Photo-induced defects in MAPbBr$_3$ single crystals

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Abstract

Single crystals of hybrid organic–inorganic halide perovskite have exhibited significantly good stability and a low trap density, leading to advantageous applications in optoelectronics. Even with recent development of high-quality perovskite single crystals, a defect analysis should be addressed to improve device performance in addition to understand the interaction between photo-generated carriers and defects. In this paper, we present a photo-induced defect characterization of CH$_3$NH$_3$PbBr$_3$ (MAPbBr$_3$) perovskite single crystals using an interpretation of photo-current and photo-capacitance measurement. The bulk and the interfacial defect densities of MAPbBr$_3$ crystals with a gold electrode are examined by the characterization of photo-capacitive response under three different wavelengths of light. The transient photo-response of the single crystals reveals the occurrence of carrier trapping and a recombination process. The photo-response under the various light conditions provides a possible origin of defects in MAPbBr$_3$ single crystals. Our comprehensive optoelectronic analysis provides the establishment of the link between the carrier transport and device performance depending on the illuminations. The fundamental understanding of photo-induced defects in perovskites can be helpful to realize the origin of electrical loss and develop highly efficient optoelectronic devices.

1. Introduction

Over the last decade, organic–inorganic hybrid perovskites CH$_3$NH$_3$PbX$_3$ (X = Cl, Br, and I) have attracted tremendous attention as a promising candidate for the development of next-generation optoelectronic device applications [1]. The outstanding performance is attributed to high absorption coefficients, direct bandgap, long carrier lifetime, and high balanced hole and electron mobility [2]. Low stability and poor charge transport in the grain boundaries of polycrystalline thin films are drawbacks for further improvement of the devices [3]. Recently, perovskite single-crystal structures have been widely utilized in device applications through the development of growth techniques and physicochemical characterization [4, 5]. In particular, the optoelectronic properties of perovskite single crystals exhibit better performance than thin films owing to low trap densities and high carrier lifetimes as well as robust interface between electrodes with the perovskites.

The fascinating evolution of optoelectronic properties for perovskite single crystals has taken place with respect to defect tolerance associated with the carrier transport and recombination [6–9]. In the case of perovskite polycrystalline thin films, the defects at surface and grain boundaries tend to lead to deep carrier trapping [10, 11]. Additionally, carrier transport by ion migration has been attributed as a possible cause of instability and the hysteresis effect [12]. A number of studies involving with defect analysis have been conducted not only on polycrystalline thin films [13, 14] but also on single-crystal structures, of which are studies on distribution of trap states [15] and the activation energy of defects [16, 17]. It is of importance to understand the carrier transport mechanism for control carrier concentration and mobility in the devices. It is widely believed that formation of defects and their effects on carrier transport are relevant to electronic structure, local structural configuration, and external perovskites including ion migration undergo reversible...
phase segregation upon illumination by the interaction between photogenerated carriers and the inorganic lattice [18]. Results of another study showed that the complex interaction suggests a light-induced change in the dielectric constant [19–21]. However, photo-generated variations in perovskites were indicated by an interfacial carrier accumulation induced by light [22]. Therefore, photo-induced carrier transport in perovskites is still a matter of debate. To develop the optoelectronic properties of perovskite single crystals, more attention should be focused on understanding the defect-related carrier transport and fundamental material properties under various illumination conditions.

In this study, we analyze the photo-current and photo-capacitance of CH$_3$NH$_3$PbBr$_3$ (MAPbBr$_3$) perovskite single crystals, which were fabricated by the inverse temperature crystallization (ITC) method, in the dark and under the different illumination conditions, i.e. 1.9 eV (red light), 2.3 eV (green light), and 3.0 eV (blue light). From the voltage-dependent current density in the dark, space-charge-limited current (SCLC) measurements were investigated to determine the trap density of MAPbBr$_3$ single crystals. Capacitance measurements with voltage and frequency dependence and drive-level capacitance profiling (DLCP) revealed the role and distribution of the defect states under different light sources. Finally, a comparison of the transient photo-current and photo-capacitance suggests that the carrier transport mechanism is related to the defect states for MAPbBr$_3$ perovskite single crystals. A tailored characterization of the defect-related optoelectronic properties for perovskite single crystals will provide a guideline for further improvement of device applications.

2. Results

CH$_3$NH$_3$PbBr$_3$ (MAPbBr$_3$) single crystals were synthesized by an ITC method [23]. As shown in figure 1(a), a Au–MAPbBr$_3$–Au simple device structure was devised to examine the intrinsic transport properties of MAPbBr$_3$ single crystals with the effects from the interlayer, such as electron or hole transport layers (ETL or HTL), minimized. The phase formation and crystal quality of the MAPbBr$_3$ single crystal were examined by x-ray diffraction (XRD) as shown in figure 1(b). The carrier transport in dark conditions was characterized by the SCLC model [24, 25], as shown in figure 1(c). The SCLC method was reasonably adapted because the low conductivity of our single crystal is within the measurement range compared to common p-doped semiconductors [26, 27]. SCLC reveals the dark current density–voltage (J–V) curves of our single crystals with the Au electrode. SCL current is voltage dependent and its carrier injection [28–30]. The J–V curves are bounded into three regions: the Ohmic (red line) trap-limited (yellow marked) and trap-filling region (blue line). Although in our SCLC plot, the trap-limited region was not clearly demarcated like the theoretical mechanism [29], the current of Ohmic region and the rapid increasing point as defined by the trap-filled limit voltage $V_{TFL}$ were checked by the abrupt change of slope in figure 1(c). The trap density ($n_{trap}$) is determined by $V_{TFL}$, which is the voltage where the current begins to increase rapidly, using the following equation [24, 25]:

$$n_{trap} = \frac{2V_{TFL}e\varepsilon_0}{\varepsilon_r eL^3} \quad (1)$$

where $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the relative dielectric constant ($\varepsilon_r = 25.5$) [31], $e$ is the elementary charge ($1.60 \times 10^{-19}$ C), and $L$ is the single-crystal thickness. The trap density of a single crystal was determined as $(2.1 \pm 0.34) \times 10^{10}$ cm$^{-3}$ according to the equation. The J–V curves of the single crystals measured under illumination as well as in dark condition are shown in figure 1(d). The lights in this experiment are red (1.9 eV), green (2.3 eV), and blue (3.0 eV) of light-emitting diodes (LED) with an intensity of 5 mW cm$^{-2}$. The current density under dark conditions was measured to be as low as $\sim 10^{-7}$ A cm$^{-2}$, while it increased to $\sim 10^{-3}$ A cm$^{-2}$ under green and blue illumination. From previous work, the photoluminescence (PL) peak of MAPbBr$_3$ single crystal was found to be at 2.29 eV [23]. The photo-current density under red illumination shows a less sensitivity, whereas green and blue lights can excite electron–hole pairs contributing to the photo-current.

Capacitance measurements of the single crystal in the dark and under the different light conditions are shown in figure 2. The voltage-dependent capacitance in the dark and under red light shows an insignificant change. However, under green and blue illumination, the capacitance–voltage (C–V) curve shows a Schottky-like behavior in figure 2(a). From the Mott–Schottky plot ($1/C^2$–V) in figure 2(a), the carrier densities ($N_{CV}$) of the MAPbBr$_3$ single crystal under green and blue light are $1.90 \times 10^{11}$ cm$^{-3}$ and $5.20 \times 10^{11}$ cm$^{-3}$, respectively. Also, the built-in potential are 0.25 V and 0.39 V under green and blue light from the fitting of $1/C^2$–V. Since the capacitance shows voltage dependence only under illumination conditions where carriers are excited, we propose that photo-induced carrier trapping should occur in the Au–MAPbBr$_3$ interface. Although the C–V curves of perovskite single-crystal devices in the dark condition have been reported [15, 17], the measured devices possessed carrier transport layers which would give additional interfacial
Figure 1. (a) The device schematics with light. (b) XRD diffraction of MAPbBr$_3$ single crystal. (c) SCLC in the dark and (d) photogenerated carrier density under the different illumination conditions.

contribution to capacitance. Capacitance of the MAPbBr$_3$ single crystals under low-energy red light will link to light-induced changes in the dielectric constant [19–21]. Figure 2(b) presents the DLCP measurement, an advanced capacitance-based technique that can provide the spatial distribution of carrier and bulk defect densities [15]. The DLCP technique focuses on the nonlinear terms of the charge response from the AC voltage, as shown in the following equation:

\[
\frac{dQ}{dV} = C_0 + C_1 dV + C_2 (dV)^2 + \ldots .
\]  

(2)

According to Heath et al [32], we determine the $N_{DL}$ at the position $\langle x \rangle$ from equations (3) and (4):

\[
\langle x \rangle = \varepsilon A/G_0
\]  

(3)

\[
N_{DL} \equiv -\frac{C_0}{2q\varepsilon A^2 G_1}
\]  

(4)

where $Q$ is the charge, $V$ is the voltage, $C_{0,1,2}$ is the coefficient of capacitance, $A$ is the area, and $\varepsilon$ is the permittivity. Also, figure 2(c) shows the admittance spectroscopy (AS) results in dark and under three light illuminations from 1 kHz to 1 MHz measuring frequencies. While the frequency-dependent capacitance in the dark and under red light shows an insignificant change. The capacitance values decrease as the frequency increases under the green and blue. The reduction of capacitance presents the accumulation of capacitance with the illumination [22], which is a clear evidence for the photo-induced defect behaviors, but no change in dielectric properties of MAPbBr$_3$ materials.

Table 1 shows the defect densities of MAPbBr$_3$ single crystals calculated from the $C$–$V$ curves and DLCP under illumination. The obtained $N_{CV}$ values under illumination are represented by the contribution of both the net charge densities ($N_p$), the bulk defect densities ($N_b$), the interface defect densities ($N_{int}$), and the photogenerated carrier densities ($N_{ph}$), i.e. $N_{CV} = N_p + N_b + N_{int} + N_{ph}$. Because the DLCP is insensitive to the response of the interface, the drive-level defect density ($N_{DL}$) includes $N_p$, $N_b$, and $N_{ph}$ under
Figure 2. Capacitance measurements of MAPbBr$_3$ single crystals under different light conditions: (a) voltage dependence, (b) DLCP and (c) AS.

Table 1. Defect densities (a) at the interface and (b) in the bulk, and (c) photogenerated carrier density.

| Illuminated light (eV) | $N_{\text{int}}$ (cm$^{-3}$) | $N_b$ (cm$^{-3}$) | $N_{\text{ph}}$ (cm$^{-3}$) |
|------------------------|------------------|------------------|------------------|
| Green (2.3)            | $(1.79 \pm 0.77) \times 10^{10}$ | $(1.08 \pm 0.54) \times 10^9$ | $(1.90 \pm 0.15) \times 10^{10}$ |
| Blue (3.0)             | $(5.19 \pm 0.15) \times 10^{11}$ | $(1.48 \pm 0.10) \times 10^9$ | $(5.20 \pm 0.32) \times 10^{11}$ |

illumination, and the interface defect density can be determined by subtracting $N_{\text{DL}}$ from $N_{\text{CV}}$ [33]. From these values, we propose that photo-induced trapping occurs near the Au–MAPbBr$_3$ interface compared within the single crystal bulk.

To examine the photo-response of MAPbBr$_3$ single crystals in detail, the time-dependent photo-current and photo-capacitance of the single crystal device under three light conditions and 0 V bias are shown in figure 3 and table 2. The photo-current signal is directly proportional to the additive contribution of the electron and hole emission, while the photo-capacitance signal is a result of the difference between the electron and hole emission [34]. Both the photo-current and photo-capacitance decrease with time under the green light conditions, whereas those under the blue light conditions increase with time despite the difference in the degree of change between the photo-current and photo-capacitance. Under the red light condition, the photo-response exhibits slightly small but obvious only in the photo-current, which is
Figure 3. Time-dependent (a), (b) photo-current and (c), (d) photo-capacitance. The part highlighted in yellow in (a), (c) is shown enlarged in (b), (d).

Interpretation of data in Figure 3:

- The part highlighted in yellow in (a), (c) is shown enlarged in (b), (d).
- Table 2 shows the decay times of (a) photo-current and (b) photo-capacitance under different illumination conditions.

| Light bias (eV) | Photo-current decay time (ms) | Photo-capacitance decay time (ms) |
|----------------|-------------------------------|----------------------------------|
|                | $\tau_1$ | $\tau_2$ | $\tau_1$ | $\tau_2$ |
| Red (1.9)      | 34       | 290      | —        | —        |
| Green (2.3)    | 94       | —        | 12       | 76       |
| Blue (3.0)     | 17       | 1540     | 41       | 85       |

These relationships can be described by the following equations:

\[
J(t) = J_1 \exp\left(\frac{-t}{\tau_1}\right) + J_2 \exp\left(\frac{-t}{\tau_2}\right) \tag{5}
\]

\[
C(t) = C_1 \exp\left(\frac{-t}{\tau_1}\right) + C_2 \exp\left(\frac{-t}{\tau_2}\right) \tag{6}
\]

where $J_{1,2}$ and $C_{1,2}$ are the pre-exponential factors, $t$ is time, and $\tau_{1,2}$ are the time constants of the decay. For the photo-current decay, the initial decrease in the transient signal is rapid under all three illumination conditions; however, the photo-current decay from the green light could be fitted with one exponential component. Additionally, the 2nd relaxation of the photo-current under the red and blue light occurred slowly. The photo-capacitance decayed more slowly under the blue light compared with the green light, which is attributed to carrier trapping and the recombination mechanism related to the defect states for...
Figure 4. Schematic of carrier transport mechanism for MAPbBr$_3$ under the blue and green illuminations.

MAPbBr$_3$ perovskite single crystals. According to the slow timescale of decay in MAPbBr$_3$ single crystals, the possible origin of defect states is considered as the ion migration [16, 20]. Our double exponential decay of photo-response would been interpreted as the release of carrier accumulation in the defect states and reorientation of ion migration [20].

According to the transient behaviors, the photo-induced carrier transport mechanism of MAPbBr$_3$ single crystals was illustrated in figure 4. Under green light, the decrease in the photo-current and photo-capacitance values with time appears to be caused by carrier recombination dominantly. The overshooting behavior of the photo-capacitance under green light supports the concept of recombination transport referred to in other similar characterization techniques [38, 39]. The increase in the photo-current and photo-capacitance values under blue light can be explained by carrier trapping at the defect states, which leads to the passivation effect for the photo-current and the charging effect for the photo-capacitance. Initially, the excitation of carriers occurs, and the carriers take main transport differently i.e. recombination and trapping of carriers at the defect states under the green and blue light respectively. Finally, the carriers are separated and diffused toward the electrode. In figure 4, the green light-induced photo-current can be estimated to be smaller than blue light-induced photo-current due to the recombination at the defect states. Furthermore, we suggest that photo-capacitance under the blue light, for which carrier trapping is a major transport, is larger than that under the green light. It can be deduced from the number of diffusing carriers in the schematic as shown in figure 4.

3. Conclusion

We analyzed the optoelectrical properties of MAPbBr$_3$ single crystals based on the ITC method with a sandwich-structure Au electrode. The measurements of photo-current and photo-capacitance under red, green, and blue light provide an understanding of the defect-related carrier transport mechanism in MAPbBr$_3$ perovskite single crystals. The SCLC and $J-V$ analysis exhibited a low trap density and high photo-response of our MAPbBr$_3$ single crystals. The C–V, AS and DLCP measurements suggest photo-induced carrier trapping at the defect near the Au–MAPbBr$_3$ interface. Finally, the behavior of transient photo-current and photo-capacitance indicate defect-related carrier transport such as recombination under green light and charge trapping under blue light. A more probable origin of defects in MAPbBr$_3$ single crystals would be the ion migration rather than the dielectric change. From the optoelectronic analysis of perovskite single crystals, we could suggest that the green light-induced defects lead the recombination loss and blue light-mediated defects cause the compensation within reduced recombination. These findings will contribute to the understanding of the fundamental transport mechanisms as well as the improvement of device performance in optoelectronic applications.

4. Experimental method

4.1. Synthesis of MAPbBr$_3$ single crystals

Methylammonium lead bromide (MAPbBr$_3$) single crystals were crystallized based on the advanced ITC method [23]. Methylammonium bromide and lead bromide (PbBr$_2$) were mixed with a ratio of 1:1 (PbBr$_2$:MABr) in N,N-dimethylformamide to prepare the growth solution. Also, it was filtered using a
0.2 µm PTFE filter. After filtration, the solution was divided among vials in 3 ml and placed on the hotplate with a computational heating system. After crystallization, the crystals were dried in a vacuum oven.

4.2. XRD
XRD patterns of the MAPbBr$_3$ powder and bulk of the single crystal were recorded with an XRD (PANalytical, X’Pert Pro MPD) using a Cu–Kα ($\lambda = 1.5418$ Å) radiation source (40 kV, 30 mA).

4.3. Deposition of electrodes
The photodetector was fabricated by depositing $\approx 100$ nm Au electrodes via vacuum sputtering on the single-crystalline perovskite MAPbBr$_3$ [23]. The size of the device is $2 \times 2 \times 1$ mm$^{-3}$.

4.4. Electrical characterization
The current and capacitance measurements were performed on a Linkam HFS350EV-PB4 probe station connected to a Keithley 4200 semiconducting analyzer with the vacuum at room temperature. For the capacitance measurements, the AC amplitude was 50 mV and the frequency range were from 1 kHz to 1 MHz. The photo-response was measured using 1.9 eV (red), 2.3 eV (green), and 3.0 eV (blue) light with an intensity of 5 mW cm$^{-2}$.

Data availability statement
No new data were created or analyzed in this study.

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Conflicts of interest
There are no conflicts of interest to declare.

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