Nanostructured thin oxide films for optical gas sensing

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Optical gas sensors, thanks to their relative simplicity, reliability, compactness, ruggedness, robustness, resistance to electromagnetic interference, and the possibility to operate at room temperature, have recently emerged as a very promising alternative to the gas detectors based on electrical properties that currently dominate the market.

The paper reviews recent results in the development of nanostructured photonic sensors made of highly transparent metallic oxides with different compositions and morphological characteristics. Special nanostructured coatings of ZnO, TiO_2, or WO_3 were applied on various optical substrates for use in m-line or Mach–Zehnder interferometers. We performed Pulsed Laser Deposition (PLD) with a KrF* (248 nm, $\tau \leq 7$ ns) excimer laser source. The coatings (of a few tens of nm up to a few microns in thickness) were applied in (0.1 – 40) Pa oxygen, while the substrates were either maintained at RT or heated at a constant rate (of 5^oC/min) up to 500^oC. In alternative experiments, we deposited nanostructures doped with (0,5-3% at.) Au, Pd, Pt, or Ag nanoparticles. Some undoped structures were partially covered with Au nanoclusters. The use of noble metal nanoclusters as either dopants or surface clusters has been predicted to help boost gas-sensing efficiency by catalyzing specific reactions with the detected gases.

All structures were optically tested by UV-VIS spectrophotometry. Transmissions as high as 90% and values of the refractive/extinction indexes quite close to tabulated ones were found. Several complementary investigation techniques were applied, including X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), and Atomic Force Microscopy (AFM).

The coatings were optimized for gas sensor applications based on gasochromic mechanisms. For optical interrogation, we used the m-line setup, a method that can detect slight variations ($\Delta n=10^{-4}$) in the refractive index. We proved that under optimum processing conditions, the obtained nanostructures were able to detect hydrocarbons traces down to 100 ppm butane or propane in a mixture with nitrogen or dry air [1]. (Note that 800 ppm is the maximum daily exposure authorized under U.S. Federal Regulations.) We observed that nanostructure doping with noble metal nanoparticles resulted in a slight decrease of detection sensitivity, which was probably due to enhanced light diffusion, scattering, and/or absorption. Coverage with nanoclusters strongly enhanced sensitivity by 2-3 times as compared with simple or doped structures.

The reproducibility of all data was very good. According to AFM, SEM, and XPS results, prolonged contact with the gas mixture under investigation did not detectably contaminate either the surface composition or the morphology of the nanostructured sensors.

[1] T. Mazingue, L. Escoubas, L. Spalluto, F. Flory, G. Socol, C. Ristoscu, E. Axente, S. Grigorescu, I.N. Mihailescu, N. A. Vainos, Journal of Applied Physics **98**, 074312 (2005)