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# Low temperature indium oxide gas sensors

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**Abstract**

$InO_x$ thin films were grown by dc magnetron sputtering. Structural and morphological investigations carried out by XRD and AFM showed a strong correlation between crystallinity, surface topology and ozone sensitivity. The electrical conductivity exhibited a large change of six orders of magnitude during the processes of photoreduction/oxidation. It was concluded that it is mainly the grain size variation that determines the sensitivity of $InO_x$ films against ozone.


*Keywords:* Metal oxide thin films; $InO_x$; Gas sensors; Ozone

## 1. Introduction

The interest in transparent conducting oxides (TCO's) for technological applications is a result of their high infrared reflectance, high luminous transmittance, and good electrical properties. These characteristics make TCO's attractive for many areas such as transparent electrodes for solar cells and flat panel displays, and coatings for architectural glasses [1–5]. Moreover, these materials are also promising for gas sensors due to their low dimension, portability, and simplicity. The electrical properties of thin films made from TCO materials are strongly influenced by the presence of oxidizing gases. Gas molecules interact with the surface of the film inducing redox reactions to take place altering the films conductivity. $InO_x$ semiconductor sensors have been successfully used for the detection of oxidizing gases such as $O_3$ and $NO_2$ in the concentration range between some ppb and ppm [6]. Takada et al. [7,8] have first reported the ozone sensing properties based on $In_2O_3$ conductivity measurements, and the optimum operating temperature for $In_2O_3$ combined with $Fe_2O_3$ additives was found to be 370 °C. On the other hand, tin-doped indium oxide (ITO) has also been tested towards and $NO_2$ by Sako et al. [9]. It was found that the highest sensitivity was obtained at 250 °C.

In this paper, we report on the correlation of surface parameters with ozone sensitivity for $InO_x$ thin films deposited by the dc sputtering technique. The films' structure, electrical and ozone sensing properties are investigated. It is concluded that it is mainly the grain size variation that determines the sensitivity of $InO_x$ films against ozone.

## 2. Experimental details

Deposition of nanocrystalline indium oxide ($InO_x$) thin films was performed by dc magnetron sputtering. Detailed description of the deposition system may be found in Refs. [4,5]. During one specific deposition, different substrates were coated to perform the structural and morphological characterization. We studied a film thickness series from 33 to 250 nm grown at room temperature (RT), constant total pressure $8 \times 10^{-3}$ mbar, 100% oxygen plasma atmosphere and deposition rate of ∼9 nm/s. A temperature film series from RT to 290 °C grown at constant total pressure $8 \times 10^{-3}$ mbar, 100% oxygen plasma atmosphere, 100 nm thickness and deposition rate of ∼9 nm/s, and a pressure series from $6 \times 10^{-3}$ to $50 \times 10^{-3}$ mbar grown at RT, 100% oxygen plasma atmosphere and 100 nm thickness is also presented.

For the structural analysis of the deposited films, X-ray diffraction (XRD) measurements were carried out using a Rigaku diffractometer with Cu Kα X-rays. The surface morphology (lateral grain size and surface roughness) was investigated

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with a NanoScope III Atomic Force Microscope (AFM) in tapping mode. The electrical characterization was performed in a special designed reactor [10] at RT in a homemade system at FORTH. For photoreduction the samples were directly irradiated in vacuum by the UV light of a mercury pencil lamp at a distance of approximately 3 cm for 20 min in order to achieve a steady state. For the subsequent oxidation the chamber was backfilled with oxygen at a pressure of 560 Torr and the samples were shielded from the lamp, which in this case served as a source for ozone production. This treatment lasted 40 min, after which no further changes of the conductivity could be observed. Finally, the chamber was evacuated and the photoreduction–oxidation cycle described above was repeated a few times. An electric field (1 or 10 V cm$^{-1}$) was applied during the whole cycling procedure to the samples and the electrical current was measured with an electrometer. Current–voltage (*I–V*) measurements were always performed before the cycling started in order to ensure the ohmic nature of the contacts.

## 3. Results

AFM characterization of the films surfaces revealed a granular, polycrystalline morphology. Fig. 1a–c shows the AFM images describing the surface morphology of $InO_x$ films with a thickness in the range of 33–250 nm, $InO_x$ films grown at different substrate temperature varying from RT to 290 °C, and $InO_x$ films grown at different total pressures varying from $6 \times 10^{-3}$ to $50 \times 10^{-3}$ mbar, respectively. From our AFM studies and XRD investigation, it has been found that both the average lateral grain size and the surface roughness mainly increased with increasing the film thickness, the deposition temperature, and the total pressure. This is clearly seen in the AFM images of Fig. 1 as well as in the plots of Fig. 2.

It was also observed that when the film thickness increases, small grains tend to be overgrown by larger neighbours. These variations are correlated with the film crystal formation. In the case of thinner films, the growth time is shorter and the surface topology reveals an inhomogeneous distribution with smaller grains. At longer deposition periods, we observed that small grains aggregation leads to the formation of larger grains with a subsequent increase in the measured lateral grain size from 11 to 24 nm and an overall rougher surface from RMS ~ 0.41 nm to RMS ~ 1.39 nm.

The observed increase in grain size with substrate temperature can be explained by the fact that substrate temperature affects the ability of atoms (or molecular species) to move across the grown surface to the low energy sites. When the mobility is high, at high thermal energy, diffusion on the surface enables material to reach regions of the surface that were flux shadowed. As a result, the grain size of the films increases as a function

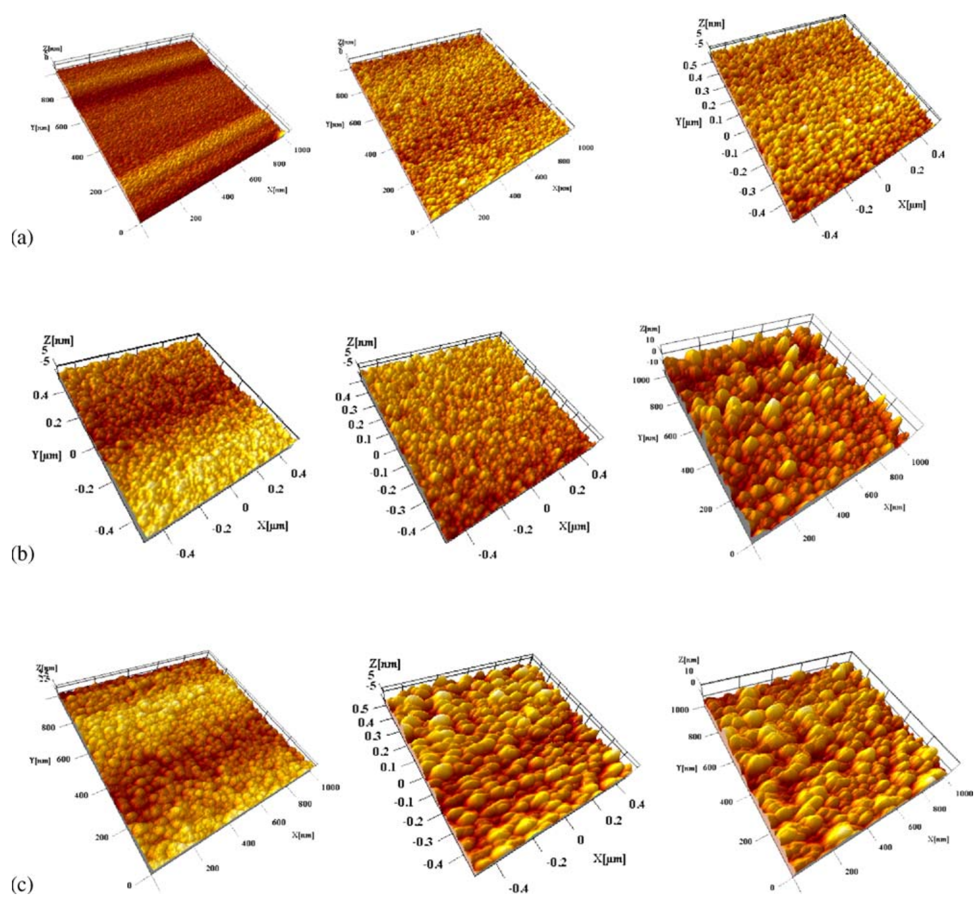

Fig. 1. (a) AFM images of $InO_x$ films with different thickness $t = 33$, 110, 230 nm. (b) AFM images of $InO_x$ films grown at different substrate temperatures $T = 27$, 140, 200 °C. (c) AFM images of $InO_x$ films grown at different total deposition pressures $p = 6$, 30, 50 μbar.

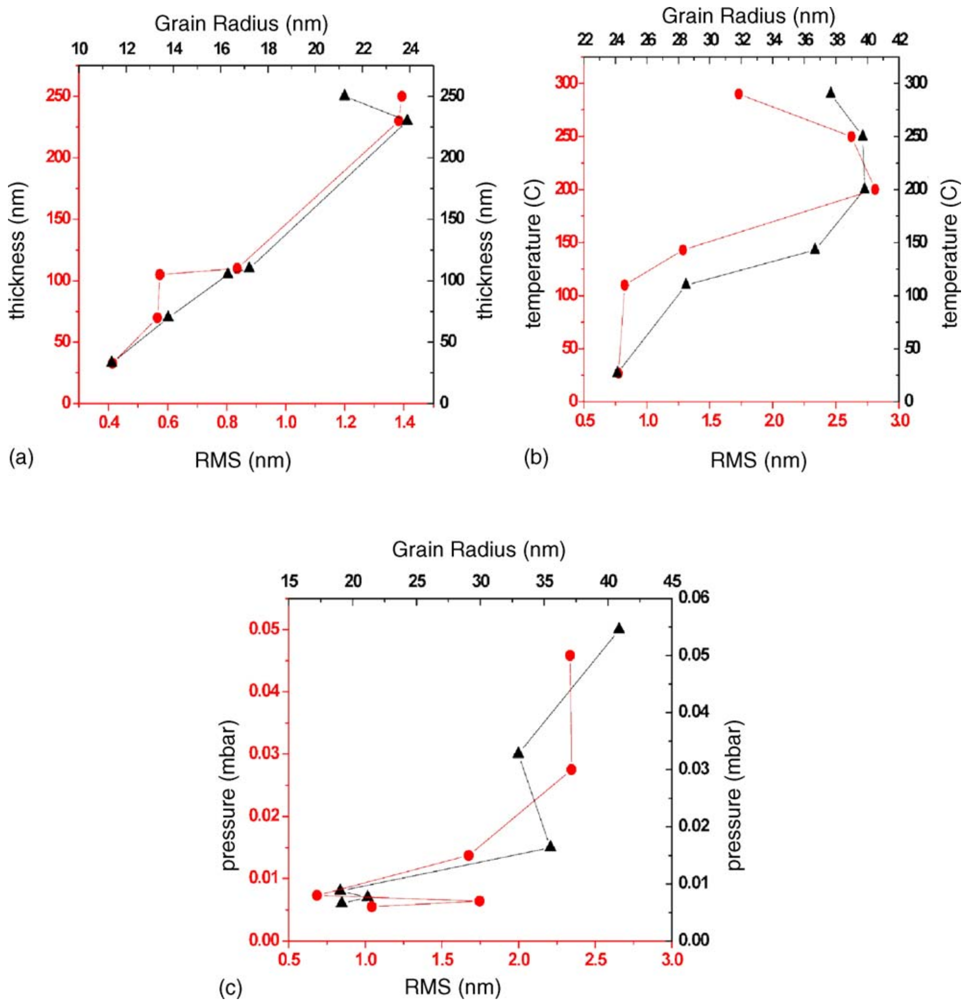


Fig. 2. (a) RMS (●) and grain size (▲) from AFM measurements as a function of film thickness. (b) RMS (●) and grain size (▲) from AFM measurements as a function of deposition temperature. (c) RMS (●) and grain size (▲) from AFM measurements as a function of deposition total pressure.

of the temperature with subsequent influence upon the surface roughness, as it is shown in Fig. 2b. The mean grain radius of the films increased from about 24 to 39 nm while the roughness increased from 0.77 to 2.81 nm, for substrate temperature variation from 27 to 290 °C due to the improvement in the crystallinity of the films in agreement with our earlier studies [11,12]. XRD studies have confirmed preferential growth orientation along the (2 2 2) direction and a corresponding improvement in crystallinity with increasing deposition temperature as shown in Fig. 3.

The surface species mobility is also affected by the deposition rate and the parameters of the vapour species energy (i.e. the vapour species translation energy, the latent heat of condensation). The RMS and grain size dependence on total pressure during the deposition was found to have generally an increasing trend. It is known that the growth rate during deposition is correlated with total pressure, with the lowest growth rate corresponding to the highest deposition pressure. This is due to the fact that at high total pressure the mean free path of the plasma species is short because of the high number of collisions that take place before they reach the substrate. The decrease in deposition rate is also the result of oxidation of the target and the resultant low sputtering yield of the oxide is reflected on film topography as increased grain size and roughness. The correspondent variation of grain size and roughness, as a function of pressure, is shown in Fig. 2c. The mean grain radius of the films increased from about 21 to 41 nm with total pressure increasing

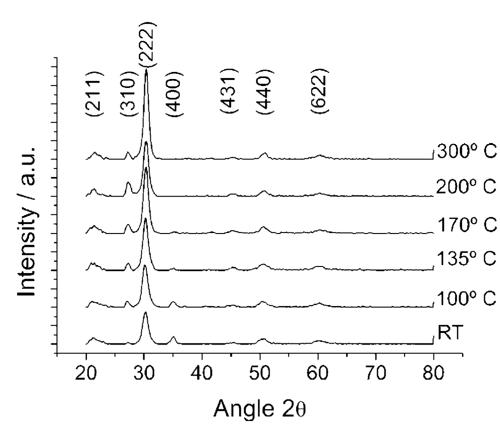


Fig. 3. X-ray diffractograms of $InO_x$ films prepared at different substrate temperatures.

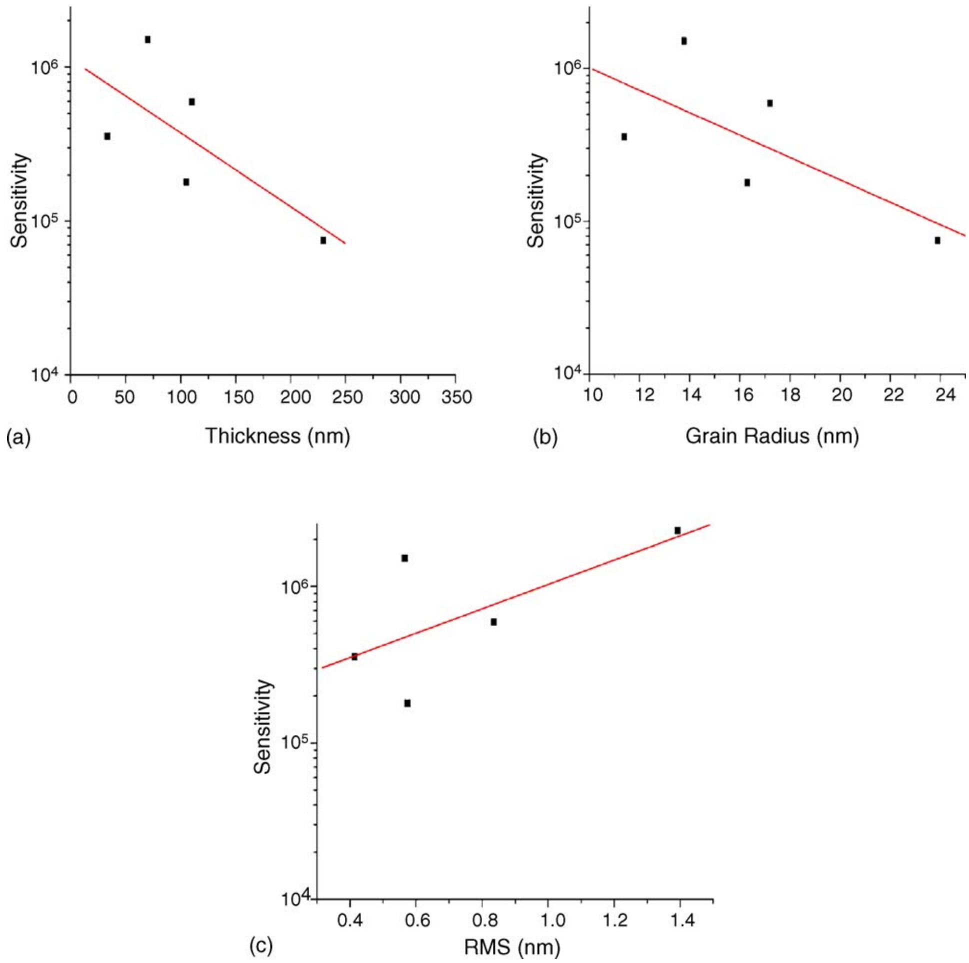


Fig. 4. Sensitivity correlations for the $InO_x$ thickness series: (a) sensitivity vs. thickness, (b) sensitivity vs. grain radius and (c) sensitivity vs. RMS.

from $6 \times 10^{-3}$ to $50 \times 10^{-3}$ mbar while RMS also increased from 0.75 to 2.35 nm in the same pressure interval [12].

In order to correlate the film surface properties with the film sensitivity to ozone (calculated from conductivity measurements in an evacuated chamber under a flow of $O_3$ at RT) defined in our work as the ratio between the maximum/minimum conductivities, we plotted the film sensitivity versus film thickness, temperature, and pressure as well as versus the AFM measured surface parameters of grain radius and surface roughness (RMS) as it is shown in Figs. 4–6.

These results are given for the film series grown as described above. The correlation shows the strong influence of film topology on film sensitivity, which allows for the optimization of sensitivity through growth parameters.

The photoreduction treatment results in an increase of conductivity up to around six orders of magnitude for the temperature and thickness series and up to almost seven orders of magnitude for the $InO_x$ total deposition pressure series. Subsequent ozone exposure leads to a decrease of conductivity to minimum values as shown in Fig. 7. This behavior was completely reversible through many cycles of photoreduction and oxidation treatments.

Increasing film thickness results in larger grain size, which in turn causes the decrease of ozone sensitivity as it can be seen in Fig. 4a and b. Comparing the conductivity changes with surface RMS and grain size from AFM measurements it can be seen that as RMS increases, the sensitivity also increases (Fig. 4c) for films with increased thickness.

The film sensitivity correlation with surface parameters can be explained using the conduction model of metal oxide gas sensors approximation given by Barsan and Weimar [13]. The base of gas detection is the interaction of the gaseous species with the surface of the semiconducting sensitive metal oxide layer. As a consequence of this surface interaction charge transfer takes place between the absorbed species and the semiconducting sensitive material [14]. According to this model, for small grains and narrow necks, when the mean free path of free charge carriers becomes comparable with the dimension of the grains, the surface influence on the mobility becomes dominant over bulk phenomena. In the presence of the ionic species on the surface, after UV photoreduction, the electronic concentration in the surface states increases. The surface states concentration is correlated with the roughness and grain size via surface-to-volume ratio. Therefore, the gas sensitivity is directly proportional with the film roughness proving the importance of surface-to-volume ratio for high sensitivity applications.

The correlations and behavior change in the case of films grown at different substrate temperatures are shown in Fig. 5.

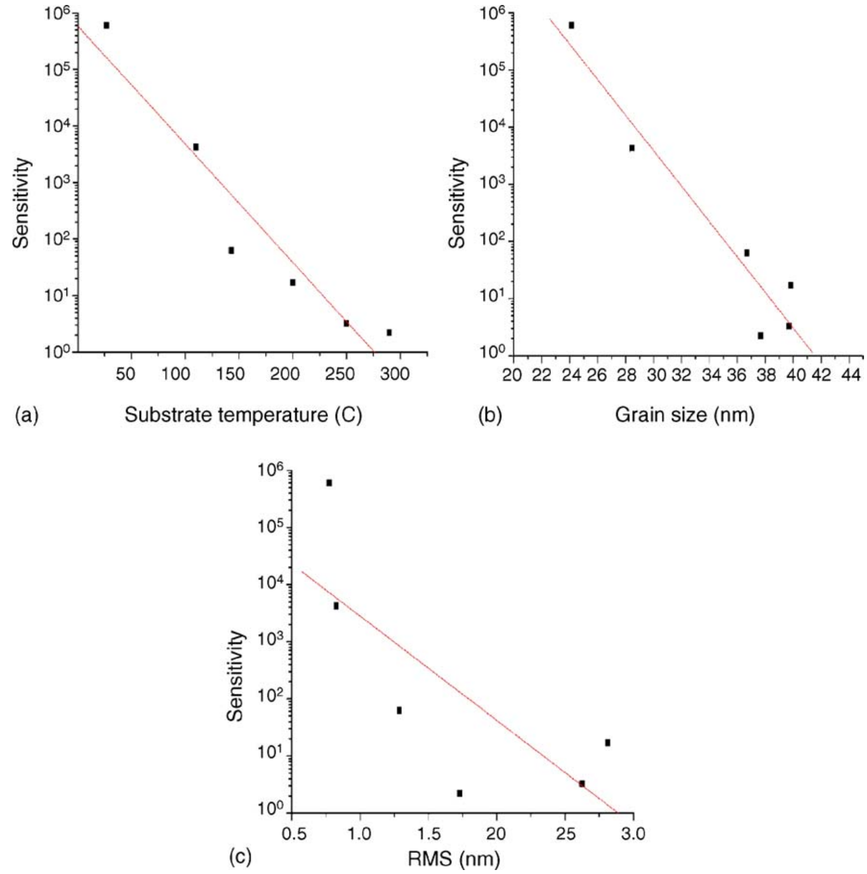


Fig. 5. Sensitivity correlations for $InO_x$ films grown at different substrate temperatures: (a) sensitivity vs. substrate temperature, (b) sensitivity vs. grain radius and (c) sensitivity vs. RMS.

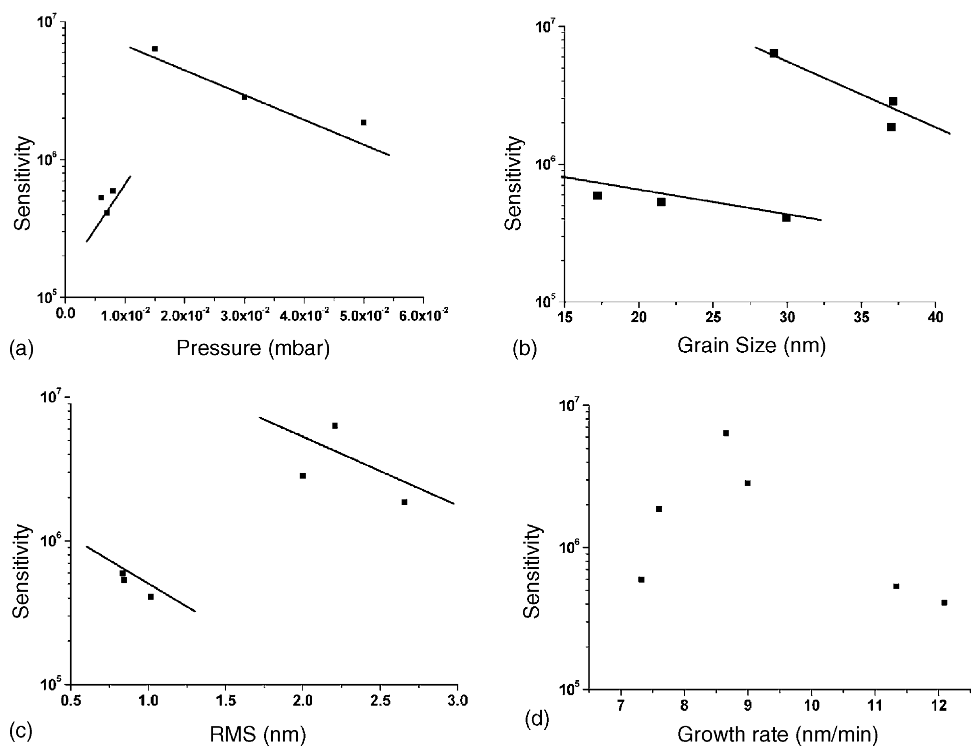


Fig. 6. Sensitivity correlations for $InO_x$ films grown at different pressures: (a) sensitivity vs. pressure, (b) sensitivity vs. grain radius, (c) sensitivity vs. RMS and (d) sensitivity vs. growth rate.

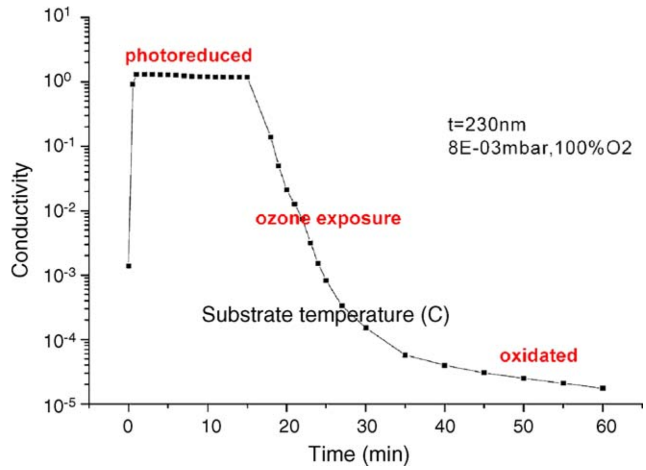


Fig. 7. Typical photoreduction–oxidation conductivity curve for $InO_x$ thin films. The photoreduced state corresponds to maximum conductivity; the oxidized state corresponds to minimum conductivity.

As the deposition temperature increases, the grain radius also increases thus the ozone sensitivity decreases (Fig. 5a and b). However, increased film RMS seems to cause a decrease in sensitivity (Fig. 5c). Since grain radius and RMS are both increasing with temperature as in the case of the thickness series, one would expect sensitivity to increase with RMS (see Fig. 4). However, increasing deposition temperature leads to better film stoichiometry and thus to less sensitivity, masking the effect of increasing RMS.

Fig. 6a and d presents the films' sensitivity correlation with total pressure in the sputtering chamber, and consequently with the growth rate. Fig. 6b and c gives the ozone sensitivity correlations with the surface parameters, grain radius and RMS. It can be seen (Fig. 6a) that there is a distinct different behavior between the sensitivities detected for films grown at pressures below and over $10^{-2}$ mbar. This is attributed to their grain size and RMS. Indeed the lower pressure films show lower RMS and grain size than the higher-pressure grown films (see Fig. 2c). The grain size local variation within the two mentioned groups of films shows an increase of sensitivity with decreasing grain size according with the previous sensitivity–grain size correlations (see Figs. 4b and 5b). What is not clear is the "jump" of sensitivity with increased grain size between the two earlier mentioned pressure groups, at a total pressure of $10^{-2}$ mbar. This can be related to a change in deposition thermodynamics with decreasing growth rate resulting in RMS values over 2 nm. The surface RMS correlation with ozone sensitivity follows the same trend with the grain size–sensitivity correlation shown in Fig. 6c.

## 4. Conclusions

Thin films of $InO_x$ (thickness, temperature and pressure series) have been fabricated using dc magnetron sputtering. XRD studies have confirmed preferential growth orientation along the (2 2 2) direction and a corresponding improvement in crystallinity by increasing substrate deposition temperature. It has also been shown from AFM studies that both the average lateral grain size and the surface roughness mainly increased with increasing the film thickness, temperature and total pressure. The effect of the deposition parameters on ozone sensitivity of $InO_x$ thin films has been investigated, while the surface characteristic parameters have been correlated with the film conductivity changes due to the ozone surface absorption. It has been shown that the grain size mainly determines the ozone sensitivity while the surface roughness plays a secondary role.

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## Biographies

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**George Kiriakidis** received his MSc from UMIST, UK and his PhD from the University of Salford, UK. Since 1981, he is an Assist. Professor in Physics Department of the University of Crete and a senior researcher at FORTH since 1985. He has founded and is the leader of the Photonic and Electronic Materials Laboratory at FORTH and is currently involved in thin-film technology with emphasis on Transparent Conducting Oxides for gas sensing, solar cells and food processing applications.