the state from a government- and rate-payer-funded toxic waste disposal model to one that puts responsibility for product disposal on manufacturers (Extended Producer Responsibility or EPR). This model not only reduces public costs, but also drives improvements in product design that promote environmental sustainability.

Solar energy can play an important role in addressing climate change and also in stimulating the “green” economic sector. As the solar industry takes off, an EPR approach will be critical to ensuring the safe disposal of decommissioned products and also to ensuring that the costs of managing this new flood of e-waste do not fall on local governments and communities.

To date, more than 15 U.S. states have passed EPR legislation based on a variety of different policy models. California has also begun implementing its E-Waste Recycling Act (SB 20, passed in 2003), which adds a \$6 to \$10 advance disposal fee to the purchase price of computer monitors and televisions to help fund e-waste collection and management efforts. Solar panels have not yet been covered, but electronics with similar toxic materials are currently regulated through this legislation. It is important to note that while the SB 20 fee supports the collection of televisions and computer monitors for recycling, it is not able to stop the export of California e-waste to developing countries that do not have the infrastructure to handle it.

Another producer-responsibility approach requires brand owners to create a plan for collection and responsible recycling of their spent items (at no cost to local governments) before products can be sold within the regulating jurisdiction, such as a U.S. state or Canadian province. This approach is being taken in Washington State, New York City, and British Columbia.

VI. Recommendations for a Clean and Just Solar Industry

The rapid growth of solar PV technologies provides an opportunity to continuously improve the safety and environmental performance of products. We also have an opportunity to ensure that the industry incorporates principles of social justice into its global supply, production, and recycling operations.

SVTC has launched the Campaign for a Just and Sustainable Future in Solar Energy to promote a lifecycle approach to the long-term safety of solar energy. The initiative calls for the following measures to help ensure a sustainable future for the solar PV industry; each of these measures is discussed in more detail later in this section.

- Reduce and eventually eliminate the use of toxic materials and develop environmentally sustainable practices. This includes design for the environment and implementation of green chemistry principles (see Green Chemistry sidebar).
- Ensure that solar PV manufacturers are responsible for the lifecycle impacts of their products through Extended Producer Responsibility (EPR).
- Ensure proper testing of new and emerging materials and processes based on a precautionary approach.
- Expand recycling technology and design products for easy recycling.
- Promote high-quality “green jobs” that protect worker health and safety and provide a living wage throughout the global PV industry, including industry supply chains and end-of-life recycling.
- Protect community health and safety throughout the global PV industry, supply chains, and recycling operations.

Green Chemistry

Green chemistry takes a lifecycle approach, in which every step from raw material extraction through product use and end-of-life are considered in the design of products. The 12 principles of green chemistry[†] include precautionary and pollution prevention measures to ensure that products are designed to incorporate safer chemicals, renewable raw materials, and minimal energy use and waste.

As detailed in this report, many of the chemicals used in the PV industry are far from green. Application of green chemistry principles will benefit everyone. Solar PV companies can save on the costs of energy and regulatory compliance, and workers and communities will risk less exposure to potential toxins. This approach is already viewed as a competitive advantage for companies seeking to market products to the E.U. and to U.S. states with proactive chemicals policies, such as California.^{††}

[†] P. Anastas and J. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, New York, 1998.

^{††} Michael Wilson, “Green Chemistry in California: A Framework for Leadership in Chemicals Policy and Innovation,” Report to the California Senate Environmental Quality Committee, California Policy Research Center, Berkeley, 2006.

A. Reduce and Eventually Eliminate the Use of Toxic Materials

Based on the information presented in this report, SVTC recommends that the following actions be taken by U.S. solar PV manufacturers to reduce the environmental and health risks presented by the PV industry:

- **Phase out use of chemicals already restricted by the E.U.'s Restriction of Hazardous Substances (RoHS).** These chemicals—including cadmium, lead, mercury, brominated flame retardants, and chromium—are considered highly dangerous and should be phased out in the U.S. as well.
- **Develop chlorine-free methods for making polysilicon feedstock that eliminate the use of trichlorosilane** (which results in waste silicon tetrachloride, an extremely toxic substance). This is the most toxic and energy-intensive phase of silicon production, and several methods are being developed to potentially replace it.¹⁰¹
- **Phase out use of sulfur hexafluoride (SF6).** One ton of sulfur hexafluoride has the greenhouse effect equivalent of 25,000 tons of CO₂.¹⁰² It is imperative that a replacement for sulfur hexafluoride be found, because accidental or fugitive emissions will greatly undermine the greenhouse gas reductions gained by the use of solar power.
- **Phase out use of hydrogen selenide.** This highly toxic material is used in the production of CIS/CIGS PV. New processes to make CIS/CIGS have been developed that avoid using hydrogen selenide.¹⁰³
- **Phase out use of arsenic.** Arsenic, used in production of gallium arsenide PV, is highly toxic and carcinogenic.
- **Phase out phosphine and arsine.** Phosphine and arsine are highly toxic gases used in the production of GaAs crystals (although they are not found in the final PV cells).
- **Reduce fugitive air emissions from facilities.** Reduce fugitive air emissions by PV manufacturing facilities, which include such chemicals as trichloroethane, acetone, ammonia, and isopropyl alcohol and greenhouse gases such as sulfur hexafluoride and nitrogen trifluoride.¹⁰⁴

B. Hold the Solar PV Industry Accountable for the Lifecycle Impacts of Its Products

The best opportunity to minimize the end-of-life hazards of solar PV lies in Extended Producer Responsibility (EPR), which makes manufacturers responsible for their products' end-of-life disposal. PV companies should take back their solar panels and recycle them responsibly without exporting waste overseas or using U.S. prison labor.

Manufacturer take-back provides an important incentive for the reduction of toxics in manufacturing and encourages the design of products that are easier and safer to recycle. It also gives companies an incentive to recycle decommissioned and defective solar PV panels into new solar panels.

The European Photovoltaic Industry Association (through its PV Cycle initiative) and the German Solar Business Association have endorsed full lifecycle accountability and product take-back for the solar PV sector. Germany accounts for both the largest solar PV market and the largest share of production.¹⁰⁵

A few companies are already establishing take-back and recycling programs. An Arizona-based firm has adopted the world's first pre-funded take-back policy for its cadmium telluride (CdTe) solar panels. A German company has established a pilot-scale recycling facility that uses defective and used crystalline silicon (c-Si) solar panels to make

new panels. Further research on recycling is being conducted on solar PV panels made from other materials and using other recovery processes.

C. Ensure Proper Testing of New and Emerging Materials and Processes

All new chemicals and materials developed for use in the solar PV industry should be properly tested. The following general guidelines should be applied:

- **Policies should incorporate a precautionary approach**, requiring that those who advocate the use of new chemicals or processes prove their safety (rather than requiring communities or workers to prove their dangers).
- **Apply green chemistry principles** as a screen for PV cell technology based on organic materials and inorganic crystals and for other emerging solar cell technologies before a prototype is available for market.

In addition, more extensive testing should be conducted on new chemicals or new materials being introduced and on the chemicals already in use. The latter category includes cadmium telluride (CdTe); cadmium telluride quantum dots; copper indium selenide (CIS) crystals; gallium arsenide (GaAs); and gallium.

D. Expand Recycling Technology and Design Products for Easy Recycling

To meet the challenges of solar PV recycling, manufacturers should be encouraged to:

- **Invest in recycling infrastructure.** Communicate with existing glass, electronics, and battery recycling companies to build the infrastructure and capacity to recycle solar PV.
- **Design for recycling.** Design all solar products for ease of recycling by reducing the use of toxic materials and designing products to be easily disassembled.
- **Use silicon recovered from consumer electronics products.** Because solar grade silicon does not have to be as pure as the c-Si used in computer microchips, the reuse of silicon recovered from consumer electronics (like televisions, computers, and cell phones) should be explored.
- **Develop recycling processes for all rare metals.** Develop plans to recover all rare metals such as tellurium (CdTe panels) and indium (CIS panels).

E. Promote High-Quality “Green Jobs” That Protect Worker Health and Safety and Provide a Living Wage

The first line of defense against dangerous toxic exposures or releases at manufacturing plants is an engaged and empowered workforce throughout the global PV industry and its supply chains. Whether solar PV manufacturing facilities are located in California or in China, it is critical that the industry establish and enforce strong labor standards for its own practices and those of its suppliers. These include standards for occupational health and safety, respect for all international labor standards including prohibitions on the use of child labor or forced labor, and the free right of all

workers to organize and have a voice at work. Workers who are deprived of these basic rights often cannot speak up against dangerous working conditions or misuse of toxic chemicals for fear of losing their jobs.

Over the past decade, dangerous working conditions and abuse of workers involved in retailers' supply chains have become a national issue. In the garment and footwear industries, for example, major brands such as Nike and Gap have been forced to defend their images against accusations of sweatshop sourcing, with at least four states and 26 cities passing legislation barring the use of public dollars to purchase clothing that does not adhere to a strict "no-sweat" code.¹⁰⁶ In microelectronics manufacturing—solar PV's close cousin—the specter of "high-tech sweatshops" tainted the industry in the late 1990s. Even IBM faced a number of lawsuits (largely settled out of court) from cancer-stricken workers who accused the computer giant of criminal negligence in exposing its employees to carcinogens.¹⁰⁷

As the solar industry rapidly grows to scale, solar PV manufacturers have an opportunity to learn from the problems faced by the electronics and apparel industries. The solar industry can be a proactive model in implementing systems to monitor worker health and safety, chemical use and exposure, and enforcement of labor and environmental laws throughout the global supply chain.

The known hazards involved in solar PV production already raise a number of red flags for worker health and safety, some of which are outlined below. In addition to these known hazards, emerging PV processes pose risks that are as yet unidentified, and further investigation is required, including input from workers and factory owners. Workers have the right to know what chemicals are being used and what potential hazards those chemicals might present.

The chemicals listed below are only a brief survey of production activity and may not reflect the most hazardous or the most prevalent chemicals in the workplace.

- **Eliminate exposure to silicon dust.** Sawing c-Si wafers creates a significant amount of silicon dust called kerf, and up to 50 percent of the material is lost in air and the water used to clean the wafers.¹⁰⁸ This process may generate silicon particulate matter that poses inhalation hazards for workers.
- **Reduce and eliminate exposure to cadmium.** The major health and safety hazards associated with CdTe cells during manufacture involve the use of cadmium. Cadmium is considered "extremely toxic" by the Environmental Protection Agency¹⁰⁹ and Occupational Safety and Health Administration (OSHA), potentially causing kidney, liver, bone, and blood damage. The potential for dust and fumes will also pose occupational hazards.
- **Eliminate potential exposure to dust from CIS/CIGS production.** Dust from copper, indium, gallium, and selenium accumulates in production equipment, presenting potential inhalation risks to workers.
- **Eliminate potential for selenium dioxide exposure.** Selenium dioxide is a tissue poison like arsenic, and great care should be used to ensure that workers are not exposed.

Finally, as part of the industry-wide effort to create green jobs, solar companies should engage with green job advocates and support federal and state green-collar jobs legislation that promotes the creation of high-quality green jobs. These jobs should include safety standards as well as provisions for education, training, and support services to ensure that all community members have the opportunity for careers in the solar industry.

F. Protect Community Health and Safety throughout the Global PV Industry and Supply Chains

We need to ensure that the communities where solar PV products are made, used, and recycled (including communities that contribute to the global supply chain) are informed about the hazards of chemicals being used nearby. Companies manufacturing and selling solar PV products must take responsibility for monitoring their supply chains and ensuring the health and safety of workers and nearby communities. This includes ensuring that workers throughout the industry earn a living wage.

As noted above, the solar PV industry received negative publicity from a recent *Washington Post* story of silicon tetrachloride waste dumping in China.¹¹⁰ That plant is owned by Luoyang Zhonggui High-Technology Co. and is a key supplier to one of the world's largest solar cell manufacturers. Supply chain audits by solar PV manufacturers are critical to avoid potential environmental damage and social injustices, especially as production shifts to countries with minimal environmental regulations.

In the U.S., toxic chemicals used in solar production, including nanomaterials, should be listed on Materials Safety Data Sheets (MSDSs), and Toxic Release Inventory (TRI) reports. Manufacturers should take steps to continuously reduce and eliminate volatile chemicals and those that have a high potential to contaminate air, water, and soil.

Manufacturers also need to be responsible for potential hazards posed by solar panels during use. It is critical that residents and fire safety personnel have information about the potential exposure to solar PV toxic materials in residential or commercial building fires.

VII. Taking Action: What You Can Do

Working together, we need to take steps to ensure that today's solar PV products are safe and sustainable throughout their lifecycles and supply chains. SVTC makes the following recommendations:

State and Federal Policymakers

- Author and support legislation that requires take-back policies for electronic waste, including solar panels.
- Enact policies regarding the import and sale of products containing toxic materials; these policies should, at a minimum, meet the standards set by recent E.U. legislation.
- Support legislation to prevent the export of hazardous waste to developing countries.
- Support legislation that promotes the creation of high-quality "green jobs." Green jobs protect worker health and safety, while providing a living wage, health and other benefits, job satisfaction, access for entry-level workers, and opportunities for career advancement.

Solar Panel Designers and Manufacturers

- Through continuous improvement in product and manufacturing design, reduce and eventually eliminate the use of toxic materials in the production of solar panels.
- Design and manufacture solar panels that can be easily and safely recycled.
- Know and disclose the chemicals used in products throughout their lifecycles.
- Assess the potential hazards of chemicals in use and avoid toxic exposure to workers, the environment, and the public.
- Establish effective take-back policies for solar panels, including strategies to collect and recycle panels when they are decommissioned.
- Monitor supply chains for the chemical inputs used in solar cell manufacturing and ensure that environmental and labor practices are safe and just.

Consumers

- Contact legislators with your concerns. Tell them you strongly support the use of solar energy and want to make sure it is advanced in a safe and just manner.
- Before purchasing solar panels, find out if the company will take back the solar panels after use and ensure responsible recycling. Also inquire whether the company actively supports legislation to require take-back programs and the use of responsible recyclers for the solar industry.
- Although manufacturers should ultimately take responsibility for ensuring product safety, consumers need information about the toxic materials used in solar panels and about any potential hazards those materials pose to users (for example, in the case of residential fires).
- When disposing of solar panels and other electronic products, be sure they are recycled in a responsible manner, without shipping waste overseas or using prison labor. For information about responsible e-waste recycling, visit the Electronics TakeBack Coalition website at: http://www.computertakeback.com/responsible_recycling/index.cfm

Appendix A

Overview of Chemicals Associated with Solar Photovoltaic (PV) Manufacturing and Disposal

- **Ammonia (NH₃)** is used to produce anti-reflective coatings for solar PV modules. High-level exposures may irritate the skin, eyes, throat, and lungs and cause burns. Lung damage and death may result from exposure to very high concentrations. Ingesting ammonia can burn the mouth, throat, and stomach, and ammonia in the eyes can cause burns and blindness.
- **Argon (Ar)** gas is used in thin-film solar cell manufacturing to apply a semiconductor onto a surface or as an inert cooling gas. Although considered non-toxic, it is known to result in death due to asphyxiation in confined spaces. In such cases, mental alertness is diminished, muscular coordination is impaired, judgment becomes faulty, and all sensations are depressed. Emotional instability often results and fatigue occurs rapidly. As the asphyxia progresses, there may be nausea and vomiting, prostration and loss of consciousness, and finally convulsions, deep coma, and death.
- **Arsenic (As)** can be released from the decomposition of discarded GaAs solar PV cells. Inhalation of high levels of arsenic causes throat soreness, lung irritation, increased lung cancer risk, nausea and vomiting, decreased production of red and white blood cells, abnormal heart rhythm, damage to blood vessels, and “pins and needles” sensations in hands and feet. Ingesting or breathing low levels of inorganic arsenic for an extended period causes skin darkening, and small “corns” or “warts” appear on the palms, soles, and torso. Skin contact may cause redness and swelling. Ingestion can increase skin, liver, bladder, and lung cancer risks. Ingesting very high levels can result in death.
- **Arsine (AsH₃)** is a doping gas used to add impurities to PV semiconductors. When inhaled, it attacks red blood cells, causing headaches, vertigo, and nausea. It can cause critically affect the kidneys and blood. Arsine is a recognized carcinogen and is similar in toxicity to the methyl isocyanate released in Bhopal. Arsine can be phased out and replaced with the less toxic tertiary butyl arsine (TBA).
- **Boron trifluoride (BF₃)** gas is used to dope silicon semiconductors. Exposure to large amounts over short periods of time can affect the stomach, intestines, liver, kidney, and brain and can eventually lead to death.
- **Brominated Flame Retardants (BFRs)** are chemicals that inhibit the ignition of combustible organic materials. BFRs are commonly used in computers, electronic products, televisions, insulating foams, and other building materials to reduce product flammability. BFRs bioaccumulate and are found at high concentrations in human breast milk. BFRs known as polybrominated diphenyl ethers (PBDEs) are used in polymers such as polystyrene foams, high-impact polystyrene, and epoxy resins (see PBDE item below).
- **Cadmium (Cd)** is a by-product of zinc, lead, or copper mining. Workers can be exposed through cadmium smelting and refining or through the air in workplaces that make Cd-based semiconductors. Acute symptoms vary depending on the specific cadmium compound, but can include pulmonary edema, cough, chest tightening, headache, chills, muscle aches, nausea, vomiting, and diarrhea. Cd is chronically toxic to the respiratory system, kidneys, prostate, and blood and can cause prostate and lung cancer. NIOSH considers cadmium dust and vapors as carcinogens. California has also determined (under AB 1807 and Proposition 65) that cadmium and cadmium compounds are carcinogens.
- **Cadmium chloride (CdCl₂)** is a soluble form of Cd that vaporizes more readily than other cadmium compounds. It is extremely toxic to workers exposed during feedstock preparation or through maintenance and fugitive emissions.

Information for this appendix was compiled from the International Labor Organization (ILO), NOAA's Office of Response and Restoration, the Intergovernmental Panel on Climate Change (IPCC), U.S. EPA, California EPA, U.S. OSHA, and California OSHA.

- **Cadmium sulfate (CdSO_4)** is used to apply CdS in CdTe and CIS/CIGS production. Cadmium compounds are toxic by inhalation and skin contact, and exposure may cause cumulative and irreversible effects. Cadmium sulfate causes nose, throat, and lung irritation, and lung edema may also occur. Symptoms are usually delayed for several hours and aggravated by physical effort. Repeated, prolonged exposure to dust may cause discoloration of teeth, loss of smell, shortness of breath, damage to liver and kidneys, and mild anemia.
- **Cadmium sulfide (CdS)** is used in CdTe and CIS/CIGS thin-film solar PV production. It is a suspected human carcinogen and is toxic to kidney, lungs, and liver. Some bacteria found in nature produce CdS, and research is underway to investigate possible use of these bacteria in solar PV manufacturing.
- **Cadmium telluride (CdTe)** is a thin-film semiconductor. Inhalation, ingestion, and dermal contact with CdTe are considered toxic, though very little CdTe toxicological data exists. The highly reactive surface of cadmium telluride quantum dots could trigger extensive reactive oxygen damage to the cell membrane, mitochondria, and cell nucleus.
- **Carbon nanotubes (CNTs)** are carbon allotropes (like diamonds and graphite) measured at the nanometer scale. Exposures are linked to mesothelioma in animals, and nanotubes are believed to present inhalation hazards similar to those of asbestos.
- **Carbon tetrachloride (CCl_4)** is used to manufacture c-Si PV cells. Exposure to very high amounts of carbon tetrachloride can damage the liver, kidneys, and nervous system (including the brain). CCl_4 can cause cancer in animals, and the Department of Health and Human Services (DHHS) has determined that it may be considered a human carcinogen.
- **Chromium VI (Cr VI)** is used in PV modules for chrome-plated hardware such as screws and frames. High levels of chromium have provoked asthma attacks, and long-term exposure is associated with lung cancer. Handling liquids or solids containing Cr VI can cause skin ulcers. Swallowing large amounts will cause upset stomach, ulcers, convulsions, kidney and liver damage, and even death. The EPA classifies Cr VI as a known human carcinogen.
- **Copper (Cu)** can be poisonous or fatal at high exposures. Inhalation exposures may occur through the vaporization of copper in CIS/CIGS production. Breathing high levels of copper can cause nasal and throat irritation. Ingestion of high levels of copper can cause nausea, vomiting, and diarrhea. Very high doses of copper can cause damage to the liver and kidneys and can ultimately cause death.
- **Copper indium diselenide (CIS)** is used in thin-film PV cells. There is limited toxicity information on CIS. Measurements of airborne concentrations of copper, indium, and cadmium from mechanical scribing and deposition operations on CIS/CdS modules were well below threshold levels. The main health issue related to CIS is the highly toxic hydrogen selenide feedstock gas (also called selenium hydride, see below).
- **Copper indium gallium diselenide (CIGS)** is similar to CIS but also contains gallium (Ga) (see below).
- **Diborane (B_2H_6)** is a doping gas used to manufacture a-Si cells. It is highly flammable and is considered highly irritating to skin tissues. In rare cases, it may cause liver and kidney damage.
- **Ethyl vinyl acetate (EVA)** is used to encapsulate solar PV cells. It is a non-toxic alternative to soft plastics like polyvinyl chloride (PVC) and bisphenyl A, but may release volatile organic compounds during manufacture.
- **Gallium (Ga)** is a rare soft metal used in GaAs PV and recovered from zinc and aluminum mining. It is not considered toxic, but may cause skin irritation after prolonged exposure. Scaling up of GaAs production is limited by the global scarcity of gallium. For use in manufacturing, Ga is converted into trimethylgallium ($\text{Ga}(\text{CH}_3)_3$).

- **Germane (GeH₄)** is often deposited with silane to dope a-Si layers with germanium. It is extremely toxic and can kill red blood cells and cause anemia and kidney failure.
- **Helium (He)** is a colorless, odorless, non-toxic gas used in solar PV to propel thin films onto a surface. Helium is absorbed by inhalation or skin contact. Inhalation causes a high voice, dizziness, dullness, headache, and possible suffocation. Containment failure can cause suffocation by displacing oxygen in confined areas. Skin frostbite is possible through contact with liquid He.
- **Hexafluoroethane (C₂F₆)** is used to etch semiconductors. It is an asphyxiant and in high concentrations may cause dizziness, nausea, vomiting, disorientation, confusion, loss of coordination, and narcosis. Very high concentrations may cause suffocation. Liquid hexafluoroethane may cause frostbite. Harmful amounts may be absorbed if skin contact is prolonged or widespread. It is listed as a potent greenhouse gas by the IPCC.
- **Hydrochloric acid (HCl)** is used to clean and etch semiconductors and to produce electrical grade silicon. Concentrated HCl is corrosive to the skin, eyes, nose, mucous membranes, and respiratory and gastrointestinal tracts. Inhalation can lead to pulmonary edema. Ingestion can cause severe injury to the mouth, throat, esophagus, and stomach. Other possible effects include shock, circulatory collapse, metabolic acidosis, and respiratory depression.
- **Hydrofluoric acid (HF)** is used to etch and remove oxidation from semiconductors. Low levels of HF gas can irritate the eyes, nose, and respiratory tract. Inhalation at high levels or in combination with skin contact can cause death from irregular heartbeat or lung fluid buildup. Splashes of HF on the skin can be fatal, but may cause no immediate signs of exposure. Swallowing even a small amount of highly concentrated HF affects internal organs and may be fatal.
- **Hydrogen (H₂)** is used to manufacture a-Si solar cells. It is considered non-toxic but is extremely flammable and explosive.
- **Hydrogen sulfide (H₂S)** is used in the manufacture of CIS/CIGS. It is considered an irritant and is extremely flammable.
- **Indium (In)** is a rare metal used as the semiconductor for CIS/CIGS, indium gallium phosphide, or indium gallium nitride solar PV. It is also used in lead-free solders. It is made from the highly reactive trimethylindium, which can spontaneously combust.
- **Indium gallium nitride (InGaN)** is a PV semiconductor. The toxicology of InGaN is not well documented, but the dust is a known skin, eye, and lung irritant. It is produced from trimethylindium, trimethylgallium, and ammonia.
- **Indium phosphide (InP)** is used in multijunction solar PV. It is listed under California Proposition 65 as a chemical known to cause cancer.
- **Lead (Pb)** is used to solder photovoltaic electrical components. Lead exposures occur in smelting and refining industries, soldering, and battery manufacturing. Workers can inadvertently bring home lead via clothing and possibly expose those most vulnerable: pregnant women and children. People who reclaim heavy metals from "recycled" electronics are also exposed. Lead is most toxic to the nervous system. Lead exposure may cause weakness in fingers, wrists, or ankles, and can also cause anemia. At high exposure levels, lead severely damages the brain and kidneys and may ultimately cause death. In pregnant women, high levels of exposure to lead may cause miscarriage. Lead is also considered a probable human carcinogen.
- **Nitric acid (HNO₃)** is used in solar PV manufacture to clean wafers, remove dopants, and clean reactors. Major occupational concerns relate to the potential for chemical burns.

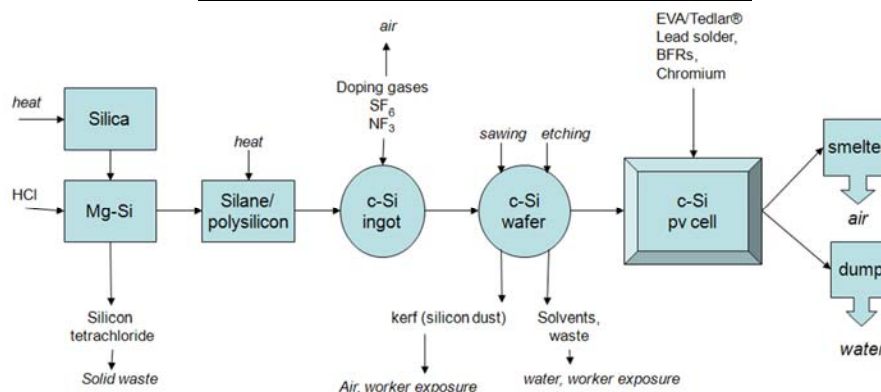
- **Nitrogen (N_2)** is used to dope semiconductors. Rapid release of nitrogen gas in an enclosed space can displace oxygen, and it therefore represents an asphyxiation hazard.
- **Nitrogen trifluoride (NF_3)** is used to clean reactors and etch polysilicon semiconductors. It emits toxic fumes when burned or reacted and can cause asphyxiation. The IPCC considers NF_3 a significant greenhouse gas, making fugitive emission control very important.
- **Phosphine (PH_3)** is a doping gas used to add impurities to photovoltaic semiconductors. It is extremely flammable and explosive and is considered a severe respiratory irritant. Phosphine can be replaced by less toxic tertiary butyl phosphine.
- **Polybrominated diphenyl ethers (PBDEs)** are flame-retardant chemicals added to plastics and foam products. Because they are mixed into plastics and foams rather than bound to them, PBDEs can leave the products and enter the environment. PBDEs undergo long-range transport and deposition, appearing in ringed seals found in the Canadian Arctic. Very little is known about the human health effects of PBDEs, but toxicity to the liver, thyroid, and neurodevelopment is reported in animals, and concerns are raised because of persistence and bioaccumulation in humans. The EPA requires special procedures for the transport, storage, or disposal of PBDE. California outlawed the sale of PBDEs and products containing them effective January 1, 2008.
- **Polysilicon** is the feedstock material used to produce silicon PV cells. It is obtained by heating silane or trichlorosilane gas.
- **Polyvinyl fluoride (Tedlar®)** is used in solar PV module backing sheets to extend product life and increase efficiency. These are preferred backing sheets due to strength and weather, moisture, and UV light resistance. Tedlar® dust may cause eye irritation, and skin contact may also produce irritation. Some formulations contain small amounts of one or more of the following compounds: lead, chromium, cadmium, selenium, arsenic, and antimony.
- **Selenium (Se)** is found in CIS/CIGS as an alloy of diselenide. Short-term exposure to high concentrations of selenium may cause nausea, vomiting, and diarrhea. Chronic exposure to high concentrations of selenium compounds can produce a disease called selenosis. Major signs of selenosis are hair loss, nail brittleness, and neurological abnormalities (such as numbness and other odd sensations in the extremities). Brief exposures to high levels of Se can result in respiratory tract irritation, bronchitis, difficulty breathing, and stomach pains.
- **Selenium dioxide (SeO_2)** is a by-product of CIS/CIGS manufacturing and an intermediary in the recovery of selenium from waste CIS/CIGS modules. It is highly toxic when inhaled and may cause skin burns and eye irritation. Chronic exposure may cause selenium-related diseases. Brief exposure to high levels of SeO_2 can result in respiratory tract irritation, bronchitis, difficulty breathing, and stomach pains.
- **Selenium hydride (H_2Se)** is used to apply the diselenide layer in CIS/CIGS. It is highly toxic and can cause respiratory irritation and selenium-related diseases. Inhalation causes a burning sensation, nausea, and sore throat. Skin contact can cause frostbite. It is extremely flammable. Methods are being developed to produce CIS/CIGS without H_2Se . Also called hydrogen selenide.
- **Silane (SiH_4)** gas is used to apply silicon thin films and make silicon crystal semiconductors. Major health hazards include respiratory tract, skin, and eye irritation. Silane gas is extremely explosive. At room temperature, silane is pyrophoric—it spontaneously combusts in air without external ignition.
- **Silicon (Si)** is the most widely used solar PV semiconductor. Crystalline silica (silicon dioxide, SiO_2) is a potent respiratory hazard, irritating skin and eyes on contact. Inhalation causes lung and mucus membrane irritation. Eye irritation results in watering and redness. Lung cancer is associated with occupational exposures to crystalline silica among miners, diatomaceous earth workers, granite workers, pottery workers, brick workers, and others.

- **Silicon tetrachloride (SiCl_4)** is a corrosive and toxic by-product and intermediary in silicon-based PV cell production. It reacts with water to form hydrochloric acid and can cause tissue damage. It causes severe respiratory problems when inhaled. Skin contact causes severe pain, and eye contact can cause permanent damage. It is one of a group of chemicals known as chlorosilanes.
- **Silver (Ag)** is used in solar PV electrical contacts or as the semiconductor in silver cells. Exposure to high levels of silver over long time periods may cause a condition called argyria, a blue-gray discoloration of the skin and other body tissues. Argyria is permanent, but it appears to be only a cosmetic problem. Exposure to high levels of silver can result in breathing problems, lung and throat irritation, and stomach pains. Skin contact with silver can cause mild allergic reactions such as rash, swelling, and inflammation.
- **Sodium hydroxide (NaOH)** is used to clean and etch semiconductors. Even very low levels can produce skin and eye irritation. High-level exposure can cause severe burns to the eyes, skin, and gastrointestinal tract, which may cause death.
- **Sulfur hexafluoride (SF_6)** is used to etch semiconductors and clean reactors in PV manufacturing. It is relatively inert and is considered an asphyxiant. The IPCC considers SF_6 the most potent greenhouse gas known.
- **Tetrobromo bisphenol A (TBBPA)** is a reactive brominated flame retardant used in the printed wiring boards of more than 90 percent of electrical and electronic products. The main use of TBBPA in solar PV is in inverters. Occupational exposure may occur from contact during production or through dust inhalation. Recent concerns focus on TBBPA as an endocrine disruptor; it is similar to bisphenol A, a known estrogen mimic. TBBPA also bioaccumulates in organisms.
- **Thiourea ($\text{CH}_4\text{N}_2\text{S}$)** is used to manufacture CdTe and CdS PV semiconductors. It is toxic to blood and causes thyroid and liver tumors. California recognizes thiourea as a carcinogen.
- **Trichlorosilane (HSiCl_3)** is the main source of electrical grade silicon. It is formed in the presence of silicon and hydrochloric acid and is toxic and flammable. Inhalation causes acute effects such as burns, difficulty breathing, headache, dizziness, bluish skin color, and lung congestion. Blurred vision results from eye contact, and ingestion can cause burns, vomiting, and diarrhea.

Appendix B

Annotated Solar Manufacturing Process Diagrams

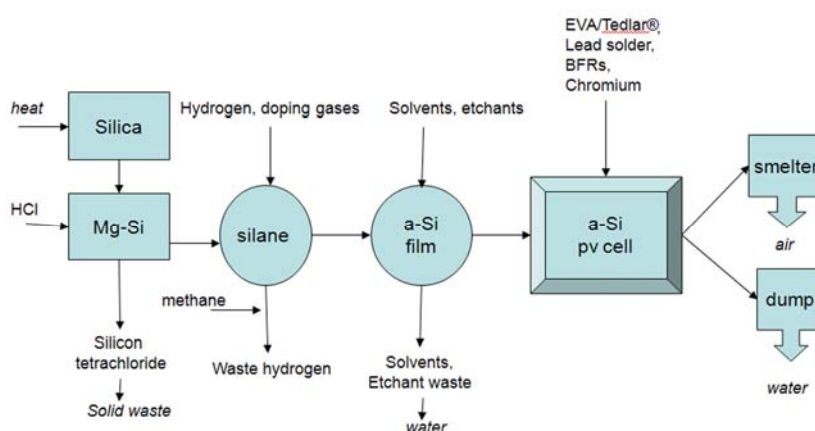
Figure 7: Crystalline Silicon Generic Process Diagram



Crystalline Silicon Generic Process Diagram Explanation (from page 11):

Silica is mined and refined into metallurgical grade silicon (Mg-Si). This is reacted with hydrochloric acid (HCl) where silane/polysilicon feedstock and silicon tetrachloride waste is produced. The resulting silane/polysilicon is heated to produce a crystalline silicon (c-Si) ingot that is doped to make c-Si into a semiconductor. The potent greenhouse gases sulfur hexafluoride (SF₆) and nitrogen fluoride (NF₃) are used in this step to clean the reactors. The c-Si ingot is cut into wafers, which are etched with reactive solvents to remove surface imperfections. Finally, the wafers are encapsulated with ethyl vinyl acetate (EVA) or Tedlar® to protect the surface, mounted onto a frame and wired into the PV cell. Without extended producer responsibility, these cells will end up in smelters and dumps where any hazardous materials will cause air and water pollution.

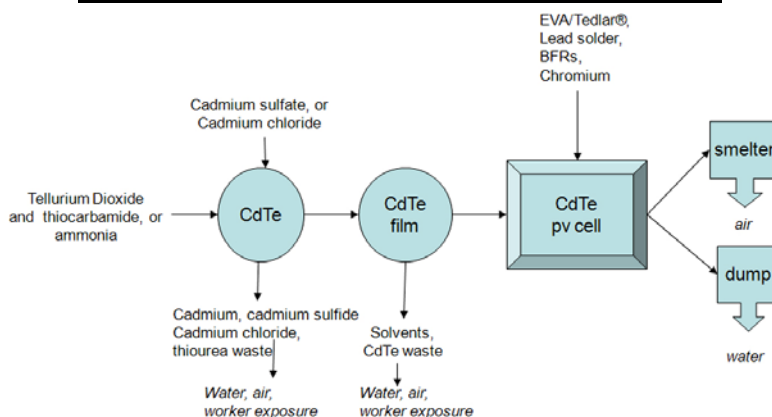
Figure 8: Amorphous Silicon (a-Si) Generic Process Diagram



Amorphous Silicon (a-Si) Generic Process Diagram Explanation (from page 13):

The first step in amorphous silicon (a-Si) PV cell production is similar to c-Si. Silane feedstock is mixed with hydrogen and doped with impurities before it is deposited onto a surface, etched, and then cleaned. The a-Si cell is mounted in a frame, encapsulated with EVA or Tedlar®, and wired to electrical components. Since many a-Si cells are put into consumer devices, their lifespan is shorter, and they often end up in smelters and dumps where hazardous materials will cause air and water pollution.

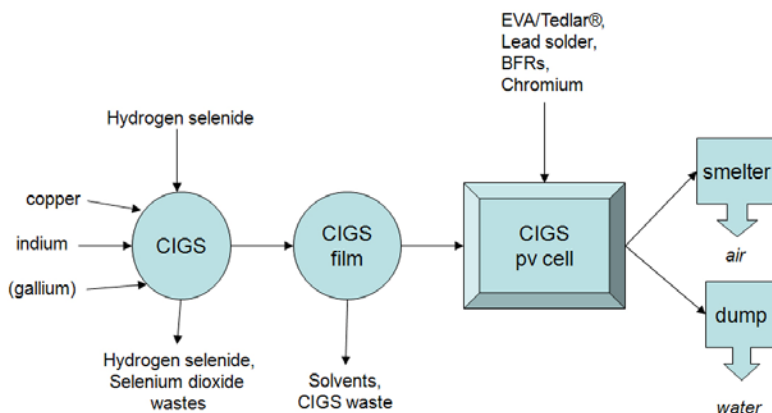
Figure 9: Cadmium Telluride (CdTe) Generic Process Diagram



Cadmium Telluride (CdTe) Generic Process Diagram Explanation (from page 14):

Cadmium Telluride (CdTe) PV cells are produced by mixing cadmium compounds, with thiocarbamide or ammonia, and tellurium dioxide, a step where cadmium and thiourea wastes are generated. The CdTe is then deposited onto a surface and the cell is mounted onto a frame, encapsulated, and wired to electrical components. Since Cd is a known carcinogen, and Te is a rare element, extended producer responsibility is important to prevent Cd from entering the water and air, and to recover Te.

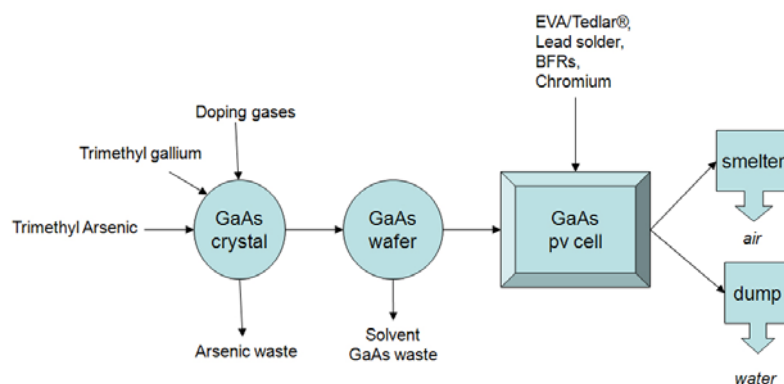
Figure 10: Copper Indium (Gallium) Selenide (CIS/CIGS) Process Diagram



Copper Indium (Gallium) Selenide (CIS/CIGS) Process Diagram Explanation (from page 16):

Copper indium (gallium) selenide (CIS/CIGS) cells are produced by mixing copper, indium, (and gallium in CIGS), and hydrogen selenide. In this step, hydrogen selenide and selenium dioxide wastes are generated. The semiconductor is then deposited on a surface, where is it etched and cleaned before being mounted in a frame, encapsulated, and wired. Since selenium is a known carcinogen, and indium is a rare element, extended producer responsibility is important to CIS/ CIGS production to prevent selenium from entering the water and air, and to recover indium.

Figure 11: Gallium Arsenide (GaAs) Generic Process Diagram



Gallium Arsenide (GaAs) Generic Process Diagram Explanation (from page 17):

Gallium arsenide (GaAs) crystals are produced by mixing trimethyl gallium and trimethyl arsenic in the presence of doping gases, often producing arsenic waste as a byproduct. The crystal is sliced into wafers, etched, and cleaned before being mounted to a frame, encapsulated, and wired. Since arsenic is a known carcinogen, it is important to ensure it does not end up in the water or air.

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