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Highly conductive Zinc-Tin-Oxide buffer layer for inverted polymer solar cells

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ABSTRACT

Thin-films of Zinc Tin Oxide (ZTO) with an extremely high charge carrier mobility and superior optical transmittance are synthesized using a simple solution method. These ZTO films have been systematically studied for the application in inverted polymer solar cells (PSCs). The Hall effects measurements show that the charge mobility of the ZTO semiconductor is over 16.5 $cm^2.V^{-1}.S^{-1}$, which is the highest mobility value ever reported for oxide buffer made by using solution process. By applying the ZTO buffer layer in the inverted PSCs of P3HT:$PC_{61}BM$, the power conversion efficiency of the device is 30% higher than that of the devices made with other common buffer layers such as ZnO and TiO_2. Light intensity-dependent JV studies and PL measurements also indicate that ZTO buffer layer reduces surface recombination. This work demonstrates that the solution-synthesized ZTO is a promising new buffer layer with superior electron extraction capability for the solar cells.

1. Introduction

Wide bandgap metal-oxide semiconductors with low work function and high optical transmittance in the visible light wavelength range have been intensively investigated as buffer layers in the polymer and perovskite solar cells [1–4], due to their low production cost, excellent stability as well as compatibility with solution processing. By using conventional wide bandgap metal oxide (e.g., ZnO,TiO_2) as the electron extracting buffer layer, the power conversion efficiency (PCE) of triple-bulk heterojunction tandem polymer solar cell [5] and perovskite solar cell have reached 11.6% and 20.1% respectively [6–8]. However, the electron mobility of conventional interfacial buffer layer materials, such as ZnO and TiO_2, is in the range of 10^{-2}–10^{-3} $cm^2.V^{-1}.S^{-1}$ [9,10], which has been considered as major obstacles to improve device performance due to the Ohmic loss. To resolve this problem, doping metal ions within oxides is one effective method. In a typical case of metal ions-doped in ZnO buffer layer, the electron mobility is greatly increased from pristine 10^{-2} $cm^2.V^{-1}.S^{-1}$ to ~10^{-1} $cm^2.V^{-1}.S^{-1}$ [11], such as gallium-doped ZnO [12], Cesium-doped zinc oxide [11], indium-doped ZnO [13], magnesium-doped ZnO [14], lithium-doped ZnO [15], and Al-doped ZnO [9]. However, with the development of promising transition metal oxides anode buffer layer such as NiO_x [16], MoO_3 [17–19] and excellent inorganic-organic hybrid perovskite active layer material [20], these solutions, although alleviate this problem to a certain extent, have not been solved thoroughly.

Recently, amorphous Zinc tin oxide (ZTO) thin films with smooth surface and charge mobility of 14.11 $cm^2.V^{-1}.S^{-1}$ have been obtained from the solution of 0.1 M $Zn(CH_3COO)_2 \cdot 2H_2O$ and 0.1 M $SnCl_2$ both dissolved in a 2-methoxyethanol solvent with a stabilizer of 12 μl ethanolamine [21,22], which improved the performance of thin film transistors. These solution processable ZTO thin films with smooth surface and high mobility have promising applications as efficient buffer layers for building high performance

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Table 1
Measured carriers concentration and mobility of ZTO thin films synthesized from precrsor solution with various ratios of $Zn(CH_3COO)$: $SnCl_2$.

Buffer layer	Weight ratios (Zn/Sn cations)	Mobility ($cm^2.V^{-1}.S^{-1}$)	Carrier concentration ($/cm^3$)
TiO_2	–	~10^{-4} ref [4]	–
ZnO	1.0:0.0	~10^{-2} ref [32]	–
ZTO	1:0.30	0.60	3.38×10^{11}
ZTO	1:0.70	8.35	1.14×10^{13}
ZTO	1:0.85	16.5	2.27×10^{14}
ZTO	1:1.20	8.44	2.71×10^{15}

inverted structure PSCs. However, the investigations of solution processable ZTO thin films as buffer layers for inverted structure PSCs have been scarce [23].

In this paper, we report a precursor solution synthesizing technique to fabricate highly conductive ZTO buffer layer with smooth surface and high transmittance at the short wavelength. The ZTO thin films were optimized by tuning mixing ratios of Zn:Sn cation in solution and electron mobility of 16.5 $cm^2.V^{-1}.S^{-1}$ was achieved as the Zn:Sn cation ratio was fixed at 1:0.85. As a demonstration, ZTO buffer layer have been applied in the inverted structure polymer solar cells (PSCs), leading to a device efficiency as high as 4.18%, which is almost 30% higher than those of reference devices with ZnO and TiO_2. The detailed physical origins on enhancement of the PCE have been studied by using a set of analytical techniques including Hall effects measurements, X-ray photoemission spectroscopy (XPS), steady-state photoluminescence (PL) spectroscopy, and light intensity-dependent current density-voltage measurement. This work indicates that ZTO thin film is a versatile buffer layer in solar cells with much improved performance through improvement in several parameters including an increase in transmittance at the short wavelength, a reduction in device series resistance, and a reduction in defect-assisted recombination at the transparent cathode interface.

2. Experimental

2.1. Material and precursor solution preparation

ZnO precursor solution was obtained from following steps: 0.1 mol Zinc acetate dihydrate [Zn(CH3COO)·$2H_2O$] (>99.0%, Sigma) was first dissolved in anhydrous ethanol [CH2CH3OH] (99.5%, Sigma) and rigorously stirred for 3 h at 80 °C and then 0.1 M ethanilamine (>99.0%, Sigma) was added to the solution as sol stabilizer [24]. Subsequently, The mixing solution was rigorously stirred on a hotplate at 60 °C for 24 h. Similarly, 0.15 M titanium diisopropoxidebis (acetylacetonate) (75 wt% in isopropanol, TCI) dissolved into 1-butanol (99.8%, TCI) and stirred over 3 h to yield TiO_2 precursor solution [25].

ZTO precursor solution was also prepared [21] by dissolving tin chloride (>98%, Sigma) and zinc acetate dihydrate in 2-methoxyethanol (>99.8%, Sigma), and molar ratio of zinc acetate and tin chloride was from 1:0.3 to 1:2, and then the mixed solution was stirred at 60 °C for 2 h and after that 12 μl ethanolamine was added as the stabilizing agent [21]. And followed the solution was stirred at 60 °C for 48 h. The P3HT:$PC_{61}BM$ (donor:acceptor) with total concentration of 18 mg/ml and weight ratio of 1:0.8 was dissolved in 1,2-dichlorobenzene (DCB, Sigma), and which was rigorously stirred overnight at 40 °C before spin-casting thin films [26].

2.2. Characterization of thin films

The films were spin-coated on the different substrates such as FTO, silicon wafer and quartz glass to characterize morphologies,

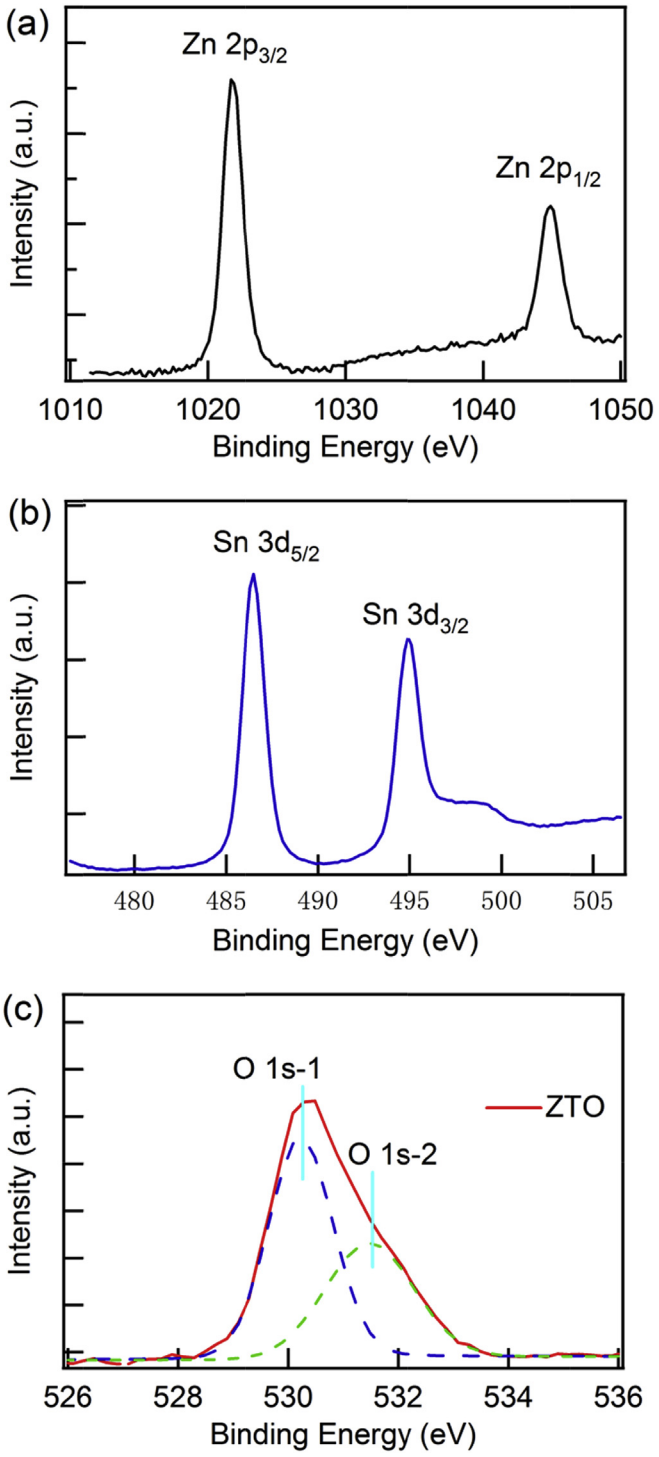

Fig. 1. XPS spectrum of ZTO buffer layer, Zn 2p peaks (a) and (b) Sn 3d peaks, and (c) XPS spectra of oxygen 1s peaks from surface of ZTO.