“Optical and electrical properties of ZnO:Al thin films deposited R.F. magnetron sputtering in Ar+H_2 and Ar atmospheres”, K. Lovchinov, O. Angelov, D. Dimova-Malinovska, (2012) Nanoscience and Nanotechnology, in press

OPTICAL AND ELECTRICAL PROPERTIES OF ZnO:Al THIN FILMS DEPOSITED BY RF MAGNETRON SPUTTERING IN Ar+H_2 AND Ar ATMOSPHERES

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Abstract: Optical and electrical properties of hydrogenated (ZnO:Al:H) and unhydrogenated (ZnO:Al) zinc oxide doped with Al thin films deposited by r.f. magnetron sputtering of sintered target (ZnO 98wt%+Al_2O_3 2 wt %) in Ar+H_2 and Ar atmospheres at different substrate temperatures, T_s, are studied. The values of the optical band gap of both kinds of films are in the same range between 3.49 and 3.58 eV. The resistivity, ρ, is in the range of 1.6-3.0 mΩ.cm (ZnO:Al:H) and 2.8-7.8 mΩ.cm (ZnO:Al). The influence of hydrogen on the optical and electrical characteristics of the obtained ZnO:Al thin films is discussed.

Keywords: magnetron sputtering, transparent conductive oxides

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1. Introduction

Recently the transparent conductive oxides with their variety of application in the electronic devices are object of different scientific studies. Their exploration has the aim improvement of oxides optical and electrical characteristics [1], achievement of doping [2], compatibility with the characteristics of the expensive ITO [3]. Al is a donor impurity and reduces the resistivity of ZnO. Thin films of ZnO:Al are widely used in different electronic devices as solar cells [4], gas sensors [5], transparent transistors [6], etc. Among the methods of preparation of thin ZnO:Al films, the r.f. magnetron sputtering has advantages: possibility for large area of deposited films with good uniformity of the thickness, low substrate deposition temperature, good density and adhesion to substrate. At the same time the thin film properties are very sensitive to the parameters of deposition and their control. The developed density function theory and total energy calculation [7] demonstrate the possibility of formation of shallow donors through hydrogen incorporation in ZnO to improve the conductivity of the ZnO thin films.

In this paper the results on the optical and electrical properties of hydrogenated (ZnO:Al:H) and unhydrogenated (ZnO:Al) zinc oxide doped with Al thin films deposited by r.f. magnetron sputtering of sintered ceramic target (ZnO 98wt% + Al_2O_3 2wt%) in Ar+H_2 and Ar atmospheres at different substrate temperatures, T_s, are reported.

2. Experimental

The ZnO:Al:H and ZnO:Al films are deposited by r.f. sputtering of sintered (ZnO 98 wt % + Al_2O_3 2 wt %) target (100 mm in diameter) in Ar (0.7 Pa)+H_2 (0.03 Pa) and Ar (0.7 Pa) atmospheres. Before deposition the substrates are ultrasonically cleaned in H_2O_2+H_2SO_4 (1:1) solution and de-ionized water. The deposition of ZnO:Al:H films is performed without heating (WH) of substrates and with heating between 80 – 150^{0}C. The r.f. sputtering power, P_s, is 150 W. The film thickness is between 150-200 nm.

The reflectance and transmittance spectra of the films are measured by Schimadzu 3100 spectrophotometer in the range of 300-1800 nm. The spectral dependence of the coefficient of absorption is calculated for direct interband transitions. The films thickness is measured by profilometer "Talystep". The surface resistance of the films is measured by a four point probe method using Veeco apparatus and the resistivity, ρ, is calculated through the measured thickness.

3. Results and discussion

The transmittance and the absorption coefficient, α, as a product $(\alpha.h\nu)^2$, versus photon wavelength and energy, hν, of the obtained thin films ZnO:Al:H and ZnO:Al at different substrate temperatures, T_s are displayed in Figures 1a and 1b, Figure 2a and 2b, respectively.

The transmittance of ZnO:Al:H and ZnO:Al thin films deposited at different T_s (Figure 1a and Figure 2a) is higher than 90% in the wavelength range between 550-1200 nm.

The spectral dependence of the absorption coefficient, α, (Figure 1b and Figure 2b) is calculated from transmittance and reflectance spectra by the equation [8]:

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

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

The optical band gap of the ZnO:Al films is calculated for direct interband transitions at higher energies, $h\nu>E_g$, according to the Tauc formula [9]:

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

where A is constant.

At photon energies $h\nu<E_g$ the spectral dependence of α is determined by the Urbach formula [10]:

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

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. The dependence of the optical absorption coefficient in the Urbach tail is related to the electron-lattice interaction. Since the phonon number is fluctuating in thermal equilibrium, the band gap energy is also fluctuating resulting in an exponential tail below the average band gap energy.

The refractive index of the films, n, is calculated from the transmittance spectra by the equation [11]:

$$n = [N + (N^2 - n_0^2)^{1/2}]^{1/2}, \qquad (4)$$

where $N = (2n_0/T) – [(n_0 + 1)/2]$.

In equation (4) n_0 is the refractive index of the substrate and T is the value of the transmittance at every λ_{min}. The values of n are calculated for a wavelength in the range of 500-550 nm in dependence on the substrate temperature. The values of n are calculated to an accuracy of 3 %.

The calculated values of E_g, E_0, resistivity, ρ, and refractiive index, n, for the ZnO:Al:H and ZnO:Al thin films deposited at a fixed sputtering power, P_s, in dependence on T_s are presented in Table 1 and Table 2, respectively. The values of E_g and E_0 are calculated to an accuracy of 2%.

Our previously published results demonstrate that the ZnO films deposited by magnetron sputtering, undoped and doped with Al, H, Er, Ta, are nanocrystalline with average grains size in nanometer scale (16-30 nm) [12, 13].

Comparison between the data for ZnO:Al:H and ZnO:Al deposited at different T_s shows that the values of the optical band gap, E_g, do not depend significantly on T_s . The changes are in the range of the calculation method accuracy.

The resistivity of the ZnO:Al:H films has lower value compared to resistivity of the unhydrogenated ZnO:Al films. A first-principles investigation, based on density function theory, give strong evidence that hydrogen improves the conductivity of ZnO [7]. It can incorporate in high concentrations and behaves as a shallow donor [7]. It has to be noted that the experimental study of hydrogen in crystalline ZnO demonstrates that after annealing of ZnO crystal at 200^0C in hydrogen atmosphere the conductivity increases due to indiffusion of hydrogen with activation energy of 0.91 eV [14]. The obtained results in the present work confirm the behavior of hydrogen as a donor impurity in ZnO thin films – the ZnO:Al:H films have lower values of the resistivity compared to ZnO:Al films.

The energy width of the Urbach tail, E_0, decreases with T_s increase which can be related to the improvement of the structural order in the films as reported in [12]. The refractive index, n, of ZnO:Al:H films have higher values than those of ZnO:Al films at all temperatures of deposition. This result could be explained with an introduction of weak polarization in the ZnO lattice due to slight increase in the length of Zn-O bonds as a result of formation of O-H bonds in the ZnO lattice [7], [15].

4. Conclusion

The optical and electrical properties of hydrogenated (ZnO:Al:H) and unhydrogenated (ZnO:Al) zinc oxide thin films doped with Al deposited by r.f. sputtering in Ar (0.7 Pa) or Ar (0.7 Pa) + H_2 (0.03 Pa) atmospheres at different substrate temperature, T_s, are studied. In the range of 550-1200 nm the transmission is higher than 90% for all deposited thin films. Comparison of the properties of ZnO:Al and ZnO:Al:H thin films shows that the optical band gaps does not depend on hydrogen incorporation in the ZnO:Al:H thin films. However, the ZnO:Al:H films have lower resistivity due to the incorporation of hydrogen during the deposition. The structural order of the film improves with increasing of deposition temperature as indicate the values of the Urbach energy. Hydrogenated ZnO:Al thin films have potential for application as transparent conductive oxides.

Acknowledgements: This work has been supported by the 7FP of EC- the Project NANO PV № 246331 and from the National Scientific Fund of Bulgaria - the Project D002-207/2008.

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Figure captions

Figure 1. Transmittance (a) and dependence of $(\alpha.h\nu)^2$ on the energy (b) for ZnO:Al:H thin films deposited at different T_s. The inset in (b) shows the dependence of ln α on the energy.

Figure 2. Transmittance (a) and dependence of $(\alpha.h\nu)^2$ on the energy (b) for ZnO:Al thin films deposited at different T_s. The inset in (b) shows the dependence of ln α on the energy.

Table 1. The calculated values of optical band gap, E_g, the Urbach tail energy width, E_0, the resistivity, ρ, and the refractive index, n, of ZnO:Al:H films deposited at a fixed sputtering power, P_s, in dependence on T_s

Table 2. The calculated values of optical band gap, E_g, the Urbach tail energy width, E_0, the resistivity, ρ, and the refractive index, n, of ZnO:Al films deposited at a fixed sputtering power, P_s, in dependence on T_s.

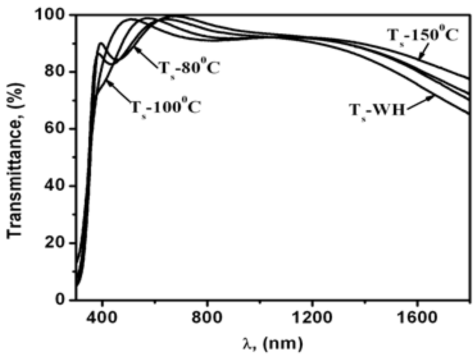

Figure 1a

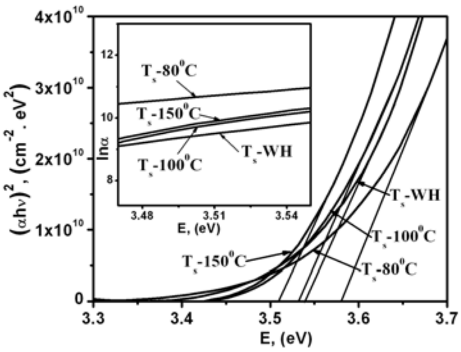

Figure 1b

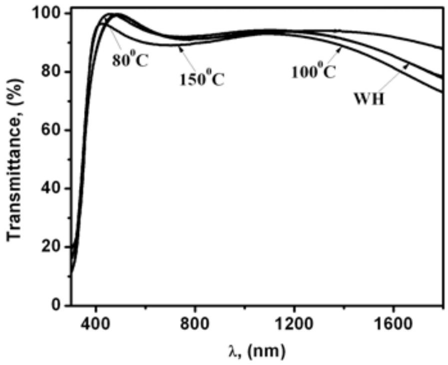

Figure 2a

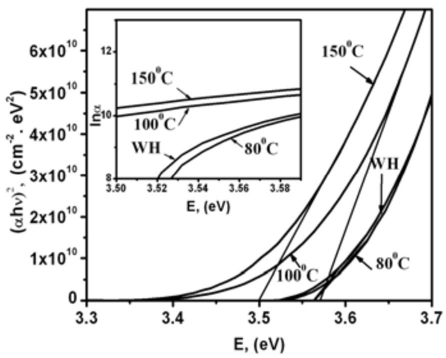

Figure 2b

Table 1

Sample	T_s, [^{o}C]	P_s, [W]	E_g, [eV]	E_0, [meV]	ρ, [mΩ.cm]	n
D297	WH	150	3.54	134	2.1	1.94
D294	80	150	3.58	118	1.6	1.96
D311	100	150	3.53	105	2.9	1.85
D312	150	150	3.51	102	3.1	1.82

Table 2

Sample	T_s, [^{o}C]	P_s, [W]	E_g, [eV]	E_0, [meV]	ρ, [mΩ.cm]	n
D407	WH	150	3.56	65	5.5	1.75
D402	80	150	3.56	63	4.4	1.76
D401	100	150	3.57	62	2.8	1.77
D400	150	150	3.50	59	7.8	1.84