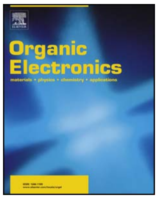
Organic Electronics 55 (2018) 90–96

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



Enhancing thermoelectric performance of the $CH_3NH_3PbI_3$ polycrystalline thin films by using the excited state on photoexcitation

Ping Wu, Yan Xiong, Lin Sun, Guo Xie, Ling Xu*

Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan 430074, China

ARTICLE INFO

Keywords:
$CH_3NH_3PbI_3$ perovskite polycrystalline thin-films
Photoexcitation generate excited state
Seebeck coefficient
Electrical conductivity
Power Factor

ABSTRACT

Recently, organic-inorganic hybrid perovskite materials ($CH_3NH_3PbI_3$) have made great progress in the solar cells field, however its thermoelectric properties are not good, one of the reason is that the carrier concentration is too low, resulting in low electrical conductivity. Another reason is that the phase structure changes from the tetragonal phase to the cubic phase when the temperature over 57 °C, which distorted the octahedron structure of PbI_6. The structural distortion restricted the carrier's transport, leading to decreasing of the carrier's mobility. And the Seebeck coefficient was also rapidly dropped with the temperature increasing. In this article, we used photoexcitation-generated excited states could effectively restrain the decrease of electrical conductivity and Seebeck coefficient of $CH_3NH_3PbI_3$ polycrystalline thin film, because the photoexcitation could greatly enhance the density of excited state, which increased charge carrier concentration and electrical conductivity. Moreover, thanks to the photoexcitation, the surface charge accumulation was increased significantly, enhancing the surface polarization at metal/Perovskite interface, simultaneously, enhancing the polarization effect of $CH_3NH_3PbI_3$. The enhanced surface polarization functions as an additional driving force to diffuse the charge carriers from hot side to cold side, thus the carrier mobility was increased effectively, restraining the Seebeck coefficient's decrease caused by the crystal phase transition. Our experimental results showed that photoexcitation increased the electrical conductivity from 7.8×10^{-6} S/m in the dark to 4×10^{-5} S/m in illumination condition, the mobility increased from the 0.141 $cm^2/v.s$ in the dark to 13.122 $cm^2/v.s$ in illumination condition. Simultaneously, the Seebeck coefficient was also increased from 26 μV/K to −17 mV/K with increasing light intensity from 0 to 100%. The Power Factor (PF) value of 11.51 nW/mK^2 in the illumination condition was further bigger than the PF of 5.27×10^{-6} nW/mK^2 in the dark condition. As a result, our experiment further demonstrated that photoexcitation can be used as an effective way to simultaneously develop high Seebeck coefficient and electrical conductivity through excited states in an organic-inorganic semiconducting material with multilayer electrode/perovskite/electrode thin-film device.

1. Introduction

Organic-inorganic hybrid perovskite ($CH_3NH_3PbI_3$) is a kind of photovoltaic material with superior performance [1–9]. These years, $CH_3NH_3PbI_3$ materials have made great progress in the solar cells field, its photoelectric conversion efficiency is increasing rapidly, now the reported maximum efficiency is 22.1% [10–14], because it has greater electron and hole mobility, smaller exciton binding energy, and long carrier free path [15–19]. Besides application on solar cell field, $CH_3NH_3PbI_3$ has also made a lot of achievements in photoelectric detection, photoluminescence et al. other fields [20–27]. However, there are few reports about the thermoelectric properties, mainly due to the too low electrical conductivity and charge carrier concentration.

In fact, we considered the $CH_3NH_3PbI_3$ perovskite should have better thermoelectric properties. The $CH_3NH_3PbI_3$ perovskite material is a kind of organic-inorganic composite material. In $CH_3NH_3PbI_3$ system, not only $(CH_3NH_3)^+$ has low thermal conductivity, but also the Pb^{+2} and I^- ion have relatively higher electrical conductivity. And some literatures have reported that the $CH_3NH_3PbI_3$ perovskite has relatively lower thermal conductivity comparing with the inorganic thermoelectric materials [28–30]. However, because the carrier concentration is very low, just about 10^{13}-10^{14} cm^{-3}, leading to low electrical conductivity, although the thermal conductivity is very low, the whole ZT value isn't high, so the $CH_3NH_3PbI_3$ perovskite material's thermoelectric property is not good. How to improve their thermoelectric ZT value? We know that traditional experimental method of adjusting the electrical conductivity (δ) is doping [31–33], which can increase the conductivity, but decrease the Seebeck coefficient (S)

---

* Corresponding author.
E-mail address: xuling@mail.hust.edu.cn (L. Xu).

https://doi.org/10.1016/j.orgel.2018.01.014
Received 1 December 2017; Received in revised form 29 December 2017; Accepted 19 January 2018

caused by the increase of the carrier density, thereby the Power Factor (PF) is still not high [34–44]. In our previous research work [45], we have found that photoexcitation-generate excited state was a good way to effectively adjust the electrical conductivity and restrain the thermal conductivity increasing, especially for $CH_3NH_3PbI_3$ such material. Using photoexcitation can easily separate electron-hole to generate a mass of free charge carriers with high mobility. On the one hand, the photoexcitation increased the density of excited states and the carrier concentration, resulting in the electrical conductivity was increased. On the other hand, these free charges could be stimulated from the ground state to excited state, enhancing the free charges' mobility, thus increasing the Seebeck coefficient. In addition, we found that the phase structure changes from the tetragonal phase to the cubic phase when the temperature over 57 °C, which meant there was a phase transition in the $CH_3NH_3PbI_3$ materials at 57 °C [46,47]. The phase structure changes of $CH_3NH_3PbI_3$ leaded to a structural distortion of PbI_6, which decreased the Seebeck coefficient. Therefore, the thermoelectric properties were also reduced rapidly with the temperature over 57 °C. Oppositely, when the $CH_3NH_3PbI_3$ material was been illuminated, its Seebeck coefficient was increased when the temperature over the 57 °C. One of the important reason is that the photoexcitation increased the charge carrier's mobility by the surface polarization effect, which can restrain the Seebeck coefficient's reduction caused by the structure change, resulting in the increase of the Seebeck coefficient.

For further understanding the $CH_3NH_3PbI_3$'s thermoelectric properties under photoexcitation to obtain a high thermoelectric performance material and device, in this article, we fabricated the $CH_3NH_3PbI_3$ polycrystalline thin film device based on the metal/Perovskite/metal architecture, and utilized the different light intensity to adjusting the Power Factor (PF), then analyzed the phtotoexcitation how to affect its thermoelectric properties.

2. Experiment section

2.1. $CH_3NH_3PbI_3$ materials preparation

We fabricated the $CH_3NH_3PbI_3$ materials using one step method. Firstly, PbI_2 and CH_3NH_3I (Purchase from Sigma-Aldrich Corporation) were mixed at a molar ratio of 1: 1, then dissolved them into a mixture of γ-butyrrolactone (GBL) and N,N-dimethylformamide (DMSO) in a volume ratio of 7: 3 to preparing perovskite solution with a concentration of 1.3 mol/L, and kept stirring for 1 h. At last, the perovskite solution was spin-coated on precleaned ITO substrates with the thickness of 300 nm by anti-solvent chlorobenzene extraction, and annealed for 5 min at 150 °C, a black $CH_3NH_3PbI_3$ thin film sample was obtained.

2.2. Device fabrication

Firstly, laser-patterned, ITO-coated glass substrates were cleaned by the ultrasonic oscillation in an alkaline, aqueous washing solution for 15 min. Afterwards, using the deionized water, ethanol and acetone to rinsing, respectively, then placed the ITO into an O_3 condition and used the ultraviolet treatment for 30 min. Secondly, The preparation $CH_3NH_3PbI_3$ was spin-coated onto ITO substrate with the film thickness of 300 nm Polycrystalline thin film of perovskite thermoelectric device with sandwich ITO/Perovskite/Au thin-film structure were used, as shown in Fig. 1. After that, the metal electrodes were evaporated. The bottom ITO electrode has a sheet resistance < 30 Ω/square. The top Au layer of 100 nm was then deposited on perovskite thin film under the vacuum of 2×10^{-6} Torr to form a thermoelectric device with ITO/Perovskite/Au architecture.

2.3. Thermoelectric properties measurement

Fig. 1 showed the device structure and the schematic diagram for Seebeck measurement under photoexcitation for the ITO/Perovskite/Au device, which was the self-built test system. In the Seebeck measurement, the type K thermocouple were connected to both the bottom (ITO) and top (Au) electrodes (see Fig. 1), the K type thermocouple's top junction was treated specially, it was a microprobe which radius was 2 μm. The thermocouples placed on the ITO and the center of cross-plane between ITO and Au, respectively, the T/C contact position is very close the points where the voltage is measured. When the ITO was heated, the temperature difference was controlled by running a current through the ITO planar substrate, which heated the Perovskite surface use the ITO side. When the temperature got to uniformity on the ITO and Au after a time, ITO could get to a balance temperature about twenty minute, to measure the temperatures of each side of the device at this time. Hot side temperature was controlled by running a current, cold side temperature was controlled by changing fan speed, and keep the different temperature was 8 K. The photoexcitation was provided by standard sunlight of AM1.5G 100 mW/cm^2 (NEWPORT company), the illumination area was greater than measurement area (0.09 mm^2). Electrical voltage data were collected using a Keithley 2400 instrument (accuracy: ± 1 μV) and temperature data were collected by an Omega Engineering temperature sensor (accuracy: ± 0.1 K).

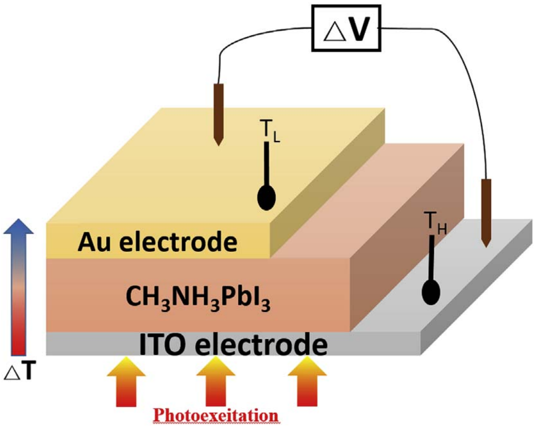


Fig. 1. Device structure and schematic diagram showed Seebeck measurement in the ITO/Perovskite/Au device under dark and different light intensity conditions.

The electrical conductivity measurement used the current-voltage curve. We also performed some characterization measurements related to thermoelectric properties for the ITO/Perovskite/Au device by using scanning Kelvin probe microscope (SKPM), X-ray diffractometer (XRD), Photoluminescence (PL) and ultraviolet visible absorption spectroscopy (UV).

In addition, we know that photoexcitation can lead to both photovoltaic and Seebeck effects in a thermoelectric device at a given temperature gradient. It was observed that the Seebeck and photovoltaic voltages have the same polarity in our device. Here, we used the following procedures to measuring the Seebeck effect. First, the entire electrical potential containing Seebeck and photovoltaic components was measured under the temperature gradient of 8 K at different temperatures from 30 °C to 70 °C with a constant photoexcitation intensity. Second, the photovoltaic voltage (Voc) was measured under zero temperature gradient ($\Delta T < 0.1$ K) at different temperatures under constant photoexcitation. Third, the Seebeck voltage data were then determined by the difference between the entire electrical voltages, measured under the temperature gradient of 8 K, and the photovoltaic voltages, measured under zero temperature gradient, for the ITO(hot)/Perovskite/Au(cold) device at different temperatures from 30 °C to 70 °C. The Seebeck coefficients were then calculated by using the Seebeck voltages under given temperature gradient between ITO and Au electrodes.