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InO_x NANOSTRUCTURED THIN FILMS: ELECTRICAL AND SENSING CHARACTERIZATION

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Abstract. The electrical and ozone sensor response characteristics of indium oxide, prepared by dc sputtering, are reviewed in this work. The electrical conductivity of these films is compared to those obtained from other deposition techniques, and found to depend upon the synthesis technique and the deposition parameters. Our sputtered-InO_x films exhibit conductivity changes of up to seven orders of magnitude under the processes of photoreduction and oxidation. A conductivity value of $\sigma = 1.5 \cdot 10^2\ \Omega^{-1} \cdot cm^{-1}$ has been achieved at room temperature, which provides the possibility to use this material as interconnect in ICs and as a sensor at ambient conditions without additional heating. The sensing properties towards ozone of these films are also investigated. Optimum operating temperatures have been found where the response to ozone of InO_x is greater and stable. The best performance of the sensitivity of our films is found at room temperature, and is of the order of $4 \cdot 10^6$. This can be applied in promoting them as promising gas sensor devices for ozone operating at ambient conditions.

1. INTRODUCTION

The use of transparent conducting oxides (TCO) in the field of photonic and electronic devices makes these thin film materials of important technological applications, and the subject of extensive studies. The history of TCO goes back in 1907 when the first cadmium oxide (CdO) films were prepared by the thermal oxidation of sputtered cadmium [1]. With the advancement of technology, the development of TCO has progressed greatly, and many TCO films based on different metals have appeared. These include films such as indium oxide (InO_x), zinc oxide (ZnO), tin oxide (SnO_2), tin-doped indium oxide (In_2O_3:Sn) symbolized by ITO, tantalum pentoxide (Ta_2O_5), etc. The interest in TCO arises because of their properties such as high infrared reflectance, high luminous transmittance, and good electrical properties (conductivity/resistivity). These characteristics make TCO attractive for many applications such as transparent electrodes for solar cells and flat panel displays, coatings for architectural glasses, hardness, excellent substrate adherence, and gas sensors [2-7]. TCO are wide band-gap materials whose characteristics depend strongly on the oxidation state (stoichiometry) and on the nature and quantity of species trapped in the film. It should be noted that the properties of TCO films are very sensitive to the deposition technique, the deposition parameters, and are subject to their operating environment.

An increasing number of gas sensor devices are nowadays found to be based on semiconducting metal oxide thin films as the gas-sensitive material. The choice of these films is based on their portability, simplicity, low cost, and reduced size. These characteristics make the gas sensors with a thin sensing layer interesting for the realization of these detectors on industrial scale. Moreover, these oxide films exhibit a significant change in their conductivity when a change in the ambient occurs, and this property forms the basis for a new generation of gas detection down to the ppb range. The change in the conductivity can generally be explained by two

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mechanisms: the transfer of electrons from the adsorbed gas to the oxide semiconductor, or the reaction of the adsorbed gas with previously chemisorbed surface oxygen. Nowadays, research on gas sensors is focused to the development of novel sensing layers, and the main goal is to find TCO films with good electrical and optical properties for specific sensing applications such as sensitivity in the ppb range and reliable selectivity of gases. For this purpose, intensive studies and investigations on a variety of materials are conducted to produce different gas sensors.

InO_x is a wide band-gap material, E_g ~ 3.70 eV, whose electrical, optical and structural characteristics are well studied [8-17]. It is characterized by a variety of properties such as, metallic, semiconducting, or insulating behavior depending on its stoichiometry. When prepared in oxygen-deficient form, it reaches n-type doping level due to oxygen vacancies [18]. However, in its stoichiometric form (In_2O_3), it behaves as an insulator. InO_x is a candidate for air monitoring applications as small and easy-use ozone (O_3) sensor. The dangers of exposure to natural gas and the fast growth in motor traffic, which leads to increasing pollution of our environment, are of important concern. The source of ozone, which is the main origin of smog, is the photolytic decomposition of NO_2 by solar radiation. It is very toxic for human health, causes inflammation and congestion of the respiratory tracts and, in the case of severe exposure, it produces serious pulmonary diseases. InO_x and doped-InO_x semiconductor sensors can be successfully used for the detection of oxidizing gases such as O_3, CO and NO_2 in the concentration range between some ppb and ppm. Ozone sensing based on In_2O_3 conductivity measurements has been first reported by Takada *et al*. in 1987 [19,20]. The optimum operating temperature for In_2O_3 combined with Fe_2O_3 additives was found to be 370 °C. However, for commercial applications there is a demand for gas sensors with low power consumption since the sensors work round the clock. Thus, there is a clear preference for sensors operating at low temperatures suppressing power consumption, since existing semiconductor gas sensors operate at elevated temperatures to ensure appropriate response time and high sensitivity.

In this work, the electrical and sensing properties, toward ozone, of thin InO_x films prepared in our laboratory by the dc-sputtering technique are reported and compared with those obtained from previous studies.

2. CONDUCTION AND SENSING MECHANISM OF InO_x

The mechanism responsible for the large conductivity changes in InO_x films is the formation and annihilation of oxygen vacancies. UV irradiation of the sample with energies above the bonding energy between In and O leads to a transformation of an oxygen atom from a bound state to the gaseous state. In this process, the two electrons of the oxygen ion are left in the vacant site. If both of these two electrons are localized at the vacancy, charge neutrality is preserved and the vacancy has zero effective charge. If one or both of the localized electrons are excited and transferred away from the vacancy, the vacancy is left with an effective positive charge. The charged oxygen vacancy (singly or doubly ionized) becomes an electron-trapping site but in this process one or two electrons are available for conduction. The formation of doubly charged oxygen vacancies can be described by the defect equation [21],

$$O_0 \rightarrow V_0 + \frac{1}{2} O_2\,(g),$$

$$V_0 \rightarrow V_0'' + 2\bar{e}\,.$$

The subsequent oxidation in ozone leads to annihilation of the charged oxygen vacancies by incorporation of oxygen into the film. Thus, the charge carrier concentration decreases drastically.

Fritzsche *et al*. [22] have investigated amorphous films with a thickness below 100 nm and demonstrated the high sensitivity of InO_x. A corresponding behavior of polycrystalline InO_x films has been explained by a simple model in which the alternate photoreduction and oxidation treatments only affect the conductivity of a thin surface layer. Fig. 1 shows a resistor model of the UV-irradiated InO_x film. More details are given by Bender *et al.* [8]. In principal, the conductivity in semiconductor materials can fluctuate because of changes that may occur in the carriers concentration and/or their mobility. Chemical mechanisms, which occur at the surface of semiconductors, have shown to significantly induce changes in the magnitude of the conductivity/resistivity of the material. Such mechanisms can be due to the adsorption of gases [5-7]. When a semiconductor surface is brought into contact with a gas the adsorption's phenomenon starts, and successful effort has been made to make use of this behavior for gas detection purposes [9-16].

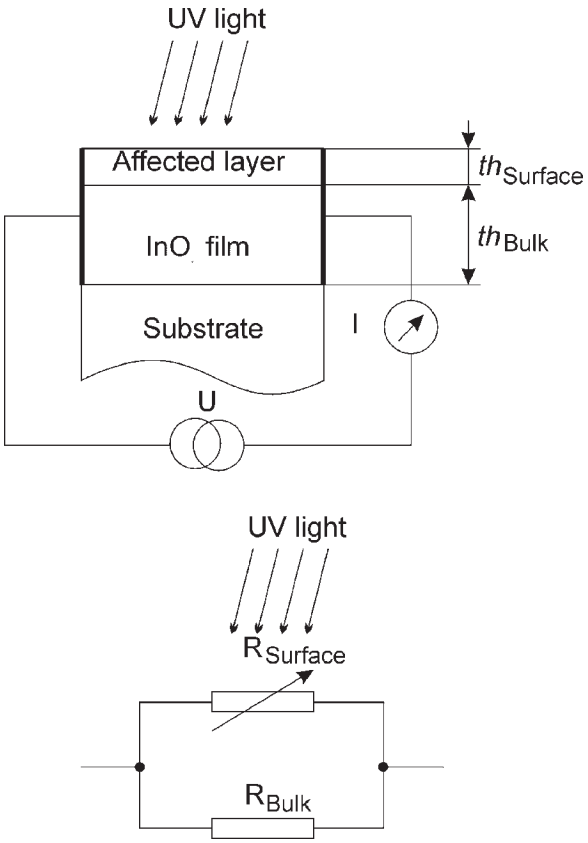

Fig. 1. Resistor model of the UV-irradiated InO_x film.

3. ELECTRICAL AND SENSING PROPERTIES OF InO_x THIN FILMS

3.1. Experimental technique

Many different deposition techniques have been used to prepare thin TCO films. Some of the early-developed methods include spray pyrolysis [23-25], reactive evaporation [26], pulsed laser deposition (PLD) [27], sol-gel method [28], and dc and RF sputtering [29]. These techniques with their associated processing parameters have an impact on the structural, optical, and electrical properties of TCO films. It is also known that the post-deposition heat treatment causes changes in the properties of these films. Thus a unique goal and achievement of these deposition techniques is to produce films with the highest sensitivity at the lowest possible temperature.

Among the existing techniques, magnetron sputtering was found to be the most widely used one for producing high quality TCO films with controlled properties. It provides good film uniformity, excellent adhesion, precise thickness control, surface smoothness, and less waste of expensive source material. By using this technique, other groups have demonstrated its superiority, showing an improvement for instance in the chemical stability of ZnO films co-doped with Al and Cr [30]. It is also reported that highly conductive and transparent films consisting of ternary compounds such as $ZnSnO_3$ and $Zn_2In_2O_5$ prepared by RF magnetron sputtering have proved more stable than ZnO, SnO_2 or In_2O_3 films in oxidizing environments at high temperatures [31]. Moreover, the formation of the platinum silicide, PtSi, by co-sputtering has shown to improve the device performance of PtSi/p-SiGe Schottky contact, reduce the total noise by 70%, while it is a promising technique for noise sensitive applications [32]. A comprehensive report on the sputtering technique can be found elsewhere [33].

In producing InO_x films in our laboratory, the depositions were carried out by dc magnetron sputtering in an Alcatel sputtering system with 99.999 % pure metallic indium target (15 cm diameter) at a pressure of $8 \cdot 10^{-3}$ mbar [34]. The base pressure of the chamber was $5 \cdot 10^{-7}$ mbar. Corning 7059 glass substrates, which had thermally evaporated NiCr electrodes for electrical measurements have been used. During the same run of the deposition of InO_x films, similar substrates with electrodes omitted were coated for performing the structural and morphological characterization of these films. In addition, InO_x films were also deposited onto silica substrate for optical characterization. The substrate temperature was varied between room temperature (RT) and 300 °C, and the film thickness from 10 to 1100 nm. The stoichiometry of the InO_x films can be changed by altering the oxygen content of the sputtering atmosphere, and the potential of these thin films for novel chemical and optoelectronic applications have been investigated [35].

3.2. Electrical properties

The electrical characterization was performed in a special designed reactor described elsewhere [17]. The as-deposited films were all in an insulating state. 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 minutes 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 50 min after which no further

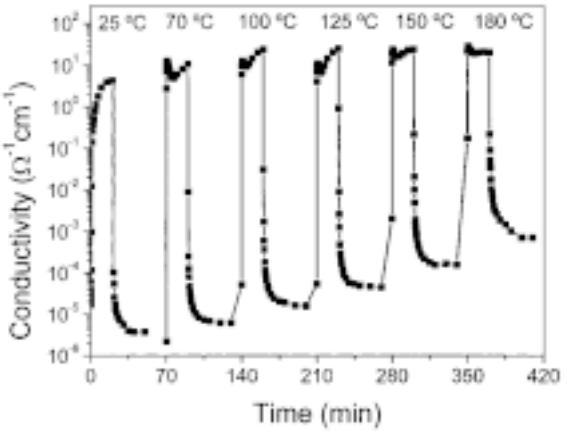

Fig. 2. Photoreduction and subsequent oxidation of a 100 nm thick InO_x film deposited at RT measured at different temperatures.

changes of the conductivity could be observed. Finally, the chamber was evacuated and the photoreduction-oxidation cycle described above was repeated for a few times. An electric field (1 or 10 V/cm) was applied during the whole cycling procedure to the samples and the electrical current was measured with an electrometer as described in detail [17]. All our conductivity measurements were carried out at RT. An I-V curve was recorded before the cycling started in order to ensure the Ohmic nature of the contacts. The photoreduction treatment results in an increase of the conductivity up to $10^2\,\Omega^{-1}\cdot cm^{-1}$ for the InO_x film with thickness of 10nm, while conductivity values as low as $10^{-6}\,\Omega^{-1}\cdot cm^{-1}$ for InO_x are obtained by subsequent ozone oxidation. This behavior was completely reversible through many cycles of photoreduction and oxidation treatments as shown in Fig. 2, which illustrates the conductivity versus time at different temperatures. It shows a degradation of less than an order of magnitude after exposure to an ambient atmosphere for more than 30 hours. The film exhibits conductivity changes of about seven orders of magnitude during the processes of photoreduction and oxidation. Furthermore, while in the conducting state the conductivity of our films did not show large temperature dependent changes. It was also found that the InO_x films have their largest response to ozone at RT after photoreduction treatment, which opens the possibility to use this material as a sensor for ozone at ambient temperatures without additional heating.

Regarding our analysis, in the following discussion, the maximum conductivity (σ_{max}) denotes the conductivity in the conducting state of the sample after the irradiation procedure, while minimum conductivity (σ_{min}) denotes the conductivity in the insulating state after re-oxidizing the sample. The sensor response of the films, *S*, in this case is defined as the ratio $S = \sigma_{max}/\sigma_{min}$.

A number of groups have studied the wide range of TCO and their compounds prepared by sputtering, under different growth conditions [6,29,31]. In comparison with their results, we have studied InO_x films over a wide range of film thickness, from 10nm to 1100 nm, and the substrate temperature was set to 200 °C. The film thickness mainly affected the maximum conductivity after irradiating the InO_x thin films with UV light as it is demonstrated in Fig. 3. The highest conductivity values were measured for the thinnest films. When the thickness of the films was increased about two orders of magnitude, from 10 nm to 1100 nm, the maximum conductivity dropped by two orders of magnitude from approximately $1.5\cdot10^2\,\Omega^{-1}\cdot cm^{-1}$ to $2\,\Omega^{-1}\cdot cm^{-1}$. The minimum conductivity, however, was almost constant in the range of $10^{-3}\,\Omega^{-1}\cdot cm^{-1}$. The difference in conductivity values found in our films and those studied by Minami *et al*., is around one order of magnitude, and can be attributed to the deposition conditions, such as, power applied for plasma generation, reactive gases, oxygen concentration, film thickness, etc. It is widely accepted that the properties of TCO films prepared by magnetron sputtering are directly dependent on such parameters [6-8]. The minimum conductivities in Fig. 3 after the oxidation process are comparable. This is due to the fact that the conductivity can be assumed to be composed of a contribution of the bulk of the film and a contribution of the surface of the film [8,36]. After photoreduction, the "surface-near-layer" contributes with a high conductivity and therefore the conductivity is thickness-dependent. When the film is re-oxidized, the surface

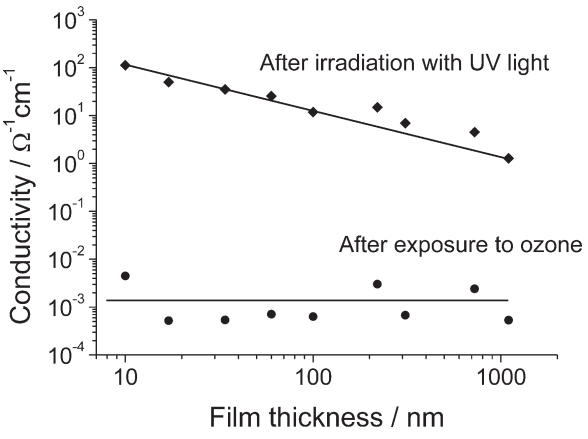

Fig. 3. Maximum and minimum conductivities of InO_x films as a function of film thickness.

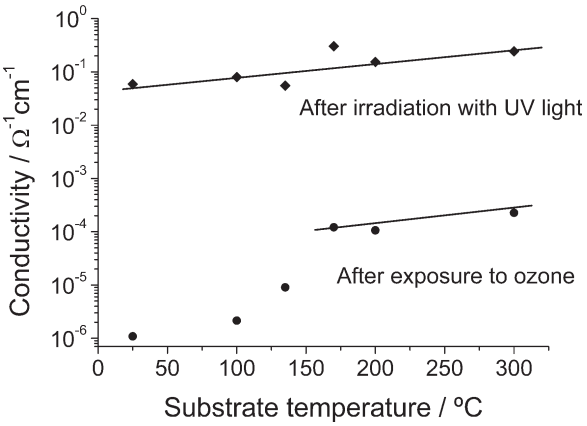

Fig. 4. Maximum and minimum conductivities of InO_x films deposited at different substrate temperatures.

is depleted from free carriers due to adsorbed oxidizing species and merely the bulk conductivity is observed. Thus, the conductivity in this state is independent of film thickness.

We also have studied the conductivities of InO_x films as a function of temperature. The electrical measurements confirmed the significant change in the film properties around 170 °C as it is seen in Fig. 4. While the maximum conductivity increased only slightly with the deposition temperature from $5.5 \cdot 10^{-2}$ $\Omega^{-1} \cdot cm^{-1}$ to $3 \cdot 10^{-1}$ $\Omega^{-1} \cdot cm^{-1}$, the minimum conductivity showed a very different behavior for the low and high temperature growth regime. Up to 170 °C the conductivity in the oxidized state increased more than two orders of magnitude, from $1.1 \cdot 10^{-6}$ $\Omega^{-1} \cdot cm^{-1}$ to $1.2 \cdot 10^{-4}$ $\Omega^{-1} \cdot cm^{-1}$. Above 170 °C, the slight increase to $2.3 \cdot 10^{-4}$ $\Omega^{-1} \cdot cm^{-1}$ followed qualitatively the behavior of the maximum conductivity. A quantitative comparison between the conductivity values found in our InO_x films and those reported by Qadri *et al*. [37] shows the enhancement of the conductivity in their In_2O_3 film doped ZrO_2 prepared by PLD technique. The improvement of the conductivity in doped-InO_x film is expected due to the fact that the doping species increase the carrier concentration, which in turn, increases the conductivity. In comparison, ITO films prepared by PLD and deposited at RT have recently shown good conductivity value of $2 \cdot 10^3$ $\Omega^{-1} \cdot cm^{-1}$ [38], and the conductivity of these films was found to be strongly dependent on the oxygen pressure P_{O_2}. The optimal P_{O_2} that yielded their highest conductivity films lies within a narrow range of $(1\text{-}1.5) \cdot 10^{-2}$ Torr. This P_{O_2} region is consistent with the previously reported P_{O_2} for achieving the best quality ITO thin films by PLD technique [39-41]. However, by using the sputtering method our films were deposited at a pressure of $8 \cdot 10^{-3}$ mbar (i.e., $6 \cdot 10^{-3}$ Torr) which is below the pressure range used in the PLD technique. In each deposition technique, the preparation of InO_x films occurs in a background atmosphere of oxygen. By varying P_{O_2}, the oxygen vacancies, which act as donors can be controlled, thus films whose conductivity characteristics range from those of metals to insulating oxides can be produced.

Beside the sputtering technique, the properties of thin films of InO_x prepared by thermal evaporation have also been investigated [42-44]. Girtan *et al*. [43] have prepared In_2O_3 thin films on a glass substrate at RT, followed by thermal oxidation in air. It was experimentally established that the heating velocity during the oxidation process has a strong influence on the electrical and optical properties of films as prepared. In these experiments, the temperature was varied between RT and 400 °C. It was found that during the first heating cycle, the conductivity of films increases with the increase in temperature and decreases during the cooling. The same behaviour was observed for the minimum conductivity of our films (see Fig.4) while the maximum conductivity was increasing slightly with the temperature. The best value obtained for the electrical resistivity was about $200 \cdot 10^{-4}$ $\Omega \cdot cm$ (i.e., the conductivity is $0.5 \cdot 10^2$ $\Omega^{-1} \cdot cm^{-1}$), for the samples oxidized by heating with 0.5 °C/s. A higher conductivity value compared to the one found by Girtan *et al*. [43] has been reported when transparent and conductive InO_x films were deposited by evaporation of indium in partial oxygen pressure [44]. As a main result on electrical and optical properties of In_2O_3 thin films, they have noted that a quite broad domain of experimental conditions (oxygen partial pressure, substrate temperature, deposition rate) allows films with good averaged properties such as a transmittance higher than 85% and a conductivity of 10^3 - $3 \cdot 10^3$ $\Omega^{-1} \cdot cm^{-1}$. The experiments demonstrated by Ali *et al*. [44] have also showed that substrate heating at 200 °C allows to obtain these films and that a post-deposition annealing treatment was not necessary. The comparison between the electrical properties of our sputtered InO_x films and those prepared by PLD, spray pyrolysis and evaporation techniques is presented in Table 1. Among the other techniques mentioned above, spray pyrolysis provides an easy route to fabricate thin films at low cost, and has been used to grow and study the material properties of In_2O_3 films. It can be easily

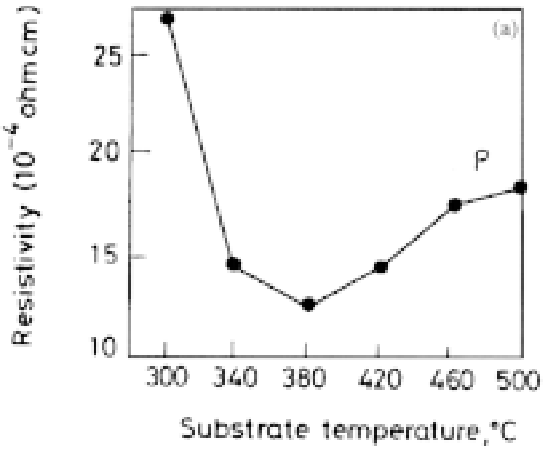

Fig. 5. Variation of resistivity of In_2O_3 films with different substrate temperatures (Ref. [45]).

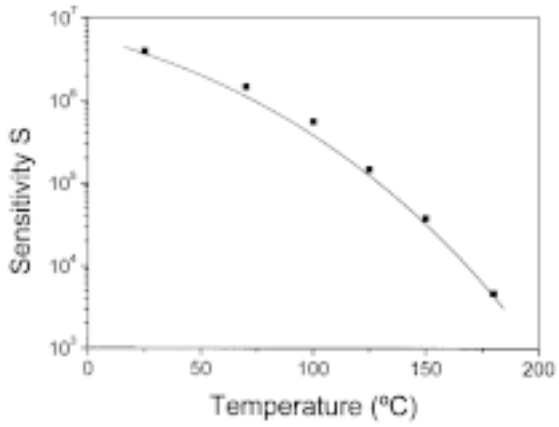

Fig. 6. Sensitivity of a 100nm thick InO_x film vs. temperature. The line is a guide to the eyes.

modified for mass production and device-quality oxide films can be obtained over a large area. By using this method, Prince *et al*. [45] have prepared In_2O_3 films and investigated their electrical properties at different substrate temperatures. It has been observed that the resistivity value of the In_2O_3 films goes on decreasing up to 380 °C and, after reaching a minimum, then increases when the substrate temperature is increased further as it is seen in Fig. 5. The best In_2O_3 film prepared in optimized conditions has a resistivity of $1.28 \cdot 10^{-3}$ Ω·cm (i.e., $\sigma = 7.8 \cdot 10^2 \Omega^{-1} \cdot cm^{-1}$). This value is comparable with the conductivity value in our InO_x film found at RT.

As can be seen from the discussion above, the electrical properties of TCO films are dependent on the synthesis techniques used to prepare them. In Table 1, some of the performances of the conductivity of InO_x and doped-In_2O_3 are summarized with the corresponding operating temperatures. However, since for many technological applications there is a limitation in the allowed substrate operating temperature, such as, in organic layers for electroluminescent diodes, flat panel displays, and solar cells, the need for good sensing characteristics at low temperature is imminent. Therefore, since our sputtered undoped-InO_x films show good conductivity at RT, which is comparable to those values found at higher temperatures, it makes them very attractive for low temperature applications and thus opens a new opportunity to use this material as a sensor at ambient conditions without additional heating.

3.3. Ozone sensing properties

Extending our investigation, we have tested films, grown under a number of parameters including

Table 1. Performance of the conductivities of some InO_x and doped-In_2O_3 films with the corresponding operating temperatures.

Deposition technique	*Substrate*	*Temperature*	*Conductivity* ($\Omega^{-1} \cdot cm^{-1}$)	*Reference*
Sputtering	InO_x	RT	$1.5 \cdot 10^2$	in this work
	ZnO-InO_x	350 °C	$5 \cdot 10^3$	[31]
	ZnO-InO_x	RT	10^3	[31]
PLD	ITO	RT	$2 \cdot 10^3$	[38]
Evaporation	InO_x	0.5 °C/s	50	[43]
Spray pyrolysis	InO_x	380 °C	$7.8 \cdot 10^2$	[45]
	ITO	350 °C	$2 \cdot 10^2$	[45]

temperature, for their sensing response in an ozone atmosphere. The sensor response to ozone of our InO_x films is defined, as mentioned above, as the ratio $S = \sigma_{max}/\sigma_{min}$. In Fig. 6, we have plotted the sensor response of a film, having a thickness of 100 nm, as a function of deposition temperature. From this figure, the sensor response to ozone is found to decrease with increasing deposition temperature by almost three orders of magnitude. The observed reduction of the film sensitivity in the higher temperature range can be attributed to the increase of the conductivity after oxidation, σ_{min}, as can be seen in Fig. 2, while the conductivity after photoreduction, σ_{max} did not show a significant dependence on temperature. The increase in σ_{min} with deposition temperature is probably due to an enhanced density of donor states, which are likely forming a donor band just below the conduction band. Furthermore, the best performance of the sensitivity of our film is found at RT, and is in the order of $S = 4 \cdot 10^6$. We have also extended our investigation, and the dependence of the ozone sensitivity of InO_x has been studied in the range from 10 to 1100 nm and the dependence on the deposition temperature for samples deposited at temperatures from RT to 300 °C. The sensitivity was found to be largest for the thinnest films and decreases when the film thickness is increased. This behaviour is attributed to a decrease of σ_{max} whereas σ_{min} remained constant regardless of the film thickness. Therefore we can conclude that the effect of the photoreduction and oxidation takes place mainly in a thin surface-near layer. Furthermore, the study of ozone sensitivity of 150 nm thick InO_x films sputtered at different substrate temperatures has shown that when the deposition temperature was increased, the maximum conductivity of these films after photoreduction remains constant whereas the conductivity after oxidation in ozone increases gradually. This results in a decrease of the sensitivity for films deposited at elevated temperature, and a higher overall sensitivity for films deposited at RT.

For gas-sensing devices the dependence between gas concentration and response is a critical parameter. In our study the test chamber was supplied with a continuous flow of ozone produced in a supplementary chamber. By varying the pressure in the measurement chamber at RT, a linear increase of the sensitivity versus ozone concentration was obtained as shown in Fig. 7. From this result it can be concluded that the photoreduction and oxidation treatment in InO_x films can be applied in promoting them as promising ozone sensor devices with a linear response operating at RT. With comparison with

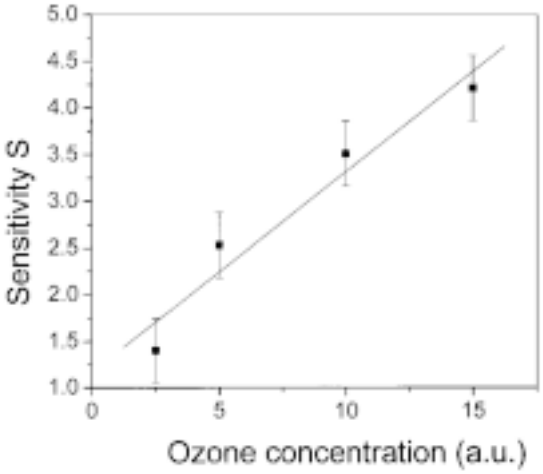

Fig. 7. Response of films to different concentrations of ozone measured at RT.

previous studies, it was reported that indium oxide is sensitive to ozone in the whole investigated temperature range, but the response is enhanced when the temperature is higher [46]. Furthermore rise and recovery rates were found to be faster when temperature is higher. The temperature of $T = 400$ °C was the optimum operating temperature where the response to ozone was found to be greater, stable and reproducible [46]. However, the low operating temperatures of our sputtered InO_x films towards ozone underlines the possibility of employing these films as sensitive layers in gas sensors for low power operating applications such as portable ozone detection.

4. CONCLUSIONS

We have reviewed the electrical and sensitivity response properties of our sputtered InO_x films and compared them with previous reports. Our InO_x films have been deposited by dc sputtering, and found to have a conductivity of around $1.5 \cdot 10^2\ \Omega^{-1} \cdot cm^{-1}$ at RT. Moreover, these films exhibit conductivity changes of about seven orders of magnitude during the processes of photoreduction and oxidation. From previous studies, doped-InO_x films showed an improvement in their conductivity due to the fact that the doping species increase the carrier concentration. The performance of the conductivity of InO_x and doped-InO_x has been summarized. Our sputtered undoped-InO_x films show good conductivity at RT, which is comparable to those values found at higher temperatures. This opens a new opportunity to use this material as a sensor at ambient conditions with-

out additional heating. Furthermore, the sensor response has been studied for a variety of substrate deposition temperatures and ozone concentration. The highest sensor response has been achieved for films deposited at RT, and was around $4 \cdot 10^6$. This high sensitivity at low operating temperatures of our sputtered InO_x films towards ozone underlines the possibility of employing these films as sensors for low power operating applications such as portable ozone detection.

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