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GAS SENSING BEHAVIOR OF ZINC OXIDE NANORODS SYNTHESIZED VIA HYDROTHERMAL METHOD

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ABSTRACT

Zinc oxide (ZnO) nanorods were grown on silicon substrate by simple hydrothermal method in an aqueous solution of mixed zinc nitrate hexahydrate ($Zn(CH_3COO)_2.2H_2O$) and hexamethylenetetramine ($C_6H_{12}N_4$, HMT). The nature of the substrate was found to have effect on the crystal structure and morphology of the grown ZnO nanorods. Pre-deposited ZnO nanoparticles on the substrate were serving as seed layer to grow ZnO nanorods. The vertically aligned ZnO nanorods were obtained by well controlling the concentration of aqueous solution and substrate temperature. The sensing behavior of grown ZnO nanorods was measured at room temperature using oxygen gas. The resistance of device is greatly changed when exposure to the oxygen gas indicates that ZnO nanorods have a potential gas sensing behavior.

Keywords: ZnO nanorods; hydrothermal; gas sensing; oxygen gas; room temperature;

INTRODUCTION

Zinc oxide nanomaterials have been extensively investigated for applications in luminescence, photocatalysts, surface acoustic wave filters, piezoelectric transducers and actuators, gas sensors, solar cells and so on [1]. This is due to the their specific electrical and optoelectronic property of being a II–VI compound semiconductor with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, high breakdown strength, cohesion, and exciton stability. Moreover, ZnO is one of the hardest materials in the family of II–VI semiconductors [2]. The properties of ZnO nanomaterials strongly depend on their dimensions and morphologies. Besides these, the density of the of ZnO nanorods also plays an important role to how the ZnO nanorods interact with each other optically, electronically, and mechanically [3].

Semiconductor metal oxide-based gas sensors have attracted great attention over several decades due to their unique advantages, such as high sensitivity, low material and fabrication cost, ease of fabrication method and good compatibility to silicon microfabrication. Among semiconductor metal oxide-based gas sensors, ZnO is one of the earliest-discovered and well established gas sensing oxides, which has been extensively studied for detection of inflammable and toxic gases [4-5].

Gas sensors based on ZnO nanorods, SnO_2 nanowires, In_2O_3 nanowires, etc. showed excellent response and recover characteristics and can potentially overcome obstacles of other type of sensors, such as sensitivity and selectivity. Among different nanomaterials, nano-ZnO is one of the most promising multifunctional materials for gas sensors, especially for H_2 sensing. ZnO nanorods also have the advantages of large surface area, thermal and mechanical stability over the other materials as a sensor [6-7].

A simple production method of ZnO is desired to ensure the large quantities to be produced in a reasonable time and in an ecologically justifiable environment. The hydrothermal synthetic route has advantages to obtain high-crystallized powders with narrow grain size-distribution and high purity without heat treatment at high temperature. The particle morphology and size can be controlled via the hydrothermal process by adjusting the source species, reaction temperature and time and so on [8-9]. The well fabrication of novel nanostructure with special size and well-defined shape may open new opportunities for exploring unique properties and more potential application.

EXPERIMENTAL DETAILS

Zinc oxide nanorods were deposited on silicon wafer and glass substrate via simple hydrothermal method. In this method, zinc oxide nanorods are formed from chemical reaction of the Zn^{2+} source and the OH^- source under certain environment condition. In order to grow highly uniform distributed and well aligned zinc oxide nanorods on the substrate surface, the growth condition has to be controlled.

A very thin ZnO seed layer was prepared by sol-gel using zinc acetate dehydrate (ZAD) (Merck, purity 99.5%), ethanolamine (Merck, purity 99.5%) and methoxyethanol (Fluka) in the molar ratio of 1:1:10. The precursor solution is then agitated for 30 min at 60 °C to yield a homogeneous and stable colloid solution. The precursor was spin coated on the substrate, dried and heated at 300 °C for 30 min.

The aqueous solution of zinc nitrate hexahydrate (ZNH) (Fluka, purity 99.0%) and hexamethylenetetramine (HMT) (Fluka, purity 99.0%) were first prepared and mixed together. The molar ratio is set to 1:1. The solution was agitated at 90 °C for 30 min in order to obtain homogeneous solution. The substrates were arranged in the Teflon holder then immersed into the aqueous solution for 3 hours at temperature of 90 °C to grow ZnO nanorods on the substrates. The substrate was removed from the solution, rinsed with deionized water and then dried at room temperature.

The microstructures, element composition and phase structures of the samples were characterized with field emission scanning electron microscope (FESEM), energy dispersion X-ray (EDX) and X-ray diffraction (XRD), respectively. The interdigital silver electrodes were deposited on the top of the sample using thermal evaporator. Finally, oxygen gas sensing properties of ZnO nanorods was investigated at room temperature using semiconductor parameter analyzer (SPA) in a closed chamber probe station.

RESULTS AND DISCUSSION

During the deposition process, the ZNH is act as Zn^{2+} ion donor while HMT as pH buffer to regulate the pH value of the solution and as a slow OH^- ions donor. The simple chemical reactions are:

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad (1)$$

$$NH_3 + H_2O \leftrightarrow NH^{4+} + OH^- \quad (2)$$

$$Zn(NO_3)_2 \rightarrow Zn^{2+} + 2NO_3^- \quad (3)$$

$$Zn^{2+} + 4NH_3 \rightarrow Zn(NH_3)_4^{2+} \quad (4)$$

$$Zn^{2+} + 4OH^- \rightarrow Zn(OH)_4^{2-} \quad (5)$$

$$Zn(NH_3)_4^{2+} + 2OH^- \rightarrow ZnO + 4NH_3 + H_2O \quad (6)$$

$$Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2OH^- \quad (7)$$

There are two precursors, $Zn(NH_3)_4^{2+}$ and $Zn(OH)_4^{2-}$ being generated in the solution. The chemical reaction of equation (4) can be neglected as the reaction rate is too slow to actually occur in the solution [10-11]. From equation (5), as the concentration of Zn^{2+} and OH^- ions exceed a significant value, the nuclei of ZnO will start form. The precipitate of $Zn(OH)_2$ is more if compared to ZnO precipitation. Therefore, the $Zn(OH)_2$ forms tend to solute and form Zn^{2+} and OH^- ions, which then form ZnO nuclei as final products.

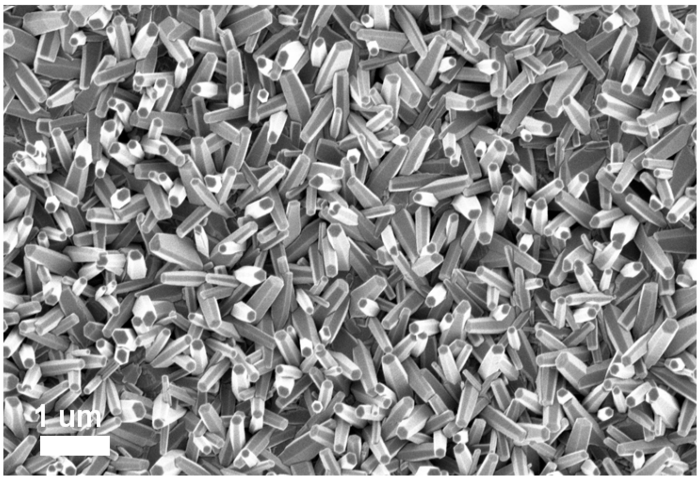

Figure 1: SEM micrograph of ZnO nanorods grown on silicon substrate

In this work, silicon wafer is used as a substrate to grow ZnO nanorods. During deposition process, the substrates were immersed into the precursor solution of a mixture of zinc nitrate hexahydrate (ZNH) and hexamethylenetetramine (HMT) in molar ratio of 1:1. After the deposition process, white powdery film can be observed on the substrates. The morphology of the ZnO is shown in Figure 1. The EDX analysis result on a selected nanorod confirmed the formation of ZnO with elemental composition of 60.5 at% Zn and 39.5 at% O (See Figure 2).

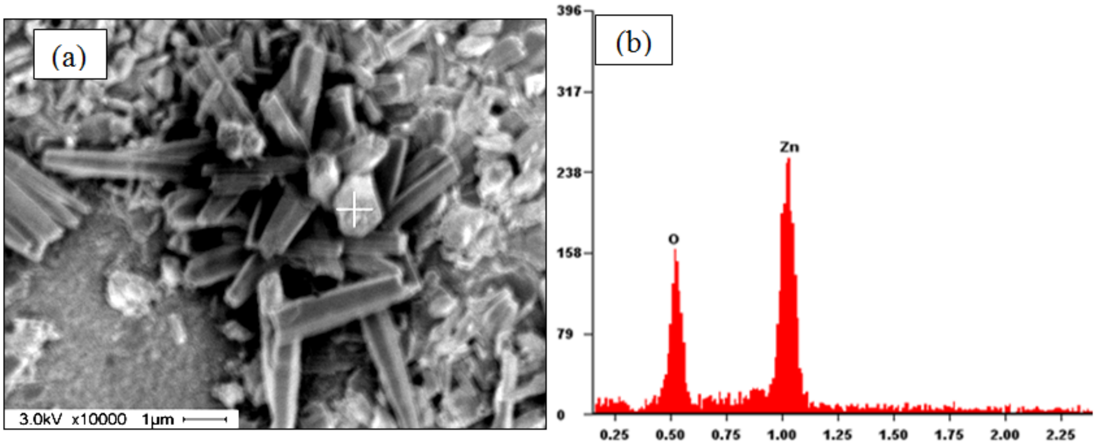

Figure 2: EDX analysis result on a selected nanorod (a) shows spectrum of Zn and O (b) with elemental composition of 60.5 at% Zn and 39.5 at% O

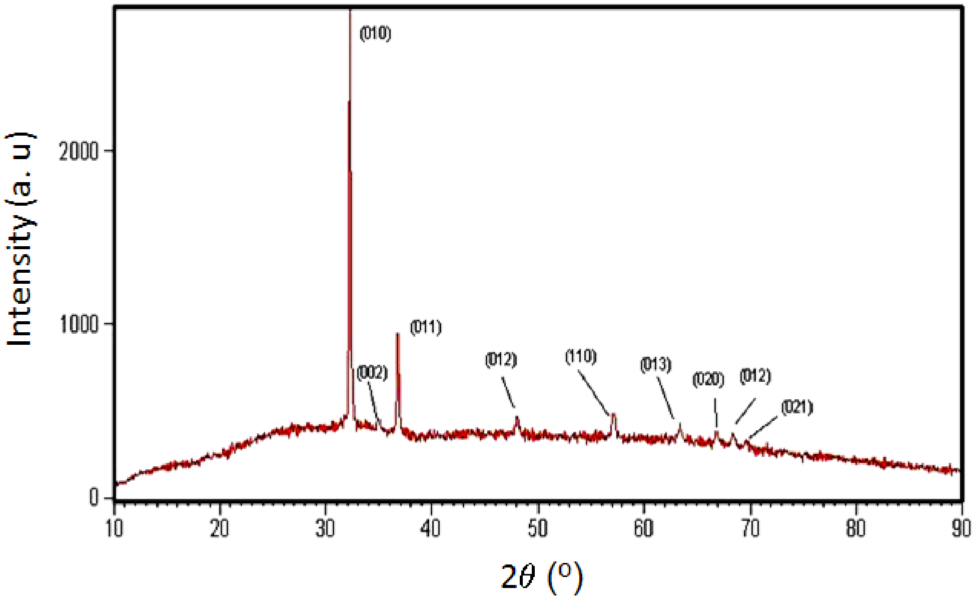

Figure 3: XRD pattern of ZnO nanorods grown on glass substrate

A typical XRD pattern of ZnO nanorods deposited on glass substrate is shown in Figure 3. All of the peaks are indexed to typical wurtzite ZnO, with calculated cell parameter *a* = 3.25 Å and c = 5.19 Å. This value is consistent with the standard value for bulk ZnO. There are no impurity peaks, such as Zn or $Zn(OH)_2$ in the XRD patterns, observed.

The intensity and half width of the XRD pattern, reveals that synthesized ZnO nanorods at the low temperature has a well-defined crystalline structure and morphology, which is very important in order to increase the response of the sensing material [12].

The interdigital silver electrodes on the surface were used to measure I-V characteristics of device under ambient (without gas) and flow oxygen gas environment. The sensing properties of device were tested at room temperature for 1 h in flow oxygen gas. The current-voltage (I-V) characteristic of the device without and with oxygen gas is shown in Figure 4. It was found that the resistance of device greatly change when exposed to the gas.

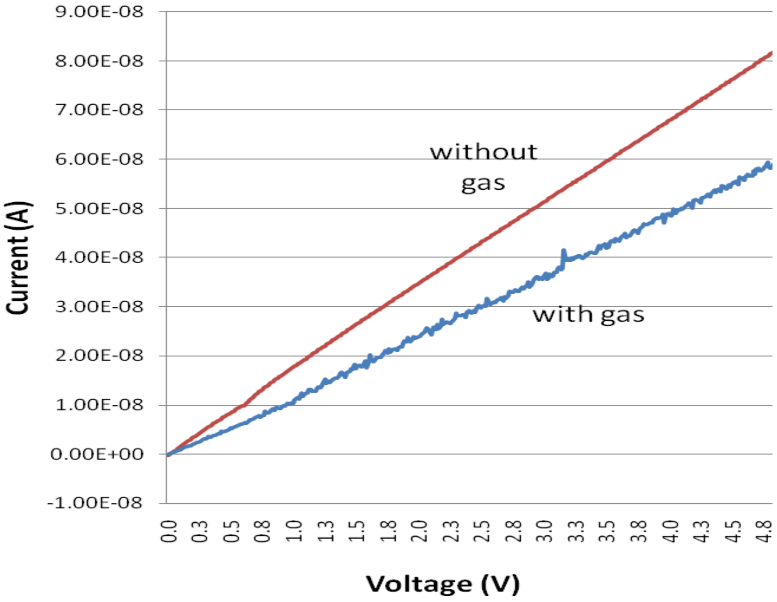

Figure 4: Current-voltage characteristics of ZnO nanorods measured under condition of without gas and with oxygen gas

ZnO sensor belongs to the surface-resistance controlled type, i.e., using the change of surface resistance to detect gases. The sensitivity is effect by the specific area and the active site on the surface of materials. The active site can adsorb oxygen and gases to be detected. Normally, the materials with higher specific surface area and oxygen adsorption quantity will exhibit high gas sensitivity [13-14]. Thus, nanomaterials with desirable morphology may help to improve their gas sensing properties. The I-V plots shown in Figure 4 reveal that the gas response of ZnO nanorods on wafer substrate to oxygen gas is very good.

Figure 4, shows the response of sensor device when exposure to oxygen. At the beginning, device measured without any gas give constant value of the resistance. When the device is subjected to the oxygen gas flow, the resistance is increased as the oxygen been absorbed by the ZnO. The electrical resistance of a metal oxide semiconductor changes in the presence of various gases. ZnO is a wide band gap semiconductor with excess metal ions, or oxygen vacancies that serve as electron donors (n-type). When oxygen molecules adsorb on the ZnO surface they act as acceptors and ionize by taking up one or two electrons from the conduction band and thus ionsorb as O^{-}/O^{2-}. This causes an electron depletion region to form in the material which increases the materials resistance [15].

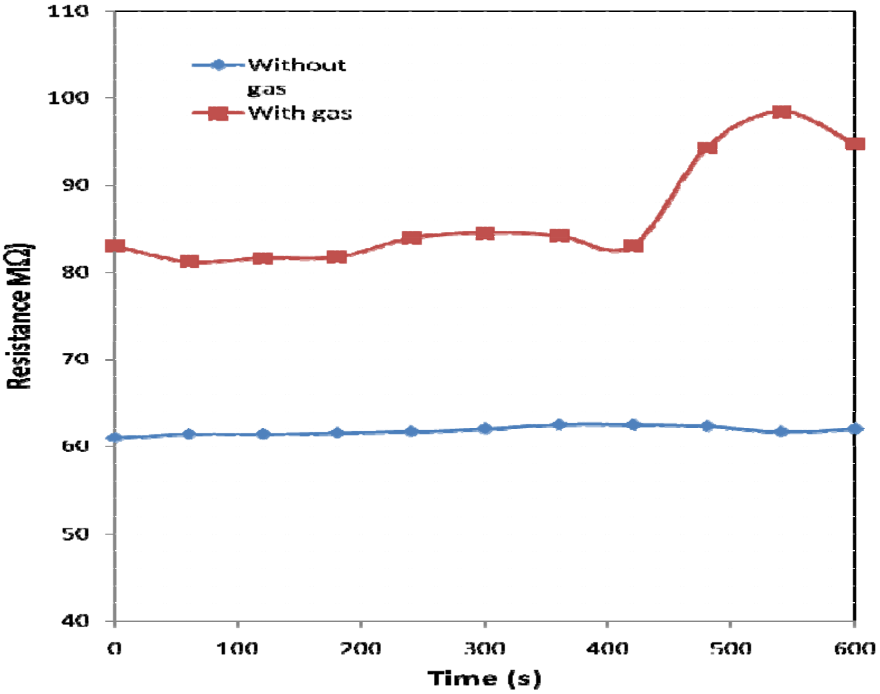

Figure 5: Time dependence of device (ZnO nanorods) resistance measured under condition of without gas and with oxygen gas for 10 min

Figure 5 shows a time dependent of ZnO nanorods sensing behavior. The resistance of ZnO nanorods is high in the oxygen environment. Lower resistance of device was observed at the ambient condition which is without the oxygen gas. Moreover, it can be seen that the resistance at the ambient condition is almost constant. However, when it exposure to oxygen gas found a significant increasing in the resistance of device. This means that the reactions might be occurring between ZnO nanorods with oxygen and resulting in changes of its electrophysical properties. Gas molecules cover the surface of a semiconductor in a gas ambience, i.e. adsorption process takes place. It lasts until the equilibrium between the gas phase and surface is reached. At the equilibrium the number of gas molecules coming on the surface equals the number of molecules, leaving it at the same time. The availability of the adsorbed molecules on the semiconductor surface causes a change of its electrical properties. A strong acceptor bond takes place in the case of oxygen adsorption on the surface of ZnO. Oxygen atoms trap free electrons from the conduction band and thus carrier depletion occurs within the Debye length [16-17]. Therefore, the resistance of sensor increases as exposure time increases.

CONCLUSION

Well aligned ZnO nanorods have been successfully grown on the silicon substrate via hydrothermal deposition method. The XRD pattern shows the formation of wurtzite type ZnO phase structure. Micrograph shows the morphology of the grown ZnO nanorods is hexagonal shape. The resistance of device is greatly changed when exposed to the oxygen gas indicating that ZnO nanorods has a potential gas sensing behavior to this particular gas. This is due to the high specific surface area of ZnO nanorods that are uniformly distributed on silicon substrate.

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