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Study of Ion Migration in $CH(NH_2)_2SnI_3$ Thin Films Using Electric-Field-Induced Optical Second-Harmonic Generation Measurement

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Abstract

Tin perovskite is attracting much attention for the preparation of Pb-free solar cell. The internal electric field formed in tin perovskite film plays an essential role for the photovoltaic effect. In this study, impacts of ion migration on I-t curves are studied by using electric-field-induced optical second-harmonic generation (EFISHG) measurement which is available for directly probing the internal electric field in tin perovskite film.

1. Introduction

Recently, organic-inorganic metal halide perovskite solar cells [1] have attracted much attention because of the high power conversion efficiency and low-cost fabrication process, but the use of toxic lead (Pb) leads to a serious environmental problem and it is severely prohibited in the European Unions and other countries. At present, tin perovskite $CH(NH_2)_2SnI_3$ ($FASnI_3$) is one of the most promising candidates for the preparation of lead-free solar cells [2].

However, the efficiency of tin perovskite solar cells is still quite low compared to lead perovskite solar cells, possibly due to the polarization mechanisms involving ionic transport [3] and ferroelectricity [4]. Ion migration has been particularly considered to influence the I-V hysteresis observed in solar cells. It is an urgent task to clarify the photovoltaic mechanism of tin perovskite solar cells, in terms of ion migration.

Here, we propose to use EFISHG measurement, which is available for directly probing the electric field in organic semiconductor layers [5]. The actual electric field formed in tin perovskite ($FASnI_3$) thin films was investigated using EFISHG, in terms of the I-t curves due to ion migration of perovskite.

2. Experiment

Figure 1 shows the sample structure of ITO/$FASnI_3$/Al. SnI_2 and $CH(NH_2)_2I$ (Formamidinium iodide, FAI) were mixed at a concentration of 1 M in γ-butyrolactone (GBL)/dimethyl sulfoxide (DMSO) mixed solvent. 20 mol% SnF_2 was also added in the solution. The perovskite solutions were spin-coated onto an ITO electrode in a glove box to fabricate perovskite thin films, followed by annealing at 100 °C for 10 min. Finally, Al electrode was thermally evaporated at the thickness of 100 nm.

In EFISHG measurement, a laser light was impinged onto the sample and second harmonic (SH) light with a half wavelength was detected by using a photomultiplier tube (PMT). For comparison, red light with a wavelength of 660 nm was impinged onto the sample by a laser diode.

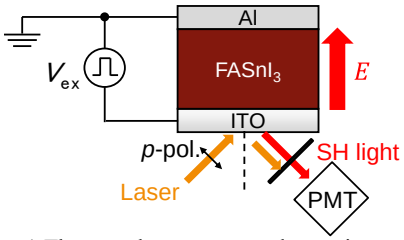

Fig. 1 The sample structure and experimental setup for EFISHG measurement.

3. Results and Discussion

EFISHG measurement was conducted by impinging 1020 nm laser light onto the ITO/$FASnI_3$/Al samples through the transparent ITO electrode, where the square-shape pulse was applied in a manner as illustrated in Fig. 2(a). The SH intensity at 510 nm in wavelength was found to be proportional to the square of the applied voltage (Fig. 2(b)). This result clearly shows that EFISHG is generated from $FASnI_3$, following the theoretical relationship

$$I_{SHG} \propto |E(0)|^2. \qquad (1)$$

Furthermore, we measured the transient current during the application of pulsed square-wave voltage. Here, the duty time is 1 μs and the amplitude is 5 V, as shown in Fig. 3(a). This condition corresponds to V_{high} = 5 V in Fig. 2(a). Fig. 3(b) shows that the decay of the current flowing across the external circuit observed under voltage application. From semi-log plot, we can see that the current does not decay with a single exponential function like a simple capacitor but a multi-exponential function as follows:

$$I = \frac{V_{ex}}{R}\sum_i a_i \exp\left(-\frac{t}{\tau_i}\right), \qquad (2)$$

where R, a_i and τ_i are external resistance (100 Ω), a prefactor and the time constant, respectively. Such current behavior including slow decay components is possibly due to the ion migration of perovskite [6]. In addition, from the increase of the current under illumination, we can confirm that the capacitance of perovskite increased [7]. On the other hand, time-resolved EFISHG measurement was conducted under the same applied voltage condition as in the current measurement. Fig. 3(c) shows that the SH intensity gradual-

ly increases with time during the application of square pulse. This result clearly indicates that the electric field in the $FASnI_3$ film was increasing while the current was decaying,

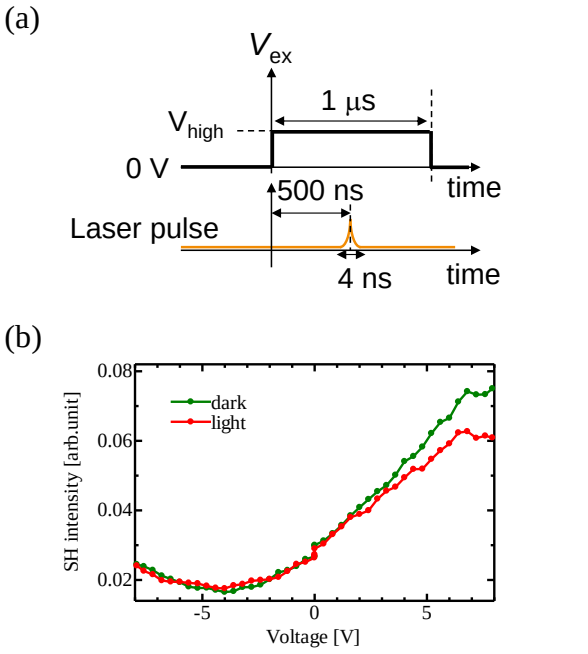

Fig. 2 (a) The timing chart of applied voltage and (b) SH-V characteristics of $FASnI_3$.

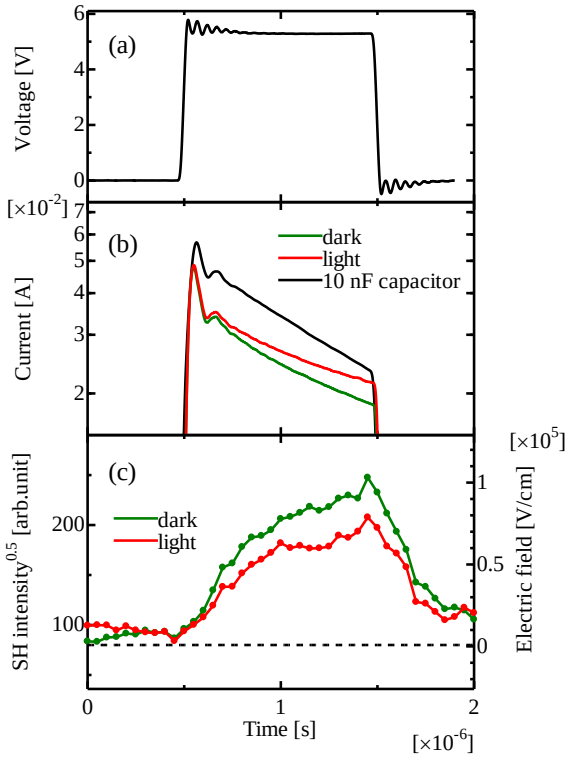

Fig. 3 The transient of (a) applied voltage, (b) current and (c) SH intensity in dark (green) and under illumination (red). The black solid line in (b) is the result of a normal capacitor of 10 nF.

where the relationship

$$RI + Ed = V_{ex} \qquad (3)$$

is satisfied. Here, d is the film thickness of the $FASnI_3$ film. Under illumination, the electric field was found to decrease compared to dark conditions, which is well consistent with the results of transient current.

Furthermore, the SH signal intensities were converted to the actual electric field, under the assumption that the electric field in the tin perovskite film can be derived from the transient current I using Eq. (3). Here we assumed that the film thickness d is 300 nm. The electric field is shown in the right axis in Fig. 3(c). By using this electric field E, ion mobility under dark conditions is estimated as

$$\mu = \frac{d}{Et_r} = 4.7 \times 10^{-4}\ \mathrm{cm^2/Vs}, \qquad (4)$$

where the transit time t_r = 1 μs. The response time of ion migration is in the range from shorter than 1 μs to longer than 10 ms depending on ion species [8], and we believe the mobility given by Eq. (4) is caused by ions such as I^-.

Consequently, EFISHG results provided the direct evidence that ions are migrated on the order of 10^4 V/cm, and current flows across the circuit due to the ion migration.

4. Conclusions

We probed the electric field in tin perovskite thin films using EFISHG measurement. Results showed that the electric field on the order of 10^4 V/cm is closely related to ion migration such as I^-, which causes the transient decay current including slow decay components. In our presentation, we will further discuss the hysteresis behaviors of $FASnI_3$ thin films in a solar cell configuration by using EFISHG.

Acknowledgements

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