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Structure and electrical property changes of ZnO:Al films, prepared by radio frequency magnetron sputtering, by thermal annealing

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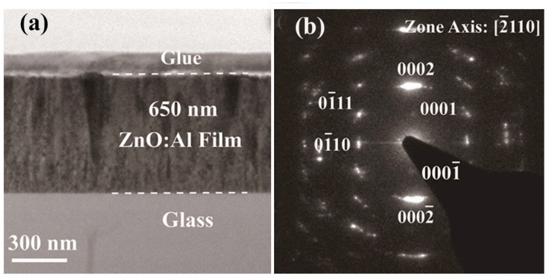
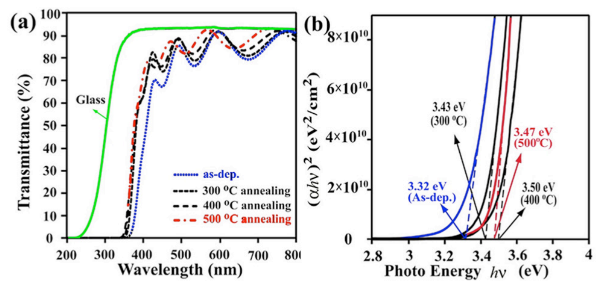
Among transparent conducting oxide films that are widely applied in optical and electronic devices such as solar cells, thin film transistors and light emitting diodes, ZnO:Al has attracted much attention because it is an abundant, inexpensive, non-toxic and environmentally friendly raw material with high crystallinity and good conductivity, and can be easily prepared. Magnetron sputtering is one of the preferred techniques to prepare the ZnO:Al films because it produces films with a composition close to that of the source material. Here, we report changes of structure and electrical properties by thermal annealing of ZnO:Al films sputtering-deposited on glass substrates

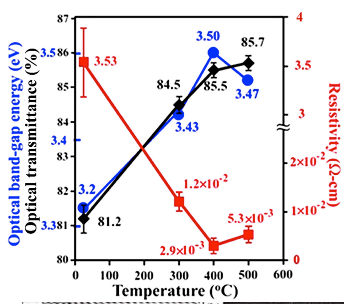
ZnO:Al thin films with a thickness of 650 nm were deposited on Corning Eagle[2000] glass substrates at a deposition rate of about 2.2 nm/min from a ZnO/2 wt.%Al_2O_3 target. After deposition, the ZnO:Al films were annealed at 300, 400, and 500^oC for 1 h in vacuum (~0.133 Pa) in a quartz-tube furnace. Optical transmittance was measured with a spectrophotometer. Electric resistivity was measured using the four-point probe method. X-ray diffraction (XRD) and electron microscopy observation were performed.

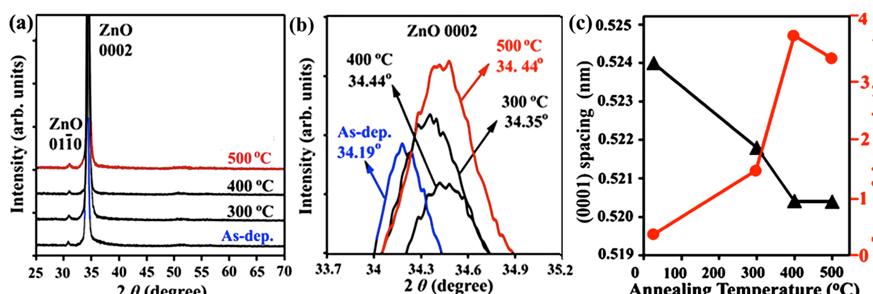
Figure 1 shows a cross-section TEM image and an ED pattern of the as-deposited film. It consisted of columnar grains perpendicular to the glass substrate surface, with the highly preferred orientation along the [0001] axis. Figure 2a reveals that the average optical transmittance of the as-deposited and post-annealed ZnO:Al films were all over 80% in a 400-800 nm wavelength range. The oscillation can be ascribed to the multiple beam interference between the top and bottom surfaces of the film, which causes the minimum transmittance through reflection of the incident light beam. So, the difference in minimum position between these curves corresponds to a small difference in thickness of the film, which was caused by the heat treatment. Plots of $(\alpha h\nu)^2$ versus $h\nu$ in Figure 2b indicate that the optical band-gap energy estimated from the intercept was significantly higher for the annealed films than the as-deposited ZnO:Al film. This blue shift of the band-gap can be attributed to the Burstein-Moss effect. Figure 3 shows the electrical resistivity as well as the optical transmittance over the 400-800 nm wavelength range and the estimated optical band-gap energy for these films. Due to the activity of the doped-Al elements and oxygen vacancies, the resistivity of the annealed ZnO:Al films significantly decreased, and the lowest resistivity occurred with annealing at 400^oC. X-ray diffraction patterns in Fig. 4a indicate the preferential (0001) orientation of the ZnO:Al film. Since the solid solubility limit of Al in ZnO:Al is 2 mol% [1] and no peaks from other crystals such as $ZnAl_2O_4$ appeared, the composition of the present films is probably approximately ZnO/1.6 mol.% Al_2O_3. Details of the 0002 peaks in Fig. 4b indicate that the (0001) lattice spacing decreased with annealing temperature until 400^oC as shown in Fig. 4c. This observed shrinking of the unit cell is ascribed to the substitution of Al^{3+} (radius 76.5 pm) for Zn^{2+} (radius 88 pm) and the formation of oxygen vacancies during the activation annealing. HRTEM images in Figure 5 reveal that the angle between the $[000\bar{1}]$ and $[01\bar{1}0]$ axes or the lean of the *c* axis increased with annealing temperature and reached a maximum of about 4^{o} (=93.7^{o}-90^{o}) at an annealing temperature of 400^{o}C (Fig. 4c). The hexagonal cell was hence deformed to a triclinic cell, leaning the *c* axis and shrinking the volume, due to the formation of point defects during the annealing. At an annealing temperature of 500^{o}C, the lean of the *c* axis was smaller than that at 400^{o}C. This is closely related with optical band-gap energy and electrical resistivity. Since the optical and electrical properties are greatly influenced by point defects, this could be ascribed to the difference of the density of point defects that are the substituted Al^{3+} ions and O^{2-} vacancies. At 400^{o}C, the point defects might be saturated in the ZnO:Al film in the most favorable state. One possible explanation for the higher resistivity and lower optical band-gap energy caused by annealing at 500^{o}C may be introduced oxygen atoms from the ambient atmosphere at elevated temperature, whereby the oxygen atoms occupy the vacancy sites without appreciably changing the unit cell volume and reducing the lean of the *c* axis.

[1] M.H. Yoon *et al*, J. Mat. Sci. Lett. **21,** 1073 (2002).









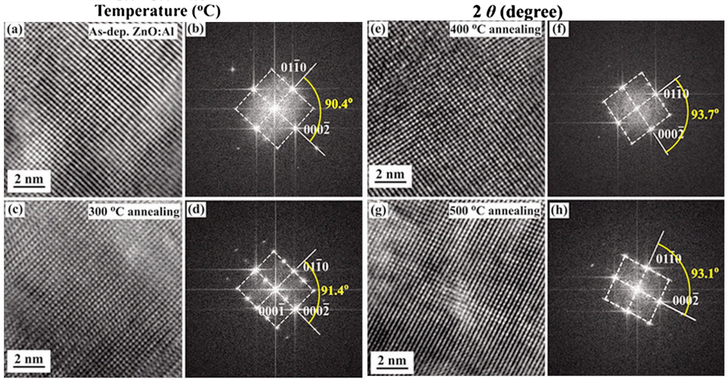


Fig. 1 (top left). TEM and ED pattern of as-deposited ZnO:Al film.

Fig. 2 (top right). (a) Optical transmittance spectra. (b) $(\alpha h\nu)^2/h\nu$ relation. α is the optical absorption coefficient.

Fig. 3 (middle left). Optical transmittance and band-gap energy, and electrical resistivity.

Fig. 4 (middle right). (a) X–ray diffraction patterns of these films. (b) the details of the 0001 peaks. (c) The (0001) spacing and the lean of the *c* axis.

Fig. 5 (bottom). HR-TEM lattice images and the corresponding FFT diagrams, showing the angle between the $[000\bar{2}]$ and $[01\bar{1}0]$ axes or the lean of the *c* axis.

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