CO sensing characteristics of In-doped ZnO semiconductor nanoparticles

R. Dhahri$^{1,2}$, M. Hjiri$^{1,2}$, L. El Mir$^{1,3}$, H. Alamri$^{4}$, A. Bonavita$^{2}$, D. Iannazzo$^{2}$, S. G. Leonardi$^{2}$ and G. Neri$^{2,*}$

$^{1}$ Laboratory of Physics of Materials and Nanomaterials Applied at Environment, Faculty of Sciences of Gabes, 6072 Gabes University, Tunisia. E-Mails: r_dhahri@yahoo.fr; Lassaad.ElMir@fsg.rnu.tn; m.hjiri@yahoo.fr.

$^{2}$ Department of Engineering, University of Messina, Messina 98166, Italy. E-Mails: leonardis@unime.it; abonavita@unime.it; diannazzo@unime.it.

$^{3}$ Al Imam Mohammad Ibn Saud Islamic University (IMSIU), College of Sciences, Department of Physics, Riyadh 11623, Saudi Arabia.

$^{4}$ Physics Department, Jamoum University College, Umm Al-Qura University, Saudi Arabia

$^{*}$ Corresponding Author; E-Mail: gneri@unime.it; Tel.: +39-090-397-7297; Fax: +39-090-397-7464
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Abstract

A study on the CO sensing characteristics of In-doped ZnO semiconductor nanoparticles (IZO NPs) prepared by a modified sol-gel technique is reported. The morphological and microstructural features of IZO NPs with various dopant concentrations (1 at.%, 2 at.%, 3 at.% and 5 at.% In) were investigated by scanning electron microscopy (SEM), and X-ray powder diffraction (XRD). The influence of indium doping on defect characteristics of ZnO was also investigated by photoluminescence (PL). A thick film of IZnO NPs was deposited by screen printing on an alumina substrate provided with a pair of Pt interdigitated electrodes to fabricate a simple conductometric sensor platform. The as fabricated In-doped ZnO sensors showed enhanced sensitivity to CO gas with respect to pure ZnO one. Sensors with low dopant loading (1 at.% and 2 at.% In) were found to be more sensitive with shorter response and recovery times than those with high dopant loading.

Keywords: In-doped ZnO; Nanoparticles; Sol-gel; Gas sensor; Carbon monoxide.
1. Introduction

Gas sensors based on metal oxide semiconductors (MOS) are widely used to detect a variety of harmful gases, such as NH\textsubscript{3}, NO\textsubscript{2}, H\textsubscript{2}, CO and volatile organic compounds (VOCs), thereby protecting both atmospheric environments and human health [1, 2]. Among these gases, CO is highly toxic and dangerous to human health because it is colorless and odorless. CO is produced by incomplete combustion of fuels and is commonly found in the emission of automobile exhausts and in domestic environments.

Due to these concerns, CO monitoring in ambient air has been deeply investigated by MOS sensors [3]. Zinc oxide (ZnO), a n-type semiconductor of the II-VI group showing several favorable characteristics for gas sensing, including low cost, high electron mobility and wide band gap, has been one of the most investigated metal oxides for detecting various gases [4, 5]. However, for the majority of gas sensors based on ZnO, the lowest detectable concentration of CO is usually several hundreds of ppm [6-7]. These values are high compared to current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for human to carbon monoxide which is 50 ppm, as an 8-hour time-weighted average (TWA) concentration. Then, it’s still a great challenge to improve the sensitivity of ZnO gas sensors for CO monitoring.

Efforts to improve the performance of ZnO-based gas sensors essentially follow two main directions: one is using ZnO nanostructures [8]; the second is doping pure ZnO with host elements [9-12]. The first approach relies on the fact that the performances of semiconducting oxides based sensors strongly depend on grain size, specific surface area and morphology of the sensing material [9, 13-15]. These properties can be tuned by properly choosing the synthesis route and process conditions, so the gas sensing properties of ZnO nanostructures with different morphologies have been extensively studied in literature [16-19]. Doping process instead enhances the gas sensing performances by changing the energy-band structure and morphology, increasing the surface-to-volume ratio and consequently creating more centers (defects) for gas interaction on the metal oxide semiconductor surface [20-22]. Many examples of doped-ZnO conductometric sensors have been reported in literature [23-24]. Han et al. [23] evaluated the doping effect of Fe, Ti and Sn on gas sensing property of ZnO. Their results showed that the secondary phases and the crystal defects detected by photoluminescence might account for the different sensing behaviors. Gaspera et al. [24] considered the effects of doping transition metal ions into ZnO, resulting in a lower detection limit of 1-2 ppm CO at 300 °C. Depending on the formal charge of the hosting
element, the electrical characteristic and charge carrier mobility of the sensing layer results largely varied.

In a previous paper, pure ZnO and ZnO-doped with 2 at.% In were compared in the monitoring of low concentration of CO in air [25]. The samples were synthesized by a sol-gel process in supercritical conditions, which was found to be a simple technique for the preparation of metal oxides for gas sensing [26]. In this respect, the sol-gel processing offers several advantages including careful control of chemical composition, high purity, and it enables very homogeneous powder preparation in a conventional environment without the need for expensive equipment. Indium was selected as a dopant for ZnO because it is recognized as one of the most efficient elements used to improve the optoelectronic properties of ZnO [27]. Despite all these advantages, a few reports have been published on sol-gel processed In-doped ZnO (IZO) [28, 29] and less papers have dealt with the sensing properties of IZO materials [30, 31].

Experiments reported previously by us for the resistive IZO-based sensor demonstrated a substantially improved CO gas sensitivity and selectivity with respect to the undoped ZnO one [25]. Therefore, we extended the study to ZnO based nanostructures with different In-doping concentrations synthesized by the above sol-gel technique to investigate in detail the effect of the doping loading on the sensor performance for CO gas detection.

2. Experimental details

2.1. Samples preparation

IZO nanoparticles were prepared by the sol–gel method using 16 g of zinc acetate dehydrate [Zn(CH₃COO)₂·2H₂O; 99%] as precursor in a 112 ml of methanol. After magnetic stirring at room temperature for 10 min, an adequate quantity of indium chloride (InCl₃) corresponding to a ratio [In]/[Zn] of 0.01, 0.02, 0.03, 0.05 was added. After 15 min magnetic stirring, the solution was placed in an autoclave and dried under ethyl alcohol (EtOH) supercritical conditions following the protocol described by L. El Mir et al. [32-34]. The obtained nanopowders were then heated in a furnace at 400 °C for 2 h in air. Sample codes are named I0ZO, I1ZO, I2ZO, I3ZO and I5ZO, according the nominal In loading of each sample (0, 1, 2, 3 and 5 at.%, respectively).
2.2. Characterization

X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence (PL) measurements are useful to get exact information about the crystal and defective structure, surface morphology, particle size, etc.

XRD patterns were recorded in the 2θ range from 20° to 80° using a Bruker diffractometer with a Ni β-filtered Cu-Kα radiation (1.54178 Å wavelength). The average crystallite size, d, has been estimated by means of the Scherrer’s equation:

\[ d = \frac{0.9\lambda}{B \cos \theta_B} \]  

where \( \lambda \) is the X-ray wavelength, \( \theta_B \) is the maximum of the Bragg diffraction peak (in radians) and B is the full width at half maximum (FWHM) of the (101) XRD peak.

SEM images of the samples surface were acquired by Zeiss CrossBeam 540 instrument, equipped by an electron-dispersive x-ray (EDX) spectrometer.

PL measurements were carried out by a NanoLog modular spectrofluorometer Horiba with a Xe lamp as the excitation light source at room temperature. An excitation wavelength of 325 nm was applied, and emission was recorded between 350 and 870 nm.

2.3. Sensing test

In order to assemble the sensor devices, the calcined nanopowders were mixed with water to obtain a paste, then screen printed (1-10 \( \mu \)m thick) on alumina substrates (6×3×0.5 mm) supplied by a pair of Pt interdigitated electrodes on a side and by a Pt heater (~4 \( \Omega \) at RT) on the other side. The experimental bench for electrical characterization of the sensors allows carrying out resistance four points measurements under controlled atmosphere. Gases coming from certified bottles can be progressively diluted in air to selectable working concentrations by mass flow controllers managed by an automated software controlled system. Sensing measurements were carried out in the 200 – 400 °C temperature range, at steps of 50 °C. A dry gas stream mixture of 100 sccm was flowed thought the sensor chamber, collecting the sensors resistance data in the four point mode. A multimeter data acquisition unit Agilent 34970A was used for this purpose, while a dual channel power supplier instrument Agilent E3632A was employed to bias the Pt heater. The gas response, S, is defined as the ratio \( R_{\text{air}}/R_g \) for reducing gases (CO), where \( R_{\text{air}} \) is the electrical resistance of the sensor in dry air and \( R_g \) its electrical resistance at the fixed reducing gas concentration.
3. Results and discussion

3.1. ZnO nanopowders characterization

The morphology of the In-doped ZnO samples annealed at 400 °C for 2 hours was investigated by SEM. Figure 1 shows typical images taken from these samples, indicating the presence of agglomerates, with a rough porous fine-grained nanostructure. The size of the grains (in the range 50-70 nm) are in agreement with the average crystallite size as estimated by XRD (see below). By increasing the In-loading, bigger agglomerates can be noted. It can be suggested that the presence of In, causing an increase of defects in ZnO structure, enhances the surface energy of grains favoring, as a consequence, their agglomeration.

XRD spectra of annealed IZO samples are shown in Figure 2. All the peaks are indexed as wurtzite hexagonal-shaped ZnO with space group P63mc (Joint Committee on Powder Diffraction Standards (JCPDS) card file 36-1451), corresponding to (100), (002), (101), (102), (110) and (103) planes of ZnO. The lattice parameters, calculated from (100) and (002) planes, are found to be \( a = 3.249 \, \text{Å} \) and \( c = 5.205 \, \text{Å} \), respectively, very close to wurtzite ZnO ones [35-36]. No other oxide based crystalline impurities, such as indium oxide (\( \text{In}_2\text{O}_3 \)) or mixed oxide (\( \text{ZnIn}_2\text{O}_4 \)) which are very common in In-doped ZnO thin films, were found [37].

Figure 2 displays a window focused on the main diffraction peak. A lower peak intensity and peak broadening are observed with increasing In loading. \( \text{In}^{3+} \) has a larger ion radius (\( r_{\text{ionic}} = 0.094 \, \text{nm} \)) than \( \text{Zn}^{2+} \) (\( r_{\text{ionic}} = 0.074 \, \text{nm} \)), so the successful incorporation of \( \text{In}^{3+} \) into the lattice, and the consequent formation of oxygen interstitials, balancing the excess of positive charge of \( \text{In}^{3+} \) dopant, could cause the generation of tensile strain [38].

By means of the Scherrer equation the average crystallite size, \( d \), has been estimated from the full width at half maximum (FWHM) of the diffraction peak. It appears that In-doping inhibits the grain growth, independently by its content. The average crystallites size was in fact 65 nm for the pure ZnO and 53, 58, 56 and 54 nm for the sample I1ZO, I2ZO, I3ZO and I5ZO, respectively. By these measurements results that, on average, grain size of the doped samples is 15% smaller than pure zinc oxide one.

Figure 3 shows the room-temperature PL spectra recorded from pure and In-doped ZnO samples in the wavelength range 350-870 nm. The intrinsic ultraviolet emission of pure ZnO, located at 380 nm, corresponds to the near band edge (NBE) peak and is responsible for the recombination of free excitons of ZnO [39, 40]. A broad visible emission band centered at around 554 nm is also evident for the pure ZnO sample. This band is commonly attributed to the defects of zinc oxide mainly due to oxygen vacancies [41].
PL spectra from the In-doped samples show the same near band edge peak at 380 nm of pure ZnO. However, it is noted the formation of a new band centred at 445 nm, related to a blue deep-level emission originated from the oxygen interstitials and In$^{3+}$ substitutionals, whose intensity is dependent on the In content [42]. In-doping causes also a red shift of the broad visible emission band related to oxygen vacancies. Further, its intensity decreases with increasing the In loading, compared to blue band. A similar finding has been reported by Ghosh et al. [43]. They pointed out that the observed behavior is related to a higher band to band recombination and shallow states to valence band recombination with the consequence diminution of radiative transition due to oxygen vacancy. This indicates that In$^{3+}$ doping in ZnO greatly affects the defect equilibrium resulting in the change in the concentration of different types of defects in the pristine ZnO. Indeed, In$^{3+}$ has a higher formal charge respect to Zn$^{2+}$ and this causes the need to balance the excess of hosted charge, introducing more oxygen to ensure the resulting mixed oxide stoichiometry.

3.2. Carbon monoxide sensing tests

The CO gas sensing properties of the pure and In-doped ZnO samples were studied at various CO gas concentrations and by varying the working temperature. Figure 4a,b summarizes the result obtained, reporting the sensors responses to 50 ppm of CO versus the operating temperature, from 200 °C to 400 °C. For clarity, sensors with low In loading (i.e. up to 2 at% In) and high In loading (i.e. > 2 at% In), respectively, are compared to pure ZnO one in two separate graphs. For all the samples, the response to CO increases with the temperature goes through a maximum ($T_M$) and then decreases. This can be explained considering the various superimposed effects which affect the sensor response [25]. The temperature dependence of gas sensing devices response arises from the concomitance of: i) occurrence of surface adsorption-reaction-desorption phenomena which, by increasing temperature, became faster; ii) occurrence of bulk interactions, controlling the sensing material conductivity, that are activated by temperature increasing since they are diffusive phenomena. Figure 5 shows the correlation between In loading and $T_M$. For pure ZnO, $T_M$ value is 250 °C and it increases at 300 °C for I1ZO and I2ZO, reaching the higher value, 350 °C, for I3ZO and I5ZO. It is clear from Figures 4 and 5 that, even if In doping increases the $T_M$ value, it allows us to obtain higher response at intermediate loading. The operating temperature of 300°C has been then chosen on the basis of the sensor performances optimization (in terms of sensitivity and response/recovery time). Indeed, at this temperature, we recorded the highest sensitivity values, coupled with reasonable fast dynamics, for I1ZO and I2ZO based sensors.
Figure 6 shows the calibration curves (response vs. [CO]) for all samples at the same working temperature (300 °C). The responses of the sensors increase as CO concentration increases. On the basis of the data reported in the plot, we can note that the sensor response increases up to an In loading of 2 at.%, then decreases for higher dopant loading, following the ranking: $I_{1ZO} > I_{2ZO} > I_{0ZO} > I_{3ZO} > I_{5ZO}$.

The response of a resistive sensor based on metal oxide semiconductors arises from the combination of different synergic and/or competitive effects. First of all, when at the device surface the adsorption of oxygen from the surrounding atmosphere occurs, this creates a depletion layer that, in an n-type semiconductor such as ZnO and In-ZnO, causes a resistance increase (because of the formation of intergrain potential barriers). During the exposure to CO - that is a reducing gas - the reaction with the oxygen species adsorbed on the sensing material surface, liberate the charge carriers, firstly trapped, and consequently the resistance decreases. This mechanism can be affected by different factors: presence and number of active sites for the gas target adsorption, activation and reaction and kinetic of products desorption. It can be supposed that the replacement of the Zn$^{2+}$ cation by the In$^{3+}$, which acts as donor, leads to formation of more active adsorption sites (indium atoms and oxygen vacancies, as suggested by PL spectra) which favor the adsorption of oxygen species [44]. It is well known that the response of sensors based on metal oxides is mainly determined by the interaction between the target gas and the sensing surface. Therefore, greater is the surface area of the sensing materials, a stronger interaction and higher response can be expected [15]. Then, the decrease of grains size at addition of In, is a way to increase the surface area and consequently to enhance the response. By way, the In$^{3+}$ sites act favoring the reaction of CO with oxygen species. However, a decrease of response occurs at higher In loading. It cannot be excluded that the grain agglomeration, evidenced by SEM on samples with high In loading, could have a role. This may reduce the response and delay the response/recovery of the sensor, as experimentally observed and discussed in detail below. The same behavior has been reported also by Pugh et al. [30]. They found that low levels of indium doping were found to increase the responsiveness of the sensors, while higher levels of doping inhibited conductivity and responsiveness to gases of IZO sensors.

Figure 7 shows a synoptic view of responses dynamics of some sensors operating at 300 °C. First, one can note that the baseline resistance value remains almost at the same value for the low loaded In sensors, while at the highest In loading an increase of one order of magnitude can be noticed. This effect arises from the bulk oxygen excess and/or the higher surface oxygen adsorption capability in order to compensate the charge effects of the In$^{3+}$.
presence as substitutional in the reticular position of $\text{Zn}^{+2}$. The observed differences in the baseline resistance may be also a consequence of reduced crystallinity, as supported by XRD. Indeed, the carrier mobility is lower in the amorphous materials than in the crystalline ones, due to enhanced carrier scattering on structural defects resulting in a higher resistance for the former materials [45].

The resistance of the $\text{ZnO}$ gas sensor in dry air abruptly decreases during the CO exposure, typical of an n-type semiconducting behavior, and this resistance variation, as above discussed, represents the response of the sensor to the target gas [22]. It is clear by the results reported that In doping not only promotes the sensitivity towards CO, but a net change of the dynamic of response/recovery curves can be registered between lower (1-2 at.%) and higher (3-5 at.%) In-doped samples. Response and recovery times are important parameters for appraising gas sensors, and they are mainly determined by the accessibility of the sensing sites. However, the response time includes the gas diffusion toward the sensing surface for reacting with chemisorbed oxygen ions, and the subsequent re-oxidation process of the sensing surface to yield oxygen species.

Figure 8 shows the relationship between CO concentration and the response/recovery time of the sensors at the operating temperature of 300 °C. Response and recovery times are defined as the time required for gas sensors to achieve 90% of the total resistance change in the case response and recovery, respectively. The response time was smaller than the recovery time at each IZO samples. A short response time was useful for detecting faster the variation of CO concentrations. The graph shows also clearly that, increasing the In content up to 2 at.%, the dynamics for the signal response/recovery is accelerated, i.e. less time is necessary for the signal equilibration after the step change in the target gas concentration. Instead, further increasing the In content tends to increase the response/recovery time.

Data here reported indicate clearly that In-doped $\text{ZnO}$ nanoparticles possess better sensing characteristic as compared to the undoped sample. Previous work on metal oxide nanoparticles for gas sensor applications, suggests that the presence of porous nanostructures assumes a key role in the gas sensing enhancement [46-47]. This, in addition to the presence of In dopant, which changes the oxygen stoichiometry of $\text{ZnO}$, is at the origin of the sensing behavior observed on In-$\text{ZnO}$ sensors. In the context of these hypotheses, our results also suggest that at low In loading the sensing mechanism relies on the surface interaction between the adsorbed CO and $\text{O}_2$ species, i.e. on the surface of these sensing layers the oxygen species are more abundant than on pristine $\text{ZnO}$. At higher In dopant loading, the sensing mechanism
is bulk controlled, due to the fact that oxygen species are more tightly bonded to the dopant sites and consequently less available for the surface reaction with CO.

4. Conclusion

The results here reported on the microstructural, electrical and sensing characterization for differently doped In-doped ZnO, can be resumed as follows:

- In doping changes the oxygen stoichiometry of the ZnO oxide, while the microstructural characteristics are substantially unaffected.
- Sensors based on IZO NPs with low In loading (1-2 at.%) possessed the most sensitive response.
- A change of the sensing mechanism, from surface-type at low In loading to bulk type at higher In loading, occurs.

In summary, IZO nanomaterials show great potential for developing low cost, sensitive carbon monoxide sensors, due to ease production of the sensing materials and tunable response changing the operating parameters (e.g., working temperature) of the conductometric sensor platform.
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Figure 1. SEM images of I0ZO, I3ZO and I5ZO samples annealed at 400 °C.
Figure 2. XRD patterns of I0ZO, I1ZO, I2ZO, I3ZO and I5ZO samples annealed at 400 °C.
Figure 3. PL spectra of IZO samples annealed at 400°C for 2 hours in air.
**Figure 4.** Response to 50 ppm CO of the IZO sensors as a function of the temperature. 
a) Low loading In-ZnO sensor; b) high loading In-ZnO sensor. Pure ZnO sensor data are also included in both a) and b) plots as a comparison.
Figure 5. Correlation between the temperature of maximum of response and In loading.
**Figure 6.** Calibration curves: relationship between CO concentration and sensor response of the pure and In-doped ZnO samples at 300°C.
Figure 7. Dynamic responses of I0ZO, I1ZO, I2ZO, and I3ZO sensors, operating at 300 °C, to different concentrations of CO in air.
Figure 8. Response/recovery time of IZO sensors to 50 ppm CO at 300°C.