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ZnO:H thin films for room temperature selective NH_3 sensors

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ZnO thin films were deposited by magnetron sputtering in Ar and $Ar+H_2$ atmospheres. The influence of the substrate temperature, Ts, on their optical, structural and electrical properties was investigated. The optical band gap, E_{opt}, of the films, from transmission and reflection spectra, ranged from 3.27 to 3.31 eV, and decreased with increasing T_s. The Urbach band tail width was also calculated - its value decreased with increasing substrate temperature. XRD analyses showed an improvement of the structural properties with increasing T_s. A discussion of the influence of T_s and hydrogen on the properties is presented. The change of the sensitivity in the presence of NH_3 vapour at room temperature is also presented.

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1. Introduction

Because of its high chemical stability, low dielectric constant and high optical transmittance, ZnO has been widely used as a dielectric ceramic, pigment, catalyst and sensing material for application in electronic and optoelectronic devices, solar cells and sensors [1-4]. In particular, an increase in the gas sensitivity and selectivity for different gases has been reported by doping ZnO with different elements [3-4].

In this work, a study of the influence of H and of the substrate temperature, T_s, on the optical, structural and electrical properties of ZnO:H thin films deposited by magnetron r.f. sputtering in an $Ar+H_2$ atmosphere is reported. The results are compared with data for ZnO films deposited in an Ar atmosphere. The sensor characteristics of the ZnO and ZnO:H films as gas sensors for NH_3 detection is also demonstrated.

2. Experimental

Thin films of ZnO:H were deposited by r.f. magnetron sputtering of a ZnO ceramic target (100 mm disc) in atmospheres of Ar (0.5 Pa)+H_2 (0.1 Pa) at T_s values between 150 and 400 ^{o}C. For comparison, ZnO thin films were deposited by sputtering in an Ar (0.5 Pa) atmosphere. The vacuum chamber was evacuated to a residual gas pressure of 2.10^{-4} Pa. Sputtering was carried out at an r.f. power of 180 W. The thickness of the films was in the range 350 to 400 nm.

The resistivity of the films was calculated from the I-V characteristics, measured in the dark using a Keithley 6517 electrometer. The co-planar evaporated Al electrodes were verified to yield ohmic behaviour. Optical transmittance and reflection spectra were obtained in the range 300-1500 nm, using a CARY UV-VIS-NIR spectrophotometer. X-ray diffraction (XRD) spectra were obtained using a DRON 3 spectrometer with CuKα radiation (λ = 1.5406 Å). The sensor characteristics such as gas sensitivity and response time were evaluated under room temperature (26±2^{0}C) and environment conditions, by changing the target gas (NH_3) concentration in the air.

3. Results and discussion

The transmission of all of the samples was about 92-93% for wavelengths higher than 600 nm, assuming a value of 100% for the transmission of the glass substrate. The absorption coefficient, α, was calculated according to [5]. The spectral dependence of α exhibited 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, [6]. The calculated energy gaps (3.27 – 3.33 eV) are typical for ZnO, and are given in Fig. 1. E_g decreases with T_s for both sets of samples. In the low 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 [7]. The exponential dependence of the absorption on hν in the Urbach region ($h\nu < E_g$) 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 [8]. The calculated values are given in Fig. 1. The ZnO:H films exhibit lower values of E_0. This is related to an improvement in the structural order of the films. Possibly, hydrogen compensates some structural defects during the

deposition of the films. It should be noted that the deposition rate, V_d, for this set of samples is the lowest (see Fig. 1), which should result in better crystallinity, as suggested from the value for the Urbach energy. The width of the Urbach tail decreases with T_s for both sets of samples, which indicates an improvement in the structure of the ZnO films [7, 8]. This is confirmed by the XRD analysis. Fig. 2 shows the XRD patterns of both sets of films prepared at different T_s. Reflections corresponding to the (002) (110), (102), (110), (103), (112) and (004) planes of wurtzite ZnO are observed. The reflection corresponding to the (002) plane becomes more pronounced with increasing T_s, and the other reflections almost disappear, which demonstrates an improvement in the structural properties, and a preferential (002) orientation of the grains in the films deposited at higher T_s.

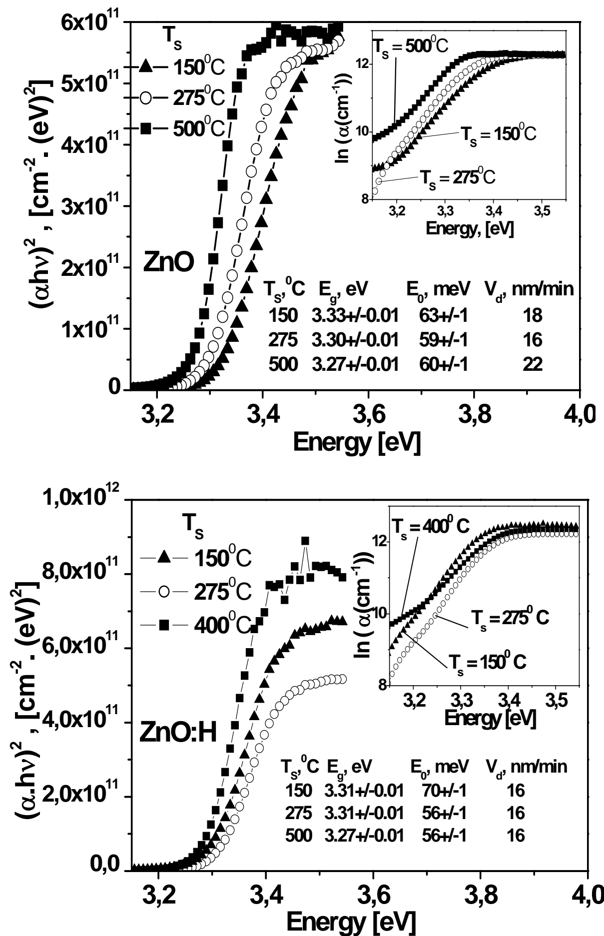


Fig. 1. A plot of $(\alpha * h\nu)^2$ against hν, for ZnO (left) and ZnO:H (right) films, deposited at different substrate temperatures, T_s. The inset shows a plot of ln α vs hν. The values of E_g, E_0, and V_d are also given.

Fig. 3 shows the resistivity as a function of T_s for both sets of samples, as deposited and after annealing at 550 °C in air for 2 hours. The resistivity of the ZnO films increases with T_s, probably due to the partial oxidation of Zn at higher T_s. The resisitivity of the ZnO:H films deposited at T_s = 150 °C is about 4.5 orders of magnitude higher than that of un-doped ZnO films. Hydrogen atoms are strong O-H bonds, and H is regarded as a new type of donor in ZnO [9]. A decrease in the resistivity of the ZnO films is observed upon H^+ ion implantation [10], and upon sputtering of a ZnO target in Ar+H_2 at 0.3 Pa with a very low H_2 partial pressure (1.10^{-3} Pa) [11].

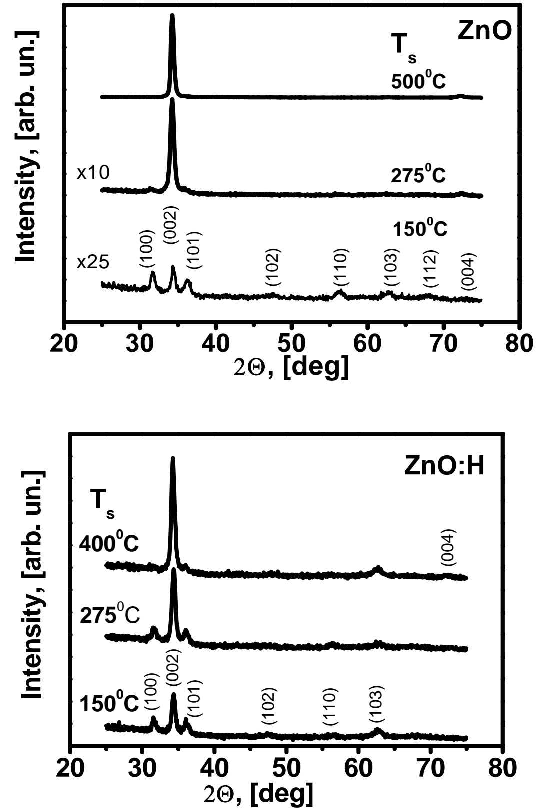


Fig. 2. XRD patterns of ZnO and ZnO:H films, deposited at different temperatures, T_s.

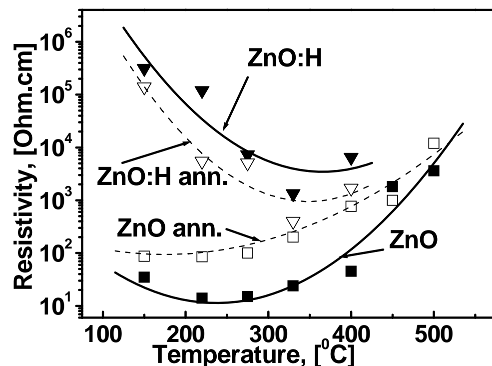
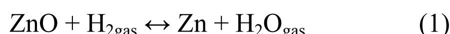


Fig. 3. Dependence of the resistivity on T_s, for ZnO and ZnO:H films, as deposited and after annealing in air at 550 °C for 2 hours.

However, these authors observed a strong increase in the resistivity of ZnO films when the H_2 pressure in the gas mixture was lower or higher than 10^{-3} Pa. In our case, the H_2 pressure was two orders of magnitude higher (0.1 Pa) than this. The role of hydrogen in the change in the

stoichiometry of the sputtered species could be: i) by reaction on the surface of the target, ii) by reactions within the sputter discharge and/or iii) by reactions at the substrate. These processes could result in changes in the growth conditions. Actually, the deposition rate of ZnO:H films decreased by 25-40% compared to that of the un-doped ZnO films for all T_s, probably due to the reduction of ZnO by H^+ on the substrate. We note that the deposition rate of ZnO:H films deposited at $T_s > 400$ °C is very low, and to obtain films of the same thickness as those of the other samples the deposition time must be increased. Thus, such films were not studied here. One of the possible reactions on the substrate during the process of sputtering in an $Ar+H_2$ atmosphere is:



$$ZnO + H_{2gas} \leftrightarrow Zn + H_2O_{gas} \quad (1)$$

Thermodynamic analyses [12] show that at T > 400 °C, the reaction will be shifted to the right. Thus, an excess of Zn should be present in the films, giving a reduction in the resistivity. However, at T < 400 °C the reaction will go to the left and the deposited material will be closer to the stoichiometric composition, giving an increased resistivity. It has to be noted that the H concentration in the ZnO:H films deposited at T_s = 150 °C is 2 at.% (from Elastic Recoil Detection Analyses) and it decreases to 1 at.% for T_s = 400°C, in conformity with reaction (1).

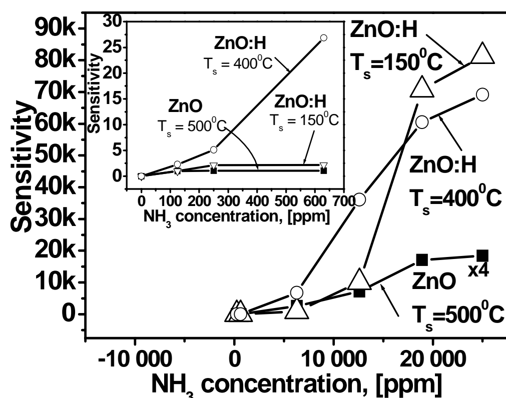


Fig. 4. A Dynamic sensitivity of ZnO:H and ZnO films toward NH_3 at room temperature. The insert is the sensitivity at lower NH_3 concentration.

It is also possible to suppose that some species absorbed in the growing films are responsible for the creation of depletion regions at the surfaces of the grains, and potential barriers for carriers, resulting in a reduced mobility [12]. This could be a reason for the increased resistivity of the films deposited in an $Ar+H_2$ plasma. Indeed, annealing of ZnO:H films at about 550 °C in air resulted in a decrease in ρ, possibly due to the desorption of the absorbants. In contrast, annealing of the ZnO films resulted in an increased resistivity (see Fig. 3).

The sensitivity of the ZnO films to NH_3 was determined as the ratio between the current, measured at room temperature in the presence of NH_3 vapor with different concentrations and that, measured in air, I_{NHs}/I_{air}. The variation in the sensitivity with NH_3 concentration is shown in Fig. 4. The sensitivity increased with the NH_3 concentration until about 20,000 ppm. It exhibited signs of saturation at higher NH_3 concentrations. It is seen that the sensitivity of the ZnO:H films is higher than that of the ZnO films. The ZnO:H film deposited at T_s = 400 °C exhibited a higher sensitivity than that deposited at 150 °C, for NH_3 concentrations less than about 18,000 ppm. For the higher sensitivity films, it was found that injection of 120 ppm of NH_3 at room temperature induced a decrease in the resisitivity, leading to a response magnitude of 2.5, while for an injection of 630 ppm, the response magnitude was about 27. Fig. 5 gives an example of the response transient of the ZnO:H films. It has to be noted that the signal could returned to its initial value after several cycles. This indicates that the adsorption of NH_3 on the film surface was reversible.

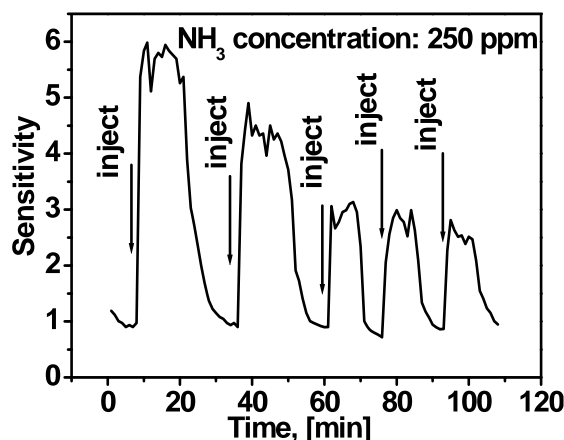


Fig. 5. Transient response of a ZnO:H film (T_s=400 °C) for a 250 ppm NH_3 concentration.

It is well accepted that the sensitivity of semiconductor gas sensors is attributed to the chemisorption of oxygen and OH^- on the oxide surface and the subsequent reaction between adsorbed species and the tested gas, which causes the resistance change [3]. It is known that atmospheric oxygen molecules and water vapor are adsorbed on the surface of the ZnO in the forms of O_2^- and OH^-, respectively, thereby reducing the electrical conductivity. When a ZnO sensor is exposed to a reductive gas, the test gas like NH_3 reacts with the surface species and the trapped electrons are returned to the conduction band of the ZnO, causing an increase in the conductivity of the sensor.

The different sizes of the grains in the films could be a reason for their different sensitivities. However, this is not so in our case - both ZnO and ZnO:H films have almost the same grain size (about 160 Å), as estimated from XRD data. The adsorbed hydrogen and H_2O (OH^-) species in the ZnO:H films during the deposition could explain the higher response of samples ZnO:H compare to the ZnO one and of the sample of ZnO:H deposited at a higher T_s. According to Eq. (1) deposition at 150 °C would result ina higher concentration of H and at 400 °C – in a higher

water vapor presence in ZnO:H films. Possibly, the presence of OH^- would accelerate the surface reaction between the reducing gas with NH_4OH as a product, additionally to the NH_3 reaction with the adsorbed oxygen species. Thus, the samples with higher OH^- concentrations (deposited at T_s = 400 ^oC in Ar+H_2) would be more sensitive to a lower NH_3 concentration.

4. Conclusion

Studies of the optical absorption and electrical resistivity of ZnO thin films, sputtered in Ar and Ar +H_2 atmospheres, and their dependences upon the substrate temperature have been performed. The optical gaps ranged from 3.27 to 3.33 eV. The Urbach tail width decreased with T_s. Sputtering in an Ar+H_2 atmosphere resulted in a better structural order and an increased resisitivity of the ZnO films. Gas sensing measurements showed that the ZnO:H films sputtered in an Ar+H_2 atmosphere have potential applications as room temperature NH_3 sensors.

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