Decoupling Structure and Composition of CH$_3$NH$_3$PbI$_{3-x}$Br$_x$ Films Prepared by Combined One- and Two-Step Deposition

Muhammad Z. Mokhtar* and Brian R. Saunders

School of Materials, University of Manchester, M13 9PL, U.K.
*Corresponding author: muhammadzulhasif.mokhtar@manchester.ac.uk

ABSTRACT Perovskite solar cells (PSCs) continue to attract great interest due to their facile preparation and outstanding properties. The solution-based methods used to prepare PSCs usually involve one-step (1-s) or two-step (2-s) deposition. Here, we investigate mixed halide perovskite films (MAPb$_{3-x}$Br$_x$) prepared using a new solution based method that combines 1-s and 2-s deposition. Mixed halide films prepared using 1 & 2-s deposition are shown to have structures and optoelectronic properties that depend strongly on the order of addition of the reactants. The results suggest a tunable competition occurred between crystal growth and anion exchange. The XRD and XPS data show that the structures and compositions of MAPb$_{3-x}$Br$_x$ prepared using 1 & 2-s deposition can be decoupled. The composition of MAPb$_{3-x}$Br$_x$ can be either stoichiometrically-controlled or diffusion-controlled depending on the addition sequence of MAI and MABr. The stoichiometrically-controlled MAPb$_{3-x}$Br$_x$ films gave devices with the highest power conversion efficiency (PCE), thermal stability and device stability.

INTRODUCTION

In a relatively short time period hybrid organic-inorganic perovskite solar cells (PSCs) have achieved remarkably high conversion efficiencies (PCEs), with certified PCEs as high as 22.1% [1] for single-junction devices and values greater than 25% for tandem devices [2]. The use of mixed halide and mixed cation perovskites to construct devices has delivered superior PCEs [3] and enhanced stability [4]. Solution-based PSC fabrication has usually involved either the reactants both being in solution [5] or one of the reactants (e.g., PbI$_2$) being pre-deposited in a solid phase followed by addition of the second reactant (e.g., MAI) in a second (sequential) deposition step [6]. The former and latter methods are denoted as one-step (1-s) or two-step (2-s) deposition, respectively. Recently, we introduced a new method for PSC film preparation which combines 1-s and 2-s deposition and is denoted as 1 & 2-s deposition [7]. In the present study we greatly extend this new approach by preparing mixed halide perovskite MAPb$_{3-x}$Br$_x$ films for the first time. We show that 1 & 2-s deposition enables a new level of composition and structural control for MAPb$_{3-x}$Br$_x$ perovskite films.

EXPERIMENTAL

All perovskite film preparations in this study employed a DMSO:DMF solvent blend containing 60 vol.% DMSO. A precursor solution containing PbBr$_2$ or PbI$_2$ (1.0 M) and MABr or MAI (0.50 M) in DMSO:DMF was prepared in a nitrogen filled glove box (humidity ~ 2%). Film and device fabrication was conducted outside of the glove box (humidity ~ 40%). The solution was maintained at 70 °C and spins coated onto the mp-TiO$_2$ layer. A two-stage spin coating procedure was employed which involved 2000 rpm for 10s followed by 4000 rpm for 20 s. The precursor films were annealed at 100 °C for 10 min and then washed with IPA for 10 s. Then, an MABr/MAI solution in IPA (100 μL, 10 mg mL$^{-1}$) was dripped onto the precursor film for 30 s and then spin coated for 30 s. This procedure was repeated twice to give the final films. These films were annealed at 100 °C for 10 min and stored in a desiccator over P$_2$O$_5$ and in the dark until investigation.

RESULTS AND DISCUSSION

MAPb$_{3-x}$Br$_x$ prepared by 1 & 2-s deposition.

SEM was used to investigate both precursor and final film morphologies (see Fig. 1). These SEM images show that the microcrystals became less distinct after the second stage reaction. Higher magnification SEM images were measured which show that nanometer-sized crystals for the precursor films prepared using PbI$_2$ (Fig. 1C, E and G) in contrast the precursor film prepared using PbBr$_2$ (Fig. 1A) did not contain such crystals. The average equivalent spherical diameter for the crystals of the final MAPB, MAPI-MAPB, MAPB-MAPI and MAPI films are 415 ± 52 nm, 154 ± 35 nm, 352 ± 66 nm and 253 ± 96 nm, respectively. The SEM image for the MAPB final film (see Fig. 1B) showed that many large crystals had been nucleated. The MAPB-MAPB final film (see Fig. 1F) contained crystals that were larger than those present on the precursor film (see Fig. 1E) which indicates that crystal growth occurred. The MAPI film (Fig. 1H) contained a high density of crystals due to heterogeneous nucleation and growth [7]. Hence, these the three MAPB, MAPB-MAPI and MAPI final films had grown via heterogeneous nucleation.
Figure 1. Representative SEM images measured for the precursor films (A, C, E and G) and final (B, D, F and H) perovskite films. (See Scheme 1). The scale bars are 500 nm.

In contrast, the MAPI-MAPI(B) film (Fig. 1D) did not show a significant increase in crystal size compared to the precursor film (see Fig. 1C). Furthermore, the nanometer-scale (Fig. 1D) for this film gave the appearance of having become more compact when compared to the respective SEM images for the precursor film. This morphological reconstruction is an indication of anion exchange involving MABr\textsuperscript{8}. The structures of the precursor and final films were investigated using XRD. The average crystallite sizes for all the final films determined from the Scherrer equation are in the range 25.5 – 40.8 nm. The values are comparable to other reports\textsuperscript{9}. The crystallite size was lowest for the MAPI-MAPI(B) film. The MAPI peaks are shown in expanded form in Fig. 2A(i) and (ii) for both the precursor and final films.

Clearly resolved doublets have been reported for the (110) peak for tetragonal perovskites\textsuperscript{10}; however, this is not always the case and less resolved shoulders are apparent from reported diffraction data for tetragonal MAP at angles slightly lower than the (110) peak for MAPI\textsuperscript{11}. The latter situation corresponds to that which can be seen from the 2θ = 13.5 to 14.2° region for Fig. 2B(ii) and 2D(ii). In contrast the same region for MAPI(B)-MAPI (Fig. 2C(ii)) appears as a (mostly) single peak and is much closer in shape to that for the (100)c peak of MAPB (Fig. 2A(ii)). The major peaks for the precursor and final films of MAPB (Fig. 2A(i) and (ii)) and MAPI (Fig. 2D(i) and (ii)) did not shift during growth, as expected. In contrast, the peaks for the mixed halide films shifted dramatically upon transformation of the precursor to final films. The (100)t and (220)t peaks of the precursor and final films shifted to higher angles upon formation of the final MAPI-MAPI(B) (see Fig. 2B(i) and (ii)). This trend is attributed to inclusion of the smaller Br\textsuperscript{-} anion in the matrix. Interestingly, the opposite trend was observed upon formation of MAPI(B)-MAPI (see Fig. 2C(i) and (ii)) where the (100)c and (200)c peaks both moved to smaller angles. In this case the inclusion of a higher proportion of larger I\textsuperscript{-} anions is responsible. Furthermore, the diffraction patterns for the final MAPI-MAPI(B) and MAPI(B)-MAPI films exhibited only single phases. Thus, efficient alloying occurred for MAPI-MAPI(B) and MAPI(B)-MAPI prepared using 1 & 2-s deposition.

XPS data were obtained to determine the compositions of the films. The Br 3d peaks (Fig. 3)
were strongest for the MAPB film and absent for MAPI, as expected. Interestingly, the Br 3d peaks shifted to higher binding energies upon incorporation of I into the lattices for both MAPI-MAPI(B) and MAPI(B)-MAPI (see table in Fig. 3). Shifts in binding energies have been linked to bonding changes for related perovskite films.[8, 12] A similar explanation should apply to MAPI-MAPI(B) and MAPI(B)-MAPI because a general decrease of the scattering angles for their most prominent X-ray diffraction peaks occurred compared to those for MAPB (compare figures 2B(ii) and 2C(ii) with 2A(iii)).

Figure 3. XPS core level spectra measured for (A) Br 3d and (B) I 3d from the surface of the final perovskite films. The legend shown in (B) also applies (A).

The atomic% for Pb, N, I and Br measured for the final films. The mole fraction of Br with respect to Br and P is denoted as ×Br. The ×Br values for MAPI-MAPI(B) and MAPI(B)-MAPI were determined as 26 and 19 mol.%, respectively, from the XPS data. Consequently, the compositions for MAPI-MAPI(B) and MAPI(B)-MAPI were MAPbI\textsubscript{2.5}Br\textsubscript{0.5} and MAPbI\textsubscript{2}Br\textsubscript{0.8} respectively. Noh et al. and Park et al. studied mixed halide perovskites containing I and Br[13] prepared using 1-s deposition. They reported transitions from tetragonal to cubic phases when ×Br was greater than ~ 20 to 30 mol%. As discussed above, MAPI(B)-MAPI and MAPI-MAPI(B) had cubic and tetragonal structures, respectively. Hence, the perovskite with the lower ×Br value (19 mol%) had a more densely packed structure than that containing a higher ×Br (of 26 mol.%). This conclusion is counter-intuitive because Br\textsuperscript{−} has a smaller ionic radius (1.96 Å) than that of I (2.2 Å). These results illustrate the potential of 1 & 2-s deposition to control perovskite structure. For both MAPI-MAPI(B) and MAPI(B)-MAPI the final structure of the respective alloy was determined by that of the perovskite phase in the precursor two-phase film. An advantage of 1 & 2-s deposition is that it separates the perovskite growth into a structure forming first stage and an alloy forming second stage.

Solar cell performance and stability.

The performance of solar cells constructed using the four films discussed above was investigated. The SEM cross-section of the best system, MAPI(B)-MAPI shows that relatively long (and large) crystals extended through the capping layer thickness. This device harvested light over much of the UV-visible range, as shown by the EQE data (see Fig. 4A). The integrated EQE data gave a J\textsubscript{sc} value of 20.6 mA/cm\textsuperscript{2} which was indistinguishable from the value obtained from the J-V data (20.4 mA/cm\textsuperscript{2}). Fig. 4B shows representative J-V curves for all of the devices which had not been optimized. We use these data for comparison because all of the cells had been prepared using similar conditions which allows differences of the photoactive layer compositions to be assessed. MAPI had the lowest J\textsubscript{sc} due to insufficient harvesting of light at higher wavelength. The V\textsubscript{oc} values increased with increasing Br content as a consequence of the widening of the bandgap that occurred. The PCEs for these devices were in the range of 4.20 to 11.33 ± 0.47 % (Fig. 4C). The maximum value was obtained for MAPI(B)-MAPI. This system had the best PCE because of a combination of relatively large crystal size from SEM (Fig. 1F), large crystallite size from X-ray diffraction, absorption of more of the visible spectrum (Fig. 4A) and higher J\textsubscript{sc}. In contrast to an earlier report for a MAPbI\textsubscript{3-x}Br\textsubscript{x} PSC prepare using 1-s deposition, we found that including Br (within MAPI(B)-MAPI) gave a much improved PCE compared to the control Br-free system (MAPI) – see Fig. 4C. The reason for this improvement is the increased crystal size for MAPI(B)-MAPI relative to MAPI, as discussed above. The long (and large) crystals for the former extended through the film thickness which will have increased J\textsubscript{sc}. In comparison, the SEM for the MAPI-MAPI(B) device showed smaller crystals and hence more grain boundaries (see Fig. 1D), which is a reason for its lower PCE. We compare the thermal stability for the MAPI(B)-MAPI film to the data obtained for the MAPI film in Fig. 4D. The thermal stability for MAPI(B)-MAPI film was very high with only minor yellowing evident after 8 h of heating at 150 °C. This system had a cubic structure (see Fig. 2C(ii)). We propose that the improved stability is due to the MA\textsuperscript{+} cations being more tightly bound[5, 13a, 14] within the lattice which slowed the rate of hydration by H\textsubscript{2}O. In contrast the MAPI film had a tetragonal structure (see Fig. 2D(ii)), which is less thermally stable.
The MAPI(B)-MAPI device stability was assessed by the change of the relative PCE as a function of time. The MAPI(B)-MAPI device had a superior stability compared to the control MAPI device (from Fig. 4E) and retained ~70% of its PCE after 30 days. The superior stability of this device agrees with that reported by Noh et al. for their MAPbI$_2$xBr$_{0.6}$ device. For the present study, the stability also benefited from the improved capping layer morphology provided by 1 & 2-s deposition.

CONCLUSIONS

The MAPI films prepared by the 1 & 2-s method provided an improvement in both thermal and device stability which was attributed to improved capping layer morphology. Overall, the study has shown that mixed anion perovskite films form alloys very efficiently even when their processing methods are greatly changed. The 1 & 2-s method enable composite perovskite films to be prepared using either stoichiometric or diffusion control and this can be switched conveniently. This method adds an additional dimension to perovskite synthesis in terms of decoupling structure and composition and is worthy of further study.

REFERENCES

[1] W. S. Yang, B.-W. Park, E. H. Jung, N. J. Jeon, Y. C. Kim, D. U. Lee, S. S. Shin, J. Seo, E. K. Kim, J. H. Noh, S. I. Seok, Science 2017, 356, 1376-1379.

[2] D. P. McMeekin, G. Sadoughi, W. Rehman, G. E. Eperon, M. Saliba, M. T. Hörantner, A. Haghighirad, N. Sakai, L. Korte, B. Rech, M. B. Johnston, L. M. Herz, H. J. Snaith, Science 2016, 351, 151-155.

[3] aD. Luo, W. Yang, Z. Wang, A. Sadhanala, Q. Hu, R. Su, R. Shrivanna, G. F. Trindade, J. F. Watts, Z. Xu, T. Liu, K. Chen, F. Ye, P. Wu, L. Zhao, J. Wu, Y. Tu, Y. Zhang, X. Yang, W. Zhang, R. H. Friend, Q. Gong, H. J. Snaith, R. Zhu, Science 2018, 360, 1442-1446; bO. Ergen, S. M. Gilbert, T. Pham, S. J. Turner, M. T. Z. Tan, M. A. Worsley, A. Zettl, Nat. Mater. 2016, 15, 522; cG. Liu, H. Zheng, L. Zhu, A. Alsaeidi, T. Hayat, X. Pan, L. e. Mo, S. Dai, ChemSusChem 2018, 11, 2436-2443.

[4] Z. Wang, D. P. McMeekin, N. Sakai, S. van Reenen, K. Wojciechowski, J. B. Patel, M. B. Johnston, H. J. Snaith, Adv. Mater. 2017, 29, 1604186.

[5] J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal, S. I. Seok, Nano Lett. 2013, 13, 1764-1769.

[6] J. Burschka, N. Pellel, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Naezeruddin, M. Gratzel, Nature 2013, 499, 316-319.

[7] M. Z. Mokhtar, M. Chen, E. Whittaker, B. Hamilton, N. Aristidou, S. Ramadan, A. Ghollina, S. A. Haque, P. O’Brien, B. R. Saunders, Phys. Chem. Chem. Phys. 2017, 19, 7204-7214.

[8] M. Yang, T. Zhang, P. Schulz, Z. Li, G. Li, D. H. Kim, N. Guo, J. J. Berry, K. Zhu, Y. Zhao, Nat. Commun. 2016, 7, 12305.

[9] B. Jeong, I. Hwang, S. H. Cho, E. H. Kim, S. Cha, J. Lee, H. S. Kang, S. M. Cho, H. Choi, C. Park, ACS Nano 2016, 10, 9026-9035.

[10] J. Dai, Y. Fu, L. H. Manger, M. T. Rea, L. Hwang, R. H. Goldsmith, S. Jin, J. Phys. Chem. Lett. 2016, 7, 5036-5043.

[11] M. Anaya, J. F. Galisteo-López, M. E. Calvo, C. López, H. Miguez, J. Phys. Chem. C. 2016, 120, 3071-3076.

[12] aJ. Chun-Ren Ke, A. S. Walton, D. J. Lewis, A. Tedstone, P. O’Brien, A. G. Thomas, W. R. Flavell, Chem. Commun. 2017, 53, 5231-5234; bJ. Liang, P. Zhao, C. Wang, Y. Wang, Y. Hu, G. Zhu, L. Ma, J. Liu, Z. Jin, J. Am. Chem. Soc. 2017, 139, 14099-14102.

[13] aJ. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal, S. I. Seok, Nano Lett. 2013, 13, 1764-1769; bB.-w. Park, B. Philippe, S. M. Jain, X. Zhang, T. Edvinsson, H. Rensmo, B. Zietz, G. Boschloo, J. Mater. Chem. A 2015, 3, 21760-21771.

[14] Z. Shi, Y. Zhang, C. Cui, B. Li, W. Zhou, Z. Ning, Q. Mi, Adv. Mater. 2017, 29, 1701656.

Figure 4. (A) EQE data for the MAPI(B)-MAPI device. (B) Representative J-V curves. (C) Variation of PCE with mole fraction of Br. (D) Digital photographs obtained of ITO/mp-TiO$_2$/perovskite after being heated at 150°C in air (humidity ~60%) for various times. (E) Normalised PCE variation with time.