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NH_3 sensing properties of ZnO thin films prepared via sol–gel method

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An 80 nm-thick ZnO film was prepared via the sol–gel method at 500 °C using zinc acetate, 2-methoxyethanol, and monoethanolamine as precursors. Characterization of the film showed that it was composed of 20–30 nm sintered ZnO nanoparticles with good crystallinity. The NH_3 sensing properties of gas-sensing devices with a 5 μm gap that utilized the prepared ZnO film were examined. The highest sensor response (57.5%) was achieved with 600 ppm NH_3 in air at 150 °C. The response and recovery times were 160 s and 660 s, respectively. This study also examined the effects of NH_3 and oxygen concentration as well as the temperature on the sensor response performance. The findings show that oxygen plays an important role in the conductivity of ZnO thin films, and thus affects the sensor response toward NH_3.

1. Introduction

Gas sensors are important tools in fields such as environmental pollution monitoring, chemical process monitoring, and personal safety [1–3]. A gas sensor typically converts the gas concentration in an environment into an electrical signal such as a voltage, current, or resistance. Metal-oxide-semiconductor gas sensors have attracted a lot of research attention due to their high sensor response, low cost, simple manufacturing process, and good process compatibility [4–6]. Metal oxides often adopted as gas sensors include SnO_2 [7], TiO_2 [8], WO_3 [9], ZnO [10], indium tin oxide [11], and CuO [12]. Seiyama et al. [13] pioneered the use of ZnO as a metal-oxide gas sensor. ZnO has been widely applied for detecting combustible and poisonous gases, such as NO_2 [14], NO [14], C_2H_5OH [15], CO [16], H_2 [17], and NH_3 [17–20].

ZnO is an n-type wide-bandgap semiconductor material with an approximate bandgap of 3.37 eV. Because of its unique properties, ZnO is extensively studied. Low-dimensional ZnO nanocrystals can be formed with stable chemical and thermal properties [21]. A ZnO thin film can be produced using many methods, including thermal evaporation [22], reactive deposition [23], sputtering [16], chemical vapor deposition [24], spray pyrolysis [25], and the sol–gel method [26]. Among these methods, the sol–gel method is relatively easy, simple, and cost-effective for mass production [27].

Wan et al. [15] synthesized ZnO nanowires and employed microelectromechanical systems (MEMS) technology to fabricate a ZnO sensing device for ethanol sensing. They found that at an operating temperature of 300 °C, this sensor could detect ethanol with a concentration of as low as 1 ppm. Wagh et al. [19] employed screen-printing technology to produce a thick ZnO film for sensing NH_3 at 300 °C. In the literature, the operating temperature for ZnO in NH_3 detection is generally higher than 250 °C [17–20], because a higher operating temperature activates and accelerates the adsorption, desorption, and reaction of NH_3 on a ZnO surface [28]. However, it is necessary to study the gas sensing properties of ZnO thin films at lower temperatures.

The present study adopts the sol–gel method to form a ZnO nanofilm. A ZnO sensing device was fabricated using photolithography. The effects of NH_3 concentration, temperature, and oxygen on the sensing properties of the device were studied.

2. Experiment at details

2.1. Synthesis of ZnO thin films

This study adopted the sol–gel method to produce a ZnO nano thin film. 1.64 g of $Zn(CH_3COO)_2{\cdot}2H_2O$, 0.45 g of monoethanolamine, and 10 mL of 2-methoxyethanol were mixed and stirred for 2 h on a hot plate at a constant temperature of 60 °C, producing a clear colloidal solution. This solution was spin-coated at 5000 rpm onto a SiO_2/Si substrate, and then the sample was heated on a hot plate at 200 °C for 10 min to remove organic solvent from the film. Finally, the sample was calcined at 500 °C for 3 h to form ZnO nanofilms.

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The surface morphology and thickness of the synthesized ZnO thin film were examined by field-emission scanning electron microscopy (FE-SEM; Hitachi S-4800). X-ray diffraction (XRD; Rigaku D/MAX2500) was used to identify the crystalline structure of the film. Transmission electron microscopy (TEM; Tecnai F20) was employed to analyze the internal structure of the film.

2.2. Setup of gas-sensing device

Fig. 1 shows the ZnO gas-sensing device. From the bottom to the top, the device is composed of a SiO_2/Si substrate, a 80 nm-thick ZnO film, a 10 nm-thick Ti film as an adhesive layer, and a set of patterned Au electrodes made using photolithography. The gap between the two electrodes is 5 μm.

Fig. 2 shows the setup of the gas sensor. The three gas cylinders contain O_2, N_2, and a mixture of NH_3 and N_2, respectively. A set of mass flow meters and a mass flow controller were employed to adjust the admitted flow and the concentration of NH_3. The total flow rate through the gas mixer to the chamber was 300 sccm. A multimeter (Keithley 2000) was used to measure variations in the resistance. The data were stored on a computer. In this study, the NH_3 concentration used for detection was in the range of 50–600 ppm, and the operating temperature was 150–300 °C. Before each measurement, the device was placed into the test chamber and allowed to sit in the air for approximately 2 h until the desired temperature was reached.

In this study, the sensor response is defined as the ratio of the resistance variation caused by the reactant gas to the initial resistance, expressed as:

$$\text{Sensor response} = \frac{|R_a - R_g|}{R_a} \times 100\% \tag{1}$$

where R_a and R_g represent the resistances of the ZnO thin film (Ω) before and after the reactant gas enters the chamber, respectively. The response time is defined as the time required for the resistance variation value to reach 90% of the maximum value, and the recovery time is defined as the time required for the resistance recovery value to reach 90% of the minimum value.

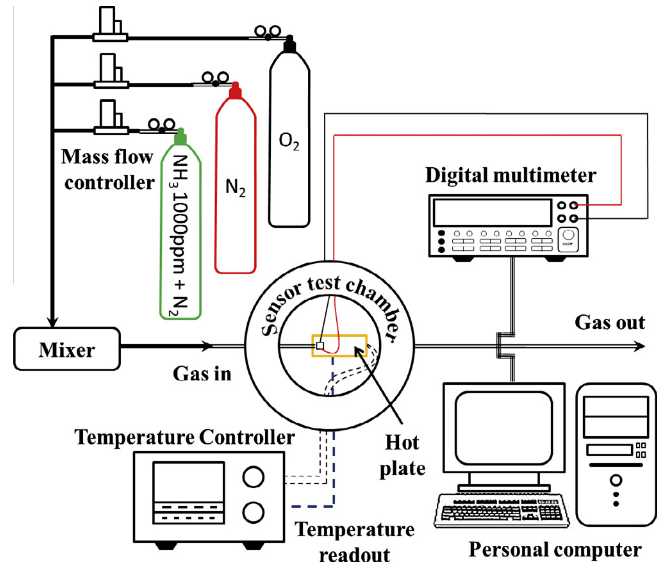

Fig. 2. Gas sensor testing apparatus.

3. Results and discussion

3.1. Synthesis of ZnO thin films

Fig. 3(a) shows a top-view SEM image of the prepared ZnO thin film. As can be seen, the film was composed 20–30 nm ZnO nanoparticles. The side-view SEM image in Fig. 3(b) shows that the film had a uniform thickness of 80 nm. The XRD pattern of the ZnO thin film is shown in Fig. 3(c). The structure was identified to be zincite (hexagonal close-packed structure). The lattice constants are $a = b = 0.322$ nm and $c = 0.521$ nm. The high-resolution TEM image in Fig. 3(d) shows that the ZnO film has a single-crystalline structure, and the selected-area electron diffraction (SAED) pattern in the inset confirms its hexagonal close-packed structure. The ultraviolet (UV) spectrum of the ZnO thin film in Fig. 4 shows an absorption peak at a wavelength of 380 nm. The band gap of the ZnO thin film was calculated to be 3.21 eV using the Kubelka–Munk equation [29]. These results confirm that ZnO nanofilms were formed using the sol–gel method.

3.2. Gas sensing studies

3.2.1. Effect of NH_3 concentration on sensor response

Fig. 5 shows the relationship between the sensor response and NH_3 concentration under an operating temperature of 150 °C. When NH_3 entered the sensing chamber, the resistance of the ZnO thin film dropped rapidly, leading to a rapid rise in sensor response. The resistance then decreased gradually and eventually reached a constant value. When the NH_3 flow was stopped, the resistance increased, leading to a gradual decrease of the sensor response to the initial level. As can be seen in Fig. 5, a rise in NH_3 concentration resulted in an elevated sensor response. For example, when the NH_3 concentration was 600 ppm, the highest sensor response (57.5%) was reached, with a response time of 160 s and a recovery time of 660 s. At the minimum concentration (50 ppm), the maximum sensor response was approximately 18%, with a response time of 660 s and a recovery time of 600 s.

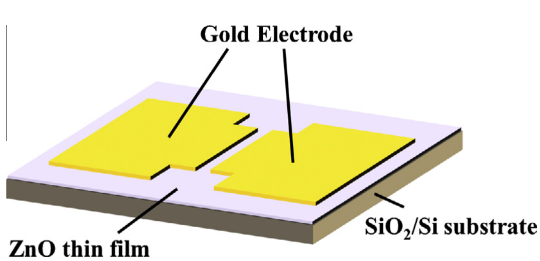

Fig. 1. ZnO gas-sensing device.

For metal oxides, gas sensors are categorized as either n- or p-type semiconductor sensors [30]. ZnO is an n-type (electron-rich) semiconductor. When the ZnO thin film was exposed in air, oxygen adsorbed on the surface of the ZnO nanoparticles. The adsorbed oxygen captured an electron from the conduction band of the ZnO nanoparticles (as shown in Fig. 6(a)), which resulted in band bending and the formation of an electron depletion region in the outer shell of the ZnO nanoparticles [31]. Therefore, a Schottky barrier formed at the boundaries of the nanoparticles in the ZnO thin film. When the purging air was admitted into the chamber, the resistance increased because of the Schottky contact. When the adsorption and desorption of the oxygen on the surface of the film reached an equilibrium, the resistance became a constant.

When NH_3 was introduced into the chamber with air, not only did O_2 react with the ZnO film, but so did NH_3. Possible reaction equations and a possible mechanism are shown in Fig. 6(b). NH_3 is regarded as a reducing gas. The admitted NH_3 gas reacted with the adsorbed oxygen ions on the surface of the nanoparticles and released electrons. The electrons then returned to the conduction band of the ZnO nanoparticles, resulting in a shrinkage of the depletion region. The Schottky barrier therefore decreased and the resistance decreased as the two reactions shown in Fig. 6(b) reached equilibrium. The resistance of the film thus became a constant value.

In general, the equation $R_a/R_g = \alpha(C_g)^\beta + 1$ [15,32] is used for the evaluation of gas sensors that employ a metal oxide as the sensing material. Here, C_g is the concentration of the reactant gas, α is a constant determined by the sensing material and operating conditions, and β is derived from the surface interaction between the chemisorbed oxygen anions and the reducing gas. For example, for the detection of NH_3 using a ZnO thin film, the ideal value for