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Hysteresis-free two-dimensional perovskite solar cells prepared by single-source physical vapour deposition

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ABSTRACT

Hysteresis-free two-dimensional (2D) pervoskite solar cells are prepared by single-source physical vapour deposition (SSPVD). The $(BA)_2(MA)_3Pb_4I_{13}$ 2D perovskite films are prepared by thermal evaporating their crystal powder and post-annealing. The dense and uniform films are formed on the surface, with high crystallization and full surface coverage. Especially, these films exhibit good chemical accordance with the precursors and optical properties. A photovoltaic efficiency of approximately 4.5% with no hysteresis was obtained for $(BA)_2(MA)_3Pb_4I_{13}$ solar cells fabricated by SSPVD. These initial results suggest that single-source physical vapour deposition is a promising method for preparing high-quality complicated multi-cation 2D perovskite films for solar application.

1. Introduction

In recent years, the rapid increase in photoelectric conversion efficiency has made the organic-inorganic metal halide perovskite materials become the candidates for the next generation thin film solar cells and optoelectronic devices (Burschka et al., 2013; Kojima et al., 2016; Kim et al., 2012). Currently, most of researches have been focused on three-dimensional perovskites, such as $CH_3NH_3PbI_3$, $HC(NH_2)_2PbI_3$ and their mixed alloys with halides, as light absorber materials because of their outstanding natural advantages (Green et al., 2014), including high extinction coefficients, electron and hole bipolar transport, medium band gap, small excitation binding energy and higher carrier diffusion length (Baikie et al., 2013; Im et al., 2011; Tiep et al., 2016). Accumulated photoelectric conversion efficiency (PCE) of perovskite solar cells under the efforts from multiple research groups reached a world record of 22.1% (Zhang et al., 2017; Yang et al., 2015). Unfortunately, the long-term stability of the three-dimensional perovskite is hindering the large-scale commercialization of perovskite solar cells (Liu et al., 2016). The poor stability is due to their low formation energy and the higher hygroscopic properties (Liao et al., 2017; Bi et al., 2016). Compared with the 3D perovskite, 2D perovskite $(CH_3(CH_2)_3NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$ ($(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$, n = 1, 2, 3, 4, ∞), especially $(CH_3(CH_2)_3NH_3)_2(CH_3NH_3)_3Pb_4I_{13}$ ($(BA)_2(MA)_3Pb_4I_{13}$), provided more tunability of their optoelectronic properties due to their greater freedom in chemistry and quantum mechanics, and more importantly environmental stability (Snaith et al., 2014; Stoumpos et al., 2017). Therefore, the development of two-dimensional perovskite films is a prioritized choice to improve the stability of perovskite solar cells (Tress et al., 2015).

Nowadays, many methods have been developed to prepare high quality perovskite films, such as solution methods (including one-step and two-step spin coating), solution evaporation deposition and vacuum dual-source heat evaporation (Stoumpos et al., 2016; Nemnes et al., 2017; Era et al., 1994; Richardson et al., 2016; Cao et al., 2015). Chemical solution methods, including one-step spin coating and two-step spin coating, are simple methods to fabricate perovskite solar cells with high power conversion efficiency (Rong et al., 2017; Nenon et al., 2016; Heo et al., 2015). Unfortunately, due to the faster reaction rate, it is difficult to control the formation of halide perovskite thin films, and sometimes resulting in the hysteresis and fast degradation of devices because of the pinholes or PbI_2 residuals formed in perovskite films. Especially, the chemical solution methods involving spin coating are facing the problem of fabricating large-area solar cells, which will be a drawback for future industrial application (Lee et al., 2016). As for 2D perovskite solar cells, the hot casting method was developed for the thin films preparation by mixing the stoichiometric raw materials into the solutions as precursors. However, the film quality prepared by this method was not uniform, and the temperature control during the spin coating process was a big challenge. Moreover, so far it was difficult to prepare large-area 2D perovskite thin films by this method (Rehman

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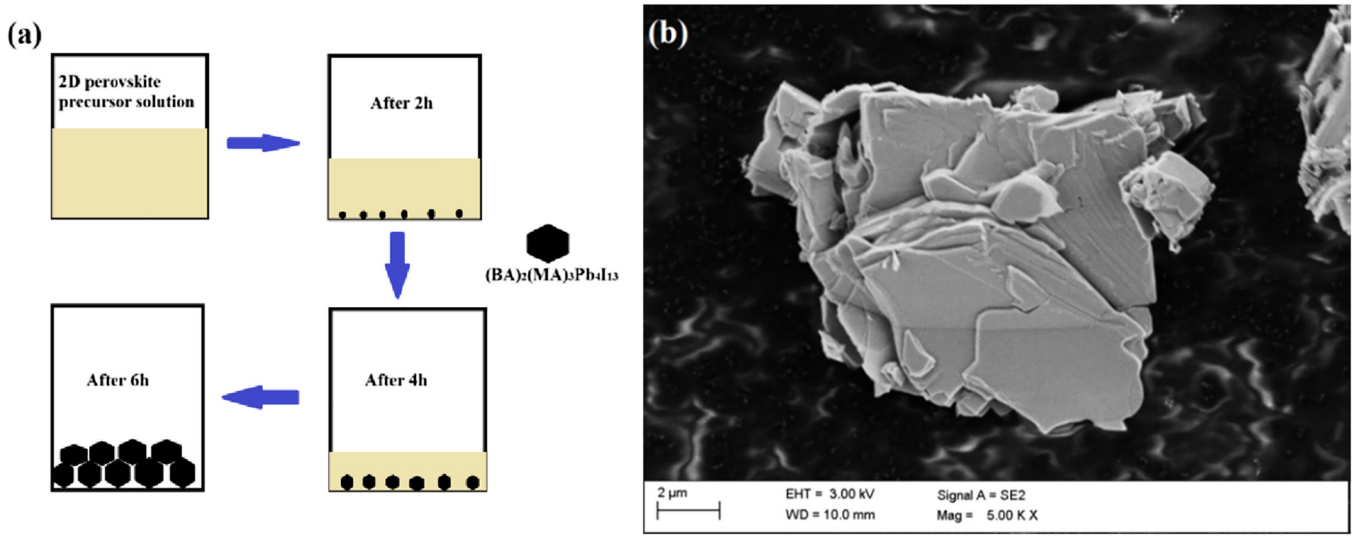

Fig. 1. (a) Progress of the $(BA)_2(MA)_3Pb_4I_{13}$ crystal growth and (b) the SEM of $(BA)_2(MA)_3Pb_4I_{13}$ crystal.

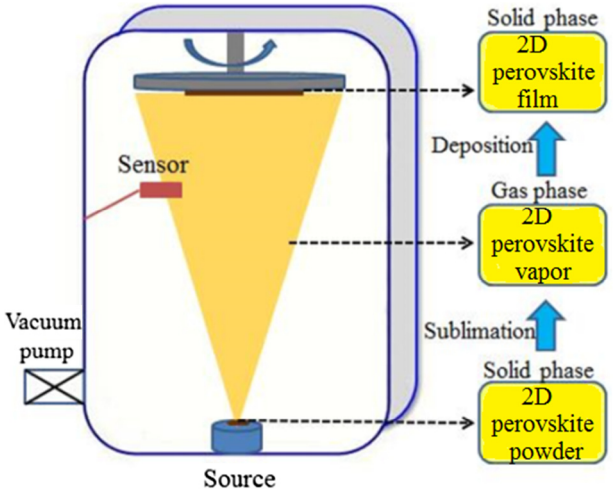

Fig. 2. Single-source physical vapour deposition process of the 2D perovskite $(BA)_2(MA)_3Pb_4I_{13}$ thin film.

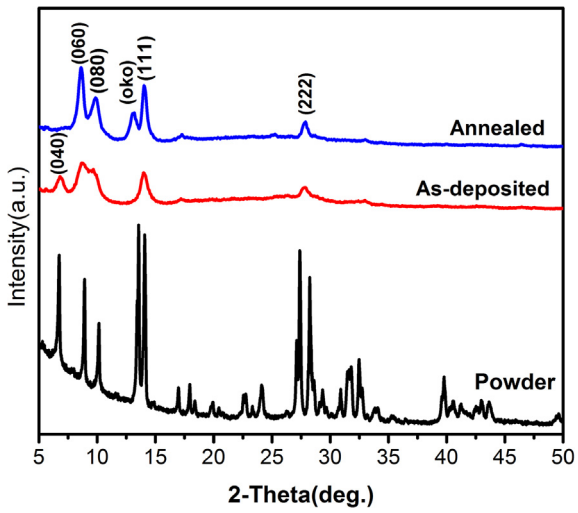

Fig. 3. XRD patterns of the 2D perovskite $(BA)_2(MA)_3Pb_4I_{13}$ powder, as-deposited, and annealed films.

et al., 2017; Yang et al., 2016; Choi et al., 2014). Therefore, the development of large-area, high-quality and high-stability perovskite thin films is an important topic for future application, especially for promising two-dimensional (2D) perovskites thin films. So far as we know, single-source physical vapour deposition (SSPVD) was a promising method for preparing high-quality 3D perovskite thin films (Liang et al., 2015; Amat et al., 2014). However, there are few reports on this method for two-dimensional (2D) perovskites thin films (Fan et al., 2016).

In this study, single-source physical vapour deposition was introduced for the preparation of an absorption layer $(BA)_2(MA)_3Pb_4I_{13}$ (n = 4) for 2D perovskite thin films and solar cells. Uniform, smooth and nonporous 2D perovskite films with full surface coverage, high purity phase and good crystallization. The solar cells based on these films show initial results of hysteresis-free characteristic and a champion PCE of 4.5%.

2. Experimental section

2.1. Material preparation

Preparation of 2D perovskite $(BA)_2(MA)_3Pb_4I_{13}$ powder: 10.05 g of BAI, 46.10 g of PbI_2 (99.99%, Sigma Aldrich) and 11.93 g of CH_3NH_3I were dissolved in γ-butyrolactone solution (100 ml, 99% Sigma Aldrich) in a 250 ml round bottom flask for 24 h with constant magnetic stirring, and then the precursor solution was transferred to a culture dish and placed on a heating table. After heating at 160°Cfor 4 h, the purple-black products were obtained. Finally, the purple-black products were ground to fine powder before use.

Table 1
The composition of $(BA)_2(MA)_3Pb_4I_{13}$ powder, as-deposited, and annealed films determined by EDS analysis.

Sample	Pb (at.%)	I (at.%)	Pb/I
Powder	23.72	76.28	0.310
As-deposited films	26.76	73.24	0.365
Annealed films	24.57	75.43	0.325

2.2. Film preparation

Preparation of 2D Perovskite $(BA)_2(MA)_3Pb_4I_{13}$ thin films by single-source physical vapour deposition method. The 2D perovskite thin films were prepared by single-source physical vapour deposition method