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Observetion of Photoexcited Carrier Recombination in Metal Halide Perovskite Materials with Single and Poly crystalline structures

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Abstract

We observed photoexcited carrier recombination processes in metal halide perovskite materials. By using time resolved photoconductivity and photoluminescence, we found trapping effects of carriers in $NH_3CH_3PbI_3$, $NH_3CH_3PbBr_3$ and $CsPbBr_3$. We also found significant surface and interface recombination in $NH_3CH_3PbBr_3$ and $CsPbBr_3$.

1. Introduction

Metal halide materials with perovskite structures (perovskite materials) are promising for solar cell application. Solar cells consist of such the material show efficiency of more than 20% [1] which is the same level those obtained from silicon solar cells. However, photoexcited carrier dynamics in the perovskite materials are not fully understood, and thus, it is not easy to design optimum cell structures with these materials. Therefore, in this study, we have observed recombination processes of photoexcited carrier in the perovskite materials by using photoconductivity and photoluminescence techniques. Then we discuss factors affecting the carrier recombination processes.

2. Experiment methods

The samples are single crystals and polycrystal pellets with composition of $NH_3CH_3PbI_3$ ($MAPbI_3$), $NH_3CH_3Br_3$ ($MAPbBr_3$) and $CsPbBr_3$. For growth of $MAPbI_3$ and $MAPbBr_3$ single crystal, antisolvent vapor-assisted crystallization approach was used [2], while for growth of $CsPbBr_3$ single crystal, vertical Bridgman technique was used [3]. Polycrystalline pellets with grain sizes of 0.1-1 μm were made by powder synthesis [4].

We used time-resolved photoluminescence (TR-PL) microwave photoconductivity decay (μ-PCD) methods to observe carrier recombination processes in the samples. Generally, TR-PL signal is proportional to product of electron and hole concentrations, while m-PCD signal is proportional to sum of electron and hole concentrations. By comparison of the signals from these two methods, we can identify presence of minority carrier traps. For a light source for photoexcitation is a pulse laser with wavelength of 355 nm and pulse width of 1 ns. Injected photon densities per pulse were fixed to $1.4x10^{13}$ and $1.4x10^{14}$ cm^{-2}.

3. Results and discussion

Figure 1 shows decay curves for TR-PL and μ-PCD observed from $MAPbI_3$. The decay curves for TR-PL are very fast and decreases noise level at ~0.2 μs. On the other hand, the decay curves for μ-PCD show an initial fast decay < 0.1 μs and subsequent gradual decay. Polycrystal samples shows almost the same or, in μ-PCD, slower decays compared with single crystals.

Figure 2 shows decay curves for TR-PL and μ-PCD observed from $MAPbBr_3$ samples. TR-PL decay cures have initial fast decays at <0.2 μs as observed from $MAPbI_3$. However, in contrast to $MAPbI_3$, single crystal samples show another slow decay component >0.2 μs.

Figure 3 shows decay curves observed from $CsPbBr_3$ samples. The TR-PL signals show relatively fast decays and decrease to noise level at ~0.4 μs. On the other hand, the m-PCD signals show more gradual decays compared with the TR-PL signals. In addition, the μ-PCD signals from the single crystal samples show significantly slower decays compared with those from the polycrystalline samples.

Slow decays in photoconductivity signals for conventional semiconductors generally originate from trapping of minority carrier by deep levels in the band gap [5]. In this case, after excitation, minority carriers do not only recombine with majority carriers but also trapped by the deep levels. Then free minority carriers in the band are

immediately exhausted after excitation, and thus the photoluminescence signal decays fast in contrast to photoconductivity signal. Because all the samples employed in this study show fast TR-PL and slow μ-PCD decays, the samples may have deep levels acting as minority carrier traps, or there are other mechanisms for trapping minority carriers, such as fluctuation of the band structure after excitation [6].

Difference in single and polycrystals is probably due to surface and interface recombination. The polycrystalline structure has much wider surface and interfaces compared with single crystals. The faster decays in μ-PCD for polycrystalline $MAPbBr_3$ and $CsPbBr_3$ compared with the single crystals, while polycrystalline $MAPbI_3$ show the even slower μ-PCD decay compared with single crystals. These results suggest that $MAPbI_3$ has negligible surface and interface recombination among the perovskite materials employed in this work.

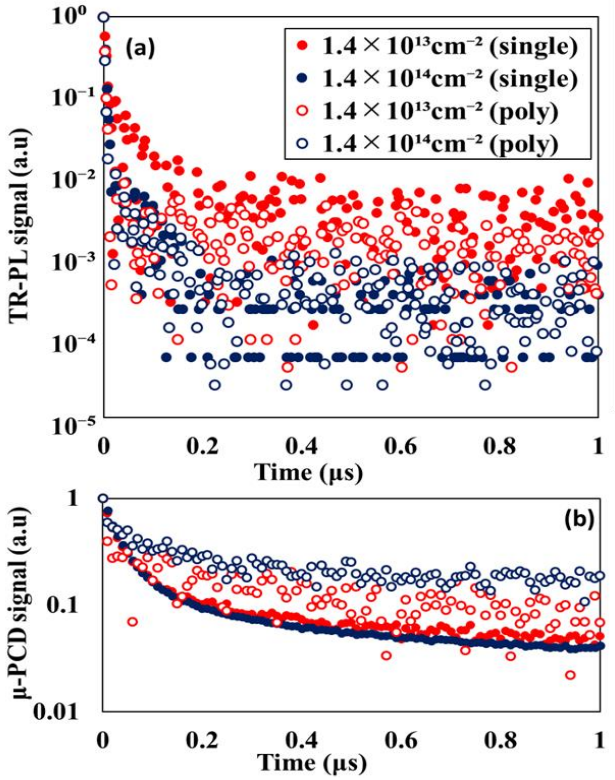

Fig. 1. Decay curves observed from the $MAPbI_3$ samples by using (a) TR-PL and (b) μ-PCD.

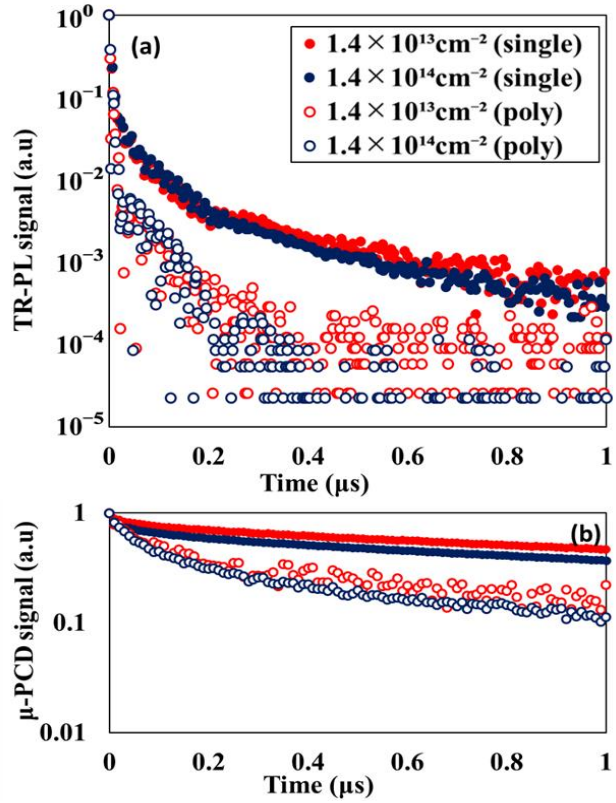

Fig. 2. Decay curves observed from the $MAPbBr_3$ samples by using (a) TR-PL and (b) μ-PCD.

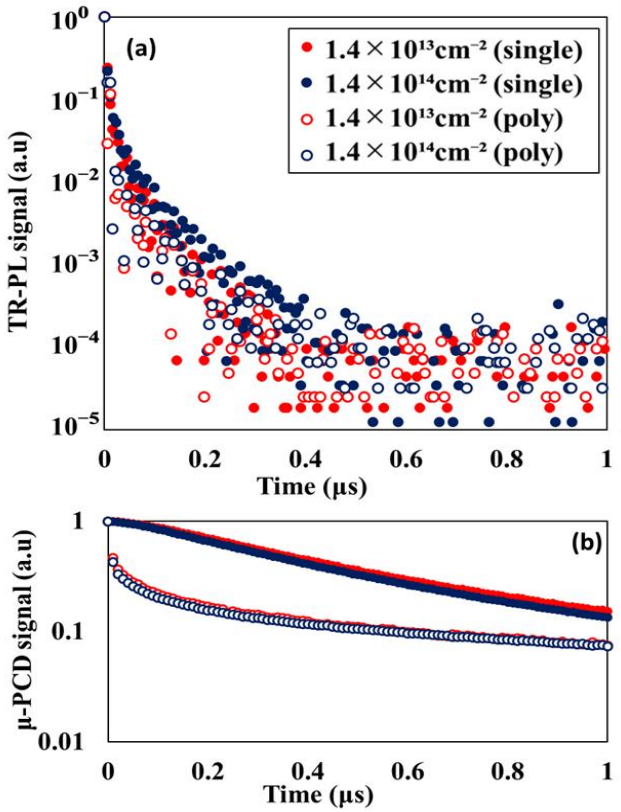

Fig. 3. Decay curves observed from the $CsPbBr_3$ samples by using (a) TR-PL and (b) μ-PCD.

4. Conclusions

From observation of carrier recombination processes in $MAPbI_3$, $MAPbBr_3$ and $CsPbBr_3$, we found trapping effects of minority carriers in these materials. Comparison with single and poly crystalline structure indicates that significant surface and interface recombination in $MAPbBr_3$ and $CsPbBr_3$.

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