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OVERVIEW ON PULSED LASER DEPOSITION OF CHALCOGENIDE-BASED THIN FILMS

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Abstract: *The application of pulsed laser deposition methods for chalcogenide-based amorphous thin films preparation is also described and current state-of-the-art is reviewed. These methods are based on vacuum evaporation of material by intensive laser pulses and subsequent deposition of vapours on a substrate and are very promising for thin films preparation of complex composition materials. The deposition in non-inert (reactive) atmosphere is possible. Low volatility and refractory materials can be also deposited without decomposition. Optical properties of obtained films are highlighted.*

Key words: *chalcogenide, amorphous thin films, pulsed laser deposition.*

1. Introduction

All the previous studies on the photo induced and waveguide properties exhibited by chalcogenide glasses have been carried out on the As-S, Ge-As-Se and Ge-Sb-Se system of glasses. However, these glasses may be relatively difficult to work mechanically and have a low devitrification temperature. The fabrication of bulk glasses of an alternative system of chalcogenide glasses, the Ga-La-S system has been reported [4], but no characterization of the photo induced properties or waveguide fabrication have been previously detailed.

The Ga-La-S system is easy to polish, hard and has crystallization temperatures of 600-700 °C.

Pulsed laser deposition (PLD) is a relatively quick, simple and highly versatile technique for depositing thin films of a wide variety of materials. Interest in the technique has experienced an explosive growth since it was first used to deposited thin films of high-T_c superconductors in 1987.

2. Pulsed Laser Deposition of Chalcogenide-based Thin Films

2.1. Pulsed Laser Deposition of $LaGa_{2.3}S_5$ Thin Films

Pulsed laser deposition has since been used to successfully grow crystalline waveguides of photorefractive material. The target used for ablation was a 12-mm diameter piece of chalcogenide glass with stoichiometry $7Ga_2S_{3.3}La_2S_3(LaGa_{2.3}S_5)$ [6]. To fabricate these glasses 99% pure, starting powders supplied by Merck were placed in glass ampoules whose interior was carbon coated. The carbon coating was required to prevent the glass melt from

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reacting with the ampoule walls. Such a reaction acts to devitrify the melt. The ampoules were pumped down to a vacuum of 10^{-6} torr and sealed. The sealed ampoule was then loaded into an electric furnace held at 1150 °C for two hours while being rotated. After two hours, the heated ampoule was removed and quenched in H_2O maintained at room temperature. The thin film deposition was carried out in a vacuum chamber at less 10^{-4} mbar pressure and the target was ablated using a KrF excimer laser, operating at a wavelength of 248 nm and pulse duration of 20 ns. The laser beam was focused to an average flux of 4 J/cm^2 and was scanned vertically over 1 cm across the target surface. The plume of ablated material was ejected perpendicular to the target surface and scanned in a vertical direction over the substrate surface, which was positioned parallel to the target surface at 5 cm distance. The two substrate materials used were CaF_2 (having 1.434 refractive index) and microscope slide glass (with 1.52 refractive index). CaF_2 was chosen because it transmits to 10 μm and would allow transmission spectra to be taken into the infrared (to 10 μm). The refractive indices of both of the substrates were lower than that of target material (n = 2.5) therefore allowing the thin films to form a waveguide. The substrate, typically of dimensions 10x10x1 mm^3, was mounted on a substrate holder which could be heated using a filament heater. Films were deposited at room temperature for 20 min. each at 40 Hz laser repetition rate (5000 pulses).

Initial observation showed that the deposited thin films had the same characteristic pale yellow colour as the target. Absorption spectra were taken of the thin films and these were in good agreement with those of the target material, with transmission ranges from 0.45 to 10 μm as expected. The thickness and surface quality of the thin films were measured using an alpha step instrument with a resolution of 0.05 μm.

The average film thickness was measured to be 1.5 μm and was uniform in the vertical direction but was 0.5 μm less on either side caused by the scanning of the ablated plume. The thickness deposited corresponded to a maximum deposition rate of 0.3 A/laser pulse.

The alpha step trace showed that the surface quality was good with only a few imperfections (each of which was less than 0.1 μm in height).

The morphology and topology were more closely investigated using electron microscopy (SEM). The film was found to be essentially featureless, implying good film quality with only one or two particulates or droplets on a sub-micrometer scale. Rutherford backscattering (RBS) was used to infer the film stoichiometry and thickness over the 1 mm^2 area analyzed.

The best fit to the experimental data was obtained for a computer simulation of 1.20 μm thickness film with composition of $LaGa_{2.2}S_{3.8}$. The thickness was in agreement with the alpha step data, although the stoichiometry was slightly sulphur deficient compared to the expected composition of $LaGa_{2.3}S_5$.

Further investigation of the stoichiometry of the film was carried out using EDX analysis. This implied a typical film composition of $LaGa_{2.3}S_{3.7}$, in close agreement with the RBS data.

The target material was also analyzed using both RBS and EDX analysis techniques, indicating that the target composition was $LaGa_{2.6}S_5$ and $LaGa_{30}S_{4.3}$, respectively, using each technique. It was inferred from this that the deposited film was slightly sulphur deficient compared with the target material.

The existence of reversible photo bleaching, photo induced refractive index changes and photo doping effects has been demonstrated in these films.

Waveguide coupling measurements show 2.53 refractive index and 1.06 μm thickness, close to the values obtained by direct measurements.

The films show great promise for optical applications and it should be possible to construct channel waveguides and integral Bragg mirrors in doped materials in order to realize a fully integrated miniature laser.

The method is likely to succeed with a wide range of chalcogenide glasses.

2.2. Pulsed Laser Deposition of Ge-Ga-Se Thin Films

Amorphous Ge-Ga-Se thin films (pure and dysprosium doped) were prepared [5] by the pulsed laser deposition technique using different energy of laser beam pulses. The optical band gap and the thickness of the thin films increased with exposure of the films and even more with the annealing.

Index of refraction has an opposite tendency. Two emission bands with maxima near 1140 and 1340 nm corresponding to electron transition of Dy^{3+} ions were identified in luminescence spectra of dysprosium doped thin films. Observed changes of optical parameters of studied Ge-Ga-Se films and infrared emission bands of dysprosium doped thin films can be interesting for potential applications in optoelectronics.

KrF excimer laser operating at 248 nm with constant output energy of 500 mJ per pulse and with a repetition rate of 10Hz was used for preparation of thin films. The energy density of the laser beam on the target was from 1-5 J/cm^2. Amorphous thin films were deposited in a vacuum chamber (background pressure being less 10^2 Pa).

2.3. Pulsed Laser Deposition of Pr-doped Chalcogenide Glass Thin Films

De Giacomo et al. [3] has used plasma assisted pulsed laser deposition (PA-PLD) to try to diminish the number of particulates in the film. Their experimental set-up consists of a KrF excimer laser (248 nm) with an optical system in order to steer and focus the laser beam, an PLD vacuum chamber, a system of gas feeding and pumping out, and a pressure controlling system. The thin films were grown under non-excited gas flow or under r.f. discharge conditions. In this way, a visible discharge surrounds the plume expansion. Praseodymium-doped chalcogenide glass was used as the target material. A scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS) was used to analyze highly polished thin sections of the deposited film surface.

The effective refractive indices and film thickness of Pr-doped chalcogenide glass films were measured at λ = 633 nm by means of the m-line prism coupling configuration in both TE and TM polarizations. The r.f. discharge affects the PLD process by improving the morphology by a partial elimination of particulates. The particulates over micron size are shown to be totally removed, while other particulates were notably reduced. Hence PA-PLD technique on Pr-doped Ge-S_2 based chalcogenide allows improving the quality of deposited films for their stoichiometry, morphology, deposition rate and optical properties.

2.4. Pulsed Laser Deposition of As_2S_3 Thin Films

Zou et al. [7] used the laser ablation technique to prepare an aqueous solution of the amorphous semiconductor As_2S_3. They used in experiments a Q-switched 1064 nm Nd:YAG laser. The laser emitted 25 ns pulses with a pulse repetition rate of 10 Hz.

The sample was placed in a quartz cell

(of 5 cm thickness) containing distilled water. The laser radiation (E = 50 mJ) was focused by a lens of focal length f = 25 cm on the surface of As_2S_3 placed near the back wall of the cell to prevent the breakdown at the front wall. The sample was exposed to laser radiation for 15 minutes. As a result of laser ablation, the nanostructures of the chalcogenide As_2S_3 entered the aqueous medium, thus forming a colloidal solution. The prepared solution had maximum absorption at 500-510 nm, compared to the maximum absorption in the initial sample at 525 nm. The homogeneity of the solution remained unchanged over a period of one month, after which sedimentation occurred in the form of crystals whose color was similar to that of the initial sample. Apparently, the ageing of the sample was associated with spontaneous clusterization of nanoparticles of the semiconductor. They claim that more prolonged storage of the solution can be ensured by adding to the solution organic stabilizers based on gelatin or polyvinylpyrrolidone. The estimates of volume part of As_2S_3 nanoparticles in aqueous solution have given the upper level of 5 x 10^{-2}. The size of As_2S_3 nanoparticles was less 10 nm, which was determined from transmission electron microscopy. The estimated volume part of nanoparticles in solution was 10^{-3}.

They used the Z-scan to measure the nonlinear optical constants of their ablated films. The nonlinear refractive index (n_2 = –2.8 x 10^{-12} CGSE units), third-order nonlinear susceptibility ($\chi^{(3)}$ = –4.7 x 10^{-12} CGSE units) and the nonlinear absorption coefficient (β = 1 cmGW^{-1}) have been measured. It was shown that the main process responsible for the self-action of laser radiation is the thermal process caused by a combined effect of linear and nonlinear absorption, which leads to self-defocusing of nanosecond radiation in aqueous solutions of As_2S_3.

3. Optical Properties of Pulsed Laser Deposited Chalcogenide Films

3.1. Optical Properties of Gallium Lanthanum Sulphide Thin-Films

Asal et al. [1] described the optical properties of Gallium Lanthanum Sulphide thin-films deposited by laser ablation technique.

A systematic investigation of the energy dependence of the refractive index, optical absorption edge, Urbach edge and Optical gap has been carried out as a function of increasing deposition energy density.

The optical absorption coefficient as a function of photon energy, deduced from transmission and reflectance measurements, shows a very large shift of the edge towards lower energies relative to that of bulk glass with increasing deposition energy density. The optical gap, as determined by Tauc extrapolation and Urbach parameter, has been determined as function of deposition energy density.

The changes in optical properties are correlated with the structural data. A remark can be made here concerning the optical quality of these thin film samples for devices applications. It is clear from the optical and EXAFS results that the deteriorating properties of the films deposited at high energy density are a result of Ga-Ga and S-S, wrong bonds.

For device applications optimum quality films are deposited at energy densities close to the ablation threshold. However the degree of near infrared absorption caused by gap narrowing and tail absorption remain inconveniently high for devices requiring very near infrared pumping (e.g., 810 nm pumped Nd^{3+} based devices) but is more promising for long wavelength based systems (e.g. 980 nm pumped Er^{3+} based devices).

3.2. Optical Properties of Ge-Ga-Se Thin-Films

Optical transmission measurements on virgin and annealed laser-ablated amorphous Ge-Ga-Se films are presented [5]. The film compositions were near those of the Pseudo binary source glasses, $(GeSe_2)_{1-x}(GaSe_2)_x$. Results are analyzed for the energy, annealing temperature, and composition dependence of the optical constants.

The Tauc energy gap and the Urbach tail width extracted from the absorption coefficient are found to vary monotonically with composition in the annealed films, in agreement with measurements of other quantities on bulk glasses in this system. This behavior is discussed in terms of homopolar-bond defects in the glass structure whose concentration evolves with annealing towards intrinsic values deriving from mechanical constraints in the relaxed glasses. Films deposition was done by ablating the targets using a Krypton-Fluoride excimer laser. The films were prepared under a vacuum of 10^{-5} Torr. The as-deposited films appear to be characterized by the presence of significant amount of frozen-in defects which cause the depression of E_g^{opt}. If the films are annealed they approach the behavior of bulk glasses.

3.3. Optical Properties of Pr^{3+}-doped Chalcogenide Films

Optical properties of laser deposited Pr^{3+}-doped chalcogenide films ($70GeS_2$-15 Ga_2S_3-15CsI) were investigated [3]. The target was ablated by using a XeCl excimer laser at the fluence of $F = 3$ J/cm^2. The target was rotated at a frequency of 3 Hz and vertically spanned during the process. The ablated material was collected on microscope glass slides at room temperature. Series of 10000-35000 pulses were directed on the target at the repetition rate of 10 Hz. SEM images showed a good planarity of the deposited films, without cracks or corrugations, and a limited number of micrometer-size droplets. From RBS measurements, the stoichiometry of the deposited films was found close to the target. The Ga_2S_3-GeS_2:Er_2S_3 films of various thicknesses (from 0.3 to 5 um) were prepared by laser ablation. The deposited films were characterized with various diagnostic techniques: optical absorption spectroscopy, X-ray fluorescence spectroscopy, secondary ion mass spectroscopy and luminescence spectroscopy. Concentrations of rare-earth ions, gallium and germanium in the target bulk glass and in the films were similar. The UV irradiation led to a large photo bleaching effect which could be explained by oxidation of films. The glass target was ablated by XeCI excimer laser operating at the wavelength 308 nm with pulsed duration 20 ns and pulse energy 10-40 mJ. The substrate was rotated at a frequency of 600 rpm and was heated under illumination.

Caricato et al. [2] have described the optical properties of Praseodymium-doped chalcogenide (GeS_2-Ga_2S_3-CsI) thin films deposited by the pulsed laser deposition technique using XeCl (308 nm) and KrF (248 nm) excimer lasers.

Optical transmission and reflectance spectra, at normal incidence, were recorded in the 200-2500 nm spectral region. The optical constants (refractive index n and extinction coefficient K) versus wavelength, as well as the film thickness, were calculated from these spectra and a computer code. The wave guiding properties of the deposited films were investigated by the prism coupling technique (m-line spectroscopy).

The presence of praseodymium in the doped chalcogenide thin film was analyzed

by exciting electrons to the $^1G_4$ level and collecting the photoluminescence spectrum in the 1.335 μm region.

Moreover, compositional, morphological and structural characteristics of the films were obtained by Rutherford backscattering Spectroscopy, Scanning electron microscopy and X-ray diffraction analysis.

These preliminary results forecast that the realization of high quality waveguides could be accomplished after the suitable reduction of surface roughness and the improvement of the film homogeneity. Thin films of GeSr based chalcogenide glass containing Pr^{3+}-ions as dopant were produced by PLD on glass, $Si0_2$ slides and $LiNbO_3$ substrates at room temperature and at 300 °C. The RBS analysis pointed out that compositional differences between the film and target were only due to small losses of sulphur.

4. Conclusions

The pulsed laser deposition method is very promising technique for thin films preparation of complex composition materials. The deposition in non-inert (reactive) atmosphere is possible. Low volatility and refractory materials can be also deposited without decomposition.

The application of PLD method for chalcogenide-based amorphous thin films preparation is successfully obtained.

In this paper, the pulsed laser deposition of chalcogenide based thin films and their optical properties have been described.

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