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Structural, optical and electrical properties of V doped ZnO thin films deposited by r.f. magnetron sputtering

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Abstract. Structural, optical and electrical properties of V doped ZnO thin films deposited by r.f. magnetron co-sputtering on glass substrates at different temperature, T_s, between 150^0C and 500^0C are studied. The EDS analyses indicate that the average vanadium content in the films is in the range of 0.86-0.89 at. %. XRD spectra demonstrate preferential (002) crystallographic orientation with *c*-axis perpendicular to the substrate surface and grains sizes of the films about 21-29 nm. The band gap energy, E_g, values are in the range of 3.44-3.47 eV. The deposited V doped ZnO films have low resistivity - $(2\text{-}8).10^{-3}$ Ω cm. Raman spectra show vibrational phonons modes typical for ZnO. Comparison with the structural, optical and electrical properties of thin films ZnO and ZnO:Al is given.

1. Introduction

The systematic study of the optical, structural, electrical and other properties of thin ZnO films in dependence on the deposition technology is topical nowadays in the development of new electronic thin film devices [1], magnetic memories [2], transparent conductive oxides (TCO) with applications in thin film solar cells [3]. ZnO doped with transition elements provide variety of applications in gas sensors [4], spintronics [5], diluted magnetic semiconductors (DMS) [6] etc. The most frequently used ZnO growth techniques are MOCVD, pulsed laser deposition (PLD), magnetron sputtering and molecular beam epitaxy (MBE). R.f. magnetron sputtering is an attractive technique for deposition of undoped and doped ZnO thin films with different concentration of doping metals [7, 8].

In this work, a study of the influence of V and of the substrate temperature, T_s, on the optical, structural and electrical properties of V doped ZnO thin films deposited by magnetron r.f. sputtering in Ar atmosphere is reported. The results are compared with data for undoped and Al doped ZnO films.

2. Experimental

Thin ZnO films doped with V (ZnO:V) were prepared by r.f. magnetron co-sputtering of ZnO target with pieces of vanadium plate in the maximum erosion zone of its surface in Ar atmosphere at a

pressure of 0.5 Pa and r.f. power of 180W. The films were deposited on glass substrates at different temperatures, T_s, between 150^0C and 500^0C. The thickness of the layers was 600 nm.

The film structure was studied by XRD and Raman spectrometry. XRD spectra were obtained using a Brucker D8 Advance spectrometer with Cu K_α radiation: λ Cu $K_{\alpha1}$ =1.540560 Å and λ Cu $K_{\alpha2}$ = 1.544426 Å (intensity half of that of λ Cu $K_{\alpha1}$). The instrumental broadening in 2θ geometry was 0.04^0. Raman spectra were recorded with a Horiba Jobin Yvon LabRam HR800 spectrometer using the 600 l/mm grating and a HeNe laser for excitation. Raman spectra were measured in back scattering geometry with resolution 1 cm^{-1}. Transmittance and reflectance spectra were measured by a spectrophotometer Shimadzu UV.3600 in the range 300-2600 nm. The vanadium content in the films was determined by Energy Dispersive X-ray Analysis (EDAX) using Link AN10000 system analysis. SEM pictures were obtained by Jeol JSM-840A with $LaBa_6$ cathode. The resistivity of the films was measured by the four point probe method using VEECO instrument.

3. Results and discussion

The concentration of vanadium in the obtained ZnO:V thin films varies little with the substrate temperature, T_s, (table 1). The presented values are averaged after measurements of the concentration at four different points on the surface of the samples. In table 1 the obtained electrical and structural parameters of the films under investigation are presented, as well. For comparison the data of undoped and Al-doped ZnO films are given too.

Table 1. The values of the optical band gap, E_g, Urbach tail, E_0, position of the (002) peak in the XRD spectra, θ, the FWHM of 2θ, Δ2θ, the average grains sizes, D, the concentration of the dopants (Al or V), c, the values of the stress, σ, and the resistivity, ρ, of the films deposited at different T_s.

Sample	T_s, [^{0}C]	E_g, [eV]	E_0, [meV]	2θ, [deg.]	Δ2θ, [deg.]	D, [nm]	c, [at.%]	σ, [GPa]	ρ, [Ω.cm]
ZnO*	150	3.33	63	34.30	0.52	16.0		-0.81	31
ZnO*	275	3.30	59	34.40	0.47	17.7		-0.18	20
ZnO*	500	3.27	60	34.40	0.33	25.2		-0.18	4300
ZnO:Al*	150	3.36	100	34.20	0.62	13.6	1	-1.52	18
ZnO:Al*	275	3.41	120	34.15	0.61	13.4	2	-1.79	5.4
ZnO:Al*	500	3.33	91	34.27	0.62	13.4	1	-0.98	6.2
ZnO:V	150	3.44	91	34.18	0.39	21.3	0.86	-1.62	0.007
ZnO:V	275	3.47	98	34.14	0.33	25.2	0.88	-1.89	0.002
ZnO:V	350	3.47	86	34.19	0.35	23.7	0.89	-1.54	0.004
ZnO:V	500	3.44	83	34.19	0.29	28.6	0.87	-1.54	0.008

*Data from reference [8]

XRD spectra of the films are presented in figure 1. The diffraction patterns show that the deposited ZnO:V films are polycrystalline with reflection corresponding to the (002) plane of the wurtzite structure with c-axis perpendicular to the substrate surface. The peak position of the ZnO:V films is shifted to the lower 2θ, compared to the undoped ZnO films, and are closed to that for Al doped films. This shift to lower 2θ is evidence for the presence of the tensile stress in the films, probably due to the presence of the doping atoms. The (002) peck position shifts slightly to the lower value of 2θ for the ZnO:V sample deposited at $T_s = 275^0$C. The stress in ZnO:V films are higher than in undoped and Al doped ZnO films. With increasing T_s, the Full Wide at Half Maximum (FWHM) of the (002) peak, Δ2θ, and the value of the stress, σ, decreases and the average grain sizes increase, which demonstrates an improvement of the structure with T_s, as in the case of undoped and Al doped ZnO films [8].

The values of the resisitivity of V doped ZnO films are lower than in the case of undoped and Al-doped ZnO deposited at the same conditions and are in the range of $2 \cdot 10^{-3} - 8 \cdot 10^{-3}$ Ω.cm. These

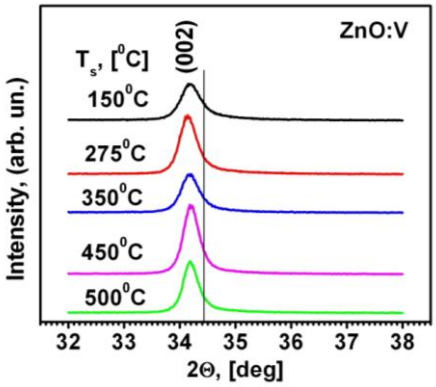


Figure 1. XRD spectra of thin films ZnO:V at different T_s.The black line indicates the position of (002) peak in crystalline ZnO [9].

values are in agreement with results reported in [10]. The average grain size is about 21 – 29 nm and increases with T_s.

Transmittance spectra of the ZnO:V thin films are presented in figure 2. The spectra are corrected for the transmittance of the glass substrate. All spectra demonstrate transmittance value higher than 85% in the range 500 – 1000 nm, independently of T_s. In the IR region beyond 1000 nm where the absorption due to the free carrier concentration (plasma resonance) takes a place, the transmission decreases. An absorption peak at about 850 nm appears for the ZnO:V deposited at $T_s > 275^0$ C more clearly pronounced for the sample with lower resistivity. The peak is attributed to the d-d absorption of V^{2+} ion in tetragonal crystal field [11].

The absorption coefficient, α, was calculated as [12]:

$$\alpha(\lambda) = 1/d \cdot \ln[(1- R(\lambda))^2 / T(\lambda)]$$

where d is the film thickness, T – transmittance and R – the reflectance.

The spectral dependence of α exhibits two regions: a power law one 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, [13]:

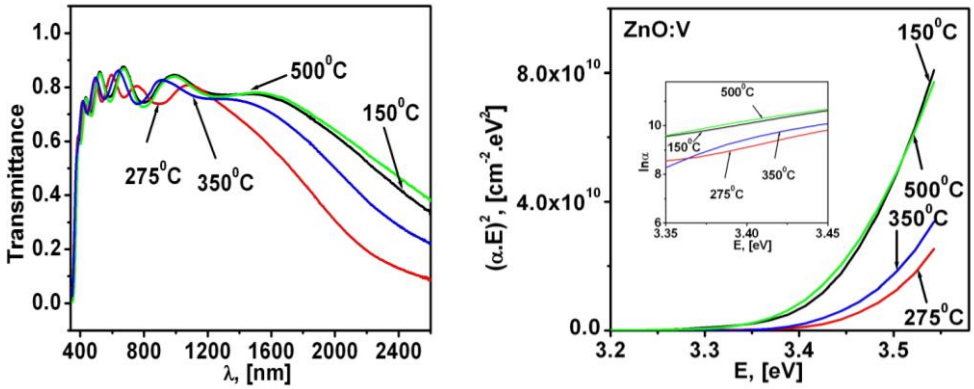
$$\alpha(h\nu) = A[(h\nu - E_g)^{1/2} / h\nu]$$

In the lower energy range ($h\nu < E_g$), where α varies exponentially with photon energy, the spectral dependence of the absorption edge follows the Urbach formula [14]:

$$\alpha(h\nu) = \alpha_0 \exp[(h\nu - E_1) / E_0]$$

where α_0 is the Urbach absorption at the edge (E_1), and E_0 is the Urbach energy. The Urbach region ($h\nu < E_g$) is due to the perturbation of the parabolic density of the states at the band edge. The increasing of the structural disorder results in an increase in Urbach energy.

The spectral dependences of α for sample deposited at different T_s are shown in figure 3. The values of the optical band gap of V doped ZnO films are in the range of 3.44 – 3.47 eV and are typical for ZnO. However they are higher than in the case of undoped and Al-doped ZnO films. The optical energy gap increases with T_s increasing until 275 ^{o}C, above which it decreases. It has to be noted that this sample demonstrates the lowest value of the resistivity (see table 1). The observed widening of E_g in ZnO:V films as compared to undoped ZnO films, could be due to an increase in the donor concentration, related to shallow V donors, as it is in the case of Al doped ZnO films [14]. The Urbach energy decreases with T_s increasing due to the improved structure in accordance with the XRD data. The values of E_o in V doped ZnO are lower than in the Al doped ZnO, however higher than in undoped



(a) (b)

Figure 2. Transmittance spectra (a) and $(\alpha.E)^2$ versus energy, E, (b) for ZnO:V films deposited at different T_s.The insert in (b) shows the plot of lnα vs hν.

ZnO. Possibly, the presence of V results in lower deterioration of the structural order in ZnO compared to Al.

Raman spectra of ZnO:V films are presented in figure 3. The glass luminescence background is substrated before drawing of plots. In the Raman spectra typical for ZnO bands are observed: 276 (B_2), 380 (A_1), 439 (E_2), 580 (LO). The band at 276 (B_2) is related to the build-in electric field in the depletion region in the grains of the films [15]. Additional bands at 509, 607 and 630 cm^{-1} are present as well. These bands cannot be attributed to bulk phonon modes and are probably due to localized ones. The band at 509 cm^{-1} could be assigned to the phonon mode highly localized near the grain boundaries as it is in the case of Al doped ZnO films [15]. This mode was observed when the crystallite size was smaller than 30 nm as in the present case. The 607 and 630 cm^{-1} bands probably have similar origin to the I_1 and I_2 modes in [16] related to dopant complexes or host defects.

The surface morphology of the films was studies by Scanning Electron Microscopy (SEM) and Atomic Force Microscope (AFM). The AFM pictures (figure 4) and SEM micrographs (figure 5) show that the films have column structures. The surface roughness decreases and the homogeneity improve with increasing of the T_s.

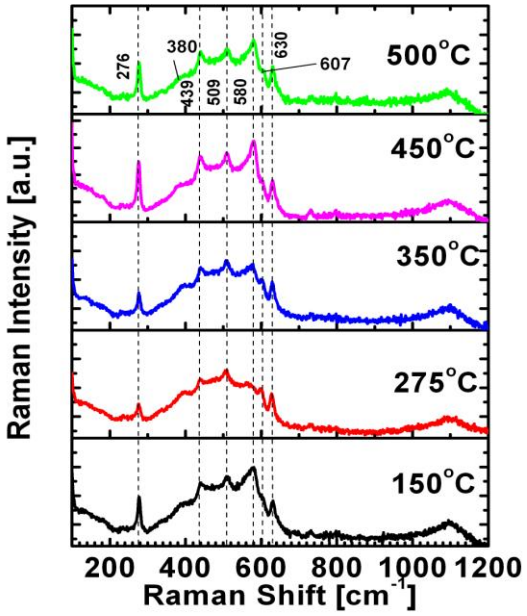


Figure 3. Raman spectra of ZnO:V films deposited at different T_s.

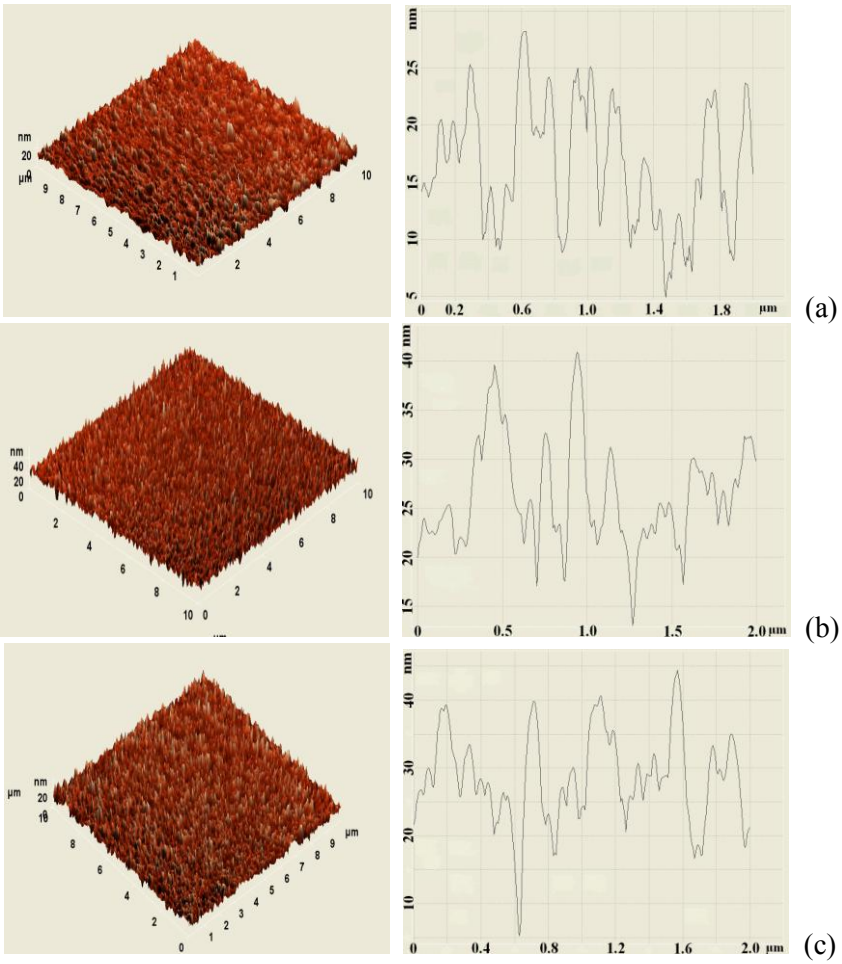


Figure 4. AFM picture of the ZnO:V deposited at T_s 150^0 C (a), 350^0 C (b) and 500^0 C (c).

4. Conclusion

The study of the structural properties of V doped ZnO thin films deposited by magnetron co-sputtering at different substrate temperatures shows wurtzite ZnO structure with c-axis perpendicular to the substrate surface. XRD analyses demonstrate that the crystalline structure improves with T_s

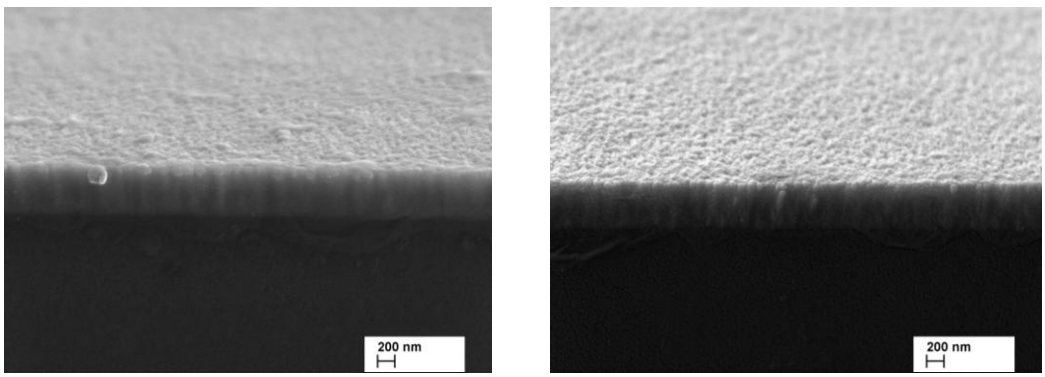


Figure 5. SEM micrographs of the ZnO:V films deposited at T_s 150^o C and 500^oC.

increasing and the grain size increases from 21 to 29 nm. The V concentration does not change with T_s and is about 0.86-0.89%. The thickness of the films is about 600 nm. The optical band gap ranges from 3.42 to 3.47 eV. The Urbach energy is higher than in undoped ZnO films, however lower than in the ZnO:Al films. The Raman spectra contain bands typical for ZnO, however bands due to the grain structure of the films are observed as well. The V doped ZnO films have transparency about 85% and low resistivity in the order of $(2\text{-}8).10^{-3}$ Ω cm. This demonstrate a potential for application of ZnO:V films as transparent conductive oxide in thin films solar cells and different optoelectronic devices.

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