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Influence of CuO nanostructures morphology on hydrogen gas sensing performances

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ABSTRACT

In this study, the impact of different morphologies of *p*-type copper oxide nanostructures on hydrogen gas response is investigated. Sensor structures based on CuO nanowire (NW) networks demonstrated much higher gas response (~340) than nanostructured films (~3) at operating temperatures of 300 °C. Such a high gas response in the case of CuO NW networks is explained by percolating phase transition of CuO NW surface to metallic Cu. The phenomenon is observed at operating temperatures higher than 275 °C, but show good reversibility at 300 °C. At a higher operating temperature of 400 °C, the gas response was found lower (~108) than at 300 °C, even if the response time and percolating time were much shorter. On the other hand, the faster recovery time (~2 s) to the initial value of electrical baseline was observed at an operating temperature of 300 °C. This latter temperature is found the best regime for stable and highly sensitive and selective detection of hydrogen with high repeatability for sensor structures based on CuO NW networks. These results will help to take full advantage of these functional nanomaterials in the new generation of sensorial nanodevices for their larger scale utilization.

1. Introduction

Cupric oxide (CuO) as a *p*-type semiconducting oxide is known for being an excellent catalyst of volatile organic compounds (VOCs), especially ethanol and acetone vapour [1–7]. Cuprous oxide (Cu_2O) and CuO with different structures such as combo-like nanorods [8] or uni-faceted crystals [9], have been widely studied as promising nanomaterials for gas sensing applications. Although the gas sensing mechanism of sensors based on semiconducting oxides is still under debate [10,11], highly sensitive hydrogen sensors based on ZnO have been developed recently [12,13]. The main mechanism responsible for such high gas response is the surface metallization of ZnO nanostructures by H_2 gas, which allows a noticeable selectivity of sensors [12,13]. Due to the formation of a Zn layer on the surface of ZnO nanoparticles, the depletion region formed between the nanograins is eliminated and facilitates the transfer of electrons [13]. Thus, the fabrication of highly selective and sensitive hydrogen sensors by reducing semiconducting oxides is a highly attractive approach which permits high selectivity. However, the case of other oxides, in particular *p*-type CuO nanostructures, including nanowires, still needs more detailed investigations. The reduction of CuO is frequently realized with H_2 and H_2S gas atmospheres [14,15]. In these cases, the reaction rate is a temperature-dependent process and occurs from the surface to the core region of the nanostructures [14,15]. The sequence of reduction process is the following: $CuO \rightarrow Cu_2O \rightarrow Cu$ [10]. As a result, the new formed percolating thin layer of metallic Cu is sufficient to radically change the resistance value of the sensor structure by an electrical breakdown [15]. In the case of H_2S gas, the lattice bound oxygens are substituted by sulfur atoms to form conducting copper sulfide (CuS) [15]. On the other hand, previous works [5,16] reported that doping CuO nanostructured films with Zn resulted in an increase of hydrogen gas response and in a decrease of ethanol vapour response. They show the potential research interest in investigating copper oxide samples with a rather high content of Zn dopant.

This work reports hydrogen gas sensing properties of a *p*-type semiconducting copper oxide nanomaterials with different morphologies, namely nanostructured films and nanowire (NW) networks. For CuO NW networks a new effect was observed due to gas-surface interaction which could be related to percolating phase transition of CuO to metallic Cu. By applying an adequate operating temperature during sensor studies, a reversible reaction of metallic Cu to CuO with highly stable base resistivity was observed. This effect is new and opens further possibilities to improve such types of sensor structures. It also extends their applications for highly selective and sensitive detection of hydrogen gas.

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2. Experimental details

The simple and cost-effective synthesis process used for the preparation of Zn-doped copper oxide nanostructured films on a glass substrate from chemical solutions (SCS approach) is described in details in our previous works [5,16–19]. Thicknesses of the investigated films ranged between 0.85 and 0.9 μm as determined by layer cross-section observations by scanning electron microscopy (SEM) (not shown here). The CuO NW networks were synthesized at 425 °C for 5 h from copper microspheres according to a technological process reported in our previous work [17]. The morphologies of copper oxide samples were analyzed using a SEM Carl Zeiss Ultra Plus instrument (7 kV, 10 μA). The compositional analysis of the specimens was carried out by energy dispersive X-ray spectroscopy (EDX, 15 kV) in combination with SEM [20]. Crystallographic information was extracted from X-ray powder diffraction (XRD) data obtained using a Seifert 3000 TT unit at 40 kV and 40 mA, with graphite monochromatized $CuK_{\alpha 1}$ radiation ($\lambda = 1.541$ Å). The step size of the XRD measurements was 0.01° with an integration total time of 5 s for each step. For transmittance measurements the copper oxide nanostructured films were deposited on the quartz substrate via the same SCS approach. The quartz substrates were cleaned exactly with the same procedure as the glass substrates. Transmittance measurements were performed at room temperature with unpolarized light at normal incidence in the wavelength range from 300 nm to 2000 nm using Cary 5000 (Varian) UV–Vis-NIR spectrophotometer. Reflectance measurements were investigated at an incidence angle of 7° in the same wavelength range. The diffuse reflectance spectra were measured on a Varian Cary 5E UV–Vis-NIR spectrophotometer equipped with an integrating sphere. A quartz substrate, cleaned by the same procedure, was used as the reference.

The optical band gap energy (E_g) was calculated using the Tauc equation [21, 22]:

$$(\alpha h\nu)^n = B(h\nu - E_g) \quad (1)$$

where α is the absorption coefficient, $h\nu$ is the incident photon energy, B is a material-dependent constant and n is equal to 2 for a direct transition (direct band gap semiconductor) or 1/2 for an indirect transition (indirect band gap semiconductor). α coefficient was calculated from the transmittance (T) and reflectance (R) data by using the following equation [22]:

$$T = (1-R)^2 \exp(-\alpha t) \quad (2)$$

where t is the sample thickness.

Different characterization techniques confirmed that the nanostructured films were crystalline materials. The gas sensing experiments were performed as reported before [5,16,17,23]. Hydrogen gas response for copper oxide nanostructured films was determined according to the relationship $S = R_{gas}/R_{air}$, where R_{gas} is the resistance of the sensor under exposure to hydrogen gas and R_{air} is the sensor resistance in the ambient air [5,16,18]. In the case of CuO NW networks, the gas response was defined as the ratio of the sensor resistance before exposure to H_2 gas and resistance after the electrical breakthrough $S = R_{air}/R_{gas}$, i.e. after considerable decrease in resistance value due to H_2 gas exposure.

3. Results and discussions

3.1. Morphological and optical properties of CuO films and CuO NWs

SEM images of Zn-doped copper oxide nanostructured and thermally annealed (TA) at 450 °C (sample set noted as TA450) films grown by SCS are presented in Fig. 1a,b. The films were made of interconnected nanocrystallites with diameters in the range of 50–200 nm which completely covered the glass substrate and formed a relatively uniform film. Effects of thermal annealing on the morphology of copper oxide nanostructured films were investigated in our previous works [5,16,18]. The inset in Fig. 1b and the Fig. S1 show the regions where CuO NWs grown on the surface of thin films. According to the EDX measurements, a Zn content of 1.3 wt% in Zn-doped copper oxide samples was detected. Compositional images taken by EDX elemental mapping at the microstructural level of Zn-doped copper oxide nanostructured films are presented in Fig. 1c. Uniform distribution of Cu, O and Zn elements is clearly seen in the film.

Optical measurements were performed to study the influence of thermal annealing and Zn doping on the optical properties of copper oxide nanostructured films. Fig. 2a shows the optical transmittance spectra of as-grown and TA450-treated sample sets, respectively. The

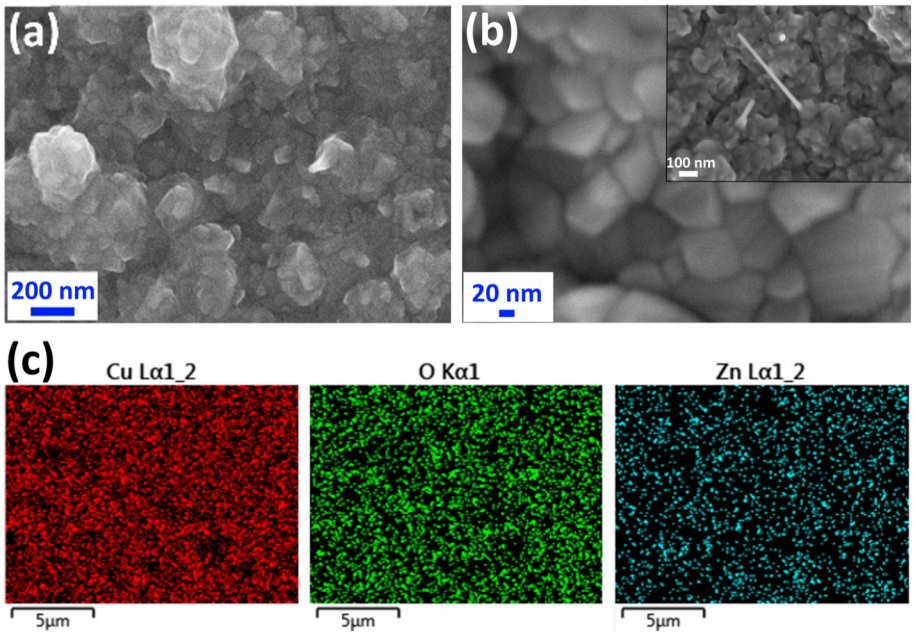

Fig. 1. SEM images of Zn-doped copper oxide nano-structured films thermal annealed (TA) at 450 °C at: (a) low magnification; and (b) high magnification; inset (b) show a region where CuO NWs grown on the surface of thin films. (c) Compositional images taken by EDX elemental mapping at the film microstructural level: Cu; O; and Zn distributions.