EFFECTS OF GAS PRESSURE AND DISCHARGE POWER ON ELECTRICAL AND OPTICAL PROPERTIES OF ZNO:AL THIN FILM DEPOSITED ON POLYMER SUBSTRATE

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(Received: 5 September 2008 / Accepted: 21 November 2008)

In this paper aluminium-doped zinc oxide(ZnO:Al) conducting layer was deposited on polyethylene terephthalate(PET) substrate by r. f. magnetron sputtering method. The effects of gas pressure and r. f. sputtering power on the structural and electrical properties of ZnO:Al thin film were investigated experimentally. The results show that the resistivity of the film was strongly influenced by the gas pressure and r. f. sputtering power. The electrical properties were improved with increase in sputtering power and gas pressure up to 180W and 5mTorr. However excessive supply of sputtering power limits the growth of crystalline grains due to too high deposition rate and may cause a degradation of the preferred orientation, giving high electrical resistivity. The lowest resistivity and optical transmittance were ~$1.1\times10^{-3}\Omega$-cm and ~85%, respectively and were obtained under the experimental conditions of 180W of sputtering power and 5mTorr of gas pressure.

Keywords: magnetron sputtering, PET substrate, ZnO:Al film, gas pressure, sputtering power, electrical resistivity

1. Introduction

Recently, deep interest has been paid in using plastic materials for replacing glass substrates with increasing applications for large scale flexible flat panel display(FPD) and flexible film-typed dye sensitized solar cell(DSCs). Indium tin oxide(ITO) for FPD and F-doped SnO_2(FTO) for DSCs are widely used as transparent conducting electrodes. However, recently, zinc oxide(ZnO) thin film has emerged as one of the most promising transparent conducting films due to its high electrical conductivity and high transmittance as well as high chemical and mechanical stability, high resistance for deoxidation, and its abundance in nature[1,2].

On using plastic materials as a substrate there are some technical limitations which we must overcome, such as lower working temperature and rougher surfaces as compared to glass substrate. That is, in fabricating the ZnO:Al film by dc or r. f. sputtering methods, the substrate heating is considered to be one of the essential processes to obtain the high electrical and optical properties. If, without substrate heating, the film shows an incomplete reaction and rough films are obtained[3,4]. But with increasing temperature the film becomes nonstoichiometric structure, which produces a decrease in the resistivity due to the oxygen vacancies and interstitial zinc atoms which act as donors. However, in the case of polymer substrate, we cannot use the substrate heating due to the poor thermal resistance of polymer substrate. Moreover, the deposition rate of ZnO:Al film deposited on the polymeric substrate cannot be comparable with that deposited on glass substrate[5]. But the systematic studies on the ZnO:Al transparent conducting film deposited on polymeric substrate cannot be performed.

In this paper in order to investigate the possible application of ZnO:Al film as a transparent conducting oxide (TCO) electrode for DSCs, aluminium doped zinc oxide films were deposited on polyethylene terephthalate (PET) substrate by r. f. magnetron sputtering method. The influences of gas pressure and r. f. discharge power on the structural, electrical and optical properties were studied and discussed. Especially the effect of position of PET substrate was studied to improve the electric and optical properties of ZnO:Al film and to increase also the deposition rate.

2. Experimentals

Fig. 1 shows electrodes arrangement of the sputtering system. In order to improve the deposition rate and to reduce the sputtering time, the substrate was placed 50mm of minimum distance apart from the target edge as shown in Fig. 1. This electrodes arrangement can protect the PET substrate from direct contact of thermal energy of plasma body, and can improve the deposition rate. ZnO:Al films were prepared on PET(20×10×0.25mm) by conventional r. f. magnetron sputtering. The sputtering

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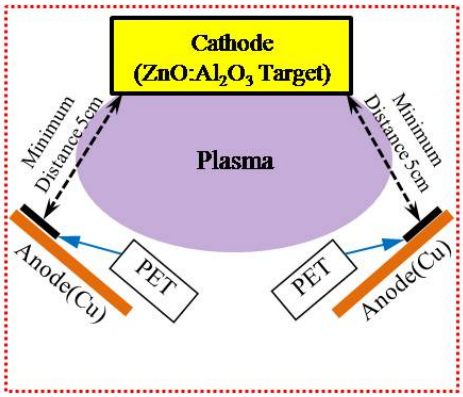

Fig. 1. Electrodes arrangement of the sputtering system.

target was a mixture of ZnO (99.99 %) and Al_2O_3(99.99%), pressed on a copper saucer with a diameter of 3inch. The minimum distance between target and PET substrate was 50mm. The PET substrate was cleaned prior to each deposition in an ultrasonic cleaner, and dried by nitrogen flow. Prior to sputtering, the sputtering chamber was evacuated to a base pressure of 10^{-6}Torr. To maintain the same target condition for each deposition, the target was also sputtered in pure argon(99.999%) environment prior to each deposition with the shutter covering the substrate. In order to study the effects of Ar gas pressure and r. f. discharge power, the Ar gas pressure and discharge power were varied from 1mTorr~10mTorr and from 160W to 240W, respectively.

Thickness and sputter yield of the films were measured using a DEKTAK 300 alpha-step or direct measurements from SEM photographs. Fig. 2 shows typical example of SEM photographs at the gas pressure of 5mTorr and r.f. power of 180W.

Crystalline structures of the films were characterized by a Rigaku D/max 2100H X-ray diffractometer (XRD). Sheet resistance was measured by a CMT-ST1000 four point probe. Surface morphology of the film was studied using atomic force microscopy (AFM). Spectral transmittance of the film was also measured using a Hitachi U 3000UV-spectrophotometer in the visible wavelength range of 400~800 nm.

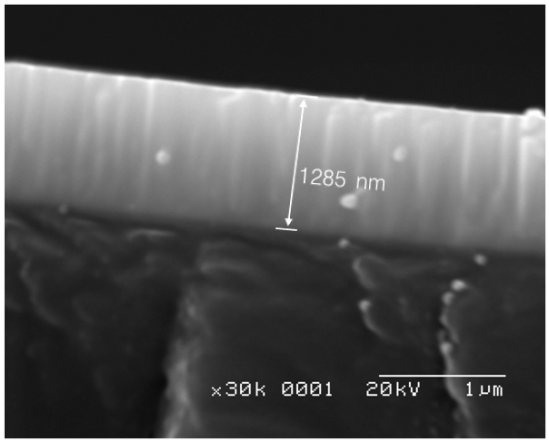

Fig. 2. SEM photograph of ZnO:Al film at gas pressure of 5mTorr and r.f. power of 180W.

3. Results and Discussions

3. 1 Structural Properties

As far as the effect of gas pressure on XRD patterns of ZnO:Al film is concerned, only the (002) diffraction peaks were observed regardless of gas pressures, and the peak intensity of the film deposited at 5mTorr was the strongest. So, all the experiments are carried out at this gas pressure condition. In this paper, to optimize the deposition conditions for sputtering power, the influence of r. f. power on the X-ray diffraction patterns of ZnO:Al films are mainly studied. The results are shown in Fig. 3. In the Fig. 3, all the patterns are those at different r. f. powers and at gas pressure of 5mTorr. As well known in Fig. 3, only the (002) diffraction peaks are observed regardless of r. f. powers, and they are located at 2θ=33.4°, which are very close to that of the standard ZnO crystal(34.45°). No additional peaks were observed as the r. f. power increases up to 240W. Moreover in the Fig. 3, it is clear that the peak intensity increases with increasing sputtering power up to 180W, and then the intensity of the (002) peak decreases from 200W of sputtering power. This can be attributed to the fact that the energy or numbers of electrons and ions in the glow discharge plasma will increase with an increment in sputtering power. From our previous study by the dc magnetron sputtering discharge current increased almost linearly with increasing dc sputtering power[6]. This means that as the sputtering power increases the positive ions can gain higher energy in the plasma and collide with target. That is, the energy of sputtered atom obtained as a result of interchange with that of positive ion in the plasma will increases with increasing sputtering power. Thus the energy of sputtered atom arriving at substrate increases due to the increase in sputtering power. This increasing energy of sputtered atom can be utilized to promote the sputtered atoms to grow in a particular order, resulting in the strong (002) preferred orientation. That is, the increase in sputtering power induces an improvement in the crystallinity of the film. In the present study this critical sputtering power was 180W. However, the excessive

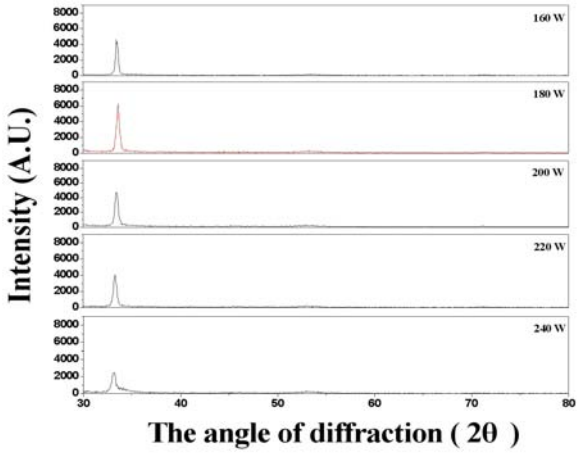

Fig. 3. XRD patterns of the ZnO:Al films deposited at gas pressure of 5mTorr and various r.f. powers.

Table 1. FWHM and Grain size of ZnO:Al film at gas pressure of 5mTorr and various r. f. powers.

Sample	160W	180W	200W	220W	240W
FWHM (Degree)	0.3725	0.3266	0.4002	0.3860	0.4154
Grain size (nm)	22.32	25.45	20.77	21.53	20.01

supply of sputtering power over than 180W may cause a degradation of the preferred orientation, resulting in the high defect density and small grain size.

In order to confirm the effect of sputtering power on the morphology of the film, the AFM morphologies of the films deposited at different sputtering powers were investigated. The results are shown in Fig. 4. In the Fig. 4, as the r. f. power increases up to the 180W, the crystallinity of the film is improved and crystalline size becomes larger. However, higher r. f. power over than 180W is expected to produce compressive stress in the films due to the different thermal expansion coefficient between the film and PET substrate, and then the film shows loose structures and small grain sizes. AFM morphology was influenced also by gas pressures. The optimized condition for crystalline growth was at 5mTorr of gas pressure, and this result agrees with the XRD result.

The grain sizes of films were calculated using Scherrer's formular. The results are summarized in Table 1. The FWHM of the (002) peak decreased with increasing r. f. power up to 180W, and thereafter increased abruptly with increasing sputtering power, which means the peak becomes more intense and sharper up to 180W of r. f. power. These results are consistent in that the crystallinity of the film deposited at 180W is improved and the crystalline size becomes larger. The largest grain size was also found to be 9.4nm for the film at 180W, and was increased by ~25% compared to the film at 240W.

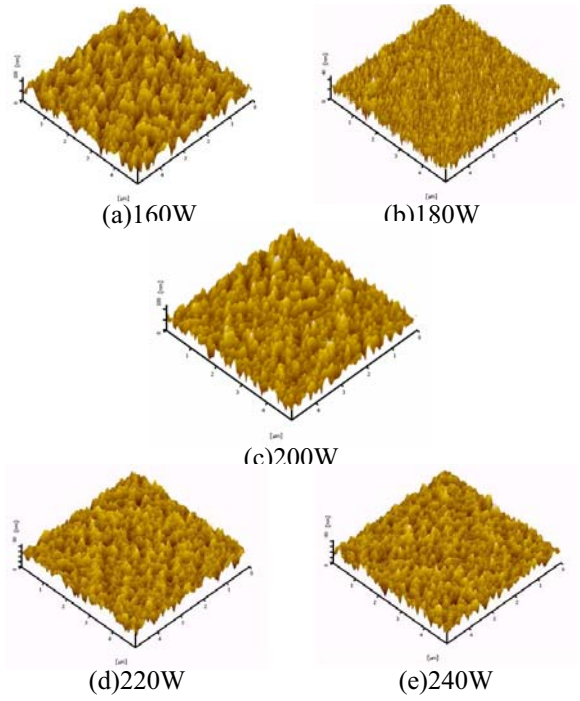

Fig. 4. The AFM of ZnO:Al thin films at working pressure of 5mTorr and various r.f. powers.

3.2 Electrical Properties

Fig. 5 represents the electrical resistivity and deposition rate as functions of Ar gas pressure. The electrical resistivity of ZnO:Al film decreases with an increase in gas pressure up to 5mTorr, and increases thereafter. The lowest resistivity was ~$1.1\times10^{-3}\Omega$-cm at gas pressure of 5mTorr. The dependence of electrical resistivity of the film on gas pressure can be understood by considering the fact that the energy of sputtered atoms increases with decreasing gas pressure from 10mTorr to 5mTorr due to an increase in mean free path. The sputtered atom has low possibility to collide with Ar gas molecules as gas pressure decreases. However, the plasma cannot be sustained stable and uniformly at lower gas pressure than 5mTorr.

The electrical resistivity and deposition rate of the ZnO:Al films with r. f. sputtering powers are shown in Fig.6. As the sputtering power increases from 160W to 200W, the deposition rate increases almost linearly from 225 Å/min to 429 Å/min, and decreases thereafter. The increase in deposition rate with increasing sputtering power is attributed to an increase in energy of sputtered atom arriving at the substrate due to the increment of sputtering power. It is also clearly seen that the electrical resistivity of the film decreases from ~$1.7\times10^{-3}\Omega$-cm to ~$1.1\times10^{-3}\Omega$-cm as the sputtering power increases from 160W to 180W, and thereafter it increases abruptly. In the case of aluminum doped zinc oxide, the variation in grain sizes at different sputtering powers is considered as one of the causes which affect the conduction mechanism [7]. In our experiment, as mentioned earlier in Fig. 3, the XRD peaks became more intense and sharper with increasing sputtering power up to 180W. Besides, the results on the FWHM and AFM morphologies in Table 1 and Fig. 4 also

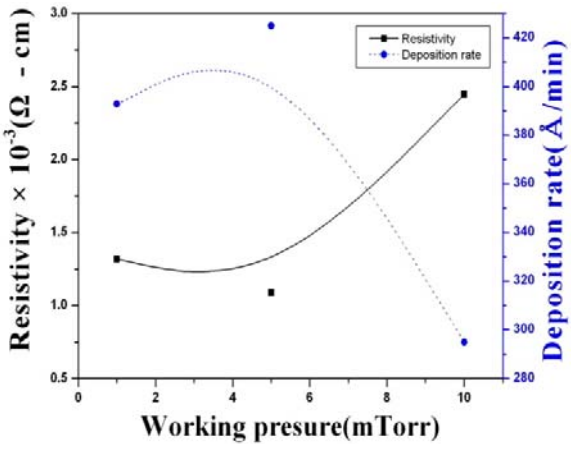

Fig. 5. Electrical resistivity and deposition rate properties as a function of Ar gas pressure.

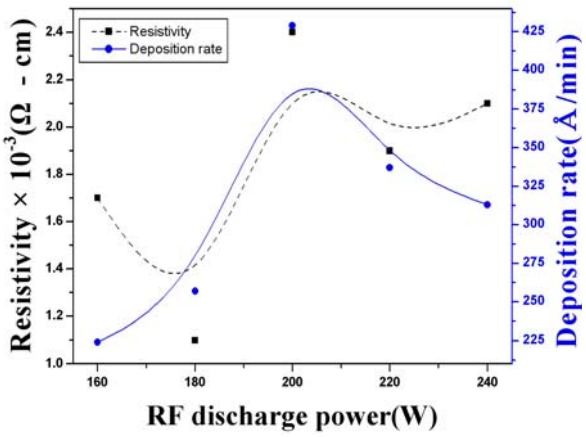

Fig. 6. Electrical resistivity and deposition rate properties as a function of sputtering power.

show that the film structure and crystalline grain size are improved with increasing sputtering power up to 180W. These results reveal that the grain size increases and grain-boundary decreases with increasing sputtering power. Therefore, the improvement in electrical resistivity with increasing sputtering power up to 180W is ascribed to decrease in the number of scattering centre for carriers, giving a low electrical resistivity. However, the excessive supply of sputtering power limits the growth of crystalline grains due to too high deposition rate (180W: 260 Å/min, 200W: 425 Å/min.) as shown in Fig. 6. The effect of self-bias voltage on the electrical properties and deposition rate cannot be recognized in this study. From the analysis of voltage waveform the self-bias voltage was around in the range of 10~16V under the present experimental conditions of r. f. power up to 160~240W.

In this experiment the PET substrate was placed as shown in Fig. 1, to improve the deposition rate and to reduce the sputtering time. The average deposition rate was around 317 Å/min., and this value is comparable to that of glass substrate and is higher than that of PET substrate of other researcher, respectively[8,9]. The film thickness was in the ranges of 1260~1320nm in the 160~240W of r. f. power ranges, and the average film thickness was 1315nm. The ZnO:Al film of the 8.2Ω/□ was also obtained at 180W of r. f. power and 5mTorr of Ar gas pressure. These results are comparable with those of ITO, and are considered enough for the film-typed DSCs as a transparent conducting layer.

3.3 Optical Properties

The band edge of the film was estimated using the relation where absorption coefficient is a parabolic function of the incident energy and the optical band gap, $\alpha=A(h\nu-Eg)^{1/2}/h\nu$, where A is a constant, $h\nu$ is the photon energy, Eg is optical band gap. Using this relationship, the band gap edge of ZnO:Al film is evaluated by plotting $(\alpha \cdot h\nu)^2$ as a function of the energy of the incident radiation, and extrapolating the linear part of the curve to intercept the energy axis. Table 2 shows transmittance of the film deposited at various r. f. sputtering powers at 5mTorr of gas pressure. From the figure, the transmittance is found to increase from ~84% to ~85% as discharge power increases from 160W to 180W, and decreases to 79% with increasing r. f. power. The optical band gap evaluated from the transmittance data is extended from 3.24 to 3.35eV at various discharge power conditions.

Table 2. Transmittance of the film deposited at various r. f. sputtering powers.

Sample	160W	180W	200W	220W	240W
Transmittance (%T)	84.2	85.2	84.2	81.8	79.0
Band gap (eV)	3.35	3.26	3.23	3.24	3.32

4. Conclusions

In this paper ZnO:Al conducting layer was deposited on polyethylene terephthalate(PET) substrate by r. f. magnetron sputtering method. The effects of gas pressure and r. f. sputtering power on the electrical and structural properties of ZnO:Al thin film were investigated experimentally. The results show that the film thickness was in the ranges of 1260~1320nm in the 160~240W of r. f. power ranges, and the deposition rate was recorded in the range of around 22~43nm/min. The electrical resistivity of the film was strongly influenced by the gas pressure and r. f. sputtering power. The electrical properties were improved with increase in sputtering power and gas pressure up to 180W and 5mTorr. However excessive supply of sputtering power limits the growth of crystalline grains, giving due to too high deposition rate and may cause a degradation of the preferred orientation, giving high electrical resistivity. The lowest resistivity and optical transmittance were ~1.1×10^{-3}Ω-cm and ~85%, respectively and were obtained under the experimental conditions of 180W of sputtering power and 5mTorr of gas pressure.

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