iJRASET
International Journal For Research in
Applied Science and Engineering Technology

# INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

**Volume:** 9 **Issue:** VI **Month of publication:** June 2021

**DOI:** https://doi.org/10.22214/ijraset.2021.35487

International Journal for Research in Applied Science & Engineering Technology (IJRASET)
*ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 7.429*
*Volume 9 Issue VI Jun 2021- Available at www.ijraset.com*

# Synthesis and Efficiency Analysis of Perovskite Solar Cells

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***Abstract: Perovskite solar cells are a new breed of solar cells belonging to the third generation of innovations that have witnessed an efficiency boost from 3.8% to 25.5% in a time frame of 10 years. There are a number of manufacturing techniques known and discovered by man to maximize the possibility of scalability across all sectors. Each synthesizing technique emerges with its own set of pros and cons which need to be correspondingly tackled based on the application scenario. The research advancements currently being carried out are discovering materials that can be exploited to replace the current PSCs and overcome the challenges of these devices, band gap engineering, and revamping metal contacts and lastly, reducing toxicity of current PSCs are few of the varied research opportunities available in this domain of renewables.***

***Keywords: Perovskite solar cells, photovoltaic technology, renewable energy, sustainability, solar energy***

## I. INTRODUCTION

Perovskite, a wondrous discovery often regarded for its capability to be a potential material, giving birth to a new generation of solar cells. Perovskite solar cells are an invention that is under rigorous research and product development to scale this impeccable solar cell on a commercial basis. Perovskite solar cells have seen a rapid increase in efficiency in a span of 10 years, from a minor power conversion efficiency (PCE) of 3.8% in 2009 to a staggering 25.5% in 2020, all this achievable with just a single junction perovskite solar cell. Researchers and several groups of scientists are meticulously exploring greater paths to scale-up the production of perovskite solar cells, overcome the disadvantages of these solar cells and greater material candidates for perovskite solar cells. In this paper we shall delve into the fundamentals of what is a perovskite, its crystal lattice structure, the different structures of perovskite solar cells, the manufacturing methods to synthesize perovskite solar cells. Using the above concepts, we shall even analyze the highest recorded efficiency using each of the manufacturing methods, the pros and cons of each synthesizing method, the advantages and disadvantages of perovskite solar cells and finally we shall examine the current trends and future scope in the domain of perovskite solar cells.

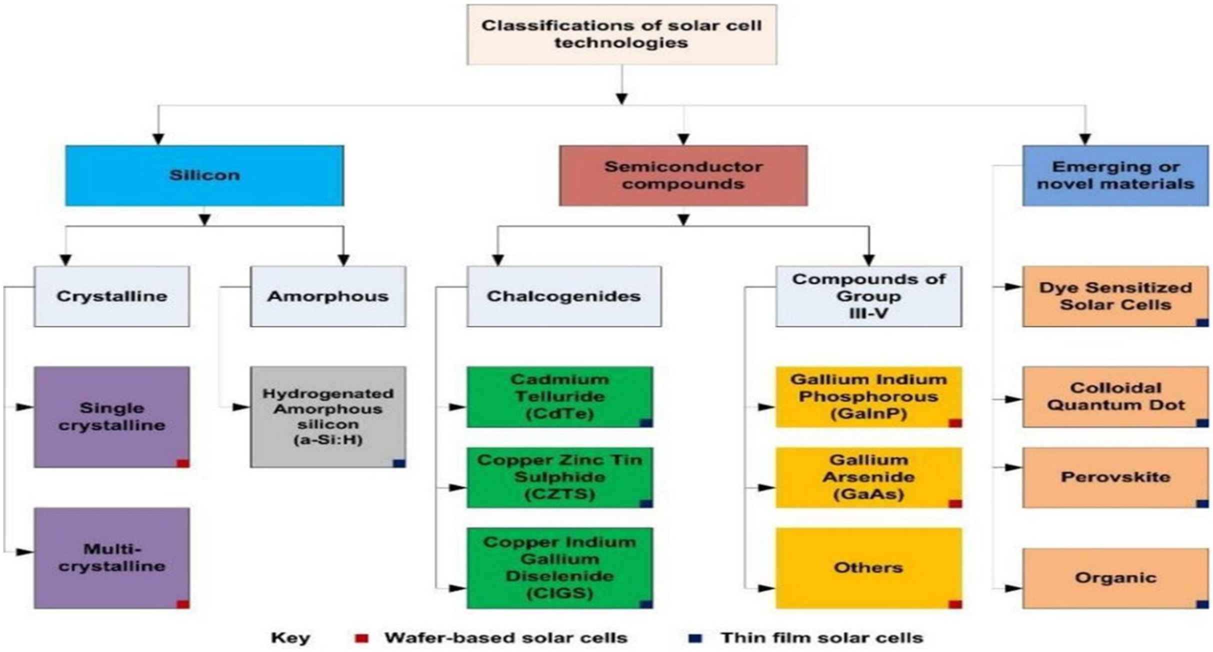

Fig. 1 Solar cell technologies

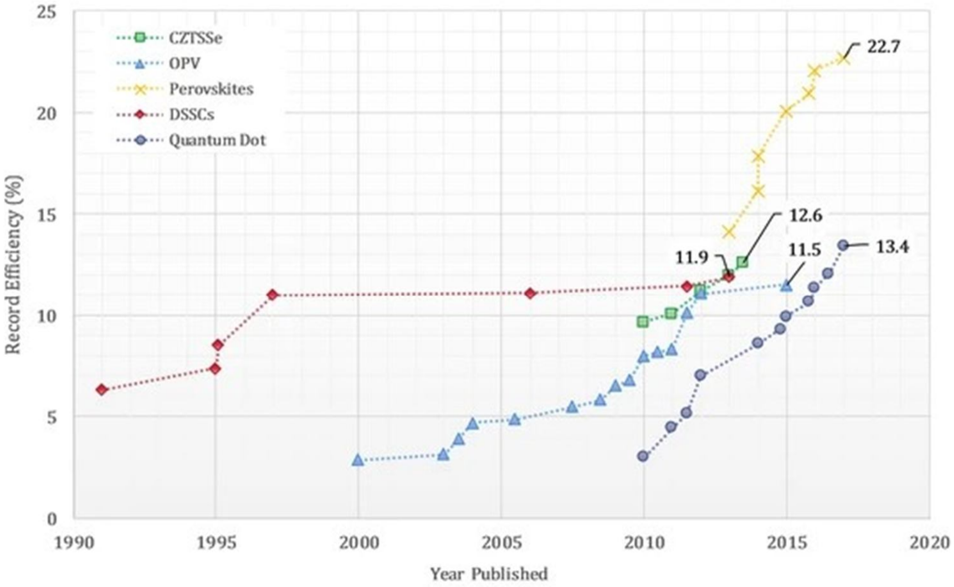

Fig. 2 Relative efficiency analysis of various solar cell technologies

## II. PEROVSKITE AND CRYSTAL STRUCTURE

With the growing culture of transitioning to renewable sources of energy, international organizations and governments have recognized the escalating importance of adopting renewable energy sources. One such renewable energy source, within this domain experiencing rapid industrial research and product development is solar energy. The study of examining greater materials as possible candidates for solar modules is known as photovoltaic technology or solar technology. In the realm of solar technology, scientists have segmented the several solar cells known to man, into three broad generations namely:-

1) *First Generation Solar Cells:* This generation of solar cells include the conventional Si-based solar modules that are generally considered extremely inefficient in today's era of photovoltaic modernity. Si-based solar modules are further divided into monocrystalline and polycrystalline solar panels with each solar panel having their own sets of advantages and disadvantages with an appropriate set of purposes.
2) *Second Generation Solar Cells:* This generation of solar cells include Thin-Film structures like CdTe and CIGS based solar cells that are often regarded to be cost-effective and have only seen a restricted application due to their low-efficiency rates and lack of development. The presence of toxic materials in these solar cells, make it less favourable for further scope in material development.
3) *Third Generation Solar Cells:* This generation of solar cells include the latest innovations within the photovoltaic industry. Solar cells like perovskite based, organic photovoltaics, dye-sensitized and quantum dot solar cells are few of the many innovations within this category. This segment includes materials that have a scope in achieving scalable efficiencies with required research and experimentations.

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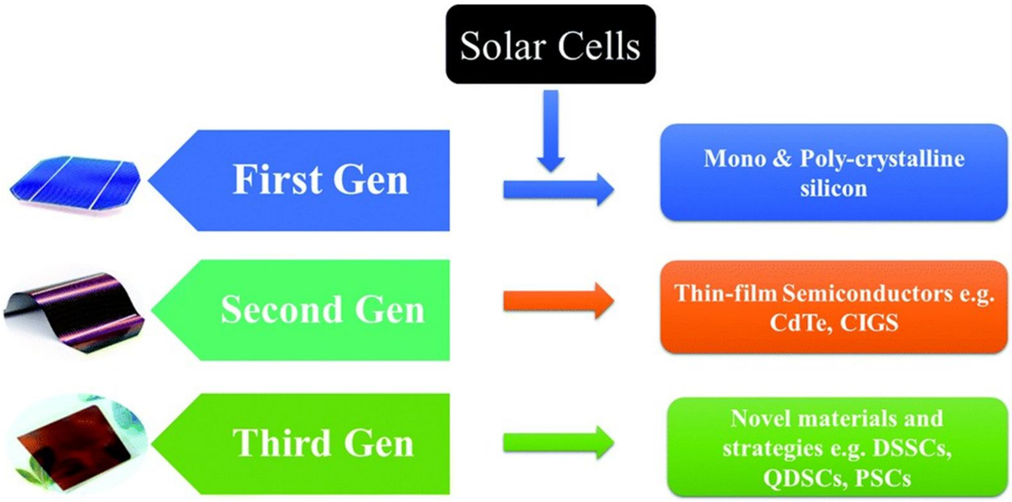

Fig. 3 Various generations of Solar technologies

Within the third generation solar cells category, we shall delve into a revolutionary material called perovskite. The very essential properties of perovskite enable these solar cells to convert incident solar radiation of nearly multiple wavelengths to produce electricity and consequently increase PCE. These compact structures permit solar power to be scaled to greater heights, opening a wider window for opportunities and innovation. The efficiency of this technology can vary from the largest of industries to the minutest of appliances and can effectively suffice a single household. Perovskites exhibit remarkable optoelectronic properties, with enhanced absorption, feasibility, and fabrication abilities. This material provides additional advantages like easier charge separation and an exceedingly slow recombination rate.

Perovskite is a hybrid of organic-inorganic compounds having a molecular configuration of $ABX_3$ , where A is typically a cationic element from group I or II of the periodic table where A can represent a charged molecule like methyl ammonium or formamidinium. B is also a cation that is from the group of transition metals usually Lead (Pb) or Tin (Sn) and X represents a halogen either Cl, Br or I, with each halogen generating peculiar properties to the PSC.

The principal structure of a perovskite is from $CaTiO_3$ with the lattice parameter as follows:-

- a = 5.404A$^{o}$
- b = 5.422A$^{o}$
- c = 7.651A$^{o}$

Cations A and B display a coordination number of 12 and 6 respectively along with X anion. The minima of the valence band is composed of hybridized antibonding orbitals from the ‘s’ state of B cation and ‘p’ state of X anion. The maxima of the conduction band is composed of $\pi$- antibonding orbitals of the p-state B cation and X anion.

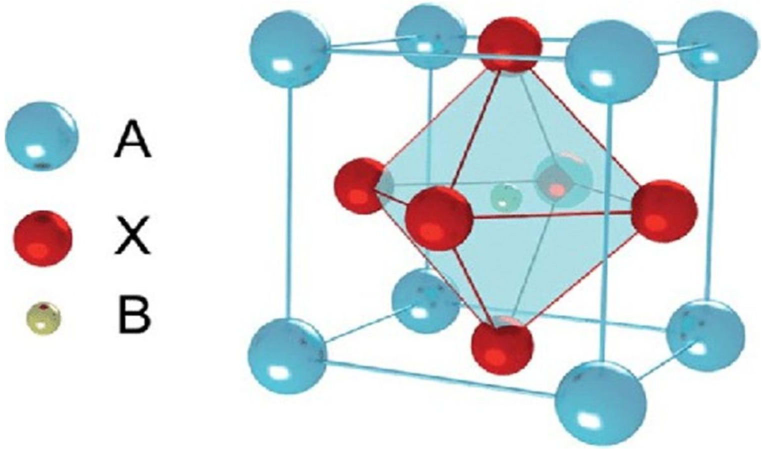

Fig. 4 Crystal lattice of a perovskite ($ABX_3$ )

Studies have shown that the action a does not strongly influence the valence and conduction bands of a perovskite but a change in A can contribute to a significant change in the overall lattice constant. Thus with notable increase of lattice parameters, constants and so on, one can observe a change in band gap of the perovskite material. An ideal perovskite lattice structure is a combination of Face Centered Cubic (FCC) unit cell and Body Centered Cubic (BCC) unit cell, where there are additional anions, X present on the faces of the unit cell. The above structure parameters and properties can be generalized for any perovskite structure following the rule $ABX_3$.

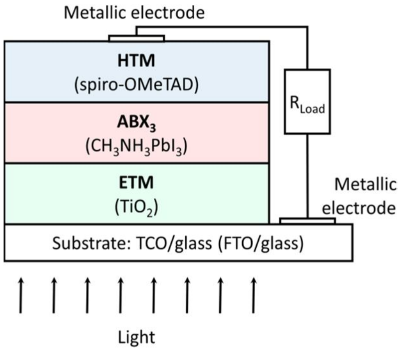

Fig.5 Circuital representation of a PSC

Perovskites possess the following qualities that make them an ideal material for extensive research in the realm of third generation solar cells:-

- Small band gap
- Ambipolar
- High carrier mobility
- High absorption
- Low temperature fabrication

However, the presence of defects is a common observation in perovskites that leads to a phenomenon known as hysteresis, that behaves as a trap for mobile charge carriers within the solar cell. We shall discuss this in greater detail as the study proceeds. A qualitatively lesser value for hysteresis would result in a more uniform perovskite formation.

## III. STABILITY OF PEROVSKITE CRYSTAL STRUCTURE

The stability of a perovskite material or a perovskite lattice is quantitatively measured by a term known as tolerance factor, t:

$t = (r+r')/(2(r''+r'))^{0.5}$

r = ionic radius of A

r’ = ionic radius of X

r’’ = ionic radius of B

A perfectly packed cubic structure of perovskite would have a tolerance factor of $t = 1$. However, a stable perovskite structure would display a tolerance factor anywhere between $0.8 < t < 1$. As stability increases, the tolerance factor increases and the band gap of the corresponding material decreases.

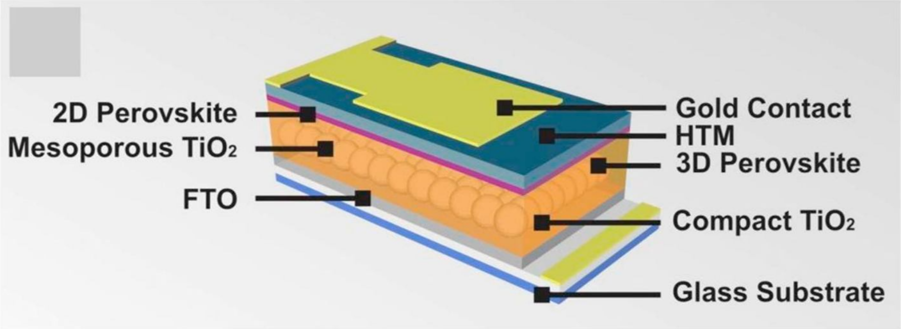

Fig.6 Pictorial Representation of a PSC

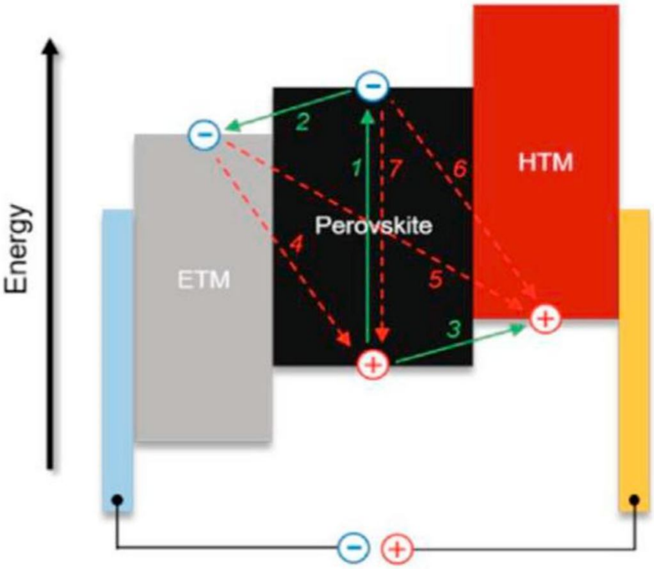

Fig.7 Energy-Band/Energy-Level Diagram during a charge-separation process in PSC

## IV. STRUCTURE OF PEROVSKITE SOLAR CELLS

With varying structural configurations, perovskite solar cells are broadly classified into 2 types:-

*A.* Planar structure
*B.* Mesoporous structure

There are derived structures from the above mentioned categories that are as shown by the figure below.

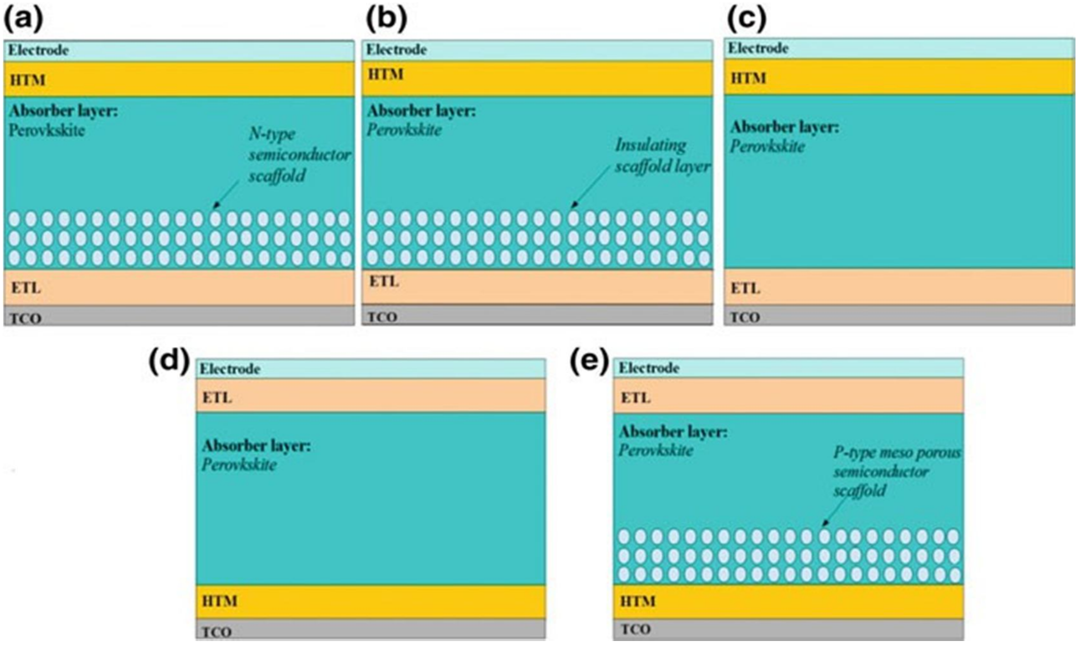

Fig.8 a) regular (b) mesostructured (c) planar heterojunction (d) inverted planar heterojunction structure (e) inverted p-type mesoporous structure

1) *Mesoporous Structure:* This category of materials have been extensively studied due to their varied properties of large specific areas and greater compatibility of an active layer for a PSC. The implementation of this material for PSC enables structures to abide by the mesoporous oxide format, to generate a light harvesting area for an active layer in a PSC. A mesoporous perovskite solar cell comprises a FTO electrode, electron transport material/layer, mesoporous oxide layer, perovskite layer, hole transport material/layer and an electrode. $TiO_2$ is the commonly used mesoporous oxide layer that permits perovskite nanocrystals to penetrate to a greater extent into the oxide layer by solution spin coating methods.$TiO_2$ offers supporting roles in other domains of a functioning of a PSC like, transporting electrons, blocking holes, inhibiting recombination and consequently enhancing the PCE of a PSC. There are additional materials used as a complement to $TiO_2$ such as $ZnO_2$ , $ZrO_2$ and so on. Using the predefined structure of mesoporous PSC effectively reduces recombination probability of charge carriers and provides these mobile charge carriers with appropriate diffusion lengths to successfully be collected at their respective electrodes and generate a sufficient output. Studies have shown that the majority of the solid state mesoporous PSC with a $MAPbI_3$ structure have reported an optimized fill factor of 0.73 and PCE of 15.0%. This increased output is mainly due to the solution based process involved in merging the perovskite nanocrystals to the mesoporous oxide layer using a two-step solution deposition method which produces an extremely uniform perovskite film of high quality. However, mesoporous PSC that use $TiO_2$ require high temperature sintering, therefore, $Al_2O_3$ is being considered as an alternative. Unlike $TiO_2$, $Al_2O_3$ does not play supplementary roles. PSC that have utilized $Al_2O_3$ witnessed a decrease in binding energy, with a significant PCE of 11.3%.
2) *Planar Structure:* The principal difference between a planar and mesoporous PSC is, the planar PSC lacks in the mesoporous oxide layer format. A planar PSC consists of an FTO electrode, electron transport layer/material, perovskite layer, hole transport layer/material and a complementary electrode. The mobile charge carriers generated when the light is incident on the perovskite layer, is transported to the respective transport layers and is effectively collected by the electrodes. The maximum efficiency obtained by using a planar PSC was 15.7% with a fill factor of 0.749 and open-circuit voltage, $V_{oc}$ of 1.03V. Researchers recognized that utilizing yttrium doped $TiO_2$, increases electron-hole mobility and results in a highly improved $V_{oc}$ and short circuit current, $I_{sc}$. Recently, substantial research is carried out on studying the structure of inverted planar PSC, that has reported a maximum efficiency of 12%, with a potential to manufacture flexible PSC.

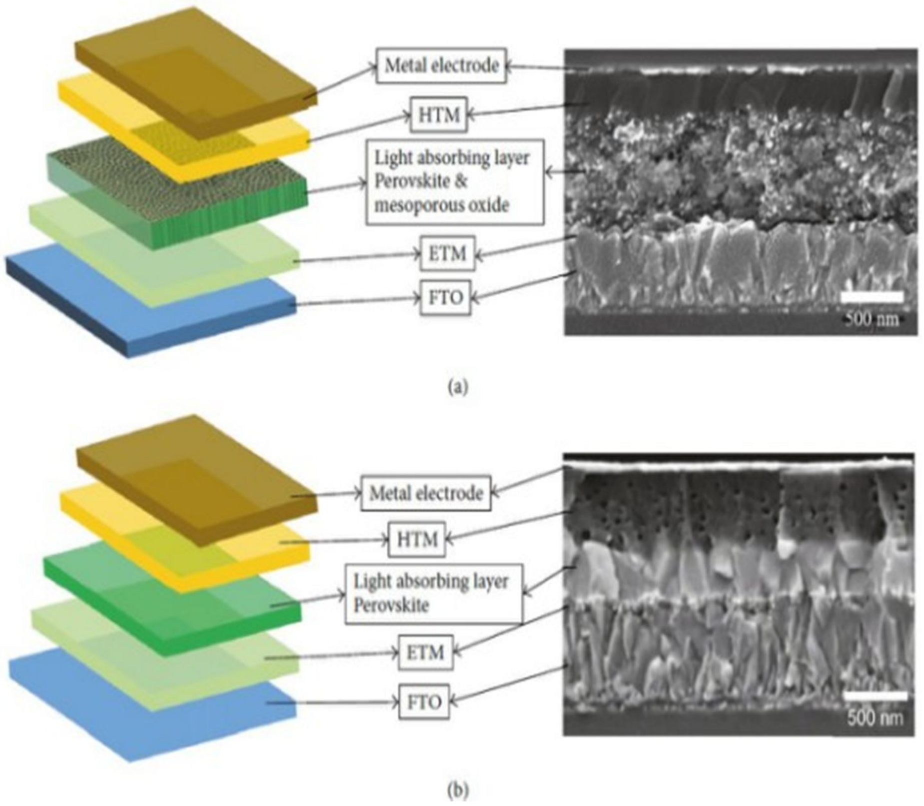

Fig.9 (a) Mesoporous structure PSC (b) Planar structure PSC

## V. MANUFACTURING TECHNIQUES OF PEROVSKITE SOLAR CELLS

Manufacturing techniques that are being explored currently are of the sole objective and that is to ensure, these processes are:-

1) Readily scalable
2) Low cost and effortlessly available
3) Low temperature processing methods
4) Dimensioning of a PSC is carried out with ease
5) Generate power efficiently

One difficulty that scientists have experienced during the development of these processes is, the synthesizing techniques are executed with ease to produce a uniform layer of perovskite solar film. However, replicating this process on a large scale is often cumbersome, as it is difficult to regulate the surface morphology of a PSC, giving a subsequent rise to variation in surface roughness and surface/ crystal layer defects. The manufacturing techniques currently available provide its own set of advantages and disadvantages that can prove to be beneficial in certain cases but detrimental in others. Manufacturing techniques are broadly divided into 2 categories, solution based deposition and vapor assisted techniques.

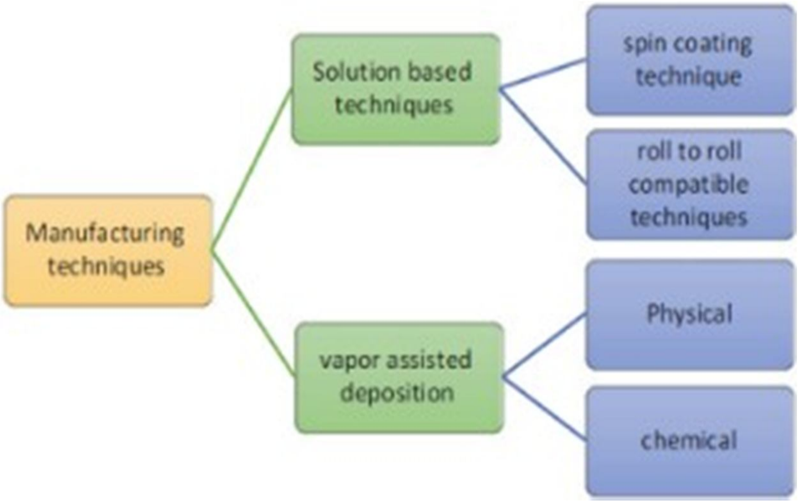

Fig.10 Classification of PSC fabrication techniques

### *A. Solution Based Processing Technique*

The solution-based techniques can be carried out in a sequential order of either one-step or two-step deposition process, based on the number of deposition steps.

1) *One-step Deposition:* The precursors are considered and deposited as an entity/mixture on the deposition surface. In this method, there is a greater probability of voids, which subsequently result in faster recombination rate of charge carriers. The $PbX_2$ and MAX are dissolved in a stoichiometric ratio to form a precursor, which is spin-coated on a $TiO_2$ substrate at appropriate temperatures. The solvents used, the annealing temperature and other physical and chemical conditions suitably determine the quality of the perovskite film formed. Using this method, the size and surface morphology of perovskite crystals cannot be regulated at ease, hence, scientists have developed an alternative regarded as two-step deposition technique.
2) *Two-step Deposition:* The precursors are considered and taken as separate entities with distinct separation characteristics. The layer obtained in this method is often more uniform, exhibits more electron lifetime and displays a greater control of surface morphology relative to one-step deposition. In this method the $PbX_2$ solvent is used as the precursor solvent to be spin-coated on the $TiO_2$ substrate. This coated substrate is now immersed in a solution of 2-propanol containing MAX with utmost precaution. Drying the substrate under favourable conditions, the reaction between MAX and $PbX_2$ is initiated to generate the perovskite film. In this method, the immersion time, quality of solvents, and concentration of solvents plays a vital role in determining the standard of perovskite film formed. The PCE obtained using a two-step deposition method was recorded to be 15%. Further studies indicated that, PSC using two-step deposition methods did not hamper the performance of the PSC at high humidities.

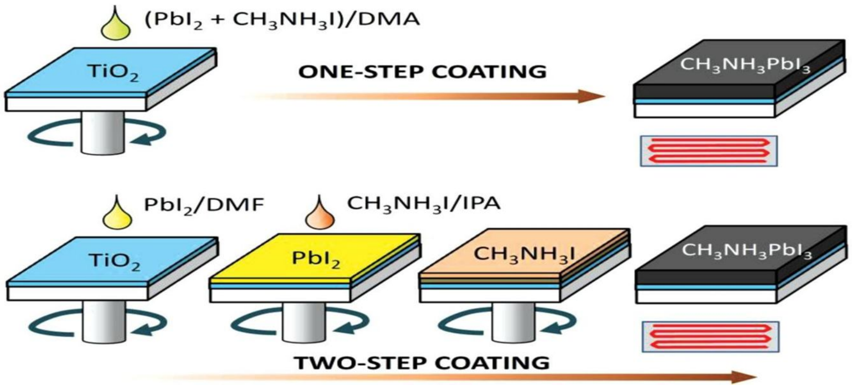

Fig.11 One-step and Two-step deposition for $CH_3NH_3PbI_3$

Solution processing based processes are the most widely and extensively used fabrication techniques for producing the perovskite active layer as they are cost effective and produce relatively unchallenging to establish. We can achieve solution based processing techniques using a subset of processes that can be derived like, spin coating, dip coating, doctor blade, spray coating and so on.

### *B. Spin Coating Technique*

The simplest and most cost effective solution based processing technique discovered for producing PSCs. In this method, a high-spinning equipment is established which will determine the acceleration, time of coating, film thickness and quality of the film produced. Spin coating is generally used for small-area PSCs. The finished product from this method has a strong adhesive force between the crystalized layers of the perovskite structure, where the cations and anions are strongly bonded. The highest recorded optimized efficiency using this method is 22.1%. However, since this technique uses a rotary disk that is difficult to regulate, the thickness levels of the film is difficult to control, secondly, due to the extremely slow processing speeds, there is an exceeding amount of material wastage that limits the scalability factor of this process.

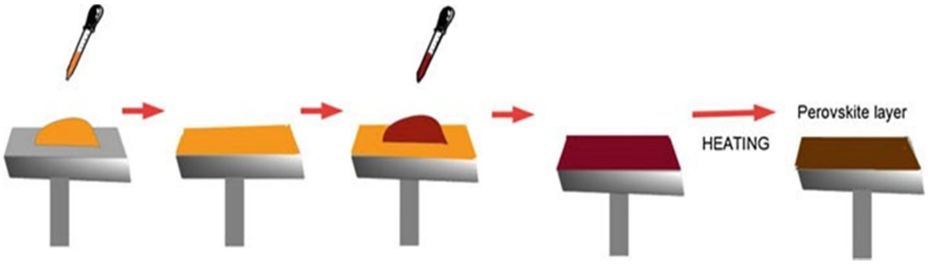

Fig. 12 Spin coating technique

### *C. Drop-Casting Technique*

This is a peculiar procedure that is uncomplicated and basic to generate perovskite films. This is a derived technique of spin coating, but in this method the spinning of the substrate is not essential. The quality and thickness of the film is determined by the volume and concentration of the dispersed phase.

Secondary parameters like the substrate temperature and wetting, rate of evaporation and drying process, influence the film quality to a certain degree. Contrary to spin-coating technique, this method does not lead to excessive material wastage and is primarily employed for volatile solvents. However, the difficulties in managing film thickness and properties has not been resolved using this particular method.

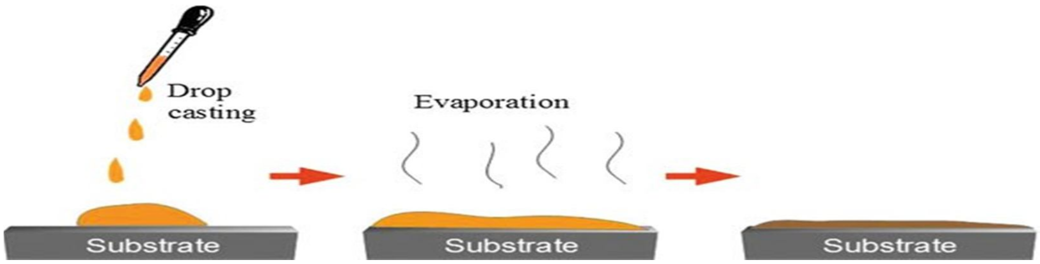

Fig. 13 Drop-casting technique

### *D. Roll-to-Roll Printing*

This manufacturing technique is a derived set of processes from solution based processing techniques. They are considered to be one of the best solution-processing techniques to manufacture PSCs. The variation in availability of generating various perovskite films enables manufacturers to weigh the pros and cons of each differing process with required modifications. The high speed coating mechanism, availability of coating on flexible substrates and uniform film deposition are few of the numerous advantages provided by roll-to-roll processing techniques in comparison to other solution based processing techniques. This manufacturing procedure uses a continuous deposition of appropriate layers on a substrate using roll-to-roll techniques. Roll-to-roll techniques enable scientists to scale, and mass produce at a rapid rate to generate cost-effective PSCs.

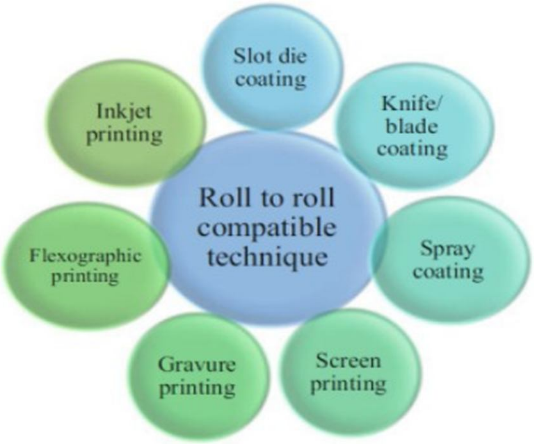

Fig. 14 Roll-to-roll technique types

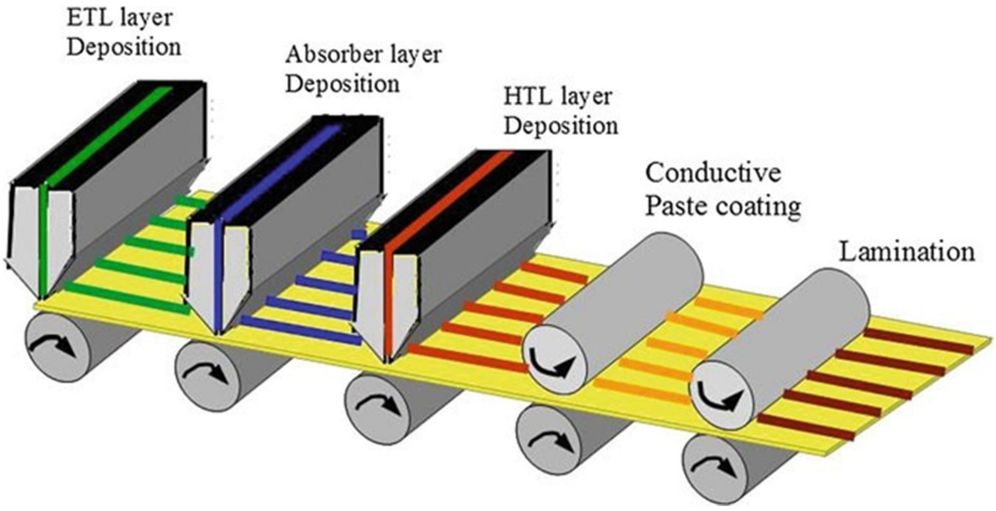

Fig.15 Principle of roll-to-roll technique

### *E. Spray Coating*

A fast and efficient mode to produce a perovskite active layer for flexible PSCs. A small-scale roll-to-roll technique that is capable of achieving 10 times the PCE of PSCs manufactured from ink jet printing or blade coating techniques. The rapid deposition rates, low-cost synthesizing, and potential to harness perovskite layers on flexible and glass substrates makes this method a dominant roll-to-roll technique. The films produced by this method have proven to show better charge transfer capabilities and higher charge carrier lifetime. This method has been typically employed for inverted and planar PSCs. The highest recorded efficiency using this method is 11%. Parameters related to carrier gas, substrate temperature and surface, annealing temperature and so on, determine the quality and uniformity of the perovskite film formed. However, in this particular method, the thickness and homogeneity of the film produced cannot be expressed as it is difficult to control it. The lack of uniformity in the film gives rise to additional internal resistances that prove to be a hindrance for mobile charge carriers and eventually decrease their lifetime and diffusion lengths. Scientists have discovered several alternatives that can treat the disadvantages offered by spray coating like, ultrasonic spray coating, pulsed spray coating, electrostatic spray coating and so on.

### *F. Ultrasonic Spray Coating*

A modified version of spray coating but in this specific method, the user is able to enhance the morphology of the perovskite film obtained. A two-step deposition process would give rise to a film with optimized morphology and photovoltaic properties. The highest recorded efficiency using this method is 7.7%. Ultrasonic spray coating generates perovskite active layers that have a larger grain size, which aids in efficient carrier diffusion and lower recombination rates. This method gives rise to perovskite films that have a lower hysteresis and hence, this method is preferably used to produce PSCs instead of the traditional spray-coating and spin-coating techniques.

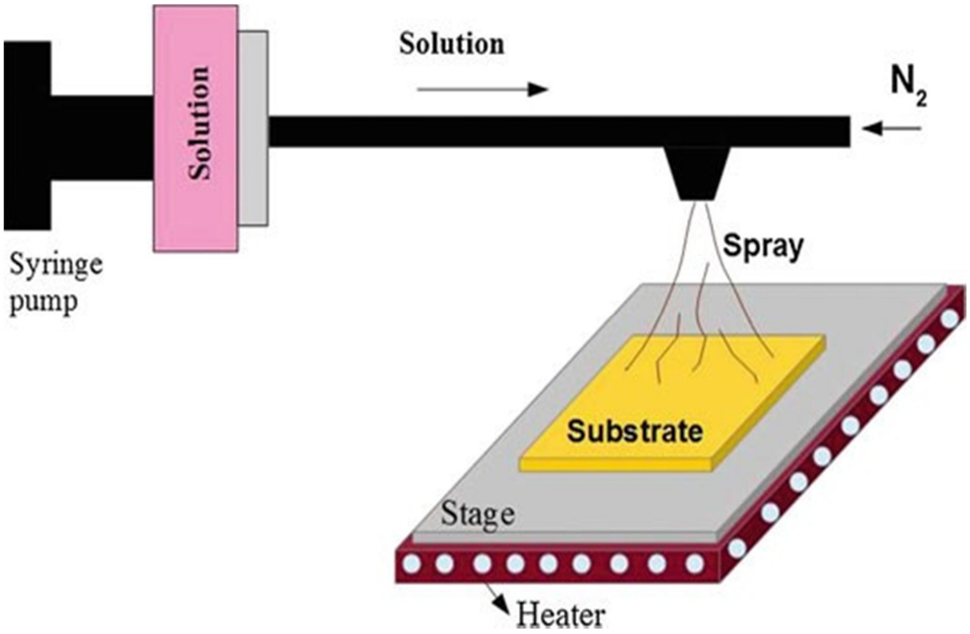

Fig.16 Ultrasonic spray coating technique

### *G. Blow Drying Technique*

A self-evident technique whose procedure is very distinct from its name. This complementary procedure does not require any additional anti-solvent or chemicals to supplement the process. The process is as simple as depositing a layer of perovskite precursor on the surface of the substrate and allowing it to dry using a blow dryer under favourable conditions. The excess deposit is then wiped out using tissue paper. This process has seen wonders by providing the end result rich in smooth, uniform and high quality films with a potential to scale it to industrial levels. The only parameter that affects the quality of films is the air flow rate of the dryer. This variable can control the coverage and can account for rapid crystallization rates of the perovskite crystals. Studies have shown that, the air flow rate from the blow dryer should optimally be at high flow rates to produce enhanced morphology of perovskite films. The air flow rate is measured using a speedometer.

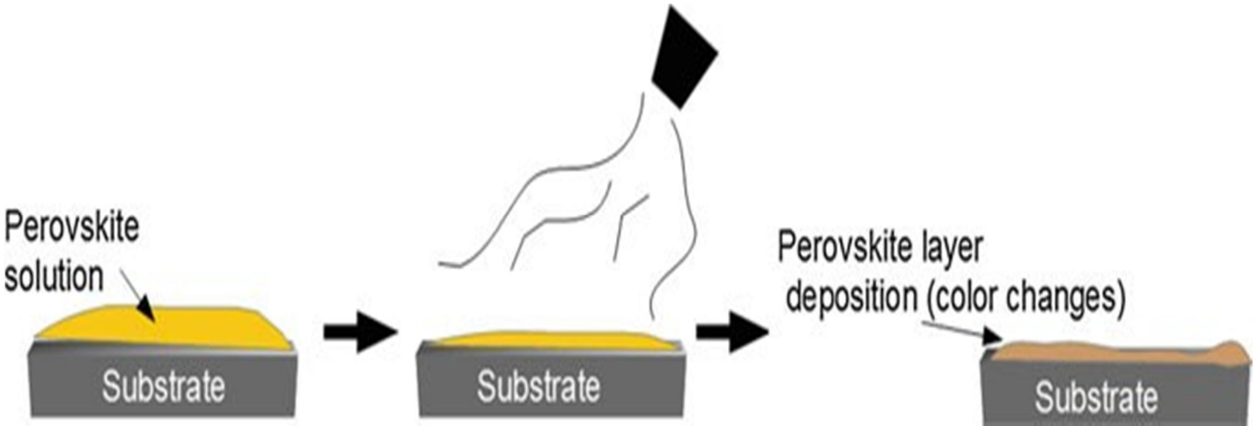

Fig.17 Blow Drying Technique

### *H. Blade Coating Technique*

A low cost, effortless, eco-friendly, improved device stability and vacuum free process that is used primarily to manufacture PSCs with optimized film morphology. A technique that uses the mechanism of a screw and a balde, where the substrate is mounted and using the screw the film height can be modified. With the help of the blade movement, the perovskite solution is made to be deposited across the surface of the substrate to produce a rather uniform surface for light harvesting. The controllable parameters that can be regulated to produce films is the evaporation of the solvent over the substrate. This can be achieved using two methods, firstly, airflow present over the substrate can be controlled and secondly, the substrate can be heated to the boiling point of the solvent. A phenomenon known as pinhole formation occurs when there is uneven distribution of solvent over the substrate which produces additional defects. To overcome this phenomenon, scientists often employ the blade coating technique to produce PSCs. The higher stability rate in this particular method is due to the slow crystallization rate, which often produces an air-protective layer against moisture. However, the drawback that follows this particular method is the excessive wastage or usage of solvent ink, which resists the exploitation to scalable standards. Hence, an alternate method known as Slot Die Coating is used.

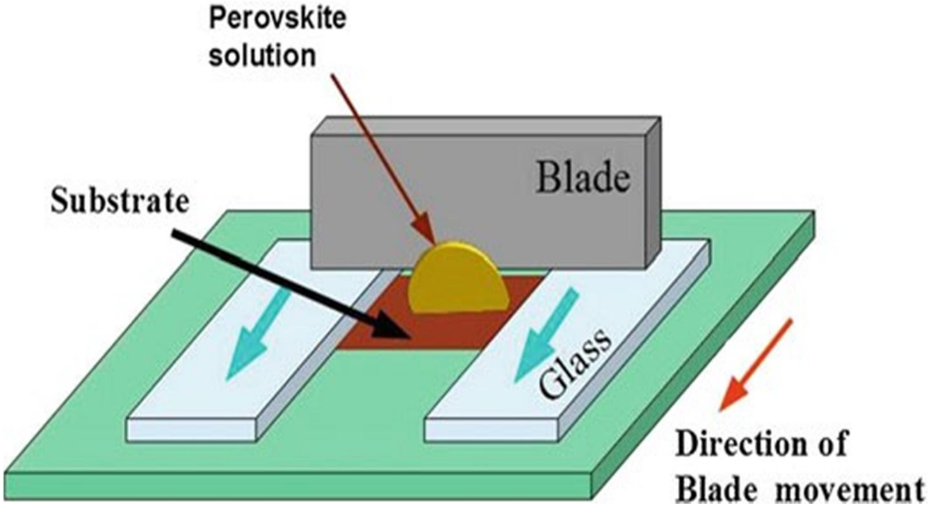

Fig. 18 Blade Coating Technique

### *I. Slot Die Coating*

Slot Die Coating is a fabrication method derived from Blade Coating technique. The only difference lies in how Slot Die coating wastes or requires a lesser amount of material or solvent. Similar to blade coating, this process is simple but offers an additional advantage of being easily scalable and producing large areas of PSCs. We can generate a uniform and controlled perovskite film using this method by varying parameters like regulating the amount of feed and material to be deposited on the substrate surface.

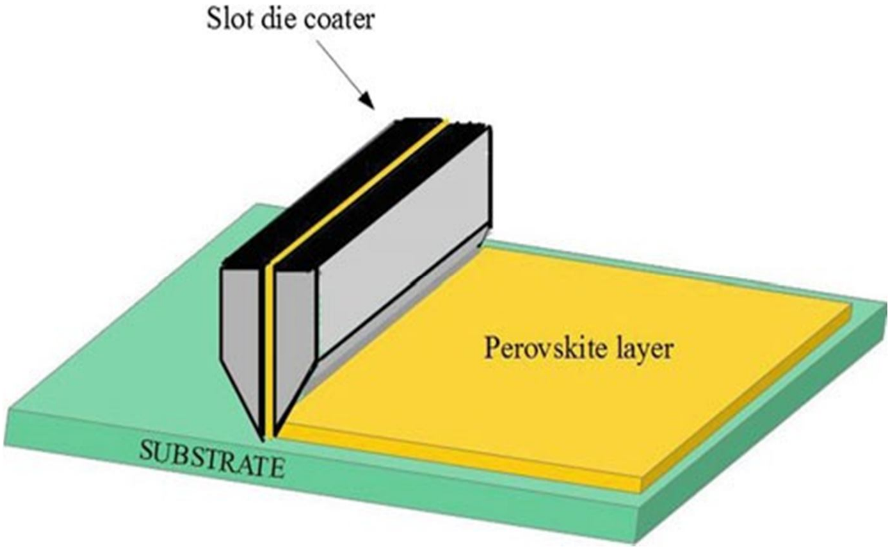

Fig. 19 Slot Die Coating

### *J. Brush Painting Technique*

A high-speed, no-annealing, cost-effective process that produces perovskite active layers with little to no loss of material. This method is typically used for the production of large-area flexible solar cells and with the variation of the solvent concentration, one can predict the quality of the output produced. This vacuum-free method does not possess the requirement of optimum procedure conditions, instead, it's as simple as using a brush to deposit the solvent/precursor over the surface of the substrate. However, this advantageous method has a set drawback, where one cannot maintain the uniformity of film thickness across the substrate.

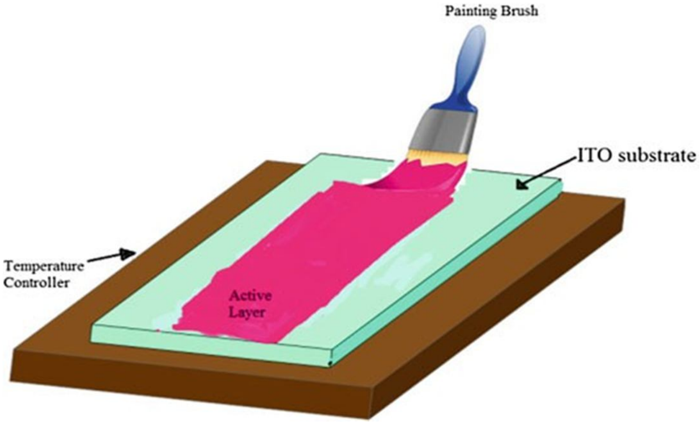

Fig.20 Brush Painting Technique

### *K. Electrodeposition*

A versatile, low-temperature, effective deposition, scalable and cost-effective technique that is a desirable technique for PSCs manufacturing. Unlike methods such as spin-coating and so on, there is no further heating of the substrate required to deposit the solvent, instead electrodeposition follows a straightforward mechanism of low-temperature synthesis and optimal use of electrical energy.

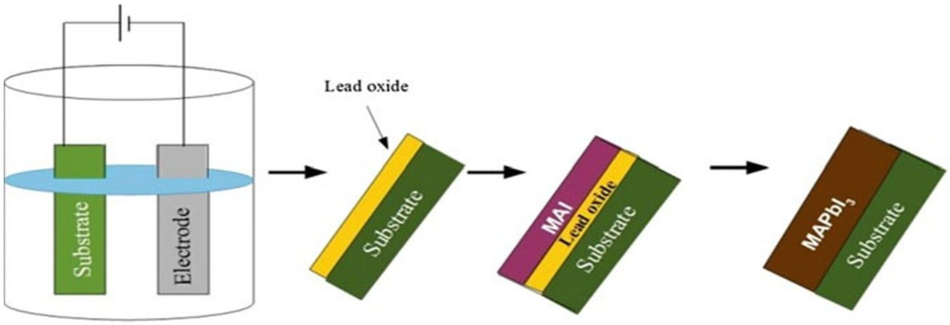

Fig.21 Electrodeposition

### *L. Ink-Jet Printing*

The advantages provided by this method are numerous:-

1) Versatile
2) Non-contact
3) Scalable and rapid deposition
4) Useful for large area PSCs production
5) Low material wastage

The mechanism of the process is exceedingly hassle-free. The process involves the selective embedment of particular ink solvents that are capable of being deposited at large and rapid rates on a substrate. Each ink solvent is stored or placed in individual chambers and with the aid of an external bias, one can observe the liquid being contracted and as a result the solvent is ejected from the nozzle to be deposited on the respective substrate. The only drawback that this method offers is the possible blockage of the nozzle or uneven ejection of solvents by the external bias.

Certain measures that one needs to ensure while practicing this particular technique are:-

*a)* Greater the ink viscosity, greater is the external bias.
*b)* A lack of definity in the bias will cause the oozing out of multiple inks
*c)* Pinch-off point is an extremely critical parameter during the process of printing
*d)* Never recombined small size droplets are a result of higher voltage parameters

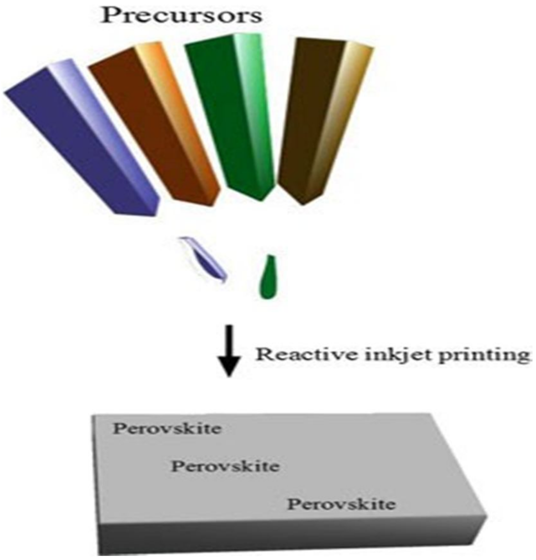

Fig.21 Ink-Jet Printing Technique

## VI. VAPOR-BASED TECHNIQUES

Amongst the various techniques known to manufacture PSCs, vapor-based techniques is one of them. There are several classifications of vapor-based methods as shown in the flowchart. The 2 broad categories that classify vapor-based techniques are physical vapor deposition (PVD) and chemical vapor deposition (CVD). Producing perovskite films using this vapor-based methods produces a high-crystalline and uniform output that often leads to higher PCE and improved surface morphology. A modified version of vapor-based deposition regarded as sequential vapor deposition was discovered. The only modification present in this method is, $PbX_2$ is initially deposited using thermal evaporation followed by MAX using vapor deposition techniques. The highest recorded efficiency using the sequential vapor deposition method is 15.4%. Scientists were successful in creating tandem PSCs using sequential vapor deposition method and delivered a PCE of 18%.Often while using vapor-based techniques, one has to ensure to obtain the appropriate thickness for light-harvesting. If the active layer is too thin, the surface for incident light reduces and if the active layer is too thick, the distance that the charge carriers have to diffuse through to reach their respective electrodes increase, as a result, the recombination rate increases. Additionally, producing a uniform and homogenous layer of perovskite is necessary across the substrate. If any region possesses a deficiency in perovskite solvent, the ETM and HTM will be in contact with each other, that will result in a condition known as a short-circuit and the obtained Fill Factor (FF), $V_{oc}$, $I_{sc}$ will be considerably lower. Vapor-based techniques are used in multiple industries as we can produce films at a rapid rate and are successful over large areas as well. The enhanced usage of vapor-based techniques permit users to fine-tune the charge collection parameters and consequently optimize the PCE at utmost ease. However, a method that provides us with innumerable advantages comes with certain irreplaceable disadvantages, like the presence of vacuum. The necessity of a vacuum in this process is exceedingly important as we wish to keep the perovskite film free from any sort of impurities or foreign substances.The basic mechanism followed in this particular method is, the precursors that are required, that is $PbX_2$ and MAX, to be deposited on the surface of the substrate are executed in alternate or continuous intervals of time. Scientists ensure to coat the substrate with $TiO_2$ prior to the depositing procedure. Using this method to produce planar heterojunction perovskite cells, researchers obtained a PCE of 15.7% with a short-circuit current density $J_{sc}$ of 21.5 mA-cm$^2$. The presence of toxic precursors like $PbX_2$ lead to the generation of harmful vapors and is not considered as a sustainable process. The above achievements, advantages and resolvable disadvantages throws light on how vapor-based techniques can greatly favour the synthesis of PSCs, with further scope for research and product development.

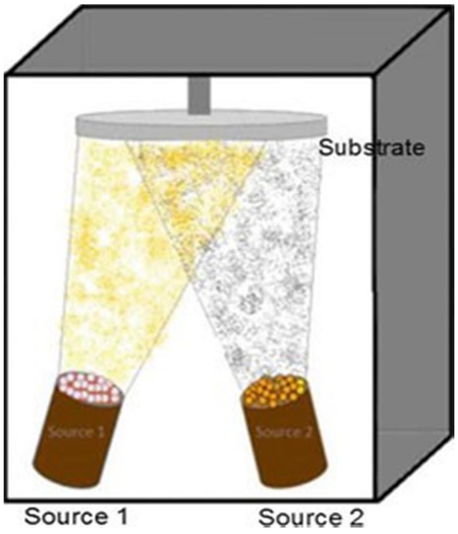

Fig.21 Vapor-based deposition technique

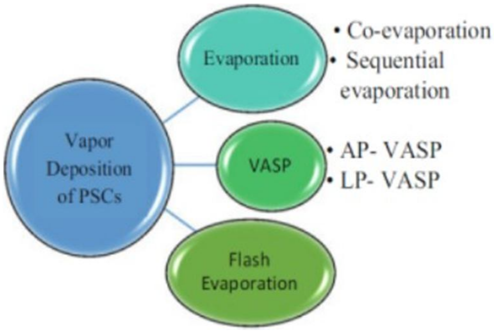

Fig.22 Classification of Vapor-deposition based techniques

### A. *Chemical Vapor Deposition (CVD)*

A pinhole free, scalable and budding process that is a dominant technique to produce perovskite films. The mechanism that this method follows is, the precursors required for the deposition are executed by co-evaporation. The precursors are thoroughly mixed, heated and transferred to a preheated substrate using a carrier gas, typically Argon, to produce highly uniform perovskite films. These perovskite films are pinhole free, have a larger grain size and longer carrier lifetime. In addition to the above mentioned benefits, this method utilizes a minimum amount of material to fabricate homogenous perovskite active layers.

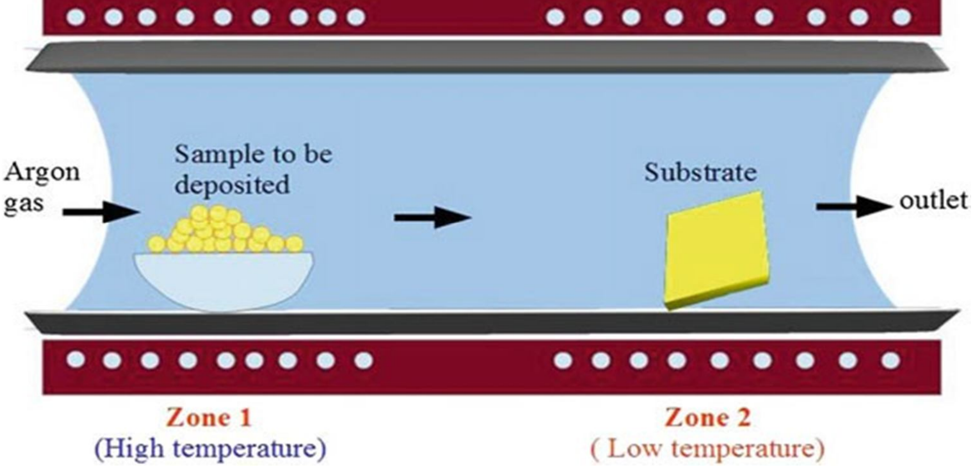

Fig. 23 Chemical Vapor Deposition

### B. *Physical Vapor Deposition (PVD)*

This is a simple and chemical-reaction free process that produces perovskite films having a full surface outreach, well-defined structure, high crystallization rates, multi-phase purity and definite control over film thickness, quality and morphology. PVD also referred to as SSPVD (Single source physical vapor deposition) has produced perovskite films of PCE 15.4%. This synthesis does not require any sort of heating or treatment procedure and avoids the complications of reaction conditions, variable parameters and so on.

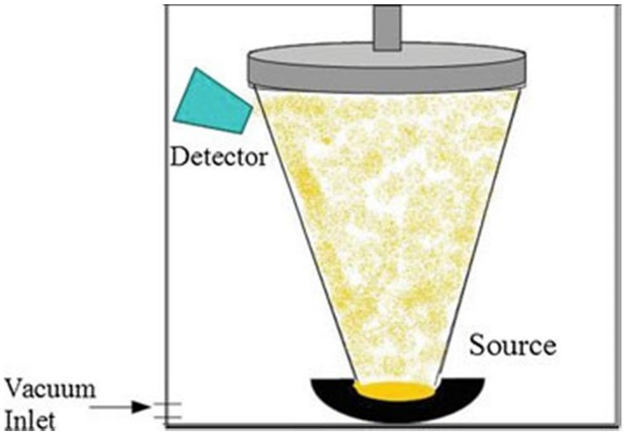

Fig. 24 Single source physical vapor deposition

## VII. VAPOR-ASSISTED SOLUTION PROCESS (VASP)

While employing the process of vapor-based deposition techniques, complications like salvation and dehydration are common encounters that one experiences while manufacturing high quality perovskite films. In VASP, these complications are resolved and one can obtain a pinhole free, cost effective and optimized surface morphology mode of producing perovskite active layers. The mechanism of this process follows a two-step sequential deposition; initially, a film of $PbX_2$ is deposited on the $TiO_2$ coated substrate, using any of the appropriate solution-based processes. Onto this, $MAPbX_3$ grains are permitted to grow using an in situ reaction in presence of a MAX vapor using vapor based deposition occurs at a temperature between 120-165°C in an atmosphere of inert gas for 2 to 4 hours, to manufacture perovskite films. Additionally, VASP techniques solve the problem of rapid degradation as experienced by solution-based perovskite films.The highest recorded efficiency using VASP to produce planar heterojunction perovskite films is 12.1%. However, the presence of toxic substances like intermediate halides, lead contents and so on, restricts the scalability of the process. The reaction between $PbX_2$ and MAX may often not lead to 100% completion, as a result, the presence of unreacted particles will be present in the system, creating a source of additional resistance, thereby reducing the power output of the PSC. This complication occurs only in extreme scenarios where the reaction and physical conditions are not favourable for the reaction to undergo at an efficient rate.

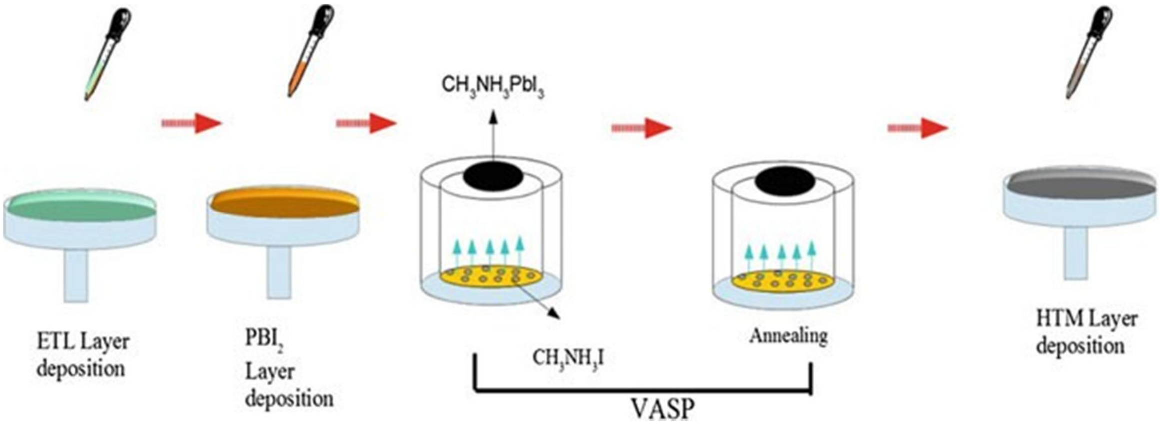

Fig. 25 Vapor-Assisted Solution Process

## VIII. ADVANTAGES AND DISADVANTAGES OF PEROVSKITE SOLAR CELLS

It is important to realize the benefits that PSCs offer consumers as a third generation type of photovoltaic technologies. Despite PSCs being in its nascent stages of research and development, the advantages that this revolutionizing technology provides the world of renewables with, is innumerable.

The following are few of the advantages of PSCs:-

*A.* High PCE while simultaneously reducing processing costs of other generations of solar cell technologies.
*B.* The capability of adjusting and behaving to various wavelengths of light unlike conventional solar cells, thereby increasing the overall power output of the cell and subsequently the PCE.
*C.* Flexible, lightweight and can range from semi-transparent to transparent light-harvesting surfaces.
*D.* Materials used in manufacturing perovskite films provide charge carriers with greater diffusion lengths, enhanced mobility, slower recombination rates and high dielectric constant, as a result, the collection efficiency of the electrodes increases.
*E.* The versatile nature of PSCs permit them to remain active and generate power from abstract surfaces like walls, cars, windows and so on.
*F.* The raw material used and disposed at the end of the fabrication process is minimal in contrast to Si-based solar cells for the same amount of electricity generated or incident radiation.

However, there are a few notable disadvantages that hinder the scalability of PSCs. The impeccable properties of perovskites do not correspondingly coincide with the resultant PCE. These challenges can affect the performance of the device to a greater scale with reasonable degradation in stability.

Few of the disadvantages/challenges are as follows:-

*1)* *Hysteresis:* In a traditional IV curve does the phenomenon of hysteresis come into play. In PSCs when the scanning direction, that is the reverse scanning of the IV curve, was conducted, scientists realized that the curve produced through scanning and the present IV curve were not coinciding. This phenomenon of difference in IV curve and scanned results is regarded as hysteresis. Researchers have stated that, due to the presence of hysteresis, it makes the process of calculating PCE extremely cumbersome as the architecture to measure such standards is not adequately developed. Hence, the occurrence of hysteresis, its origin and eradicating it from a photovoltaic device is nearly unknown to man. The root cause of hysteresis has not been identified yet but researchers have claimed certain possibilities based on trial and error speculations and well-devised experiments.

The governing mechanisms are:-

*a)* Ferroelectric polarization
*b)* Ion migration
*c)* Charge trapping
*d)* Capacitive effects

Hence, during recording of efficiencies using IV data, scientists should pay key attention to the recording of PCE. There have been certain measures that organizations like the NREL have suggested to adopt while measuring the PCE of PSCs such as:-

- Sealing or laminating the PSC accurately to record an error-free value.
- Precisely calibrating the light source with a valid reference node.
- Measuring the $I_{sc}$ or $J_{sc}$ and $V_{oc}$ simultaneously whilst recording the stability.
- Recording the IV curves in forward and reverse directions for various scan rates.
- Determining the $I_{ph}$ at voltages approximately close to the MPPT.
- Comparing the obtained data using literature from the IPCE data spectrum analysis.
- Performing a qualitative/quantitative analysis for vast datasets.

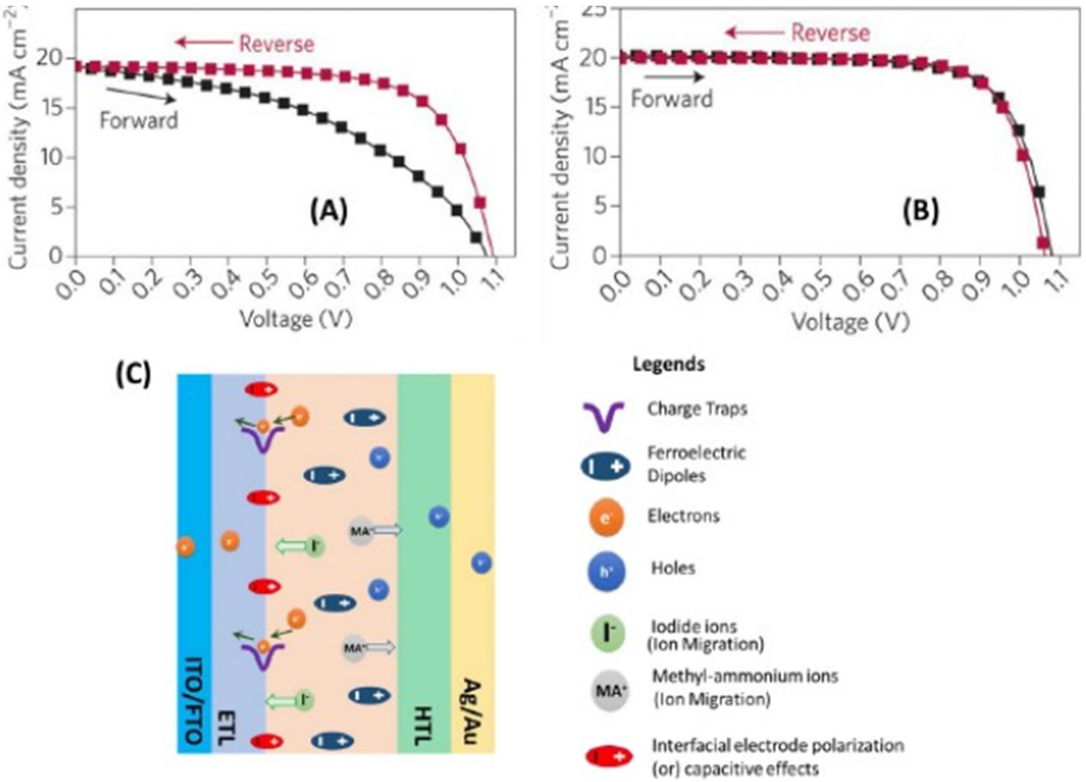

Fig. 26 (A) IV curve with hysteresis loop (B) IV curve with negligible hysteresis loop (C) Possible governing hysteresis mechanisms

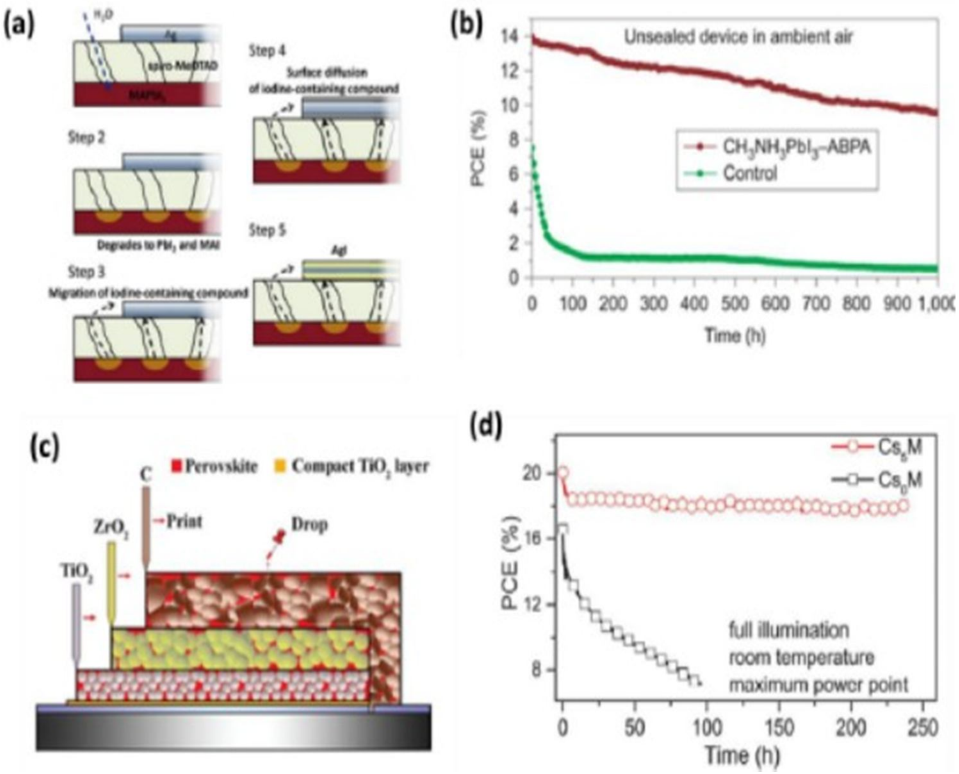

Fig. 27 (a) Degradation mechanism in a PSC (b) Variation of PCE with and without an encapsulation varying with time (c) Triple layer PSC (d) Variation of PCE with Cesium additive

2) *Stability:* The major disadvantage of PSC is the low lifetime and high degradation capabilities of this photovoltaic device. With increasing degradation, the PCE of PSCs continues to decrease at non-uniform rates that prove to be destructive for any power-producing equipment. Through experimental damp heat tests at conditions 85$^o$C, 85% relative humidity (RH), it has been proved that the efficiency of a PSC degrades by a percentage of 10% in less than 1000 hours of operation. Hence, PSCs are far from usable conditions on an industrial level even to this day. It has been proved that degradation levels elevate when thermal stress, temperature and moisture on a continuous medium, can rapidly decline the performance of a PSC. Taking into consideration a simple perovskite molecule that is used for manufacturing of PSC, $CH_3NH_3PbI_3$, on exposure to elevated levels of heat and moisture, the molecule decomposes using the following reaction:-

$$CH_3NH_3PbI_3 \rightarrow PbI_2 + CH_3NH_2 (\uparrow) + HI (\uparrow)$$

To generalize the degradation conditions, the thermal temperature can vary between 110$^o$C - 140$^o$C and as temperature increases, the degradation increases with rapid decrease in PCE. In recent applications, the use of phosphonic acid as an additive to improve the stability of PSCs has been widely recognized as the crosslink produced between phosphonic acid and the perovskite active layer molecule, tends to resist degradation with increase in moisture, heat, stress and so on. Researchers have also resorted to the use of carbon infused PSCs as it provides additional protection to stress and moisture particularly. Using encapsulating material like glass, thermosetting epoxy glue can provide the solar cell with an additional layer of protection against moisture and oxygen, providing long term stability to the device. Adding a small amount of Caesium to the precursor solutions during the fabrication of PSCs promotes phase separation and enhances device stability. For PSCs to achieve the goal of being cost-effective it should prove to the consumers that it can sustain harsh conditions, suit industrial standards and generate a constant PCE over long periods of time. Unfortunately, at the moment this utopia has not been accomplished at favourable conditions that researchers can replicate effectively. The first generation solar cells available in the market today can produce a constant PCE over a period of 25 to 30 years, hence, for a PSC to revolutionize the photovoltaic industry further, it should pass the experimental tests in every manner to generate beneficial results.

3) *Toxicity:* The materials of perovskite active layers often contain transition metals like lead (Pb) and tin (Sn) that are extremely harmful to humans in calculated levels. Through lead and tin poisoning, diseases that damage the lungs, kidneys and nervous system are possible. The lack of clarity in disposing of PSCs poses a threat to the environment as Pb and Sn are in direct contact with the ecosystem, which can directly or indirectly affect biodiversity. Hence, reducing the amount of Pb and Sn or replacing it with viable alternatives is a greater medium for research by scientists.

4) *Scalability:* The PSCs manufactured to date are miniature models that are lesser than 1 $cm^2$ in area and these models have reported a PCE greater than 20%. The need for scalability, rapid development in equipment and product awareness are domains that researchers and global organizations need to explicitly tap into. Scientists discovered that using PSCs of 1$cm^2$ the PCE is nearly 15%, hence the need of higher dopant concentration would be needed to achieve a greater PCE, ensuring that these devices are equipped for industrial purposes. Additionally, since the metal contacts/electrodes in PSCs are gold or silver, whilst scaling these devices on a commercial level, one should look at key alternatives that can replace these economically-intensive materials. Manufacturing large scale PSCs can also be a challenge when the appropriate synthesizing technique is not practised and thus prove to be an economical and technical burden. Lastly, while developing large scale PSCs the need to maintain uniformity and a constant perovskite film thickness is another challenge that we are bound to encounter. This is where the requirement of appropriate equipment, technique and technology will come into light.

## IX. COMMERCIAL ACTIVITIES OF PEROVSKITE SOLAR CELLS

Across the globe, there are several organizations and companies deeply exploring technologies that hold great potential to revolutionize the existing PSCs. There have been considerable modifications to develop defect-free PSCs and improve the lifespan of these photovoltaic devices but this would require greater depths of research to overcome the challenges encountered in modern day PSCs.

1) *Oxford PV, United Kingdom:* This institution developed a 1 $cm^2$ tandem PSC which is capable of absorbing multiple wavelengths of incident radiation particularly belonging to a segment of Infrared and Ultraviolet radiations and the entirety of visible radiations. The device recorded its highest PCE of 28% which was verified by the National Renewable Energy Laboratory (NREL). The next objective that they wish to achieve is to reach an all-time high of 30% PCE. The device even sustained the experimental damp heat tests with a degradation time of 2000 hours. In order to produce these PSCs on an industrial scale, Oxford PV has established a contract with an institution in Berlin, Germany to mass produce these devices at a rapid rate.

2) *Energy Materials, United States of America:* This institution has begun ramping up and evolving its institution facilities to produce PSCs on an industrial scale. The high-speed manufacturing assembly system has attracted worldwide attention where investors have extensively financed the institution with more than 4 million USD to successfully execute its venture. The authorities of Energy Materials have stated that, with their technology they can transform the face of renewables, particularly photovoltaics, by reducing the cost of production by 95% and selling price by 50%.
3) *Microquanta Semiconductor, China:* This institution predominantly focuses on manufacturing stable state PSCs and was successful in attaining a steady PCE of 17.3%. Microquanta has been successful in fabricating a large surface area PSC of 200x800 $cm^2$ with a PCE of 14.24%. The institution is looking into expanding its production facility as its next endeavour to produce stable state PSCs on an industrial scale and is chiefly focussing on large-area perovskite photovoltaics. An additional feature of Microquanta is, the organization has been extremely successful in terms of their research and development where investors have extensively financed their venture to carry out further findings and consequently, commericalize perovskite solar devices.
4) *Indian Institute of Technology Bombay (IIT Bombay) and Bharat Heavy Electricals (BHEL), India:* Recently, the Indian government announced an allocated budget to support the production of photovoltaic cells production, particularly third generation solar cells, with emphasis on the research programs of IIT Bombay and BHEL to develop high efficiency perovskite solar cells. Through this partnership, the end-goal would be to establish improved efficiency, cost-effective and optimized technological outputs in the fabricated PSC.
5) *International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), India:* A research-based institute that has developed various applications for PSCs. The institution has been successful in manufacturing high-efficiency and optimum-performance PSCs using solution and vapor based processes, exceedingly stable PSCs in high moisture environments, and transparent PSCs for smart window applications. Currently, ARCI is looking to develop these and additional technologies at cost-effective possibilities, replacing toxic materials with viable alternatives and overcome further challenges of conventional PSCs with readily available technology and defect-free throughput.

## X. FUTURE SCOPE OF PEROVSKITE SOLAR CELLS

1) Researchers are looking into developing PSCs using mixed halide cations as they are more stable and efficient. Molecules like $CH_3NH_3PbI_2Cl$ that can be used to model the active layer of a PSC have seen PCE of 10.90%. Modifying the halide ions to Br and I observed an approximate efficiency of 16.20% and with additional changes to the cation, including methyl ammonium ions have improved the efficiency and stability of the device. By using the method of deposition of $FAPbI_3$ and intermolecular exchange between $PbI_2$, the PSC attained a PCE of 20% with a halide active layer. Using Cesium as an additive to enhance stability, optimized the efficiency to 21.1%, which is regarded as the highest PCE for a mixed-halide PSC.
2) Due to the toxic element of Pb and Sn present in PSCs, scientists have examined predominantly lead-free alternatives that will be capable of tuning the band gap, subsequently elevating the PCE. Noel and his team of researchers, recorded a PCE of 6% using lead-free alternatives in PSCs but since then the progress in replacing these toxic materials have been extremely restricted. Researchers modelled a PSC using $SnF_2$ with an additive of $FASnI_3$ which improved the PCE to 6.22%. Adjusting the annealing temperatures and varying the concentration of Pb altered the PCE to 13.60%. Additionally, using a Sn-Pb alloy in the perovskite layer with solvents like DMSO and DMF, revised the crystallinity rates and improved the PCE to 15.20%

Table I
Lead Free Alternatives In PSCS

| ‘Device Structure | PCE (%) |
|---|---|
| $FTO/c\text{-}TiO_2/m\text{-}TiO_2/CH_3NH_3SnI_{3-x}Br_x/Spiro\text{-}OMeTAD/Au$ | 5.73 |
| $ITO/PEDOT:PSS/FASnI_3/C_{60}/BCP/Ag$ | 6.22 |
| $ITO/PEDOT:PSS/CH_3NH_3Pb_{0.5}Sn_{0.5}I_3/C_{60}/BCP/Ag$ | 13.60 |
| $ITO/PEDOT:PSS/MASn_{0.25}Pb_{0.75}I_3/PC_{61}BM:C_{60}/ZrAcac/Ag$ | 15.20 |

*3)* The metal electrodes generally present in PSCs to complete the circuit are gold or silver contacts. During commercialization one cannot implement these electrodes as the cost of production increases to a large extent. Hence, the pressing need to transition towards carbon or copper based electrodes are the need of the hour. Carbon has been regarded as the most suited alternative as carbon derived electrodes do not require high processing temperatures, vacuum based conditions and expensive production methods. Carbon derived electrodes can be of the form, carbon nanotubes, carbon paste and carbon black, with each form reporting exceedingly high values of PCE. To deposit carbon as an electrode, techniques such as screen printing technique was implemented, where $(5\text{-AVA})_xPbI_3$ was used as the perovskite active layer, the thickness of $TiO_2$ layer was increased to 25nm, using this particular PSC configuration, the PCE was seen to be 13.41%.

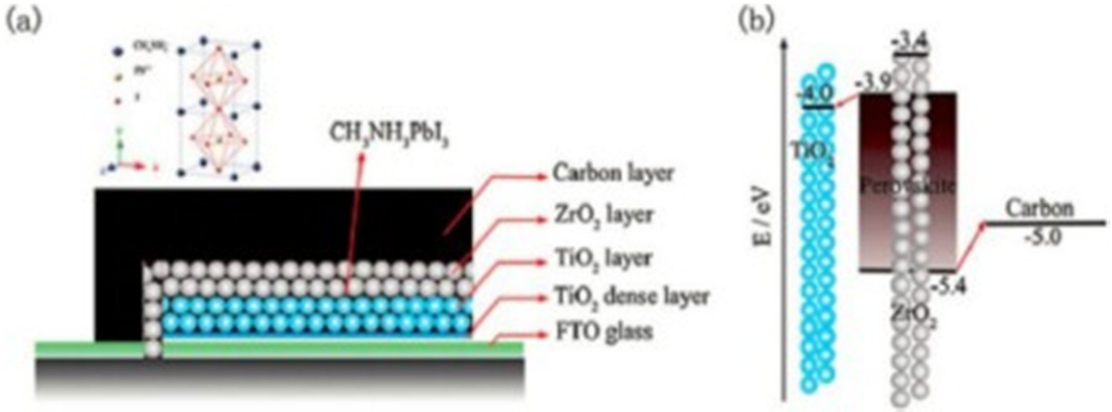

Fig. 28 (a) Carbon electrode PSC (b) Energy band diagram using Carbon electrodes in PSCs

*4)* Studies pertaining to the ETM have been pursued in great detail. Researchers are looking into examining the use of $ZnO/TiO_2$ to manufacture cost-effective PSCs. Additionally, experiments to incorporate the utilization of Ag and Cu nanoparticles using techniques such as sol-gel and colloidal-based are being reviewed carefully. The effect of manufacturing techniques on efficiency analysis are being investigated lately, to comprehend the variation of efficiency with synthesizing procedures, where processes like spray coating, spin coating and so on are being studied.

*5)* Currently, greater materials are being studied in contrast to the organic and inorganic halide perovskites that are capable of absorbing nearly all the wavelengths of the incident radiation. The need for altering the cation and anion for a given perovskite has seen a significant change in band gap and this study is known as band gap engineering. One way to tackle this is by using tandem PSCs but cost of production subsequently increases making it hard for commercialization. The direct change in cation of a perovskite does not affect the band gap as the band gap constitutes the combination of bands from the halide and anion of the perovskite. The need for altering appropriate halogens is of utmost importance as using Br in a PSC can shift the absorption band edge, using Cl does not produce significant changes in the band gap whereas I is relatively pristine. The use of Cl in PSCs can increase charge mobility to a greater degree thus making it a suitable halogen for manufacturing PSCs. Researchers have even used multiple halogen atoms in a particular configuration to get the cross-benefits of each halide.

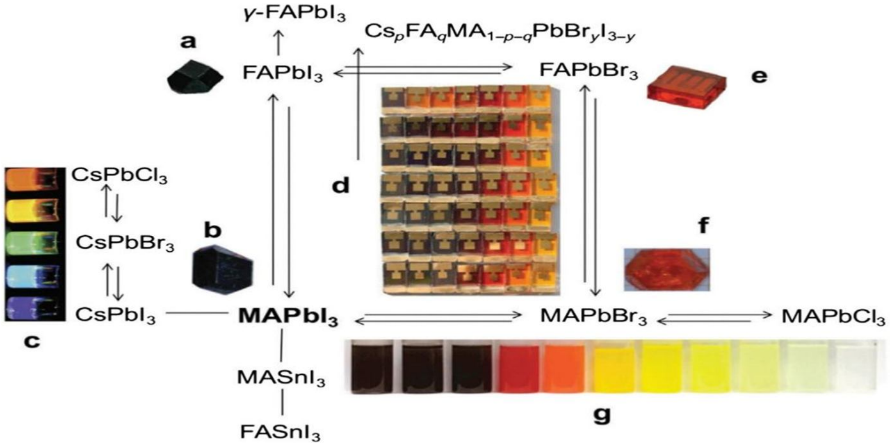

Fig. 29 Absorption tunability and versatility of hybrid PSCs

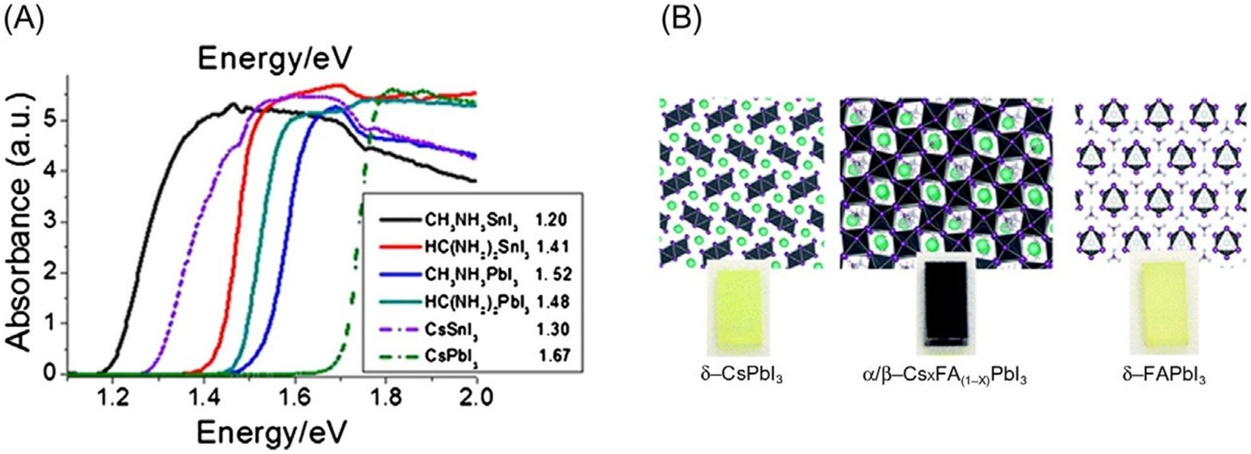

Fig. 30 (A) Absorbance and band gap values for various materials (B) Crystal photos of modified band gap materials

*6)* Researchers in Korea at Pohang University of Science and Technology discovered PSCs that were extremely efficient. In addition to this advantage, the invented PSC was capable of achieving phenomenal results in stability, heat and moisture tests. The architecture of the PSC used a hydrophobic conducting polymer with high hole mobility as the HTM without any need of further additives. Using this composition, the device was capable of absorbing moisture in the air that would traditionally hamper the device's performance. The PSC was capable of recording a PCE of 17.3% and an average lifetime of 1400 hours under 75% RH. The future endeavour of the institution is to develop greater findings to commercialize a similar concept of perovskite solar cells and spend an extensive amount of resources in this regard to attain it.

*7)* Saule Technologies, an establishment that is looking to integrate PSCs with Internet of Things (IoT). The company believes that this product integration could provide the renewables industry with a revamped industrial image. The need for IoT being merged with renewables can aid the journey towards sustainability, support businesses and optimize daily functioning by taking smarter data-driven decisions. Analysts have suggested that the IoT market is forecasted to attain a 1 trillion dollar industry, with the addition of renewables, the market value and need for research is enhanced.

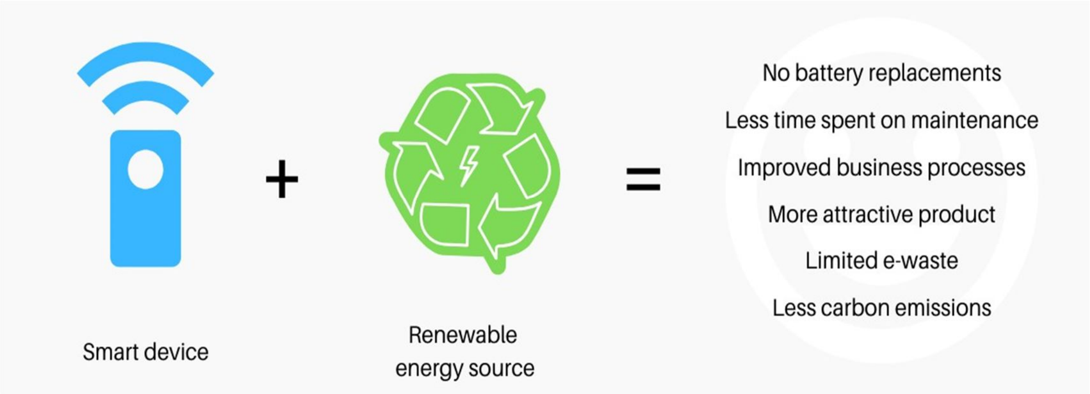

Fig. 31 Benefits of IoT integration with renewables

## XI. CONCLUSION

Through the course of this study, we were able to recognize certain key aspects like the fundamentals of perovskite, its properties that make them a candidate for solar cells, manufacturing techniques of PSCs along with an efficiency analysis and an understanding of the key benefits and notable disadvantages for each method, the advantages and disadvantages of PSCs, current progress of PSCs through commercial examples and lastly the future prospects for research in PSCs. As consumers we can be affirmative of the fact that over the next 5 years, third generation solar cells, particularly PSCs will replace the conventional Si-based solar cells with varied changes in efficiency and power generation. The appropriate use of technology and identification of appropriate materials are the only hindrances that prevent the commercialization of PSCs. On solving these complications we can witness a revamped definition of the term "photovoltaic technology".

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