O_2 Sensing Properties of Zn- and Au-Doped Fe_2O_3 Thin Films

Giovanni Neri, Anna Bonavita, Signorino Galvagno, Y. X. Li, Kosmas Galatsis, and Wojtek Wlodarski

***Abstract*—Zn- and Au-doped iron oxide thin films have been prepared by liquid phase deposition. These films have been characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Their performance as oxygen gas sensors has been measured. It has been shown that both the Zn and Au dopants increase the oxygen response of the pure iron oxide films. The XRD and SEM results show that Zn changes both the microstructure and the particles size of the sensing layer through the formation of a solid solution with iron oxide. However, the strong increase in sensitivity to oxygen of the Au-doped Fe_2O_3 film has been related to the more favorable chemisorption of oxygen on the small gold particles at the interface with the semiconductor oxide. The results show that Au-doped iron oxide sensors are most promising for oxygen gas sensing.**

I. INTRODUCTION

COMMERCIAL oxygen sensors are predominantly based on solid-electrolytes such as ZrO_2 [1]. Such sensors are used for monitoring oxygen partial pressure in control systems of combustion engines exhausts, waste gases, chemical processes, etc. Conductometric sensors based on semiconducting oxides such as TiO_2, Nb_2O_5, $SrTiO_3$, Ga_2O_3, and CeO_2 are simpler and cheaper to fabricate. They can operate at lower temperatures (< 450 °C) than solid-electrolyte sensors, and do not require a references gas [2].

Fe_2O_3 has been widely investigated for gas sensing, yet so far it has received little attention as an oxygen gas sensing material. Recently, it has been reported that thick films of Fe_2O_3–ZrO_2 solid solutions show good responses to O_2 gas [3]. In this paper, we focus on Fe_2O_3 thin films doped with Zn and Au, prepared by liquid-phase deposition (LPD). This method allows the thin films to be prepared with high surface area to volume ratio, and ensures a strong interaction between the dopant(s) and the semiconducting oxide. Such characteristics are favorable for the improvement of the interaction between oxygen and the surface of sensing layer, leading to an enhancement of the sensing properties. In previous reports, Fe_2O_3 thin films prepared by this technique and doped with Li, Zn, and Au have been investigated as sensors of humidity, CO and NO_2 [4], [5]. Here, we report O_2 gas sensing performance of such films.

II. EXPERIMENTAL

The doped Fe_2O_3 sensors were fabricated by depositing thin films on alumina substrates (3×3 mm^2) with gold interdigital electrodes. A Pt heater is located on the backside of the substrate. Thin films were deposited by LPD according to the following procedure: an aqueous mixture containing $Fe(NO_3)_3\ 9H_2O$ was prepared first. To obtain doped films, $Zn(NO_3)_2$ or $HAuCl_4$ were added in appropriate amounts to this solution then 10 μl of the resulting solution was deposited on the alumina substrate by micropipetting. The sample was successively introduced in the deposition chamber and flushed with an NH_3/He mixture. After the deposition was completed, the chamber was evacuated and the film calcined in the same apparatus at the temperatures of 400 °C in air for 2 h.

Three iron-based oxide sensors have been prepared, namely a) undoped Fe_2O_3, b) Au/Fe_2O_3 with 5% in moles of Au, and c) ZnO–Fe_2O_3 with 50% in moles of Zn. The morphology and microstructure of the films was investigated by x-ray diffraction (XRD) and scanning electron microscopy (SEM) coupled with energy dispersive x-ray (EDX) analyzer. The electrical and gas sensing tests were carried out in a multi channel gas calibration system. Measurements were carried out at different operating temperatures, ranging from 350–450 °C. The operating temperature of the sensors was adjusted by a regulated dc power supply to the heater.

The gas response S is defined as $S = R_g/R_b$, where R_g is the electrical resistance at different O_2 concentrations and R_b is the resistance of the baseline which consisted of 10 ppm O_2 gas. Certificated O_2 gas bottles between 10 ppm and 1% balanced with dry N_2 were used for the gas sensing measurements.

III. RESULTS AND DISCUSSION

A. Film Microstructure

Film microstructure was investigated by XRD and SEM-EDX. XRD analysis of the films after calcination at 400 °C is reported in Fig. 1. Hematite (α-Fe_2O_3) was the only identified phase on the undoped Fe_2O_3 film. These peaks have also been observed on the film doped with Au. Moreover, a very weak reflection, barely discernible form the baseline, at about 38.3 $2-\theta$ was noted. This peak is characteristic of metallic gold and due to its low intensity, the noble metal can be supposed in a finely dispersed state. On the other hand, the XRD pattern of the Zn-promoted film is instead dominated by broad peaks, which do not correspond to any pure phase of iron or zinc oxides. This strongly suggests the formation of Zn-Fe mixed phases. Reflections observed are in strong agreement with those reported in the JCPDS data file for franklinite

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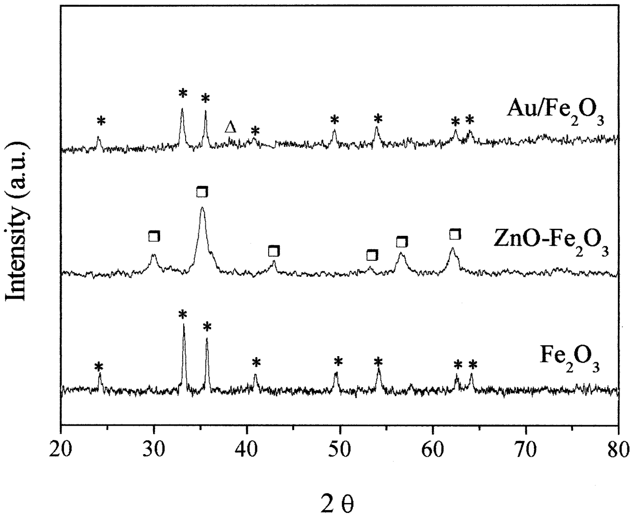

Fig. 1. XRD analysis of the investigated films; ($*$) hematite; ($\square$) franklinite; (Δ) metallic gold.

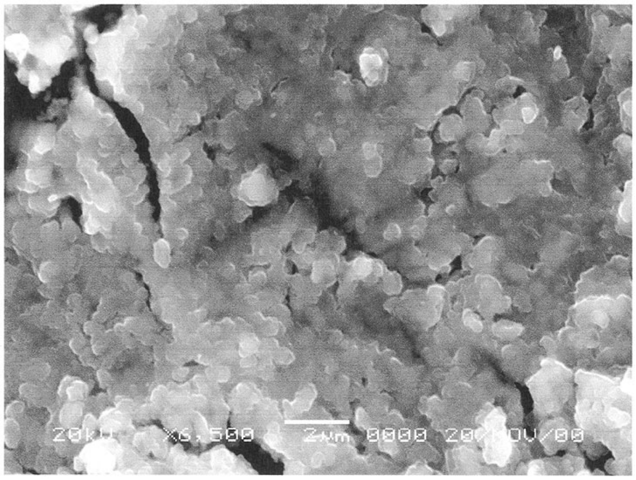

Fig. 2. SEM micrograph of the ZnO–Fe_2O_3 film.

($ZnFe_2O_4$) [6]. The large peaks width also indicate the occurrence of a defective structure, lower degree of crystallinity and smaller particle size with respect to both undoped and doped Au films. Line broadening analysis of the diffraction peaks was undertaken and from this, the mean diameter was calculated using the Scherrer equation. A mean diameter of approximately 10 nm was calculated for the mixed Zn–Fe oxide particles whereas a higher value, 35 nm, was calculated for the iron oxide particles in the pure and Au-doped films.

The SEM micrograph in Fig. 2 shows the typical morphology of the investigated films. The film appears to be uniform, with a structure made up of rod-like grains, cracks and pores. These characteristics are favorable for the diffusion of oxygen in the films and enhance the sensitivity [7]. The larger surface to volume ratio of the thin film results in greater interaction between the oxygen gas and the sensing layer leading to a higher sensitivity. Elemental EDX-mapping of the Au-doped film has shown that gold is homogeneously distributed in the structure of the iron oxide film and exists in the form of nanometer particles. This is in agreement with XRD results.

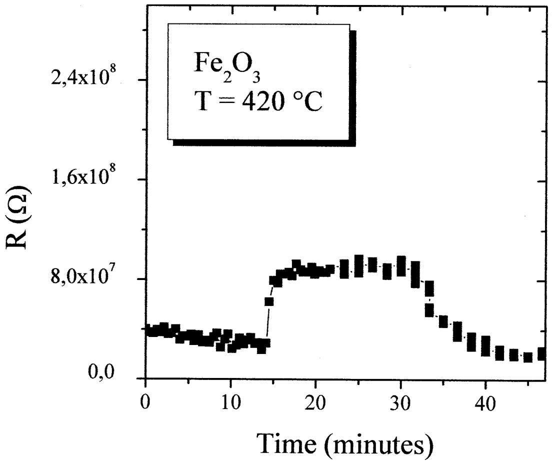

Fig. 3. Response of the Fe_2O_3 sensor to 1000 ppm of O_2. T = 420 °C.

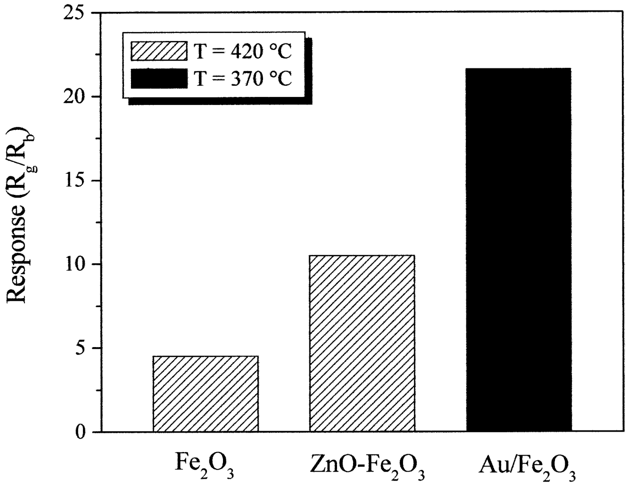

Fig. 4. Comparison of the response of pure and doped sensors to 1000 ppm of O_2.

B. Electrical Properties

A prior investigation has shown that iron oxide-films present n-type semiconductor behavior, i.e., their conductance, in air or nitrogen, increases with the temperature [5]. The Fe_2O_3 and ZnO–Fe_2O_3 films show a high baseline electrical resistance (around 10^7 Ω), which is not suitable for practical applications. However, the Au-promoted film shows instead a lower baseline resistance (up to 2 order of magnitude), most likely due to the increase in the number of conduction states of the host material from the addition of gold.

To test the oxygen response, sensors were baselined in ultra-high purity nitrogen gas and subsequently exposed to successive pulses of: 100, 1000, and 10 000 ppm of O_2, each for a period of 15 min. The operating temperature was varied between 350–450 °C. Fig. 3 illustrates the electrical response of the undoped film to 1000 ppm of oxygen balanced in nitrogen at an operating temperature of 420 °C. The response and recovery times are defined as the times the resistance takes to reach 90% of saturation value when the mixture containing the O_2 gas is introduced and when the baseline flux is restored, respectively. The undoped film exhibits a response time, τ_{90}, of about one minute, while the recovery time is longer ($\tau_{90} = 10$ min).

The responses of the pure and undoped iron oxide films to 1000 ppm of O_2 are reported and compared in Fig. 4. The un-

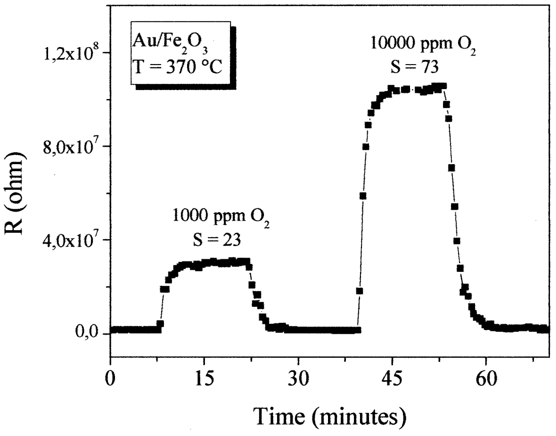

Fig. 5. Response of the Au/Fe_2O_3 sensor to different O_2 concentration in N_2. Baseline is 10 ppm of O_2. T = 370 °C.

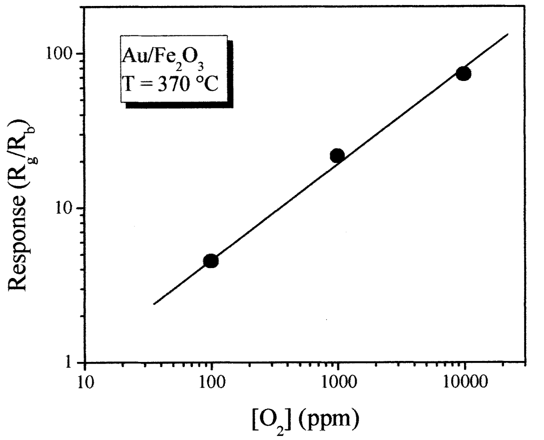

Fig. 6. O_2 calibration curve for the Au/Fe_2O_3 sensor.

doped sensor shows a response of approximately 4 at 420 °C. At the same temperature, the Zn-doped sensor presents a sensitivity that is increased by a factor two. The Au/Fe_2O_3 film is the most sensitive. Its enhanced oxygen sensing allows it to operate at lower temperatures (370 °C) than the undoped and Zn-doped sensors. This is in agreement with previous data from literature; noble metal promoters are in fact reported to increase the O_2 sensitivity of thin or thick films while decreasing the operating temperature and the response time [8], [9].

The performance of the Au/Fe_2O_3 sensor at 370 °C for different concentrations of O_2 in nitrogen is presented in Figs. 5 and 6. It is observed the sensor has a high response to oxygen ($S = 23$) at 1000 ppm of O_2 and good linearity in a wide range of concentration (100 ppm—0.1% of oxygen). Moreover, the recovery time has been greatly reduced ($\tau_{90} =$ about 2 min).

C. Microstructure-O_2 Sensing Correlation

The sensing mechanism of semiconducting metal oxide based oxygen sensors is very complicated, involving structural defects, spillover phenomena, particle-size effects, metal-semiconductor junctions, space-charge layers, and adsorption–desorption effects [10], [11]. These variables are strongly dependent on the microstructural properties of the sensing material. The characterization reported in Section III-B highlights the promoter's effect on the microstructure of the undoped iron oxide film. Zn changes the microstructure of the sensing layer through the formation of a solid solution with iron oxide, as witnessed by XRD. The substitution of Zn^{+2} ions into the Fe_2O_3 lattice, creates oxygen vacancies that act as O_2 adsorption center. The substitution of ZnO in the Fe_2O_3 structure can be represented as

$$2\mathrm{ZnO} \rightarrow 2\mathrm{Zn}'_{\mathrm{Fe}} + V_O^{\bullet\bullet} + 2\mathrm{O}_O \tag{1}$$

where $\mathrm{Zn}'_{\mathrm{Fe}}$ represent the Zn^{++} ions at the Fe lattice site, $V_O^{\bullet\bullet}$ the oxygen vacancy and O_O is the oxygen ion at the oxygen lattice site. The oxygen vacancies $[V_O^{\bullet\bullet}]$ created through (1) are a critical factor for oxygen sensing. When the oxygen concentration increases, $[V_O^{\bullet\bullet}]$ decrease and vice versa, according to the equilibrium (2)

$$V_O^{\bullet\bullet} + 2e' + \frac{1}{2}\mathrm{O}_2(g) \leftrightarrow \mathrm{O}_O. \tag{2}$$

The dissociation of oxygen molecules is however an activated process that requires rather elevated temperatures to occur. At the operating temperature of the sensors, process (2) does not occur and the conductivity variations are assumed to come from surface controlled processes, which are not in equilibrium with the bulk.

Furthermore, the addition of Zn also induces a remarkable decrease in the grain size of the sensitive layer. This implies a higher surface to volume ratio and consequently, an increase of defects on which oxygen is chemisorbed [6]. The enhancement of the sensitivity to gases with the decrease of the grain size is well known [12]. Hence, the increased sensitivity of the Zn-doped sensor can be attributed to this increased surface area of the sensitive layer.

The strong enhancement of sensitivity noted on the Au-doped sensor cannot be related to reduction of grain size and/or modification of the microstructure of the sensing layer. Both the microstructure and the size of the iron oxide particles are in fact the same as those present in the undoped film. It appears reasonable then to hypothesize that the increase in sensitivity is linked to the more favorable chemisorption of oxygen on the Au-doped sensing film. This is in agreement with the literature on Au/metal oxides, which emphasize the ability of the noble metal to chemisorb O_2 molecules [13]–[15]. Where the O_2 chemisorption sites are located is yet an open question. In some cases, oxygen adsorption has been postulated to proceed directly on nanometer gold particles [13]. More likely it occurs on the support (or at the metal-support interface) [14], [15]. Oxygen adsorbs on these sites in a molecular form, probably as an O_2^- surface specie, evolving, at higher temperature, into the $O^=$ form

$$\begin{aligned}[\mathrm{Au}]\mathrm{Fe} + e' + \mathrm{O}_2(g) &\leftrightarrow \mathrm{O}^-_{2(\mathrm{ads})} + e' \leftrightarrow 2\mathrm{O}^-_{2(\mathrm{ads})}\\ &+2e' \leftrightarrow 2\mathrm{O}^=_{(\mathrm{ads})}.\end{aligned} \tag{3}$$

The nanometer gold particles located at the metal-support interface, [Au]Fe, are assumed to be the site at which oxygen dissociates with lower activation energy. This should promote the sensitivity, response kinetic and allow operation at lower temperatures, which was well observed on the Au–Fe_2O_3-based sensor.

IV. CONCLUSION

Doped Fe_2O_3 thin films prepared by LPD have been characterized and investigated with respect to their oxygen sensing properties. Characterization results reveal Zn affects both the microstructure and the grain size of the sensing layer, forming a mixed oxide with iron. The increased sensitivity of the ZnO–Fe_2O_3 sensor was related to the decrease in grain size. The Au-doped sensor shows a higher sensitivity and a lower operating temperature. This was related to the ability of the finely dispersed Au to dissociate O_2 molecules at the interface with the support. Results presented show that the Au-doped Fe_2O_3 sensors are most promising for O_2 sensing at low temperatures.

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