Annealing Effect on (FAPbI\textsubscript{3})\textsubscript{1-x}(MAPbBr\textsubscript{3})\textsubscript{x} Perovskite Films in Inverted-Type Perovskite Solar Cells

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Abstract: This study determines the effects of annealing treatment on the structure and the optical and electronic behaviors of the mixed (FAPbI\textsubscript{3})\textsubscript{1-x}(MAPbBr\textsubscript{3})\textsubscript{x} perovskite system. The experimental results reveal that (FAPbI\textsubscript{3})\textsubscript{1-x}(MAPbBr\textsubscript{3})\textsubscript{x} is an effective light-absorbing material for use in inverted planar perovskite solar cells owing to its large absorbance and tunable band gap. Therefore, good band-matching between the (FAPbI\textsubscript{3})\textsubscript{1-x}(MAPbBr\textsubscript{3})\textsubscript{x} and C\textsubscript{60} in photovoltaic devices can be controlled by annealing at various temperatures. Accordingly, an inverted mixed perovskite solar cell with a record efficiency of 12.0% under AM1.5G irradiation is realized.

Keywords: MAPbI\textsubscript{3}; FAI; organic solar cells; perovskite

1. Introduction

Organic/inorganic hybrid perovskite materials of the form APbX\textsubscript{3} (A = CH\textsubscript{3}NH\textsubscript{3} or HC(NH\textsubscript{2})\textsubscript{2}; X = I, Br or Cl) are attracting considerable interest owing to their potential for absorbing light in solar cells due to their broad spectral absorption, strong light harvesting, and long exciton diffusion length [1-6]. Perovskite solar cells (PSCs), which include perovskite materials as active absorption layers, have yielded good device performance with the highest power conversion efficiencies (PCEs) that have risen from approximately $\eta = 3\%$ efficiencies [7] to almost 20.2% [8]. Additionally, perovskite thin films of the form MAPbI\textsubscript{3} can be prepared by the vapor-assisted solution method [9], the sequential deposition process [10-12], the one-step spin-coating method [13] and the two-step sequential method [14]; the corresponding processes are fast, simple, and low-cost. PSCs have been developed with two types of device architecture—conventional [10-14] and inverted [15]. Recently, Jeon et al. [16] reported on the compositional engineering of high-performance PSCs. They used mixed CH\textsubscript{3}NH\textsubscript{3}PbBr\textsubscript{3} (MAPbBr\textsubscript{3}) and HC(NH\textsubscript{2})\textsubscript{2}PbI\textsubscript{3} (FAPbI\textsubscript{3}) in a solvent as a precursor to deposit (FAPbI\textsubscript{3})\textsubscript{1-x}(MAPbBr\textsubscript{3})\textsubscript{x} perovskite films on mesoporous TiO\textsubscript{2} to form conventional PSCs. However, to the best of our knowledge, no detailed study of the mixing of FAPbI\textsubscript{3} and MAPbBr\textsubscript{3} perovskite in inverted PSCs has been published.

This work reports solution-process (FAPbI\textsubscript{3})\textsubscript{1-x}(MAPbBr\textsubscript{3})\textsubscript{x} perovskites (that are formed using a mixed solution of HC(NH\textsubscript{2})\textsubscript{2}PbI\textsubscript{3} (FAPbI\textsubscript{3}) and CH\textsubscript{3}NH\textsubscript{3}PbBr\textsubscript{3} (MAPbBr\textsubscript{3})) for use in PSCs with an inverted architecture. The (FAPbI\textsubscript{3})\textsubscript{1-x}(MAPbBr\textsubscript{3})\textsubscript{x} perovskites are formed by a one-step spin-coating
process on PEDOT:PSS-coated ITO substrates. The optical, structural, and surface properties of the \((\text{FAPbI}_3)_1-x\)(\text{MAPbBr}_3)_x perovskite films are investigated as functions of the thermal annealing temperature; the relationship between the performance of the PSC and the properties of the perovskite films is discussed.

2. Methods

In this study, a PEDOT:PSS film using a Triton X-100 (volume ratio PEDOT:PSS:Triton X-100 = 150:1) surfactant was spin-coated on a pre-cleaned ITO substrate at 5000 rpm for 30 s. After spin coating, the film was annealed at 140 °C for 10 min. The perovskite layer was deposited using the solvent-engineering technique \([13]\) using a mixing solvent (in which the volume ratio of dimethyl sulfoxide (DMSO) to γ-butyrolactone (GBL) was 1:1). Then 0.96 mmol of FAPbI3 and 0.24 mmol of mmol MAPbBr3 (i.e., 165 mg of FAI, 27 mg of MAB, 443 mg of PbI2 and 88 mg of PbBr2) were dissolved in the mixing solvent (1 mL) as a \((\text{FAPbI}_3)_0.8\)(\text{MAPbBr}_3)_0.2 precursor solution. The perovskite precursor solution was coated onto the PEDOT:PSS/ITO substrate in two consecutive spin-coating steps at 1000 rpm and 5000 rpm for 10 s and 20 s, respectively. At 5000 rpm, the wet spinning film was quenched by dropping 50 µL of anhydrous toluene onto it. After spin coating, the film was annealed at 100 °C for 10 min. Subsequently, C60, Bathocuproine (BCP), and a silver (Ag) electrode were deposited to thicknesses of 50, 5, and 100 nm, respectively, using a thermal evaporator. The sample was covered with a shadow mask to define an active area of 0.5 cm × 0.2 cm during C60/BCP/Ag deposition. Figure 1a schematically depicts the complete structure.

![Figure 1.](image.png)

**Figure 1.** (a) Schematically depicts the complete structure and (b) corresponding energy band diagram in this study.

**Material and Device Measurement**

The crystalline microstructures of the films were determined using a PANalytical X’Pert Pro DY2840 X-ray diffractometer with Cu-Kα radiation (PANalytical, Naerum, Denmark) \((\lambda = 0.1541 \text{ nm})\). A field-emission scanning electron microscope (GeminiSEM, ZEISS, Oberkochen, Germany) was used to observe the surface morphology of the cells. Photoluminescence (PL) and absorption spectra were measured using a fluorescence spectrophotometer (Hitachi F-7000) (Hitachi High-Technologies Co., Tokyo, Japan) and a UV/VIS/NIR spectrophotometer (Hitachi U-4100 spectrometers) (Hitachi High-Technologies Co., Tokyo, Japan), respectively. Moreover, the current density-voltage (J-V) characteristics were measured using a Keithley 2420 programmable source meter (Keithley, Cleveland, OH, USA) under irradiation by a 1000 W xenon lamp. The scan rate is 0.1 V/s. Finally, the irradiation power density on the surface of the each sample was calibrated as 1000 W/m².

3. Results and Discussion

Mixed perovskite can be flexibly modified by changing the concentration ratio of the mixed halogen precursors \([16,17]\); this process is useful for photovoltaic applications. The LUMOs of FAPbI3, MAPbBr3 and C60 are \(-4.0\), \(-3.6\) and \(-3.9\) eV, respectively \([18,19]\). To optimize the band matching with C60, the mole ratio of FAPbI3 to MAPbBr3 in the mixed perovskite was set to 80:20 (i.e., \(x = 0.2\)) because the LUMO of the \((\text{FAPbI}_3)_0.8\)(\text{MAPbBr}_3)_0.2 was determined by interpolation to be \(-3.92\), as presented in Figure 1b. Figure 2a displays the PL spectra of the MAPbBr3, \((\text{FAPbI}_3)_{1-x}(\text{MAPbBr}_3)_x\),
and FAPbI3 films with annealing treatment at 135 °C. The spectra include peaks at 530, 762 and 800 nm, respectively. The ratio of the concentration of the (FAPbI3)1−x(MAPbBr3)x film, x, is estimated to be around 0.2 which is similar to the mole ratio in the precursor solution. The absorption edges of the three perovskite films are clearly shifted, as shown in Figure 2b.

![Figure 2](image1)

Figure 2. (a) PL and (b) absorption spectra of MAPbBr3, (FAPbI3)1−x(MAPbBr3)x, and FAPbI3 films deposited on glass substrates.

Figure 3 shows the XRD patterns of (FAPbI3)1−x(MAPbBr3)x perovskite films after thermal annealing at various temperatures. The spectra include four main diffraction peaks at 11.67°, 12.28°, 12.71°, and 14.11°, which correspond to the δ-FAPbI3, PbI1.0Br1.0, PbI2, and α-FAPbI3 phases, respectively. As the annealing temperature increases, the intensity of the α-FAPbI3 phase peak increases and that of the δ-FAPbI3 phase peak decreases because δ-FAPbI3 transitions to the α-FAPbI3 phase or the crystallinity of the α-FAPbI3 phase is increased. Annealing at 175 °C completely suppresses the formation of the δ-FAPbI3 phase, suggesting that perovskite films must be thermally annealed to drive the inter-diffusion of precursors [20]. The δ-FAPbI3 powders can also be converted to α-FAPbI3 powders by annealing and this process is reversible even after the δ-FAPbI3 powders have been stored in air for 10 h [16]. The peak intensity of the PbI1.0Br1.0 phase decreased as the annealing temperature increased, vanishing at 175 °C, whereas the peak intensity of the PbI2 phase increased with an annealing temperature over 135 °C, perhaps because methylammonium bromide (MABr) and methylammonium iodide (MAI) were thermally decomposed from the films, forming the PbI2 phase. Furthermore, the intensity of the α-FAPbI3 phase peak increased with the annealing temperature owing to the stability of formamidinium iodide (FAI) at high temperatures.

![Figure 3](image2)

Figure 3. XRD patterns of (FAPbI3)0.8(MAPbBr3)0.2 perovskite films following annealing at various temperatures.
Figure 4 presents SEM images of (FAPbI$_3$)$_{1-x}$(MAPbBr$_3$)$_x$ perovskite films that have been thermally annealed at various temperatures. The grain size increased with the annealing temperature. A smooth, dense perovskite film was obtained when the annealing temperature exceeded 135 °C. Lower annealing temperatures yielded rough films with some defects (or pinholes). A high-quality perovskite film is crucial in the fabrication of well-performing photovoltaic devices, as revealed by the SEM micrographs in Figure 4. Clearly, the grains merged into each other as more PbI$_2$ was formed at the grain boundaries as the annealing temperature rose above 175 °C, increasing the scattering of carriers, and thereby reducing the mobility of carriers during their transportation in the perovskite film [21].

Figure 5a displays the room-temperature PL spectra of (FAPbI$_3$)$_{1-x}$(MAPbBr$_3$)$_x$ that was deposited on glass substrates following annealing at various temperatures. Table 1 presents the peak positions. As the annealing temperature increases from 75 to 175 °C, the PL peak shifts from 762.1 to 782.5 nm. Figure 5b shows the absorption spectra from 400 to 800 nm of (FAPbI$_3$)$_{1-x}$(MAPbBr$_3$)$_x$ that was deposited on glass substrates following annealing at various temperatures. The absorption increased with the annealing temperature because the grains became larger (Figure 4). The inset presents an enlarged view of Figure 5b. The PL observations indicate that the absorption edges shift to longer wavelengths as the annealing temperature increases, owing to an offset of the stoichiometric ratio of α-FAPbI$_3$ to MAPbBr$_3$ since more α-FAPbI$_3$ is formed and transitions to δ-FAPbI$_3$ and more MAI and MABr decompose in the films. Therefore, the semiconducting band gap of the films downshifts to approaching that of the pure α-FAPbI$_3$ phase. This result reveals that the composition of mixed perovskite is extremely sensitive to the temperature of annealing.

Table 1. Peak positions in PL spectra of (FAPbI$_3$)$_{1-x}$(MAPbBr$_3$)$_x$ deposited on glass substrates and annealed various temperatures.

| Thermal Annealing Temperatures | As-Deposited | 75  | 95  | 115 | 135 | 155 | 175 |
|-------------------------------|-------------|-----|-----|-----|-----|-----|-----|
| PL peak (nm)                  | 762.3       | 762.1| 762.1| 770.6| 775.8| 780.0| 782.5|
The band gap of the (MAPbBr₃)ₓ(FAPbI₃)₁₋ₓ film is reduced as more of the α-FAPbI₃ phase is formed in the films (Figure 5). Therefore, annealing at 135 °C reduces the LUMO of the (MAPbBr₃)ₓ(FAPbI₃)₁₋ₓ film to match that of the C₆₀ layer and reduces the energy barrier to the transportation of electrons, resulting in a high FF. The value of V₉C is positively correlated with the difference between the HOMO of the (MAPbBr₃)ₓ(FAPbI₃)₁₋ₓ film and the LUMO of the C₆₀ layer (Figure 1b) [15]. Therefore, the V₉C following annealing at 135 °C is determined by the increase in the HOMO of the (MAPbBr₃)ₓ(FAPbI₃)₁₋ₓ film. However, annealing at temperatures above 135 °C worsens the performance of the solar cell. The band gap of (MAPbBr₃)ₓ(FAPbI₃)₁₋ₓ film continues to fall as the annealing temperature increases, reducing the V₉C. Moreover, the LUMO level of (MAPbBr₃)ₓ(FAPbI₃)₁₋ₓ film is lower than that of C₆₀, so an energy barrier is formed, lowering the FF.

Figure 6b shows the IPCE of the best device and the integrated current density that is calculated from IPCE data is 19.4 mA/cm². The difference between the current density from the IPCE data and that obtained from the J-V curves is only 5.8%. Therefore, the current density data are reliable. Figure 6c plots the J-V curves of the best cell under forward and reverse scanning under AM 1.5 G illumination. The efficiency difference between the forward and reverse scans is only 3.2% (Effforward = 12.0% and

| Temperature (°C) | Number of Devices | V₉C (V) | Jsc (mA/cm²) | FF (%) | Eff (%) |
|------------------|--------------------|--------|--------------|--------|--------|
| 75               | 4                  | 1.04 ± 0.02 | 8.9 ± 4.4 | 51.7 ± 2.4 | 4.11 ± 0.20 |
| 95               | 6                  | 0.94 ± 0.09 | 14.2 ± 1.9 | 49.4 ± 5.9 | 6.68 ± 0.69 |
| 115              | 8                  | 0.93 ± 0.03 | 14.9 ± 0.6 | 53.6 ± 2.5 | 7.21 ± 0.42 |
| 135              | 10                 | 0.87 ± 0.008 | 20.1 ± 0.5 | 66.4 ± 1.2 | 11.8 ± 0.20 |
| 155              | 8                  | 0.84 ± 0.01 | 20.3 ± 0.6 | 42.9 ± 2.1 | 7.52 ± 0.61 |
| 175              | 6                  | 0.83 ± 0.02 | 17.2 ± 1.0 | 42.0 ± 6.4 | 6.02 ± 0.88 |

The band gap of the (MAPbBr₃)ₓ(FAPbI₃)₁₋ₓ film is lower than that of C₆₀, so an energy barrier is formed, lowering the FF.
Eff_{reverse} = 12.4\%). The hysteresis in our case is much weaker than has been reported elsewhere [16,22], indicating that high-quality (MAPbBr_3)_x(FAPbI_3)_{1−x} films were formed herein by annealing.

**Figure 6.** (a) Photocurrent J-V curves of perovskite solar cell (Ag/BCP/C_60/(FAPbI_3)_0.8(MAPbBr_3)_0.2 / PEDOT:PSS/ITO) obtained under standard 1 sun AM 1.5 simulated solar irradiation; (b) IPCE spectrum and (c) J-V curves of best device under forward and reverse scanning.

4. Conclusions

In summary, the characteristics of (FAPbI_3)_{1−x} (MAPbBr_3)_x perovskite films that were thermally annealed at temperatures from 75 to 175 °C were elucidated. The optimal device that was obtained by annealing at 135 °C performed outstandingly, with short-circuit current density (J_{sc}) = 20.6 mA/cm^2, open-circuit voltage (V_{oc}) = 0.88 V, fill factor (FF) = 65.9%, and power conversion efficiency (Eff) = 12.0%.

The composition of the mixed (FAPbI_3)_{1−x}(MAPbBr_3)_x perovskite system is extremely sensitive to the temperature of annealing. Therefore, the annealing of mixed (FAPbI_3)_{1−x}(MAPbBr_3)_x perovskite is important to control the quality of a film of that material and (ensuring OR providing) band matching in the device.

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**Conflicts of Interest:** The authors declare no conflicts of interest.

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