Pulsed laser deposition of Ga-La-S chalcogenide glass thin film optical waveguides

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Thin film optical waveguides of the chalcogenide glass Ga-La-S have been deposited on substrates of CaF_2 and microscope glass by the technique of pulsed laser deposition. The chalcogenide properties of photobleaching, photodoping, and photoinduced refractive index changes have been observed and preliminary experiments carried out. The refractive index and thickness of the layer were verified using a waveguide "dark mode" analysis technique.

Non-oxide, chalcogenide glasses are of interest for applications in infrared technology, including the fabrication of optical elements such as mirrors and filters.[1] In particular, thin film waveguides of these glasses are highly desirable for novel infrared integrated optical components and devices. The low characteristic vibrational frequencies of the chalcogenide bonds allow them to transmit far out into the infrared, and typical transmission is from 0.5 to 10 μm.[1-3] This low maximum phonon energy also ensures low nonradiative relaxation rates which makes them ideal candidates for laser host media.[4,5]

The majority of chalcogenide glasses exhibit a wide range of interesting photostimulated properties. These include subtle effects such as shifts in the absorption edge (photobleaching and photodarkening), and more substantial atomic and molecular reconfigurations such as photoinduced refractive index changes and photodoping effects.[6] The changes in refractive index induced by illumination (with optical radiation of a suitable wavelength) can be up to 1%, corresponding to an absolute index change of 0.02.[7] In addition, photodoping of these materials with silver can increase the refractive index change to as much as 20% corresponding to an absolute index change of 0.5.[1]

All the previous studies on the photoinduced and waveguide properties exhibited by chalcogenide glasses have been carried out on the As-S, Ge-Sb-Se, and Ge-As-Se systems of glasses. However, these glasses suffer from problems of toxicity, and are 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[8] but no characterization of the photoinduced properties or waveguide fabrication has been previously detailed. The Ga-La-S system does not suffer from the problems mentioned above for the As systems, and it is nontoxic, easy to polish, hard, and has crystallization temperatures of 600–700 °C. In this letter, thin film optical wavelengths of gallium lanthanum sulphide have been fabricated and the photostimulated properties of this system investigated for the first time to our knowledge.

Pulsed laser deposition is a relatively quick, simple and highly versatile technique for depositing thin films of a wide variety of materials.[9,10] Interest in the technique has experienced an explosive growth since it was first used to deposit thin films of high-T_c superconductors in 1987.[11]

The technique has since been used to successfully grow crystalline waveguides of the photorefractive material $Bi_{12}GeO_{20}$.[12] The experimental arrangement for pulsed laser deposition is shown in Fig. 1. The target used for ablation was a 12-mm-diam piece of chalcogenide glass with nominal stoichiometry $7Ga_2S_3 \cdot 3La_2S_3(LaGa_{2.3}S_5)$. 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 reacting with the ampoule walls. Such a reaction acts to devitrify the melt. The ampoules were pumped down to a vacuum of $\sim 10^{-6}$ Torr and sealed. The sealed ampoule was then loaded into an electric furnace held at 1150 °C for two hours while being rotated. After 2 h, 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 a pressure of $\leqslant 10^{-4}$ mbar 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 a distance of 5 cm.

The two substrate materials used were CaF_2 (having a refractive index 1.434) and microscope slide glass (with refractive index 1.52). CaF_2 was chosen because it transmits to 10 μm and would allow transmission spectra to be

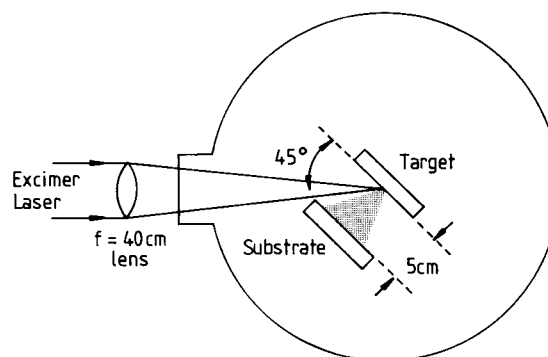
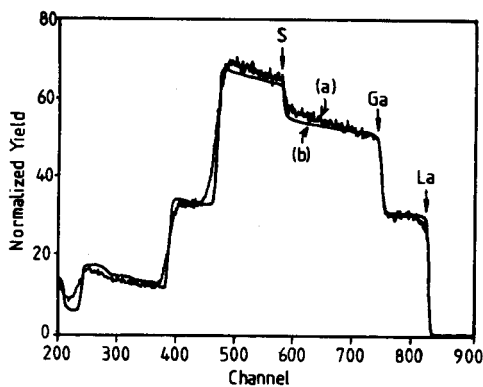FIG. 1. Experimental arrangement for pulsed laser deposition.

FIG. 2. RBS spectrum from a typical film, (a) experimental data, (b) simulation of 1.2 μm LaGa$_{2.2}$S$_{3.8}$.

FIG. 3. Transmission spectra of a typical film, (a) before and (b) after photobleaching.

taken into the infrared (to 10 μm). The refractive indices of both of the substrates were lower than that of the target material ($n = 2.5$) therefore allowing the thin film to form a waveguide. The substrates, typically of dimensions 10 $\times 10 \times 1$ mm^3, were mounted on a substrate holder which could be heated using a filament heater. Films were deposited at room temperature for 20 min each, at a laser repetition rate of 40 Hz ($\approx 50\,000$ pulses).

Initial observations showed that the deposited thin films had the same characteristic pale yellow color 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 alphastep 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 Å per laser pulse. The alphastep 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 topography were more closely investigated using scanning 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 submicrometer 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 a film of 1.20 μm and a composition of LaGa$_{2.2}$S$_{3.8}$, as shown in Fig. 2. The thickness was in agreement with the alphastep 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$_{3.0}$S$_{4.3}$, respectively, using each technique. It was inferred from this

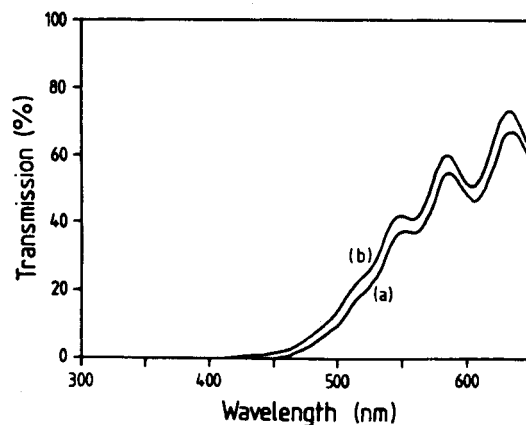that the deposited film was slightly sulphur deficient compared with the target material.

Despite the possible nonstoichiometry in the film composition many of the characteristic photostimulated properties of chalcogenide glasses were observed. Figure 3 shows transmission spectra for a film before and after photobleaching. The photobleaching was performed by exposing the film for 5 h to light from an Ar$^+$ laser at a wavelength of 514 nm, at an intensity of 0.16 W/cm^2. An increase in the film's transmission at visible wavelengths, is indicated in Fig. 3(b), and is clearly seen by eye, showing up as a more transparent region in the film. The photobleaching effect could be reversed by annealing the film at a temperature of 250 °C in air for 2-h.

Photodiffusion into the thin films was also carried out. A 10-nm-thick layer of silver was evaporated onto the film which was then illuminated for 30 min through the substrate with laser radiation at 514 nm focused to an intensity of 2 W/cm^2. The residual silver coating was then removed by dissolving it in a solution of Fe(NO$_3$)$_3$. EDX analysis showed that 0.3 at. % of silver was present in the regions which had been illuminated but was not present in the unilluminated regions. Previous experiments[13] on the As system of chalcogenides had shown that the undoped regions could be etched in NaOH, but this did not remove the film in our case. A thorough systematic search would be required to find the correct etchant for the thin films.

To investigate photoinduced changes in the refractive index of the thin films, two laser beams at a wavelength (λ) of 514 nm were overlapped, producing an interference pattern in the film. The intensities of the writing beams were 30 and 60 mW, respectively, and intersected at an external angle of 36°(2θ). The interference pattern between the two beams produced a refractive index grating from which a He-Ne laser operating at 633 nm could be diffracted. A diffracted beam was observed, which monotonically increased in intensity over the first 5 min, but due to vibrational instabilities in the experimental arrangement, the grating did not reach its saturated value. It is likely that an optimized experimental arrangement, which incorporated a facility for interferometric stabilization would pro-

duce much stronger gratings and correspondingly higher diffraction efficiencies. The first order diffraction efficiency (η) obtained with the unoptimized setup was 0.01%. Using the expression[14]

$$\Delta n = \frac{\lambda \cos \theta}{2\pi d} \cosh^{-1}\left(\frac{1}{1-2\eta}\right), \quad (1)$$

where d is the thickness of the grating, the refractive index variation (Δn) in the grating was calculated to be 2×10^{-3}. This is somewhat smaller than the 1% reported for the As system of chalcogenides, but this result can presumably be improved after correction of the vibrational instability problems.

The waveguide properties of the films were analyzed using a prism coupling technique. For a waveguide of 1 μm thickness, 7 transverse electric (TE) and 7 transverse magnetic (TM) modes were predicted. Not all of these modes could be accessed using the prisms available (which had apex angles of 90°, 80°, and 60°), but 4 TE and 3 TM modes were observed using a 60° prism. The effective indices of the first 2 TE modes were determined by measuring the angles at which they were coupled into the film. Using this information the refractive index of the thin film was calculated to be 2.53, and the thickness of the film over the ≈ 1 mm coupling area was determined to be 1.06 μm, both in excellent agreement with the expected values.

Unfortunately, no waveguide loss measurements were possible in these films because the area of the films was too small to facilitate the use of the sliding prisms technique.[15] The films were also too thin and the edge quality insufficient to facilitate end launching. Longer (several cm) and thicker (~ 5 μm) films would be needed in order to allow waveguide losses to be made, and work is continuing to grow films to these specifications.

In conclusion, we have shown that high quality chalcogenide glass films of nominal composition $7Ga_2S_3.3La_2S_3$ can be readily deposited by the pulsed laser deposition technique. The existence of reversible photobleaching, photoinduced refractive index changes, and photodoping effects has been demonstrated in these films. Waveguide coupling measurements show an index of 2.53 and a thickness of 1.06 μm, close to the values obtained by direct measurement. 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 construct a fully integrated miniature laser. The method is likely to succeed with a wide range of chalcogenide glasses.

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