Effect of substrate temperature on the properties of aluminum doped zinc oxide by DC magnetron sputtering

Hong-Mo Koo, Se-Hyun Kim, Yeon-Keon Moon, Jong-Wang Park
Division of Materials Science and Engineering, Hanyang University Haengdang-Dong, Seongdong-Ku, Seoul, Korea
Chang-Ho Jeong[1]
LCD R&D Center, Samsung Electronics Co., Ltd., Yongin-City, Gyonggi-Do, Korea

Abstract
Transparent conducting aluminum-doped zinc oxide (AZO) thin films have been deposited on corning 1737 glass by DC magnetron sputter. The structural, electrical and optical properties of the films were investigated as a function of various substrate temperatures. AZO thin films were fabricated by dc magnetron sputtering with AZO ceramic target (Al_2O_3: 2wt %). The obtained films were poly crystalline 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 $20.426 cm^2/Vs$. The average transmittance in the visible range was above 90%.

1. Introduction
Transparent conductive oxide (TCO) films, mainly indium tin oxide (ITO) films, have been widely applied to manufacture transparent electrodes for flat panel displays, solar cells, organic light-emitting diodes, integrated optics, piezoelectronic, gas sensor and surface acoustic wave (SAW) devices due to the high luminous transmittance, good electrical conductivity, good adhesion to substrate and chemical inertness. However, high cost of ITO has motivated efforts to develop substitutes. 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.

ZnO:Al films can be produced by various deposition techniques including pulsed laser deposition[1], chemical vapor deposition[2], sol-gel process[3], spray pyrolysis[4], evaporation[5] and magnetron sputtering[6].

Among all, magnetron sputtering is characterized by several advantages, low processing temperature, good adhesion of films on substrates, very good thickness uniformity, high deposition rates possible, high density of the films and the relative ease of scaling to large areas. Also, it is simple process and process parameter control possible.

In this paper, we showed the effect of substrate temperatures 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. A 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 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 substrate temperatures was controlled in the

[1] If necessary, you may place some address information in a footnote, or in a named section at the end of your paper.

range from R.T to 500℃.

The structural, electrical and optical properties of AZO thin films deposited at different temperatures 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

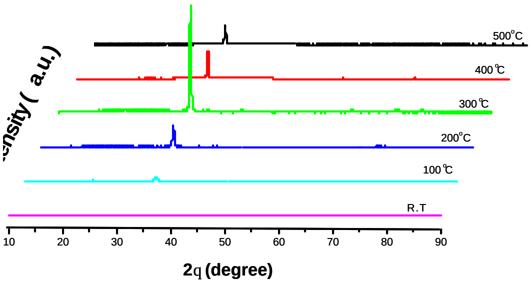

Fig 1. X-ray diffraction patterns of ZnO:Al films deposited with various substrate temperatures.

The thin film of ZnO:Al is deposited at 40 W, 5 mtorr with various substrate temperature (RT~500℃). The effect of substrate temperature on the microstructure of AZO thin film was investigated using XRD. Fig.1 show the X-ray diffraction pattern of ZnO:Al films. As substrate temperature is increased, the peak intensity is improved. At substrate temperature of 300 ℃, the peak intensity is the largest. But the substrate temperature is increasing over the 300 ℃, 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 substrate temperature is 300 ℃, grain size of ZnO:Al film is the largest

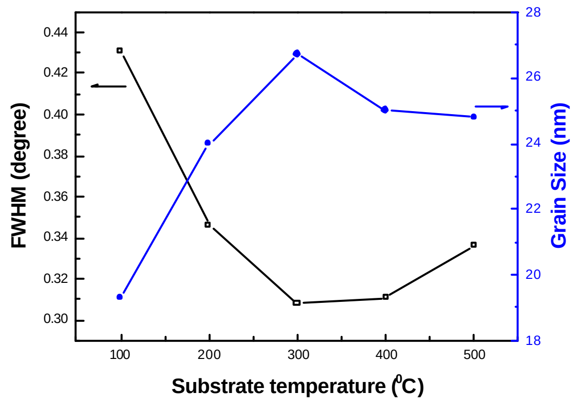

Fig 2. Full width at half maximum (FWHM) of XRD (002) peaks and the grain sizes for ZnO:Al films deposited with various substrate temperatures.

3.2 Electrical properties

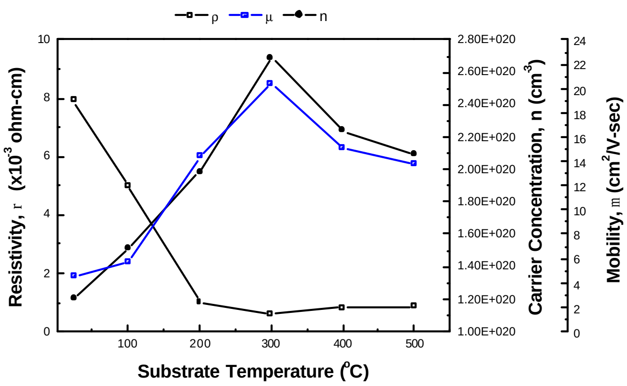

Fig 3. Electrical resistivity (?), carrier concentration (n) and Hall mobility (μ) of ZnO:Al films deposited with various substrate temperatures.

Fig. 3 shows dependence of the electrical properties presented by the ZnO:Al thin films deposited with various substrate temperatures. The resistivity of the films is decreased with the increase of substrate temperature in the range from R.T to 300 ℃. A minimal value for the resistivity of 6.0×10^{-4} Ωcm is obtained at 300 ℃. A further increase in substrate temperature causes resistivity to increase slightly. The carrier concentration and Hall mobility are respect to the variation of substrate temperature. Substrate temperature increase from R.T to 300 ℃, 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 300 ℃, which results in a minimum resistivity of film. But as substrate temperature increases further, an opposite variation tendency occurs for the carrier concentration and Hall mobility.

3.3 Optical properties

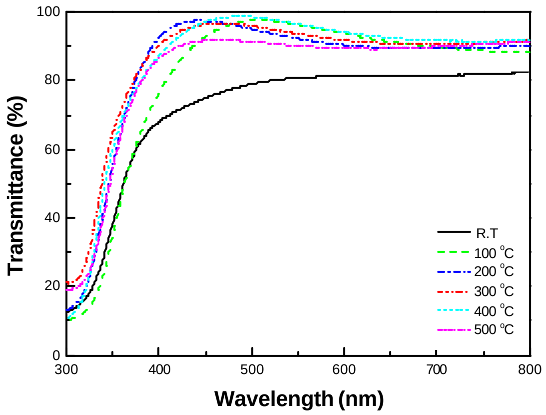

Fig 4. Optical transmittance spectra of ZnO:Al films deposited with various substrate temperatures.

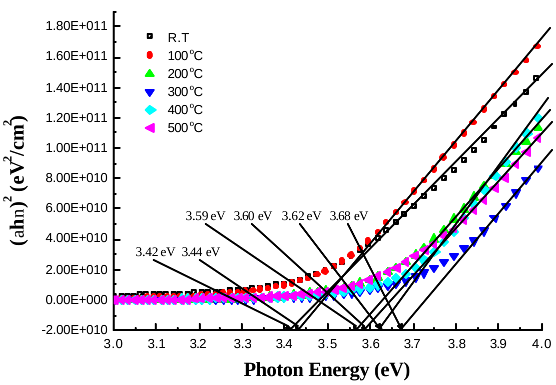

Fig 5. (a·h?)^2-h? plot properties of ZnO:Al films deposited with various substrate temperatures.

The transmittance spectra as a function of wavelength in the range of 300-800 nm for AZO films deposited at various Substrate temperature is shown in Fig. 4. The Substrate temperature was controlled in the between R.T and 500 ℃. The film deposited at R.T has relatively lower transparency, but it still exhibits a visible light transmittance of about 80%. It is seen that all films exclude film deposited at R.T exhibit average transmittance of above 90% in the visible region. The optical band gap width AZO films were estimated to be 3.42, 3.44, 3.59, 3.68, 3.62 and 3.60 eV at a discharge power of R.T, 100, 200 300, 400 and 500 ℃, 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 300 ℃, which is believed to be due to Burstein-Moss effect. 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.

4. Structure and surface morphology

Substrate temperature (℃)	R.T	100	200	300	400	500
RMS (nm)	11.0	1.15	0.72	0.59	0.66	0.73

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

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 [7,8]. 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.

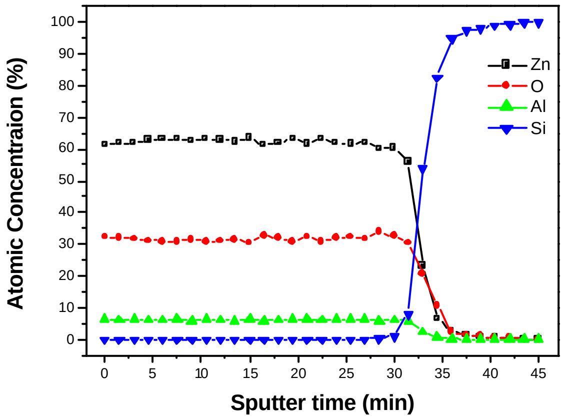

Fig 21. SIMS depth profiles of ZnO:Al thin film deposited at 40 W.

Composition of AZO thin films was determined using SIMS referenced by RBS, which shown in Fig. . 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 [9,10]. 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 [11].

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 objective of study was to investigate the structure, electrical and optical properties of thin films as a function of various substrate temperatures. 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}Ωcm with the carrier concentration of 2.694×10^{20} cm^{-3} and Hall mobility of 20.426cm^2/Vs. The average transmittance of the visible light 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 substrate temperature. The more result will be presented in the meeting.

6. Acknowledgements

This work was supported by Samsung Electronics Co. through the Brain Korea 21 project under the ministry of Education and Human Resources Development.

7. References

[1] J. H. Kim, Kyoung-cheol Lee, and Cheon Lee,. Proc. SPIE Int. Soc. Opt. Eng. 5063, 49 (2003)

[2] Teresa M. Barnes, Steve Hand, Jackie Leaf, and Colin A. Wolden, J. Vac. Sci. Technol. A 22, 2118 (2004)

[3] M. J. Alam and D. C. Cameron , J. Vac. Sci. Technol. A 19, 1642 (2001)

[4] J. M. Bian, X. M. Li, X. D. Gao, W. D. Yu, and L. D. Chen Appl. Phys. Lett. 84, 541 (2004)

[5] Toshihiro Miyata, Youhei Minamino, Satoshi Ida, and Tadatsugu Minami,. J. Vac. Sci. Technol. A 22, 1711 (2004)

[6] Bo Huang, Suntao Wu, Jing Li, Shigang Sun, and Zhong-Qun Tian Proc. SPIE Int. Soc. Opt. Eng. 5774, 152 (2004)

[7] Y. Igasaki, H. Satio, Thin Solid Films 199 (1991) 233.

[8] S.S. Lin, J.l. Huang, Ceram. Int. 30 (2004) 497

[9] K. L. Chopra, S. Major and D.K. Pandya, Thin Solid Films, 102, (1983) 1.

[10] C. M. Lampert, Sol. Energy Mater.,6, 6 (191) 1.

[11] MILTON OHRING, in Materials Science of Thin Films, ACADEMIC, second edition, p. 176