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Optical and electrical properties of transparent conducting gallium-doped ZnO electrodes prepared by atomic layer deposition for application in organic solar cells

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ABSTRACT

Transparent and conducting gallium-doped ZnO electrodes were fabricated by means of atomic layer deposition. The electrode showed the lowest resistivity of 7.19×10^{-4} Ω cm at a 5% cyclic layer deposition ratio of Trimethyl-gallium and Diethyl-zinc chemicals. The electrodes showed minimum resistivity when deposited at a temperature of 250 °C. The electrode also showed optical transmittance of about 82%–89% with film thicknesses between 100 nm and 300 nm. An organic solar cell made with a 300-nm-thick gallium-doped ZnO electrode exhibited 2.5% power conversion efficiency, and an efficiency equivalent to that of cells made with conventional indium tin oxide electrodes.

1. Introduction

As the world energy demand continues to grow and the cost of natural resources increases, solutions for cheaper and cleaner energy resources are required. Photovoltaic cells have become more and more attractive as a clean, renewable energy source. Silicon has been considered as a premier candidate. However, the biggest obstacle regarding crystalline silicon-based solar cells is high manufacturing cost. Organic solar cells (OSCs) offer great technological potential as a renewable, alternative source of electrical energy [1–3].

For developing low-cost OSCs, the use of indium-free transparent conducting oxide (TCO) electrodes and TCO deposition techniques has become an important issue. Even though most OSCs have been deposited on indium tin oxide (ITO) electrodes, the use of this material increases the fabrication cost of OSCs due to the high cost and limited availability of indium. The increase in demand for large-area flat panel displays and thin film transistors has resulted in an increase in the cost of indium [4,5].

Recently, In_2O_3 [6], CdO [7], and ZnO have been studied as replacements for ITO electrodes. Most of the studies on ZnO-based films have involved Al-doped ZnO (AZO), but Al presents a very high reactivity with oxygen during growth processing. However, Ga-doped ZnO (GZO) electrodes are relatively stable compared to AZO electrodes, because Ga dopants are less reactive and more resistive to oxidation compared to Al dopants [8].

Many techniques have been introduced for the growth of Ga-doped ZnO thin films, such as sputtering [9], pulse laser deposition[10] and chemical vapor deposition [11]. Even though AZO and GZO films grown by batch-type DC/RF magnetron sputtering have been suggested for potential use in fabricating low-cost electrodes for OSCs, their low power conversion efficiencies still remain as drawbacks [12]. In addition, the conventional DC/RF magnetron sputtering process with a planar-type cathode is not acceptable for low-cost OSCs, because such cathodes have a low target usage of 20–30%, which increases the fabrication cost of the anode layer [13].

The atomic layer deposition (ALD) technique has been proposed as a promising growth method to deposit conductive ZnO-based thin films on large-area substrates at relatively low temperatures. It is possible to deposit one atomic monolayer in one cycle by chemisorption and physisorption (desorption of precursors) reactions, and to obtain highly uniform and reproducible growth. In addition, TCO thin films grown by ALD show a very flat surface and are dense. The exact dopant concentration can also be controlled in the ALD process. However, until now, the ALD of Ga-doped ZnO thin films has rarely been reported.

In this study, we compare the electrical and optical properties of OSCs based on ITO and GZO electrodes. We have also characterized the thin film properties of indium-free GZO electrodes prepared by an atomic layer deposition process prior to the application of OSC devices.

2. Experimental details

The precursors used to deposit Ga-doped ZnO thin films were Trimethyl-Gallium (TMG, $Ga(CH_3)_3$) for Ga, and Diethyl-zinc (DEZ,

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$Zn(C_2H_5)_2$) for ZnO. H_2O was used as a reactant gas. During deposition, the pulse times of DEZ and TMG were maintained at 0.1 s, and the N_2 pulse time was maintained at 5 s. An experiment with doped ZnO electrode layers was conducted in Lucida D-100 equipment, manufactured by the NCD Corporation. Devices with ITO electrodes were also fabricated as reference cells. The ITO electrode has a resistivity of 10 ± 2 Ω sq, 90% transmission at 550 nm, and a thickness of 185 ± 20 nm.

The OSCs fabricated in this study comprise a photoactive layer consisting of a P3HT(poly(3-hexylthiophene)):PCBM-C61([6,6]-phenyl C61-butyric acid methyl ester, 99%) and is based on the bulk heterojunction structure. The P3HT, an electron donor, was obtained from Rieke Metals (absorption wavelength: 443–568 nm), and the PCBM, an electron acceptor, was obtained from NANO-C (absorption wavelength: 284–341 nm). The photoactive materials, P3HT, and PCBM-C61, were prepared by dissolving them in O-Dichlorobenzene (1.2 wt.%) and Mono-chlorobenzene (1.2 wt.%), respectively, and then stirred for 12 h in order to ensure complete dissolution. The P3HT and PCBM solutions were then mixed at ratios of 1:0.7 by weight.

The prepared ITO and GZO substrates were cleaned and patterned using a contact aligner and etched with acid ($HCl:HNO_3:H_2O$). The cleaned ITO and GZO substrates were then treated by a UV ozone surface treatment for 15 min.

Polyethylenedioxythiopene:poly-styrenesulfonate (PEDOT:PSS) was deposited as a hole transport layer onto the ITO or GZO substrate using a spin coating method, and baked at 90 °C for 1 h to dry the solvents. The thickness of the active layers was fixed at around 100 nm to minimize other physical effects. Pristine LiF (0.5 nm) and Al (150 nm) metal electrodes were subsequently deposited on the active layer using a metal evaporator (SUNICELL PLUS 200) under the high vacuum conditions of 10^{-5} Pa. All of the solution stirring and spin coating processes were conducted under ambient conditions.

All of the light absorption layers had the same dimensions of 2×4 mm^2. The thicknesses of each active layer were measured using a spectroscopic ellipsometer (VB-400), and the optical absorption spectrums were investigated using UV–vis spectroscopy (UV 1601PC UV–visible Photometer). The power conversion efficiencies and the fill factor were calculated from the current density–voltage (J–V) characteristics under simulated solar light irradiation of 100 mW/cm^2 in ambient conditions (using an ORIEL solar simulator with a 150-W Xe lamp and a KEITHLY SMU 2400). Before the devices were measured, the light source was calibrated using a reference cell (ORIEL Solar reference cell).

3. Results and discussion

Ga-doped ZnO thin films were prepared with various amounts of Ga in the film. The amount of Ga doped was controlled by the unique cyclic deposition feature of ALD process. The total thicknesses of Ga-doped ZnO thin films were acquired from the following equation:

$$(\mathrm{Ga-doped\ ZnO\ film})_{\mathrm{thickness}} = [(\mathrm{ZnO\ \ cycle}) \times n + (\mathrm{Ga_2O_3\ \ cycle}) \times m] \times N$$

where m was fixed to 1, and n and N were variables. Therefore, the relative amount of Ga-doping could be expressed by the cyclic deposition ratio Ga/(Ga + Zn). If we increase the number of deposition cycles of Zn, the amount of Ga in the film becomes relatively low. The amount of doped Ga was expressed as a percentage value of the total number of deposition cycles. The prepared Ga-doped ZnO thin films were characterized with three essential parameters: the resistivity, carrier mobility, and carrier concentration, in accordance with the Ga/(Ga + Zn) deposition cycles at the process temperature of 250 °C. Fig. 1 shows a clear dependence of the resistivity on the amount of Ga in the film. In this experiment, films with cyclic deposition ratios (Ga/(Ga + Zn)) of 0% (ZnO only), 3%, 4%, 5%, and 8% were prepared and characterized. As the amount of Ga was increased to a cyclic deposition ratio of 5%, the resistivity of Ga-doped ZnO was

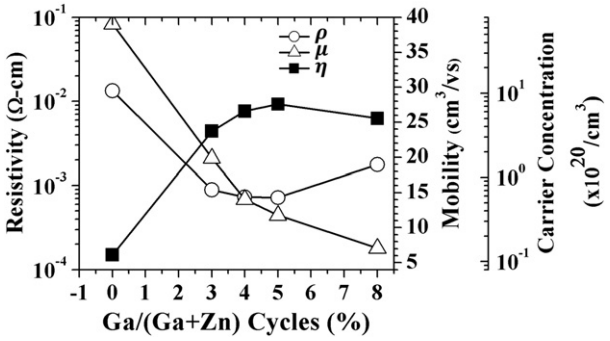

Fig. 1. Resistivity, Hall mobility, and carrier concentration as a function of cyclic layer deposition ratio of TMG and DEZ chemicals processed at 250 °C.

decreased to as low as 7.19×10^{-4} Ω cm. The resistivity was about two orders of magnitude lower than that of ZnO-only films. The films with a cyclic deposition ratio above 5% showed small increases in resistivity, which indicates that spontaneous Ga incorporation into Zn sites may not readily happen in these conditions. The resistivity change in Fig. 1 shows an inversely symmetrical pattern compared to the carrier concentration, in accordance with the cyclic deposition ratio. As Ga incorporation in the film was enhanced, the carrier concentration was increased up to 7.3×10^{20}/cm^3. The carrier concentration showed a maximum value at a cyclic deposition ratio of 5%, and saturated to 5.0×10^{20}/cm^3. The slight increase in resistivity at cyclic deposition ratios above 5% may have been caused by a gradual decrease in mobility as Ga incorporation progressed. Ga atoms in the ZnO film act as impurities. Therefore, the initial decrease in resistivity in the Ga-doped ZnO by the increased carrier concentration was compensated for by the mobility decrease when a larger amount of Ga was incorporated into the system.

Fig. 2 exhibits the process temperature dependency of the Ga-doped ZnO thin film characteristics of resistivity, mobility, and carrier concentration. The process temperatures were varied from 150 °C to 280 °C at a fixed cyclic deposition ratio of 5%. The resistivity reached a minimum value at the deposition temperature of 250 °C. At the same point, the carrier concentration of the thin film showed a maximum value of 7.4×10^{20}/cm^3, as well as a maximum carrier mobility. It has often been reported in the case of RF-sputtered films that the crystallographic film orientation is highly oriented, with their crystallographic c-axis perpendicular to the substrate at deposition temperature around 300 °C [8]. For the ALD-processed Ga-doped ZnO, the Ga incorporation into ZnO seemed to happen at an even lower temperature of 250 °C, due to its low-temperature deposition characteristics. However, at deposition temperature above 280 °C, the resistivity was again increased as the mobility and the carrier concentration were decreased, which indicates solubility limits for the Ga atoms in the ZnO system differs at each deposition temperature.

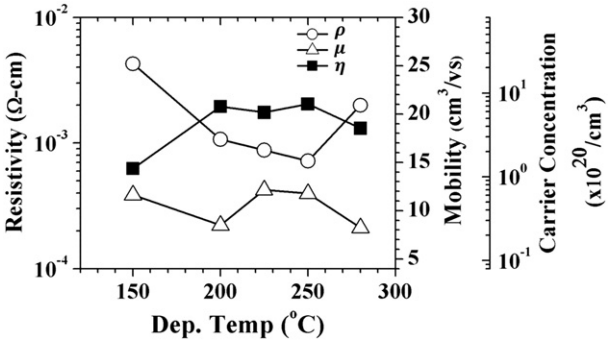

Fig. 2. Resistivity, Hall mobility, and carrier concentration as a function of deposition temperature.