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# Growth orientation transition and metal-like conductivity of Ti, Al co-doped ZnO films

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Ti, Al co-doped ZnO thin films have been fabricated by radio frequency magnetron sputtering and post-vacuum-annealing techniques on glass substrates. For annealing temperatures below 723 K, the room temperature resistivity of these films was found to decrease as the annealing temperature increased. The lowest resistivity ($6.75\times10^{-4}$ Ω·cm), indicating metal-like conductivity, was found at 723 K. The post-annealing temperature dependent on the resistivity of these films also showed a metal –semiconductor transition at 723 K. It was also found a growth orientation transition of these films from (002) to (100) with the annealing temperature up to 773 K.

Keywords: *growth-orientation transition; metal-like conductivity; Ti, Al co-doped; ZnO thin film; vacuum annealing*

## 1. Introduction

Transparent conducting oxides (TCOs) have found applications in several optoelectronic devices such as light emitting diodes (LEDs), solar cells, and flat panels as well as flexible displays [1–3]. Indium tin oxide (ITO) is the most commonly used TCO for these applications because of its high transmittance in the visible region and the resistivity close to $1.0\times10^{-4}$ Ω·cm [4, 5]. However, a high cost and scarce resources of In limit its usage in these devices. This has led researchers to explore alternative materials for TCO devices. Some of the TCOs which have shown transmittance and resistivity values close to those of ITO are ZnO:Al, ZnO:Ga, $SnO_2$:F, $TiO_2$:Nb etc. Among these, ZnO is the most favourable material, because of its benign nature, relatively low cost, good stability in hydrogen plasma process, and non-toxicity [5, 6]. Therefore, there is a considerable interest in understanding the electrical and transport properties of doped ZnO films which is critical for further improvement of TCOs characteristics.

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Most of the careful doping studies have been performed by several techniques of various types in order to improve the performance of ZnO films [5, 7–10]. Doped ZnO, especially Al-doped ZnO (ZATO), shows excellent transparency over the entire visible spectrum and has better transport properties, due to higher electron mobility. For further improvement of properties of ZATO films, the co-doping effect of some impurity and $Al^{3+}$ has been reported earlier [8, 11]. But the co-doping effect of $Ti^{4+}$ and $Al^{3+}$ has not been reported so far. $TiO_2$ has a particular and useful physical property for optical applications [12, 13]. $TiO_2$ was selected as dopant and expected to improve the transmittance and transport properties for ZATO film. In this paper, we have investigated the post-annealing, temperature dependent, transport properties of ZATO films grown on glass substrates at room temperature using the radio frequency (rf) magnetron sputtering technique. The investigation of a metal-like behaviour at low temperature has been investigated, being probably due to weak localization of the charge carries at the defect sites, surface scattering and the annealing temperature. In the paper, a new observation of the growth-orientation transition from (002) to (100) with an annealing temperature of up to 773 K has also been reported; it is probably related to the change of crystal surface energy induced by ionized impurities and massive formation of oxygen vacancies and defects in ZnO films grown on glass substrates during annealing.

## 2. Experimental

The ZATO ceramic sputtering targets, of which the raw materials were mechanical mixed powders, were fabricated by the conventional solid state sintering process in air. The following compositions were chosen: 97% ZnO + 1.5% $Al_2O_3$ + 1.5 $TiO_2$ (wt. %). The raw materials were commercially available ZnO, $Al_2O_3$ (99.95% in purity) and $TiO_2$ (99.96% in purity) powders. The compacted targets were sintered at 1573 K for 3 h in air.

ZATO thin films were grown on glass substrates at room temperature by the rf magnetron sputtering technique. The glass substrates were thoroughly cleaned using absolute ethanol, acetone and distilled water as solvents and ultrasonic technology, and then dried before loading in a deposition chamber. The chamber was evacuated to the pressure of $8\times10^{-5}$ Pa, and the deposition was carried out under 1.6 Pa argon pressure. The ZATO films of 400–500 nm thick were annealed in the temperature range of 298–823 K for 3 h under vacuum (ca. $10^{-1}$ Pa).

Crystallographic and phase structures of the ZATO thin films were determined using a D8-Advance X-ray diffractometer with Cu $K_\alpha$ radiation. A JSM-5610LV scanning electron microscope (SEM) was used to investigate the surface morphologies of the deposited films. The electrical resistivity was measured using a standard four-point probe technique at room temperature.

## 3. Results and discussion

Figure 1 shows X-ray diffraction (XRD) patterns of the ZATO films annealed at various temperatures under vacuum for 3 h. The (100), (002) peaks are observed in the XRD patterns. The peaks correspond to a hexagonal wurtzite structure. The patterns show that the ZATO films deposited and annealed are highly textured along the *c* axis, except for the films annealed at 773 K. The absence of additional peaks excludes the possibility of any extra phases and/or large-size precipitates in the films. The above indicates that Al, Ti co-doping did not distort the original crystalline structure.

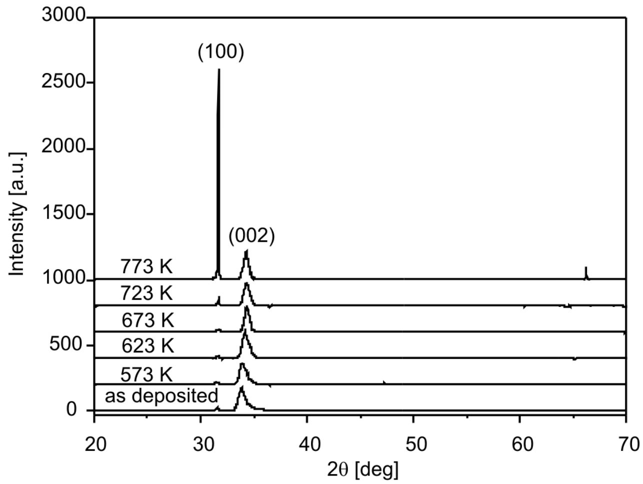


Fig. 1. X-ray diffraction (XRD) patterns OF ZATO films annealed at various temperatures under vacuum (ca. $10^{-1}$ Pa) for 3 h

However, for the film annealed at 773 K, very strong (100) and weak (200), (002) peaks were observed, which suggests that the preferred growth orientation undergoes a transition from (002) to (100), which is related to the change of surface energy of the film crystals during the annealing. Theoretically, for the ZnO films, (002) plane is the close-packed surface, and thus the value (1.6 J/m$^2$) of its surface energy is the lowest among all the planes, which is the reason that ZnO film crystals preferentially grow along the *c* axis [14, 15]. However, after the high temperature (773 K) annealing, Al, Ti ions sufficiently substitute the sites of Zn ions in the ZATO film, which probably results in the change of the closely-packed surface, and makes the surface energy value of the (100) plane be lowest being the reason for the change in the orientation of the recrystallization growth. In order to prove that $Al^{3+}$, $Ti^{4+}$ ions occupy Zn substitutional sites, the dependences of the lattice parameters *a* and *c* and the step-scanned (002) XRD line profiles of ZATO films on the annealing temperature have been recorded (Fig. 2).

The lattice parameter *c* decreases as the annealing temperature increases to 723 K, and then it slightly increases till 773 K. The lattice parameter *a* also initially tends to decrease and then subsequently increases. This is a universal trend with the shift of 2$\theta$

in the XRD patterns, as is seen from the (002) XRD line profiles of ZATO films at various annealing temperatures (Fig. 2) suggesting that the Al and Ti atoms occupy Zn substitutional sites.

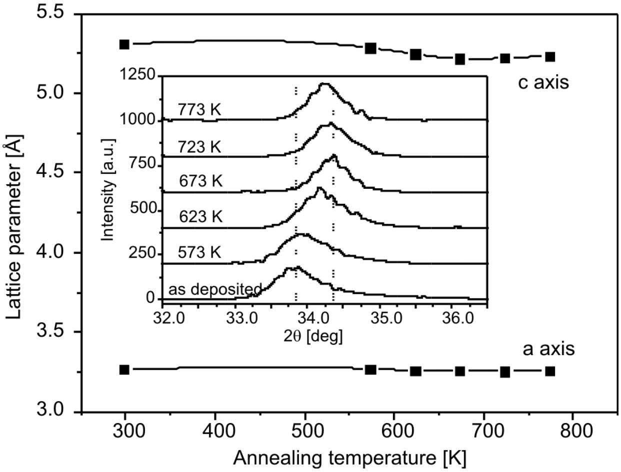


Fig. 2. Annealing temperature dependence of the lattice parameters ($a$, $c$) and step-scanned (002) XRD line profiles of ZATO films

Annealing of ZnO under vacuum at 773 K also leads to massive formation of oxygen vacancies and defects in ZnO films grown on glass substrates. In order to verify this supposition, ZATO films were annealed under oxygen atmosphere at 773 K for 3 h. In their XRD patterns (Fig. 3), only the (002) peak is observed, which supports the above supposition.

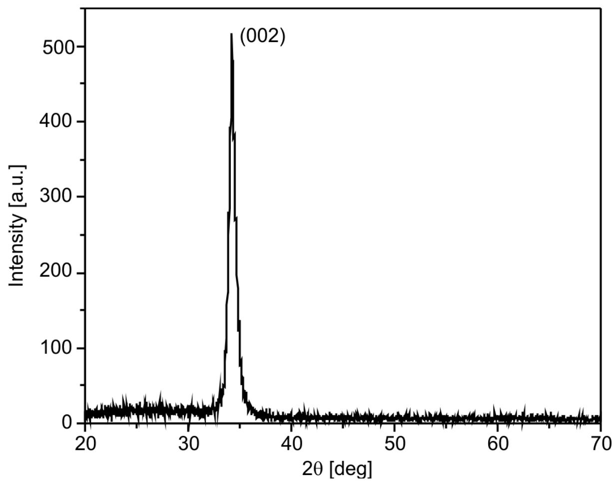


Fig. 3. X-ray diffraction (XRD) patterns OF ZATO films annealed at 773 K under oxygen atmosphere for 3 h

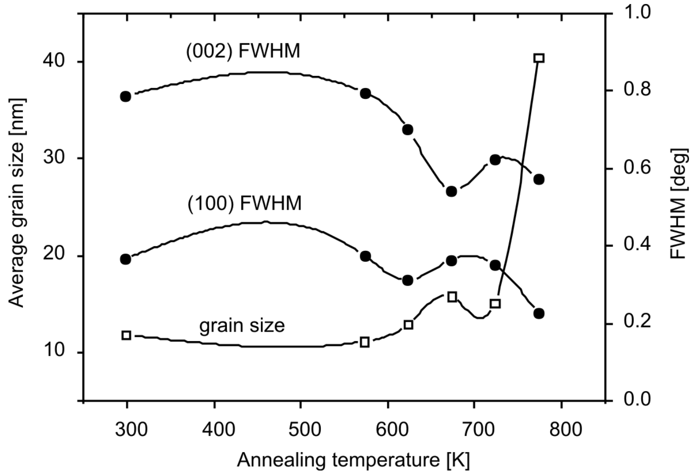


Fig. 4. Dependences of FWHM of (002) peak and average grain size of ZATO films on annealing temperature

Figure 4 shows the dependence of the full width at half maximum (FWHM) and average grain size on the annealing temperature. The FWHM decreased, that is, the average grain size became larger, as the annealing temperature increased. The smallest (100) peak FWHM exists when the annealing temperature is 773 K; this is the temperature at which the largest grain size can be obtained. Figure 4 also shows that the annealing temperature dependence of both the (100) peak FWHM and the (002) peak FWHM is similar, that is, initially both the (100) peak FWHM and the (002) peak FWHM decrease as the annealing temperature increases up to 623 K, then slightly increase till 673 K, and then decrease till 773 K.

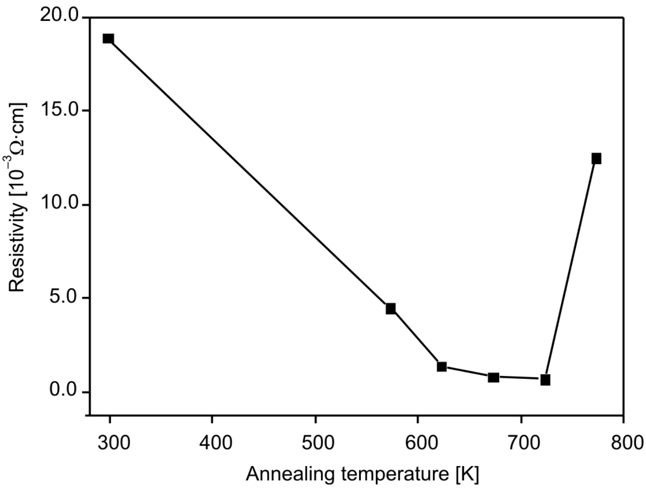


Fig. 5. Dependence of the resistivity of ZATO films on the annealing temperature

Figure 5 shows the dependence of the resistivity of ZATO films on the annealing temperature. The resistivity decreases as the annealing temperature increases up to 723 K, due to the increased grain size and the decreasing scattering to electrons. Then it clearly increases to 773 K, due to the growth-orientation transition from (002) to (100) as discussed previously, weak localization of the charge carriers at the defect sites and surface scattering. When the annealing temperature is 723 K, the semiconductor–metal transition appears, at which, the lowest resistivity, $6.75\times10^{-4}$ Ω·cm, is achieved. The lower resistivity of ZATO films after thermal annealing can be explained by the presence of Al, Ti ions at the substitutional sites of Zn ions. Furthermore, Al, Ti interstitial atoms change the oxygen vacancy characteristics, and desorption of oxygen atoms under vacuum, thereby causing a shift in the Fermi level. By raising the annealing temperature, the atoms receive energy and migrate to relative equilibrium positions. This induces a series of effects, for example, it reduces the lattice strain and the oxygen defect levels. In particular, it results in the appearance of a more perfect crystallite, and a pilling-up of donor, thereby weakening the grain boundary scattering and increasing the number of current carriers. The other reason for the lower resistivity is the growth of the average grain size as the annealing temperature increases, which reduces the grain boundary scattering [3, 4]. When the annealing temperature is increased even further, a serious diffusion appears however between the glass substrates and the ZnO films, and consequently more defects are produced in the films. Excessive defect levels and disorder caused by the impurities strengthen the grain boundary scattering and reduce the number of current carriers.

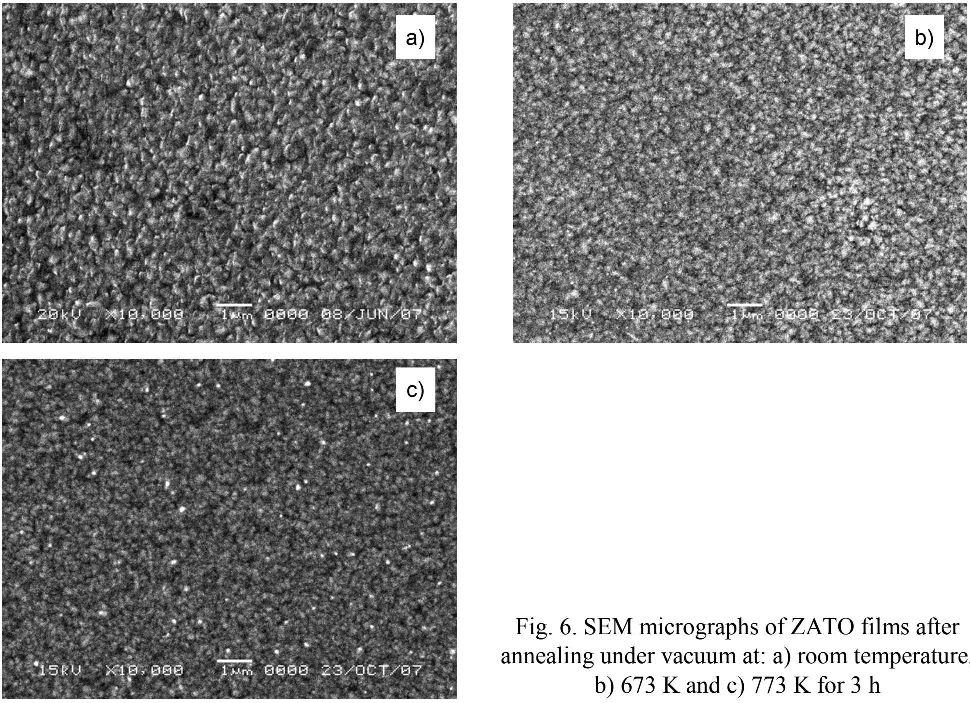


Fig. 6. SEM micrographs of ZATO films after annealing under vacuum at: a) room temperature, b) 673 K and c) 773 K for 3 h

Thus, the resistivity of the films starts to increase when annealing occurs at 773 K. Otherwise, the preferred growth orientation changes for a few grains in the films, and maybe also increases the resistivity of the films. A novel preferred orientation might offer different properties.

In order to illustrate the surface morphology of the ZATO films, scanning electronic microscopy (SEM) images are shown in Fig. 6. For the obtained ZATO films, uniform and dense surfaces with small grain sizes are observed, but these nanocrystalline surfaces do not show evident differences. The crystallite size, which can be estimated using the Scherrer formula, increases as the annealing temperature increases up to 773 K, as shown in Fig. 4 and is in the 10–45 nm range. This indicates the coalescence of the grains in ZATO films after thermal annealing at a different temperature. During deposition of ZATO films by sputtering onto glass substrates the growth took place by the nucleation and coalescence process. Randomly distributed nuclei may have formed first and then may have grown to form some observable "islands" which come closer to each other [8]. The larger ones appeared to grow by coalescence of smaller ones during annealing.

## 4. Conclusion

High-quality conducting ZATO films were grown on glass substrate by the rf magnetron sputtering technique, showing stronger *c* axis orientation. After thermal annealing in vacuum at 723 K, the preferred growth orientation of ZATO films changes from the (002) to the (100) plane. The resistivity of ZATO films decreases as the annealing temperature increases up to 723 K, and then clearly increases till 773 K. At 723 K, the semiconductor–metal transition appears, at which, the lowest resistivity, $6.75\times10^{-4}$, is achieved. For the obtained ZATO films, uniform and dense surfaces with small grain size are observed, but these nanocrystalline surfaces do not show evident differences. The crystallite size is in the 10–45 nm range.

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