

Chapter 22

Material and Process-Related Contaminants in Solar Photovoltaics: Key Issues, and Future Prospects



Venkata S. N. Chava and Sreeprasad T. Sreenivasan

Abstract The limited availability of fossil fuel sources coupled with the health and environmental risks associated with their use lead to the increased focus on renewable energy resources such as solar photovoltaics (PV) as a potential energy source for the future. Currently, significant research is focused on improving the efficiency (i.e., reducing the cost per watt power) and long-term reliability of solar cells to make PV cells competent with fossil fuels. On the other hand, little attention is given to understanding and assessing long-term environmental impacts associated with the contaminants produced during the manufacturing and application of solar cells. Hence, it is imperative to review and evaluate the critical environmental issues relevant to solar PV, especially in emerging PV technologies. This chapter will introduce different PV technologies, including silicon PV, thin-film PV, and perovskite solar cells, and outline the materials and the processes used in PV technologies. A review of the health and environmental impact of Sn- and Pb- based PV technologies and the need for alternative technologies such as Sn- and Pb-free perovskite PV will be presented. The potential environmental, energy, and health impacts and a review of possible mitigation strategies related to perovskite solar cells-induced hazards are also presented.

Keywords Sustainable energy · CO₂ emissions · Photovoltaics · Solar panel · Module · Silicon · CdTe · CIGS · Perovskite · Recycling · Toxicity · Health and safety · Environmental impact

22.1 Introduction

Land, energy, and water are among the most precious and critical resources for human survival. The mismanagement of these resources has, however, contributed negatively to climate change. Currently, fossil fuels are the primary energy sources from which

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we generate energy for our daily needs, including industries, transportation, etc. In the last century, due to huge scientific and technological advancements, there has been a significant rise in the consumption of energy derived from fossil fuels (Smalley 2005). In this process, the adverse effects of fossil fuel emissions on climate are largely ignored, which led to a significant rise in global temperatures. Now, there is a consensus (Carlton et al. 2015), after decades of arguments (Oreskes 1686), about the negative consequences of the emissions, including severe human health and safety concerns, due to the production and use of these fossil fuels. Addressing climate change has been identified as one of the top 10 global challenges for the twenty-first century (Smalley 2005). Two major initiatives, including the Kyoto protocol (1995) and the Paris climate agreement (2015), are launched to address the climate challenge. However, the progress made is negligible when compared to the threat we are facing (Climate Change 2019). In the last couple of decades, there is a shift towards the use of alternative energy sources. These alternative energy sources include solar, wind, biomass, hydrogen, geothermal, etc. There is a non-uniform shift across the globe when it comes to adopting the renewable energy sources for public and industrial applications (Fig. 22.1) (Xu et al. 2019). A major reason for this disparity could be the lack of government support in the form of incentives to the companies and customers that can lead to the cost per watt of these alternative energy sources comparable to the fossil fuel sources (Lund 2009; Koseoglu et al. 2013). Moreover, the shift toward alternative sources has taken place at much slower rates than the increased CO₂ emissions from fossil fuels. In this scenario, an important question arises: why do countries across the globe rely heavily on fossil-fuel-based energy sources? One important reason for this could be the lack of alternative energy sources that can meet the existing energy demand (Smalley 2005; Armaroli and Balzani 2007; Dorian et al. 2006).

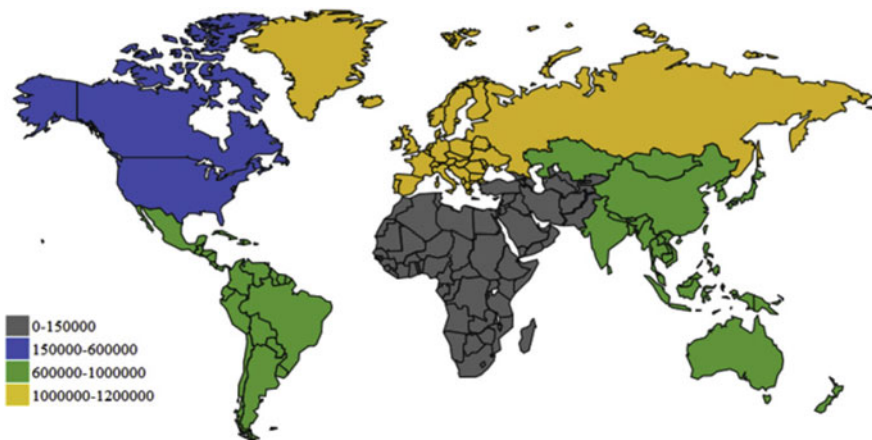


Fig. 22.1 Renewable energy generation by region in 2016 Unit: Gwh *Sources* International Energy Agency, the World Bank). Reproduced with permission from Elsevier (Xu et al. 2019)

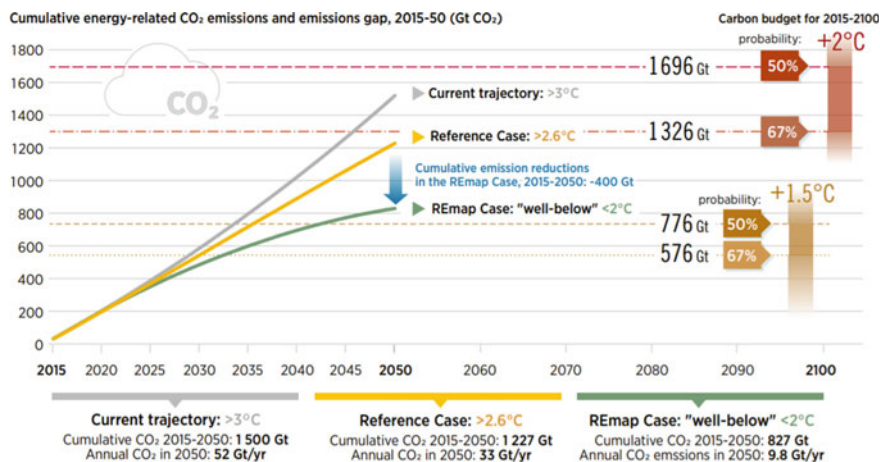


Fig. 22.2 A pathway for a well-below 2 °C climate target, towards 1.5 °C. Cumulative energy-related CO₂ emissions for the period 2015–2050 and emission budgets for 2015–2100 for 1.5 and 2 °C scenarios (Gt CO₂) (Global energy transformation: a roadmap to 2050 2019).

It is predicted that if renewable energy resources can provide two-thirds of the total global energy demand, this can help restrict the global temperature rise under 2 °C (Fig. 22.2) (Gielen et al. 2019). Therefore, immediate action for a fast transition towards renewable and clean energy sources is needed for addressing climate change problems. Such transition in global energy use is multi-faceted that is constantly progressing due to evolving technologies, socioeconomics, and government policies. Figure 22.2 summarizes a trajectory of cumulative energy-related CO₂ emissions with corresponding changes in global temperatures. To restrict the increase in temperature below 2 °C, the CO₂ emissions should drop below 9.8 GT/Year by 2050 from the current 52 GT/Year rate.

Electric power generation using solar photovoltaics has always been considered the primary choice for a clean and renewable energy economy. The belief in PV technologies is due to the significant availability of solar radiation that can be harnessed to generate power across the world. Given the increasing demand for renewable energy production, considerable investments are made in this sector, including research and manufacturing. However, the health and safety concerns arising due to the generation and consumption of solar PV are often overlooked. Therefore, it is imperative for both scientists and engineers to seriously consider and evaluate all possible scenarios of solar PV manufacturing and applications that could lead to undesirable health and safety consequences. Finally, both the government and policymakers must encourage new R&D innovations, manufacturing, and installations in solar PV. They should also consider imposing strict regulations on PV technologies, especially on those that may pose serious health and safety concerns. Hence, this chapter aims to provide a comprehensive overview of the safety and health concerns related

to various materials, processes used to manufacture different types of photovoltaic cells and modules, and their practical use.

22.2 Solar Cell Technologies

The photovoltaic effect is fundamental for the design and operation of solar cells. The photovoltaic effect is defined as the process that generates either voltage or current when the device (or solar cell) is exposed to a light source of a suitable wavelength. Solar photovoltaics (PV) employs the photovoltaic effect to produce electricity from solar radiation. A major milestone in the history of solar PV technology is the first demonstration of a practical silicon photovoltaic (PV) cell, at Bell Laboratories in 1953 (Perlin 2004), that converted solar energy into electricity. Since then, different PV technologies have emerged, including silicon PV, thin-film PV, dye-sensitized PV, perovskite PV, etc. (Amin et al. 2017). The classification of these technologies (or devices) is based on the absorbing film (or active layer) used in the PV cell. Among these technologies, Si and thin-film (CdTe) based solar panels have been used for practical applications for almost > 2 decades. Figure 22.3 shows a comparison of the share of the total PV installations worldwide by technology.

22.2.1 Overview of the Material Properties of Absorbing Materials Used in Different PV Technologies

In a solar cell, the absorbing material (or active layer) is the key component that absorbs light and generates e-h pairs and a photovoltage using the photovoltaic effect.

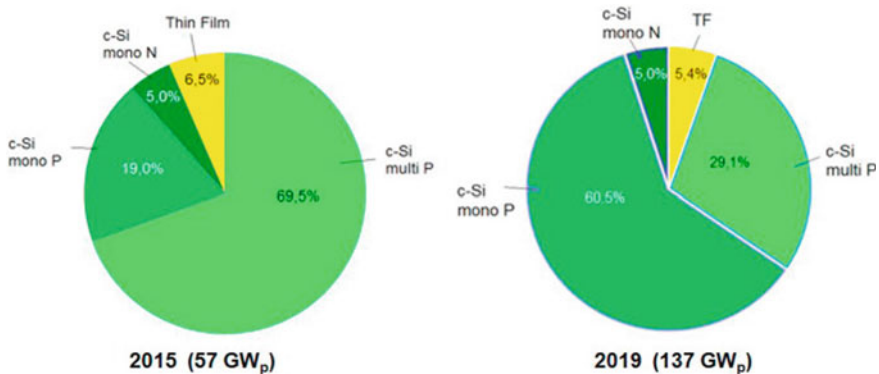


Fig. 22.3 Comparison of market share of different PV technologies. Reproduced with permission from Elsevier (Benda and Černá 2020)

Conventionally, the solar cells are designed and fabricated by forming suitable junctions (e.g., p-n, Schottky) using inorganic semiconductors as absorbing films. While there exist several semiconductors with a suitable bandgap to absorb incoming solar radiation and produce a measurable current, only a few of them are used in PV cells due to constraints related to material quality, cost, and availability that are critical for commercialization. Semiconducting materials with a direct bandgap of 1.5 eV, high optical absorption coefficient (10^5 cm^{-1}), high quantum efficiency are considered as an ideal choice for terrestrial solar cell applications (Wadia et al. 2009). In addition, the semiconducting absorber should be able to form a good electronic junction (homo/hetero/Schottky) with suitably compatible materials. While elemental semiconductors are preferable from the manufacturing point of view, there are no suitable materials available with a direct bandgap close to 1.5 eV. Interestingly, even though silicon (indirect bandgap of $E_g = 1.1 \text{ eV}$), is not an ideal material for PV, it still dominates the PV market due to various reasons including advancements in silicon microelectronics and reliability, as will be discussed later in other sections. Due to indirect bandgap nature of Si, the Si wafers used in PV must be at least 50 mm thick for effective solar absorption, unless the optical absorption is enhanced using some additional design and process steps. Besides silicon, other elemental semiconductor materials that showed some promise in laboratory research are diamond-like carbon (Ma and Liu 2001), and fullerene films (Narayanan and Yamaguchi 2003). However, the synthesis and formation of electrical contacts with these materials is a challenging task. There also exists a big library of compound semiconductor or alloys that are suitable for PV applications. A metastable film of a-Si:H, with advantages including large tailorable bandgap, and high optical absorption coefficient, is also a suitable semiconductor material for PV applications (Rech and Wagner 1999). In the early days, the a-Si:H-based solar PV technology was considered as a major contender to challenge the crystalline Si photovoltaics dominance. Despite of its promise, the a-Si:H technology is not a commercial success. become a reality. A few other compound semiconductors based thin-film solar cells, including GaAs, CdTe, Cu_2S , Cu_2O , InP, Zn_3P_2 , etc., are also reported. Of these, GaAs and InP with direct bandgaps of 1.4 eV and 1.34 eV, respectively, are ideal for photovoltaic applications, but the high wafer costs together with device processing challenges severely restricted their commercialization. Besides the active semiconductor material, careful consideration of other materials required for device fabrication is paramount. With increasing number of components, the number of possible materials increases in geometrical proportion. On the other hand, the phase diagram of the compound semiconductors and alloys in bulk form is quite complex, and therefore poses a significant challenge in the quality and control of the material growth (Altamura and Vidal 2016; Bosson et al. 2017). In addition to binary semiconductors, there are various ternary semiconductor based PV cells. $\text{Cu}_2\text{ZnSnS}_4$ (popularly referred to as CZTS) is a quaternary absorber materials with an optimal bandgap (1.5 eV) and high absorption coefficient ($>10^4 \text{ cm}^{-1}$) (Katagiri et al. 2009). Even though inorganic semiconductors can offer high structural stability critical for long term reliability, organic semiconductors (e.g., fullerenes), which combine superior optoelectronic properties and processing properties have attracted significant research attention (Brabec and Durrant 2008).

The absorption of incoming photons by organic semiconductors, creates an exciton, which is bound pair of electron and hole, with a binding energy of approximately 0.5 eV. Each excitons when dissociated will generate an unbound electron–hole pair at the dissociation sites, and these charge carriers (electron and holes) are subsequently separated and transported to the suitable contact electrodes. A majority of semiconducting polymers are not optimal absorber of incoming solar radiation as they have $E_g > 2.0$ eV (Hoppe and Sariciftci 2004). In addition, owing to low charge-carrier and exciton mobility, the thickness of the polymer absorbing film cannot be above 100 nm. In these materials, Similar to silicon, light-trapping strategies can be employed to enhance the optical absorption. Despite of these limitations, organic semiconductors provide unique benefits such as solution based device processing at room temperature on flexible substrates. Further, the device fabrication by employing low-energy deposition methods such as spin or blade coating, substantially reduces the device costs (Brabec and Durrant 2008; Zhao et al. 2018). Perovskite solar cells and quantum dot solar cells are a recent addition to the family of solar cells that have shown tremendous research progress in the last decade (Park 2015; Kamat 2013). Perovskites have unique material properties, including direct bandgap, high charge-carrier mobilities, low exciton binding energies, wide-wavelength absorption, which makes them good candidates for solar cell applications. There are significant scientific developments in these new device technologies that exploited low dimensional quantum confinement effects for achieving enhanced device performance (Wright et al. 2020). Figure 22.4 summarizes the historical progress of the different solar cell technologies with corresponding best cell efficiencies certified by NREL.

While Si and thin-film PV technologies have shown tremendous growth in terms of their installations, owing to their cost advantages, emerging PV technologies such as DSSC and perovskite solar cells (PSC) have the potential to reach the commercial

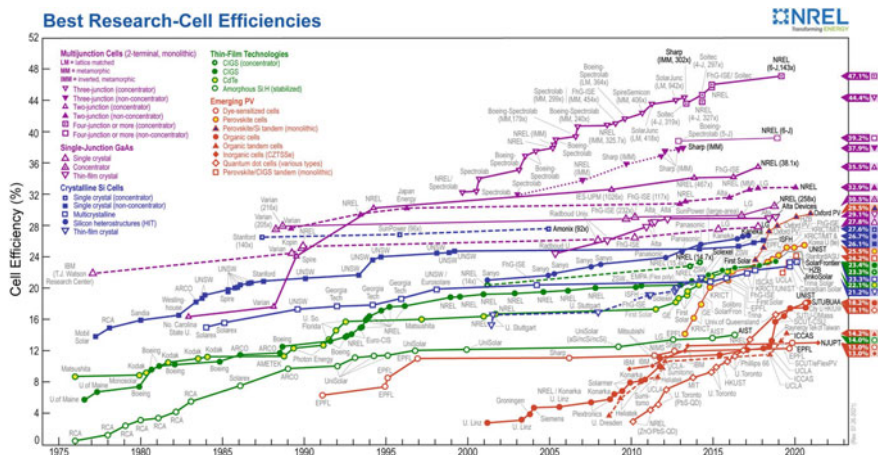


Fig. 22.4 A plot showing the historical data of highest certified cell efficiencies of different PV cells (Best research-cell efficiency chart 1976)

market and compete with Si and thin-film PV technologies. Hence, considerable research efforts have been devoted in the last decade to improve the efficiency and stability of the PSC technology.

The solar cells based on silicon wafers are generally referred to as the first-generation PV technologies. Currently, about 90% of the commercial solar cells are manufactured using silicon wafers, either single crystalline or multi-crystalline (Fig. 22.3). The dominance of silicon solar cells stems from the high efficiencies of Si PV modules with demonstrated long-term stability. Starting from wafer manufacturing to solar cell fabrication technology, the early success in the field of silicon PV was driven by R&D advances in silicon microelectronics. The major share of Si PV technology cost lies in the silicon wafer, which is more than fifty-percent of the total module manufacturing cost. Alternatively, the thin-film solar cells are expected to lower the PV module costs due to the relatively inexpensive absorbing films used in them. The thin film based photovoltaics are commonly referred to as second-generation PV technologies. In addition to their lower module cost, the silicon supply shortage has also contributed for the rapid commercialization of thin-film photovoltaics modules. Several distinct thin-film technologies are now available, based on a-Si, poly-crystalline Si, mixed phases, or chalcogenides. There is also a third generation of solar cell technologies that include dye-sensitized solar cells, organic solar cells, perovskite solar cells, etc. The primary difference between the third generation differs from the first and second generation is in terms of materials used for cell formation or in terms of the operation principle of the device. The third-generation PV solar cells have entered the commercial market recently, and the 3rd generation PV technologies are yet to prove their full potential in the PV market (Kim et al. 2018a).

22.2.2 *First-Generation (or Silicon) Solar Cells*

Silicon solar cells are classified into three categories based on the silicon used. These include monocrystalline (m-Si), multi-crystalline (mc-Si), and amorphous silicon (a-Si). Silicon is an indirect bandgap material that is successfully used to make commercial solar cell modules for almost 4 decades. Several different silicon solar cell structures are designed and optimized for achieving high efficiency are emerged in the last 20 years. These structures are presented in Fig. 22.5.

22.2.2.1 **Silicon Solar Cell Fabrication Process Steps**

While there are different types of Si solar cell technologies (Fig. 22.6), the process steps discussed below are common and applicable in most Si solar cell fabrication with minor changes in the cell design and process. The fabrication of silicon solar

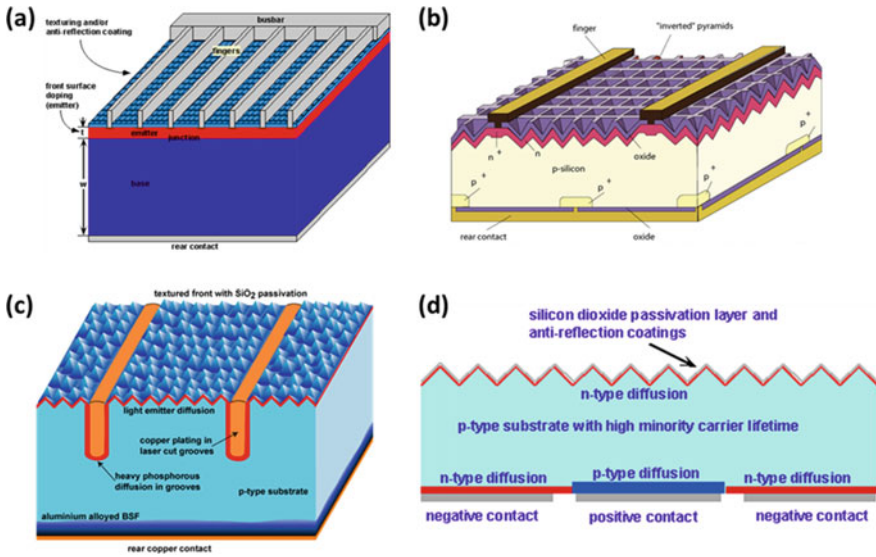


Fig. 22.5 Schematic showing various types of silicon solar cell structures. **a** Standard screen-printed silicon solar cell **b** passivated emitter rear localized (PERL), **c** buried-contact cell structure **d** back contact, back junction (BC-BJ). Reproduced with permission from www.pveducation.org Honsberg and Bowden (2019)

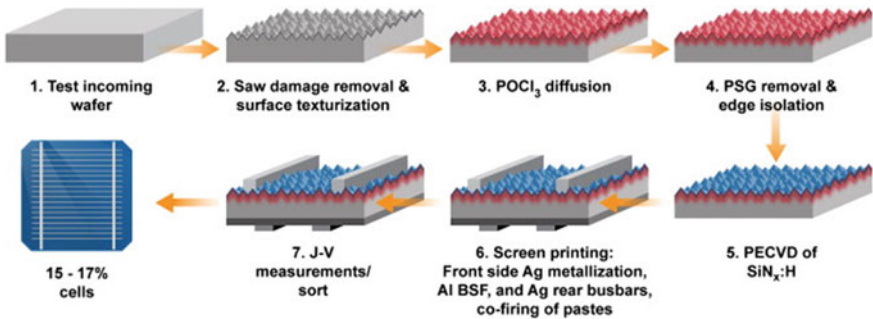


Fig. 22.6 Process flow for fabricating a standard c-Si solar cell. Reproduced with permission from Elsevier (Goodrich et al. 2013)

cells begins with a monocrystalline or multi-crystalline silicon wafer substrate (p-type, ~ 300–500 μm thick, 6 inch wafer). The cell fabrication process steps are discussed below.

Saw damage removal: The silicon wafers used in PV manufacturing are obtained by cutting ingots using either slurry based sawing or diamond wire sawing. In general, the sawing process results in a small mechanical damage and a surface contamination layer on each face of the wafer. Therefore, as a first step of the cell manufacturing

process, this damage and surface contamination should be removed. Typically, 10–20 μm of silicon is etched from both top and bottom faces of wafers. The etch depth is based on the type of sawing used i.e. diamond wire sawing or slurry based sawing. The saw damage removal is typically done using acidic (mixture of HNO_3 , HF and CH_3COOH) or hot alkaline (NaOH or KOH in water) solution (Park et al. 2009).

Surface Texturization: After the saw damage removal etching step, the silicon wafer surface reflects more than 30% of the incident light. To minimize the optical absorption losses due to surface reflection, the wafer surface undergoes a process called “texturing” (Abdullah et al. 2016). The reflection losses in commercial silicon solar cells are reduced mainly by random chemical texturing. The texturization of mono-crystalline silicon wafers with randomly distributed pyramids on the surface can be achieved by treating the wafer in a mixture of diluted NaOH and KOH with isopropanol (IPA) at 80 °C. This random texturization process is not so effective in case of multi-crystalline silicon wafers compared to mono-crystalline silicon wafers. Through this texturization process, the optical reflection losses from the silicon wafer surface can be lowered down to 10% from 30% seen at the end of the saw damage removal step.

Emitter diffusion (junction formation): As described previously, the photovoltaic cell operation requires a semiconductor junction to separate the photogenerated electron–hole pairs and develop photovoltage. Therefore, an n-type impurity (e.g. phosphorus) is introduced into the starting p-type silicon wafers in this step to form the junction. POCl_3 is the commonly used source for phosphorous doping in silicon solar cell manufacturing (Wolf et al. 2015). Typically the diffusion of POCl_3 is done inside a furnace at a temperature of ~ 900 °C. The p–n junction is formed about 0.5 μm below the top surface when the phosphorous diffusion is carried for 30 min at 900 °C.

There exist alternatives technologies to POCl_3 furnace diffusion for dopant deposition, including screen printing (Kwon et al. 2011), spin-on dopants (SOD) (Yadav et al. 2015), or chemical vapor deposition (CVD) (Schmich et al. 2007).

PSG Removal and Edge isolation: In the previous step, the diffusion of phosphorous dopant source happens via the gas phase, and as a result, the emitter layer is usually formed on the entire surface of the wafer. This results in the formation of shunts between the n-type and the p-type region of the device. To address this issue or isolate the front and the rear side emitter, edge isolation is done after the emitter diffusion step. Typical edge isolation methods (Comparison of different techniques for edge isolation 2001) include mechanical (Arumugan et al. 2005), laser cutting (Abbott et al. 2007; Kray et al. 2007; Zhang et al. 2010), or plasma etching. Plasma etching is the most common and popular method used in industrial silicon solar cell manufacturing. By using fluoride or oxide plasma environment, electrical isolation of the front and the rear emitter is achieved by removing $\sim 2\text{--}5$ μm of silicon from the edges.

Antireflection coating (ARC): As discussed earlier, the top surface of silicon reflects $\sim 10\%$ of the incident light after the surface texturing step, and this results in a significant loss in terms of the device efficiency. Therefore, further reduction of surface reflectance from silicon solar cell can help improve the cell efficiency. This

can be achieved by depositing an antireflection coating (ARC) on the top surface. A critical material requirement for ARC is the suitable refractive index of the ARC film. In general, materials with refractive index between 1.4 and 2.7 can be used as an antireflective coating (ARC) for silicon solar cells. Silicon nitride (SiN_x) is the popular choice as ARC for silicon solar cells due to its optimal refractive index and bulk passivation of surface states (Sopori 2003), and as a result enhancement in the short circuit current density (J_{sc}) and open circuit voltage (V_{OC}) can be observed. Typically, the SiN_x is deposited using plasma enhanced chemical vapor deposition (PECVD).

Double layer ARC coatings [e.g., $\text{SiN}_x/\text{SiO}_2$ (Kim et al. 2013), $\text{MgF}_2/\text{SiN}_x$ (Chu 2011)] have also been shown to mitigate the surface reflection losses and improve the passivation. In the last decade, plasmonic solar cells (Matheu et al. 2008) that leveraged plasmonic scattering of metal nanoparticles has emerged as a new paradigm in solar cells. Owing to silicon's indirect bandgap, plasmonic scattering can enhance the absorption in conventional silicon solar cells (Green and Pillai 2012). Plasmonic silicon solar cells with improved efficiencies are reported by leveraging the surface plasmon resonance (SPR) of metal nanoparticles [e.g., Ag NPs (Sardana et al. 2015; Sardana 2014)] deposited on the top surface of silicon.

Metal contact formation (metallization): The process of contact formation is a vital solar cell processing step because it strongly affects various properties of the silicon solar cell, such as short circuit current, open-circuit voltage, series resistance, shunt resistance, and the fill factor. For high-efficiency solar cells, the front electrodes should have low series resistance and low area coverage (Schroder and Meier 1984). The most widely used metal contacting technique for silicon solar cells is screen-printing (Hoenig et al. 2012). The front side contact is achieved by a screen-printed silver paste (Hilali et al. 2006). In contrast, the rear side electrode formation and surface passivation are attained by alloying a screen-printed aluminum paste with silicon (Gatz et al. 2011). The pastes are subsequently dried in an oven at a temperature of approximately 300 °C.

Contact firing: The screen-printed contacts initially lie on top of the insulating antireflection coating. The silicon solar cells undergo a short heat treatment at temperatures up to 900 °C, using an IR belt furnace (Cooper et al. 2010). During the firing process, the antireflection coating layer experiences selective dissolution such that the front Ag contacts penetrate through the antireflection coating onto the emitter while avoiding deep penetration into bulk silicon. Simultaneously, the back surface field (BSF) formation with aluminum is achieved.

22.2.3 Second-Generation (or Thin-Film) PV Cells

Second-generation photovoltaics primarily include thin-film solar cells such as a-Si or Cadmium Telluride (CdTe) or (CIGS) (Chopra et al. 2004; Lee and Ebong 2017). These technologies are already matured and have been in the market for almost 2 decades.

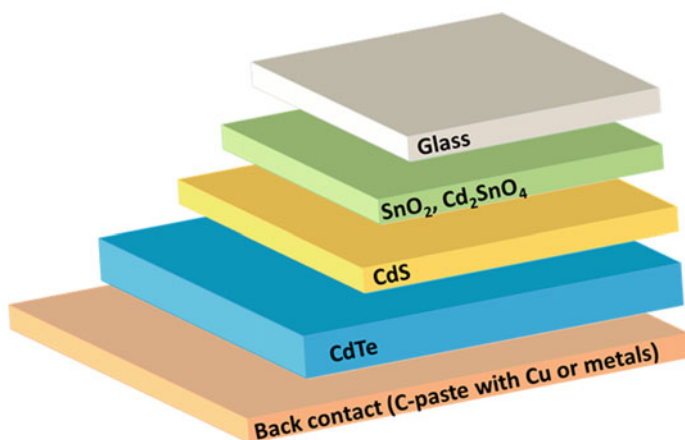


Fig. 22.7 Schematic of a CdTe solar cell device structure

22.2.3.1 CdTe Solar Cells

The CdTe is the leading contender to the Si PV and comprises ~ 5% of the total installation worldwide in 2019 (Fig. 22.3). Also, this technology entered the commercial market almost 2 decades ago.

CdTe Solar Cell Fabrication Process

The most commonly used CdTe solar cell is fabricated by forming a heterojunction between CdS and CdTe. Figure 22.7 shows the cross-sectional image of CdTe solar cell structure fabricated on glass substrate with a junction formed between CdTe and CdS. The first step in the CdTe solar cell device fabrication is the substrate cleaning. The commonly used substrate in CdTe solar cells is SnO₂-coated glass that can be obtained commercially. After cleaning the SnO₂-glass substrate, CdS film is deposited using chemical-bath deposition (CBD). This is followed by the deposition of absorbing CdTe thin-film. Different techniques including close-spaced sublimation, vapor-transport deposition, or electrodeposition for CdTe deposition. After CdTe deposition, CdTe is prepared (chemical etching) for back contact formation. The back contact can be carbon paste containing Cu_xTe and HgTe, or other metals (e.g. Cu). The inclusion Cu in the back contact improves both the performance and stability of the CdTe solar cells.

22.2.3.2 CIGS Solar Cells

CuIn_xGa_{1-x}Se₂ (or CIGS) solar cell is another prominent example for thin-film solar cells. A schematic of the device is shown in Fig. 22.8. In these devices, the absorbing

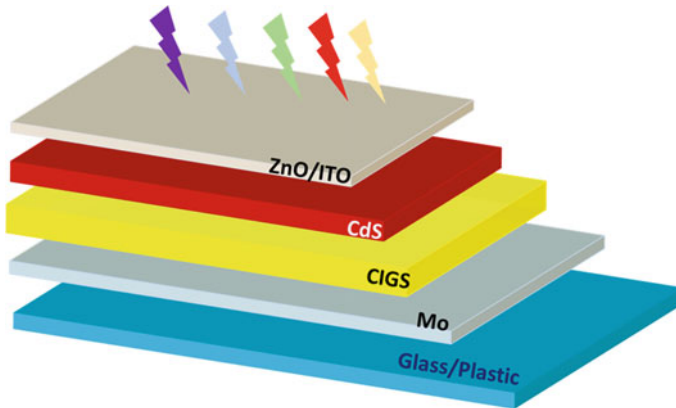


Fig. 22.8 Schematic of a CIGS solar cell device structure

film is formed by alloying CuInSe_2 and CuGaSe_2 , and the bandgap of the absorbing film can be tuned by modifying the composition of In and Ga. Both CuInSe_2 and CuGaSe_2 have a direct bandgap, very high absorption coefficient (10^5 cm^{-1}), and typically 1–2 μm thick active absorbing films are used in the devices.

CIGS Solar Cell Fabrication Process

The substrates used for CIGS cell fabrication includes either glass, metal foil, or plastic. The first step in the device fabrication is coating of 0.5–1 μm Mo film on glass (i.e., substrate) using sputtering process. The next step after Mo film coating is the formation of active CIGS absorber film. The CIGS film can be deposited on top of Mo film using different methods such as evaporation of elements, sputtering of metals followed by selenization with H_2Se , reactive sputtering of metals with Se vapor, or printing of metals from ink precursors followed by selenization. The growth of CIGS is assisted by Na atoms that are diffused through Mo film into the CIGS. After this CdS layer is formed on top of CIGS film by using CBD technique. This is followed by deposition of a bilayer consisting of intrinsic and conducting ZnO. ZnO can be deposited using either sputtering or CVD. The absence of Na in the device may lower the device efficiency by 2–3%. Therefore, when non-Na-containing substrates are used, alternative steps are required to improve the efficiency such as introducing NaF during the CIGS deposition or forming a 6–12 nm NaF layer on Mo back contact. These cells can be further processed to make CIGS modules for practical applications. The schematic for the CIGS module fabrication process flow is shown in Fig. 22.9.

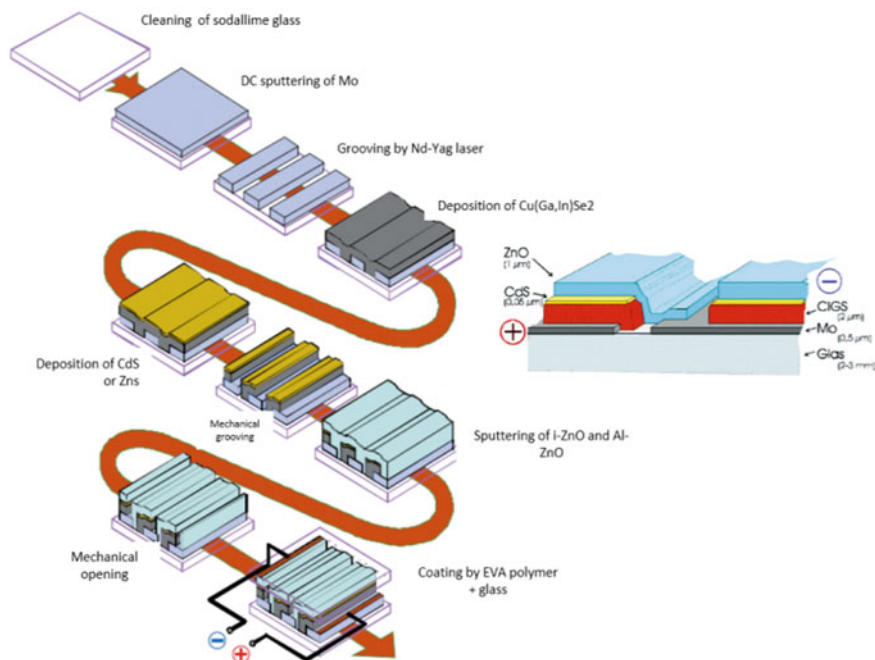


Fig. 22.9 (Left) A schematic showing the CIGS photovoltaic module fabrication process steps starting from cleaning of the glass substrate. (Right) A cross-section view of CIGS solar cell depicting different layers in the device. Reproduced with permission from EDP Sciences-SIF (Slaoui 2017)

22.2.4 Third Generation (or Emerging) Solar PV Cells

Third-generation solar cell technology includes dye-sensitized solar cells, perovskite solar cells (PSCs), quantum dot (QD) solar cells, etc. In this section, we limit our discussion to PSC-based solar cells owing to their potential for commercialization and multiples environmental issues related to the processing and use of PSCs.

22.2.4.1 Perovskite Solar Cells (PSCs)

Perovskite solar cells are the devices in which the light-harvesting active layer has a perovskite structure. The perovskites have a general formula of ABX_3 with a cubic structure. In ABX_3 , A is a monovalent cation (cesium (Cs), methylammonium (MA), or formamidinium (FA)); B is a divalent cation (Pb or Sn); and X is a halogen (e.g., Cl, Br, or I) (Fig. 22.10). Several perovskite compounds are reported in the literature, and only a few are actively pursued for PSCs applications. Among them, organic–inorganic hybrid perovskites (OIHP) have been the leading candidates. The OIHP compounds have shown great promise in applications, including solar cells,

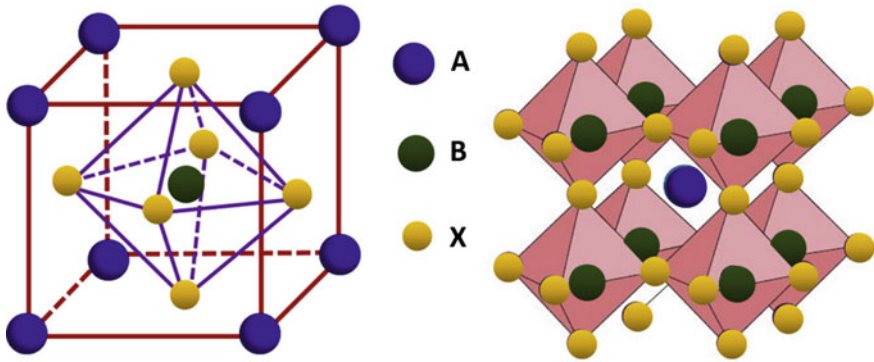


Fig. 22.10 a Schematic of perovskite crystal structure. Reproduced with permission from Elsevier (Zhao and Wang 2018)

light-emitting diodes (LEDs), photodetectors, and transistors (Kojima et al. 2009). In particular, the Methyl Ammonium Lead Iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) perovskite owing to its excellent material properties, including *direct bandgap*, *tunable visible and near-infrared light absorption*, *ambipolar transport*, *long diffusion lengths*, *high absorption coefficient* (10^4 cm^{-1}), *low exciton binding energy* ($\sim 10 \text{ meV}$), and *high charge carrier mobilities* combinedly contributed significantly to the progress of perovskite solar cells (PSCs) (Stranks et al. 2013; Herz 2017; Tan et al. 2014; Xing et al. 2013).

22.2.4.2 Perovskite Solar Cell (PSC) Fabrication Process

Perovskite solar cell (PSC) fabrication predominately uses solution methods for depositing different films that are part of the device structure. Besides their exciting optoelectronic properties, the feasibility of solution-based synthesis and fabrication is also a major reason for tremendous progress of PSCs through university laboratory research. The fabrication technology of PSCs has evolved significantly (Park and Zhu 2020). Optimization of each process step in the device fabrication is critical for the enhancing the respective film properties and also the overall device efficiency and stability. Beside the absorbing perovskite film, the PSC device structure may require two additional layers, that are deposited on either side of the perovskite film. These layers are often referred to as charge transport layers, and one of these two layers function as electron transport layer (ETL) and the other one as hole transport layer (HTL). In literature, a huge library of materials are reported that can function as either ETL or HTL.

In this section, we introduce general steps involved in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite device fabrication (Dharmadasa et al. 2019). The first step in the PSC device fabrication process is the preparation of materials and solutions required for depositing

each film in the device structure. In the device structure presented below, the PCBM and PEDOT:PSS are used as ETL and HTL, respectively.

Perovskite Solar Cell (PSC) device fabrication steps:

The device process flow is summarized in Fig. 22.11. Pre-cleaned conducting ITO-glass or FTO-glass substrates are used as substrates for the device fabrication. Note that, typically, all the process steps, except substrate preparation, related to device fabrication are done inside a glove box. The substrate is first pre-cleaned using commercial soap solution (e.g. Hellmannex). The pre-cleaning step is followed by solvent cleaning which includes cleaning in an ultrasonic bath with DI water,

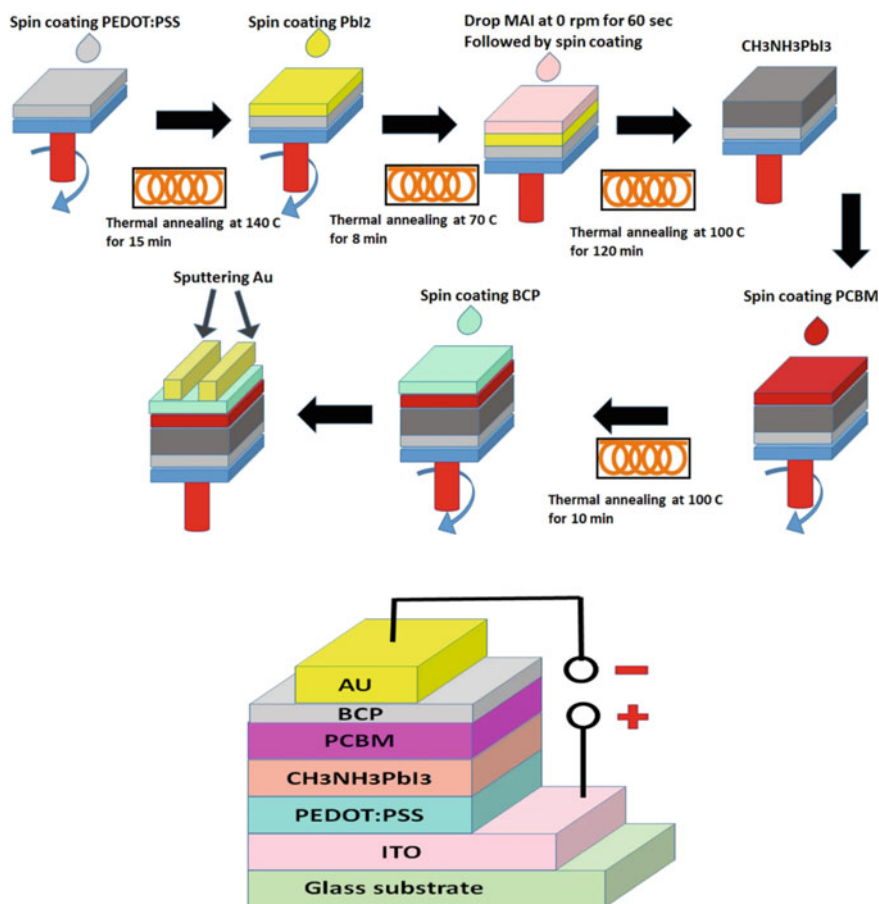


Fig. 22.11 Sample device process fabrication steps. (Top) Schematic diagram depicting different process steps involved in the fabrication of a typical PSC device with CH₃NH₃PbI₃ perovskite absorbing film. (Bottom) Schematic of completed PSC device with PCBM and PEDOT:PSS as electron transport layer (ETL) and hole transport layer (HTL), respectively. Reproduced with permission from Springer Science (Dharmadasa et al. 2019)

acetone, and Isopropanol, in that order, for 20 min each. The cleaned substrates can be subjected to ultraviolet-ozone treatment for 30 min to improve the surface adhesion. A thin film of PEDOT:PSS is uniformly coated onto the cleaned ITO substrate. The film is then annealed at 140 °C for 15 min. After this, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ (1.2 M in 0.7 ml DMF and 0.3 ml DMSO) solution prepared overnight is spin-coated on the sample with spinner programmed to 1000 rpm for 5 s and 6000 rpm for 45 s. After 10 s, in the second step, 500 μL of toluene can be dripped on the sample. The spin-coated films are annealed at 100 °C for 10 min. The PCBM dissolved in chlorobenzene (20 mg/mL) is spin-coated onto the perovskite layer at 1000 rpm for 60 s and annealed at 80 °C for 15 min. Then, 1 mg/mL of BCP solution in ethanol is spin coated at 4000 rpm for 30 s. Finally, 100 nm thick Ag electrodes are deposited using thermally evaporation or sputtering ($\sim 1 \times 10^{-6}$ Torr pressure) through a shadow mask on the surface of the BCP layer.

The fabrication process described above primarily deals with p-i-n type perovskite device. Other device structures can also be fabricated using solution processes with slight modifications in the process steps to optimize film properties. Different types of PSC device architectures that exist in literature are shown in Fig. 22.12. Mesoporous is among the first PSC architecture that was developed. The planar perovskite solar cell (p-i-n or n-i-p) which is dominating the PSC technology currently has been developed later.

22.3 Metrics for Evaluating the Economic and Environmental Impact of Photovoltaic (PV) Technologies

Before discussing the environmental, health, and safety aspects, we summarize some critical metrics used to assess different PV technologies. Table 22.1 compares the cumulative energy demand (CED), energy payback time (EPBT), and Greenhouse as emission rate (GHG) values of different technologies (Ludin et al. 2018) These are key metrics while assessing the technology of choice for future energy needs.

Cumulative energy demand (CED): CED represents the amount of primary energy used within the solar cell entire life cycle from raw materials extraction until the end-of-life stage, including installation, transportation, and energy-mix used.

Energy payback time (EPBT): EPBT is an indicator that represents the amount of time required for the installed solar PV system to generate the equivalent amount of energy used in the whole life cycle of PV module, including raw materials extraction, cell and module fabrication, and decommissioning phase.

Green House Gas (GHG) emissions rate: A key goal in moving towards the renewable energy technologies such as solar is to reduce the GHG emissions. Therefore, it is essential to develop an metric to understand the respective trends. In this

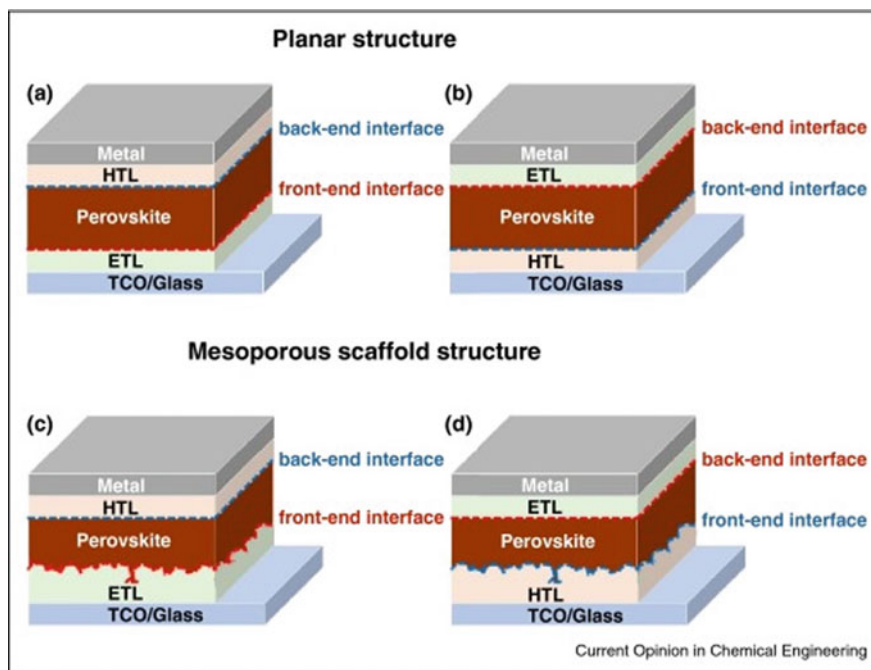


Fig. 22.12 Schematics of PSC and module architecture. **a** planar n-i-p PSCs, **b** planar p-i-n PSCs, **c** mesoporous n-i-p, and **d** mesoporous p-i-n device structures. Reproduced with permission from Elsevier (Manspecker et al. 2017)

Table 22.1 A comparison of different PV technologies using CED, EPBT, and range of GHG emissions based on literature reports from the year 2000

Solar PV technology	Range of CED	Range of EPBT	Range of GHG emissions (g CO ₂ eq/kWh)
Mono-Si	1123–8050	1.4–7.3	29–671
Multi-Si	1034–5150	0.8–4.17	12.1–569
a-Si	862–1731	1.1–3.2	8.1–57
CdTe	811–1803	0.79–2.7	8.9–66
CIS	1105–1684	1.3–2.8	33–95
DSSC	277–365	0.6–1.8	9.8–25
Perovskite	379–821	0.2–5.4	56.65–497.2
Quantum dot	370–1030	0.9–1.51	2.89–5

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regard, the GHG emissions rate, expressed as CO₂-equivalents, is a valuable index for determining how effective a PV system is in terms of reducing the temperatures on earth's surface.

22.4 Environmental, Health, and Safety (EHS) Impacts

So far we have discussed key semiconductor materials, their properties and fabrication process that led to different solar PV technologies. In this section, we discuss the EHS hazards associated with the manufacturing, use, and disposal of PV cells and modules. The use of hazardous, toxic, and flammable substances during solar cell or module manufacturing, even in small amounts, can present occupational and environmental hazards (Solar Energy Isn't Always as Green as You Think 2014). In this section, we give a comprehensive review of the environmental, health, and safety concerns of each PV technology discussed in the previous sections.

22.4.1 Silicon Solar Cells

In this section, we review the toxic effects of silicon-PV cells. The first life cycle assessment (LCA) research on silicon-solar cells was reported 15 years ago (Koroneos et al. 2006). Despite being the oldest PV technology with more than 3 decades of field performance studies, the number of studies investigating different types of toxic effects at different stages of silicon solar cell life cycle is limited in the literature.

22.4.1.1 Occupational Health Issues

As discussed in the silicon solar cell process steps, multiple acids including hydrofluoric acid (HF), nitric acid (HNO₃) as well as alkalis (e.g., NaOH) are used at different stages in the silicon solar cell processing. The potential hazards from using these acids and solvents include acid burns and fumes inhalation (Fthenakis 2018). The inhalation of dopant gases and vapors, e.g., POCl₃ and B₂H₆ that are commonly used as dopant sources for silicon, is hazardous. Even though POCl₃ is in liquid form, the generation of toxic P₂O₅ and Cl₂ gaseous effluents in the diffusion furnaces is a significant health concern for the safety of the workers. Therefore, adequately designed ventilation should be in place in the process area to avoid any possible inhalation hazards. The flammability of silane (SiH₄) used in SiN_x deposition using PECVD poses significant safety hazard. Further, the by-products from SiN_x deposition are also considered occupational health hazards (Moskowitz and Fthenakis 1991). There were reports of workers being affected by the silane leak in plants (Biello 2010). One pathway to avoid silane transport and frequent installations is

storing locally and avoid frequent transport and installation. Engineering and safety protocols such as proper gas-handling systems are used to minimize the risks of fire and explosion from explosive and hazardous gases and their by products in PV manufacturing (Fthenakis 2018; Moskowitz and Fthenakis 1991).

22.4.1.2 Environmental Issues

The environmental issues in silicon solar cell technology primarily arise in liquid and solid waste generation. The first step in silicon solar cell manufacturing is obtaining polysilicon wafers from metallurgical grade silicon (Zulehner 2000). In this step, metallurgical-grade silicon is treated with hydrochloric acid to form trichlorosilane (SiHCl_3). Then, this SiHCl_3 reacts with hydrogen to form polysilicon. A by-product of this refinement process is liquid silicon tetrachloride (SiCl_4). The SiCl_4 can form corrosive and toxic hydrogen chloride (HCl) upon its reaction with water or air. On average the production of every ton of polysilicon involves producing three to four tons of SiCl_4 (Wu et al. 2010). In addition, there is solid and liquid waste generated during wafer slicing, cleaning, and etching process steps. There is also solid waste generated during module assembly (e.g., stainless-steel wire) and the wafers slicing from ingots (abrasive slurry), and liquid slurry waste (Li 2021).

The fabrication of crystalline silicon panels requires various materials such as silicon, glass, polymers, silver, copper, boron, phosphorous, tin, tin oxide, lead (Sica et al. 2018). Even though there may not be any environmental concern during the silicon PV module operation, the pH dependent leaching of heavy metals such as Al, Cu, Ni, and Pb from module pieces is a significant concern. Therefore, it is critical to recycle the solar panels safely to avoid any problems related to drinking water, aquatic life, soil, agriculture, etc.

22.4.1.3 Solutions for Safer and Environmentally Friendly Silicon PV Technology

Since the waste produced by using oil-based slurry during silicon wafer slicing can have significant negative environmental impact, extensive cleaning of the wafers prior to silicon solar cell fabrication is required. Therefore, slurries based on glycol or water should be preferred as an alternative to oil-based slurry. The generation of toxic effluents from the belt-furnaces or tube-furnaces during the POCl_3 diffusion step demands regular cleaning of the diffusion chamber with acids such as HF. The use of belt-furnaces, on the other hand, can offer an environmentally friendly process technology because of the water-soluble and non-toxic materials or gases used for the doping step (Yadav et al. 2015). Typically, laser cutting or plasma etching are used for edge isolation after POCl_3 diffusion step. Also, the use of CF_4 in plasma etching should be avoided as it is a dangerous greenhouse gas. Hence, safer alternatives to CF_4 should be considered in future for plasma etching step. Also, a safer non-pyrophoric alternative to SiH_4 for ARC coating step should be considered. The

soldering residues formed while making the interconnections in a PV module requires cleaning with chlorofluorocarbons (CFC) compounds, which can cause atmospheric ozone depletion. The CFC usage should be avoided, and instead, low-residue fluxes should be used in PV manufacturing facilities (Fthenakis and Moskowitz 2000). If the residues or fluxes on the cells cannot be avoided, materials that produces water soluble fluxes or residues should be given priority for safer practices (Evans 2007; Tsuo et al. 1998).

22.4.2 Thin-Film Solar Cells

In the case of thin-film solar cells, including a-Si, CdTe, CIGS, etc., the environmental, health, and safety concerns are more severe compared to silicon solar cells as discussed below. Table 22.2 shows the total mass of different elements used to manufacture crystalline and thin-film solar cells.

22.4.2.1 Occupational Health and Safety Issues

The degree of occupational health hazards related to Cd and Te compounds can vary. This is because each process step in the device fabrication can produce compounds with different toxicities. In addition, the physical state and the mode of exposure can

Table 22.2 Total mass of elements in one module piece for c-Si, a-Si, CdTe, and CIGS

Element	Total mass (in mg) per 1 module piece ($5 \times 5 \text{ cm}^2$)			
	c-Si	a-Si	CdTe	CIGS
Ag	7.8 ± 0.9	2.2 ± 0.3	0.05 ± 0.005	1.2 ± 0.4
Sn	21.3 ± 1.1	31.0 ± 1.7	12.5 ± 3.9	19.1 ± 0.4
Zn				16.1 ± 1.6
Cd			14.9 ± 1.6	0.2 ± 0.001
Te			15.9 ± 1.1	
In				19.2 ± 0.7
Ga				0.7 ± 0.2
Se				8.2 ± 0.8
Al	167.2 ± 49.9			
Mo			13.0 ± 1.8	5.0 ± 0.2
Cu	7.8 ± 0.9	130.4 ± 16.7	74.5 ± 4.7	146.2 ± 5.7
Ni		1.0 ± 0.2		
Pb	15.9 ± 1.2			

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Table 22.3 Summary of the hazardous materials used in silicon and thin film solar cell manufacturing

PV technology	Material/precursor	Purpose	Safety concerns
Si	HF	Etchant	Noxious, corrosive
	Chlorosilane	Si deposition	Toxic fumes upon decomposition
a-Si	Chlorosilane	a-Si deposition	Toxic fumes upon decomposition
	Diborane	a-Si deposition	Highly toxic
	Hydrogen	a-Si deposition	Fire hazard
	Phosphine	a-Si deposition	Toxic and flammable
	Silane	a-Si deposition	Fire and explosive
CdTe	Cd compounds	CIS film deposition	Carcinogenic
CIS	Cd Compounds	CIS film deposition	Carcinogenic
CIS	Hydrogen selenide	CIS film deposition	Highly toxic and flammable
CIS	Hydrogen sulfide	CIS film deposition	Highly toxic and flammable

lead to health hazards of varying severities (Table 22.3). The Occupational Safety and Health Administration (OSHA) agency of the US has regulated the use of Cd (including CdTe) due to reasons related to its toxicity and potential for causing lung carcinogen (Occupational Safety and Health Administration (1971)). The accidental ingestion of Cd compounds by personnel in the research laboratories and production environments is possible when proper and safe handling practices of these toxic and hazardous gases are not in place (Elinder and Järup 1996; Genchi et al. 2020). The environmental risks can vary depending on the physical state of the Cd compound used or Cd products released to the environment. For instance, as with many metal particulate matter, fabrication processes in which fine particles of Cd compounds are used or produced present more significant health risks. Hence, the laboratories and industrial facilities that uses volatile or soluble Cd compounds must take significant care during their use, and must discharge volatile by products into the environment only after careful treatment.

CdTe is typically deposited using spray pyrolysis. Given that spray pyrolysis is not an efficient process, a high amount of by products and fine particles are generated during the CdTe deposition step. Furthermore, these by products/particles can also get deposited on the spray process chamber wall. As a consequence, periodic cleaning (either scraping or chemical removal) of the reactors is required. More importantly, spray pyrolysis deposition of CdTe can produce dangerous by products such as Cd and CdO. Therefore, proper care must be taken while operating the spray pyrolysis reactors to avoid accidental exposure to Cd and CdO fumes (Kolesnikov et al. 2017).

Currently, there is only a limited information on the toxicity of process related emissions for the CIS and CGS solar cells. One known major hazard in CIS processing is the use of hydrogen selenide feedstock which is highly toxic. While mechanical scribing and deposition are known to produce airborne hazards (e.g., Cu, In,

and Cd) in CIS and CdS processing, existing data, which is not extensive, suggest concentrations of these elements are below their threshold levels.

22.4.2.2 Environmental Issues

Chronic exposure to Cd compounds poses serious health concerns to the public (Järup and Åkesson 2009). The Cd compounds may be released into the environment as a by product of different manufacturing steps or as a waste from the uncontrolled disposal of used photovoltaic modules at the end of their life. However, the magnitude of potential emission from different manufacturing and laboratory facilities can vary depending on the fabrication processes used and the implementation of emission controls.

As mentioned before, the techniques used for the deposition of CdTe also play a key role in determining the amount of effluents generated in CdTe cell manufacturing. For example, electrodeposition is considered as a less hazardous process. On the other hand, a less efficient deposition methods such as processes spray pyrolysis (with an estimated efficiency of 10%) would generate significant amount of hazardous (e.g. CdCl₂, CdO, HCl, H₂S, and thiourea) by products (Fthenakis and Moskowitz 2000). Even though some of these by products will be deposited on the spray pyrolysis reactor's walls, most of them will escape through exhaust in gaseous form. Previous studies indicates significantly less CO₂ emissions (20 g /kWh) from CdTe photovoltaics during the lifecycle compared to that emitted from fossil fuel plants (500–1000 g CO₂/kWh). Also, emission of other priority pollutants such as SO₂, NO_x, particulates, etc., amounts to only 2–4% of that emitted from fossil-fuel plants (Fthenakis et al. 2008).

Beyond the traditional pollutants, the heavy-metal emissions (e.g., Cd, Se) are also important in case of CdTe and CdS, CIGS solar cells. Experimental investigations also confirmed that the Cd can be safely encapsulated in the module using molten glass which makes it less fire-proof for residential use (Fthenakis 2004). In addition, the direct cadmium emissions in the life cycle of CdTe solar cells amount to 0.02 g per GWh of energy produced under average US conditions (Fthenakis et al. 2005). It is worth noting that the magnitude of cadmium emission from CdTe PV cells is two orders less compared to an average coal-burning plant that emits 2 g Cd per GWh (Fthenakis 2004). First Solar, a leading manufacturer of CdTe solar modules, expressed strong confidence about the green nature of this PV technology. Their studies confirmed there is no occupational exposure hazard to Cd based on tests conducted over 15 years. The sample size for this assessment is approximately 1100 Cd exposure tests performed on the workers. These results indicate thin-film PV can be benign to the environment compared to fossil-fuel-based energy sources.

It is also essential to consider the potential risks involved with thin-film technology at the end of their lifetime. In spite of serious concerns about the cadmium in CdTe, and CIGS/CdS solar cells, the hazardous level is not directly related to the amount of toxic compounds used in a module but it mainly depends on leaching out potential of cadmium (Nover et al. 2017). Moreover, there is a possibility for cadmium release into

atmosphere if the PV modules are disposed in landfills. The simulation studies using Toxic Characteristic Leaching Procedure (TCLP) can help understand the potential for leaching of the toxic elements. All three cadmium based photovoltaic modules i.e., CdTe, CIGS and CdS have passed TCLP studies and thus confirming that these thinfilm PV modules are safe to use under normal conditions. In contrast, recent investigation suggested that long-term leaching studies can provide better insights on potential harms due to leaching out of toxic elements by considering different conditions (e. g. pH, environment) (Nover et al. 2017). Even though existing literature did not provide any direct evidence of significant hazards under normal scenarios, the recycling of the heavy metal based solar panels should be done with carefully at the end of their life. Hence, the recollection of used modules should be a major priority for both manufacturers and the governments. Toxic emissions are much lower in the life cycle of thin-film photovoltaics than in the life cycles of alternative photovoltaic- and conventional-power systems (Fthenakis et al. 2008).

22.4.3 Perovskite Solar Cell (PSCs)

As mentioned in the first section of this chapter, the PSCs offer unique advantages compared to Silicon or thin-film (CdTe or CIGS) based PV technologies, such as the ease of chemical tunability, solution processability. However, these same advantages can be the downside with significant negative environmental impact. An important downside of the PSC technology is that the presence of heavy metals in the perovskite absorbing film. A schematic of the perovskite solar cell life cycle is shown in Fig. 22.13.

22.4.3.1 Occupational Safety and Health Hazards

While the Pb presents a significant health hazard, perovskite solar cell device processing is typically conducted in a glove box (Salvador et al. 2020). This can potentially minimize the exposure to Pb-containing compounds. Even though the perovskite device fabrication takes place inside glove box, the unintentional or accidental exposure to Pb present in perovskite can occur at other times, including testing in ambient conditions. Upon contact with Pb-containing materials or devices, the ingestion and uptake can possibly happen via different routes (e.g., gastrointestinal, respiratory, and dermal). Besides the intoxication by the perovskites, the use of the toxic solvents such as dimethylformamide (DMF) and dimethylsulfoxide (DMSO) in the solution processing of the PSCs presents significant occupational safety and health challenges. In addition, the high miscibility of these solvents with water can increase their bioavailability. As a result, there is a significant risk of absorbing these toxic solvents by oral ingestion, dermal contact or permeable cell membrane (Ménorval et al. 2012). Due to these reasons, sufficient personal protection should be in place when working with these solvents. (e.g. 15 mil latex gloves, dust masks

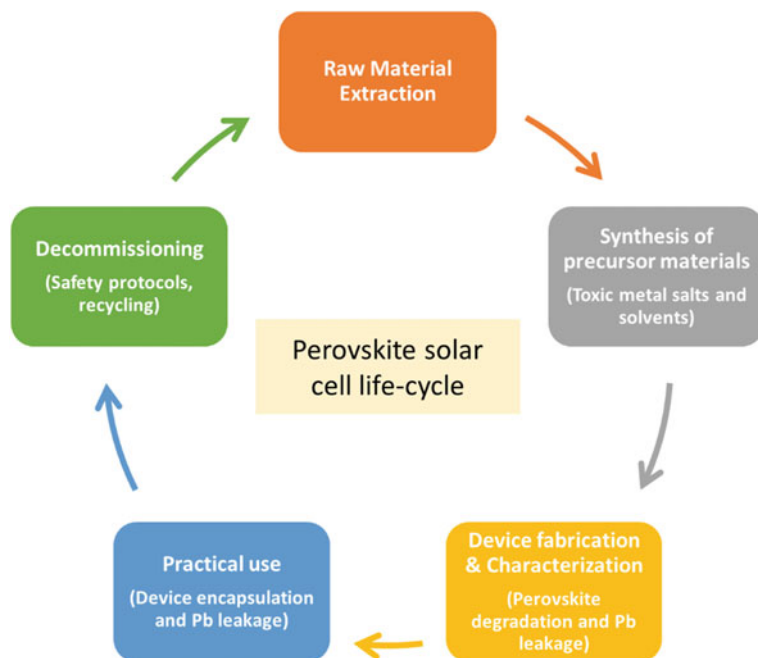


Fig. 22.13 Schematic of the life cycle of perovskite solar cells and associated hazards

and glasses). Further, the safe storage of waste products in the perovskite solar cell fabrication laboratories is paramount. Owing to the toxicity of DMSO and DMF, alternative solutions should be pursued in PSC processing. Recent studies show the feasibility of using tetraethyl orthocarbonate (with perovskite precursors) and anisole (with PCBM) as potential alternatives that can lead to avoiding the use of DMSO or DMF in PSC processing in future (Gardner et al. 2016; Zhang et al. 2020; Tian et al. 2019; Wang et al. 2017).

The Sn based perovskites also poses some toxic effect (Babayigit et al. 2016a). Owing to its lower reduction potential Sn(II) can be converted into Sn(IV) easily in ambient. As a result, the operators can be easily exposed to Sn(II) and Sn(IV) during the perovskite synthesis. This is a serious health hazard as the net gastrointestinal absorption of Sn depends on the oxidation state, and, Sn(II) and Sn(IV) are not readily interconverted when being transported in the human body. The conversion to Sn(IV) can be slowed down in laboratories where low-oxygen and dry environment is maintained. A summary of health hazards that may arise due to exposure to Pb and Sn are shown in Fig. 22.14.

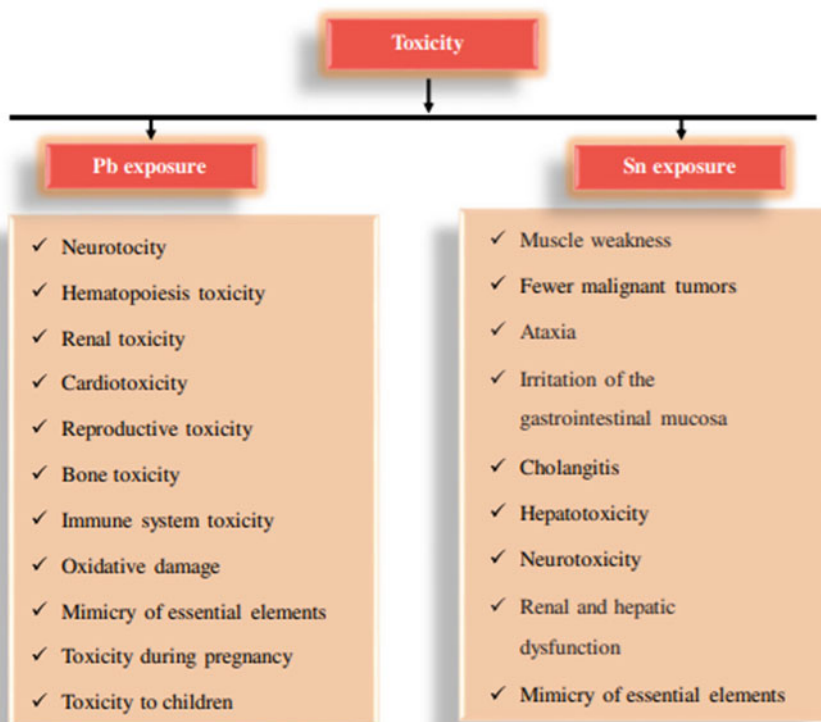


Fig. 22.14 Schematic diagram showing the health hazards for living beings upon exposure to Pb and Sn, which are the popular metal constituents present in perovskite films. Reproduced with permission from Wiley (Debnath et al. 2020)

22.4.3.2 Environmental Impact

A major challenge with $\text{CH}_3\text{NH}_3\text{PbI}_3$ based PSCs is the presence of heavy metal Pb. Lead is known to damage the nervous system and cause brain disorders. The solubility product (K_{sp}) of PbI_2 in water is on the order of 10^{-8} , which is much higher than those of other common heavy metal compounds used in solar cells (Fabini 2015). For instance, the K_{sp} values for CdS, PbS, and CdTe lie in the range of 10^{-27} – 10^{-34} . Furthermore, unlike PbI_2 with three-atoms, CdS, PbS and CdTe are binary compounds, with up to 14 orders of smaller solubilities than PbI_2 in water (<https://pubs.acs.org/doi/full/10.1021/acs.jpcllett.5b00504>). It can decompose into $\text{CH}_3\text{NH}_3\text{I}$ – HI – CH_3NH_2 (methylamine). Hence, soil, rivers, and groundwater may be contaminated by Pb when the installed PSC modules are disposed without proper care. Also, the PbI_2 (lead iodide) formed upon decomposition of perovskite, can be further decomposed into Pb. This Pb can find its way into the groundwater via the effluent in significant quantities that can cause severe health risks. There is very little history available on the perovskite module life cycle analysis, and hence

simulation studies must be conducted to predict their potential environmental impact. In a recent study (Hailegnaw et al. 2015), the possible environmental effects of PSCs are evaluated by considering the complete exposure of a damaged Pb-based perovskite device to rain as the worst-case scenario. The study considered a PSCs module with a 300 nm thick perovskite layer, and it is assumed that this PSC module would contain $\sim 0.4 \text{ g m}^{-2}$ of Pb. When the PSC module is exposed to rain, there would be an increase of Pb by ≈ 70 ppm in the first centimeter of ground under the panel. This study concluded that the practical use of PSCs results in a low level contamination (<400 ppm), as the Pb concentration in uncontaminated soil varies from less than 10–200 ppm or even higher (Hailegnaw et al. 2015; Kim et al. 2018b). Again similar to the case of Cd in thin film solar cells, any release of Pb from perovskites into the environment should be avoided or at least minimized. While the lead present in organic–inorganic lead halide perovskites can leak into the environment by rainwater, the Pb^{2+} can be recovered by simple solution treatment. Despite of these studies, the toxic effect of Pb are still a major concern and is a major bottleneck for their commercialization.

Even though Sn based perovskites are generally believed as environmental friendly and safe alternative to Pb based perovskite, Sn-based PSCs' application can also pose environmental and health risks. In case of Sn based perovskites, SnI_2 and SnI_4 have been identified as potential toxic products (Babayigit et al. 2016b). There are several different sources for heavy metal intoxication from Pb- and Sn-based perovskites. With widely varying water solubility, these sources are ordered according to their water solubility as: $\text{SnBr}_2 > \text{SnCl}_2 > \text{Pb}(\text{NO}_3)_2 > \text{Pb}(\text{CH}_3\text{COO})_2 > \text{Pb}(\text{OH})_2 > \text{PbCl}_2 > \text{PbBr}_2 > \text{PbI}_2 > \text{SnI}_4 > \text{SnI}_2 > \text{SnO}_2$.

Moderate exposure to different environments including humidity, oxygen, elevated temperature, etc., can degrade perovskites into harmful heavy metal compounds. Furthermore, the structural failure of a photovoltaic module can lead to leaching of these compounds into the environment. Like CdTe modules, even if the PSC modules are encapsulated there is potentially a higher environmental risk when these panels are exposed to rain. Especially during their practical use, the PSC modules need to be installed in outdoors or rooftops, and there is a potential for these panels to get damaged and consequently exposed to moisture, rain, etc.

Even though recent studies indicated that the amount of Pb spilled from defective PSCs would be orders of magnitude smaller than that emitted from other energy-related activities, we need to remember that this conclusion is based on a limited data. Hence, careful toxicological investigation is highly required to further understand the dangers associated with local accumulation of perovskites (Fabini 2015). It is also possible, in a worst-case scenario, the perovskite degradation products could be transported by soil water and eventually accumulate in unpredictable locations (Nelson and Campbell 1991). The composition of Pb penetrated into soil is highly dependent on soil composition and acidity (McBride et al. 1997).

One may think that the total metal content per square meter of a solar panel is only a few hundred milligrams which is less risky. However, the large scale implementation of the PSC technologies may cause severe safety and health hazards. At this point, due to limited field data, it is better not to conclude the environmental impacts of PSCs

as either positive or negative. Similar to thin film solar cells, the safe deployment of PSC technology relies entirely on adopting precautionary measures against contamination at each stage of the device's life, from fabrication to disposal/recycling. In this direction, dedicated EHS standards should be developed as part of academic research during their development. Such standards can be beneficial especially when multiple personnel work on PSC device fabrication at the same time. Finally, the safety protocols developed in academic research labs can be easily implemented in industrial settings where the expected risks can be further mitigated by the automation of production processes.

22.5 Summary and Conclusion

Solar PV technologies have tremendous potential to offer sustainable and cleaner energy resources for future energy demands. While Si and thin-film solar cell technologies currently lead the worldwide PV installations, emerging technologies such as DSSC and perovskite solar cells can potentially enter the commercial market in the next decade. Especially considering the material shortage issues with thin-film technologies such as CdTe, there is a strong need for these emerging PV technologies to be commercially available and compete with Si PV in terms of price and long-term durability. Currently, significant research efforts are underway to address the stability issues, especially for perovskite solar cells. But, in perovskite solar cells, the researcher community should also look for alternative materials to the currently used Pb and Sn containing perovskites. Simultaneously, the PSC research community should consider using safe chemical processing technologies to minimize health and safety impacts on the researchers and workforce. Still, solar PV technology is deemed a green technology and can significantly contribute to addressing climate challenges. However, more studies are required to understand the emerging PV technologies' environmental impacts and life cycle, mainly based on PSCs. Considering the relatively less data available on the LCA of PSC technologies, simulation studies should be conducted to understand the potential future challenges in this area. Furthermore, the ecotoxicity of leached chemicals from different types of solar cell devices should be investigated further as currently there is only limited literature exists in this area. In future studies, significant attention should be given to accumulating more ecotoxicological data. Moreover, the governments and industries across the globe should work together to develop sustainable practices to address the occupational safety and health concerns of the personnel working in PV manufacturing, waste management, environmental impacts. Finally, a greater emphasis on recycling PV panels should be given to minimize the hazardous waste from the PV cells and minimize their environmental footprint.

References

- Abbott MD, Trupke T, Hartmann HP, Gupta R, Breitenstein O (2007) Laser isolation of shunted regions in industrial solar cells. *Prog Photovoltaics Res Appl* 15:613–620
- Abdullah MF et al (2016) Research and development efforts on texturization to reduce the optical losses at front surface of silicon solar cell. *Renew Sustain Energy Rev* 66:380–398
- Act An (1970) Occupational safety and health act of 1970. Public Law 91:596
- Altamura G, Vidal J (2016) Impact of minor phases on the performances of CZTSSe thin-film solar cells. *Chem Mater* 28:3540–3563
- Amin N et al (2017) Solar photovoltaic technologies: from inception toward the most reliable energy resource. In: *Encyclopedia of sustainable technologies*, pp 11–26. <https://doi.org/10.1016/B978-0-12-409548-9.10092-2>
- Amaroli N, Balzani V (2007) The future of energy supply: challenges and opportunities. *Angew Chemie Int Ed* 46:52–66
- Arumughan J, Pernau T, Hauser A, Melnyk I (2005) Simplified edge isolation of buried contact solar cells. *Sol Energy Mater Sol Cells* 87:705–714
- Babayigit A, Ethirajan A, Muller M, Conings B (2016a) Toxicity of organometal halide perovskite solar cells. *Nat Mater* 15:247–251
- Babayigit A et al (2016b) Assessing the toxicity of Pb- and Sn-based perovskite solar cells in model organism *Danio rerio*. *Sci Rep* 6:18721
- Benda V, Černá L (2020) PV cells and modules—State of the art, limits and trends. *Heliyon* 6
- Best research-cell efficiency chart (1976). <https://www.nrel.gov/pv/cell-efficiency.html>
- Biello D (2010) Explosive silicon gas casts shadow on solar power industry. *Scientific American* <https://www.scientificamerican.com/article/explosive-gas-silane-used-to-make-photovoltaics/>
- Bosson CJ et al (2017) Cation disorder and phase transitions in the structurally complex solar cell material $\text{Cu}_2\text{ZnSnS}_4$. *J Mater Chem A* 5:16672–16680
- Brabec CJ, Durrant JR (2008) Solution-processed organic solar cells. *MRS Bull* 33:670–675
- Carlton JS, Perry-Hill R, Huber M, Prokopy LS (2015) The climate change consensus extends beyond climate scientists. *Environ Res Lett* 10:094025
- Chopra KL, Paulson PD, Dutta V (2004) Thin-film solar cells: an overview. *Prog Photovoltaics Res Appl* 12:69–92
- Chu J-Y (2011) 17.2% efficiency multicrystalline solar cells by optimizing structure of the MgF_2/SiNx double antireflection layer. *J Photonics Energy* 1:017001
- Climate Change (2019). <https://www.un.org/en/global-issues/climate-change>
- Cooper IB et al (2010) Understanding and use of IR belt furnace for rapid thermal firing of screen-printed contacts to Si solar cells. *IEEE Electron Device Lett* 31:461–463
- Debnath T, Kim E, Lee K, Nath NCD (2020) Halide perovskite solar cells with biocompatibility. *Adv Energy Sustain Res* 1:2000028
- Dharmadasa IM, Rahaq Y, Ojo AA, Alanazi TI (2019) Perovskite solar cells: a deep analysis using current–voltage and capacitance–voltage techniques. *J Mater Sci Mater Electron* 30:1227–1235
- Dorian JP, Franssen HT, Simbeck DR (2006) Global challenges in energy. *Energy Policy* 34:1984–1991
- Elinder CG, Järup L (1996) Cadmium exposure and health risks: recent findings. *Ambio* 25:370–373
- Evans JW (2007) *A guide to lead-free solders: physical metallurgy and reliability*. Springer Science & Business Media
- Fabiani D (2015) Quantifying the potential for lead pollution from halide perovskite photovoltaics. *J Phys Chem Lett* 6:3536–3548
- Fthenakis VM (2004) Life cycle impact analysis of cadmium in CdTe PV production. *Renew Sustain Energy Rev* 8:303–334
- Fthenakis VM, Moskowitz PD (2000) Photovoltaics: environmental, health and safety issues and perspectives. *Prog Photovoltaics Res Appl* 8:27–38
- Fthenakis VM et al (2005) Emissions and encapsulation of cadmium in CdTe PV modules during fires. *Prog Photovoltaics Res Appl* 13:713–723

- Fthenakis VM, Hyung CK, Alsema E (2008) Emissions from photovoltaic life cycles. *Environ Sci Technol* 42:2168–2174
- Fthenakis VM (2018) Overview of potential hazards. In: McEvoy's handbook of photovoltaics: fundamentals and applications (2018). <https://doi.org/10.1016/B978-0-12-809921-6.00035-5>
- Gardner KL et al (2016) Nonhazardous solvent systems for processing perovskite photovoltaics. *Adv Energy Mater* 6:1600386
- Gatz S et al (2011) 19.4%-efficient large-area fully screen-printed silicon solar cells. *Phys Status Solidi Rapid Res Lett* 5:147–149
- Genchi G, Sinicropi MS, Lauria G, Carocci A, Catalano A (2020) The effects of cadmium toxicity. *Int J Environ Res Public Health* 17:3782
- Gielen D, Gorini R, Wagner N, Leme R, Gutierrez L, Prakash G, Asmelash E et al (2019) Global energy transformation: a roadmap to 2050
- National Renewable Energy Laboratory (NREL) (2021) Best research-cell efficiencies. <https://www.nrel.gov/pv/cell-efficiency.html>. Accessed June 15 2021
- Goodrich A et al (2013) A wafer-based monocrystalline silicon photovoltaics road map: utilizing known technology improvement opportunities for further reductions in manufacturing costs. *Sol Energy Mater Sol Cells* 114:110–135
- Green MA, Pillai S (2012) Harnessing plasmonics for solar cells. *Nat Photonics* 6:130–132
- Hailegnaw B, Kirmayer S, Edri E, Hodes G, Cahen D (2015) Rain on methylammonium lead iodide based perovskites: possible environmental effects of perovskite solar cells. *J Phys Chem Lett* 6:1543–1547
- Hauser A, Hahn G, Spiegel M, Fath P, Bucher E, Feist H, Breitenstein O, Rakotonjainia JP (2001) Comparison of different techniques for edge isolation. In: 17th European photovoltaic solar energy conference, pp 1739–1742
- Herz LM (2017) Charge-carrier mobilities in metal halide perovskites: fundamental mechanisms and limits. *ACS Energy Lett* 2:1539–1548
- Hilali MM et al (2006) Effect of Ag Particle Size in Thick-Film Ag Paste on the Electrical and Physical Properties of Screen Printed Contacts and Silicon Solar Cells. *J Electrochem Soc* 153:A5
- Hoenig R et al (2012) Impact of screen printing silver paste components on the space charge region recombination losses of industrial silicon solar cells. *Sol Energy Mater Sol Cells* 106:7–10
- Honsberg CB, Bowden SG (2019) Photovoltaics Education Website. www.pveducation.org
- Hoppe H, Sariciftci NS (2004) Organic solar cells: an overview. *J Mater Res* 19:1924–1945
- Järup L, Åkesson A (2009) Current status of cadmium as an environmental health problem. *Toxicol Appl Pharmacol* 238:201–208
- Kamat PV (2013) Quantum dot solar cells. The next big thing in photovoltaics. *J Phys Chem Lett* 4:908–918
- Katagiri H et al (2009) Development of CZTS-based thin film solar cells. *Thin Solid Films* 517:2455–2460
- Kim J et al (2013) Double antireflection coating layer with silicon nitride and silicon oxide for crystalline silicon solar cell. *J. Electroceramics* 30:41–45
- Kim DH, Whitaker JB, Li Z, van Hest MFAM, Zhu K (2018a) Outlook and challenges of perovskite solar cells toward terawatt-scale photovoltaic module technology. *Joule* 2:1437–1451
- Kim BJ, Lee S, Jung HS (2018b) Recent progressive efforts in perovskite solar cells toward commercialization. *J Mater Chem A* 6:12215–12236
- Kojima A, Teshima K, Shirai Y, Miyasaka T (2009) Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *J Am Chem Soc* 131:6050–6051
- Kolesnikov E et al (2017) Investigation of discharged aerosol nanoparticles during chemical precipitation and spray pyrolysis for developing safety measures in the nano research laboratory. *Ecotoxicol Environ Saf* 139:116–123
- Koseoglu NM, van den Bergh JCJM, Lacerda JS (2013) Allocating subsidies to R&D or to market applications of renewable energy? Balance and geographical relevance. *Energy Sustain Dev* 17:536–545

- Kray D, Hopman S, Spiegel A, Richerzhagen B, Willeke GP (2007) Study on the edge isolation of industrial silicon solar cells with waterjet-guided laser. *Sol Energy Mater Sol Cells* 91:1638–1644
- Kwon TY et al (2011) Screen printed phosphorus diffusion for low-cost and simplified industrial mono-crystalline silicon solar cells. *Sol Energy Mater Sol Cells* 95:14–17
- Lee TD, Ebong AU (2017) A review of thin film solar cell technologies and challenges. *Renew Sustain Energy Rev* 70:1286–1297
- Li J et al (2021) Progress in recovery and recycling of kerf loss silicon waste in photovoltaic industry. *Sep Purif Technol* 254:117581
- Ludin NA et al (2018) Prospects of life cycle assessment of renewable energy from solar photovoltaic technologies: A review. *Renew Sustain Energy Rev* 96:11–28
- Lund PD (2009) Effects of energy policies on industry expansion in renewable energy. *Renew Energy* 34:53–64
- Ma ZQ, Liu BX (2001) Boron-doped diamond-like amorphous carbon as photovoltaic films in solar cell. *Sol Energy Mater Sol Cells* 69:339–344
- Manspeaker C, Venkatesan S, Zakhidov A, Martirosyan KS (2017) Role of interface in stability of perovskite solar cells. *Curr Opin Chem Eng* 15:1–7
- Matheu P, Lim SH, Derkacs D, McPheeters C, Yu ET (2008) Metal and dielectric nanoparticle scattering for improved optical absorption in photovoltaic devices. *Appl Phys Lett* 93:113108
- McBride M, Sauvé S, Hendershot W (1997) Solubility control of Cu, Zn, Cd and Pb in contaminated soils. *Eur J Soil Sci* 48:337–346
- de Ménorval MA, Mir LM, Fernández ML, Reigada R (2012) Effects of dimethyl sulfoxide in cholesterol-containing lipid membranes: a comparative study of experiments in silico and with cells. *PLoS One* 7:e41733
- Moskowitz PD, Fthenakis VM (1991) A checklist of suggested safe practices for the storage, distribution, use and disposal of toxic and hazardous gases in photovoltaic cell production. *Sol Cells* 31:513–525
- Narayanan KL, Yamaguchi M (2003) Photovoltaic effects of a:C/C60/Si (p-i-n) solar cell structures. *Sol Energy Mater Sol Cells* 75:345–350
- Nelson WO, Campbell PGC (1991) The effects of acidification on the geochemistry of Al, Cd, Pb and Hg in freshwater environments: a literature review. *Environ Pollut* 71:91–130
- Nover J et al (2017) Long-term leaching of photovoltaic modules. *Jpn J Appl Phys* 56:08MD02
- Occupational Safety and Health Administration (1971)
- Oreskes N (2004) The scientific consensus on climate change. *Science* (80):306, 1686
- Park NG (2015) Perovskite solar cells: an emerging photovoltaic technology. *Mater Today* 18:65–72
- Park NG, Zhu K (2020) Scalable fabrication and coating methods for perovskite solar cells and solar modules. *Nat Rev Mater* 5:333–350
- Park H et al (2009) Improvement on surface texturing of single crystalline silicon for solar cells by saw-damage etching using an acidic solution. *Sol Energy Mater Sol Cells* 93:1773–1778
- Perlin J (2004) Silicon solar cell turns 50. NREL/BR-520–33947. National Renewable Energy Lab., Golden, CO. (US)
- Koroneos C, Stylos N, Moussiopoulos N (2006) LCA of multicrystalline silicon photovoltaic systems. Part 1: present situation and future perspectives. *Int J Life Cycle Assess* 11:129–136
- Rech B, Wagner H (1999) Potential of amorphous silicon for solar cells. *Appl Phys A Mater Sci Process* 69:155–167
- Salvador M, Motter CE, McCulloch I (2020) Hidden perils of lead in the lab: guidelines for containing, monitoring, and decontaminating lead in the context of perovskite research. *Chem Mater* 32:7141–7149
- Sardana SK et al (204) Influence of surface plasmon resonances of silver nanoparticles on optical and electrical properties of textured silicon solar cell. *Appl Phys Lett* 104:073903
- Sardana SK, Chava VSN, Komarala VK (2015) Morphology and optical properties of sputter deposited silver nanoparticles on plain, textured and antireflection layer coated textured silicon. *Appl Surf Sci* 347:651–656

- Schmich E, Schillinger N, Reber S (2007) Silicon CVD deposition for low cost applications in photovoltaics. *Surf Coat Technol* 201:9325–9329
- Schroder DK, Meier DL (1984) Solar cell contact resistance—a review. *IEEE Trans Electron Devices* 31:637–647
- Sica D, Malandrino O, Supino S, Testa M, Lucchetti MC (2018) Management of end-of-life photovoltaic panels as a step towards a circular economy. *Renew Sustain Energy Rev* 82
- Slaoui A (2017) Inorganic materials for photovoltaics: status and futures challenges. In: EPJ web of conferences, vol 148. EDP Sciences, p 00007. https://www.epj-conferences.org/articles/epjconf/abs/2017/17/epjconf_epssif2017_00007/epjconf_eps-sif2017_00007.html
- Smalley RE (2005) Future global energy prosperity: the terawatt challenge. *MRS Bull* 30:412–417
- Solar Energy Isn't Always as Green as You Think (2014). <https://spectrum.ieee.org/green-tech/solar/solar-energy-isnt-always-as-green-as-you-think>
- Sopori B (2003) Silicon nitride processing for control of optical and electronic properties of silicon solar cells. *J Electron Mater* 32:1034–1042
- Stranks SD et al (2013) Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber. *Science* 342(80):341–344
- Tan ZK et al (2014) Bright light-emitting diodes based on organometal halide perovskite. *Nat Nanotechnol* 9:687–692
- Tian S et al (2019) A facile green solvent engineering for up-scaling perovskite solar cell modules. *Sol Energy* 183:386–391
- Tsuo Y, Gee J, Menna P, Strebkov D (1998) Environmentally benign silicon solar cell manufacturing. In: Photovoltaic solar energy conversion (1998)
- Wadia C, Alivisatos AP, Kammen DM (2009) Materials availability expands the opportunity for large-scale photovoltaics deployment. *Environ Sci Technol* 43:2072–2077
- Wang J et al (2017) Highly efficient perovskite solar cells using non-toxic industry compatible solvent system. *Sol RRL* 1:1700091
- Wolf A et al (2015) Status and perspective of emitter formation by POCL₃-diffusion. In: 31st European PV solar energy conference and exhibition, pp 414–419
- Wright AD et al (2020) Intrinsic quantum confinement in formamidinium lead triiodide perovskite. *Nat Mater* 19:1201–1206
- Wu L, Ma Z, He A, Wang J (2010) Studies on destruction of silicon tetrachloride using microwave plasma jet. *J Hazard Mater* 173:305–309
- Xing G et al (2013) Long-range balanced electron-and hole-transport lengths in organic-inorganic CH₃NH₃PbI₃. *Science* 342(80):344–347
- Xu X, Wei Z, Ji Q, Wang C, Gao G (201) Global renewable energy development: influencing factors, trend predictions and countermeasures. *Resour Policy* 63:101470
- Yadav A, Singh G, Nekovei R, Jeyakumar R (2015) c-Si solar cells formed from spin-on phosphoric acid and boric acid. *Renew Energy* 80:80–84
- Zhang L, Shen H, Yang Z, Jin J (2010) Shunt removal and patching for crystalline silicon solar cells using infrared imaging and laser cutting. *Prog Photovoltaics Res Appl* 18:54–60
- Zhang M, Xin D, Zheng X, Chen Q, Zhang WH (2020) Toward greener solution processing of perovskite solar cells. *ACS Sustain Chem Eng* 8:13126–13138
- Zhao X, Wang M (2018) Organic hole-transporting materials for efficient perovskite solar cells. *Mater Today Energy* 7:208–220
- Zhao W et al (2018) Environmentally friendly solvent-processed organic solar cells that are highly efficient and adaptable for the blade-coating method. *Adv Mater* 30:1704837
- Zulehner W (2000) Historical overview of silicon crystal pulling development. *Mater Sci Eng B Solid-State Mater Adv Technol* 73:7–15