Optical and electrical properties of ZnO doped thin films doped with Al, V and Nb

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This study addresses the optical and electrical properties of ZnO thin films doped with Al, V and Nb (ZnO:Al, ZnO:V and ZnO:Nb, respectively) deposited by r.f. magnetron sputtering in Ar atmosphere. The films are deposited on glass substrates without heating and heated at 100^0C, 150^0C and 275^0C. The optical spectra of transmittance and reflectance are measured and the optical band gap of the films is determined. The different films have band gap values in the range of 3.37-3.57 eV. The films have about 90% transmittance and their resistivity is in the range of 8.5-2.0 mΩ.cm. The influence of doping elements on the optical and electrical characteristics of the obtained thin films is discussed.

1 Introduction The transparent conductive oxides (TCO) have an important role for the conversion efficiency of the thin film solar cells, e.g., collection of generated charges and improvement of device absorption [1]. The TCO based on undoped and doped ZnO films are widely used because they are cheap, can be textured for light trapping and readily produced for large scale coatings [2]. They allow tailoring of the absorption in the UV region and have a low temperature of deposition [3].

Different technologies are used for preparation of transparent and conductive layers in dependence on the technique of deposition - chemical vapor deposition [4], sol-gel method [5], pulsed laser ablation [6], magnetron sputtering [7]. The magnetron sputtering is attractive and widely used because of possibility of large deposition area, film packing density and uniformity, low substrate temperature, etc. The films properties are very sensitive to the parameters of deposition and their control. It is established that the process of thin films doping with Al, In, Ga improves their electrical properties [8]. Recently transition metals (V, Nb) are used as dopants of ZnO to obtain transparent conductive oxide thin films and this encourages the preparation and study of doped ZnO thin films [9, 10].

In this article we report the results on the optical and electrical properties of ZnO films doped with Al, V and Nb (ZnO:Al, ZnO:V and ZnO:Nb, respectively) deposited by r.f. magnetron sputtering at different substrate temperatures.

2 Experimental The films are deposited on glass substrates ultrasonically cleaned in H_2O_2 + H_2SO_4 (1:1) solution and rinsed in deionized water. During the deposition the substrates are kept without heating (WH) and heated at 100^0C and 150^0C, and additionally at 275^0C in the case of ZnO:V. ZnO:Al films are deposited by r.f. magnetron sputtering of sintered ZnO+Al_2O_3 target (100 mm diameter, with 2 wt% Al_2O_3) in Ar (0.7 Pa) atmosphere with sputtering power of 150 W. ZnO:V films are obtained by r.f. magnetron sputtering of sintered ZnO target (100 mm diameter) with small plates of V (total area of 150 mm^2) in the maximum erosion zone on its surface in Ar (0.5 Pa) atmosphere and sputtering power of 180 W. ZnO:Nb films are deposited by r.f. magnetron sputtering of sintered target ZnO (100 mm diameter) with small plates of Nb (total area of 80 mm^2) in the maximum erosion zone on its surface in Ar (0.5 Pa) atmosphere with sputtering power of 160 W. Our preliminary results demonstrate that the lowest values of the resistivity, ρ, are

Table 1 Calculated values of the optical band gap, E_g, the Urbach tail energy width, E_0, the parameter B^2, the refractive index, n and the resistivity, ρ of ZnO:Al, ZnO:V and ZnO:Nb films in dependence on T_s.

Sample	T_s, (^{0}C)	Thickness, (nm)	E_g, (eV)	E_0, (meV)	B^2, (cm^2.eV)	n, refractive index	ρ, (mΩ.cm)
ZnO:Al	WH	200	3.56	65	8.88E11	1.75	5.5
ZnO:Al	100	200	3.57	62	1.17E12	1.77	2.8
ZnO:Al	150	200	3.50	59	5.90E11	1.84	7.8
ZnO:V	WH	830	3.37	96	8.15E11	2.02	8.5
ZnO:V	100	780	3.48	97	8.43E11	2.10	3.4
ZnO:V	150	970	3.56	126	6.76E11	2.14	2.0
ZnO:V	275	890	3.46	118	6.66E11	2.18	5.7
ZnO:Nb	WH	800	3.48	77	8.42E11	1.99	2.2
ZnO:Nb	100	900	3.56	76	7.79E11	1.97	2.5
ZnO:Nb	150	700	3.49	77	9.84E11	2.00	3.9

obtained at the presented values of r.f sputtering power for three series of samples with different doping. The thicknesses of the obtained films are listed in Table 1 and they are in the range of 200-900 nm. The spectra of optical transmittance and reflectance of the films are measured by Schimadzu 3100 spectrophotometer in the range of 300 - 1800 nm. The calculation of the absorption coefficient is based on the optical spectra for direct interband electron transitions. The values of the refractive index, n, are calculated from the films transmittance spectra. The thickness of the films is measured by a profilometer „Talystep". The sheet resistance of the films is measured by a four point probe method using Veeco apparatus and the resistivity, ρ, is calculated.

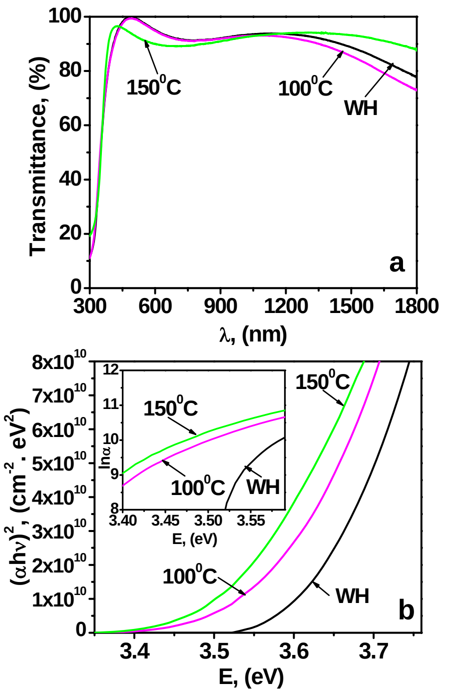

Figure 1 Dependence of the transmittance of the wave lendth (a) and of the absorption coefficient as a product $(\alpha.h\upsilon)^2$ on energy (b) of ZnO:Al thin film deposited at different substrate temperatures.

3 Results and discussion Table 1 presents the values of the measured and calculated characteristics of the obtained films.

The values of the resistivity of the films are in the range of 2.0-8.5 mΩ.cm and they vary slightly with the substrate temperature, T_s. The minimal values are obtained for ZnO:Al and ZnO:Nb films deposited at T_s=100^{0}C and for ZnO:V at T_s=150^{0}C.Figures 1a, 2a and 3a show the spectra of transmittance VS photon energy of ZnO:Al, ZnO:V and ZnO:Nb films, respectively. The spectra are corrected for the transmittance of the glass substrate.

Figures 1b, 2b and 3b present the dependence of the coefficient of absorption, as a product $(\alpha.h\upsilon)^2$, of the ZnO:Al, ZnO:V and ZnO:Nb, respectively, on energy.

The transmittance of the ZnO:Al and ZnO:Nb films is about 90 % in the wavelength range between 550-1200 nm. The samples ZnO:V (Fig. 2a) demonstrate lower transmittance values of 75-85% in the same wavelength range. The absorption bands at about 480–560 nm and 800-820 nm are observed in the spectrum of the samples ZnO:V, more pronounced in the spectrum of the film deposited at T_s=150^{0}C. These bands are typical for transitions of d-d electrons in V^{+2} ions that substitute for Zn in the ZnO:V lattice [9]. In the IR region beyond 1200 nm the transmission decreases for the ZnO:V film deposited at T_s= 100^{0}C, 150^{0}C and 275^{0}C due to the absorption of free carriers (plasma resonance). The transmittance spectrum of the ZnO:V film demonstrates that plasmonic absorption has maximum for the ZnO:V films deposited at T_s=150^{0}C. This is confirmed by the fact that the resistivities of the V doped ZnO films deposited at these temperatures have the lowest values. The vanadium concentration according to EDS analysis [11] varies between 0.86-0.89 at.% at T_s in the range of 150-500^{0}C.

The spectral dependences of the absorption coefficient, α, (Fig. 1b, 2b and 3b), are calculated from the optical spectra of transmittance and reflectance by the equation [12]:

$$\alpha_\lambda=(1/d).\ln[(1-R_\lambda)^2/T_\lambda] \qquad (1),$$

where R_λ – reflectance and T_λ – transmittance spectra, d – film thickness.

The optical band gap of the films is calculated for direct interband electron transitions at higher energies, $h\upsilon>E_g$, according to the Tauc formula [13]:

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

where B is a constant.

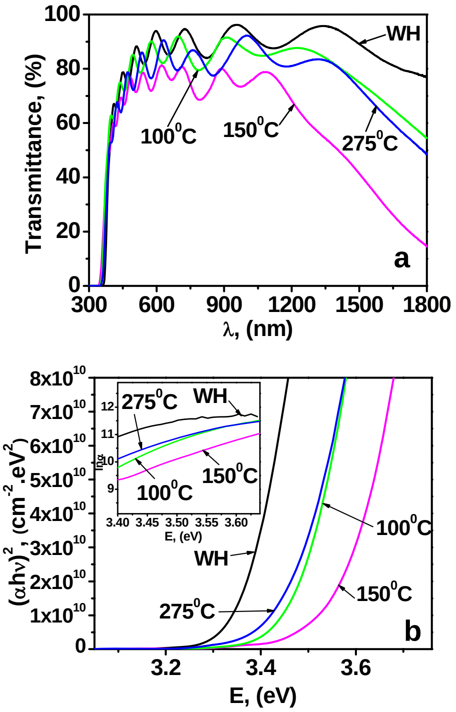

Figure 2 Dependence of the transmittance of the wave lendth (a) and of the absorption coefficient as a product $(\alpha.h\upsilon)^2$ on energy (b) of ZnO:V thin film deposited at different substrate temperatures.

The value of the parameter B is inversely proportional to the extent of the tail state at the conduction and valence band [14].

In the region where $h\upsilon<E_g$ the spectral dependence of α is determined by the Urbach formula [15]:

$$\alpha(h\nu) = \alpha_0 \exp[(h\nu - E_l)/E_0] \qquad (3),$$

where α_0 – absorption coefficient at the edge E_l, E_0 - the energy width of the Urbach tail, related to the film structural disorder. In the Urbach tail the optical absorption is related to the electron-lattice interaction. This results in an exponential tail below the average band gap energy.

The calculated values of E_g, E_0, parameter B^2, refractive index, *n*, and resistivity, ρ, for the ZnO:Al, ZnO:V, and ZnO:Nb thin films in dependence on T_s are presented in Table 1. The values of E_g and E_0 are calculated to an accuracy of 2% and the values of n to an accuracy of 3%.

All of the deposited films have value of the energy gap in the range of 3.37 – 3.57 eV which are typical for ZnO. In the case of ZnO:Al thin films (Fig. 1b) the energy band gap value decreases, but for ZnO:V (Fig. 2b) it increases with T_s increase. The value of E_g of ZnO:V and ZnO:Nb films has a maximum at T_s of 150^0C and 100^0C, respectively.

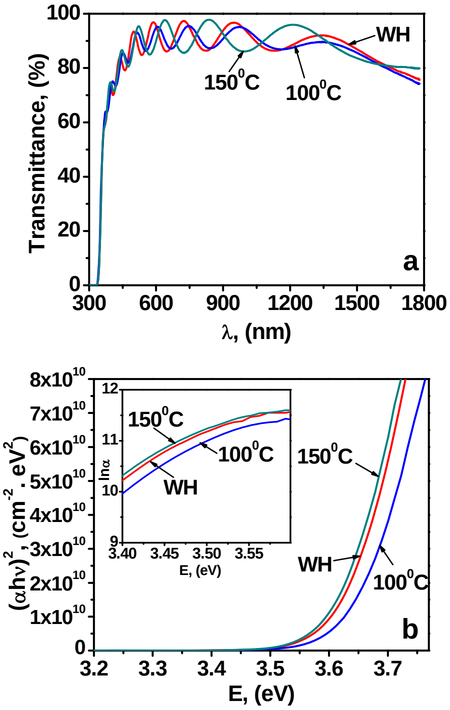

Figure 3 Dependence of the transmittance of the wave lendth (a) and of the absorption coefficient as a product $(\alpha.h\upsilon)^2$ on energy (b) of ZnO:Nb thin film deposited at different substrate temperatures.

The Urbach energy of ZnO:Al films decreases with T_s which demonstrates improvement of their structure as reported earlier [16]. In the case of ZnO:V E_0 has maximum for the film deposited at T_s of 150^0C. It has to be noted that this sample has the lowest value of the resistivity and the film is highly doped with V which results in deterioration of the lattice and increase of the band tails width. The Urbach energy of ZnO:Nb does not change significantly with T_s, so doping with Nb improves the conductivity and does not deteriorate significantly the ZnO lattice.

The values of Urbah energy in V doped ZnO films are higher than those in doped with Nb and Al ZnO films. The doping impurities substitute for the Zn^{2+} ions in the crystalline lattice. The ionic radius, r, of Al^{3+} (0.55 Å), Nb^{2+} (0.77 Å) and V^{2+} (0.94 Å) ions are different from the Zn^{2+}

(0.74) ionic radius [17]. Thus, the doping of ZnO leads to deformation of the lattice and residual stress, more pronounced in the case of ZnO doped with V. This results in increasing of the Urbach energy, more pronounced in the case of ZnO:V.

The changes of the coefficient B (its increasing or decreasing) correlate with the changes of the Urbach energy (its increasing or decreasing, respectively) which indicates change in the band tails energy of the doped ZnO films in dependence on the substrate temperature and doping.

The values of the refractive index, *n*, (Table 1) at $\lambda \sim 550$ nm are calculated from the transmittance spectra by the method of Swanepoel [18]. The values of *n* of the doped with Al and Nb ZnO films are close to those of undoped ZnO films (~ 1.89) prepared by r.f. magnetron sputtering [19]. The V dopant in ZnO films results in more pronounced increase in the value of the film refractive index. The doping leads to increasing of the energy band tails width and increasing of the refractive index that could be related with the ZnO lattice deformation due to the difference in the doping impurities ionic radius.

Conclusion The study of the optical and electrical properties of ZnO films doped with Al, V and Nb deposited by magnetron sputtering at relatively low substrate temperatures demonstrates that the films are highly transparent and have high conductivity. The ZnO:Al and ZnO:Nb films deposited on glass substrates without heating and heated at 100^0C and 150^0C have a transmittance of about 90%. The doping with V leads to decrease of the ZnO:V transmittance. The optical band gap is in the range of 3.37- 3.57 eV and the refractive index is between 1.75 and 2.14. ZnO:V films demonstrate plasmonic absorption of free electrons in the near IR region. The resistivity of the films is in the range of 2.0 – 8.5 mΩ.cm. The results demonstrate that the ZnO films deposited at relatively low temperatures could be applied as transparent conductive oxide.

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