Improved semiconducting CuO/CuFe2O4 nanostructured thin films for CO2 gas sensing

Audrey Chapelle, Imane El Younsi, Stefania Vitale, Yohan Thimont, Thomas
Nelis, Lionel Presmanes, Antoine Barnabé, Philippe Tailhades

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

A. Chapelle[a], I. El Younsi[a], S. Vitale[b,c], Y. Thimont[a], Th. Nelis[b], L. Presmanes[a,*], A. Barnabé[a], Ph. Tailhades[a]

[a] Institut Carnot CIRIMAT–UMR CNRS 5085, Université Paul Sabatier Toulouse III, 118 route de Narbonne, 31062 Toulouse Cedex 9, France
[b] Bern University of Applied Sciences, Engineering and Information Technology, rue de la source 21, 2501 Bienne, Switzerland
[c] Dipartimento di Scienze Chimiche, Universita' di Catania, Viale A. Doria 6, 95125 Catania, Italy

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

---

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
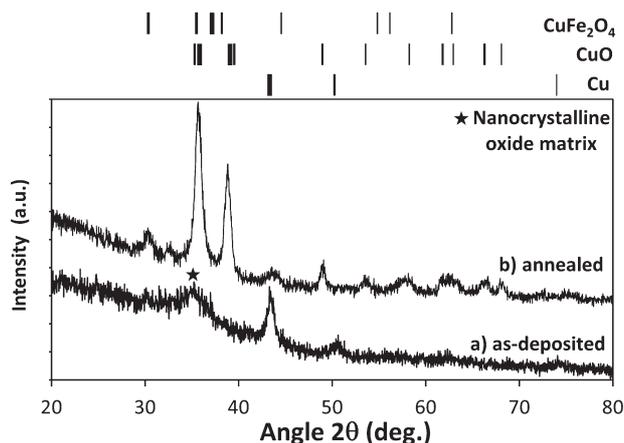

Fig. 1. X-ray diffraction patterns of (a) as-deposited layer and (b) the bilayer obtained after air annealing at 450 °C.

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).

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
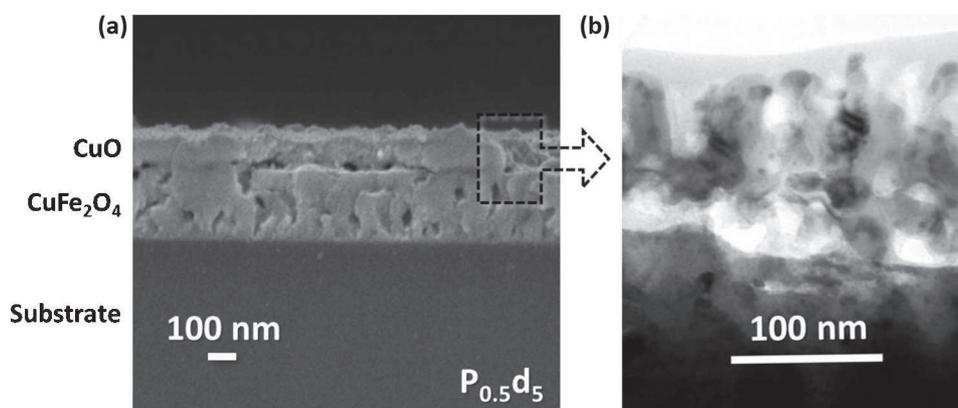

Fig. 2. (a) SEM and (b) TEM micrographs in cross section view of $P_{0.5}d_5$ sample annealed 12 h at 450 °C in air.
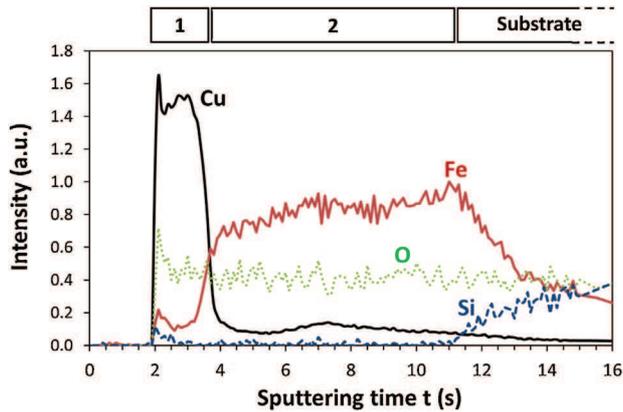
Fig. 3. GD-OES profiles of a 50 nm thick film deposited at $P_{0.5}d_5$ on quartz substrate and annealed in air. Zones 1 and 2 represent the CuO cover layer and the $CuO/CuFe_2O_4$ heart layer respectively.

Fig. 4. FEG-SEM planar and cross section micrographs of sample annealed (a) 12 h at 450 °C in vacuum and then (b) 12 h at 450 °C in air.

revealed that the surface layer consisted of CuO upper layer while the heart layer was composed of $CuFe_2O_4$ [15]. However these measurements were only performed on 300 nm thick films, and have not been carried out on thinner ones.

Although, GD-OES experiments were realized on 300 and 50 nm thick deposited films. This technique allows us to establish a rapid elemental concentration profiling along the depth of the film/substrate, faster than dynamic secondary ion mass spectroscopy and the results are more easily quantified [16]. The bilayer structure was observed for both 300 and 50 nm thick films, annealed at 450 °C in air. Fig. 3 shows the profile of the different elements present in the 50 nm thick film. The analytical signal is significantly above the background signal. The three areas identified are consistent with the structure previously revealed by XPS measurements [15]: zones 1 and 2 correspond to the bilayer $CuO/CuFe_2O_4$, respectively, and zone 3 to the substrate. Thus, GD-OES experiments confirm that the $CuO/CuFe_2O_4$ bi-layer structure that was only observed previously in the 300 nm thick films is also obtained with our two-step process (deposition/oxidation) on thinner sensitive films.

In the case of the composite $CuO/BaTiO_3$, Liao *et al.* [6] proved that the elements CuO and $BaTiO_3$ taken separately were not sensitive to CO_2, whereas the $CuO/BaTiO_3$ composite exhibited good performances. In the other hand, we have already demonstrated [12] that the $CuO/CuFe_2O_4$ bilayer was sensitive to CO_2 but the sensitivity of the single $CuFe_2O_4$ phase toward this gas was however never checked. We then prepared a $CuFe_2O_4$ layer by chemical attack with NH_4OH (28%) on the annealed composite bilayer to dissolve the CuO layer located on top of the copper ferrite layer. Single $CuFe_2O_4$ phase characteristic peaks were observed by X-ray diffraction and Raman spectroscopy (not shown here) after the complete removal of the CuO cover layer by this selective chemical etching. Finally, no electrical measurement could be carried out on the $CuFe_2O_4$ single layer below 400 °C due to its resistance which becomes too high. Finally, the original rearrangement of the as-deposited thin film into two layers, during the oxidizing annealing, offers the possibility to detect CO_2, whereas the two elements which are separated are not sensitive to this gas.

This composite material is new and until now no sensing mechanism has been clearly established. It remains quite similar to the $CuO–BaTiO_3$ composite material studied by Herran et al. [5], the most probable assumption is that sensing mechanism of $CuO–CuFe_2O_4$ bilayer could be controlled by the work function variations of p–n heterojunction between $CuFe_2O_4$ (n type) and CuO (p type). Sensing reactions remain to be studied and defined precisely. In our case, the use of dry air in our experiment can lead
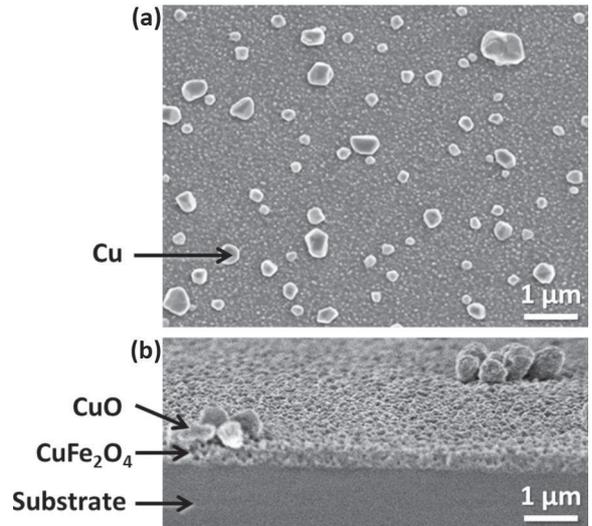
to the formation of iron and/or copper carbonates activated both by oxygen and carbon dioxide. According to research work of Mendayo et al. [17], CO_2 sensing tests under wet air could lead to an enhancement of the response due to the formation of bicarbonate species concomitantly at the surface of the material. Such experiments will be carried out in a near future.

This specific two-stacked sensitive layers architecture was obtained by a controlled *ex situ* oxidation process [15] of as-deposited film nanocomposite [13]. In this process, metallic copper and copper (I) species oxidize in copper (II) oxide and diffuse up to the cover layer concomitantly. If the metallic copper particles first migrate to the surface and then, oxidize into CuO in two independent thermal treatments, this could affect the crystallite size and shape of the active cover layer. According to the literature [18,19], these microstructural characteristics could have an influence on the electrical properties of metal oxides, and then onto the response to CO_2. The microstructure of a $P_{0.5}d_5$ as-deposited sample was then investigated by SEM after an alternative preparation process consisting in two successive annealing treatments under vacuum (12 h at 450 °C) and under air (12 h at 450 °C) instead of a direct air annealing of the as deposited sample. During the first annealing, metallic copper particles contained in the as-deposited sample migrate to the surface by a phenomenon of coalescence and then, during the second annealing, CuO grains gathered at the surface of $CuFe_2O_4$ heart layer as shown in SEM micrographs in Fig. 4a and b, respectively. As a result, none electrical measurement could be recorded due to the discontinuity of the CuO upper layer and the highly resistive $CuFe_2O_4$ under layer. This confirms that stacking CuO over $CuFe_2O_4$ is not a sufficient condition to be CO_2 sensitive, microstructure has also a large influence on the sensing properties and our two steps (deposition/oxidation) process play also a great role during the preparation of the bilayer.

3.2. Influence of the thickness

Samples with two different thicknesses have been deposited under low argon pressure and low target-to-substrate distance ($P = 0.5$ Pa and $d = 5$ cm, respectively, and called $P_{0.5}d_5$ in this work) in order to compare the response of $CuO/CuFe_2O_4$ bilayer within carbon dioxide atmosphere (5000 ppm CO_2). Fig. 5 shows the evolution of the response as a function of operating temperature for these two samples with thicknesses set at 50 and 300 nm for the as-deposited samples. We can see that the thinner film presents
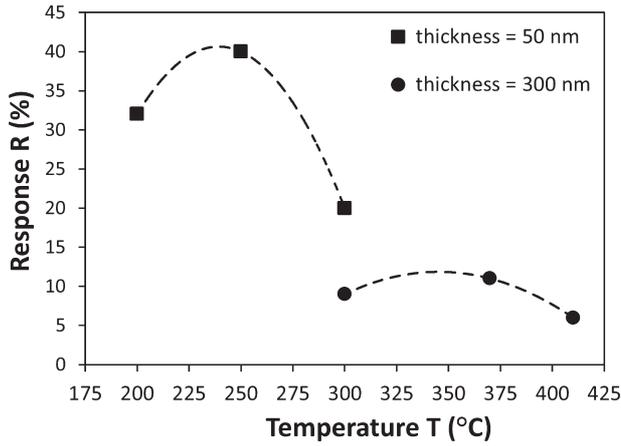
Fig. 5. Response evolution (under 5000 ppm CO_2) as a function of operating temperature for 50 and 300 nm thick samples.

Table 2
Sensing characteristics of 50 and 300 nm thick samples for 50 and 300 nm thick samples, $|R|$, $t_{90\%}$ and $tr_{90\%}$ are response, response time and recovery time, respectively (tests carried out under 5000 ppm CO_2).

Thickness (nm)	$T_{operating}$ (°C)	$|R|$ (%)	$t_{90\%}$ (min)	$tr_{90\%}$ (min)
50	250	40	55	8
300	370	15	150	15

both high response of 40% and low optimal operating temperature around 250 °C. In comparison, the 300 nm thick film has an optimal operating temperature that is shifted to about 350 °C associated to a strong decrease of the response.

Table 2 gives response (R) and recovery times ($t_{90\%}$) of these films deposited with two different thicknesses. Both values decrease when the thickness decreases. These results are in good agreement with the literature [9,20].

Seo *et al.* [21] demonstrated that the control of morphology of the sensing layer is very important to optimize the response characteristics of a material. They proposed especially [22] a model that describes the relation between the sensitivity and the gas diffusion. Thus, the sensitivity and response rate tend to increase when the thickness of the sensing layer decreases and its porosity increases. The microstructural characteristics [15] of the sample deposited with $P_{0.5}d_5$ conditions are given in Table 3. Initially,

the as-deposited layer had a thickness of 300 nm. After the heat treatment carried out to oxidize the film, the thickness became 390 nm and the cross-section observation by SEM determined that the thickness of the CuO cover layer was about 120 nm. GD-OES measurements proved that the bilayer structure was conserved in the thinner film. Then, by using a proportionality relationship, we estimated that for the 50 nm thick as-deposited sample, the thickness of the copper oxide cover layer after the oxidation step is near 20 nm. The porosity is assumed to stay at a constant value of 40% due to the similar oxidation phenomena of metallic copper during the oxidation phase. According to the sensing mechanism expected, the work-function of p–n heterojunction should change due to the carbonation of the surface. The fastest and the highest CO_2 response with a lower operating temperature of the thinnest $P_{0.5}d_5$ sample that has a thinner CuO cover layer (20 nm instead 120 nm for the thicker sample) could be due to a better gas diffusion from surrounding atmosphere to the p–n interface through the CuO porous layer. Moreover, the comparison of the SEM view of these samples shows that thinner CuO cover layer has much smaller grains than the thicker one (Fig. 6), which can also lead to an increased response [23].

3.3. Influence of the deposition conditions

The electric response towards CO_2 of the $P_{0.5}d_5$ sample was in a second time compared with a new sample elaborated at high argon pressure and high target-to-substrate distance ($P = 2.0$ Pa and $d = 8$ cm, respectively, and called $P_{2.0}d_8$ in this work). These experimental conditions were chosen because they lead to a different microstructure than that of $P_{0.5}d_5$ samples. To compare the two-stacked architecture with those obtained with $P_{0.5}d_5$ condition, the microstructural characteristics of the sample deposited with $P_{2.0}d_8$ conditions were investigated for an initial as-deposited film thickness of 300 nm. They are reported in Table 3. However, for the sensing measurements, the as-deposited thickness of this second sample was fixed at 50 nm to enhance the response of the sensitive layer according to the results showed previously. The response as a function of operating temperature for the sample $P_{2.0}d_8$ had a trend similar to that seen for the $P_{0.5}d_5$ film. Particularly, the optimal temperature was also obtained for an operating temperature close to 250 °C. The sensing characteristics of these two samples, determined at 250 °C, are compared in Table 4.

The best response is obtained for the sample $P_{0.5}d_5$. Moreover, response and recovery times are twice shorter in the case of the
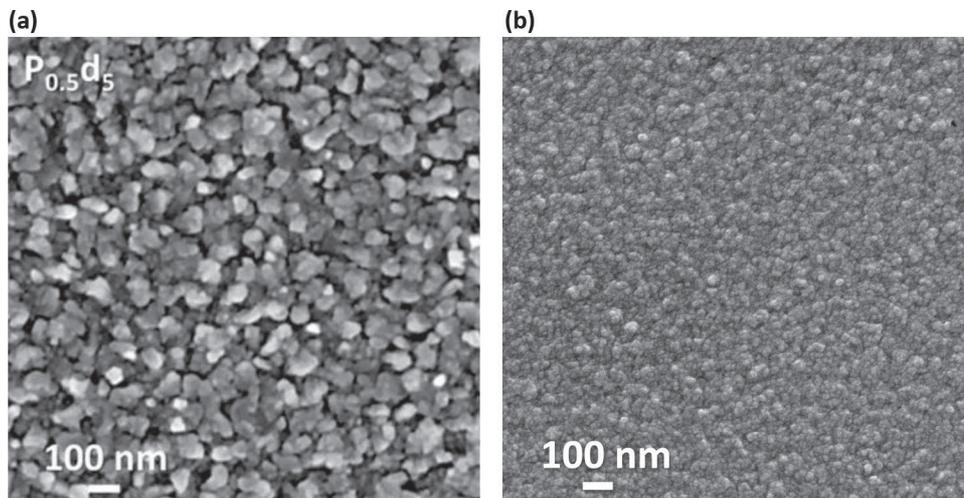

Fig. 6. FE-SEM micrographs in-plane view of $P_{0.5}d_5$ samples annealed 12 h at 450 °C under air: (a) thickness of the CuO cover layer closed to 120 nm and (b) thickness of the CuO cover layer estimated at 20 nm (see Table 3).

Table 3
Microstructural characteristics of the samples deposited at $P_{0.5}d_5$ and $P_{2.0}d_8$. The total thickness and the thickness of the CuO cover layer for the 50 nm thick samples were estimated by using a proportionality relationship.

Sample	$P_{0.5}d_5$		$P_{2.0}d_8$	
Thickness of the as-deposited film	300 nm	50 nm	300 nm	50 nm
Total thickness of the film after 450 °C/12 h air annealing	390 nm	$50 \times 390/300 = 65$ nm (estimated)	310 nm	$50 \times 310/300 = 52$ nm (estimated)
Thickness of the CuO cover layer	120 nm	$50 \times 120/300 = 20$ nm (estimated)	60 nm	$50 \times 60/300 = 10$ nm (estimated)
Porosity of the CuO cover layer	40%		<5%	

Table 4
Sensing characteristics of the samples deposited at $P_{0.5}d_5$ and $P_{2.0}d_8$ |R|, $t_{90\%}$ and $tr_{90\%}$ are responses, responses times and recovery times respectively (tests carried out under 5000 ppm CO_2).

Sample	$T_{operating}$ (°C)	$|R|$ (%)	$t_{90\%}$ (min)	$tr_{90\%}$ (min)
$P_{0.5}d_5$	250	40	55	8
$P_{2.0}d_8$	250	32	100	20

$P_{0.5}d_5$ sample than the $P_{2.0}d_8$ one. These improvements are linked to the two-stacked layers microstructures.

Microstructural characteristics (Table 3) show that the $P_{2.0}d_8$ sample has a CuO cover layer which is dense. Fig. 7 exhibits the variation of the porosity of the CuO cover layer as a function of the deposition conditions. In comparison, the $P_{0.5}d_5$ sample has a cover layer which is two times thicker and has a high porosity close to 40%. Using a proportional relationship for a 50 nm thick as-deposited sample, we estimated that after oxidation annealing we obtain, for the $P_{2.0}d_8$ sample, a dense CuO layer with a thickness of 10 nm, and for the $P_{0.5}d_5$ condition a 20 nm thick layer of copper oxide highly porous. The accessibility which is then much better in the case of the latter can then explain the higher response and the lower response time of the sample deposited with $P_{0.5}d_5$ conditions.

3.4. Influence of the substrate

XPS measurements were realized on films deposited on conventional glass substrate. After annealing in air for long duration at 500 °C, some alkaline elements are supposed to diffuse into the thin film [24–26]. Fig. 8 presents a survey scan of a 100 nm $P_{0.5}d_5$ sample after 12 h of air annealing at 500 °C. The spectrum shows photoelectron lines of a Cu2p, O1s, C1s, Au4f, Na1s and the Auger lines LMM. The presence of gold is due to the electrodes deposited on the surface of the sensing layer for a better electrical contact during the gas sensing tests. The XPS peak of Na observed in the high resolution scan (Fig. 8, inset) imply that sodium migrates from the glass substrate into the thin film. This diffusion of the sodium
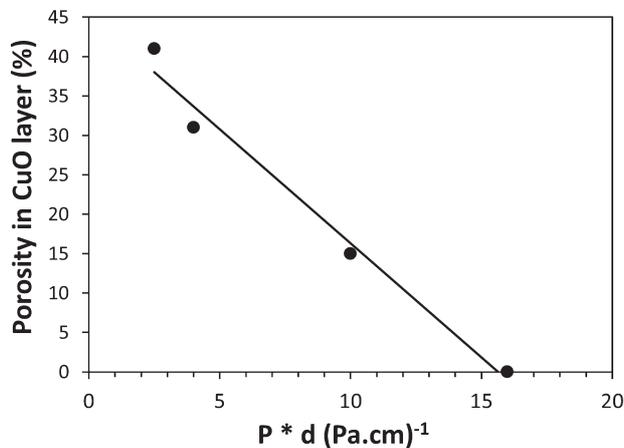

Fig. 8. XPS of 100 nm CuO/CuFe$_2$O$_4$ sample deposited on glass substrate Survey scan and high resolution scan for Na1s inset.

contained in the substrate could have an influence on the sensing response of the composite layer.

In order to avoid the migration of any alkaline element, sensitive layers were deposited on quartz substrate with the same sputtering conditions ($P_{0.5}d_5$). As for layers already prepared on glass substrates, the samples were oxidized at 450 °C for 12 h to form the CuO/CuFe$_2$O$_4$ composite layer and then mounted in the cell to be tested. Due to the use of this substrate, no alkaline elements could migrate during the annealing step. Fig. 9 presents a transient response of the sample under 5000 ppm CO_2 with one hour pulse duration. High and repeatable response values closed to 30% were obtained. However, for 3 h pulse duration which is enough to get the saturated response, we measured a value close to 40% which is similar to the recorded response of the samples deposited on glass substrates. In conclusion, we have not noticed any influence of the sodium diffusion into the sensitive layer.

Fig. 7. Variation of the porosity in the CuO layer after air annealing as a function of the factor pressure × distance (deposition conditions).
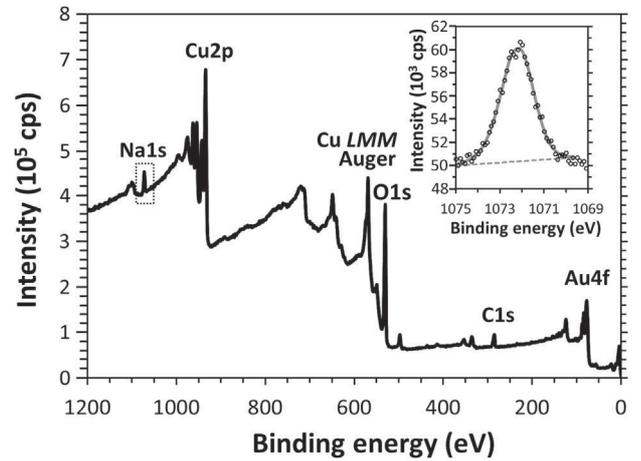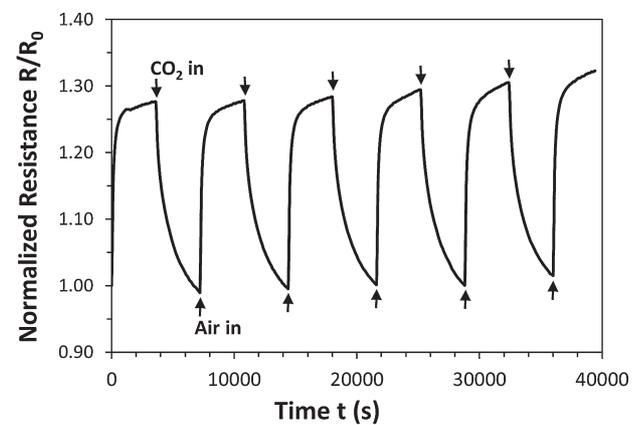

Fig. 9. Transient response at 250 °C (under 5000 ppm CO_2) for a 50 nm thick sample deposited on quartz substrate.
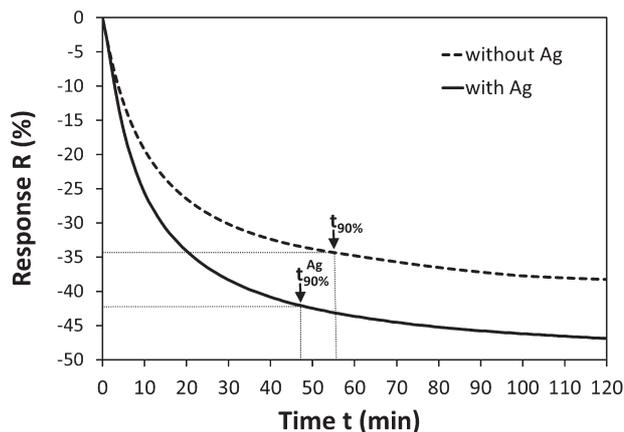
Fig. 10. Response evolution of samples with or without silver additive ($t_{90\%}$ is response time).

3.5. Influence of silver as additive

The presence of additive nanoparticles at the surface or in volume can modify significantly the metal oxide behavior leading to the enhancement of the response towards a gas, as well as to a better gas selectivity [8]. About three nanometers of silver were then sputtered on the surface of a 50 nm $P_{0.5}d_5$ deposited sample. The silver film is too thin to be continuous and then nanometric islands grow on the surface of the bilayer. The size of the silver particles after annealing at 450 °C is difficult to determine and could not be obtained by FEG-Scanning Electron Microscopy or Atomic Force Microscopy. Due to the temperature used for the sensing test (250 °C) the silver remains at the metallic state [27]. Fig. 10 shows that the metallic silver, which cannot be substituted for the cations of iron or copper, improves the response of about 25% compared to a layer without this ultra-thin silver deposition.

Herrán *et al.* [5] demonstrated that the main physical detection mechanism is based on a work function variation of the p-/n-semiconductor hetero-junction. The introduction of silver as a metallic additive enhances the sensitivity. This phenomenon is explained by a metal/semiconductor junction. Ishihara et al. [28] also demonstrated that the addition of small amounts of metal or metal oxide onto $CuO/BaTiO_3$ was effective in increasing the sensitivity and selectivity to CO_2. They especially found that Ag was the most desirable additive from the standpoint of sensitivity and operating temperature. However the mechanisms remain not clear at the present.

4. Conclusion

Thin films were deposited by RF-sputtering from a $CuFeO_2$ target varying argon pressure and target-to-substrate distance. The sensing layer was obtained after an air annealing for 12 h at 450 °C. Self-organization of the sample after air annealing induced a p-CuO/n-$CuFe_2O_4$ bilayer structure. GD-OES experiments confirm that the $CuO/CuFe_2O_4$ bi-layer structure is obtained on film deposited with $P_{0.5}d_5$ conditions and for thicknesses of 50 nm measured in the as-deposited state. This latter film was found to be the sample exhibiting the highest response to 5000 ppm of CO_2 due to thin and highly porous CuO upper layer. XPS experiment showed that alkaline element could diffuse from the interface with the conventional glass substrate during the oxidation annealing. However, sensing layer deposited on pure quartz substrate could not lead to a higher response to CO_2. On the other side, deposition of sputtered silver nanoparticles at the surface of the bilayer could improve the response by 25%. These results confirm that nanostructured

$CuO/CuFe_2O_4$ bilayers are promising candidates for future cheap semiconductors CO_2 sensors. However, to be fully interesting for a future industrial application, further additional tests have to be carried out to determine the cross-sensitivity with various gases and the influence of the humidity on the response.

References

[1] T. Ishihara, K. Kometani, M. Hasida, Y. Takita, Application of mixed oxide capacitor to the selective carbon dioxide sensor, J. Electrochem. Soc. 138 (1991) 173–176.
[2] Y.F. Gu, H.M. Ji, B. Zhang, T.X. Xu, Preparation and CO_2 gas sensitive properties of CuO–$SrTiO_3$-based semiconductor thin films, Key Eng. Mater. 280-283 (2007) 311–314.
[3] J.C. Xu, G.W. Hunter, D. Lukco, C.C. Liu, B.J. Ward, Novel carbon dioxide microsensor based on tin oxide nanomaterial doped with copper oxide, IEEE Sens. J. 9 (3) (2009) 235–236.
[4] G. Zhang, M. Liu, Effect of particle size and dopant on properties of SnO_2-based gas sensors, Sens. Actuators B: Chem. 69 (2000) 144–152.
[5] J. Herrán, G.G. Mandayo, E. Castano, Physical behaviour of $BaTiO_3$–CuO thin-film under carbon dioxide atmospheres, Sens. Actuators B: Chem. 127 (2007) 370–375.
[6] B. Liao, Q. Wei, K. Wang, Y. Liu, Study on CuO–$BaTiO_3$ semiconductor CO_2 sensor, Sens. Actuators B: Chem. 80 (2001) 208–214.
[7] M.I. Baraton, L. Merhari, Determination of the gas sensing potentiality of nano-sized powders by FTIR spectrometry, Scr. Mater. 44 (2001) 1643–1648.
[8] Z. Jiao, F. Chen, R. Su, X. Huang, W. Liu, J. Liu, Study on the characteristics of Ag doped CuO–$BaTiO_3$ CO_2 sensors, Sensors 2 (2002) 366–373.
[9] J. Herrán, G.G. Mandayo, E. Castano, Solid state gas sensor for fast carbon dioxide detection, Sens. Actuators B 129 (2008) 705–709.
[10] J. Herrán, O. Fernandez-Gonzalez, I. Castro-Hurtado, T. Romero, G.G. Mandayo, E. Castano, Photoactivated solid-state gas sensor for carbon dioxide detection at room temperature, Sens. Actuators B 149 (2010) 368–372.
[11] M.I. Baraton, L. Merhari, P. Keller, K. Zweiacker, J.U. Meyer, Novel electronic conductance CO_2 sensors based on nanocrystalline semiconductors, Mater. Res. Soc. 536 (1999) 341–346.
[12] A. Chapelle, F. Oudrhiri-Hassani, L. Presmanes, A. Barnabé, Ph. Tailhades, CO_2 sensing properties of semiconducting copper oxide and spinel ferrite nanocomposite thin film, Appl. Surf. Sci. 256 (2010) 4715–4719.
[13] A. Chapelle, A. Barnabé, L. Presmanes, Ph. Tailhades, Copper and iron based thin film nanocomposites prepared by radio frequency sputtering. Part I: elaboration and characterization of metal/oxide thin film nanocomposites using controlled in situ reduction process, J. Mater. Sci. 48 (2013) 3386–3394.
[14] Th. Neils, M. Aeberhard, M. Hohl, L. Rohr, J. Michler, Characterisation of a pulsed RF-glow discharge in view of its use in OES, J. Anal. At. Spectrom. 21 (2006) 112–125.
[15] A. Barnabé, A. Chapelle, L. Presmanes, Ph. Tailhades, Copper and iron based thin film nanocomposites prepared by radio frequency sputtering., Part II: elaboration and characterization of oxide/oxide thin film nanocomposites using controlled ex-situ oxidation process, J. Mat. Sci. 48 (2013) 3304–3314.
[16] T. Nelis, J. Pallosi, Glow Discharge as a Tool for Surface and Interface Analysis, Applied Spectroscopy Reviews (2006) 227–258.
[17] G. Mandayo, J. Herran, I. Castro-Hurtado, E. Castaño, Performance of a CO_2 impedimetric sensor prototype for air quality monitoring, Sensors 11 (2011) 5047–5057.
[18] N. Murakami, K. Tanaka, K. Sasaki, K. Ihokura, The influence of sintering temperature on the characteristics of tin dioxide combustion monitor sensors, Anal. Chem. 17 (1983) 165–170.
[19] X. Wang, S.S. Yee, W.P. Carey, Transition between neck-controlled and grain-boundary-controlled sensitivity of metal-oxide gas sensors, Sens. Actuators B: Chem. 25 (1–3) (1995) 454–457.
[20] N. Yamazoe, G. Sakai, K. Shimanoe, Oxide semiconductor gas sensors, Catal. Surv. Asia 7 (2003) 63–75.
[21] M.H. Seo, M. Yuasa, T. Kida, J.S. Huh, K. Shimanoe, N. Yamazoe, Gas sensing characteristics and porosity control of nanostructured films composed of TiO_2 nanotubes, Sens. Actuators B 137 (2009) 513–520.
[22] G. Sakai, N. Matsunaga, K. Shimanoe, N. Yamazoe, Theory of gas-diffusion controlled sensitivity for thin film semiconductor gas sensor, Sens. Actuators B 80 (2001) 125–131.
[23] G. Korotcenkov, Gas response control through structural and chemical modification of metal oxide films: state of the art and approaches, Sens. Actuators B 107 (2005) 209–232.
[24] C. Lim, D.E. Day, Sodium diffusion in glass: II. Mixed sodium–potassium silicate glasses, J. Am. Ceram. Soc. 60 (1977) 473–477.
[25] A. Kolitsch, R. Kuechler, E. Richter, W. Hinz, Tracer diffusion in sodium silicate glasses. I. Studies on sodium self-diffusion, Silikattechnik 29 (10) (1978) 302–304.
[26] R. Hempelmann, C.J. Carlile, D. Beyer, Ch. Kaps, Sodium self-diffusion coefficient in sodium silicate glass by quasielastic neutron scattering, Z. Phys. B 95 (1994) 49–53.
[27] K. Kiryukhina, H. Le Trong, Ph. Tailhades, J. Lacaze, V. Baco, M. Gougeon, F. Courtade, S. Dareys, O. Vendier, L. Raynaud, Silver oxalate-based solders: New

materials for high thermal conductivity Microjoining, Scripta Materialia 68 (2013) 623–626.

[28] T. Ishihara, K. Kometani, Y. Nishi, Y. Takita, Improved sensitivity of CuO–BaTiO$_3$ capacitive-type CO$_2$ sensor by additives, Sens. Actuators B 28 (1995) 49–54.

Biographies

A. Chapelle received her MSc in materials for energy storage and conversion from University Paul Sabatier of Toulouse in 2008. She obtained her PhD degree in 2012 from CIRIMAT laboratory, Toulouse, France. Her research is now focused on metal oxide sensors in LAAS-CNRS laboratory, Toulouse, France.

I. El Younsi obtained her master's degree in materials engineering: thin metal layers from University of Strasbourg in 2012. She is currently pursuing her PhD degree on preparation and characterization of new sensitive layers for CO$_2$ gas sensors in CIRIMAT laboratory at Paul Sabatier University, Toulouse, France.

S. Vitale obtained her MSc in materials chemistry at the University of Catania (Italy) in 2011. She has worked for two years (2012–2013) at the Bern University of Applied Sciences (Switzerland), were she was involved in multilayered materials characterization by GDOES. She is currently PhD student at the Department of Chemical Sciences of the University of Catania, in LAMSUN laboratory, where she is working on surface engineering *via* molecular self-assembly for nanotechnology applications.

Y. Thimont is an assistant professor at the CIRIMAT laboratory (Toulouse-France) since September 2013. He received his PhD degree in chemistry of materials at the University de Caen Basse-Normandie (France) in 2009 for YBa$_2$Cu$_3$O$_7$ thin films depositions and characterization. He held a nine month post-doctoral position based on the study and the deposition of TCO thin films at the LRCS laboratory (Amiens-France). He then returns to Caen as temporary teacher and researcher in superconductor thematic for two years then held another post-doctoral position at Caen for one year which devoted to the synthesis and characterization of thermoelectric silicides. His research interests include the thin films synthesis and topographic, electrical, magnetic and optical characterizations.

T. Nelis received his PhD degree for work on free radical spectroscopy in Bonn, Germany. Since then he has worked several years for major scientific instrument manufactures in the field of glow discharge emission spectroscopy. Since 2011, he is professor for physics at the Bern University of Applied Sciences in Biel Switzerland. His current field of research is plasma processes for thin film deposition and surface modification.

L. Presmanes received his PhD degree, for his thesis-work on ferrite thin films for magneto-optical storage. Since 1997, he has been working in CIRIMAT laboratory at University Paul Sabatier (Toulouse) and he is also CNRS researcher since 2001. His research interests are focused on the preparation of sputtered oxide and nano-composites thin films and the study of their microstructure as well as their electrical, magnetic and optical properties. He developed sputtered ferrite thin films to be integrated as sensitive layers in magneto-optical disks and micro-bolometers (IR sensors). His work is currently focused on transparent conducting oxides and semiconductor sensitive layers for gas sensors.

A. Barnabé is a professor at the CIRIMAT laboratory, Paul Sabatier University, France. He received his PhD degree in chemistry of materials from University de Caen-Basse Normandie (France) in 1999. He held a post-doctoral position in Northwestern University, Evanston (USA), in 2000. His current research interests are mainly focused in functional metal oxide powders, ceramics and thin films prepared by PVD technique.

P. Tailhades received his PhD degree in material science in 1988 and the Habilitation à Diriger les Recherches in 1994. He is currently the vice director of the Centre Interuniversitaire de Recherche et d'Ingénierie des Matériaux (CIRIMAT), Toulouse, France. His research interests include the preparation of original metallic oxides, especially spinel ferrites, in the form of fine powders, thin films, or bulk ceramics and the study of their magnetic, electric, and optical properties. He also works on the preparation of special metallic powders. He received the silver medal of CNRS in France in 2000.