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A study of photocurrent spectrum of porous ZnO film sensitized by metal chloride solutions

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ABSTRACT

In order to study the ZnO photoresponse mechanism, a platform that can perform the photocurrent spectrum measurement has been designed. By using our platform, the photocurrent spectrum of porous ZnO film sensitized by metal chloride solutions was obtained. We used the screen printing technique to fabricate the material chip. The measurements were performed in dry air (relative humidity 15%) and at room temperature. We observed two peaks in the photocurrent spectrum. The peak at 380 nm is assigned to the exciton transition. The shoulder peak at 480 nm is owed to surface states introduced by sensitization and we find V_{Zn} plays an important role on this phenomenon. A model is proposed to explain the phenomenon. Furthermore, it is suggested that our platform is a useful tool for photoresponse research and can offer an effective guidance for further investment of light activated gas sensors.

1. Introduction

With the development of technology, the world awareness about environmental problems and human safety is increasing. The requirement for the detection and degradation of volatile organic pollutant has been enhanced in future. The degradation of volatile organic pollutants using semiconductors such as TiO_2 [1–3] and ZnO [4–6] has aroused intensive interests due to their larger specific surface, higher surface activity, low cost and nontoxic. Photocurrent measurement, an important method for evaluation of the separation of the photogenerated electron and hole within the semiconductor materials, was applied by many researchers as an effective guidance for further investigation of the photocatalytic activity [7–9].

In our previous work, we designed several ingredient triangles and used the high-throughput screening platform developed independently by our laboratory to perform the photocurrent measurement [10] and study the photoconductivity and trap-related decay in porous TiO_2/ZnO nanocomposites [11]. Different recombination such as band-to-band recombination or trap related recombination has intensively effect to the photocurrent intensity. The traps in ZnO, which can act as recombination center and affect mobility, conductivity and surface properties of ZnO, dominate its optical, electrical to a certain extent [12]. Several methods have been adopted to reveal recombination centers responsible for photosensitivity [13]. So far, the defects which are responsible for photoresponse are still not fully understood. It is supposed that the light response of the as-selected semiconductors could be verified in photoelectrical properties measurement. By changing the wavelength of the incident light, the traps can react with ambient gas under the light with certain energy [14,15]. Compared with the conventional photocurrent measurement, the information about photochemical and photophysical progress can be acquired conveniently. We can use this in situ measurement to know which defects are directly responsible for photocurrent and study the reaction between semiconductor and ambience under illumination, which can offer an effective guidance for further investment of light activated gas sensors. The sensitization of nanoparticles by metal chloride solutions is a method widely used in gas sensing to improve the response and selectivity of the sensors [16]. Furthermore, the method is very suitable for synthesizing plenty of material at the same time. We use the method to study the surface properties and traps of porous ZnO film sensitized by $AlCl_3$ solutions and find the photoresponse mechanism.

2. Experiment

2.1. Sample preparation

Commercial ZnO (average size 80 nm) was used without any further treatments. Firstly, we homogeneously mix the powders and a certain amount of organic solvent (composed of ethyl-cellulose, terpineol, butyl carbitol, span 85, and din-butyl phthalate) into agate jar. After Ball milling for 2 h at the milling speed of 200 rpm,

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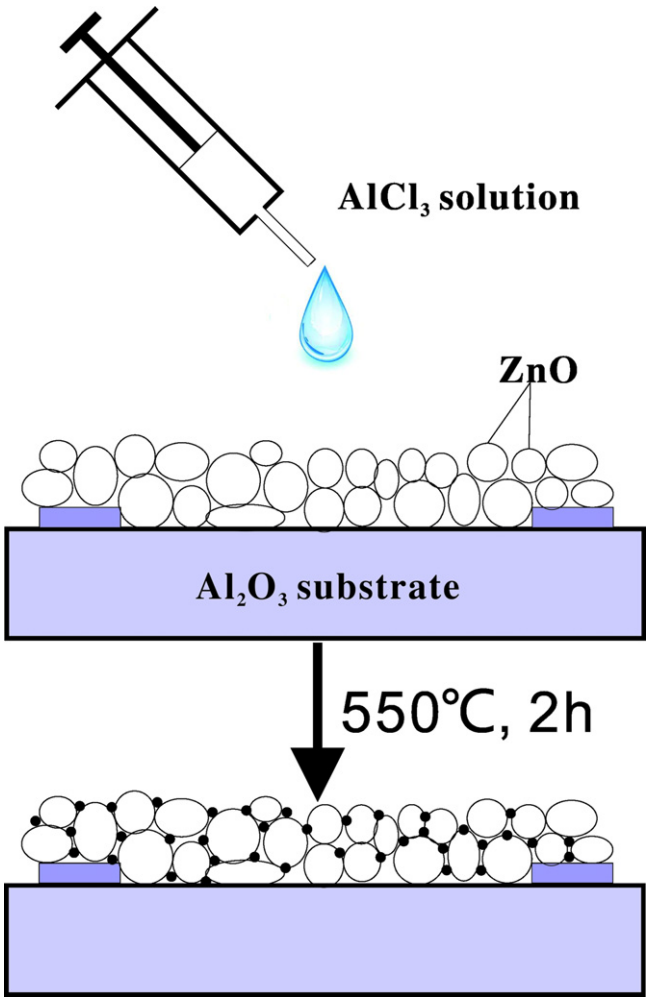

Fig. 1. Schematic diagram of the sample preparation.

we got a paste, which can be used for screen printing. The paste was screen printed onto the Au counter electrode preprinted on the alumina substrate.

The Au electrode was printed on the cleaned alumina ceramic substrate by screen printing too. After that, the electrode was sintered at 850 °C for 15 min in air after drying at 250 °C for 2 h. Finally, zinc oxide paste was printed on the substrate, 16 films on a substrate. The area of each ZnO film is about 1 mm × 1 mm, and thickness is about 10 μm [10].

After drying at 300 °C for 2 h, we got a kind of porous sponge-like thick film, which is made up of nano-ZnO particles. Then 0.01 mol/L solutions of $AlCl_3$ was injected onto the zinc oxide thick films, with volumes of 0 μL (sample a) and 0.2 μL (sample b). Each sample had eight copies to make symmetry in the environment. We used the deionized water as the solvent for aluminum chloride hexahydrate. Then, the devices were sintered for 2 h in air at the temperature of 550 °C after drying at room temperature and cooled in the furnace. Finally, we got the material chip that can be tested with our own development platform. Schematic diagram of the sample preparation is shown in Fig. 1.

2.2. The platform and the testing process of the photocurrent spectrum

To measure the photocurrent spectrum of the material chip, we developed a high-throughput screening platform. One of the most significant features of the testing platform was that the photocurrent of 16 films could be evaluated quickly and conveniently each time. At the same time, we can change the atmosphere of the chamber, and the future with the superposition of some certain external fields, such as magnetic field and temperature grade. The testing photocurrent range of the platform was 10^{-8} to 10^{-4} A.

The light was obtained by passing light from a 500 W xenon lamp (7ILX500, Beijing 7-Star Optical Instruments Co., Ltd.) through a monochromator (7IMS102, Beijing 7-Star Optical Instruments Co., Ltd.). Then, we use the optical fiber cable (UV–vis Step index multimode fiber, Beijing Xing-Yuan-Ao-Te Optoelectronics Tech. Co., Ltd.) to conduct the light to the chamber and make uniform in illumination intensity. The computer was used to control the monochromator to change the wavelength of the incident light at the speed of 0.2 nm/s from 200 nm to 600 nm and use the mass flow controller (D07-11C, Beijing Sevenstar Electronics Co., Ltd.) to change the gas concentration and type. In our measurement, we controlled the gas fluxes at 600 milliliter per minute to keep the relative humidity at 15%. By means of data acquiring using the data acquisition card (PCI-6225, National Instrument Co.) which was performed by LabVIEW in the testing platform, the instantaneous current in the circuit could be obtained easily and expediently. The schematic diagram of the platform was shown in Fig. 2.

3. Results and discussion

3.1. SEM and PL measurements

The as-prepared ZnO nanoparticles were characterized by a SEM and PL spectroscopy. Fig. 3a shows the surface images of the pure ZnO films. Fig. 3b shows the surface images of the ZnO films sensitized by $AlCl_3$ solutions. Generally speaking, sensitization had not made a big difference in the geometrical morphology. Compared with pure ZnO, grain size increases slightly, but surface roughness increases heavily with the sensitization. And the existence of Al ions in ZnO nanoparticles was confirmed by the EDS results (Fig. 4). The peak of Pt is also observed. During the sample preparation for SEM, Pt was introduced. It is believed that the Al_2O_3 exists on the surface of ZnO nanoparticles with much smaller nanoparticles and makes the surface much rougher. Fig. 5 shows the PL spectroscopy of two samples. The main peak of ZnO is 386 nm, which is the optical band gap of ZnO. The UV band emission of ZnO has been well demonstrated to be related to the exciton emission [17]. For the ZnO sensitized by $AlCl_3$ solutions the main peek moved to 391 nm, a red shift of 5 nm is obviously observed. It is widely accepted that the red shift is produced by changing the carrier concentrations [18]. That is a result of the dissolution of Al ions in the surface ZnO nanoparticles.

3.2. Testing curve of photocurrent spectrum

According to the features of the material chip, the photocurrent spectrum of all samples were measured. Fig. 6 shows the photocurrent-wavelength testing curves of sample a and sample b using our platform under the illumination. Considering the low intensity of the incident light and high resistance of the device with counter electrode, a bias voltage of 10 V was used. A dark current was formed which could be detected in the external circuit. With the increment of the incident light's wavelength, the photocurrent was increased rapidly. At 380 nm, the photocurrent reached to a maximum value, a response peak, which is very close to the optical band gap of ZnO (3.24 eV) though calculation. Then the response decreased with the increment of the incident light's wavelength.

Generally speaking, the photocurrent spectrum response of sample b is weaker than that of sample a. The reason for this is