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Nanostructured Silicon Oxide–Nickel Oxide Sol–Gel Films with Enhanced Optical Carbon Monoxide Gas Sensitivity

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Sol–gel derived silica (SiO₂) films doped with nickel oxide (NiO) nanocrystals were fabricated. A bifunctional ligand was used, bearing amine groups capable of coordinating the nickel ions and hydrolysable siloxane groups for anchoring the metal complex moiety to the silicate matrix. Nickel oxide nanocrystals precipitated at 500°C while the film was still porous. The nanocomposite films showed a reversible change in the optical transmittance in the VIS–NIR range when exposed to carbon monoxide gas. The effects of residual porosity, testing temperature, and carbon monoxide gas concentration on optical transmittance were studied.

I. Introduction

RECENTLY, nanocomposites with sensor functionality are becoming a new area of interest for optical gas-sensing applications. In fact, the optical transmittance of nanoparticles or thin films has been reported^{1,2} to change on exposure to some gases. In particular, it was found² that NiO, Co₃O₄, and Mn₃O₄ thin films showed a reversible decrease in the VIS–NIR absorption when exposed to CO at temperatures ~250°–350°C. The CO-sensitive decrease of the absorbance of NiO films can be ascribed² to a decrease of positive hole density in the NiO caused by a decrease in oxygen anion density on the NiO surface during the catalytic oxidation of CO. As the gas-sensing mechanism is a surface-related phenomenon, the increase of the specific surface area of the functional oxide is expected to enhance the CO-sensing effect. In this work we synthesized, by sol–gel methods, porous SiO₂ films doped with homogeneously dispersed NiO nanocrystals. The nanoporosity of the sol–gel matrix provides a path for the gas molecules to reach the functional ultrafine particles embedded in the glass matrix, and the nanocomposite films showed a reversible change in optical transmittance when exposed to CO gas.

II. Experimental Procedure

The nanocomposites were obtained by mixing a matrix solution of tetraethylorthosilicate (TEOS; Aldrich Chemical Co., Milwaukee, WI) and methyltriethoxysilane (MTES; Aldrich) as SiO₂ precursors, with a doping solution containing NiCl₂ as precursor

for the NiO particles. 3-(2-Aminoethylamino)propyltrimethoxysilane (AEAPTMS; Aldrich) was used as the bifunctional ligand. This ligand bears both amine groups capable of coordinating the nickel ions, and hydrolysable silyl groups for anchoring the metal complex moiety to the silicate matrix. The matrix solution was obtained by using the following molar ratios: MTES:TEOS:H₂O:HCl = 1:1:1:0.005. In the doping solution the molar ratio between AEAPTMS and NiCl₂ was 1. The solvent was ethanol and the nominal oxide concentration in the deposition solution was 50 g/L.

Films of composition 60SiO₂·40NiO were deposited by dipping at 35% RH on silicon or SiO₂ glass substrates and heat-treated for 1 h in air at 500°, 700°, 800°, or 900°C.

The films were characterized by X-ray diffraction (XRD; Philips, Eindhoven, The Netherlands) using a diffractometer equipped with glancing-incidence X-ray optics. The analysis was performed using CuK_α nickel-filtered radiation at 40 kV and 50 mA. The average crystallite size was calculated from the Scherrer equation after fitting the experimental profiles.

Transmission electron microscope (TEM; Philips) characterization was conducted at 200 kV. Scratched fragments of the film deposited on a holey carbon copper grid were used for the analysis. The average diameter of the NiO particles was measured from TEM images by evaluating about 200 particles.

Rutherford backscattering spectrometry (RBS; 2.2 MeV ⁴He⁺) was used to evaluate the concentration profiles of silicon, nickel, oxygen, and carbon in the film and to measure the composition of the film with respect to the different elements by simulating the RBS experimental spectra. The hydrogen content of the films was measured by elastic recoil detection analysis (ERDA). The film density (mol·cm⁻³) was calculated by combining thickness data (cm), obtained from profilometer measurements, and the film dose (mol·cm⁻²) from RBS and ERDA data.

The sensing properties of the nanocomposite films were evaluated by measuring the variation of the optical transmittance of the film when exposed to CO in air. The films were mounted on a custom-fabricated heater in a gas flow chamber, with a design to permit unimpeded radiation transmission through the whole assembly. Transmission data in the 200 nm < λ < 900 nm range were recorded using a spectrophotometer (Model Cary1E, Varian, Palo Alto, CA) with films heated at temperatures between room temperature and 350°C and with CO concentrations of 1, 0.1, and 0.01 vol% CO in air. Details of the experimental setup are reported in Ref. 3.

III. Results and Discussion

TEOS and MTES were used as sol–gel precursors to obtain thicker films. In fact it has been shown⁴ that by using MTES it is possible to obtain single-layer films ~2 μm thick at 500°C. It is

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also reported⁵ that the porosity of the films can be tailored using different MTES/TEOS ratios.

In the doping solution, NiCl_2 was used because of its good solubility in ethanol. Moreover, to improve the homogenous distribution of the NiO particles, a bifunctional ligand, AEAPTMS, was used. The amine groups present in the AEAPTMS are capable of coordinating the nickel ions through the formation of metal complexes that can be anchored to the silicate matrix by the hydrolysable silyl groups.⁶ As reported by Breitscheidel *et al.*,⁶ the metal complexes form in solution through the reaction between the AEAPTMS and the nickel salt, and NiO precipitates at 500°C after removal of the organic part. As reported by Piccaluga *et al.*,⁷ metal oxide nanoparticles in the sol-gel matrix probably form in the cavities of the matrix, substituting for a part of the adsorbed water.

TEM measurement of films heated at 500°C showed the presence of round-shaped nanocrystals with a mean diameter of 3.8 nm and a standard deviation of 1.2 nm. Figure 1 shows the XRD spectra of films heated at different temperatures. Peaks belonging to NiO cubic crystals (Powder Diffraction File No.78-0643, International Centre for Diffraction Data, Newtown Square, PA) have been observed in films heated at 500°C or at higher temperatures, whereas in films heated at lower temperatures no diffraction peaks were detected. The mean diameter of NiO crystallites, estimated from the linewidth of the most intense diffraction peak, was ~ 6 nm for both films heated at 800° and 900°C, whereas in films heated at lower temperatures the broadness of the diffraction peaks did not allow a reliable estimation of the mean crystallite size. Comparing the values of the mean diameter of NiO nanoparticles in films heated at 500°C, estimated from TEM measurements, with those in films heated at 800° and 900°C, estimated from XRD measurements, there is an increase in crystal size with the heat-treatment temperature, even though the mean diameter remains in the nanometer range.

The silicon/nickel ratio evaluated from RBS and ERDA analysis was in good agreement with the nominal one (nominal silicon/nickel = 1.5, see Table I). Moreover, the profile concentration was uniform throughout the film thickness. The hydrogen content decreases with the heat-treatment temperature whereas the carbon content remains constant. The density of the films increases with the heat-treatment temperature because of the progress of the sol-gel film densification.

Figure 2 shows the FTIR spectra of films treated at different temperatures. In all the spectra two dominant peaks of the Si-O bond⁸ at 1070 and 800 cm^{-1} are evident. In the spectra of films heated at 500° and 700°C there are more bands, one very broad at 3400–3500 cm^{-1} , and one around 1630 cm^{-2} caused by OH vibrations, and one between 910 and 940 cm^{-1} , attributed to stretching vibrations of Si-OH or SiO^- groups.⁹ These bands are absent in films heated at 800° and 900°C, indicating a higher degree of densification, in agreement with the variation of the hydrogen content measured by RBS-ERDA. All the spectra also

Table I. Results of RBS-ERDA Analysis on $60\text{SiO}_2\cdot 40\text{NiO}$ Films Heated at Different Temperatures

Temperature (°C)	Relative composition (%)					Density ($\text{g}\cdot\text{cm}^{-3}$)
	Si	Ni	O	C	H	
500	17	13.5	39.5	13	17	1.91
700	16	14	44	13	13	2.12
800	18	15	42	13	12	2.45
900	18.5	15	46.5	13	7	2.51

have a shoulder at ~ 1200 cm^{-1} , which, as reported by Almeida and Pantano,¹⁰ is related to the total porosity of the films.

The optical transmittance over the $200\text{ nm} < \lambda < 900\text{ nm}$ range for films heat-treated at 500°C or higher temperatures increased reversibly on exposure to CO for film testing temperatures $> 200^\circ\text{C}$. Transmission data at $\lambda = 650\text{ nm}$ for a series of four different films, all at testing temperatures of 330°C during gas exposure, obtained as a function of exposure time to 1% CO in air is shown in Fig. 3. The films were heat-treated at 500°, 700°, 800°, and 900°C, and data of this type are reproducible over many cycles of CO/air exposure. In the series of measurements reported in Fig. 3, the two films that were heat-treated at the lower temperatures were exposed to two sequential pulses of 1% CO with air exposure in between, whereas the other two films experienced only one CO pulse. It is clear that both the relative increase in transmittance and the rate of response decrease with the film heat-treatment temperature. The films densify to a greater extent when heat-treated at the higher temperatures, as shown by RBS-ERDA and FTIR measurements, so there exists a correlation between film density and the magnitude and speed of sensor response. With increased densification, the porosity of the films decreases, and this constricts and limits the availability of paths of the gas molecules for reaching the surface of the NiO nanocrystals in the SiO_2 matrix. However, other factors, such as NiO particle size and matrix stoichiometry, may play a role in these observed effects, and the relative importance of these factors on sensor functionality has not yet been determined conclusively. Figure 4 shows the effect of film testing temperature on the transmittance response at $\lambda = 650\text{ nm}$. For this data, a film heat-treated at 500°C was used, and the exposure gas was 1% CO/air, but the film test temperature was varied in four steps from 220° to 330°C. It is clear that both the magnitude of response (i.e., change in transmittance) and the reversibility are enhanced at the higher testing temperatures. As the proposed detection mechanism is thermally activated,² the relative variation in optical transmittance would be expected to decrease as the testing temperature decreases. Even so, at 220°C transmittance changes are still easily detectable although the response characteristics are poorer than at the higher temperatures.

Fig. 1. XRD spectra of $60\text{SiO}_2\cdot 40\text{NiO}$ films heat-treated at different temperatures.

Fig. 2. FTIR spectra of $60\text{SiO}_2\cdot 40\text{NiO}$ films heat-treated at different temperatures.

Fig. 3. Variation of the optical transmittance of $60\text{SiO}_2\cdot 40\text{NiO}$ at $\lambda = 650$ nm and $T = 330^\circ\text{C}$ for films heat-treated at different temperatures exposed to 1 vol% CO in air.

The transmittance dependence of the films on CO concentration was also measured. Figure 5 shows transmittance data obtained at $\lambda = 650$ nm for a film at a test temperature of 280°C . Three CO concentrations in air have been used (0.01%, 0.1%, and 1% CO in air). Clearly a CO concentration dependence is evident, and transmittance changes are easily observable even at concentrations of 0.01% CO. The relative transmittance changes, based on the initial (air) base line are $\sim 1.3\%$, 2.0% , and 2.7% for 0.01%, 0.1%, and 1% CO in air, respectively, indicating a log concentration dependence on transmittance response. Other features of the response characteristics in this data need to be noted. For example, reversibility is generally good except at the final stage where a longer tail out is present, although an eventual return to the original base line is achieved over time. An explanation of this observation is that a portion of the response at the lower CO concentrations is accompanied by the CO or its reaction products being more strongly chemisorbed or adsorbed in the NiO/SiO_2 matrix. This results in less lability with a consequential deterioration to reversibility. In general, for the data reported, the achievement of good return to base line before and after CO exposure is improved with

Fig. 4. Variation of the optical transmittance of $60\text{SiO}_2\cdot 40\text{NiO}$ at $\lambda = 650$ nm for films heat-treated at 500°C and exposed to 1 vol% CO in air at four different testing temperatures.

Fig. 5. Variation of the optical transmittance of $60\text{SiO}_2\cdot 40\text{NiO}$ at $\lambda = 650$ nm and $T = 280^\circ\text{C}$ for films heat-treated at 700°C and exposed to three different CO concentrations.

increasing testing temperature. This would be predicted for a mechanism that is thermally activated and involves desorption of strongly bound adsorbed or chemisorbed species.

IV. Conclusions

Nanoporous SiO_2 glass films doped with monodispersed NiO nanocrystals were obtained by the sol-gel technique. Films heat-treated between 500° and 900°C showed the presence of NiO nanocrystals and a residual porosity that allowed the reaction between the surface of the NiO particles dispersed in the SiO_2 glass matrix and CO gas. The optical transmittance of $40\text{NiO}\cdot 60\text{SiO}_2$ films increases on exposure to CO in air over the 300–800 nm wavelength range. For films that have been heat-treated at $T < 700^\circ\text{C}$ and are exposed to CO in air at $T > 250^\circ\text{C}$, a rapid and reversible change in transmittance occurs. The change in transmittance is clearly demonstrated, even at concentrations at the 0.01% CO level. The transmittance response of the films indicates a logarithmic proportionality to CO concentration. The CO-gas-sensing properties depend on heat-treatment conditions during sol-gel preparation, the residual porosity, and the testing temperature during CO exposure.

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