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Improved semiconducting $CuO/CuFe_2O_4$ nanostructured thin films for CO_2 gas sensing

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ABSTRACT

Promising results on the behavior of $CuO/CuFe_2O_4$ sputtered thin films as a sensing material under carbon dioxide atmospheres are presented in this article. More specifically, we report the effects of preparation parameters and microstructure of the sensing layer on the response to CO_2. FEG-SEM images and XPS measurements revealed the two-stacked layers rearrangement of samples after air annealing as a key parameter in gas sensing test. The influence of the sensing layer thickness and the influence of Ag as an additive in the film on the response are also reported. The best response was obtained at the optimal operating temperature of 250 °C with a thin film deposited under low argon pressure and low target-to-substrate distance, reaching 40% towards 5000 ppm of CO_2.

1. Introduction

Semiconductor nanocomposites with p–n junction were reported in the literature as the most performing materials for gas sensing regarding operating temperature and response. Ishihara et *al.* [1] introduced the CO_2 gas sensing using a composite oxide/$BaTiO_3$ junction. Several studies were performed on the comparison of different oxides combined with $BaTiO_3$ such as PbO, MgO, CaO, NiO or CuO [1]. As a result, $CuO/BaTiO_3$ exhibited the highest response to CO_2 with a relatively low operating temperature in comparison with other oxides. Other groups replaced the perovskite phase by either another perovskite phase [2] or other oxides having rutile structure [3,4]. From then on, several research groups worked on this composite [5–8] by changing the way of elaborating this material. Indeed, many studies have been carried out on thin [5,9,10] and thick films [1,6,8,11]. Thin films show higher repeatability in fabrication process, better control on fabrication parameters and better conditions in mass production, which allows lower costs than thick film techniques. In this work, radio-frequency (RF) sputtered $CuO/CuFe_2O_4$ semiconductor thin films are used as sensitive material. It has been already demonstrated [12] that the $CuO/CuFe_2O_4$ composite was sensitive to CO_2.

In the present work, some of the key aspects concerning the electric response under CO_2 of $CuO/CuFe_2O_4$ thin-films are correlated with the microstructure characterization thanks to scanning and transmission electron microscopy and X-ray photoelectron spectroscopy analyses. The effects of preparation parameters, microstructure, as well as the influence of silver doping on the sensitivity of the CO_2 sensor are also described.

2. Experimental

2.1. Preparation of the gas sensitive elements

Thin films were deposited by RF-sputtering technique using a $CuFeO_2$ ceramic target according to the preparation described by Chapelle *et al.* [13]. Thickness calibrations were performed with a Dektak 3030ST profilometer. Process parameters for the as-deposited samples are given in Table 1. In order to obtain the $CuO/CuFe_2O_4$ nanocomposite, the as-deposited films were annealed at 450 °C in air for 12 h. After heat treatment, gold interdigitated electrodes were deposited on the surface by direct current

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Table 1
Summary of deposition parameters.

Referencing of deposition conditions	$P_{0.5}d_5$	P_2d_8
Target material	$CuFeO_2$	
Substrates	Fused silica glass, silicon, quartz	
Power (W/cm^2)	3.5	
Argon pressure P (Pa)	0.5	2.0
Target to substrate distance d (cm)	5	8
$P \times d$ (Pa cm)	2.5	16
Deposition rates (nm/min)	6.77	3.75

(DC)-sputtering. Finally, our simplified test device consisted of a substrate, the oxide sensitive layer and two gold electrodes.

2.2. Microstructural characterizations

The microstructure of thin films were examined with a Jeol 2100 field emission gun Transmission Electron Microscope (TEM) and a Jeol JSM 6400 field emission gun Scanning Electron Microscope (SEM). A Thermo Scientific K-Alpha apparatus was used for X-ray photoelectron spectroscopy (XPS) measurements, using a monochromatic Cu Kα radiation with a 400 μm spot size. Peaks were scanned at 50 eV pass energy. The spectrometer was equipped with ions gun to realize depth profile by etching technique. Flood gun was used to minimize charging effects. The binding energies (BE) were referenced to the 1s carbon peak (atmospheric contamination) at 284.6 eV. The structure of thin films was examined by Glow-Discharge Optical Emission Spectrometry (GD-OES) measurements. GD-OES allows fast compositional depth-profiling from the nanometer range up to several hundreds of micron in depths. The depth resolution of this technique is of a few nanometers for thin layers, but increases for thicker layers to reach a few percent of the total sputtered depth. The major advantages of the technique are its speed and ease of use. The optical emission measurements were all conducted on the instrument referred to elsewhere [14], a Jobin Yvon JY 5000 RF instrument equipped with a Hi Light^{TM} 133-Dressler GmbH 13.56 MHz RF generator capable of supplying constant real power, constant applied RF-voltage, or constant DC-bias voltage, and also capable of being operated with continuous or pulsed RF power.

2.3. CO_2 sensing measurements

The impedance of the sensing layer was measured by a Fluke PM6306 RCL-meter. The experiments were carried out from room temperature to 500 °C, using a tube-type furnace with a programmable temperature controller. The total gas flow was fixed at 100 cm^3/min. Two gas bottles were used, one with synthetic dry air and the other one with the same dry air including a concentration of 5000 ppm CO_2 which is the most often used in the bibliography. The response to CO_2 is defined as the relative difference of the film resistance between air and CO_2 atmosphere $(R_{CO_2} - R_{air})/R_{air}$, where R_{CO_2} is the resistance of the film registered in CO_2 atmosphere and R_{air} is the resistance in air (both measured in two probes mode).

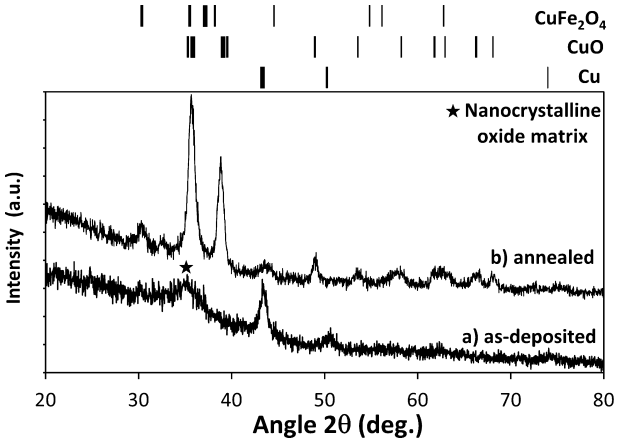

Fig. 1. X-ray diffraction patterns of (a) as-deposited layer and (b) the bilayer obtained after air annealing at 450 °C.

3. Results and discussion

3.1. Importance of the two-stacked sensitive layers architecture: the key role of the elaboration process

The microstructure of the CuO/$CuFe_2O_4$ composite has been detailed previously [15] by the present authors. This material can be described as a self-organized bi-layered architecture made of a thin CuO porous cover layer on the top of a thicker $CuFe_2O_4$ heart layer. Due to their specific self-organization in p- and n-type layers, such films prepared by simple air annealing on as-deposited samples, exhibited significant response to CO_2 [12]. X-ray diffraction studies have shown that as-deposited layers contain metallic copper particles dispersed in a nanocrystalline oxide matrix (Fig. 1, pattern a). After post-deposition annealing, the metallic copper and copper (I) species oxidize in cupric oxide (CuO) (Fig. 1, pattern b) which is obtained at the surface of the film.

This particular self-organization in two-stacked layers after annealing step was systematically observed for all samples analyzed as shown in Fig. 2a and b by SEM and TEM cross section views respectively. XPS and electron probe micro-analysis studies

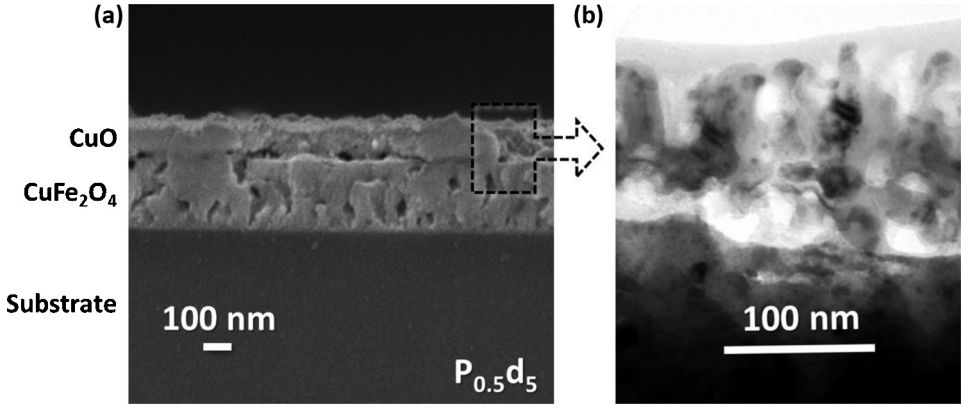

Fig. 2. (a) SEM and (b) TEM micrographs in cross section view of $P_{0.5}d_5$ sample annealed 12 h at 450 °C in air.