Structural, electrical and optical properties of ZnO:Al films deposited on flexible organic substrates for solar cell applications

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Abstract

Aluminum doped ZnO thin films (ZnO:Al) were deposited on glass and poly carbonate (PC) substrate by r.f. magnetron sputtering. In addition, the electrical, optical properties of the films prepared at various sputtering powers were investigated. The XRD measurements revealed that all of the obtained films were polycrystalline with the hexagonal structure and had a preferred orientation with the c-axis perpendicular to the substrate. The ZnO:Al films were increasingly dark gray colored as the sputter power increased, resulting in the loss of transmittance. High quality films with the resistivity as low as 9.7×10⁻⁴ Ω-cm and transmittance over 90% have been obtained by suitably controlling the r.f. power.

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1. Introduction

Transparent conducting zinc oxide (ZnO) films have been extensively studied in recent years because they exhibit high optical transmission and electrical conduction and have a lower material cost [1]. Furthermore, ZnO films are more stable in hydrogen plasma environments than other transparent conducting oxide films such as tin-doped In₂O₃ (ITO) and tin oxide (SnO₂). These advantages are of considerable interest for practical applications such as transparent electrodes, window material in displays, solar cells, and various opto-electronic devices [2–4]. Recently, magnetron sputtered ZnO films have been used as a window and contact layer for flexible thin film solar cells with absorber materials such as amorphous silicon or Cu(In, Ga)Se₂ [5–7].

Comparing with undoped ZnO, Al-doped ZnO (ZnO:Al) films have lower resistivity and better stability. In most device applications, ZnO:Al films deposition was accomplished at high processing temperatures (500 °C). Fabrication of high-quality ZnO:Al at lower temperature would enable the production of devices and contacts on polymer substrates and on temperature-sensitive components. ZnO:Al films have been prepared by various deposition techniques, such as sputtering [1,8,9], pulsed laser deposition [10], chemical vapor deposition [11], spray pyrolysis [12], and metal–organic chemical vapor deposition (MOCVD) [13]. Among them, the most commonly used technique is r.f. magnetron sputtering, because it is possible to obtain good orientation and uniform films even at low substrate temperature [14]. The most important deposition parameters in this technique are r.f. power, deposition pressure, gas flux, and the distance between the target and the substrate, which should be well determined and controlled in order to obtain thin films with the desired properties.

In this study, highly conductive ZnO:Al films were deposited by r.f. magnetron sputtering at room temperature. The influence of sputtering power on the electrical, optical and structural properties was investigated.

2. Experimental

The ZnO:Al films were deposited on Corning 7059 glass and polycarbonate (PC) substrates in a conventional r.f. magnetron sputtering system. A sintered oxide ceramic disk of ZnO (diameter 3 in.) mixed with 2 wt.% Al₂O₃ was used as a target. The base pressure in the sputter chamber was below 6.6×10⁻⁴ Pa. The separation between target and substrate was about 6 cm.
After the chamber was evacuated to a base pressure below $6.6 \times 10^{-4}$ Pa, pre-sputtering of 20 min was carried out at an argon gas pressure of 1.0 Pa in order to clean the target surface. The sputtering power was varied from 50 to 200 W, and the argon gas pressure was controlled from 0.3 to 2.7 Pa. All the films were deposited at room temperature. In order to reveal the genuine effect of r.f. power excluding the film thickness effect, we have fixed the film thickness to about 200 nm.

The thicknesses of the films were obtained using an $\alpha$-Step 500 surface-profile measurement system. The crystal structure of the films was determined by X-ray diffraction (XRD) technique, using a Siemens D5000 system with Cu Kα radiation ($\lambda = 0.1540562$ nm). The surface morphology was observed by a Hitachi S4500 field-emission scanning electron microscope (FE-SEM). The Hall measurements were made with the Van der Pauw technique at room temperature. The optical transmittance measurements were performed with a Hitachi UV-3200 spectrophotometer. For transmittance measurement, the beam was made to enter the film through the glass substrate and a blank glass slide was kept in the path of the reference beam for compensation.

3. Results and discussions

ZnO:Al films prepared in this work were physically stable and had good adherence to the polymeric substrate. Fig. 1 shows the relation between the sputtering power and deposition rate of ZnO:Al films on glass substrate. A linear increase on growth rate was observed as sputtering power increase. This increase indicates the number of atoms sputtered from the target is proportional to the r.f. power. For higher sputtering power, the sputtered species get a higher energy that contributes to the film growth. These high energy particles have high surface mobility and therefore a higher growing process at the surface takes place.

Fig. 2 shows the XRD patterns for ZnO:Al films deposited on glass and PC substrate at several r.f powers (ranging from 50 to 125 W). ZnO:Al films on glass have a strong diffraction peak at $2\theta \sim 34.4^\circ$ and very weak peak at $2\theta \sim 72.5^\circ$, regardless of sputter pressure and substrate types. These peaks are associated with the (0 0 2) and (0 0 4) plane of hexagonal phase ZnO. The presence of a strong diffraction peak of (0 0 2) indicates that films have a (0 0 2) preferred orientation. Neither metallic zinc or aluminum characteristic peaks nor aluminum oxide peak was observed from the XRD patterns, which implies that aluminum atoms replace zinc in the hexagonal lattice or aluminum segregate to the noncrystalline region in grain boundary. With increasing the sputtering power the intensity of the (0 0 2) peak increases. This means that the crystallinity of the resulting films improves when the r.f. power is higher. It is noteworthy that the intensity of (002) diffraction peak decreases when the sputtering power exceeds 100 W. High r.f. power induces faster reaction rate and it damages the surface, resulting to a poor crystalline quality. Accordingly, the sputtering power must be sufficiently...
low to have an efficient nucleation and growth. For PC substrate, the XRD spectra are very similar to those of glass substrate. This means that the films deposited on PC have the same structure, and both of them are polycrystalline with a hexagonal structure and a preferred orientation with the c-axis perpendicular to the substrates. By comparing the results with the same film deposited onto glass substrates, however, the intensity of the diffraction peaks for PC substrate is not so intense, which might be due to the surface roughness exhibited by the polymer substrate.

The SEM photographs of ZnO:Al thin films with various sputtering powers are shown in Fig. 3. The morphology of ZnO:Al grains is found to be continuous and dense. The surface grain size tends to be bigger when r.f. power increases, regardless of substrate types. High r.f. power allows that the deposited particles may grow with bigger grains, improving thus the surface state density. Besides, the particles have higher kinetic energy, being obtained more compact films. However, Kim et al. [15] reported that the grain size of the ZnO film is not much dependent on the r.f. power in the range of 80–250 W, even though there is a slight increase in the grain size at higher r.f. powers. They concluded that the temperature elevation at higher r.f. power helps to obtain the slightly larger grain structure. The crystallite sizes of the films deposited on PC substrates are larger than that on glass under the same deposition conditions, as seen in Fig. 3 (b) and (d).

Fig. 4 illustrates the resistivity, carrier concentration, and Hall mobility of ZnO:Al deposited on glass and PC substrate as a function of sputtering power. It can be seen that as the sputtering power increases from 25 to 125 W, the resistivity of the films on glass decreased significantly from $5.8 \times 10^{-2}$ to $9.7 \times 10^{-4}$ Ω·cm. This behavior could be explained by the effect of the sputtering power on the mobility and carrier concentration (Fig. 4(b)). When the sputtering power increases, the carrier concentration increases slightly while the mobility increases significantly. These variations originate from improved crystallinity and enhanced substitutional doping as the sputtering power increases. The former effect increases the crystallite size and, subsequently, reduces charge carriers scattering due to grain boundaries, thus increasing the mobility, while the latter effect increases the carrier concentration. Both of them reduce the resistivity of the films. The maximum value of the Hall mobility was obtained for the r.f. power of 100 W and then a slight decrease was observed. This could be attributed to the increase in the scattering from ionized impurities. The low value of the mobility obtained at 25 W is related to the fact that the
films were deposited at room temperature. At low temperature, the sputtered ions from the target cannot obtain enough heat energy to adjust the bond direction and length in order to obtain an optimum bonding to the adjacent atoms (including substrate atoms and film atoms). This leads to difficulties, not only due to a nucleation on the substrate for the sputtered ions and ion clusters, but also to a growth of large grains from the nucleated molecules. The former effect leads to a bad adherence to the substrate for obtained films and the latter causes a low mobility and a high resistivity due to a strong contribution of grain boundaries in charge carriers scattering. For PC substrates, meanwhile, the resistivity increases with the sputtering power, as seen in Fig. 4. At high r.f. power, enhanced high energetic ion bombardment leads to damage of organic substrate, and the quality of ZnO thin film will become poorer. Accordingly, the sputtering power must be sufficiently low to have an efficient nucleation and growth for organic substrate.

Fig. 5 shows the optical transmittance of ZnO:Al films deposited at various sputter powers. The optical transmittance spectra of ZnO:Al films represent a strong dependence on the sputter power. It is seen that the average transmittance of these samples in the range 400–800 nm was over 90%, regardless of sputtering voltage and substrate types. Fortunato et al. [9] reported that ZnO:Al films deposited on PET substrate showed the average transmittance of 85% in the visible part of the spectrum. As the r.f. power increases, the average transmittance of the films reduces slightly. It would be noted that the film deposited at 125 W becomes nearly opaque to near-infrared region. However, the dependence of substrate types on transmittance is not as sensitive as the resistivity’s.

4. Conclusions

ZnO:Al films were deposited on glass and PC substrate by r.f. magnetron sputtering at room temperature. The obtained films were polycrystalline with the hexagonal structure and had a preferred orientation with the c-axis perpendicular to the substrates, regardless substrate types. The improvement in the electrical properties is obtained by the increase of the r.f. power essentially due to a substantial increase in the carrier concentration and Hall mobility. This behavior could be related to the increase in the sputtering rate and also to the enhancement in the crystallinity of the films. The optical transmittance of the
films was over 90% in the visible region, regardless of r.f. power and substrate types. The transmittance in the near-infrared region reduced with the r.f. power. Although the quality of the ZnO:Al films deposited on organic substrates is somewhat worse than that for glass substrate, ZnO:Al films on PC might be suitable for solar cells.

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References