Gradient engineered light absorption layer for enhanced carrier separation efficiency in perovskite solar cells

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Abstract

Carrier transport behavior in perovskite light absorption layer significantly impacts the performance of perovskite solar cells (PSCs). In this work, reduced carrier recombination losses were achieved by the design of band structure in perovskite materials. An ultrathin $(\text{PbI}_2/\text{PbBr}_2)_n$ film with a gradient thickness ratio was deposited as the lead halide precursor layer by thermal evaporation method, and PSCs with a gradient band structure in perovskite absorption layer were fabricated by a two-step method in ambient atmosphere. For comparison, PSCs with homogeneous perovskite materials of MAPbI_3 and $\text{MAPbI}_x\text{Br}_{3-x}$ were fabricated as well. It is found that the gradient type-II band structure greatly reduces the carrier lifetime and enhances the carrier separation efficiency. As a result, the PSCs with a gradient band structure exhibit an average power conversion efficiency of 17.5%, which is 1-2% higher than that of traditional PSCs. This work provides a novel method for developing high-efficient PSCs.

Keywords

Perovskite solar cells; Gradient band structure; Carrier separation efficiency; Carrier recombination loss;

Introduction

Since the organic-inorganic hybrid perovskite was first used as the light-absorbing material in solar cells in 2009, perovskite solar cells (PSCs) went through a period of rapid development in recent years¹⁻⁶. Many efforts have been focused on the improvement of cell performance or power conversion efficiency (PCE)⁷⁻¹³. As we know, the cell performance essentially depends on incident photon-to-electron conversion efficiency (IPCE) and light absorption efficiency, whereas efficient carrier separation efficiency is the key to improve IPCE. Therefore, it becomes crucial to control the transport of photon-generated carriers in perovskite materials. In traditional planar structure PSCs, carriers (or electron-hole pairs) are separated at the interface between electron transfer layer (ETL) and perovskite material, and only the carriers diffusing to the separation interface can have an effect on cell performance. Hence, much work has been devoted to reduce carrier recombination losses during its diffusion. Different methods, such as solvent annealing¹⁴⁻¹⁵, additive engineering¹⁶⁻¹⁸, surface passivation¹⁹⁻²², etc., have been employed to improve perovskite crystal quality. Actually, band alignment control is an alternative method to reduce recombination losses²³⁻²⁵. For example, Jing Zhang *et al.* introduced extrinsic movable ions Li^+/I^- in MAPbI_3 , and the aggregation of Li^+/I^- tuned the energy level of the perovskite, which made charge extraction quite efficient from perovskite materials to both ETL and hole transport layer (HTL) in PSCs²⁶. Interestingly, the band structure of organometal halide perovskite materials can be easily adjusted by changing the component or content of halogen element in perovskite materials²⁷⁻³⁰.

For instance, Wei Ruan¹ et al. fabricated MAPbI₃/MAPb(I_xBr_{1-x})₃ heterostructure with a type-II band structure and achieved HTL-free PSCs³¹. In essence, it is an ideal approach to directly reduce recombination losses through the design of a gradient band structure in perovskite light absorption layer³²⁻³³, which supports the carrier separation as fast as possible. However, to the best of our knowledge, it has not been reported so far about the fabrication of perovskite materials with a gradient band structure.

In this work, ultrathin PbI₂ or PbBr₂ films were alternately deposited onto the substrate as the lead halide precursor layers by thermal evaporation method, and PSCs with a gradient engineered perovskite absorption layer were fabricated by gradually tuning the thickness ratio of PbI₂ to PbBr₂ films. For comparison, PSCs with homogeneous perovskite materials of MAPbI₃ and MAPbI_xBr_{3-x} were fabricated as well. Scanning electron microscopy (SEM), energy dispersive X-Ray spectroscopy (EDS), X-ray diffraction (XRD), absorption spectra, photoluminescence (PL) spectra, and time-resolved photoluminescence (TRPL) spectra were performed to investigate the morphologies, element distribution, crystal structures, chemical compositions, optical properties, and carrier lifetime of perovskite materials. It is found that the gradient type-II band structure in perovskite light absorption layer significantly reduces the carrier lifetime and enhances the carrier separation efficiency. As a result, the PSCs with a gradient band structure exhibit an average power conversion efficiency of 17.5%, which is 1-2% higher than that of traditional PSCs.

Experimental section

Device fabrication

Fluorine-doped tin oxide (FTO) glass substrates ($15\ \Omega/\text{sq}$) were etched by a laser and cleaned by sequential ultra-sonication in acetone, ethanol, and deionized water for 15 min in each. A compact SnO_2 (c- SnO_2) layer was deposited on the cleaned FTO substrates by spin-coating 0.1 M tin oxide ethanol solution (Xi'an Polymer) at 3000 rpm for 30 s, and then annealed at $200\ ^\circ\text{C}$ for 120 min. After the substrates were naturally cooled to room temperature, they were immersed in tin tetrachloride solution for 20 min at $75\ ^\circ\text{C}$, and then rinsed with deionized water and dried by nitrogen flow. Three kinds of perovskite layers, i.e. MAPbI_3 , $\text{MAPbI}_x\text{Br}_{3-x}$, and gradient $\text{MAPbI}_x\text{Br}_{3-x}$, were prepared by a two-step method. To fabricate homogeneous MAPbI_3 or $\text{MAPbI}_x\text{Br}_{3-x}$ perovskite films, PbI_2 (99.99%, Xi'an Polymer) with the thickness of 180 nm was first evaporated on the prepared substrate at a rate of 0.5 nm/s. To convert lead halides to MAPbI_3 materials, the precursor film with a solution of $\text{CH}_3\text{NH}_3\text{I}$ (MAI) in isopropanol (40 mg/mL) was spin-coated on the substrates. Whereas converting lead halides to $\text{MAPbI}_x\text{Br}_{3-x}$, a MAI and $\text{CH}_3\text{NH}_3\text{Br}$ (MABr) mixed isopropanol solution (mole ratio: 4:1) was used as the precursor and spin-coated on the as-prepared FTO/c- SnO_2 / PbI_2 substrates. As for the fabrication of gradient $\text{MAPbI}_x\text{Br}_{3-x}$ perovskite films, PbI_2 and PbBr_2 were alternately evaporated onto the FTO/c- SnO_2 substrate as the lead halide precursor layers, As shown in Fig. 1, by accurately controlling the evaporation time of PbI_2 and PbBr_2 , a 180 nm heterogeneous lead halides layer with a gradient thickness ratio, consisting of (11.6

nm PbI₂/0.4 nm PbBr₂)/(11.2 nm PbI₂/0.8 nm PbBr₂)/...../(6 nm PbI₂/6 nm PbBr₂), was obtained. And then the precursor film with a solution of MAI in isopropanol (40 mg/mL) was spin-coated on the as-prepared FTO/c-SnO₂/(PbI₂/PbBr₂)₁₅ substrates. All the above spin-coating speeds were set to 5500 rpm, and all the samples were annealed at 110 ° C for 60 min. The hole transport material (HTM) was deposited by spin-coating at 4000 rpm for 30 s, which was composed of 72 mg/L (spiro-OMeTAD), 28.8μL of 4tert-butylpyridine, and 17.5μL of 520 mg/mL lithium bis-(trifluoromethanesulfonyl) imide in acetonitrile in 1 mL of chlorobenzene. All the above processes are operated in ambient atmosphere with a relative humidity of 35%. Finally, 80 nm thick gold electrodes were deposited on the top of the devices by a thermal evaporation method. The active area of the cell was measured to be 0.07 cm².

Characterization

Morphologies of the samples and EDS mapping images were examined by a high-resolution field emission SEM (FE-SEM, Zeiss Sigma). Crystal structures were analyzed by XRD (Ultima IV, Rigaku, Cu Kα:λ=0.15406 nm). The absorption spectra of perovskite films were characterized by an UV/Vis spectrophotometer (PerkinElmer, Lambda 850). The current density-voltage (*J-V*) curves were measured by a digital source meter (B2901A, Keysight) under an AM 1.5 solar simulator (SS150, Zolix). The incident photon-to-electron conversion efficiency (IPCE) was measured in AC mode on a testing system (QE-R, Enli Technology Co. Ltd.) with a tungsten-halogen lamp as the light source. PL and TRPL spectra were measured by steady state transient near infrared fluorescence spectrometer (FLS 980) at the laser wavelength of

377 nm as an excitation source.

Results and discussion

The surface and cross-section morphologies of the perovskite films were characterized by SEM. Figures 2(a-c) show the surface images of the perovskite samples of MAPbI₃, MAPbI_xBr_{3-x} and gradient MAPbI_xBr_{3-x} (labeled as G-MAPbI_xBr_{3-x}), respectively. The inserts are their cross-sectional images. All the samples exhibit a uniform and compact surface, indicating the good crystal quality of perovskite materials. Notably, the samples demonstrate the different grain sizes. The MAPbI_xBr_{3-x} sample has the average grain size on the order of micrometer, whereas for the MAPbI₃ and G-MAPbI_xBr_{3-x} samples, the grain sizes are ~350 nm and ~450 nm, respectively. The size difference should be related to the material growth process. As for the MAPbI_xBr_{3-x} sample, a MAI and MABr mixed isopropanol solution was used as the precursor, whereas, for the other two samples, only the MAI isopropanol solution was adopted. Br atoms in the precursor solution tend to slowly displace I atoms during the growth process because of their different atomic radii, which is conducive to reduce the growth rate and increase the grain size. This behavior is also observed in other literatures³⁴⁻³⁵. In addition, as shown in the inserts of Fig. 2, the thickness for all the three samples is controlled to ~ 350 nm, which is similar to the optimized value in previous reports³⁶.

To elucidate the crystal structures and compositions of different samples, XRD measurements were performed with the results in Fig. 3(a). The diffraction peaks at

around 14.1° , 28.4° , 31.8° , and 40.9° are indexed to (110), (220), (312), and (330) planes of MAPbI_3 material, respectively. There is no characteristic peak corresponding to hexagonal PbI_2 or PbBr_2 , revealing the complete conversion. With respect to the MAPbI_3 sample, as shown in the Fig. 3(b), the diffraction peaks of the $\text{MAPbI}_x\text{Br}_{3-x}$ and G- $\text{MAPbI}_x\text{Br}_{3-x}$ samples slightly shift to the larger 2θ degrees with the same position, indicating the analogous doping content of Br atoms³⁰. Figure 3(c) shows their absorption spectra. For the MAPbI_3 sample, obvious absorption edge at ~ 785 nm is observed, corresponding to a bandgap of ~ 1.58 eV. For the other two samples, both the absorption edges move to ~ 755 nm, corresponding to a band gap of ~ 1.64 eV. Empirically, the bandgap E_g can be estimated by the following quadratic equation:

$$E_g(\text{MAPbI}_x\text{Br}_{3-x}) = 2.29 - 0.35x + 0.037x^2,$$

hence, the Br content can be estimated to be $\sim 16\%$ ³⁰. It is worth noting that although the $\text{MAPbI}_x\text{Br}_{3-x}$ and G- $\text{MAPbI}_x\text{Br}_{3-x}$ samples have almost same absorption edges, their curve slopes exhibit a certain difference. As shown in the insert of Fig. 3(c), the absorption edge for the G- $\text{MAPbI}_x\text{Br}_{3-x}$ sample is relatively gentle, which might be because of the non-homogeneous perovskite material possessing a non-identical bandgap.

The PSCs were fabricated by using the above three samples and labeled as PSC-I, PSC-I/Br, and PSC-G-I/Br, respectively. Figure 4(a) displays the J - V characteristic curves. The detailed performance parameters are summarized in the inserted table. It can be seen that the PSC-G-I/Br exhibits the best performance with a PCE of 18.2%,

corresponding to an open-circuit voltage (V_{oc}) of 1.07 V, a short-circuit current density (J_{sc}) of 22.5 mA/cm², and a filling factor (FF) of 75.6%. Understandably, the V_{oc} of PSC-I/Br and PSC-G-I/Br is 0.06 V higher than that of PSC-I, since the Br-doping expands the band gap of perovskite material and improve the V_{oc} [4]. In addition, compared with the other two cells, the PSC-I/Br has a significantly reduced J_{sc} (21.7 mA/cm²). This might be because of the less light absorption in perovskite materials owing to its larger band gap. To confirm the effectiveness of the experiment, we fabricated 80 devices for each kind of cell. Figure 4(b) exhibits the PCE histograms. Obviously, the PSC-G-I/Br devices have the highest average PCE of 17.5%, whereas the PSC-I and PSC-I/Br devices exhibit the lower average PCEs, corresponding to ~15.8 % and ~16.7%, respectively. Here, it should be mentioned that our experiment is fully operated in ambient atmosphere (relative humidity: 35%), and PSCs with the higher performance can be hopefully achieved when they are fabricated in a low-humidity environment.

To reveal the mechanism of the improved performance in PSC-G-I/Br devices, the measurements of IPCE, PL, EDS, and TRPL for the different samples were performed. Figure 5 shows their IPCE curves with the wavelength range from 300 nm to 800 nm. There are slight differences in cut-off wavelength and IPCE intensity. As for PSC-I device, it shows the largest effective region from 300 nm to 780 nm, contributing to the maximal J_{sc} . By contrast, the Br-containing devices (i.e. PSC-I/Br and PSC-G-I/Br) exhibit a shorter cut-off wavelength due to the larger band gap. Notably, compared with the PSC-I/Br device, the PSC-G-I/Br device has the higher

IPCE in the range from 500 nm to 750 nm, resulting to the larger J_{sc} . These behaviors are consistent with the $J-V$ results in Fig. 4(a). Figure 6 (a) shows their PL spectra. In the case of MAPbI_3 and $\text{MAPbI}_x\text{Br}_{3-x}$ materials, their peak positions locates at 780 nm and 752 nm, corresponding to the bandgap of 1.59 eV and 1.65 eV, respectively, which agree well with the results in Fig. 3(c). Considering the non-identical bandgap in G- $\text{MAPbI}_x\text{Br}_{3-x}$ material, its PL spectra were measured in the front and back sides. Interestingly, as indicated in the inset of Fig. 6(a), the two PL spectra exhibit the different peak positions locating at 734 nm and 771 nm, respectively, corresponding to a bandgap difference of 81 meV; moreover, the full width at half maximum (FWHM) of PL spectra are broader than that of MAPbI_3 or $\text{MAPbI}_x\text{Br}_{3-x}$ materials. These phenomena mean the achievement of the non-homogeneous Br distribution in perovskite materials. To further analyze the Br element distribution, EDS mapping of I and Br elements were performed for the $\text{MAPbI}_x\text{Br}_{3-x}$ and G- $\text{MAPbI}_x\text{Br}_{3-x}$ samples. As shown in Fig. 6(c-g), the I and Br elements almost uniformly distribute on the whole perovskite layer for the $\text{MAPbI}_x\text{Br}_{3-x}$ sample; whereas a gradient I and Br distribution along the longitudinal direction can be clearly observed for the G- $\text{MAPbI}_x\text{Br}_{3-x}$, as shown in Fig. 6(h-l), and moreover, the closer to the FTO substrate, the smaller the Br content. These results are in line with the design expectation. Based on previous reports^{4, 31, 37}, the conductive band for lightly Br-doped perovskite material ($\text{MAPbI}_x\text{Br}_{3-x}$) will gradually increase with the Br content while the valance band almost keeping fixed. In the light of this, a gradient type-II band structure is formed in the perovskite material. In addition, it can be seen

from Fig. 6(a) that the PL intensities for the G-MAPbI_xBr_{3-x} material is markedly lower than that for the other two samples. As we know, the emission intensity is significantly impacted by carrier lifetime of perovskite material. Figure 6(b) plots the TRPL spectra measured at 770 nm for different samples. We fitted the carrier lifetime through a two-component exponential decay function:

$$F(t) = A + B_1 \exp\left(\frac{-t}{\tau_1}\right) + B_2 \exp\left(\frac{-t}{\tau_2}\right),$$

where τ_1 and τ_2 represent the decay times, B_1 and B_2 are the corresponding decay amplitudes of the component, and A is a constant for the base-line offset. The average recombination lifetime (τ_{ave}) is estimated from the fitting parameters according to equation:

$$\tau_{ave} = \frac{\sum B_i \tau_i^2}{\sum B_i \tau_i}.$$

The fitting values of τ_{ave} for MAPbI₃ and MAPbI_xBr_{3-x} and G-MAPbI_xBr_{3-x}, are 18.4 ns, 18.1 ns, and 13.1 ns, respectively. It can be seen that the G-MAPbI_xBr_{3-x} sample has the shortest carrier lifetime. This is because the sample owns a gradient type-II band structure, as revealed in Fig. 6(h-l), leading to a fast carrier separation and a short carrier lifetime, which contribute to the high IPCE (see Fig. 5) and the low PL intensity (see Fig. 6(a)). In this sense, the designed gradient band structure in our experiment is beneficial for the carrier separation and device performance compared with traditional homogeneous band structure.

In order to further elaborate how the gradient band structure affects the performance of PSCs, schematic diagrams of working principle for PSCs with or without a gradient band structure in perovskite material were drawn in Fig. 7. As for

the traditional structure PSC shown in Fig. 7(a), electron-hole pairs are firstly generated in perovskite materials under light irradiation, and then they are separated at the interface between SnO_2 and perovskite material, leading to the current output. From this point of view, only the electron-hole pairs diffusing to the separation interface can contribute to the output current. Hence, improving crystal quality has been extensively employed to enhance cell performance due to the increased number of electron-hole pairs reaching separation interface. As for the PSC with a gradient type-II band structure shown in Fig. 7(b), the gradient band alignment supports carrier separation inside perovskite materials, which significantly reduces carrier radiative or non-radiative recombination during the diffusion process, thereby improves the carrier separation efficiency and cell performance. These analyses are well consistent with the result discussed in Fig. 4(a), Fig. 5 and 6(a).

Conclusions

In this work, perovskite absorption layers with a gradient or non-gradient band structure were designed and fabricated by a two-step method, and three kinds of PSCs, i.e. PSC-I, PSC-I/Br and PSC-G-I/Br, were achieved. The results reveal that the gradient type-II band structure in perovskite absorption layers is beneficial for the reduction of carrier recombination losses. An enhanced carrier separation efficiency and IPCE was achieved in the PSC with a gradient band structure. As a result, the kind of PSCs exhibits an average PCE of 17.5%, which is 1-2% higher than that of traditional PSCs. This work paves a way to design high-efficiency PSCs.

Competing interests

The authors declare that they have no competing interests.

Acknowledgements

This work was supported by the National Key Research and Development Program of China (grant no. 2016YFB0400801), the National Natural Science Foundation of China (grant nos., 61774128, 61974123, 61874092, and 61804129), the Natural Science Foundation of Fujian Province of China (grant no 2018I0017), Science and Technology Key Projects of Xiamen (Grant No. 3502ZCQ20191001), the Fundamental Research Funds for Xiamen Universities, China (20720170085).

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Figure captions

Figure 1 Schematics of the fabrication process of gradient $\text{MAPbI}_x\text{Br}_{3-x}$ perovskite films.

Figure 2 The surface and cross-section morphologies of perovskite films, (a) MAPbI_3 , (b) $\text{MAPbI}_x\text{Br}_{3-x}$, and (c) $\text{G-MAPbI}_x\text{Br}_{3-x}$. The inserts are their cross-sectional images.

Figure 3 (a) XRD patterns of perovskite films, (b) their partial enlargement, and (c) absorption spectra.

Figure 4 (a) $J-V$ curves of the PSCs, the insert is their parameter results; (b) The PCE histograms of PSC devices.

Figure 5 IPCE curves of the PSCs.

Figure 6 (a) Steady PL spectra; (b) TRPL spectra; (c) Cross-section image of an $\text{MAPbI}_x\text{Br}_{3-x}$ film; (d) and (e) EDS mapping images of I and Br elements in the area marked in (c), respectively; (f) and (g) Relative intensity of I and Br element based on (d) and (e) images along the longitudinal direction; (h) Cross-section image of an $\text{G-MAPbI}_x\text{Br}_{3-x}$ film; (i) and (j) EDS mapping images of I and Br elements in the area marked in (h), respectively; (k) and (l) Relative intensity of I and Br element based on (i) and (j) images along the longitudinal direction.

Figure 7 Schematic diagrams of working principle for different PSCs, (a) PSC without a gradient type-II band structure; (b) PSC with a gradient band structure.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7