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Post-annealing properties of aluminum-doped zinc oxide films fabricated by ion beam co-sputtering

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ABSTRACT

Aluminum-doped zinc oxide (AZO) films were fabricated by using the ion beam sputter deposition (IBSD) method with dual metallic targets, Al and Zn, co-sputtered by argon ion beam in an oxygen ambient. Structural and electrical properties of AZO films before and after annealing were *ex situ* investigated by the X-ray diffractometer and Hall measurement with the Van der Pauw method, respectively. The intense (002) diffraction peak and simultaneously the low resistivity were observed in the as-deposited film. The resistivity of the film after 400 °C post-anneal increased more than two orders of magnitude than that of the as-deposited film resulting from the decrease of the donor concentration and mobility in the AZO film. The residual stress was derived from the results of the XRD patterns. Finally, it was found that the film resistivity increased as the annealing temperature increased and a corresponding shift of the energy band gap was observed.

1. Introduction

Aluminum-doped zinc oxide (AZO) with a large band gap is one of the promising materials for the applications of conductive transparent oxides. Nowadays, the AZO thin film attracts more attention as a substitution for indium tin oxide films due to its low resistivity, high transparency, less toxicity and abundant raw material. Various technologies for preparing AZO thin films have been used, such as magnetron sputtering [1–3], pulsed laser deposition [4,5], sol-gel [6,7] and so on.

It is well known that the physical properties of the film depend on its microstructure which is determined by the deposition conditions and post-annealing [8,9]. In general, the properties of the as-deposited films are influenced significantly by the certain amount of structural defects which are requisite for thin films to maintain their stable film properties after the post-annealing treatment [9]. The primary contribution of the post-annealing process for the films may be derived from the variation of the stoichiometry in the films, the improvement of crystallinity as well as the physical desorption or the chemisorption of oxygen from the grain boundaries of films [10,11].

Ion beam sputtering process, a relatively unique method for preparing AZO films, was used in this study due to its capability to fabricate high-packing-density films by the atom-by-atom or molecule-by-molecule transport growth mechanism at low substrate temperature [12]. During the process the Al and Zn components in the AZO films can be controlled by adjusting the relative sputtered areas of two pure metal targets mounted side by side. The setup of the deposition chamber is schematically shown in Fig. 1. In our previous work [13], not only the properties of AZO films deposited at room temperature with different components were reported but also the *in situ* XRD results during annealing. To further understand the resistivity changes after annealing the detailed property changes of the film such as the mobility, grain size, the thermal induced stress, and optical band gap after annealing up to 400 °C were investigated *ex situ* and reported in this work.

2. Experiments

AZO films were deposited on the B270 glass substrates of size 1.3 cm × 1.3 cm by the ion beam sputtering system at room

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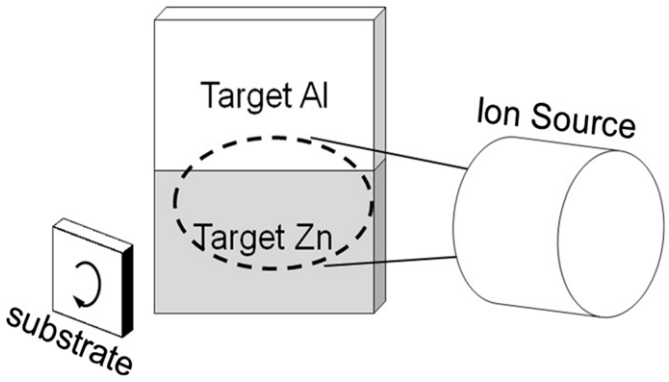

Fig. 1. Schematic diagram of the ion-beam co-sputtering system. Two metallic targets, Zn and Al, are simultaneously co-sputtered by an ion beam.

temperature. The substrates were not heated intentionally during the deposition. Two metallic targets Al and Zn with the purity of 99.99% were mounted side by side on the water-cooled copper block. The substrate was cleaned by ethanol in an ultrasonic cleaner and blown dry by nitrogen gas prior to the deposition process. The incident angle between ion beam and the normal of target surface was 45°. The chamber was pumped down to a base pressure of 5.3×10^{-6} mbar. The argon ion beam cleaned the targets for about 30 min before removing the shutter which covered the substrate. The ion beam voltage was kept at 1000 V with the ion beam current of 20 mA and the thickness of the as-deposited film, controlled by a quartz monitor, was around 200 nm. During the deposition the argon gas was fed into the ion source as a working gas and oxygen as ambient gas fed into the chamber as well. The total pressure was maintained at 3.1×10^{-4} mbar.

The component ratio of AZO film was appropriately adjusted by controlling the position of the two targets relative to the sputtering ion beam and the Al concentration of AZO film measured by the EDS (Hitachi S-4800) was 0.7 wt.% [13]. Then the as-deposited AZO films were post-annealed in air at 100, 200, 300 and 400 °C, respectively. An X-ray diffraction (XRD) apparatus (Rigaku Multiflex) with a Cu K_α line (1.54055 Å) was used to identify the crystallinity of the films. The electrical resistivity/conductivity, carrier concentration and Hall mobility in the films were measured at room temperature by Hall measurement (Ecopia HMS-3000) with the Van der Pauw method. The transmittance spectra were measured by UV–VIS–NIR spectrometer (Varian Cary-5E). The band gaps of the films after different post-annealing temperatures were calculated by using the extrapolation from the plots of $(\alpha h\nu)^2$ vs. $h\nu$. The optical absorption coefficient α of a semiconductor can be derived from $\alpha = A(h\nu - E_g)^{1/2}$, where A is a constant, $h\nu$ is the phonon energy and the E_g is the energy band gap [14]. All the properties of films studied in this work were *ex situ* investigated before and after the annealing process.

3. Results and discussion

3.1. Structural characteristics

Fig. 2 shows the XRD spectra of AZO films before and after annealing at various temperatures. The crystalline orientations of the films were similar to our previous work [13]. The stronger ZnO (002) diffraction peak was detected in the films before and after annealing. It indicates that the films have a high texture of the crystalline (002) orientation along the c-axis perpendicular to the substrate surface.

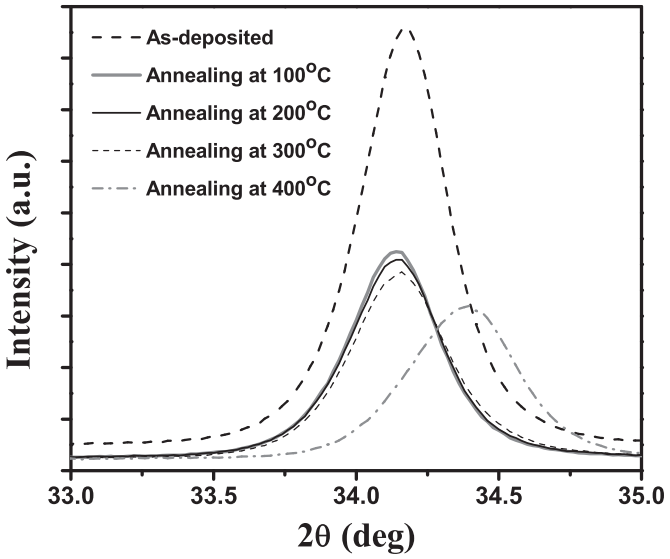

Fig. 2. The XRD spectra of AZO film before and after annealing at various temperatures.

From the XRD results, the grain sizes calculated by the Scherrer formula and the full width at half maximum (FWHM) of (002) peak with respect to the annealing temperature are shown in Fig. 3. After annealing, poor crystallinity and the smaller grain size were deduced from the broadening of the FWHMs and decrease in the peak intensities. In general, the structures of the ZnO film were improved by the post-annealing process [15]. However, the crystallinity, i.e., XRD peak intensity, of the films after the annealing process were obviously lower than that of the as-deposited film in Fig. 2. It means that better crystallinity of the AZO film just after deposited by ion beam sputtering at room temperature was achieved. Further annealing of the film results in a film with worse crystallinity. The decrease of the grain size was either caused by the release of the compressive stress in the film or the oxidation of the dopant aluminum in the AZO film during annealing in air as discussed below.

In order to realize the influence of the annealing effect on the stress of the AZO films, the film stress was calculated based on the biaxial strain model [16]. The strain in the c-axis direction determined by XRD is $\varepsilon = (C_{film} - C_0)/C_0$, where C_0, 0.5206 nm, is the unstrained lattice parameter from the ZnO powder [17] and C_{film} is

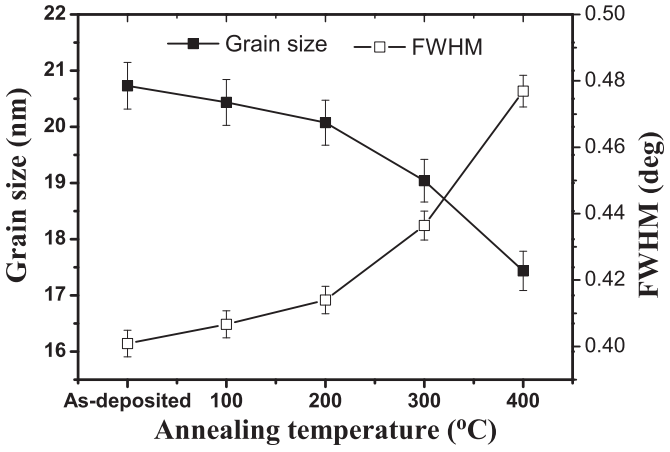

Fig. 3. The grain size and FWHM of AZO film before and after annealing.