Study of properties of absorber layer in Perovskite solar cell

A Project Report Submitted

By

Puneet Kaur

(Reg. No. 11615700)

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Puneet Kaur

(11615700)

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ABSTRACT

This report aims at developing an understanding of different constituent layers of Perovskite solar cell with emphasis on the absorber layer, in particular. In order to have a better appreciation of the basics of solar cell the evolution of different generation of solar cells realized with various materials has been discussed. A comprehensive study of literature is carried out in order to examine the properties of absorber layer in Perovskite solar cell. The investigation of the optical, electronic and physical properties of the absorber layer is carried out through literature review, to establish our research problem. We find that although Perovskite solar cells have achieved a huge recognition over a very short period of time span, yet there remains a lot of scope and challenges to realize a long-lasting high efficiency Perovskite solar cell which can become an alternative to Si-based solar cells.

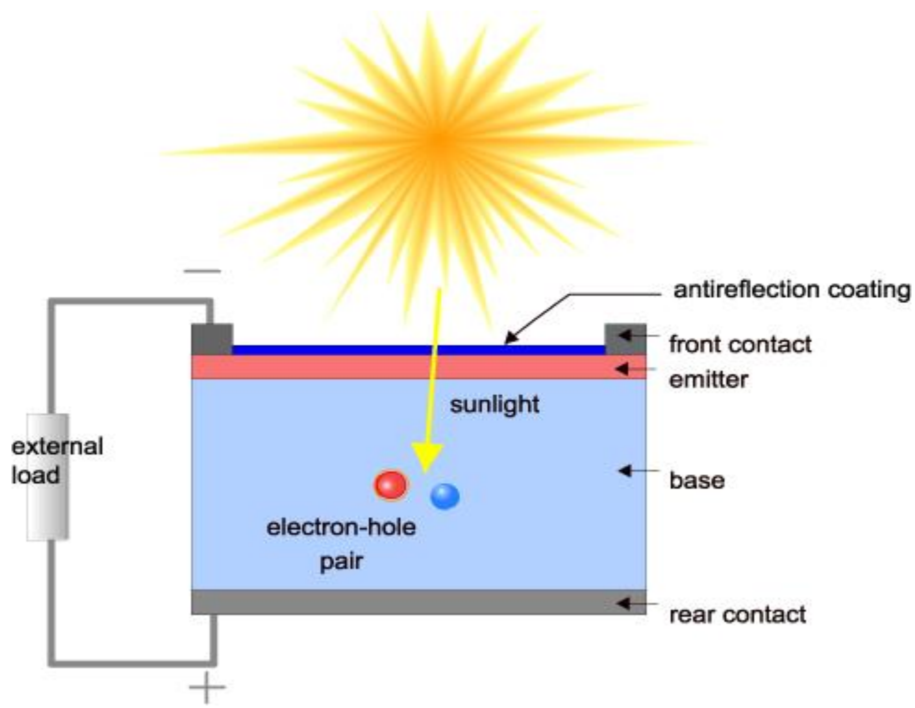
We finally conclude that the absorber layer of Perovskite solar cell needs attention so far as choice of material as well as processing is concerned and hence we decide to carry out the experiments in order to improve the performance of solar cells by tailoring the properties of the absorber layer.

CHAPTER1

1. INTRODUCTION

1.1 Solar cell

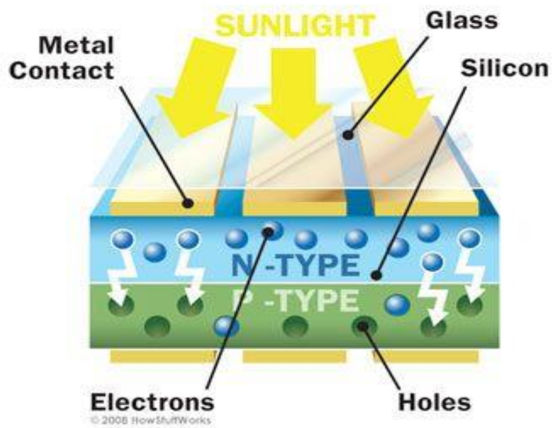
An electronic device that converts the light energy of sunlight into the electricity by the photovoltaic effect is known as the solar cell. When light shines on the solar cell than it produces current and voltage, which generates the electric power. Firstly we need a material which absorbs the light and promote the electron to the higher energy state and then after that this higher energy electron moves to the external circuit from the solar cell. Energy of this electron is dissipates in the external circuit and the electron returns back to the solar cell. This photovoltaic energy conversion needs semiconductor materials in the form of p-n junction. Most of the solar cells fabricated from the silicon, which increases its efficiency. [1], [2]



Schematic of conversion of sunlight into electricity [1]

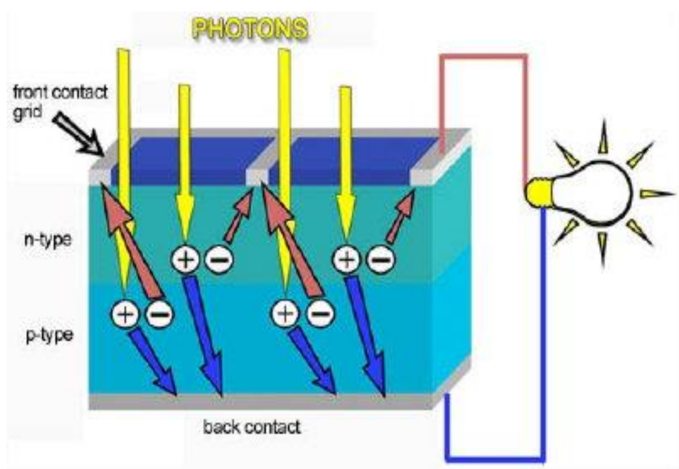
For the operation of solar cell the steps are as follows:

- Generation of the charge carriers due to light.



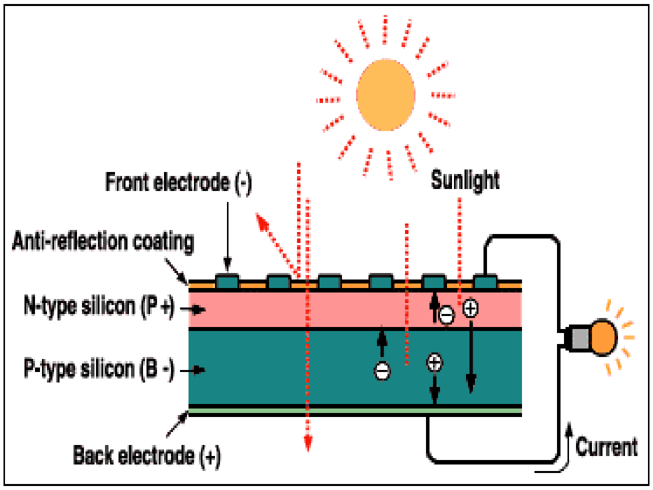
Schematic of generation of charge carriers [3]

- Transportation of the charge carriers due to the electric field across the cell.



Schematic of separation of charge carriers [4]

- The collection of these charge carriers till the external circuit.
- Large voltage is produced across the solar cell.



Schematic of power generation [5]

- Power is dissipated in load and in parasitic resistances. [1]

1.1.1 Three generations of solar cell

- **Wafer based:**

  (1) Monocrystalline silicon

  (2) Polycrystalline silicon

- **Thin films based single junction:**

  (1) Amorphous thin film silicon

  (2) Cadmium telluride

  (3) Copper indium gallium selenium

- **Thin films based multi junction:**

  (1) Perovskite solar cell

  (2) Biohybrid solar cell

  (3) Amorphous silicon solar cell

  (4) Cadmium telluride solar cell

  (5) Micromorph

- **Others:**

  (1) Dye-sensitized solar cell

  (2) Quantum dot-sensitized solar cell

  (3) Organic photovoltaic

  (4) QDs-polymer hybrid solar cell

(5) Perovskite solar cell [2]

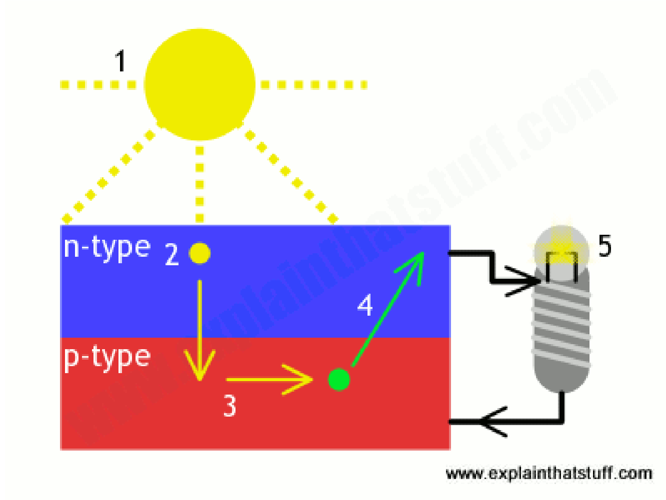
1.1.2 Si-based solar cell

A solar cell is sandwich of two different layers of silicon and these are doped. There is p-type, in which electrons are negatively charged and it is called positive type silicon and there are holes, which are charge carriers. The another upper layer is n-type layer or it is called negative type layer, in this layer charge carriers are electrons.

When layer of n-type silicon is placed on the layer of p-type silicon then the barrier is created at the junction of two materials. Electrons cannot cross the barrier and so that no current will flow even this silicon sandwich connect to the flashlight and the bulb will not light up. Something happened if the light shines on the sandwich. The light as a steam of energetic light particles called photons. When the photons enter into the sandwich then they give their energy to the atoms present in the silicon. When this incoming energy knocks the electrons out of the lower p-type layer than the electrons jumps to the n-type layer above across the barrier. After that the electrons will flow out about the circuit. If the light shines more than more the electrons jump up and more current will flows. This is called the photoelectric effect because here light makes the voltage.

Solar cell is a sandwich of n-type silicon and p-type silicon. In this, by using the sunlight electricity produced than between the different layers of silicon electrons hop across the junction by the sunlight:

- Photons bombard the upper surface, when the sunlight shines onto the cell.
- Photons carried their energy down through the cell.
- In the lower p-type layer photons give up their energy to the electrons.
- By using this energy electrons jumps across the barrier into the upper n-type layer.
- By flowing around the circuit electrons makes the lamp light up. [6]

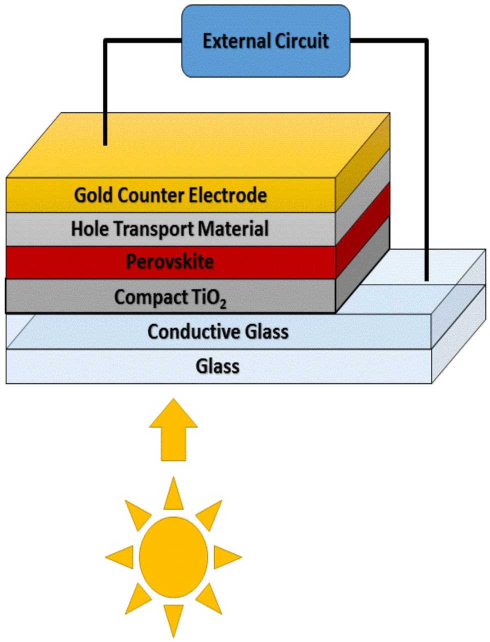


Schematic of working of Si-based solar cell [6]

1.2 Perovskite solar cell

1.2.1 Layers and working of Perovskite solar cell

In the Perovskite for absorbing the light there is a layer of Perovskite material. Than the holes and electrons are separate out and they are transported to an external circuit and then produce the electricity in the solar cell. The charge generate in the Perovskite structure can move very fastly away from one another, because the Perovskite solar cell doesn't need the thick layer of porous , which allows the hole-electron pairs to separate out from each other. Hole transport materials are used to transport the holes away from the Perovskite organic molecules. These hole transport materials are deposited on the top of Perovskite as a thin film and than due this the cell takes the solid state form and here no need of the liquid electrolyte which can be prone to leaking as used in the dye-sensitized solar cell. [7]

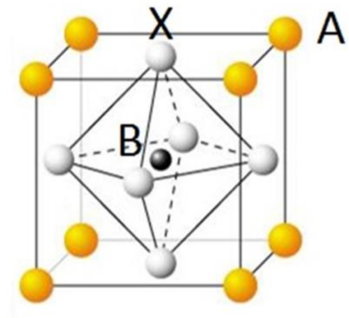


Schematic of different layers of Perovskite solar cell [7]

1.2.2 Crystal structure of absorber layer in Perovskite solar cell

Perovskites that do not contain the carbon-hydrogen bond, these are the natural Perovskites. They are metal oxides and also considered as the inorganic materials. The mixture of the the Perovskite solar contains the organic and inorganic ions. The basic formula for the Perovskite is ABX_3

The stoichiometry of the Perovskite is ABX_3. Here A is the corner position (it can be Ca, K, Na, Pb, Sr and other rare metals). B is the body centered position (it can be the metal cation) and X_3 is face centered position (it can be oxide or halide anion such as Cl, Br, I). Examples are lead titanate, calcium titanate, strontium titanate etc. [7]



Schematic of crystal structure of Perovskite solar cell [7]

1.2.3 Advantages

The power conversion efficiency of Perovskite solar cells is high as compare to other solar cells. So that the Perovskite solar cell becomes popular over the past few years. Its currently recorded efficiency is around 22.3%. Perovskite solar cells are well suited for the solid state hole-transport material and because of this the problem of corrosive electrolyte which can leak out of cell is avoided. Perovskite solar cells can be fabricated by the printing from solution so with the higher efficiency they can share it with the dye-sensitized solar cell and organic photovoltaics. [7]

1.2.4 Future challenges of the Perovskite solar cell

When the Perovskite material comes in contact with the moisture than they degrades, so when the cell left out in the atmosphere it will lose all activity. So firstly improving its stability and also improves the techniques which prints the larger area cells that enables its use in the electricity generation. We can also increase its efficiency to exceed the thin film CdTe solar cells by studying their cell designs and material properties. In future increase its temperature and air stability and replace lead with other element. [7]

CHAPTER2

2. REVIEW OF LITERATURE

Hui-Seon Kim *et al.* (2013) have analyzed that by the gathering of photogenerated charge and charge separation photovoltaic conversion is done. In this report we analyzed the mechanism of carrier gathering in the lead-halide Perovskite. First time we observed the gathering of charge in the light absorbing material, which is $CH_3NH_3PbI_3$ Perovskite in the NS solar cell, so that it creates a new kind of photovoltaic device, which different from the sensitized solar cells. This is observed from the capacitance which is extracted from the IS measurements for the electrodes NS TiO_2 and ZrO_2. [8]

Jeffrey A. Christians *et al.* (2013) have studied about the organo lead halide Perovskite solar cells. These are expensive and having low hole mobility. For the thin film photovoltaics as for hole conducting material, the new copper iodide is identified as in the Perovskite material. By using this copper iodide in the Perovskite we can achieve the 6% power conversion efficiency with a good photocurrent stability. Because of higher electrical conductivity, copper iodide gives the better fill factor than the spiro-OMeTAD. Copper iodide becomes a low cost hole conductor for the organo lead halide Perovskite and also achieve the good power conversion efficiency. [9]

Olga Malinkiewicz *et al.* (2013) have studied that for the clean and the renewable energy thin film photovoltaics. The efficiencies of perovskites are improved and increased from the last few years. For the yielding of high frequency we need the metal oxides, but these metal oxides need the higher temperature sintering process. But in this report methylammonium lead iodide is used as an absorber layers. This is sandwiched between the two layers of organic charge transporting, these layers act as an electron and hole blockers. Than this comes in contact with the indium tin oxide, so that the electrons and holes are extracted, than we getting the efficiency of 12%. By using the sublimation process in the high vacuum chamber than we get the high purity Perovskite layers. [10]

Teck Ming Koh *et al.* (2013) have analyzed that organic-inorganic methylammonium lead halide based solar cells have obtained the efficiencies more than 15%, which has superseded thin film based photovoltaics and liquid dye sensitized cells. In this report, they introduced a new metal halide Perovskite, which is the formamidinium cation. This shows the significant bandgap, which is 1.47ev. Formamidinium cation also shows the broader absorption as compare to the methylammonium cation. The fill factor and open circuit voltage of formamidinium cation yields the efficiency of 4.3%. so this material becomes good for the Perovskite solar cell. In this report they also analyzed the formation of black trigonal Perovskite polymorph and yellow hexagonal non-perovskite polymorph. The measurements of absorption shows the bandgap of 1.47ev for the formamidinium lead iodide compound, so the absorption extends toward the longer wavelength as compare to the Perovskite containing the methylammonium group. In the future they work on the stabilization of the black Perovskite polymorph. [11]

Eran Edri *et al.* (2014) have analyzed that the cells are operate as p-i-n device in the thin film and in inert mesoporous configuration, with the good electronic quality of i- layer and in these layers the quasi-fermi levels are divided. When the quasi Fermi levels are divided than the p-n junctions can take place outer the region of space charge so that they are known as selective contacts. In this report we studied that there are two prime locations are present, one is present near the hole blocking layer and the other one is present near the electron blocking layer interfaces. We observed that p-i-n solar cell has the good electronic quality semiconductor in between the p and n layer, but this solar cell having a layer which is low doped. [12]

Feng Hao *et al.* (2014) have analyzed that lead free perovskites can also work. He used the tin (Sn) instead of lead in the methylammonium tin iodide Perovskite. In this the band gap is 1.3ev which is less as compare to the band gap in methylammonium lead iodide, which is 1.55. Sn-based perovskites shows the excellent mobility in the transistors. Here he studied that Sn shows the high open circuit voltage and also good photovoltaic properties and there is less loss of voltage. Tin crystallizes at room temperature and displays a strong photoluminescence at 950nm, which corresponds to onset absorption. He used the x-ray spectroscopy for the structure and purity of the material and for the estimation of band gap photo-thermal deflection spectroscopy is used. Further optimization of this material proves should prove to be a non-toxic and viable alternative to the lead based Perovskite solar cell. Tin based perovskites prove to be low cost and high efficient for the future time. [13]

Hairong Li *et al.* (2014) have studied about 3,4-ethylenedioxythiophene, which is the electron rich molecule. The power conversion efficiency is increased to 13.8%, when we use the 3,4-ethylenedioxythiophene as the hole transporting the Perovskite solar cell under the AM 1.5G solar simulations. This material contains the hetrocycle so that it helps to achieve the efficiency more than 10% and this material has great tendency to replace the costly spiro- OMETAD and then we get the cheaper synthesis. [14]

Jarvist M. frost *et al.* (2014) have analyzed that methylammonium lead iodide is the mostly used hybrid Perovskite solar cell material, $CH_3NH_3PbI_3$ or $MAPbI_3$, where MA is the organic cation which is positively charged and present at the center of the lead iodide cage structure. In the mesoporous dye cell it employs as a light sensitizer and it also works as an absorber and transport layer in this cell. Here we can calculate the electronic band energies, energetic barriers in the hybrid lead iodide perovskites for the rotation, electronic cohesion energies and also the optical transitions. Here we can also shows the lattice polarization which is affected by the polar organic cation so it gives rise to the ferroelectric behavior and increases the photovoltaic performance. [15]

Jeong-Hyeok Im *et al.* (2014) have analyzed the average efficiency 12% with the new efficiency 16% than now getting the best efficiency of 17%. This much efficiency is getting by the two step spin coating method of the material $CH_3NH_3PbI_3$ cuboids by the growth of this with the controlled size. The $CH_3NH_3PbI_3$ cuboid size depends upon the concentration CH_3NH_3I . Charge carrier extraction and also the light harvesting efficiency are affected by the cuboid size. In this report we analyzed that we can achieve the 17.01% efficiency by controlling the size of cuboid during the growth time. In this paper we developed a new reproducible method for the preparation of $MAPbI_3$ based solar cell for achieving the highest efficiencies. [16]

Nakita K. Noel *et al.* (2014) have analyzed that we already obtained the power conversion efficiencies of more than 16% by using organic-inorganic lead halide Perovskite solar cells, but due to the toxicity of lead, they thought the replacement of lead is with the tin. Tin is also the member of group 14 metals and tin halide Perovskite also shows the good semiconducting behavior. But the tin is instable in its 2+ oxidation state. So here it is the challenge to improve its stability in its oxidation state. Here by using the methylammonium tin iodide Perovskite material we obtained the efficiencies more than 6% and also get the open circuit voltages over the 0.88V from the material with bandgap 1.23ev. Tin based perovskites shows the good photovoltaic properties. Sn shows the high open circuit voltage and there is less voltage loss. Sn crystallizes at room temperature and displays a strong photoluminescence at 950nm, which corresponds to onset absorption edge. For the crystal structure and purity of material x-ray diffraction is used and for the good estimation of band photo thermal deflection spectroscopy is used. [17]

Peng Qin *et al.* (2014) have studied that due to the unique electrical and optical properties, perovskites by the organo-lead halide are good for the applications of solar cell. By the last 2 years the power conversion efficiencies are increased over 15% by the organic hole transport material which uses the process of either vacuum evaporation or low temperature solution processing. But this material is expensive because its synthetic procedure is complicated and it requires high purity. So here use the hole transporting p-type material, which has effective applications and it is less expensive. The material is copper thiocyanate which is absorbed on the lead halide based Perovskite device. The power conversion efficiency obtained is 12.4% by using the process of low-temperature solution process deposition under the presence of full sun illumination. By using the copper thiocyanate, the efficiency increased through the short circuit current which is increased by 65% and open circuit potential is increased by 9%. [18]

Yixin Zhao and Kai Zhu *et al.* (2014) have studied the one step solution process for the formation of $CH_3NH_3PbI_3$ Perovskite films. In this solution add CH_3NH_3Cl with the standard $CH_3NH_3PbI_3$ precursor solution. By using the MACI, we obtained the pure $CH_3NH_3PbI_3$ and also the absorption of $CH_3NH_3PbI_3$ is increased and it also improves its coverage on the planer substrate. MACI also improves the performance of the solar cell from 2% to 12% and from 8% to 10% for the planer cell structure and mesostructured device. By the one step solution process we can control the $CH_3NH_3PbI_3$ growth for achieving the high performance Perovskite solar cells. [19]

Giles E. Eperon *et al.* (2015) have studied the working of inorganic cesium lead iodide. At the room temperature $CSPbI_3$ resides in a yellow non Perovskite phase but we also stabilize this material in the black Perovskite phase at the room temperature by the low temperature phase transition route and the processing control. In this material, the devices which are well functioning planar shows the long range hole and electron transportation. In this report we studied that organic cation is not needed, without this we get the lead triiodide Perovskite with good photovoltaic properties. In the $CSPbI_3$ devices, in the absence of organic polar molecule we observe the rate dependent current voltage hysteresis. The material $CSPbI_3$ cannot be the ferroelectric because of its space group, so in the Perovskite solar cells for the explanation of current voltage hysteresis, ferroelectricity is not needed. [20]

Mohammad Khaja Nazeeruddin and Henry Snaith (2015) have analyzed that by the methylammonium lead triiodide based Perovskite solar cells the power conversion efficiency is increased by 20% and getting the good photovoltaic properties of Perovskite devices as compare to the thin film and crystalline silicon solar cells. The long carrier lifetimes combination, electronic defects and charge carrier mobilities are responsible for the high power conversion efficiencies. The uses of this methyl ammonium lead triiodide based perovskites as a solar cell are- photo detector, light emitting diodes. But their disadvantages are that the sensitivity toward the humidity and under the heat and light conditions they are not stable. [21]

Thirumal Krishnamoorthy *et al.* (2015) have studied that Germanium is suitable element for the replacement of lead in the halide Perovskite compounds. It has suitable values of bandgap for the light harvesting. Instead of methylammonium, Cesium germanium iodide based perovskites shows higher photocurrents, but their film forming abilities and oxidizing tendencies are not so good. Cesium germanium iodide has greater bandgap than the methylammonium lead iodide. The larger bandgap materials are good for achieving high open circuit voltage, which required for making the tandem cells. Photoemission spectroscopy is used to measure the valence band energy of the Ge based Perovskite compounds. Cesium germanium iodide has stable rhombohedral crystal structure, which has been synthesized and do not shows the phase changes in the device of working temperatures. The photocurrent density of the Ge based Perovskite compounds is higher than that of the Sn based Perovskite compounds, however the solar suffered from very poor open circuit voltages. For the next time Ge based perovskites are prepared without the addition of hypophosphorus acid and take care about the synthesis atmosphere so that the precursor obtained the film quality of significant improvement. [22]

CHAPTER3

3. SCOPE OF THE STUDY

This study should be able to contribute in improving the performance and stability of Perovskite solar cell through proper choice of material for absorber layer and the optimization of process parameters. The stability of Perovskite solar cells is of ultimate priority so far as viability of the cells for long term usage are concerned.

So this study has a wide scope of modifying the processing and materials to help Perovskite solar cell evolve as an alternative to currently used Si-based photovoltaics.

CHAPTER4

4. OBJECTIVES OF THE STUDY

Currents, the photovoltaic market is dominated by Si-technology, which has its own limitation so far as the efficiency limit and cost of the solar cell is concerned. Perovskite solar cell is comparatively very new technology, which has seen a sharp growth in terms of academic interest. This technology is full of potential to provide a low cost alternative to the currently available Si-technology, however we remains a lot of challenges.

The objective of this study is to improve the performance and stability of perovskite solar cell.

CHAPTER5

5. RESEARCH METHODOLOGY

We plan to spin-coat the absorber layer of PB-based, SN-based and SN-GE based absorber layer. The optical properties will be studied using UV-visible spectrophotometer and the band gap will also be measured. The structural information will be deduced from FTIR and Raman spectra.

The analysis of properties of absorber layer spin coated with different process parameters will be done in order to find the optimum process parameters. Find the favored material for best performance of absorber layer in the perovskite solar cell.

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