Characterization of ZnO:Al(AZO) Transparent Conduction Film produced by DC Magnetron Sputtering Method

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Abstract

Al-doped ZnO (ZnO:Al) thin films were grown on corning 1737 glass substrates by dc magnetron sputtering. The structural, electrical and optical properties of the films were investigated as a function of various discharge power. The obtained films were polycrystalline with a hexagonal wurtzite structure and preferentially oriented in the (002) crystallographic direction. The lowest resistivity is 6.0×10^{-4}Ocm with the carrier concentration of 2.694×10^{20} cm^{-3} and Hall mobility of 20.426cm^2/Vs. The average transmittance in the visible range was above 90%.

1. Introduction

Transparent conductive oxides (TCOs) have been widely used in optoelectronic devices because of their low electrical resistivity and high transmittance in the visible light wavelength region. The most commonly used TCO material for high-quality applications is indium-tin-oxide (ITO). In recent years, however, doped zinc oxides have been attracting much attention as an alternative candidate to ITO due to their inexpensive, abundance, and non-toxic features. Zinc oxide is an II–VI semiconductor with wide direct band gap of 3.2eV at room temperature and 3.44eV at 4K, and wurtzite structure. In particular, ZnO film doped with Al, an n-type dopant, has attracted attention as TCO because of its low resistance and high transparency to visible lights. ZnO-based TCOs are relatively inexpensive and they also have desirable properties such as nontoxicity, long-term environmental stability and excellent IR shielding[1]. ZnO films are are widely applied to manufacture transparent electrodes for FPD (flat panel displays)[2], organic light-emitting diodes[3], solar cells[4] , ultraviolet laser devices[5], integrated optics[6], piezoelectronic, gas sensor[1] and surface acoustic wave (SAW) devices.

The good quality ZnO films have been prepared by many methods, such as sputtering[7], reactive thermal and electron-beam evaporation[7,8], pulse laser deposition[9], chemical vapor deposition[10], spray pyrolysis[11] and molecular beam epitaxy. Among these, sputtering technique has been widely used to deposit thin films of a broad range of materials because of its advantageous features such as simple apparatus, low deposition temperature and gives deposits of better adhesion and high density than other methods.

In this paper, we showed the effect of DC power on the structural, electrical and optical properties of ZnO:Al(AZO) films deposited on corning glass(1737) substrates. AZO thin films were fabricated by dc magnetron sputtering with AZO ceramic target (Al_2O_3: 2wt %).

2. Experimental

Aluminum-doped zinc oxide (ZnO:Al) films on Corning glass 1737 (0.7mm thick) have been prepared using a conventional DC magnetron sputtering system. The targets used in this study were sintered stoichiometric ZnO:Al (99.999% purity, 4in diameter, 0.5in thickness, High purity chemicals Inc.). The content of Al_2O_3 added to the ZnO power target ranged from 2wt%. The glass substrate (corning 1737 (thickness: 0.7mm, Samsung corning)) was ultrasonically cleaned in acetone, methanol rinsed an ultrasonic bath for 10 min in deionized water, and subsequently dried in a flowing nitrogen gas before deposition. The sputtering was performed in an Ar atmosphere with a target-to substrate distance of 40 mm. An oil diffusion pump with a rotary pump was used to achieve 2.0×10^{-3}Torr pressure before introducing argon gas. The substrate temperature was measured using a thermocouple gauge and a hot

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cathode gauge. The temperature was controlled using a feed back controlled heater. The variation in substrate temperature during deposition process was maintained within ±5 ℃. AZO films deposited at various dc powers were controlled in the range from 20 to 80 W.

The structural, electrical and optical properties of AZO thin films deposited at various dc plasma powers were characterized by various techniques. The film thickness was measured using a surface profiler (Alpha-Step 500, TENCOR, USA) and FE-SEM (field emission scanning electron microscope, S-4300, Hitachi). X-ray diffraction (High resolution X-ray diffractometer, Bruker D8 DISCOVER, Germany) was used to investigate the crystallinity and crystal orientation of films. The surface morphologies and the surface roughness of the ZnO:Al films were examined by AFM (atomic force microscopy, AP0190, Auto-Probe CP Multitask Microscopy). The electrical resistivity and Hall mobility were measured at room temperature by the van der Pauw method. The optical transmittance of the ZnO:Al films was measured in the wavelength range of 300–800 nm by using an UV-Vis NIR spectrophotometer (UV-Visible-near-IR spectrometer, Japan Shimadzu UV-3101PC). The elemental compositions were (of ZnO:Al films carried out by) investigated by RBS(Rutherford Back Scattering, NEC 53DH-2) and SIMS (Secondary Ion Mass Spectroscopy, PH17200 TOF-SIMS)

3. Results and discussion

3.1 Crystallinity properties

Thin film of ZnO:Al is deposited at 300℃, 5 mtorr with various discharge power (20~80W). The effect of discharge power on the microstructure of AZO thin film was investigated using XRD. Fig.1 show the X-ray diffraction pattern of ZnO:Al films. As discharge power is increased, the peak intensity is improved. At discharge power of 40 W, the peak intensity is the largest. But the power is increasing over the 40 W, the peak is bargain to decrease. Fig.2 shows the FWHM (Full Width Half Maximum) and grain size of the ZnO:Al films using the scherrer' s formula. Grain size is in reverse proportional to FWHM. At the discharge power is 40 W, grain size of ZnO:Al film is the largest while the FWHM is the smallest.

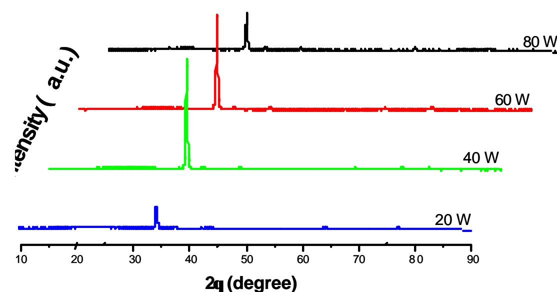

Fig 1. X-ray diffraction patterns of ZnO:Al films deposited with various \discharge power.

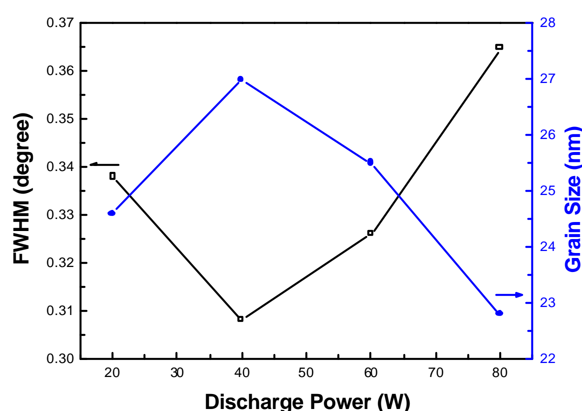

Fig 2. Full width at half maximum (FWHM) of XRD (002) peaks and the grain sizes for ZnO:Al films deposited with various DC power.

3.2 Electrical properties

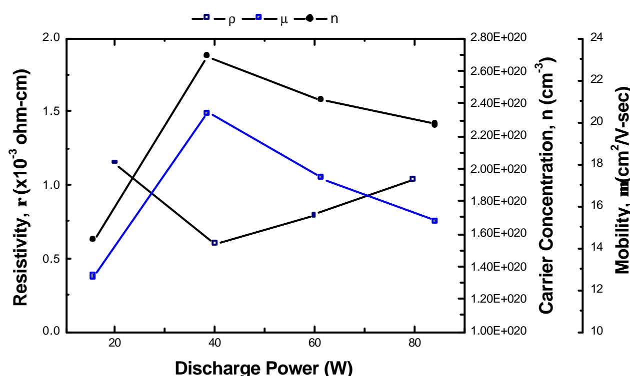

Fig 3. Electrical resistivity (?), carrier concentration (n) and Hall mobility (μ) of ZnO:Al films deposited with various DC power.

Fig.3 shows the dependence of the electrical properties on the substrate temperature for AZO thin films deposited of the AZO films with various DC power. The resistivity of the films is decreased with the increase of DC power in the range from 20 to 40 W. A minimal value for the resistivity of 6.0×10^{-4} Ocm is obtained at 40 W. A further increase in DC power causes resistivity to increase slightly. The carrier concentration and Hall mobility are respect to the variation of DC power. DC power increase from 20 to 40 W, both carrier concentration and Hall motilities increase. The carrier concentration of 2.694×10^{20} cm^{-3} and the Hall mobility of 20.426 cm^2/Vs are the maximum values for the film obtained at 40 W, which results in a minimum resistivity of film. But as DC power increases further, an opposite variation tendency occurs for the carrier concentration and Hall mobility. The resistivity decreases as DC power increases up to 40 W and then reversely increases at 60 W. Resistivity of the films is mainly affected by carrier concentration and mobility.

3.3 Optical properties

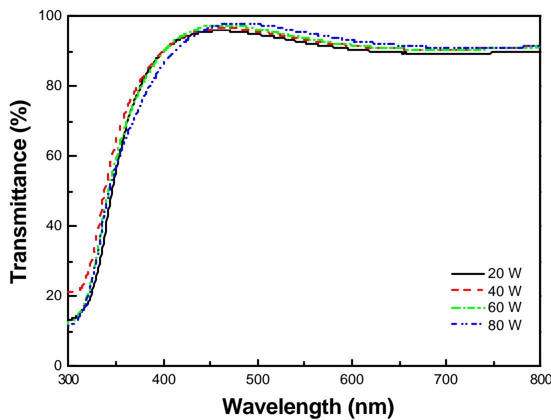

Fig 4. Optical transmittance spectra of ZnO:Al films deposited with various DC power.

The transmittance spectra as a function of wavelength in the range of 300-800 nm for AZO films deposited at various discharge power is shown in Fig. 4. The discharge power was controlled in the between 20 W and 80 W. It is seen that all films exhibit average transmittance of above 90 % in the visible region. The optical band gap of AZO films were estimated to be 3.53, 3.68, 3.56 and 3.61 eV at a discharge power of 20, 40, 60 and 80 W, respectively. It is shown in Fig. 5. The absorption edge of the transmittance shifted to the shorter wavelength (blue-shift) region up to the discharge power of 40W, which is believed to be due to Burstein-Moss effect[12]. It is describing that the Fermi level inside the conduction band moves upward with increasing donor concentration due to the filling of conduction band by the increase of electron carriers.

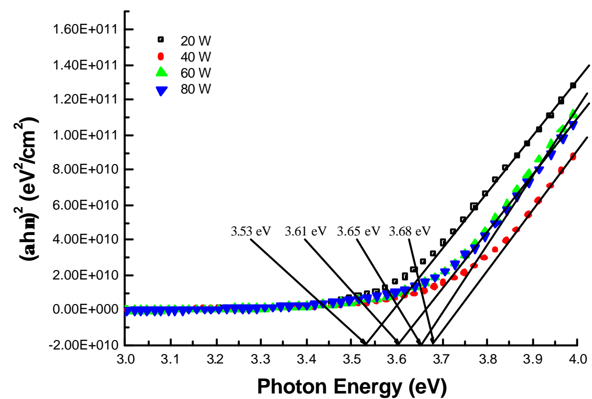

Fig 5. (a·*h?*)^2-*h?* plot properties of ZnO:Al films deposited with various DC power.

4. Structure and surface morphology

DC power (W)	20	40	60	80
RMS (nm)	0.19	0.59	0.66	0.78

***Table 1.* The DC power of AZO films prepared in different substrate temperature, measured by AFM**

Table. 1 shows the AFM images of ZnO:Al films deposited with various DC powers. The measured root-mean-square (RMS) roughness values were 0.19, 0.59, 0.66, and 0.78 nm for the films deposited with the DC power of 20, 40, 60, and 80 W, respectively. This indicates that the surface roughness increases with increase DC power. Increase in surface roughness of the films promotes oxygen absorption on the surface of the crystallites to form dangling bonds which then act as electron traps. These electron traps are responsible for the decrease in carrier concentration and Hall mobility. Besides, the rough surface morphology scatters the incident light

reducing optical efficiencies. However, the morphology change with increasing DC power seems to be rather small. Therefore, electronic and optical properties of ZnO:Al films would not be affected by the surface roughness in the present case.

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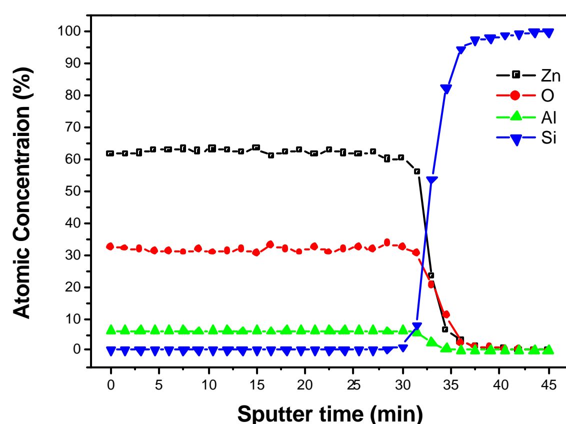

Fig 6. SIMS depth profiles of ZnO:Al thin film deposited at 40 W.

Composition of AZO thin films was determined using SIMS referenced by RBS, which shown in Fig. 6. The analysis shows that AZO exhibit homogenous composition but the ratio of Zn/O is in general greater than 1. This showed non-soichiometric structure properties of ZnO. The depth profile of AZO film obtained atomic ratio of Zn / O / Al with 62.27 / 31.46 / 5.93 %. The ratio of Al / Zn by weight is therefore 1.1%, which is greater than that in the target (2 wt %). This is perhaps due to sputter yield property of Zn and Al atoms

5. Conclusion

AZO films have been deposited by dc magnetron sputtering using a ZnO target mixed with Al_2O_3 of 2wt% on coring 1737 glass. The structural, electrical and optical properties of there films were investigated as a function of various discharge power. The obtained films were polycrystalline with a hexagonal wurtzite structure and preferentially oriented in the (002) crystallographic direction. The lowest resistivity is 6.0×10^{-4}Ocm with the carrier concentration of 2.694×10^{20} cm^{-3} and Hall mobility of 20.426cm^2/Vs. The average transmittance in the visible range was above 90%. From this work, we could expect the possibility of producing TCO films based on ZnO with good electrical and optical properties by optimizing the discharge power.

6. Acknowledgements

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7. References

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