

Full Paper

ZnO:Al Thin Film Gas Sensor for Detection of Ethanol Vapor

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Abstract: The ZnO:Al thin films were prepared by RF magnetron sputtering on Si substrate using Pt as interdigitated electrodes. The structure was characterized by XRD and SEM analyses, and the ethanol vapor gas sensing as well as electrical properties have been investigated and discussed. The gas sensing results show that the sensitivity for detecting 400 ppm ethanol vapor was ~20 at an operating temperature of 250°C. The high sensitivity, fast recovery, and reliability suggest that ZnO:Al thin film prepared by RF magnetron sputtering can be used for ethanol vapor gas sensing.

Keywords: ZnO:Al, sputtering, ethanol gas sensor, thin films.

1. Introduction

Gas monitoring devices are in demand for a rapidly growing range of applications. Metal oxide-based chemical sensors have been used extensively for the detection of toxic pollutant gases, combustible gases and organic vapors. The main advantages of chemical sensors are their low price, small size, high sensitivity, and low power consumption. Ethanol is one of the most commonly used and widespread alcohols, and thus there is a need to develop sensors for its detection. The most

common application of ethanol sensors is as a breath analyzer, since the ethanol vapor in human breath is said to be correlated with the concentration in the blood.

Recently, gas sensors based on the semiconducting metal-oxides such as SnO₂ and ZnO [1–5] have been found to be very useful for detecting ethanol vapor. Pure and doped ZnO films have been investigated as sensors for O₂ [6], H₂ [7], NO_x [8], and ethanol [9]. One of the requirements of the gas sensors is low power consumption, because the sensors need to work reliably and continuously. A low resistance material has lower driving power when it is used as a sensor. Appropriate donor doping can produce the electronic defects that increase the influence of oxygen partial pressure on the conductivity. Nanto et al. showed that a lower operating temperature may be achieved by the doping effect, and a significant resistance change can be obtained in the doped ZnO rather than the undoped ZnO sensor, which results in a higher sensitivity [10].

Several techniques have been used to prepare doped ZnO films, such as RF magnetron sputtering [11], chemical vapor deposition [12], sol-gel [13], and spray pyrolysis [14]. In this study, the Al doped ZnO (defined as ZnO:Al) thin film sensors deposited by RF magnetron sputtering using Pt as the electrode are reported. X-ray diffraction (XRD), scanning electron microscopy (SEM), and conductivity measurements were used to characterize the microstructure and electrical properties of ZnO:Al gas-sensing films that were deposited on Si substrate.

2. Experimental

Pt electrodes with interdigital structure were deposited on Si substrate by an RF magnetron sputtering process. The ZnO:Al sensing film was sputtered over the interdigitated electrodes. The target was a 3 in. 98 wt % Zn-2 wt% Al alloy, and the distance between the target and substrate was held at 45 mm. Figure 1 (a) shows the sensor configuration. A mixed Ar + O₂ gas was introduced into the chamber and metered by mass flow controllers for a total flow rate fixed at 15 cm³/s. Sputtering deposition was carried out at various RF powers and a pressure of 3 × 10⁻³ torr. Before deposition, the chamber was evacuated to an ultimate background pressure of 10⁻⁶ Torr, and then a presputtering process was employed to clean the target surface. The surface and cross-section morphologies were characterized by a scanning electron microscope (FE-SEM, Philips, XL-40FEG). X-ray diffractometer (RIGAKU-D-max) with Cu K α radiation was used to determine the crystallographic structures. The as-deposited films were used for the measurement of gas sensing properties. The gas sensing properties were evaluated at various operating temperatures, from 120 to 250 °C, by measuring the changes of resistance of the sensor in air and in ethanol gas. The sensitivity in the experiment was defined as

$$S=R_a/R_g$$

where R_a is the sample resistance measured in the ambient environment while R_g is that under the test gas.

3. Results and discussion

The ZnO:Al thin films sputtered onto Si substrates were used as an ethanol gas sensor. Figure 2 represents the XRD diffraction patterns of ZnO:Al film of thickness 100 nm deposited at various RF powers and a pressure of 3 × 10⁻³ Torr on Si substrates. XRD analysis reveals that all films exhibit

only the (0002) peak, indicating that they have ZnO (0002) preferred orientation, implying a c-axis growth perpendicular to the substrate surface. This was due to the lowest surface free energy [15] of the most densely packed (0002) planes in the wurtzite ZnO structure. With increasing RF power the locations of the measured diffraction angle do not change significantly and the dominant (0002) peak becomes sharper, indicating the well-established c-axis orientation of ZnO:Al films. This suggests that the crystallinity of the resulting film increases and the grain size becomes larger with increasing RF power (under the oxide region of the Shinoki model [16], where the crystallinity was enhanced with increasing RF power).

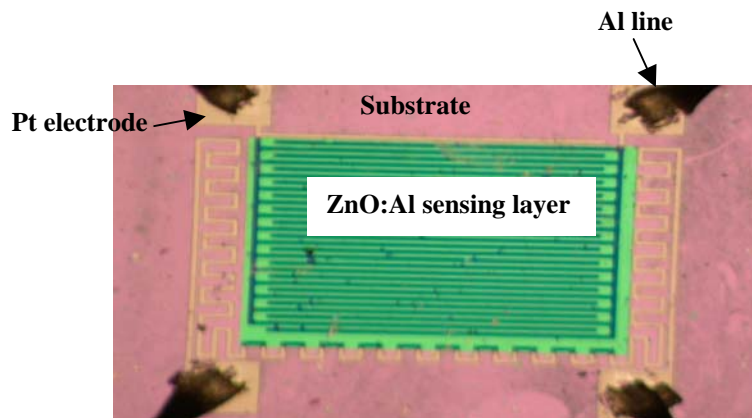


Figure 1. The sensor configuration

The grain size of ZnO:Al film was estimated using the Debye-Scherrer equation [17] and the full width at half maximum (FWHM) of (0002) peaks is shown in Figure 2. The calculated grain sizes of the films were more or less uniform for all films, ranging from 51 to 69 nm, for the ZnO:Al films sputtered at the RF powers of 100~140 W, respectively.

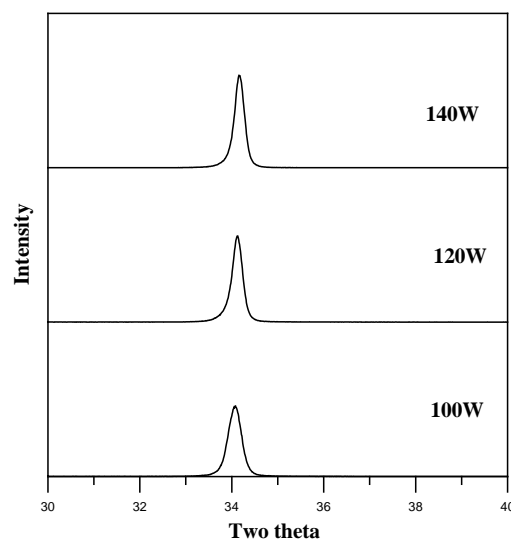


Figure 2. XRD diffraction patterns for ZnO:Al films deposited at various RF powers and pressure of 3×10^{-3} Torr.

The SEM surface and cross-section morphologies for the film deposited at 120 W are shown in Figure 3. It is seen that the deposits are flat and smooth in morphology, while the cross-section micrograph reveals a columnar structure as it grew on the substrate. The columnar morphology of films deposited on silicon substrate helps enhance the chemical interaction of ethanol gas with ZnO:Al film, which strengthens the output signal and sensitivity of the sensor.

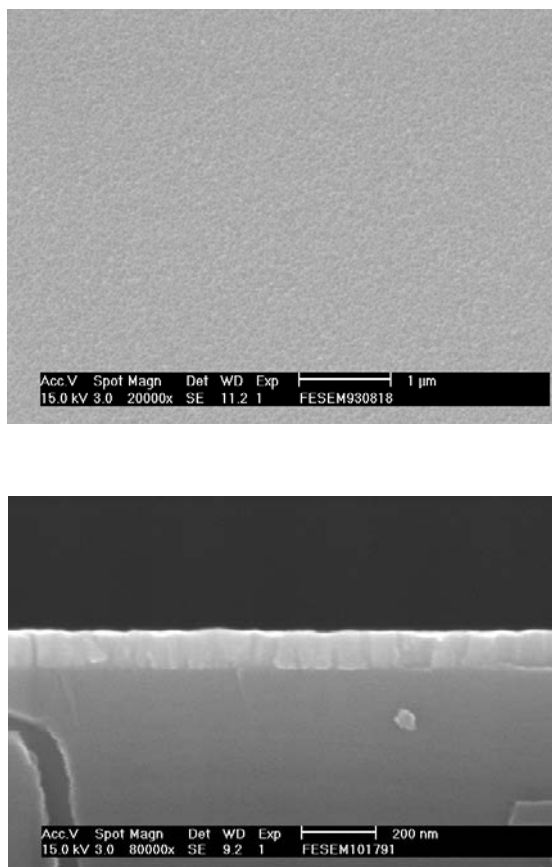


Figure 3. SEM surface and cross-section morphologies for ZnO:Al film deposited at RF power of 120 W.

Sensitivity of a ZnO:Al thin film to 400 ppm ethanol vapors from 120 to 250°C is shown in Figure 4(a), and it can be seen that the sensitivity increases with increasing operating temperature. The characteristic behavior of the resistance decrease of the sensor upon detecting ethanol vapors is typical for n-type semiconductor oxide gas sensors. When the ethanol vapors were introduced into the test chamber, the resistance of the sensor decreased and soon afterwards it became saturated. When the gas was turned-off, the resistance of the sensor increased. After initial resistance was stabilized, ethanol vapors were injected into the closed chamber in the batch system and the gas was vented after being maintained for 5 min. Figure 4(b) presents the response and recovery transients of the sensor to 400 ppm ethanol vapors at 250°C. The response and recovery time (time for 90% of resistance change) for ethanol vapors/air mixture for 400 ppm concentration at 250°C is about 2-4 min, with good reproducibility.

The calibration curve shown in Figure 5 indicates that the relation between sensitivity and concentration is linear, which benefits an actuator by enabling it to detect different concentrations of combustible gases and organic vapors.

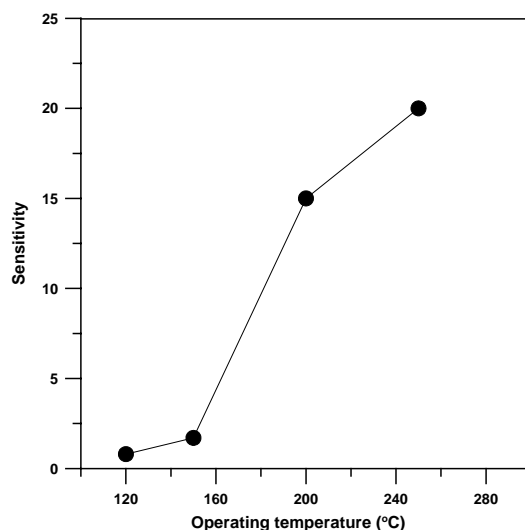


Figure 4. (a) Relationship between operating temperature and sensitivity for ZnO:Al thin film at 400 ppm.

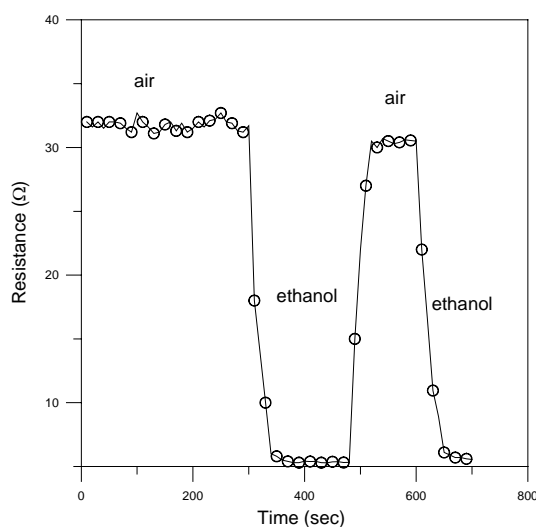


Figure 4. (b) Electrical response of the sensor at operating temperature of 250°C.

The gas sensing mechanisms normally accepted for semiconductor sensors assume that the oxygen adsorbed on the surface of the oxide removes some of the electronic density and thus decreases the material's conductivity. When reduction gas molecules come into contact with this surface, they may interact with this oxygen, leading to an inverse charge transference [18]. Upon the return of the electrons to the conduction band, conductivity increases. This utilizes the gas-induced resistance variations in potential barrier height at grain boundaries (i.e. changes in thickness of the space charge layer) to detect ethanol vapors in air. For polycrystalline substances, grain boundaries contribute most of the resistance.

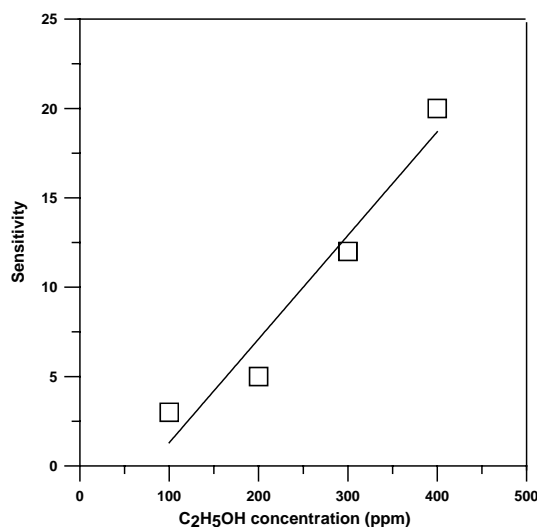
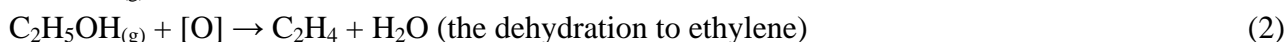
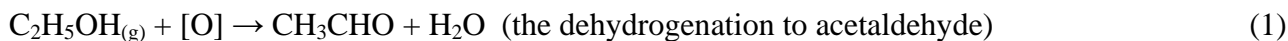


Figure 5. Sensitivity variation as a function of ethanol concentration for ZnO:Al thin film as operated at 250°C.

It may also be concluded that the surface conductivity of a semiconducting oxide crystal depends on the electron concentration near the surface, which in turn is affected by the nature of the chemisorbed species. The sensitivity characteristics of the sensor are associated with a modification of the ZnO surface by the electron transfer mechanism. In this study, the reason for a decrease in the resistance may be due to the oxidation of the ethanol vapors upon coming in contact with the ZnO:Al film surface, which liberates free electrons and H₂O. The atmospheric oxygen chemisorbs on the surface of the ZnO:Al film as O₂⁻ or O⁻, removing an electron from the conduction band of the ZnO:Al semiconductor, developing a depletion region on the surface. Ethanol vapors react with the chemisorbed oxygen and reinject the carrier, thereby reducing the resistance of the ZnO:Al material. The possibility of a reaction of ethanol with the ZnO:Al sensing layers can be explained as two oxidation states [19]:



in which [O] represents the surface oxygen ions.

The first reaction is a process initiating the oxidation by the dehydrogenation to CH₃CHO intermediate, and the second reaction is initiated by the dehydration to C₂H₄. But the selectivity for the two reactions is initiated by the acid–base properties of the oxide surface. The dehydrogenation process is more probable on the oxide surface with basic properties, while the dehydration is favored on the acid surface [19]. The intermediate products, acetaldehyde and ethylene, are subsequently reduced to CO₂ and H₂O. At higher temperature, the depletion region created by the chemisorption of oxygen on the surface extends more deeply, providing larger scope for more gaseous elements to be adsorbed, thereby giving a better response. Also, the hydroxyl group desorbs at higher temperatures [20]. Thus for lower temperature operation (<150°C), the surface of the sensor does not get completely desorbed, which causes a smaller change in resistance. ZnO:Al has thus been found to markedly and effectively promote the sensitivity to ethanol vapor.

4. Conclusions

In this study, the structures and sensing properties of ZnO:Al films as an ethanol vapor gas sensor obtained by RF magnetron sputtering system were investigated. The structural characteristics reveal that flat and well-defined columnar films with c-axis textured were formed. The film exhibited good sensitivity to the ethanol vapors with quick response-recovery characteristics, and it was found that the sensitivity for detecting 400 ppm ethanol vapor was ~20 at an operating temperature of 250°C. ZnO:Al seems to be a promising semiconducting material for the detection of ethanol vapor.

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