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Electrical and optical properties of ZnO thin films doped with Nb deposited by rf magnetron sputtering

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Abstract. The optical and electrical properties are investigated of Nb doped ZnO (ZnO:Nb) thin films deposited by r.f. magnetron co-sputtering on glass substrates at different temperatures, T_s , between 50 °C and 500 °C. The optical transmittance and reflectance spectra are measured and used to determine the optical band gap. The values of the optical band gap are in the range 3.29- 3.44 eV and are typical for ZnO thin films. The films have about 90 % transparency, while their resistivity increases in the range of $2.2 \times 10^{-3} \Omega \text{ cm}$ - $6.4 \times 10^2 \Omega \text{ cm}$ as T_s is raised. The results demonstrate the potential of using Nb-doped ZnO films as a transparent conductive oxide in thin films solar cells and various optoelectronic devices.

1. Introduction

The thin film technologies and ZnO have been studied for the development of new electronic thin film devices [1], magnetic memories [2], transparent conductive oxides (TCO) for applications in thin film solar cells [3] etc. ZnO thin films doped with transition elements provide a variety of applications in gas sensors [4], diluted magnetic semiconductors (DMS) [5], etc. Studying the properties of doped ZnO with different metal (Al, V, Ga, Nb, Tb, etc.) [6-9] has led to the attractive idea of developing a new kind of highly conductive transparent thin films.

In this paper, a study is reported of the influence of varying the substrate temperature (50 °C – 500 °C) on the optical and electrical properties of Nbdoped ZnO thin films (ZnO:Nb) deposited by magnetron r.f. sputtering in Ar atmosphere.

2. Experimental

The ZnO thin films doped with Nb (ZnO:Nb) were prepared by r.f. magnetron co-sputtering of a ZnO target with pieces of Nb plates with area of 80 mm² in the maximum erosion zone on its surface in Ar atmosphere at pressure of 0.5 Pa and r.f. power of 160 W using ALCATEL-DION 420 equipment. The films were deposited on glass substrates at different temperatures, T_s , in the range 50 °C – 500 °C. The thickness of the layers was between 700 and 950 nm, as measured by a Talystep Hobson profilometer.

Transmittance and reflectance spectra were obtained by a Shimadzu UV.3600 spectrophotometer in the range of 320 - 1800 nm. The resistivity of the films was measured by the four-point probe method using a VEECO instrument.

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3. Results and discussion

The values of the resistivity, ρ , of ZnO:Nb films are in the range $2.2 \times 10^{-3} \Omega \text{ cm} - 6.4 \times 10^2 \Omega \text{ cm}$ (table 1) and are close to the ones reported in [10]. The values of ρ increase with T_s , particularly for $T_s > 350 \text{ }^\circ\text{C}$ (figure 1). This is probably due to the changes in the stoichiometry of the films deposited at higher temperatures, as reported in [10]. At higher T_s , the deposition conditions favor a higher rate of reflection of ZnO atoms arriving at the substrate during the sputtering process from the substrate, thus increasing the concentration of O atoms in the lattice of ZnO films deposited (respectively decreasing the O vacancies). This results in an increased ZnO films resistivity of, as Zn in the ZnO lattice is a donor.

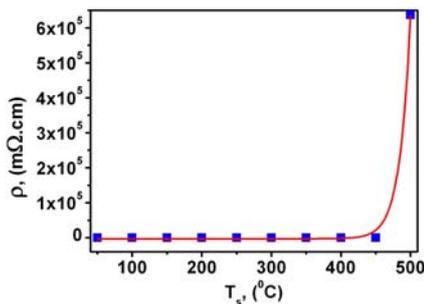


Figure 1. Dependence of ZnO:Nb films resistivity on the substrate temperature.

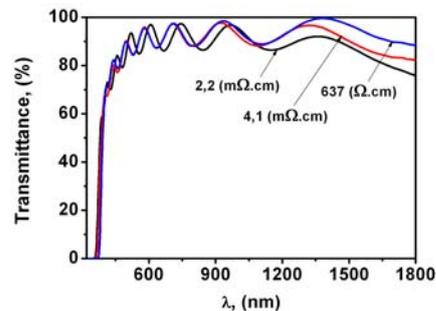


Figure 2. Transmittance of ZnO:Nb films with different resistivity.

Transmittance spectra of the ZnO:Nb thin films are presented in figure 2. The spectra are corrected for the transmittance of the glass substrate. All spectra demonstrate transmittance value about 90% in the range 550 – 1000 nm. In the IR region beyond 1200 nm, the transmission of the films with resistivity $< 4.1 \times 10^{-3} \Omega \cdot \text{cm}$ decreases due to the absorption of by free carriers (plasma resonance).

The values of n are calculated from the transmittance [11] in the range 500 – 1200 nm and are given in table 1. The value of n is about 1.99 and decreases slightly as T_s increases. This could be related to the oxidation of interstitial Zn in the films or to the decreasing concentration of O vacancies at higher T_s , which results in a decrease in the free carrier concentration. It is probable that the effect of any possible increase in the mobility, μ , upon ρ is less pronounced than the changes in the film stoichiometry [12].

The dependences of the absorption coefficient, α , on the energy, $h\nu$, for the ZnO:Nb films are presented in figure 3. The absorption coefficient was calculated as in [9].

The value of the energy band gap, E_g , the Urbach energy, E_0 , and the coefficient B^2 (table 1) are calculated for direct inter-band electron transitions as described in [8, 13, 14]. The spectral dependence of α exhibits two regions: a power law at high photon energies and an exponential one at lower energies. The formula for direct allowed transitions can be used to obtain the optical gap, E_g :

$$\alpha(h\nu) = B[(h\nu - E_g)^{1/2}/h\nu] . \quad (1)$$

In the lower energy range ($h\nu < E_g$), where α varies exponentially with the photon energy, the spectral dependence of the absorption edge follows the Urbach formula [10, 15, 16]:

$$\alpha(h\nu) = \alpha_0 \exp[(h\nu - E_l)/E_0] , \quad (2)$$

where α_0 is the Urbach absorption at the edge (E_l , where $E_l < E_g$), and E_0 is the Urbach energy.

Table 1. The values of the optical band gap, E_g , Urbach tail, E_0 , the coefficient B (values of B^2 are given), refractive index, n , the thickness and the resistivity, ρ , of ZnO:Nb films deposited at different substrate temperature T_s .

sample	T_s , ($^{\circ}$ C)	Thickness, (nm)	E_g , (eV)	E_0 , (meV)	B^2 , ($\text{cm}^2 \cdot \text{eV}$)	n , refractive index	ρ , ($\text{m}\Omega \cdot \text{cm}$)
D262 ZnO:Nb	50	860	3.42	77	8.42E11	1.99	2.2
D263 ZnO:Nb	100	950	3.44	76	7.79E11	1.97	2.5
D264 ZnO:Nb	150	760	3.43	77	9.84E11	2.00	3.95
D265 ZnO:Nb	200	710	3.37	72	1.15E12	1.96	4.1
D337 ZnO:Nb	250	810	3.37	71	1.14E12	1.95	4.2
D268 ZnO:Nb	300	750	3.38	69	1.22E12	1.99	4.9
D269 ZnO:Nb	350	850	3.38	69	1.25E12	1.99	3.5
D270 ZnO:Nb	400	750	3.34	67	1.32E12	1.95	13.5
D338 ZnO:Nb	450	860	3.32	62	1.44E12	1.94	15
D271 ZnO:Nb	500	770	3.29	59	1.52E12	1.93	6.37×10^5

The spectral dependence of the absorption coefficient of ZnO:Nb films is shown in figure 4. The values obtained of the band gap are in the range 3.29 – 3.44 eV and are typical for ZnO. The value of the band gap decreases as T_s increased, as seen in figure 4. The blue shift is observed for the films with lower resistivity which is attributed to the Burstein–Moss effect [17].

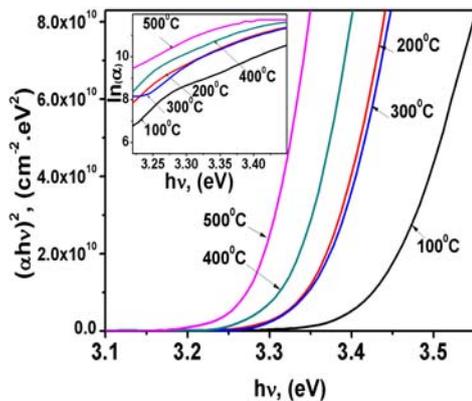


Figure 3. Dependence of $(\alpha hv)^2$ on $h\nu$. The inset shows the plot of $\ln \alpha$ vs. $h\nu$.

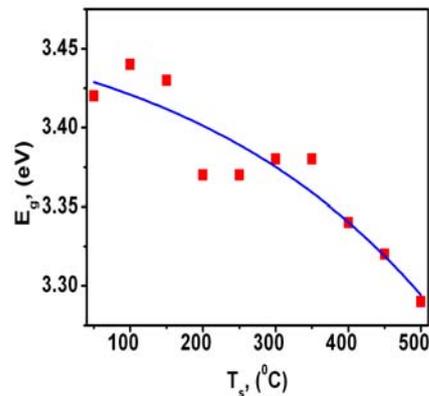


Figure 4. Dependence of the optical band gap on the T_s .

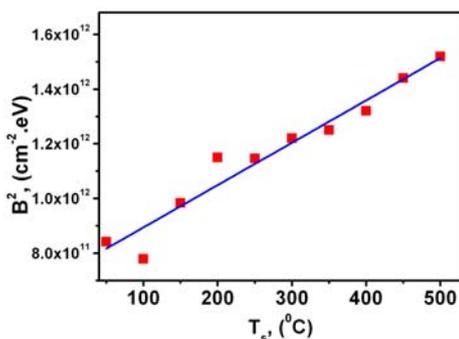


Figure 5. Dependence of the coefficient B^2 on the substrate temperature.

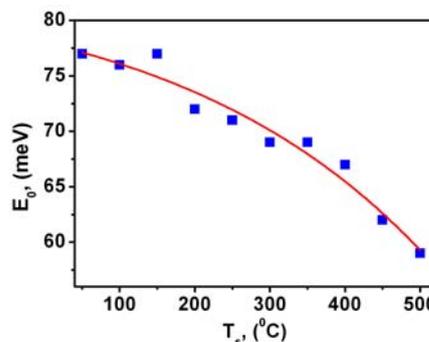


Figure 6. Dependence of the Urbach energy E_0 on the substrate temperature.

The variation of the coefficient B^2 and the Urbach energy, E_0 , with the substrate temperature is shown in figures 5 and 6, respectively. The values of the coefficient B^2 increase with the substrate temperature. In contrast, the Urbach energy has an inverse dependence on T_s . The Urbach region ($h\nu < E_g$) is due to the perturbation of the parabolic density of the states at the band edge. The increase of the structural disorder results in an increase in Urbach energy. The coefficient B^2 and the Urbach energy are assumed as being parameters of the conduction and valence band tail states, respectively [18, 19]. A decrease in B^2 and an increase in E_0 imply an increase in the band tails' width. The dependences observed for ZnO:Nb demonstrate that the band tails width decreases with the increase of the substrate temperature, probably due to the better structural properties of the films deposited at higher T_s , as is reported in [10,13].

Conclusions

The influence was studied of the substrate temperature on the optical properties and electrical resistivity of ZnO thin films doped with Nb. The films have transmittance about 90% in the visible range. The resistivity of the deposited films decreases with T_s . The films deposited at substrate temperature $T_s = 50$ °C exhibited lower resistivity (2.2×10^{-3} Ω.cm). The values of the optical band gap of the ZnO:Nb films are in the range of 3.29 – 3.44 eV and decrease as T_s is raised. The refractive index is in the range 1.93 – 2.00 at about 500 nm. The ZnO:Nb film deposited at lower T_s (50 – 100°C) are transparent (~90%). They have low resistivity and demonstrate a potential for application as a transparent conductive oxide in thin film solar cells and LED.

Acknowledgements

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