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Optical Gas Sensing Properties of Silica Film Doped with Cobalt Oxide Nanocrystals

A. MARTUCCI*, D. BUSO AND M. GUGLIELMI
INSTM and Università di Padova, Dipartimento di Ingegneria Meccanica Set. Materiali, Via Marzolo 9, 35131 Padova, Italy
alex.martucci@unipd.it

L. ZBRONIEC AND N. KOSHIZAKI
National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 8565, Japan

M. POST
ICPET, National Research Council of Canada, Ottawa, Canada

Abstract. SiO_2 sol-gel films doped with cobalt oxide nanocrystals have been fabricated. The nanocrystals precipitate in the glass film at 500°C, while the film is still porous. The nanocomposite films showed a reversible change in the optical transmittance when exposed to CO in the $250 < \lambda < 850$ nm range. The effects of the residual porosity and testing temperature have been studied. The gas sensing properties of the cobalt oxide nanocrystals doped films are compared with those of nickel oxide nanocrystals doped silica film, previously reported.

Keywords: nanocrystals, optics, gas sensor, cobalt oxide, nanoporosity

Introduction

Semiconductor-doped glasses have received a growing interest in the last two decades both for fundamental studies and for applications. The interest in such nanostructured materials arises from the unique optical properties that nanocrystals can give to the glass nanocomposite. The nanocomposite can have different optical functionalities depending on the nature of the embedded semiconductor nanocrystals. Nanocomposites with sensoring function are becoming a new area of interest in the field of optical gas sensor. In fact, it has been reported that the optical transmittance of nanoparticles or thin films may be changed by gas atmosphere [1, 2]. In particular it was found that NiO, Co_3O_4 and Mn_3O_4 thin films showed reversible decrease in the Vis-NIR absorption due to CO at temperatures around 250–350°C [2]. As the gas sensing mechanism is a surface related phenomenon, the increase of the specific surface area of the functional oxide will enhance the sensing effect.

In a previous work [3] we described the synthesis and the optical gas sensing properties of nonporous silica film doped with nickel oxide nanocrystals. In this paper we report the preliminary results on the optical gas sensing properties of films doped with cobalt oxide nanocrystals comparing the gas sensing response of the two nanocomposites.

Experimental

For the preparation of the cobalt oxide doped silica films we used a procedure similar to that used for the nickel oxide nanocomposites [3]. Briefly, a

*To whom all correspondence should be addressed.

matrix solution of $Si(OC_2H_5)_4$ (TEOS) and $CH_3Si(OC_2H_5)_3$ (MTES) was mixed with a doping solution containing cobalt chloride salt. 3-(2-aminoethylamino)propyltrimethoxysilane (AEAPTMS) was used as the bifunctional ligand. As a matter of fact it bears either amine groups capable of coordinating the cobalt 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: EtOH:MTES:TEOS:H_2O:HCl = 1:1:1:1:0.01. In the doping solution an AEAPTMS/Co = 1 molar ratio was used. In the deposition solution the Si/Co molar ratio was 3/2 and the nominal oxide concentration was 40 g/l. Films were deposited by dipping on SiO_2 glass substrates and heated at different temperatures in air.

The films were characterized by X-ray diffraction (XRD) using a diffractometer equipped with glancing-incidence X-ray optics. The analysis was performed using Cu K_α Ni filtered radiation at 40 kV and 50 mA. The average crystallite size was calculated from the Sherrer equation after fitting the experimental profiles by the method described in [4].

Transmission electron microscope (TEM) characterization was conducted at 200 kV. Scratched fragments of the film deposited on a holey carbon copper grid were used for the analysis.

Infrared absorption spectra, in the range 400–4000 cm^{-1}, were recorded by Fourier transform infrared spectroscopy (FTIR).

The sensing properties of the nanostructured films were evaluated by measuring the variation of the optical transmittance of the film when exposed to CO. The samples 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 200–900 nm range were recorded using a Shimadzu UV-2100PC spectrophotometer. The gas sensing properties of the doped films were tested exposing the samples to 1 vol% CO in air at temperatures ranging from room temperature and 350°C.

Results and Discussion

Figure 1 shows the XRD spectra of films heated at different temperatures. Peaks belonging to Co_3O_4 crystals (#JCPDS 42-1476) have been observed in films heated at 500°C or at higher temperatures up to 800°C,

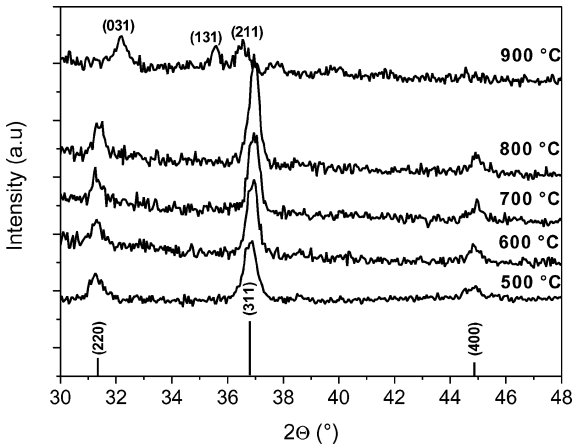

Figure 1. XRD spectra of films heated at different temperatures. The diffraction peaks in film heated at 500, 600, 700 and 800°C belong to Co_3O_4 crystals (#JCPDS 42-1476), those in film heated at 900°C belong to Co_2SiO_4 crystals (#JCPDS 15-865).

while in films heated at lower temperatures no diffraction peaks have been detected. The mean diameter of Co_3O_4 crystallites, estimated from the linewidth of the most intense diffraction peak, was 14 nm for films heated at 500°C. As expected, the crystal size increases with the heat treatment temperature (18 nm at 600°C, 20 nm at 700 and 800°C), even though the mean diameter remains in the nanometer range. At 900°C only peaks belonging to Co_2SiO_4 crystals (#JCPDS 15-865) have been observed (see Fig. 1) indicating the transformation of cobalt oxide in cobalt silicate.

TEM images confirmed the presence of nanoparticles homogenously dispersed in an amorphous matrix for film heated at 500°C [5].

In the case of NiO doped films we also have found that the nanocrystals precipitate at 500°C [3], but no silicate formation have been observed up to 1000°C.

Figure 2 shows the absorption spectra of films heated at 500°C, in air and upon exposure to 1 vol% CO in air. Two different absorption bands can be seen around 410 and 720 nm, which can be assigned to Co^{3+} and Co^{2+} sites of the octahedral and tetrahedral centers of Co_3O_4 elementary cell [6]. The optical the transmittance increases reversibly upon exposure to CO over the $250 < \lambda < 800$ nm range for testing temperature as low as 200°C. At lower temperature no variations have been observed, while for higher temperatures the magnitude of response (i.e. the change in optical transmittance) increases. The highest enhancement has been detected between 300 and

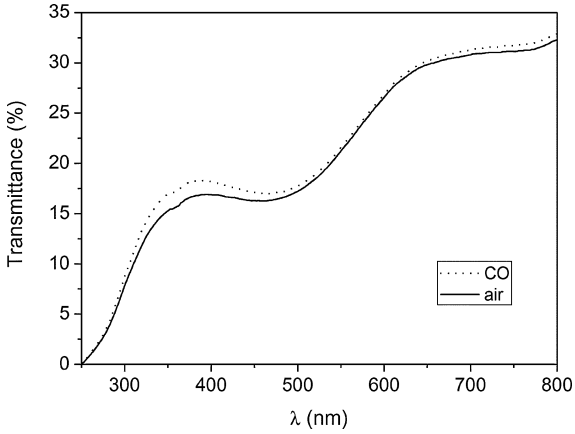

Figure 2. Optical transmittance spectra of films heated at 500°C in air (straight line) and in 1 vol%CO in air (dot line) at 300°C. The transmittance in CO was measured after 2 min exposure.

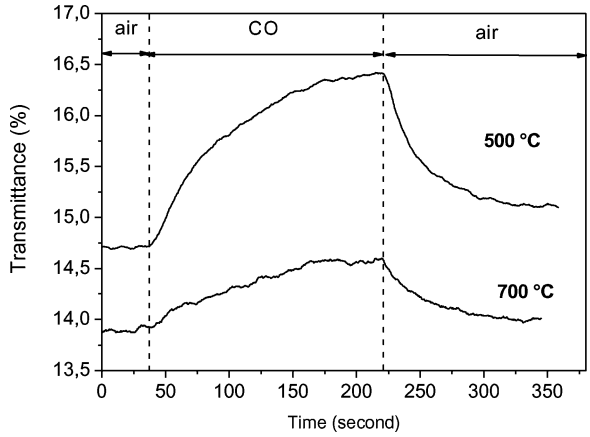

Figure 4. Variation of the optical transmittance at $\lambda = 400$ nm and at testing temperature of 350°C for films heat treated at 500 and 700°C exposed to 1 vol% CO in air.

350°C. Similar results have been obtained also for the NiO doped films [3].

The optical transmittance CO-sensitive increase of transition metal oxide films has be ascribed to a decrease of positive hole density in metal oxide due to a decrease in oxygen anion density on the surface of oxides during the catalytic oxidation of CO [2]. This detection mechanism is thermally activated, hence the relative variation in optical transmittance is expected to decrease as the testing temperature decreases.

Contrary to what we have found for NiO doped films [3], the optical transmittance did not increase constantly along the $250 < \lambda < 800$ nm range (see Fig. 2). In Fig. 3 it was plotted the difference between the optical transmittance in CO and in air ($\Delta T = T(\text{CO})$-$T(\text{air})$) vs. wavelengths. The highest ΔT values have been found between 350–400 nm, roughly corresponding to the absorption band due to Co^{3+} center in the octahedral sublattices of the Co_3O_4 spinel. Similar behaviors have been already observed for cobalt oxide thin films [7] and can be attributed to a higher catalytic activity of trivalent cobalt ions in octahedral sites [8].

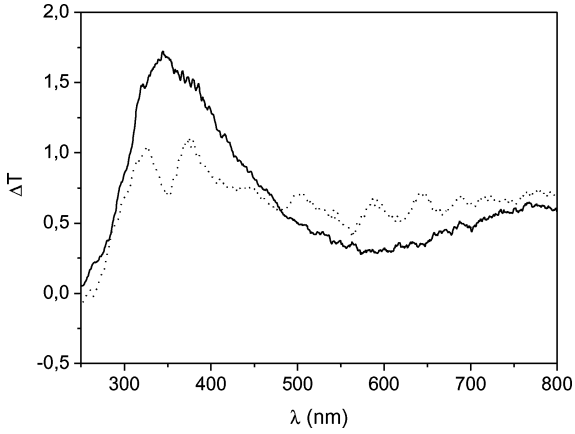

Figure 3. Variation of the increase in transmittance ΔT (Transmittance in CO—Transmittance in air) with wavelength at 300°C, for films heated at 500°C (straight line) and at 700°C (dot line).

Films heated at 700°C showed the same optical features as the film heated 500°C, but both the relative increase in transmittance (see Fig. 3) and the rate of response (see Fig. 4) were lower. This can be ascribed mainly to a higher degree of densification of film heated at higher temperatures. In fact FTIR measurements showed that the vibration bands related to OH species (i.e. the broad band at 3400–3500 cm^{-1} and the band at 1630 cm^{-1} due to OH vibrations, and that at 910–940 cm^{-1}, attributed to stretching vibrations of Si—OH or SiO^- groups [9]) were no more present in films heated between 700 and 800°C. Moreover the position of the main Si—O vibration band (i.e. 1050–1100 cm^{-1}) shifts to higher wavenumbers by increasing the film heat treatment temperature (see Table 1).

Transmission data at $\lambda = 400$ nm for films densified at 500 and 700°C, both at testing temperatures of 350°C during gas exposure, and obtained as a function of exposure time to 1%CO in air is shown in Fig. 4. Both the relative increase in transmittance and the rate of response decreases with the film heat treatment temperature, due to the progress and evolution of film densification during heat treatment, in agreement with the

Table 1. Variation of the position of the main Si—O vibration band in films heated at different temperatures.

Heat treatment temperature (°C)	Peak position of main Si—O vibration (cm^{-1})
500	1052
600	1053
700	1073
800	1077

FTIR measurements. 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 cobalt oxide nanocrystals in the SiO_2 matrix. However other factors such as cobalt oxide nanocrystals size and matrix stochiometry may play a role in the observed effect. Figure 4 also shows a saturation time of about 120 min in agreement with the data reported by Ando et al. [7]. The reversibility is generally good even if a complete recover of the original baseline is achieved over long time.

Conclusions

Nanoporous SiO_2 glass films doped with cobalt oxide nanocrystals were obtained by the sol-gel technique. Co_3O_4 nanocrystals precipitate in silica films at 500°C and grow with heat treatment temperature, while at 900°C cobalt silicate is formed. For films doped with Co_3O_4 nanocrystals the optical transmittance increases reversibly upon exposure to CO over the $250 < \lambda < 800$ nm range.

Respect to the previous results obtained on NiO nanocomposites [3], which showed almost the same increase in transmittance all over the $250 < \lambda < 850$ nm range, the Co_3O_4 nanocrystals doped silica films showed a maximum around 400 nm roughly corresponding to the absorption band of the Co^{3+} center in the octahedral sublattices of the Co_3O_4 spinel. The increase in transmittance and the rate of transmittance change were very similar for both nanocomposites films, while the response of NiO doped films was faster. Experiments are in course to understand the nature of the observed differences.

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