Impedance Spectroscopy Study of Porous ITO Based Gas Sensor

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Abstract

In this work, Tin-doped indium oxide (ITO) films were prepared by the screen printing technique onto glass substrates then annealed in a furnace at a temperature of 570°C during 45 minutes. The crystallinity, roughness and morphology of the obtained films were analyzed by X-Ray Diffraction (XRD), Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM). The energy dispersive spectroscopy (EDX) analysis has been used to determine the atomic composition of the films. The activation energies calculated from the plot of the resistance R versus temperature T indicate that different scattering mechanisms are operative. From Lennard-Jones equation, we can estimate the operating temperature range to activate the chemisorption process that leads to the maximum response of the sensor. AC impedance spectroscopy has been used to investigate the nature of the conduction processes and modeling the sensing mechanisms. All impedance spectra seem to have a single half circle shape without shift along the Z’ axis, the equivalent circuit can be decomposed as a parallel R-C circuit. We found that the resistance and capacitance values depend on temperature and atmosphere change.

Keywords: Metallic oxide gas sensors; Screen-printing; ITO; AC measurements

1. Introduction

Many transparent conducting oxides (TCO) such as ZnO, In₂O₃, SnO₂... were reported to be usable in gas sensor [1]. Their popularity as a gas sensing materials is due to its suitable physical-chemical properties such as natural non-stoichiometric structures [2] and free electrons originating from oxygen vacancies contribute to electron conductivity change when the composition of the surrounding atmosphere is altered [3]. We studied in previous works [4] the gas sensing properties of an ITO films in direct current (DC) measurements. While direct current (DC) measurements give information on the global sensor response, alternating current (AC) impedance study is necessary to understand the nature of the conduction processes and the mechanism of gas/solid interactions [5]. The objective of this work is to study the nature of the conduction processes and modeling the sensing mechanisms in alternating current (AC) impedance of an ITO films prepared by the screen printing technique.

2. Experimental details

The ITO films were prepared by screen printing a viscous organometallic paste (ESL # 3050) of a dissolved combination of metallic indium and tin onto glass substrates. The samples are dried in air in an oven at a temperature

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of about 150 °C during 15 min, in order to remove a part of the solvents and to prepare the samples to the sintering process. The ITO deposits were annealed in an infrared furnace at a temperature of 570°C during 45 minutes in order to stabilize the chemical composition and the crystalline structure [4]. The composition, cristallinity, roughness and morphology of the obtained ITO films were analyzed using Energy Dispersive Spectroscopy (EDX), X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). To investigate the ITO sensing properties towards NO₂, the films were introduced in a special chamber, which offers several possibilities of measurements. Further details on this set-up are described elsewhere [4, 6]. Alternating current (AC) measurements were acquired using HP4192A standard analyzer impedance in the 1 Hz to 13 MHz frequency range, a constant voltage (10V) and different temperatures. A multimeter (Agilent 34970 A) was used to record the temperature and the impedance of the sensor. We will note Z’ as the real part and Z” as the imaginary part of the complex impedance. Indeed, it is frequently mentioned that the electrical response is very sensitive to humidity, so humidity values in test rig-humidity and air flow composition can alter NO₂ sensitivity. Therefore, humidity values should be known or not varied; in this work, all measurements are made under the same conditions so that we neglect the effect of humidity and air flow composition.

3. Results and discussion

3.1. Chemical composition, structure and morphology

Various ITO films having a thickness of about 1μm were prepared. An EDX analysis done on different crystallites revealed uniform chemical composition. The particles contain roughly about 90% of Indium and about 10% of Tin. X-ray diffraction (Fig. 1) shows that only peaks corresponding to In₂O₃ appear for all samples. The peaks agree with that corresponding to the In₂O₃ cubic structure (JCPDS No.89-4595) and the estimated lattice constant is a=10.122 Å. From HRTEM (Fig. 2) we identify three interplanar spacing, corresponding to the (222), (400) and (440) plans of In₂O₃. From TEM and AFM images (Fig. 3 and Fig. 4) one may notice uniform distributed crystallites forming a granular, rough and porous structure. The estimated roughness is about 10.8 nm and the crystallite size in the range of 10-14 nm.

Fig. 1: XRD patterns of the screen printed ITO film

Fig. 2: HRTEM image of the screen printed ITO film.

Fig. 3: AFM image of the screen printed ITO film.

Fig. 4: TEM image of the screen printed ITO film.
3.2. Electrical conductivity; I-V characteristic and activation energy

Fig. 5 shows I-V characteristic of the screen printed ITO film measured in air using KEITHLEY 2400 Source Meter. The measured current increased linearly with the applied bias and the plot is found to be linear and symmetrical, indicating good ohmic-contacts. Confirmation of ohmic-contacts would ensure that the change in the resistance could only be due to the influence of temperature and gas exposure.

Fig. 6 shows the resistance variation of the ITO film versus temperature (Ln(R) = f (1/K_bT)) in the range of 50°C and 250°C. It is clear from the graph that the electrical conductivity increases with the temperature and the resistance change of is a thermally activated process that can be expressed as an Arrhenius equation [7]:

\[ R = R_0 \exp \left( \frac{E_a}{k_bT} \right) \]  

(1)

Where, R is the resistance at temperature T, R_0 is the pre-exponential factor, k_b is Boltzmann's constant, T is the absolute temperature and E_a is the activation energy.

By applying the Arrhenius equation, we found various activation energies (fig. 6), which indicate the presence of different scattering mechanisms. We note that the increase of the temperature from about 100°C to about 180 °C (region 2) increases significantly the activation energy, probably due to further oxygen adsorption on the film surface and to thermal excitation of electrons in the conduction band.

As a summary:
- The value of conductivity strongly depends on the nature of the predominant defects involved in the conduction mechanism (mainly oxygen defects in semiconducting oxides and deep donor states introduced by Tin and Indium).
- Defects and charge carriers may be activated by increasing the temperature leading to an increase of the conductivity.

The phenomenon could be interpreted as a competition between the rates of adsorption and desorption, which is shown in the Lennard-Jones equation [5, 8, 9]:

\[ \frac{d \theta}{dt} = K_{ads} \exp \left( -\Delta E_a / K_bT \right) - K_{des} \exp \left[ - \left( \Delta E_a + \Delta H_{chem.} \right) / K_bT \right] \]  

(2)

Where \( \theta \) is the fraction of available surface sites covered, K_{ads} and K_{des} are respectively the rate constants for adsorption and desorption, \( \Delta E_a \) the activation barrier for chemisorption and \( \Delta H_{chem.} \) is the heat of chemisorption.

According to equation 2 and to fig. 6 a physisorption process dominates in region 1 which is reduced with increasing the temperature \( (\Delta E_a \geq K_bT) \); in region 2 the chemisorption process will be activated and the rate of desorption became negligible \( (\Delta E_a \leq K_bT) \); in region 3 we notice a physisorption increase, while the chemisorption phenomenon become negligible like in region 1.

During gas detection, the chemisorption activation leads to the maximum response of the sensor, consequently the operating temperature must be chosen in the range between 100°C and 180°C (region 2). This result is in good agreement with previous results [4, 6].

3.3. Alternating current spectroscopy: measurements and modeling

Fig. 7 shows the Nyquist plots shape at various operating temperature in ambient air. We note that the impedance spectra have a semi-cycle shape indicating the homogeneity of the grains.

In previous works [4, 6], we demonstrate that the optimal operating temperature of ITO films for NO_2 detection is around 180°C (high sensitivity). In order to test the stability and the repetitivity of the measurements at this
temperature, we inject 200 ppm of NO2 during 30min, 60min and 180min and we plot Nyquist spectra (Fig. 8) after an average waiting time of about 300 seconds (stabilization before measurement). As shown in the plot (Fig. 8), the spectrum remains quasi-stable and no memory effects were observed.

Fig. 9 illustrates the effect of NO2 concentration on the Nyquist diagram. As shown in the plot, the impedance \( Z' \) increases upon exposure to NO2 and begins saturating as concentration exceeds 160 ppm. All impedance spectra seem to be single half circles without shift along the \( Z' \) axis. The equivalent circuit can be decomposed in the simplest case as a parallel R-C circuit, similar to other transparent conducting oxides.

**Fig. 7:** Nyquist diagram at various operating temperature in ambient air.  
**Fig. 8:** Impedance variation consecutive to repetitive excitation by 200 ppm of NO2.  
**Fig. 9:** Impedance spectroscopy of the screen printed ITO film versus NO2 concentration.

**4. Conclusion**

ITO films were prepared by the screen-printing technique. The activation energies calculated from the resistance variation of the ITO film versus temperature and deduced from Arrhenius equation indicates that different scattering mechanisms are operative. These results can be explained by deep donor states introduced by Tin and Indium in addition to the thermally activation process. During gas detection, the chemisorption process leads to the maximum response of the sensor; in that the operating temperature range can be estimated from the Lennard-Jones equation.

AC impedance spectroscopy has been used to investigate the nature of the conduction processes and modeling the sensing mechanisms. All impedance spectra to be single half circles without shift along the \( Z' \) axis, the equivalent circuit can be decomposed as a parallel R-C circuit.

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**References**

[1] T.-J. Hsueh, C.-L. Hsu. Fabrication of gas sensing devices with ZnO nanostructure by the low-temperature oxidation of zinc particles. Sens. Actuators 2008; B 131: 572-576.

[2] J. Kaur, R. Kumar, M.C. Bhattachar. Effect of Indium nanoparticles on NO2 gas sensing properties. Sens. Actuators 2007; B 126: 478-484.

[3] D. Chu, Y.-P. Zeng, D. Jiang, Y. Masuda. In2O3-SnO2 nano-toasts and nonorods: Precipitation preparation, formation mechanism, and gas sensing properties. Sens. Actuators 2009; B 137: 630-636.

[4] M. Saadoun, M.F. Boujmil, L. El Mir, B.Bessais. Nanostructured Zinc Oxide Thin Films for NO2 Gas Sensing. Sensor Letters 2009; Vol. 7: 1-6.

[5] A. Labidi, C. Jacolin, M. Bendahan, A. Abdelghani, J. Guérin, K. Aguir, M. Maaref. Impedance spectroscopy on WO3 gas sensor. Sens. Actuators 2005; B 106: 713-718.

[6] I. Madhi, M. Saadoun, B. Bessais. Screen Printed ITO-SnO2 Nanocomposite Films for NO2 Detection. Sensor Letters 2011; Vol. 9:1726-1730.

[7] Y.-H. Hee, I.-H. Choi, S. Moon, C.-S. Son. Characteristics of Vanadium-Tungsten-Oxide Bolometric Thin Films for Uncooled IR Detectors. Journal of the Korean Physical Society 2004; Vol. 45: pp. S902-S905.

[8] M. Batzill, U. Diebold. The surface and materials science of tin oxide. Progress in Surface Science 2008; 79: 47-154.

[9] Matthias Batzill. Surface Science Studies of Gas Sensing Materials: SnO2. Sensors 2006; 6: 1345-1366.