**Nanodimensioned NiO in Porous $SiO_2$ Films for CO Sensing using Optical Transmittance Modulation**

Michael Post[a], Alessandro Martucci[b] and Massimo Guglielmi[b]

[a] ICPET, National Research Council of Canada, Ottawa, Ontario, Canada
[b] Dipartimento di Ingegneria Mechanica S. Materiali, Università di Padova, Italy

Overview. $SiO_2$ sol-gel films doped with NiO nanocrystals with 2.5nm diameter have been fabricated. For the sol-gel process, a bifunctional ligand was used, with an amine group for coordinating the Ni ions and a siloxane group for anchoring the metal complex moiety to the silicate matrix. The NiO nanocrystals precipitate at 500°C while the film is still porous. The nanocomposite films showed a reversible change in the optical transmittance in the Vis-NIR range when exposed to CO. The effects of the residual porosity, testing temperature and gas concentration will be reported.

Introduction. Nanocomposites which possess sensor functionality are an expanding area of focus for optical gas sensing applications. Earlier reported data on the optical transmittance of nano-particles or thin films has shown that modulation of optical density can accompany exposure to some gases [1,2]. In particular it was found that NiO, $Co_3O_4$ and $Mn_3O_4$ thin films, at temperatures around 250-350°C, showed a reversible decrease in Vis-NIR absorbance when exposed to CO. The CO-sensitive decrease of the absorbance of NiO films can be ascribed, [2], to a decrease of positive hole density in NiO due to a decrease in oxygen anion density on the surface of NiO during the catalytic oxidation of CO. As the gas sensing mechanism is surface related, an increase in the specific surface area of the functional oxide is expected to enhance the sensing effect. In order to increase the surface area of NiO in this work, porous $SiO_2$ sol-gel films were synthesized with doped and homogeneously dispersed NiO nano-crystals. The optical transmittance of the $SiO_2$/NiO nanocomposite films, when exposed to CO, have been determined as a function of gas concentration, film temperature and $SiO_2$ matrix porosity/density.

Experimental. The nanocomposites were prepared by mixing a matrix solution of tetraethylorthosilicate (TEOS) and methyltriethoxysilane (MTES) as $SiO_2$ precursors, with a doping solution containing $NiCl_2$ as precursor for NiO particles. The bifunctional ligand was 3-(2–amino ethylamino)propyltrimethoxysilane (AEAPTMS). Films with a composition 60%$SiO_2$-40%NiO were deposited by dipping on Si or $SiO_2$ glass substrates and heated at 500, 700, 800 and 900 °C in air for 1 hour. A combination of techniques was used for characterisation. X-Ray diffraction (XRD) using $CuK_\alpha$ Ni filtered radiation, was used to determine phase purity and crystallite size from line broadening. From transmission electron microscopy (TEM) the average diameter of the NiO particles was measured from TEM images. Rutherford Backscattering Spectrometry (RBS) was used to evaluate the concentration profile of Si, Ni, O, and C in the film; the hydrogen content of the films was measured by Elastic Recoil Detection Analysis (ERDA). The film density was calculated by combining thickness data, obtained from profilometry, and the film dose from RBS and ERDA data. The CO sensing properties of the nanocomposite films grown on $SiO_2$ glass substrates were evaluated by measuring the variation of the optical transmittance of the films in the 300 - 800nm range, when exposed to 1, 0.1 and 0.01 vol% CO in air, with the film at temperatures between room temperature and 350°C. Details of this experimental apparatus are reported elsewhere [3].

Results & Discussion. The $SiO_2$/NiO composite films were shown to be of high quality by the combined characterisation techniques used. Film thicknesses were about 200nm with NiO particles, of diameter 2.5nm and with a narrow size distribution, uniformly dispersed in the $SiO_2$ matrix. Film density increases with the temperature of heat treatment, and in films heated at 500 °C it is about 30% less than for films heated at 900°C.

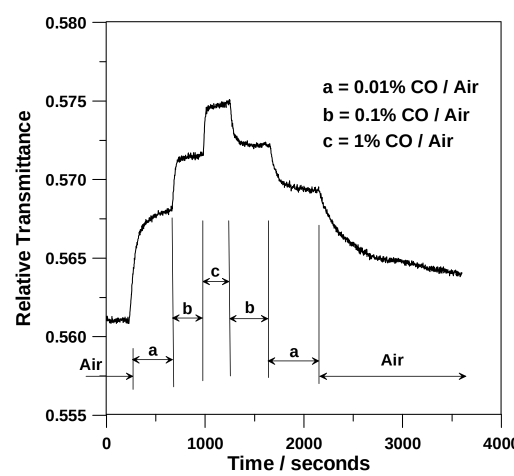


Figure. CO sensing response for nanoparticulate NiO in a porous $SiO_2$ matrix. Temperature 280°C; $\lambda$=650nm.

The optical transmittance of $SiO_2$/NiO films increased rapidly and reversibly upon exposure to CO over the 300-800 nm range at film temperatures higher than 200°C. In the Figure is shown this variation at $\lambda$=650nm for the 3 CO concentrations, demonstrating that the change in optical transmittance is proportional to the concentration of CO in air over a large dynamic range. Appreciable transmittance variations are detected even for CO concentrations as low as 0.01 vol%. Other parameters of the CO sensor response, such as temperature and wavelength dependence will be reported, as will the deleterious effect of increased densification of the films – which results in limiting the access of the CO *via* the film pore structure to the surfaces of the NiO nanoparticles.

Conclusions. Nanoporous $SiO_2$ glass films doped with uniformly distributed NiO nanocrystals have been obtained by the sol-gel technique. The films have NiO nano-crystals and a residual porosity which facilitates penetration of the gas phase into the film and allows the reaction between the surface of the NiO particles dispersed in the glass matrix and CO gas. For $T$>200°C the optical transmittance of $SiO_2$/NiO films increases rapidly and reversibly upon exposure to CO in air over the 300-800 nm wavelength range and is proportional to the CO concentration. The CO gas sensing properties depend both on the film temperature and the residual porosity.

References.

1. K. Yasumoto, N. Koshizaki, K. Suga, in: J.D. Mackenzie (ed.), Proc. SPIE **1758**, 604, (1992).
2. M. Ando, T. Kobayashi, M. Haruta, *Catalysis Today*, **36**, 135, (1997).
3. M. Post, J. Yao, *MRS. Symp. Proc.* **403**, 533, (1996).