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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1166/sl.2011.1571>

Sensor letters, 9, 2, pp. 600-604, 2011-04-01

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ZnO-NiO thin films containing Au nanoparticles for CO optical sensing

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Abstract

ZnO-NiO sol-gel thin films doped with Au nanoparticles have been prepared with NiO amounts ranging from 0% to 30%. X-ray diffraction, UV-visible spectroscopy and electron microscopy confirm the crystallization of Au, ZnO and NiO, and the high residual porosity of the nanocomposites. Optical sensor functionality towards CO detection has been presented, showing an increase in sensitivity with NiO amount when the wavelength of analysis is far from the Au surface plasmon resonance peak, while in the 500-750nm range there is a strong wavelength dependence of the response with a decrease in sensitivity for a certain range of operative frequencies. This allows tuning of the sensor performance, and makes this material useful for multiple gases analysis.

Keywords: Au nanoparticles, nanocomposite film, optical sensor, ZnO, NiO

Introduction

Gas recognition through a fully optical device is a recent trend in gas sensor research, due to the numerous improvements that optical detection presents compared to the well established conductometric approach, because of electromagnetic noise independence and the possibility of

optical fiber device implementation^{1,2}. Au nanoparticles (NPs) dispersed inside a porous semiconductive matrix represent an effective design for a gas sensor material, due to their catalytic and surface plasmon resonance (SPR) properties that enhance the semiconductor sensing performance^{3,4}.

ZnO and NiO have been widely investigated in the past as active materials for sensing and catalysis^{5,6,7,8}; in this paper we present a simple and straightforward synthesis of ZnO-NiO thin films doped with Au NPs and the films properties as optical gas sensors for CO detection.

Experimental

ZnO and ZnO-NiO thin films doped with Au NPs have been prepared by sol gel technique. First, two 0.5M ethanolic solutions of Zinc Acetate dihydrate and Nickel Chloride hexahydrate were prepared; then ethanolamine was added dropwise under fast stirring to both solutions, keeping the ratio between the metal ion and the amine equal to 1. After 45 minutes stirring, the two solutions were mixed together according to the desired Zn:Ni molar ratio (7:3, 8:2, 9:1 or 1:0) and letting it stir a further 10 minutes. Eventually, a 0.2M tetrachloroauric ethanolic solution was added, keeping the ratio $\text{Au}:(\text{Zn}+\text{Ni})=0.05$; for comparison purposes, Au-free samples were also prepared, by substituting the gold precursor solution with the same amount of ethanol. After an additional 5 minutes stirring, the solutions were deposited by spin-coating at 2500rpm for 30 seconds on SiO₂ substrates. Thin films were thermally stabilized at 400°C for 10 minutes and then the spinning/stabilization procedure was repeated another 4 times. A final annealing at 500°C for 1 hour was performed.

The films were characterized by X-Ray Diffraction (XRD) by using a diffractometer equipped with glancing-incidence X-Ray optics. The analysis was performed at 0.5° incidence angle, using CuK α Ni filtered radiation at 30 kV and 40 mA. The average crystallite size was calculated from the Scherrer equation after fitting the experimental profiles.

Transmission Electron Microscopy (TEM) images were obtained with a Philips CM20 STEM system operating at 200 kV, equipped with EDX spectroscopy for elemental analysis. Scratched fragments of the film deposited on a carbon copper grid were used for the analysis.

The surface structure of the nanocomposite films has been investigated with a Field Emission Scanning Electron Microscope (FE-SEM).

Optical absorption spectra of samples were measured in the 250-900 nm range using a Jasco V-570 standard spectrophotometer. Optical sensor functionality was studied over the wavelength range $400\text{ nm} < \lambda < 800\text{ nm}$ using a custom-built gas flow cell coupled with a Varian Cary1E spectrophotometer. Details are reported elsewhere⁹. Films annealed at 300°C were exposed to three different concentrations of CO (0.01%, 0.1% and 1%), balanced in dry air, at a flow rate of about 0.4 L/min. The substrate size was approximately 1 cm × 2 cm and the incident beam was normal to the film surface with a 6 mm × 1.5 mm section area.

Results and Discussion

Zinc oxide films obtained from alcoholic solutions of zinc acetate with ethanolamine as a complexing agent are known to crystallize with orientated grains along the *c*-axis. Various explanations of the orientation mechanism have been presented^{10,11,12}, and so a clear understanding of the process is not achieved yet. Figure 1 shows the XRD patterns of the samples containing 5% molar Au with different NiO amounts after the final annealing at 500°C: theoretical diffraction peaks for ZnO (PDF #36-1451), NiO (PDF #471049) and Au (PDF #04-0784) are reported at the bottom. All samples show crystalline phases, indicating that 500°C is high enough to pyrolyse the organics inside the film, promote the reduction of Au ions dispersed inside the oxide films, and also to crystallize both Ni and Zn oxides. Analyzing the ZnO reflections, it is clear that the (002) diffraction peak is much more intense than the tabulated value, while all the other ZnO peaks are absent or very weak, indicating an extensive orientation along the *c*-axis. It can be also noticed that

NiO peaks are progressively increasing in intensity as the Ni content in the starting solution increases, clearly indicating a higher amount of Nickel oxide in the films, as expected.

Diffraction peaks for the same phase are very similar in intensity and broadening in all samples, apart from the above mentioned increase in intensity of NiO peaks, confirming a similar crystalline structure of the different nanocomposites, at least as far as Au and ZnO are concerned. In fact, performing a Lorentzian fit on the XRD peaks and measuring the full width at half maximum (FWHM), the crystallite size can be estimated by means of the Scherrer's relationship: ZnO, NiO and Au crystals sizes are respectively between 24-29 nm 11-16 nm and 14-18 nm in all the samples. Optical absorption measurements in the UV-Vis range (Figure 2) show in all samples the sharp absorption edge of ZnO around 370 nm and the Au Surface Plasmon Resonance (SPR) peak between 570 nm and 600 nm. The ZnO absorption edge is almost the same in all samples, and the energy associated with the band gap (around 3.3 eV) is very close to values reported in the literature for similar sol-gel films¹³ and also for bulk ZnO¹⁴, indicating that the structure of zinc oxide is not influenced by the NiO. However, the Au SPR peak undergoes some changes, being red shifted and broadened with increasing NiO content. The red shift can be explained considering the different refractive indexes of the two oxides: for ZnO it is 2.01¹⁵, while for NiO it 2.33¹⁶, so if the amount of nickel inside the film is increased, an increase of the average refractive index of the nanocomposite results, and this causes the observed red shift of the Au SPR peak.

The broadening of the Au SPR band could be ascribed to the interaction of the noble metal NPs with the active NiO surface: in fact it has been shown¹⁷ that Au and NiO, having the same cubic crystalline structure with very small lattice mismatch, can form particular two-fold structures in which gold and nickel oxide crystals are coupled along the Au (111) and NiO (200) planes. This fact leads to a broadening and a strong red shift of the SPR peak, due to the high extent of interaction between the two materials. So the broadening is again due to the higher refractive index of NiO, but while the red shift is associated with an average increase in refractive index of the films,

the broadening is related to a specific local interaction between NiO and Au crystals due to their low lattice mismatch.

Figure 3 shows bright field TEM images of ZnO-Au films without NiO (Figure 3a) and with 30% NiO (Figure 3b). Polydispersed Au NPs can be recognized as darker spots because of their higher mass-thickness contrast and scattering (diffraction) contrast, compared to the lighter oxide matrix components. It is difficult to distinguish between ZnO and NiO nanocrystals, because TEM images have not been taken at sufficiently high resolution and EDX analysis scans an area larger than the crystallite size. Nevertheless, EDX data showed the presence of Zn, Au, O, and also Ni with the exception, of course, of the sample with 0%NiO, confirming the composition of the oxide matrix (ZnO and NiO), as previously discussed.

SEM micrographs of the nanocomposite film surface are reported in figure 3c and 3b. Zinc oxide crystalline grains are easily detectable, as well as the presence of a residual porosity. The observed morphology is desirable for gas sensor thin films, in order to obtain a sensing material with high specific surface area and to have an easy path for the gaseous species entering and exiting the nanocomposite.

Gas sensing tests have been performed at different operative temperatures (OT): below 200°C sensors response was very small and the dynamics of absorption/desorption were quite long. For higher temperatures the response was acceptable, so it was determined to perform all sensing tests at 300°C OT, a good compromise between high performances and an acceptably low enough temperature of analysis. Figure 4 reports the OAC parameter (Optical Absorption Change, defined as the difference between absorption spectra collected during CO and air exposure, i.e. $OAC = A_{gas} - A_{air}$) versus wavelength for Au-free samples (Figure 4a) and Au-doped samples (Figure 4b). It can be noticed that pure ZnO films do not show any detectable OAC optical signal, while with increasing NiO content, the sensitivity of Au-free films increases, confirming the optical response of nickel oxide towards reducing gases¹⁸. The absorbance of the films decreases when exposed to the target gas, as expected from the interaction between reducing gases like CO and p-type

semiconductors like NiO^{19,20}. Samples containing Au NPs show the typical wavelength dependence of sensing response⁴, especially in the SPR range (500-700nm). ZnO-Au response is symmetric, with positive and negative maxima of about the same intensity. With increasing NiO content, this behavior is added to the NiO response, so the total optical variation is no longer symmetric. The resultant effect of Au NPs is to reduce the response at low wavelengths and to increase it at higher wavelengths. Interestingly, the highest response is observed with 10% NiO, while for larger NiO content the response is lower. This can be explained by analyzing the shape of the plasmon peak, which becomes broader as the Ni content is increased, and so its modification caused by the reducing gas happens to be damped. Nevertheless, outside the Au SPR region, a higher NiO amount produces a higher response of the nanocomposite film, as expected considering the behavior of Au-free samples.

A useful parameter to compare Au-doped samples performances is the Response Intensity (RI), that can be defined as the following:

$$RI = \left| 1 - \frac{Abs_{CO}}{Abs_{Air}} \right|$$

In Figure 5 the RI parameter at three different wavelengths (at 450 nm and at the two wavelengths corresponding to positive and negative maximum of OAC curves reported in Figure 4b) has been plotted versus the CO concentration. The response intensity for all the samples increases linearly with order of magnitude of target gas concentrations, highlighting good sensitivity for low concentrations. A linear fit has been performed on data plotted in a linear-logarithmic scale, obtaining a good fit of experimental values: so the intensity of the response of all films at each wavelength can be described as linear with respect to the logarithm of the target gas concentration, giving the opportunity to easily create calibration curves for the sensitivity at different wavelengths. As expected, outside the Au NPs plasmon range (Figure 5a) increasing the NiO content causes an increase in the response, while the introduction of Au NPs with their absorption peak in the visible

range causes a decrease in the response when operating at a wavelength near the OAC positive maximum (Figure 5b) and an increase when operating near the OAC negative maximum (Figure 5c). The response decrease experienced for a particular range of wavelength suggests the possibility to test these materials in multiple gas detection configurations. Nevertheless, for samples with a low amount of Ni (0%, 10%) this decrease is not evident, since the intensity of the response due to NiO was absent or very small; thus the presence of Au NPs causes an improvement in the sensor performance also in the range of wavelength near the OAC positive maximum.

The dynamics of absorption and desorption of the target gas are fast, as can be seen in Figure 6, where the temporal response of the sample with 10% NiO and 5% Au exposed to different CO concentrations is reported. The behavior is almost step-like, with both response and recovery times (calculated as the time needed to reach 90% of the total absorption variation) between 30 seconds and 1 minute.

Conclusions

A simple and reproducible sol-gel synthesis of ZnO-NiO thin films has been presented and a dispersion of Au NPs inside the porous film has also been achieved. XRD and electron microscopy characterizations confirm the crystallization of both oxides and of Au NPs, while UV-Vis spectroscopy shows the Au SPR peak red shifting and broadening with an increase in NiO content, as a consequence of the interaction between the two materials.

An increase of optical CO sensitivity with NiO content is demonstrated in the whole analyzed range of wavelengths for Au-free samples, and also outside Au SPR region in Au-doped samples. For wavelengths between 500 nm and 750 nm, the sensor response becomes wavelength dependent, giving rise to the opportunity of tuning the sensitivity by selecting the operative wavelength, and consequently making these nanocomposite films of potential use for multiple gases analysis.

Acknowledgements

E.D.G. thanks Fondazione CARIPARO for financial support. This paper is recorded as National Research Council of Canada; NRCC# 52181.

References

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1. K. Educhi, Optical gas sensors, in *Gas Sensors*, Edited by G. Sberveglieri, Kluwer Academics Publishers, Dordrecht (1992), pp. 307-328
 2. J.J. Robillard, U.S. Patent 5436167 (1995), assigned to Board of Regents, University of Texas System, Austin, Tex.
 3. H. Tsunoyama, T. Tsukuda and H. Sakurai, Chem. Lett. 36, 212 (2007)
 4. T. Kobayashi, M. Haruta and M. Ando, Sens. Actuators B 13-14, 545 (1993)
 5. X.L. Cheng, H. Zhao, L.H. Huo, S. Gao and J.G. Zhao, Sens. Actuators B 102, 248 (2004)
 6. Nikos Brilis, Chara Foukaraki, Eleftherios Bourithis, Dimitris Tsamakis, Aggelos Giannoudakos, Michael Kompitsas, Theodora Xenidou and Andreas Boudouvis, Thin Solid Films 515, 8484 (2007)
 7. J. Kubota, A. Bandara, A. Wada, K. Domen and C. Hirose, Surface Science 368, 361 (1996)
 8. M. Miyauchi, A. Nakajima, T. Watanabe and K. Hashimoto, Chem. Mater. 14, 2812 (2002)
 9. A. Martucci, M. Pasquale, M. Guglielmi, M. Post and J.C. Pivin, J. Am. Ceram. Soc. 86, 1638 (2003)
 10. D. Bao, H. Gu and A. Kuang, Thin Solid Films 312, 37 (1998)
 11. S. Amirhaghi, V. Craciun, D. Craciun, J. Elder and I.W. Boyd, Microelectron. Eng. 25, 321 (1994)
 12. A. Yavuz Oral, Z. Banu Bahs and M. Hasan Aslan, Appl. Surf. Sci. 253, 4593 (2007)
 13. L. Armelao, M. Fabrizio, S. Gialanella and F. Zordan, Thin Solid Films 394, 90 (2001)
 14. J.J. Cavalieri, D.E. Skinner, D.P. Colombo and R.M. Bowman, J. Chem. Phys. 103, 5378 (1995)
 15. D.R. Lide, Handbook of Chemistry and Physics, CRC press, 72nd Edition, 4-112 (1991)

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- 16.** R.J. Powell and W.E. Spicer, Phys. Rev. B 2, 2182 (**1970**)
 - 17.** D. Buso, M. Guglielmi, A. Martucci, G. Mattei, P. Mazzoldi, C. Sada and M. Post, Cryst. Growth Des. 8, 744 (**2008**)
 - 18.** A. Martucci, D. Buso, M. De Monte, M. Guglielmi, C. Cantalini and C. Sada, J. Mater. Chem. 14, 2889 (**2004**)
 - 19.** F. Boccuzzi, A. Chiorino, S. Tsubota and M. Haruta, Sens. Actuators B 24–25, 540 (**1995**)
 - 20.** M. Ando, T. Kobayashi, S. Iijima and M. Haruta, J. Mater. Chem. 7, 1779 (**1997**)

Figure Captions

Figure 1. XRD patterns of ZnO-NiO-Au films with the NiO amount increasing from 0% to 30%, annealed at 500°C. Theoretical diffraction lines for ZnO (PDF #36-1451, letter Z), NiO (PDF #471049, letter N) and Au (PDF #04-0784, letter A) are reported at the bottom.

Figure 2. Optical absorption spectra of the 4 samples with NiO amount increasing from 0% to 30%

Figure 3. Transmission Electron Microscopy images of a) ZnO-Au and b) ZnO-30%NiO-Au scratched fragments from the thin films annealed at 500°C. Scanning Electron Microscopy of c) ZnO and d) ZnO-Au films annealed at 500°C.

Figure 4. Optical absorption change ($OAC = A_{\text{gas}} - A_{\text{air}}$) curves for a) ZnO-NiO films and b) ZnO-NiO-Au, collected at 300°C OT. Zero value for OAC is highlighted with a dotted line.

Figure 5. Response intensity plots at three different CO concentrations for ZnO-NiO-Au films: a) at 450nm. b) at the wavelength corresponding to the negative maximum of OAC curve. c) at the wavelength corresponding to the positive maximum of OAC curve.

Figure 6. Dynamic response of ZnO-Au sample with 10%NiO with different CO concentrations measured at 680nm and 300°C OT.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6