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Transparent and conductive ZnO thin films doped with V

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Abstract

Influence of the vanadium concentrations, C_V, on the structural, optical and electrical properties of V doped ZnO thin films deposited by R.F. magnetron sputtering is studied. The C_V in the films (0.41-2.46 at.%) is determined by EDAX analysis. XRD spectra show a preferential c-axis orientation along the (002) plane and average grain size is in the range 19-28 nm. The surface morphology is studied by SEM and AFM. The deposited ZnO:V films have a transmittance value in the visible above 85% and resistivity $1.6\text{-}74.10^{-3}$ Ω.cm for different C_V. The lowest resistivity and better structural properties are observed for the films with C_V=1.41 at.%.

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Keywords: polycristalline thin film, transparent conductive oxide, r.f. magnetron sputtering, ZnO:V

1. Introduction

The development of thin film coating with high transmission and lower resistivity have been in the focus of the extensively study because of their application for large area devices such as solar cells, flat panel displays, sensors etc. [1-3]. Different technique for deposition of ZnO films have been applied - thermal evaporation, e-beam evaporation, magnetron sputtering, molecular beam epitaxy, pulsed laser deposition, etc. [4-6]. R.F. magnetron sputtering is a well established technique for deposition of undoped

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and doped ZnO thin films with different concentration of doping metals [4, 7-9]. Low resistivity ZnO films can be obtained by doping with Al, Ga, V and other doping impurities [3, 4, 8-11].

In this work the influence of the V concentration, C_V, on the optical, structural and electrical properties of V doped ZnO films (ZnO:V) deposited by magnetron R.F. sputtering is studied.

2. Experimental

Thin ZnO:V films were prepared by R.F. magnetron co-sputtering of ZnO target (10 cm diameter) with pieces of vanadium plate on in the maximum erosion zone of its surface in Ar atmosphere at a pressure of 0.5 Pa and r.f. power of 180W. In order to obtain ZnO:V films with different C_V different areas of vanadium plates in the range of 110-660 mm^2 were used. The films were deposited on glass substrates at temperature, T_s, of 150^0C. The thickness of the layers was between 700 and 860 nm.

The vanadium content in the films was determined by Energy Dispersive X-ray Analysis (EDAX) using Link AN10000 system analysis. The film structure were studied by X-Rays Diffraction spectrometry (XRD) 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. Transmittance and reflectance spectra were used for investigation of optical properties and were measured by a spectrophotometer Shimadzu UV.3600 in the range 320-1800 nm. Scanning Electron Microscope (SEM) pictures were obtained by Jeol JSM-840A with $LaBa_6$ cathode. The surface morphology was studied by Atomic Force Microscope (AFM) as well. The resistivity of the films was measured by the four-point probe method using VEECO instrument. The thickness of the ZnO:V films was measured by a profilometer Talystep Hobson.

3. Results and discussion

The concentration of V in the obtained ZnO:V thin films varies with the area of vanadium plates on the surface of ZnO target. The C_V in the deposited films varies between 0.41 and 2.46 at.% (Table 1). The presented values of the C_V are averaged after their measurements at four different points on the films surface. The obtained optical, electrical and structural characteristics of the ZnO:V films are given in Table 1, too.

The values of the resistivity, ρ, of the obtained ZnO:V films are in the range 1.6-74.10-3 Ω.cm (table 1) and are close to the reported ones in [12]. The values of ρ decrease with increasing in vanadium concentration up to 1.41 at.% V. Further increasing of the CV results in increasing of the resistivity.

The surface morphology of the films is studied by SEM and AFM. The AFM and SEM pictures are shown in Fig. 1 and 2, respectively, for the films with C_V of 0.81 at.%, 1.41 at.% and 2.46 at.%. The average surface roughness passes through the maximum for the sample with at C_V = 1.41 at.% (Table 1). The SEM pictures show a columnar structure of the films (Fig. 2).

XRD spectra of the films are presented in Fig. 3a. The diffraction patterns show the polycrystalline structure of the deposited ZnO:V films with preferential reflection corresponding to (002) crystallographic plane of the ZnO wurtzite structure with c-axis perpendicular to the substrate surface.

The peak position of the ZnO:V films is shifted to the lower 2θ values, compared to the spectra of undoped powdery ZnO (34.45^0) [13].

Table 1. The values of: the optical band gap, Eg, Urbach tail, E_0, the coefficient B (value of B^2 is given), the position of the (002) peak in the XRD spectra, 2θ, the FWHM of 2θ, Δ2θ, the average grains sizes, D, the roughness, the c- axis, c_{film}, the concentration of V, C_V , the stress, σ, and the resistivity, ρ.

Sample	C_V, *(at.%)*	2θ, *(deg.)*	Δ2θ, *(deg.)*	D, *(nm)*	Roughness, *(nm)*	C_{film}, *(nm)*	σ, *(GPa)*	Eg, *(eV)*	E_0, *(meV)*	B^2, *($cm^2.eV$)*	ρ, *(Ω.cm)*
1. ZnO:V	0.41	34.06	0.44	19	3.41	0.5261	-2.44	3.38	80	1.10E12	$1.3x10^{-2}$
2. ZnO:V	0.83	34.07	0.39	21	4.18	0.5259	-2.37	3.49	104	1.69E12	$2.9x10^{-3}$
3. ZnO:V	1.41	34.05	0.30	28	4.64	0.5262	-2.51	3.55	122	4.50E11	$1.6x10^{-3}$
4. ZnO:V	1.44	34.03	0.35	24	4.18	0.5265	-2.64	3.45	135	6.80E11	$5.3x10^{-3}$
5. ZnO:V	2.46	33.94	0.36	23	3.71	0.5279	-3.23	3.49	190	6.82E11	$7.4x10^{-2}$

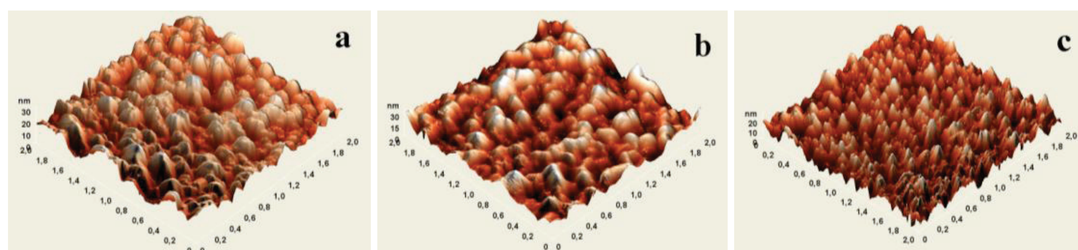

Fig.1. AFM pictures of the ZnO:V films deposited at different concentrations – 0.41at.% (a), 1.41at.% (b) and 2.46 at.% (c).

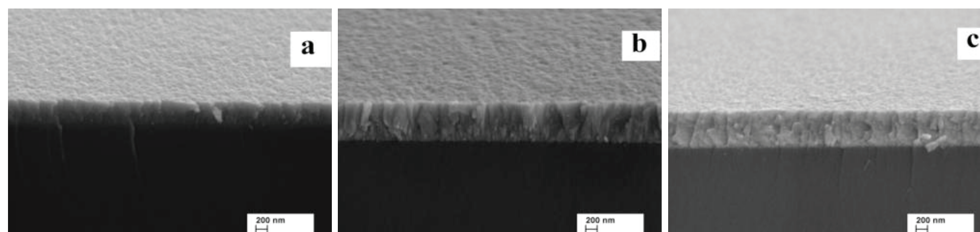

Fig. 2. SEM pictures of the ZnO:V films deposited at different concentrations – 0.41at.% (a), 1.41at.% (b) and 2.46 at.% (c).

This shift to lower 2θ value and the increase of the values of the c-axis calculated from XRD data are evidence for the tensile stress in the V doped films, probably due to the presence of the doping atoms (vanadium atoms partially substitute for zinc atoms and V^{2+} has higher ionic radius (0.88 Å) than Zn^{2+} ion (0.74 Å)) and the mismatch between the lattice parameters of the films and substrate. The (002) peak of the ZnO:V film with the highest C_V has the largest shift to the lower value of 2θ and the highest value of the stress. The Full Width at Half Maximum (FWHM) of (002) XRD peak decreases with increasing in C_V till 1.41 at.%, thus the calculated from the XRD spectra average grains sizes increase from 19 till 28 nm. Further increasing of the C_V leads to decreasing of the intensity of the (002) peak, to its shift to the lower 2θ and to light decreasing of the average grain size to 23 nm at C_V =2.46 at.%. Thus, the ZnO film with V concentration of about 1.41 at.% has better structural properties.

Transmittance spectra of the ZnO:V thin films are presented in Fig. 3b. The spectra are corrected for the transmittance of the glass substrate. All spectra demonstrate transmittance value above 80% in the range of 500–1000 nm. The absorption edge of the ZnO:V films is at 380 nm and is typical for ZnO. An absorption band about 806 nm is observed for the film with C_V in the range of 0.83 – 1.44 at.%. It is more pronounced in the film with C_V = 1.41 at.%. This band is typical for transitions of d-d electrons in the vanadium ions that substitute for zinc in the ZnO:V lattice [14]. In the IR region beyond 1000 nm the transmission decreases for the film with resistivity < 5.3 x 10^{-2} Ω.cm due to the absorption of free carrier concentration (plasma resonance).

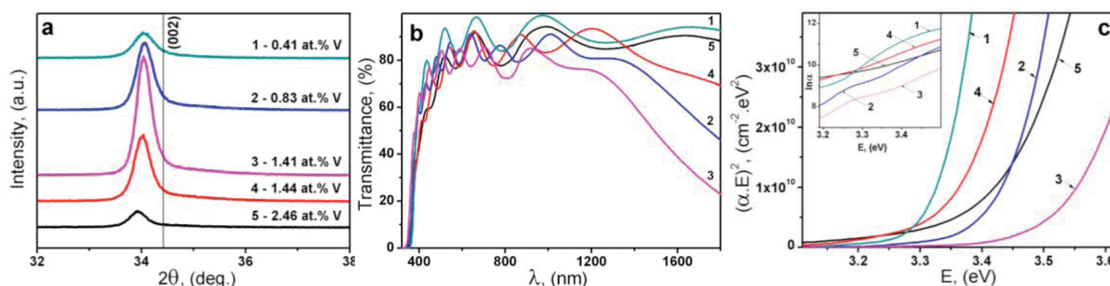

Fig. 3. XRD (a), transmittance (b) and absorption coefficient, α, (c) spectra of thin films ZnO:V at different concentration.. The black line at the XRD spectra indicates the position of (002) peak of ZnO powder [13]. The insert in (c) shows the plot of lnα vs hν. The numbers of the curves correspond to the numbers of the samples given in the table 1.

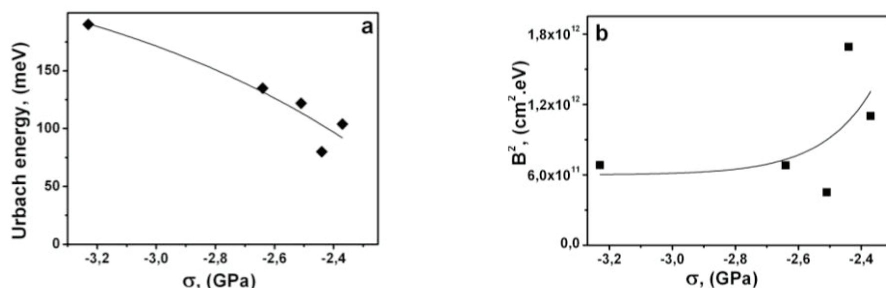

Fig. 4. Dependence of the Urbach energy, E_0, (a) and the coefficient B^2 (b) on the stress σ. The lines are for guiding the eye.

The dependence of coefficient of absorption on the energy for the ZnO:V films are presented in Fig. 3 c. The value of the energy band gap, E_g, Urbach energy, E_0, and the coefficient B (Table 1) are calculated as described in [7, 10, 15] for direct inter-band electron transitions. The obtained values of the band gap are in the range 3.38 – 3.55 eV and are typical for ZnO. It is observed the blue shift for the films with lower resistivity which is attributed to the Burstein–Moss effect [16]. Larger shift is obtained for the film with C_V = 1.41 at.% and lowest value of the resistivity [4]. The value of the optical band gap, Eg, decreases with further increasing of C_V (Table 1 and Fig. 3 c). Probably at higher C_V part of V atoms segregate on the grains boundaries and do not form shallow donor level in the band gap in ZnO.

Fig. 4 a and b display the dependence of the E_0 and B on the tensile stress in the films. E_0 and B are assumed as parameters for the band tail states [17, 18]. Decreasing of B and increasing of E_0 imply an increase in the disorder of the structure and an increase in the band tail width [7, 17, 18]. This could be connected to the presence of V ion in the ZnO lattice and in the intergrain's boundaries. The latter prevail

at higher C_V. A correlation between the stress and the structural disorder in the films is observed - the increase of the structural disorder due to the doping with V is accompanied by increasing of the tensile stress in the films.

4. Conclusion

Structural, optical and electrical properties of V doped ZnO thin films doped with different content of V (0.41 at.% ÷2.46 at.%) are studied. The XRD spectra show polycrystalline structure of the deposited ZnO:V films with preferential peak reflection corresponding to (002) crystallographic plane of the ZnO wurtzite structure with c-axis perpendicular to the substrate surface. Films deposited with C_V =1.41 at.% demonstrate better crystalline structure – the intensity of the (002) peak is higher and the average grain size are larger - about 28 nm. The films have a transmittance above 80 % in the visible range. The values of the optical band gap of ZnO:V films are in the range of 3.38–3.55 eV and are typical for ZnO. The resisitivity of the ZnO:V films with C_V = 1.41 at.% is 1.6 x 10^{-3} Ω.cm. This is encouraging for application of these films as a transparent conductive oxide. This vanadium concentration of 1.41 at.% is established to be a boundary value for the changes in the structural, optical and electrical properties of the ZnO:V thin films.

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