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Gas sensor applications of zinc oxide thin film grown by the polymeric precursor method

G. Biasotto^a, M.G.A. Ranieri^{b,1}, C.R Foschini^{b,1}, A.Z. Simões^{c,*}, E. Longo^a, M.A. Zaghete^a

^aLaboratório Interdisciplinar em Cerâmica (LIEC), Departamento de Físico-Química, Instituto de Química, UNESP, CEP 14800-900,

Araraquara, SP, Brazil

^bUniversidade Estadual Paulista—UNESP, Faculdade de Engenharia de Bauru, Dept. de Eng. Mecânica, Av. Eng. Luiz Edmundo C. Coube 14-01,

Zip-Code 17033-360, Bauru, SP, Brazil

^cUniversidade Estadual Paulista—UNESP, Faculdade de Engenharia de Guaratinguetá, Av. Dr. Ariberto Pereira da Cunha, 333, Bairro Pedregulho, CEP 12516-410, Guaratinguetá, SP, Brazil

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Abstract

Good quality zinc oxide ZnO films were deposited on alumina substrates by the polymeric precursor method (PPM) using zinc acetate as the precursor. X-ray diffraction (XRD) was used to confirm the crystallinity of the zinc oxide films which were free of impurities and SEM study revealed the uniform deposition of fine grains with a thickness of 120 nm. ZnO films were used for CO gas detection at different times by recording the change in the film conductance. The faster response of ZnO sensors to CO gas is believed to be due to high porous sensing films which show higher surface-to-volume ratio. The O_2' , O'', O species concentration emerging from the [ZnO₅ · VO•]+1/2O₂ \rightarrow [ZnO₆] chemisorptions reaction affects the ZnO gas sensor response owing to the fact that the oxygen ion acts as a trap for electrons from the bulk of films. © 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

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1. Introduction

ZnO is an important multifunctional material with applications for varistors, gas sensors, SAW devices, transparent electrodes, catalysts etc. By virtue of its specific chemical, surface and microstructural properties, ZnO has a wide range of applications. It is extensively used as a commercial varistor material with good performance characteristics thanks to its high density at temperatures as low as 800 °C. Although extensive research regarding CO gas sensing based on SnO₂ and ZnO heterostructures is ongoing [1–3], experimental results for pure ZnO system are lacking due to the fast grain growth and densification of this system. It is factually wellknown that gas sensors require porous microstructure with a

E-mail address: alezipo@yahoo.com (A.Z. Simões).

small particle size, thereby yielding a large ratio of the surface area to the bulk [4]. The microstructural and physical properties of ZnO can be modified by introducing chemical synthesis changes in the procedure. A porous microstructure of the materials with controlled pore sizes is largely preferred, especially for the application of ZnO as a gas sensor. The sensitivity and response time of ZnO-based sensors strongly depend on the porosity of the material. Furthermore, the grain size of the polycrystalline material is known to have a noticeable effect on its gas sensing properties. It has been experimentally observed [5] that the gas sensitivity of ZnO sensors decreases given an increase in the mean grain size.

Solution-based methods have been widely used in the preparation of thin oxide films [6,7]. The most commonly used methods for solution preparation can be grouped into the following categories: (1) the sol–gel process; (2) metallorganic decomposition; (3) colloidal sol–gel processes; and (4) gel routes involving the formation of an organic polymeric complex—the

^{*}Corresponding author. Tel.: +55 12 3123 2765.

¹Tel.: +55 14 3103 6119.

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polymeric precursor method (PPM). The PPM can be further divided into two groups [8]: (1) In situ polymerization of organometallic monomers; and (2) the preparation of a viscous solution system containing metal ions, polymers and a solvent. This viscous solution can be easily converted into a thermoplastic gel at high polymer concentrations. The in situ PPM has been used to a larger extent to obtain ceramic powders with small particle sizes and a single phase [9]. This method originally developed by Pechini [10] is based on the chelation of a metallic cation by a carboxylic acid (such as citric acid) where further polymerization is promoted by the addition of ethylene glycol and a consequent polyesterification. An intrinsic problem with solution-based methods lies in the large volume change that occurs when the liquid solution transforms into a solid inorganic oxide thin film. This volume change can cause cracking in the film during pyrolysis and sintering processes. In general, the appearance of cracks is found to be lower in thinner films once adhesion on the interface film-substrate is higher while the lateral shrinkage of film is suppressed in thinner coatings. When the critical film thickness value is reached, cracks are undoubtedly unvoidable. To obtain the crack-free films, it is worth noting that a number of characteristics of the solution must be controlled, including viscosity and ionic concentration, substrate-film adhesion, heating conditions, atmosphere, substrate and withdrawal speed. Differences between the thermal expansion coefficients of the film and the substrate have also been found to influence this behavior [11]. In addition, the main purpose of improving cleanliness in sensor applications is to reduce chemical and atmospheric contaminations.

The predominant electrical characteristics of semiconductor oxides can be classified according to the resistance change direction relative to the oxidant atmosphere. This classification is related to the intrinsic conductivity type of semiconductor oxides which in turn is determined by the nature of the dominant charge carriers; i.e., electrons or holes. Besides that, the conductance in n-type semiconductor oxides is known to be dependent upon oxygen partial pressure, and it is found to decrease given an increase in the oxygen partial pressure (the inverse is valid for p-type semiconductor oxides) [12,13].

In recent times, there has been a growing interest in material and electrical properties of inorganic compounds that are insulators at low temperatures, yet good conductors at high temperatures [14]. Among them, SnO₂, TiO₂, ZnO, Fe₂O₃, and ZrO₂ have been used for applications such as gas sensors, varistors, and electrodes [15-21]. In particular, n-type semiconductors including SnO₂, TiO₂, Fe₂O₃, and ZnO have been extensively used for the detection of reducing gases such as CO, CH_4 and alcohol [22–25]. In this study, we investigated the optimum processing condition for ZnO film preparation, phase and morphological characterization and its electrical properties as a CO gas sensor. Compared to the existing literature on ZnO-based gas sensing, the merit of this technology lies in it being capable of easily modifying electrical, morphological and sensing properties of zinc oxide films by controlling the growth regimes, rotation speed as well as the treatment conditions. Moreover, no solid solution is required for the detection of the sensor response to CO gas by

the spin-coating technique depositing three layers of crystalline ZnO film on the substrate surface.

2. Experimental procedure

Zinc acetate dihydrate ((CH_3CO_2)₂Zn · 2H₂O) with 99.9% purity (Aldrich) was dissolved in a solution of citric acid and ethylene glycol in line with the PPM [26]. The films were spin coated by a commercial spinner operating at 5000 revolutions/ min for 30 s (spin coater KW-4B, Chemat Technology) on Pt wires (0.25 mm diameter) attached to Au pads on an alumina substrate with a printed Au electrode in a comb-tooth configuration. The ZnO sensor film was placed on top of the electrode using the spin coating technique followed by annealing at 600 °C for 2 h before electrical and sensing measurements. Thin films were annealed in a conventional furnace under static air atmosphere repeating the spin-coating and heating treatment cycles 3 times. A mass flow controller (MFC) controlled the concentration of CO gas. The two-probe dc measurement technique was used to measure electrical and sensing properties. The ZnO films were deposited on Al₂O₃ substrates and interdigitated Au-electrodes (100 µm Au fingers spaced by 200 µm) were sputtered at room temperature on the film surface to characterize its sensor response. Sensing tests were performed at 300 °C by applying a d.c. voltage of 20 V. The sensor response of ZnO thin films was studied by the cyclic exposure to CO gas varying the concentration between 5, 10 and 15 cm³/min. Conductance-time measurements were taken using a stabilized high voltage source measuring unit (Keithley, Model 237) with a one second delay. The thermal effect was investigated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in the STA 409 apparatus (Netzsch—Germany). Synthetic air flow (30 cm³/ min) with a constant heating rate of 5 °C/min from room temperature up to 1200 °C was used. The obtained film was characterized by XRD using a diffractometer (Rigaku-DMax/ 2500PC, Japan) with Cu-K\alpha radiation ($\lambda = 1.5406$ Å) in the 2θ range from 20 to 80° with 0.2°/min. The ZnO crystallite size (d) was calculated using the Scherrer equation $d = k\lambda/\beta \cos\theta$, where k is constant, λ being the wavelength of X-rays, and β the full width at half maximum (FWHM) for (1e0t1) reflection measured from a slow scan with θ being the diffraction angle of the main peak. The morphology of the as-prepared film was observed using high resolution field-emission gun scanning electron microscopy FEG-SEM (Supra 35-VP, Carl Zeiss, Germany). The annealed thin film thickness was determined using scanning electron microscopy (SEM) (Topcom SM-300) and checking the transversal section where back-scattered electrons were utilized. Surface roughness (RMS) was examined by atomic force microscopy (AFM) using tapping mode techniques.

3. Results and discussion

Fig. 1 shows TG/DTA curves of the ZnO precursor powder obtained from room temperature up to 1200 $^{\circ}$ C at a heating rate of 5 $^{\circ}$ C/min. In this figure, three stages of weight loss can



Fig. 1. TG/DTA curves of a ZnO precursor powder synthesized at 300 $^\circ C$ for 4 h in a conventional furnace.



Fig. 2. XRD pattern of a ZnO thin film annealed at 600 $^\circ$ C for 2 h repeating the spin-coating cycle 3 times.

be observed. The first stage (from room temperature to 275 $^{\circ}$ C) is related to the elimination of water produced during the esterification process and excess ethylene glycol. The second stage (275 to 400 °C) corresponds to a break-away of polymeric chains formed by a polyesterification reaction and the last stage (between 400 and 460 $^{\circ}$ C) as depicted in the figure is due to the decomposition of organic compounds which is in agreement with the information found in the literature [27]. After this procedure, no trace of weight loss is detected once the decomposition of organic material is completed. Endothermic signals, in the range of 110–150 °C and 190–230 °C, were attributed to the evaporation of water and solvents, respectively (DTA curve). A very intense exotherm signal observed in the range of 400-450 °C was assigned to the pyrolysis of organic ligands and the main phase crystallization. It is worth pointing out that the ZnO stable phase was formed above 460 °C as can be observed.

Fig. 2 shows the XRD diffraction pattern of ZnO films. Diffraction peaks in the pattern can be indexed to the hexagonal wurtzite structured ZnO (space group: P63mc (1 (16); a=0.3249 nm, c=0.5206 nm) diffraction results



Fig. 3. Micrographs of a ZnO thin film annealed at 600 $^\circ C$ for 2 h: (a) FE-SEM and (b) cross-section.

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which are in agreement with (JCPDS card 036-1451) [28]. Peak intensities relative to the background signal demonstrate a hexagonal phase of the products as well as a high main phase crystallinity. The unobserved characteristic peaks of $Zn(OH)_2$ indicate a single hexagonal ZnO phase. Nanocrystallites are oriented along the *c* axis, [1 ax1] direction. The mean grain size (*d*) was calculated using Scherrer's equation. The average grain size determined from the XRD pattern was 5.8 nm.

For surface morphology and film thickness estimation, FEG-SEM and SEM techniques were used (Fig. 3a and b). Zinc oxide has a wurtzite (zinc blende) crystal structure where both metal and oxygen ions are tetrahedrally coordinated. Morphological studies reveal that randomly oriented grains are in the range of a nanometer size, which is very useful for gas sensing applications. ZnO consists of non-stoichiometric ZnO, which contains bulk and surface oxygen vacancies (VO^x (VO and VÖ) that act as donor and acceptor states [29]; these states permit the adsorption of oxygen. When an oxygen molecule is adsorbed on the ZnO film surface or on the grain boundaries, it extracts electrons from the semiconductor and thus reduces the concentration of electrons thereby promoting an increase in the film resistivity [30]. For our study purpose, we proposed a cluster model, as basic units of materials to explain gas sensor of complex metal device of ZnO. In this cluster model, the magnitude and structural order–disorder effects determine the physical properties. We consider ZnO as a noncentrosymmetric oxide, where a [ZnO₄] with 4-fold tetrahedro is the constituent basic unit. The cluster-to-cluster charge-transfer (CCCT) process provides direct insight into the charge carrier dynamics in materials, and hole polaron trap states are localized on oxygen anions in both the bulk and surface. Oxygen vacancies in a disordered structure with $[ZnO_4]^x/[ZnO_3 \cdot V O^x]$ complex clusters are hole trapping centers, according to the following equations:

 $[\operatorname{ZnO}_4]^{x} + [\operatorname{ZnO}_3 \cdot \operatorname{V} \operatorname{O}^{x}] \to [\operatorname{ZnO}_4]' + [\operatorname{ZnO}_3 \cdot \operatorname{VO}^{\bullet}]$ (1)

 $[ZnO_3 \cdot VO^x] + O_2 \rightarrow [ZnO_3 \cdot VO^x] \cdots O_2 \text{ (ads)}$ ⁽²⁾

$$[ZnO_3 \cdot VO^x] \cdots O_2 \rightarrow [ZnO_3 \cdot VO^{\bullet}] \cdots O_2' \text{ (ads)}$$
(3)

 $[ZnO_3 \cdot VO^x] + [ZnO_3 \cdot VO'] \cdots O_2' \rightarrow 2[ZnO_3 \cdot VO^{\bullet}] \cdots O' \quad (4)$

 $[ZnO_3 \cdot VO^{\bullet}] \dots O' \to [ZnO_3 \cdot V\ddot{O}] \dots O''$ (5)

ZnO film topography was evaluated by AFM measurements (see Fig. 4). The film exhibits an inhomogeneous microstructure consisting of small grains randomly oriented with a statistical roughness, root mean square (RMS) of approximately 6.2 nm and an average grain size of 25 nm with a degree of porosity. The bottom electrode was critical for the surface morphology of the synthesized film owing to the fact that the precursor underwent optimized nucleation and growth process which produce films with small randomly oriented grains.

The sensing along with the recovery behavior for CO gas is shown in Fig. 5a and b. The sensor signal is defined as the relation between the sensor response G (conductance) and the response free of stimulus denoted as G_0 (conductance from a transport gas). In this case, the sensor response is related to the conductance of an atmosphere composed of a gas transport



Fig. 4. AFM of a ZnO thin film annealed at 600 $^{\circ}$ C for 2 h repeating the spin-coating cycle 3 times.



Fig. 5. Changes in the sensor response of ZnO thin film annealed at 600 $^{\circ}$ C for 2 h: (a) Conductance as a function of gas flow and (b) signal as a function of gas flow.

 (N_2) and a defined CO gas concentration. The sensitivity describes changes in the G sensor response as a result of the specific modifications in the gas concentration [31]. A typical curve is depicted showing the sensitivity of the nanostructured zinc oxide thin film sensor element measured against the increase in the CO gas concentration at 300 °C; the sensor signal depends on the CO partial pressure, and an increase in the conductance is found to lead to an increase in the CO concentration (see Fig. 5a). This result corroborates the n-type charge carrier of a ZnO thin film prepared by the PPM. A number of examples are reported in the literature for ceria- and zirconia-based thin films where the near-ordering of oxygencation bonds can be substantially affected by the initial processing route [32–35]. The sensor signal of ZnO thin films is found to increase when the material is exposed to a CO atmosphere, indicating a predominant n-type (electronic) conductivity for the PPM processing. We thoughtfully suggest that oxygen adsorbs onto the surface of ZnO film and ionizes to O^{-} or O^{2-} by trapping electrons from the lattice. The increase in conductance with the CO flow is related to the low concentration of the adsorbed oxygen or the trapped electrons on the surface given that the ratio of the surface area to bulk



Fig. 6. Changes in the sensor response of ZnO thin film annealed at 600 $^{\circ}$ C for 2 h: (a) Sensitivity as a function of gas flow and (b) conductance as a function of time.

prompts a decrease in the adsorbed oxygen concentration with an increase in grain size.

The ZnO sensor exhibits greater sensitivity to 15 cm³/min flow at 300 °C (see Fig. 6b). These results confirm the application of this method in the development of a nanostructured ZnO thin film for the detection of CO above 15 cm³/min. A certain degree of selectivity can be noted by controlling the operating temperature [36] when the sensing film is sensitive to several gases. The nanostructured ZnO gas elements sensitivity is relatively high and it is said to be related to the grain size effect [37]. The high sensitivity of the ZnO film can be associated to the small grain size that provides a high surface area for gas-solid reactions. In that sense, for a good CO gas sensor based on ZnO, it is necessary to synthesize very thin films with a small grain size with high degree of crystallinity rather than a large grain size. For gas sensing characterizations, the sensor elements were placed in a gas chamber. The readings were taken every 2 h following the introduction of the gases into the test chamber, where a signal change $S = G/G_0$ was observed. For the CO gas the said signal was found to increase given a reduction in the gas flow. The sensitivity of the sensor element to gases (CO reducer) was calculated using the formula $m_{red} = \partial G / \partial c$ [38]. The conductivity was found to increase rapidly upon the exposure of the sensor to CO gas, while reverting to the original value after the introduction of clean air. The reducing gas influences the sensor resistance owing to a decrease in the oxygen on the surface and as a result of the reduced sensor resistance.

$[ZnO_3 \cdot VO^{\bullet}] \cdots O_2' + CO \rightarrow [ZnO_3 \cdot VO^x] \cdots CO (ads) + O_2$	(6)
$2[ZnO_3 \cdot VO^{\bullet}] \cdots O' + 2CO \rightarrow 2[ZnO_3 \cdot VO^x] \cdots CO(ads) + O_2$	(7)
$2 [ZnO_3 \cdot V\ddot{O}] \cdots O'' + 2CO \rightarrow [ZnO_3 \cdot VO^x] \cdots CO (ads) + O_2$	(8)

The action of CO gas on the ZnO surface can be addressed by Eqs. (1)–(8) which shows that the sensor response is quite fast, though the saturation time for the adsorption and desorption processes was unalike. The faster response is believed to be as a result of the high porous sensing ZnO films with smaller granules. This porous nature was confirmed by SEM and AFM images (see Figs. 3 and 4), showing higher surface-to-volume ratios for nanostructured films. Both surface defects and configuration affected the detection. ZnO thin films produce electronic defects and heightens the influence of oxygen partial pressure on the film conductivity. The ZnO gas sensor response is controlled by the surface reaction. The O_2' , O", O species concentration is changed by the $[ZnO_5 \cdot VO \bullet] + 1/2 \quad O_2 \rightarrow ZnO_6]$ chemisorptions reaction. Thus, an oxygen ion acts as a trap for electrons from the bulk of films. Electron polarons are taken from ionized donors through a semiconductor and the density of the majority of charge carriers at the gas-solid interface is reduced. The formation of a potential barrier for electrons gives rise to an increase in the oxygen ion density on the surface and inhibits oxygen adsorption. In view of that, at junctions between ZnO grains, the depletion layer and potential barrier increase the electrical resistivity value, which is known to be strongly dependent on the concentration of adsorbed oxygen ions of the surface. The observed quick response of the ZnO sensor to CO gas as well as the recovery to initial conditions is associated to the negligible quantity of the surface reaction product.

4. Conclusions

In this study, nanostructured ZnO thin films as a CO gas sensor obtained by the PPM were investigated. The merit of this technology lies in the simplicity of the process, economy in energy structures with high efficiency, short duration, energy savings, accessible auxiliary materials and nonsophisticated equipment. The electrical, morphological and sensing properties of zinc oxide films can be easily modified controlling the growth regimes, rotation of the substrate, rotation speed and treatment conditions. ZnO thin films can be said to have a very high sensing response to CO gas. The gas sensing characteristics of ZnO films were found to improve drastically by the porous nature of the sensing films. The CO gas response of a ZnO sensor is controlled by the surface reaction with a concentration of O²⁻ and O⁻ species which is changed by chemisorption. The sensitivity of n-type ZnO films can be associated with a variation in the sensor baseline, which thus

produces electronic defects and increases the influence of CO partial pressure on the conductivity of the films.

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