Available online at www.sciencedirect.com
SCIENCE DIRECT®

Thin Solid Films 496 (2006) 227 – 233

thin solid films

www.elsevier.com/locate/tsf

Structural and optical properties of *n*-propoxide sol–gel derived ZrO_2 thin films

G. Ehrhart [a,*], B. Capoen [b], O. Robbe [a], Ph. Boy [c], S. Turrell [a], M. Bouazaoui [b]

[a] *Laboratoire de Spectrochimie Infrarouge et Raman (CNRS, UMR 8516), Bât. C-5, France*
[b] *Laboratoire de Physique des Lasers, Atomes et Molécules (CNRS, UMR 8523), Bât. P-5, Centre d'Etudes et de Recherches Lasers et Applications (CERLA-FR CNRS 2416), Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France*
[c] *Sol–Gel Laboratory, CEA/Le Ripault, BP 16 37260 Monts, France*

Received 11 April 2005; received in revised form 23 June 2005; accepted 18 August 2005
Available online 19 September 2005

Abstract

In this work, we present a sol–gel method for the preparation of zirconia films. Using zirconium *n*-propoxide as the starting precursor, a ZrO_2 sol has been synthesized that remains stable for several months. Thin films were deposited using the dip-coating method. The structural characterization was performed using waveguide Raman spectroscopy. The films present an amorphous phase up to an annealing temperature of 400 °C. Both monoclinic and tetragonal phases were obtained for annealing temperatures higher than 450 °C. The proportions of these two phases were calculated from the Raman spectra and the size of the crystallites was evaluated using the low-wavenumber Raman band. The optical properties were characterized by the m-lines technique ($n=1.96$) and UV–visible spectroscopy. The optical losses for a TE_0 mode were measured to be 0.29 ± 0.03 dB cm^{-1} for a sample annealed at 400 °C. To optimize the protocol for thermal annealing, a powder obtained from a dried sol was characterized by Thermal Gravimetric Analysis. Rutherford Back Scattering was employed to determine the chemical composition and the stoichiometry of the zirconia films.

Keywords: Sol–gel; Zirconia; Raman scattering; Optical properties

1. Introduction

Zirconium oxide glasses are widely studied for optical applications due to their high refractive indices (greater than 2 in dense phases) and transparency in the near-UV–visible. These materials are considered to be among the most chemically and photochemically stable and their excellent mechanical, electrical, thermal and optical properties make them ideal media for applications in photonics [1]. In the amorphous phase, such oxides are good candidates for waveguide applications, as they can be deposited on silicate substrates.

Another consideration is that these films can subsequently be doped with semiconductor nanoparticles (CdS, PbS) [2,3] in order to obtain non-linear optical properties [4]. In fact, the increase of the non-linear refractive index of waveguides would make it possible to fabricate components like all-optical switches. In principle, the sol–gel process is ideal for obtaining such materials, as it presents numerous advantages like low-cost and low-temperature processing, easy coating and versatile doping, not to mention the yield of homogeneous and high purity materials with controlled stoichiometry. However, for many systems a great deal of progress must be made concerning the stabilization of the sol as well as with the doping efficiency.

Zirconia has already been used for the preparation of sol–gel thin films [5–9] for waveguide applications. However it was found that the sol based on zirconyl chloride octahydrate yielded thin films of much poorer optical quality than those with zirconium alkoxides precursors. Unfortunately these latter are very sensitive to humidity in the laboratory, thus rendering syntheses extremely difficult.

The high reactivity of zirconium alkoxides can be reduced by adding a stabilizing agent such as β-diketone [8] or acetic

* Corresponding author.
E-mail address: gilles.ehrhart@ed.univ-lille1.fr (G. Ehrhart).

0040-6090/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2005.08.309

acid [9]. In the present work, we present a sol–gel method, using acetic acid as the stabilizer, which yields a very stable sol. ZrO_2 thin films obtained by dip-coating are characterized using a variety of physical and optical techniques, in order to study the evolution of the properties of the material as a function of the temperature of heat-treatment.

2. Experimental details

2.1. Sample preparation

The synthesis of the ZrO_2 sol is described in Fig. 1. First, zirconium *n*-propoxide $Zr(OC_3H_7)_4$ at 70 wt.% in *n*-propanol (Fluka) is mixed with acetic acid (Aldrich 99.7+%, ACS reagent) in a molar ratio (acetic acid/Zr)=6. As suggested by Balamurugan et al. [9], a large excess of distilled water was then introduced into the mixture in order to complete the hydrolysis until a clear and light yellow transparent sol was obtained. The viscosity was then adjusted to 2.6 cP by the addition of methanol (Aldrich 99.8+%, ACS reagent) and absolute ethanol (Alcohol Society Flourent-Brabant). The final concentration of zirconium in the sol was about 0.6 mol l^{-1}. If kept in a closed bottle at ambient temperature this sol was stable for a long period. In fact, the viscosity remains stable and there is no trace of precipitation for 60 days. After this time the viscosity increases slowly until gelification of the sol occurs around 4 months later.

The ZrO_2 polymeric sol was aged for two weeks and passed through a 0.2 μm filter. The films were deposited in a clean room to preserve a good optical quality of ZrO_2. Different kinds of substrates were used in the present work such as SiO_2/Si wafers and pure silica or soda glass (ISO 8037/1) slides, depending on the heat-treatment temperature and the methods used for characterization. Prior to coating, the substrates were cleaned with optical detergent and washed with distilled water and ethanol. The films were deposited on both sides of the substrate using the dip-coating technique. In order to remove organic residues, the films were then heat-treated in oxygen atmosphere in a tubular furnace. This process can be repeated to make multilayer films (Fig. 1). In order to identify the various phase transitions, the films were then annealed for about 1 h at various temperatures ranging from 300 to 1000 °C.

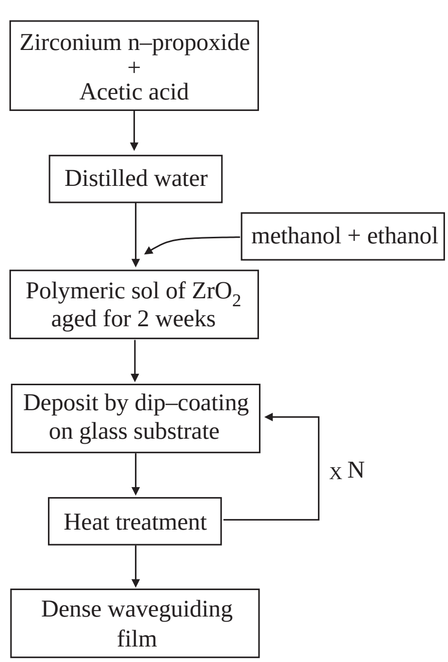

Fig. 1. Flow diagram for the preparation of the ZrO_2 thin films using the sol–gel method.

2.2. Characterization

Thermal Gravimetric Analysis (TGA) measurements were performed with a Netzch STA 409 apparatus. For these studies a powder obtained from a dried ZrO_2 sol was heated up to 800 °C at a rate of 1 °C min^{-1} and with steps of 1 h in a helium gas flow. The molecular structure of the material was characterized after each annealing treatment by waveguide Raman Spectroscopy. Using the prism-coupling technique, the excitation radiation from the 514.5 nm line of an Ar-ion laser was injected into the waveguide. The VV polarized light scattered from the film was then collected and analyzed using a T64000 spectrometer (Jobin-Yvon). Optical losses were measured using a method based on the detection of the light scattered from the waveguides when excited with the 632.8 nm wavelength line of a He–Ne laser. The image of the scattered light was collected by a CCD camera and treated numerically. The refractive indices and the thicknesses of the films were measured using the m-lines technique with an excitation at 632.8 nm. The transmission measurements of ZrO_2 thin films were obtained with a Varian Cary 1 UV–visible spectrophotometer. Rutherford Back Scattering (RBS) was used to check the chemical and stoichiometric composition of the layers. For these measurements the samples were put in a 2.4 MeV helium beam generated by a Van de Graff accelerator.

3. Results and discussion

3.1. TGA and Raman spectroscopy

Fig. 2 presents the evolution of mass losses of a ZrO_2 gel powder measured by TGA. One hour steps at different temperatures were programmed to reproduce the heat-treatment process on a film. Up to 300 °C we observe a large weight loss corresponding to the departure of ethanol, methanol and water. However, it is obvious that all the organic components are not evacuated at this temperature, as the sample mass loss continues at temperatures greater than 300 °C.

Fig. 3a presents Raman spectra of the sol and of a ZrO_2 waveguide annealed at different temperatures. This waveguide was a one layer film of 0.1 μm thickness deposited on a pure silica substrate. After annealing at 300 °C, several bands remain in the spectral region of ν C–O vibrations (1350, 1421 and 1450 cm^{-1}). In addition, the COO^- rocking and deformation modes are apparent as a shoulder around 650 cm^{-1} [10]. These bands confirm the presence of a metallic acetate salt which comes from the complexing of zirconium