JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 7, July 2008, p. 1810 - 1813

High performance gas sensing materials based on nanostructured zinc oxide films

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ZnO and ZnO:(Sn, Al) thin films and their sensing properties are presented with respect on their surface texture and composition. Thin films were prepared by vacuum thermal evaporation technique and deposited on different substrates. The thin film structure, crystallinity and morphology were investigated by using X-ray diffraction analysis and Atomic Force Microscopy (AFM). The ZnO gas sensor was exposed to different concentration of gases at elevated temperatures to evaluate the gas sensitivity of ZnO gas sensors. It was found that the highest sensitivity was obtained for temperatures arround 250^{o}C and that sensitivity to a certain gases is influenced by dopants and substrate nature.

(Received April 1, 2008; accepted June 30, 2008)

Keywords: Thin films, Gas sensor, Sensibility

1. Introduction

Zinc Oxide (ZnO) is a unique material that exhibits semiconducting, optical, piezoelectric and pyroelectric properties. ZnO has the same Wurtzite crystal structure as GaN and a very close optical band gap of 3.37eV, however, it has larger excitation binding energy (59meV) at room temperature than GaN (28meV) and ZnSe (20meV), resulting in efficient excitonic optical devices [1,2].

ZnO thin films have also been used as gas sensors, solar cell electrodes and optical waveguide devices. ZnO can be prepared by numerous methods, such as sputtering, sol-gel, spray pyrolysis, MOCVD, etc. Pure and doped ZnO films have been investigated as sensors for O_2, H_2, NO_x and ethanol [3-5]. Nanto et al. showed that by doping a significant change in sensitivity may be achieved due to significant change in electrical resistivity [6-8].

In the present study, undoped and doped ZnO thin films were prepared by thermal oxidation of metallic films (Zn or mixture of Zn, Sn, Al) deposited onto glass and Si substrates by vacuum thermal evaporation.

2. Experimental

Pure 0.024g Zn or a mixture made from 0.023Zn, 0.0005g Sn and 0.0005g Al were evaporated from a resistive molybdenum crucible onto unheated (111) p^+ Si and glass substrates, by using the vacuum thermal evaporation technique (p = 0.003 Pa). The obtained thin films were annealed at 623K in air for 3h. The structure of the thin film was examined by X-ray diffraction technique (DRON2 diffractometer, CuK_α) and the thin film morphology and roughness were investigated by using home made AFM equipment. The thickness of thin films was measured by using a DEKTAK profilometer, and was of about 400 nm. The electrical resistance of ZnO thin films was measured by using a two-point method and silver electrodes was deposited on the surface by vacuum thermal evaporation technique.

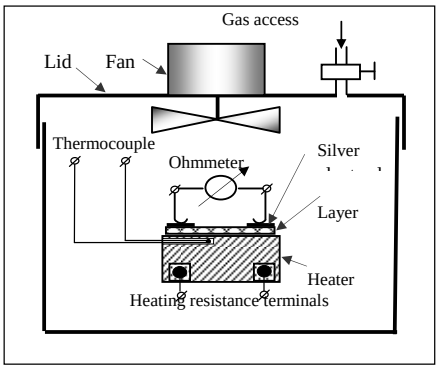


Fig. 1. Experimental set-up

For sensing measurements, the sample was mounted on a heater and placed in a glass enclosure capable of controlling the different gas concentrations. The gas sensing was performed in the temperature range from 150^{o}C to 350^{o}C. A chromel - alumel thermocouple placed in the glass chamber indicates the working temperature. As test gases were used: acetone (CH_3COCH_3), ethanol (C_2H_5OH), methane (CH_4) and liquid petroleum gas (LPG).

The electric resistance of the thin film sensor in test gases (R_g) and in pure air (R_a) was measured, and the gas sensitivity (S) was determined as

$$S = \frac{\Delta R}{R_a} = \frac{\left|R_a - R_g\right|}{R_a}, \qquad (1)$$

3. Results and discussions

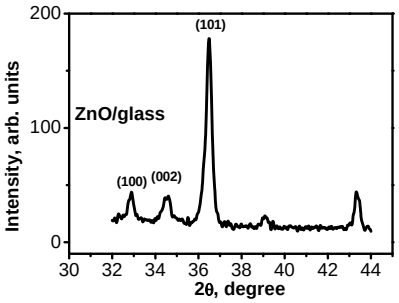


Fig. 2 XRD pattern of ZnO thin films

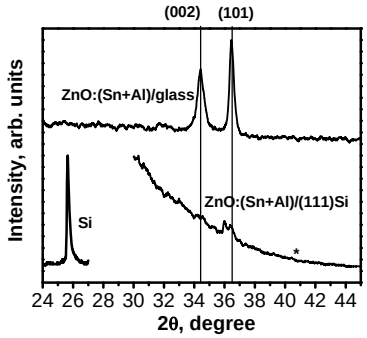


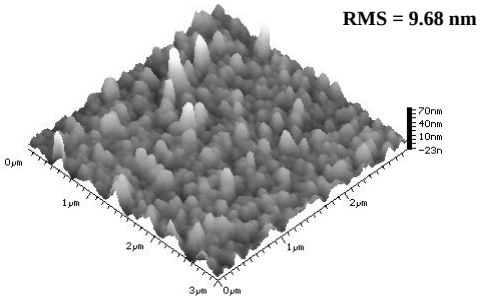
Fig. 3 XRD patterns of doped ZnO thin films
** - amplified XRD pattern of ZnO(Si+Al)/(111)Si thin film*

The X-ray diffraction patterns of doped and undoped thin films are shown in Figure 2 and 3.

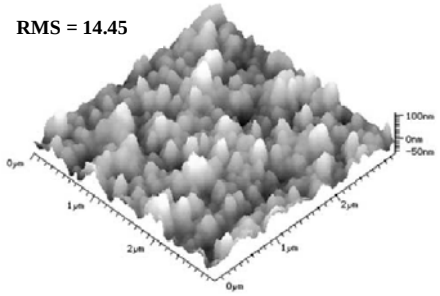
XRD pattern of undoped ZnO thin film deposited on glass (Figure 1) shows a nanocrystalline structure of Wurtzite type with a (101) prefered orientation.

The doped ZnO thin film deposited on glass (Figure 2) shows peaks that correlate to ZnO peaks and a change in XRD peak intensities and positions. The ratio of (101)/(002) peak intensities is changed from 4.6 to 1.2 indicating that dopants entered into the structure. Due to the strong intensity of XRD peaks belonging to the Si substrate, the XRD peaks belonging to ZnO thin film were observed only when the XRD pattern was highly amplified in the 2θ region of 30 - 45 degrees (Figure 3). By using the Scherer's formula ($D = (0.9\lambda)/(\omega\cos(\theta))$, where $\lambda = 0.154$ nm, ω is the (101) peak broadening) it was evidenced that the grain size is influenced not only by the dopants but also by the substrate nature (D = 25.6 nm for ZnO thin film deposited on glass; D = 22.6 nm for ZnO:(Sn+Al)/glass and D = 33.16 nm for ZnO:(Sn+Al)/(111)Si).

The AFM images of thin films deposited on (111)Si and glass are shown in Figure 4. Thin films have smooth nanometer granular structures. The surface roughness and grain size of thin film deposited on (111)Si have higher values as compared with those corresponding to films deposited on glass in agreement with XRD results. It is also visible that thin film deposited on (111)Si has a more columnar morphology as compared with thin film deposited on glass.



a)



b)

Fig. 4 AFM images of thin films: a) ZnO:(Sn+Al)/glass; b) ZnO:(Sn+Al)/(111)Si

The electrical resistivity for doped ZnO films, at room temperature, is presented in Figure 5.

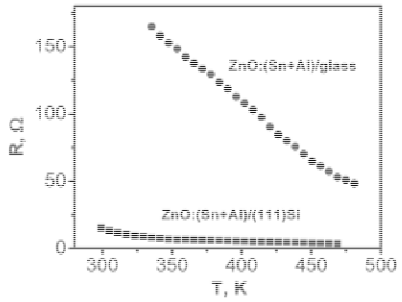
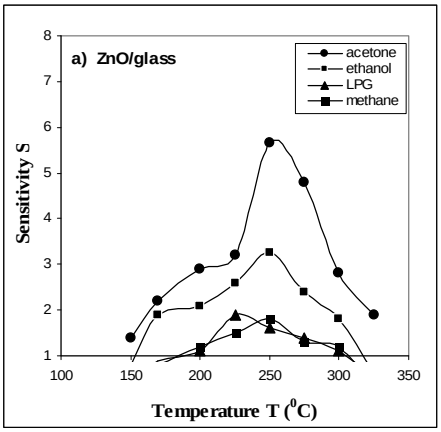
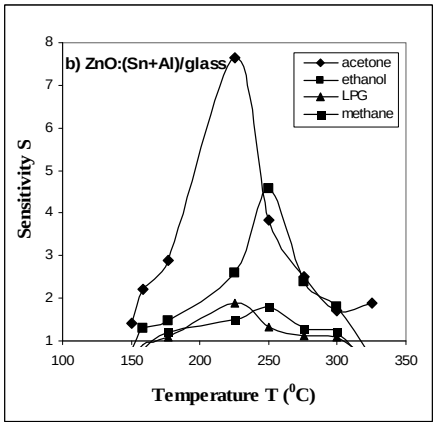


Fig. 5 Influence of substrate nature on the temperature dependence of electrical resistivity of doped ZnO thin films

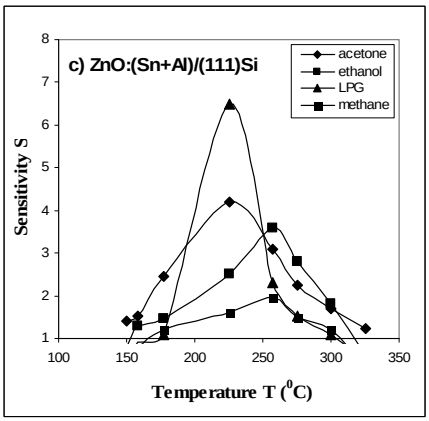
The substrate nature strongly influences the electrical resistivity, indicating different conduction mechanisms. It seems that thin films deposited on (111)Si have carriers with higher mobilities than thin films deposited on glass. The nearly temperature independence of the electrical resistivity of ZnO:(Sn+Al)/(111)Si thin film confirms that the semiconductor is a degenetate one.



a) ZnO/glass;



b) ZnO:(Sn+Al)/glass;



c) ZnO:(Sn+Al)/(111)Si.

Fig. 6 Relationship between operating temperature and sensitivity, for different gases:

The diminishing of grain size and columnar morphology of the sensor material are generally considered facilitating higher surface area and sensitivity.

The surface conductivity of semiconducting ZnO thin films depend on electron concentration near the surface and may be affected by the nature of the chemisorbed species. Vapors of acetone, ethanol, liquefied petroleum gas and gases, like methane, react with the chemisorbed oxygen reducing the resistance of the doped or undoped ZnO thin films. Dopants and substrate nature influence the morphology and the mechanism of the electrical conductivity and consequently the sensitivity of thin films.

Sensitivity of undoped and doped ZnO thin films deposited on glass and (111)Si increases with increasing operating temperature (Fig.6a-c).

The results obtained for the sensitivity of the films, as a function of temperature, evidenced a best sensitivity of ZnO thin films deposited on glass to acetone and ethanol.

The thin film sensitivity was increased by the presence of Sn and Al dopants. When doped ZnO thin films were deposited on (111)Si the sensitivity of thin films to LPG strongly increased. This result suggests that carrier mobility and columnar morphology are probably the most important factors in the reactivity of thin film with LPG.

If ZnO/glass thin films have a maximum sensitivity to acetone (5.65) at a temperature of 250°C, ZnO:(Sn+Al)/glass thin films exhibit a higher maximum sensitivity value (7.65), at a lower temperature of 225°C.

Sensitivity studies on ZnO:(Al+Sn) thin films deposited on (111)Si substrates showed a highest sensitivity to LPG (6.45) at a temperature of 225°C.

In order to explain the selectivity for the surface reaction of LPG, future structural and electrical studies are necessary.

4. Conclusions

Sensitivity studies were performed on ZnO/glass and ZnO:(Sn+Al)/glass and ZnO:(Sn+Al)/(111)Si thin films grown by vacuum thermal evaporation technique.

The thin film electrical proprieties and sensitivities to different vapors or gases were influenced by thin film structure, morphology and substrate nature.

Thin films deposited on glass were more sensitive to acetone and ethanol and thin films deposited on (111)Si were more sensitive to LPG.

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