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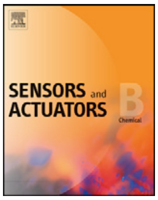

Mn-doped zinc oxide nanopowders for humidity sensors

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ABSTRACT

Mn-doped ZnO nanopowders have been prepared by the sol–gel technique using zinc and manganese (II) acetates as precursors. The as-prepared nanopowders were characterized by scanning electron microscopy and Micro-Raman spectroscopy. Humidity sensors based on ZnO nanopowders with different Mn concentrations of 0, 1, 3 and 6 at% were fabricated. Linear behavior of the *I–V* curves at various relative humidity (RH) indicates the ohmic contact between the sensing material and gold electrodes. Sensing characterization reveals that the 6 at% Mn-doped ZnO nanopowders have linear response to RH over the range of 11–95%, which offers higher sensitivity than the commonly reported exponential response. The response and recovery time of the sensor are 6 s and 20 s, respectively, versus the changes of RH from 20% to 80%. The sensors with high reproducibility and stability, as well as high sensitivity throughout a large dynamic range have been obtained.

1. Introduction

Humidity control is very important in a wide range of our daily life, such as service, air conditioning, electronics processing, etc. In the past years, the detection techniques have gone through from wet and dry bulb thermometry to modern capacitive, resistive, and thermal conductive moisture detectors. In order to further promote the properties of humidity sensors, intensive efforts have been made in the exploration of humidity sensor based on different nanomaterials such as carbon [1,2], polymer [3,4] and especially ceramics [5]. The principle of humidity measurement with metal oxide based sensors is the change in electrical capacitance or conductivity owing to water vapor chemisorption and physisorption on the surface of sensing element.

Being an important n-type semiconductor with a wide band gap (3.37 eV), ZnO has attracted the interest of many researchers during the last few years. It has been applied in many fields, such as light emitting or laser diodes, transparent conducting oxides, high temperature radiation-hard and transparent electronic circuits, diluted- and ferro-magnetic material for semiconductor spintronics, electron-acceptor in hybrid solar cells, cantilevers production, photocatalysis, piezoelectric applications and humidity sensor, etc. [6–9]. Although many successes have been obtained, however, the humidity sensor based on Mn-doped ZnO nanopowders has not yet been reported. Mn doping would cause the deformation of ZnO, which would consequently influence the sensing properties.

In this paper, we present a simple approach to fabricate humidity sensors based on Mn-doped ZnO nanopowders. Experimental data reveal that the obtained sensors have long-term reproducibility and stability, as well as high sensitivity at room temperature, indicating that the Mn-doped ZnO is a good candidate for fabricating practical humidity sensors with high performance.

2. Experiment details

2.1. Preparations of the Mn-doped ZnO nanopowders

Zinc and manganese (II) acetates were used as precursors in the sol–gel process. Certain amounts of zinc and manganese (II) acetates were dissolved in 30 ml of dimethyl-formamide at room temperature. These two solutions were mixed to a clear solution under vigorous stirring. The gel products of the powders were prepared by vaporizing the mixture solutions at 70 °C for 24 h, and Mn-doped ZnO nanopowders were obtained by thermal decomposition of the precursors at 350 °C for 4 h. The concentration of Mn in the final products was 1, 3, and 6 at% respectively. Detailed description of method for preparing the nanopowders can be found in our previous work [10].

2.2. Characterizations

The morphologies of ZnO nanopowders were characterized by Scanning Electron Microscope (SEM). Micro Raman scattering was performed using a Jobin-Yvon T64000 Triple-mate system with the radiation of 514.5 nm from a coherent argon ion laser and a

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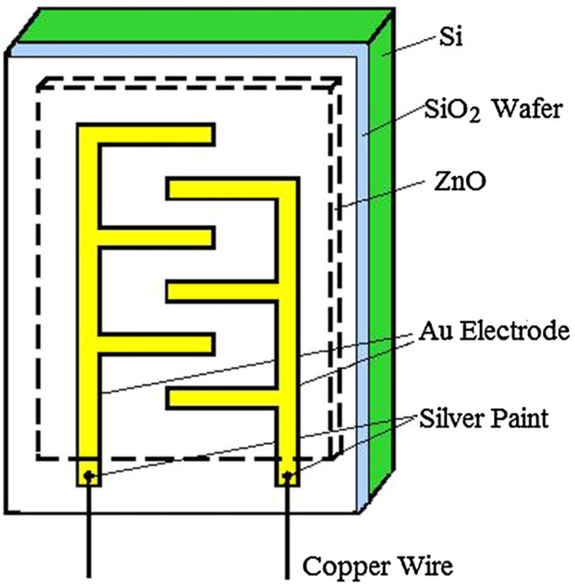

Fig. 1. Schematic sketches of prototype sensor device.

liquid nitrogen cooled charge coupled device was used to collect and process the scattered data (made by HORIBA Group in Japan).

2.3. Preparation of prototypic sensors

To explore the response to humidity, the Mn-doped ZnO nanopowders based sensors were built (Fig. 1). The pure and Mn-doped ZnO nanopowders were mixed with deionized water to form a paste, respectively. The paste was screen-printed on silicon (1 0 0) substrate with a pair of comb-like sputtered gold electrodes deposited on the SiO_2 buffer layer to form a film with about 200 μm in thickness, 10 mm in length and 6 mm in width. The introducing of comb-like electrodes ensures the contact of the nanopowders and thus increases the conductivity of the sensors. The gold electrodes were sputtered on the SiO_2 layer at room temperature for 30 s inducing a thickness of 30 nm. The contact for the gold electrodes with copper wires was made by silver paint. Then the sensors were dried naturally.

2.4. Measurement of sensing properties

Fig. 2 shows a schematic diagram of the measurement system that consists of a stainless steel chamber with a volume of 1 L, pipelines and valves to transfer and control gases relative humidity (RH) inside the test chamber, a dryer device to dry the sensors, and an electrical circuit to acquire the electrical signal from the sensors. The desired level of humidity was regulated by mixing different percentages of humid air and dry air, and the humidity was measured by a standard hydrothermal. The humidity response of the sensors was surveyed through monitoring the variation of the resistance of the sensors, which was completed by measuring an external testing circuit: the samples were serially connected to a precise resistor ($R = 2\,\mathrm{M\Omega}$) and an AC power supply (1 V, 1000 Hz) to form a voltage–current–resistor (V–I–R) electrical circuit. The variation of sensor's impedance was estimated based on the measurement of the voltage drop across the precise resistor according to the formula: $Z_{\text{sensor}}/R_{\text{precise}} = V_{\text{sensor}}/V_{\text{precise}}$, where the Z_{sensor}, R_{precise}, V_{sensor} and V_{precise} are the impedance, resistance and voltage drop across the ZnO based sensors and the precise resistor, respectively.

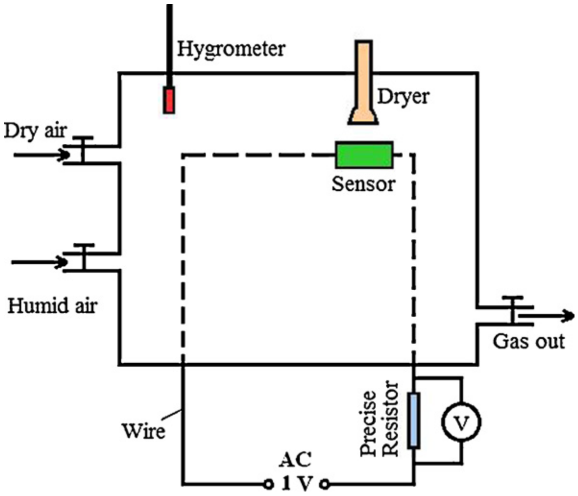

Fig. 2. A schematic diagram of device assembly.

3. Results and discussions

3.1. Characterizations of the Mn-doped ZnO nanopowders

Energy Dispersive X-ray Spectrometry (EDS) data indicate that the Mn concentration in ZnO nanopowders are 1, 3 and 6 at%, respectively. Fig. 3 shows the SEM images of pure and 6 at% Mn-doped ZnO nanopowders. It is interesting to note that the pure ZnO nanopowders can be classified as two groups. The size of particles in the first group (identified as A in Fig. 3(a)) are around 20–40 nm, but in the second group (identified as B), it is around 400–500 nm. Each

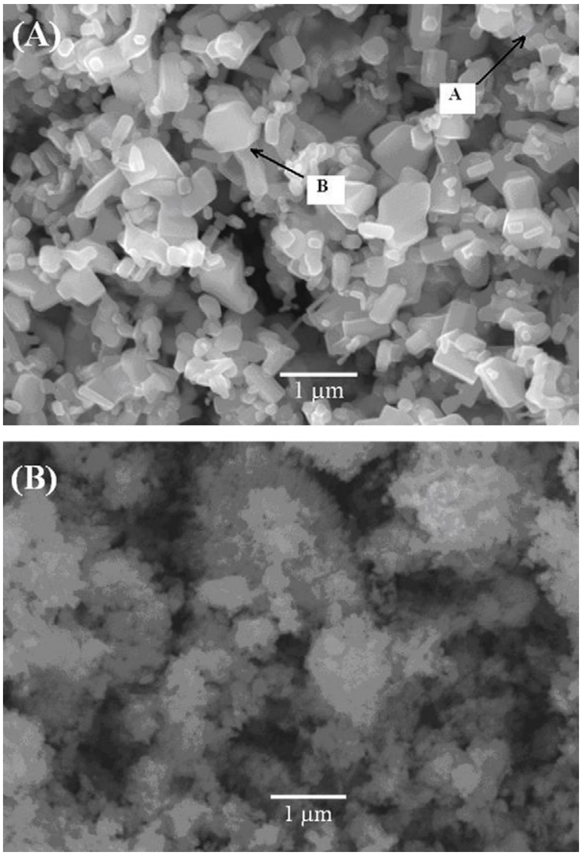

Fig. 3. SEM images of pure ZnO and 6 at% Mn doped ZnO nanopowders.