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Study on TiO_2-doped ZnO thick film gas sensors enhanced by UV light at room temperature

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Abstract

The gas-sensing properties of titanium oxide (TiO_2)-doped zinc oxide (ZnO) thick film sensor specimens to typical ethanol vapor under UV light activation at room temperature have been investigated. Zinc nanoparticles were mixed with commercial TiO_2 in various weight percentage (0%, 1%, 5%, and 10%) and sintered at 650 °C for 2 h to prepare the thick film sensors. The sensors exhibit better photosensitivity and gas sensitivity to ethanol analyte. The response and recovery times are within 8 s. TiO_2 doping can improve the sensors stability and reproducibility. X-ray diffraction (XRD) and scanning electron microscopy (SEM) characterization of the film materials revealed that Zn_2TiO_4 and TiO_2 phases hindered the rod- or needle-like structure growth and subsequently affected the gas sensitivity. UV absorption spectra of the sensing film material completely dispersed in ethanol solution exhibited that the red shifts were caused with the doping of a small amount of TiO_2 into ZnO then blue shift was caused with higher TiO_2 level. The results of the UV spectra are well consistent with the photosensitive performance. The maximum sensitivity can be achieved by doping the amount of TiO_2 (5 wt%).

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Keywords: ZnO; TiO_2; UV light; Gas sensing; Room temperature

1. Introduction

Semiconductor metal oxide (MOS) gas sensor has attracted great attention in the past few years due to its many advantages such as simple manufacture technique, low cost, rapid response, and recovery. However, commercial MOS gas sensor always operated at higher temperature (>300 °C) influences its wide application. Therefore, new approaches must be explored to make the gas sensor operated at low or room temperature. UV light irradiation is a very useful way to improve the gas-sensing properties and reduces the working temperature [1,2]. To the best of our knowledge, few papers have been reported on the zinc oxide (ZnO) sensors gas-sensing performance under light illumination to reduce working temperature yet, although ZnO has been deeply studied in many aspects compared with the other metal oxide gas-sensing materials [3].

ZnO and titanium oxide (TiO_2) are two typically photocatalytic materials and also often used as MOS gas-sensing materials [4–12]. Several studies reported that the properties of ZnO-based gas sensor could be remarkably improved by introducing TiO_2 dopant into the sensing films [10,12], and the peculiar structure and morphology of the sensing materials can also be conducive to the low-temperature gas-sensing performance [11]. ZnO is proved to be one of the richest families of nanostructures among all materials, both in structures and properties [13]. Preparation of high quality and purity ZnO from the thermal oxidation of metallic Zn is one of the most important methods [14–16].

In the present study, we report the preparation of ZnO-based sensing film materials from the oxidation of metal zinc nanoparticles and the sensing properties of TiO_2-doped

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ZnO thick film gas sensors using UV light activation at room temperature for the typical ethanol analyte in air.

2. Experimental

Zinc nanoparticles with mean size of 35 nm and purity of 99.99% used as the Zn resource to produce ZnO were prepared by thermal evaporation method [14]. The obtained Zn nanoparticles show sphere shape [16]. The paste of mixed powder of Zn nanoparticles with content of 1, 5, and 10 wt% commercial TiO_2 (99.9% purity) were formed by adding suitable amount distilled water and then to be coated on Al_2O_3 tubes on which Pt electrode wires had been fixed at each end. The thick film element and the remainder of the paste were both sintered at 650 °C for 2 h, and TiO_2-doped ZnO thick film sensors and powders were obtained. The sensors after aging were employed to implement gas-sensing test, and the powders obtained were used for X-ray diffraction (XRD) characterization and UV absorption spectra. The doped ZnO specimens with content of 1, 5, and 10 wt% TiO_2 were named as Ti (1), Ti (5), and Ti (10), respectively. The gas-sensing properties were tested on HWC-30A gas-sensing measurer. The graphic for the gas sensitivity measurement is shown in Fig. 1. The sensors were operated using a simple circuit voltage (V_C), which was applied to allow a measurement of the output voltage (V_{RL}) across the load resistor (R_L). The sensitivity measurements with UV exposure have been carried out by employing an F4T5/BLB UV lamp with a power of 24 W at the main wavelength of 365 nm. The absorption spectra of the samples were tested using UV-2102PC spectral photometer after the powders completely dispersed in the ethanol solution.

XRD with CuKα incident radiation at 40 kV (PAN, X'Pert PRO) and scanning electron microscope (SEM, SIRION‖) were employed to characterize the phase structure and morphology.

3. Results and discussion

3.1. Gas-sensing properties

Fig. 2 shows the response curves of pure ZnO, Ti (1), Ti (5), and Ti (10) sensors to 100 ppm of ethanol vapor. All the sensors show good sensitivity under UV light activation but nearly insensitive without UV light illumination at room temperature. For easier discussion, the sensitivity including photosensitivity (ΔV_p) and gas sensitivity (ΔV_g) are defined as the difference of voltage, which are the differences of the voltages on sensors before and after exposing to the UV light in the air and introducing the tested gas with the UV illumination simultaneously, respectively. The total sensitivity is ΔV_s ($\Delta V_s = \Delta V_p + \Delta V_g$), which expresses the sensor voltage change coming from the resistance change between base-line resistance in air- and the gas-sensing resistance under UV illumination. The detailed scheme of the definition is shown in Fig. 3.

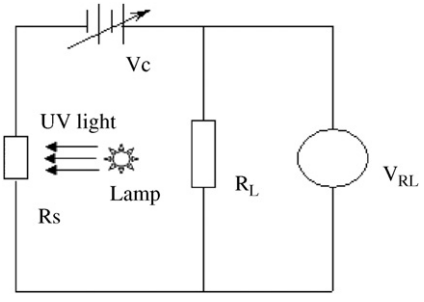

Fig. 1. Graphic of the gas sensitivity measurement circuit with voltage, V_C; output voltage, V_{RL}; and load resistance, R_L.

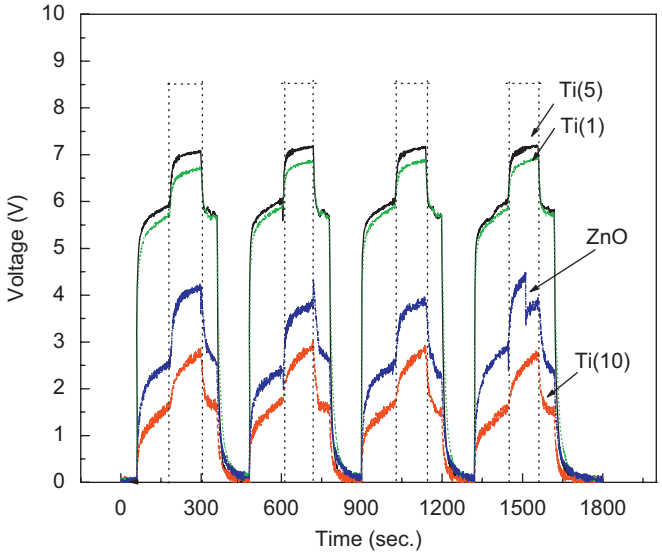

Fig. 2. Response curves of ZnO- and TiO_2-doped ZnO sensors to 100 ppm ethanol vapor in air at room temperature and 80% RH.

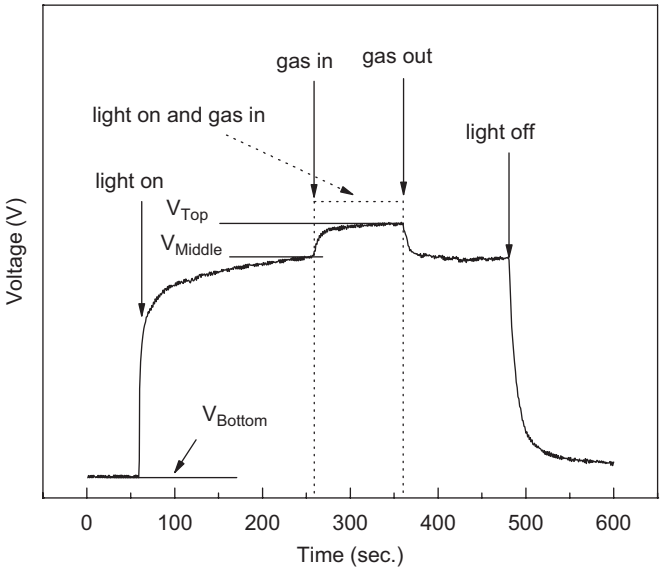

Fig. 3. Scheme of definition of the photosensitivity ($\Delta V_p = V_{Middle} - V_{Bottom}$) and gas sensitivity ($\Delta V_g = V_{Top} - V_{Middle}$) on the response curve.