

# Manufacturing Techniques of Perovskite Solar Cells

Priyanka Kajal, Kunal Ghosh and Satvasheel Powar

**Abstract** Perovskite solar cells (PSCs) are in focus of the solar cell development research for the last few years due to their high efficiency, cost-effective fabrication, and band gap tunability. Perovskite solar cell efficiency sharply increased from its initial reported efficiency of 3.8% in 2009 to 22.1% in 2016. This makes PSCs as the technology with the fastest growth rate in terms of the efficiency. Different device architectures have also been developed in an attempt to improve the PSC efficiency. At laboratory scale, a spin-coating process is employed to deposit different layers of PSCs. Though spin-coating process helps to achieve high efficiency, for large-scale production viability, researchers are developing different deposition techniques. A broad range of manufacturing techniques for perovskite-based solar cells have been tested and reported comprising drop casting, spray coating, ultrasonic spray coating, slot die coating, electrodeposition, CVD, thermal vapor deposition, vacuum deposition, screen printing, ink-jet printing, etc., with different device architectures. This chapter summarizes different PSC structures along with the corresponding manufacturing techniques.

**Keywords** Perovskite solar cells · Scale-up · Manufacturing techniques

## 1 Introduction

Energy demand is rapidly increasing across the globe, and it is estimated that by 2030, the global energy demand will increase to 16 terawatts (TWs) [1]. The growing demand cannot be fulfilled by fossil fuels-based energy sources because of

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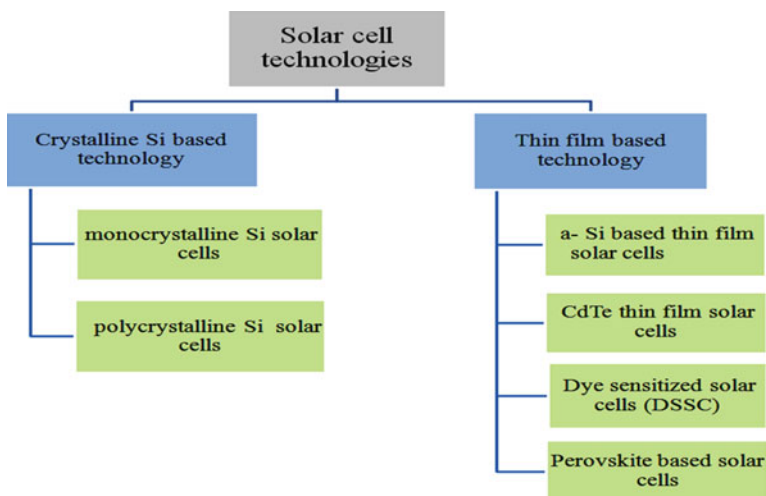
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their harmful impact on the environment. So there is a strong need to harness the energy using renewable sources like solar [2], the wind [3], biogas [4, 5]. Among all other sources, solar is the most abundant source of energy which is available throughout the year. Hence, solar is the best alternative to fossil-based non-renewable energy sources [6]. Solar energy can be produced through thermal and photovoltaic (PV) converters. Out of these, PV is a preferred technique for electricity generation because of direct conversion of sunlight into electricity [7].

Photovoltaic effect was first discovered by Alexandre-Edmond Becquerel in 1839. However, it is in 1954 that Bell Labs first designed the modern solar cell, which is based on separating junction. In a solar cell, when a photon of energy greater than the band gap strikes the material, electron-hole pairs are created. Under the influence of electric field, they are separated and transported to their respective contacts from which they are extracted as current. The fundamental factors which limit the commercialization of solar cells are durability, efficiency, and price, while material availability and its impact on the environment are also considered. Layer thickness, material type, defects, and device architecture directly affect the fill factor (FF), power conversion efficiency (PCE), losses, and absorption capacity of the solar cell. The limiting parameters such as layer thickness, its properties, and defects can be controlled depending upon the type of the manufacturing technique used. Hence, depending upon the designing approaches, solar cell technology may be classified into two categories, i.e., crystalline Si-based technology and thin film-based technology, which are as shown in Fig. 1, and their corresponding merits and challenges are discussed further.

Crystalline silicon (c-Si) solar cell dominates the commercial PV landscape. At laboratory scale, these solar cells exhibit the highest efficiency of 26.3% and achieved efficiency on a commercial scale of about 25% [8]. The basic silicon



**Fig. 1** Classification of solar cells by technologies

(Si)-based *p-n* junction solar cell consists of p- and n-doped Si region and anti-reflective coating with metal contacts in front and back of the solar cell. Depending on the crystal structure, c-Si solar cells are further classified as monocrystalline and polycrystalline. The main advantage of Si-based solar cells is high durability. However, because of the complicated process development, researchers are exploring alternatives to Si-based technology [8, 9].

Thin film-based solar cells are an alternative to crystalline Si solar cell technology [10]. Thin film-based technology is further classified into various categories depending on the material type used as depicted in Fig. 1. In the thin film-based technology, the thickness is from few nanometers to few micrometers, which results in faster charge collection. Inorganic thin film-based solar cells require high vacuum and higher processing temperature which limits their large-scale production for solar cell application [11]. Multiple techniques including a-Si [12], QDSSC [13, 14], DSSC [15], and PSCs [16] exist within thin film-based technology out of which PSCs have shown phenomenal increase in efficiency from 3.8 to 22.1% [17–19] within few years. Keeping all these facts into consideration, this monograph chapter focuses on perovskite solar cells, different perovskite solar cell architectures, and their manufacturing processes.

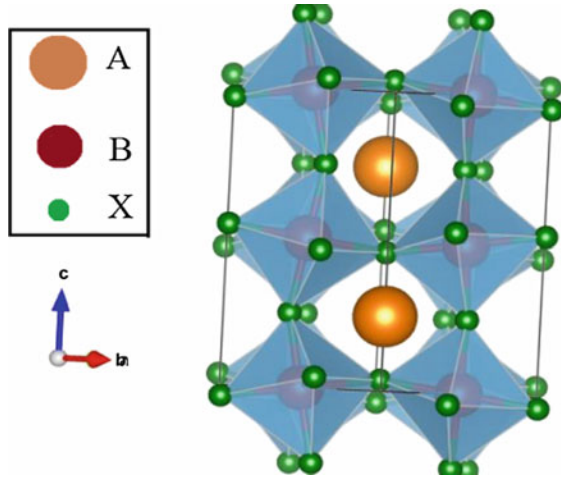
### ***Perovskite solar cells (PSCs)***

Perovskite solar cells have most significant improvement in terms of the efficiency in recent years. These solar cells have shown remarkable efficiency increase from 3.8% reported by Miyasaka and co-workers in 2009 [20] to 22.1% up to 2016 [17–19, 21]; the reported increase in efficiency within these few years makes it a very attractive light absorbing the material. Moreover, perovskites exhibit excellent optical and electrical properties. Thus, Perovskite solar cells exhibit improvement in optical absorption, synthetic feasibility, ease of fabrication, easy charge separation, and slow charge recombination rate [4, 22].

Perovskite is an organic–inorganic hybrid compound having an  $ABX_3$  crystal structure. The basic crystal structure of perovskite following  $CaTiO_3$ -type structure with lattice parameters  $a = 5.404 \text{ \AA}$ ,  $b = 5.422 \text{ \AA}$ , and  $c = 7.651 \text{ \AA}$  drawn using VESTA is as shown in Fig. 2.

In this structure, X represents halogens such as  $I^-$ ,  $Br^-$ ,  $Cl^-$ , or oxygen, whereas A and B are cations of different sizes having 12 and 6 coordinates with X anions, respectively [23]. Site A is occupied by the elements from the group I or II of the periodic table, whereas the site B is filled by the cations such as transition metals. The valence band maxima of perovskite are made by antibonding hybridization of “B = Pb, Sn” s-state and “X = Br, Cl, I” p-state, whereas conduction band minima are formed by  $\pi$ -antibonding of “B = Pb, Sn” p-state and “X = Br, Cl, I” p-state. Cation A, i.e., methyl ammonium, formamidinium does not directly contribute to valence band maxima and conduction band minima, but it does affect the lattice constants, and it was found that band gap increases with increasing lattice parameters. The ideal structure of the perovskite is similar to bcc with additional anions on the faces of the unit cell.

**Fig. 2** Crystal structure of perovskite using VESTA



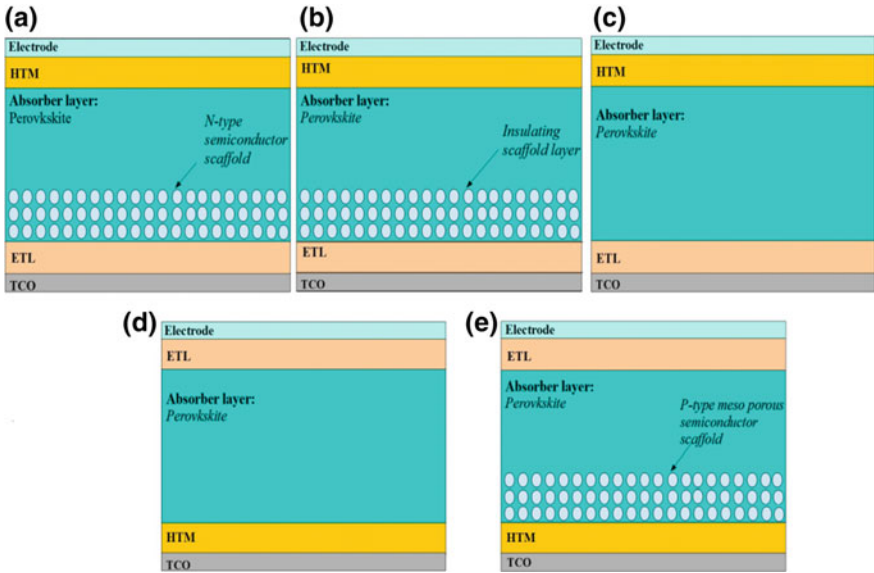
Perovskites are ambipolar and have attracted so much attention within a few years due to their small band gap, high carrier mobility, high absorption, and easy fabrication at low temperature [24–26]. Defects in perovskite solar cells lead to hysteresis effect which acts like traps for both electrons and holes. Less hysteresis indicates more uniform perovskite layer with lesser defects. The stability of perovskites is calculated using *tolerance factor* ( $t$ ) [23] which is given by:

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (1)$$

where  $r_X$ ,  $r_A$ ,  $r_B$  are ionic radii of ions for X, A, B sites, respectively. Tolerance factor affects the size of ionic radius. For  $t = 1$ , perovskite exhibits perfectly packed cubic structure; for  $0.8 < t < 1$ , perovskites exhibit highly stabilized structure, and with the increase in the value of  $t$ , symmetry value increases, resulting in band gap reduction [27, 28]. Depending on structural configurations, there are five types of PSC architectures, which again are classified into two categories, namely planar and mesoporous. Further, subclassification into various subcategories is as shown (Fig. 3).

Various factors such as device architecture, compositional engineering, and technique of film formation greatly affect the device performance. Film formation technique directly affects the efficiency of the solar cell. Perovskite films can be deposited by a variety of deposition techniques such as spin coating, drop casting, spray coating, ultrasonic spray coating, slot die coating, electrodeposition, CVD, thermal vapor deposition, vacuum deposition, screen printing, ink-jet printing [31–35].

The most common structures of Perovskite solar cells mainly consist of ITO, an electron-transporting layer, perovskite layer, hole-transporting layer, and the metal electrode [36]. Their efficiency depends on the materials used in various layers and



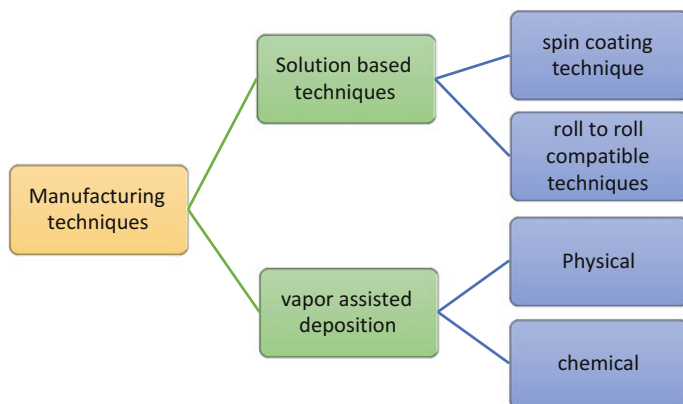
**Fig. 3** Different structures of PSC: **a** regular, **b** mesostructured, **c** planar heterojunction, **d** inverted planar heterojunction structure, **e** inverted p-type mesoporous structure [29, 30]

on the type of deposition technique used. This article attempts to report different techniques of depositing perovskite materials and their industrial scalability.

## 2 Manufacturing Techniques

The primary objective of the PV devices is to generate power efficiently and its large-scale applicability. However, while scaling the dimensions of the PV device, various challenges are encountered which are not found in small-area solar cells [37]. In the case of PSCs, one such difficulty is to control the morphology of perovskites over a large area [38, 39]. Depending on manufacturing technique, layer roughness also gets affected. Hence, manufacturing technique needs to be selected carefully [40, 41]. Thin film-based solar cells are rectangular so as to reduce the length that charge carriers move [42]. The reported scalable techniques for PSCs are solution-based deposition and vapor-assisted deposition techniques, which are further classified into subcategories as shown in Fig. 4.

PSC fabrication may either be carried out using *one-step* or *two-step* deposition technique. Electron lifetime directly depends on the type of the film deposited. One-step deposition of perovskite is the thin film deposition using a mixture of both  $\text{CH}_3\text{NH}_3\text{I}$  and  $\text{PbI}_2$ , while the two-step deposition is carried out using the separate



**Fig. 4** Classification of PSC manufacturing techniques

layer deposition of both  $\text{CH}_3\text{NH}_3\text{I}$  and  $\text{PbI}_2$  to produce highly uniform and defect-free layers. Layers obtained by using one-step deposition contain voids which result in faster recombination. Hence, the two-step deposited perovskite layer exhibits electron lifetime of about one order of magnitude greater than one-step deposited films. Also, two-step deposition offers better morphology control over one-step deposition [43]. The solution- and vapor-assisted manufacturing techniques and their subcategories are discussed as follows.

## 2.1 Solution Processing-Based Techniques

Solution processing-based technique is the most widely used technique for depositing perovskite thin films. Solution-processed deposition is carried out using various techniques such as spin coating, dip coating, doctor blade, spray coating, ink-jet printing, screen printing, drop casting, slot die coating. These techniques are illustrated as follows.

**Spin-coating technique:** Spin coating is the simplest and cost-effective solution-processed technique used for uniform deposition of the perovskite layers of the PSCs. This technique is mainly used for producing small-area solar cells. Generally, after spin coating, the film is baked to produce well-crystallized layers of the perovskite, since the baking results in strong adhesion and bonding between metal cations and halogen anions [44]. By setting up spin speed, acceleration, and time of spin coating, the film thickness and quality can be optimized. Highest recorded efficiency at laboratory scale using this technique is about 22.1% [17–19]. This technique can be used for the fabrication of inverted as well as regular PSC structures [32, 45, 46]. Achieved efficiency using spin-coating technique is very high, but this technique has the limitation of not producing a uniform film on larger

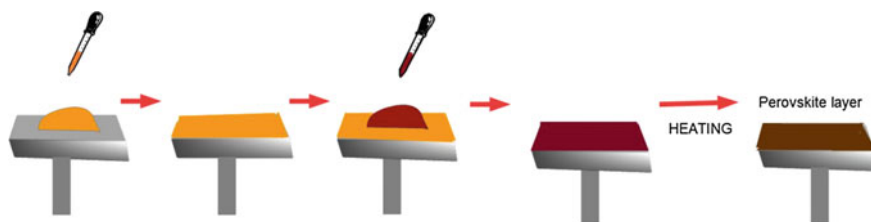


Fig. 5 Sequential steps of spin-coating process [44]

areas. Also, the film thickness varies from center to the end of substrate mostly in case of bigger substrates [47, 48]. The efficiency achieved using this technique is very high with a good level of reproducibility and morphology control in case of smaller sizes of modules. However, because of slow processing technique and also due to more material wastage, this technique is not a good solution for PSC manufacturing at large scale [42]. The two-step deposition of the perovskite using spin-coating technique is as shown in Fig. 5.

**Drop-casting technique:** Drop casting is a basic and low-cost method for the production of PSCs. This technique is similar to spin coating, but the major difference is that no substrate spinning is required. Also, the film thickness and properties depend on the volume of the dispersion and concentration. Other variables which affect the film structure are substrate wetting, the rate of evaporation, and drying process.

Volatile solvents are generally preferred for this technique which can wet the substrate. One of the advantages over spin coating is less material wastage. On the other hand, there are various shortcomings of this method including difficulty in controlling film thickness and non-uniform film formation on large size wafers [49].

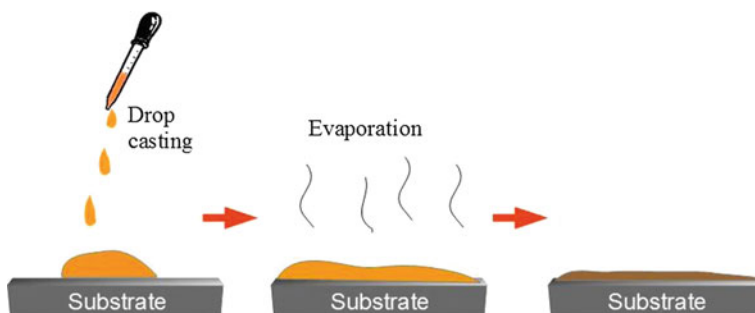
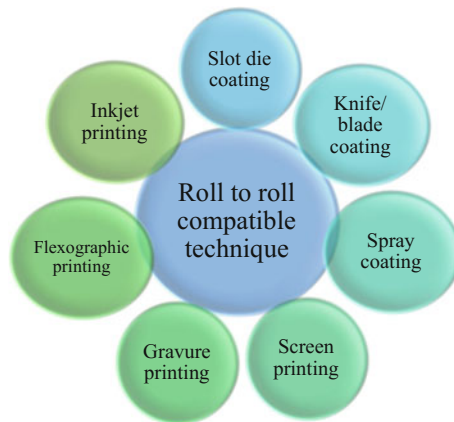


Fig. 6 Perovskite deposition using drop-casting technique [99]



**Fig. 7** Types of roll-to-roll fabrication techniques [51]

## 2.2 Roll-to-Roll Printing

Roll-to-roll printing is one of the best solution processing techniques used for the manufacturing of PSCs. This is a highly reproducible technique with an enormous potential of producing flexible PSCs at large scale with high throughput [50]. It includes different coating methods which are used to form a thin film on moving substrate by using rotating rolls. Roll-to-roll compatible printing techniques are shown in the Fig. 7.

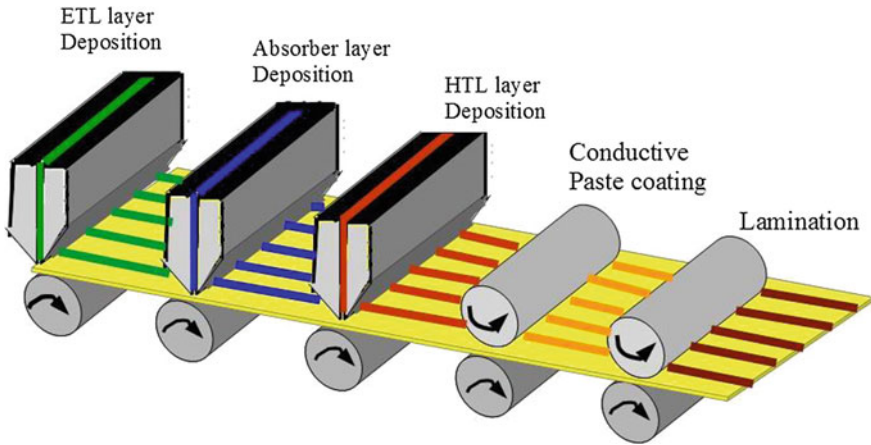
These techniques can be employed for fabrication of solar cells on flexible substrates. The continuous deposition is carried out at high coating speed [52]. For deposition of the active HTL and ETL layers, deposition by roll-to-roll printing technique, slot die coating is one the most preferred techniques because of the highly uniform film deposition by this method [42]. Using various roll-to-roll compatible methods, the PSC fabrication is as shown in Fig. 8.

Roll-to-roll deposition is the continuous process of depositing layers on the substrate for making solar cells by using various types of the roll-to-roll compatible techniques [53]. The biggest advantage of this kind of deposition is that very long wafers can be used leading to the bulk production of solar cells, faster technique, highly scalable and cost-effective technique.

### 2.2.1 Spray Coating

It is one of the most efficient and faster solution-based approaches for producing flexible solar cells. It is not dominating technique, but still it exhibits various advantages over one of the most dominating spin-coating techniques. As already discussed, spin coating is a small-scale thin film deposition technique due to scalability issue [54], while spray coating is a highly scalable thin film deposition





**Fig. 8** PSC solar cell production using roll-to-roll printing techniques [42]

technique [54, 55]. There are various other scalable thin film deposition techniques that include ink-jet printing [56], slot die coating [57, 58], doctor blade [51], out of which blade coating is one of the fastest and cheapest thin film deposition techniques, but still PCE achieved using spray-coating technique is about ten times greater than blade-coating technique. Along with this, various other advantages of this technique are rapid film deposition, low-cost processing, and deposition capability for large scale both on flexible and glass-based substrates. Moreover, the spray-coated films exhibit higher thermal stability and also show better optoelectronic properties as compared to spin-coated films due to better charge transfer capability and higher minority carrier lifetime [59].

This technique is compatible for deposition of both planar and inverted perovskite solar cell devices [60]. Recorded efficiency till now using this method is about 11%. Proper control over processing parameters such as carrier gas, substrate temperature, and annealing temperature is necessary [42]. Despite so many advantages, there are certain shortcomings of this technique such as difficulty in achieving fully covered and highly homogeneous layers. These shortcomings arise due to the liquid atomization phenomenon in which random spraying of different size droplets takes place which leaves patches of varying sizes on drying, and hence, the film shows unpredictable characteristics. This leads to an increase in series resistance, affecting the device performance. To overcome this problem, further modified spraying processes such as airbrush pen spray [61], electrostatic spray-coating technique [62], pulsed spray coating [63], ultrasonic spray-coating technique [64] are used.

**Ultrasonic spray coating:** It is one of the modified forms of spray-coating technique with the additional feature like proper morphology control of perovskite layer in ambience. The highest PCE achieved so far using this technique is 7.7% [64]. As previously discussed, two types of deposition, i.e., one-step and two-step

deposition, processes are used for perovskite deposition [43], out of which two-step deposition is preferred for better morphology control. However, in the case of spin coating (which is highly preferred technique at laboratory scale), it is difficult to control chemical reaction speed. Hence, ultrasonic spray-coating technique is a highly preferred technique for two-step deposition due to proper control over the rate of deposition. Thin films with larger grain size are obtained by this technique which helps in achieving high carrier mobility with low charge recombination.

Moreover, the hysteresis effect in the films obtained using this technique is less than that of spin-coating technique and conventional spray-coating technique. Hence, this is highly preferred technique over spin-coating and conventional spray-coating technique for the uniform deposition of the perovskite layer [65]. The basic schematic for the ultrasonic spray-coating technique is as shown in Fig. 9.

**Blow drying:** This is one of the complementary processes in manufacturing perovskite solar cells. This process can be clubbed with any solution-processed film deposition techniques such as spraying. Blow drying is a roll-to-roll compatible process and does not require any additional anti-solvent or the sacrificial component. The films produced by this method are very smooth and of excellent quality with the scalable solution processing sequence [66]. This method does not require sophisticated environmental conditions and complicated equipment. The whole process is carried out by dispensing perovskite solution onto the substrate and then absorbing of the excess solution by tissue paper followed by blow drying in the compressed air which leads to faster crystallization and good coverage [67]. The films prepared by blow-drying technique are reported to be darker which indicates higher absorbance of blow-dried films. Blow-dried films are smoother than the spin-coated films on the glass substrate (Fig. 10).

In blow-drying technique, airflow speed greatly affects the film uniformity and the airflow speed depends on the distance between the compressed air outlet and substrate and is measured by wind speedometer. As per the published articles, at

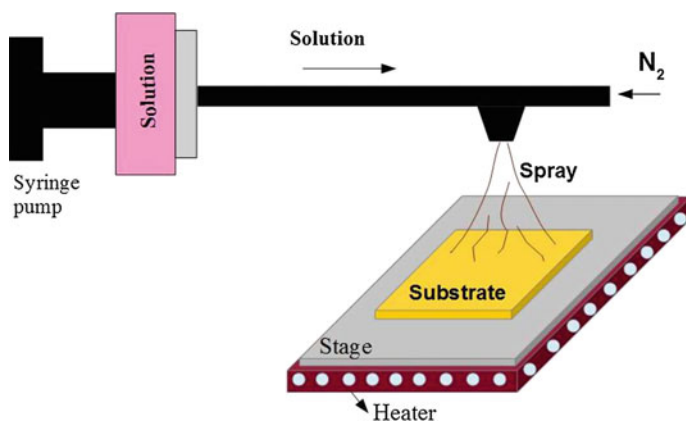
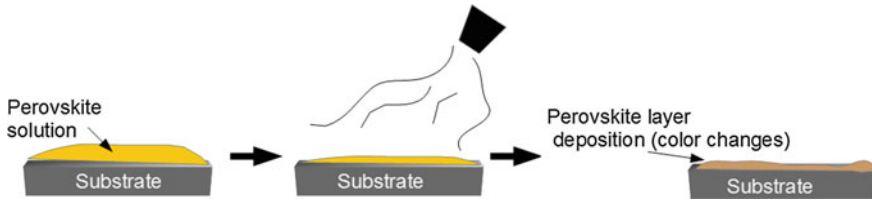


Fig. 9 Schematic diagram of ultrasonic spray-coating process [65]

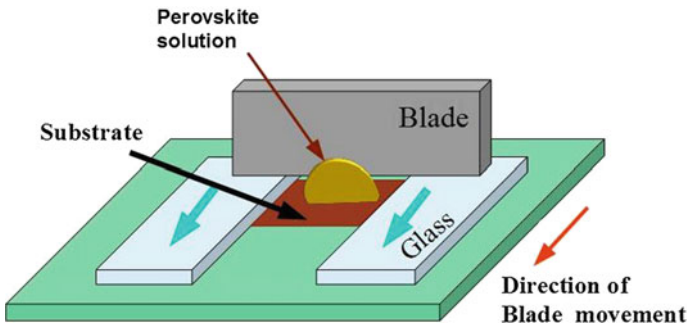


**Fig. 10** Basic schematic of blow-drying process [67]

low speed perovskite films exhibit branch like morphology which is commonly found in spin-coated films. As the airflow speed increases, the grain size reduces, and with further increase in speed ( $>25 \pm 2$  m/s), highly smooth film is obtained. So the advantages of blow drying over other solution-based techniques are that it does not require any time window for compressed air blowing, is of low cost, and has greater control on the film uniformity. Several other advantages of this technique include highly smooth and good quality films; no additional sacrificial component is required; highly scalable technique; easy component specification [68].

### 2.2.2 Blade Coating

It is one of the simple, environment-friendly, vacuum free, and low-cost solution-processed methods for the fabricating PSC at industrial scale using blade coater applicator [32]. Blade coater applicator is a simple coating system which consists of a screw of micrometer size used to adjust the height of the blade with respect to the substrate surface [42]. In this technique, film uniformity and quality can be controlled by controlling evaporation rate of inks by adjusting airflow over the substrate or by heating up the substrate to the boiling point of the solvent. The basic arrangement is as shown (Fig. 11).



**Fig. 11** Perovskite solar cell fabrication by blade-coating technique at laboratory scale [51]

This process delivers better film morphology control as compared to spray-coating and other roll-to-roll compatible techniques. This technique is used for the fabrication of planar heterojunction PSCs (Fig. 3c). Generally, most of the perovskite deposition techniques result in pinhole formation in the perovskite layers due to non-uniform deposition and the presence of moisture and air which often leads to performance degradation of photovoltaic devices. So as to overcome these challenges, blade coating is preferred [69]. It is one of the highly recommended processes for the growth of self-assembled perovskite crystalline domains with the features like uniform film coverage and improved device stability. Furthermore, this technique has advantages of uniform, high-throughput deposition and easy application on flexible substrates [51].

Yang et al. [70] have reported slow crystallization rate in case of blade-coating technique which often leads to large size agglomeration forming air protection patches and thus restricts the moisture permeability of the perovskite layer. Hence, the films obtained by this technique are highly stable with better morphology.

According to Kim et al. [71], due to the feature of depositing electron-transporting layer (ETL) and hole transporting-material (HTM) layer along with perovskite layer, this technique can be implemented at large scale. However, the major loophole behind the implementation of this method is precise control of ink used, and for overcoming that problem, the use of slot die coating is made, which is having same operating principle as blade-coating technique.

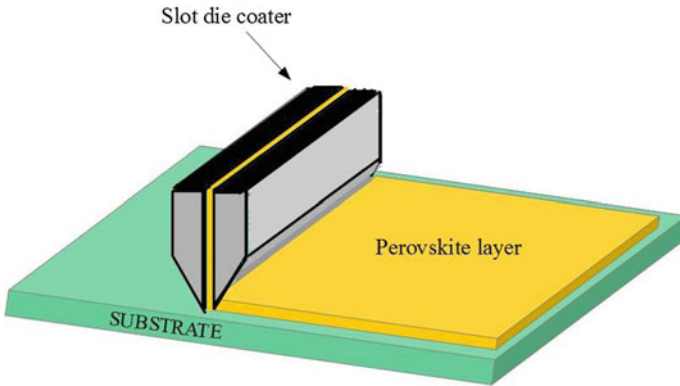
### 2.2.3 Slot Die Coating

This is a solution-processed, roll-to-roll compatible, highly scalable process and is almost similar to blade-coating technique with the advantage of less or no material wastage which is seen in the case of blade-coating technique. Among other techniques, this technique has achieved large success in the production of PVs. This process produces uniform and controlled thickness film in the material and is called as premetered coating process [57]. By controlling the amount of the material feeding, thickness of the film can be controlled.

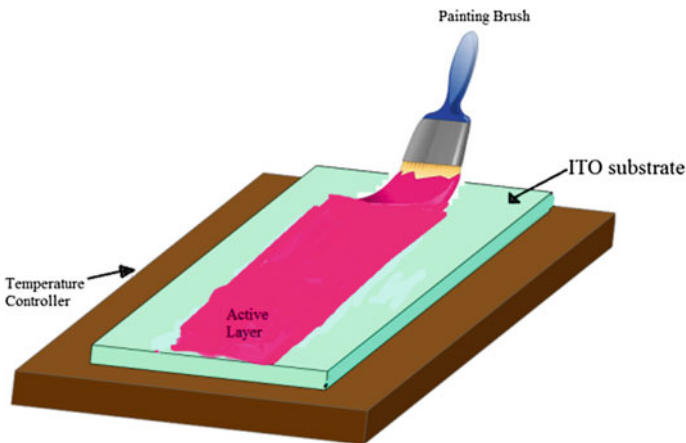
It is a laboratory to fab transition technique, i.e., having high potential to be used at industrial scale for PSC manufacturing [72]. This process is advantageous over the spin-coating technique in terms of scalability over a large-scale and less material wastage. The basic schematic of the slot die coater using mini roll coater unit is as shown in Fig. 12.

### 2.2.4 Brush Painting

Brush painting is one of the simplest methods for manufacturing perovskite solar cells. It is a high-speed fabrication technique with the low material loss. It is a faster technique as no annealing process is involved in this process. It is a highly



**Fig. 12** Perovskite layer deposition using slot die coating technique [73]



**Fig. 13** Perovskite layer deposition using brush painting technique [76]

cost-efficient technique and can be used in large-area flexible solar cells. With proper optimization of the concentration of the solvent and the perovskite material, a high-efficiency solar cell can be attained. Moreover, while using this process, there is no need to control the experimental condition or any other time-consuming procedures [74, 75]. An illustration of PSC fabrication using brush painting technique is shown in Fig. 13.

Advantages of brush painting include the absence of vacuum and fast processing which makes it very cost-effective technique. Brush-painted devices exhibit improvement in efficiency as compared to spin-coating technique as no thermal annealing is required. The downside of brush painting may be controlling the uniform thickness.

### 2.2.5 Electrodeposition

Electrodeposition is versatile, and roll-to-roll compatible technique is used for producing PSCs. Its cost-effectiveness, rapidness, and a high degree of uniformity make it a desirable technique for perovskite layer deposition [77]. The basic features of this technique are as follows:

- A versatile technique for producing surface coatings,
- Low-temperature variation technique,
- The rapid deposition technique,
- Large-scale productivity,
- Low cost,
- Well-controlled film thickness.

Unlike spin-coating technique, no heating of the substrate takes place in this procedure since heating results in the rough film. When heat is applied, then the film breakdown and island formation take place randomly on the surface of the substrate [78]. The schematic illustration of the PSC fabrication using electrodeposition technique is shown in Fig. 14.

Thin films produced by electrodeposition are highly uniform with large-area coverage with no shear forces [79, 80]. Perovskite layer deposition on complex shaped substrates, which is not possible using other techniques discussed so far, makes it a very attractive approach for manufacturing at large scale [77].

### 2.2.6 Ink-Jet Printing

This is a versatile, non-contact, additive patterning technique used for the production of the solar cells, optoelectronic devices, and field-effect transistors. Less

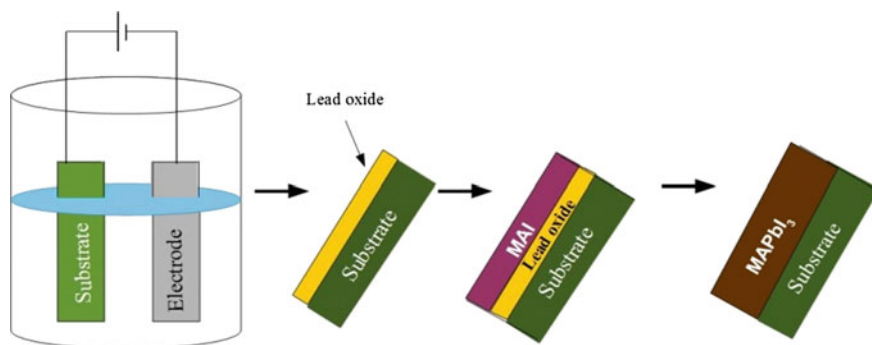
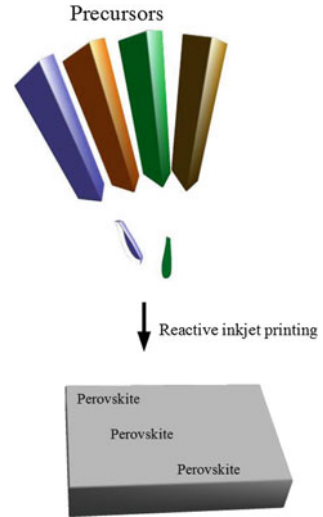


Fig. 14 PSC fabrication using electrochemical deposition [78]

**Fig. 15** Schematic illustration of the fabrication of perovskite material using reactive ink-jet printing technique [82]



material wastage, high scalability, and fast deposition of the material on large area make it an attractive approach for large-scale production of the perovskite solar cells [81, 56]. It is used for the highly specific in situ synthesis of the material on the large substrate and thus simplifies the fabrication process. The basic schematic of perovskite solar cell fabrication using ink-jet printing technique is shown in Fig. 15.

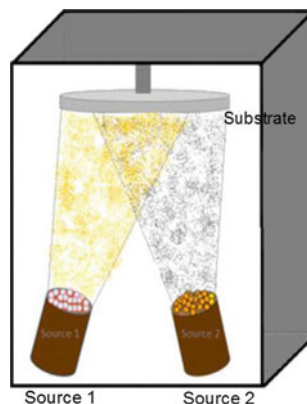
This process involves the selective ejection of the ink from the chamber through the nozzle on the substrate. Due to the external bias application, the chambers filled with liquid get contracted, which leads to a shock wave in the liquid and causes ejection of a liquid droplet from the nozzle. According to Jiang et al. [82], the main issue with this technique is blocking of the nozzle which is due to poor solubility of material solvents. Various observations made during ink-jet printing technique are as follows:

- a. More viscous ink requires more applied bias and thus results in the formation of the small droplets.
- b. If intermediate bias is applied in two different inks, then it results in the jetting of the inks.
- c. Higher voltage results in the never recombined small size droplets.
- d. Pinch-off point of different liquids matters a lot during printing.

### 2.3 Vapor-Based Techniques

Solution- and vapor-based techniques are the most dominating techniques for fabricating perovskite absorber layers. Out of both, vapor-assisted approach has better film uniformity. Vapor-based techniques are further classified into two main

**Fig. 16** Vapor deposition of perovskite layers [31]



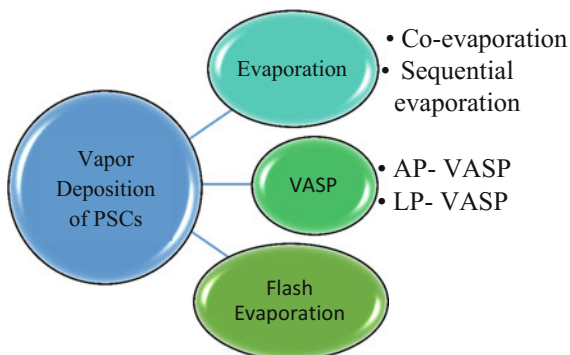
categories, i.e., physical- and chemical-based techniques. Vapor deposition process results in highly crystalline and uniform films with thickness in nanometers, as compared to micrometer thick films by solution-processed techniques. Moreover, the vapor-deposited thin films are uniform, while the solution-processed layered thin films are of much larger crystal grain sizes than the field of view. As per the reported work, vapor-deposited PSCs are more efficient than the solution deposited. Till now, the reported highest PSC efficiency fabricated by vapor-based technique has reached an efficiency of 15.4% [31] (Fig. 16).

The thickness of perovskite layer significantly affects the optical (absorption) efficiency of the solar cell. If the film is very thin, then the solar cell will not be able to absorb much sunlight, whereas with thick films, the time needed for the electron and hole to reach the contacts increases, resulting in more recombination. If the film is missing in certain areas, then it results in direct contact between ETM and HTM and thus results in the shunting path which leads to lower fill factor (FF) and open-circuit voltage ( $V_{oc}$ ). The main advantage of the vapor deposition process over the solution processing technique is that by using vapor deposition process, multi-stack thin films over large areas can be produced. Vapor technique is most widely used on the industrial scale including glazing industry, liquid crystal display industry, and thin film solar industry. Moreover, with vapor deposition technique, charge collection at interfaces can be easily tuned. Thus, the vapor deposition is one of the preferred routes for manufacturing uniform thickness solar cell layers [64] (Fig. 17).

The shortcoming of vapor-based techniques is the requirement of vacuum. In vapor-based techniques, a vacuum is employed to increase the mean free path of the vapors for producing highly uniform thin films of very high purity. Various types of the vapor-assisted approach used for deposition of perovskite layers are discussed as follows.



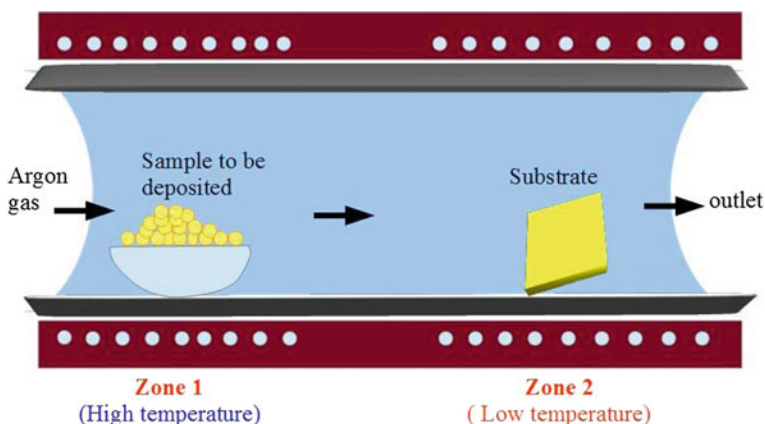
**Fig. 17** Classification of various vapor phase deposition techniques for PSCs [64]



### 2.3.1 CVD

This is one of the promising vapor deposition techniques for large-scale production of highly scalable and uniform pinhole-free perovskite thin films. Unlike other vapor deposition method where challenges were like low material utilization, difficulty in controlling flux deposition, CVD technique was employed for fabricating perovskite films [83–85]. Merits of CVD technique including high material yield ratio and scalability makes it a desirable technique for depositing perovskite layers [86, 87]. The basic schematic of the perovskite layer deposition using a round tube by CVD technique is shown in Fig. 18.

Perovskite layers are deposited by co-evaporation of two different precursors which are heated, mixed, and then transferred to a preheated substrate using carrier gas to form highly uniform, pinhole-free films with larger grain size and long carrier



**Fig. 18** Schematic of perovskite film fabrication using chemical vapor deposition technique [83]

lifetime. However, this technique requires very high vacuum and uniform co-evaporation of material, which is very challenging for mass production.

### 2.3.2 Physical Vapor Deposition

This is a very simple and non-reactive thin film deposition process which allows the complete surface coverage of the substrate along with the great stability of the solution against the moisture. Various advantages of this technique are as follows:

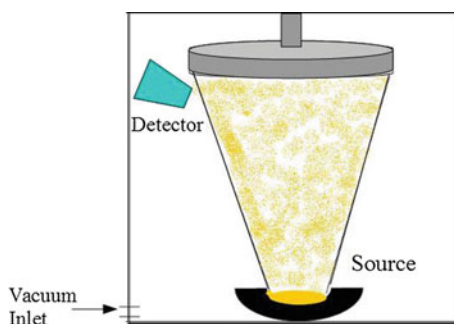
- full surface coverage,
- well-defined grain structure,
- high crystallization and reproducibility,
- the tetragonal phase purity,
- more control on film quality, thickness, and morphology (better than the solution process technique).

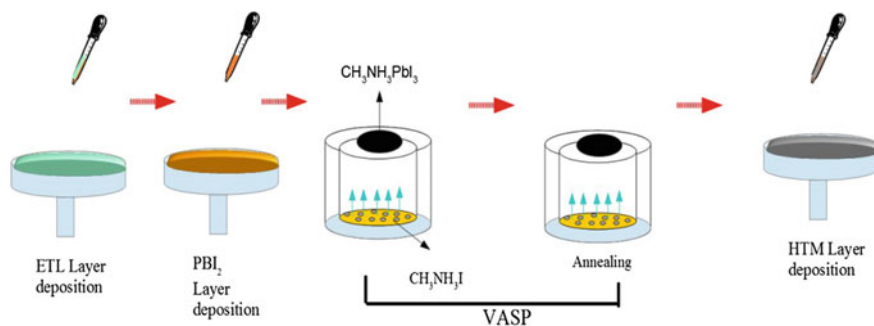
This method is different from other techniques such as one-step coating technique, two-step sequential vapor-assisted solution process, and dual source vapor deposition method [88]. This method avoids the problems such as high reaction rate, impurities, improper heat treatment.

This approach results in the production of the uniform, smooth, and non-porous films with uniform surface coverage with good crystallization. Hence, we can say that this process is one of the attractive methods for fabrication of high-quality perovskite films. As per the reported data, about 15.4% of efficiency has been attained. The basic schematic diagram of SSPVD technique is shown in Fig. 19.

Very dense, uniform, and compact films can be obtained by using SSPVD technique which indicates that this method can be used at large scale for bulk production of PSCs [88]. The formation of uniform, smooth, and complete surface covering film indicates that no heat treatment is required in this process. PCE about 10.9% was obtained using this process. Hence, it is one of the most promising techniques for the fabrication of the PSCs.

**Fig. 19** Single-source physical vapor deposition process of the perovskite  $\text{MAPbI}_3$  thin film [88]





**Fig. 20** PSC deposition including VASP process for perovskite deposition [94]

### 2.3.3 Vapor-Assisted Solution Process

This technique is used for deposition of pinhole-free perovskite layer. Salivation and dehydration problems are encountered in vapor deposition process. In VASP technique,  $\text{CH}_3\text{NH}_3\text{I}$  vapors react with  $\text{PBI}_2$  forming larger grain size perovskite films. The film morphology obtained by solution-based approach is different from the VASP-based technique [89–93] (Fig. 20).

VASP is a two-step sequential deposition technique where the first step is film deposition in solution-based deposition process, while the second step is vapor deposition process. In the case of solution-assisted techniques, the films get degraded very rapidly. Hence, gas-assisted VASP technique is used to overcome that problem [95–97]. The problem in the deposition of the mixed halides mainly restricts the application of this technique at industrial scale [98].

## 3 Conclusion

PSCs are thin film-based solar cells with tremendous increase in efficiency up to 22.1% in quite few years, makes it to be the best alternative of the current wafer-based solar cells. Low-cost, thin film-based technology, less bulkiness, etc., make it the next choice of the industry. Manufacturing techniques of perovskite solar cells, i.e., liquid- and vapor-assisted techniques, were discussed, and it was found that both the techniques have their own dos and dont's which directly affect their manufacturing at large scale. Solution-based techniques are very fast and cost-effective, but they have uniformity and stability issues. On the other hand, vapor-based techniques carried out in a vacuum-based environment which helps in achieving uniform films of high purity but makes the deposition costlier and slow too. Depending on all these facts, the major concern is on roll-to-roll compatible

techniques to produce large size, flexible PSCs. Apart from the scalable process development, perovskite research is focused on improving the long-term stability of these solar cells and development of new cost-effective materials.

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