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Full Length Article

Aluminosilicate glass thin films elaborated by pulsed laser deposition

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ABSTRACT

In the present work, we report the elaboration of aluminosilicate glass thin films by Pulsed Laser Deposition at various temperatures deposition. The amorphous nature of glass thin films was highlighted by Grazing Incidence X-Ray Diffraction and no nanocristallites were observed in the glassy matrix. Chemical analysis, obtained with X-ray Photoelectron Spectroscopy and Time of Flight Secondary Ion Mass Spectroscopy, showed a good transfer and homogeneous elementary distribution with of chemical species from the target to the film a. Structural studies performed by Infrared Spectroscopy showed that the substrate temperature plays an important role on the bonding configuration of the layers. A slight shift of Si-O modes to larger wavenumber was observed with the synthesis temperature, assigned to a more strained sub-oxide network. Finally, optical properties of thins film measured by Spectroscopic Ellipsometry are similar to those of the bulk aluminosilicate glass, which indicate a good deposition of aluminosilicate bulk glass.

1. Introduction

In the last three decades, the development of glassy materials as thin films has a growing interest due to their large domain of application. One of the main fields of application relates to the bioengineering industry with the development of bioactive glasses [1,2] allowing to improve tissue repair [3] or the creation of scaffolds for bone regeneration [4]. These biocompatible glass coatings may be deposited on polymeric substrates [5] or metallic implants [6] to promote fribovascular intergrowth and avoid the risk of inflammation or rejection [7]. They can also be used to develop biosensors [8].

Chalcogenide glasses are also widely studied as thin film for their optical properties with various applications such as infrared detectors, lenses [9,10], infrared optical waveguides [11,12] or photonic devices [13]. Chalcogenide glasses are also the active materials used for optical storage media [14,15] such as ReWritable Compact Disk (CD-RW), ReWritable Digital Versatile Disk (DVD-RW) or Phase-Change Random Access Memory (PRAM) [16]. The principle is based on the switching between amorphous and crystalline states induced by an increase in temperature (produced by during laser irradiation). More recently, chalcogenide glassy thin films were also developed for photovoltaic solar cell materials [17]. These two latter glass families have therefore been extensively studied in the literature in the recent years. In the present work, we focus on aluminosilicate glasses deposited as thin films, which have been much less studied. The aluminosilicate glasses are known to withstand high temperatures and have a high resistance to thermal shock, mechanical shock, chemical attack and oxygen permeation [18]. They are employed in order to realize combustion tubes, gauges glasses able to work under extreme conditions, tungsten halogen lamps operated at high temperatures [19] or as sealing glass in Solid Oxide Fuel Cells (SOFC) [20]. They can be used also as glass for flat panel displays or as protective alloys coating to avoid oxidation at high temperatures [18]. Deposited as thin films, they can be attractive for various applications. For example, the alkaline earth aluminosilicate glasses can be used as **i**) protective coating on metals or alloys in reactors for high temperature and pressure application [21]; **ii**) dielectric layer in the packaging of semiconductors (the electrical resistance is comparable, or even better in some cases, than the vitreous silica [22]); **iii)** planar waveguide or as phosphor layers when doped with rare earths in the optic devices [23]; **iv)** sealing glass in miniaturized SOFC technology; and **v)** gas barrier in plastic packaging especially to replace Al-coated polymers [24]. Alkali aluminosilicate glasses, due to their

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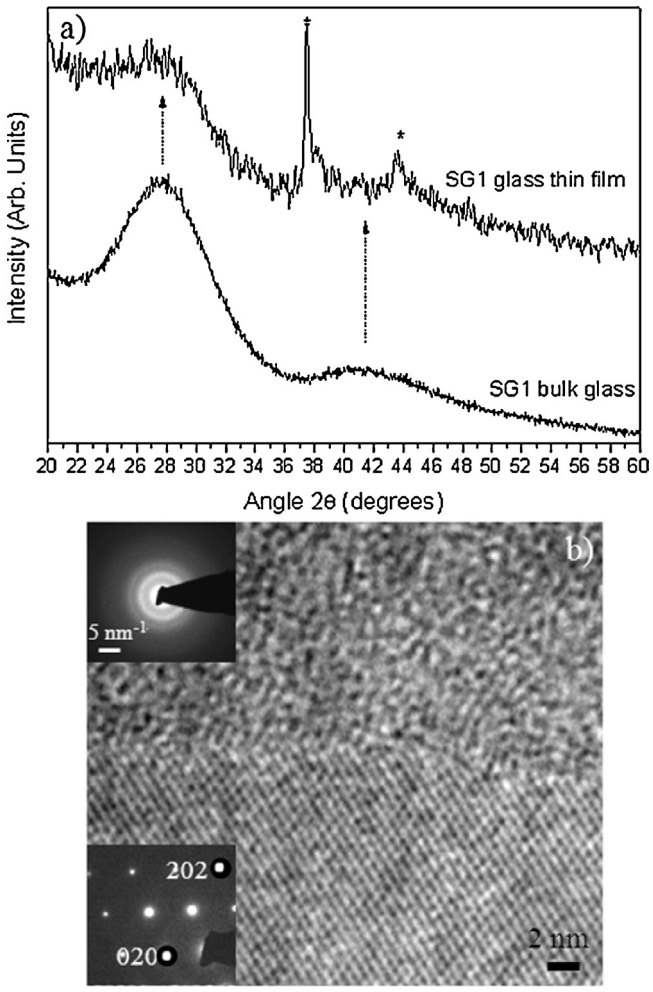

Fig. 1. a) GI-XRD patterns of SG1 glass target and SG1 thin film synthetized at 600 °C; b) TEM image and corresponding ED patterns, of SG1 glass thin film deposited on silicon substrate, showing the interface between the amorphous glass and the Si substrate along [101] zone axis.

high scratch-resistance, are especially suitable for protective coating on active materials subject to high stresses [25].

To the best of your knowledge, there are few studies that dealt with the synthesis of these aluminosilicate glasses as thin films. For example, the main techniques used are the sol-gel route [26,27], the magnetron sputtering [28], the Chemical Vapor Deposition (CVD) [29] or the pulsed microwave plasma [30]. In the present paper, we propose a study on the alternative synthesis of these glass thin films by a Pulsed Laser Deposition (PLD). It is well-known that the advantage of this technique is much better transfer of the stoichiometry of a multicomponent target to a film deposited on a substrate [31]. This technique based on plasma condensation, presents the advantage of achieving denser films compared to the sol-gel method (whose porosity is induced by the removal of the solvent as well as the unreacted organic groups), which may be advantageous for the implementation of a protective layer.

We have characterized the glass thin films deposited on silicon substrate by various methods such as Grazing Incidence X-Ray Diffraction (GI-XRD), Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS), Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR), Atomic Force Microscopy (AFM) and Spectroscopic Ellipsometry (SE).

2. Experimental section

An aluminosilicate glass (SG1), with the composition (% mol) 47.6 SiO_2 –28.6 BaO – 14.3 CaO – 9.5 Al_2O_3 was prepared from $BaCO_3$, $Al(OH)_3$, $CaCO_3$ and SiO_2 [32]. These starting materials were weighed, mixed, calcined at 1100 °C, and then melted in a 90Pt-10Rh crucible at 1600 °C for 2 h. The glass was obtained by pouring the melt on a stainless steel plate. The PLD target, 1 inch diameter, was shaped by isostatic pressing at P = 180 MPa and then densified by heat treatment at 750 °C for 5 h.

Glass thin films were synthetized by PLD technique on (100)-oriented silicon substrate. Before the deposition step, polished silicon substrates were firstly ultrasonically cleaned in acetone then in ethanol for 5 min. Each substrate was attached to a heating plate using silver paste. Deposits were obtained using a KrF excimer laser (Compex Pro, λ = 248 nm). Based on our previous work [33], the laser pulse rate and the fluence were 5 Hz and 2 J/cm^2, respectively. The target-substrate distance was fixed to d = 5.5 cm to avoid the formation of Ca/Ba-rich droplets on the film [33]. All films were deposited with 2.10^4 laser pulses and under dynamical vacuum controlled at 10^{-5} mbar. The deposits were performed at several temperatures (200 °C, 400 °C and 600 °C) using an halogen lamp for heating the sample holder.

The structural characterization of the films was performed using a Rigaku SmartLab high resolution X-ray diffractometer equipped with a 9 kW rotating anode X-ray generator ($\lambda_{K_{\alpha 1}}$ = 1.54059 nm). Thin films were studied under grazing incidence mode with a grazing angle of 2°. The scans were performed in the range of 20°- 60°, with a step size of 0.02° and with a speed of 1°/min.

Observations were performed by TEM on an FEI Technai G220 microscope. Cross-sections were prepared by Focused Ions Beam (FIB). The images and diffraction patterns were directly recorded on a CCD camera.

The surface morphology of the thin films was investigated using an AFM (MultiMode, Bruker) working under environmental conditions. AFM measurements were performed in contact mode using silicon nitride (Si_3N_4) tips.

ATR-FTIR experiments were carried out in the 1200–700 cm^{-1} region with a spectral resolution of 2 cm^{-1} on a Shimadzu IR Prestige-21 spectrometer equipped with a germanium prism.

XPS analyses were realized with a Kratos Axis Ultra DLD (Kratos Analytical, U.K.) spectrometer using a monochromatic Al Kα source (1486.69 eV). 150 W of power was applied to the X-ray anode. The instrument work function was calibrated to give a Binding Energy (BE) of 83.95 eV for the Au $4f_{7/2}$ line for metallic gold, and the spectrometer dispersion was adjusted to give a BE of 392.63 eV for the Cu $2p_{3/2}$ line of metallic copper. The pressure in the analysis chamber during XPS analysis was in the 10^{-9} mbar range. All spectra were recorded at a 90° take-off angle. Survey spectra were recorded with 1 eV step and 160 eV analyzer pass energy and the high-resolution regions with 0.1 eV step and 40 eV pass energy. In both cases, we have employed the hybrid lens mode and the charge compensation. XPS spectra were analyzed using CasaXPS software. All spectra were rescaled in binding energy by fixing the Ba $3d_{5/2}$ peak of the different samples at 780.5 eV.

ToF-SIMS experiments were performed using a TOF SIMS 5 spectrometer from Iontof. The non-interlaced dual beam mode was used for depth profiling with a 25 keV analysis Bi^+ gun alterning with a 1 kV O_2^+ gun for sputtering. The bismuth primary ion source delivered a 1 pA current over an (100 μm × 100 μm) area. The Bi^+ analysis raster was centered in the (300 μm × 300 μm) O_2^+ crater. The oxygen current was 240 nA, and both ion beams hit the surface at an angle of 45°. Positive ion signals were recorded and followed with the profiles of ^{27}Al, ^{28}Si, ^{40}Ca and ^{138}Ba.

The thicknesses of thin films were measured by ellipsometric spectroscopy at room temperature using a phase-modulated ellip-