Solar Energy Materials & Solar Cells 95 (2011) 657–663

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

Effects of deposition temperature on characteristics of Ga-doped ZnO film prepared by highly efficient cylindrical rotating magnetron sputtering for organic solar cells

Jun-Hyuk Park [a], Kyung-Jun Ahn [b], Seok-In Na [c], Han-Ki Kim [a,*]

[a] Department of Advanced Materials Engineering for Information and Electronics, Kyung Hee University, 1 Seocheon-dong, Yongin-si, Gyeonggi-do 446-701, South Korea
[b] SNTEK, 987-1,Gosaek-dong, Suwon-si, Gyeonggi-do 441-813, South Korea
[c] Korea Institute of Science and Technology (KIST), 864-9 Dunsan-ri, Bongdong-eup, Wanju-gun, Jeollabuk-do 565-902, South Korea

ARTICLE INFO

Article history:
Received 16 July 2010
Received in revised form
27 September 2010
Accepted 28 September 2010
Available online 23 October 2010

Keywords:
Ga-doped ZnO
Cylindrical rotating magnetron sputtering
Organic solar cells
Transparent conducting electrodes
Transmittance

ABSTRACT

We report the characteristics of Ga-doped zinc oxide (GZO) films prepared by a highly efficient cylindrical rotating magnetron sputtering (CRMS) system as a function of substrate temperature for use as a transparent conducting electrode in bulk hetero-junction organic solar cells (OSCs). Using a rotating cylindrical GZO target, low sheet resistance (~11.67 Ω/square) and highly transparent (90%) GZO films were deposited with high usage (~80%) of the cylindrical GZO target. High usage of the cylindrical GZO target in the CRMS system indicates that CRMS is a promising deposition technique to prepare cost-efficient GZO electrodes for low cost OSCs. Resistivity and optical transmittance of the CRMS-grown GZO film were mainly affected by substrate temperature because the grain size and activation of the Ga dopant were critically dependent on the substrate temperature. In addition, the performance of OSC fabricated on GZO electrode sputtered at 230 °C (11.67 Ω/square) is better than OSC fabricated on as-deposited GZO electrode (29.20 Ω/square). OSCs fabricated on the GZO electrode sputtered at 230 °C showed an open circuit voltage of 0.558 V, short circuit current of 8.987 m A/cm^2, fill factor of 0.628 and power conversion efficiency of 3.149%.

1. Introduction

Organic solar cells (OSCs) are a promising alternative to Si-based thin film solar cells due to their unique advantages such as simple structure, easy fabrication, possibility of scale-up production and low fabrication cost [1–3]. Due to simple bulk-heterojunction structure, large area OSCs can be fabricated by simple coating of an organic active layer and electrode layer (cathode and anode) using a roll-to-roll processing [4,5]. To reduce the fabrication cost of OSCs, the development of low cost and indium free transparent conducting oxide (TCO) electrodes and an efficient TCO deposition technique is imperative. Although most OSCs have been prepared on indium tin oxide (Sn-doped In_2O_3: ITO) electrodes, the use of ITO increases fabrication cost of OSCs due to the high cost and its limited availability of indium [6,7]. In particular, the rapid increase in demand for large area flat panel displays and touch panels has resulted in a steep rise in the cost of indium. Recently Krebs et al. [8] reported that the step costs for ITO coating, including process and materials cost, account in large part (~29%) for total OSCs module costs. Therefore, when considering the cost advantage of OSCs, high cost ITO electrode should be replaced by cost-efficient TCO electrodes and deposition technique. Although low cost indium free TCO electrodes, such as Al-doped ZnO (AZO) and Ga-doped ZnO (GZO) films grown by batch type DC/RF magnetron sputtering, have been suggested as potential low cost electrodes for OSCs, their low power conversion efficiencies still remain as drawbacks [9,10]. In addition, the conventional DC/RF magnetron sputtering process with a planar type cathode is not acceptable for low cost OSCs, because a planar type cathode has low target usage of 20–30%, which increases the fabrication cost of the anode layer. Recently, cylindrical rotating magnetron sputtering (CRMS) has attracted a great deal of attention as a cost efficient sputtering technique for photovoltaics, due to its high target usage greater than 80%, process stability and enhanced process efficiency [11–14]. In our previous work, we also reported that the CRMS-grown AZO electrode with high cathode target usage could be a promising cost-efficient anode material to substitute ITO electrode for OSCs [13]. However, despite the high AZO target usage in the CRMS technique, we were only able to obtain a resistivity of 1.2×10^{-3} Ω cm, which is higher than resistivity of conventional AZO electrode, due to a low quality of cylindrical AZO target. As an alternative to ITO electrodes, GZO film has also been investigated as a promising indium free anode materials due to its several advantages [15,16]. Due to the similarity between the radius of Ga^{3+} ion and Zn^{2+} ion, it resulted in only a small

* Corresponding author. Fax: +82 31 204 8114.
E-mail address: imdlhkkim@khu.ac.kr (H.-K. Kim).

0927-0248/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2010.09.036

lattice deformation even for high Ga concentration. In addition, GZO electrodes are more stable than AZO electrodes because Ga dopants are less reactive and more resistive to oxidation compared to Al dopants [17]. However, there are no reports on the characteristics of GZO film fabricated by the CRMS technique, which would be beneficial for the low-cost production of TCO for OSCs, even though the GZO electrode has better stability than AZO electrode.

In this work, we report the electrical, optical and structural properties of indium free GZO electrodes prepared by a specially designed CRMS system as a function of the substrate temperature as well as characteristics of CRMS technique for the cost-efficient TCO coating in OSCs. We were able to deposit a GZO electrode with much higher GZO target usage (~80%) than conventional DC sputtering by rotating cylindrical GZO target due to a homogeneous and continuous sputtering of rotating cylindrical target. It was found that the resistivity and optical transmittance of the CRMS-grown GZO electrode were mainly affected by substrate temperature because the grain size of the GZO and activation of Ga dopants were determined by substrate temperature. In addition, the power conversion efficiency of the neutral poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) based OSC fabricated on the GZO electrode grown at 230 °C is higher than that of OSC fabricated on the as-deposited GZO electrode due to lower sheet resistance.

2. Experimental details

400 nm-thick GZO films were sputtered on glass substrates by a specially designed CRMS system [13]. Fig. 1(a) shows a picture of the rotating cathode with a cylindrical GZO target with a length of 256 mm and diameter of 100 mm (3 wt% Ga_2O_3 doped ZnO) and the race track formed on the cylindrical GZO target during the CRMS process. In general, the race track formed on a planar type GZO cathode results in a groove, leading to the localized thinning and inhomogeneous sputtering of the GZO target. This could lead to degraded electrical and optical properties of the GZO film with increasing processing time. However, in the case of CRMS, the GZO target is homogeneously sputtered along the target length, because the cylindrical GZO target is continuously rotating. The homogenous sputtering of the cylindrical GZO target leads to the gradual thinning of the target and increases its material usage to as much as 80%. In addition, thermal load or localized temperature on the target is homogenously spread because the cooling time for the cylindrical rotating target is enough to reduce the localized temperature of the target during each rotation outside the plasma [12]. Therefore, it is possible to provide a high-density power on the cylindrical target without crack or melting of the target unlike planar type sputtering target. This indicates that the GZO film can be deposited at a higher sputter rate, resulting in a higher throughput. Using this highly efficient CRMS system, GZO electrode can be produced with high throughput and low fabrication cost due to its high target usage, sputter rate, process efficiency and improved process stability. Fig. 1(b) shows schematic diagram of the CRMS system for continuous sputtering of GZO films. At a constant direct current (DC) power of 2 kW, an Ar flow rate of 30 sccm, working pressure of 3 m Torr and rotating speed of 10 rpm, the GZO film were sputtered using various substrate temperatures (25, 100, 150 and 230 °C) in the CRMS system. The thickness of the GZO film was measured using a surface profiler (Dektak 150, Veeco). The electrical resistivity and optical transmittance of the CRMS-grown GZO films were measured by means of the Hall effect measurement and a UV/Vis spectrometer, respectively, as a function of the substrate temperature. The structural properties and grain size of the GZO films were investigated by X-ray diffraction (XRD) using Cu K_α radiation. XRD spectra were collected in θ–2θ scan (25°–55°) with a measurement step of 0.02°. The morphology of the CRMS-grown GZO electrodes was investigated by field emission scanning electron microscopy (FESEM) and atomic force microscope (AFM) as a function of the substrate temperature. Finally, bulk

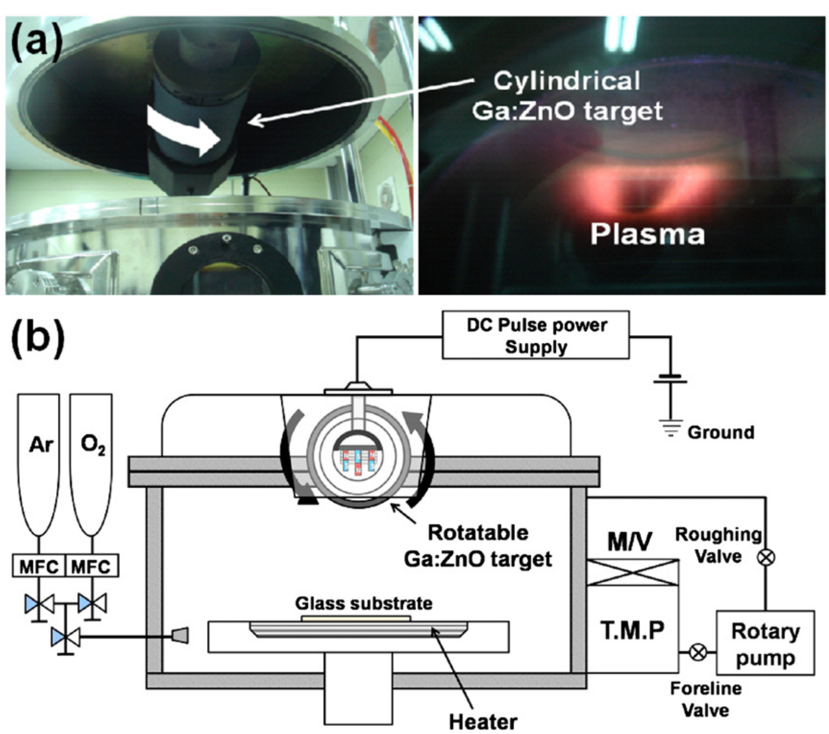

Fig. 1. (a) Picture of the highly efficient cylindrical rotation cathode and race track formed on the rotating GZO target. (b) Schematics of the cylindrical rotating sputtering for sputtering of the GZO electrodes.