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Pulsed laser deposited alumino-silicate thin films and amorphous chalcogenide/alumino-silicate structures

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ABSTRACT

Alumino-silicate coatings and structures formed from alumino-silicate and amorphous chalcogenide submicrometer layers were prepared by pulsed laser deposition. Fabricated thin films were characterized in terms of their structure, morphology, topography, chemical composition, optical properties, and basic anticorrosive functionality. Prepared coatings are amorphous, smooth, without micrometer-sized droplets, with chemical composition close to parent targets. Spectral dependencies of refractive indices and extinction coefficients were derived from variable angle spectroscopic ellipsometry data. Amorphous chalcogenide/alumino-silicate structures present large refractive index differences of individual layers ($\Delta n \sim 1.2$ at 1550 nm) which could be useful for optical systems working at infrared telecommunication band wavelengths. Basic anticorrosion data of alumino-silicate layers show promising anticorrosion behavior.

1. Introduction

Silicon-based ceramics, being represented by silicon carbide and silicon nitride, are widely studied for high-temperature applications such as combustion systems and heat exchangers. At high temperatures, silicon-based ceramics naturally form a protective SiO_2 layer at the surface, which provides effective passivation of the material against dry, oxidizing atmosphere. On the other hand, the surface SiO_2 layer can be degraded and finally destroyed by the presence of water vapor or alkali salts. To eliminate the problem of hot corrosion, environmental barrier coatings, in other words additional protective coatings, are needed for effective protection of silicon-based ceramics [1–6].

Several different coating systems were investigated to protect silicon-based ceramics, for example alumina, zirconia or alumino-silicates. Alumina and zirconia possess excellent corrosion resistance, but both of them differ substantially in the coefficient of thermal expansion when compared with silicon-based ceramics to be protected [2]. Alumino-silicate coatings were shown to be suitable protecting layers having a coefficient of thermal expansion reasonably close to the underlying ceramics. Moreover, such coatings have high-temperature strength, thermal shock resistance and creep resistance, low thermal conductivity and remarkable chemical stability [2,5,6].

Inspecting the Al_2O_3–SiO_2 phase diagram, a dramatic increase in refractoriness or temperature resistance is observed at the composition of the incongruently melting intermediate compound mullite with ideal stoichiometry $3Al_2O_3$–$2SiO_2$. This is why mullite is a subject of research in the field of silicon-based protective coatings discussed above. It should be noted that the term mullite is often used to describe more generally the entire range of oxide solid solutions with the general formula $Al_2[Al_{2+2x}Si_{2-2x}]O_{10-x}$, where x is a stoichiometry factor describing the oxygen vacancy concentration in the material [3–5].

In addition to high-temperature protecting layer applications, alumino-silicates could be useful for classical anticorrosive thermally-stable coatings similar to spinels or perovskites [7,8]. It is worthy to mention also the potential use of alumino-silicate coatings as adhesion enhancing layers for organic coatings on inorganic substrates.

Finally, due to the expected lower values of refractive indices in comparison with amorphous chalcogenides, it is of interest to use alumino-silicate thin films as a low refractive index layer in multilayered

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optical systems, potentially useful in mirrors/planar laser cavities designated for infrared telecommunication bands [9–11].

In principle, different deposition techniques can be used for the fabrication of thin alumino-silicate (mullite) coatings: chemical vapor deposition [2,12,13], plasma spraying [5], dual-source metal plasma immersion [6], sol–gel [14], pulsed laser deposition (PLD) [4,15,16], etc.; each of them possessing its own advantages and disadvantages. The PLD technique seems to be favorable according to its simplicity, easy control of the process, often stoichiometric transfer of the target material to the films, and possibility to fabricate multilayered structures or films of unusual compositions [17–21].

The PLD technique for mullite coating preparation described in the literature available used pulsed CO_2 laser operating at 10.6 μm with 170 μs pulses only [4,15,16]. On the other hand, classical PLD systems employ UV pulsed lasers with ns pulses.

The aim of this work is to use the classical UV PLD system for the preparation of alumino-silicate thin films and to describe their characteristics in terms of the structure (by using X-ray diffraction), composition (via energy-dispersive X-ray analysis), morphology and topography (with scanning electron and atomic force microscopy, respectively), optical properties (employing variable angle spectroscopic ellipsometry, VASE), element depth profiles performed by nano secondary ion mass spectrometry, and basic anticorrosive properties. As first step for fabrication of optical structures for infrared telecommunication bands, double or triple layers (alumino-silicate/amorphous chalcogenide double layers or alumino-silicate/amorphous chalcogenide/alumino-silicate triple layers) are fabricated and characterized.

2. Experimental details

Alumino-silicate thin films were prepared by PLD using hot-pressed targets. The targets were fabricated from commercial kaolin at a temperature of 1100 °C and a pressure of 40 MPa in the carbon matrix. Hybrid alumino-silicate/amorphous chalcogenide structures were prepared by sequential PLD runs from the above-mentioned hot-pressed kaoline and chalcogenide glass targets, respectively. Chalcogenide glass targets with As_2Se_3 composition (selected as a prototype chalcogenide glass with high refractive index ~2.78 at a telecommunication wavelength of 1550 nm and interesting non linear refractive index [22]) were made by the conventional melt quenching method.

The off-axis PLD technique combining rotating substrates and targets was used for the fabrication of appropriate quality films in terms of homogeneity in thickness. In detail, a KrF excimer laser operating at 248 nm with a constant output energy of 300 ± 3 mJ per pulse, with a pulse duration of 30 ns and with a repetition rate of 20 Hz was used for the PLD of the coatings under study. The energy fluence on the target was constant (~10 J cm^{-2}). The laser beam was incident on the target under an angle of about 45°. Amorphous thin films were deposited in a vacuum chamber (background pressure ~$2.7–4 \times 10^{-4}$ Pa). The substrates used for PLD (chemically cleaned microscope glass slides, Si wafers, Sn foil, and steel panels) were positioned parallel to the target surface. The target to the substrate distance was 5 cm. The number of laser pulses used for the preparation of the simple alumino-silicate films was 36,000, 72,000 or 216,000; a larger number of pulses was used for the preparation of thicker coatings on steel panels, which were used for the study of anticorrosive properties of mullite-based layers. An energy fluence of ~2.6 J cm^{-2} and 13,200 laser pulses, respectively, were used when fabricating amorphous chalcogenide thin films.

The homogeneity of prepared samples, their morphology and amorphous state as well as the chemical composition of used targets and prepared coatings were determined by a scanning electron microscope (SEM, JEOL JSM-6400 instrument) employing energy-dispersive X-ray microanalyzer with an operating voltage of 10 kV and collecting time 60–120 s. The coatings prepared on the Sn foil were used for the analysis to avoid the undesirable presence of substrate elements in the spectra. X-ray diffraction (XRD) of targets/coatings (on glass substrates) was performed using D8-Advance (Bruker AXE) instrument with CuKα excitation line. An Atomic Force Microscope (AFM, Dimension 3100, Nanoscope V, Digital Instruments, Santa Barbara CA, USA) was employed to study the surfaces of fabricated layers; silicon probes (resonant frequency 300 kHz, tip radius <10 nm) were used. AFM was calibrated with 10 μm, 3 μm grid pitch of 200 nm and 23 nm depths, respectively. For low roughness surfaces, Si atomic steps (0.314 nm, Si (111)) were used to calibrate the Z axis.

Nano secondary ion mass spectroscopy (NanoSIMS) analyses were performed on a NanoSIMS 50 standard ion microprobe (Cameca). Samples were cut, gold-coated and directly introduced into the instrument. A cesium primary ionic source was used for the measurement. A 16-keV Cs^+ beam was focused and raster-scanned on the surface sample. Sputtered singly charged negative secondary ions were extracted for mass analysis and collected in an electron multiplier. Depth profile was realised on a 15 μm × 15 μm area, with a blanking frame of 25%, under a 115 pA primary beam. The ^{28}Si image of the target (15 μm × 15 μm) was recorded for 87 s under a 2 pA primary beam. The ^{28}Si image of the film (10 μm × 10 μm) was recorded for 22 s under 2 pA primary beam. For all the analyses, a mass resolving power of ~4000 (M/ΔM) enabled to remove potential mass interferences was used. The spatial resolution for images was about 120 nm.

The optical parameters of the prepared layers were obtained from the analysis of spectroscopic ellipsometry data measured using an ellipsometer with automatic rotating analyzer (VASE, J. A. Woollam Co., Inc.). The measurement parameters are as follows: spectral region 400–2300 nm (i.e. 3.1–0.54 eV) with wavelengths steps of 10 nm, angles of incidence 65°, 70°, and 75°. The films deposited on the Si substrate were used for ellipsometry measurements due to large enough refractive indices contrast between the coatings and the substrate making analysis of measured data easier.

The anticorrosive properties of the prepared coatings were evaluated by means of the corrosion weight losses of steel panels with the top layer formed from the thin alumino-silicate film after 28 days in aqueous solutions of selected salts (0.1% NaCl, 1% NaCl, 0.1% K_2SO_4) and water. To exclude the influence of different thicknesses of the individual coatings, the corrosion weight losses of steel panels were recalculated dividing by weights of the alumino-silicate layers.

3. Results and discussion

The XRD patterns of used hot-pressed targets show that mullite ($3Al_2O_3$–$2SiO_2$ or $2Al_2O_3$–SiO_2, usually identified as the two ends of the thermodynamically stable phases of the solid solution) is their main component, but quartz (SiO_2) and cristobalite (SiO_2) crystalline phases are also present (Fig. 1a). In thin film XRD patterns (Fig. 1b), the diffraction peaks are absent completely, which is an indication of amorphous state of the coatings prepared. Thin films obtained by PLD were confirmed to be amorphous and homogeneous according to optical and electron microscopy as well.

The chemical composition of mullite-based targets and corresponding films, as measured by energy-dispersive X-ray analysis, was found to be, in accordance with XRD results, SiO_2 overstoichiometric when compared with pure mullite (Table 1). Table 1 shows generally good agreement between the chemical composition of the target and prepared thin films; this fact confirms PLD as a thin film deposition technique usually preserving the chemical composition of the material. We report ~3% oxygen deficiency of fabricated coatings when compared with the used target, which is a much better result than 20% oxygen deficiency found in [16]. It should be however noted that the oxygen determination could be influenced by its surface adsorption which might lead to oxygen signal