ORGANIC-INORGANIC HYBRID PEROVSKITE SOLAR CELL FABRICATION

A Project Report

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(Electrical Engineering)

by

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June 2016

CERTIFICATE

This is to certify that the thesis entitled **“ORGANIC-INORGANIC HYBRID PEROVSKITE SOLAR CELL FABRICATION”** Submitted by **Deepak Tripathi, (EE14M051)** to the **Indian Institute of Technology Madras** in partial fulfilment of the requirements for the award of the degree in **Master of Technology** in **Microelectronics and VLSI** a bona-fide record of project work by him under my supervision.

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Deepak Tripathi

ABSTRACT

KEYWORDS: *Organic Solar cell; Perovskite; fabrication, Dark Current*

Solar Cells have proven to be a reliable and alternate source of energy. Various types of solar cells have been evolving over the years: p-n junction crystalline (first generation) to Dye Sensitized Solar Cells (fourth generation). The main emphasis being the cost, efficiency and environmental cleanliness while processing and over usage. Perovskite solar cells are the recent addition towards this direction. They are the fourth generation solar cells which work on the same principle as the Dye Sensitized Solar cells (DSSC). In the DSSC, the photo-generated carriers are produced with a sensitizer (dye molecules) and these carriers are collected on the sides by selective contacts. Similarly, Perovskite solar cells have an organic-inorganic hybrid Perovskite layer as the absorber and on either side of this absorber layer, lies the hole transport layer and Electron transport layer. Various material combinations have been tested. Among the several Perovskite materials studied, methyl ammonium lead iodated ($CH_3NH_3PbI_3$) shows good promise; PEDOT-PSS seems to give a good performance as hole transport layer and PCBM as ETL. In the present study, solution processed technique is chosen to prepare both $CH_3NH_3PbI_3$, PCBM and PEDOT-PSS thin films.

The main aim of the present study is (i) to optimize the thermal spin casting parameters for $CH_3NH_3PbI_3$ thin film deposition to obtain optimal thickness for good optical absorption (ii) to characterize the Perovskite layer for optical, structural and electrical properties (iii) to optimize PCBM the electron transport layer by spin coating to achieve a thickness of 30nm-50nm and (iv) to deposit PEDOT-PSS, the Hole transport layer by solution processed spin casting technique. Methyl Ammonium Lead Iodide thin film are prepared at room temperature (300 K) on ITO glass substrates by the process of sequential deposition of methyl ammonium iodide (CH_3NH_3I) and lead iodide (PbI_2) by spin casting technique. The deposition is carried out for different ratios of $CH_3NH_3PbI_3$: PbI_2: 1:1 to $CH_3NH_3PbI_3$: PbI2: 3:1. Along with the precursor ratio, the e spinning speed and annealing temperature has been varied after several trails, approximately 300nm is achieved for spinning speed 3000RPM and 35wt% solution it may be noted that $CH_3NH_3PbI_3$ thin films are hygroscopic.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABBREVIATION/ACRONYMS

EHP	Electron hole pair
DSSC	Dye sensitized solar cell
BHJ	Bulk hetrojunction
UNDP	United Nations development program
XRD	X-ray Diffraction
FF	Fill factor
SEM	Surface electron microscope
PEDOT-PSS	Poly (3, 4-ethylenedioxythiophene) polystyrene sulfonate
PCBM	Phenyl-C61-butyric acid methyl ester
΄Y-GBL	Gamma-Butyrolactone
DMF	Dimethyl form amide
DCB	Dichlorobenzene
ITO	Indium Tin-oxide

CHAPTER 1

INTRODUCTION

Energy is required to do work. In today's world energy demand is increasing rapidly because of various applications such as transportation, office requirement, domestic requirement, and industries. We can use energy in different forms for example thermal energy, nuclear energy, wind energy, mechanical energy, and chemical energy. Before industrial revolution, we used to burn wood for energy, later we burnt coal in steam engine. As human discovered internal Combustion engine, we started using Petroleum products for our energy requirements. We burnt fossil fuels (coal, petroleum and gas) to get energy directly or converted in to electrical energy then transported to consumer. However burning of fuels increases carbon footprint and more specifically increases the amount of carbon dioxide in our atmosphere that leads to problem like Global warming etc. to get clean energy, it is better to focus on renewable energy sources (wind energy, solar energy, tidal energy, hydra etc.). Among them solar energy is the most easily affordable source of energy. Solar energy is coming from sun to earth in the form of light and heat. We can deploy this energy either by converting to different form using a range of ever-evolving technologies such as solar heating, Solar photovoltaic's [1], solar thermal energy, solar architecture and artificial photosynthesis.

The Sun is powerhouse of energy. UNDP in its 2000 World Energy Assessment found that the annual potential of solar energy was 1,575–49,837EJ(10^{18} J) .Total consumption of every type of energy on this planet by human being is nearly 567.8 EJ(10^{18} J) in 2013 (given by EIA). That means Sun can solve our problem and give us clean and renewable energy for life time and free of cost. We can cultivate and harness from this energy through different techniques and one of the efficient techniques is Photovoltaic. This involves conversion of solar energy into electrical energy so we are trying to develop a technology with advantage of having light weight, thin film and low cost.

1.1 PHOTOVOLTAIC EFFECT

Solar cell works on the principle of photovoltaic effect. It takes solar irradiance as input power and provides electrical power as output. Photovoltaic world originated from two words photo (light particle) and volt (Static charge potential) .Conversion of energy from sunlight to electrical energy known as "**Photovoltaic effect**". In 1839 it was first discovered by "**Edmund Becquerel**".

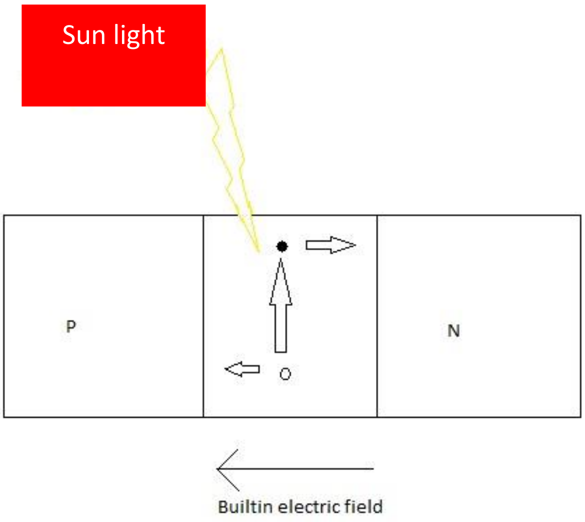


Fig 1.1 Photovoltaic effect

Principle of operation: When light photon, having energy greater than band-gap of active material, falls on the material, electron in valence band jump to conduction band leaving hole at valence band. Both electron and hole can be separated and collected at contacts with the help of built in electric field before recombination. If contacts are closed circuit and connected to a load, a current will flow in the circuit.

1.2 SOLAR IRRADIANCE

Sun can be modelled as black body with temp 5800 K, emitting Electromagnetic radiation with Peak at yellow –Green region wavelength. When light passes through earth atmosphere some wavelength we can see sharp attenuation because of absorption, solar irradiance unit is Watt/meter^2/wavelength [2].

Plank radiation law-

$$B_v(v.T) = \frac{2hvv^3}{c^2}\frac{1}{(e^{\frac{hv}{K_BT}} - 1)} \tag{1.1}$$

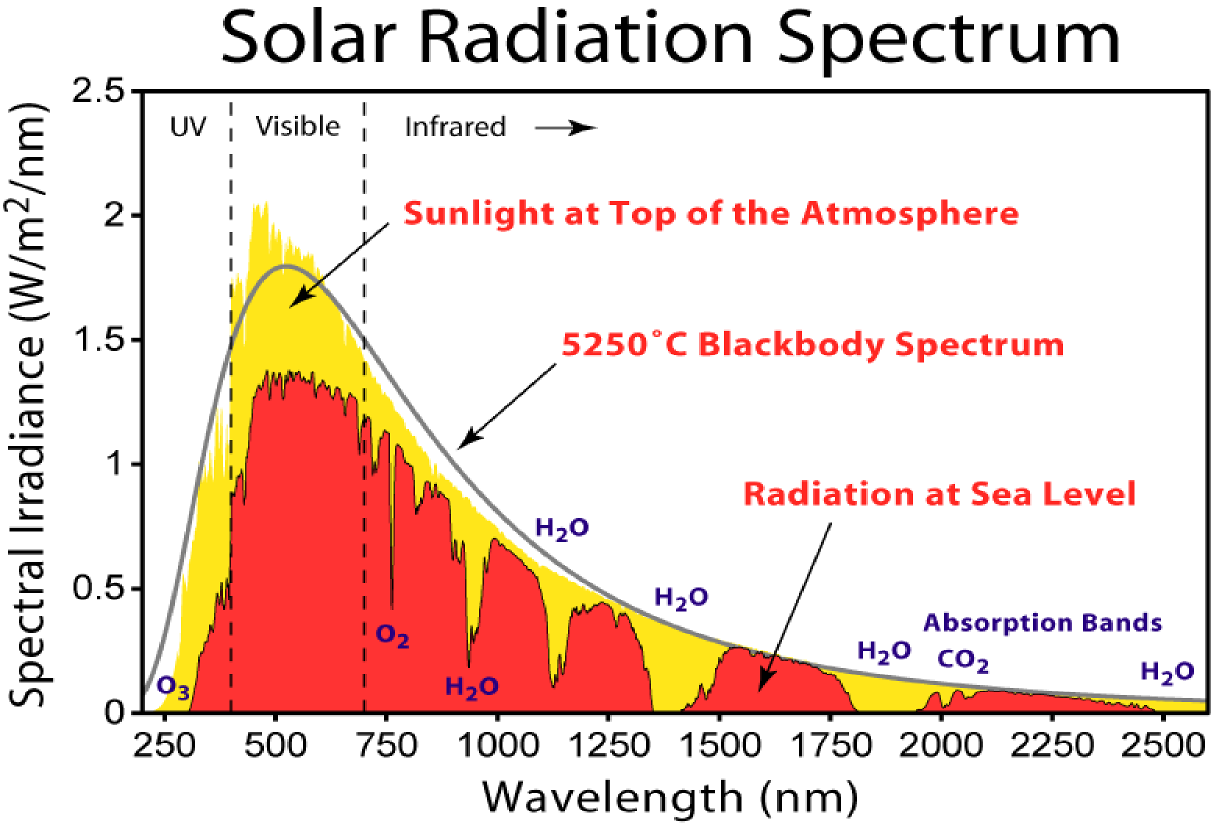


Fig 1.2 Solar radiation on earth

Solar radiation received on the surface of the earth in a clear sky day is subject to variations due to the change in the extraterrestrial radiation and two additional phenomenons:

1. Atmospheric scattering by air molecules, water and dust.
2. Atmospheric absorption by O3, H2O and CO2.

Ozone layer at 30km away from earth surface absorbs nearly all UV radiation having wavelength below 290nm coming from Sun. Similarly water vapour at 2-3 km height absorbs all infrared radiation having wavelength more than 1000nm.

1.3 AIR MASS

Air Mass is the path length taken by the light while coming from Sun through the atmosphere normal to the zenith path length. The Air Mass quantifies the reduction in the power of light as it passes through the atmosphere and is absorbed by air and dust.

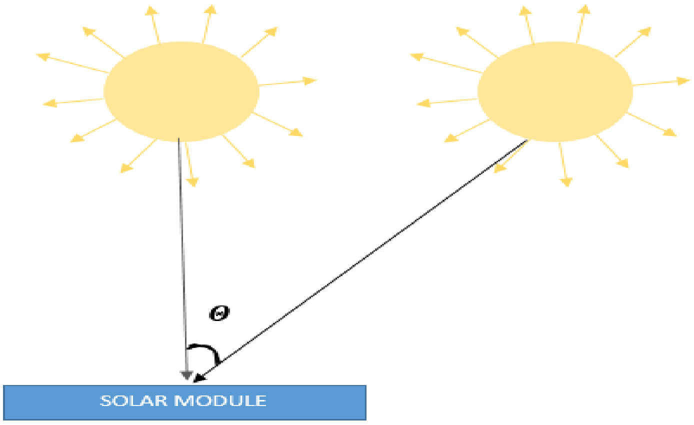


Fig1.3 Air mass

The Air Mass is defined as,

$$AM = \frac{L}{L_0} = cos\boldsymbol{\Theta} \qquad (1.2)$$

L_0--------- *Shortest path length when Sun is on top (at noon)*

L------------Path length covered by Light

1.4 TYPES OF SOLAR CELL

As time progressed different types of solar cell technologies came into existence depending on device architecture and working principle .We can divide this journey into four generations which are explained in further sections.

First generation solar cell: Journey of solar cell started with the first generation solar cell. Main work started in 1960. In this era, Solar cell mainly used for satellite applications where high stability, low efficiency and long life time were essential properties required, although Cost per watt is very high for first generation solar cell. To fulfil all the requirements we use single crystal silicon and germanium for fabrication of solar cell [1].

Second generation solar cell: These solar cells are made from amorphous silicon and polycrystalline silicon to reduce cost. Efficiency is lower than first generation solar cell. Cost per watt is lower compared to the first generation solar cell. In amorphous type of solar cell, hydrogen was introduced so that one can dope with boron and phosphorous. In polycrystalline solar cell, antireflection coating was used. The surface was textured on both sides to capture higher wavelength light by increasing path length. In CIS type of solar cell CIS (Copper Indium di-selenide) is the best absorber till now.

Third generation solar cell: There are many types in this generation .One of them is Quantum dot solar cell, in which one photon can generate multiple electron hole-pair at a time. In this generation, we started looking beyond Silicon. Organic solar cell immerged as promising alternative to above solar cells and explored in the next generation era.

Fourth generation solar cell: Today, fourth generation solar cells are the most popular structures to provide cheaper and highly efficient solar cell. Perovskite solar cells have shown promising results in terms of the cost of fabrication and efficiency. We tried to fabricate hybrid organic and inorganic material to make Dye sensitized solar cells. Perovskite solar cells are the key devices in the latest generation of solar energy. Both have similar working principle with few modifications from one to another. DSSCs emerged as new class of cells which were cheap and simple manufacturing procedures. In DSSC, addition of dye molecules in wide band gap semiconductor electrodes is the key. DSSC were first prepared by Michael Gratzel and co-workers at Ecole Polytechnique Federale de Lausanne. It is also known as “Gratzel cell”.

1.5 DIFFERENCE BETWEEN DSSC AND PEROVSKITE SOLAR CELL

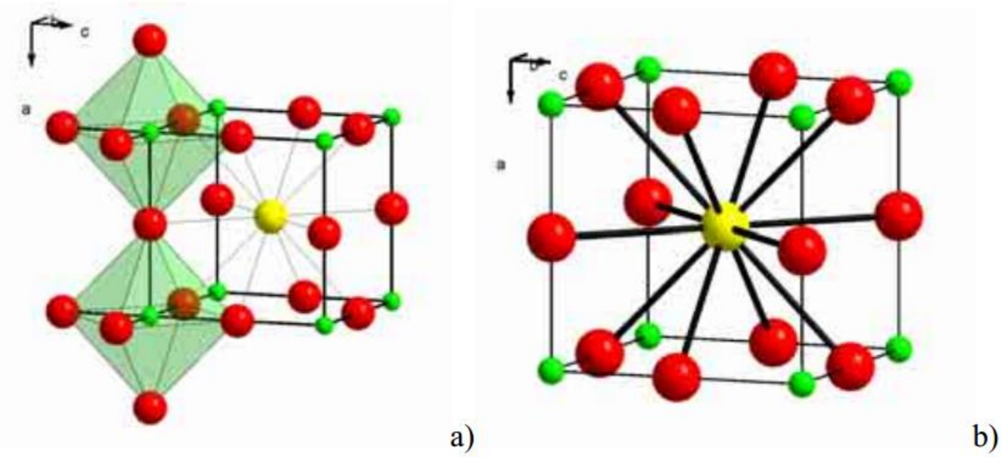
S/No	PEROVSKITE SOLAR CELL	DSSC SOLAR CELL
1	Low cost material used	High cost material use such as platinum and ruthenium.
2	No electrolyte required	Electrolyte required
3	Prepared by chemical process or physical vapour deposition	Only through Chemical route

Table 1.1 Difference between DSSC and BHJ Perovskite solar cell

Adsorption of sensitizers is necessary in operation of DSSC. Nano-crystalline TiO2 is deposited on conducting electrode to provide larger surface area which is necessary to adsorb sensitizers. As photons are absorbed, dye molecules are excited from the HOMO level to LUMO level. Injection of electron into the conduction band of the wide band gap semiconductor i.e. Nano-structured TiO_2 is followed by oxidization of the TiO_2 film. The injected electron is transported between the TiO_2 Nano-particles and then extracted to a load where the work done is delivered as the electrical energy. A mediator, for instance Electrolyte containing I^- / I_3^- is used between photo electrode and carbon coated counter electrode. Therefore, oxidized dye molecules are regenerated by receiving electrons from the I^- ion red-Ox mediator that get oxidized to I_3^- .These tri-iodide ions substitute internally donated electron with the electron from the external load and reduces back to I^- ion. The diffusion of charge compensating cat-ions in the electrolyte close to Nano particle surface accompanies the movement of electron in the conduction band of wide band gap, Nano-structured semiconductor.

Perovskite material was initially introduced into DSSC as the sensitizer. Later modifications of the DSSC lead to removal of the electrolyte and produced planar architecture cells which had Perovskite material as the absorber layer. The working principle of this Perovskite solar cell is very similar to that of a DSSC. Perovskite layer produces the electron hole pairs which are then transported to the side contacts selectively. Fourth generation solar cells have been in focus now and hence a comparison between them is inevitable.

1.6 PEROVSKITE CRYSTAL STRUCTURE



a) b)

Fig 1.4 Perovskite crystal structure

A Cat-ion --corner centre

B Cat-ion -—Body centre

X An-ion --Face centre

Perovskite is a special type of materials, having a chemical formula as calcium titanium oxide ($CaTiO_3$). Perovskite name was given by Russian mineralogist L.A.Perovski, who discovered first Perovskite mineral. In Perovskite crystal structure an-ion is oxygen. If the large oxide ion is combined with a metal ion having a small radius the resulting crystal structure can be looked upon as close packed oxygen ions with metal ions in the interstitials. This is observed for many compounds with oxygen ions and transition metals of valence +2, e.g. NiO, CoO, and MnO. In these crystal structures the oxygen ions form a cubic close packed lattice (CCP) with the metal ion in octahedral interstitials (i.e. the rock salt structure) [3].

Replacing one fourth of the oxygen with a cat-ion of approximately the same radius as oxygen (e.g. alkali, alkali earth or rare earth element) reduces the number of octahedral voids, occupied by a small cat-ion, to one fourth. The chemical formula can be written as ABX_3 and the crystal structure is called Perovskite. X is often oxygen but also other large ions such as F^- and Cl^- are possible.

ATOM	TYPE	LOCATION	NO OF ATOMS	CO-ORDINATION NUMBER
A	Cation	(0,0,0),(0,0,1),(0,1,0),(1,0,0),(1,1,0),(1,0,1),(0,1,1),(1,1,1)	8	12
B	Cation	(1/2,1/2,1/2)	1	6
X	Anion	(1/2,1/2,0),(1/2,1/2,1),(1,1/2,1/2),(0,1/2,1/2),(1/2,0,1/2),(1/2,1/2,0)	6	2

Table 1.2 Crystal structure of Perovskite

1.6.1 Factors responsible for distortion in crystal structure

There are two main factors responsible for defects and distortion in crystal structure, which are given below:

- **Jahn –Teller Effects**: In some Perovskite the distortion of the structure can be assigned to Jahn-Teller active ions at the B position. For example in LaMnO3 with Mn3+ ions the 3d4 electrons divide up into 3tg and 1eg electron. The odd number of electrons in the e.g. orbital causes an elongation of the octahedron [MnO6]
- **Size effects:** In the ideal cubic case the cell axis, a, is geometrically related to the ionic radii (r_A, r_B and r_O) as described in equation (1).

$$\boldsymbol{a = \sqrt{2}(r_A+r_B) = 2(r_B+r_O)} \tag{1.3}$$

The ratio of the two expressions for the cell length is called the Goldschmidt’s **tolerance Factor t** and allows us to estimate the degree of distortion. It is based on ionic radii i.e. purely ionic bonding is assumed, but can be regarded as an indication for compounds with a high degree of ionic bonding; it is described in equation below,

(1.4)

$$t = \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)}$$

If the A ion is smaller than the ideal value then t becomes smaller than 1. As a result the [BO6] octahedral will tilt in order to fill space. However, the cubic structure occurs if $0.89 < t < 1$ Lower values of t will lower the symmetry of the crystal structure. Since Perovskite are not truly ionic compounds and since the *t* values also depend on what values are taken for the ionic radii, the tolerance factor is only a rough estimate.

1.6.2 Material of interest

Organ-lead halide Perovskite is emerging solution process enable material with outstanding optoelectronic properties. Among them, methyl ammonium lead iodide $CH_3NH_3PbI_3$ has proven to be an exceptional light harvester for hybrid organic-inorganic solar cells, which in just four years achieved an impressive NREL-certified power conversion efficiency of 20.1%, and remarkable performance in a variety of device architectures. Thanks to their cost-effectiveness and ease of processing, hybrid Perovskite have naturally attracted a vast interest for applications beyond photovoltaic energy conversion, such as water splitting, light-emitting diodes and tuneable, electrically pumped lasers So far transport parameters of Perovskite materials were mostly deduced from the study of photovoltaic devices, which indicated bipolar transport of holes and electrons within the Perovskite active region, and long electron-hole pair diffusion length [4].

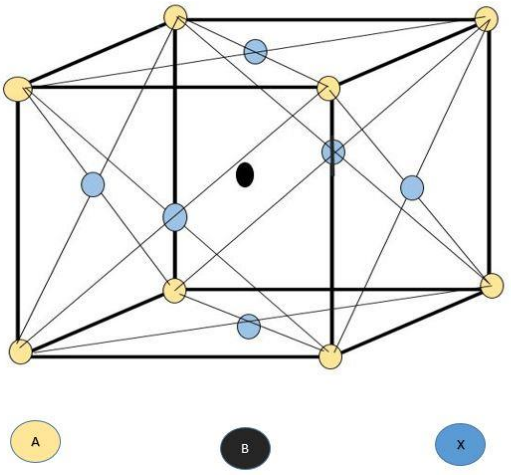


Fig. 1.5 Generalize Perovskite structure

Methyl ammonium led iodide structure is that of a Perovskite (ABX_3) .Where methyl ammonium as (CH_3NH_3) as A lead (Pb) as B and Iodine (I) as X in our crystal structure [5]

1.7 Mathematical formulations: Solar Cell

Dark Current Diode equation: When no light fall on solar cell it behaves as normal diode and act as passive device. Current increases exponentially with respect to voltage. Current and voltage relationship given below,

$$J = J_0 \left(\exp\left(\frac{V}{\eta V_T}\right) - 1\right) \tag{1.5}$$

J_0 -------*Reverse saturation current*

V -------*Applied voltage*

V_T ------*Thermal Voltage*

η--------*Ideality Factor*

Short circuit current density: Short circuit current density in solar cell is maximum possible light current when solar cell acts as current source. This current density represented as $J_{sc;}$ let's say total current J_{net}, dark current is J_{dark}, and light current is J_{light}.

Open circuit voltage: Voltage at which there is no current flow across terminals in solar cell, known as open circuit voltage. Open circuit voltage, represented as V_{oc}. This is the maximum possible voltage which we can get across solar cell as current source.

$$V_{oc} = \eta V_T \ln\left(\frac{J_{Light}}{J_0} + 1\right) \tag{1.6}$$

Fill factor: Fill factor is the ratio of area covered by V_m and J_m and V_{oc} and $J_{sc.}$ It is qualitative measure of quality of our solar cell. Fill factor is ratio of maximum possible power generate to multiplication of V_{oc} and $I_{sc.}$ Fill factor is represented by FF.

$$FF = \frac{V_m J_m}{V_{oc} J_{sc}} \tag{1.7}$$

Power conversion efficiency: Power conversion efficiency is ratio of power falling on solar cell as incoming light to maximum possible power generated as output. Power conversion efficiency is represented as PCE.

$$PCE = \frac{V_m J_m}{P_{in}} \tag{1.8}$$

External quantum efficiency: External quantum efficiency is ratio of electron collected at output per second to number of Photon having energy greater than band gap of semiconductor falling on solar cell per second.

$$EQE = \frac{Number\ of\ electron\ collected\ at\ contact\ per\ second}{Number\ of\ photon\ falling\ on\ solar\ cell\ per\ second} \tag{1.9}$$

Internal quantum efficiency: Internal quantum efficiency is ratio of electron collected at output per second to number of Photon absorbed of energy,

$$IQE = \frac{Number\ of\ electron\ collected\ as\ contacts\ per\ second}{Number\ of\ absorbed\ \ photon\ falling\ on\ solar\ second} \tag{1.10}$$

1.8 EQUIVALENT CIRCUIT DIAGRAM OF SOLAR CELL

When light fall on solar cell, EHP generated collected at contact and current flow, this current know as light current generated from solar radiation. Diode starts working as solar cell. Diode can be modelled as non-ideal current.

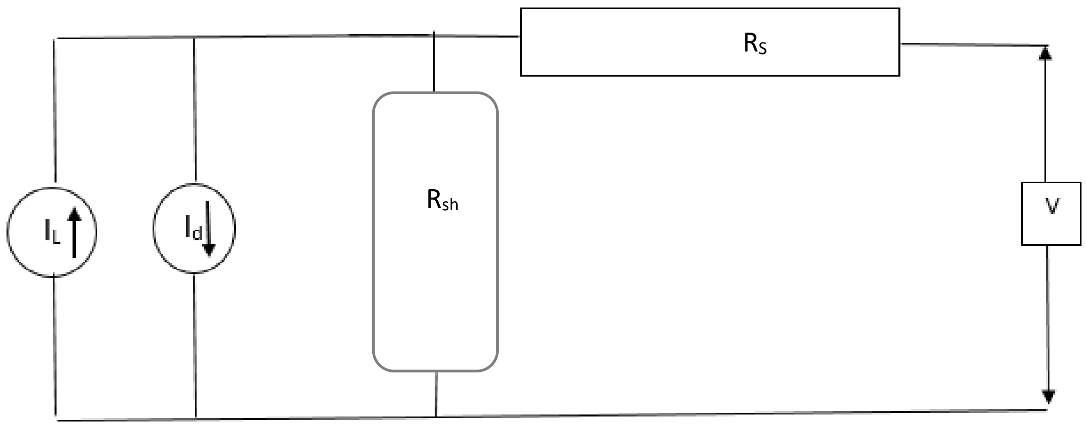


Fig 1.6 Circuit diagram of typical solar cell

Where,

I_L- *Light current*

I_d- *Dark current*

R_s- *Series Resistance*

R_{sh} -*Parallel Resistance*

R_{sh}- (Shunt Resistance): We use this resistance to model current leakage inside device because of short circuit. Ideally R_{sh} value should be as large as possible.

Rs (Series Resistance): Series resistance included in circuit equivalent of solar cell to model material resistivity of material. Resistivity property of material can be model with this resistance value. Generally in good solar cell series resistance should be as small as possible [6].

I_D (Diode Current): When we connect load parallel to solar cell. Every time dark current will flow exponential to voltage drop across solar cell. This current flows in passive direction.

I_L (Light current): When light radiation fall on solar cell, absorbed by intrinsic layer and thus EHP will generate. Now these EHP will be separated and collected at cathode and anode of our cell. Current will flow from N to P inside solar cell and outside from P to N. This value is nearly constant depends only on incoming radiation. Generally this current is constant for a particular light radiation.

CHAPTER 2

EXPERIMENTAL METHODS

2.1 INTRODUCTION

In this part of the thesis we will explain all techniques and processes used to fabricate and synthesize our different kinds of layers. This also includes explanation of working principle of different measuring instrument used in characterization.

2.2 METALLIZATION

This process to deposit film on substrate is one of the oldest technologies used for physical vapour deposition. Using this process we can achieve thickness between few Nano meters to few micrometers. Typical deposition rate we used varies between 20A^0/sec-100A^0/sec. We can form thick multilayer using different materials [7].

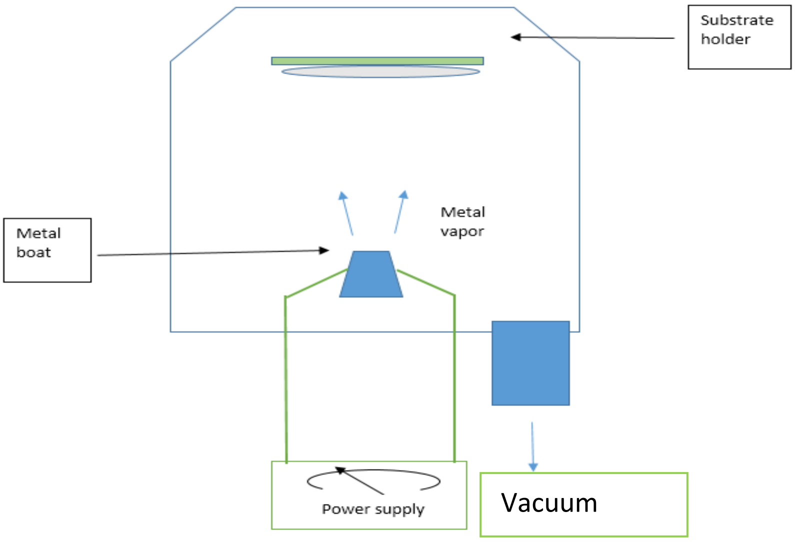


Fig 2.1 Thermal Evaporation Chamber

We place our sample on substrate holder; processed raw material is placed in a metal boat. To provide high temperature we use Tungsten wire or use high energy electron beam on source metal, so that source material gets heat up to a point and starts to sublimate. A high current flows in order of amps and according to ohmic law electrical energy gets converted into heat $(P=I^2R)$ .Now temperature of material in the boat reaches up to its melting point ,material starts to sublimate or starts melting .Kinetic energy of molecules of metal increases further. This all process is happen inside glove box and we need high vacuum and low pressure ($2*10^{-6}$mbar) for it. We do this process under high vacuum because we do not want collision between metal molecule and ambient. Low pressure and high vacuum reduces this probability .Trajectory of vaporized metal is known as “Line of sight”. During metallization substrate rotates on its axis at the speed of 60rpm -100rpm to provide equal thickness everywhere.

When metallization starts we do not want to destroy our top surface of substrate (expose to metal) because high energy vaporized atoms hit substrate and can damage substrate if they hit with high velocity. We control the rate of metallization to .02A^0/Sec up to 20nm.Once it reaches to 20nm we increase our metallization rate to .250A^0/Sec [8].

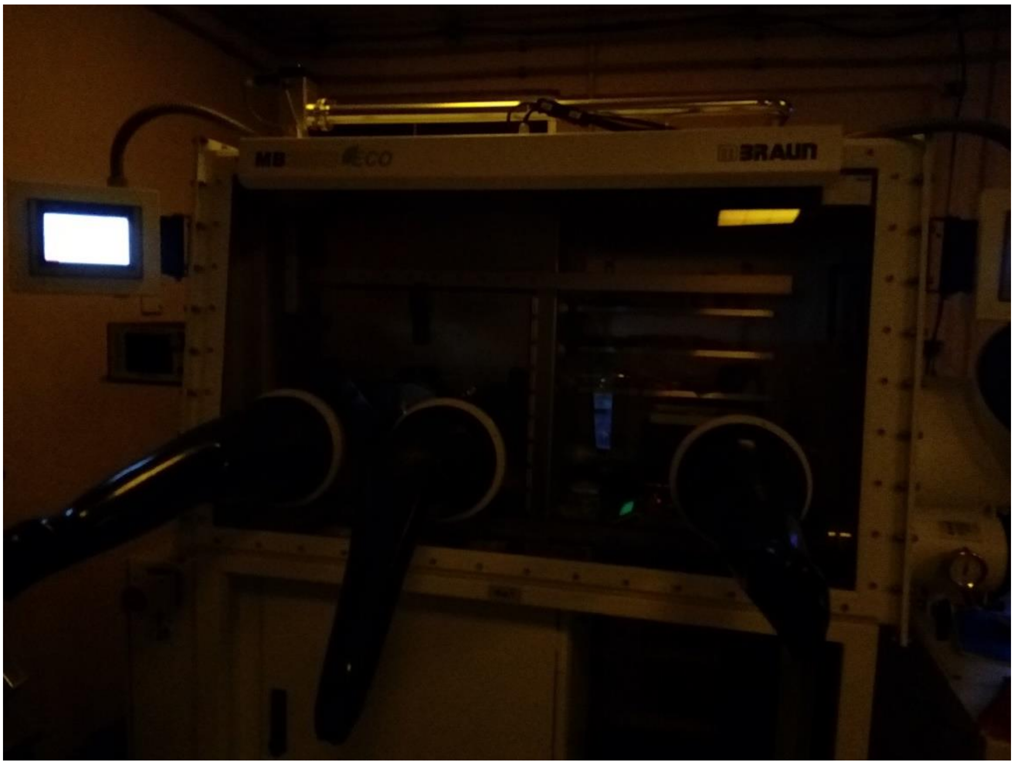


Fig. 2.2 Mbraun Metallization Box (Organic Lab- IIT Madras)

2.3 SPIN COATER

Spin coating is one of the most famous and cheapest techniques available to produce thin films. When we are fabricating our solar cell with solution processed materials, we can use this technique. We can control thickness of our layers between few micrometres to few nanometres by varying RPM and Wt. % of solute in solvent.

We put our sample on chuck and to hold substrate on it we use vacuum pump. When Chuck starts rotating, Centrifugal force starts acting on our solution and this force drives the liquid radial outward. The viscous force and surface tension causes a thin residual film to be retained on the flat substrate. The key steps involved in this deposition are [9]:

Dispense Step: This step helps to deposit resin fluid on the substrate surface. We use pipette to deposit our solution on substrate .This can be of two type Static and dynamic type.

Spin Up: Step by step we increase our RPM so that we can reach up to our desire RPM and get thin film. Generally we follow ramp variation.

Stable fluid outflow: In this stage, substrate is rotating at constant rate and fluid viscous forces dominate fluid thinning behaviour. Fluid thinning is generally quite uniform, though with solutions containing volatile solvents; it is often possible to see interference colours “spinning off”, and doing so progressively more slowly as the coating thickness is reduced. Edge effects are often seen because the fluid flows uniformly outward, but must form droplets at the edge to be flung off. Thus, depending on the surface tension, viscosity, rotation rate, etc., there may be a small bead of coating thickness difference around the rim of the final substrate.

Drying: When the switch off of the spin coater than our film starts drying. Due to loss of solvent in deposited film starts further shrinkage and Outflow due to centrifugal force stops.

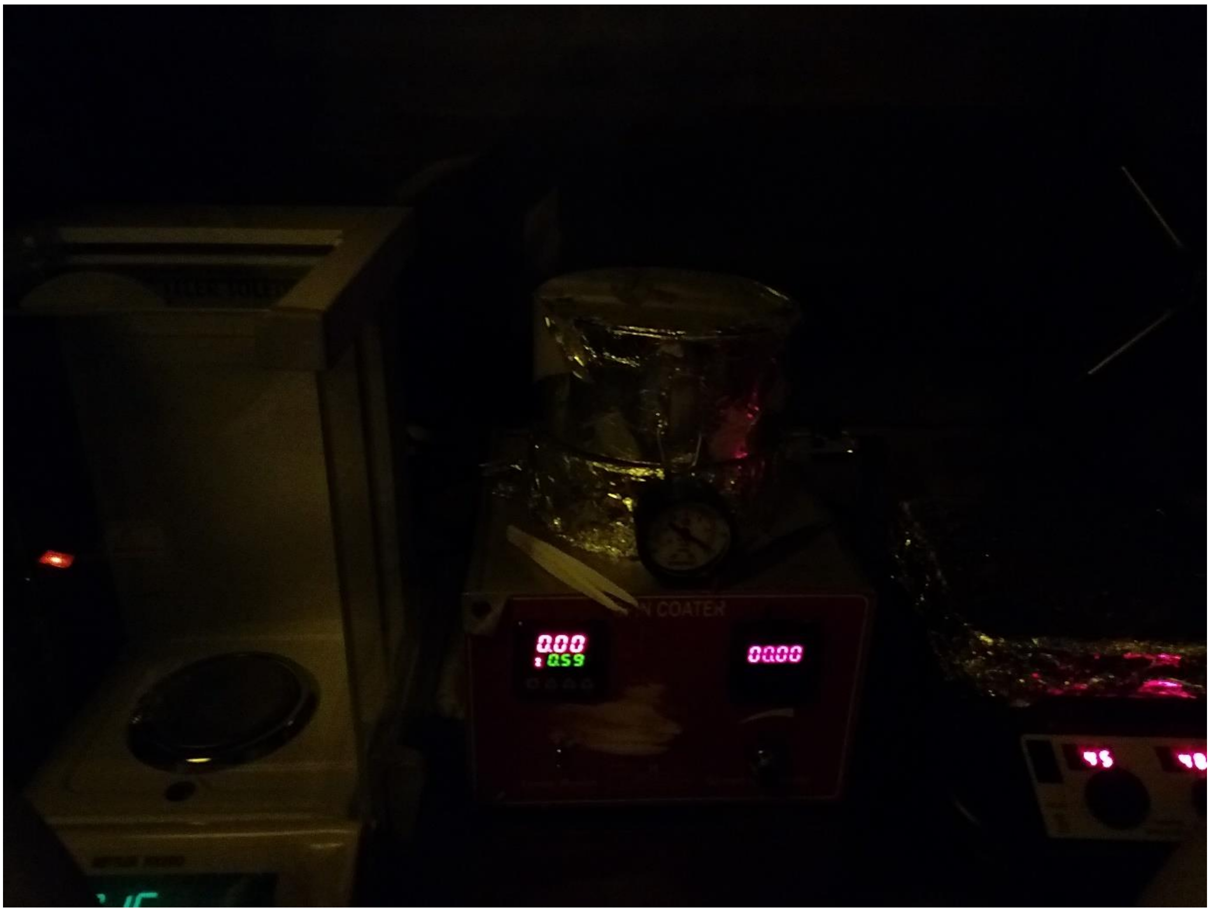


Fig. 2.3 Spin-Coater (Organic Lab- IIT Madras)

2.4 X- RAY DIFFRACTION

In X-ray diffraction process, analysis and data collection have been based mainly on one dimensional diffraction (1D) profiles .These diffraction profiles measured with scanning point detectors or linear position sensitive detectors (PSD). Therefore, almost all the x-ray powder diffraction applications, such as phase identification, texture (orientation), residual stress, crystallite size, percent crystalline, lattice dimensions and structure refinement, are developed in accordance with the 1D profile collected by conventional diffract meters. The diffraction measurement in the conventional Diffracto-meter is confined within a plane, here referred to as plane. A point detector makes 2θ scan along a detection circle. If a one-dimensional position sensitive detector (PSD) is used in the Diffract-meter, it will be mounted on the detection circle. Since the variation of diffraction pattern in the direction (Z) perpendicular to the Diffracto-meter plane are not considered in the conventional Diffracto-meter, the x-ray beam is normally extended in Z direction (line focus). The actual diffraction pattern measured by a conventional Diffracto-meter is an average over a range defined by beam size in Z-direction.

Incident X ray strikes the electrons in atoms. These electrons undergo vibrations and give out secondary circular waves emanating from each electron. This phenomenon is known as Elastic Scattering. A regular array of waves emanating from electrons produces spherical waves. These waves undergo constructive interference in some directions. These specific directions are determined by

Bragg's Law
$$n\lambda = 2dsin\boldsymbol{\Theta} \qquad (2.1)$$

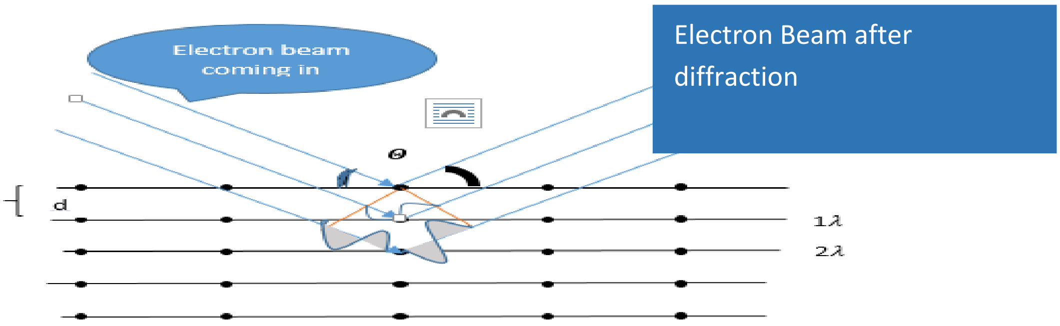


Fig 2.4 X-RAY Diffraction

In Bragg's law equation, order of diffraction is n and θ is diffraction angle. In a typical XRD pattern, the plot is obtained between the intensity and the diffraction angle 2θ. This data is then compared with the International standard database. The crystallite size is calculated using the Scherer formula: $t = 0.9\lambda/\beta\cos\theta$ B is the broadening of diffraction line measured at half of its maximum intensity.

2.5 GLOVE BOX

Perovskite is very unstable material and when we exposed Perovskite to atmosphere, degradation of Perovskite starts because it gets oxidized. To avoid humidity, Oxidation and contamination we use Glove box, inside Glove box Nitrogen is present and Oxygen level remains less than 12 PPM. Pressure inside glove box varies between 40psi -80psi.

Fig. 2.5 Glove box (Organic lab IIT Madras)

2.6 SCANNING ELECTRON MICROSCOPY

Like optical microscopy we use light, in Florescent microscopy we use Photon to illuminate object and can see it by zooming feature of Microscope, similarly in Electron microscopy we use electron for illumination. Electron microscopy can be divided into two types,

- Scanning electron microscopy
- Transmission electron microscopy

Scanning electron microscopy-(SEM):

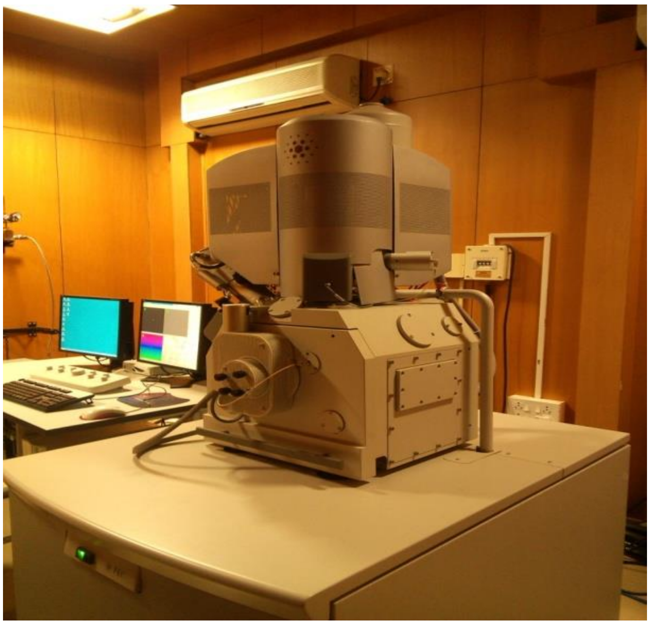


Fig. 2.6 Quanta 3D FE-SEM (NFMTC IIT Madras)

By seeing SEM images of surface we can analyse surface quality. To measure thickness of our layers we do cross-sectional SEM. In an optical microscope, the maximum level of magnification is about 1000x. To increase the resolution of microscope the wavelength of the radiation used for imaging must be reduced. In SEM we use high energy electron beam with falls on film. These electrons are high energy electrons and energy of each electron varies between 1KeV to 1MeV. If the specimen is very thin, these energetic electrons can pass through unaffected or if the specimen is thicker then these electrons are no longer transmitted and therefore only particles which are emerging from the surface can give us information.

We do study of different parameters SEM can provide information on topography, crystalline structure, chemical composition and electrical behaviour of top 1μm or so of specimen [10]. In an SEM the incident electrons have energies in the range of 2-40keV. There are three types of electrons guns used in SEM. They are tungsten hairpin filament, Lanthanum hexaboride filament and field emission guns. Two or three electromagnetic condenser lenses de-magnify the electron beam in to a fine probe which is then scanned across a selected area of the specimen surface in a raster by scan coils. The electrons penetrate the specimen in a teardrop-shaped volume whose overall dimensions are determined by the energy of the electron beam, the atomic masses of elements in the specimen and the angle at which the electron beam hits the specimen. The penetration depth increases with higher electron beam energy, incidence angle and lighter mass, e.g. 1μm into GaAs for 20keV electron and normal incidence. Whenever an electron beam interacts with the specimen it produces secondary electrons, back scattered electrons, Auger electrons, X rays and light. These are collected by various detectors. The signal from each of these detectors can be fed to a monitor, which is restored in synchronization with the electron beam. The magnification of the image is determined by the ration of the side length of the monitor display to the side length of the raster on the specimen, like other electron microscopy in SEM depends on release of electron to illuminate an object under study. But electron can heat the surface under analysis. When electron coming from source hit surface after hitting surface we can divide electron into many types as following-

- **Absorbed Electron**: Some electrons get absorbed by material under study.
- **Reflected or back scattered electron beam**: After hitting surface of the film, some electron gets reflected.
- **Secondary Electron**: Some electron with high energy when hit the surface they can transfer an electron from ground state to excited state and these excited state electron known as Secondary electron.

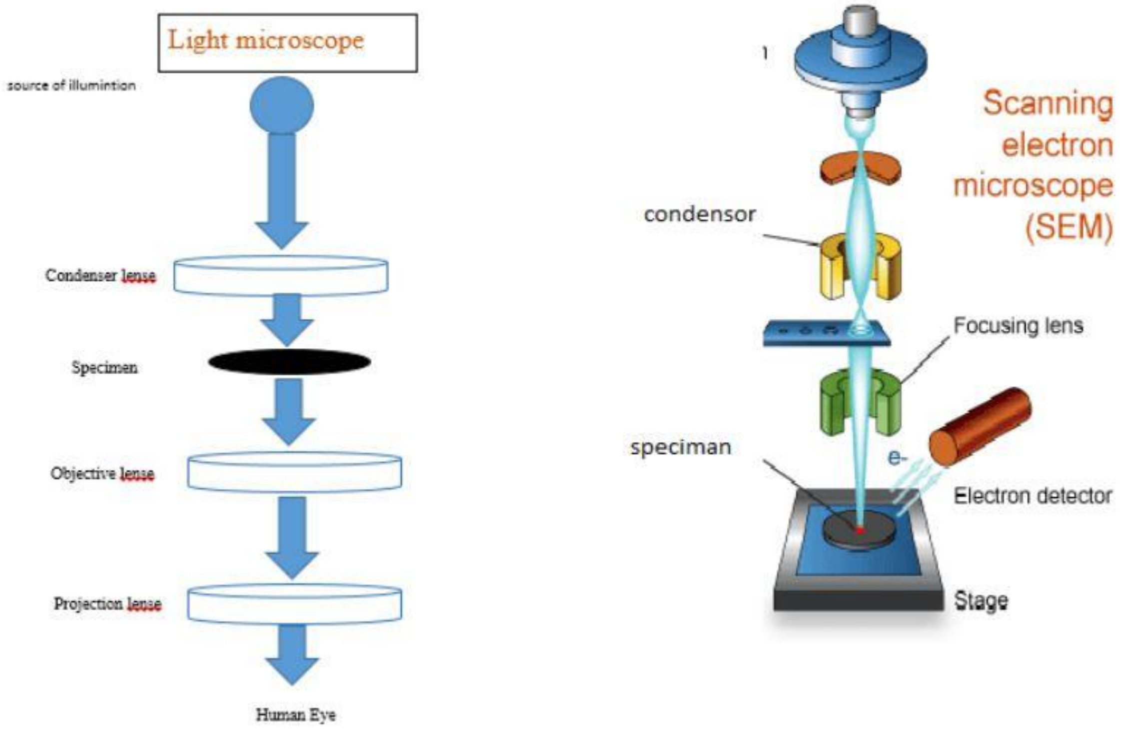


Fig. 2.7 Optical and scanning electron microscope

By detecting all types of electron and after analysis we can tell about surface structure of the molecule, as well as composition and type of molecule depending upon percentage variation. Most important types of electron as back scattered electron and secondary electron .Back scattered electron are reflected electron. Some electron gets absorbed give rise to X-ray. Generally secondary electron gets released from surface area when an electron with high energy strikes on that surface. These all types of electron collected by different detectors and after analysis we can have a clear idea of surface texture, type of molecule, and molar concentration and many more [11].

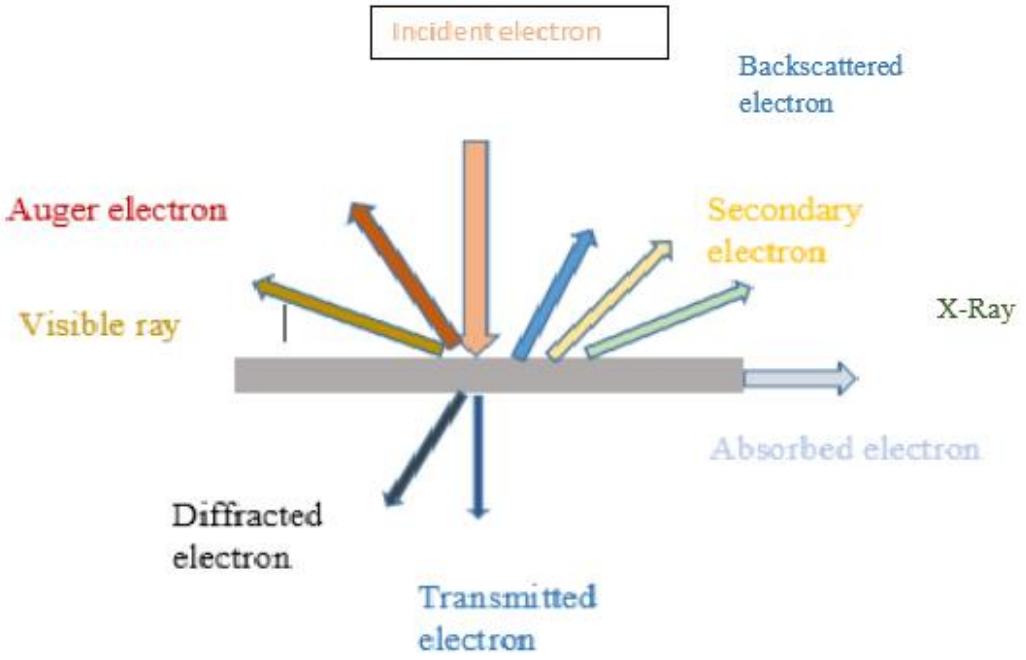


Fig. 2.8 Electron ray

2.7 UV visible spectroscopy

UV Visible spectroscopy is useful in calculating band gap calculation. We can get concentration vs. absorption graph with the help of UV visible spectroscopy. In UV Visible spectroscopy we are swapping our wavelength range from 300nm to 900nm.In UV visible spectroscopy we are producing White light with the help of Xenon and Quartz lamp. Now with the help of monochromatic light source we are selecting only one frequency at a time. When this monochromatic light pass through sample transmitted light collected at detector, detector record intensity and compare sample data with reference data.

We can do different calculation with the help of this data.

- We can calculate concentration of our solution.
- We can calculate band gap of our material using Tauc formula

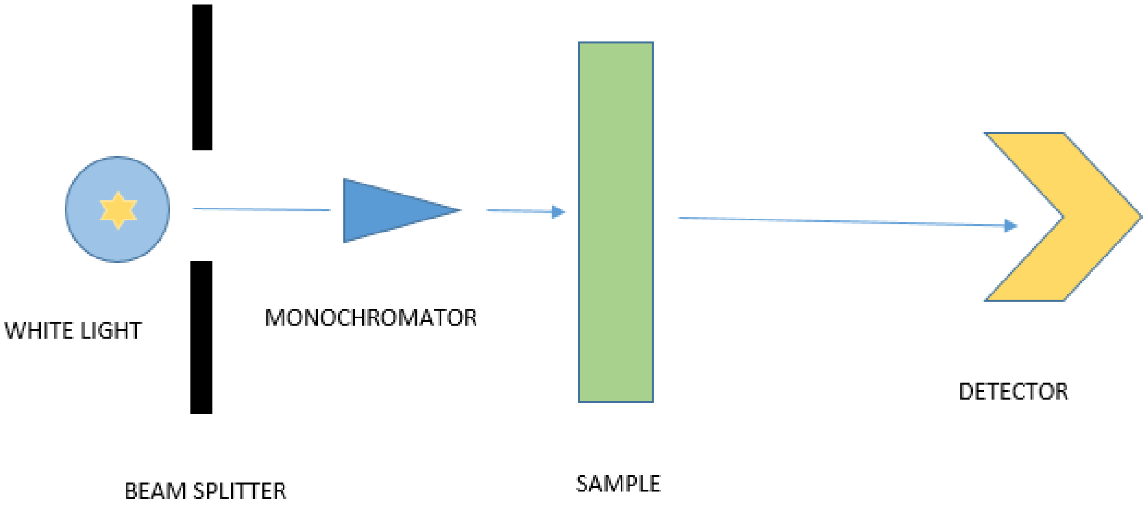


Fig. 2.9 UV Visible spectroscopy

2.8 UV O_3 cleaner

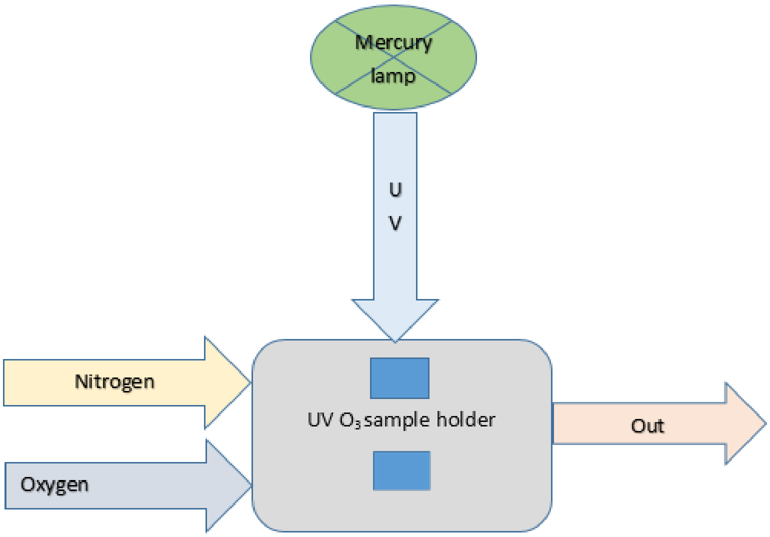


Fig. 2.10 UV O_3 Cleaner

UV O_3 cleaning is an important step in thin film fabrication. We remove molecular hydrocarbon contamination with the UV-O_3 cleaning. To make is effective and more intense we use UV radiation of wavelength of range 195nm to 254nm.When we expose UV light on substrate contaminated with Hydrocarbon in presence of Oxygen and Ozone. Hydrocarbon and other organic contamination molecule go into excited state or dissociate. Excited organic molecule reacts with Oxygen and Ozone and form volatile products and gases such as water, and carbon dioxide. These volatile products can be removed from chamber by purging Nitrogen into chamber. First purge oxygen inside chamber containing sample for 60 sec after oxygen purging switch on UV radiation source mercury lamp for 600 sec this will convert oxygen into ozone now ozone will reacts with molecular organic contamination and break them into small molecules. These small molecules can be thrown out by again purging nitrogen into chamber for 600 sec.

CHAPTER 3

FABRICATION

3.1 SOLUTION PREPARATION

PEDOT –PSS Solution: We purchased PEDOT-PSS from market. We filtered with PVDF filter of .45µm size.

Perovskite solution: We use Perovskite as intrinsic film. To make our fabrication soluble process able takes PbI$_2$ and CH$_3$NH$_3$I as solute and mixes them together into DMF or γ- GBL [3].

MOLAR RATIO CH3NH$_3$I :PbI$_2$	WEIGHT PERCENTAGE	MATERIAL QUANTITIY IN DMF AS SOLVENT		MATERIAL QUANTITY IN GBLAS SOLVENT	
1:1	45%	CH$_3$NH$_3$I	199.3mg	CH$_3$NH$_3$I	236.3mg
		PbI$_2$	577.9mg	PbI$_2$	686.6mg
		DMF	1ml	γ-GBL	1ml
3:1	45%	CH$_3$NH$_3$I	395.2mg	CH$_3$NH3I	469mg
		PbI$_2$	382mg	PbI$_2$	454mg
		DMF	1ml	γ-GBL	1ml
1:1	35%	CH$_3$NH$_3$I	131.16mg	CH$_3$NH$_3$I	155.8mg
		PbI$_2$	380.374mg	PbI$_2$	452.08mg
		DMF	1ml	γ-GBL	1ml

3:1	35%	CH_3NH_3I	260.09mg	CH_3NH_3I	308.9mg
		PbI_2	251.mg	PbI_2	298.8mg
		DMF	1ml	γ-GBL	1ml

Table 3.1 Perovskite solution

To calculate above table we used reference data for solution concentration calculations:

GBL	1129gm/litre
PbI2	461.1gm/mole
CH3NH3I	158.96gm/mole
DMF	950gm/litre

Table 3.2 Material quantity parameter

PCBM Solution:

CONCENTRATION	PCBM(IN MILIGRAM)	DCB(IN MILI LETER)
15mg/ml	15mg	1ml
20mg/ml	20mg	1ml

Table 3.3 PCBM solution

We used DCB as solvent. PCBM as solute .We mix both together put on stirrer at 45^0c for 12 hours.

Al etchant preparation: Before metallization starts every time we need to clean aluminium wire with Al etchant to remove impurity and other contamination from outer surface. We prepare solution which can work as aluminium etchant we used following recipe

CONSTITUENTS	QUANTITY
Ortho phosphoric acid	114ml
Acetic acid	22.5ml
Nitric acid	4.5ml
DI water	7.5ml

Table 3.4 Aluminium etchant

3.2 PROPOSED STRUCTURE

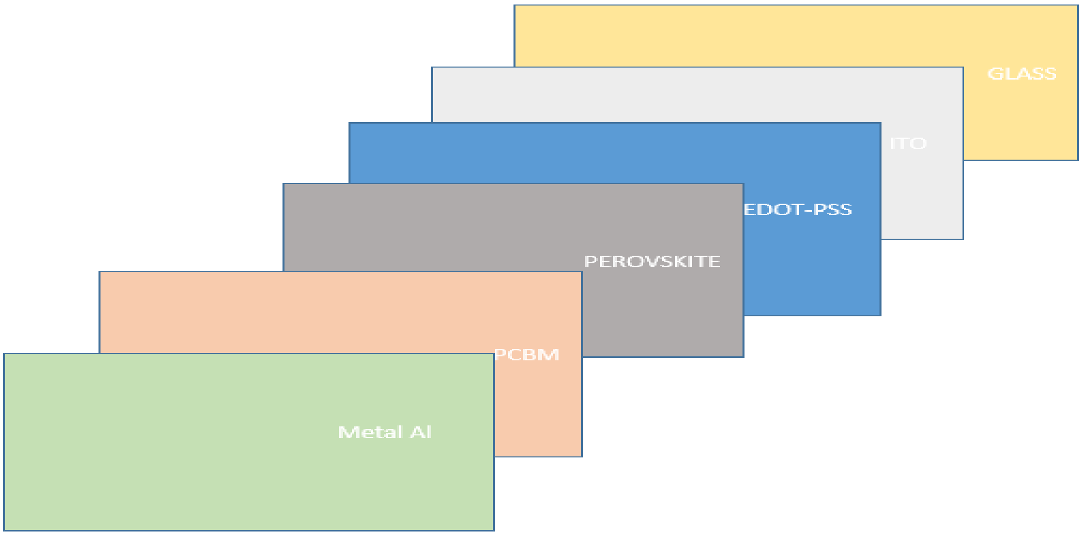


Fig. 3.1 proposed structure

To fabricate our solar cell we choose planer regular P-I-N structure with five different layers.

1. Glass substrate
2. ITO
3. PEDOT-PSS
4. Perovskite
5. PCBM
6. Aluminium

PEDOT-PSS acts as hole transport layer and electron blocking layer at same time. Perovskite acts as intrinsic layer absorb most of the light. PCBM acts as electron transport layer (blocking layer). Lithium fluoride acts as buffer layer between Perovskite and Aluminium. As top layer we use aluminium acts as cathode in our device.

3.3 CLEANING AND ETCHING OF ITO SUBSTRATE

Glass ITO substrate cutting:

First we cut our Glass substrate into small pieces with the help of Diamond cutter as square having length of every side 2.3 centimetres.

ITO etching:

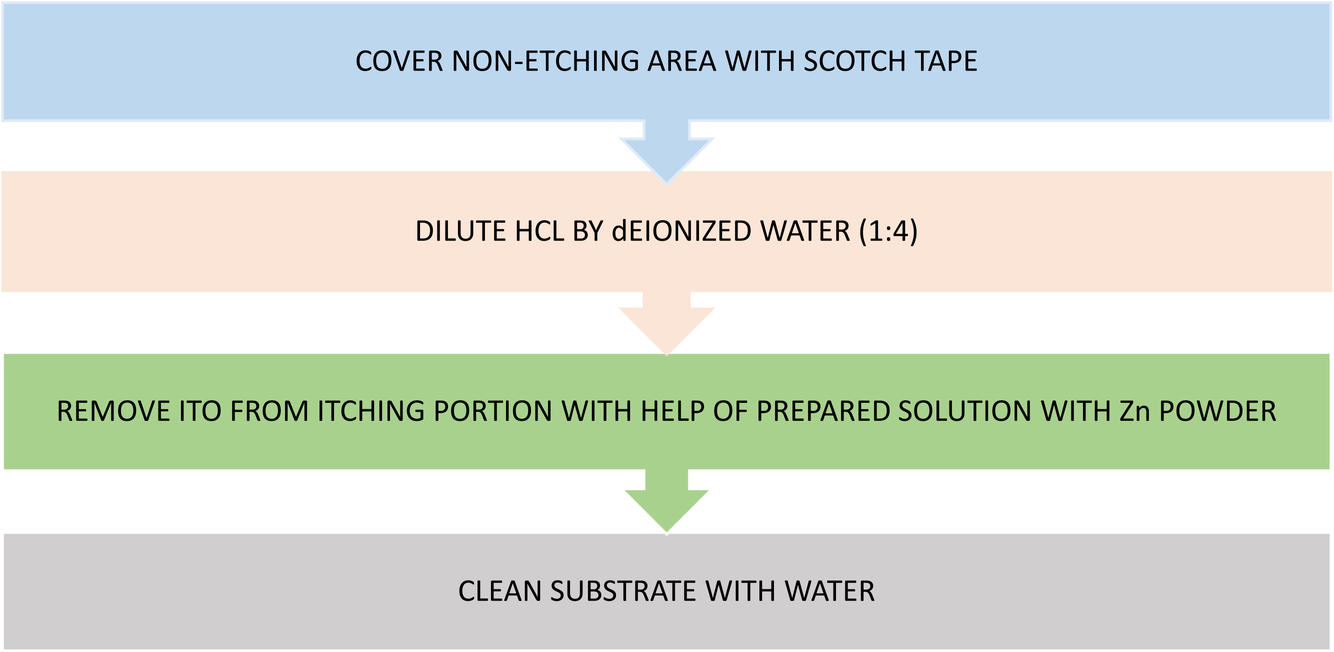


FIG. 3.2 Etching ITO process char

As shown in above figure first covered unwanted area which we do not want to itch cover with scotch tape. We take anhydrous HCl and make it dilute HCl (1:4) with help of deionised water. Rinse cotton bud into diluted HCl and drop some Zn powder on itching portion of substrate. Now rub exposed surface slowly with cotton. Solution reacts with ITO and able to remove ITO from glass substrate. Once ITO get remove from Substrate we can see difference in colour and conductivity between itched portion and non-etching portion. We now clean our sample substrate with water. After cleaning with water three or four times, we remove scotch tape from substrate.

ITO Cleaning:

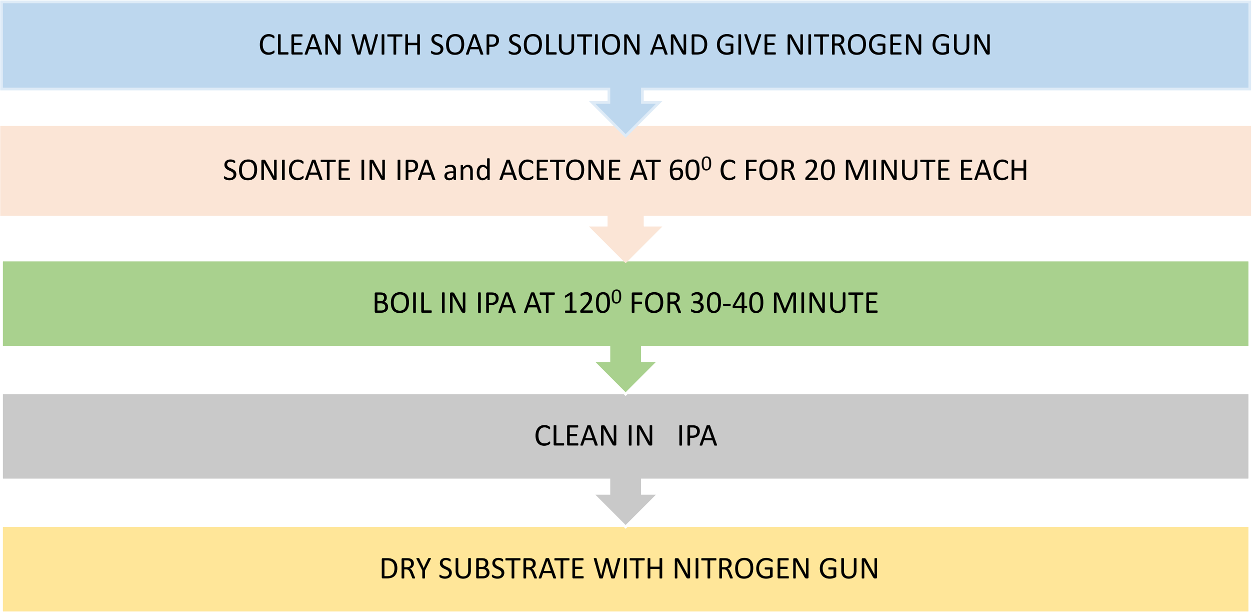


Fig 3.3 Cleaning ITO substrate

After etching ITO from side walls, we start cleaning our sample substrate to remove dust and contamination from our substrate to get good film on it. First we clean our sample with soap solution with the help of brush. Now after cleaning with soap solution we dip into Deionised water Three or four times to remove soap from our substrate. To dry our sample we use Nitrogen gun. After cleaning with soap solution, give Ultra-sonitation to agitate dust particle from glass substrate. In Sonication we use frequency more than 20 KHz. First Ultra-Sonication in Acetone at 60^{0}C for 20 ~30 minute, now we will do in IPA (Iso propyl alcohol).

After Sonication we boil our samples in IPA to remove oil, and other impurities .We boil our samples at 120^0C for 45 minute. After boiling our samples we clean them in IPA. After rinse our sample in IPA we give Nitrogen gun to make them dry and clean.

UV-O_3 cleaning

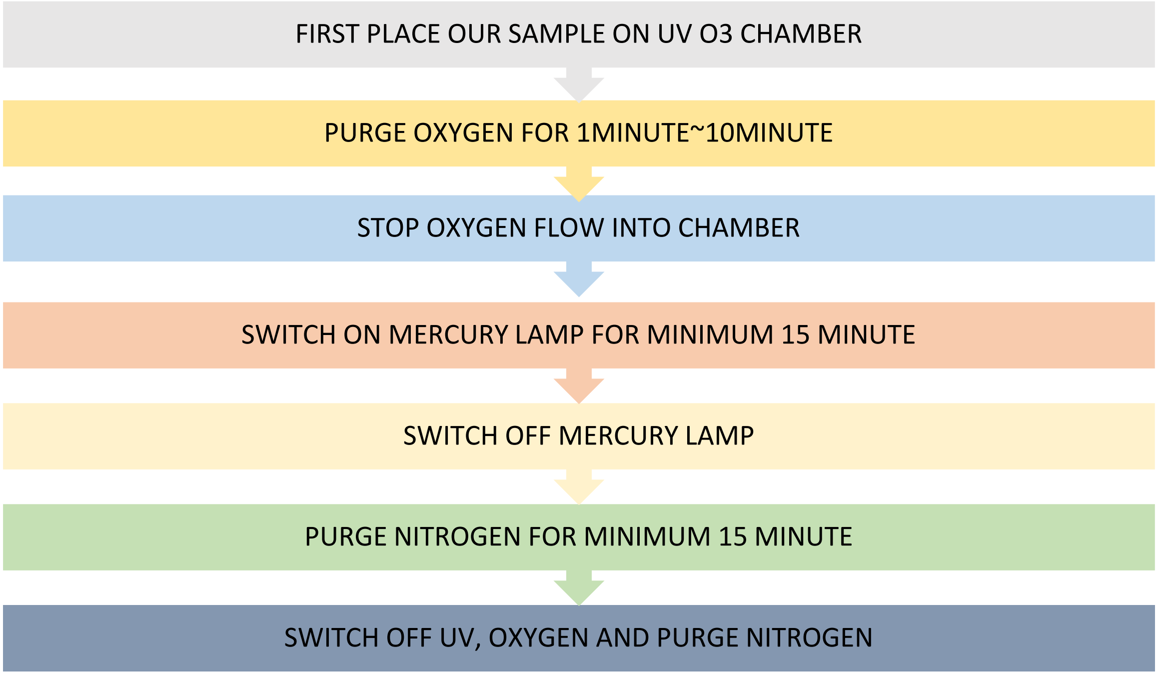


Fig. 3.4 UV O_3 Cleaning

As shown in above figure first we will place our sample in UV-O_3 chamber .Process will starts with nitrogen purging into chamber for 60 sec. After purging oxygen mercury lamp go switch on for 600sec. UV radiation will fall on oxygen and convert it into ozone. Ozone is very reactive and remove organic molecule into small molecule like CO_2, H_2O .To remove contamination from sample substrate we again flow nitrogen inside chamber for 600 sec. Now after this whole process we take out our sample from UV-O_3 cleaner

3.4 SPIN COATING

PEDOT-PSS:

PARAMETER	VALUE
Spinning speed (in RPM)	4000~5000
Spinning time	60sec
Ramp	10sec
Annealing temperature	120^0c~150^0c
Annealing time	10 min ~30 min
Removal of unwanted PEDOT-PSS	With H_20 and cotton bud.

Table 3.5 PEDOT-PSS spin coating parameter

This layer works as hole transport layer (HTL) and electron blocking layer (EBL) .We purchase PEDOT-PSS solution directly from market and used it. First we place our cleaned sample substrate on chuck .Now with the help of vacuum pump; we hold our sample on rotating chuck. Now we select speed 4000 ~5000RPM with ramp of 10sec. Before 10 Sec we drop 70µl filtered PEDOT –PSS on sample with help of Pipette. Now for remaining 50sec our sample rotates at 4000~5000 RPM .After spinning

After spinning for 60sec remove sample from spin coater and anneal it at 120^0c~150^0c.After annealing we remove PEDOT-PSS with deionised water from unwanted place (ITO itched area) by cotton bud. Again after removing PEDOT-PSS from unwanted area we again anneal sample at 120^0c~150^0c for 10 min ~30 to dry and improve thin film.

Perovskite:

PARAMETER	NUMERICAL VALUE
Spinning speed (in RPM)	2500~3500
Spinning time	60sec
Ramp	10sec
Annealing temperature	90^0c~150^0c
Annealing time	10 min ~60 min
Removal of unwanted PEDOT-PSS	With DMF or GBL and cotton bud.

Table 3.6 Perovskite film synthesis parameter

Perovskite material acts as intrinsic layer in solar cell. Perovskite material use in fabrication process is Methyl ammonium lead iodide ($CH_3NH_3PbI_2$).We purchased methyl ammonium iodide and lead iodide .We made equimolar, and 3:1 molar solution with different concentration (35wt%, 45wt%) in different solvent (GBL, DMF). After preparing solution take 60µl~70µl into pipette and drop on sample coated with PEDOT-PSS. Now place our sample on chuck. Use vacuum pump to hold sample with the help of vacuum at the time of spinning. Select Spinning speed 2500rpm~3500rpm for 60sec with ramp of 10sec. After depositing Perovskite sample colour changes into yellow colour [5].

After coating material anneal sample on hot plate at temp 90^0c~150^0c for variable time period from 20 min to 60 min. Annealing helps in crystallization and we can confirm it by seeing change in colour from yellow to black. Once colour of layer change into black we stop annealing and cool sample at room temp for 10 min.

After Annealing remove Perovskite material from unwanted area by cotton bud and solvent (GBL, DMF). Once we removed material from unwanted area we again anneal sample.

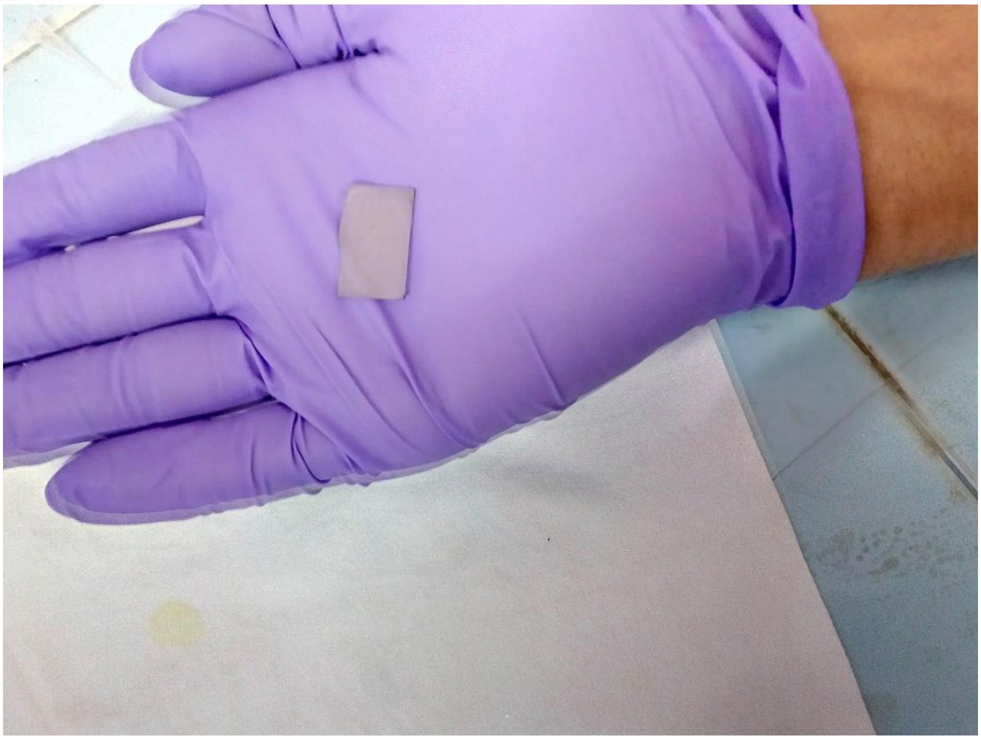


Fig. 3.5 Perovskite thin-film (annealed at 90^0 C for 40 min.)

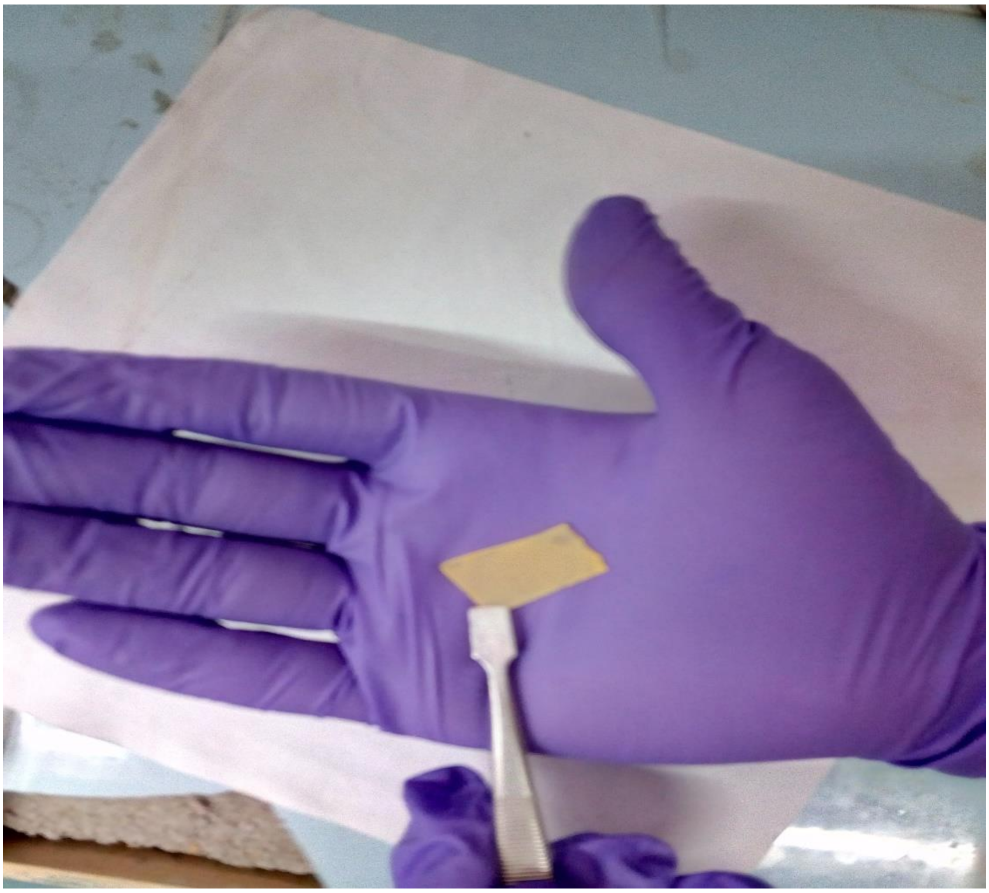


Fig. 3.6 Perovskite thin-film (annealed at 120^0 C for 20 min.)

PCBM:

PARAMETER	**NUMERICAL VALUE**
Spinning speed (in RPM)	900~1100
Spinning time	60sec
Ramp	10sec
Annealing temperature	90^0c~120^0c
Annealing time	10 min ~30 min
Removal of unwanted PEDOT-PSS	With DCB

Table 3.7 PCBM thin film synthesis parameter

PCBM acts as electron transport layer and hole blocking layer. PCBM is derivative of Fullerene. Fullerene is highly conducting layer but not soluble in organic solvent, to make it soluble we add organic chain (methyl group) to make it soluble into organic solvent. We purchase our material from Sigma–Aldrich. Prepare solution of different concentration 15mg/ml~30mg/ml. Now take 55µl ~65µl into pipette. Place our sample on chuck .Hold sample by creating vacuum with the help of vacuum pump. Drop solution on top of Perovskite layer. Spin sample at spinning rate of 900rpm~1100rpm for 60sec with ramp of 10sec. After successful spin coat PCBM anneal sample at 90^0c~150^0c for 10min~20min.Remove PCBM from unwanted place with help of DCB. Again anneal sample.

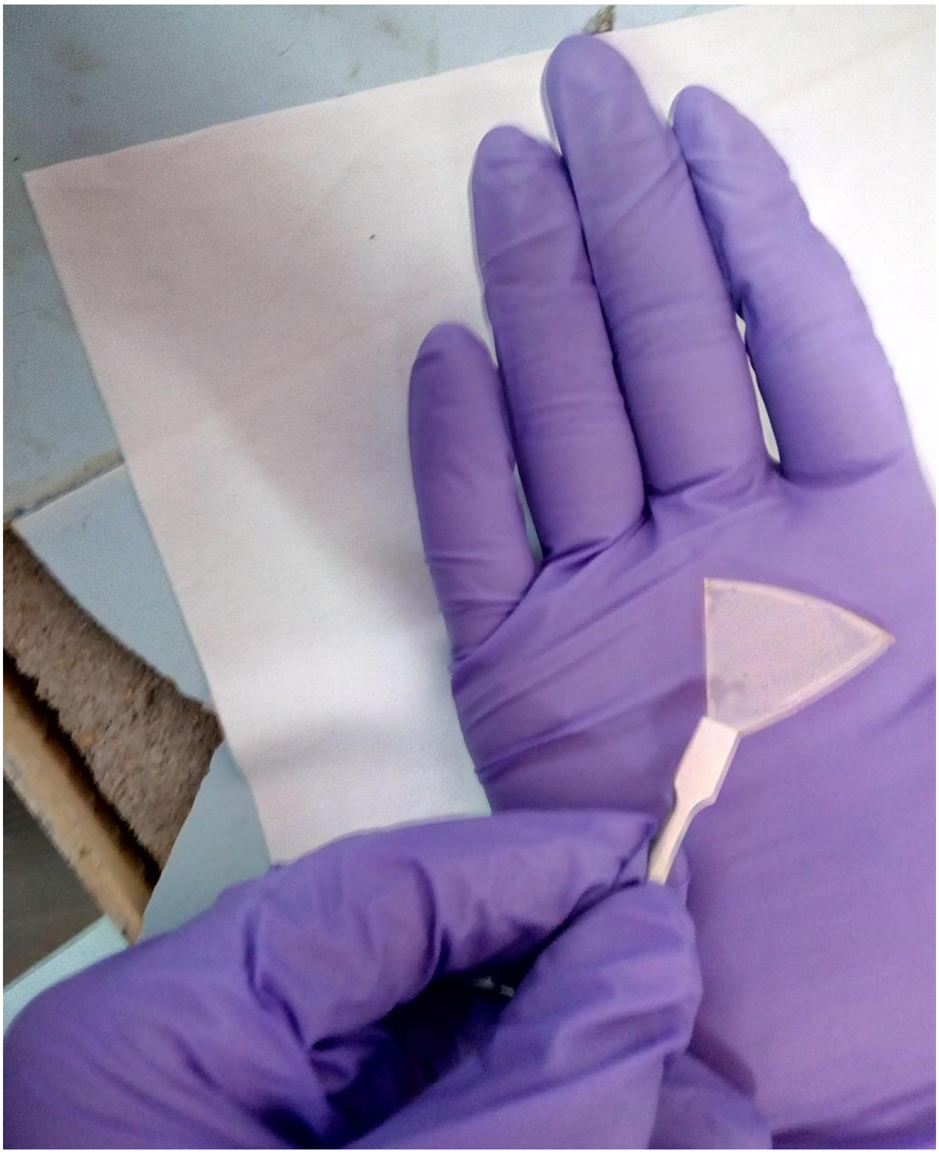


Fig 3.7 PCBM thin-film (annealed at 90^0 c for 60 min.)

3.5 PHYSICAL VAPOR DEPOSITION

LiF as buffer layer: Lithium fluoride is insulator in nature. We will use this layer as buffer layer to improve flatness of our film which helps in metallization. This layer avoids Al penetration into PCBM. First we put our sample substrate on substrate holder. This layer thickness varies from 2nm~5nm. We put lithium fluoride on chromium boat inside metallization chamber. We do this process in high vacuum to avoid collision. A high current flows through boat and dissipate high energy which starts sublimation or melting [6].

Once sublimation starts, molecule with high energy reach to top surface or our sample substrate. At starting time we do not open substrate shutter because of instability inside chamber. When pressure reaches up to $2 * 10^{-6}$ mbar, we open substrate shutter. Now molecule hit surface of perovskite it can damage our layer to avoid it initial time do vapour deposition slowly by controlling current and voltage.

Metallization: We select Aluminium as top layer of solar cell. We clean aluminium wire with aluminium etchant. We dip aluminium wire into Al etchant and boil it for 20 min at 150^0c. We can see cleaning by seeing grey colour .It will remove Al_2O_3 and other contamination from outer surface of aluminium wire.

Put clean aluminium wire on aluminium boat. Put sample on substrate holder. Create high vacuum inside metallization chamber. Now start flowing high current through aluminium boat. This high current will starts sublimate and melting of aluminium. Aluminium molecule having high kinetic energy will attack on lithium fluoride layer. To avoid lithium fluoride layer damage initially rate of deposition should be small. When thickness of aluminium reaches up to 20 nm, we can increase our rate of deposition by increasing current flow into circuit. We do metallization of thickness varying from 50-100 nm.

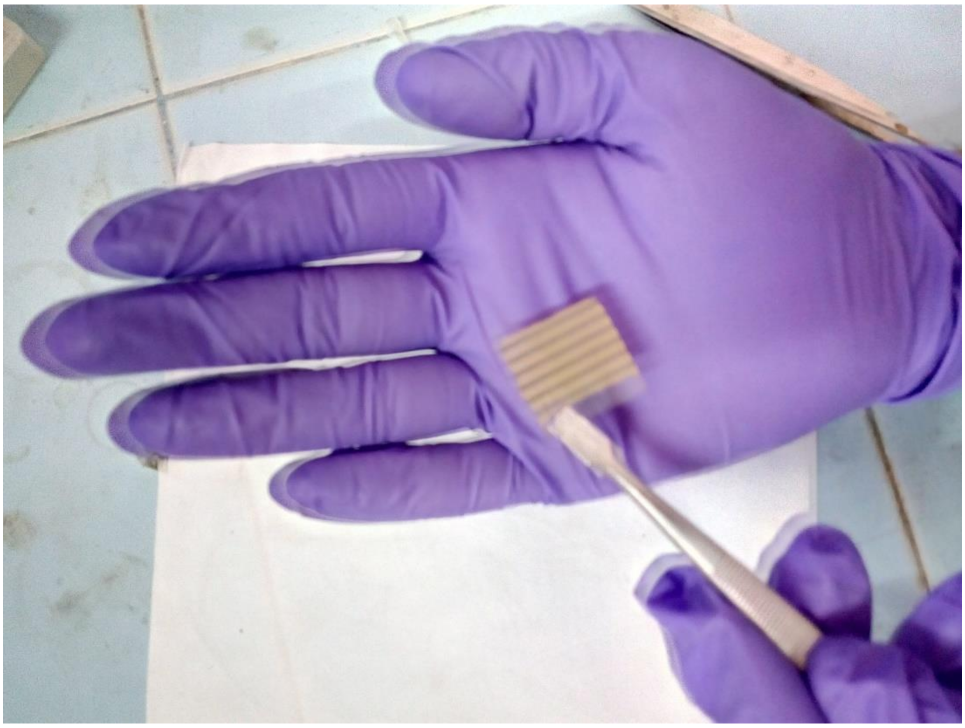


Fig. 3.8 Solar cell after metallisation (Al metal)

CHAPTER 4

RESULT AND ANALYSIS

4.1 UV VISIBLE SPECTROSCOPY

S/N	SPINNING SPEED	CONCENTRATION
1	2000	1:1 Equimolar 45wt% in GBL

Table 4.1 UV Visible Spectroscopy (Perovskite thin film)

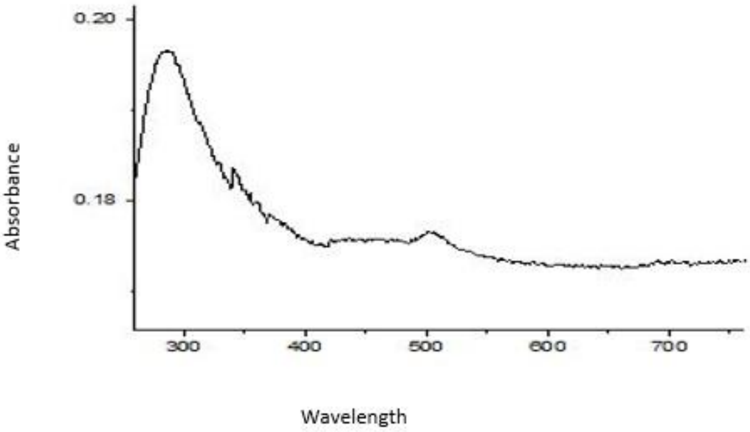


Fig. 4.1 UV-Vis absorbance Perovskite (equimolar45 wt% in GBL)

Conclusion: As we know band gap of methyl ammonium lead iodide can be vary from 1.55eV to 2.29 eV by varying composition of lead iodide and methyl ammonium iodide. As we can see in above fig. it covers whole visible spectrum.

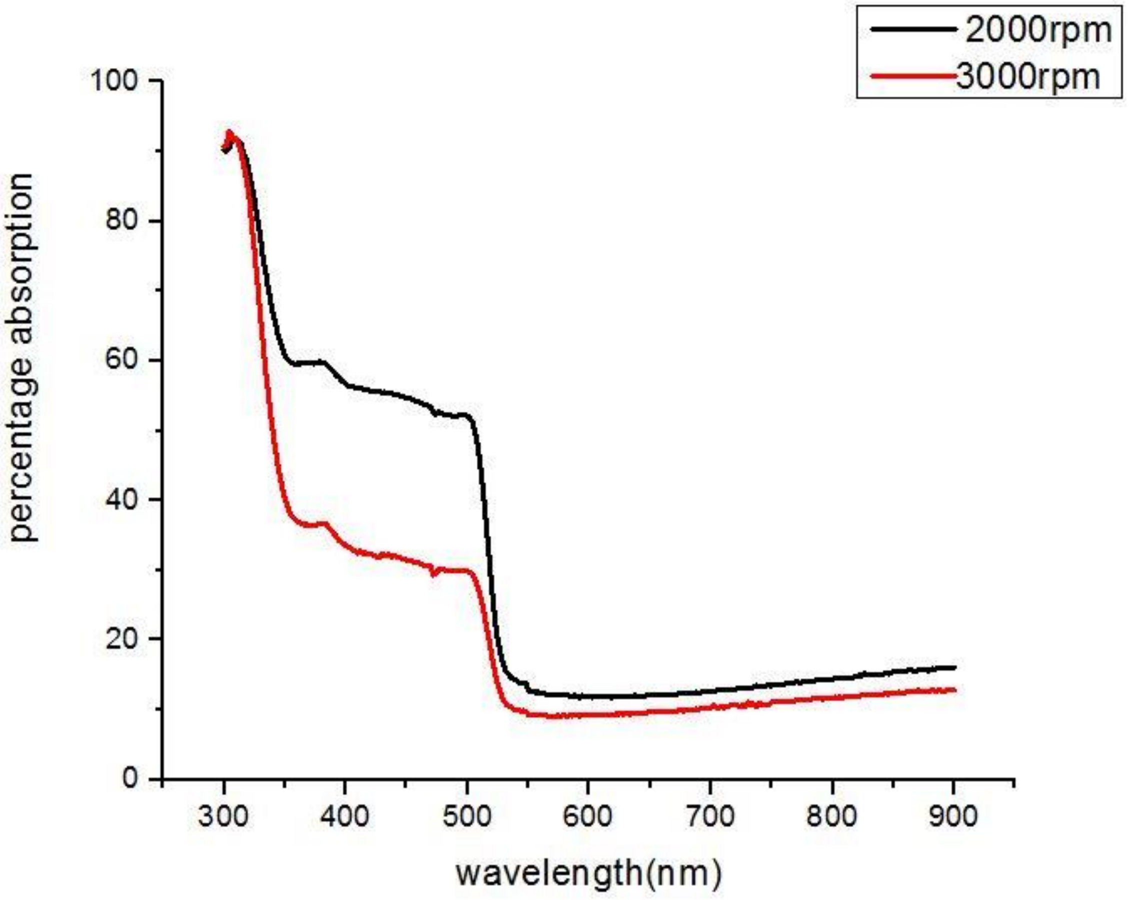
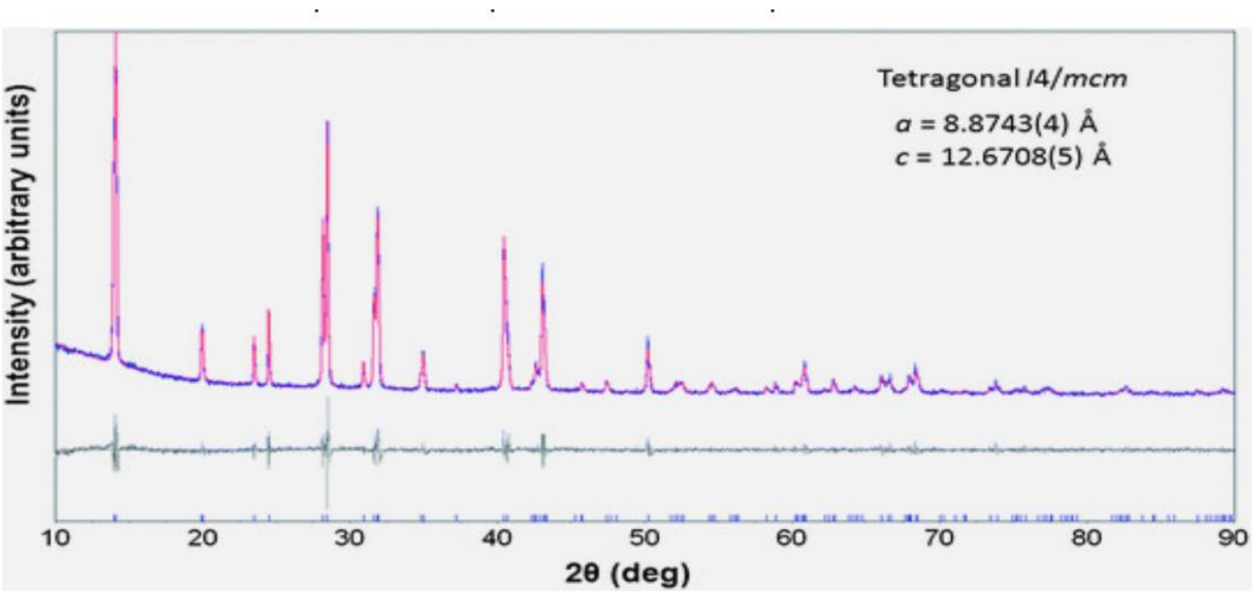


Fig. 4.2 Absorption (Bentham instruments)

Conclusion: From above figure we can clearly tell as spinning speed is increasing thickness of active layer decreasing. There is a transition in absorption graph at 550 nm, so this is critical wavelength. Below the critical wavelength there is large absorption and for wavelength larger than critical wavelength absorption is less.

4.2 XRD RESULT



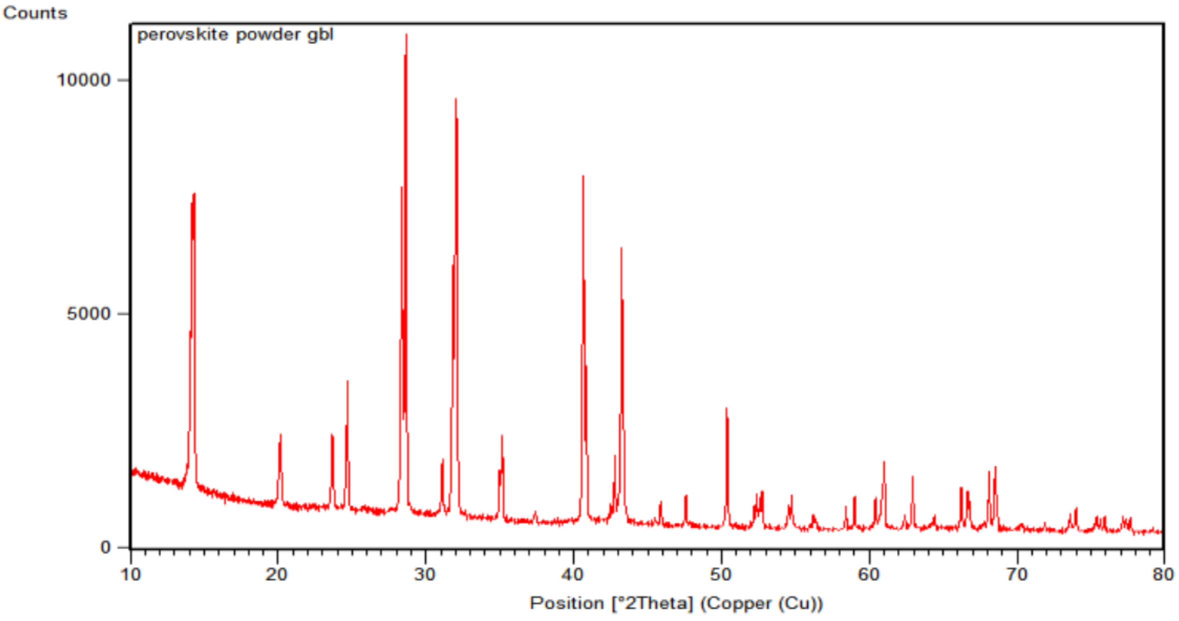


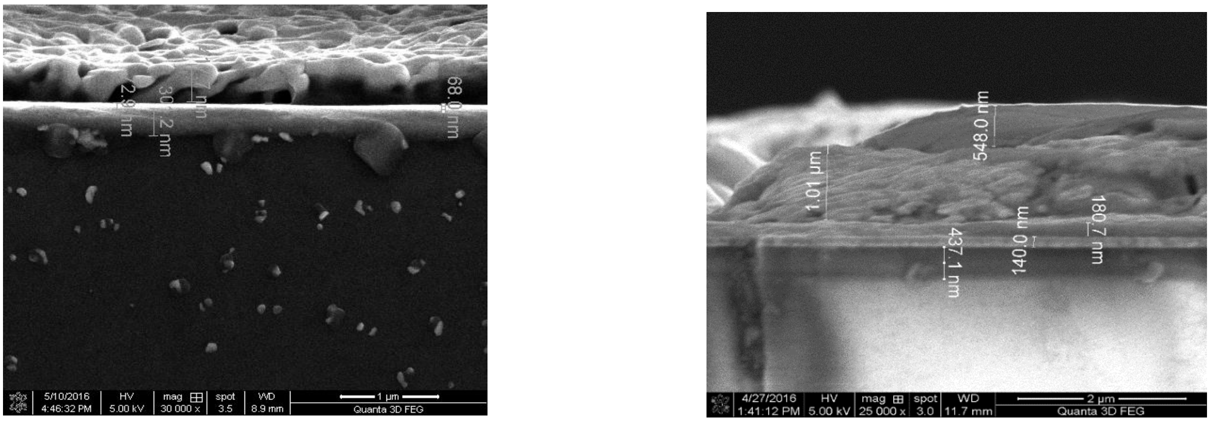
Fig. 4.3 XRD result of Perovskite

Conclusion: Our standard and sample results both are matching. Only at Lead Iodide peak at 16 ^{0} is less compared to standard result due to less concentration of lead in our sample.

4.3 CROSSSECTIONAL SEM RESULT

PERVOSKITE SOLUTION	SAMPLE1	SAMPLE 2
Spinning speed in rpm	2500	1000
Solution	1:1(45wt%inGBL)	1:1(45wt% in DMF)

Table 4.2 Cross-sectional SEM



Sample 1 sample 2

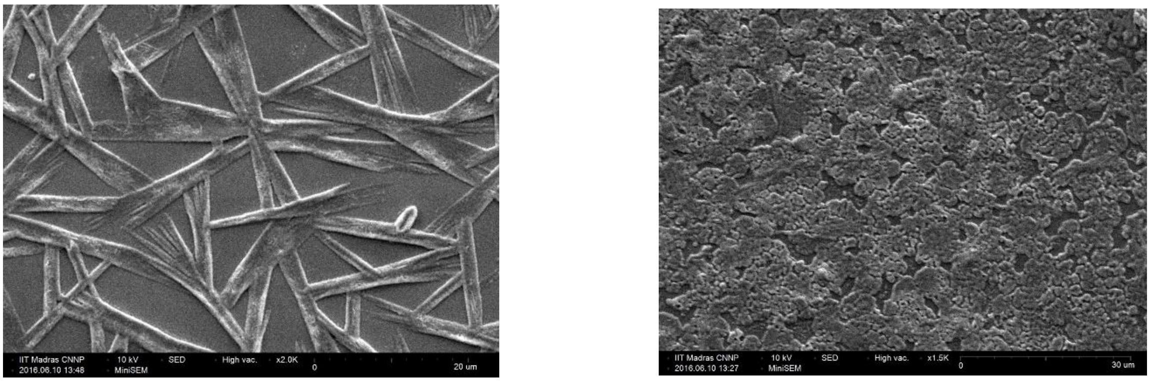
Fig. 4.4 Cross-section SEM image of Perovskite

Conclusion: We can see from figure we followed same process to fabricate our device only changed process steps for perovskite layer. In sample 1 we coated our material at 1000 rpm and 2500rpm for sample 2.As we are increasing our spinning speed we can see variation in thickness. At 1000 rpm we get thickness in the range of micrometers. At 2500 rpm we get thickness less than 500 nm . we can vary thickness by either varrying spining speed or concentration of perovskite solution. Optimum thickness is 250~350nm for optimum result. So increase rpm to 3000 rpm or reduce concentration of solution to get desired thickness.

4.4 SURFACE SEM RESULT

SAMPLE NUMBER	SPINNING SPEED IN RPM	PEROVSKITE SOLUTION
Sample 1	3000	3:1 MAI:PbI$_2$ 35 wt. % In DMF
Sample 2	3000	1:1 MAI:PbI$_2$ 35 wt. % In DMF

Table 4.3 Surface SEM



Sample1 Sample 2

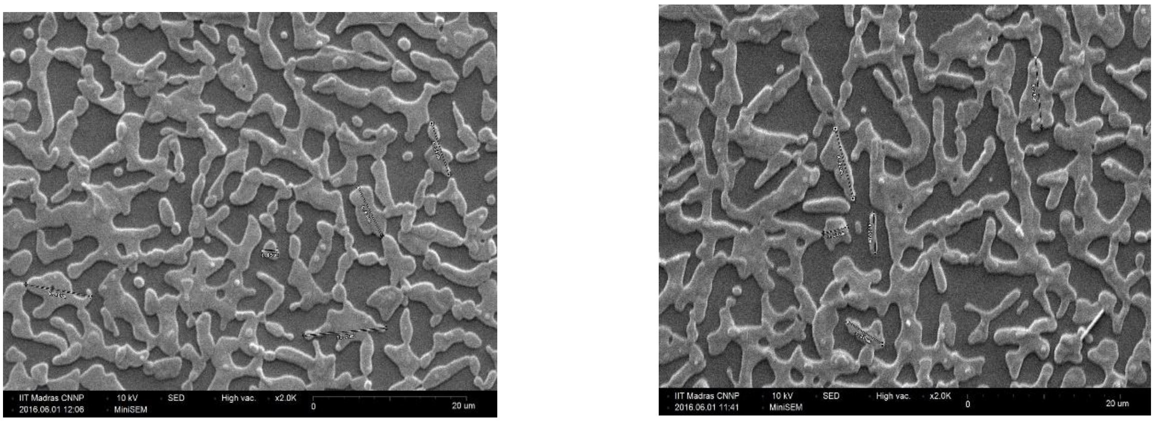
Fig. 4.5 Surface SEM image of Perovskite

Conclusion: We can conclude from above figure sample 1 surface is not uniform because there is ionic bonding . But sample 2 is more uniform because we used equimolar concentrated solution

Degradation in Perovskite surface:

SAMPLE NUMBER	SPINNING SPEED IN RPM	PEROVSKITE SOLUTION
Sample 3	3000	3:1 MAI:PbI_2 35 wt. % In DMF
Sample 4	3000	1:1 MAI:PbI_2 35 wt. % In DMF

Table 4.4 Degradation in Perovskite thin film



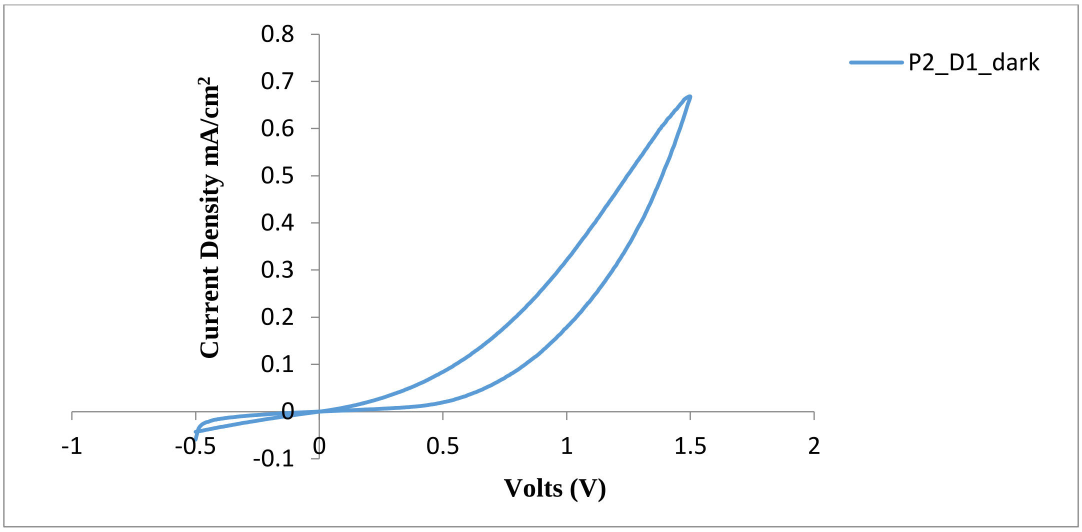
Sample 3

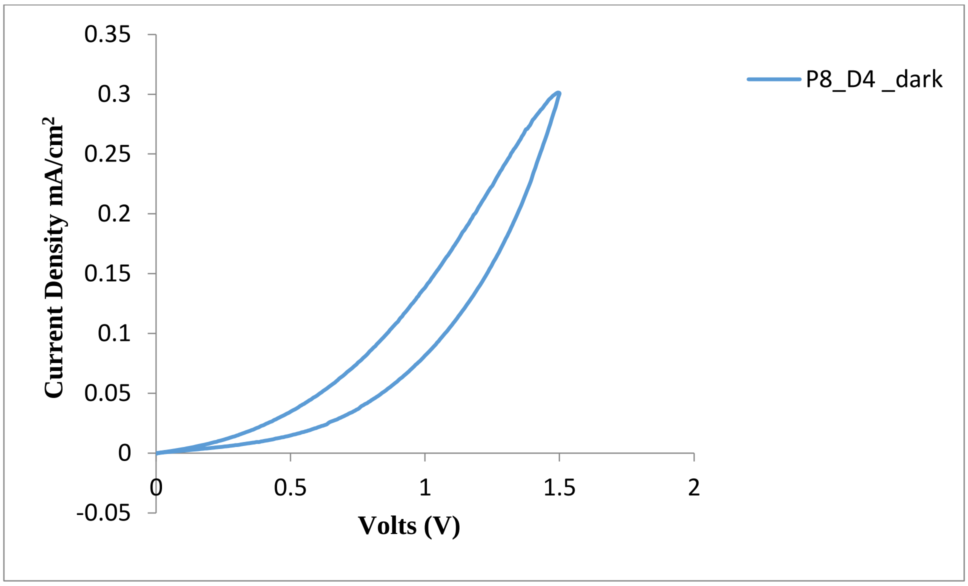
Sample 4

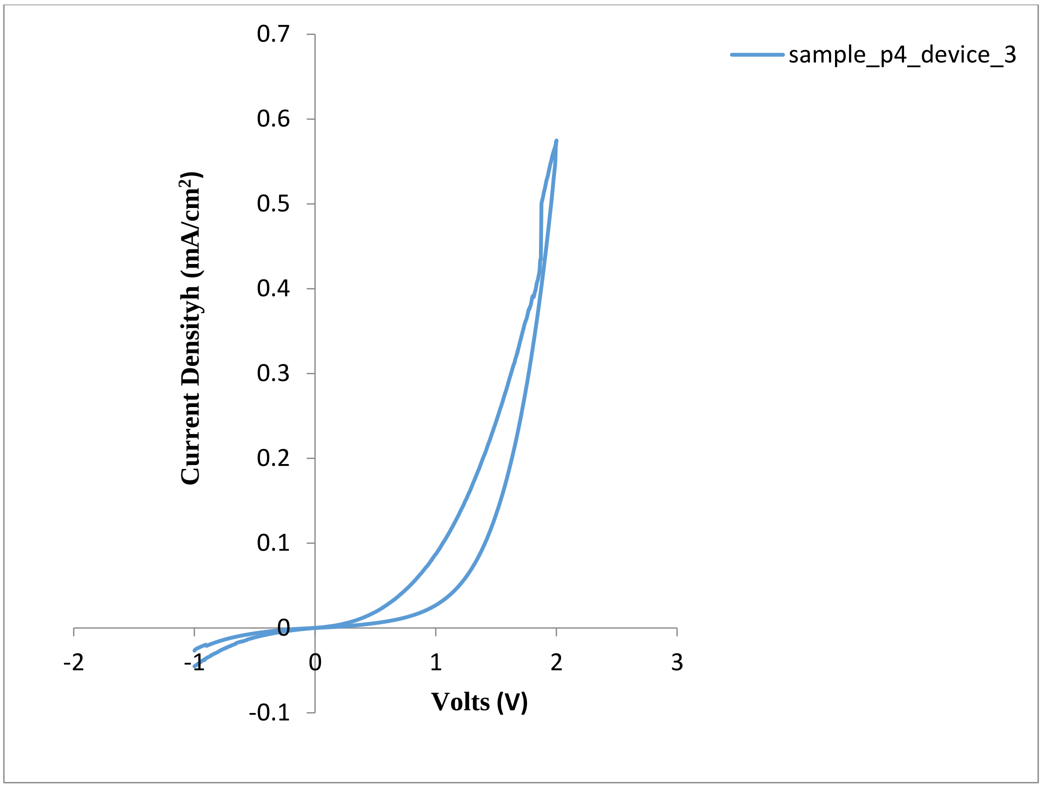
Fig. 4.6 Degraded surface SEM images of Perovskite

Conclusion: We again took SEM images of surface of our same sample after 10 days but we saw there is complete change in surface because of degradation of Perovskite material.

4.5 DARK CURRENT RESULT







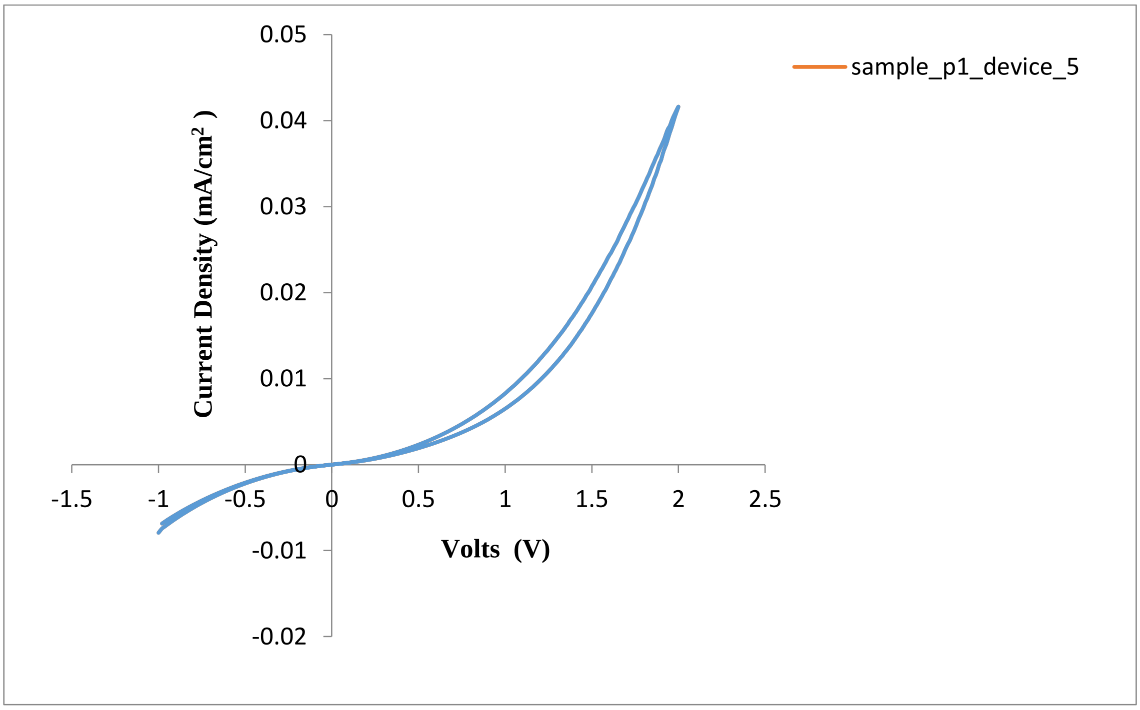


Fig. 4.7 Dark Current Results

LAYER		**P2 10/06/**	**P810/06**	**P4 17/04**	**P1,12/05**
PEDOT-PSS	Spinning speed in rpm	4000	4000	4000	4000
	Annealing temp in Celsius	150	150	150	150
	Annealing time	20	20	20	20
Perovskite	concentration	1:1 35wt% in DMF	3:1 35wt% in DMF	1:1 45wt%in GBL	1:1 35wt%in DMF
	Spinning speed in rpm	3000	3000	3000	3500
	Annealing temp in Celsius	90	90	150	150
	Annealing time in minutes	40	40	20	20
PCBM	Concentration in mg/ml	20	20	15	20
	Spinning speed in rpm	1000	1000	1200	1000
	Annealing temp in Celsius	90	90	150	150

	Annealing time in minutes	60	60	20	20
Lithium Fluoride thickness in nm		2	2	0	2
Aluminium thickness in nm		100	100	70	50

Table 4.5 Solar cell fabrication parameter

CONCLUSION: From above graphs we can conclude that;

- We used different molar concentration Perovskite solution; from above table we can say equimolar solution is best.
- We are getting high current density when PCBM concentration is 20mg/ml.
- When we annealed our sample at 90^{0}c for 40 min. Perovskite gives us best result.
- Optimum annealing temperature for PCBM is 90^{0}c for 1hour.
- LiF as buffer layer avoid aluminium penetration into intrinsic layer and save our device from short circuiting but we are getting less current because of LiF.
- Metal layer thickness should be 100nm.

CHAPTER 5

FUTURE SCOPE

The news that Perovskite perform extraordinarily well in solar cells has spread fast, and many academic and industrial researchers are already discussing their potential for commercialization. Most are optimistic that the efficiencies of Perovskite cells will continue to improve until they are competitive with, or better than existing commercially available solar cells. However, there are concerns that lead toxicity will be a problem, because the Perovskite are soluble in water and could be washed out of a leaky module. The race is on to discover Perovskite containing non-toxic elements that have the same desirable properties as the lead compounds. [7]

Another possible issue is the long-term stability of Perovskite. The results of preliminary tests performed on short timescales are promising, but some researchers remain concerned that a water-soluble material that can be sublimed at a low temperature (as Perovskites can) will lack the rock-like stability that enables silicon solar cells to last for more than 25 years.

Perovskites and crystalline silicon need not compete with each other as solar-cell materials. Because silicon has a smaller band gap (the energy required to generate conducting electrons) than the Perovskite, it absorbs a chunk of the solar spectrum that Perovskite do not. One could therefore place a silicon cell underneath a Perovskite cell to form a tandem cell. Perovskites could be printed on top of silicon in a way that would add little to the manufacturing cost, and because Perovskite generate a higher voltage than silicon, the tandem cell would be more efficient than a silicon cell.

Further breakthroughs in Perovskite solar cells can certainly be expected in months to come. [7][8]

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