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Pulsed laser deposition of transparent fluoride glass

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ABSTRACT

The presence of reduced zirconium in fluorozirconate (FZ) glasses is highly unfavorable due to its detrimental effect on glass quality. Previous researchers have relied upon the use of a fluorine-containing processing gas to prevent the reduction of zirconium in FZ glasses deposited as thin films by pulsed laser deposition (PLD). However, the use of a fluorine-containing processing gas as an oxidizing agent is disadvantageous, due to its toxicity. Eliminating the need for the processing gas would lead to a significantly safer and simpler process. Our approach is to incorporate indium, which is multivalent, into the PLD ablation target in order to stabilize the zirconium and remove the need for a processing gas. A ZLANI glass, based on the composition 60.24ZrF_4-4.13LaF_3-3.54AlF_3-31.49NaF-0.59InF_3 (values are in mol%), was synthesized for use as an ablation target. Using the ZLANI target, FZ glass films were successfully deposited on fused silica substrates by PLD, without the need for any processing gas. Multiple depositions were performed to observe the effects of deposition duration on growth rate and on film roughness. The deposited films are transparent with a brownish coloration. The source of this coloration is postulated to be color centers that are created during synthesis. Thermal annealing increases light transmission through the films up to 400%, depending upon wavelength, in the UV and visible spectrum (350–600 nm), after a series of heat treatments culminating at 300 °C. The fact that the transparency of the films can be correlated to annealing temperature suggests that the films may be of use as passive temperature sensors.

1. Introduction

Fluoride glasses are notable for their extended transparency out to infrared wavelengths, with ultra-low loss of 0.001 dB/km in the infrared regions, which can be can be exploited for fiber optic applications [1,2]. In addition, the low phonon energy of fluoride glass matrices makes them a favorable host for optically-active rare earth elements, which can be employed for a variety of applications [3]. Rare earth-doped fluoride glasses have shown potential for such applications as optical amplification, fiber lasers, and wavelength shifters for solar cells and light emitting diodes [4,5]. The addition of a second halide, such as chlorine, to the glass composition allows for the precipitation of halide crystals in the matrix, yielding novel glass ceramics with further applications, such as computed radiography and dosimetry [6–9]. The most common fluoride glasses found in literature are ZBLAN compositions, consisting of the fluorides of zirconium, barium, lanthanum, aluminum, and sodium.

PLD deposition of fluorozirconate (FZ) glass thin films has utilized a fluorine-containing processing gas [10,11],which is used to prevent the reduction of zirconium in the glass matrix during synthesis. Reduced zirconium is highly unfavorable in FZ glasses dues to its detrimental effect on glass quality including the formation of black particulates in the matrix [12]. The use of a fluorine-containing processing gas as an oxidizing agent is disadvantageous due to its toxicity. Furthermore, removing the need for a processing gas would lead to a significantly safer and simpler process. We hypothesized that the incorporation of indium, which is multivalent, into the PLD ablation target would stabilize the zirconium and remove the need for a processing gas. It has been shown that In^{3+} becomes reduced to In^{+}, which allows reduced zirconium (Zr^{3+}) to oxidize to Zr^{4+} [13–15].Reduced indium in the glass is colorless and does not negatively affect its transmission properties in the visible range.

This study presents preliminary work to an ultimate goal of synthesizing a multilayer ZBLAN design glass ceramic. In this study, a series of transparent FZ glass thin films were deposited by PLD onto fused silica substrates using a ZLANI ablation target, consisting of the fluorides of zirconium, lanthanum, aluminum, sodium, and indium, and without a processing gas. Successful deposition of fluoride glass without

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an oxidizing process gas has not been reported in the literature and represents a significant process improvement. In future work, barium chloride and europium portions will be added to the ablation target. The vitreous nature of the films was confirmed by x-ray diffraction (XRD). Thermal characteristics were ascertained by differential scanning calorimetry (DSC). The optical transmission of the films, both as-made and after thermal annealing, was determined by spectrophotometry; the effects of heat treatments on the transparency of fluoride glass thin films have not been previously investigated. Surface roughness and film thickness were established by optical profilometry.

2. Materials and methods

A ZLANI fluoride glass target was made with composition $60.24ZrF_4$–$4.13LaF_3$–$3.54AlF_3$–$31.49NaF$-$0.59InF_3$ (values are in mol %) via the melt-quench method. The synthesis was performed in an argon atmosphere glovebox with a connected furnace. The total weight for the sample mixture was approximately 20 g. After mixing, the components were heated in the furnace at a temperature of 825 °C for 20 min, within a platinum crucible. Following a 5-minute fining step at 750 °C, the crucible was removed from the furnace and the molten glass was poured into brass mold held at 200 °C, which allowed the glass to cool gradually to ambient temperature over a period of 4 h. An ablation target with dimensions 51 × 38 × 1.3 mm was cut from the as-made glass, with the remainder reserved for characterization. The same ablation target was utilized for the synthesis of all samples pertaining to this article.

The ZLANI glass films were deposited via PLD on UV Grade fused silica substrates (University Wafer). Each deposition utilized four fused silica substrates that were approximately 25 × 25 × 0.5 mm, mounted to a rotating substrate holder. The securing created witness marks on the films during the deposition process, which allowed for consistent positioning of the film during subsequent characterization. Before deposition, the substrates were ultrasonically cleaned in high purity acetone (VWR Analytical, assay ≥99.5%) and methanol (VWR Analytical assay ≥99.8%) for 10 min in each solution, respectively, followed by a 2-minute soak in piranha solution that consisted of a 1:1 volume ratio of H_2SO_4 (Fisher Scientific, 66 Be) and H_2O_2 (Acros Organics, 95% solution in H_2O).

Depositions were performed using a 193 nm ArF excimer laser with a repetition rate of 50 Hz and a rated pulse length of 15 ns. Five depositions were done with durations of 0.5, 1, 2, 3, and 4 h over a 9-day period. During deposition, the background chamber pressure remained $< 7.0 \times 10^{-6}$ Torr, and the substrate temperature was 21 ± 3 °C. Details of the PLD deposition system are given in Leonard et al., 2012 [16]. The incident laser pulse energy, measured before interaction with the focusing lens, was 6.82 ± 0.3 mJ during all depositions. This laser pulse energy is attenuated by the focusing lens, chamber window, and shielding glass before it interacts with the target. Although the energy at the target cannot be measured directly while the deposition chamber is closed, it can be estimated, based upon 50% attenuation and a focus spot size of 0.13 mm^2, yielding an average fluence of 2.62 J/cm^2. The films were kept in a light tight box within a vacuum desiccator when not being characterized.

The film thickness and surface roughness were measured with white light interferometry using a Bruker GTK 3-D optical microscope (Billerica, MA) and the Vison64 software. The roughness was measured over a 48 μm lateral field of view, while an 860 μm lateral field of view was used for thickness measurements. The film surface and exposed substrate were sputter coated with gold for uniform reflectivity, and the thickness measurement was made using the step height adjacent to the witness mark. The thickness of a film deposited using PLD will vary with proximity to the plume. While rotating the substrate holder provides for a more even coating, the film thickness will still vary radially; using the witness marks from the retaining screws allows for film thickness measurements to be made at a uniform radial distance for more meaningful comparison. The intrinsic machine uncertainty was determined to be 0.057 μm due to illumination variation during measurements.

The transmission properties of the films were observed using ultraviolet/visible light (UV/Vis) spectrophotometer (TU-1901, Beijing Purkinje General Instrument Co.; Beijing, China) equipped with UVWin5.0 analysis software. Transmission was measured for incident light wavelengths between 350 nm and 600 nm at 1.0 nm spectral resolution. The measurements were performed using an uncoated fused silica reference. The witness marks were used to position the sample in the spectrophotometer to ensure that the same region of the film was observed through multiple measurements.

The thermal characteristics of the films were determined by differential scanning calorimetry (Netzsch DSC 200 F3; Selb, Germany). Scans were performed from 100 °C to 550 °C at a rate of 10 °C/min. The deposited ZLANI films were scraped off the substrate, and compared to the DSC data for the ZLANI glass target. The thickest deposited thin film (4-hour deposition) was used to ensure the largest possible DSC signal. Sample masses were 0.9 and 21.6 (± 0.1) mg for the thin film and target glass respectively.

X-ray diffraction measurement for the 4-hour deposition film was performed on a Philips X'Pert MRD X-ray Diffractometer (PANalytical Inc., Westborough, MA) with a Cu anode x-ray source. The x-ray diffraction spectrum was recorded over a 2θ range from 20° to 80° with a step size of 0.05° and a time step of 10 s. The amorphous nature of materials can be determined by x-ray or electron diffraction. The material is deemed to be vitreous if no crystals are detected [17].

Thermal annealing was performed in an argon atmosphere. The temperature in the sample chamber was proportional-integral-derivative (PID) controlled, using cartridge heaters as the heat source and thermocouples to monitor the temperature. Two annealing protocols were used. In the first case the sample was annealed at a temperature of 125 °C for 10 min, then removed and allowed to cool to ambient temperature, followed by transmittance measurement. The annealing/measurement process was repeated ten times on the same sample. In the second case the sample was annealed for 1 h at temperatures from 75 to 300 °C in 25 °C increments; after each 1 h anneal, the sample was removed from the chamber, allowed to cool to ambient temperature, and its transmittance was measured.

3. Results and discussion

3.1. Structural characterization

Examples of the deposited films are shown in Fig. 1 along with the as-made ZLANI glass used for the deposition target. No buckling or cracking was observed, indicating the films had adequately adhered to the substrate. With increasing deposition time, the samples become less transparent in visible light. The films exhibited a brown coloration, but no black particulates associated with reduced zirconium species [12]. A possible explanation for the brown coloration will be discussed in the upcoming Optical Characterization section.

The film roughness shows a direct correlation to deposition time, as seen in Fig. 2. Using the kinetic roughening theory, the roughness can be related to growth time via a power law:

$$\omega \sim t^{\beta}, \tag{1}$$

where ω is the average roughness (R_A) of the film, t is the deposition time, and β is the scaling exponent, which shows the roughness development [18]. Based upon the data, the fitted β value for the fluoride glass roughness development is 1.07, indicating that roughness increases with respect to time at a near-linear growth. An alternate explanation to kinetic roughening, for the increase in roughness, is that there can be a buildup of relatively large particulates ejected from the ablation target over time [19].

The thickness and calculated deposition rate for the five films are