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Effect of deposition temperature and F_2 flow rate on the characteristics of F-doped ZnO films

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In this study, we would investigate the fluorine (F)-doped ZnO films (FZO) using radio frequency (RF) magnetron sputtering method at room temperature (RT) and 200°C. At first, ZnO powder was used to form the ZnO ceramic target. The F_2 flow rate ($F_2/(Ar + F_2)$) was changed in the range of 0–0.25%, and the F_2 ratio was controlled using the mixing gases of (F_2(5%) + 95% Ar) and pure Ar. FZO films were deposited on the EagleXG glass (Corning) and the films' thickness was about 330 nm by controlling the deposition time. After the FZO films were deposited, their crystalline structure and optical and electrical characteristics were well investigated as a function of deposition temperature and F_2 flow rate. We would prove that the characteristics of the 200°C-deposited FZO films were better than those of the RT-deposited FZO films.

Keywords: Deposition temperature; F_2 flow rate; optical and electrical characteristics.

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1. Introduction

Tin-doped indium oxide (ITO) is the most used material for transparent conductive metal-oxide films in today's industries, but in the ITO films In is a toxic material and it has the problems of few quantities of output and high price, and ITO films are easily to produce the reduction reaction with hydrogen plasma.[1] For that, many researches have investigated the properties of the ZnO-based films because the ZnO is a non-toxic material. Even the transmittance of the ZnO-based films is high and competed with ITO films in the visible wavelength range, they have the shortcoming of high resistivity. The low resistivity of ZnO-based films can be obtained from the presences of oxygen vacancies and zinc interstitials and from the addition of different dopants, like Ti, Al, and Ga.[2–4] Recently, many studies had used F^--based ions as the dopants of the ZnO-based films to investigate their characteristics.[5,6] In this study, we would investigate the F-doped ZnO (FZO) films using ZnO ceramic as target and radio frequency (RF) sputtering as deposition method, the different flow rates of F_2 were introduced during the deposition process. The effect of different F_2 flow rates on the properties of FZO films would be well investigated in this study.

2. Experimental Procedure

In this work, ZnO powders (99.999%) were ground and sintered at 1350°C to form the ZnO target. The chamber pressure of RF magnetron sputtering was pumped to less than 5×10^{-6} Torr, and the deposition parameters were controlled at deposition pressure and power of 5×10^{-3} Torr and 100 W, working distance of 8 cm, and deposition temperatures of room temperature (RT) and 200°C. Pure argon with 20 sccm was introduced into the chamber and the different F_2 flow rates ($F_2/(Ar+F_2) = 0$, 0.05%, 0.1%, and 0.25%) were achieved by introducing the mixing atmosphere of 5% F_2 + 95% Ar into the chamber. The EagleXG glass with the area of 2.5×2.5 cm^2 and the thickness of 0.7 mm was used as substrate. FZO films' thicknesses of ∼330 nm were achieved by controlling the deposition time, while the FZO films' crystalline structure was identified by X-ray diffraction (XRD) pattern. A Hall effect measurement system was used to find the electrical properties of the FZO films. Optical transmission spectra were recorded using a JASCO V-570 UV-Vis-NIR spectrophotometer in the 300–2500 nm wavelength range.

3. Results and Discussion

The XRD patterns of the FZO films are shown in Fig. 1 as a function of F_2 flow rate and deposition temperature. The diffraction peak of the (002) plane was observed in all FZO films and diffraction peak of the (004) plane was only observed in 200°C-deposited ZnO films. However, as the same F_2 flow rate was used, the diffraction intensity of the FZO films deposited at 200°C was higher than that deposited at RT. As higher deposition temperature is used, the FZO particles will have higher activation energy, that will be the reason for the enhancement of the crystallization.

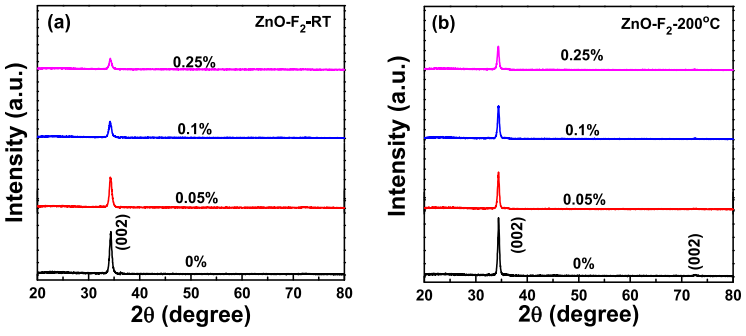

Fig. 1. (Color online) XRD patterns of the FZO films as a function of F_2 flow rate, deposited at (a) RT and (b) 200°C.

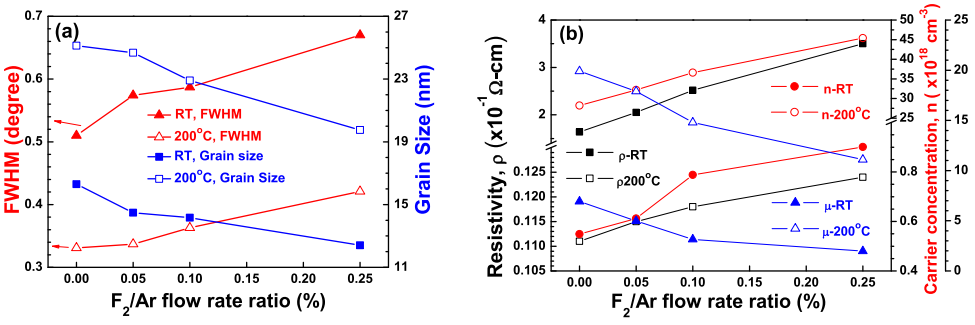

Fig. 2. (Color online) (a) FWHM values and grain sizes and (b) Hall effect measurements of the FZO films as a function of F_2 flow rate and deposition temperature.

Figure 2(a) shows the full width at half maximum (FWHM) values of the (002) plane and the grain sizes of the FZO films. When the deposition temperature was RT (200°C), the 2θ value of the (002) plane changed from 34.31° (34.43°) to 34.35° (34.44°) as the F_2 flow rate increased from 0% to 0.25%. The Zn^{2+} and O^{2-} ions have the radii of 0.74 Å and 1.38 Å, respectively, and F^- ions have the radius of 1.31 Å. The radius of F^- ions is similar to and smaller than that of O^{2-} ions, for that F^- ions will substitute the sites of O^{2-} ions to increase their conductivity and the 2θ value of the (002) plane is shifted to higher value. Equation (1) is the Scherrer formula, which can be used to find the grain sizes of the FZO films.

$$D = (0.9\lambda)/(\beta \cos\theta)\,, \tag{1}$$

where D is the grain sizes, λ is 1.054056 nm, β is FWHM value, and θ is diffraction angle. The results in Fig. 2(a) indicate that the grain sizes decreased and FWHM value increased with increasing F_2 flow rate. However, the research of Cullity and Stock found that as grain size decreases, the grain boundary in the unit area increases, the electronic mobility degenerates, and the resistivity increases.[7]

Hall effect measurements of the FZO films for resistivity (ρ), Hall mobility (μ), and carrier concentration (n) are shown in Fig. 2(b). As Fig. 2(b) shows, the n increased, the μ value decreased, and thus the ρ value increased with the increasing F_2 flow rate. The addition of F^{-1} ions is hoped to substitute the sites of O^{-2} ions and increase the conductivity of the FZO films. But we believe that F^{-1} ions do not substitute the sites of O^{-2} ions to become the active dopant, but they will cause many defects in the internal part or boundaries of the FZO grains. For that, the crystallization and the μ value of the FZO films decrease as the F_2 flow rate increases. As the deposition temperature was 200°C, the films' structure became more densified, the n value and the μ value apparently increased and then the ρ value decreased. The 200°C-deposited undoped ZnO films had the optimum properties of $\mu = 19.9$ cm^2/V-s, $n = 2.82 \times 10^{19}$ cm^{-3}, $\rho = 1.11 \times 10^{-2}$ Ω-cm.

The transmission spectra of the FZO films are shown in Fig. 3. The average transmittance of all the FZO films in the visible light range was higher than 87%, independent of the F_2 flow rate. As Figs. 3(a) and 3(b) show, when the deposition temperature was RT (200°C), the F_2 flow rate was 0%, 0.05%, 0.1%, and 0.25%, the average transmittance of the FZO films was 90.3% (91.3%), 87.9% (91.3%), 88.5% (90.4%), and 89.2% (88.7%), respectively. As the F_2 flow rate increased, the optical absorption edge at the UV region of transmission spectra experienced an apparent shift to a shorter wavelength regardless of the deposition temperature, and the greater sharpness was also noticeable in the absorption edge. Also, the optical plasma oscillation frequency was not observed in all FZO films. The energy band gap (E_g) value can be obtained using Eq. (2).

$$\alpha h\nu = C(h\nu - E_g)^{1/2}, \tag{2}$$

where α, C, and $h\nu$ are absorption coefficient, a constant, and the incident light energy, respectively. The variation of $(\alpha h\nu)^2$ against $h\nu$ (energy) is plotted in Fig. 4, and the E_g values can be found by extrapolating a straight line at $(\alpha h\nu)^2 = 0$. As the F_2 flow rate increased from 0% to 0.25% and the deposition temperature was

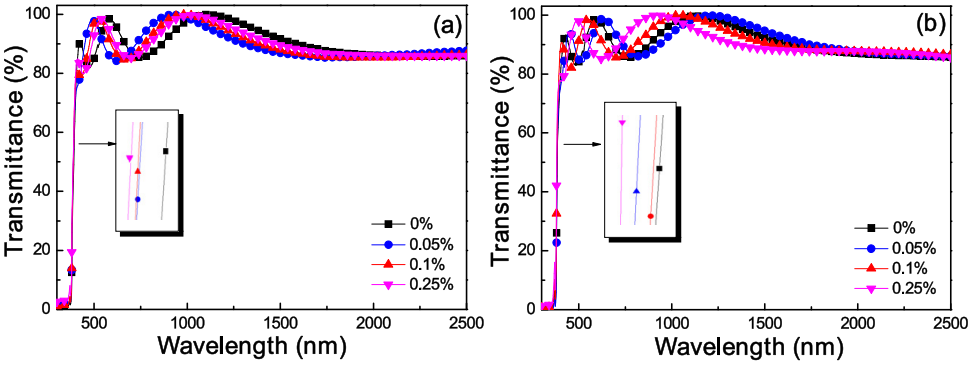

Fig. 3. (Color online) Transmission spectra of the FZO films as a function of F_2 flow rate, deposited at (a) RT and (b) 200°C.

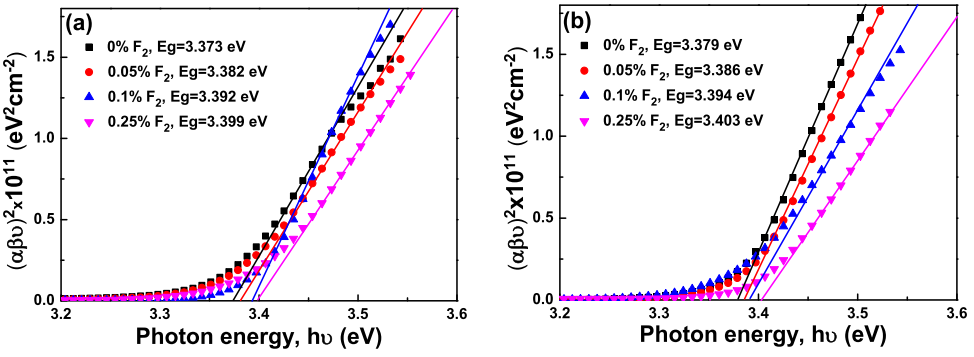

Fig. 4. (Color online) $(\alpha hv)^2$ against hv (energy) plots of the FZO films, deposited at (a) RT and (b) 200°C.

RT (200°C), the Eg value increased from 3.373 (3.379) eV to 3.399 (3.403) eV. The calculated results prove that FZO films deposited at 200°C will have larger E_g value. Many factors will affect the transmission spectra of the FZO films. At first, the results in Fig. 1 suggest that the defects in the FZO films decrease with increasing deposition temperature. Second, the results in Fig. 2(a) suggest that as the FZO films have fewer defects, the increase in the E_g value is caused by the increase in carrier density.

4. Conclusions

When the deposition temperature of the FZO films was RT (200°C) and the F_2 flow rate was increased from 0% to 0.25%, the average transmittance was in the range of 90.3–91.3% (88.7–91.3%), and the E_g value increased from 3.373 (3.379) eV to 3.399 (3.403) eV. In this study, we had proven that the 200°C-deposited FZO films had better crystallinity and electrical properties and larger E_g value as compared with those of the RT-deposited ones.

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