Gas-Sensing Properties of Sprayed Films of \((\text{CdO})_x(\text{ZnO})_{1-x}\) Mixed Oxide

R. Ferro, J. A. Rodríguez, I. Jiménez, A. Cirera, J. Cerda, and J. R. Morante

Abstract—A novel \(\text{NO}_2\) sensor based on \((\text{CdO})_x(\text{ZnO})_{1-x}\) mixed-oxide thin films deposited by the spray pyrolysis technique is developed. The sensor response to 3-ppm \(\text{NO}_2\) is studied in the range 50 °C–350 °C for three different film compositions. The device is also tested for other harmful gases, such as CO (300 ppm) and \(\text{CH}_4\) (3000 ppm). The sensor response to these reducing gases is different at different temperatures varying from the response typical for the p-type semiconductor to that typical for the n-type semiconductor. Satisfactory response to \(\text{NO}_2\) and dynamic behavior at 230 °C, as well as low resistivity, are observed for the mixed-oxide film with 30% Cd. The response to interfering gas is poor at working temperature (230 °C). On the basis of this study, a possible sensing mechanism is proposed.

Index Terms—Gas sensor, mixed oxide, \(\text{NO}_2\), spray pyrolysis.

I. INTRODUCTION

A

IR-QUALITY monitoring has received a great deal of attention in the last years. Nitrogen dioxide (\(\text{NO}_2\)) is one of the main harmful gases, which provokes noxious effects on environment and human health. Resistive-type sensors based on metal-oxide semiconductors have been intensively studied in the last decades due to the low cost, technological simplicity, small size, and ease of handling. Besides, thin-film gas sensors show high performance features such as high stability and fast response [1]–[3]. Furthermore, the compatibility with micromachined structures allows sensor miniaturization, reduction of the production cost, and power consumption.

Several metal oxides have been tested for \(\text{NO}_2\) detection, tungsten trioxide (\(\text{WO}_3\)) being one of the most promising materials in view of its high sensitivity. However, thin films of this oxide generally exhibit high resistivity, which is the main drawback of sensors based on this material [4]. It is well known that the resistivity of the n-type semiconductor increases upon exposure to oxidizing gases like \(\text{NO}_2\). High-output sensor impedance is undesirable since a complex electronic circuit would be required in this case, thus complicating the construction of a portable miniaturized device.

Zinc oxide (\(\text{ZnO}\)) was the first metal oxide used for chemical sensors [5], but thin films of this material also have a high resistivity. On the contrary, as-deposited cadmium oxide (\(\text{CdO}\))

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R. Ferro and J. A. Rodríguez are with the Faculty of Physics, University of Havana, 10400 Vedado, Havana, Cuba (e-mail: rferro2000@yahoo.com).

I. Jiménez, A. Cirera, J. Cerda, and J. R. Morante are with the Electronic Materials and Engineering Faculty, Physics, University of Barcelona, E-08028 Barcelona, Spain.

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II. EXPERIMENTAL

Two solutions (0.1 M) were prepared using nitrates of Zn and Cd diluted in distilled water. Different compositions for the starting solutions were investigated (see Table I for the corresponding denomination of the samples). The resulting solution was sprayed onto alumina substrates having interdigitated Pt electrodes (length = 1.6 mm and width of spacing = 0.2 mm) on the front side and a Pt heating resistor on the bottom. Other technological parameters used were substrate temperature 130 °C, solution flow 3 ml/min, carrier gas flow (nitrogen) 5 l/min, and nozzle height 0.3 m. The details concerning the experimental setup can be found elsewhere [14]. All as-deposited \((\text{CdO})_x(\text{ZnO})_{1-x}\) films were subsequently annealed in static air at 600 °C for 2 h in order to stabilize the sensing properties.

The layer thickness was measured by means of a periplometer DEKTAK 3030. Energy-dispersive X-ray spectroscopy (EDS) analysis was used to determine the chemical composition at several points of the layers. The spectra were analyzed with ZAF software and the results were averaged for each layer. Gas-sensing tests were carried out in a stainless-steel chamber under a dynamic regime. The chamber volume was 200 ml, and the total gas flux was fixed at 200 ml/min. The gas composition
was regulated by mixing the target gas and synthetic air, coming from the certified bottles, in appropriate proportions by means of a mass flow controller (MFC). Automatic control of MFC, as well as measurements of electrical parameters, were performed with the help of a PC by using data acquisition boards. Further details can be found elsewhere [13].

III. RESULTS AND DISCUSSION

Mixed-oxide layers having thickness values in the interval of 400–500 nm were obtained. Such thickness was considered optimal to avoid the usual increase of resistance in ultrathin sensors, but keeping the main properties of thin layers. From X-ray patterns, it was established that the films are constituted of a mixture of cubic CdO and hexagonal ZnO phases [15]. Table I shows the EDS data corresponding to film composition. The atomic percent of Cd is considered with respect to the sum of the atomic percent of Zn and Cd in the samples and corresponds to the x value in the formula \((\text{CdO})_{x}(\text{ZnO})_{1-x}\). As can be observed, there is a good correspondence between those values of x estimated from the composition of the sprayed solution (nominal values) and those calculated from the experimental data.

Fig. 1 depicts the temperature variation of the conductance of the films exposed to oxygen. It should be noted that, in all cases, the conductance increases as temperature increases and a maximum value is reached in the temperature range 200 °C–230 °C. The initial increase of the conductance below 230 °C can be related with the typical semiconductor behavior, that is, an increase of the electron concentration is produced by thermal excitation of the valence electrons. The ulterior behavior observed in Fig. 1, to a great extent, reveals a typical surface-controlled sensor model [16], which has been applied for SnO2 films as well as for CdO-doped Fe2O3 [8] and ZnFe2O4 [10] films. It is known that at low temperatures, the surface is populated by physisorbed and chemisorbed species such as \(\text{O}^{2-}\), \(\text{OH}^{-}\), and \(\text{H}_2\text{O}\) while, at higher temperatures (above 300 °C), the ions \(\text{O}^{2-}\) and \(\text{O}^{2-}\) predominate [17], [18]. The maximum observed for the sensor response in our experiments might be associated with the occurrence of the following reactions as temperature increases [10]

\[
\begin{align*}
\text{O}_2\text{gas} + e^{-} & \rightarrow \text{O}^{2-}_{\text{ads}} \\
\text{O}^{2-}_{\text{ads}} + e^{-} & \rightarrow 2\text{O}^{2-}_{\text{ads}}
\end{align*}
\]

where subscripts “gas” and “ads” refer to species in gaseous phase and adsorbed on the film surface, respectively. It seems that at temperatures higher than 200 °C, the effect of these reactions is more significant than the thermal excitation and the conductivity finally decreases due to capture of electrons, thus diminishing their concentration in the conduction band.

The explained behavior also predicts the response of the material to the presence of oxidizing gases, which results in an increase of the resistance. Fig. 2 depicts the sensor response to NO2 measured in the temperature interval 50 °C–350 °C for the three different samples studied. The sensor response (S) in our case is defined as the resistance ratio \(R_{\text{gas}}/R_{\text{air}}\). \(R_{\text{gas}}\) and \(R_{\text{air}}\) being the sensor resistance in presence of the target gas and air, respectively. The gas concentration was fixed at 3 ppm since it is the concentration listed in the safety standard by American Conference of Governmental Industrial Hygienist (ACGIH). It is observed that the sensor resistance rises in presence of NO2 for all temperatures and a well-defined maximum on sensor response is achieved at about 200 °C. A somewhat similar result was reported by Leo et al. for sprayed SNO2 film-based sensors [19]. The observed behavior may be understood by considering that the kinetic of the surface interaction is thermally ac-

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**TABLE I**

**RATIO OF THE ATOMIC PERCENT OF Cd WITH REGARD TO THE SUM OF THE ATOMIC PERCENT OF Zn AND Cd IN THE SAMPLES**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cd nominal concentration (x)</th>
<th>Cd experimental concentration (x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZC1</td>
<td>0.15</td>
<td>0.14</td>
</tr>
<tr>
<td>ZC2</td>
<td>0.30</td>
<td>0.28</td>
</tr>
<tr>
<td>ZC3</td>
<td>0.50</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Fig. 1. Dependence of conductance on sensor temperature, in oxygen, for \((\text{CdO})_{x}(\text{ZnO})_{1-x}\) films with different compositions according to Table I (ZC1 : x = 0.14, ZC2 : x = 0.28, and ZC3 : x = 0.52).

Fig. 2. Effect of temperature on sensor response to 3-ppm NO2 for \((\text{CdO})_{x}(\text{ZnO})_{1-x}\) films with different compositions according to Table I (ZC1 : x = 0.14, ZC2 : x = 0.28, and ZC3 : x = 0.52).
ivated and determined by the concurrence of several processes of adsorption, reaction, and desorption of previously adsorbed molecules of NO$_2$. At temperatures below 200 °C, the sensor response change might be attributed mainly to the adsorption and/or reaction of NO$_2$ molecules on the solid surface according to the following mechanisms [20]:

$$\text{NO}_2^{\text{gas}} + e^- \rightarrow \text{NO}_2^{\text{ads}} \quad (3)$$

$$\text{NO}_2^{\text{gas}} + \text{O}_2^{\text{ads}} + 2e^- \rightarrow \text{NO}_2^{\text{ads}} + 2\text{O}^{\text{ads}}. \quad (4)$$

These processes reduce the electron concentration in the conduction band with a corresponding increase in sensor response. On the other hand, if temperature increases, the following reaction might take place even though the concentration of O$_{\text{ads}}^-$ at temperatures below 300 °C might still be low [21]

$$\text{NO}_2^{\text{gas}} + \text{O}^{\text{ads}} \rightarrow \text{NO}_\text{gas} + \text{O}_2^{\text{gas}} + e^- \quad (5)$$

It seems that the decrease of adsorption rate together with the possible desorption of some adsorbed molecules of NO$_2$ and the occurrence of the reaction (5) lead to a decrease in the sensor response at temperature higher than 200 °C, as observed in the experimental results.

According to Fig. 2, the maximum sensor response is obtained at around 200 °C (sample ZC1). However, the working temperature was fixed at 230 °C by making a compromise between sensor response and dynamic characteristics (response and recovery times), which are derived from a time resistance variation, as shown in Fig. 3. This dependence was obtained at 230 °C, by exposing the samples for 30 min to dry air, 3 ppm of NO$_2$, and dry air, alternatively. No drift of the baseline was observed, corresponding to an oxidizing reaction of molecules adsorbed on the film surface, whereas at high temperature (300 °C), a contrary effect is manifested. At intermediate temperatures, a transitory process occurs. This phenomenon evidences the presence, in this material, of several concurrent sensitivity mechanisms thermally activated. It is known that the oxidizing or reducing character of a gas in contact with an oxide metal semiconductor depends on the gas pressure, surface temperature, kind of species adsorbed on the surface, and other morphological, structural, and electronic factors which determine the concentration of surface active sites of adsorption and surface catalytic activity. It has been reported about the oxidizing character of nitrous oxides (NO and NO$_2$) in contact with samples of SnO$_2$ [20]. However, the same interactions have produced an increase or decrease of the sensor resistance, depending on the temperature range and gas concentration [21].

In our case, a somewhat similar situation might be taking place. The rise of the resistance of the sensor upon exposure to CO and CH$_4$ observed at temperatures as low as 100 °C might be attributed to the reaction of the gas molecules with the ionosorbed oxygen according to the following possible reactions:

$$\text{CO}^{\text{gas}} + \text{O}^{\text{ads}} + e^- \rightarrow \text{CO}^{\text{ads}} + \text{O}^{\text{ads}} \quad (6)$$
mixed oxide under NO₂ is associated to reaction (4) with a further dissociation of the NO₂ ion according to the reaction proposed in [21]

\[
\text{NO}_2^{\text{ads}} \rightarrow \text{NO}_{\text{g}} + \text{O}_\text{ads}^-. \quad (11)
\]

Of course, the process described by reaction (3) might also take place under the same suppositions. The dissociation of adsorbed NO₂ molecules on In₂O₃ film surface was confirmed in [23] by analyzing O 1 s and N 1 s core level signals in XPS spectra.

IV. Conclusion

A novel NO₂ gas sensor based on (CdO)ₓ(ZnO)₁₋ₓ mixed-oxide thin films deposited by spray pyrolysis has been studied. The sensor follows a typical surface-controlled gas-sensing model. A different behavior was observed when the sensor surface was exposed to reducing gases at different temperatures. Thus, the sensor resistance increases at low temperature (100 °C), while it decreases at high temperature (300 °C) as a consequence of different surface interaction mechanisms.

The dependence of sensor response on the test gas concentration follows a power law with an exponent equal to 0.54, which allowed us to propose a possible gas-sensing mechanism at working temperature. A device with 30% Cd exhibits satisfactory sensor properties to 3-ppm NO₂.

REFERENCES


R. Ferro received the M.Sc. degree from Havana University, Havana, Cuba, in 1999. He is currently pursuing the Ph.D. degree in new materials for solar cells and gas sensors at the Catholic University of Louvain, Louvain, Belgium.

J. A. Rodríguez was born in Havana, Cuba, in 1949. He received the B.S., M.S., and Ph.D. degrees in physics from the University of Havana in 1973, 1977, and 1989, respectively.

J. R. Morante was born in Mataró, Spain. He received the Ph.D. degree in physics from the University of Barcelona, Barcelona, Spain, in 1980.

I. Jiménez received the degree in physics and the Ph.D. degree from the University of Barcelona, Barcelona, Spain, in 1999 and 2003, respectively.

A. Cirera received the degree in physics and the Ph.D. degree in developing new technologies and their characterization for tin-oxide gas-sensor devices from the University of Barcelona, Barcelona, Spain, in 1996 and 2000, respectively.

J. Cerdà received the degree in physics from the University of Barcelona, Barcelona, Spain, in 1998, where he is currently pursuing the Ph.D. degree in the development of materials for gas sensors.

J. R. Morante was born in Mataró, Spain. He received the Ph.D. degree in physics from the University of Barcelona, Barcelona, Spain, in 1980.

He was a Full Professor of electronics and Director of the Electronic Materials and Engineering (EME) Group, Faculty of Physics, University of Barcelona. He was also Dean of the Physics Faculty, Academic Advisor of the electronic engineering degree, and Director of the Electronics Department. Currently, he is the Research Head of the EME Group, Co-Director of the Center for Engineering of Microsystems, and Director of the Center of Reference of Advanced Materials for Energy, University of Barcelona. He has collaborated in international R&D projects, including BRIT, GROWTH (micromechanics, microengineering, gas sensors, etc.), ESPRIT, IST (advanced devices, sensors, actuators, microsystems, electronic systems, etc.), JOULE, etc., and industrial projects, including EUREKA, IBEROEKA, and CRAFT. He is coauthor of more than 400 papers in international specialized journals and member of international committees and editorial boards in the field of electronic materials and technology, sensors and actuators and microsystems, and electronic systems. His activity is devoted to electronic materials and technology, physics and chemical sensors, actuators, and microsystems, and he has a special interest in nanoscience and nanotechnologies.

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