

Emerging Solar Technologies: Perovskite Solar Cell

Amruta Mutalikdesai and Sheela K Ramasesha

Conversion of sunlight to electricity with high conversion efficiencies at low cost is possible with emerging photovoltaic technologies. Organic–inorganic halide perovskite, a newcomer in the solar cell industry has proved its potential for increasing efficiency rapidly from 3.8% in 2009 to 22.1% in 2016. High efficiency, flexibility, and cell architecture of the emerging hybrid halide perovskite have caught the attention of researchers and technologists in the field. This article focuses on the emergence, properties, and current research status of hybrid perovskite solar cells.

1. Introduction

Gradually, primary energy resources such as fossil fuels, coal, and natural gas are depleting, while the global energy consumption is increasing. Solar energy, along with wind, biomass, tidal, and geothermal sources is emerging as an answer to our energy-starved planet. These renewable energy resources are freely available in nature, are non-polluting, and help in reducing global CO₂ emissions. The impact of industrialization, global warming, and their effects on the environment are discussed in detail in the first part of the series of articles – ‘Challenges in the Quest for Clean Energies’ [1]. Out of the mix of available sources of energy, solar energy is the cleanest and the most abundant (*Figure 1*). Conversion of solar energy into electricity by photovoltaic solar cells is one of the most promising approaches to cope with the current energy shortage. Second part of the series – ‘Challenges in the Quest for Clean Energies’ is focused on different solar technologies and materials that can be used to make an efficient photovoltaic (PV) cell [2].

Available PV cells can be broadly classified into first, second, and



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Keywords

Photovoltaic technologies, perovskite, solar cell, conversion efficiency.



Figure 1. Different renewable energies. Sizes of the blobs indicate relative abundances.

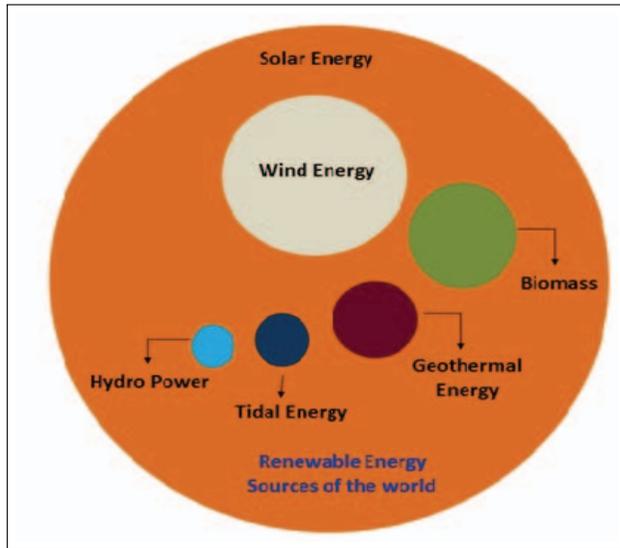
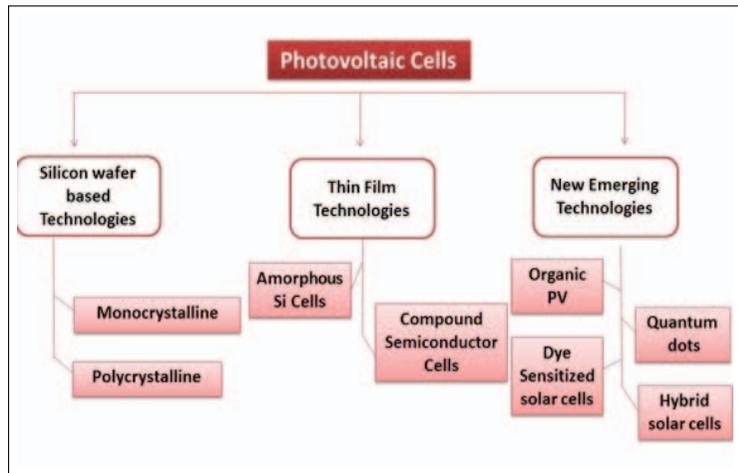


Figure 2. Classification of solar cells.



third generation solar cells. First generation cells are basically silicon based crystalline cells while second generation cells are thin film based, and third generation cells comprise new emerging technologies (*Figure 2*).

Solar cells used for power generation must possess certain char-



acteristics like high efficiency, low cost of raw materials, simple fabrication technique, ease of solar panel installation, and long-term stability. Unfortunately, there is not yet a device that can simultaneously meet all the above requirements.

First and second generation solar cells have high efficiency and stability except for the amorphous silicon solar cells. However, they also possess some disadvantages. Majority of these solar cells employ high-efficiency silicon-based materials which are expensive. The scarcity of indium which is used in copper indium gallium silicon (CIGS) solar cells is a potential challenge for the widespread use of these cells. The toxicity of cadmium and the low earth abundance of tellurium are often regarded as the drawbacks of cadmium tellurium (CdTe) solar cells.

In the recent years, research has focused on the development of cost-effective and feasible non-silicon solar cell technologies. The new (third) generation solar cells are primarily organic solar cells, dye sensitized solar cells (DSSCs), quantum dots, conjugated polymers, and perovskites. Perovskite-based photovoltaics is still a nascent technology. However, the distinct properties of perovskites such as high absorption coefficient, tunable band gap, longer carrier diffusion length, and the rapid increase in efficiency, makes it a very interesting technology. A considerable amount of research is being carried out in this field.

2. Perovskite: Structure

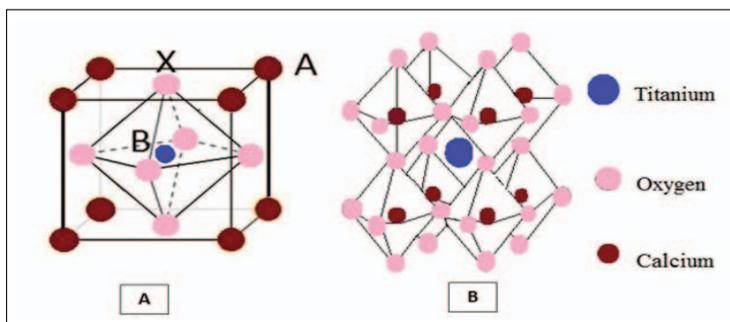
Perovskite is calcium titanium oxide (CaTiO_3) mineral. It was discovered in 1839 in the Ural Mountains of Russia and named after the Russian mineralogist L A Perovski. Generically, the term perovskite is used for the class of ABX_3 compounds which have the same crystal structure as CaTiO_3 . Structure of perovskite was first described by Victor Goldschmidt in 1926.

Figure 3 depicts the structure of mineral perovskite. The general chemical formula of perovskite is ABX_3 , where 'A' and 'B' are cations of different sizes, and 'X' is an anion that bonds with both the cations. 'A' ions are larger than 'B' ions. In the ideal

Perovskite-based photovoltaics is still a nascent technology. However, the distinct properties of perovskites such as high absorption coefficient, tunable band gap, longer carrier diffusion length, and the rapid increase in efficiency, makes it a very interesting technology.



Figure 3. Structure of perovskite (ABX_3) and mineral perovskite ($CaTiO_3$).



The ideal cubic perovskite structure is not very common, and also the mineral perovskite itself is slightly distorted.

form, the crystal structure of cubic ABX_3 perovskite consists of corner-sharing $[BX_6]$ octahedra with the 'A' cation surrounded by twelve 'X' anions. It can also be equivalently described as a cube with 'A' cations at the corners, 'X' anions at the face centers, and 'B' cations at the body center. Here 'A' can be Ca, K, Na, Pb, Sr or some rare earth metals. 'B' corresponds to a metal cation with coordination number six, and 'X' is an anion like oxide or halide. The oxidation states are such that the formula unit is neutral. The ideal cubic perovskite structure is not very common, and also the mineral perovskite itself is slightly distorted. Because of this distortion, perovskite materials exhibit many different properties such as ferromagnetism, ferroelectricity, multiferrocity, colossal magneto-resonance, and superconductivity to name a few. The materials with perovskite structure are widely studied in solid state chemistry and materials science. With the invention of perovskite solar cells, they have also entered the field of photovoltaics.

The first organic–inorganic halide perovskite was discovered by Weber by replacing cesium in $CsPbX_3$ with methylammonium cations. *Figure 4* represents the structure of organic-inorganic halide perovskite. The most efficient perovskite solar devices so far have been produced with the following combination of materials in the usual perovskite form ABX_3 :

A = An organic cation such as RNH_3 where R is an alkyl, phenethyl, etc. Methylammonium $(CH_3NH_3)^+$ is commonly used.

B = A large inorganic cation such as lead (Pb) or tin (Sn) in +2

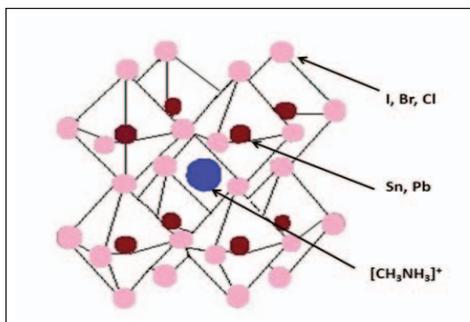


Figure 4. Organic–inorganic halide perovskite.

oxidation state.

X = A slightly smaller halide ion such as iodide (I^-), bromide (Br^-) or chloride (Cl^-).

The inorganic (BX_2) and organic (AX) layers are stacked alternately. The inorganic layers are covalently bonded in-plane, while the Van der Waals force between the organic layers exists perpendicular to the inorganic layers.

3. Emergence of Perovskite Solar Cells: Evolution to Revolution

The ability of halide perovskite to convert electricity to light was initially discovered by Mitzi and group in 1990, in the light emitting diode (LED) configuration. The reverse, *i.e.*, light to electricity conversion was reported almost after two decades.

Basically, perovskite solar cell has evolved from dye sensitized solar cells (DSSCs). The evolution of perovskite solar cells [3] is schematically represented in *Figure 5*.

Dye Sensitized Solar Cell (DSSC)

Typical DSSC consists of mesoporous n-type titania sensitized with a light absorbing dye in a redox active electrolyte. Porous titania provides a greater internal surface area to the excited dye molecule for efficient electron transfer to its conduction band. The film thickness of the dye of the order of $10\ \mu\text{m}$ is required for complete absorption over the absorbing range.

The ability of halide perovskite to convert electricity to light was initially discovered in 1990 in the LED configuration while light to electricity conversion was reported almost two decades later.



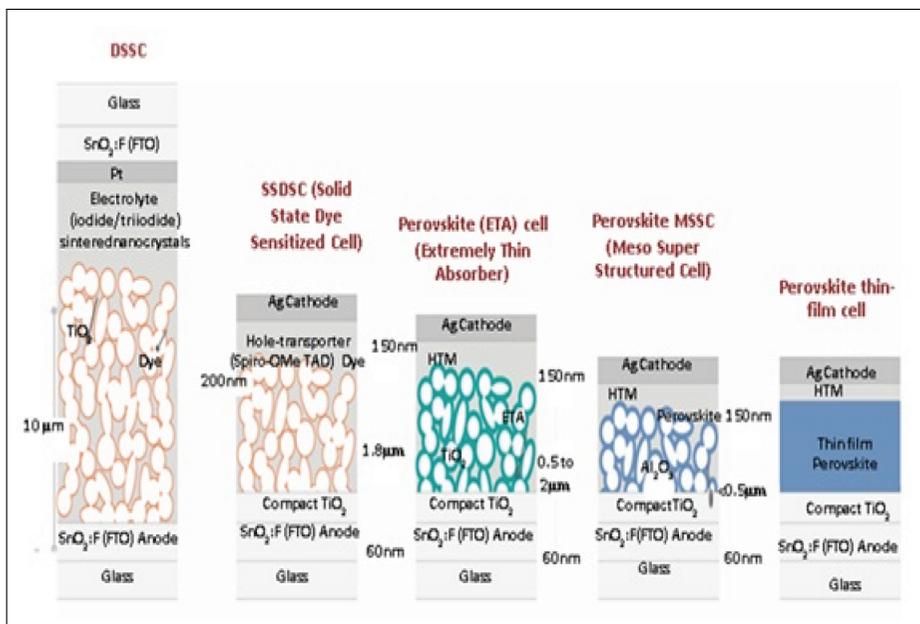


Figure 5. Evolution of perovskite solar cell (Source: Christopher Case, EU PVSEC 2014, Amsterdam, NL).

Solid State Dye Sensitized Cell (SSDSC)

In SSDSC cell, a solid hole conductor is used instead of liquid electrolyte, and the film thickness is reduced to $2 \mu\text{m}$. The hole conductor is typically made from a wide band gap material such as spiro-OMeTAD or semiconducting polymers such as PEDOT or P3HT (see *Figure 6* for their structure). SSDSCs are in principle, more industrially compatible than standard DSSCs because they do not contain corrosive liquid electrolyte, which requires careful packaging.

Extremely Thin Absorber (ETA) Perovskite Cell

As an alternate approach, thin film semiconductor active layers and quantum dot layers are also in vogue. These enable complete light absorption in much thinner layers while at the same time pushes the photosensitivity further into near infrared (NIR) range. This alternate approach was the motivation to find more efficient light sensitizers for DSSCs. Miyasaka's group at the University of Tokyo, Japan, reported the first perovskite solar cell using organometallic perovskite and liquid electrolyte in 2006. An

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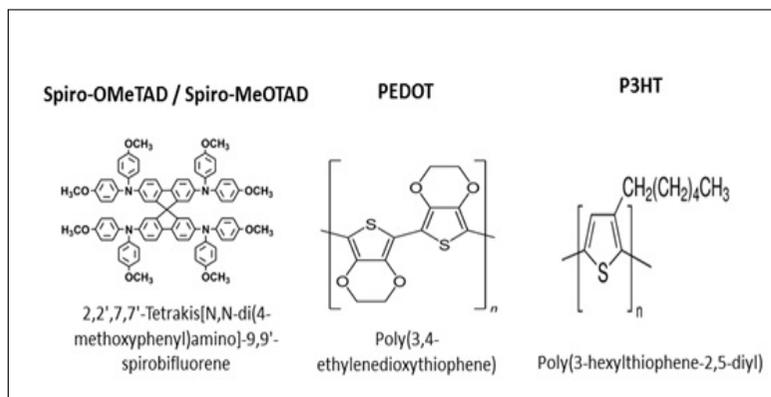


Figure 6. Materials used to make hole conductors for SSDSC.

efficiency of 2% was achieved in this cell. Power conversion efficiency (PCE) of 0.4% was reported with a solid state electrolyte. The first peer-reviewed report for perovskite-sensitized solar cell was published in 2009. In this series, CH₃NH₃PbI₃ absorber in an iodide/triiodide redox couple achieved an efficiency of 3.5%. N G Park and co-workers at Sungkyunkwan University, Korea, achieved an improved efficiency of 6.5% by optimizing the titania surface morphology and perovskite processing.

The major drawback in the liquid electrolyte based perovskite-sensitized solar cell was the dissolution and decomposition of perovskite in the liquid electrolyte. As a consequence, these solar cells exhibited poor stability and would degrade within minutes. The solution to this problem was in the adoption of solid state hole transport medium in place of liquid electrolyte as was originally attempted by Kojima and co-workers in 2006. Methylammonium trihalogen plumbates, being relatively insoluble in non-polar organic solvents, paved the way for realizing first perovskite sensitization and made subsequent infilling with organic hole conductor possible. The primary advantage of perovskite absorbers over dyes is their stronger absorption over a broader range, enabling greater and broader light absorption in films as thin as 500 nm.

Meso-Super Structured Cell (MSSC)

Henry Snaith further investigated meso-super structured cells (MSSC)



A planar device made using perovskite *via* vapor deposition achieved an efficiency of 15%, categorically confirming the ambipolar nature of perovskite.

to understand the charge-transport properties of perovskite-sensitized solar cells. He noticed that the charge extraction rates were significantly faster for perovskite-sensitized cells compared to conventional DSSCs. Furthermore, he constructed solar cells replacing the mesoporous TiO₂ with insulating mesoporous Al₂O₃ with a very similar meso-morphology; the primary intention being to elucidate the mechanism of electron transport through the perovskite phase and find out whether the mesoporous TiO₂ is required at all. Surprisingly, not only was the charge transport faster and the photocurrent unaffected when the insulating Al₂O₃ replaced the TiO₂, the open-circuit voltage increased by 200 to 300 mV, leading very quickly to an efficiency of 10.9%. This indicated that perovskite could also act as an absorber rather than being just a sensitizer.

Perovskite Thin Film Cell

A planar device made using perovskite *via* vapor deposition achieved an efficiency of 15%. This categorically confirmed the ambipolar nature of perovskite, *i.e.*, comparable electron and hole mobility in these systems.

4. Preparation of Perovskite Solar Cell

The perovskite solar cells can be prepared quite easily by the solution process. A simple, low-cost technique like spin-coating can be employed. But the drawback in this solar cell processing is that the complete processing has to be carried out in a glove box under a controlled atmosphere, without exposing the cell to moisture.

For the synthesis of active perovskite layers, different thin film deposition techniques such as one-step precursor solution deposition, two-step sequential deposition, dual-source vapor deposition, vapor assisted solution process, and sequential vapor deposition approaches are reported. In one-step coating, iodide perovskite is produced by first reacting equimolar CH₃NH₂ and HI in an appropriate solvent. The white precipitate obtained is washed with diethyl ether and finally dried in vacuum for about 24 h at



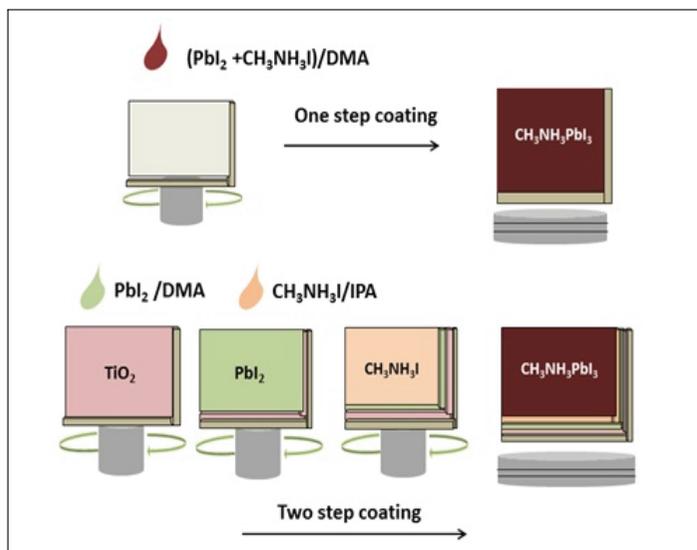


Figure 7. Schematic representation of preparation of perovskite solar cell by solution process.

60 °C. The synthesized $\text{CH}_3\text{NH}_3\text{I}$ is then mixed with PbI_2 in a 1:1 molar ratio in γ -butyrolactone at 60 °C. This solution can be used for coating to make the perovskite solar cells [4]. For two-step coating method, PbI_2 is first introduced into the TiO_2 nanopores by spin-coating a solution of PbI_2 in N, N-dimethylformamide (DMF) at 70 °C. The layer thus formed is immersed in $\text{CH}_3\text{NH}_3\text{I}$ solution [5]. *Figure 7* illustrates perovskite active layer coating by spin-coating technique. For making chloride/iodide mixed halide perovskites, PbCl_2 is used along with $\text{CH}_3\text{NH}_3\text{I}$ [6].

Properties of the solvent, additives, annealing and processing temperatures, and environments have a profound impact on the final film quality.

Properties of the solvent, additives, annealing and processing temperatures, and environments have a profound impact on the final film quality. Lower annealing temperature results in poor film convergence while higher annealing temperature causes decomposition of the active layer. Optimum annealing condition is reported to be slow annealing at 100 °C forming particles of 100–1000 nm.

5. Perovskite Solar Cells: Device Architecture

Operating mechanisms of the organometal halide perovskite solar cells are of great interest. When the perovskite solar cell was



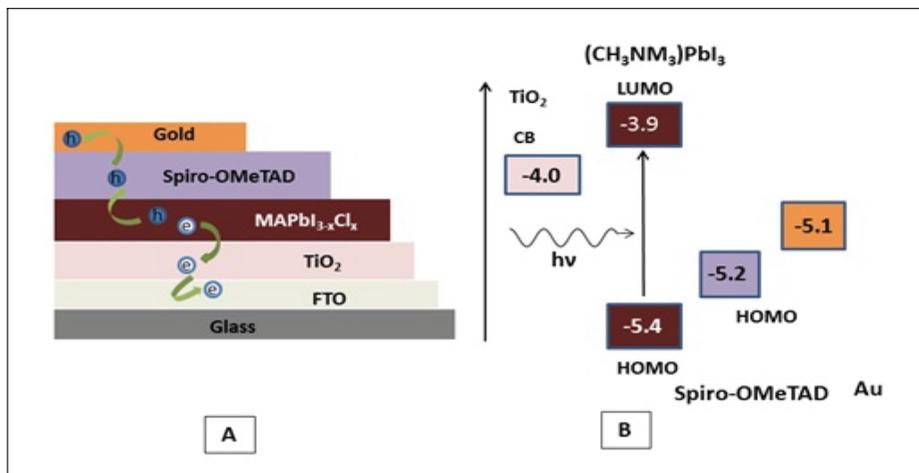


Figure 8. (A) Perovskite solar cell, and (B) Working of perovskite solar cell.

first discovered, it was a TiO₂ sensitized cell. So, it was natural to believe that electron injection to the wide band gap metal oxide was the main transport pathway. However, the observation of significant efficiencies in perovskite solar cells with neither electron nor hole transporting materials, or even in thin film configuration indicated that in perovskite solar cells the operating mechanism was quite different from that of DSSCs. These results strongly point to the coexistence of photo-generated electrons and holes in CH₃NH₃PbX₃ absorber material and that they travel to the selective contacts where they are separately collected. The device architecture of perovskite solar cell is shown in *Figure 8* (A). The proper band alignments between spiro-OMeTAD and perovskites as well as between perovskites and TiO₂ make both spiro-OMeTAD and TiO₂ good candidates for carrier transportation. When photoexcited, electrons and holes are generated at the conduction bands (CBs) and valence bands (VBs) of a perovskite respectively. The electrons will move to the CB of TiO₂, while the holes will move to the VB of the hole transport material (HTM) layer (as illustrated in *Figure 8* (B)).

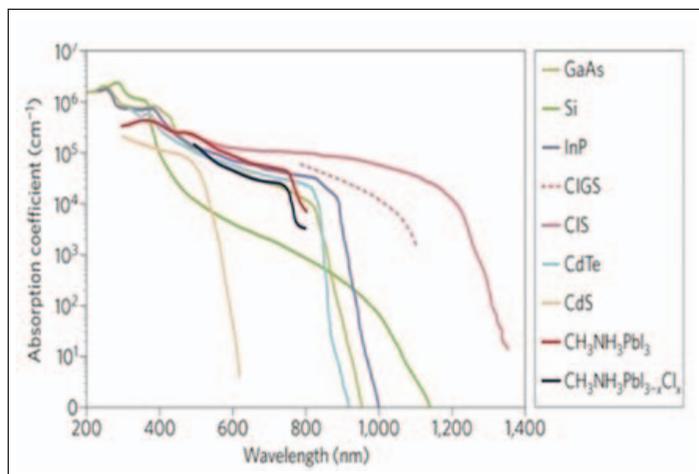


Figure 9. Optical absorption of different materials [7].

6. Perovskite Solar Cell: Properties

6.1 High Optical Absorption

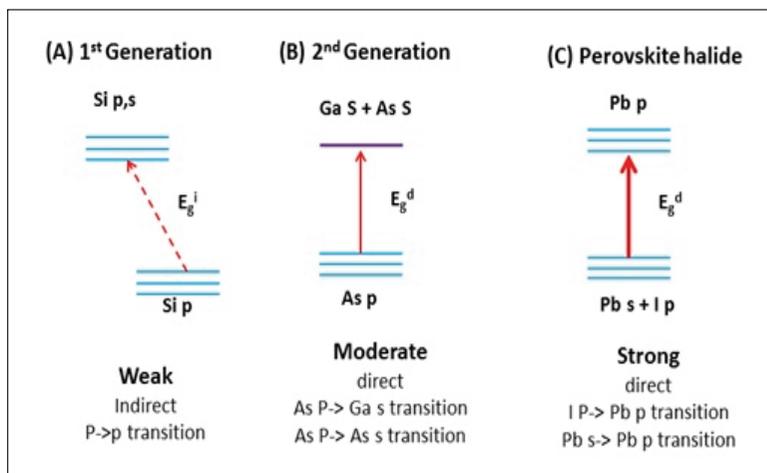
The absorber layer is the heart of the solar cell. *Figure 9* depicts absorption coefficient of different solar absorber materials. Organic–inorganic hybrid perovskite absorber materials have a direct band gap with high absorption coefficient. This property allows the absorber film to be as thin as several hundred nanometers for light harvesting, while in traditional CIGS and silicon based solar cells, the film thickness required are usually a few micrometers and a few hundred micrometers, respectively.

The mechanisms of optical absorption for the first generation, second generation, and perovskite-based solar cell absorbers are shown schematically in *Figure 10*. The first generation absorber (silicon) is an indirect band gap semiconductor. This means that the momentum of the electron at the top of the VB is not the same as the momentum at the bottom of the CB. A transition between these levels is forbidden, and it becomes weakly allowed only because lattice vibrations also participate in the excitation. Hence, the transition probability between the VB and CB extrema is about two orders of magnitude lower than in those of direct band gap materials. Thus, for the same number of photons to be absorbed per unit area, the thickness of the absorber

Organic–inorganic hybrid perovskite absorber materials have a direct band gap with high absorption coefficient.



Figure 10. The schematic optical absorption of materials used in (A) first-generation, (B) second-generation, and (C) halide perovskite solar cell absorbers [8]. The orbitals involved in the initial and final states are indicated at the bottom.



layer of an indirect band gap material needs to be about two orders of magnitude more than that of direct band gap materials. This leads to an increase in the cost of material required for an indirect band gap semiconductor based solar cell, operating at the same efficiency as a direct band gap material based solar cell. The second-generation absorber (such as GaAs) and halide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) are direct band gap materials, and thus their optical absorption is much stronger than that of silicon. However, the electronic structures of GaAs and perovskite halide are different. The lower part of the CB of GaAs is derived from the dispersive ‘s’ band (delocalized ‘s’ orbitals), whereas the lower part of the perovskite halide CB is mainly composed of degenerate Pb ‘p’ bands. The atomic ‘p’ orbitals are less dispersed than the ‘s’ orbitals. As a result, transition intensity is moderate in GaAs. Additionally, the edge transition for perovskite comes from the initial state which is made up largely of Pb ‘s’ and I ‘p’ orbitals to the conduction band edge which is essentially Pb ‘p’ orbitals. The intra-atomic Pb ‘s’ to Pb ‘p’ transition probability is high, which makes the VB–CB transition probability of perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) higher than that of GaAs. Therefore, halide perovskites show stronger optical absorption than GaAs. Visible light accounts for the major usable portion of the full solar spectrum, and high absorption in this range

Tailoring the band gap of the light absorber in solar cells is important in designing a device architecture for maximizing the absorption of sunlight.



is critical for achieving high-efficiency cell.

6.2 Tunable Band Gap

Tailoring the band gap of the light absorber in solar cells is important in designing a device architecture for maximizing the absorption of sunlight, especially in the heterojunction and tandem solar cells. Therefore, the band-gap-controllable mixed perovskite is greatly advantageous as a light absorber in solar cells. In inorganic-organic hybrid perovskite materials of type ABX_3 , the band gap of the absorber layer can be fine-tuned by changing the organic cation (A) or the metal atom (B) or the halide (X).

Influence of Organic Cation (A): In cubic perovskite structures, although position 'A' does not significantly influence the band structures, the change in 'A' can still tailor the band structure to a small extent. Actually, the band structure of $MAPbI_3$ ($MA = CH_3NH_3$) is close to the optimum value for solar cell application. To narrow the bandgap of $[CH_3NH_3]^+PbI_3$, formamidinium (FA) cation has been utilized for the perovskite absorbers, forming $[H_2N-CH=NH_2]^+PbI_3$ ($FAPbI_3$) with a band gap of 1.4 eV. A trend is that with the increase in the size of 'A' cation, *i.e.*, from Cs^+ to $CH_3NH_3^+$ and $NH_2CH_2 = NH_2^+$, the value of the band gap gradually decreases (*Table 1*). However, on further increasing the size of 'A' to $CH_3CH_2NH_2$ (EA), the perovskite $[CH_3CH_2NH_3]^+PbI_3$ structure turns into orthorhombic symmetry with a band gap of 2.2 eV.

Influence of Metal Cation (M): Lead (Pb) is a toxic element; its use is restricted in many countries. This has led to the development of leadless or lead-free perovskites. Tin (Sn), which belongs to the same group as lead, is an alternate which can replace lead. The ratio between Sn and Pb has been experimentally worked out to get perovskite $CH_3NH_3Sn_{1-x}Pb_xI_3$, and the band gap can be tuned between 1.17 eV to 1.55 eV as listed in *Table 1*. Thus, Sn substitution can extend the light absorption from visible to near-infrared region (1060 nm). The problem with the Sn-based solar cell is that it is difficult to form uniform and dense absorber films



A Substitution		M Substitution		X Substitution	
Material	Bandgap eV	Material	Bandgap eV	Material	Bandgap eV
EAPbI ₃	2.2	MAPbI ₃	1.5	MAPbI ₃	1.5
MAPbI ₃	1.5	MASn _{0.3} Pb _{0.7} I ₃	1.31	MAPbI ₂ Br	1.8
FAPbI ₃	1.4	MASn _{0.5} Pb _{0.5} I ₃	1.28	MAPbBr ₃	2.20
CspPI ₃	1.67	MASn _{0.9} Pb _{0.1} I ₃	1.18	MAPbCl ₃	3.11
		MASnI ₃	1.10		

Table 1. Band gap of different ABX₃ materials.

over the device area, and as a consequence, the solar cell efficiency drops. Furthermore, due to the downshifting of the CB edge, there is always a decrease of open-circuit voltage in the Sn-based perovskite when compared to the Pb equivalents.

Influence of Halide Anion (X): Group VII elements, Cl, Br, and I are the most widely used candidates for substitution in the ‘X’ position of perovskite. The alteration in the element can bring forth large changes in the band gap. In CH₃NH₃PbX₃, the band gaps are 3.11, 2.22, and 1.51 eV for X = Cl, Br, and I respectively (Table 1). It is also noted that lowest band gap obtained by changing CH₃NH₃PbX₃ (X = Cl, Br, I) is 1.51 eV. To obtain the desired band gap, researchers resort to altering the substitutions in both the M and X positions simultaneously. By partial replacement of I with Br and complete replacement of Pb with Sn, Hao *et al.*, [9] observed that the band gap could be tuned from 1.30 to 2.15 eV in CH₃NH₃SnI_{3-x}Br_x. The optimization of the ratio between I and Br shows that CH₃NH₃SnIBr₂ can generate better PCE.

While both radiative and non-radiative recombination are detrimental to the performance of a solar cell, non-radiative recombination also heats up the device, further reducing the solar cell efficiency.

6.3 Low Recombination

Recombination is the process by which the excited electron in the CB falls back to occupy an empty state in the VB. This is also called electron-hole recombination. This process competes with the process of separation of the excitation to electron and hole and their collection at the electrodes. Hence, this process leads to a drop in the current of the solar cell and consequently the effi-

ciency. There are two types of recombination – radiative and non-radiative. In radiative recombination, a photon is emitted, and in a non-radiative recombination, the energy of the excited electron is dissipated as heat. While both are detrimental to the performance of a solar cell, non-radiative recombination also heats up the device, further reducing the solar cell efficiency.

The diffusion length of the charge carrier is an important parameter for assessing the recombination probabilities in the materials. Longer diffusion lengths will aid in better collection of carriers at the electrodes. Stranks and co-workers reported that the electron and hole diffusion length of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ is over one micron which is about three times the typical film thickness in a solar cell. This ensures the migration of charges to the interfaces before recombination and is significant for the fabrication of planar heterojunction solar devices. However, in $\text{CH}_3\text{NH}_3\text{PbI}_3$ based solar cells, a mesoporous TiO_2 nanoparticle network is necessary for transporting charges to the collecting electrode as the diffusion length of carriers is only ~ 100 nm.

6.4 High Open Circuit Voltage (V_{oc})

Compared to other thin film polycrystalline semiconductors, the perovskite absorber materials show lower non-radiative recombination rate. *Figure 11* shows the graph of open-circuit voltage versus band gap of current and emerging solar technologies. Per-

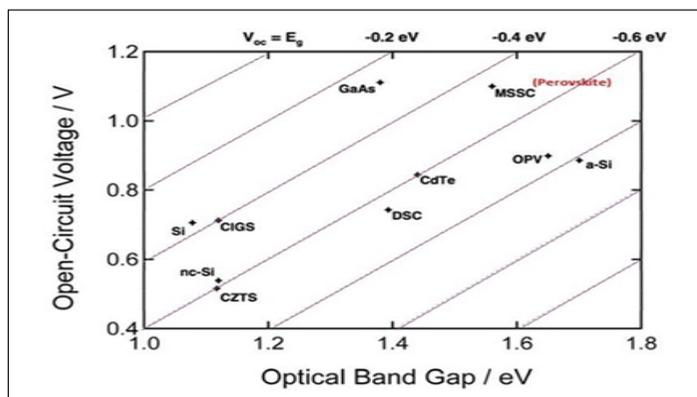


Figure 11. Open-circuit voltage (V) versus optical band gap (eV) for current and emerging solar technologies [3]. The OCV of perovskite solar cells falls on the same line as most solar cells. Since the band gap is high (1.51 eV), the OCV is also large, which results in greater efficiency.

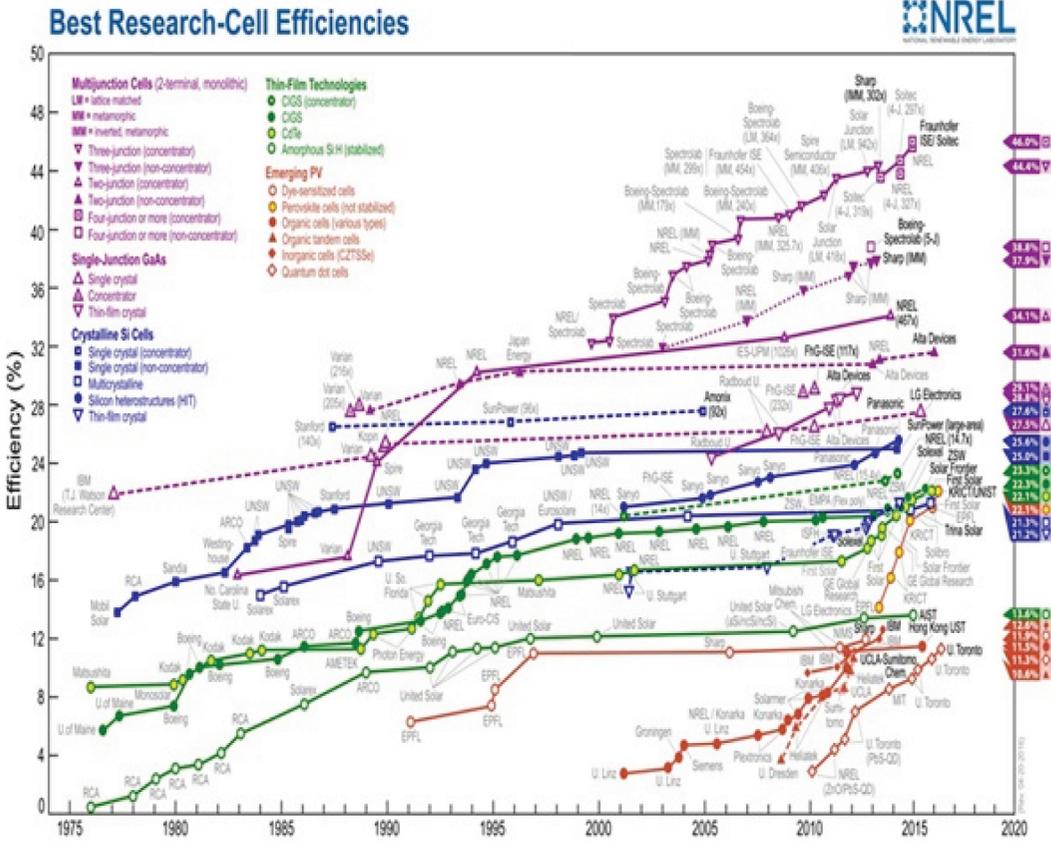


Figure 12. Efficiencies of different solar technologies [11].

ovskite is very well positioned compared to all other materials for solar cell technologies. High V_{oc} is the second factor that contributes to high PCE.

6.5 Rapidly Increasing Efficiency

The power conversion efficiencies of perovskite solar cells have risen from 3.8% in the year 2009 to 22.10% in 2016 (Figure 12). A certified efficiency of 19.6% is achieved with an aperture area of 1 cm² [10]. Since perovskite band gaps are tunable and can be optimized for the solar spectrum, these cells can approach the

Characteristics	CIGS	CdTe	C-Si	Perovskite
Raw materials cost	Low	Medium	Low	Low
Finished material cost	Low	High	High	Low
Fabrication cost	Medium	Medium	High	Low
Energy payback period	Medium	High	High	Low
Efficiency	Medium	Medium	High	High

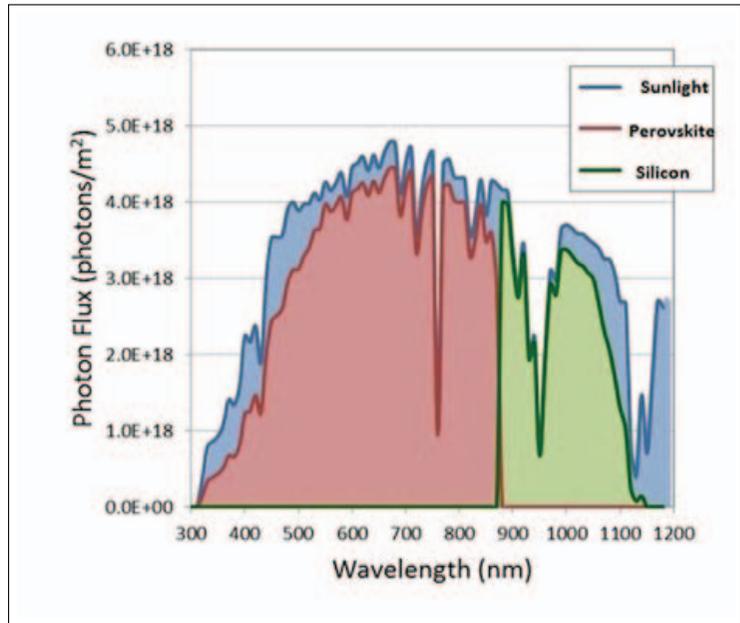
Figure 13. Why perovskite solar cells have enormous potential when compared to other solar cells! (Source: Christopher Case, EU PVSEC 2014, Amsterdam, NL).

Shockley–Queisser efficiency limit, which is about 31% under an AM1.5G solar spectrum at one sun illumination (1000 W/m^2), for a perovskite band gap of 1.55 eV.

Perovskite has enormous potential (*Figure 13*). As a raw material, its fabrication, finished material cost, and energy payback time are low compared to existing solar technologies, while at the same time, PCE is very high (as shown in *Table 1*). Perovskites have several advantages over traditional solar cell materials. Perovskites can be processed using very simple, low-cost methods – the precursor solution contains a mixture of inexpensive salts, annealed at very low temperatures, and sandwiched with a top electrode. This allows printing of these solar cells using a large area inkjet printer. These can also be processed on flexible substrates, such as plastic or fabric and can be used as portable electronic devices. The band gap and optical properties of perovskite can be widely tuned by tweaking the halide composition in AMX_3 structure, and different colors of solar cells can be produced which can be used in building integrated PV.



Figure 14. Combining wide band gap (1.5 eV) perovskite on top of 1.1 eV Si captures more photons from sunlight (Source: Christopher Case, EU PVSEC 2014, Amsterdam, NL).



With the current state-of-the-art, perovskite solar cell can be used effectively as a top cell, in a tandem cell configuration, with existing technologies like crystalline silicon, and thin film solar cells like CZTSSe, CIGS, and CIS. Efficiency as high as 29.6% could be achieved with top perovskite cell and bottom c-Si cell in tandem cell configuration [3]. *Figure 14* shows the advantages of combining c-Si and perovskite cells because these tandem solar cells can absorb over a wider solar spectral range. All this can be achieved with the existing technologies, with little optimization in terms of band gap widening, FF enhancement, and integration into tandem cell architecture. At present, 16% efficient tandem thin perovskite/polymer solar cells with graded recombination layer are fabricated with efficiency 65% greater than that of the polymer single-junction device [12].

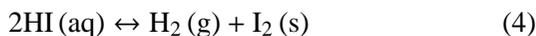
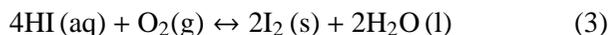
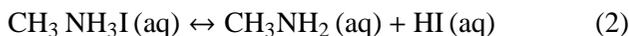
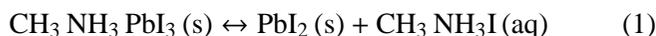


7. Drawbacks of Perovskite Solar Cells

7.1 Stability

Considerable research effort has been focused on enhancing the efficiency of perovskite devices by the adoption of various device architectures, compositions, and manufacturing techniques. This has resulted in substantial increase in the efficiencies to a proven efficiency of 19.6%. The limiting factor to this success story is the lack of stability. High-efficiency devices reported are synthesized under controlled environments, and their efficiencies drop rapidly upon exposure to ambient atmosphere. Degradation in perovskite solar cells is a synergistic effect of exposure to humidity, oxygen, UV radiation, and temperatures.

$\text{CH}_3\text{NH}_3\text{PbI}_3$ is highly sensitive to humidity; it tends to hydrolyze in the presence of moisture and degrade as follows:



The equilibrium species, in the presence of water, oxygen, and UV radiation, are thus, $\text{CH}_3\text{NH}_3\text{I}$, CH_3NH_2 , and HI . HI can either decompose by a one-step redox reaction or by photochemical reaction under UV radiation to H_2 and I_2 . This sensitivity requires synthesis in a controlled environment like a glove box. A humidity of 55% is reported to deteriorate the performance and is evident by a color change from dark brown to yellow due to the decomposition to PbI_2 in $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ ($x = 0, 0.06$) solar cells.

Liu *et al.*, used an HTM with long alkyl chains, which can reduce the infiltration of water through the HTM layer to the perovskite.

Degradation in perovskite solar cells is a synergistic effect of exposure to humidity, oxygen, UV radiation, and temperatures.



Perovskite cells have led to the rise of a new era of low-cost, high-efficiency cells in the solar industry.

In this case, the PCE of the device did not show a decrease after storing in the air for long periods, and the stability reached up to 1008 hours.

The perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ films are normally annealed at 100 °C for ten minutes after the synthesis of the layer. Dualeh and co-workers found that when the annealing temperature is higher than 120 °C, the perovskite starts to decompose into PbI_2 , $\text{CH}_3\text{NH}_3\text{I}$, and $\text{CH}_3\text{NH}_3\text{Cl}$. Once the temperature reaches 300 °C, the perovskite decomposes into PbI_2 , CH_3NH_2 , and HI. The instability of the device would also stem from TiO_2 in some cases, owing to the non-stoichiometric TiO_2 induced deep electron traps in the crystals which lead to oxidation. This phenomenon is especially notable under an inert atmosphere. This poses a great challenge in terms of avoiding oxidation of the dye or perovskite in sealed devices.

While the stability has been improved to some extent, it is still far below the stringent requirements for long-term practical applications. Therefore, further improvement in stability is necessary in terms of both materials and device at the laboratory and more importantly, on the module scale.

7.2 Toxicity of Lead

Lead (Pb) compounds are highly toxic and can harm the environment. Pb is known to adversely affect the ecosystem by harming the microorganisms in the soil. This is an unsettling concern about perovskite solar cells because the high light conversion efficiencies are Pb based. There is emphasis on replacing Pb ion with safer ion like tin.

Conclusion

In summary, various researchers with backgrounds in chemistry, physics, engineering, and materials science have investigated and contributed to the development of perovskite semiconductor material. Within a few years since its invention, perovskite solar



cells have proved that they have the desired properties and enormous potential. This has led to the rise of a new era of low-cost, high-efficiency cells in the solar industry. The drawback though is their instability under ambient conditions and Pb toxicity. If these issues are addressed, undoubtedly, perovskite solar cells will play a major role in the solar PV industry.

Box 1. Annexure

Van der Waals Forces: Molecules can attract each other at moderate distances and repel each other at close range. The attractive forces between molecules are collectively called the 'Van der Waals forces'. Van der Waals forces are much weaker than chemical bonds, and random thermal motion at room temperature is usually enough to break them. Van der Waals forces include all intermolecular forces that act between electrically neutral molecules. These forces govern many properties including crystal structures, melting points, boiling points, heats of fusion and vaporization, surface tension, and densities.

Light Emitting Diode: LED is a semiconductor device that creates light using solid-state electronics. A diode is composed of a layer of electron rich (n-type) material separated by a layer of electron deficient (p-type) material which forms a junction. Under a bias voltage, electrons move from n-type region to p-type region and holes from p-type region to n-type. This facilitates the recombination of electrons in the conduction band with holes in the valence band leading to the emission of light. Depending on the chemical composition of the semiconductor layers, the color of light emission will vary within the electromagnetic spectrum.

Valence Band: It is a band of fully occupied (at absolute zero temperature) continuous (or gapless) highest energy states.

Conduction Band: Conduction band is a continuous set of partially occupied or empty (at absolute zero temperature) lowest energy states.

Band Gap: The band gap refers to the energy difference between the top of the valence band and the bottom of the conduction band in insulators and semiconductors. Semiconductors distinguish themselves from metals and insulators by the fact that they contain an empty conduction band and a completely filled valence band at absolute zero temperature. At finite temperatures, due to thermal activation, some of the electrons in the valence band are promoted to the conduction band. The empty states in the valence band are referred to as hole states or simply holes.

p-Type Semiconductor: The addition of trivalent impurities such as boron, aluminum or gallium to an intrinsic silicon semiconductor creates deficiencies of valence electrons, called 'holes'. This type of doping results in p-type semiconductors. Holes notionally have a positive charge equal in magnitude to that of the electron. Holes are the majority carriers in p-type semiconductors (*Figure A*).

Contd.



Box 1. Contd.

n-Type Semiconductor: The addition of pentavalent impurity atoms such as antimony, arsenic, phosphorous or silicon contributes an electron to the conduction band, contributing to the conductivity of the resulting n-type semiconductor. Electrons are the majority carriers in n-type semiconductors. When p-type and n-type materials are placed in contact with each other, the positively charged donor impurities on the n-doped side and the negatively charged acceptor impurities on the p-doped side diffuse towards the junction. This leads to a high repulsive potential for electrons on the p-side and holes on the n-side. This blocks the electrons in the conduction band on the n-side and holes in the valence band on the p-side from crossing the junction (*Figure A*).

Diffusion Length: Diffusion length is the average length a carrier moves between its generation and recombination. Semiconductor materials that are heavily doped have greater recombination rates and consequently shorter diffusion lengths. Higher diffusion length is indicative of materials with longer recombination lifetimes and is, therefore, an important parameter in evaluating a semiconductor’s solar cell application.

Shockley–Queisser Efficiency Limit: Shockley–Queisser Efficiency Limit or SQ Limit refers to the maximum theoretical efficiency of a solar cell using a single p-n junction to collect power from the cell.

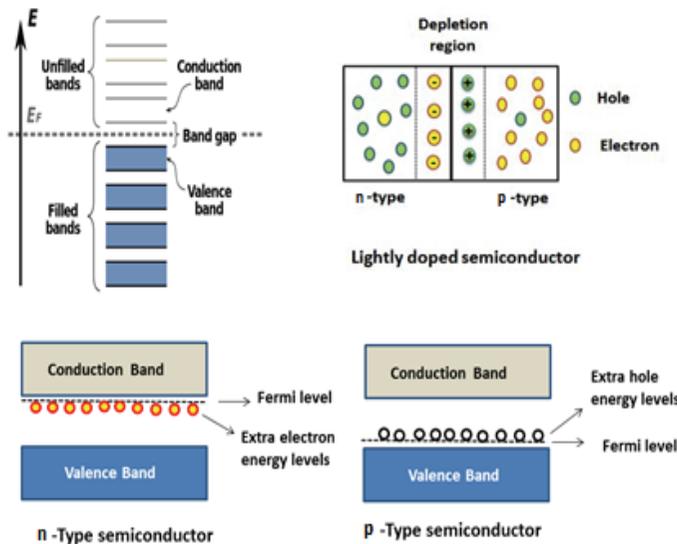


Figure A. p-Type and n-Type Semiconductors.

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