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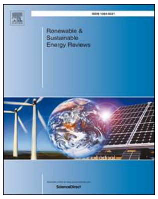

Fabrication techniques and morphological analysis of perovskite absorber layer for high-efficiency perovskite solar cell: A review

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ABSTRACT

Organolead trihalide perovskite absorber layers are potential contenders in solar energy harvesting technologies because of their competitive lower fabrication cost, high power conversion efficiency, and ease of processing. The structural, interfacial and morphological properties are the key aspects to determine the stability and photon-to-current conversion efficiency of Perovskite solar cells (PSCs). Most contemporary research has emphasised on enhancing the power conversion efficiency (PCE) of perovskites by changing the fabrication process, solvent engineering, or precursor solution. With changes in these variables, the structure and morphology of perovskites also change, which affects the photon-to-current conversion efficiency and the stability of the PSCs. However, no stockpiled records have aided in conducting corresponding research outcomes on this perspective. In this review, we summarise the effect of fabrication method on the structure and morphology, as well as the PCE and stability of PSCs. This review will help readers decipher the scientific and technological challenges concerning hybrid inorganic–organic PSCs.

1. Introduction

The conversion of solar radiation to electricity by a photovoltaic cell was first demonstrated in 1954. Due to the formation of a p–n barrier in silicon, photons were observed to generate electron–hole pairs which could be successfully transported to an external circuit [1]. Over the past five decades, silicon solar cells (SCs) have shown significant progress with high energy output and affordable production cost [2,3]. At present, the current global photovoltaic (PV) market is fully dominated by the crystalline silicon technology, in which 55% and 36% are polycrystalline and monocrystalline silicon modules, respectively. The remaining share of the PV market is open to the development of organic PVs (OPVs), perovskite solar cells (PSCs), dye-sensitised solar cells (DSSCs), quantum dot solar cells (QDSCs) and polycrystalline thin-film solar cells [4,5]. In comparison with other 1st generation SCs, Si-SCs have led to reduce cost with few limitations. Due to dependency on vacuum and temperature conditions during manufacturing, the processing costs of these SCs are still high. Although the PV market is dominated by silicon-based solar cells, the price range of these solar cells remains below an affordable level for individual users due to their complex manufacturing process, high energy consumption, and high throughput cost [6–8]. The 3rd-generation SCs such as PSCs, OPVs, QDSCs, and DSSCs have offered a great versatility in terms of lighter weight, flexibility, choice of various synthesised material, simple device fabrication techniques, and most importantly, commercial-scale production with low cost [9–13]. Although the overall performance of 3rd-generation SCs has exhibited rapid evolution at the research scale, they lag behind other types of solar cells. Critical bottlenecks, such as limited efficiency, toxicity, and cost, and challenges with stability, reproducibility, and scalability hinder their ability to compete with existing solar technologies in power grid applications and the current electronics market. Considering the above-mentioned pros and cons, hybrid inorganic–organic PSCs are considered as one of the rising stars in the PV industry due to their high efficiency, low-temperature processing, and

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easy fabrication techniques.

Hybrid inorganic–organic perovskites indicate high absorption coefficients, high charge-carrier mobility, low exciton binding energy, long exciton diffusion length, and an easily tuneable band gap [14–19]. The staggering properties of the perovskite absorber have led to an increase in PCE from 3.8% to 22.1% within a period of only eight years [20,21]. However, PSCs are challenged with long-term stability and reproducibility problems, mainly due to the unstable behaviour of perovskite compounds in an ambient environment, and the synergistic factors of the functional components in PSCs [22]. Salhi et al. reviewed in depth the latest developments and shortcoming in the stability of PSCs. They presented moisture, elevated temperature, UV light, and exposure to the environmental condition as the leading causes of degradation in the PSCs [23]. Ansari et al. extensively reviewed the challenges and opportunities of perovskite solar cells. They focussed on the role of structure and composition of perovskite materials, and the deposition methods used for the perovskite layer [24]. Understanding the role of fabrication procedures in perovskite absorbers is important to further enhancing PV performance and reducing the overall production costs for role-to-role production. Low cost, easy reproduction, and facile deposition techniques are preferred for the fabrication of perovskite films. Various methods have already been subjectto intense investigation, and have been verified for the fabrication of high-quality perovskite layers for high-efficiency PSCs. Given that the film quality of perovskite plays a pivotal role in the overall performance of solar cells, obtaining high-quality perovskite films with high phase purity, fewer structural defects, suitable morphology, and high crystallinity are necessary.

In this review, we elaborate on the structure of perovskite materials and their development chronologically to the present day. The main part of this work discusses existing fabrication methods of perovskite film for PSCs applications. By considering the aforementioned technical and theoretical aspects, we discuss all existing fabrication methods of perovskite film with structural and morphological analysis for PSCs applications. Notably, the phase transition, microstructure, defect states, band gap, and optical properties of perovskite films are strongly affected by the post-operating temperatures and deposition methods. Moreover, the band gap, optical constant, and optical absorption may also be affected by processing techniques. Therefore, in this review, we focus on the correlation of the structural and morphological properties of perovskite films with their corresponding deposition techniques at the end of each section.

1.1. Structure and properties of perovskite compounds

Universally, the general chemical formula for perovskite material is AMX_3. It consists of two different sizes of cations (‘A’ and ‘M’) and one anion (‘X’), in which the ideal cubic symmetry of the 'M' cation is located in six-fold coordination while it is encircled by an octahedron of anions, while the 'A' cation is in a twelve-fold cuboid octahedral coordination, as shown in Fig. 1.

The most attractive features of perovskite structures are organic molecule cations that are based on amine ($CH_3NH_3^+$) at 'A' sites, metal cations (Ge^{2+}, Sn^{2+} and Pb^{2+}) at 'M' sites, and halide anions (Cl^-, Br^- and I^-) at 'X' sites. The extraordinary properties of this unique structure has led to significant interest among scientists worldwide [26]. In 1978, Weber synthesised the first organic–inorganic halide perovskite $CH_3NH_3PbX_3$ [27], which exhibited different colours when the stoichiometric parameter was varied. The ion 'A' balances the charge of the framework without distressing the band gap; however, the size may lead to shrinking or expansion of the crystal lattice and a final effect on the band gap [28–30]. A series of materials with different band gaps can be obtained by controlling the size of the 'A' ion. Metal–halide bond angle also indicates a significant effect on the band gap. The band gap of the metal halide increases with the decrease in bond angle. The band gap of various metal halides is shown in Table 1. Studies also show that the stability of the perovskite group follows the trend $AGeI_3 < ASnI_3 < APbI_3$ [31].

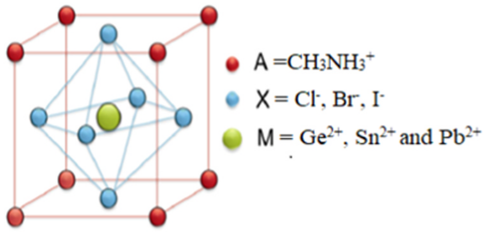

Fig. 1. Molecular structure of perovskite compound (Reprint permission from Ref. [25]).

Table 1
Effect of M cations on perovskite energy gap [32].

Material	LUMO/eV	HOMO/eV	E_g/eV
$CH_3NH_3PbI_3$	− 3.88	− 5.39	1.51
$CH_3NH_3Sn_{0.3}Pb_{0.7}I_3$	− 3.81	− 5.12	1.31
$CH_3NH_3Sn_{0.5}Pb_{0.5}I_3$	− 3.67	− 4.95	1.28
$CH_3NH_3Sn_{0.7}Pb_{0.3}I_3$	− 3.69	− 4.92	1.23
$CH_3NH_3Sn_{0.9}Pb_{0.1}I_3$	− 3.57	− 4.75	1.18
$CH_3NH_3SnI_3$	− 3.63	− 4.73	1.10

Other mixed-lead halide perovskite compounds, such as $CH_3NH_3PbI_{3-x}Cl_x$, have direct band gaps in the range of 1.61–1.96 eV [33]. $CH_3NH_3PbI_{3-x}Br_x$ shows direct band gaps of 1.58–2.28 eV [30], which depend on the value of x. Therefore, these materials are excellent light absorbers that can effectively cover a wide range of solar emission spectra from ultraviolet to infrared wavelength regions. $CH_3NH_3PbI_3$ contains weak bond exciton binding energy ranging from 37 meV to 50 meV and provides a pathway for easy movement of free carriers [34–36]. It shows exceptional charge carrier transportation properties that make it a popular choice for optoelectronic device fabrication. As a single crystal, $CH_3NH_3PbI_3$ has large diffusion length that exceeds 175 µm, whereas in the form of thin film, $CH_3NH_3PbI_{3-x}Cl_x$ has a diffusion length of up to 1 µm, as presented in Table 2. Carrier mobility and recombination were measured for single crystals using Hall effect measurement and impedance spectroscopy, respectively, at 1 sun illumination. However, diffusion lengths of single crystals and thin films were measured by combining the mobility and lifetime. The Hall effect measurement was conducted with a sample size of 1.5 mm × 1.5 mm × 1 mm in dark conditions. All four electrodes were made of Ga. A source meter (Keithley 2400) was used to apply DC current, and a different source meter (Keithley 4200) was used to record the Hall voltage. The carrier recombination of thin film was measured by a laser flash spectrometer (LP920). The measurement was based on a standard transient absorption setup. During this observation, a nanosecond laser pulse is used to excite the sample. The time evolution of the differential absorption changes induced by the pump which is monitored by a continuous wave light source probe.

Fig. 2 provides the electronic band structure of AMX_3 perovskite (A = CH_3NH_3, CH_2NHCH_2, Cs; M = Pb, Sn; X = I, Br, Cl) with several crystal structures. In Fig. 2(a)–(d), the band gaps increase with increasing electronegativity of M–site and X-sites, and decreasing symmetry of the crystal structures (orthorhombic > tetragonal > cubic). However, there is no existing mechanism to explain the change in band gap with the variation in the A cation [37].

1.2. Chronological development of PSCs

The chronological development of PSCs is shown in Table 3. In 2009, Miyasaka first introduced PSCs with mesoporous TiO_2 as the template for $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$ as a photoactive layer, which resulted in a PCE of 3.81% [21]. Park et al. optimised a method