Sensing Properties of Nanostructured Zinc Oxide-based Gas Sensor Fabricated using Immersion Method

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ABSTRACT

Zinc oxide (ZnO) is a unique semiconducting material that popular among researchers due to its potential in various applications. ZnO has wide optical band gap energy of 3.37 eV and high excitation binding energy of 60 meV. Numerous methods can be used to fabricate nanostructured ZnO-based gas sensor, such as, physical vapor deposition (PVD), chemical vapor deposition (CVD), immersion method and etc. Immersion method is considered as a low cost and easy method to obtain nanostructured ZnO. In this work, the nanostructured ZnO-based gas sensor have been fabricated by immersion

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method using zinc acetate dehydrate ($Zn(CH_3COO)_2 2H_2O$) as the precursor. The ZnO solution's molarity was varied ranging from 0.02 M to 0.10 M. The effect of different molarity on its structural, electrical and sensing properties was investigated. The structural properties were characterized using atomic force microscopy (AFM). All samples have roughness value in range of 13 nm to 21 nm. The electrical properties were measured using current-voltage (IV) measurement. The highest conductivity of $3.3 \times 10^{-3} S \cdot cm^{-1}$ was obtained by 0.06 M. The sensing properties were characterized using simple gas testing setup. The samples were tested to 5% methane gas at operating temperature of 150 ^oC. The 0.06 M exhibited the highest sensitivity of 14.3%.

Keywords: *ZnO, CH_4 Gas Sensor, Immersion Method, Molarity*

Introduction

During the past 10 years much more information has become available on nanostructured semiconductor because of their compact size which always has high demand in fabricating electronic devices. Among n-type semiconducting materials, zinc oxide (ZnO) attracted considerable attention due to their unique properties for use in gas sensor applications. They observed on the change in the surface resistance of the sensing element with the presence of gases [1-3]. Methane (CH_4), the main constituent of natural gas, is a colorless, highly volatile, odorless and flammable gas. The development of a reliable, low cost methane sensor is thus of great interest, especially to monitor CH_4 from escaping into the atmosphere during industrial operation in order to protect public health and safe environment [1].

Several deposition techniques has been applied by numerous researchers to grow nanostructured ZnO, such as chemical vapor deposition (CVD) [4], physical vapour deposition (PVD) [5], spray pyrolysis [6] and sol-gel process [7]. Comparing to other deposition techniques sol-gel technique has not required expensive and complicated equipment. It has advantage of being easy to be coated on the desired shape and area [8]. There have been few ZnO-based methane sensors reported so far [9]. J.P. Cheng et al. have reported that the structural properties of the ZnO films depend on the zinc concentration [10].

In this paper, we report on the sensing properties of nanostructured ZnO-based gas sensor fabricated using immersion method. The effect of different molarity on its structural and electrical properties was investigated. Then the thin films were tested to 5% methane (CH_4) using simple gas chamber setup at operating temperature of 150^{o}C.

Experimental

The ZnO nano-template layer was prepared on glass substrate using sol-gel spin-coating technique. The solution of 0.4 M was prepared using zinc acetate dehydrate ($Zn(CH_3COO)_2 2H_2O$, 98% Sigma-Aldrich) as a starting material, aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, 98%, Sigma-Aldrich) as a dopant source, monoethanolamine (MEA, $C_2H_7N_{14}$) as a stabilizerand 2-methoxyethanol ($C_3H_8O_2$, 99%, Sigma-Aldrich) as a solvent. The molar ratio of MEA to zinc acetate was fixed at 1 with 1 at.% of Al doping [11].

The nanostructured ZnO were grown on the ZnO nano-template layer using immersion method. The immersion solution was prepared at different molarity ranging from 0.02 M to 0.10 M. The certain amounts of zinc acetate dehydrate was dissolved in hexamethylenetetramine (HMT, $C_6H_{12}N_4$, 99% Sigma-Aldrich) and deionized (DI) water. The molar ratio of HMT to zinc acetate was fixed at 1. The solution was sonicated at 50 ^oC for 30 minute using an ultrasonic water bath (Hwasin Technology Powersonic 405, 40 kHz). Then the solution was magnetically stirred and aged for 3 hour at room temperature. The aged solution was poured into a Schott bottle, which had been placed the spin-coated ZnO nano-template layer at the bottom. The immersion process was done in water bath at 95 ^oC for one hour. After an hour, the sample was withdrawn from the solution, thoroughly rinsed with DI water and allowed to dry at 150^oC for 10 minute before annealed in air ambient at 500^oC for 1 hour.

Gold electrode coating process

In order to inspect the conductivity of nanostructured ZnO, gold (Au) was deposited on top of the sample as an ohmic electrode. Au with thickness of 60 nm was deposited with the use of a physical mask using thermal evaporator (ULVAC, VCP 1100) in a vacuum environment.

Thin film characterization method

The structural properties were characterized using atomic force microscopy (AFM, Park System). The electrical and methane gas (CH_4) sensing properties were measured using two point probe current-voltage (IV) measurement (Keithley 2400).

Result and Discussion

Structural properties

The AFM images of the nanostructured ZnO that prepared at different molarity were investigated. Figures 1 and 2 showed the AFM 3D and watershed images of the nanostructured ZnO scanned over an area of 5.0 x

5.0 μm^2, respectively. The numerical analysis of AFM is listed in Table 1. The hexagonally faceted columnar structure was observed dominating the surface morphology when the molarity was increased, as shown in Figure 1. The results also showed that the root-mean-square (rms) roughness value increased from 13 nm to 21 nm with the increase of molarity. However, at the molarity over than 0.06 M, the roughness value was slightly decreased up to 15 nm. The rough surface properties increased the specific surface area that exposed to the target gases and hence, improve the sensor response [12].

The total of grain boundary that calculated from the watershed analysis is also presented in Table 1. It was seen from Figure 3 that, the total of grain boundary was decreased as the molarity increased and reached an optimum point at 0.06 M. However, at molarity over 0.06 M, the total of grain boundary was increased and this might due to larger particle size obtained at higher molarity. This is similar to pattern result obtained by J.P. Cheng et al. [10], where a high molarity resulted to a denser film. These results suggested that the surface morphology was strongly affected by the molarity.

Table 1: Numerical analysis of AFM 3D image

Molarity (M)	Roughness, Rq (nm)	Total of grain boundary (N)
0.02	13	269
0.04	18	257
0.06	21	153
0.08	17	195
0.10	15	236

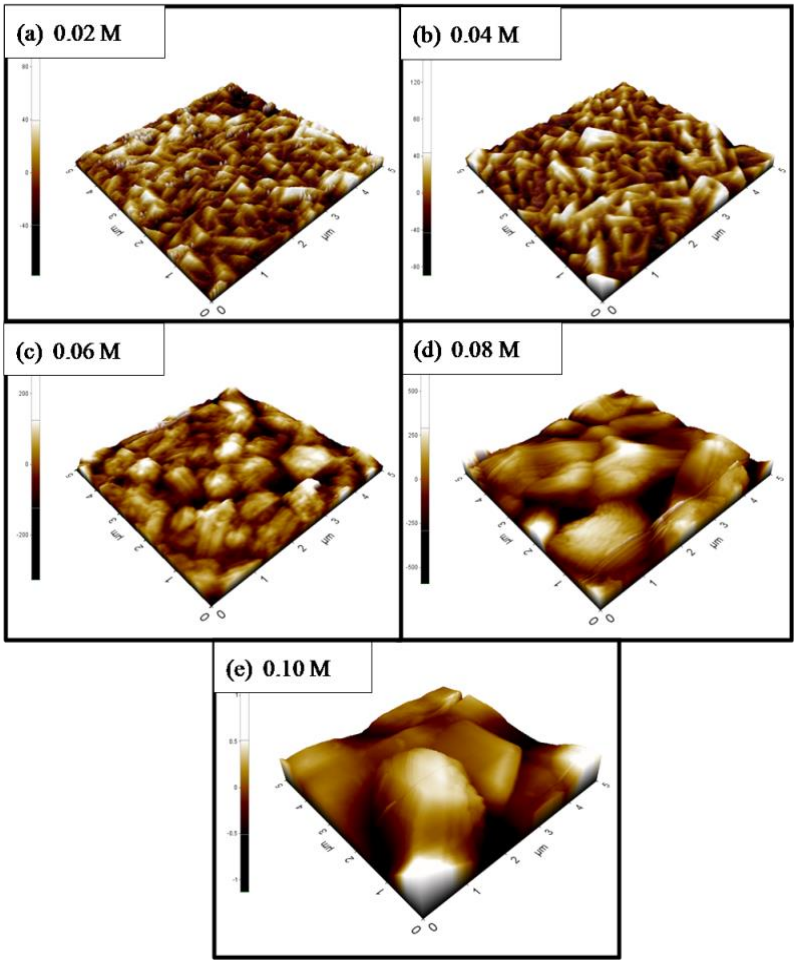

Figure 1: AFM morphology images of nanostructured ZnO prepared at different molarity of (a) 0.02, (b) 0.04, (c) 0.06, (d) 0.08 and (e) 0.10 M

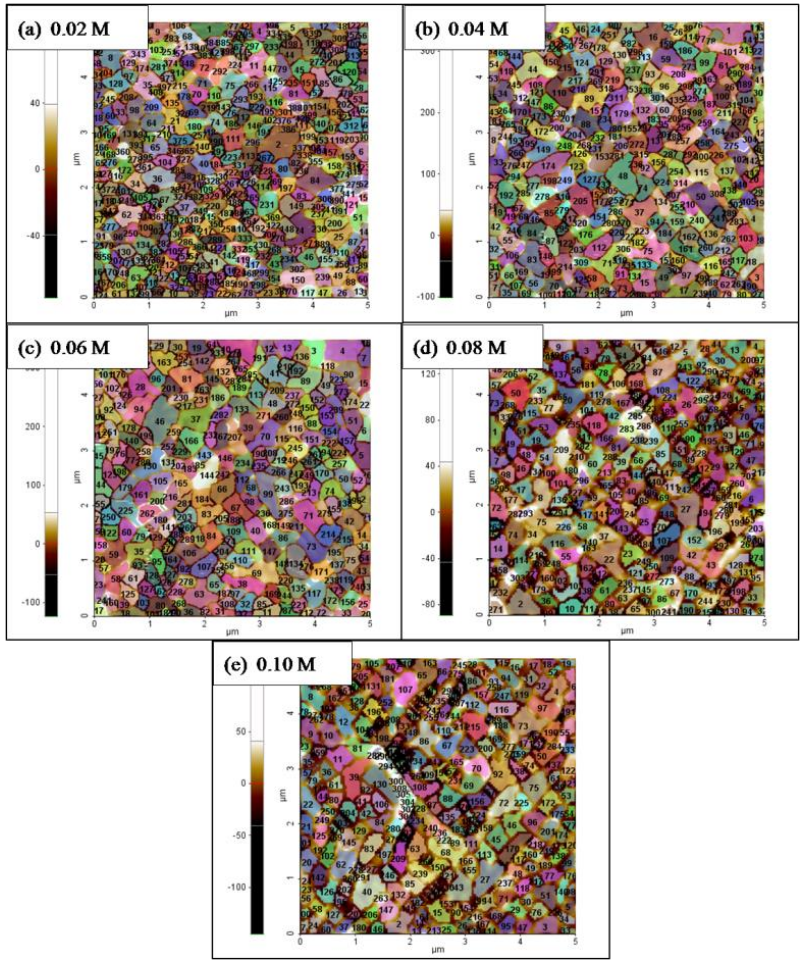

Figure 2: Watershed analysis of AFM 5 x 5 µm^2 images of nanostructured ZnO deposited at different molarity of (a) 0.02, (b) 0.04, (c) 0.06, (d) 0.08 and (e) 0.10 M

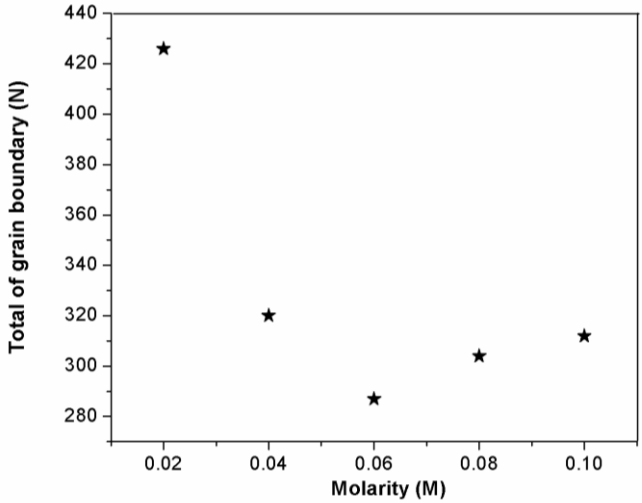

Figure 3: The total number of grain boundary calculated at different molarity

From the analysis of AFM watershed, the less number of total grain boundary resulted better electrical conductivity. Previous researchers imply that the less grain boundary can improve the electron mobility that hence increases the electrical conductivity. However, the high number of total grain boundary may behave like barriers against the electron mobility which causes poor electrical conductivity [13]. These results suggest the optimal molarity was 0.06 M sample.

Electrical properties

Figure 4 showed the IV characteristics of the nanostructured ZnO when the voltage sweep from -10 V to +10 V. The current linearly increased with the increase of the molarity. The optimum value of conductive sample was observed at the 0.06 M. Figure 5 showed the electrical conductivity that was calculated for each sample. The electrical conductivity can be calculated using formula (1) and (2),

$$\text{Resistivity, } \rho = \left(\frac{V}{I}\right)\left(\frac{A}{l}\right) \quad (1)$$

$$\text{Conductivity, } \sigma = \frac{1}{\rho} \quad (2)$$

Where, V is voltage, I is current, l is distance between contact and A is area of contact. Figure 5 showed that the electrical conductivity of the nanostructured ZnO was increased from 2.3×10^{-3} S·cm^{-1} to 3.3×10^{-3} S·cm^{-1}, as the molarity increased from 0.02 M to 0.06 M. However, as the molarity increased more

than 0.06 M, it was seen that the electrical conductivity was gradually decreased up to 2.7 × 10^{-3} S·cm^{-1}. The highest conductivity was obtained by 0.06 M and it is comparable to others which lied in the range of normal semiconductor (10^{3} to $10^{-3}$$Scm^{-1}$) [14].

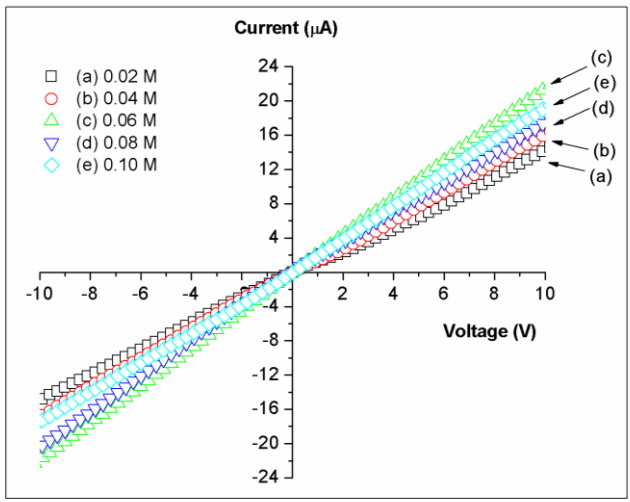

Figure 4: IV curve of nanostructured ZnO at different molarity

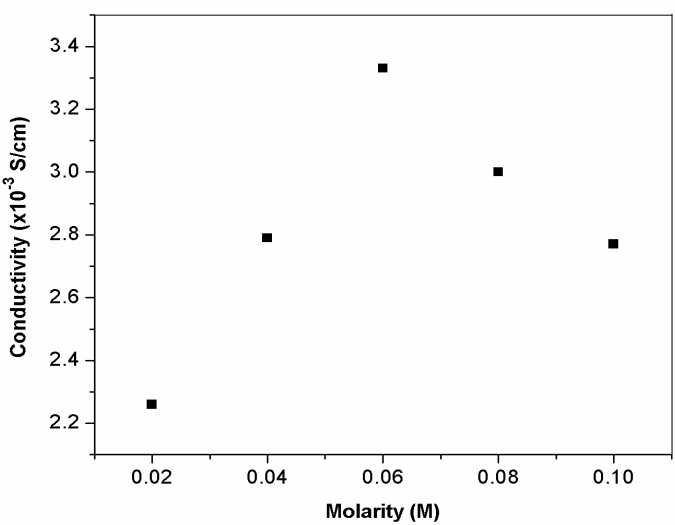

Figure 5: Conductivity of nanostructured ZnO at different molarity

CH_4 gas sensing properties

The sensing mechanism depends on the chemical reaction that happened on the surface and at the grain boundary. High surface roughness provides higher surface area of gas to be absorbed which thus induce the resistance change. Figure 6 showed a reduction of sensor resistance ratio (R_{gas}/R_{air}) with time. The ration is less than one for reducing gases, since the sensor resistance decreases in a reducing environment. As expected, the sensor resistance was significantly decreased when CH_4 gas was allowed to flow inside the chamber and thereafter reached a stable value as shown in Figure 6. The stable value is also known as equilibrium resistance value (R_{gas}) which then the percent sensitivity can be calculated. The gas sensitivity (S) is defined as the percent reduction of resistance of the thin films in the presence of target gas given by equation (3):

$$S\,(\%) = \frac{R_{air} - R_{gas}}{R_{air}} \times 100 \qquad (3)$$

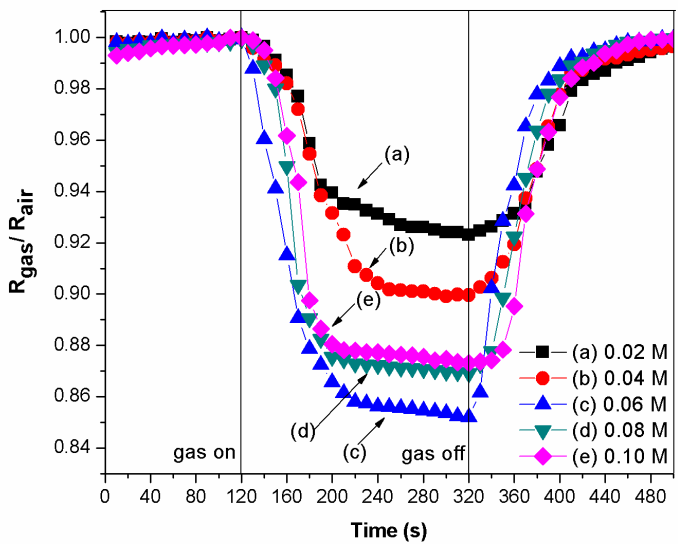

Figure 6: The response of ZnO thin film in presence of CH_4 gas at 150 ^oC

Table 2: **S**ensitivity value of nanostructured ZnO based gas sensor

Molarity (M)	Sensitivity (%)
0.02	7.5
0.04	10.0
0.06	14.3
0.08	13.0
0.10	12.5

It is notable that the increase in molarity enhanced the sensor response which may due to less grain boundary. As discussed earlier, at higher molarity (i.e. 0.08 and 0.10 M), the particle size become larger and thus increase the grain boundary scattering which act as barriers. It can retard the movement of electron which resulted poor sensor response. The highest sensitivity was obtained by 0.06 M with sensitivity value of 14.3%. These results are consistent with AFM watershed analysis and IV measurement. These results suggest that the molarity of ZnO solution play important roles in the gas sensing performance.

Conclusion

The nanostructured zinc oxide-based gas sensor had successfully fabricated using immersion method. Based on the studies, dense nanostructured film was obtained as the molarity increased. The electrical conductivity was increased and optimum point was obtained at 0.06 M. The improvement of structural and electrical properties leads to an enhancement in gas sensor response. The sensor element exhibited sensitivity of about 14.3% at 150^{o}C in presence of 5% methane (CH_4) in air for 0.06 M.

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