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Thickness effects of ZnO thin film on the performance of tri-iodide perovskite absorber based photovoltaics

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Abstract

Comprehensive studies were carried out to understand the thickness effects of ZnO thin films for tri-iodide perovskite absorber (TPA) based photovoltaics, including the absorption spectrum, photoluminescence, nanosecond time-resolved photoluminescence (NTRPL), and photo-induced absorption (PIA) of TPA/ZnO/ITO/glass. These were carried out in order to explore the Urbach energy of TPA films and the exciton dissociation at the interface between TPA and ZnO. The results show that the thickness of the ZnO thin film significantly influences the photovoltaic performance in terms of open-circuit voltage (V_{OC}), fill factor (FF), and short-circuit current density (J_{SC}). In the case of the thicker ZnO film, the photovoltaics have the better FF and V_{oc}, as a result of the smaller electron recombination. This means that a thicker ZnO film can block the electron recombination from the Fermi level of the ITO to the valance band of the TPA. On the other hand, the thicker ZnO film results in a higher J_{SC} due to the better exciton dissociation at the interface between TPA and ZnO, which means that the electron mobility of the thicker ZnO is higher. Consequently, the photovoltaic performance can be expected to be improved by using a transparent cathode electrode with high conductivity and electron mobility.

Keywords: Time-resolved photoluminescence; Photo-induced absorption; Energy transfer; Photovoltaic

1. Introduction

Mixed halide ($CH_3NH_3PbI_{3-x}Cl_x$) and tri-iodide ($CH_3NH_3PbI_3$) perovskite absorbers (PAs) have been intensively investigated because with them a power conversion efficiency (PCE) of 15% can be achieved by using a solution process under low temperatures (Burschka et al., 2013; Liu and Kelly, 2014). In order to absorb more sun-light, the optical bandgap of PA has been engineered to range from 2.2 eV to 1.1 eV (Eperon et al., 2014; Stoumpos et al., 2013). The exciton binding energy and Urbach energy of PA can be determined by analyzing the temperature-dependent absorption spectrum (D'Innocenzo et al., 2014; Wolf et al., 2014). The exciton binding energy (Urbach energy) of PA is about 50 meV (15 meV), which is slightly larger than that of GaAs. The small exciton binding energy (Urbach energy) and the low optical bandgap are the

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reasons why the PCE of PA based photovoltaics can be larger than 15%. The first attempt of using $CH_3NH_3PbX_3$ (X = Br and I) as light absorber was made in dye-sensitized liquid-type photovoltaic (Kojima et al., 2009), which was significantly improved to 6.5% by optimizing perovsikte fabrication process (Im et al., 2011). However, the perovskite absorber suffers from liquid-type dye-sensitized photovoltaic because it tends to easily dissolved in polar liquid electrolyte. Long-term durable all solid state perovskite solar cell was first developed and reported in literature (Kim et al., 2012). The first high efficient PA based photovoltaic device was realized using the following structure: Ag/Sprio-OMeTAD/PA/TiO_2/FTO/glass (Lee et al., 2012), where Spiro-OMeTAD and mesoporous TiO_2 were used as the hole acceptor and electron acceptor, respectively. The main drawback is that the sintering temperature for anatase TiO_2 has to be higher than 450 °C (Schattauer et al., 2012) which can damage the plastic substrate. For low-temperature fabrication, ZnO thin films have been used to replace the mesoporous TiO_2 as an electron acceptor (Liu and Kelly, 2014; Kumar et al., 2013; Son et al., 2014). ZnO nanoparticle film and Spiro-OMeTAD film were used to extract the electrons and holes, respectively (Liu and Kelly, 2014). The optimized thickness of a ZnO nanoparticle film for PA based photovoltaics is 25 nm, which results in a high PCE of 15.7%. In contrast, in this study we investigate the thickness effects of ZnO thin film fabricated by atomic layer deposition (ALD) method (Wang et al., 2010).

We seek to understand the thickness effects of ZnO thin film on the performance of PA based photovoltaics. Nanosecond time-resolved photoluminescence (NTRPL) and photo-induced absorption (PIA) were carried out to observe the exciton dynamics of PA/ZnO/ITO/glass for different thicknesses of ZnO thin film.

2. Fabrication

ZnO thin film was deposited on top of ITO/glass with a sheet resistance of 10 Ω/sq under a temperature of 80 °C using the ALD method. The detailed fabrication process of the ZnO thin film is described in our previous report (Wang et al., 2010). A two-step process was used to grow the TPA film. This consisted of spin coating a film of PbI_2 onto the ZnO/ITO/glass, followed by spin coating a solution of CH_3NH_3I in isopropyl alcohol. After the two-setp spin coating process, the films were heated at 100 °C for 30 s. The detailed fabrication process of the TPA film is described in our previous report (Chiang et al., 2014). Spiro-OMeTAD was spin coated on top of TPA/ZnO/ITO/glass as the hole acceptor. Then, MoO_3 and Ag were thermally evaporated onto the sample to act as the anode electrode. The final photovoltaic structure was comprised of Ag/MoO_3/Sprio-OMeTAD/TPA/ZnO/ITO/glass. The thicknesses of ITO, TPA, Spiro-OMeTAD, MoO_3, and Ag were controlled at ca. 250 nm, 350 nm, 150 nm, 5 nm, and 100 nm, respectively. The thickness of ZnO thin film was varied from 5 nm to 40 nm by controlling the ALD cycle times.

3. Results and discussion

Fig. 1 presents the X-ray diffraction (XRD) patterns of ZnO thin film and TPA film. The XRD characteristics of ZnO thin film cannot be obtained due to the thin thickness. The four diffraction peaks of 13.4°, 19.5°, 24.0° and 27.4° indicate the formation of crystalline $CH_3NH_3PbI_3$ (Kojima et al., 2009). The diffraction peak of 12.1° originates from the unreacted PbI_2, which is presented in twe-step depostion because of dense PbI_2 layer for planar structure. The substrate-induced changes in the energy band position of TPA film has been investigated (Miller et al., 2014). In order to include the substrate-induced changes in the optical and electrical properties of the TPA films, the ZnO/ITO/galss substrate is used in the optical characterizations of TPA films. Fig. 2 presents the absorbance and PL spectra of the TPA/ZnO/ITO/glass. In the linear absorbance spectrum, there are two prominent peaks located at 480 nm and 760 nm, which is in agreement with the perivously reported values (Xing et al., 2013). In the PL spectrum, there is an emission peak located at 768 nm when pumping at $\lambda = 532$ nm, which is the direct bandgap emission from the first conduction band to the first valence band (Xing et al., 2013). The exciton binding energy ranging from 30 meV to 50 meV (D'Innocenzo et al., 2014; Koutselas et al., 1996; Ishihara, 1994), which is slightly larger than the thermal energy (~25 meV) at room temperature. For an exciton binding erngy of 50 meV (30 meV), the faction of the photo-generated excitons can be calculated from statistical physics to yield: 34% (45%) of the excitons dissociating spontaneously and remaining 66% (55%) of the excitons (Sum and Mathews, 2014). Therefore, the PL originages mainly from the radiative recombination of electron–hole pair (exciton). The PL intensity can be used to eavuate the exciton quenching (exciton dissociation) at the interface between TPA and ZnO. The thickness of ZnO thin film highly influensces

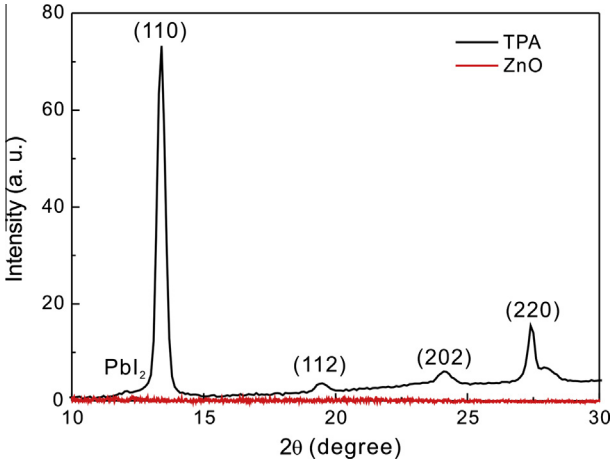

Fig. 1. X-ray diffraction patterns of ZnO/glass and TPA/glass.