

ZnO Nanowire-film Hybrid Nanostructure for Oxygen Sensor Applications

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(Received December 28 2005, Accepted February 2, 2006)

Carefully designed ZnO nanowire-film hybrid nanostructure, composed of a bottom ZnO film, ZnO nanowire arrays, and a top ZnO film, was consecutively fabricated by adjusting the supersaturation conditions using a metal-organic chemical vapor deposition (MOCVD) to utilize the vertically aligned ZnO nanowires as the oxygen sensors. The decrease of current flow through ZnO nanowire arrays increasing oxygen pressure showed the high potential for the application of the ZnO hybrid nanostructure to the oxygen sensors. In addition, it was confirmed that the oxygen sensing characteristics of this hybrid nanostructure were attributed to the defects near the surface of the nanowires.

Keywords : ZnO, Nanowires, Oxygen sensors, MOCVD

1. INTRODUCTION

Metal oxide semiconductors have been applied to solid-state gas sensors for medical care, personal safety, and environmental monitoring applications to improve sustainability of society and quality of life by digitalizing the amount of gas[1,2]. The function of gas sensors is based on the modification of electrical transport characteristics which comes from the adsorbed oxygen-species-related reactions on the surface of metal oxide semiconductors. Thin metal oxide films have been investigated as solid-state gas sensors but their sensitivity is limited because of the small and buried surface area of grain boundary[3-5]. In recent years, one-dimensional (1D) nanowires have been applied to gas sensors for overcoming the structural limitation of thin films as the various fabrication techniques of 1D structures have been widely investigated[6-13]. The high surface-to-volume ratio of nanowires maximizes sensitivity of solid-state gas sensors. However, the fabrication and manipulation processes of nanowires for the sensing device applications seem to be complicate and most device structures suggested to date have been based on single nanowire or irregularly entangled nanowires demonstrating the development potentials.

ZnO nanowire is one of the most promising active elements for the development of room-temperature gas sensor[11-13]. In addition, the recent reports of self-assembled formation of the vertically aligned ZnO

nanowire array encouraged the fabrication and manipulation of devices based on ZnO nanowires [14,15]. As the vertically aligned nanowire array is a convenient structure to integrate individual nanowires and has larger surface area compared to the nanowires dispersed on substrates, a sensitive room-temperature gas sensor is possibly developed by using vertically aligned nanowires. However, a fabricable advanced structure has not been reported to apply the vertical ZnO nanowires to a gas sensor as a whole.

In this paper, a carefully designed ZnO nanowire-film hybrid nanostructure for utilizing vertically aligned ZnO nanowires as a gas sensor application is introduced. The hybrid nanostructure, composed of a bottom ZnO film, ZnO nanowire arrays, and a top ZnO film, was fabricated by the adjustment of supersaturation conditions which are the critical factor to determine growth modes of nanowires and films[16]. Through the continuous growth of a bottom film, nanowire arrays, and a top film, the both ends of ZnO nanowires for active elements in the gas sensor were successively interlinked bottom and top ZnO films for electrode applications without crystalline mismatch and contact resistance. This ZnO hybrid nanostructure was conventionally fabricated using a metalorganic chemical vapor deposition (MOCVD) method and enabled much simplified observation of the oxygen-sensing characteristics of ZnO nanowires at room temperature.

2. EXPERIMENTS

The ZnO nanowire-film hybrid nanostructure was fabricated on a *c*-plane Al₂O₃ substrate by controlling supersaturation conditions which was mainly affected by growth temperature when the flow rates of source materials were fixed in MOCVD. The consecutive transition of ZnO structures from a bottom film to nanowires was achieved by increasing the fabrication temperature of 570 K to over 870 K and the top ZnO film was successively fabricated on the nanowire arrays by decreasing the fabrication temperature to 520 K. A high growth temperature results in the low supersaturation condition because the synthesis of ZnO is an exothermic reaction and this promotes the nanowire formation. On the other hand, the film growth is preferred at a low growth temperature, which brings the high supersaturation condition.

The oxygen-sensing characteristics of the hybrid nanostructure were observed in the vacuum chamber with auto-pressure controller. The indium films were formed on ZnO films for ohmic contacts and the hybrid nanostructures. The ultraviolet was always irradiated to the ZnO hybrid nanostructure before measuring the current-voltage (*I-V*) using semiconductor parameter analyzer to remove the oxygen species on the surface of the ZnO nanowires and the *I-V* measurements were performed in the dark. Considering the adsorption of oxygen species on the ZnO nanowires, *I-V* was measured after 5 min from when the controlled oxygen pressure was saturated. In addition, Thermal treatment in the hydrogen ambient was performed in the conventional furnace to study the oxygen-sensing mechanism of ZnO nanowires. The high purity (5 N) hydrogen ambient was introduced to the furnace and the atmosphere pressure was maintained. The annealing temperature and time were 570 K and 60 min, respectively.

3. RESULTS AND DISCUSSION

Figure 1(a) and (b) are a scanning electron microscopy (SEM) image and a schematic configuration to observe the oxygen-sensing characteristics of the ZnO nanowire-film hybrid nanostructure, respectively. As shown in Fig. 1(a), the thickness of the polycrystalline ZnO films grown on the substrate were ~ 400 nm and the highly densified ZnO film-like structure fabricated on the nanowires made it possible to deposit metal contacts on them. In the resulting ZnO hybrid nanostructures, ZnO nanowire arrays were parallelly connected to the metal electrodes through the ZnO films without contact resistance as shown in Fig. 1(b). This hybrid nanostructure was optimized to characterize the oxygen-sensing properties of the ZnO nanowires without complicated post processes.

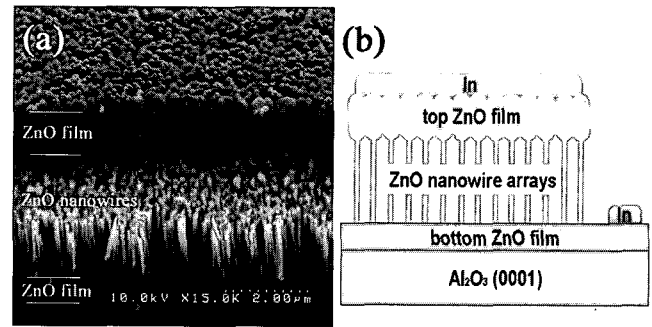


Fig. 1. (a) SEM image of ZnO nanowire-film hybrid nanostructure and (b) schematic configuration of the hybrid nanostructure for *I-V* measurement.

The oxygen-sensing properties of the hybrid nanostructure were explored in the chamber where the oxygen pressure was controllable. The voltage was applied across the bottom and top ZnO films to induce the electric field through the whole ZnO nanowire arrays. Figure 2(a) is the *I-V* characteristics of the hybrid nanostructure and the linear relationship of the *I-V* indicates that carriers transported through the ZnO nanowires without any interruption due to the perfect interface between the ZnO nanowires and films. The current flow through the ZnO nanowire arrays decreased as increasing the oxygen pressures from 10⁻⁶ torr to 150 torr at room temperature. The sensitivity of the hybrid nanostructure for the oxygen sensor application was further estimated by plotting the relative conductance, the ratio of conductance in the oxygen ambient to that in the absence of oxygen, as a function of the oxygen pressure in log scale as displayed on Fig. 2(b). The linear relationship between the relative conductance and the oxygen pressure in log scale indicates the hybrid nanostructure can detect not only the high pressure of oxygen species (150 torr) but also the very low pressure of oxygen species (10⁻⁶ torr) at room temperature.

The oxygen sensing characteristics of the hybrid nanostructures are affected by the density of defects near the surface and the radius of the ZnO nanowires. Adsorbed oxygen species on the surface of the nanowires deplete the electrons by becoming the negative ions and the negatively charged oxygen species form the depletion region in the nanowires, resulting in decreasing the conductivity of the nanowires as shown in Fig. 2(c). This electron depleted depth, defined by the Debye length, is a critical value for the fabrication of the gas sensors based on nanowires[11]. The radius of the nanowires should be smaller than the Debye length to make a distinctive electrical signal, the change of the conductivity of the nanowires dependent on the oxygen pressure. The Debye length of the polycrystalline ZnO films has been known as 26.9 nm at 1000 K[12], and it is

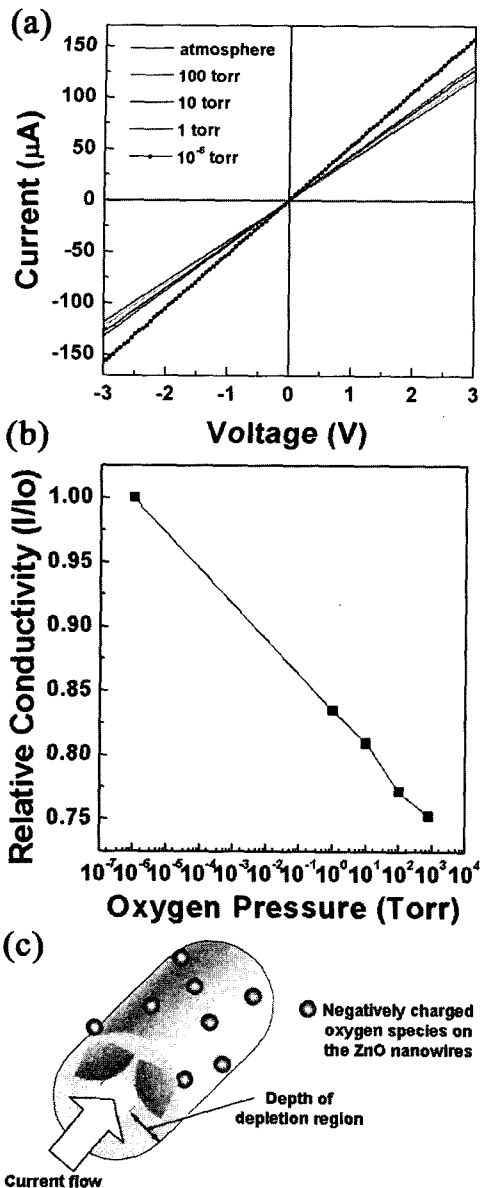


Fig. 2. (a) I - V characteristics of the hybrid nanostructure in different oxygen pressures. (b) Linear relationship between relative conductivity of ZnO nanowire arrays and oxygen pressures in log scale. (c) Schematic feature of oxygen-sensing mechanism of ZnO nanowire.

assumed that the single crystalline ZnO nanowires have the longer Debye length because the defect density in the nanowires is very low compared to the films and the oxygen sensing properties of the nanowires are measured at room temperature[9]. The Debye length of single crystalline ZnO crystals is reasonably larger than the nanowire's average radius of 27.7 nm.

Thermal treatment in the hydrogen ambient was performed to confirm the oxygen-sensing mechanism of

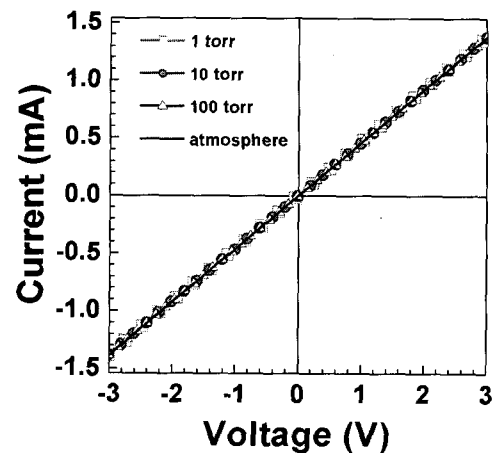


Fig. 3. I - V characteristics of the hybrid structure which is thermal-treated in hydrogen ambient.

the ZnO nanowires and the I - V characteristics of the hydrogen-treated ZnO hybrid nanostructure are shown in Fig. 3. The oxygen-sensing properties of the polycrystalline ZnO films have been known due to the dangling bond on the surfaces of grain boundaries where the oxygen species could be attached and form the depletion regions[3,4]. It could be assumed that the oxygen-sensing mechanism of the ZnO nanowires is the same as that of the ZnO films and the hydrogen passivation is performed to degenerate the dangling bonding on the surface of ZnO nanowires[17]. The differences of current flow through the nanowires are not observed even though the oxygen pressure changes as exhibited in Fig. 3. This result indicates that the dangling bonds on the surface of the ZnO nanowire are successfully passivated and it is deducible that the oxygen-sensing properties of the ZnO hybrid nanostructure are attributed from the dangling bonds on the surface of the nanowires, i.e. active sites for taking the oxygen species, in the ZnO hybrid nanostructures.

4. SUMMARY

The ZnO nanowire-film hybrid nanostructure showed the performance and the great potentials as oxygen sensors and the oxygen sensing mechanism of ZnO nanowires were studied. In addition, it was proved that the fabrication of this hybrid structure was a simple process for utilizing the ZnO nanowires as active elements in devices. It is believed that the hybrid nanostructure proposed in this study could be applied to the development of various nanowire devices by researching more about the surface reactions of the ZnO nanowires.

ACKNOWLEDGMENTS

This work was supported by National R&D Project for Nano Science and Technology.

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