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# Laser-deposited As<sub>2</sub>S<sub>3</sub> chalcogenide films for waveguide applications

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## Abstract

We have shown that high-repetition rate short-pulse laser deposition can be used to successfully fabricate low loss waveguide films in As<sub>2</sub>S<sub>3</sub> chalcogenide glasses. The resulting films are highly photosensitive and can be used without thermal annealing in waveguide fabrication. Waveguide losses as low as 0.2 dB/cm in laser written waveguides have been measured at 1550 nm. The results suggest that ultra-fast pulsed laser deposition may be an important process for the production of low loss waveguides in the chalcogenides. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Laser deposition; Chalcogenide glass films; Optical waveguide

## 1. Introduction

Chalcogenide glasses are low phonon energy materials and hence are transparent from the visible up to the infrared. These glasses are susceptible to electromagnetic radiation and show a wide variety of photo-induced effects as a result of illumination [1]. Various models have been put forward to explain these effects [2–4], which can be used to fabricate diffractive as well as waveguide structures in the chalcogenide glasses [4–7].

Up to now thermally evaporated and sputtered films have been used to fabricate these structures into chalcogenide glasses. Vacuum evaporated films have been used [7] to fabricate waveguides in As–S–Se system of glasses while attempts to use of rapid thermally annealed sputter deposited films to fabricate

very low loss (<0.3 dB/cm) channel waveguides were also quite successful [8]. A significant problem encountered with these films is associated with the need to anneal them prior to exposure for waveguide writing. In general their thermal expansion coefficient is very large compared to common substrate materials leading to cracking or film lift off during annealing. Whilst rapid thermal annealing has proven an useful approach to minimise these problems, any process that removed the need for annealing would have a significant advantage. This lent impetus to a successful search for another way for deposition of chalcogenide films.

Pulsed laser deposition (PLD) involves the evaporation of a target material with an intense laser pulse and subsequent deposition of the vapours onto a suitable substrate. Since each laser pulse completely ablates a thin surface layer of the target, an useful property of PLD is its ability to transfer the stoichiometry of the target to the deposited film. In addition the surface

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layer is ablated with moderately high kinetic energy, and this helps to densify the resulting films.

In general PLD is performed using high-energy ( $\approx 100$  mJ–1 J) pulses from UV excimer lasers using pulse repetition rates up to 100 Hz. Under such conditions it is generally observed that films become contaminated with particles caused by the ejection of lumps of target material by the high-energy laser pulses. As a result the optical losses of films produced by conventional PLD are rather high due to scattering. We have proposed the process called ultra-fast PLD to overcome this problem [9]. In ultra-fast PLD the laser pulse energy is lowered so that it is no longer possible to evaporate sufficient material during each laser pulse to create a large particle. Pulse energies in the 100 nJ–1  $\mu$ J range are generally used. In addition the pulse repetition rate is increased into the 1 MHz–100 MHz range to increase the overall mass ablation rate. Importantly, the on-target intensity is chosen so that sufficient energy is available to ablate the surface to a depth equal to the penetration of the thermal wave. This ensures that the ablation process reaches its maximum efficiency and occurs without significant heating of the target.

The process has been demonstrated to work very effectively and to eliminate the production of particles within ultra-fast PLD produced films. We have applied ultra-fast PLD to the production of  $\text{As}_2\text{S}_3$  films with the aim of determining the resulting film properties and the suitability of the films for waveguide applications.

## 2. Film deposition

$\text{As}_2\text{S}_3$  flats were prepared by Amorphous Materials, and used as ablation targets. Films of up to 5  $\mu\text{m}$  thick were deposited onto fused silica substrates either in the form of microscope slides or 100 mm diameter oxidised silicon wafers using the ultra-fast laser deposition method [9]. The  $\text{As}_2\text{S}_3$  films depositions were performed using second harmonic of a mode-locked Coherent Antares Nd:YAG laser ( $\lambda = 532$  nm,  $t_p = 50$  ps). Up to 7 W of second harmonic output was available at 76 MHz repetition rate (pulse energy  $\approx 80$  nJ). The laser beam was directed into a vacuum chamber pumped to  $\sim 3 \times 10^{-7}$  Torr, and focused on a target with a special telecentric scanning lens,

providing intensity up to  $5 \times 10^8$  W/cm<sup>2</sup> on the target surface. The beam could be scanned over a 10 cm<sup>2</sup> region of the target surface to minimise the influence of crater formation on the deposition rate. The targets were angled approximately 25° to the incoming beam axis whilst the substrates were positioned along the target normal. This prevented specularly reflected light from hitting the substrate, which is essential in case of laser deposition of photosensitive materials.

The ablation rate studies were performed by evaluation of the ablated volume, which was determined by measuring the crater volume after a certain number of pulses. The ablation threshold value was extrapolated from the experimental data of the ablated depth vs. the laser fluence.

The measured ablation rates at the intensity range  $1 \times 10^8$ – $5 \times 10^8$  W/cm<sup>2</sup> are summarised in Fig. 1. The ablation threshold fluence  $F_{\text{th}}$  was found to be  $\sim 6.5$  mJ/cm<sup>2</sup> for 50 ps, 532 nm pulses. This value corresponds to the bonding energy of 2.3 eV, or to the heat of vaporisation of 222 kJ/mol for  $\text{As}_2\text{S}_3$ . The solid curve was calculated with the help of [9]:

$$d_{\text{ev}} = \frac{AI_1 t_p}{\varepsilon_b n_a} \quad (1)$$

where  $d_{\text{ev}}$  is the depth of the crater ablated per single pulse,  $AI_1$  the absorbed laser energy,  $t_p$  the pulse duration,  $\varepsilon_b$  the binding energy, and  $n_a$  is the atomic number density for  $\text{As}_2\text{S}_3$ :  $n_a = 3.92 \times 10^{22}$  cm<sup>-3</sup>.

The deposition rate measured at the target–substrate distance of 250 mm, the longest target-to-substrate distance in the experimental chamber, was up to 20 Å/s when using the full mode-locked pulse train (Fig. 2). At this distance the deposited film thickness variation over a 10 cm wafer used as a substrate was of the order of  $\pm 5\%$ . The film thickness homogeneity can be arbitrarily improved by mounting substrate on carousel. The solid curve in Fig. 2 represents the deposition rate fitting based on the evaporation rate  $R_{\text{ev}}$  determined using [9]:

$$R_{\text{ev}} = \frac{AI_1}{\varepsilon_b + 3.3k_B T} \left( \frac{\text{atoms}}{\text{cm}^2 \text{ s}} \right) \quad (2)$$

where  $k_B T$  is the vapour temperature. The vapour temperature is proportional to the absorbed laser intensity, so the evaporation rate saturates with the increase of laser intensity. This leads to an important

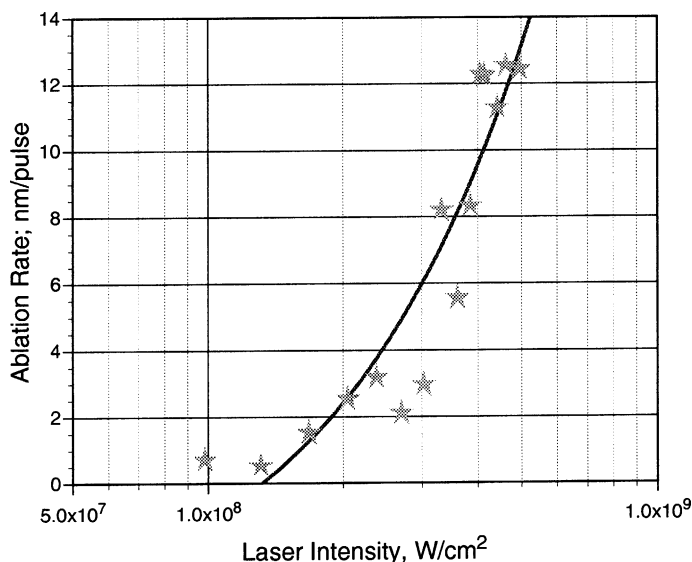


Fig. 1. Ablation depth per pulse with 50 ps, 532 nm laser pulses vs. laser intensity. The solid curve is fitting the Eq. (1) to the experimental data. The intersection with the 'zero' depth gives the threshold laser intensity, which corresponds to the binding energy of 2.3 eV, or the heat of vaporisation 222 kJ/mol for  $\text{As}_2\text{S}_3$ .

conclusion that, as soon as the steady state regime of ablation is achieved at the intensity level a few times the threshold, there is no need to increase further the laser intensity in order to boost the deposition rate.

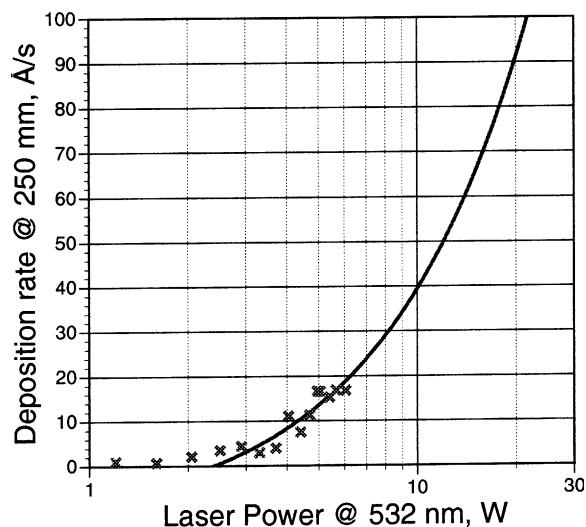


Fig. 2. Deposition rate achieved at the target–substrate distance of 250 mm. The solid curve represents the rate for higher laser power based on steady state regime of ablation, suggesting that the rate of 100 Å/s is achievable at the mode-locked laser power of 25–30 W at 532 nm.

The deposition rate should be increased via the increase in the pulse repetition rate.

The stoichiometry of the film was tested by electron diffraction X-ray analysis in a JEOL-6400 scanning electron microscope (SEM). The analysis showed that the deposited film composition reflects that of the target with the accuracy of  $\pm 0.5\%$  (atomic). There was no particulates on the deposited films, but we found evidence of photo-decomposition on the surface of the films left exposed to daylight. The rms roughness determined by atomic force microscopy was  $\sim 0.4 \text{ nm}$  over  $200 \mu\text{m}^2$ .

### 3. Photosensitivity

The films were exposed at various intensities and fluences using the 514 nm line of an argon ion laser and the refractive indices were measured before and after exposure. The films were also annealed in a  $\text{N}_2$  gas atmosphere for 2 h at  $150^\circ\text{C}$  to assess the stability of the photo-induced index changes. Annealing was also used to prepare the films prior to photodarkening. Similar to the observations reported in [7], regions of "permanent" photo-induced changes were identified for high intensity and high fluence. Our samples

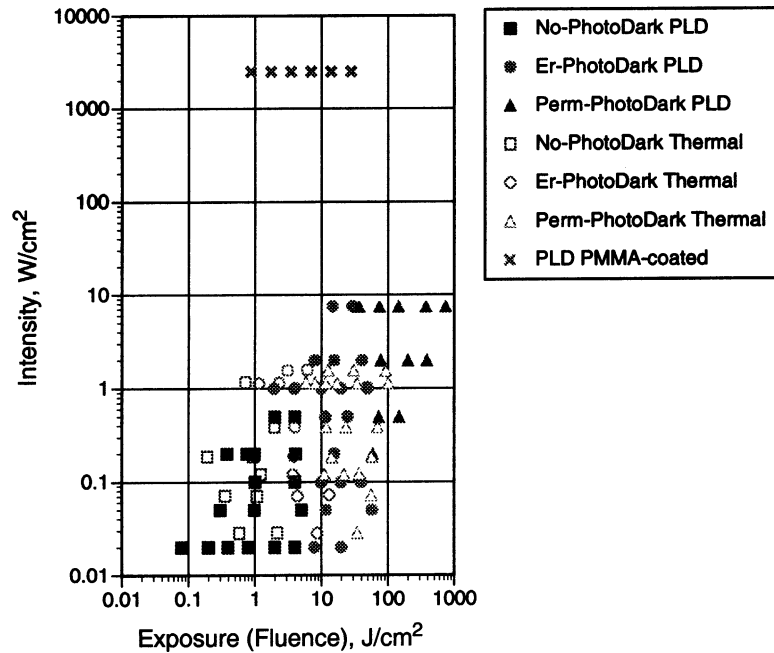


Fig. 3. Photodarkening data for laser-deposited (filled squares, circles, and triangles) and thermally evaporated (Ref. [7], empty squares, circles, and triangles)  $\text{As}_2\text{S}_3$  films. The squares represent no photodarkening, circles: erasable photodarkening, triangles: permanent photodarkening. The crosses indicate permanent photodarkening of the PMMA-coated films.

seemed to be slightly less photosensitive than the thermally evaporated films reported in [7], see Fig. 3. Index changes of 0.04 were typically obtained.

The films exposed to day light for a few days showed significant surface deterioration. Analysis using SEM demonstrated extensive growing of As and S crystals on the surface, presumably via the photo-decomposition of the film. In order to prevent surface decomposition, the films were spin-coated with a thin ( $0.8 \mu\text{m}$ ) layer of PMMA. An additional benefit from the PMMA-coating was a significant increase in the allowable laser intensity to induce photodarkening without thermal damage of the film. The laser intensity of up to  $2.5 \times 10^3 \text{ W/cm}^2$  produced well-defined waveguide channels in the PMMA-coated  $\text{As}_2\text{S}_3$  films, while the uncoated films demonstrated noticeable thermal damage at the laser intensity above  $40 \text{ W/cm}^2$ .

The photosensitivity of  $\text{As}_2\text{S}_3$  enables single-mode channel waveguides to be formed in planar samples through preferential exposure to visible radiation. Since the fluences required are large for conventional mask based processes, direct laser writing [10], was

used to define channel waveguides. The laser direct writing system is based around a computer controlled 2-axis air bearing translation stage (Dover Instruments,  $\pm 10 \text{ nm}$  position accuracy), and a frequency doubled, diode pumped Nd:YAG laser. The system was configured to deliver  $4 \text{ mW}$  onto the photosensitive sample in a  $3.5 \mu\text{m}$  spot diameter Gaussian beam. By controlling the scan rate of the sample under the focussed beam, the exposure of the material could be varied. Straight channel waveguides were written in confined geometry of PMMA-coated samples for a series of writing velocities in the range from 1 to  $16 \text{ mm/s}$ . This was an improvement of the waveguide writing speed over two orders in magnitude compared with the uncoated films (Fig. 4).

The following optical properties of the deposited films were obtained:

- Optical losses down to  $<0.1 \text{ dB/cm}$  for as-deposited films at  $1550 \text{ nm}$ .
- Optical losses  $<0.2 \text{ dB/cm}$  for films fully photodarkened using Ar ion  $514 \text{ nm}$  laser light or Nd:YAG  $532 \text{ nm}$  laser.

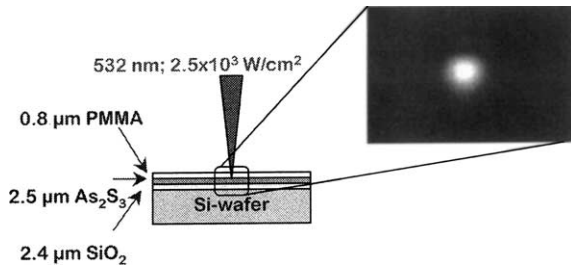


Fig. 4. Near-field output of a single-mode 800 nm light confined in a 3.5  $\mu\text{m}$  wide photo-induced channel.

- The refractive index increases with photodarkening from 2.46 at 810 nm up to 0.06, with an average increase 0.04–0.05.
- Nonlinear optical coefficients determined at 800 nm via degenerative four-wave mixing using a 150 fs Ti:sapphire laser indicated that the films had a moderate instantaneous third order nonlinearity of Kerr type with  $|n_2| \approx 2.7 \times 10^{-14} \text{ cm}^2/\text{W}$ .

#### 4. Conclusions

We have shown that ultra-fast PLD can be used to successfully fabricate low loss waveguide films in  $\text{As}_2\text{S}_3$  chalcogenide glasses. The surface quality of the deposited films was almost down to the atomic level with a rms roughness of the order of 0.4 nm. The resulting films are highly photosensitive and can be used without thermal annealing in waveguide fabrication. Waveguide losses as low as 0.2 dB/cm in laser

written waveguides have been measured at 1550 nm. Protective PMMA-coating on the  $\text{As}_2\text{S}_3$  film surface allowed the laser writing intensity to be increased by over two orders of magnitude, compared to the uncoated films, without any collateral damage to the film. This led to the increase of waveguide writing speed up to 16 mm/s for a 3.5  $\mu\text{m}$  single-mode waveguide. The results suggest that ultra-fast PLD may be an important process for the production of low loss waveguides in the chalcogenides.

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