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Effects of Electron Irradiation on the Properties of ZnO/Au/ZnO Films Deposited on Poly-Imide Substrates

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Abstract: Transparent and conductive ZnO 50 nm/Au 8 nm/ZnO 50 nm tri-layer films were deposited on poly-imide films by radio frequency (RF) and direct current (DC) magnetron sputtering at room temperature, and then the effect of electron irradiation on the crystallization, electrical resistivity and optical properties of the films was considered with X-ray diffraction, UV-visible spectrometer, Atomic force microscope and Hall measurement system. All the films were deposited at a fixed sputtering power, Ar gas flow rate, and distance between target and substrate, while the post-deposition electron irradiation energy was varied from 300 to 900 eV. The electron irradiated films exhibited a flatter surface than the as deposited films that were not electron irradiated, and the XRD patterns also revealed that the electron irradiated films had larger grain sizes than that of as deposited films. The films electron irradiated at 900 eV also showed a higher visible transmittance of 79.8% and a lower sheet resistance of 56.0 Ω/□. Post-deposition films electron irradiated at 900 eV showed a higher figure of merit of 1.86×10^{-3} Ω^{-1} than that of the as deposited film of 1.29×10^{-3} Ω^{-1}. The optical band gap was also enhanced by electron irradiation. The films electron irradiated at 900 eV showed a higher optical band gap of 4.07 eV.

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Keywords: ZnO, Au, XRD, AFM, Figure of merit

1. INTRODUCTION

Growing industrial demand for transparent and conductive metal oxide (TCO) films for various display device applications has promoted the development of new TCO materials and innovative TCO/metal/TCO tri-layered films [1] that can provide enhanced opto-electrical performance to conventional small amount tin (Sn) doped In_2O_3 (ITO) thin films. Particularly for solar cell applications, many research works have focused on molybdenum (Mo) doped zinc oxide (ZnO) [2] and gold (Au) doped ZnO [3] thin films because of their high visible transmittance and low electrical resistivity, which can be comparable to conventional gallium (Ga) doped ZnO (GZO) films [4]. Also, it is well known that some metal doped ZnO films need high substrate treatment temperatures of up to 300°C to ensure the necessary electrical resistivity (2.7×10^{-3} Ωcm) and high visible transmittance (84.5%) [5]. However, that high substrate temperature is a major obstacle to the application of metal doped ZnO films to broad flexible displays. Such high substrate temperatures are not suitable for plastic substrates, due to their low melting temperature and weak thermal shock properties.

Recently, Y. Park reported the opto-electrical properties of ZnO thin films with an Au interlayer, and suggested the effective thickness of the Au interlayer was 8 nm [6]. In this study, 8 nm thick Au interlayered ZnO (ZAZ) films were deposited on poly-imide (PI) films with a radio frequency (13.56 MHz) and direct current magnetron sputtering process. Then, the film surface was irradiated with intense electron beam to enhance the opto-electrical performance of the films. The effect of electron irradiation on the film's property was investigated by observing the crystallization, surface roughness, optical band gap and figure of merit, respectively.

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2. EXPERIMENTAL PROCEDURES

Tri-layered ZnO 50/Au 8/ZnO 50 nm films were deposited on transparent PI film (2×2 cm^2) at room temperature. Prior to deposition, the chamber was evacuated to 6.5×10^{-7} Torr and then high purity argon (Ar) gases were injected to an ideal deposition condition of 1×10^{-3} Torr. Table 1(a) and (b) shows the experimental deposition and electron beam irradiation [7] conditions of this study. After deposition, an electrical power of 250 W was biased on the RF (13.56 MHz) coil antenna of the electron irradiation source and the electron irradiation energy was varied from 300 to 900 eV. The film thickness was confirmed with a surface profilometer (Dektak 150, Veeco), and thin film crystallinity was analyzed using high resolution X-ray diffraction (HR-XRD) at the KBSI, Daegu Center.

In addition, the cross section image, chemical component, visible transmittance and sheet resistance were measured with a scanning electron microscope (SEM), an energy dispersive x-ray spectroscopy (EDS), a UV-Visible spectrometer and a four-point probe system. The bare PI substrates had a visible transmittance of 91%. The surface morphology and root mean square (RMS) roughness of the films were observed with an atomic force microscope (AFM).

To evaluate the influence of electron irradiation on the opto-electrical performance of the films, the figure of merits were compared. To investigate the flexibility of the ZAZ films electron irradiated at optimal incident energy, bending tests were also performed under various bending radius conditions. To compare the flexibility of the ZAZ film, 100 nm thick ITO films were deposited on PI films with the same ZnO sputtering conditions.

Table 1(a). Experimental deposition conditions of ZnO and Au thin film.

Base pressure (Torr)	6.5×10^{-7}
Deposition pressure (Torr)	1.0×10^{-3}
DC sputtering power density (W/cm²)	Au, 3.3
RF sputtering power density (W/cm²)	ZnO, 3.5
Ar gas flow rate (sccm)	10
Deposition rate (nm/min)	ZnO : 10, Au : 50
Film thickness (nm)	ZnO : 50, Au 8

Table 1(b). Post-deposition electron irradiation conditions.

Base pressure (Torr)	6.5×10^{-7}
Working pressure (Torr)	5.0×10^{-5}
Irradiation time (min)	10
RF Power (W)	250
Ar gas flow rate (sccm)	3
Irradiation energy (eV)	300, 600, 900

3. RESULTS AND DISCUSSION

Fig. 1(a) and (b) show a cross-section image of the ZAZ film, and the results of component analysis (SEM-EDS). The XRD patterns of the ZAZ films electron irradiated at different electron energy conditions are shown in Fig. 2. Recently, P. H. Xiang et al. investigated the crystallization mode of ITO films deposited on mica substrate over a substrate temperature range of 100-500°C [8]. They reported that the ITO film formed an amorphous phase at substrate temperatures below 200°C. However, all of the ZAZ films in Fig. 2 show diffraction peaks for ZnO (002) and Au (111) regardless of electron irradiation energy.

Fig. 3(a) and (b) show the full width at half maximum (FWHM) and average grain size measured by the Scherrer formula. While the as deposited films show a grain size of

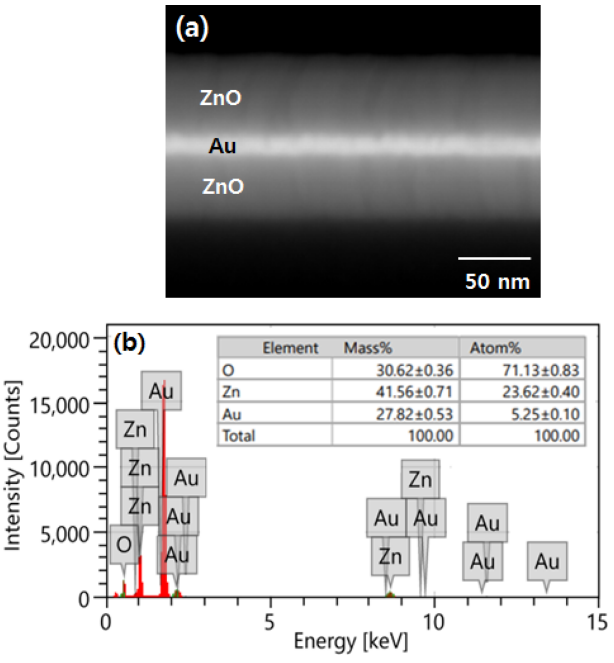

Fig. 1. The cross-section image of ZAZ film (a) and the result of component analysis (b).

11.53 nm (ZnO (002)), the films electron irradiated at 900 eV show a larger grain size of 14.32 nm, respectively.

Fig. 4 shows the visible transmittance of the ZAZ films. The as deposited films show a high visible transmittance of 79.0%. Although the as deposited and electron irradiated films did not show a big difference in visible transmittance, the films electron irradiated at 900 eV show a higher optical transmittance of 79.8%. It is well known that the optical transmittance of TCO film depends upon crystallization, because grain boundaries can scatter visible light and result in low visible transmittance [9]. From Fig. 1, the little enhancement in visible transmittance produced by electron irradiation is attributed to an increase in the grain of ZnO and Au in the films.

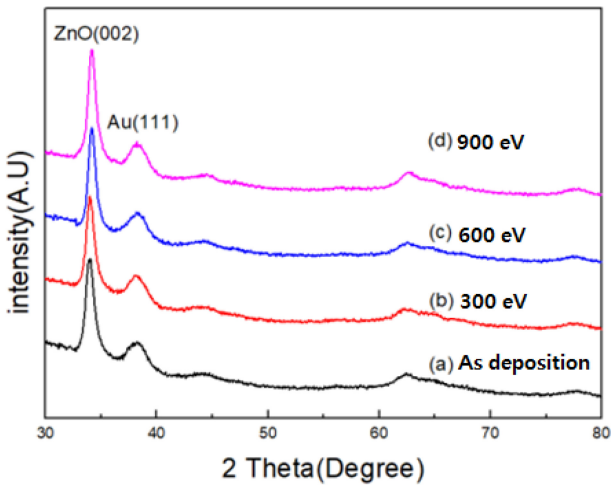

Fig. 2. XRD patterns of ZnO 50 /Au 8 /ZnO 50 nm films electron irradiated at different energies.

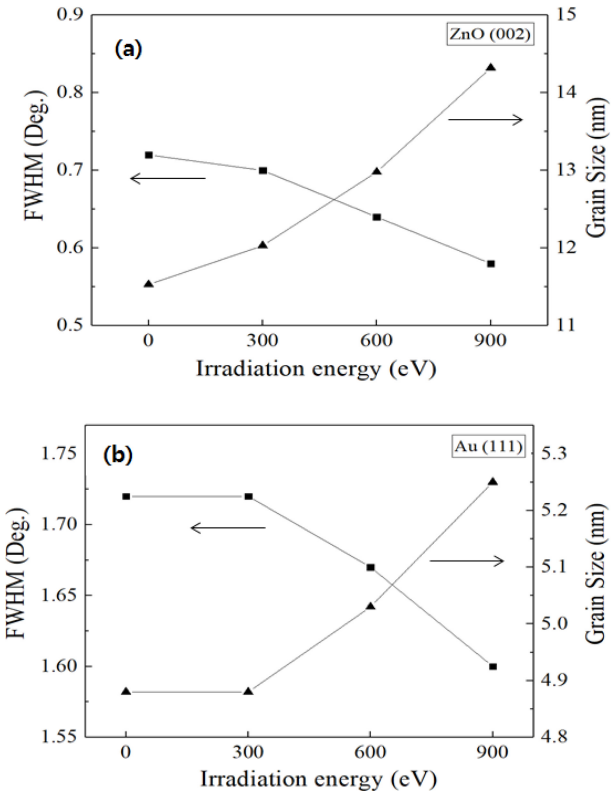

Fig. 3. Average grain size and full width at half maximum of the ZnO (002) (a) and Au (111) (b) as a function of electron irradiation energies.

Table 2 shows the figure of merit (FOM) as a function of electron irradiation energy. The FOM is a criterion for measuring the opto-electrical performance of transparent electrode applications [10]. The FOM is defined as

$$FOM = T^{10} / R_{sh} \quad (1)$$

where T is the visible transmittance and R_{sh} is the sheet resistance. With increasing electron irradiation energy (~900 eV), the FOM was enhanced to 1.86×10^{-3} Ω^{-1}.

Fig. 5 shows AFM images of the ZAZ films. The electron irradiated films exhibit a flatter surface than the as deposited

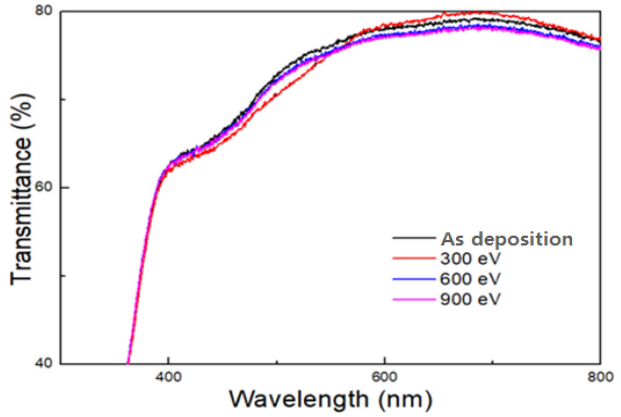

Fig. 4. The visible transmittance of ZAZ films electron irradiated at different energies.

Table 2. Effect of electron irradiation on the figure of merit of ZAZ films.

ZAZ film	Sheet resistance (Ω/□)	Visible Transmittance (%)	Figure of merit ($\times10^{-3}\Omega^{-1}$)
As deposition	73.3	79.0	1.29
300 eV	63.5	79.3	1.54
600 eV	59.3	79.5	1.69
900 eV	56.0	79.8	1.86

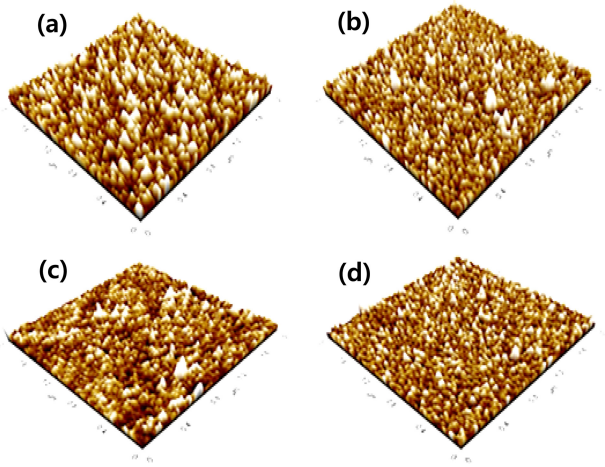

Fig. 5. Surface AFM images and RMS roughness of ZAZ films electron irradiated at different energies. (a) As deposition: 1.5 nm, (b) 300 eV: 1.4 nm, (c) 600 eV: 1.3 nm, (d) 900 eV: 1.1 nm.

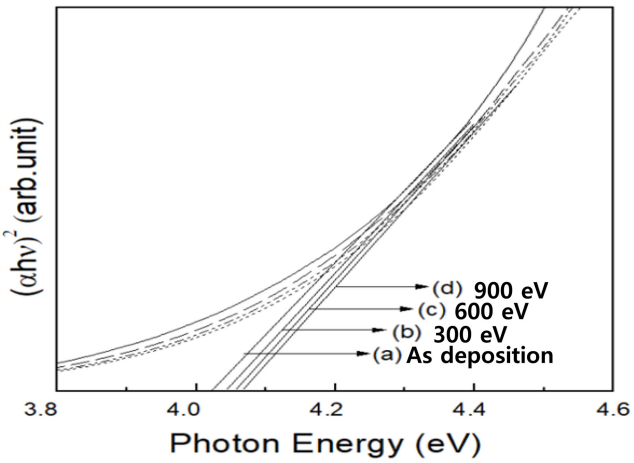

Fig. 6. Optical band gap energy of ZAZ films as a function of electron irradiation energy.

films that were not electron irradiated. Surface roughness is a critical factor for all opto-electronic applications of TCO films, because the rough surface allows more optical scattering than a flat surface, and electrical conductivity is also degraded by reduced carrier mobility due to the rough surface. In Fig. 3, the higher visible transmittance observed for the films electron irradiated at 900 eV is attributed to their having a flatter surface than the other films. This suggests that electron irradiation is a useful method for forming a flat surface on ZAZ films, resulting in higher visible transmittance.

Table 3 shows the dependence of electrical properties and optical band gap energy on the electron irradiation energy. The carrier density, mobility and optical band gap energy were enhanced by the increase in electron irradiation energy. The decrease in resistivity (6.1×10^{-4} Ωcm) with the increase in electron irradiation energy up to 900 eV is thought to be due to an enlarged grain size, as shown in Table 1, and the flat surface observed in AFM images.

Fig. 6 shows a plot of $(\alpha h\nu)^2$ of the ZAZ films as a function of the photon energy ($h\nu$). The optical band gap energy (Eg) is estimated by extrapolation of the linear part on the $h\nu$ axis. The absorption coefficient (α) is evaluated using Eq. (2) [11]:

$$\alpha = (1/t)\ \ln(1/T) \quad (2)$$

where t is the thickness and T is the visible transmittance. The Tauc formula in Eq. (3) shows the relationship between the absorption coefficient (α) and optical band gap (Eg) [12]:

$$(\alpha h\nu)^2 = A(h\nu - Eg) \quad (3)$$

where A is the absorption edge width parameter. From the observed electrical properties and optical band gap energy, it is supposed that the band gap movement is related to the carrier concentration. The band gap was enhanced, from 4.03 to 4.07 eV, as the carrier concentration increased from 2.7 $\times10^{21}$ (at deposition) to 3.0×10^{21} cm^{-3} (at 900 eV).

Fig. 7 shows the results of the bending test of the ZAZ films electron beam irradiated at 900 eV, and as deposited ITO films (sheet resistance: 250 Ω/□).While the ZAZ films

Table 3. Effect of electron irradiation on the electrical properties and optical band gap energy of ZAZ films.

ZAZ film	Carrier density ($\times10^{21}$ cm^{-3})	Carrier mobility (cm^2 $V^{-1}s^{-1}$)	Electrical resistivity ($\times10^{-4}$ Ωcm)	Optical band gap [eV]
As deposition	2.7	2.8	8.0	4.03
300 eV	2.8	3.1	7.0	4.05
600 eV	2.9	3.2	6.5	4.06
900 eV	3.0	3.4	6.1	4.07

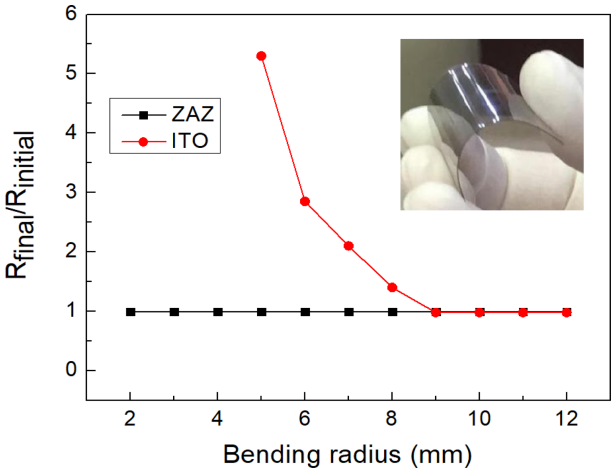

Fig. 7. Compared sheet resistance change of electron irradiated ZAZ and as deposited ITO films as a function of bending radius.

did not exhibit any increase in sheet resistance until the bending radius reached 2 mm, the sheet resistance of the ITO films increased starting at bending radius of 9 mm. Since the ZAZ films did not show any change in sheet resistance after 10,000 trials of the bending test at 2 mm bending radius, it is concluded that electron irradiated ZAZ films have better flexibility than conventional ITO films.

4. CONCLUSIONS

Thin Au interlayered ZnO films were deposited by DC and RF magnetron sputtering on PI substrates, and then the effects of post-deposition electron irradiation on the optical and electrical properties were investigated. The opto-electrical performance was enhanced by electron irradiation at 900 eV, from 1.29×10^{-3} to $1.86\times10^{-3}\,\Omega^{-1}$. From the experimental results, it is concluded that electron irradiation is an effective surface treatment technology for improving the optical and electrical performance, and the flexibility of ZAZ films without substrate deformation.

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