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Schottky barrier effect of ZnO modified methyl glycol thin films for detection of hydrogen sulfide gas

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Abstract

Highly nanocrystalline ZnO modified methyl glycol thin films have been deposited on a p-type silicon substrate via the sol–gel spin coating manner. The morphology of the as-deposited film was scrutinized using scanning electron microscopy. *I–V* characteristics of the as-prepared ZnO film under vacuum and in open air were monitored. The results showed that the ZnO films have a barrier height of 0.38 eV under vacuum and 0.62 eV in open air. The Schottky barrier height between ZnO grains was determined for different reducing gases. The ZnO film showed high sensitivity to H_2S gas compared with other reducing gases due to the reduction of barrier height between ZnO grains. The as-prepared ZnO film was annealed at four different temperatures. X-ray diffraction manifested that the wurtzite hexagonal structure of ZnO deviated from ideality at annealing temperature greater than 650 °C. The barrier height of ZnO film decreased due to the increase of annealing temperature up to 650 °C and then decreased. The results also confirmed that the change of barrier height strongly affected the sensitivity of ZnO film.

Keywords: Spin coating; Annealing; Schottky barrier; Gas sensitivity

1. Introduction

Recently, metal oxide gas sensor devices have found prevalent application [1–3]. These sensor devices are being substantially monopolized for the automotive and municipal applications to control the air ventilation flutters or to monitor natural gas seepages. These implementations entail metal oxides with low price, light weight, small extent, un-convoluted, low consuming power and high sensibility to a spacious assortment of gases. Among these metal oxides, zinc oxide is rated as one of the utmost auspicious n-type metal oxide semiconductor gas sensor due to wide band energy gap, 3.37 eV, with exciton binding energy, 60 meV, at ambient temperature [4–6], high transparency in visible region [7–10], low cost and non-toxicity.

Many attempts have been made for embellishing the selectivity of zinc oxide gas sensors either by doping zinc oxide with other metal oxides [11–15] or by controlling its structure stiochiometry [16–18] to enhance the gas discrimination. The control of zinc oxide structure stiochiometry is mainly dependent on the process of preparation techniques. Yoon et al. [19] have prepared ZnO thin film on alumina substrate via the RF magnetron. They showed that this preparation technique enabled ZnO to detect acetone at low concentrations efficiently. Chougule et al. [20] have synthesized ZnO thin film on glass substrate using the sol–gel spin coating technique. They showed that such preparation technique was useful for detection of NO_2 with a sensitivity of 40% at an operating temperature of 200 °C. Pawar et al. [21] reported the effect of different polymers kinds on the structure of zinc oxide. Their results confirmed that each kind of polymer affected the structure and sensation of acetone gas. In spite of ZnO films showing a reasonable sensitivity for different gases such as acetone, ammonia and nitrous, the operation temperature and response time are still high from commercial application point of view [21,22].

As far as we know, no reports mentioned the synthesis of ZnO film on p-type silicon substrate via the sol–gel spin

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coating technique based methyl glycol for detection of H_2S gas at room temperature. Moreover, the effect of Schottky barrier height of ZnO film on the sensitivity of H_2S has not been reported yet. Here, we reported the relation between Schottky barrier height and H_2S gas sensitivity of ZnO film at different annealing temperatures.

2. Experimental

2.1. Samples preparation

Zinc oxide thin films have been obtained via the sol–gel spin coating methodology on p-type silicon substrate according to the following procedure. Firstly, a solution of zinc acetate has been prepared by dissolving 1 mmol of zinc acetate into 40 ml of isopropanol and kept stirring for 30 min at ambient temperature. Then 1 mmol of methyl glycol is added to the zinc acetate solution and kept stirring for 2 h at a temperature of 60 °C and left to cool down naturally at ambient condition for 24 h until getting a clear and homogeneous viscous solution was obtained. This viscous solution was utilized as the coating exporter. Silicon substrates p-Si (100) were cleaned by hydrogen fluoride (HF), ethanol and acetone for about 10 min in ultrasonic bathtub. Therefore, these silicon substrates were laved with de-ionized water and dehydrated in the presence of nitrogen. The viscous gel was deposited onto silicon substrate followed by rotation at 2000 rpm for 60 s using a spin coater. After the spin coating process, the deposited films were exsiccated at 100 °C for 10 min in an electric oven to vaporize the solvent and to evict organic boosts. This process was reiterated multiple times to get desirable thickness. These films have been annealed at different temperatures of 400, 650, 850 and 1000 °C for 2 h with a heating rate of 25 °C/min.

2.2. Measurements

All of the samples investigated in this study were thoroughly characterized using Regaku–Ultima-IV X-ray diffraction, $\lambda_{cu(k\alpha1)} = 1.5406$ Å, working at 40 kV and 30 mA with scan speed 0.05°/s. A complete scan has been performed between 30° and 70° (2θ). Field emission scanning electron microscopy of the prepared films has been performed by using JEOL 7001F. For gas sensitivity measurement, the resistance was measured using a Keithley 6514 Electrometer. The film was mounted in 3000 cm^3 airtight glass container. Definite concentration of the tested gas has been squirted through the glass chamber. The sensor sensitivity during gas detection was determined as the ratio $G_{gas} - G_{air}/G_{air}$, where G_{air} is the ZnO conductance in open air and G_{gas} is the ZnO conductance in the subsistence of target gas. All measurements were conducted at ambient temperature.

3. Results and discussion

3.1. Characterization

Fig. 1 reveals the SEM photography for the as synthesized zinc oxide thin film via the sol–gel spin coating technique based methyl glycol. It is obvious that the film has smooth surface and the ZnO nanoparticles are homogeneously distributed along the surface of silicon substrate. The side view of SEM image (inset of Fig. 1) indicates that the average thickness of the as-prepared film is 186 ± 11 nm.

Fig. 2 depicts the current–voltage characteristics of ZnO film under vacuum and in open air at forward and reverse biases. Such figure indicates that the deposited ZnO thin film on the p-Si substrate shows Schottky diode like behavior with rectification of three in the voltage range

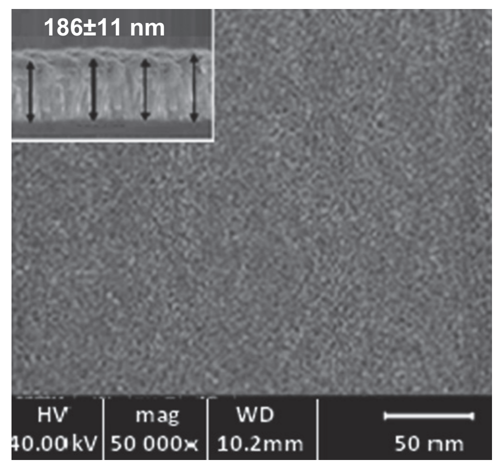

Fig. 1. SEM image for the as-prepared ZnO thin film via the sol–gel spin coating technique (inset: side view for monitoring thickness).

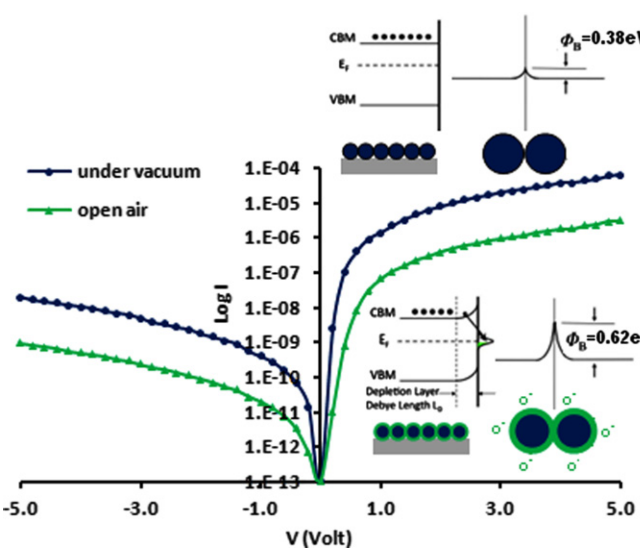

Fig. 2. I–V characteristics for Ag/n-ZnO/p-Si under vacuum and in open air.

from −5 to +5 V. The second observation is that at a constant voltage, the current under vacuum is higher than in open air. This means the resistance of the zinc oxide film increased in open air. This increase of resistance is mainly due to the absorbance of oxygen gas molecules from the surrounding atmosphere on the zinc oxide surface. This reaction mechanism can be described as

$$O_2(\mathrm{gas}) \leftrightarrow O_2(\mathrm{ads})$$

$$O_2(\mathrm{ads}) + e^- \leftrightarrow O_2^-(\mathrm{ads})$$

$$O_2^-(\mathrm{ads}) + e^- \leftrightarrow 2O^-(\mathrm{ads})$$

The adsorbed oxygen molecules on the zinc oxide surface tend to extract electrons from the conduction band which resulted in trapping of oxygen atoms in the form of ions on the zinc oxide surface. This mechanism leads to band bending in the conduction band and the formation of depletion layer. The depletion layer and band bending are strongly affecting the Schottky barrier height. The height of this barrier is illustrated in the inset of Fig. 2. Thermionic emission model is mainly used for determination of the value of Schottky barrier height [23]:

$$J = J_s\left[\exp\left(\frac{qV}{nkT}\right) - 1\right] \quad (1)$$

where V is the applied potential, n is the ideality factor, k is the Stefan–Boltzmann constant, T is the absolute temperature, and J_s is the saturation current which is defined as

$$J_s = A^* T^2 \exp\left(\frac{-q\phi_b}{kT}\right) \quad (2)$$

where q is the electronic charge, $,\phi_b$ is the barrier height between zinc oxide grains and A^* is the Richardson constant which equals 32 $\mathrm{Acm^{-2}\,K^{-2}}$, for n-type ZnO [24]. The saturation current was determined from the intercept at zero voltage of the logarithmic current vs. voltage curve shown in Fig. 2. The barrier height value was estimated from Eq. (2). The barrier height under vacuum is found to be 0.38 eV and in open air it is found to be 0.62 eV. The increase in the barrier height in open air gives rise to an increase in the resistivity of ZnO film.

3.2. Gas selectivity

Fig. 3 shows the *I–V* characteristic curves for the as-prepared ZnO film under the influence of different gases at the same concentration of 0.15 ppm. It is clear that the current is strongly affected by the type of tested gas. The Schottky barrier height was determined based on Eqs. (1) and (2) and the values are represented in Fig. 4. The sensitivity of ZnO film for these gases at the same concentration was also monitored and is represented in Fig. 4. Regarding Fig. 4, one may observe that the Schottky barrier height has the lowest value when ZnO film is subjected to H_2S gas. This reduction of barrier height may be attributed to the following. When ZnO thin film is subjected to H_2S, this gas is oxidized by negatively

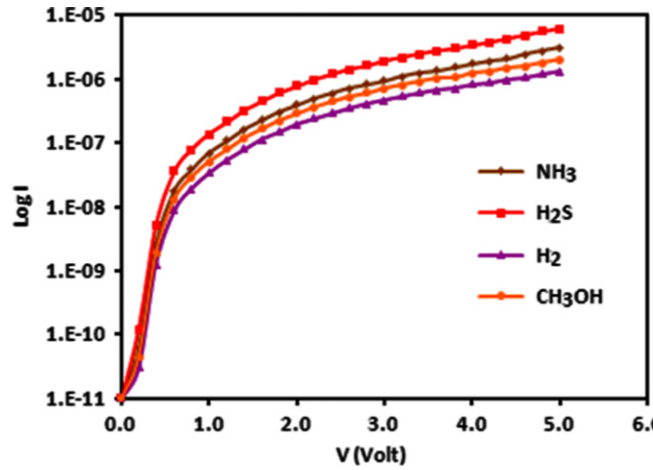

Fig. 3. I–V characteristics of ZnO film at different gases.

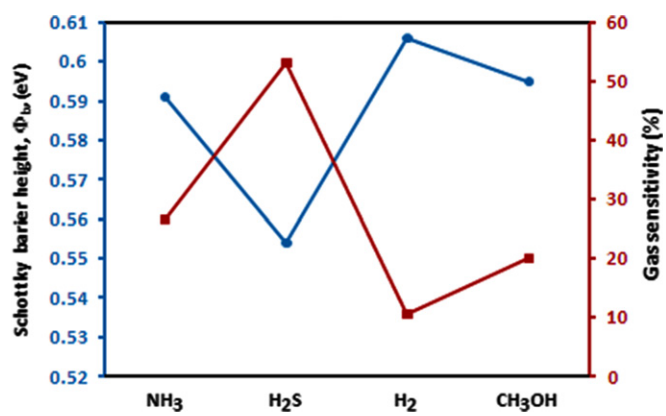

Fig. 4. Schottky barrier height and gas sensitivity of ZnO film at different gases.

charged oxygen ions and released electrons back to the conduction band. In addition to the reduction of the number of negatively charged oxygen ions on the zinc oxide surface, the thickness of depletion layer decreases. Therefore, the Schottky barrier between zinc oxide grains is reduced and it would be convenient for electrons to travel through various zinc oxide grains.

Among all tested gases, the prepared ZnO film was most sensitive for H_2S gas. The sensitivity of ZnO film for H_2S gas was 53%, 26% for NH_3, 12% for H_2 and 20% for CH_3OH. This variation in sensitivity can be explained according to the following reaction mechanisms.

$$NH_3 + 1.5O^- \leftrightarrow 1.5\,H_2O + 0.5\,N_2 + 1.5e^-$$

$$H_2S + 3O^- \leftrightarrow H_2O + SO_2 + 3e^-$$

$$H_2 + O^- \leftrightarrow H_2O + e^-$$

$$CH_3OH + 2O^- \leftrightarrow CO + 2\,H_2O + 2e^-$$

When the ZnO film is exposed to reducing gases, the adsorbed oxygen species react with these gases and relieve electrons back to the ZnO film and steer for an increase of the ZnO conductivity. Among all gases, the interaction of H_2S with oxygen species results in the liberation of three electrons. Therefore, the change of conductivity will be higher than in other gases which liberated lower number of electrons.

3.3. Effect of annealing temperature on structure of ZnO film

Fig. 5a depicts the X-ray diffraction patterns for the ZnO thin film at four different annealing temperatures. These diffraction patterns appear at about 31.72°, 34.4°, 36.24°, 47.52° and 56.6° corresponding to the (100), (002), (101), (102) and (110) planes. These patterns match the pure hexagonal wurtzite ZnO structure [25]. The lattice parameters of ZnO have been calculated using the Bond method [26] and tabulated in Table 1. One may note that the calculated lattice parameters and c/a ratio are in good agreement with ideal wurtzite ZnO hexagonal structure up to an annealing temperature of 650 °C [27]. At elevated temperatures, from 800 to 1000 °C, the c/a ratio altered from ideal value 1.602 to 1.597. This slight deviation from the ideal wurtzite hexagonal crystal structure is perhaps due to crystal ionization and formation of free charges.

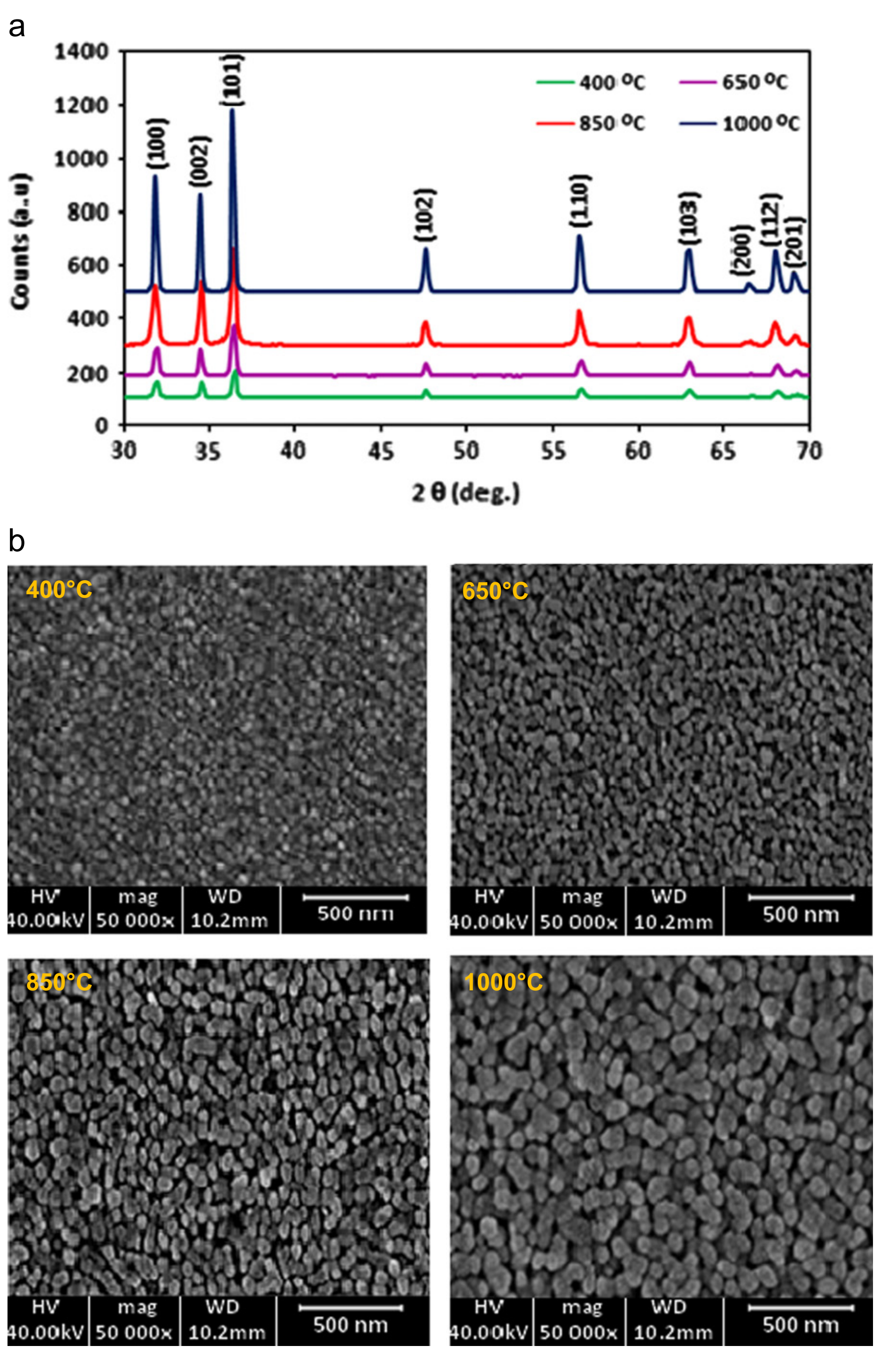

Fig. 5. (a) XRD patterns and (b) SEM images of ZnO thin films at different annealing temperatures.

Table 1
Calculated lattice parameters of wurtzite ZnO hexagonal structure.

Annealing temperature (°C)	a (Å)	c (Å)	c/a ratio
400	3.249 ± 0.002	5.208 ± 0.004	1.602
650	3.248 ± 0.002	5.209 ± 0.004	1.603
850	3.251 ± 0.003	5.201 ± 0.007	1.599
1000	3.251 ± 0.001	5.196 ± 0.003	1.597

It has been claimed that the free charges are the prevailing laborer responsible for lattice expanding [28]. Accordingly, one may expect that at elevated temperature, above 650 °C, the deviation of ZnO structure from ideality will negatively reduce its gas sensitivity.

The morphology of the annealed films was studied by using scanning electron microscopy (SEM) to elucidate the shape and particle size of the annealed ZnO films. Fig. 5b depicts SEM images for ZnO thin films annealed at different temperatures of 400, 650, 850 and 1000 °C. It is clear that the zinc oxide particle size is increased as the annealing temperature increased. The average particle sizes were 23, 49, 97 and 143 corresponding to annealing temperatures 400, 650, 850 and 1000 °C, respectively.

3.4. Effect of Schottky barrier height on annealed ZnO film for H_2S detection

Fig. 6a shows the change of Schottky barrier height for the annealed ZnO films when subjected to H_2S gas at a concentration of 0.15 ppm. It is clear that the barrier height decreases until the annealing temperature of 650 °C. Such decrease in the barrier height resulted in an increase in the rate of adsorption of H_2S gas on ZnO nanoparticles surface. At higher annealing temperature the ZnO particles are increased and formed large grains. Therefore, the rate of adsorption of H_2S gas will be decreased and these grains will not be fully covered with gas. Such mechanism is indicated in the inset of Fig. 6a. For confirming such assumption, the sensitivity of the annealed films for H_2S gas was monitored as shown in Fig. 6b. One can notice that the ZnO film annealed at 650 °C has the highest sensitivity.

In general one may conclude that, when the size of the grain is large, almost all available electrons are trapped in surface states and the grains are depleted from free carriers. This depletion inhibits the transport of electrons through the nano-crystalline structure of semiconductor device. This makes the device more resistive than bulk. In case of small grain diameter, the whole nano-crystallites are completely covered with gas ions which results in a dramatic change in the conduction of ZnO sensor device.

4. Conclusion

ZnO thin film has been prepared based on methyl glycol by the sol–gel spin coating technique on p-Si substrate. According to SEM, the ZnO film has an average thickness about 186 nm. The Ag/n-ZnO/p-Si heterostructure film showed Schottky diode like behavior. The barrier height between ZnO grains under vacuum was 0.38 eV and in open air was 0.62 eV. The barrier height of ZnO film was strongly affected by the tested gases. The lowest barrier height is obtained when ZnO film is subjected to H_2S gas which resulted in an enhancement of the sensitivity of ZnO film for H_2S gas among other tested gases. The as-prepared ZnO film was annealed at four different temperatures. XRD measurements showed that the annealing temperature results in an enhancement of ZnO crystallinity up to 650 °C, followed by deviation from ideality. SEM images

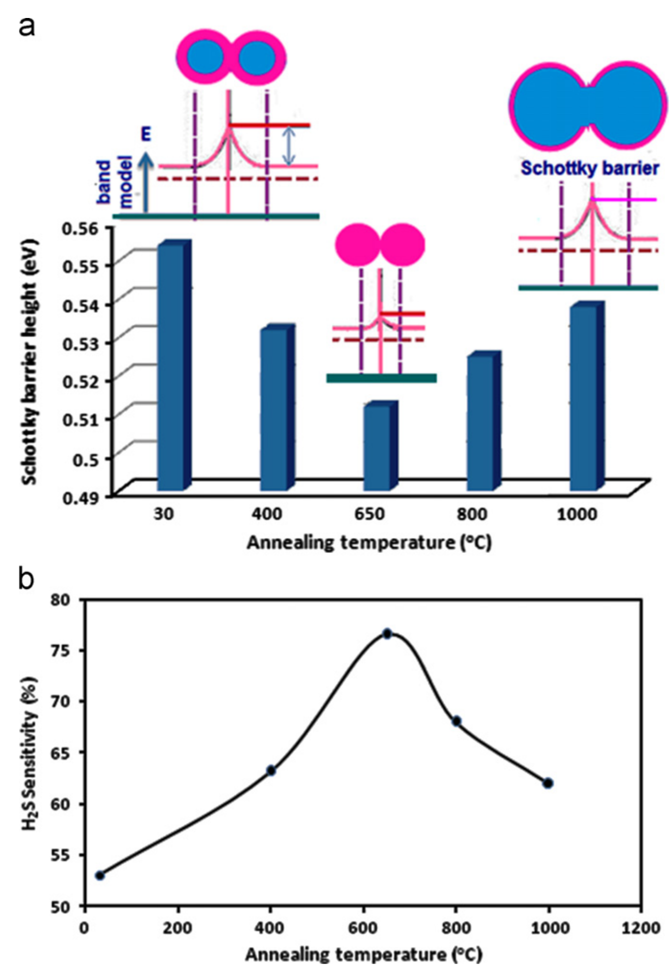

Fig. 6. Schottky barrier height (a) and H_2S gas sensitivity (b) for annealed ZnO films.

showed that the annealing temperature results in an increase of ZnO nanoparticles. The barrier height between ZnO grains decreased and then increased as a function of annealing temperature. The optimum barrier height was achieved at 650 °C. At this annealing temperature the ZnO film showed a high sensitivity for H_2S gas.

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