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Electrical, optical and structural properties of transparent and conducting ZnO thin films doped with Al and F by rf magnetron sputter

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Abstract

Al and F-doped ZnO films of 200 nm thicknesses were prepared on glass substrates by co-sputtering ZnO targets composed of 2 wt.% Al_2O_3, 1.3 wt.% ZnF and pure ZnO targets, respectively. After annealing in vacuum pressure of 10^{-6} Torr at 300 °C for 2 h, the resistivity of ZnO films decreased down to $4.75 \times 10^{-4}\ \Omega$ cm and ZnO film which composed of Al-doped ZnO 25% and F-doped ZnO 75% by volume fraction showed the highest mobility of 42.2 cm^2/V s. From XRD measurements it was found that F dopants improved crystallization of ZnO films. Form XPS spectra of oxygen 1 s binding energy and Hall measurements it was confirmed that by vacuum annealing chemisorbed oxygens at the grain boundary desorbed and reduced grain boundary scattering. Also figure of merit (FOM) defined as ratio of electrical conductivity to optical absorption coefficient increased up to 2.67 Ω^{-1} after post annealing.

Keywords: Electrical properties; ZnO; Transparent and conducting oxide

1. Introduction

ZnO thin films doped with Al, Ga or In have low electrical resistivity and high optical transmittance due to their high carrier concentrations above 10^{20} cm^{-3} and wide optical band gap energy of above 3.3 eV.[1] Recently, Al doped ZnO thin films (AZO) have drawn a great deal of attention due to their low material cost, non-toxicity and the stability under the hydrogen plasma compared to ITO (Sn-doped indium oxide).[2] Most of the studies on doped ZnO thin films were carried out using trivalent cation dopants such as Al, Ga and B.[3] However, only a few studies on fluorine doped ZnO (FZO) can be found in the literature despite the fact that fluorine can be an adequate anion doping candidate due to its similar ionic radius to the oxygen. Most of the studies on FZO thin films were made using chemical process of sol–gel or spray pyrolysis, and the resistivity of FZO prepared by spray pyrolysis was in the range of 10^{-1} to $10^{-2}\ \Omega$ cm.[4] The most notable result was obtained for FZO thin films deposited using CVD technique by Hu and Gordon, in which the resistivity as low as of $4 \times 10^{-4}\ \Omega$ cm and high mobility as high as 40 cm^2/V s were reported.[5] The low resistivity combined with high mobility of FZO film was attributed to the restricted perturbation effect of fluorine anion to valence band.[5] Unlike metallic dopants, however, fluorine is known to be difficult to be incorporated into ZnO films by PVD technique like sputtering.[6]

In this study, to make advantage of Al dopants which can be easily incorporated into Zn sites and F dopants which can not be easily incorporated but give high mobility, Al and F dually doped ZnO films (AFZO) were prepared by co-sputtering of ZnO target containing Al_2O_3 (AZO) and ZnO target containing ZnF_2 (FZO), and their electrical, optical and structural properties were investigated.

2. Experimental details

AZO, FZO and AFZO thin films were deposited on corning glass substrates (Eagle 2000) by rf magnetron sputtering with 2 in. diameter targets. ZnO:Al_2O_3 (AZO) and ZnO:ZnF_2

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(FZO) targets contained 2.0 wt.% Al_2O_3 and 1.3 wt.% ZnF_2, respectively. By varying the rf power applied on each target during co-sputtering, ZnO films with five different chemical compositions were prepared (AFZO series). The volume ratios of FZO to AZO in AFZO film series, which were determined from deposition rates of each film, were 1:0, 3:1, 1:1, 1:3, and 0:1, and the corresponding AZO volume fraction was 0% (FZO), 25% (AFZO25), 50% (AFZO50), 75% (AFZO75) and 100% (AZO), respectively. Only Al doped ZnO films (APZO series, co-sputtered with pure ZnO and AZO targets), in which AZO volume fraction was varied 0% (ZnO), 25% (APZO25), 50% (APZO50) and 75% (APZO75) were also prepared by co-sputtering of pure ZnO and AZO targets, and their electrical and structural properties were compared with those of AFZO films. Sputter deposition was carried out at working pressure of 1 mTorr using pure Ar gas and the substrate was not heated intentionally during the deposition. Annealing test of the deposited films was performed at the temperature of 300 °C for 2 h inside the vacuum chamber pumped down to below 10^{-6} Torr. The electrical resistivity, Hall mobility and carrier concentration were determined from the Hall effect measurement equipment using van der Pauw method. For all the films, the thickness was kept at about 200 nm. The grain sizes of films were analyzed using X-ray diffractometer with Cu Kα radiation ($\lambda = 1.540562$ Å). The optical transmittance and reflectance spectra were obtained on UV–vis spectrophotometer in the wavelength range from 250 to 1100 nm. For analysis of chemical binding energy of oxygen ions, XPS characterization was made for as-deposited and annealed films after surface pre-cleaning for 3 min by sputtering.

3. Results and discussion

3.1. Structural properties

The Fig. 1 shows the XRD profiles of the as-deposited and the vacuum annealed AFZO25, AZO films, respectively. All the as-deposited and the annealed films show strong (0 0 2) peaks of preferred orientation, together with relatively weak (1 0 1) and (1 0 3) peaks. It is notable that the intensity of (1 0 1) and (1 0 3) peaks for the as-deposited films slightly increased with increasing amount of AZO in the films, and that intensity of these peaks increased for the annealed films. Inactive Al atoms in the AZO films have been reported to be segregated into grain boundaries and to inhibit the crystallization and preferred orientation of ZnO.[7] Very weak (1 0 1) and (1 0 3) peaks of AZO 100% film could be attributed to these inactive Al atoms. APZO film series also showed very similar preferred orientation.

In Fig. 2, the full width at half maximum (FWHM) of (0 0 2) peaks obtained for AFZO series and APZO series samples are compared. For both AFZO and APZO film series, FWHM decreased with increasing AZO content, and vacuum annealing resulted in slight reduction of FWHM. These implies that the average crystallite size with (0 0 2) orientation increases with increasing Al contents in the films, and that annealing causes an increase of the average crystallite size with (0 0 2) orientation. Before annealing and also after annealing AFZO films had lower FWHM than APZO films in the same AZO volume contents. These observations imply that the addition of Al, F enhances crystal growth in ZnO films.

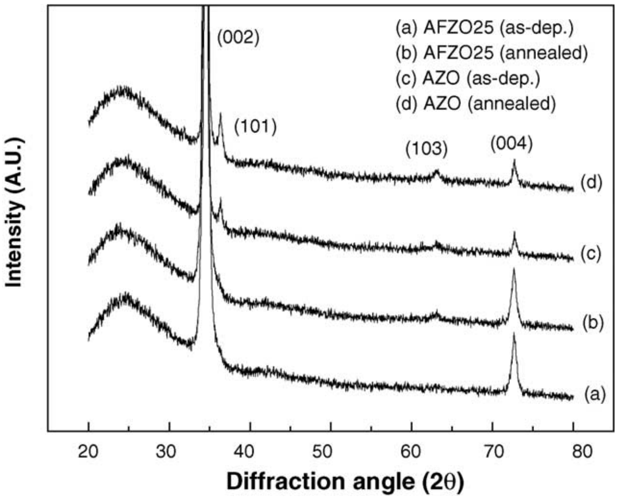

Fig. 1. X-ray diffraction pattern of AFZO25, AZO films as-deposited and vacuum annealed at 300 °C.

3.2. Electrical properties

In Fig. 3(a)–(c), the carrier concentration, Hall mobility and the resistivity obtained for both AFZO and APZO series films before and after annealing are compared, respectively. The carriers of Al and F-doped ZnO films are generated from both the intrinsic type of donors stemming from the interstitial Zn metals or the oxygen vacancies and the extrinsic

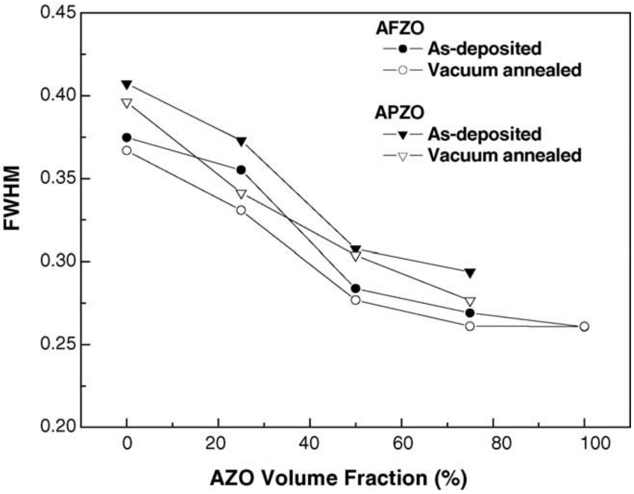

Fig. 2. Full width at half maximum (FWHM) of AFZO and APZO series films with different AZO volume fraction.

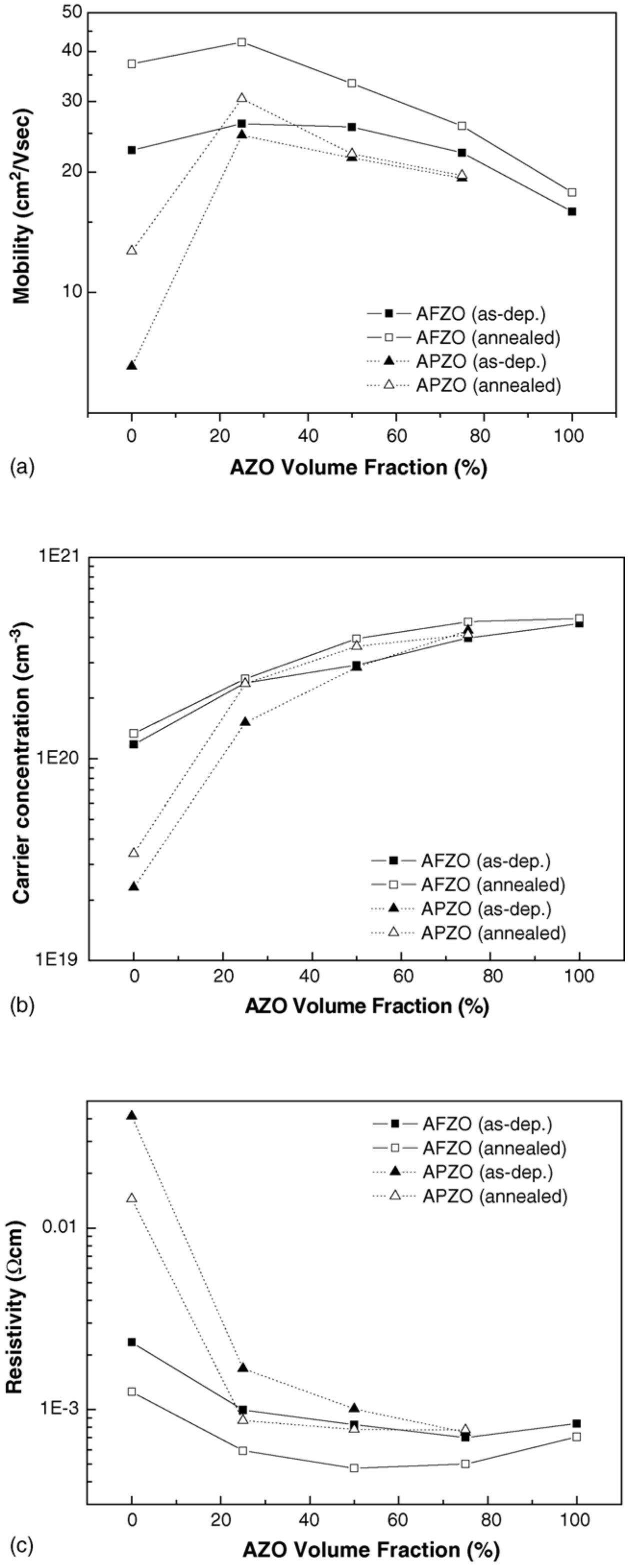

Fig. 3. (a) Carrier concentration; (b) Hall mobility and (c) resistivity of AFZO and APZO series films with different AZO volume fraction as-deposited and vacuum annealed at 300 °C.

type of donors stemming from the substitution of Al and F. By vacuum annealing the oxygen vacancies and the interstitial Zn metals can be created and the carrier concentration will increase.[8] After vacuum annealing the resistivity of all ZnO films became lowered due to the increase of both carrier concentration and mobility. The minimum resistivity of $4.75 \times 10^{-4}\,\Omega\,\mathrm{cm}$ could be obtained for AFZO50 films due to their high mobility and carrier concentration. Vacuum annealed AFZO25 film showed the maximum mobility of $42.2\,\mathrm{cm}^2/\mathrm{V\,s}$. Fig. 4 shows the XPS oxygen 1s binding energy of as-deposited APZO25, AFZO25, annealed APZO25 and AFZO25 films. The binding energy for O 1s of ZnO structure is 530 eV and that of Al_2O_3 is 531.6 eV. Chen et al. reported that the component of the O 1s located at about 531.25 eV is attributed to O^{2-} ions in oxygen deficient regions.[9] The components of O 1s in Al_2O_3 and oxygen deficient regions could not be fitted clearly. The small O 1s component located at about 532 eV is mainly due to the chemisorbed oxygen impurities such as O^{2-}, O^{-} and $O_2{}^{-}$. ZnO thin films are chemically active and the oxygen will be adsorbed easily at the surface and grain boundary. These chemisorbed oxygen acts as trap site of free electrons and increase the potential barrier of grain boundary. Minami reported that the mobility of doped ZnO films with carrier concentrations of 10^{20}–$10^{21}\,\mathrm{cm}^{-3}$ was mainly limited by the ionized impurity scattering, and ZnO films with carrier concentrations of 10^{19}–$10^{20}\,\mathrm{cm}^{-3}$ was dominated by the grain boundary scattering.[7] Since all the films except pure ZnO film have carrier concentration in the range of 1×10^{20}–$5 \times 10^{20}\,\mathrm{cm}^{-3}$, grain boundary scattering mechanism cannot be excluded completely. After vacuum annealing of AFZO25 and APZO25, the reduction of the high binding energy oxygen peak at about 532 eV can be seen clearly in Fig. 4, which implies that the grain boundary potential decreases due to the removal of the chemisorbed oxygen at the grain boundary. It is notable from Fig. 3 that vacuum annealing gives rise to a pronounced increase in mobility while only a slight increase in carrier concentration is observed for all AFZO series films. This cannot be explained only by ionized impurity scattering because the mobility of highly degenerate semiconductor is known to be disproportional to carrier concentrations as $\mu \propto n^{-2/3}$.[10] Although the average crystallite size estimated from FWHM was all in the range of 30–40 nm and is larger than the electronic mean free path of all our ZnO films (below 6 nm), the grain boundary potential barrier is believed to influence the mobility of our ZnO films. The mobility decrease of AFZO films with the increase of AZO volume fraction might be explained by the ionized impurity scattering together with the grain boundary scattering. Upon comparing the electrical properties of APZO and AFZO series films, it is clear that vacuum annealing of APZO films also give rise to an increase of mobility but not as much as in the case of AFZO series films. Furthermore, the carrier concentration and the mobility of APZO series films lay below those of AFZO series films at the same volume fraction of AZO. Although Shanthi et al. reported that fluorine did not cause an increase in grain boundary potential in

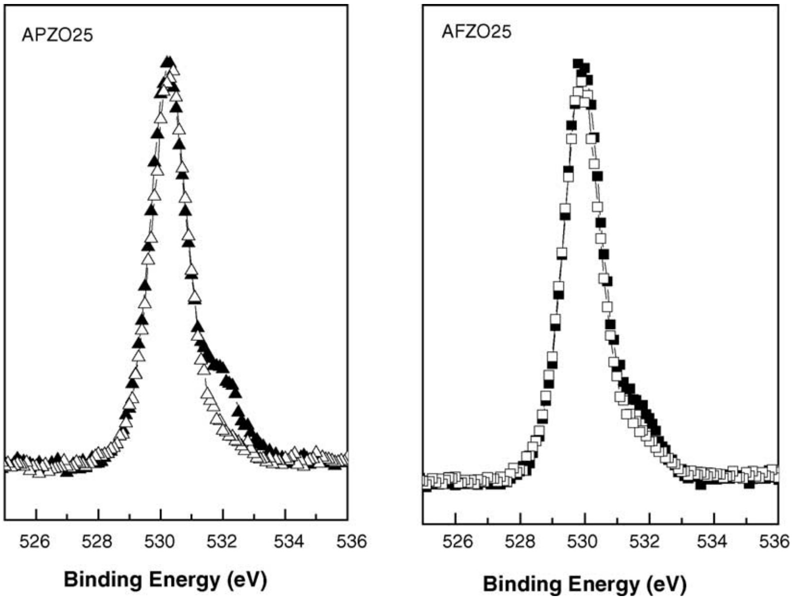

Fig. 4. Oxygen 1s XPS spectra of as-deposited (solid triangle) and annealed (open) AFZO25 and as-deposited (solid square) and annealed (open) APZO25 films.

their F-doped tin oxide films,[11] this could not be confirmed in our films. As shown in Fig. 2, FWHM values of annealed APZO series films are lower than those of AFZO series films. This indicates that the fluorine dopant promotes the crystallization of ZnO films and reduces grain boundary scattering, which eventually would lead to higher mobility observed in AFZO films.

3.3. Optical properties

Fig. 5 shows the plot of the absorption coefficients obtained for the as-deposited and the annealed AFZO, APZO film series. The absorption coefficient was calculated from the measured optical transmittance and reflectance according to the following relation and averaged from the visible wavelength 400–800 nm, where no absorption band occurs:

$$\alpha = \frac{1}{d} \ln \left(\frac{1 - R}{T} \right) \tag{1}$$

where T and R are the optical transmittance and reflectance of the films and d, the thickness of the films. By vacuum annealing, the average absorption coefficients of all the films reduced for the most of visible and near IR range measured in this study. The decrease of absorption in the short wavelength region (about 400–600 nm) after annealing is due to the increase of the optical band gap according to Burstein–Moss effect. After vacuum annealing, the optical band gap of AFZO, APZO films all increased due to the increase of the carrier concentrations. The decrease of absorption coefficient in the long wavelength region (about 600–800 nm) for the vacuum annealed films is thought to be caused by the increase of mobility as this can be explained by the decrease of the low free carrier absorption. Free carrier absorption has been described by Eq. (2) following Drude model:[12]

$$\alpha = \frac{ne^3\lambda^2}{4\pi^2c^3N\mu\varepsilon_0m^{*2}} \tag{2}$$

where n, λ, c, N, ε_0, m^* and μ are carrier concentration, wavelength, light speed, refractive index, vacuum permittivity, effective mass and mobility, respectively. The free carrier absorption is proportional to n/μ and the increase of mobility reduces the free carrier absorption. Annealed AFZO films have lower absorption coefficients than annealed APZO film series because of higher mobility and higher optical band gap of AFZO films. Good transparent and conducting oxides (TCOs) should have low resistivity and visible absorption. Quantitative measure of performance of transparent

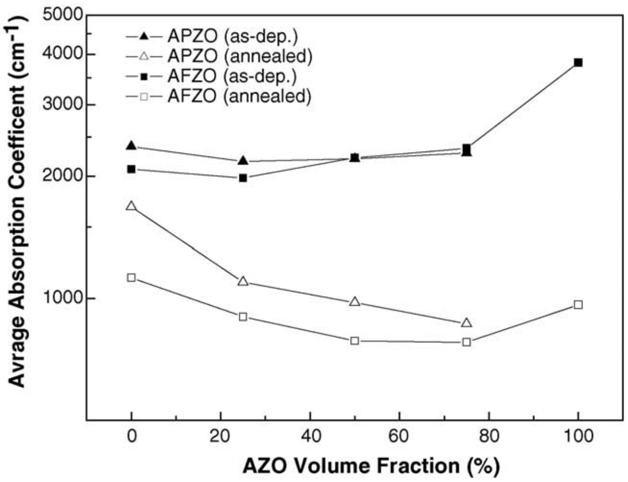

Fig. 5. Average absorption coefficients of as-deposited and vacuum annealed AFZO, APZO films with different AZO volume fraction.

conducting oxide is figure of merit (FOM) defined as:[8]

$$\mathrm{FOM} = \frac{1}{\rho\alpha} \tag{3}$$

After annealing, FOM of all ZnO films increased noticeably due to lower visible absorption and higher conductivity than before annealing and FOM of AFZO films series are higher than APZO films at the same AZO volume fraction. AFZO50 had the highest FOM value of 2.67 Ω^{-1} after annealing.

4. Conclusions

Transparent and conducting ZnO films doped with Al and F have been deposited on glass by co-sputtering ZnO:ZnF_2 and ZnO:Al_2O_3 ceramic targets. After annealing at 300 °C for 2 h in vacuum, the minimum resistivity of $4.75 \times 10^{-4}\ \Omega\,\mathrm{cm}$ was obtained for AFZO50 film, and the highest mobility of $42.2\ \mathrm{cm^2/V\,s}$ was found in AFZO25 thin film. From XRD measurements it was found that fluorine dopants enhanced the crystallization of ZnO and reduce grain boundary scattering. The analysis of XPS spectra for the as-deposited and the annealed AFZO25 films revealed that chemisorbed oxygen ions reduce the mobility of ZnO films, and that after vacuum annealing most of chemisorbed oxygen was removed giving in the increase in mobility. Vacuum annealing of the AFZO films resulted in the decrease in both the optical absorption and the resistivity, giving the highest FOM of 2.67 Ω^{-1} for AFZO50 thin film. It can be concluded that dual doping of F and Al might be a plausible method for obtainment of transparent conducting ZnO films with higher performance.

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