WAVEGUIDE RAMAN SPECTROSCOPY AND OPTICAL STUDIES OF UNDOPED AND CdS-DOPED SOL-GEL DERIVED ZrO_2 THIN FILMS

G. Ehrhart[1], B.Capoen[2], M.Bouazaoui[2] and S. Turrell[1*]

[1]Laboratoire de Spectrochimie Infrarouge et Raman (CNRS, UMR 8516);
E-MAIL: sylvia.turrell@univ-lille1.fr and
[2]Laboratoire de Physique des Lasers, Atomes et Molécules (CNRS, UMR 8523) ;
Centre d'Etudes et de Recherches Lasers et Applications (CERLA), Université des Sciences et Technologies de Lille, F-59655 Villeneuve d'Ascq, France

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Abstract : This communication presents waveguide Raman spectra of ZrO_2 thin films. The evolution of structural and optical properties is studied as a function of increased annealing temperatures and doping with CdS nanoparticles.

Zirconium and titanium oxide materials are of wide interest because of their excellent mechanical, thermal and optical properties. In particular, ZrO_2 with its low optical losses and very high linear refractive index is an excellent candidate for integrated devices for all-optical switching. Moreover, doping ZrO_2 with semiconductor nanoparticles such as CdS or PbS can confer an appreciable enhancement of the third order optical non-linearity, thus yielding glasses of interest for active components for telecommunications [1-2]. However, since optical properties are closely related to the microstructure, an understanding of the relation between the two is essential for every preparation technique. To date, very few publications have been devoted to structural studies of nanoparticle-doped ZrO_2 films.

In the present work, polymeric solutions of ZrO_2 were synthesized by hydrolysis of zirconium n-propoxide in n-propanol, acetic acid, water and methanol. The resulting sols are colorless and stable for at least one month. This solution was filtered and dip-coated on pure silica substrates. Heat treatments under oxygen flow yielded homogeneous amorphous thin films. Five successive coatings provided crack-free two-mode waveguides which were used for optical loss measurements and waveguide Raman spectroscopic (WRS) studies. All optical measurements were performed using the prism coupling technique. M-lines spectra of the films (using λ= 633 nm) showed a gradual increase of the refractive index from 1.80 at 300°C to 1.93 at 500°C. The corresponding film thicknesses were observed to decrease from 100 to 80 nm. Finally, attenuation measurements demonstrated optical losses of less than 1 dB/cm.

Figure 1 displays representative Stokes WRS spectra of undoped ZrO_2 waveguides for annealing temperatures varying from 300°C to 1000°C. At 300°C the vitreous structure is evidenced by the boson peak at 96 cm^{-1} and bands centered around 460 cm^{-1} and 550 cm^{-1} assigned to vibrations of matrix Zr-O-Zr groups and Zr-O ring structures, respectively. For temperatures up to 500°C, the shifts of these bands

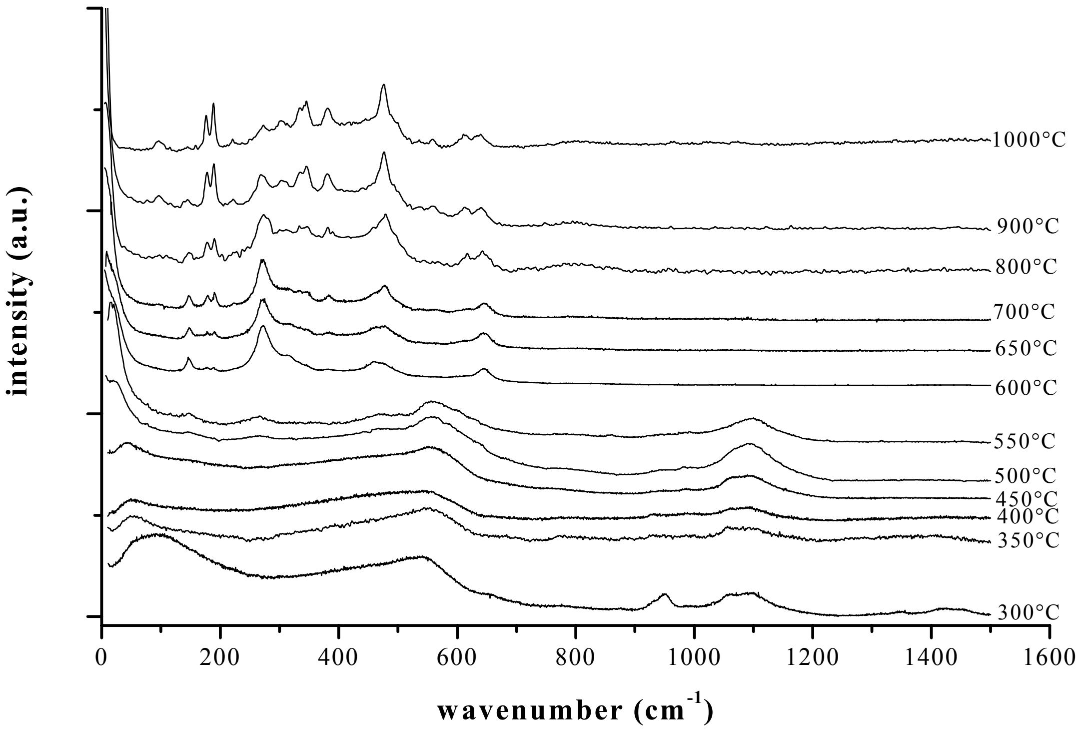

Figure 1: Waveguide Raman spectra for ZrO_2 at varying annealing temperatures.

to lower frequencies, as well as the gradual changes in relative intensities of the peaks around 1100 cm^{-1} attributed to Zr - non-bridging-oxygen vibrations attest to the structural changes which accompany densification. A beginning of crystallisation into a tetragonal phase [3,4] is observed around 500°C. The sharp low-frequency band which replaces the boson peak allows an estimation of about 5nm for the average size of the crystallites [5]. This crystal phase is metastable and from 700°C to 900°C the spectra show a gradual transformation into the more stable monoclinic structure [6]. In parallel, we have demonstrated that, although heat treatment is essential for obtaining optical-quality thin films, annealing at temperatures above 500°C results in decreased film quality due to the appearance of microcrystals. Preliminary WRS results on ZrO_2 films doped with CdS nanoparticles and annealed at 300°C, show changes for the Zr – non-bridging oxygen vibrational bands. Interpretations are made of the nature of the interactions between the matrix and the dopant species.

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