Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 145 (2015) 145–154

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Microstructure and optical dispersion characterization of nanocomposite sol–gel TiO_2–SiO_2 thin films with different compositions

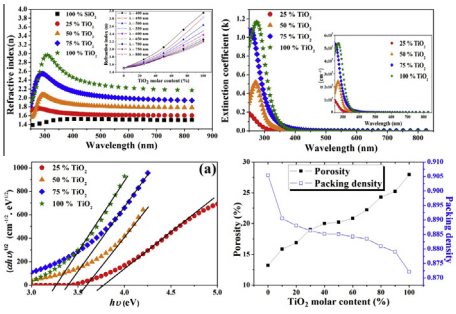
S. Kermadi [a,*], N. Agoudjil [b], S. Sali [a], L. Zougar [a], M. Boumaour [a], L. Broch [c], A. En Naciri [c], F. Placido [d]

[a] CRTSE- Division DDCS 02, Bd Dr Frantz Fanon BP: 140, les 07 merveilles, 16038 Algiers, Algeria
[b] Department of Chemistry, Laboratory of Physico-Chemistry of Materials and Environment USTHB University, BO Box 32 El Alia, 16111 Algiers, Algeria
[c] Laboratoire de Chimie Physique-Approche Multi-échelle des milieux complexes (LCP-A2MC, EA4632), Université de Lorraine, 1 Boulevard Dominique François Arago, 57070 METZ Technopôle, France
[d] Thin Film Centre, University of the West of Scotland, Paisley, PA1 2BE, SUPA (Scottish Universities Physics Alliance), Scotland, United Kingdom

HIGHLIGHTS

- Nanocomposites TiO_2–SiO_2 thin films were prepared by sol–gel dip-coating process.
- The composition-dependent structural and optical properties were examined.
- The refractive index dispersion fit well the Wemple-DiDomenico single oscillator model.
- The optical parameters were tunable by a simple control on the film composition.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 June 2014
Received in revised form 24 February 2015
Accepted 26 February 2015
Available online 5 March 2015

Keywords:
Sol–gel
Nanocomposite thin films
Dispersion parameters
Optical conductivity
Energy loss

ABSTRACT

Nanocomposite TiO_2–SiO_2 thin films with different compositions (from 0 to 100 mol% TiO_2) were deposited by sol–gel dip-coating method on silicon substrate. Crystal structure, chemical bonding configuration, composition and morphology evolutions with composition were followed by Raman scattering, Fourier transform infrared spectroscopy, energy-dispersive X-ray spectroscopy and scanning electron microscopy respectively. The refractive index and the extinction coefficient were derived in a broad band wavelength (250–900 nm) from spectroscopic ellipsometry data with high accuracy and correlated with composition and microstructure. Results showed an anatase structure for 100% TiO_2 with a grain size in 6–10 nm range. Whereas, the inclusion of SiO_2 enlarges the optical band gap and suppresses the grain growth up to 4 nm in size. High TiO_2 dispersion in SiO_2 matrix was observed for all mixed materials. The refractive index (at $\lambda = 600$ nm) increases linearly with composition from 1.48 (in 100% SiO_2) to 2.22 (in 100% TiO_2) leading to lower dense material, its dispersion being discussed in terms of the Wemple-DiDomenico single oscillator model. Hence, the optical parameters, such optical dispersion energies E_0 and E_d, the average oscillators, strength S_0 and wavelength λ_0 and the ratio of the carrier concentration to the effective mass N/m^* have been derived. The analysis revealed a strong dependence on composition and structure. The optical response was also investigated in term of complex optical conductivity (σ) and both volume and surface energy loss functions (*VELF* and *SELF*).

© 2015 Elsevier B.V. All rights reserved.

* Corresponding author. Tel./fax: +213 21433511.
E-mail address: kermadisalim@yahoo.fr (S. Kermadi).

http://dx.doi.org/10.1016/j.saa.2015.02.110
1386-1425/© 2015 Elsevier B.V. All rights reserved.

Introduction

Combining various different compounds (composite materials) has attracted a great deal of attention in the recent years, in the goal to achieve novel materials with structural, optical or electrical properties different from those of the individual pure materials. By now, various combinations (binary, ternary or more) have been investigated using a variety of inorganic oxides such as TiO_2, SiO_2, ZrO_2, CaO, CeO_2, MgO and Al_2O_3 [1–6].

Because of the large difference between their optical constants of band gap and refractive index, TiO_2 and SiO_2 appear well suited for these purposes and several advantages can be derived from their binary composite. Both TiO_2 and SiO_2 are typical optical thin films with high transparency and low absorption in visible and near infrared regions. Furthermore, as they are low cost, safe and abundant materials with high chemical, thermal and mechanical stabilities, they have been widely used for various optical applications, such as antireflective coatings [6,7], high reflecting, mirrors [8], photocatalyst [9] and integrated optical waveguides [10].

To our knowledge, Although many studies have investigated TiO_2-SiO_2 composites films [8,9,11,12], detailed correlation between microstructure and optical parameters such as dielectric functions or dispersion parameters have not yet been reported.

The aim of this work was to investigate the influence of the composition nanocomposite TiO_2 -SiO_2 thin films on their microstructure, optical and electrical properties. For this purpose, films with different compositions as well as the single materials have been elaborated by a sol–gel process and dip-coated on (1 0 0) polished silicon. Structural and elementary characterizations were carried out with Raman and Fourier Transform Infrared Spectroscopy (FTIR) characterization respectively while the nanostructure was observed by Scanning Electron Microscopy (SEM). The optical properties were studied using spectroscopic ellipsometry (SE) in a large spectral range of 250–900 nm which represents the major motivation of our work.

Experimental

Silica coating sols were prepared by refluxing at 80 °C under stirring for 90 min a mixture of silicon tetraethoxide (TEOS) (TEOS, Aldrich 99.99%), propanol (Prolabo 99.5%) as solvent, H_2O as hydrolysis agent and HCl (Cheminova 37 wt%) as acid catalyst. The molar ratio of TEOS/2-Propanol/H_2O was 1:42:4. For Titania sols a mixture of titanium tetra-isopropoxide (TTIP, Fluka 99.99%), iso-propanol as solvent, acetylacetone (acacH, Aldrich 99%) as ligand, and water as hydrolysis agent and acetic acid as an acid catalyst were stirred under room temperature for 30 min with the molar ratio. The molar ratio of TTIP/2-Propanol/acacH/H_2O is 1:30.6:0.3:4. The sols for composite materials were prepared by mixing for 2 h the same sol prepared for single titania (with H_2O/TEOS equal to 2) with the same sol prepared for single silica (pre-refluxed only for 30 min) with different compositions (25, 50 and 75 mol%TiO_2). But the water silicon tetraethoxide molar ratio was kept equal to two in this case, and the sol was pre-refluxed only for 30 min.

The film deposition was carried out on silicon wafers by dipping-withdrawing at 50 mm/minute speed in an ambient atmosphere. Afterwards, the samples were dried at 100 °C followed by sintering in air at 500 °C for 1 h.

Characterization

The phase structure was investigated by micro-Raman spectrometer (Jobin–Yvon T64000) working in back-scattering configuration. The excitation line at $\lambda = 514.5$ nm was provided by Ar–Kr ion laser. The chemical structure identification was performed with FTIR Thermo Nicolet NEXUS 670. Scanning electronic microscope (SEM) (JEOL JSM-6360LV) equipped with energy-dispersive X-ray spectroscopy (EDS) was used to investigate the surface morphology and the composition. The relationship of ellipsometric angles with wavelength were recorded with a phase modulated spectroscopic ellipsometer (UVISEL, Horiba Scientific) at angle of 69.5° in the range of $\lambda = 250$ to $\lambda = 900$ nm with a step of 5 nm.

Results and discussion

Structural and morphological studies

Raman shift characterization

From Raman scattering spectra displayed in Fig. 1, we can observe only the active mode of silicon substrate located at 300, 425, 520, 617 and 660 cm^{-1} in 75% TiO_2 sample [13]. Similar spectra were obtained for 25% TiO_2, 50% TiO_2 and 100% SiO_2 films confirming the amorphous structure. The 100% TiO_2 spectra shows the appearance of other extra features assigned to the allowed active modes of anatase structure determined by Ohsaka et al. [14], A_{1g} (515 cm^{-1}), $2B_{1g}$ (399 and 519 cm^{-1}), $3E_g$ (144,197 and 640 cm^{-1}).

The absence of any peak corresponding to anatase phase in the mixed films attests to the homogeneous and regular dispersion of Ti and Si atoms in the mixed films. This is in agreement with other works reporting the growth of amorphous sol–gel TiO_2–SiO_2 films annealed at 400 °C for low SiO_2 concentrations around 25% mole [15].

FTIR characterization

To follow clearly the effect of the heat-treatment on film structure, FTIR spectra were recorded on unsupported materials (in KBr pellets) corresponding to as deposited and sintered films of each composition. From Fig. 2(a) in all composition of unsintered samples, one can observe a broad band between 3255 and 3386 cm^{-1} assigned to the fundamental stretching vibration of free or bonded hydroxyl groups belonging to adsorbed water, which are proved by a weak band at 1630 cm^{-1} [16]. The weak band at 2975 cm^{-1} is attributed to –C–H stretching vibration [17]. The bands at 1110, 1350, 1433 and 1543 cm^{-1} are assigned to wagging, rocking and scissoring of the $-CH_2$ vibration from acetyl and propoxide groups of organic compounds. However, those between 573 and 657 cm^{-1} are assigned to C–H deformation mode [18]. The bands below 445 cm^{-1} are assigned to stretching modes of Si–O and Ti–O vibrations [19]. Whereas the band at 740 cm^{-1} belongs to the Ti–O

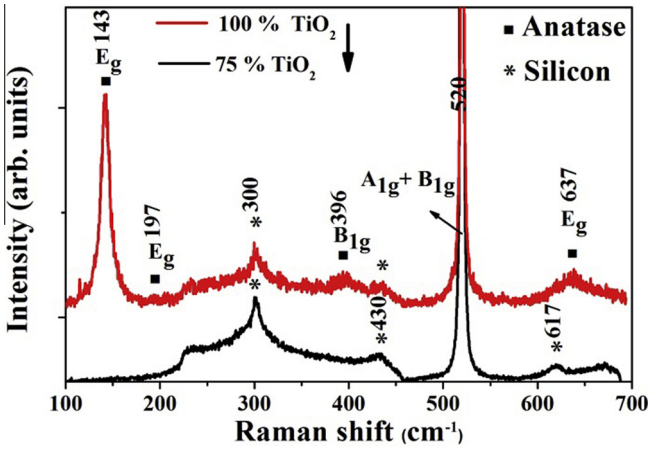


Fig. 1. Raman spectra of thin 75% TiO_2 and 100% TiO_2 films on Si substrate.

Download English Version:

https://daneshyari.com/en/article/1228969

Download Persian Version:

https://daneshyari.com/article/1228969

Daneshyari.com