Available online at www.sciencedirect.com

ScienceDirect

Solar Energy 106 (2014) 95–101

SOLAR ENERGY

www.elsevier.com/locate/solener

Nanocrystalline Ga-doped ZnO thin films for inverted polymer solar cells

M. Thambidurai [a,*], Jun Young Kim [a], Jiyun Song [a], Youngjun Ko [a], N. Muthukumarasamy [b], Dhayalan Velauthapillai [c], Changhee Lee [a,*]

[a] Department of Electrical and Computer Engineering, Global Frontier Center for Multiscale Energy Systems, Seoul National University, Seoul 151-744, Republic of Korea

[b] Department of Physics, Coimbatore Institute of Technology, Coimbatore, India

[c] Department of Engineering, University College of Bergen, Bergen, Norway

Available online 26 December 2013

Communicated by: Associate Editor Smagul Zh. Karazhanov

Abstract

Nanocrystalline ZnO and Ga-doped ZnO thin films have been prepared by sol–gel spin coating technique. X-ray diffraction results indicated that the grain size of Ga-doped ZnO is smaller than that of ZnO. The EDAX analysis confirmed that Zn, O and Ga elements are present in the samples. HRTEM image shows the formation of ZnO and Ga-doped ZnO nanocrystalline thin films with an average grain size of 22.5 and 12.5 nm. Inverted polymer solar cell containing Ga-doped ZnO as an electron transport layer with device structure ITO/Ga-doped ZnO/poly(3-hexylthiophene) (P3HT):[6,6]-phenyl C_{71}-butyric acid methyl ester ($PC_{71}BM$)/MoO_3/Al has been fabricated. The power conversion efficiency of inverted polymer solar cell with Ga-doped ZnO is 3.25%, which is higher than that of ZnO (1.96%).

Keywords: Inverted polymer solar cells; Doping; P3HT:$PC_{71}BM$

1. Introduction

ZnO is an important n-type semiconductor with a wide-band gap of 3.4 eV at room temperature. It has attracted considerable attention because of its large exciton binding energy of 60 meV. ZnO thin films have been extensively investigated because of their important technological applications in areas like solar cells (Thambidurai et al., 2011, 2012, 2013) organic light emitting diodes (Lua et al., 2012) and gas sensors (Hassan et al., 2013). Impurity doped zinc oxide is also considered as a possible alternative to ITO due to its unique electrical and optical properties (De Sio et al., 2012). The group-III atoms such as Al, In and Ga have been used as n-type dopants in ZnO because they can replace Zn in the ZnO crystal (Aprilia et al., 2013; Luna-Arredondo et al., 2005; Gabás et al., 2011). Al-doped ZnO and Ga-doped ZnO films have been widely researched. Jun-ichi Nomoto et al. have reported that the resistivity stability of Al–ZnO thin films was lower than that of Ga-doped ZnO films (Nomoto et al., 2010). Especially, Ga-doped ZnO thin films are more attractive than Al-doped ZnO thin films, because Ga-doped ZnO thin films are more resistant to oxidation and exhibit small lattice mismatch upon doping as compared with Al-doped ZnO films. Among the metal dopants, Ga seems to be the best for ZnO due to fact that the atomic radius of Ga^{3+} is similar to that of Zn^{2+} and also owing to the lower reactivity of Ga^{3+} towards oxygen (Assuncao et al., 2003).

In addition, Ga-doped ZnO has some merits due to its stability, lower material cost, and high transparency. The

* Corresponding authors. Tel.: +82 2 880 9093; fax: +82 2 877 6668.
E-mail addresses: phy_thambi@rediffmail.com (M. Thambidurai), chlee7@snu.ac.kr (C. Lee).

0038-092X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.solener.2013.12.009

optical and electrical properties of ZnO thin films can be improved by doping gallium into the ZnO structure, which can generate excess free electrons in the conduction band (Shin et al., 2011). Prasada Rao and Santhosh Kumar, 2010 have prepared Ga-doped ZnO thin films and have investigated the effects of Ga-doping on the crystallinity, microstructure and the optical properties of ZnO thin films. Moreover, recent studies have reported the use of ZnO as an air stable anode in organic light emitting diode (OLED), providing additional evidence to show Ga-doped ZnO as a promising transparent conducting oxide for organic device applications (Ko et al., 2012; Fortunato et al., 2008). Ga-doped ZnO film has been prepared by different workers using various techniques such as DC reactive magnetron sputtering (Ma et al., 2008), molecular-beam epitaxy (Mandalapu et al., 2007), pulsed laser deposition (Park et al., 2006) and sol–gel (Tsay et al., 2010) method.

In most of the organic photovoltaics devices (ITO/poly(3,4-ethylene dioxythiophene):(polystyrene sulfonic acid) (PEDOT:PSS)/P3HT:$PC_{71}BM$/Ca), the front hole-collecting electrode is a high work function transparent conducting oxide and the back electron-collecting electrode is a low work function metal such as Ba or Ca. In such a device, diffusion of oxygen into the active layer (P3HT:$PC_{71}BM$) through pinholes and gain boundaries in Ba or Ca cathode causes the degradation of the active layer (P3HT:$PC_{71}BM$), leading to device instability in air (Hames et al., 2010; Wong et al., 2012; Seemann et al., 2011). In order to overcome these problems of conventional organic devices, solar cells with inverted structures have been developed in recent years because of their potential for superior device stability and manufacturing compatibility. To enhance the electron transport properties in the ZnO films, Ga was used in this work as a doped impurity. The efficiency of solar cell has been improved by using Ga-doped ZnO interfacial layers. In the present work, sol–gel method has been used to synthesize Ga-doped ZnO nanocrystalline thin films. Inverted polymer solar cell containing Ga-doped ZnO as an electron transport layer with device structure ITO/Ga-doped ZnO/poly(3-hexylthiophene) (P3HT):[6,6]-phenyl C_{71}-butyric acid methyl ester ($PC_{71}BM$)/MoO_3/Al has been fabricated and its characteristics have been studied.

2. Experimental

Ga-doped ZnO nanocrystalline thin films have been prepared using sol–gel spin coating method. Zinc acetate dihydrate ($(CH_3COO)_2$ Zn·$2H_2O$, 0.548 g) (0.25 M) and gallium (III) nitrate hydrate (Ga $(NO_3)_3$·xH_2O, 0.127 g) (0.05 M) were dissolved in a mixture of ethanol (10 ml) and ethanolamine ($H_2NCH_2CH_2OH$, 0.15 ml) (0.25 M) at room temperature. The resultant solution was stirred for 2 h to yield a homogeneous, clear and transparent solution using magnetic stirrer. The spin coating method was used to prepare thin films of Ga-doped ZnO onto ITO substrates using the prepared sol. The films were observed to have good adhesion to the substrate. Ga-doped ZnO thin films of thickness 30 nm were formed after post annealing at 450 °C for 2 h. The Ga-doped ZnO coated substrates were transferred into a nitrogen-filled glove box for polymer coating. An organic active layer was spin coated on the top of the Ga-doped ZnO thin films using the solution of P3HT and $PC_{71}BM$ blend with a weight ratio of 1:0.8 in chlorobenzene. After the organic layer was slowly dried in air, a layer of MoO_3 (10 nm)/Al (100 nm) as electrode was thermally evaporated on top of the active layer through a shadow mask under a pressure of $\sim 10^{-6}$ Torr. The effective area of the device was measured to be 0.196 cm^2. Inverted organic solar cell devices with structure ITO/Ga-doped ZnO/P3HT:$PC_{71}BM$/MoO_3/Al were fabricated and the schematic diagram of the fabricated cell is shown in Fig. 1.

The X-ray diffraction studies have been carried out using X-ray diffractometer (New D8 Advance), surface morphology and energy dispersive X-ray analysis (EDAX) of the samples has been studied using Zeiss Supra 55VP field emission scanning electron microscope (SEM), high resolution transmission electron microscope (HRTEM) images of the prepared ZnO and Ga-doped ZnO have been recorded using a JEM-3010 Electron Microscope. The optical properties have been studied using the absorbance spectra recorded using Beckman DU-70 spectrophotometer. Electrical resistivity measurements have been carried out using the current–voltage (I–V) measurement. The mobility was measured by bottom-gate top-contact thin film transistor (TFT) method with semiconductor parameter analyzer (Agilent 4155C). Current density–voltage (J–V) characteristics of the devices have been measured with a Keithley 237 source measurement unit using a 100 mW/cm^2 AM 1.5G solar simulator (Newport, 91160A). Light intensity was calibrated using a standard silicon solar cell as reference. The incident photon to current conversion efficiency (IPCE) spectra of the devices have been recorded using a lock-in amplifier (Model 7265, Signal Recovery) and monochromatic light from a xenon lamp through the monochromator (SpectroPro-150, Acton Research Corporation).

3. Results and discussion

The X-ray diffraction patterns of the ZnO and Ga-doped ZnO films are shown in Fig. 2. The diffraction peaks at 2θ (°) 31.77°, 34.40°, 36.26°, 47.51°, 56.55° 62.79° and 67.89° are indexed as (100), (002), (101), (102), (110), (103) and (112) planes of ZnO. The lattice constants have been found to be $a = 3.248$ Å and $c = 5.207$ Å and are in agreement with the standard data of JCPDS (card no. 36-1451). It is observed that the diffraction peaks of the Ga-doped ZnO show a small shift towards higher 2θ values when compared to that of ZnO. This shift may be due to the occupation of Ga ions at the Zn sites. The lattice constants of Ga-doped ZnO films are $a = 3.245$ Å and $c = 5.200$ Å, which are smaller than those of ZnO. The diffraction pattern reveals that both