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Enhanced gas sensing performance of Li-doped ZnO nanoparticle film by the synergistic effect of oxygen interstitials and oxygen vacancies

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ABSTRACT

Li doped ZnO ($Zn_{1-x}Li_xO$) nanoparticles with different content were synthesized. X-ray photoelectron spectroscopy (XPS) indicated that the ratio of oxygen to zinc for ZnO increased with increasing of Li content from $x = 0$ to 0.2, which had been attributed to the introduction of oxygen interstitial by Li dopant. The sensing performance and the temperature-dependent conductivity were investigated. It is observed that Li doped ZnO showed higher sensitivity and selectivity compared to the undoped ZnO. The 0.1 Li doped ZnO performed the maximum responses of 71.5 and 40.2 for 100 ppm methanol and formaldehyde, respectively, at 350 °C. The research showed that the oxygen vacancies served as active sites which supported the oxygen adsorption and reaction, oxygen interstitials served as active sites to oxidize the reducing gases and produce electrons. The enhanced sensing performance of Li doped ZnO was attributed to the synergistic effect of oxygen interstitials and oxygen vacancies.

1. Introduction

Zinc oxide (ZnO), one of the most promising metal oxide semiconductors (MOS), which has a wide band gap of 3.37 eV with a high exciton binding energy of 60 meV [1], has found a wide range of applications, such as gas sensors [2–4], transparent electrodes [5], varistors [6] and etc. It has been proved that ZnO is a naturally n-type conductivity semiconductor caused by excess zinc [7]. The excess zinc gives origin to the intrinsic donors in ZnO, which can be assigned either to the interstitial zinc (Frenkel defect), or to the oxygen vacancy (Schottky defect).

A promising exploitation of ZnO is in the field of gas sensing application. It has been widely recognized that the sensing performance of ZnO highly depends on its defect chemistry properties [8,9]. Generally, oxygen vacancy (V_O) is considered to be the determining factor in the chemiresistive behavior of ZnO [10]. In a typical sensing process, V_O plays a crucial role in the following reversible process: (1) reducing gases remove oxygen from the surface of ZnO to give oxidation products, thereby producing oxygen vacancies; (2) the vacancies become ionized, thereby introducing electrons into the conduction band and increasing the conductivity; (3) if oxygen is present, it fills the vacancy and electrons are taken from the conduction band, which results in the decrease of conductivity [11]. Obviously, in this process the oxygen vacancy serves as the active center. And for exactly that reason, plenty of works have been done to tailor the oxygen vacancies in ZnO, such as doping, heat treating, and modified synthesis method [13–16]. The above approaches do change the defect chemistry of ZnO, including introduction of metal ions or change the configuration of oxygen defects. However, as is well known that the gas sensing process is really complex, which involves the oxygen adsorption/desorption, oxygen diffusion, surface catalyst, and transfer of electrons etc. [11,12]. Therefore, it is not enough to just consider the role of oxygen vacancies in sensing process, especially for the introduction of other doping element. The effects of minority defects, which mainly consist of oxygen interstitials, zinc vacancies and antisites, should be taken into account in order to better understand and develop the sensing mechanism. Oxygen interstitial (O_i) as one of the most important minority defects in ZnO has been studied intensively in the field of oxygen diffusion [17] and photocatalysis [18]. However, few researchers have focused the effect of oxygen interstitials in gas sensing field. This is due largely to the difficulty of characterizing defects behaviors in sensing process. Spectroscopic techniques are the common ways to study defects in semiconductor, but they can merely apply to static states, usually in vacuum or constant/room temperature condition. Therefore, there is a great gap between the conditions of characterization and the sensing process where a dynamic change of defects is taken place.

Fortunately, the temperature-dependent conductivity (σ–T) measurement appeared as a significant method to study defects

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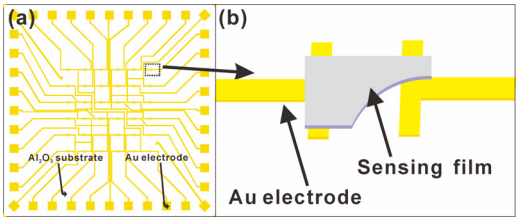

Fig. 1. (a) Schematic diagram of test chip. (b) Configuration of sensing film and Au electrode.

and surface reactions under dynamic conditions, such as the varying temperature or atmosphere. With temperature programming, the change of conductivity can not only offer the information of defects ionization but also the interactions between solid surface and atmosphere [19–22]. The processes of surface adsorption/desorption, reactions of adsorbates, and ionization of defects etc., can be recorded by the change of conductivity in σ–T curves. These will powerfully contribute to the illumination of the gas sensing mechanism.

In this present work, ZnO and Li doped ZnO at various Li content were prepared. By using a self-designed platform, the gas sensing characteristics and temperature-dependent conductivity properties of Li doped ZnO were investigated in detail. Furthermore, the influence of oxygen interstitials as the minority defects in sensing processes was emphasized. It was found that the effects of oxygen interstitials in sensing process are very distinct from the oxygen vacancies. Great enhancement of sensing performance of Li doped ZnO was attributed to the synergistic effect of oxygen vacancies and oxygen interstitials.

2. Experimental

2.1. Preparation of sensitive materials and fabrication of gas sensors

The $Zn_{1-x}Li_xO$ (x = 0, 0.05, 0.1 and 0.2) nanoparticles were prepared by using zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), lithium acetate dihydrate ($CH_3COOLi{\cdot}2H_2O$) as starting materials and urea ($CO(NH_2)_2$) as the homogeneous precipitant. A mixture with equal volumes of ethanol and deionized water was used as the solvent. In a typical synthesis procedure, 18 mmol $Zn(NO_3)_2{\cdot}6H_2O$ and 50 mmol $CO(NH_2)_2$ were dissolved in 100 ml mixed solvent, and then transfer the reacting solutions to a thermostat water bath to react for 3 h at 90 °C with vigorous stirring. The resulting precipitates were filtered and washed several times by using deionized water and absolute ethyl alcohol and finally dried at 80 °C for 24 h and calcining the precursors at 500 °C in air for 3 h. The ZnO with different Li content was synthesized by the same steps except adding the desired amount of $CH_3COOLi{\cdot}2H_2O$ to the reactant.

Porous thick film gas sensors were fabricated by screen printing technique. In order to get a suitable printing paste, the obtained powders were ground in an agate mortar with an appropriate amount of organic solvent (composed of terpineol, butyl carbitol, ethyl-cellulose, span 85 and din-butyl phthalate). Afterwards, the pastes were printed onto a self-designed test chip as shown in Fig. 1, each of the material film has an area of 0.6 mm × 0.8 mm and a thickness of 8 μm. The obtained sensors were dried at 80 °C for 30 min and then, 200 °C and 500 °C calcinations were processed to remove the organic solvent and to improve the mechanical bond of particles in the film respectively.

2.2. Characterization of the samples and gas response testing of sensors

The structure of the samples was characterized by X-ray diffraction (XRD) using a Philips X-Pert diffractometer with Cu-Kα radiation (λ = 1.5406 Å). The surface morphology of the materials was characterized by a Hitachi S-4800 field-emission scanning electron microscopy (FE-SEM) at a voltage of 10 kV. In order to check the surface chemical states of the samples, X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Kratos XSAM800 spectrometer employing Mg-Kα source radiation and the incident photon energy is 1253.6 eV. The overall spectral resolution of the system is 0.48 eV for Ag $3d_{5/2}$ peak with peak intensity over 400 kcps.

Gas sensing properties of the sensors were investigated in a self-designed experimental platform named high throughput screening platform of gas-sensing materials (HTSP-GM), which could real-time record the variation of resistance (R). The detail information of the HTSP-GM can be seen in our earlier work [23,24]. Temperature-dependent conductivity was also studied by the platform integrated with temperature-programmed system in air.

3. Results and discussion

3.1. Materials characterization

Fig. 2 depicts the XRD patterns of the ZnO with Li content x = 0, x = 0.05 (0.05LZO), x = 0.1 (0.1LZO) and x = 0.2 (0.2LZO). Fig. 2(a) shows that all the diffraction peaks of samples can be matched with hexagonal wurtzite ZnO (JCPDS card no. 36-1451) and no prefer orientations and second phases diffraction peaks in the patterns. Fig. 2(b) shows the enlarged region around the three strongest peaks (1 0 0) (0 0 2) (1 0 1), which show a slight shift toward lower side for Li-doped ZnO. As described by Bragg's law ($2d_{(hkl)}\sin\theta = \lambda$), the decrease of diffraction angle (θ) indicates the increase of crystalline interplanar spacing ($d_{(hkl)}$), namely it means that the lattice parameters of ZnO increased. In other words, some atoms (e.g. Li) may be incorporated into the lattice interstitial of ZnO. Depending on the positions of Li in ZnO, one can distinguish two kinds of doping behaviors [25]: (i) lithium atoms enter into ZnO interstitial sites, and (ii) lithium atoms substitute for the Zn sites in ZnO. The above two can be described by the following defect chemistry Eqs. (1) and (2), respectively.

$$Li_2O \xrightarrow{ZnO} 2Li_i^{\bullet} + O_i'' \quad (1)$$

$$Li_2O \xrightarrow{ZnO} 2Li_{Zn}' + O_O^{\times} + V_O^{\bullet\bullet} \quad (2)$$

where we have adopted the Kröger–Vink's notation for the defects: $Li_i^{\bullet}$ is a lithium ion in interstitial site, O_i'' is an oxygen ion in interstitial site, Li_{Zn}' is a lithium ion in lattice Zn site, $O_O^{\times}$ is an oxygen ion in its regular site and $V_O^{\bullet\bullet}$ is an oxygen vacancy. Since Li^+ has a smaller ionic radius of 0.068 nm than that of Zn^{2+} (0.074 nm) [26], lattice expansion occurs only when Li incorporate into ZnO by interstitials. Thus, it can be concluded that Li doped ZnO mainly in the way of Eq. (1).

Fig. 3 shows the microstructures of undoped and Li-doped ZnO. The average grain size and morphologies of all the samples are very similar. SEM analysis identifies spherical particles as well as irregular ellipsoid particles in all the samples. The inset enlarged images in Fig. 3 reveal that the particles with a size range from 40 nm to 60 nm.

Based on the results of XRD and FE-SEM, it can be concluded that the crystal structure and morphology are barely changed through doping lithium element. Thus, it is a reasonable assumption that