

Design and Simulation of Efficient Perovskite Solar Cells

A Project Submitted
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This is to certify that this Project is our original work. No part of this work has been submitted elsewhere partially or fully for the award of Master of Science in Applied Physics and Electronics. Any material reproduced in this project has been properly acknowledged.

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Abstract

The demand of electricity is increasing day by day. Today this demand is mostly met by burning coal, oil and natural gas. After depletion of these sources renewable energy will become the main source of electricity for the next generation. Among all the renewable energy sources, solar photovoltaic will be the potential source of energy. Solar cell can convert sunlight directly into electricity. Thin film solar cell becomes more popular because of its low material cost. Perovskite solar cell is recently invented in recent years due to its advantageous features including high absorption, low cost, ease of fabrication and rapidly improving efficiencies. Using organometallic halide Perovskite as absorber layer the efficiency has already increased above 20% in recent years. A Perovskite solar cell is made of three main layers where a Perovskite layer is sandwiched between the n type and p type material. The standard design for a Perovskite solar cell is: Back contact/ Hole transporting material (HTM)/ Perovskite as absorber layer/ Electron transport material (ETM)/ transparent electrode. By increasing the conductivity of the hole transport materials by doping and optimizing charge collection by adjusting the absorber thickness and band gap the efficiency can be improved. Electron transporting materials are also an important component in perovskite based solar cells. Several PV parameters such as thickness of the absorber, Hole transporting material (HTM) and Electron transport material (ETM) respectively can be optimized by simulation methods and subsequently implemented by experimentalists. In this work, we designed a Perovskite solar cell using ZnO as n-type and Cu₂O as p-type material, CH₃NH₃PbI₃ (Perovskite) as intrinsic layer material. Considering 300K as room temperature we found the maximum efficiency of 25.29%, with $V_{oc} = 0.8082$ V, $J_{sc} = 36.92$ mA/cm² and FF of 84.74% when absorber layer (CH₃NH₃PbI₃) thickness was 15 μ m.

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List of Symbols and Abbreviation

χ	Electron affinity
ϵ	Permittivity
ψ	Electrostatic potential
ξ	Electrostatic field
q	Charge of Electron
N_c	Density of States In the Conduction Band
N_v	Density of The State In the Valance Band
N_A	Acceptor density
N_D	Donor density
NREL	National Renewable Energy Laboratory
AMPS	Analysis Of Microelectronic and Photonic Structure
SCAPS	Solar Cell Capacitance Simulator
AM 1.5	Standard Terrestrial Solar Spectrum 'Air Mass 1.5'

Chapter 1

Introduction

1.1 Introduction

A Secured and sustainable supply of energy is a key to the prolongation and development of prosperous and modern society. Day by day energy consumption has been increased steadily with civilization development. In the future the energy consumption will be further increased to sustain the current human development. Worldwide energy consumption is 104,216TWh [1] and 41.3% of that energy comes from coal/peat,21.7% from natural gas, 16.3% from Hydro, 10% from nuclear, 4.4% form oil and finally only 5.7% from renewable sources etc. The main issue of those sources is sustainability, especially with the continuous increase of the demand for energy. The energy consumption by sources in 2013 is shown in Fig 1.1.

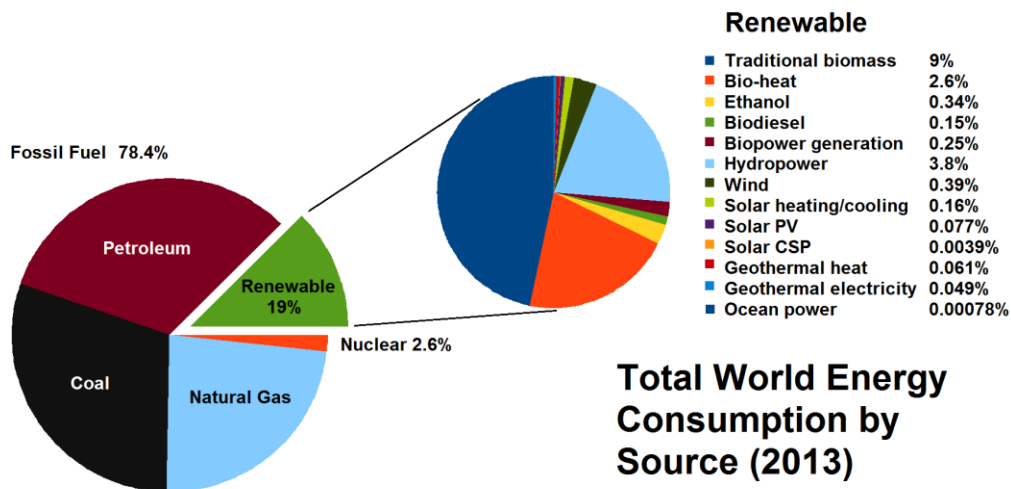


Fig 1.1 Total world energy consumption in 2013[2]

One quarter of the total energy used in the world was consumed in the US alone and 85% of that energy depended on fossil fuels (coal, oil and natural gas). The energy Demands have kept on increasing very quickly and the consumption will increase even faster with the population growth and the development of underdeveloped regions. The predicted energy consumption for 2050 will amount to as much as 30 TW [3].

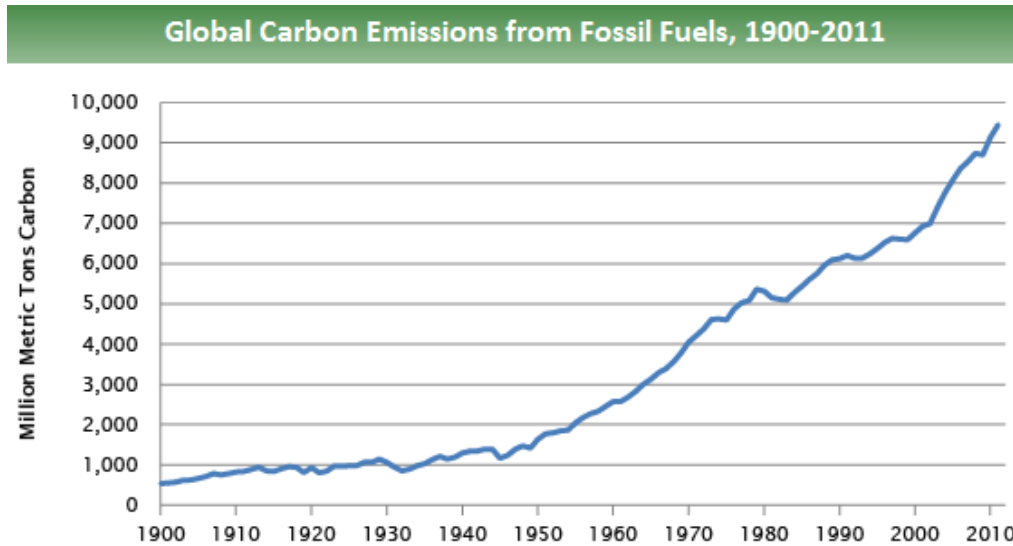


Fig 1.2 Global CO₂ emissions per region from fossil fuel burning 1971-2012 [4]

It can be seen from the Figure that after 1950 the CO₂ emission due to fossil fuel has been increased rapidly. After 2000, the CO₂ emission has crossed over 10000 million tons. Thus, fossil fuel usage has a detrimental effect on environment such as greenhouse gas emission, air pollution, and water and soil contamination and so on. The enhanced uses of fossil fuel increase the amount of CO₂ emission which is responsible for global warming. A cumulative total of 210 billion tons of CO₂ were emitted between 2000 and 2011. Emissions from the 34 developed country members of the Organization for Economic Cooperation and Development now account for only one third of global CO₂ emissions.

Moreover fossil fuels are a finite source of energy. Oil and gas will be running out in the near future. It took millions of years to generate, but finished in a single life time. For these reasons we have to think of alternative sources of energy. Nuclear energy would not meet nuclear is very difficult, any disaster may arises at any time and disposal of nuclear product is another problem.

1.2 Renewable Energy

Renewable energy is energy that is collected from renewable resources, which are naturally replenished. The major sources of renewable energy are solar energy, wind energy, biogas energy, tidal energy, ocean wave energy, geothermal energy and so on. The origin of most of these energies is the solar radiation incident on earth. However tidal power is dependent on gravitational pull of sun and moon. Geothermal energy also doesn't depend on sun. The sun's

heat drives the wind, whose energy is captured by wind turbines. The winds and suns heat cause water to evaporate. When these water vapors turn into rain or snow and fall downhill to rivers and streams, its energy can be captured using hydroelectric power. Also, sunlight causes plants to grow. The organic materials that make up these plants is known as biomass. It can be used to produce electricity.

Based on REN21's 2016 report, renewables contributed 19.2% to humans' global energy consumption and 23.7% to their generation of electricity in 2014 and 2015, respectively. This energy consumption is divided as 8.9% coming from traditional biomass, 4.2% as heat energy (modern biomass, geothermal and solar heat), 3.9% hydroelectricity and 2.2% is electricity from wind, solar, geothermal, and biomass. Worldwide investments in renewable technologies amounted to more than US \$286 billion in 2015, with countries like China and the United States heavily investing in wind, hydro, solar and biofuels [5]. Globally, there are an estimated 7.7 million jobs associated with the renewable energy industries, with solar photovoltaic being the largest renewable employer [6]. As of 2015 worldwide, more than half of all new electricity capacity installed was renewable [7].

Hydropower is the most widely used renewable resource for generation of electricity. More than 150 countries generate large amounts of electricity using hydropower. World hydroelectric power generation has risen steadily by an average 3 percent annually over the past four decades. In 2011, at 3,500 billion kilowatt-hours, hydroelectricity accounted for roughly 16 percent of global electricity generation, almost all produced by the world's 224,000-plus large dams. Today hydropower is generated in over 147 countries.

World Hydroelectric Generation, 1965-2011

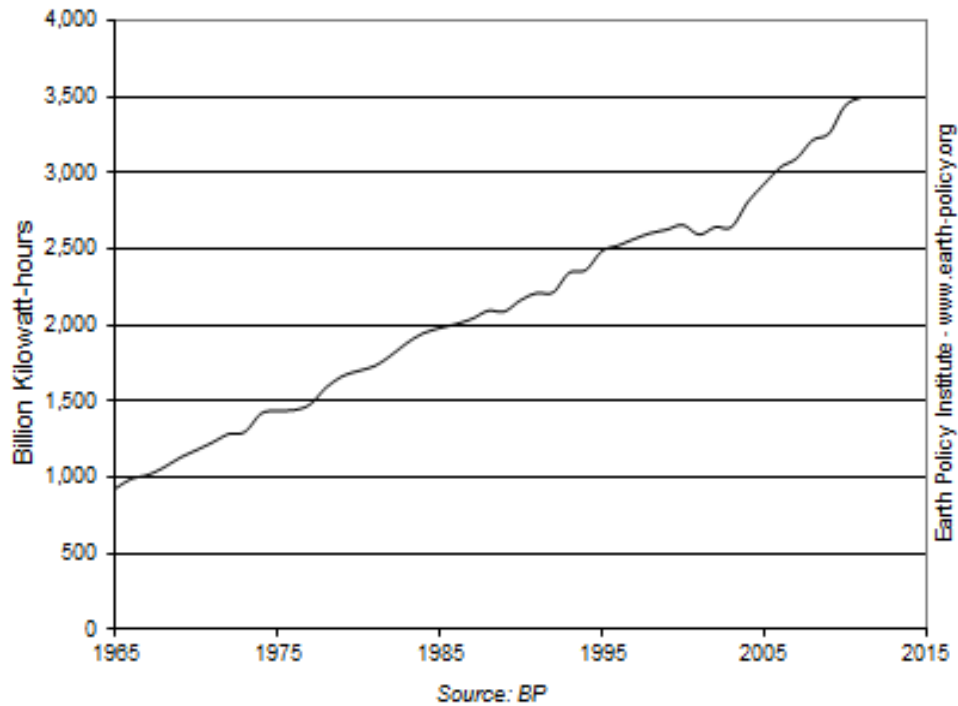


Fig. 1.3: World hydropower generation

Four countries dominate the hydropower landscape: China, Brazil, Canada, and the United States. Together they produce more than half of the world's hydroelectricity [8]. The world already uses most of the feasible hydropower. So, further extension of hydropower is limited.

Wind energy is generated by thermal current which is produced by the warming of equatorial air and the cooling of the polar air. As of the end of 2015, the world wide total cumulative installed electricity generation capacity from wind power amounted to 222,883 MW, an increase of 17% compared to the previous year.

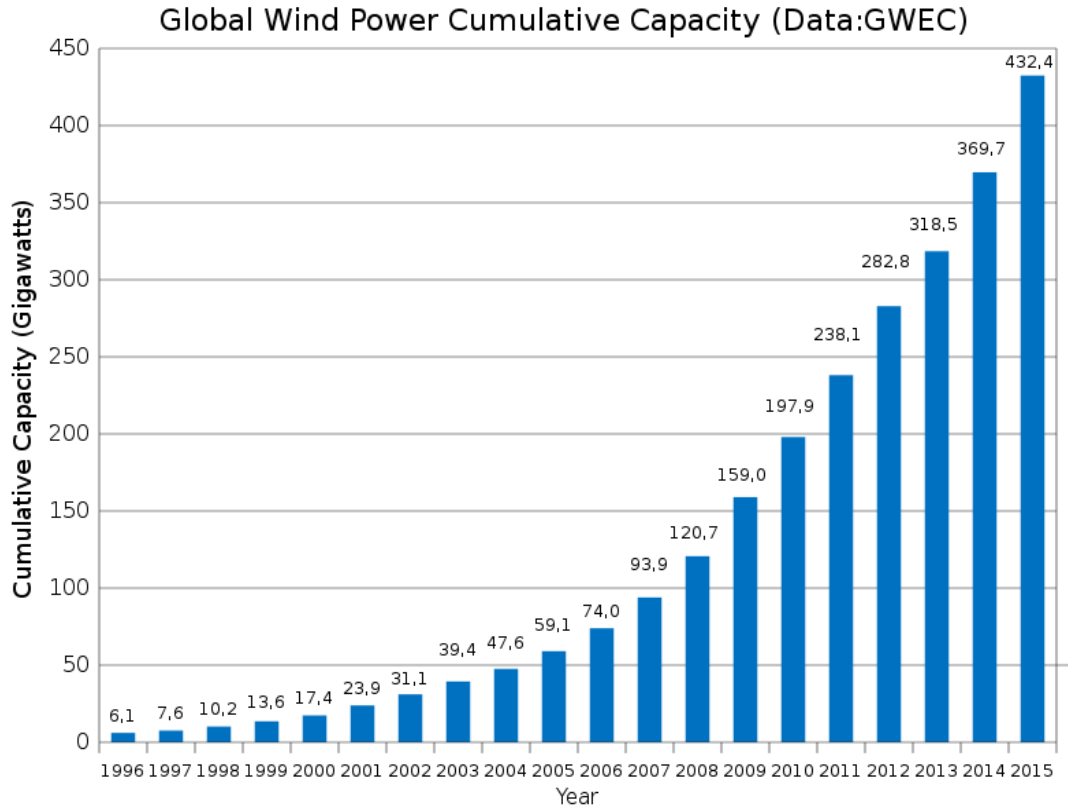


Fig. 1.4: Global wind power cumulative capacity [9]

Global wind power installations increased by 63,209 MW, 51,237 MW and 35,467 MW in 2015, 2014 and 2013 respectively. Since 2010 more than half of all new wind power was added outside of the traditional markets of Europe and North America, mainly driven by the continuing boom in China and India. At the end of 2015, China had 1224GW of wind power capacity [9]. Wind energy can't be getting all time at all the areas of the world to produce electricity. So, it is not reliable.

Biomass is organic matter derived from living, or recently living organism. Biomass can be used as a source of energy and it most often refers to plants or plant-based materials that are not used for food or feed, and are specifically called lignocellulosic biomass. As an energy source, biomass can either be used directly via combustion to produce heat, or indirectly after converting it to various forms of bio-fuel. Conversion of biomass to bio-fuel can be achieved by different methods which are broadly classified into: thermal, chemical and biochemical methods which are broadly classified into: thermal, chemical and biochemical method. Biomass can be

converted into: thermal, chemical and biochemical method. Biomass can be converted into electric power through several methods. The most common is direct combustion of biomass material, such as agricultural waste or woody materials. Other options include gasification, pyrolysis, and anaerobic digestion. Gasification produces a synthesis gas with unusable energy content by heating the biomass with less oxygen than needed for completing combustion. Pyrolysis yields bio-oil by rapidly heating the biomass in the absence of oxygen. Anaerobic digestion produces a renewable natural gas when organic matter is decomposed by bacteria in the absence of oxygen. Biomass has some limitations. There are also some problems in using biomass energy to produce electricity. Biomass crops need to occupy more lands. They are threat for food crops. Because electric motors can be 2-3 times more efficient than internal combustion engines, PV can result in 200-190 times more usable energy for vehicle transport than bioenergy [10]. Biomass energy also has some environmental effect.

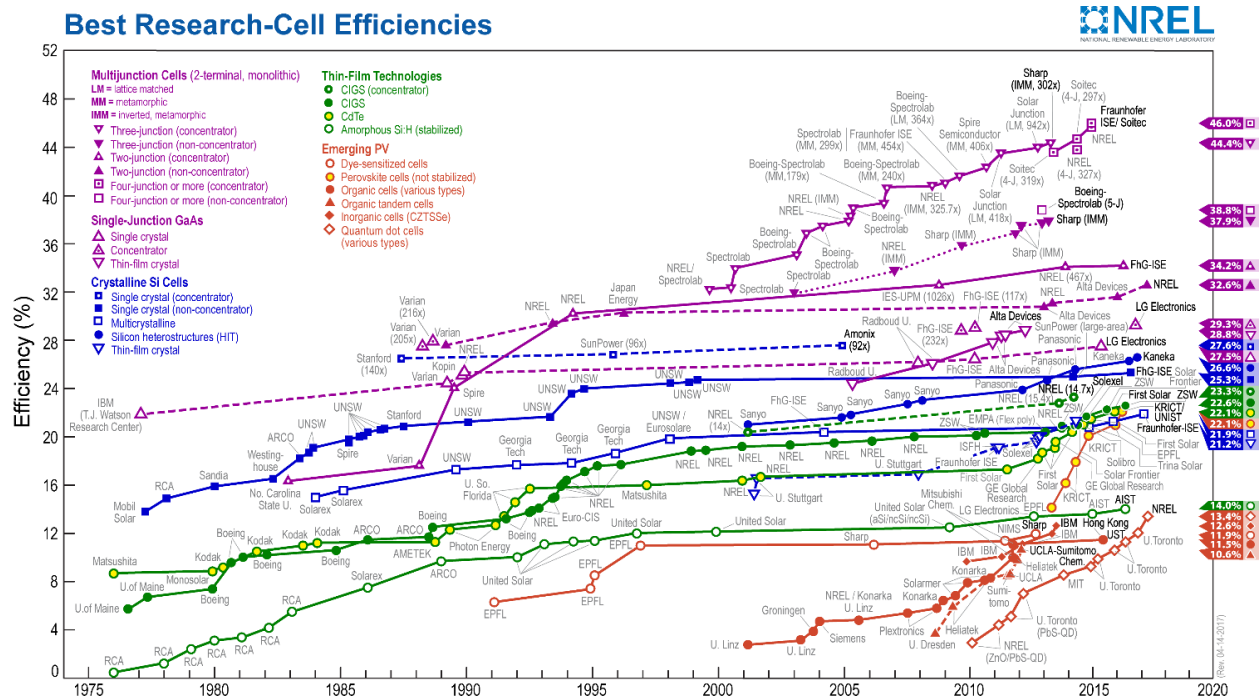
Geothermal energy is the heat from the Earth. It's clean and sustainable. Resources of geothermal energy range from the shallow ground to hot water and hot rock found a few miles beneath the Earth's surface, and down even deeper to the extremely high temperatures of molten rock called magma. Almost everywhere, the shallow ground or upper 10 feet of the Earth's surface and down even deeper to the extremely high temperature of molten rock called magma. Almost everywhere, the shallow ground or upper 10 feet of the Earth's surface maintains a nearly constant temperature between 50°F and 47°F. Geothermal heat pumps can tap into this resource to heat and cool buildings. A geothermal heat pump system consists of a heat pump, an air and cool buildings. A geothermal heat pump system consists of a heat pump, an air delivery system (ductwork), and a heat exchanger-a system of pipes buried in the shallow ground near the building. In the winter, the heat pump removes heat from the heat exchanger and pumps it into the indoor air delivery system. In the summer, the process is reversed, and the heat pump moves heat from the indoor air into the heat exchanger. The heat removed from the indoor air during the summer can also be used to provide a free source of hot water. Some geothermal power plants use the steam from a reservoir to power a turbine/generator, while others use the hot water to boil a working fluid that vaporizes and then turns a turbine. Hot water near the surface of earth can be used directly for heat. But, all areas are not suitable for geothermal energy. It can't be the main source of energy in the future.

Moreover, tidal and wave energy of the ocean can't be the sound alternative of energy crisis in the future because the electricity produced from these sources is not sufficient and there is also transformation problem of the electricity.

Moreover, tidal and wave energy of the ocean can't be sound alternative of energy crisis in the future because the electricity produced from these sources is not sufficient and there is also transformation problem of the electricity.

1.3 Motivation of this work

As a source of energy, solar energy is free, inexhaustible, accessible, non-hazardous unlimited and available everywhere in this world. The sun is a fusion reactor that has been operation maintenance free for four and a half billion years, and will continue to do so for another three and a half billion years. Every day it provides more energy than mankind consumes in one year in the form of fossil fuels. The utilization of those renewable resources is a chance to meet the demand for energy that is constantly rising and will continue to rise due to increasing population and modernization. So the best alternative to this energy crisis might be solar cells have limited its use. Thus, increasing efficiency and decreasing cost of solar cell is the major challenge to the researchers. Perovskite solar cell is a recently invented, it was first used in solar cell is increasing rapidly. From 2009 to 2016 its efficiency has been achieved by 22.1% [NREL]. So, there is a great hope for high performance for Perovskite solar cell [11]



Efficiency chart from NREL

Fig.1.5 best research cell efficiency

1.4 Thesis Objectives

In this thesis, a through literature review on Perovskite solar cell has been carried out. A numerical modeling and simulation of the performance of Perovskite solar cell has been carried out using wxAMPS device simulation program to study the cell performance (efficiency, V_{oc} , J_{sc} , and Fill factor) on material parameters. The simulation result suggest that the thickness of absorber, ETM, HTM, Dopant and acceptor concentration and operating temperature influence the cell performance.

The main objectives of the project are

1. To Study the Literature of Perovskite solar cell.
2. Design and simulate a Perovskite solar cell.
3. To enhance the efficiency of the cell through parameter optimization.

Chapter 2

Literature Review

Introduction

The development and prolongation of any society depends mainly on the safe and reliable supply of energy. Now the energy supply depends mainly on the fossil fuel such as coal, oil, natural gas etc. But the sources are limited and they will be running out one day. Also they emit greenhouse gases and cause global warming by emitting greenhouse gases. To solve these problems renewable energy could be the sound alternative. Renewable energy resources exist over wide geographical areas, in contrast to other energy sources, which are concentrated in a limited number of countries. Rapid deployment of renewable energy and energy efficiency is resulting in significant energy security, climate change mitigation, and economic benefits [12]. The results of a recent review of the literature [13] concluded that as greenhouse gas (GHG) emitters begin to be held liable for damages resulting from GHG emissions resulting in climate change, a high value for liability mitigation would provide powerful incentives for development of renewable energy technologies. The sources of renewable energy are solar, wind, hydro, biogas, geothermal, tidal, wave energy etc. Solar energy is the best alternative of the energy crisis problem because as a source of energy, solar energy is free, inexhaustible, accessible, non-hazardous, unlimited and available everywhere in this world.

2.1 Solar energy

Solar energy radiant light and heat from the Sun that is harnessed using a range of ever-evolving technologies such as solar heating, photovoltaics, solar thermal energy, solar architecture, molten salt power plants and artificial photosynthesis etc. It is an important source of renewable energy and its technologies are broadly characterized as passive solar or active solar depending on how they capture and distribute solar energy or convert it into solar power. Active solar techniques include the use of photovoltaic system, concentrated solar power and solar water heating to harness the energy. Passive solar techniques include orienting a building to the Sun, selecting materials with favorable thermal mass or light-dispersing properties, and designing spaces that naturally circulate air. The large magnitude of solar energy available makes it highly appealing

source of electricity. The United Nations Development program in its 2000 World Energy Assessment found that the annual potential of solar energy was 1255-49837 exajoules (EJ). This is several times larger than the total world energy consumption, which was 4451.8 EJ in 2012 [14, 15]

The radiation spectrum of the Sun can be approximated by a black-body with a temperature of approximately 4700k and can therefore be well described with Plank’s radiation law. The intensity and spectral distribution that arrives on the Earth’s surface is significantly altered due to atmospheric scattering and absorption. The radiant powers per unit are is strongly dependent on the path length of Sun’s rays through the Earth’s atmosphere. The term air mass intensity (AM) is often used to denote the ratio of optical path to a normal path at sea level on cloudless day.

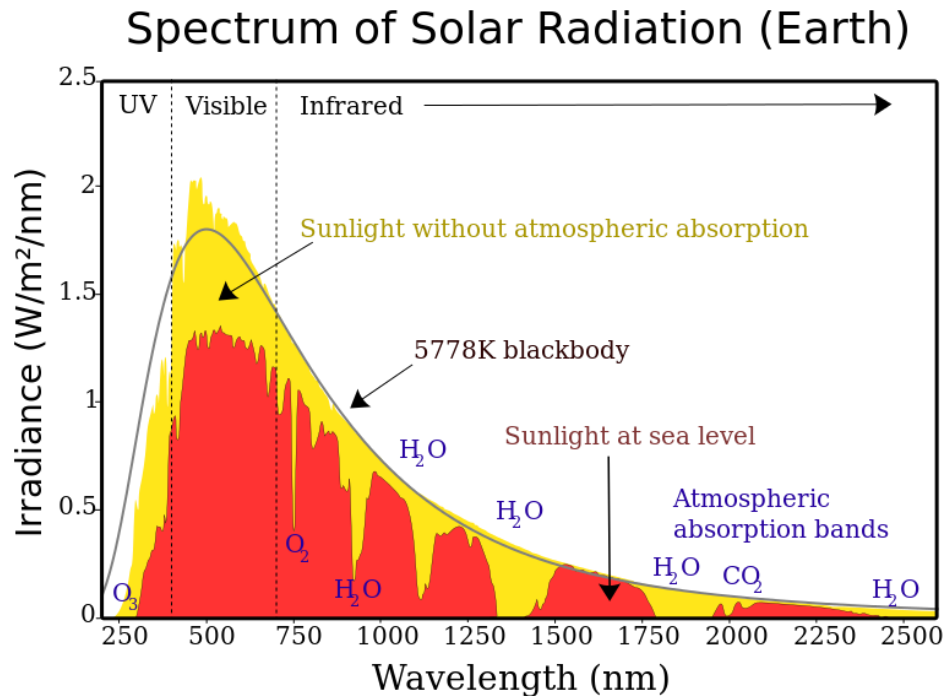


Fig. 2.1: Spectra irradiance vs wavelength [16]

2.1.1 Concentrated solar power and solar photovoltaics

Solar power is the conversion of sunlight into electricity, either directly using photovoltaics (PV), or indirectly using concentrated solar power. Concentrated solar power systems use lenses or mirrors and tracking systems to focus a large area of sunlight into a small beam, Photovoltaic cells convert light into current using photovoltaic effect.

A photovoltaic system, also solar PV power system, or PV system, is a power system designed to supply usable solar power by means of photovoltaics. It consists of an arrangement of several components, including solar panels to absorb and convert sunlight into electricity, a solar inverter to change the electric current from DC to AC, as well as mounting, cabling and other electrical accessories to set up a working system. It may also use a solar tracking system to improve the system's overall performance and include an integrated battery solution, as prices for storage devices are expected to decline. Strictly speaking, a solar array only encompasses the ensemble of solar panels, the visible part of the PV system, and does not include all the other hardware, often summarized as balance of system (BOS). Moreover, PV systems convert light directly into electricity.

2.1.2 Worldwide growth of PV

Worldwide growth of photovoltaics has been fitting and exponential curve for more than two decades. During this period of time, photovoltaics (PV), also known as solar PV, has evolved from a pure niche market of small scale applications towards becoming a mainstreams electricity source. When solar PV systems were first recognized as a promising renewable energy technology, programs, such as feed-in tariffs, were implemented by a number of governments in order to provide economic incentives for investments. For several years, growth was mainly driven by Japan and pioneering European countries. As a consequence, cost of solar declined significantly due to improvements in technology and economies of scale, even more so when production of solar cells and modules started to ramp up in China [19]. Since then, Deployment of photovoltaics is gaining momentum on a worldwide scale, particularly in Asia but also in North America and other regions, where solar PV is now increasingly competing with conventional energy sources as grid parity has already been reached in about 19 country [20].

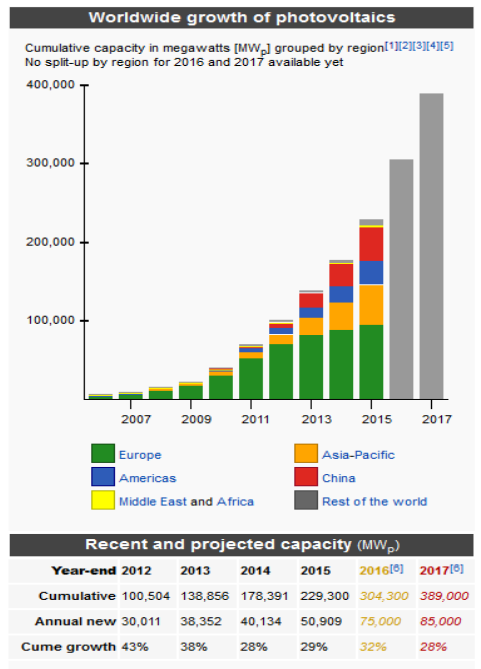


Fig 2.2 shows worldwide growth of PV technology from 2000 to 2017[18]

Historically, the United States had been the leader of installed photovoltaic for many years, and its total capacity mounted to 77 megawatts in 1996 more than any other country at that time. Then, Japan stayed ahead as the world's leader of produced solar electricity until 2005, when Germany took the lead. The country is currently approaching the 40,000 megawatt mark. China is expected to continue its rapid growth and to triple its PV capacity to 34,000 megawatt by 2017 [21, 22]. In 2015, China became world's largest producer of photovoltaic power [23, 14, and 25]. By the end of 2015, cumulative photovoltaic capacity reached at least 227 gigawatts (GW), sufficient to supply 1 percent of global electricity demands. Solar now contributes 8%, 7.4% and 7.1 % to the respective annual domestic consumption in Italy, Greece and Germany [26]. For 2016 worldwide deployment of 77GW is being forecasted, and installed capacity is projected to more than double or even triple beyond 500GW between now and 2020 [27]. By 2050, solar powers us anticipated to become world's largest source of electricity, with solar photovoltaic and concentrated solar power contributing 16 and 11% respectively. This will require PV capacity to grow to 4,470GW, of which more than half is forecasted to be deployed in China and India [28]

2.2 Solar cells:

Solar cells or solar PV modules are solid state semiconductor devices with no moving parts those convert sunlight directly into electricity. Solar cells usually called photovoltaic which means conversion of light or photon into electricity. It was first discovered by Becquerel in 1839 by illuminating silver chloride in an acidic solution and measuring current [28]. The efficiency of the first solar cell was 6% in 1883. Physicsts at Bell Labotratories discovered that silicon is more efficient than selenium, creating the first practical solar cell and that was 6% efficient [28]. After years of experiments to improve the efficiency and commercialization of solar power, solar energy gained support when the government used it to power space exploration equipment. The first solar-powered satellite, Vanguard1 has traveled more than 197,000 revolutions around Earth in the 50 years it has been in orbit. This application paved the way for more research to decrease costs and increase production [28]. In 1994, the National Renewable Energy Laboratory developed a new solar cell from gallium indium phosphide and gallium arsenide that exceeded 19% conversion efficiency. By the end of the century, the laboratory created thin-film solar cells that converted 32% of the sun light it collected into usable energy [28]. DIY solar panels started hitting the market in 2005 and have become more prevalent with each New Year.

2.2.1 Working principle of solar cells:

In order to design a solar cells and realize the role of different components we must know the working principle of solar cell. The basic steps undertaken in solar cell are as follows-

Absorption of incident light by an absorber layer i.e. interaction between photons and an absorber to create electron-hole pairs. So, an electron can jump to the conduction band from the valance band.

The separation of charge carriers of opposite types and to move in opposite direction toward the anode and cathode.

The separate extraction of these carriers to and external circuit via contacts where energetic electrode leaves the electrode leaves the electrode, does something useful in the load, hereby loose energy and finally returns back to the initial position through anther electrode.

At the end of the round trip, the electron recombines with a hole so that the absorber returns back to the ground state and ready to absorb another photon for next trip.

A solar cell is a sandwich of n-type silicon (blue) and p-type silicon (red). It generates electricity by using sunlight to make electrons hop across the junction between the different flavors of silicon:

1. When sunlight shines on the cell, photons (light particles) bombard the upper surface.
2. The photons (yellow blobs) carry their energy down through the cell.
3. The photons give up their energy to electrons (green blobs) in the lower, p-type layer.
4. The electrons use this energy to jump across the barrier into the upper, n-type layer and escape out into the circuit.
5. Flowing around the circuit, the electrons make the lamp light up.

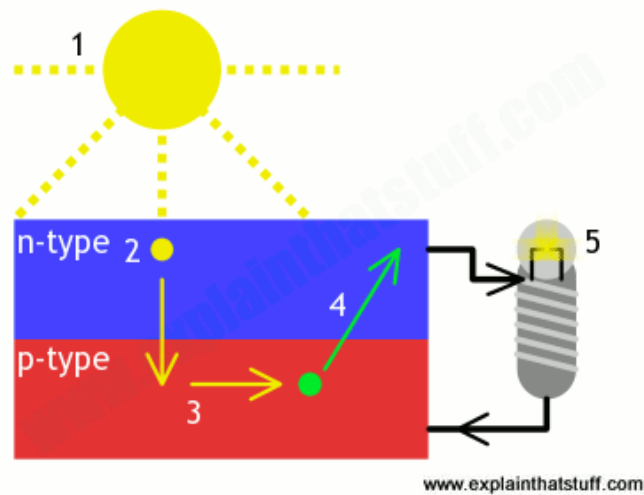


Fig:2.3 Working principle of solar cell [19]

2.2.2 Thin film solar cell

A thin-film solar cell is a second generation solar cell that is made by depositing one or more thin layers, or thin film (TF) of photovoltaic material on a substrate, such as glass, plastic or metal. Thin-film solar cells are commercially used in several technologies, including cadmium

telluride (CdTe), copper indium gallium diselenide (CIGS), and amorphous thin-film silicon (a-Si, TF-Si).

Film thickness varies from a few nanometers (nm) to tens of micrometers (μm), much thinner than thin-film's rival technology, the conventional, first-generation crystalline silicon solar cell (c-Si), that uses wafers of up to 200 μm . This allows thin film cells to be flexible, and lower in weight. It is used in building integrated photovoltaic and as semi-transparent, photovoltaic glazing material that can be laminated onto windows. Other commercial applications use rigid thin film solar panels (sandwiched between two panes of glass) in some of the world's largest photovoltaic power stations.

Thin-film technology has always been cheaper but less efficient than conventional c-Si technology. However, it has significantly improved over the years. The lab cell efficiency for CdTe and CIGS is now beyond 21 percent, outperforming multi-crystalline silicon, the dominant material currently used in most solar PV systems. Accelerated life testing of thin film modules under laboratory conditions measured a somewhat faster degradation compared to conventional PV, while a lifetime of 20 years or more is generally expected.^[2] Despite these enhancements, market-share of thin-film never reached more than 20 percent in the last two decades and has been declining in recent years to about 9 percent of worldwide photovoltaic installations in 2013.

Other thin-film technologies that are still in an early stage of ongoing research or with limited commercial availability are often classified as emerging or third generation photovoltaic cells and include organic, dye-sensitized, and polymer solar cells, as well as quantum dot, copper zinc tin sulfide, nanocrystal, micromorph, and perovskite solar cells. [20]

Difference between conventional and Perovskite solar cell: The main difference between the conventional solar cell and perovskite solar cell is that there is an intrinsic layer in the perovskite solar cell between the n-type and p type material whereas in conventional solar cell only p type and n type material forms the solar cell. In perovskite solar cell, the perovskite layer acts as an intrinsic layer and it is the absorber layer of the solar cell. In perovskite solar cell more photons are absorbed in the absorber layer and more electron hole pair is created. The structure of conventional and perovskite solar cell is given below-

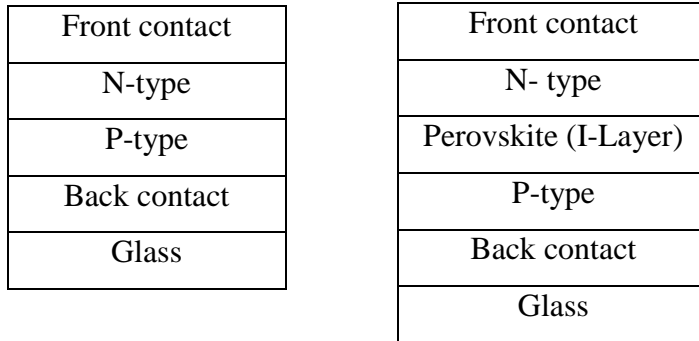


Fig: 2.4 Structure of conventional (left) and Perovskite (right) solar cell

2.3 Perovskite

Perovskite is a recently invented material that is used in solar cell since 2009 and shows a trend of rapidly increasing efficiency. A perovskite is any material with the same type of crystal structure as calcium titanium oxide, known as Perovskite structure, or $A^{2+}B^{4+}X_{2-3}$ with the oxygen in the face centers [41]. Perovskites take their name from the mineral, which was first discovered in the Ural Mountains of Russia by Gustav Rose in 1839 and is named after Russian mineralogist L.A. Perovskite (1792-1846).



Fig. 2.5: Perovskite mineral [21]

It can be found in nature in the form of such minerals, and then they are processed to use them in solar cells.

2.3.1 Structural Properties

The general chemical formula for perovskite compounds is ABX_3 , where 'A' and 'B' are two cations of very different sizes, and X is an anion that bonds to both. The 'A' atoms are larger than the 'B' atoms. The ideal cubic-symmetry structure has the B cation in 6-fold coordination, surrounded by an octahedron of anions, and the A cation in 12-fold cuboctahedral coordination. The relative ion size requirements for stability of the cubic structure are quite stringent, so slight buckling and distortion can produce several lower-symmetry distorted versions, in which the coordination numbers of A cations, B, cations or both are reduced. Fig 2.6 is the 3D crystal structure of perovskite.

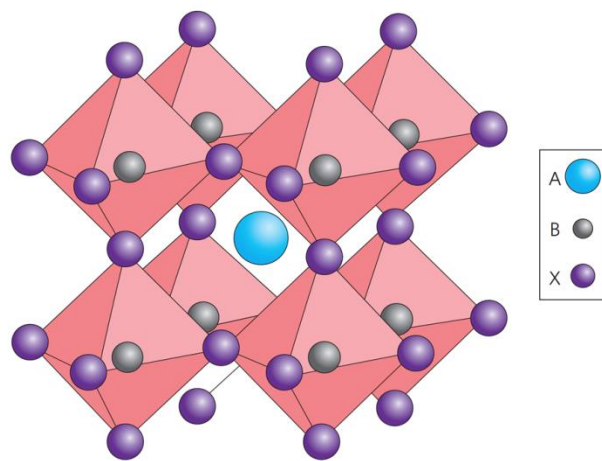


Fig 2.6: 3D structure of Perovskite [22]

Although the most common Perovskite compounds contain oxygen, there are a few perovskite compounds that form without oxygen. Instead of oxygen there are some other atoms such as halides (X).

They are two types of Perovskite, these are

- a) Inorganic oxide Perovskite
- b) Halide Perovskite

We are concerned to use organo metal halide Perovskite. In the case of perovskite Solar cells, the most efficient devices so far have been produced with the following combination of materials in the usual Perovskite form ABX_3 :

- A = An organic cation - methylammonium (CH_3NH_3)⁺
- B = A big inorganic cation - usually lead(II) (Pb^{2+})
- X_3 = A slightly smaller halogen anion – usually chloride (Cl^-) or iodide (I^-)

2.3.2 Electrical Properties:

Perovskite gets ionic and covalent, dual nature in electronic structures. Experimental/ research works show the different values of band gap for Perovskites. Band gap of Perovskite depends on the synthesizing process and the size of organic / inorganic cation, metallic ion and very less on halide ion. Band gap of $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{PbBr}_3$, $\text{CH}_3\text{NH}_3\text{PbCl}_3$, $\text{CH}_3\text{NH}_3\text{Pb}_3 - \text{xCl}$ are 1.49-1.26, 1.95, 2.46 and 1.21 eV respectively [23, 224], whereas mostly used band gap for $\text{CH}_3\text{NH}_3\text{PbI}_3$ 1.5eV [46]

2.3.3 Optical properties:

Absorber layer is a very important element in any solar cell to achieve a good performance. So, optical absorption strength is a crucial factor of the materials. Perovskite is a direct band gap material and hence it has high optical absorption strength and wider range to absorb sufficient solar energy to achieve high value of power conversion efficiency.

In solar cell Perovskite works as an intrinsic layer. So, in Perovskite solar cell, p-i-n junction is formed. It works as the same way as p-n solar cell except that the depletion layer become wider because of intrinsic layer. In the Perovskite solar cell the intrinsic region i.e. Perovskite layer works as light absorber

As the cell has wider depletion layer, it occupies more area for light absorption. Perovskite has high absorption coefficient. The absorption coefficient of various solar cell material for different wavelength is compared in Fig 2.7

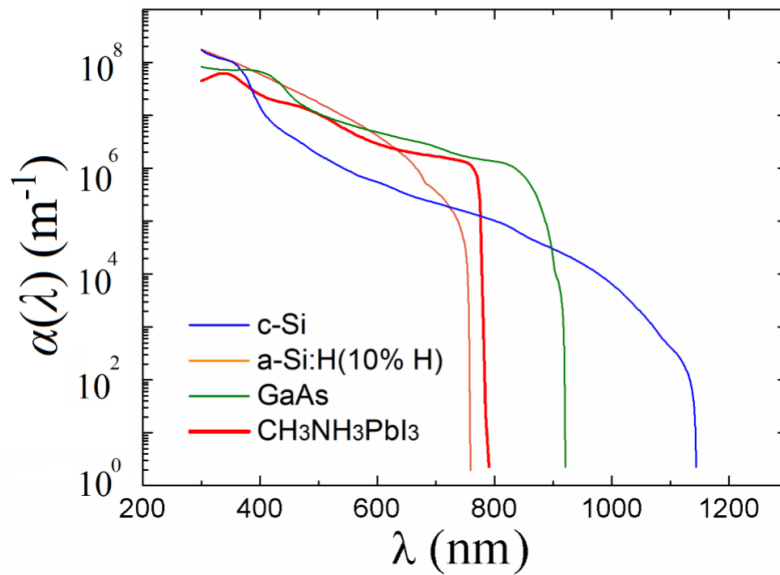


Fig: 2.7 Absorption coefficient vs wavelength for different solar cell materials [46]

From the fig. 2.7 it can be seen that in the visible wavelength the absorption coefficient of perovskite is higher. As in the visible range from 400 to 340nm the solar irradiance is highest [Fig. 2.1], so Perovskite can absorb more photons. So, Perovskite material is suitable for solar cell application.

The perovskite layer also acts as charge carrier between the n-type and p-type material. Normally, Perovskite is sandwiched between the n-type and p-type material. After absorbing photon from the sun's radiation electron-hole pair is generated. Perovskite carries electron to the n-type material and carries holes to the p-type materials.

2.3.4 Evaluation of Perovskite solar cell

Perovskite-based hybrid organic halide materials are not new materials and have been extensively studied because of their useful physical properties, electroluminescence, organic-like mobility, magnetic properties and conductivity [44-45]. Perovskite materials are used in solar cell since 2009. Scientists from the University of Yokohama firstly started working on perovskite in 2009. The first perovskite sensitized TiO₂ solar cell used liquid electrolytes based on iodide and bromide. The corresponding devices gave PCEs of 3.8% and 3.1%, respectively. Later, in 2012 when Henry Saith and Mike Lee from University of Oxford showed that efficiencies of almost

10% were achievable using the ‘sensitized’ TiO_2 architecture with the solid state hole transporter. In 2013 both the planar and sensitized architectures saw a number of developments. Burschka et al. demonstrated a deposition technique for the sensitized architecture exceeding 15% efficiency by a two-step solution processing [46]. Meanwhile, a simple planar-heterojunction(p-i-n) solar cell incorporating vapor- deposited perovskite as the absorbing layer has been developed, and demonstrated a solar-to-electrical PCE of 15.4%. A range of new deposition techniques and even higher efficiencies were reported in 2014. A reverse- scan efficiency of 19.3% was claimed by Yang Yang at UCLA using the planar thin- film architecture [46] In November 2014, a device by researchers from KRICT achieved a record with the certification of a non-stabilized efficiency of 20.1%. In December 2015, a new record efficiency of 21.0% was achieved by researchers at EPFL. The newest record of efficiency have been increased to 22.1% at KRICTIUNIST [35].

2.4 Fabrication of Perovskite solar cell

Perovskite solar cell can be fabricated by spin coating process. We need $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ precursor ink, Cu_2O , ZnO , ITO substrate, glove box, filters and so on. $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ can be produced by adding the $\text{CH}_3\text{NH}_3\text{I}$ and $\text{CH}_3\text{NH}_3\text{Br}$ with the PbI_2 / PbBr_2 .

The details fabrication process will be discussed in chapter 5

2.5 Solar cell physics

For the development of solar cell, basic device physics is very important. The basic physics behind junction, Junction formation, carrier generation, transportation and recombination are important to understand the basic principle of solar cells. Here, the basic physics of solar cell are discussed.

2.5.1 Photovoltaic effect

Photovoltaic effect is the creation of potential barrier between the n-type and p-type material. Photovoltaic effect is defined by the generation of charge carriers by the absorption of photons in the materials that forms the junction Photovoltaic effect is shown in Fig. 2.8

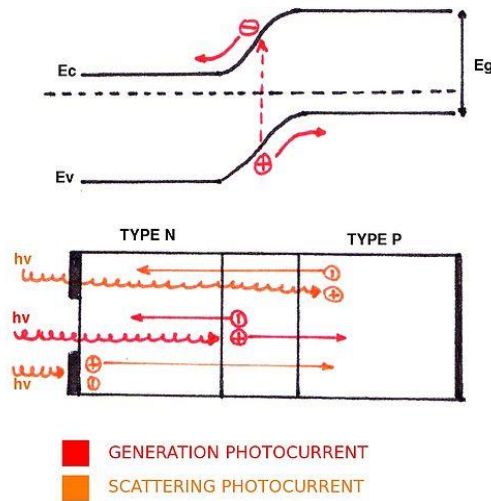


Fig 2.8 Photovoltaic effect

Absorption of photon in a material means that its energy is used to excite an electron from an lower energy level to a higher energy level. Photon can only be absorbed if the band gap energy of the materials equals to photon energy, if photon-energy is higher than the band gap energy then the extra energy will be lost as heat.

2.5.2 Energy band gap

The band gap generally refers to the energy difference (in electronVolts) between the top of the valence band and the bottom of the conduction band in insulators and semiconductors. It is the energy required to promote a valence electron bound to an atom to become a conduction electron, which is free to move within the crystal lattice and serve as a charge carrier to conduct electric current. Thus, the band gap-energy (E_g) is the difference between the bottom of the conduction band and the top of the valence band ($E_c - E_v$) Fig 2.9 shows the band diagram of metal, semiconductor and insulator.

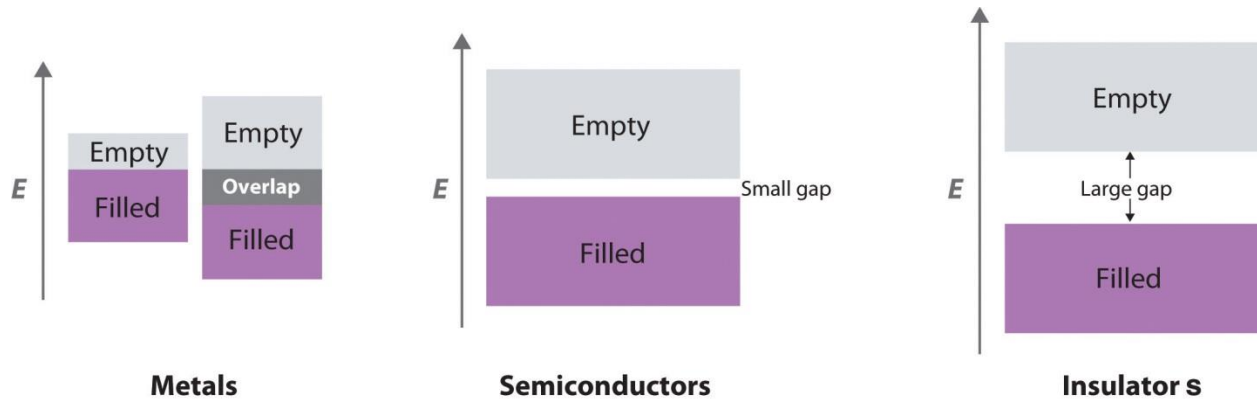


Fig 2.9: Band diagram of metal, semiconductor and insulator [25]

In the metal, the valence and conduction band may overlap in the equilibrium interionic distance. The band gaps of semiconductor are in the order of I-V. Insulator has larger band gap than semiconductor.

2.5.3 Absorbance and absorption coefficient

When an absorbing material of thickness d is being illuminated by sunlight of wavelength and intensity $I(\lambda)$, some light is reflected (R), some is absorbed (A) and remaining is transmitted (T) through the material. Now absorbance [$A_{\text{abs}}(\lambda)$] and absorption coefficient [$\alpha(\lambda)$] can be defined as [43]

$$A_{\text{abs}}(\lambda) = -\log_{10} [T(\lambda) / I(\lambda) - R(\lambda)]$$

$$\alpha(\lambda) = A_{\text{abs}}(\lambda) / d$$

The absorption coefficient determines how far into a material light of a particular wavelength can penetrate before it is absorbed. In a material with a low absorption coefficient, light is only poorly absorbed, and if the material is thin enough, it will appear transparent to that wavelength. The absorption coefficient depends on the material and also on the length of light which is being absorbed.

Semiconductor materials have a sharp edge in their absorption coefficient below the band gap electron into the conduction band does not have sufficient energy to excite a conduction band from the valence band consequently this light is not absorbed.

The absorption coefficient, α , is related to the extinction coefficient k , by the following formula [21]

$$\alpha = \frac{4\pi k}{\lambda}$$

Where λ is the wavelength, λ is in nm. Fig 2.10 shows the relationship between absorption coefficient and wavelength of light

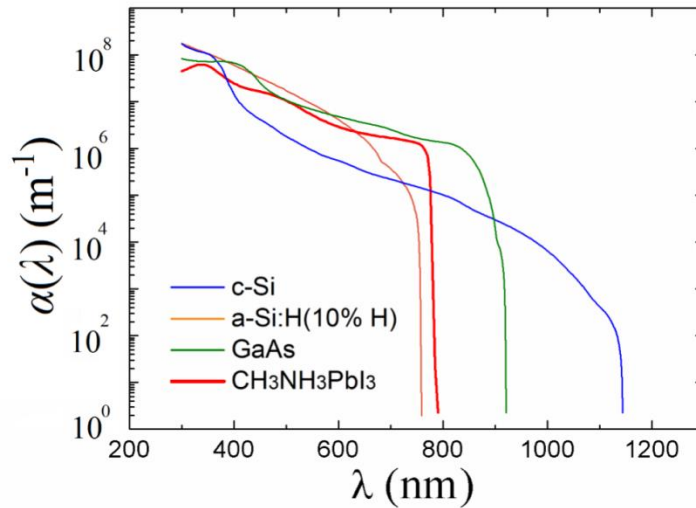


Fig 2.10 Absorption coefficient versus wavelength graph

The above graph shows that even for those photons which have energy above the band gap the absorption coefficient is not constant, but still depends strongly on wavelength. The probability of absorbing a photon depends on the likelihood of having a photon and an electron interact in such a way as to move from one energy band to another. For photons which have an energy very close to absorption to that of the band gap, the probability is relatively low since only those electrons directly at the valence band edge can interact with the photon to cause absorption. As the photon energy increases, not just the electrons already having energy close to that of the band gap can interact with the photon. Therefore, a larger number of electrons can interact with the photon and result in the photon being absorbed.

2.5.4 Density of states

In solid-state and condensed matter physics, the density of states (Dos) of a system describes the number of states per interval of energy at each energy level that are available to be occupied. Unlike isolated systems, like atoms or molecules in the gas phase, the density distributions are not discrete like a spectral density but continuous. A high DOS at a specific energy level means that there are many states available for occupation. A Dos of zero means that no states can be occupied at that energy level. In general, a DOS is an average over the space and time domains occupied by the system. Local variations, most often due to distortions of the original system, are often called local density of states (LDOS). If the Dos of an undisturbed system is zero, the LDOS in the conduction band (N_c) and effective densities of states are temperature-dependent material properties which are given by formulae [58]

$$N_V = \frac{m_p^* \sqrt{2}}{\pi^2 h^3} \sqrt{(E - E_V)}$$
$$N_C = \frac{(m_n^*) \sqrt{2}}{\pi^2 h^3} \sqrt{(E - E_C)}$$

Where m_p^* and m_n^* are effective mass of hole and electron, E_V and E_C are energy levels at steady state, valence band edge and conduction band edge respectively.

2.5.5 Fermi function

How many of the states at the energy E will be filled with an electron is defined by the

Following equation-

$$f(E) = \frac{1}{1 + e^{(E - E_F)/KT}}$$

$f(E)$ under equilibrium conditions, the probability that an available state at an energy E will be occupied by an electron.

$1 - f(E)$, under equilibrium conditions, the probability that an available state at an energy E will not be occupied by an electron.

2.46 Carrier concentration

Semiconductor material which has not had impurities added to it in order to change the carrier concentrations is called intrinsic material. The intrinsic carrier concentration is the number of electrons in the conduction band or the number of holes in the valence band in intrinsic material. In thermal equilibrium, number of free electrons and holes charge densities, n and p respectively are given by-

$$n = N_c \exp\left(\frac{E_F - E_C}{kT_n}\right) = N_o \exp\left(\frac{V_n}{kT_n}\right)$$

$$p = N_v \exp\left(\frac{E_V - E_F}{kT_p}\right) = N_o \exp\left(\frac{V_p}{kT_p}\right)$$

Where, E_F is Fermi level and V is built-in potential, k Boltzmann constant and T is spatially varying electron and hole temperature.

2.5.7 Doping

Doping intentionally introduces impurities in an extremely pure intrinsic semiconductor for the purpose of modulating its electrical properties. The impurities are dependent upon the type of semiconductor and the properties that it needs to have for its intended purpose. Lightly and moderately doped semiconductors are referred to as extrinsic semiconductors. A semiconductor doped to such high levels that it acts more like a conductor than a semiconductor is referred to as a degenerate semiconductor. Donor-type impurity atoms donate an electron to the conduction band and add electron to the conduction band without creating a hole in the valence band to create an n-type semiconductor. The acceptor atom accepts an electron from the valence band and generates holes in the valence band without generating electron in the conduction band.

This type of semiconductor is p-type semiconductor; Fig. 2.11 shows the detailed energy

Band diagram of n-type and p-type semiconductor material.

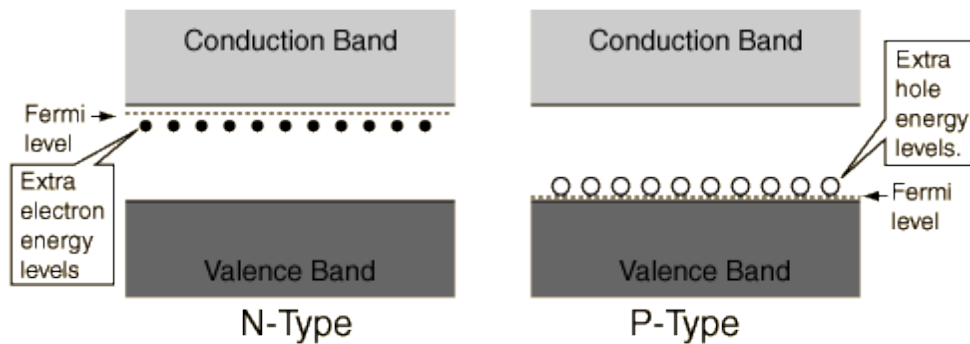


Fig 2 11: Energy band diagram of n-type and p-type semiconductor [26]

Doping influences the position of Fermi energy. When increasing concentration of electrons by increasing the concentration of donors. The Fermi energy will increase, thus Fermi energy will be closer to conduction band in n-type semiconductor. In the p-type semiconductor Fermi energy will be closer to valence band.

2.5.8 p-n junction

When one side of intrinsic semiconductor is doped with acceptor i.e., one side is made p-type by doping with n-type material, a p-n junction diode is formed. This is a two-terminal device. p-n junction can be step graded or linearly graded. In step graded the concentration of dopants both, on n side and in p side are constant up to the junction. But in linearly graded junction, the doping concentration varies almost linearly with the distance from the junction [28]. When the p-n diode is in unbiased condition that no voltage is applied across it, electrons will diffuse through the junction to p side and holes will diffuse through the junction to n-side and they combine with each other. The acceptor atom near the p-side and donor atom near n-side are left unused. An electric field is generated by these uncovered charges. This opposes further diffusion of carriers so, no movement of region is known as space charge or depletion region.

2.5.8.1 p-n homo-junction

A homo-junction is a semiconductor interface that occurs between layers of similar semiconductor material, these materials have equal band gaps but typically have different doping. In most practical cases a homo-junction occurs at the interface between an n-type (donor doped) and p-type (acceptor doped semiconductor such as silicon, this called a p-n junction. So, if a p-n junction is fabricated in the same material is called p-n homo-junction. In a p-i-n junction, the internal electric field is increased by inserting an intrinsic layer between the n-type and p-type material. The intrinsic layer behaves like a capacitor and it stretches the electric field formed by the p-n junction across it. When a p-type and n-type material are brought together, a very large difference in electron concentration between n-type and p-type material causes a diffusion current to flow from the n-type material across the junction into the p-type material. Similarly, the difference in hole concentration causes a diffusion current of hole to flow from the p-type to n-type material. Due to this diffusion, the region close to the junction becomes completely depleted of mobile charge carriers, This gives rise to space charge. This region of the space charge is called the space charge region or depletion region. Fig 2.12 shows the depletion layer formation between p-type and n-type material

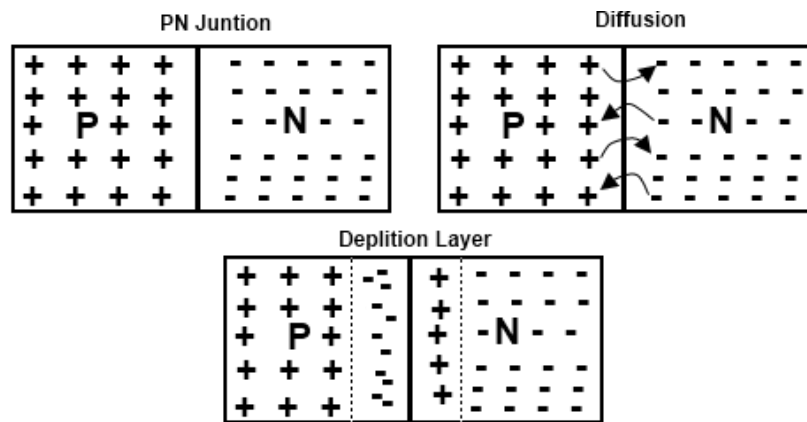


Fig 2 12: Depletion laver formation

The energy band diagram of p-n homojunction is shown in Fig. 2.13

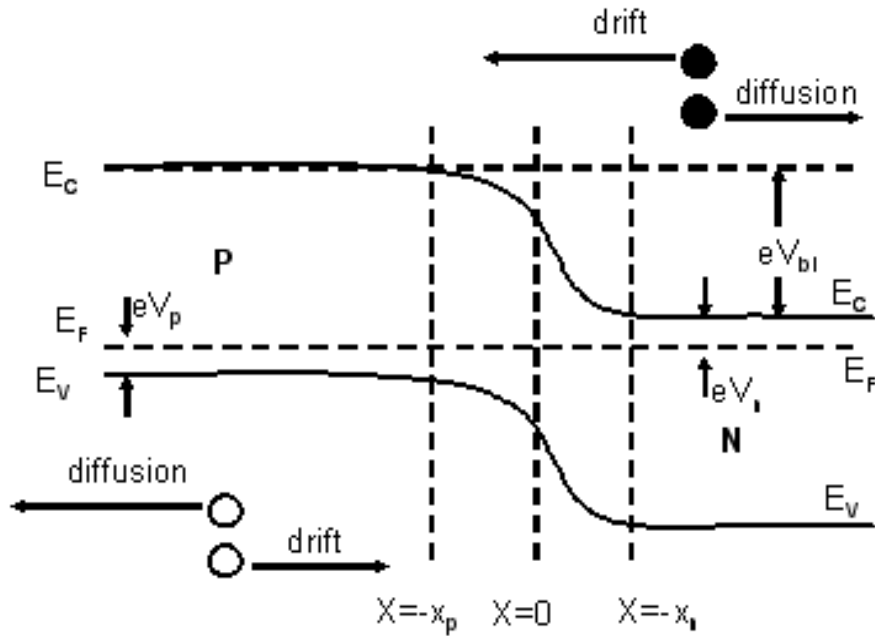


Fig 2.13: Energy band diagram of p-n homojunction

When p-type and n-type materials are interconnected, a band bending occurs in the space charge region. Accumulated positive and negative charge in the space charge region creates an electric field inside the p-n junction means that there is an electrostatic potential difference across the space charge region. Electric field adjacent to p-type material forces on holes and electric field adjacent to n-type material forces on electron. The electric field helps to collect and separate electrons and holes. Electrons are forced to move to the n doped side, and holes are forced to move to the p doped side. Fig 2.14 shows this phenomenon

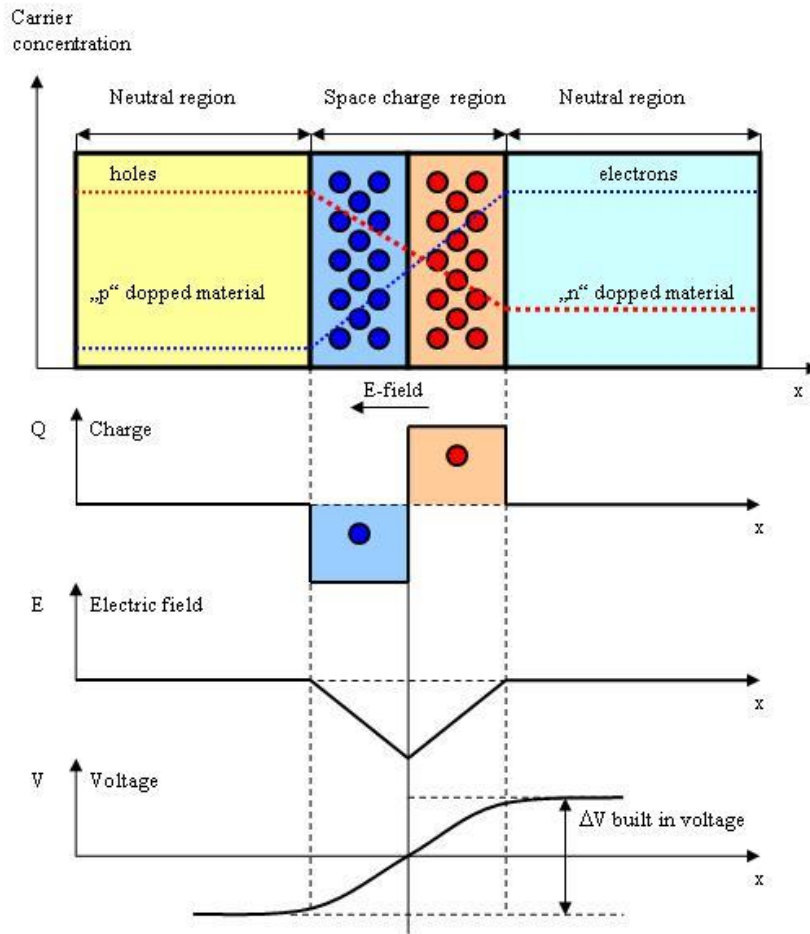


Fig. 2.14. Electric field in space charge region

When a p n junction is illuminated, additional electron hole pair is generated in the semiconductor. The concentration of minority carriers strongly increases. It leads to the flow of minority carriers across the depletion region. The electrostatic potential barrier across the junction is lowered by the open circuit voltage, v_{oc} .

2.5.8.2 p-n hetero-junction

A heterojunction is the interface that occurs between two layers or regions of dissimilar crystalline semiconductors. These semiconducting materials have unequal band gaps as opposed to a homojunction. It is often advantageous to engineer the electronic energy bands in many

solid-state device applications, including semiconductor lasers, solar cells and transistors (heterotransistors) to name a few. The combination of multiple heterojunctions together in a device is called heterostructure, although the two terms are commonly used interchangeably. The requirement that each material be a semiconductor with unequal band gaps is somewhat losses, especially on small length scales, where electronic properties depend on spatial properties. A more modern definition of heterojunction is the interface between any two solid-state materials, concluding crystalline and amorphous structures of metallic, insulating, fast ion conductor and semiconducting materials. Figer.2.15shows the band diagram of p-type and n-type material formed from different semiconductor material.



Fig. 2.15 band diagram of semiconductors

When a junction is formed between these two materials, the Fermi level on both sides of the junction should coincide in equilibrium. This leads to discontinuities in the conduction and valance band edges. They act as barriers to the mobile charge carriers. This acts as barriers to the mobile electron flow from the p side to the n side of the junction when it is illuminated. The energy band diagram of p-n heterojunction is shown in fig.2.16.

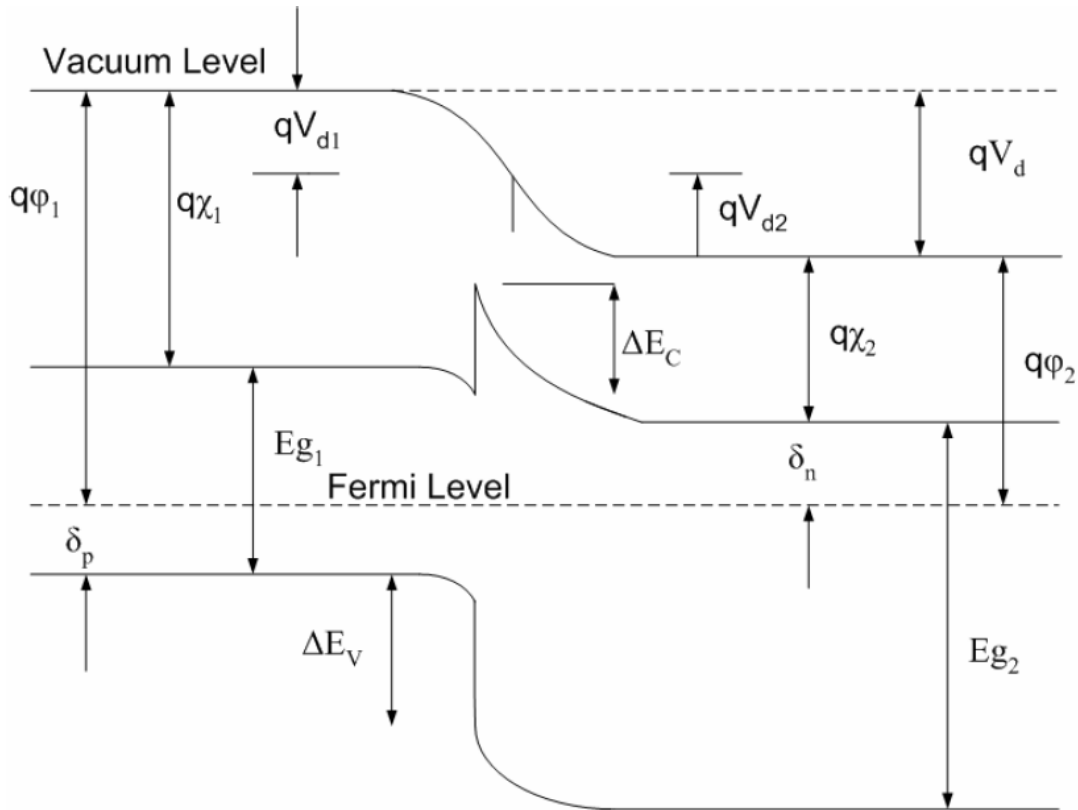


Fig. 2.16 energy band diagram of p-n heterojunction

A spike formed in the conduction band which is called the conduction band offset. The misalignment of the conduction bands is defined by the electron affinity of the both the materials.

2.5.8.3 Multi-junction

Multi-junction (MJ) solar cells are solar cell with multiple p-n junctions made of different semiconductor materials. Each material's p-n junction will produce electric current in response to different wavelengths of light. The use of multiple semiconducting materials allows the absorbance of a broader range of wavelengths, improving the cell's sunlight to electrical energy conversion efficiency.

Traditional single- junction cells have a maximum theoretical efficiency of 33.16% [28]. Theoretically, an infinite number of junctions would have a limiting efficiency of 86.8% under highly concentrated sunlight [29]. Currently, the best lab examples of traditional crystalline silicon solar cells have efficiencies between 20% and 25% while lab examples of multi-

junctioncells have demonstrated performance over 46% under concentrated sunlight [30].commercial examples of tandem cells are widely available at 19% under one- sun illumination [20] and improve to around 40% under concentrated sunlight. However, this efficiency is gained at the cost of increased complexity and manufacturing price. To date, their higher price and higher price-to-performance ratio have limited their use to special roles, notably in aerospace where their higher power- to- weight ratio is desirable. In terrestrial applications, these solar cells are emerging in concentrated photovoltaic (CPV), with a growing number of installations around the world. Tandem fabrication techniques have been used to improve the performance of existing design. In particular, the technique can be applied to lower cost thin-film solar cells using amorphous silicon, as opposed to conventional crystalline silicon, to produce a cell with about 10% efficiency that is lightweight and flexible. This approach has been used by several commercial vendors, but these products are currently limited to certain niche roles, like roofing materials.

2.5.8.4 Metal semiconductor junctions

Metal-semiconductor (M-S) junction is a type of junction in which a metal comes in close contact with a semiconductor material. It is the oldest practical semiconductor device (M-S) junctions can either be rectifying or non- rectifying. The rectifying metal semiconductor junction forms a Schottky barrier, making a device known as a Schottky diode, while the non- rectifying junction is called an ohmic contact.(In contrast, a rectifying semiconductor- semiconductor junction, the most common semiconductor device today , is known as a p-n junction.)

Metal-semiconductor junctions are crucial to the operation of all semiconductor devices. Usually an ohmic contact is desired, so that electrical charge can be conducted easily between the active region of a transistor and the external circuitry. Occasionally however a Schottky barrier is useful, as in Schottky diodes, Schottkytransistors, and Metal-semiconductor field effect transistors.

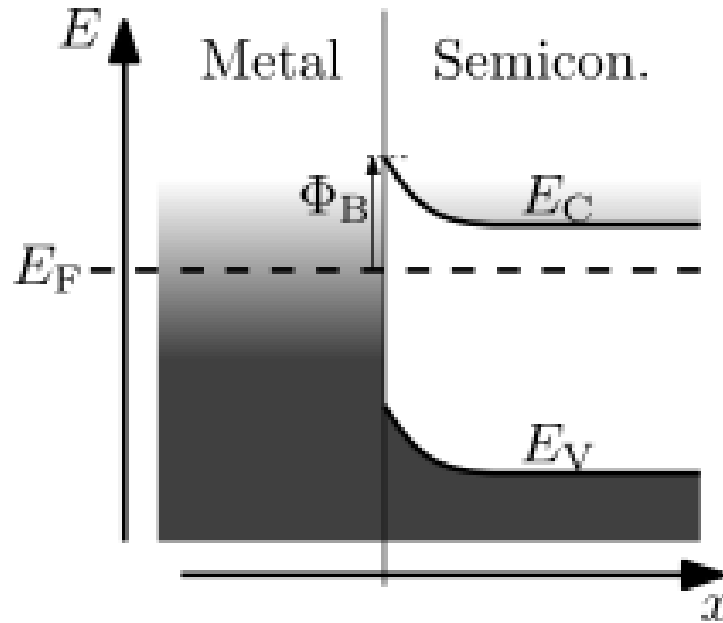


Fig. 2.17 band diagram of metal semiconductor junction

2.5.8.5 p-i-n junction

The p-i-n junction consists of three differently doped regions. As the name suggests there is an intrinsic or un-doped layer sandwiched between a p- and an n- doped region. Typically this kind of junction is fabricated from amorphous silicon with a band gap of about 1.8eV. The p-type and n-type region are typically heavily doped because they are used for ohmic contacts. The wide intrinsic region is in contrast to an ordinary p-n diode. The wide intrinsic region makes the p-i-n diode an inferior rectifier (one typical function of a diode), but it makes it suitable for attenuators, fast switches, photo detectors, and high voltage power electronics applications. A p-i-n diode operates under what is known as high-level injection. In other words, the intrinsic “i” region is flooded with charge carriers from the “p” and “n” regions. Its function can be likened to filling up a water bucket with a hole on the side. Once the water reaches the holes level it will begin to pour out. Similarly, the diode will conduct current once the flooded electrons and holes reach an equilibrium point, where the number of electrons is equal to the number of holes in the intrinsic region. When the diode is forward biased, the injected carrier concentration is typically several orders of magnitude higher than the intrinsic carrier concentration. Due to this high level injection, this in turn is due to the depletion process, the electric field extends deeply (almost the

entire length) into the region. This electric field helps in speeding up of the transport of charge carriers from the p to the n region, which results in faster operation of the diode, making it a suitable device for high frequency operations. The band diagram of pin junction is shown in Fig2.18

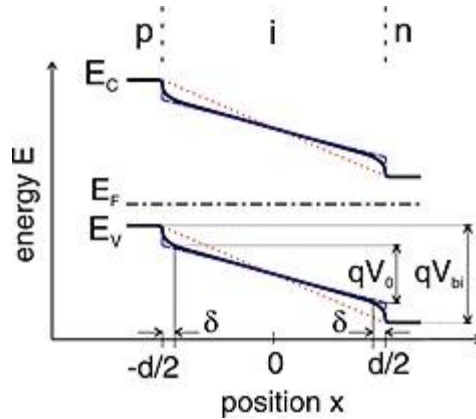


Fig.2.18 band diagram of p-i-n junction

A p-i-n diode obeys the standard diode equation for low frequency signals. At higher frequencies, the diode looks like an almost perfect (very linear, even for large signals) resistor. There is a lot of stored charge in the intrinsic region. At low frequencies, the charge can be removed and the diode turns off. At higher frequencies, there is not enough time to remove the charge, so the diode never turns off. The PIN diode has a poor reverse recovery time. The high-frequency resistance is inversely proportional to the DC bias current through the diode. A p-i-n diode, suitably biased, therefore acts as a variable resistor. This high-frequency resistance may vary over a wide range (from 0.1Ω to $10\text{ K}\Omega$ in some cases; the useful range is smaller, though). The wide intrinsic region also means the diode will have a low capacitance when reverse-biased. In a p-i-n diode, the depletion region exists almost completely within the intrinsic region. This depletion region is much larger than in a p-n diode, and almost constant-size, independent of the reverse bias applied to the diode. This increases the volume where electron-hole pairs can be generated by an incident photon. Some photo detector devices, such as p-i-n photodiodes and phototransistor (in which the base-collector junction is a p-i-n diode) use a p-i-n junction in their construction. In a Perovskite solar cell, Perovskite layer works as intrinsic layer and it is a p-i-n structure.

2.5.8.6 p-n junction diode characteristics

Lets a voltage V is applied across a p-n junction and total current I , flows through the junction. It is given as.

$$I=I_s[\exp(eV/\eta k_B T)-1]$$

Here, I_s = reverse saturation current

e = charge of electron

η =emission co-efficient

k_B = Boltzmann constant

T =temperature

The current voltage characteristics plot is given in Fig 2.23. The current voltage characteristics.

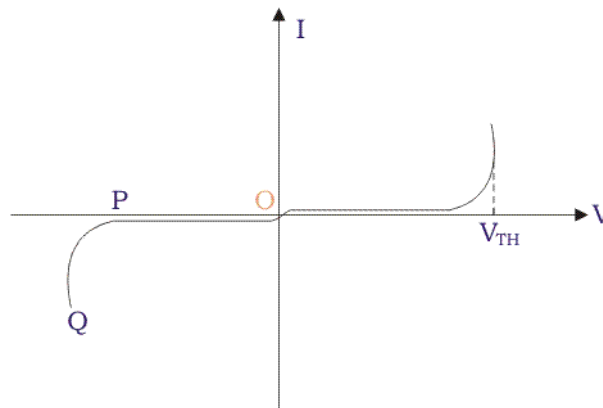


Fig. 2.19 p-n junction characteristic

When V is positive the junction is forward biased and when V is negative, the junction is reversing biased. When V is negative and less than V_{th} , the current is very small. But when V exceeds V_{th} , the current suddenly becomes very high. The voltage V_{th} , is known as threshold or cut in voltage. For Silicon diode V_{th} , = 0.6 V. At a reverse voltage corresponding to the point P , there is abrupt increment in reverse current. The PQ portion of the characteristics is known as breakdown region.

2.5.8.7 p-n junction diode equation

The voltage and current in ideal diode are given by the equation as below:

$$V_0 = \frac{KT}{q} \ln\left(\frac{N_A N_D}{N_i^2}\right)$$

$$I = I_0 \left[\exp\left(\frac{qV}{KT}\right) - 1 \right]$$

Where n_i is intrinsic carriers concentrations and I_0 is saturation current.

2.5.8.8 Solar Cell Equation

A Solar cell in the dark behaves like a p-n junction. If there is a positive voltage over the diode/pn-junction (+connected to the p-side of the junction), the current will increase exponentially as the voltage increases. If there is a negative voltage over the diode/pn-junction (-connected to the p-side of the junction), almost no current will flow, even when the voltage increases. Solar cell current in dark condition is-

$$I_D = I_0 \left[\exp(qv/KT) - 1 \right]$$

The solar cell under illumination, can be regarded as a current source (Where the amount of current is proportional to the intensity of the illumination), connected in parallel with a diode. The current generated by the illumination equals I_L and flows in the opposite direction of the diode (dark) current I_D .

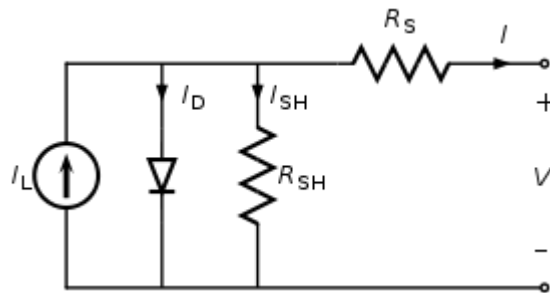


Fig 2.20 solar cell under illumination

Fig 2.21 shows the I-V characteristic curve of solar cell

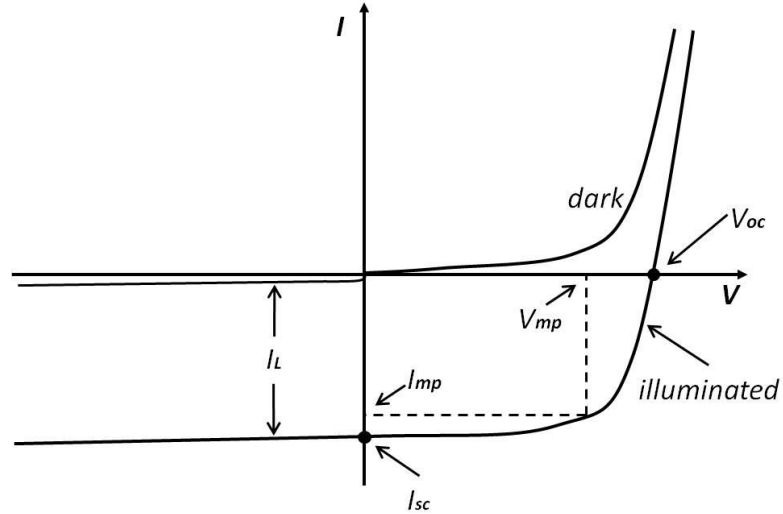


Fig. 2.21 I-V characteristic curve of solar cell

So, the equation of current becomes-

$$I_{total} = I_0 [\exp(qv/KT) - 1] - I_D$$

The equation of open circuit voltage and current density of solar cell are –

$$V_{oc} = \frac{nKT}{q} \ln\left(\frac{I_{sc}}{I_0} + 1\right)$$

$$J = J_0 \left[\exp\left(\frac{qT}{nKT}\right) - 1 \right] - J_{sc}$$

Where J_0 and J_{sc} are the saturation and short circuit current density respectively.

2.5.9 Electron and hole diffusion length

The diffusion length, L_d , of electrons or hole in a semiconductor is defined by the average distance the relevant charge moves in the semiconductor. It is influenced by the average distance the relevant charge moves in the semiconductor. It is influenced by the average distance the relevant charge moves in the semiconductor (for example, in photovoltaic cells) and recombination/extraction from the semiconductor. Diffusion implies movement of charge carriers directed by a concentration gradient. If the movement is due to an electric field, then the

“drift” is used. The diffusion coefficient (D) and the equivalent term in the presence of a field, mobility (μ), are related to each other by the Einstein relation-

$$D = \mu(Kt/q)$$

and

$$L_d = (D\tau)^{1/2}$$

Where τ is the charge lifetime from generating until recombination or extraction.

$$\text{Electron diffusion length } L_n = (D_n\tau_n)^{1/2}$$

$$\text{Hole diffusion length, } L_p = (D_p\tau_p)^{1/2}$$

2.5.10 Recombination

Shockley- Read-Hall (SRH), Radiative and Auger recombination are the possible Recombination mechanisms in solar cells [27], they are given as-

SRH recombination:

$$R^L = \frac{v\sigma_n\sigma_p N_T [np - n_i^2]}{\sigma_p [p + p_1] + \sigma_n [n + n_1]}$$

Radiative recombination:

$$R^R = \left[\frac{g_{th}^R}{n_i^2} \right] (pn - n_i^2)$$

Auger recombination:

$$R^A = \left[\frac{n - n_0}{\tau_n^A} \right]$$

$$R_n^A = \left[\frac{p-p_0}{\tau_n^A} \right]$$

Where σ_s are capture cross-sections for electrons and holes, v electron thermal velocity, N_T number of gap states per volume, n_i intrinsic number density, g_{th}^R gives the number of electrons in conduction band and holes in valence band generated per unit time per unit volume and τ_n^R & τ_p^R are electron and hole lifetimes.

2.5.11 Work function

The work function is the minimum thermodynamic work (i.e. energy) needed to remove an electron from a solid to appoint in the vacuum immediately outside the solid surface. Here “immediately” means that the final electron position is far from the surface on the atomic scale, but still too close to the solid to be influenced by ambient electric fields in the vacuum. The work function is not a characteristic of a bulk material, but rather a property of the surface of the material (depending on crystal face and contamination) [32].

In most of the cases work function of the front and back contacts are well defined. Otherwise, in flat band case the work function of contact (s) is calculated as follows [43]:

When contact is n-type-

$$\Phi_m = \chi + K_B T \ln \left(\frac{N_C}{N_D - N_A} \right)$$

When contact is p-type-

$$\Phi_m = \chi + E_g - K_B T \ln \left(\frac{N_C}{N_A - N_D} \right)$$

When contact is intrinsic-

$$\Phi_m = \chi + K_B T \ln \left(\frac{N_C}{n} \right)$$

Where ϕ_m is work function of metal/material, χ is electron affinity; K_B is Boltzmann constant is operating temperature, N_C is conduction band effective density of states, and N_A and N_D are shallow acceptor and donor dopant concentrations respectively.

2.5.12 Short Circuit Current

The short circuit current is the current through the solar cell when the voltage across the solar cell is zero (i.e., when the solar cell is short circuited). Usually written as I_{SC} , the short-circuit current is shown on the I-V curve in Fig 2.22. The short circuit current is due to the generation and collection of light-generated carriers. For an ideal solar cell at most moderate resistive loss mechanism, the short circuit current and the light generated current are identical. Therefore, the short circuit current is the largest current which may be drawn from the solar cell.

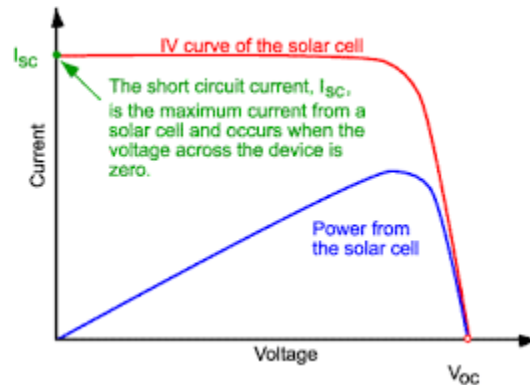


Fig. 2.22 I-V curve of solar cell

The maximum current that the solar cell deliver depend strongly on the optical properties of solar cell i.e. absorber layer and reflection. When comparing solar cells of the same material type, the most critical material parameter is the diffusion length and surface passivation. In a cell with perfectly passivated surface and uniform generation, the equation for the short-circuit current can be approximated as:

$$J_{sc} = qG(L_n + L_p)$$

Where G is the generation rate, and L_n and L_p are the electron and hole diffusion lengths respectively. Although this equation makes several assumptions which are not true for the conditions encountered in the most solar cells, the above equation nevertheless indicates that the short-circuit current depends strongly on the generation rate and the diffusion length.

2.5.13 Open circuit voltage

The Open circuit voltage, V_{OC} , is the maximum voltage available from a solar cell, and this occurs at zero current. The open-circuit voltage corresponds to the amount of forward bias on the solar cell due to the bias of the solar cell junction with the light-generated current. An equation for V_{oc} is found by setting the net current equal to zero in the solar cell equation to give:

$$V_{oc} = \frac{nKT}{q} \ln\left(\frac{I_L}{I_0} + 1\right)$$

Where I_L is the photo generated current, I_0 is the saturated current and k is the Boltzmann constant. The saturation current density depends on the recombination rate in the solar cell. V_{oc} is the measure of the amount of recombination in the device.

2.5.14 Fill Factor

Fill factor is the ratio of the product of the maximum voltage and current density to the product of the open circuit voltage and short circuit current density.

$$FF = \frac{V_{mp} J_{mp}}{V_{oc} J_{sc}}$$

2.5.15 Conversion Efficiency

Solar cell efficiency refers to the portion of energy in the form of sunlight that can be converted via photovoltaic into electricity. The fraction of incident power converted into useful electricity by the solar cells is termed into power conversion efficiency. It is given below:

$$\eta = \frac{P_{out}}{P_{in}} = \frac{FF V_{oc} J_{sc}}{P_{in}}$$

At room temperature and standard AM 1.5 illumination, $P_{in} = 100 \text{ mW/cm}^2$ so, then the efficiency = $V_{oc} J_{sc} \times FF$

2.5.16 Loss Mechanism

Different type of loss such as optical loss, collection loss, transmission loss. Are responsible for lower efficiency of solar cell.

2.5.16.1 Optical Losses

Optical losses chiefly affect the power from a solar cell by lowering the short circuit current. Optical losses consist of light which could have generated an electron-hole pair but does not, because the light is reflected from the front surface, or because it is not absorbed in the solar cell. For the most common semiconductor solar cells, the entire visible spectrum (350-780 nm) has enough energy to create electron-hole pairs and therefore all visible light would ideally be absorbed. Fig. 2.23 shows different types of optical losses.

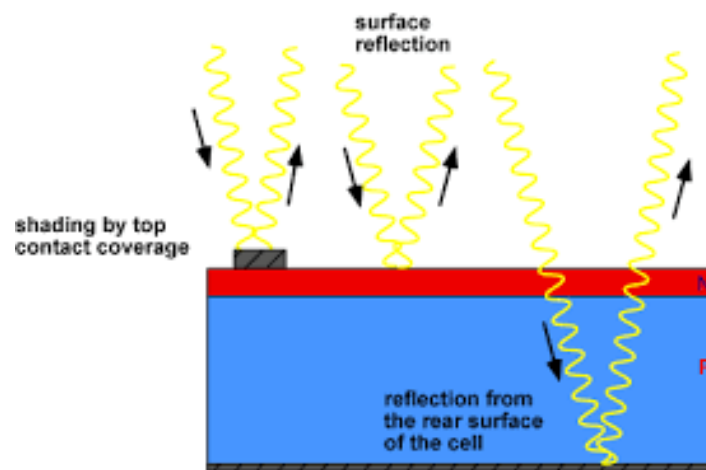


Fig. 2.23 Optical Losses

Optical losses caused by reflection, parasitic absorption, shading, incomplete absorption etc. A part of the incident light that can be converted into usable energy by solar cell is lost by reflection in the different interface in the solar cell. The layers different from the absorber layer is also a loss factor. Sometimes shading prevents light to enter all part of the solar cell.

2.5.16.2 Recombination losses

The entire photo generated carrier in a solar cell is not collected in electrode. Some carriers are subjected to recombination. Recombination losses effect both the current collection (and therefore the short circuit current) as well as the forward bias injection current (and therefore the open-circuit voltage). Recombination is frequently classified according to the region of the cell

in which it occurs. Typically, Recombination at the surface (surface recombination) or in the bulk of the solar cell (bulk recombination) are the main areas of Recombination. The depletion region is another area in which Recombination can occur (depletion region recombination).

2.5.16.3 Losses due to spectral mismatch

There are two principal losses that strongly reduce the energy conversion efficiency of today's solar cells. An important part of a solar cell is the absorber layer, in which the photons of the incident radiation are efficiently absorbed resulting in a creation of electron-hole pairs. The absorber layer of the solar cells is in most cases formed by a semiconductor material, which has its distinct optical properties characterized by the band gap energy, E_g , and the complex refractive index. In principle, only photons with energy higher than the band gap energy of the absorber generate electron-hole pairs. Since the electrons and holes tend to occupy energy levels at the bottom of the conduction band and the top of the valence band, respectively, the extra energy that the electron-hole pairs receive from the photons is released as heat into the semiconductor lattice in the thermalization process. Photons with energy lower than the band gap energy of the semiconductor absorber are in principle not absorbed and cannot generate electron-hole pairs. Therefore these photons are not involved in the energy conversion process. The non-absorption of photons carrying less energy than the semiconductor band gap and the excess energy of photons, larger than the band gap, are the two main losses in the energy conversion process using solar cells. Both of these losses are thus related to the spectral mismatch of the energy distribution of photons in the solar spectrum and the band gap of a semiconductor material

Chapter 3

Methodology

3.1 Introductions

The main important thing that needs to be done before simulation of a solar cell is to establish a model based on different verified parameter. Numerical designing is the first step for solar cell simulation. This chapter includes cell designing, characterization of different parameters of different layers and studying about different simulating software. There is much simulation software for simulating solar cell. They are AMPS (Analysis of Microelectronics and Photonic Structures) SCAPS (Solar Cells Capacitance Simulator), PC-ID, ISE-TCAD (DESSIS), ASA etc. for this work, wxAMPS is used.

3.2 Cell designing

For starting the simulation, the first task is to design a cell structure and it is very important task. It is necessary to characterize the whole cell according to the characterization of different layers. The values of the different parameters can be changed according to the allowable range those are obtained from material properties. The characteristics curve, energy band diagram, generation and recombination rate, electric field, quantum efficiency curve can be obtained after simulation. The open circuit voltage, V_{oc} , short circuit current density, J_{sc} , Fill Factor, FF and efficiency can be observed from the simulation result.

3.3 Simulation software

In the simulation software the simulation is processed by a set of mathematical equations. There are many software for simulating solar cell. There are AMPS-ID, wxAMPS, SCAPS, ASA, ISE-TCAD (DESSIS) etc.

3.3.1 AMPS-ID

AMPS is the abbreviation of Analysis of Microelectronics and Photonic Structures was written by S.Fonash and coworkers of Pennsylvania State University. It was engineered to be a general

and versatile computer simulation tool for the analysis of device Physics and for device design. This software is compatible with Windows 95 or higher with AMPS it is possible to work on several problems simultaneously, and each device (or case as it is called in AMPS) is shown in a separate window. Defining a new problem is an easy task, and it also provides a clean and intuitive user interface [33]. A single device can have up to 19 layers, each layer having its own set of parameters. All parameters (band-gap, effective density of states, mobility) are independent of temperature. An issue of AMPS is that wavelengths and corresponding absorption coefficients and spectrum intensities have to be entered manually. AMPS is slow in solving the problem comparing with other simulation programs. Therefore it does not encourage an interactive use of the program. The AMPS has the ability to solve several cases simultaneously. Once the results are calculated, they can be analyzed with the excellent built-in plotting facility. Simulations with different excitation parameters on a single device or simulations on different devices can be compared [33].

Advantages of AMPS-ID

- AMPS-ID has a good user interface and the plotting program is flexible.
- AMPS-ID software is provided with a well documented user manual.
- Very stable in general, but complex device may introduce some instabilities.
- Allow batch processing of simulation.
- Both band-to-band and Shockley-Read-Hole recombination.
- Provides a gap state model that allows capture cross sections to vary with energy.
- Gap state distributions whose properties vary with position.
- Mobility gaps that can differ from optical gaps.
- The ability to analyze device structures fabricated using single crystal polycrystalline or amorphous materials [33].

Limitations of AMPS-ID:

- Limited to 400 mesh points and 19 layers.
- No treatment of interface requires definition of “interfacial layers”.
- All information needs to be entered manually by hand.

- Only binary case file can be read in AMPS-ID, manipulation of text file is not possible [33].

3.3.2 SCAPS

This numerical simulation program is written and maintained at the University of Gen. it is designed as general polycrystalline thin-film device simulator and is mainly used for modeling CdTe and CIGS-based solar cells. The discussion is based on version 2.3 for the operating system windows. Up to seven layers can be added to the device and for each layer or contact all physical and electronic properties can be shown and altered inside a separate window. Simple models are used for the temperature dependence of the effective density of states and thermal velocity, other parameters such as the band gap and the mobility are independent of temperature. Recombination in deep bulk levels and their occupation is described by Shockley-Read-Hall (SRH) formalism [34]

SCAPS has among the studied simulation programs the largest number of electrical measurements that can be simulated. Each measurement can be calculated for light or dark condition and as a function of temperature. When solving the desired simulation, the energy band diagram and the charge and currents in the device are shown on screen for each intermediate bias voltage or wavelength. This intermediate solution can then be saved to a file. When the simulation is completed, the characteristics can be viewed and compared with characteristics from other simulation. This feature makes SCAPS a very interactive program [34].

Advantage of SCAPS:

- All input files are user accessible text file including spectral response and device definition file.
- Sophisticated treatment of interface recombination and interface trapping.
- Very fast and inclusion of series resistance, capacitance-voltage and capacitance frequency response.
- Loading and saving of all setting, start of SCAPS in a personalized configuration; a script language including a free user functions.
- Batch calculation is possible.

- Presentation of results and settings as a function of batch parameters.
- A built-in curve fitting capacity.
- A panel for the interpretation of admittance measurement.
- Optical property direct excitation with light is possible.
- Recombination mechanism: Band-to-band, Auger, SRH-type.
- Tunneling: intra band Tunneling, Tunneling to and fro from the from interface states.
- Almost all parameters can be graded [34].

Limitations of SCAPS:

- May be unstable when the device is far from ideal and secondary barrier.
- No batch processing, every model has to be performed by hand.
- Plotting is not flexible and of little use.
- May be unstable when the device is far from ideal.
- Interface is not user friendly, excess data input is required.

3.3.3 ISE-TCAD (DESSIS)

Integrated systems Engineering (ISE), recently acquired by synopsis Inc., offers a comprehensive simulation solution. The entire software Package is referred to as “ISF- TCAD” and licensed on a modular basis to the end user. At the heart of the device simulations is the code DESSIS, which is a multidimensional, electrothermal, mixed mode device and circuit simulator for one, two, and three dimensional semiconductor devices”. In ISE-TCAD, these functions are separated into different application, to name only the ones most relevant to this work.

GENESISe: the “host “of the application suite, manages project, and ties all other applications together by organizing data transfer between individual components.

MDRAW: Graphical drawing programs in which the user specifies geometry, material associations, and mesh details.

DESSIS: performs the calculation and supports many physical models specific to Si and 111-V semiconductors. Defect distributions, interface definitions, illumination spectrum, etc., are all input to this calculation.

Tecplot-ISE: plotting utility that allows two- and three-dimensional analysis of the results and the creation of cuts, contour plots, vector plots, etc.

Advantage of ISE-TCAD:

- Two dimensional'
- Extremely comprehensive and flexible.
- Excellent batch capabilities including distributed computing.
- Documentation can easily be understood.

Limitations of ISE-TCAD:

- Difficult to get started.
- Establishing a first model is difficult.
- No built-in support for solar cell application.
- Expensive [35].

3.3.4 PCID

This program is developed by Basore and coworkers but was originally written at Sandia National Labs and was developed at UNSW, Australia. As it is considered a standard for crystalline Si cells, it is widely spread in PV research community, and hence also used for thin-film cells, though it is not particularly designed for those cells. PCID has a very clean user interface and defining a new problem is simple. For each layer and contact in the device there is parameter list displayed on screen and, by clicking on a parameter, its value can be changed. There is a layer limitation in this program comparing with other programs; only five layers are allowed per device. For CdTe/CdS-based devices this number is almost certainly too low. The standard $j(V)$ and spectral response measurements, transients can be simulated. The results of the simulations can be viewed in a separate window and the data can easily be copied and pasted in external programs such as spreadsheet [36].

Advantage of PCID:

- It provides a very clean user interface.
- It is also very fast.

- The parameter can be changed through a menu system.

Limitations of PCID:

- Problem with modeling 11-V1 and a-Si solar cells.
- Layer limitation; only 5 layer can be added.
- For CIGS devices, the number of graded layer is too low

3.3.5 wxAMPS

AMPS stand for Analysis of Microelectronics and Photonic Structures. It was engineered to be a very general and versatile computer simulation tool for the analysis of device design. It is a one dimensional (1-D) device physics code which is applicable to any two terminal devices. It can be for diode, sensor, photo-diode and photovoltaic device analysis. The objective of AMPS is to teach how material properties (e.g., band gap, affinity, doping, mobilities, doping gap state defect distribution in the bulk and at interfaces, etc) and device design/structure together control device response to light, impressed voltage, temperature. AMPS allows user learn the “whys” of device response to a given situation (i.e., light bias, voltage bias, and temperature) through exploring and comparing band diagram, current component, recombination, generation, and electric field plot available from AMPS as a function of light intensity, voltage, temperature and position. The wxAMPS program is newly developed solar cell simulation software based on the original AMPS (Analysis of Microelectronics and Photonic Structures) code [36]. The interface of wxAMPS is developed using a cross-platform library, wx Widgets, and the kernel is based on an updated version of the AMPS (Analysis of Microelectronics and Photonic Structures) code [37]. wxAMPS has two different tunneling models, one is drift-diffusion model and another is intra-band tunneling model. The second model is more suitable for hetero-junction solar cell [38].

The main physical principles are derived from AMPS and in addition two different tunneling models, intra-band tunneling and trap-assisted tunneling, are incorporated to the program. The algorithm of wxAMPS has been modified to combine the Newton and Gummel methods, which convergence and stability. Improves the effects of series and shunt resistance unrelated to the main diode are also added.

A database-oriented WIKI has been set up for sharing the simulation files of devices and helping users find and discuss the parameters used in solar cell simulations. wxAMPS is a good tool to simulate various kinds and structures of solar cells, which can be made from crystalline and amorphous Si material, as well as CdTe and CIGS thin films, and other materials. Tandem structure solar cells can also be simulated through using the trap-assisted tunneling model in which carrier mobilities are enhanced as functions of electric fields.

Advantage of wxAMPS:

- wxAMPS program is an update of popular solar cell simulation tool AMPS.
- It is so designed that the previous successfully simulated results will be available so that users will not lose their information if the simulation doesn't converge at a certain bias voltage.
- It is a high performance simulator to simulate the hetero-junction solar cell.
- Can read any files, e.g. spectral files and result data import and export is also possible
- Quick data entry and enhanced visualization are possible.
- User friendly.
- Based on the options for an unlimited number of layers in the simulation modeling graded solar cells can be implemented easily in wxAMPS.
- Combines Newton and Gummel model which convergence and stability.
- Database-oriented WIKI helps the user to find and discuss the parameter.
- The effects of series and shunt resistance unrelated to the main diode are also added.
- Any number of wavelengths can be entered for analysis [37].

3.4 Comparison among different simulation soft-wares

A comparative study among different simulation soft-wares is described in Table 3.1.

	AMPS-ID	SCAPS	wxAMPS	PCID
Maximum number of layers	19	7	unlimited	5
Band discontinuities $\Delta E_c, \Delta E_v$	All program use the Anderson model: $\Delta E_c = \Delta \kappa$ and $\Delta E_v = \Delta \kappa + \Delta e g$			
Graded band gaps	No	No	Possible	No
Deep bulk states	50	3	50	No charge
Deep interface states	No	Yes	No	No
Charge in Deep states	Yes	Yes	Yes	No
Simulation of nonroutine measurement	No	C-V C-f	No	Transients
Numerical robustness(convergence)	High	Ok	High	Ok
Speed	Low	Fast	Fast	Fast
User friendliness, interactivity	Good	Very good	Very good	Good

Table 3.1 Comparison among different simulation software

3.5 wxAMPS

In this research work, simulation software wxAMPS is chosen for simulating perovskite solar cell due to its simplicity, user friendliness and large scale of analysis on performance parameters. The wxAMPS is an updated version of popular solar cell simulation software AMPS. The updated features of wxAMPS are user interface and algorithm modification.

3.5.1 User interface:

The graphical user interface (GUI) of wxAMPS is designed with a cross-platform C++ library, wxWidgets, and allows quick data entry as well as enhanced visualization of results for comparison and analysis. The main user interface window is shown in fig.3.1

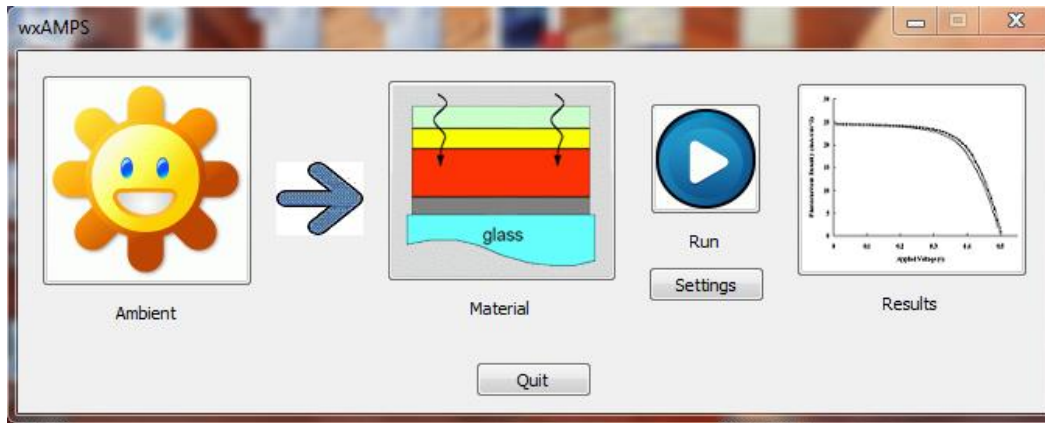


Fig. 3.1 User interface of wxAMPS

In wxAMPS, the simulation procedure is carried out in three steps. First, the ambient operational environment, including temperature, solar spectrum, and bias voltages, is set up. Standard values can be used or the operator can adjust the data. Unlike the original AMPS code any number of wavelengths can be entered for analysis. Second, the materials properties are entered for each layer of device. These are provided through a database, editable using common spreadsheet programs, simplifying entering data for many layers and for quick manipulation of properties such as absorption coefficient. Finally, the case is run and the results are returned for analysis by the user. Output is provided in a variety of forms, including files readable by both spreadsheet programs and directly through the graphical user interface. These steps are implemented in three dialog boxes that can be called from a simplified user interface.

In AMPS, there are five separate dialog boxes for inputting voltages biases, illumination condition, operating temperature, and front and back contact data. In wxAMPS, these are combined into one window for quick editing and viewing. To help users who do not know the values of PHIB (the barrier height defined as $(E_c - E_f)$ for the front and back contacts, a check box to incorporate flat bands is included. Inputting bias voltages has been stream lined by allowing user to write the values of every voltage of interest into a text file and load it. The ambient conditions, entered once, are cached automatically to reduce time spent by the user tweaking the simulation environment. However, new ambient conditions can be entered easily at any time by loading from an external file. When entering material properties, the parameters of each layer are categorized into four groups, accessed by separate tabs. Materials data can be entered and scrutinized conveniently in the panels selected by these tabs. Absorption coefficients

can be loaded from external data files. An editable grid is displayed that can clearly view and modify the structure of the device.

Users are not only able to save and load a entire device, but also may save and load any single layer. This helps users define a new device quickly by picking and choosing among existing material files. During a simulation run, a dynamic progress dialog will pop up to inform users which step the program is running at that moment. The calculation can also be canceled part way through husing this dialog box if needed. If canceled any results obtained to that point are available in output files. Upon completion, the results are displayed based on a third dialog box. The output graphs for different variables can be promptly viewed by selecting items from a list. User can move, zoom, and select an area to display in the graphs. Figures can be copied, printed, and saved as bitmaps. For assisting user in analyzing the results, three slider bars for voltage as well as shunt and series resistance (unrelated to the diode) are included. Unlike the original AMPS simulation this allows easy addition of external resistances to the device simulation. To support further data analysis, results can be exported in comma-delimited (CSV) formal that is compatible with spreadsheet-based software [38].

3.5.2 Algorithm modification

To consider tunneling effects, there are two tunneling models incorporated into wxAMPS: trap-assisted tunneling and the intra-band tunneling.

Trap-assisted tunneling model:

The trap-assisted tunneling model is necessary when high electric fields exist at junction, such as when simulating tandem solar cell. The intra-band tunneling model provides more realistic results for heterojunction solar cells. The algorithm of the simulation system was modified to solve these tunneling models, which extends the drift-diffusion model that AMPS employs. In the trap-assisted tunneling model, the expression for recombination rate is changed from the typical Shockley-Read-Hall model to a new form:

$$R = \frac{N_t V_{th} \sigma (1 + \Gamma n) (1 + \Gamma p) \sigma_p (np - n_i^2)}{\sigma n (1 + \Gamma n) (n + n_t + \sigma_p (1 + \Gamma p) (p + p_t))}$$

Where R is the recombination rate, N_t is the defect density, V_{th} is the thermal velocity and p are the concentrations of electrons and holes, n_i is the intrinsic carrier density, and s_n and s_p are the

capture cross-section for electrons and holes, respectively. G_n and G_p are field-driven tunneling functions that account for the contribution of trap-assisted tunneling to recombination and trap occupation.

Intra-band tunneling model:

The intra-band tunneling model is implemented by adding a thermionic emission boundary condition at any layer interface, including the primary junction. When tunneling dominates the behavior at an interface, the current through that interface, π , is composed of a thermionic emission current J_{TE} and an intra-band tunneling current, expressed as-

$$J_I = (1 + \delta) J_{TE}$$

Where δ is the tunneling coefficient that incorporates the tunneling contribution across the energy band to states at the interface. The coefficient δ is a complex integral term that is calculated by a numerical interrogation of the current through a barrier using the trapezoidal rule and based on the spacing and energy band edge profiles creating a given barrier [74].

3.6 Input parameters

There are three types of input parameters: the ambient parameters, the material properties and the simulation settings.

Ambient parameter modeling

The ambient operational parameter such as temperature, light, QE, front and back contact setting and bias voltage are setup in the ‘ambient’ dialog box of the wxAMPS software. There are five separate dialog boxes for inserting voltage biases, illumination conditions, front and back contact data. The ambient parameter insertion window is shown in Fig.3.2

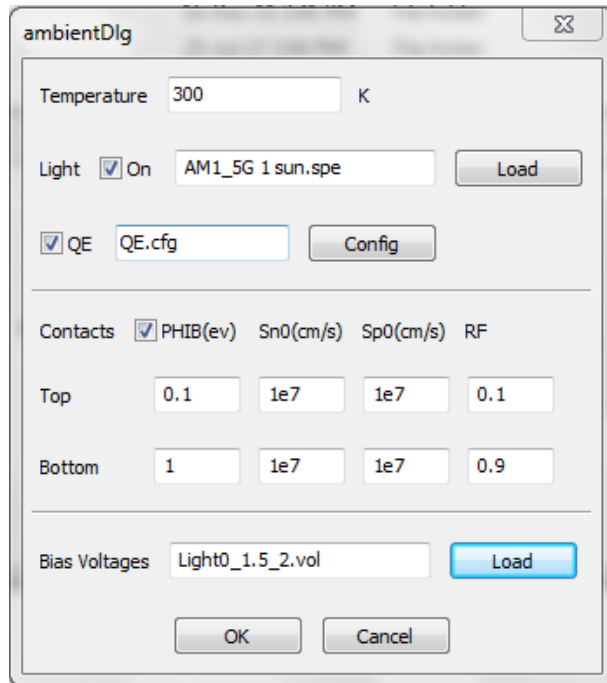


Fig. 3.2 Ambient modeling of wxAMPS

These are combined into one window for quick editing and viewing. The ambient conditions entered once, are caught automatically to save time of the user. New ambient condition can also be entered easily.

Layer properties modeling

In order to simulate a device all the basic input parameters should be well defined so that it behaves as a real counterpart. The parameters of the solar cell materials such as: Thickness, permittivity, band gap (E_g), electron affinity (χ), dielectric constant (ϵ) valence and conduction band density of states (N_v and N_c), charge carriers mobility (μ_n and μ_p), acceptor and donor dopant concentration (N_a , N_d) are inserted in the electrical parameter window.

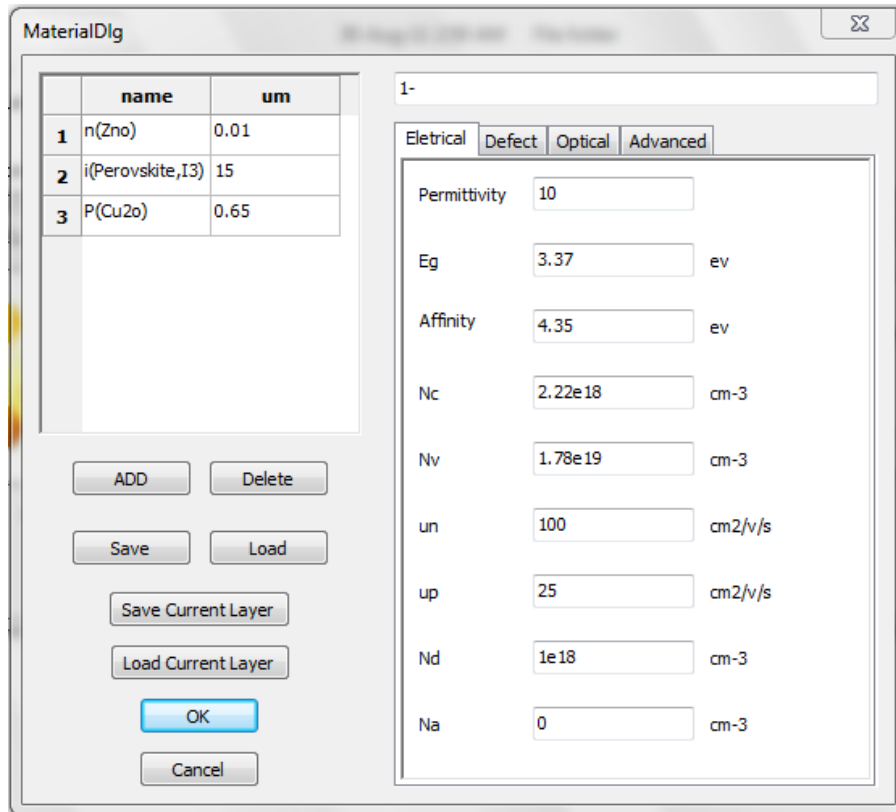


Fig. 3.3 Insertion of electrical parameter in wxAMPS

Every material has some defects. So, for simulating solar cell, the defect parameters should be inserted in the wxAMPS software. Then the defect parameters are inserted for every layer in the defect parameter insertion window. There are three types of defects such as discrete defect, banded defect and Gaussian defect etc. one of these three types of defect should be selected. The defect insertion window is shown in Fig. 3.4.

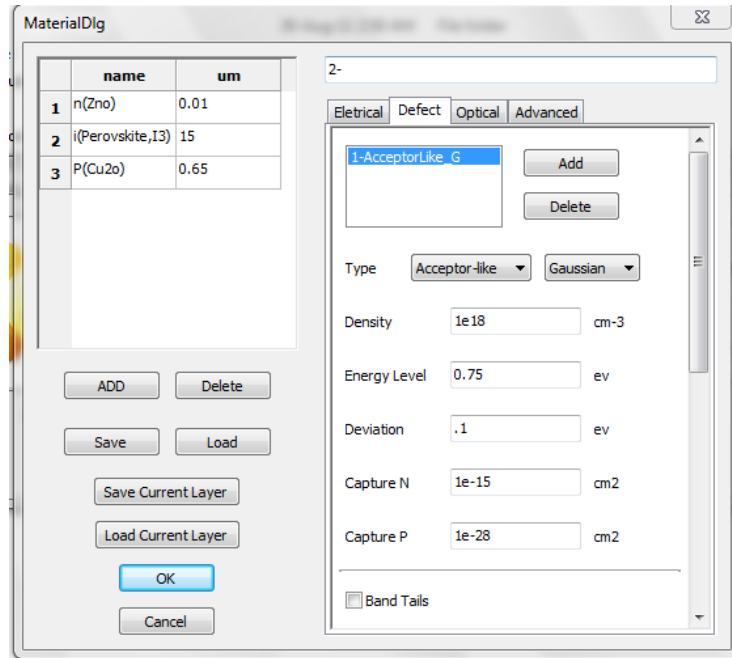


Fig. 3.4 Insertion of defect parameter

After that, the optical properties of different layers are inserting as shown in Fig. 3.5

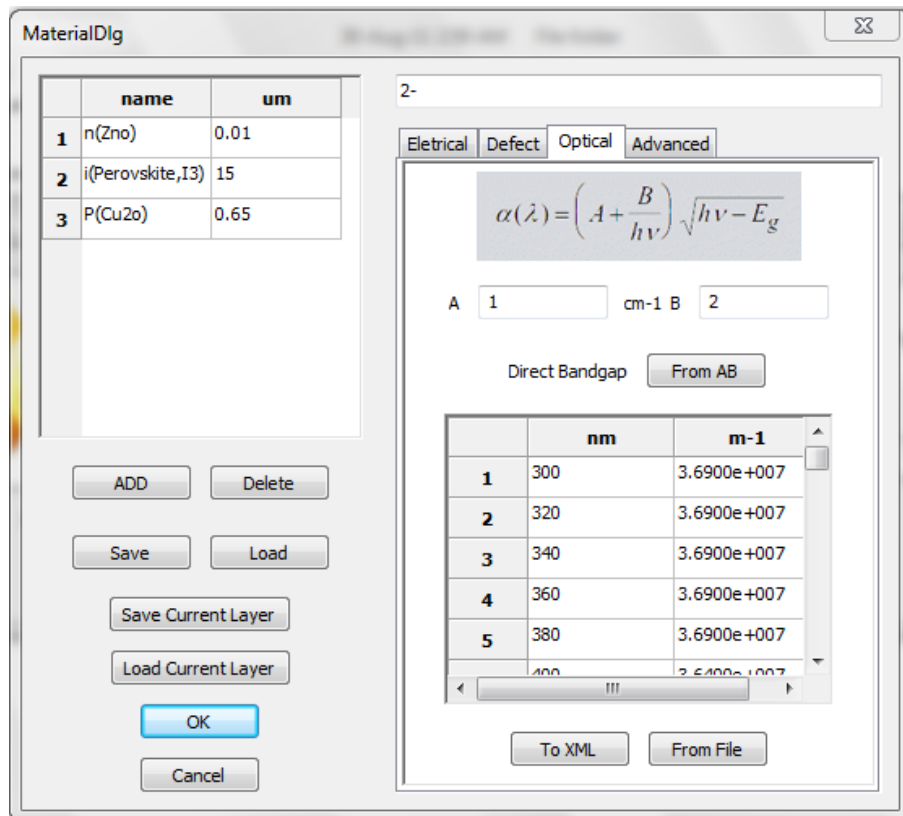


Fig. 3.5 Insertion of optical parameter

Optical absorption file should be written in notepad according to specific manner and the file should be saved in abs or abs format. Then the absorption file can be inserted by clicking the radio button “From file”.

3.7 Outputs

After insertion of the ambient parameters, layer properties and settings, the run button should be clicked to let the simulator to perform simulation. The simulator shows the results in the portion “Results”. The results are the I-V characteristics curve, energy band diagram, carrier profile, and Electric field inside the device, generation and recombination of electrons and, lifetime of carriers and quantum efficiency curve Fig. 3.7 shows the I-V curve of a Perovskite solar cell.

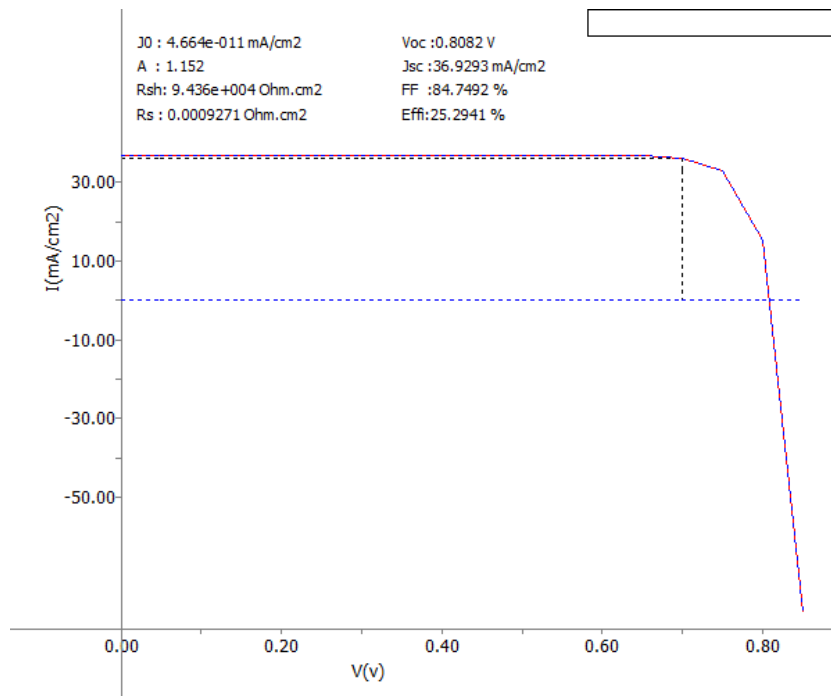


Fig. 3.6 I-V curve of simulation cell

Some important parameter can be obtained from this window such as V_{oc} , J_{sc} , and FF and efficiency of the simulated cell.

The other result such as energy band diagram, carrier profiles, Electric field inside the device, generation and recombination of electrons and holes, lifetime of carriers and quantum efficiency also shows curves in this window.

Chapter 4

Design and simulation

Introduction

In Perovskite solar cell there are three main layers, Cu_2O as p-type, Perovskite as intrinsic and ZnO as n-type material. To additional layers, front contact and back contact are also necessary. Before simulation the materials properties must be characterized into numerical values. After simulation, detail observation of results is needed to analyze the performance parameter.

4.1 Design of the cells

At the starting, we studied about different Perovskite materials such as $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{PbBr}_3$, $\text{CH}_3\text{NH}_3\text{PbCl}_3$, $\text{CH}_3\text{NH}_3\text{Pb}_{3-x}\text{Cl}_x$ etc and their various properties are analyzed. The properties of different hole transporting material and electron transporting material are also analyzed. For solar cell suitable band gap is 1.5 eV. We choose $\text{CH}_3\text{NH}_3\text{PbI}_3$ as absorber for single absorber cell. The band gap of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is 1.5 eV. Thus for structure with $\text{CH}_3\text{NH}_3\text{PbI}_3$ i.e. with single absorbed layer, we get high J_{sc} and high power conversion efficiency. The characteristics of Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ is used to get high PCE and short circuit current (J_{sc}) as well as high open circuit voltage (V_{oc}) which result in an overall efficiency to be higher.

The structure of single absorber layer is shown in Fig 4.1

Front contact (All)
ZnO (n-type) 0.05 μm
Perovskite($\text{CH}_3 \text{NH}_3 \text{PbI}_3$) 15 μm
Cu_2O (p-type) 0.7 μm
Back contact(Mo)
Glass

Figure. 4.1 cell structure

Cell proposed structure of a Perovskite solar cell with single absorber layer of $\text{CH}_3\text{NH}_3\text{PbI}_3$

The structure of the employed device here is a p-i-n solar cell where ZnO is used as n-type and Cu₂O is used as p-type material. As intrinsic layer CH₃NH₃PbI₃ is used. The p-type Cu₂O has good transparency, high hole mobility and good chemical stability. Also it is nontoxic and abundantly available on the earth. By adjusting the thickness of Perovskite layers, the PCE of the cell can be improved.

The Perovskite solar cells with spiro-OMeTAD as p-type material have achieved high PCEs of about 20%. However, the synthesis of spiro-OMeTAD becomes a barrier for future commercialization because of its high cost. So it is necessary to use other p-type materials as a substitute for spiro-OMeTAD (74). Compared with organic spiro-OMeTAD, inorganic p-type Cu₂O with similar physical property, good chemical stability, ease of synthesis procedure, and low cost is an ideal kind of p-type material.

ZnO has energy band structure and physical properties similar to those of TiO₂. But ZnO has substantially higher electron mobility than that of TiO₂, which would make it an ideal kind of n-type material[39-40]. Therefore, Cu₂O as HTM and ZnO as ETM are widely utilized to perovskite solar cells

4.2 simulation parameters

Numerical simulation of the perovskite solar cell is performed by solar cell simulation software wxAMPS. Before simulation, different electrical, optical, defect properties of the cell materials are analyzed as they are needed for simulation. Also the operating temperature, front contact and back contact data are needed for simulation.

4.2.1 Ambient parameters

Ambient parameter describes the surrounding condition of a solar cell such as temperature sun spectrum etc.

Ambient temperature:

The operating temperature at which solar cell works is called the ambient temperature. The ambient temperature of should be considered properly as the performance of a solar cell depends greatly on ambient temperature. Efficiency depends on temperature because the electron and

hole mobility changes with temperature. Generally the ambient temperature is selected at room temperature (25°C or 288k)

Illumination:

Solar radiation closely matches a black body radiator at about 5,800K. As it passes through the atmosphere, sunlight is attenuated by scattering and absorption; the more atmosphere through which it passes, the greater the attenuation.

As the sunlight travels through the atmosphere, chemicals interact with the sunlight and absorb certain wavelength. The amount of short- wavelength light reaches the Earth's surface. A more active component of this process is water vapor, which results in a wide variety of absorption bands at many wavelengths, while molecular nitrogen, oxygen and carbon dioxide add to this process. By the time it reaches the Earth's surface, the spectrum is strongly confined between the far infrared and near ultraviolet.

The most important parameter that determines the solar irradiance under the condition of clear sky is the distance that the sunlight has to travel through. The ratio of the actual path length of the actual path length of the sunlight to the minimum path length when sun is directly overhead is known as Air Mass. When sun is directly overhead, the Air Mass is 1 (AM 1). When the sun is situated at an angle Θ , then Air Mass is $=\frac{1}{\cos\Theta}$. For simulation the sun spectrum is set to AM1.5 which corresponds to the angle 48.2°.

Bias voltage:

Bias voltage is the operating voltage at which solar cell works. For thin film solar cell, spectral response depends on bias voltage is set to 0-0.4/1V.

4.2.2 Front contact parameters

Front contact material property is defined by Schottly barrier at the front contact and n type ZnO window interface and the reflectivity of the contact. Φ_{bn} of the front contact should be zero that means that the Fermi level of metal and semiconductor are in the same level. But in practice, some of the photons reflect from the front contact. For this research work Φ_{bn} PHIB (E_c-E_p) of front contact is at 0.3 eV and reflectivity of front contact is 0.15.

4.2.3 Back contact parameters

Back contact material property is defined by Schottly barrier at the p-type Cu₂O layer and back contact layer interface and the reflection of light towards the cell from back contact region. For being the contact ohmic for hole, the work function of back contact materials chosen in such a manner that the Schottly barrier for p-type semiconductor, Φ_{bn} is equal to zero i.e. $(E_c - E_p)$ is equal to the band gap of p-type semiconductor. 100% reflectivity of back contact is ideal, but in practice it is not possible. We chose the value of reflectivity is 0.85 and the value of PHIB, Φ_{bp} is 1.2 eV.

4.2.3 Simulation of the cells

Various electrical properties of the p-type, n-type and intrinsic materials are needed simulating the cells. The properties of the materials are given at table 4.1

properties	ZnO(n-type)	MAPbI ₃ (i-layer)	Cu ₂ O(p-type)
Thickness (μm)	0.05	15	0.7
permittivity	10	19	7.5
E _g (eV)	3.37	1.5	2.22
Affinity(eV)	4.35	3.93	3.6
N _c (cm ³)	2.22x10 ¹⁸	2.5 x10 ²⁰	1x10 ¹⁹
N _v (cm ³)	1.78x10 ¹⁹	2.5 x10 ²⁰	1x10 ¹⁹
μ _n (cm ² /V/s)	100	50	19
μ _p (cm ² /V/s)	25	50	19
N _d (cm ³)	1x10 ¹⁸	0	0
N _a (cm ³)	0	0	1.5 x10 ¹⁵

Table 4.1 Various electrical properties for simulation

4.3 Result analysis

We got an efficiency of 25.29%, J_{sc} = 36.92mA/cm², V_{oc} = 0.8082V, fill factor = 84.75% for cell with the thickness of 15μm Perovskite layer (CH₃NH₃PbI₃). We analyzed the performance of

the structure by changing the thickness of different layers of the structures, by varying the doping concentration of the N-type and p-type materials and by varying the operating temperature.

4.3.1 Role of absorber

As absorber is the key component in the solar cell devices the deep knowledge and understanding about this matter is crucial to design and fabricate a solar cell. Here our study has focused on realization of role of absorber to make more practical and optimization of the performance of the PV devices. Simulation with different aspect of the absorbing materials are discussed below-

4.3.1.1 Effect of thickness of the absorber

Performance of the cell depends mainly on optoelectronic characteristics and thickness of the absorber layer. Thus simulations are carried out to examine the device parameters with thickness of the absorber layer is 15 μm then output efficient 25.29%.

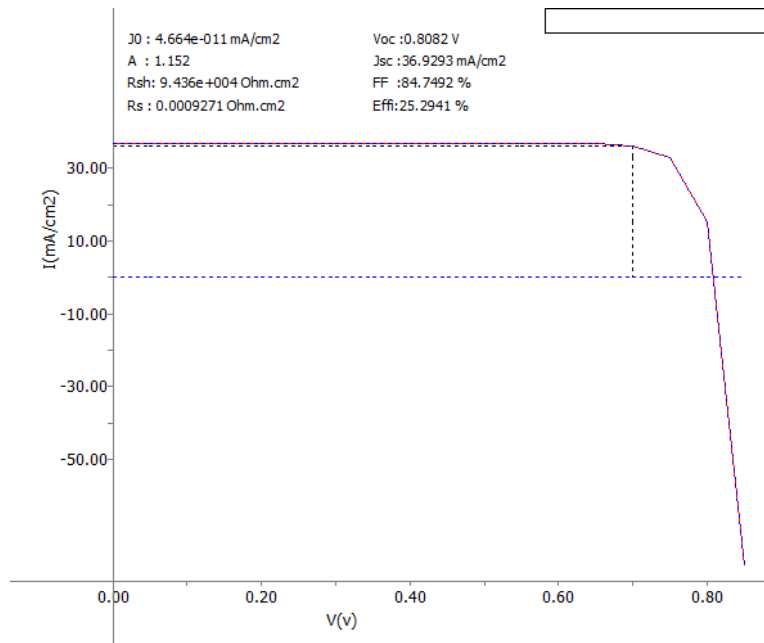


Fig 4.2 I-V curve of simulation cell

The absorber layer thickness is 13 μm then output efficient 25.26%.

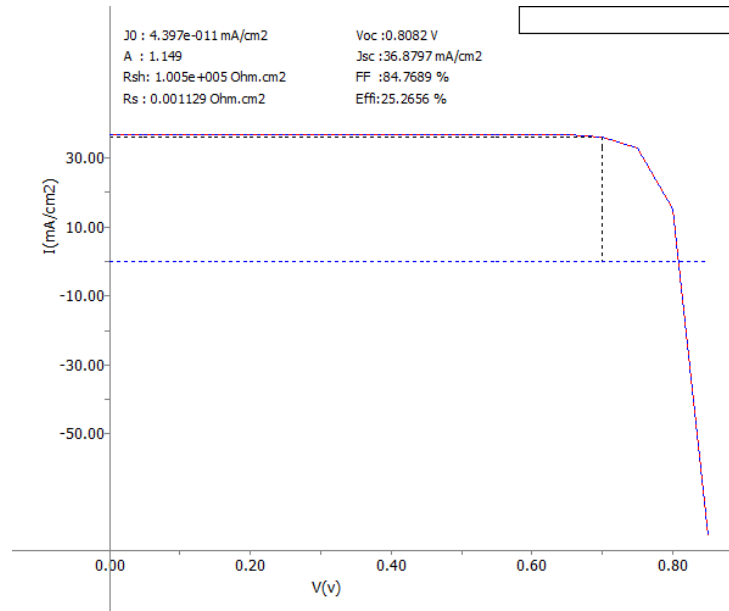


Fig 4.3 I-V curve of simulation cell

The absorber layer thickness is 17 μm then output efficient 25.31%.

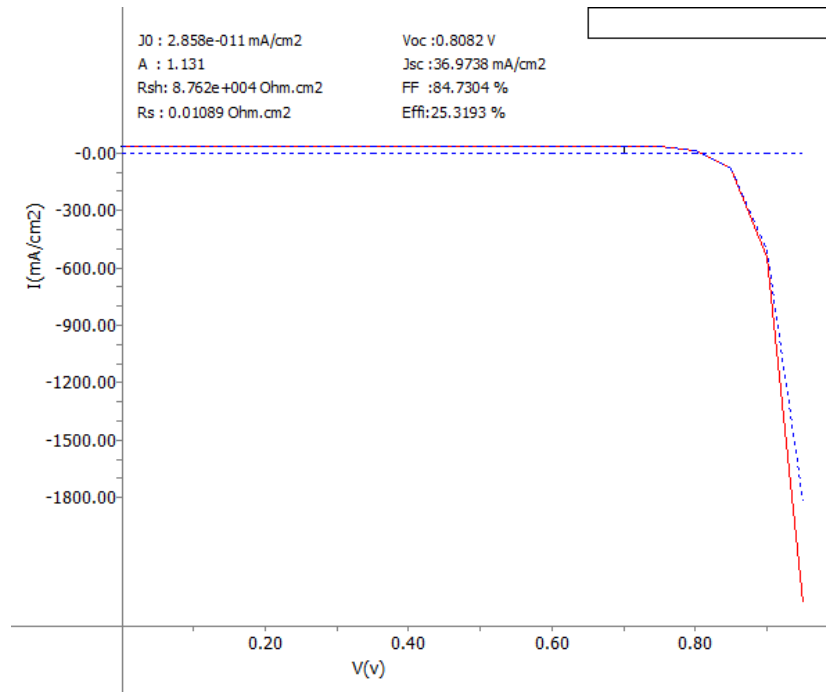


Fig4.4 I-V curve of simulation cell

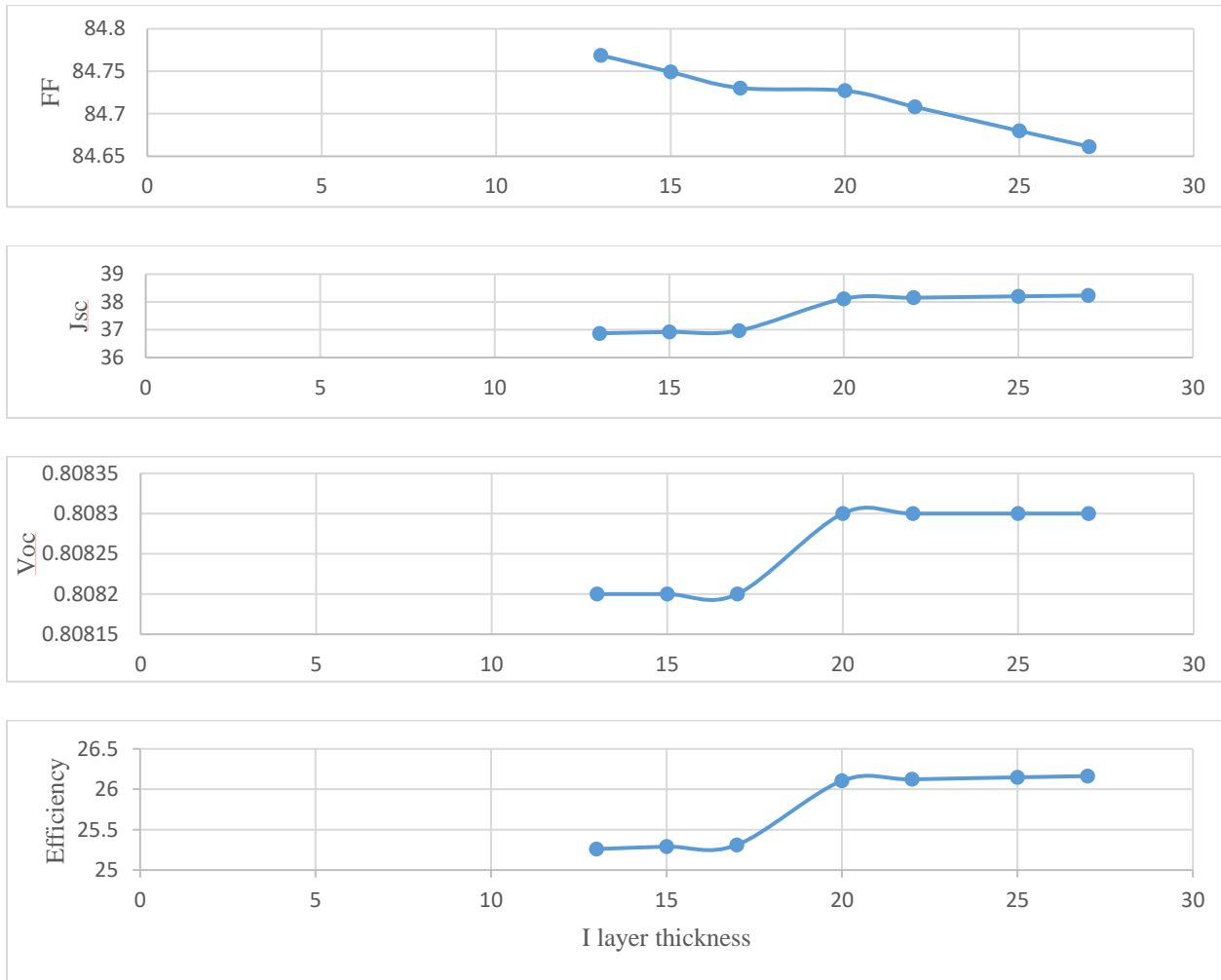


Fig 4.5: I layer thickness vs Efficiency, V_{oc} , J_{sc} , and Fill Factor.

We choose $15\mu\text{m}$ thickness for $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer, in $15\mu\text{m}$ thickness the efficiency of solar cell is 25.28%.

4.3.2 Effect of temperature

With increasing temperature, the short-circuit current of the cell increases, whereas the open-circuit voltage decreases. The effect of temperature on the power is quantitatively evaluated by examining the effects on the current and the voltage separately. Say I_o and V_o are the short-circuit current and open-circuit voltage at the reference temperature T , and α and β are their respective temperature coefficients. If the operating temperature is increased by ΔT , then the new current and voltage are given by the following

$$I_{sc}=I_0(1+\alpha\Delta T) \text{ and } V_{oc}=V_0(1-\beta\Delta T)$$

Since the operating current and the voltage change approximately in the same proportion as the short-circuit current and open-circuit voltage, respectively, the new power is as follows:

$$P=V.I= I_0(1+\alpha\Delta T). V_0(1-\beta\Delta T)$$

This can be simplified in the following expression by ignoring a small term:

$$P=P_0[1+(\alpha-\beta)\Delta T]$$

for typical signal crystal silicon cells, α is $500\mu\mu$ per $^\circ\text{C}$ and β is $5\text{m}\mu$ per $^\circ\text{C}$. The power is therefore:

$$P=P_0[1+(500\mu\mu-5\text{m}\mu).\Delta T] \text{ or } P_0[1-0.0045\Delta T]$$

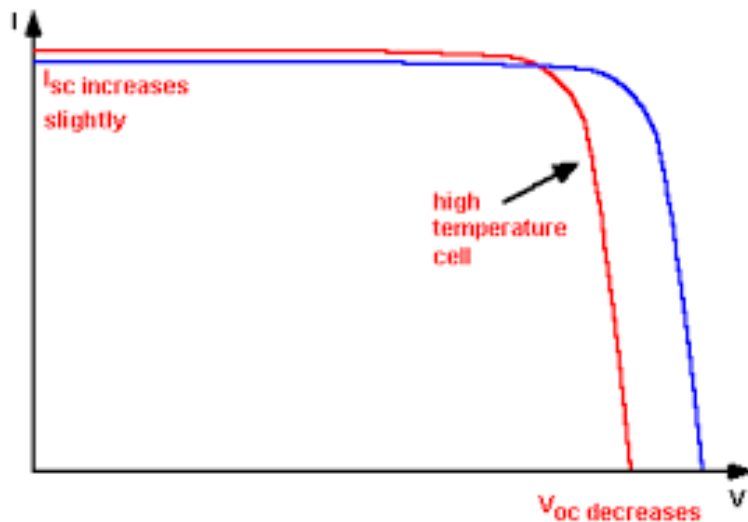


Fig.4.6 power output curve of I-V

This expression indicates that for every $^\circ\text{C}$ rise in the operating temperature above the reference temperature, the silicon cell power output decreases by 0.45 %. Since the increase in the current is much less than the decrease in the voltage, the net effect in the decrease in power at high operating temperature.

The effect of varying temperature on the power output is shown in the power versus voltage characteristics at two operating temperature in figure 4.5. The figure shows that the maximum power available at lower temperature is higher than that at higher temperature. Thus, cold

temperature is actually better for the PV cell, as it generates more power. However, the two P_{max} points are not at the same voltage. In order to extract maximum power at all temperature, the PV system must be designed such that the module output voltage can increase to V_2 for capturing P_{max2} at lower temperature and can decrease to V_1 for capturing P_{max1} AT higher temperature.

At standard temperature that means $300^{\circ}K$ the output efficiency is 25.29%:

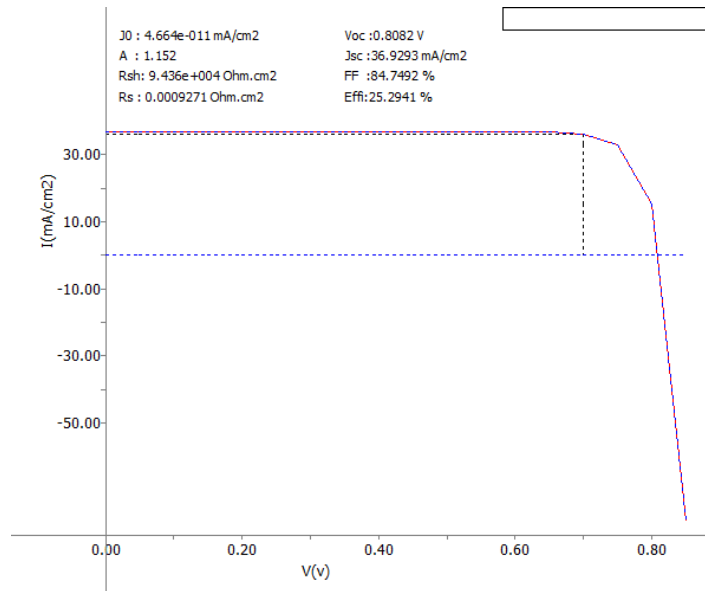


Fig. 4.7 I-V curve of simulated cell

At $310^{\circ} K$ the output efficiency is 25.13%.

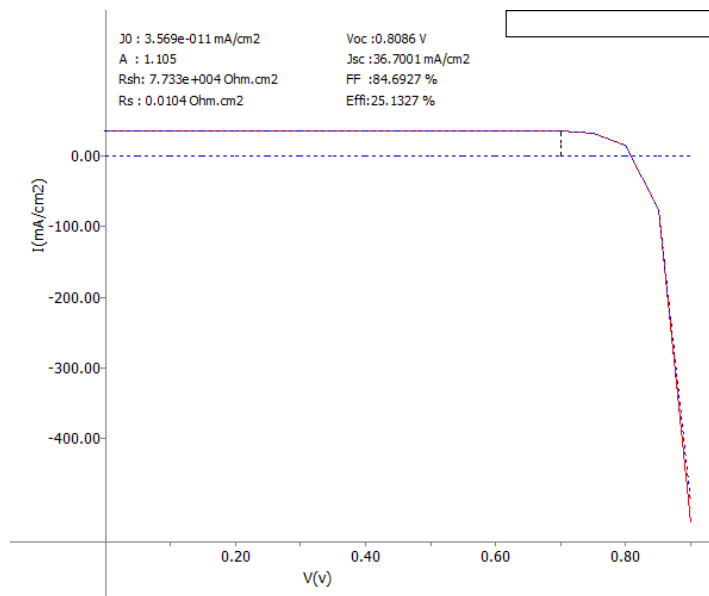


Fig. 4.9 I-V curve of simulation cell

At 295° K the output efficiency is 25.64%.

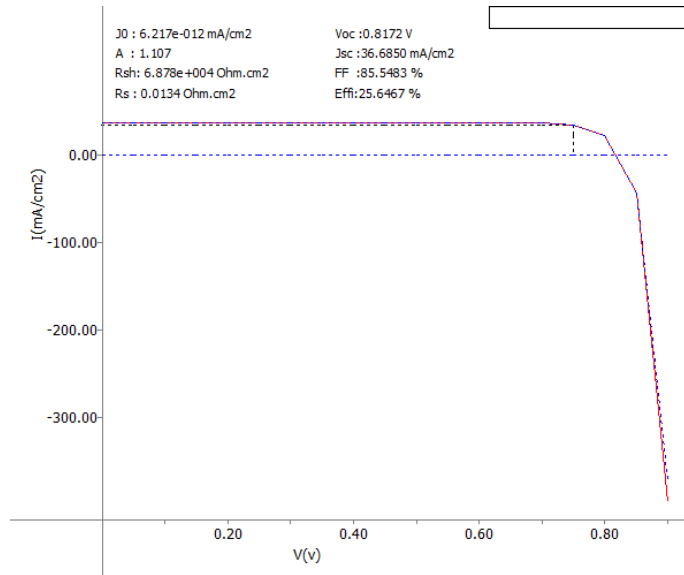


Fig. 4.10 I-V curve of simulation cell

At 290° k the output efficiency is 25.92%.

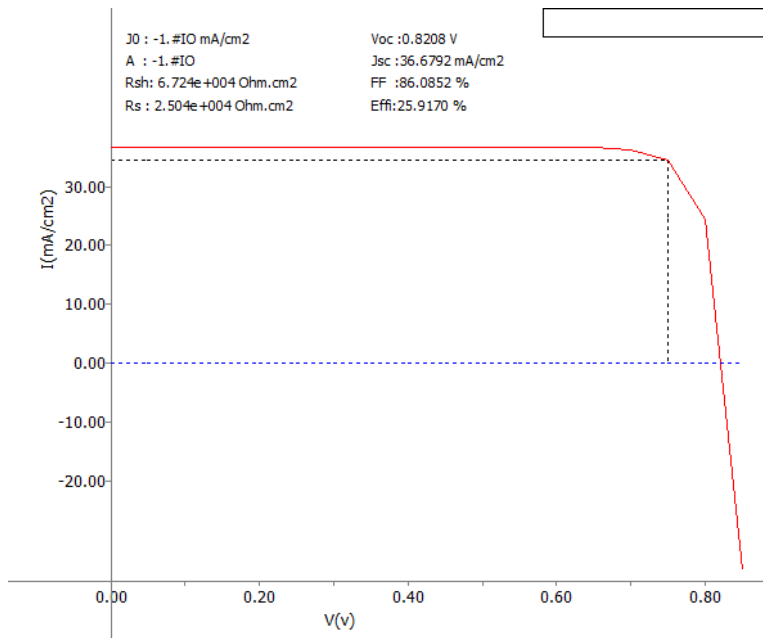


Fig. 4.11 I-V curve of simulation cell

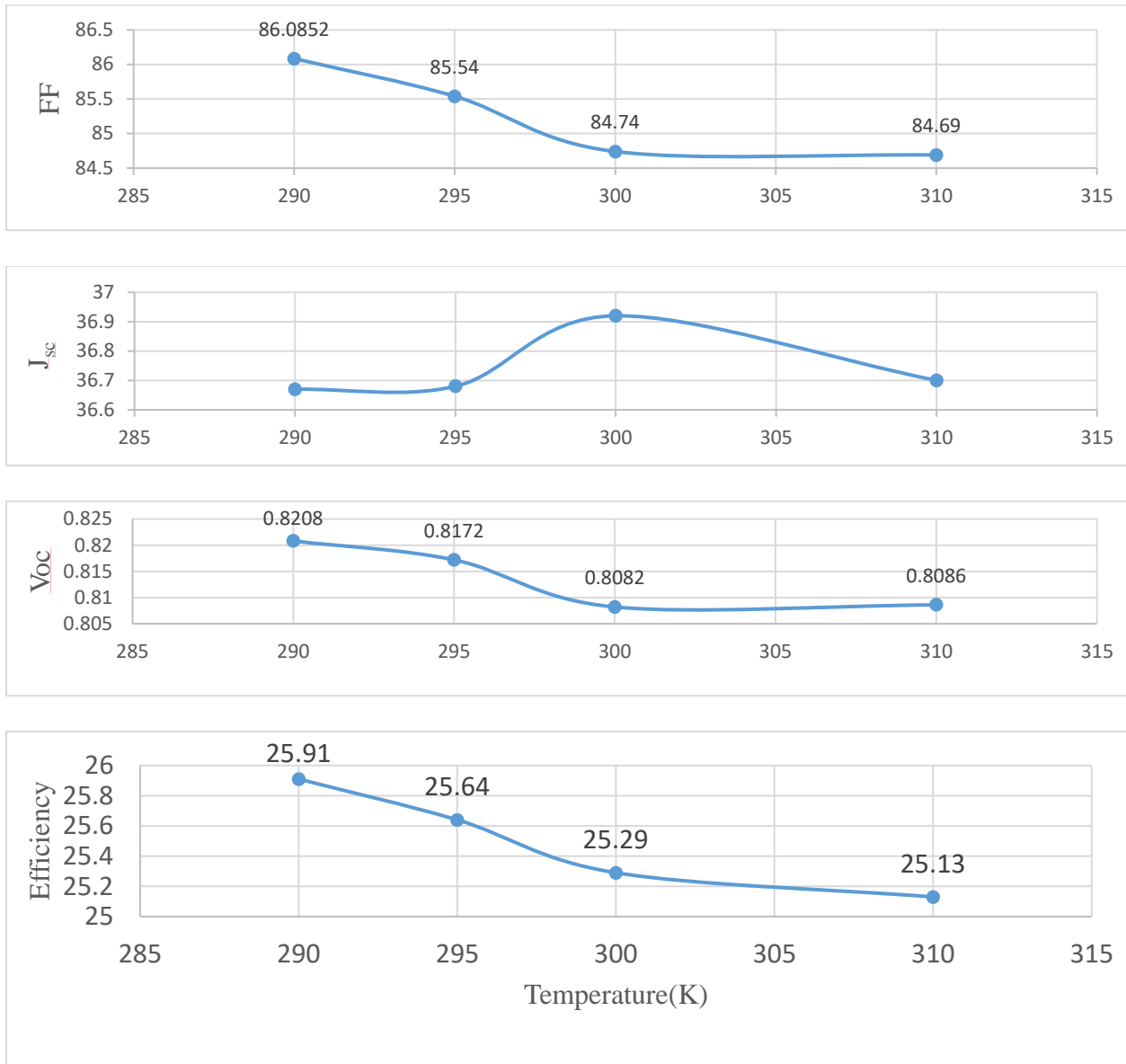


Fig 4.12: Temperature vs Efficiency, V_{oc} , J_{sc} , and Fill Factor.

So, maximum power can be tracing form PV panel at lower temperature that means in winter session.

Effect of climate:

On a party cloud day, the PV module can produce up to 80% of their full sun power. Even on an extremely overcast day, it can produce about 20% power. Snow does not usually collect on the

modules, because they are angled to catch the sun. If snow does collect, it quickly melts. Mechanically, modules are designed to withstand golf ball size hail.

Chapter 5

Conclusion

6.1 Summary of the works done

Final simulated high performance Perovskite solar cell with one absorber layer ($\text{CH}_3\text{NH}_3\text{PbI}_3$) of thickness 15 μm has the open circuit voltage, V_{oc} is 0.8082 V and the short circuit current density, J_{sc} is 36.92 mA/cm^2 , FF of the cell is 84.74%. We can improve the performance of the cell by using the absorber layer thickness of about 17 μm . The efficiency is 25.20% which is slightly greater than the current highest Perovskite solar cell's efficiency of 25.28% and other parameters are $V_{oc}=0.8082\text{V}$, $J_{sc}= 36.97 \text{ mA}/\text{cm}^2$.

6.2 Future Works

Research can be done on increasing the performance and stability of Perovskite solar cell. Also research work can be done in reducing the cost associated with Perovskite solar cell. Fabrication of the proposed cell can be done to observe the practical performance of the proposed cells. Perovskite solar cell could be a sound alternative to other thin film solar cell such as CdTe, GaAs, GIGS, CZTS, and CIS etc. From 2009 to 2016 its efficiency has been reached up to 22.1% from 3.2%. The increase in efficiency is so rapid compared to other cell. So there is a great possibility for Perovskite solar cell. Further work can be done on the fabrication of Perovskite solar cell.

6.3 Final conclusion

The possibility of high performance thin film Perovskite solar cell with single and absorber layer has been explored by the numerical simulation. We achieved an efficiency of 25.28 % ($V_{oc}=0.808\text{V}$ $J_{sc} =36.92 \text{ mA}/\text{cm}^2$ and $\text{FF} = 84.74\%$) for single absorber layer. The proposed cells provide higher conversion efficiency and also show better thermal stability. The proposed cells can be fabricated by standard fabrication process. Much more research will be anticipated in this arena.

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