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Visualization of Carrier Transport in Organic-Inorganic Hybrid Perovskite Thin Film by Photoluminescence Decay Method

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Abstract

Photoluminescence (PL) decay imaging measurement was conducted to study the carrier transport phenomena in spin-coated $CH_3NH_3PbI_3$ perovskite thin film. Carrier transport processes was visualized by utilizing the quenching of light emission intensity due to the injected charges. We successfully observed two steps change of the transient PL imaging indicating different transport processes. The fast PL decay corresponds to the hole transport phenomena, and the slow PL decay is possibly due to the migration of intrinsic ions in the perovskite. In this studies, we confirmed the PL quenching is corresponding the charge injection and obtained electron and hole transport with motilities of $2 \times 10^{-2}\mathrm{cm}^2/\mathrm{Vs}$ and $1.0 \times 10^{-2}\mathrm{cm}^2/\mathrm{Vs}$ respectively. Our experiment approaches further investigations into the ion migrations that is one of the key factors of hysteresis behavior in perovskite solar cells.

1. Introduction

The hybrid halide perovskites combine the solution processablity and low-cost manufacturing of organic materials with the high performance of inorganic compounds. Recently the power conversion efficiencies of perovskite solar cells have reached a value of 20%. [1] Even though the dramatic rise of efficiencies of perovskite solar cells, the fundamental carrier transport properties are still under investigations. The fundamental properties of optical and electrical properties of the organic-inorganic hybrid trihalide perovskites (OTPs) are a target of intense research, in parallel with promising developments in semiconductor device application. A direct observation of carrier injection from the electrode and its transport would be very useful for a further understanding of the carrier behavior in semiconducting devices. [2,3] The carrier transport properties in the OTPs is influenced by the fabrication process, morphology, defects, grain boundaries and environmental effects. [4] We developed a novel method to visualize the carrier motion in an organic semiconductor on the basics of the optical second harmonic generation (SHG) measurement. [5] But some difficulty exists when we apply the SHG technique to fluorescent materials because of the interference of two-photon excited PL and the SHG signal. Our previous experiment reveals the injected charges are responsible for PL decay phenomena in perovskite material. In this paper, we demonstrate the charge transport process in spin-coated $CH_3NH_3PbI_3$ perovskite thin film to be successfully visualized through the PL decay imaging.

2. Experiments

Carrier transport process was visualized using thin film transistor (TFT) structure. For fabrication of the top contact TFT device, highly-doped Si wafer with 500nm thick SiO_2 gate insulator was used. For semiconducting channel layer, 40 wt% DMF solution of $CH_3NH_3PbI_3$ was spin-coated on Si wafer with a rotating speed of 3000 rpm for 60 seconds then 15 minutes annealing at 100º C in the glove box. Finally, the source and drain gold electrodes were deposited by thermal evaporation through a shadow mask. The experimental setup of PL decay imaging is shown in Fig. 1.

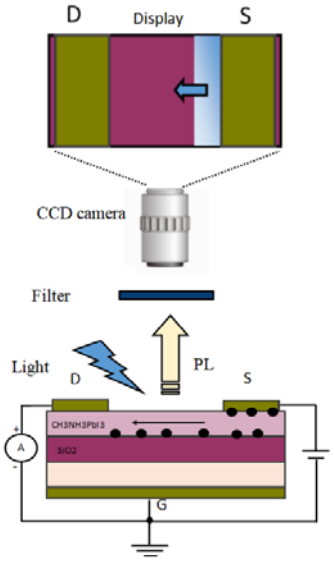

Fig. 1 Experiment setup for PL decay imaging

PL takes place when the excited molecular state produced by photo irradiation goes back to the ground state. However, under the electric field, excitons may dissociate because of large dielectric constant of perovskite materials, and the energy of excited molecule may transfer to the charged molecule under the presence of injected charges according to the Foster model, and PL intensity decreases. We can visualize the transient change in the fluorescence images by CCD camera that reflect directly the carrier motion as shown in Fig. 2. Interestingly, we can clearly see two-step change in these transient images in 50 frames per second. Before PL decay, for the first 0.02s, we can see the enhancement of PL spreading from the source electrode after negative voltage application, probably due to the extraction of intrinsic holes. After that, the PL intensity slightly decreased because of motion of the

intrinsic ions in the perovskite. The enhancement of the PL spreads faster than the PL decay process, indicating the difference in the mobility between the electron and intrinsic ion. Interestingly carrier motion and ionic motion can be discriminated by using the PL decay imaging.

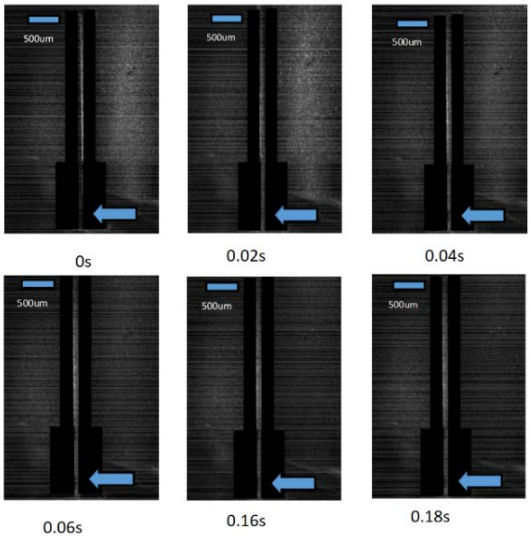

Fig. 2 Time dependent fluorescence images

To confirm that the transient PL decay images correspond to the carrier motion, lateral time-of-flight (TOF) measurement was also conducted. The transient current from the drain electrode was measured using the device with long channel length (L=6.8mm) to avoid effect of the charging current. For the lateral TOF measurement, transient fluorescence images were also captured with a time interval of 0.02s during the current measurement. Fig. 3 shows the transient current change and the PL decay motion. As shown in Fig. 3, the current observed at drain electrode began to increase when the PL decay area approached the drain electrode. These results also indicate the transient PL decay corresponds to the carrier motion.

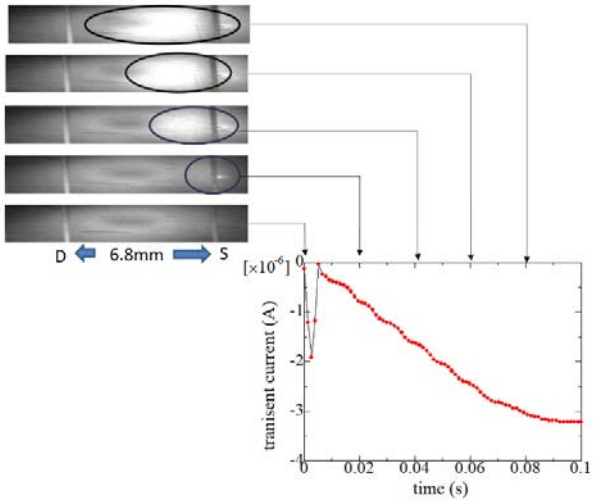

Fig. 3 Time dependent fluorescence images and transient current from opposite electrode

Carrier mobility is evaluated by analyzing the transient behavior of the time-dependent fluorescent images according to Eq. (1), where μ is mobility, x is transport distance, V is pulse voltage, and t is transit time. [6]

$$\mu = \frac{x^2}{2Vt} \qquad (1)$$

From this measurement, we can also confirm our PL decay corresponds the carrier distribution and calculate electron and hole motilities according to Fig. 3. We can calculate electron and hole mobility as $2 \times 10^{-2}\mathrm{cm}^2/\mathrm{Vs}$ and $1 \times 10^{-2}\mathrm{cm}^2/\mathrm{Vs}$ respectively. This is much lower than mobility measured using single crystals and vertical TOF. [7] In the lateral TOF configuration, transport can be expected to be strongly influenced by surface morphology and crystal structure. The complexity of the carrier transport properties in perovskite materials is induced by the fabrication process, defects, grain boundaries and environmental effects.

3. Conclusions

We have successfully visualized the charge transport phenomena in spin-coated $CH_3NH_3PbI_3$ perovskite thin film through the PL decay imaging. Perovskite materials can provide ambipolar electrical properties with high luminescence efficiency. The experimental results reveal the intrinsic ions predominantly exist throughout the film. Discriminate evaluation of the carrier and ion current is quite important to discuss the fundamental electrical transport properties of perovskite materials but is yet still under further studies.

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