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CO_2 sensing properties of semiconducting copper oxide and spinel ferrite nanocomposite thin film

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A B S T R A C T

A new active layer for CO_2 sensing based on semiconducting CuO–$Cu_xFe_{3-x}O_4$ (with $0 \leq x \leq 1$) nanocomposite was prepared by radiofrequency sputtering from a delafossite $CuFeO_2$ target using a specific in situ reduction method followed by post annealing treatment in air. The tenorite–spinel ferrite nanocomposite layer was deposited on a simplified test device and the response in a carbon dioxide atmosphere was measured by varying the concentration up to 5000 ppm, at different working temperatures (130–475 °C) and frequencies (0.5–250 kHz). The results showed a high response of 50% ($R_{air}/R_{CO_2} = 1.9$) at 250 °C and 700 Hz for a CO_2 concentration of 5000 ppm.

Keywords:
Gas sensor
Carbon dioxide
Nanocomposite
Thin film
Sputtering
CuO
Spinel ferrite

1. Introduction

Carbon dioxide detection is currently in demand in key fields such as indoor air quality monitoring [1,2]. Most of the currently available carbon dioxide sensing devices are based on optical principles but they are usually bulky and expensive. This has fuelled the research of several groups in the development of an alternative sensor for CO_2 monitoring which is cheap and efficient. In this context, semiconductors are always a competitive low-cost choice because they are efficient [3], cheap and easy to integrate into electronic and control devices. Concretely for carbon dioxide detection, $BaTiO_3$–CuO mixed oxide composites have been studied by several research groups [4–7] ever since Ishihara et al. [8] reported that the resulting capacitance of this composite depends strongly on the CO_2 concentration in air. A theory based on the behaviour of the p–n heterojunction between n-type $BaTiO_3$ and p-type CuO has been developed by Herran et al. [9] to explain how AC electrical properties change with CO_2 concentration in this system. Other oxides have also been reported [10–15], but research work focused on semiconducting oxides for CO_2 sensing is still limited and only a few systems have been tested.

On one hand, spinel oxides have never been studied for CO_2 detection to date, while for the detection of other gases such as Cl_2, H_2 and NH_3, these oxides, i.e. $NiFe_2O_4$, $CoFe_2O_4$, $ZnFe_2O_4$ [16,17] and $CuFe_2O_4$ [16,18,19] have been widely studied in the form of thick and thin films, and pellets prepared by various methods. On the other hand, even though some spinel structures like $Cu_xFe_{3-x}O_4$ [18,20] exhibit n-type semiconducting properties, they have never been reported for use in p–n heterojunction in cooperation with p-type CuO [21,22].

Furthermore, thick film technology and sintering are commonly used to synthesize materials for such applications, while thin film technology is used only by a few groups [3,10,23] even though it allows mass production of devices at low cost with high control and repeatability. Moreover, due to its high intrinsic surface-to-volume ratio, thin film technology exhibits high capabilities for miniaturization and very short response. Among the different processes to prepare thin films, radiofrequency (RF) sputtering ensures relatively high deposition rates and high versatility, allowing the deposition of different materials and the possibility of preparing out-of-equilibrium phases [24–26].

In this study, thin films of copper oxide and spinel ferrite have been deposited by RF sputtering with the aim to achieve CO_2 sensing. The size, content, distribution and microstructure of this nanocomposite has been varied by using specific in situ reduction method during the deposition [24]. The gas-sensing characteristics of the $Cu_xFe_{3-x}O_4$ and CuO nanocomposites have been tested for carbon dioxide monitoring.

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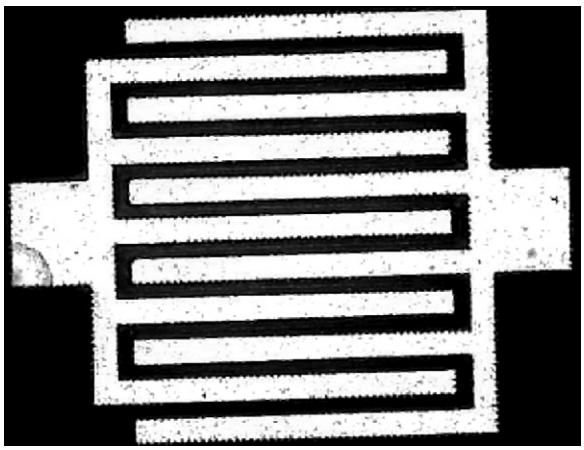


Fig. 1. Optical micrograph of the test device before deposition of nanocomposite sensing layer. The bright grids correspond to the gold electrode.

2. Experimental

The thin films were deposited with an Alcatel A450 apparatus using a sintered ceramic target of pure $CuFeO_2$ with a relative density of 70%. The RF power was fixed at 4 W/cm^2 and the pressure inside the deposition chamber was 5×10^{-6} mbar or lower before deposition is commenced. During the deposition of the films, the argon pressure and the target-to-substrate distance were kept at 0.5 Pa and 5 cm respectively. Thin films of 300 nm were deposited on glass substrate for structural characterizations. The film thickness was fixed to a value of 50 nm when making the sensor device for CO_2 sensing tests.

Thickness calibrations were performed with a DEKTAK 3030ST profilometer. The structural properties were determined by Grazing incidence ($\alpha = 1^\circ$) X-ray Diffraction (GXRD) using a Siemens D5000 diffractometer with the Cu Kα radiation ($\lambda = 1.5418$ Å).

Microscopic studies were carried out with a Veeco Dimension 3000 Atomic Force Microscope (AFM) equipped with a super sharp TESP-SS Nanoworld©tip (nominal resonance frequency 320 kHz, nominal radius curvature 2 nm), and a JEOL 2100 Transmission Electron Microscope (TEM) operating at 200 kV equipped with a X-ray Energy Dispersive Spectroscopy (X-EDS) system.

Our simplified CO_2 sensor consists of a substrate, two interdigitated electrodes and the sensitive oxide layer. The substrate is a piece of 17 mm × 17 mm silicon wafer electrically insulated with a 1 μm thick SiO_2 blanket-layer. Two gold interdigitated electrodes were screen-printed onto the surface of the silicon dioxide layer. The drying and densification of the gold paste was made by thermal annealing at 700 °C. This device is presented in Fig. 1. The sensing nanocomposite layer was then deposited on the top of the electrode by RF-sputtering with the electrical contacts at each sides of the electrodes left uncovered.

The electrical response of the sensing layer was investigated by registering the variations in impedance with a RCL-meter (FLUKE PM6306) as a function of temperature, time, frequency and CO_2 concentration. The test device was placed in a furnace operating under controlled atmosphere with the temperature range of 20–475 °C. The total gas flow was fixed at 100 cm^3/min. Two gas cylinders were used to set the CO_2 concentrations between 0 and 5000 ppm with the use of mass flow regulators.

Impedance measurements were done under two atmospheres: synthetic air and a mixture of air + CO_2 (5000 ppm), which will be referred to as CO_2 henceforth. During these measurements, an alternating current of 1 V was applied to avoid polarization effects. High frequencies are not effective for this study because depletion sites located at grain interfaces are not mobilized as the electrical oscillation is too fast [9]. Therefore, a low frequency was used to avoid the relaxation phenomena and to acquire signals due to spatial-charge phenomena. An arbitrary value of 700 Hz was chosen.

The response S is defined by Eq. (1) as follows:

$$S(\%) = 100 \times \frac{Z_{CO_2} - Z_{air}}{Z_{air}} \quad (1)$$

where Z_{air} and Z_{CO_2} are the electrical impedances of the sensor measured in air and in CO_2 respectively.

The electrical responses were recorded using dynamic tests whereby the sensor was exposed to alternating air and CO_2 pulses at a constant temperature.

In this report, tests have only been made in dry atmospheres. In our future work, we plan to investigate the effect of humidity by testing the sensing layer in an atmosphere with controlled water partial pressures. This nanocomposite thin film can only be used in a practical device if the CO_2 response is reproducible even in varying humidity atmospheres.

3. Results and discussion

3.1. Structural characterization

Fig. 2a shows the GXRD pattern of the thin film deposited on glass substrate, which constitutes the first step of the deposition process. The GXRD data clearly demonstrates the presence of metallic copper with the characteristic (1 1 1) and (2 0 0) Bragg's peaks located at $2\theta = 43.3^\circ$ and $2\theta = 50.43^\circ$ respectively. The broad peak located at $2\theta = 35.5^\circ$, i.e. with $d_{hkl} \approx 2.5$ Å, can be attributed to the various mixed oxide phases, such as Cu_2O ($d_{1\,1\,1} = 2.46$ Å), CuO ($d_{1\,1\,\bar{1}} = 2.52$ Å), $CuFeO_2$ ($d_{0\,1\,2} = 2.51$ Å), and/or $CuFe_2O_4$ ($d_{2\,1\,1} = 2.50$ Å). The oxide phase cannot be unambiguously identified using GXRD in the as-deposited films due to the nanocrystallinity of the material [24]. TEM image of a as-deposited sample of 50 nm thickness (Fig. 3a) shows a homogenous distribution of particles of about 50 nm which are attributed to metallic copper according to X-EDS measurements. The grainy area between the copper particles belongs to the mixed oxide phase. These are in agreement with the GXRD results. AFM done on the same sample shows a regular surface morphology as shown in Fig. 3b.

Thermal annealing at 450 °C under vacuum increases the crystallite size of each phase and magnifies the diffraction peaks related to copper, delafossite and cuprospinel phases as shown in Fig. 2b. This allows clearer identification of the thin film composition. It has been previously demonstrated [27] that deposition by RF sput-

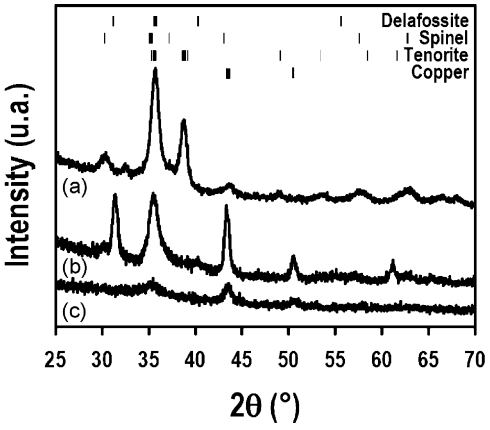


Fig. 2. Grazing angle X-ray diffraction patterns of the deposited film on glass substrate from a $CuFeO_2$ target, (a) as-deposited film, (b) after annealing film under vacuum at 450 °C and (c) after annealing in air at 450 °C for 21 h. Thickness = 300 nm.

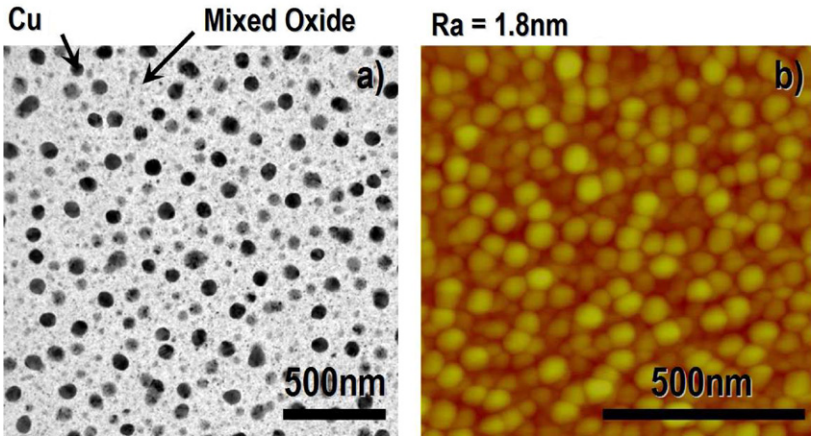


Fig. 3. TEM (a) and AFM (b) images of a as-deposited sample of 50 nm thickness.

tering from a delafossite $CuFeO_2$ target leads to the presence of reduced species in the film. Metallic copper and spinel oxide can then be obtained at a temperature close to ambient. This reduction is favored by several factors, including low oxygen pressure during the deposition, and the bombardment of the target and the substrate by energetic species during the deposition. The formation of these two reduced phases is expected from Cu–Fe–O phase diagram [28] at high temperature and low oxygen partial pressures, according to Eq. (2).

$$CuFeO_2 \rightarrow (1/(3-x))Cu_xFe_{3-x}O_4 + ((3-2x)/(3-x))Cu + ((1-x)/(3-x))O_2 \quad (2)$$

However, sputtering deposition is an out-of-equilibrium process and during the thin film deposition, Eq. (2) is not complete. In addition to spinel and metallic copper, the delafossite phase is also present in the final deposited compound. The as-deposited film is then made of nanometric copper metal particles homogeneously distributed in a copper and iron oxide matrix consisting of spinel and delafossite phases.

The second step in the preparation of $CuO–Cu_xFe_{3-x}O_4$ composite consists of heat treatment of the as-deposited film in air at 450 °C. This treatment leads to the oxidation of metallic copper into CuO and the decomposition of nano-crystallized delafossite $CuFeO_2$ into CuO and $Cu_xFe_{3-x}O_4$. As a result, the film is only constituted of CuO and spinel oxide, in line with the GXRD pattern (Fig. 2c) and according to the phase diagram [29]. This in situ reduction of the target, followed by ex situ oxidation of the thin film, lead to a homogeneous and nanosized composite thin film comprising of CuO and $Cu_xFe_{3-x}O_4$. Due to their individual n and p-type semiconducting properties already reported in the literature [18,20–22], this material can be described as a thin layer made of nanometric p–n heterojunctions.

3.2. CO_2 gas-sensing properties

The electrical properties depend on several parameters such as for example temperature, frequency and gas concentration. Temperature plays a crucial role on the electrical response of semiconductor-based gas sensors. In fact, the adsorption of gases is directly related to the temperature at the surface of the sensing layer.

Fig. 4 shows the response of the layer operating at different temperatures with alternating air and CO_2 pulses. The measurements were performed at 50 °C intervals between 150 °C and 400 °C. The carbon dioxide concentration was fixed at 5000 ppm in order to obtain the maximum signal. The curve shows a classical evolution of the response with respect to temperature, with a maximum at around 250 °C. Below 250 °C, the increase of the response with the temperature, is due to the increase of the depletion layer width [30] and the desorption of contaminating species adsorbed at the material surface, both of which are promoted by higher temperature. The desorption of contaminants also make more sites available for the adsorption of sensory species. At higher temperature, the decrease of the response results from the surface desorption of the sensory species which are responsible for changing the response factor. The best response was found to be −48% at 250 °C, which corresponds to a Z_{air}/Z_{CO_2} ratio of 1.9 approximately.A few hypothesis on the sensing reaction of $CuO–Cu_xFe_{3-x}O_4$ can be introduced on the basis of the results reported on the $CuO–BaTiO_3$ system: in this system, the authors claimed that the capacitance changes of the sensing layer were caused by the carbonation of either the copper oxide [8] or barium oxides [9,31]. However, this carbonation effect could not lead to capacitance or impedance variations without the coupling of the two oxides [32]. Grain boundary effect of the semiconductor must also be taken into account in order to explain the sensitivity of the material [32]. In our system, we assume a sensing mechanism based on the carbonation of the oxides that affects the potential barrier at the boundary between p-type CuO and n-type $Cu_xFe_{3-x}O_4$.Fig. 5 shows the impedance transient of the nanocomposite layer recorded at the optimum temperature of 250 °C and a CO_2 concentration of 5000 ppm. The decrease in impedance when CO_2 gas is injected reveals that Z_{CO_2} is lower than Z_{air}. CO_2 is an oxidizing gas which leads to a decrease in impedance in our case; it behaves like in the presence of a p-type semiconductor. The sig-

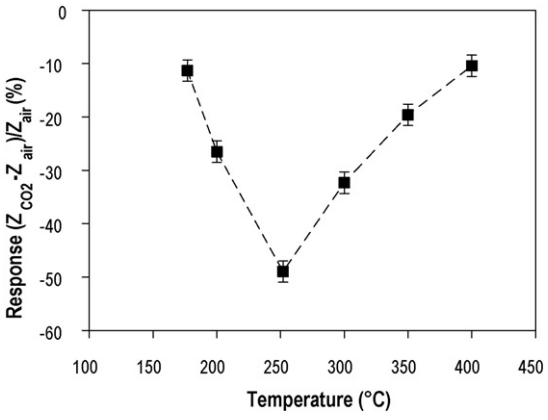


Fig. 4. Response of the sensing layer as a function of temperature, f = 700 Hz, thickness = 50 nm.

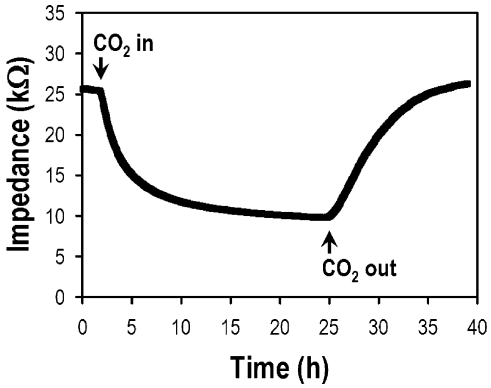


Fig. 5. Impedance transient (at 700 Hz) for response and recovery of a 50 nm $CuO/Cu_xFe_{3-x}O_4$ sensing layer.

nal is totally reversible but the stabilization under CO_2 gas requires very long time. The response time (time to obtain 90% of the total response) is 9.5 h. This value is too high to be considered for application in a sensory device.

A sensitive layer is usually modeled by a porous layer whose constituents are grains of oxides which are in contact at the grain boundaries. Because of its morphology, this layer may be the site of many phenomena when exposed to a gas: competitive adsorption on the surface of the grains, reaction with the molecules that are pre-adsorbed and diffusion between the grains through the pores and grain boundaries. The magnitude and kinetics of each of these processes are different and strongly influenced by the morphology of the film, i.e. by the deposition conditions. In our case, the long response time observed is probably the result of a mechanism limited by diffusion between the grains. A modification of the deposition conditions to obtain more inter-granular porosity and decrease of the layer thickness may be a suitable method to improve the response time.

The aim of this work is to report the unprecedented use of n-type spinel $Cu_xFe_{3-x}O_4$ coupled with a p-type CuO to form a p–n heterojunction which can be used as CO_2 sensing layer. The two-step process to fabricate an active thin film of nanometric $CuO–Cu_xFe_{3-x}O_4$ heterojunction is both simple and convenient. Parameters for the active layer, for example, deposition conditions, film thickness, and composition and doping, can be modified in order to improve the response time. Similar, there exists plenty of room for optimization of the device in terms of the nature of the electrodes, stacking design, and the use of micro-heater platform to perform temperature modulated measurements, etc. These works to optimize the overall performance of the sensor are currently underway and will be reported in another publication at a later time.

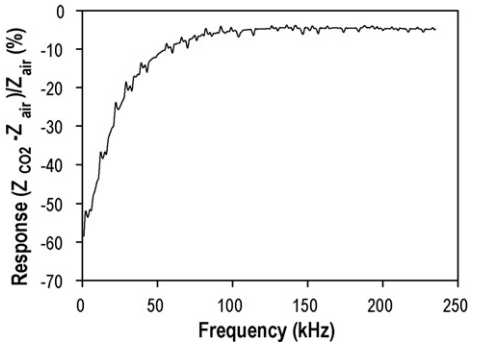


Fig. 6. Variation of the response of $CuO–Cu_xFe_{3-x}O_4$ film as a function of the frequency. $T = 250\,^{\circ}C$, CO_2 concentration = 5000 ppm, thickness = 50 nm.

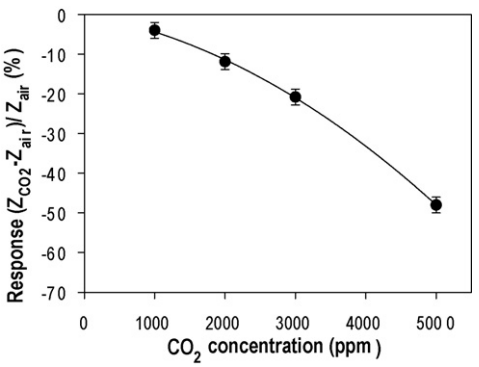


Fig. 7. Response of $CuO–Cu_xFe_{3-x}O_4$ layer as a function of CO_2 concentration. $T = 250\,^{\circ}C$, $f = 700$ Hz, thickness = 50 nm.

The influence of frequency on the electrical responses of the $CuO–Cu_xFe_{3-x}O_4$ semiconducting nanocomposite thin films was also verified. Impedance was measured between 700 Hz and 235 kHz, in air and subsequently under 5000 ppm CO_2. The response was then calculated at each frequency. At $250\,^{\circ}C$, the best results were obtained at low frequencies (Fig. 6). When the frequency increases, the absolute value of the response decreases abruptly until it reaches a plateau at around 5% for frequencies over 100 kHz. As mentioned previously, this variation of the response with the frequency can be attributed to the relaxation phenomena present in the layer as explained in the literature [9]. At high frequencies, the charge transfer at the depletion region appears to be constant because the oscillation of the electrical signal is too fast to detect this physical phenomenon.

The response of the sensing layer as a function of CO_2 concentration ranging from 1000 to 5000 ppm was studied at the optimum temperature of $250\,^{\circ}C$ (Fig. 7). An increase of the sensitivity is evident when the concentration of CO_2 increases. This is in accordance with the increase in the number of molecules arriving at the sites of adsorption. The signal remains significant even for the lowest CO_2 concentrations (< 2000 ppm).

4. Conclusion

Novel thin films of semiconducting nanocomposite $CuO–Cu_xFe_{3-x}O_4$ were tested for CO_2 gas sensing. These films were deposited by radiofrequency sputtering from a delafossite $CuFeO_2$ target. Si/SiO_2 substrates covered with gold interdigitated electrodes were used for gas-sensing measurement. Impedance variations were recorded under two different atmospheres: air then a mixture of air and 5000 ppm of CO_2. The optimal response was obtained at a temperature of $250\,^{\circ}C$ with a value of 48% ($Z_{air}/Z_{CO_2} \sim 1.9$). Best results were achieved at low frequencies (<1000 Hz), and the layer remained still sensitive even for CO_2 concentration lower than 2000 ppm.

In comparison with the bibliographical data, these results obtained with a simplified test device are very promising due to the low operating temperature and the high sensitivity of the material. However, the transient impedance showed a very long response time of about 9.5 h. This time is too long to allow the use of this sensitive layer in a CO_2 gas sensor for the moment. Ongoing work is now focused on the optimization of the sensing layer and the design of the test device to improve the response time.

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