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High sensitivity of a ZnO nanowire-based ammonia gas sensor with Pt nano-particles

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ABSTRACT

We report the growth of high-density single crystalline ZnO nanowires on a patterned ZnO:Ga/SiO_2/Si template, the adsorption of Pt nano-particles on the nanowire surface, and the fabrication of a ZnO nanowire-based NH_3 gas sensor. It was found that the sensor responses were 22.5% and 36% for the nanowires without and with Pt adsorption when the chamber was injected with 1000 ppm of NH_3 gas at 300 °C. With Pt adsorption, it was found that the measured sensitivities were around 16%, 22%, 26% and 36% when the concentration of the injected NH_3 gas was 100, 200, 500 and 1000 ppm, respectively.

1. Introduction

Ammonia (NH_3) is a colorless gas with a distinctive odor. Traditionally, the detection of gaseous NH_3 was performed either by potentiometric electrodes [15] or by infrared devices [13]. However, these devices are expensive and bulky. Recently, it was found that semiconducting metal oxide materials such as SnO_2 [24], MoO_3 [18], ZnO [19], WO_3 [10], In_2O_3 [3], and TiO_2 [11] can all be used to detect NH_3 vapor concentration. Of these, ZnO is an interesting chemically and thermally stable *n*-type semiconductor with a large exciton binding energy of 60 meV and a large bandgap energy of 3.37 eV at room temperature [21]. With these properties, ZnO has become widely used in detectors sensitive to toxic and combustible gases [4].

ZnO gas sensors with various forms, such as thick films [22], thin films [25], heterojunctions [17], nanoparticles [14] and nanowires [19], have all been demonstrated. It should be noted that the gas sensing of the semi-conducting metal oxide materials generally involves the chemical reaction of gas molecules on the oxide surface [6]. In recent years, one-dimensional (1D) ZnO nanowires have attracted considerable attention since they provide a much larger surface-to-volume ratio than bulk ZnO and ZnO films [9]. With a large surface area, nanowire-based gas sensors should be able to provide a larger sensitivity. The other possible way to enhance the sensitivity of the metal oxide gas sensor is to use noble metal catalyst such as Pt, Pd and Au. It has been shown that the presence of these noble metal elements on the surface of a metal oxide can enhance its interaction with the reducing gases [1,12]. In this study, we report the growth of high density ZnO nanowires on a patterned ZnO:Ga/SiO_2/Si template and the adsorption of platinum (Pt) on nanowire surfaces. In addition, the sensing properties of the ZnO nanowires to NH_3 gas will also be discussed.

2. Experiments

Prior to the growth of ZnO nanowires, a Si substrate was thermally oxidized to form a 500 nm-thick SiO_2 film. A 100 nm-thick Ga-doped ZnO thin film was subsequently

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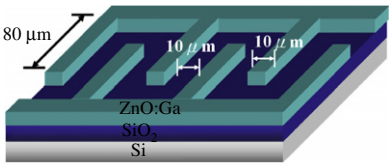

Fig. 1. Schematic diagram of the patterned ZnO:Ga film after the etching process.

deposited onto the SiO_2 film by RF magnetron sputtering. Standard photolithography was then performed to partially etch away the ZnO:Ga film and define the pattern. During wet etching, the template was dipped in 2% HCl for 3 min to remove the exposed ZnO:Ga. Then, the etching mask was designed to make the fingers of the comb-like pattern 10 μm wide and 80 μm long with a spacing of 10 μm. Fig. 1 shows a schematic diagram of the patterned ZnO:Ga/SiO_2/Si template used in this study. Two small pieces of glass were used to cover the two electrodes of the patterned ZnO:Ga film so that no ZnO nanowires were grown in these regions. We then placed the patterned ZnO:Ga/SiO_2/Si template and 99.9% pure zinc metal powder on an alumina boat, and inserted them into a quartz tube to grow the ZnO nanowires. During the growth, we introduced argon and oxygen gases into the reaction system and kept the Ar flow rate at 54.4 sccm. On the other hand, we kept the O_2 flow rate at 0.8 sccm. We also kept the pressure inside the quartz tube, the reaction temperature and the total growth time at 10 Torr, 600 °C and 60 min, respectively.

To adsorb the Pt, we prepared an ethanol solution of $PtCl_2$ with an ethanol: $PtCl_2$ ratio of either 50:1 or 2000:1 in a square alumina bath. We then immersed the sample in the solution and placed the alumina bath in a Kinsten KVB-30D ultraviolet (UV) box. Subsequently, the solution and the alumina bath were irradiated by UV light for 4 min to absorb the Pt particles onto the surface of the ZnO nanowires. During irradiation, the UV wavelength and the UV power were kept at 380 nm and 100 W, respectively. Finally, the sample was annealed at 480 °C for 1 h in Ar ambient to remove any chlorine. A JEOL JSM-7000F field emission scanning electron microscope (FESEM) operating at 5 keV and an energy dispersive X-ray (EDX) spectroscopy operating at 10 keV were then used to characterize the structural properties of the ZnO nanowires. To measure the gas sensing properties of the nanowires, the sample was placed in a sealed chamber and the resistivity of the sample in air was measured from the two electrodes of the patterned ZnO:Ga film. We then injected NH_3 gas into the chamber and measured the resistivity of the sample again in the presence of NH_3 gas.

3. Results and discussion

Fig. 2(a) shows a top view FESEM image of the as-grown ZnO nanowires prepared on the patterned ZnO:Ga/SiO_2/Si template. It was found that ZnO nanowires were grown vertically on the conducting ZnO:Ga finger regions. This can be attributed the fact that these ZnO nanowires were grown along the columnar grains of the underneath sputtered ZnO:Ga film [8]. In contrast, the ZnO nanowires

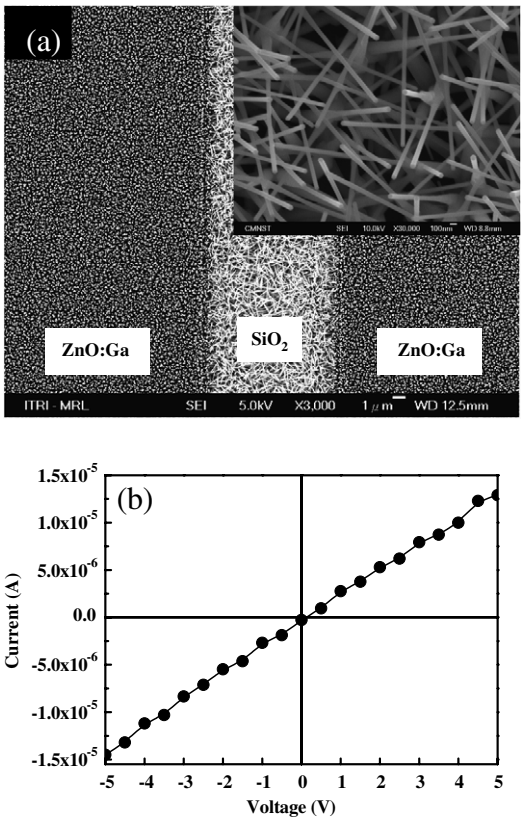

Fig. 2. (a) FESEM image of the ZnO nanowires grown on the ZnO:Ga/SiO_2/Si template. The inset shows Enlarged SEM photographs of the ZnO nanowires grown on the SiO_2 spacer regions. (b) I–V characteristics measured from the two electrodes of the sample.

grown on SiO_2 spacer regions were randomly oriented. The inset in Fig. 2(a) shows an enlarged SEM photograph of the ZnO nanowires grown on the SiO_2 spacer regions. It could be estimated from the inset of Fig. 2(a) that the density of randomly oriented ZnO nanowires is $\sim 1.9 \times 10^{12}$ cm^{-3}. Notably, these randomly oriented ZnO nanowires provided electrical paths between the neighboring fingers. With these randomly oriented ZnO nanowires in the spacer regions, the two electrodes were no longer electrically open. Fig. 2(b) plots the current–voltage (I–V) characteristics measured from the two electrodes in air. The active area of randomly oriented ZnO nanowires is 4.4 mm^2. Since the resistivity, mobility and electron concentration of the sputtered ZnO:Ga film are 2.14×10^{-4} Ω cm, 8.32 cm^2/V s and 3.51×10^{21} cm^{-3}, respectively, we should be able to neglect the resistance of the ZnO:Ga film. In other words, the resistance measured from the sample should originate from the resistance of the randomly oriented ZnO nanowires in the spacer regions.

Fig. 3(a) and (b) show SEM photographs of the ZnO nanowires treated with ethanol: $PtCl_2$ ratio of 50:1 and 2000:1, respectively. As shown in Fig. 3(a), it was found that large size Pt particles almost covered the entire surface of the ZnO nanowires due to the extremely high $PtCl_2$ concentration used during Pt adsorption. This could result in a smaller sensitivity of the gas sensor due to the fact that the exposed ZnO surface was significantly