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Room temperature sensitivity of Ta doped nanocrystalline ZnO films to NH_3 exposure[♣]

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Undoped (ZnO) and doped with Ta (ZnO:Ta) films have been deposited by magnetron sputtering of a ZnO target and co-sputtering of the target with Ta chips on its surface respectively. The structural and optical properties of the films have been performed by X-ray Diffraction Spectroscopy (XRD), optical transmittance and reflectance measurements. The sensitivity of the undoped ZnO thin films and those doped with Ta (ZnO:Ta) to exposure to NH_3 was measured by the ratio of the resistivity in air to that in the presence of the target gas. A higher sensitivity was observed in the Ta doped ZnO film.. It is shown that ZnO thin films doped with Ta have a potential application as room temperature sensors.

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1. Introduction

ZnO is a material widely used in industry for decades. Because of its chemical sensitivity to different adsorbed gases, high chemical stability, amenability to doping, non-toxicity and low cost, it has attracted much attention as gas sensor [1-3].

The catalytic functions of the ZnO thin film surface have been changed by intentional introduction of different elements into the sensing film [4, 5]. In this work, a comparison of the room temperature sensitivity, S, of nanocrystalline undoped (ZnO) and Ta-doped (ZnO:Ta) thin films to NH_3 exposure has been performed. The sensitivity has been measured by the ratio of the resistivity in air to that in the presence of the target gas. The influence of the substrate temperature, T_s, of the nanocrystalline thin films deposition by magnetron sputtering on their optical and structural properties and on the sensitivity is also analysed.

2. Experimental

Thin nanocrystalline films of ZnO and ZnO:Ta were prepared by r.f. magnetron sputtering in an Ar (0.5 Pa) atmosphere, from a sintered ZnO target and by co-sputtering of a ZnO target with Ta chips on its surface, respectively, as described earlier in [6].

The samples were deposited on glass substrates at different T_s, in the range 150^0C - 500^0C. The optical and structural properties were measured on samples 500 nm thick.

X-ray diffraction spectra (XRD) of the samples were obtained using a Brucker D8 Advance spectrophotometer with CuKα radiation: λ $CuK_{\alpha1}$= 1.540560 Å and λ $CuK_{\alpha2}$ = 1.544426 Å (intensity half that of λ $CuK_{\alpha1}$). The instrumental broadening was 0.04^0 in 2Θ geometry. Optical transmittance and reflectance spectra were measured in the range 350-1500 nm, using a CARY UV-VIS-NIR spectrophotometer. The Ta concentration was determined by Energy Dispersive X- Ray (EDX) microanalysis using Link AN10000 system analysis. Co-planar Al electrodes on the film surface were evaporated to provide ohmic contacts for measurement of the resisitivity changes under NH_3 exposure. The gas sensitivity, *S*, of the thin films on glass substrates was determined by the ratio of the resistivity in air to that in a NH_3 atmosphere at different target gas concentrations, calculated from the I-V measurements with a Keithley 6517 electrometer.

3. Results and discussion

The values of the Ta contents, in dependence on the substrate temperature of the thin film

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Table 1. The values of the 2Θ of (002) XRD peaks, their FWHM, the average grain size, D, the Ta content and the optical band gap, E_g, of ZnO and ZnO:Ta thin films, deposited at different T_s.

Samples	T_s, ^{0}C	2θ, deg (ZnO)	FWHM, deg, (ZnO)	D, nm (ZnO)	2θ, deg ($ZnTa_2O_6$)	FWHM, deg ($ZnTa_2O_6$)	D, nm ($ZnTa_2O_6$)	E_g, eV	E_0, meV	Ta, at.%
ZnO	150	34.30	0.52	16	-	-	-	3.33	63	0
ZnO	275	34.40	0.47	18	-	-	-	3.30	59	0
ZnO	500	34.40	0.33	25	-	-	-	3.27	60	0
ZnO:Ta	150	33.55	1.53	54	33.09	0.37	22	3.33	124	4
ZnO:Ta	275	33.55	1.34	62	32.95	0.48	17	3.39	95	4.5
ZnO:Ta	500	-	-	-	32.74	1.05	8	3.46	95	7

deposition, are displayed in Table 1. The Ta content increased with increasing T_s. The XRD spectra shown in Fig. 1a reveal reflections corresponding to the (002) crystallographic plane of wurtzite ZnO, in the case of undoped ZnO films. Only in the case of a ZnO film deposited at a low $T_s = 150^0$ C were the reflections of the (100) and (101) planes observed together with the (002) peak. The peak intensity increased, the peak position shifted to the angle corresponding to powder ZnO (34.44^0) on a 2Θ scale, and its Full Width at Half Maximum, FWHM, decreased with increasing T_s. In the case of Ta doped ZnO films, the bands in the XRD spectra (Fig 1 b) of the samples deposited at lower $T_s = 150^0$C and 275^0C are very large and could be related to the presence of different phases – ZnO and $ZnTa_2O_6$ [7].

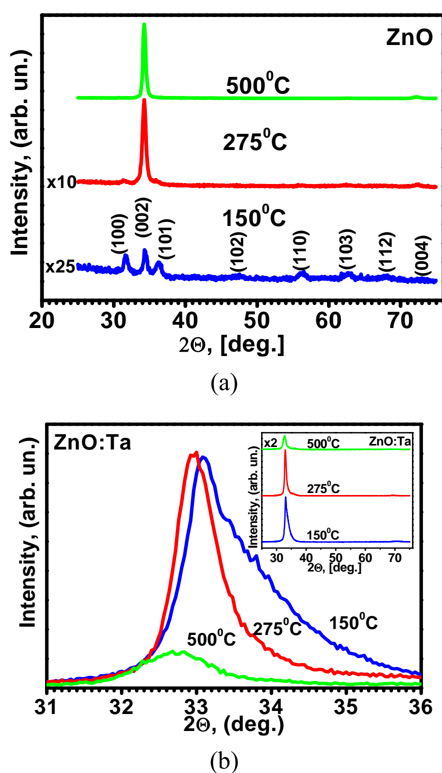

Fig. 1. XRD spectra of ZnO (a) and ZnO:Ta(b) thin films, deposited at different T_s.

Actually, the best fit was obtained introducing only two bands – of ZnO (002) at 33.55^0 and $ZnTa_20_6$ (051) in the range 33.09^0 – 33.87^0 [7]. Fig. 2 displays the fits of the XRD spectra (Lorentzian low was used) of ZnO:Ta films deposited at different T_s. Increasing the Ta concentration in the doped ZnO:Ta films with T_s increasing was accompanying by a decrease in the intensity of the XRD band related to ZnO. In the XRD spectrum of the sample deposited at $T_s = 500^0$C (the Ta concentration increased to about 7%), this band disappears and only the band of orthorhombic $ZnTa_2O_6$ (051) is observed [7], however its intensity decreased. An increasing T_s resulted in a shift of the position of the XRD peak of (051) band to a lower 2Θ, from 33.09^0 to 32.74^0. The shift of its position to the higher value of 2Θ than that reported for the $ZnTa_20_6$ powder (2Θ =32.373^0 [7]) could be due to the presence of the compressive stress. Increasing values of T_s and of the Ta concentration caused a decrease in the stress.

The average grain sizes, *D*, for ZnO and $ZnTa_2O_6$ nanocrystallites were calculated to an accuracy of 10% by the Debye-Scherrer equation [8] to the FWHM of ZnO (002) and $ZnTa_2O_6$ (051) peaks, and are shown in Table 1. The increase of the T_s stimulated a better structural order of undoped ZnO films, and led to an increase in the average grain sizes. In the case of ZnO:Ta films, the average grain size of the nanocrystallites of the ZnO phase increased slightly.However, the *D* value of the nanocrystallites of the $ZnTa_2O_6$ phase decreased from about 22 to 8 nm with T_s increasing from 150^0C to 500^0C. The absorption coefficient, α, in dependence on the incident photons energy, is shown in Figs. 3 a and b. It is calculated for direct allowed electron transitions, from the reflectance and transmittance spectra [9]. The values of the optical band gaps decreased from 3.33 to 3.27 eV in the case of undoped ZnO films, and increased from 3.33 3.46 eV in the case of Ta doped ZnO films (Table 1). The changes of E_g with T_s for undoped ZnO films can be explained using the Burstein-Moss effect, as reported earlier [9]. The optical band of ZnO:Ta films increased with increasing T_s, probably due to an increasedof the Ta concentration (as the EDX analysis shows) and with an increasing presence of the $ZnTa_2O_5$ and other tantalum oxide phases (according to the XRD spectra). For example, the band gap of Ta_2O_5 is reported to be about 4.1-4.2 eV which value is higher than that of ZnO [10].

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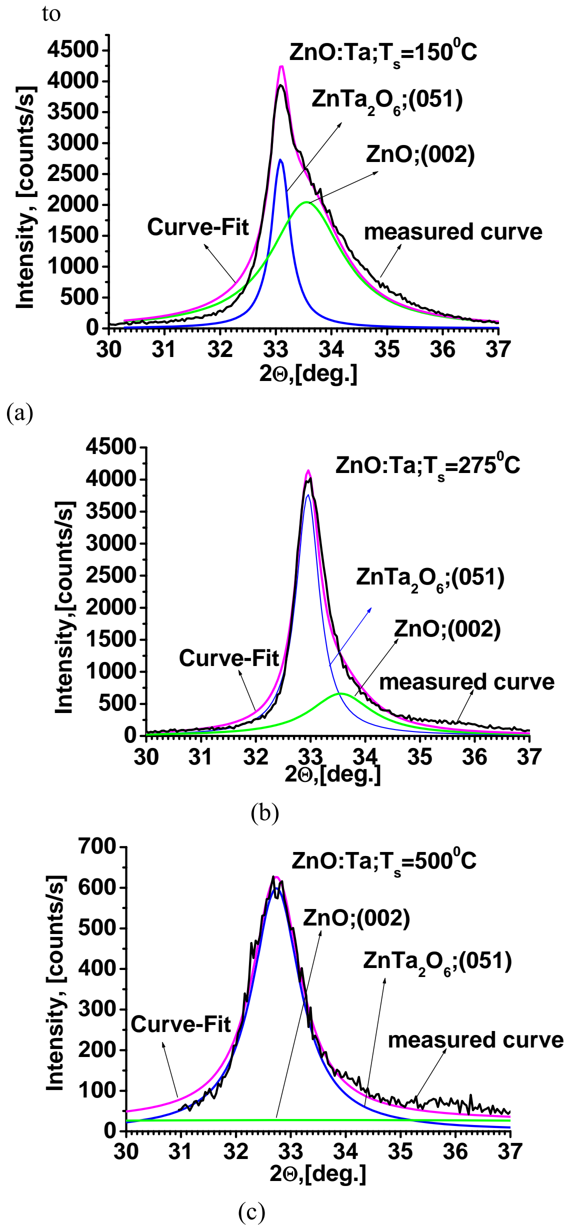

Fig. 2. Fits with two Lorentzian bands of the experimental XRD data of the ZnO:Ta samples, deposited at (a) 150^0C, (b) 275^0C and (c) 500^0C.

In the lower energy range, where α varies exponentially with photon energy, it is possible to assume that the spectral dependence of the absorption edge follows the Urbach formula [11]. The exponential dependence of the absorption on $h\nu$ in the Urbach region is due to the perturbation of the parabolic density of the states at the band edge – increasing structural disorder results in an increase in the Urbach energy, E_0 [11]. The energy dependences of α at lower photon energies is displayed in the inserts of Fig. 3a and b. The calculated values for the Urbach energy (resolution of ±4 meV) are given in Table 1. The Ta doped ZnO films exhibited significant band tailing in the lower energy region, compared to undoped ZnO films. This could be attributed to structural defects due to the mixed phase in the doped samples, and to the lower size of the crystallites as well. The results show that E_0 decreases with increasing substrate temperature for two sets of samples, indicating an improvement of the structural ordering which coincides with the XRD observation.

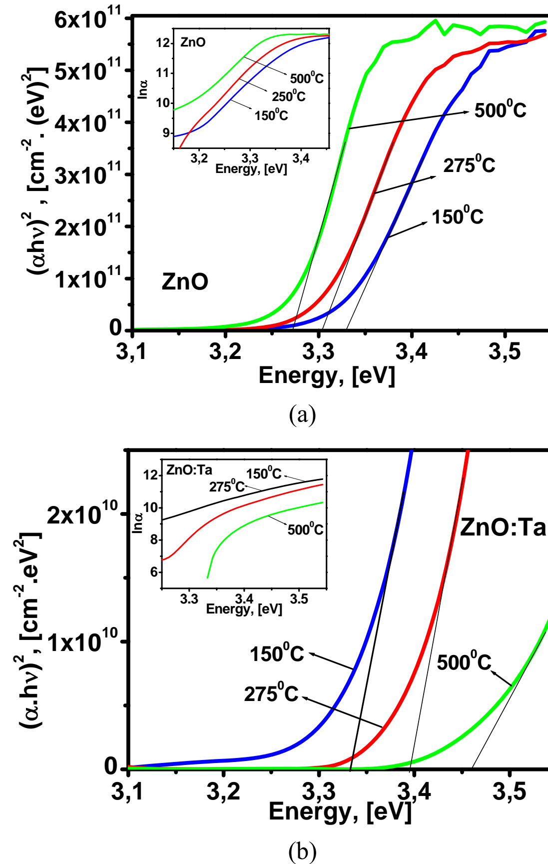

Fig. 3. $(\alpha * h\nu)^2$ plot against the photon energy for ZnO (a) and ZnO:Ta (b) films deposited at different T_s. The inserts show the plot of ln α vs. hν.

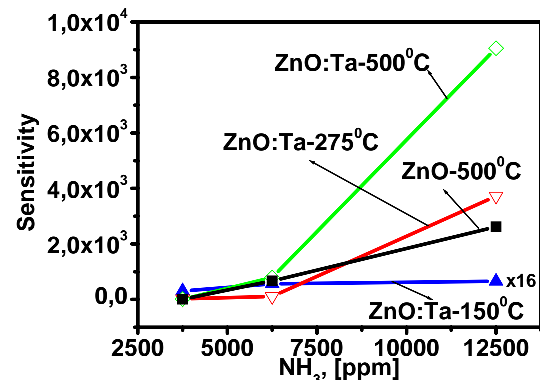

Fig. 4. Sensitivity of ZnO ($T_s=500^0C$) and ZnO:Ta thin films vs. NH_3 concentration.

The variation in the sensitivity of ZnO, deposited at T_s=500^{0}C and ZnO:Ta, deposited at different T_s, with NH_3 concentrations up to 12,500 ppm is shown in Fig. 4. The sensitivity of ZnO films deposited at 150^{0}C and 275^{0}C is not shown, because it is lower than the used NH_3 concentration. The sensitivity of ZnO:Ta films to NH_3 increased with increasing T_s. It has to be pointed out that the ZnO:Ta film had a sensitivity 3 times higher than that of the ZnO film deposited at the same T_s = 500^{0}C with 12,500 ppm of NH_3.

It is well accepted that NH_3 reacts with the surface species and the trapped electrons are returned to the conduction band, causing an increase in the conductivity of the material and the sensitivity of the sensor [3]. Usually, the gas sensitivity increases with decreasing grain sizes in the films [12].

The higher sensitivity of the Ta doped ZnO films compared to the undoped ones reported here could be due to the presence of a higher concentration of defects at the surface of the grains (as suggested from the observed band tailing), where higher quantity of O_2^- and OH^- could be absorbed. Lower crystallite sizes in the Ta doped ZnO film compared to undoped ZnO deposited at T_s = 500^{0}C result in an increase in their effective surface and as a consequence the concentration of point and packing defects. The presence of the phases of $ZnTa_2O_6$ could be a reason for the higher sensitivity of the ZnO:Ta, as well.

4. Conclusions

Study on the influence of the substrate temperature of nanocrystalline ZnO and ZnO:Ta thin films deposited by r.f. magnetron sputtering on their structural and optical properties, and sensitivity to ammonia, has been performed. The optical band gap decreased with T_s for the undoped ZnO films and increased in the case of ZnO:Ta films. The sensitivity to NH_3 of ZnO and ZnO:Ta films increased with increasing T_s. The ZnO:Ta film demonstrated a higher sensitivity than the undoped ZnO film deposited at the same T_s = 500^{0}C. A higher sensitivity was observed in ZnO:Ta films, compared to the undoped ZnO films. The higher concentration of defects and different phases (ZnO and $ZnTa_2O_6$), or only one phase of $ZnTa_2O_6$ in Ta-doped ZnO films, could be one of the reasons for the different behaviours of the sensors with undoped and Ta doped ZnO films. It is shown that nanocrystalline Ta doped ZnO thin films have a potential application as room temperature sensors.

Acknowledgements

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