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Short communication

Preparation of ZnO nanorod arrays with tailored defect-related characterisitcs and their effect on the ethanol gas sensing performance

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ABSTRACT

In this study gas sensors using ZnO nanorod arrays (NRs) with different surface-to-volume ratios and tailored defect-related properties are prepared and used to fabricate gas sensors. There are three kinds of ZnO gas sensors (ZnO seed layer and different ZnO NRs) grown by sol–gel route and subsequent aqueous chemical growth (ACG). The variation in sensing performance to ethanol gas of those gas sensors will be discussed in terms of morphology and the defect-related carrier behavior of ZnO NRs. Furthermore, the *I–V* characteristics (metal–semiconductor contact) of ZnO NRs are used to elucidate the defect-related properties affecting the electrical properties of ZnO as well as the sensitivities of those ZnO NRs. The ZnO NRs grown with Zn salt/KOH solution have a larger intensity of deep level emission and a higher Fermi level than that grown with Zn salt/HMTA solution, and sensitivity to ethanol gas of the former is superior. Therefore, it is proposed that more oxygen vacancy inducing more free carriers for gas sensing will result in a higher sensitivity to ethanol gas for sensors based on ZnO nanorod arrays.

1. Introduction

Among the metal oxide semiconductors (MOS), ZnO has been widely used as gas sensing materials because of its chemical sensitivity to different adsorbed gases, high thermal and chemical stabilities, amenability to doping, non-toxicity and low cost. At the earliest, ZnO thin film is used for detecting H_2 gas and it is suggested that the variation of electrical conductivity in gas sensing results from the adsorption and successive desorption processes of oxygen gas on the surface of semiconductor [1]. Consequently, thin film gas sensors based on ZnO have been extensively studied, especially focused on increasing the surface adsorption sites of material to obtain outstanding performance. Chang et al. improved the sensitivity to CO gas of ZnO thin film sensor through modulation of film thickness and reduced grain sizes; moreover, Al doping in ZnO film was employed to compensate for the conductivity degradation as a result of considerable grain boundaries [2]. However, the limited surface-to-volume ratio of gas sensor based on thin film will impede the promotion of sensing performance even though the above-mentioned procedure works. Recently the one-dimensional (1D) ZnO nanostructures have attracted much attention due to their potential application, such as materials for gas sensors with great possibility for overcoming the fundamental limitations owing to their ultrahigh surface-to-volume ratio [3]. Besides, single crystalline 1D ZnO nanostructure arrays have much better electron transportation capability by providing a direct conduction path for electron transport and reducing the number of grain boundaries greatly. Therefore, the study of ZnO nanorod/wire arrays grown for various gas sensing has been reported extensively, including H_2, C_2H_5OH, CO and NH_3 [4–6].

As is well known, the sensing mechanism of gas sensor is mainly based on the capture and release of electrons by the adsorption and desorption of specific gases on the surface, respectively. Therefore, the surface for reactions is crucial to the sensing performance of ZnO gas sensor and many groups devote to raising the surface-to-volume ratio of the sensing materials by reducing feature sizes [6,7] or building hierarchical structures [8–10] to enhance the sensitivity of gas sensor device. When ZnO is exposed to air, the oxygen molecules adsorb on the surface of ZnO and form oxygen ions by capturing electrons from the conductance band at a moderate temperature. As ZnO is exposed to reducing gas, the gas reacts with the oxygen ions on ZnO surface, which decreases the concentration of oxygen ions and increases the conductivity of ZnO. On the other hand, the oxygen vacancies in ZnO nanorod usually act as an electron donor, which provide electrons to the conduction band of ZnO and make it an n-type semiconductor. Additionally, the gas sensing processes are based on the transition of electrons between surface and bulk, therefore the density of oxygen vacancy is a significant factor. Although the defect density in ZnO that involved with oxygen vacancy (V_o) is usually exploited for explaining the superior sensitivity of gas sensor in the literature [6,7,10], the correlation between the concentration of V_o and gas sensing properties

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(sensitivity) has rarely been reported. Hsueh et al. [7] raised the number of oxygen vacancy and length-to-diameter ratio of ZnO nanowires to enhance the sensitivity to CO gas by modulating the growth temperature from 600 °C to 800 °C. Liao et al. [6] proposed that the thinner ZnO nanorods have a better sensing performance due to a larger quantity of oxygen vacancies and larger surface area, resulting in a larger quantity of adsorbed oxygen than thicker ZnO nanorods. In contrast with the procedures of vapor phase synthesis mentioned above, the more convenient aqueous routes are chosen in this study for growing ZnO nanorod arrays which can be tailored to have different defect-related characteristics, those including mild Zn salt/HMTA (Hexamethylenetetramine) and alkaline Zn salt/KOH aqueous solution growths. According to the results of above-mentioned studies, both the sizes and the defect-related characteristics of 1D nanostructure arrays will influence the sensing performance of ZnO gas sensor. It is recognized that the specific surface area increases with the decreasing diameter (or increasing length) of 1D nanostructure arrays, which affects the amount of adsorbed oxygen as well as the sensing properties in ZnO gas sensor device. However, the exact parameter to determine the contribution of V_o to gas sensor deserves to be studied in more detail. In the present study, ZnO with a larger quantity of V_o to bring about more free carriers (electrons) in ZnO nanorod arrays will be obtained using different solution processes and verified via PL analysis and *I–V* characterization. The consequent effect of higher V_o for enhancing the sensitivity in ethanol gas sensor device will be discussed, and the relative importance of specific surface area and the concentration of V_o for sensing performance will be determined.

2. Experiment procedure

2.1. Preparation of ZnO seed layer and nanorod arrays

The preparation of the sol–gel solution as the precursor for coating the substrates with a seed layer was similar to that reported in the literature [11]. $Zn(CH_3COO)_2 \cdot 2H_2O$ was first dissolved in a 2-methoxyethanol (MEA) solution at room temperature and the molar ratio of zinc acetate to MEA was kept at 1. In this study, the concentration of zinc acetate was 2.0 M and the solution was stirred at 60 °C for 2 h to yield a homogeneous solution that served as the precursor solution. A pair of interdigital Au/Cr electrodes with a thickness around 300/100 nm was deposited on the silica by sputtering through photolithography and lift-off, with a 50 μm gap between adjacent electrodes. The precursor solution was dropped onto the interdigital electrode and coated by a spinner, and then the substrates were dried at 300 °C for several minutes until the solvent was evaporated. The resulting substrates (sol–gel film) were used for growing of ZnO nanorod arrays after annealing at 300 °C for 1 h to form the ZnO seed layer. The nanorod arrays were fabricated on the sol–gel-derived seed layer through aqueous chemical growth (ACG). There were two kinds of ACG solutions used in the present study, including the Zn salt/HMTA and Zn salt/KOH solution following the methods of Vayssieres et al. [12] and Shi et al. [13], respectively. The ZnO nanorod arrays grown with Zn salt/HMTA solution were from a solution composed of 0.025 M $Zn(NO_3)_2 \cdot 6H_2O$ and 0.025 M $C_6H_{12}N_4$, and heated at 95 °C in a sealed quartz bottle for 3.5 h. The growth of nanorod arrays in Zn salt/KOH solution used a mixture of 0.5 M $Zn(NO_3)_2 \cdot 6H_2O$ and 4 M KOH with a volume ratio 1:1, which was performed at room temperature (around 25 °C) for 10 min.

2.2. Characterization

The top-view and cross-section morphologies of all the samples were characterized by field emission (FE-SEM, XL-40FEG, PHILIPS) and high resolution scanning electron microscopy (HR-SEM, S4200, HITACHI). The structures of the samples were identified by X-ray powder diffraction (Rigaku MultiFlex) with a scan speed of 4°/min and a scan step of 0.01°. The photoluminescent spectra of the samples were analyzed by Fluoresce Spectrometer (MFS230) at an excitation of 325 nm. The layout of ZnO sensing device is depicted in Fig. 1, and the details of the gas detection system using a digital multimeter (Agilent 3458A) had been described previously [2]. The gas sensing properties were evaluated at 300 °C by measuring the variation of resistance of the sensors at the ambient gas (air) condition and that of ethanol-mixed condition. These were measured at a bias voltage of 5 V. Current–voltage (*I–V*) characteristics of the samples were recorded with a semiconductor parameter analyzer (Agilent 4156C) by employing pressed tungsten contacts.

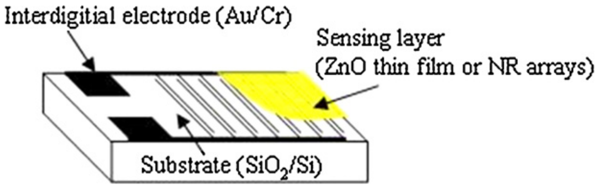

Fig. 1. Schematic diagram of the configuration of the ZnO gas sensor.

3. Results and discussion

Fig. 2 is a typical FE-SEM top view of the ZnO seed layer and the ZnO nanorod arrays grown with Zn salt/HMTA and Zn salt/KOH solutions on the seed layer. The SEM shows a uniform particle size of about 23 nm in the ZnO seed layer, and average nanorod diameters of 51 and 33 nm in ZnO NRs grown with Zn salt/HMTA and Zn salt/KOH solutions, respectively. The inserts in Fig. 2 are the cross-section view of samples, which reveal the thickness of seed layer and length of nanorods of about 262, 748, and 470 nm. As shown in Fig. 2(b) and (c), dense ZnO nanorods in a large area are deposited on the sol–gel-derived seed-layers, at which the nanorods grow almost perpendicularly to the substrates. Herein, the sol–gel-derived seed layers are composed of bonded nanocrystallites and form a continuous thin film structure. Accordingly, the oxygen molecule or analyte is difficult to penetrate the seed layer to form absorbed oxygen or react with the absorbed oxygen on the interface of ZnO nanocrystals, whereas it is easy in the case of NRs. Therefore, the surface area (reactive surface) of seed layer is thought to be far smaller than freestanding NRs.

Fig. 3 shows the XRD patterns of the samples, all diffraction peaks can be indexed to the wurtzite structure of ZnO (36-1451). The spectrum of the ZnO seed layer shows the typical characteristics for polycrystalline films with (0 0 2) and (1 0 1) peaks having comparable intensities at 34.4° and 36.25°. However, the NRs display only the (0 0 2) diffraction peak at 34.4° of the wurtzite ZnO, indicating the significant preferential orientation in the *c*-axis direction, which corresponds well with the result of SEM. In addition, both the ZnO nanorods grown with Zn salt/HMTA and Zn salt/KOH solution are single crystals (as characterized by TEM, but not shown here).

Most gas sensors based on metal-oxide semiconductor are operated on the basis of the resistance variation of sensing materials arising from the interactions between the oxygen on the oxide and the gas molecules to be sensed. The conduction band bottom of ZnO is about 4.4 eV below the vacuum energy level, which is higher than the chemical potential of oxygen (about 5.7 eV below the vacuum energy level) [14]. When ZnO is exposed to air, oxygen will be adsorbed on ZnO surface and acts as electron acceptors. The adsorbed oxygen species will capture electrons from ZnO and form oxygen ions (O^-, O^{2-} or O_2^-), which leads to surface depletion in the conductance channel of ZnO [15]. The carrier density in the ZnO