Properties of Al doped zinc oxide films prepared by electron beam-PVD

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Al doped ZnO (AZO) films were prepared on quartz substrates by the co-evaporation of ZnO and Al₂O₃ by EB-PVD. Structural, optical and electrical properties of AZO films were investigated, focusing on the effect of the electron beam power applied to the Al₂O₃ ingot. X-ray diffraction measurement showed that the AZO films were highly c-axis oriented. Transmittance of all the AZO films was over 85% in the visible range. The highest reflectance in the near IR range was obtained at the EB power on Al₂O₃ of 7.5 kW, 73% at 2500 nm. The lowest resistivity of 2.34 × 10⁻⁴ Ω cm was obtained for the film deposited with the EB power on Al₂O₃ of 7.5 kW.

Key-words : EB-PVD, Transparent conductive oxides, Al-doped ZnO, Near-IR reflective

1. Introduction

Transparent conductive oxides (TCOs) are transparent in visible range and shows the high reflectance in the near-infrared (IR) region. Therefore, TCOs are good candidate for application as the coatings for IR-reflectors on super-insulating window, which realize a considerable energy-saving effect in air conditioning of houses and buildings. Among TCOs, ZnO is a promising material, due to its low cost, abundant and nontoxicity. It is well known that group III elements such as Al, In and Ga act as donors in ZnO.¹ Among them, the Al doped ZnO (AZO) films have been widely studied for its excellent electrical and optical properties. AZO films can be prepared by many deposition methods, including electron beam physical vapor deposition (EB-PVD),²⁴ magnetron sputtering,⁵⁻⁷ and pulsed laser deposition (PLD).⁸⁻⁹ Among the deposition methods, EB-PVD has advantages such as high speed, large area deposition, and economical, efficient usage and easy preparation of evaporant. At present, to our knowledge, there are few reports on the IR-reflective property of Al doped ZnO (AZO) films prepared by EB-PVD.¹³

In EB-PVD process, source material is evaporated from an ingot molten by local irradiation of high power electron beam. In the case where the vapor pressures of two constituents in the source material ingot differ too much, a homogeneous composition of the films cannot be achieved by single source evaporation of a mixture of the materials. Therefore, it is difficult to deposit AZO films from single source material, because AZO is composed of two oxides exhibiting different evaporation characteristics: ZnO is subliming material and Al₂O₃ is melting material. Therefore, evaporation from two sources can overcome the problem in the case of EB-PVD of AZO films.

In this work, structural, optical and electrical properties of AZO films prepared by co-evaporation EB-PVD were investigated, addressing the effect of the EB power applied on the Al₂O₃ evaporation source.

2. Experimental

The AZO films were prepared on quartz glass substrates (30 mm × 30 mm × 1 mm) by electron beam physical vapor deposition. The source material ingots used in this study were a 40 mm diameter × 20 mm thickness of ZnO (Hakusui Tech.), and a 63 mm diameter × 50 mm thickness of Al₂O₃ (Kyoto Thin-Film Materials Institute). As shown in Fig. 1, the source materials were co-evaporated by a 100 kW EB gun, using electron beam jumping technique.¹⁰ In co-deposition using the electron beam jumping technique, the electron beam is scanned over one target (ZnO) for a certain amount of time and then moved to the next target (Al₂O₃). Electron beam power applied to the ceramic targets, EBₓ (x = ZnO, Al₂O₃) was controlled by dividing the dwell time of electron beam among the evaporation sources with the ratio of EBₓ to EB_total (=EB_zno + EB_alo). The EB_zno was fixed at 5.1 kW. EB alo was varied from 5.1 to 8.7 kW. The substrate was placed directly above the center of two evaporation source and parallel to the ingot surface at a distance of 600 mm. The vacuum chamber was evacuated to a background pressure below 5 × 10⁻³ Pa. The deposition was carried out in the pressure range of 0.2 to 0.3 Pa. Quartz glass substrates were heated to 400°C which was found to be the optimum growth temperature in this study. The substrates were rotated at 30 rpm during deposition. Deposition time was fixed at 450 s. Crystal structure...
and texture were analyzed by X-ray diffraction (XRD, Rigaku 20000V/PC) with a Cu Kα radiation (λ = 0.1541 nm). Micro-
structures of AZO films were investigated by field emission scanning electron microscope (FE-SEM, Hitachi S-8000). The thick-
ness of the AZO films was estimated from cross-sectional SEM images. The electrical resistivity ρ, Hall mobility μ and carrier concentration N were measured using a four-point probe and Hall effect apparatus (TOYO Corporation ResiTest 8300) at room temperature. Optical transmittance and reflectance were measured in the range of 190–2500 nm by UV–VIS–NIR spectro-photo-
rometer (Perkin Elmer Lambda 950).

3. Results and discussion

Figure 2 shows the XRD patterns of AZO films deposited by different $E_{Al:O}$. The peaks at about 34.5 and 72.8° correspond to the diffraction from (002) and (004) planes, respectively. Compared with the standard diffraction pattern, the AZO films exhibit highly (002) preferential orientation. The 2θ values of (002) diffraction peaks are about 34.5°, slightly higher than that of the standard ZnO crystal (34.422°) (JCPDS Card No. 36-1451). With increasing $E_{Al:O}$, the positions of measured diffraction peaks were not changed significantly, but the intensity of the (002) and (004) peaks increased, that means the crystal-

linity of AZO film improves with the increase in $E_{Al:O}$.

The surface SEM images of AZO films are shown in Figs. 3(a)–
3(d). The AZO films show relatively rough surface morphology and a poly-
crystalline structure with grain size of around 100 nm. The grain size of AZO film deposited with $E_{Al:O}$ of 8.7 kW was around 200 nm, larger than that of other AZO films. The thickness of the AZO films was about 300–320 nm. The thickness of the AZO film deposited at $E_{Al:O}$ of 8.7 kW was about 410 nm. The grain size and thickness of the AZO film deposited at $E_{Al:O}$ of 8.7 kW is different from that of other AZO films. Deposition rate in this study was about 0.67 to 0.91 nm/s. These values are comparable to that of sputtering,7) and faster than that of the reported AZO films prepared by EB-PVD3) and PLD.9),10) Using our EB-PVD equipment, higher deposition rate could be achieved by decreasing the distance between substrate–evaporation source and/or increasing EB power. However, we managed the deposi-
tion rate in this range, in order to achieve the uniformity of film thickness on large area substrates. AZO films deposited at a distance of 600 mm, thickness drop at the edge of the substrate holder (approximately 135 mm from the center) was within only 10%. In addition, positions in the substrate holder insignifi-
cantly affected optical and electrical properties of AZO films deposited at a distance of 600 mm.

Figure 4 shows resistivity, carrier concentration and Hall mobility of AZO films as a function of $E_{Al:O}$. The carrier concentration initially increased up to $E_{Al:O}$ of 7.5 kW with increasing $E_{Al:O}$, and the highest carrier concentration of $9.31 \times 10^{20} \text{cm}^{-3}$ was obtained at the $E_{Al:O}$ of 7.5 kW. After that, the carrier concentration decreased. The resistivity decreased with increasing $E_{Al:O}$ up to 7.5 kW, after that the resistivity decreased. The lowest resistivity of $2.34 \times 10^{-4} \Omega \cdot \text{cm}$ was obtained. The Hall mobility initially increases as the $E_{Al:O}$ increased up to 7.5 kW, after which the Hall mobility decreased. The highest mobility of $28.7 \text{cm}^2/\text{Vs}$ is obtained at the $E_{Al:O}$ of 7.5 kW. The mobility in polycrystalline ZnO films is generally limited by scattering from grain boundaries and ionized impu-
rities. The grain size of the AZO films of 100–200 nm is rela-
tively large, hence, the Hall mobility of AZO films is consid-
erably affected by scattering from ionized impurities. The decrease of the resistivity is caused by the increase of the carrier density. The resistivity is inversely proportional to the product of the carrier concentration and the Hall mobility. Therefore, the change in resistivity with $E_{Al:O}$ is ascribed to the change in carrier concentration and Hall mobility. These values are comparable to that of the reported AZO films prepared by EB-
PVD,3) sputtering,7) and PLD.9),10) Optical properties were shown in Figs. 5(a) and 5(b). All the AZO films show high transmittance above 85% in visible range, regardless of the $E_{Al:O}$. [Fig. 5(a)]. The drop of transmittance in near-IR region mainly comes from the increase of reflectance which is due to the plasma resonance of electron gas in the conduction band. Therefore, the transmittance drop is related to
the carrier concentration. The lowest transmittance in the near-IR range is obtained at the $E_{\text{BAlO}_3}$ of 8.7 kW, which is below 30% at 1500 nm. Near-IR-reflectance was observed in all the AZO films. Near-IR-reflectance initially increases with increasing the $E_{\text{BAlO}_3}$ up to 7.5 kW, after which IR-reflectance slightly decreases. Highest IR-reflectance was obtained at the $E_{\text{BAlO}_3}$ of 7.5 kW, up to 73% at 2500 nm [Fig. 5(b)], which is much higher than that of reported films by EB-PVD$^3$ and comparable with that of reported films by sputtering$^7$ and PLD.$^{8,9}$ The near-IR reflectance behavior of AZO film can be explained by the classical Drude theory. The IR reflection of transparent conductive films originates from the plasma resonance resulting from the high electron density. The cut-off wavelength where IR reflection changes to visible transmission is called the plasma wavelength, and this shifts towards higher wavelength with decrease in carrier density. In order to obtain a lower plasma wavelength and improve both the reflectance in the near-IR range and the transmittance in the visible range of AZO films, the electron density of the layers must be as high as $2 \times 10^{21} \text{ cm}^{-3}$$^{11}$ and the higher Hall mobility is indispensable. In this work, the carrier density ($7.08-9.31 \times 10^{20} \text{ cm}^{-3}$) and the Hall mobility (23.8–28.7 cm$^2$/Vs) seemed to be enough to obtain high IR-reflectance.

The Al content in AZO films measured by Energy Dispersive X-ray Spectrometry was increased from 1.68 at% (the $E_{\text{BAlO}_3}$ of 5.1 kW) to 3.12 at% (the $E_{\text{BAlO}_3}$ of 8.7 kW) almost linearly. However, carrier concentration first increases and then decreases, reaching a maximum value of $9.31 \times 10^{20} \text{ cm}^{-3}$ at the $E_{\text{BAlO}_3}$ of 7.5 kW, as mentioned above. The above behavior of carrier concentration suggests that not all the Al atoms in the film contribute to carrier generation. In AZO films, the carrier concentration is mainly attributed to the conduction of shallow donors which are formed by substitutional incorporation of Al on a regular Zn lattice site. With increasing the $E_{\text{BAlO}_3}$, the vapor pressure of Al$_2$O$_3$ increases, resulting in increase of the flux of Al atoms to the film surface. However, not all Al atoms incoming to the film thought to substitute Zn lattice sites adequately. Al atoms, which do not substitute Zn lattice sites, are possible to result in the intragrain segregation and/or grain boundary segregation forming Al–Al and Al–O clusters such as Al$_2$O$_3$ suboxides. These Al atoms seem to be electrically inactive, acting as donor killers, thereby inducing low carrier concentration. Other possible reason for decrease in the carrier concentration is increase in chemisorbed oxygen trapped at the boundaries, which acts as electron trap and results in the decrease of carrier concentration. Role of oxygen chemisorbed at the grain boundaries was mentioned in the literatures.$^{41,9,12}$ As the $E_{\text{BAlO}_3}$ rose, more oxygen may be also induced into the films coming from the Al$_2$O$_3$ evaporation source, due to increase of the flux of O atoms caused by raising the vapor pressure of Al$_2$O$_3$. Such excess oxygen trapped at the boundaries might annihilate shallow donor levels which originated from oxygen vacancies and/or excess zinc.$^{12}$ A further study is necessary to reveal that.

### 4. Conclusions

Highly transparent, conductive and near-infrared reflective Al doped ZnO (AZO) films were prepared on quartz glass substrates by the co-evaporation of ZnO and Al$_2$O$_3$ by EB-PVD. The effect of EB power applied to the Al$_2$O$_3$ source ($E_{\text{BAlO}_3}$) on the structure, optical and electrical properties of AZO film was investigated. X-ray diffraction measurement showed that the AZO films were highly c-axis oriented and exhibited high crystallinity. Transmittance of all the AZO films was over 85% in the visible range. The highest reflectance in the near IR range was obtained at $E_{\text{BAlO}_3}$ of 7.5 kW. The lowest resistivity of $2.34 \times 10^{-4} \Omega \text{m}$ was obtained for the film deposited with the $E_{\text{BAlO}_3}$ of 7.5 kW. Hall mobility of 28.7 cm$^2$/V$s$ was obtained for the film deposited with the $E_{\text{BAlO}_3}$ of 7.5 kW. These results show that AZO films deposited by EB-PVD are promising for near-IR reflecting mirrors and heat reflectors.

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### References