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Low-loss waveguides in ultrafast laser-deposited As_2S_3 chalcogenide films

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Ultrafast pulsed laser deposition was used to successfully deposit atomically smooth 5-μm-thick As_2S_3 films. The As-deposited films were photosensitive at wavelengths close to the band edge ($\approx$520 nm), and waveguides could be directly patterned into them by photodarkening using an argon-ion or frequency-doubled Nd:YAG laser. The linear and nonlinear optical properties of the films were measured as well as the photosensitivity of the material. The optical losses in photodarkened waveguides were $<$0.2 dB/cm at wavelengths beyond 1200 nm and $<$0.1 dB/cm in As-deposited films. The third-order nonlinearity, n_{2,As_2S_3}, was measured using both four-wave mixing and the Z-scan technique and varied with wavelength from 100 to 200 times fused silica ($n_{2,\mathrm{Silica}} \approx 3 \times 10^{-16}\ \mathrm{cm}^2/\mathrm{W}$) between 1500 nm and 1100 nm with low nonlinear absorption.

OCIS codes: 160.2750, 160.4330, 310.1860, 230.7370.

1. INTRODUCTION

Chalcogenide glasses are low-phonon-energy materials transparent from the visible to the midinfrared. In the case of arsenic trisulphide (As_2S_3) glass, the nonlinear refractive index n_2 has been measured at $\lambda = 1550$ nm to be $\sim$100 times that of silica with a nonlinear figure of merit $n_2/\beta\lambda \approx 2$ (here β is the two-photon absorption coefficient), making this chalcogenide glass an attractive material for ultrafast all-optical switching.[1] Chalcogenide glasses are also frequently sensitive to optical radiation and show a wide variety of photoinduced effects as a result of illumination.[1–3] Various models have been put forward to explain these effects,[4–6] and the index change accompanying the common photodarkening phenomenon can be used to fabricate diffractive as well as waveguide structures.[7–10]

Up to now, thermal evaporation and sputtering have been used to create the chalcogenide glass thin films. Vacuum-evaporated films were used to fabricate waveguides in a As-S_x-Se_y system of glasses,[9] while attempts to use rapid thermally annealed sputter-deposited films to fabricate very low loss ($<$0.3 dB/cm) channel waveguides were also successful.[10] A significant problem encountered with these films is associated with the need to anneal them before exposure for waveguide writing. In general, their thermal-expansion coefficient is much larger than common substrate materials such as fused silica or silicon, leading to cracking or film lift off during or after annealing. While rapid thermal annealing has proven a useful approach to minimize these problems, any deposition process that removes the need for annealing would have a significant advantage. This motivated the search for a better way of depositing chalcogenide glass films.

In this paper, we study the properties of chalcogenide glasses deposited using pulsed laser deposition (PLD) using a high-repetition-rate picosecond-range laser pulses. A well-known advantage of the PLD technique is that it can accurately transfer the stoichiometry of a multicomponent target to a film deposited on a substrate. This is particularly important in materials containing weakly bonded volatile components such as sulphur, where thermal evaporation often results in marked changes in stoichiometry. In addition, PLD can result in bombardment of the substrate by relatively high-energy ions or neutrals, and this assists in densification of the film in a way analogous to the use of ion bombardment during thermal evaporation. It is possible, therefore, for PLD to produce high-quality films that do not require annealing, as is generally essential for thermally evaporated films. A disadvantage of the conventional PLD process, which uses high-energy ($\sim$1 J), low-repetition-rate (10–100 Hz) nanosecond laser pulses, is the production of particulates that can lead to high scattering losses in the films. Until now, there have been only a few reports of the fabrication of waveguide structures in pulsed laser-deposited films of

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chalcogenide glasses, and these have been mainly concentrated on the Ga-La-S system of glasses. Thin-film optical waveguides of Ga-La-S glasses were deposited[11] by PLD although the losses were rather high (6 dB/cm at 632.8 nm).[12]

We have previously shown that the problem of particulates produced by conventional PLD can be eliminated by using the ultrafast PLD process that employs short (<50 ps), low-energy ($\approx\mu$J), high-repetition-rate (10^5–10^8 Hz) pulse trains.[13,14] Indeed, we were able to produce high optical quality As_2S_3 chalcogenide glass films using ultrafast PLD.[15] The surface quality of the deposited films was almost down to the atomic level with rms roughness of the order of 0.42 nm. The resulting films were highly photosensitive and could be used without thermal annealing for waveguide fabrication using the photodarkening process.

In the present work we report studies of the linear and nonlinear optical constants of As_2S_3 films deposited by ultrafast PLD. The use of these films for waveguiding is also demonstrated. The films were produced by ablating solid glass targets in vacuum using a 25-W cw Nd:YAG laser in one of two different modes. In the first case, the laser was operated in the *Q*-switched mode-locked (QSML) regime and produced pulse trains at a repetition rate of 10 kHz. The laser output was frequency doubled to 532 nm, where up to 12 W of average power was available. In the second case, the laser was operated in the pure mode-locked (ML) regime again with an external frequency doubler and produced 50-ps pulses at a 76-MHz repetition rate with an average power up to 7 W at 532 nm. Significant differences were observed in the properties of the films resulting from these two operating regimes. The films produced in the QSML regime appeared to be generally less photosensitive and required annealing after deposition before they could be used for waveguide fabrication. The ML laser produced films of higher photosensitivity, demonstrated higher change in refractive index as a result of photodarkening, and showed low scattering losses such that they did not require annealing before waveguide fabrication.

Waveguides were fabricated in the ML films by photodarkening the film using a scanned focused beam at either 514 nm from an argon-ion laser or 532 nm from a frequency-doubled Nd laser. The waveguide losses were measured to be <0.2 dB/cm at 1550 nm, an acceptable value for use in the fabrication of planar light-wave circuits, and equal to the values obtained for bulk samples of photodarkened material. Loss in the as-deposited films was at least a factor of 3 lower.

2. PHOTOSENSITIVITY

Arsenic sulphide glasses are known to exhibit a wide variety of photostructural effects. Of these, photodarkening can be used to define waveguides as well as diffractive structures into chalcogenide glasses. Photodarkening is normally accompanied by a redshift in the absorption edge, a decrease in the transmission, and an increase in the refractive index of the glass.[16–18] This effect has been explained by a metastable double-well potential model.[4] It was concluded in the model that the origin of this photostructural change is not directly related to the native defects (i.e., dangling bonds), but to bulk-oriented features in a disordered network. It is believed that some extensive feature of the disorder, such as fluctuations in bond angle, is associated with the photostructural behavior. A configurational model of bistable local-bonding geometries has been proposed, in which the action of light is to cause minor bond rearrangements involving chalcogen atoms. As a result, the potential energy of the system can relax between the minima of a double-well potential. A unified model for reversible photostructural effects in chalcogenide glasses in terms of both intermolecular and intramolecular bond-weakening mechanisms has also been presented.[5] An intermolecular bond-breaking mechanism in which the weak, attractive (interlayer) interactions are particularly vulnerable to optical excitation has been proposed. Two intramolecular bond-breaking mechanisms, namely, the self-trapped exciton model and a random covalent network transformation model in which two heteropolar bonds are transformed into two different homopolar bonds, have also been suggested.[5] In As-S glasses, photodarkening has been attributed to the formation of As-As bonds as a result of illumination,[16] and their results on the compositional dependence of the effect in As-S system has been explained satisfactorily based on this hypothesis. It is possible to use this photodarkening effect to fabricate waveguide structures into As-S films. Before starting this task of direct writing of waveguides, a material characterization of the glassy films is needed to fully exploit this effect.

3. FILM DEPOSITION BY MODE-LOCKED PULSES AND BY *Q*-SWITCHED MODE-LOCKED PULSE TRAINS

As_2S_3 flats obtained from Amorphous Materials, Inc., were used as the targets for laser ablation. Films of up to 5-μm thickness were deposited onto fused-silica or (oxidized) silicon wafers as substrates using the ultrafast laser deposition method.[13,14] The As_2S_3 film depositions were performed using the second harmonic of a mode-locked Nd:YAG laser in either *Q*-switched mode-locked or cw mode-locked regimes. The QSML regime produced 10–12-kHz trains of high-power pulses, each train containing 30 to 35 pulses ~60 ps in duration and separated by ~13.2 ns. A noncritically phase-matched lithium triborate (LiB_3O_5) frequency-doubler converted the IR output to second harmonic for efficient absorption by the As_2S_3 target. In QSML mode, $\sim(3.0–3.5)\times10^5$ pulses per second were produced at 532 nm with an average pulse energy of ~20 μJ. The laser beam was directed into a vacuum chamber pumped to 3×10^{-7} Torr and focused on a target with a special telecentric scanning lens, providing intensity up to 5×10^{10} W/cm^2 on the target surface.

In cw mode-locked mode, laser pulses at a repetition rate of 76 MHz were converted into second harmonic using the same lithium triborate doubler. The average power at 532 nm was 6–7 W, which corresponded to pulse

energy of 70–80 nJ. The laser beam was directed into the vacuum chamber and focused onto the target with the telecentric lens to a focal spot of ~20-μm diameter, providing intensity up to 5×10^8 W/cm^2 at the target surface.

With the available laser power, the deposition rate for a separation of the target and substrate of 250 mm was up to 2 nm/s. The laser beam was rapidly scanned over the target area of 5 cm $\times$ 5 cm using a pair of scan mirrors external to the target chamber to prevent the formation of craters in the target, which would eventually reduce the ablation rate. By using a large target to substrate separation, the deposited films were uniform in thickness to better than 5% over the surface of a 100-mm-diameter silicon wafer. The targets were angled approximately 25° to the incoming beam axis, while the substrates were positioned along the target normal. This prevented specularly reflected light from hitting the substrate, which is important when depositing photosensitive materials.

It should be noted that 532-nm light is not quite optimum for the ultrafast PLD method with As_2S_3 because the absorption depth of 532-nm radiation in the As_2S_3 target is ~2 μm. Ultrafast PLD is optimum when the thickness of the material ablated matches the distance of heat-front penetration from the strongly absorbing surface during the pulse. When the radiation can propagate into the material further than the heat wave, the ablation efficiency reduces because significant heating of the target occurs beyond the ablation front. This can also affect the ablation by introducing some thermal evaporation in addition to laser ablation. The use of a shorter laser wavelength would have eliminated this problem but was not available for these experiments.

The quality of the films was assessed by examination under optical and scanning electron microscopes. Similar to the results reported earlier for evaporation of graphite and deposition of diamondlike films,[14] QSML operation does not lead to the complete elimination of particle contamination from the films. Films deposited in the ML regime, however, demonstrated total absence of particles on the surface. For these films, the rms roughness was determined by atomic force microscopy to be 0.42 nm over a 15 μm $\times$ 15 μm film area (Fig. 1). The quality of these ML laser deposited films was sufficiently high for them to be used later for the fabrication of waveguides using photodarkening.

An interesting observation was made on the stability of these laser-deposited films, where it was found that exposure to daylight in air for a few days resulted in a significant deterioration of the surface. Analysis using a scanning electron microscope showed that arsenic and sulphur crystals were growing on the surface, presumably through the photodecomposition of the film followed by surface diffusion and crystallization of As and S atoms. Surface deterioration was even more pronounced in the case of QSML films. In order to prevent surface decomposition, it was found adequate to coat the films with a thin, ~0.8-μm layer of polymethyl methacrylate (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. A

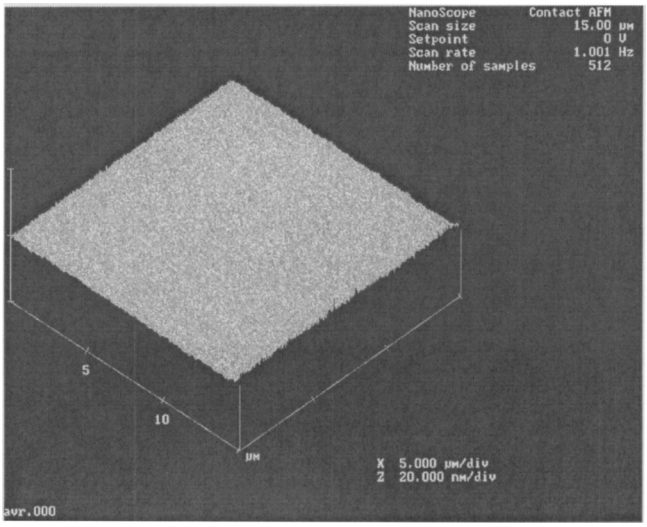

Fig. 1. Atomic force microscopy image of a 15 μm $\times$ 15 μm area of a ML deposited film. Rms roughness of the film was 0.42 nm (the vertical scale is 20 nm/division).

laser intensity of up to 2.5×10^3 W/cm^2 produced well-defined waveguide channels in the PMMA-coated As_2S_3 films,[15] while the uncoated films demonstrated noticeable thermal damage at a laser intensity above 40 W/cm^2 (see Subsections 4.C and 4.D below).

The stoichiometry of films was tested by both Rutherford backscattering and energy-dispersive x-ray analysis, which allows quantitative (accuracy of the order of 0.1 at.%) and qualitative elemental mapping of the laser-deposited films. The chemical composition of the films was compared with that of the target material. In all cases, the target composition was accurate to 40/60 of As/S ratio within 1 at.%, which was within the manufacturer's specifications, while film composition was usually slightly different from the source by up to 1.5 at.%, the films being slightly sulphur deficient. Sulphur deficiency was also observed in the conventional preparation of As-S amorphous glass films by the thermal evaporation technique and was attributed to preferential evaporation of sulphur.[16] As noted above, this may have been due to the presence of some thermal evaporation as well as ablation for the reasons noted above.

4. OPTICAL PROPERTIES OF LASER-DEPOSITED As_2S_3 FILMS

A. Refractive-Index Measurements

The prism-coupling technique was used to measure the refractive index at 632.8 nm, 810 nm, and 1064 nm for films deposited either onto fused-silica microscope slides or onto silicon wafers covered by an oxidized layer 2.4 μm thick. During these measurements, the ability of the films to act as waveguides could also be assessed from the propagation of the excited slab waveguide modes. In general, rather poor propagation was observed at 633 nm due to strong absorption (10–20 dB/cm) due to the proximity of the band edge at 2 eV, while at longer wavelengths, the losses were low and the guided beam would

propagate across the full wafer, indicating losses in the dB/cm range or lower. The loss measurements are discussed in more detail below.

In order to characterize more broadly the refractive indices of the films, a transmissivity measurement was performed using a spectrophotometer. The dispersion characteristics of the material were extracted from interference fringes presented on the transmission curve, through the Swanepoel technique[19] in the wavelength range 500–2400 nm. The accuracy of the measurements, which is always an issue in the Swanepoel technique due to a possible thickness variation in the film, was tested by comparison with results obtained from ellipsometry from the same sample, though in a much narrower range of 500–750 nm. The ellipsometry results of the refractive-index measurements were, on average, 0.01 lower, which is within a reasonable agreement with that derived from the transmission curves.

Figure 2 shows a typical spectral dependence of the refractive index for QSML and ML films, for both as-deposited and after the photodarkening. The results were reproducible to $\Delta n \leqslant 0.01$ over different deposition runs.

In order to examine the effect of laser exposure on these films, an area of a few cm^2 on each sample was illuminated with a 514.5-nm cw laser beam (the illumination intensity was 1 W/cm^2, and the total exposure time was 100 s). A significant difference in the refractive indices was observed for the QSML and ML laser-deposited films. A change of $\Delta n_{\mathrm{QSML}} \approx +0.01$ on average was measured, while the $\Delta n_{\mathrm{ML}} \approx +0.04$ was much larger in the whole range of wavelengths. It is not clear why these materials show such a difference. The results indicated though that ML laser-deposited films offer better potential for waveguide fabrication through photoinduced changes in the refractive index.

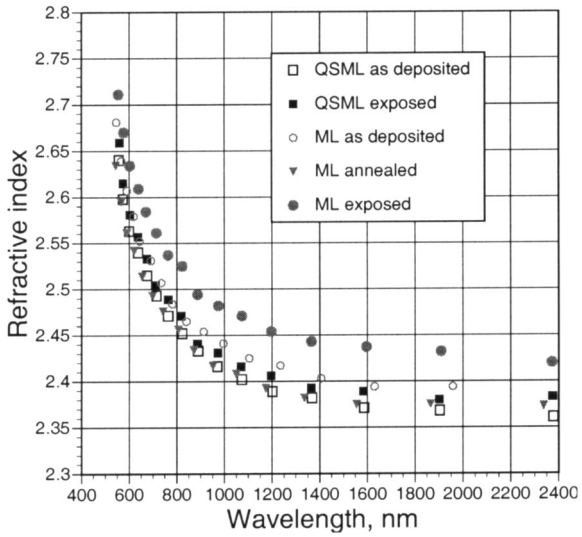

Fig. 2. Spectral dependence of the refractive index in the *Q*-switched mode-locked (QSML, squares) laser and mode-locked (ML, circles) laser-deposited films. Empty squares and circles indicate as-deposited films, and the filled ones indicate photodarkened films after illumination. The result of thermal annealing of a ML laser-deposited film is also shown for comparison (triangles).

B. Thermal Annealing

In order to prepare films to potentially give a larger change in refractive index by photodarkening, extensive work was carried out on the effect of annealing on the refractive index. As a result of either exposure or annealing, the film is transferred between metastable states, which depend upon the exposure or annealing history of the film. It has been known that annealing removes the stress in films and hence can lead to a more relaxed amorphous glass structure suitable for waveguide device fabrication.

Initial tests indicated that annealing the films in an inert atmosphere at temperatures of 150 °C for 2 h generally resulted in a reduction in the refractive index of the film. The effect was largest for the QSML films where the index change was $\Delta n_{\mathrm{QSML}} = -0.04$ at 800 nm, while for the ML films, the corresponding change was $\Delta n_{\mathrm{ML}} = -0.02$. Hence annealing and photodarkening have the opposite effect on the refractive index, with annealing tending to reduce the index (associated with bleaching of the absorption due to a change of the absorption edge to shorter wavelengths). Photodarkening, however, results in an increase in the index associated with movement of the absorption edge to longer wavelengths.

A problem, however, with the annealing process was that it led to microcracking of the films, rendering them useless for waveguide fabrication. This was attributed to a mismatch in the expansion coefficient of the film and the fused-silica substrate. It has been suggested in the literature[10] that rapid thermal annealing was effective in improving the properties of as-deposited films while avoiding cracking. Rapid thermal annealing (RTA) was therefore carried out under a nitrogen flow for annealing time up to 800 s and nominal temperatures up to 600 °C. At a short annealing time, up to 50 s, no noticeable change in refractive index could be detected, while beyond 300 s, the index change was nearly the same as that previously measured with oven annealing. Although it was suggested in Ref. 10 that RTA was effective in improving the properties of as-deposited sputtered films while avoiding cracking, for our relatively thick, up to 5-μm-thick, laser-deposited films, RTA always led to cracking. We thus concluded that the RTA process is inapplicable for use with few-micrometer-thick laser-deposited As_2S_3 films, and hence for waveguide fabrication, as-deposited films could only be used.

C. Photodarkening Characteristics

In order to explore the photodarkening further, a map of the photodarkening behavior as a function of exposure intensity and fluence was measured similar to that reported in Ref. 9. A 514.5-nm, cw argon-ion laser beam was used for illumination. Photodarkening was measured by monitoring the change in transmission of the sample versus illumination time. The transmission generally decreased with time, approaching a saturation level for long exposures.

Figure 3 illustrates the result of photodarkening of the laser-deposited films at various laser intensities in W/cm^2 and exposure time expressed in units of laser fluence J/cm^2. We have divided the exposure/intensity map into three distinctly different regions: no photodarkening, re-

versible, and permanent photodarkening. In order to establish whether the photodarkening was reversible or permanent, the samples were annealed at 150 °C for 2 h under a nitrogen flow after exposure. If the absorption returned to the value before exposure (±10%), the photodarkening was classified reversible. For comparison, the results of illumination of thermally evaporated As_2S_3 films from Ref. 9 are presented in the same graph. Our results show similar behavior to that reported in Ref. 9, although laser-deposited films seem to be three to ten times less sensitive. This could be explained by the fact that the films have been illuminated with 532-nm laser light scattered from the target surface during the deposition in the PLD chamber.

D. Direct Laser Waveguide Writing

The index increase associated with photodarkening can be used to define waveguides in the films by scanning a focused laser beam across the film surface at a fluence within the regime for "permanent" photodarkening, thereby creating narrow channels of enhanced index. A laser direct-writing system was available to photodefine such waveguides. It consisted of a computer-controlled two-axis air-bearing translation stage (Dover Instruments with ±10-nm position accuracy), and a frequency-doubled, diode-pumped Nd:YAG laser focused onto the film surface using a microscope objective. The system could deliver up to 4 mW in a 3.5-μm spot-diameter Gaussian beam onto the sample. The exposure of the material could be varied by controlling the scan rate of the sample under the focused beam and by attenuating the beam.

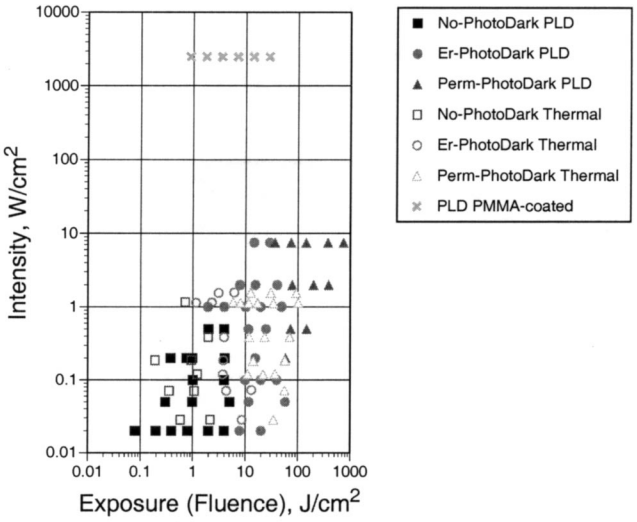

Fig. 3. Photodarkening data for laser-deposited (filled squares, circles, and triangles) and thermally evaporated (Ref. 9, empty squares, circles, and triangles) A_2S_3 films. The squares represent no photodarkening, circles represent erasable photodarkening, and triangles represent permanent photodarkening. The crosses indicate permanent photodarkening of the PMMA-coated films.

When using photodarkening for direct laser writing, it is important to know the threshold for the onset of damage where the film is ablated or melted off the substrate. For an uncoated film in air, this threshold was found to be ~40–50 W/cm^2 for both 514.5-nm (Ar laser) and 532-nm (second-harmonic of Nd:YAG laser) wavelengths. From Fig. 4, permanent photodarkening could then be achieved using a 3.5-μm-wide beam at speeds up to 100 μm/s at subdamage irradiances of 30 W/cm^2.

The application of a PMMA coating remarkably increased the damage threshold by up to two orders of magnitude. The combination of inhibited surface diffusion combined with the increased thermal conduction from the As_2S_3 layer in the presence of PMMA is most likely responsible for this dramatic change. Hence with the PMMA coating, a laser intensity of 2.5×10^3 W/cm^2 could be used, and the writing speeds increased into the 1 mm/s to 16 mm/s range, a two order of magnitude improvement compared with the uncoated films.

E. Measurements of the Absorption Coefficients

The absorption coefficient, α, of the films was measured using several techniques for the as-deposited, annealed, and photodarkened films as well as in the fabricated waveguides. At short wavelengths, where the absorption was high, a conventional spectrophotometer could be used, with corrections for reflection losses using the method described in Ref. 20. At wavelengths beyond the band edge, however, the absorption is too small for the technique to be useful. We therefore used photothermal deflection spectroscopy (PDS) to measure the relative ab-

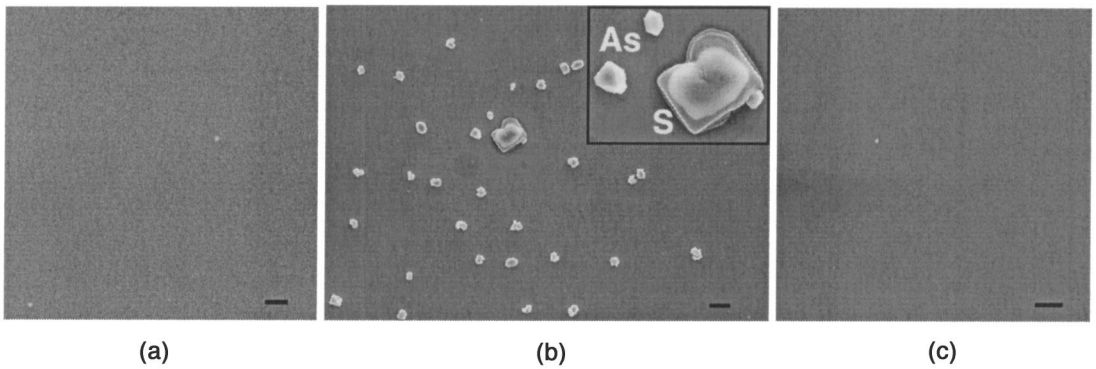

Fig. 4. Scanning electron micrographs of the surface of ML laser deposited films: (a) as deposited; (b) after a few days of storage under the daylight (in the corner is a magnified image of As and S crystals); (c) PMMA-coated after the deposition and stored under daylight. The scale bars are 10 μm in all images. Photodecomposition of the film clearly shows up in (b) as growth of pure crystal arsenic and sulphur on the surface, while the PMMA coating protects against decomposition of the films in (c).

sorption coefficient in the long-wavelength region. To calibrate the PDS data, absorption values from the spectrophotometer and the PDS were overlapped in the region of moderate absorption just beyond the band edge, where both give an accurate measurement. In addition, the loss was determined at spot wavelengths from propagation measurements that were made in slab waveguides. For these measurements, films deposited onto oxidized Si wafers were placed in a prism coupler, and the lowest-order slab waveguide mode was excited. Some radiation was scattered from the surface of the sample and could be detected using a cooled CCD camera. At wavelengths close to the absorption edge (633 nm), the decay of the intensity with distance was assumed dominated by film absorption, and hence the absorption coefficient for the film could be determined and used to calibrate the PDS data.

Figure 5 shows a calibrated PDS spectrum for a 5-μm-thick ML sample before and after exposure in the regime of permanent photodarkening. Notice the noise level of the PDS is reached for the as-deposited films at wavelengths beyond ~1000 nm (the noise level increases at longer wavelengths due to reducing power from the Xe arc lamp used in the PDS). Hence as-deposited films have losses below 0.1 dB/cm across the telecommunications bands at 1300 and 1550 nm. Photodarkening increases the losses to 0.3 dB/cm at 1000 nm and 0.2 dB/cm at 1600 nm. These are still sufficiently low values for the films to be potentially useful for waveguide applications.

Films 2.5 μm thick were used for single-mode waveguide fabrication using the direct-writing system. To assess the losses in fabricated waveguides, it was found possible to image the light scattered from the waveguides (without PMMA overcoat) and to monitor the decay of power in the waveguide as a function of distance using an IR-sensitive video camera. Light from laser-diode sources at 780, 1300, and 1550 nm was end coupled into the waveguides using a microscope lens for these measurements. The losses obtained in this way were ~4 dB/cm at 780 nm, ~0.24 dB/cm at 1300 nm, and 0.2 dB/cm at 1550 nm. These values are in good agreement with those obtained from the PDS measurements as shown in Fig. 5. The output from the waveguides was imaged with a microscope objective onto a video camera. The waveguides were single mode at 1300 nm and 1550 nm. A typical output beam pattern at 780 nm is shown in Fig. 6, where the lowest-order mode was excited by careful alignment of the input beam. The near-field pattern shows reasonable symmetry, although some influence of the upper air–As_2S_3 interface is apparent.

Band theory for crystalline semiconductors suggests that the absorption coefficient for indirect transitions can be written as

$$\alpha = \text{const} \times M^2 \frac{(h\nu - E_g)^2}{h\nu}, \tag{1}$$

where M is the matrix element of the optical transition and E_g is the bandgap energy. With the assumption of parabolic bands, the absorption in many amorphous semiconductors is observed to obey this relation above the exponential edge.[21] If M is constant, plotting $(\alpha \times h\nu)^{1/2}$ versus $h\nu$ (Tauc plot) should result in a straight line. The optical gap is obtained from the intersection of this line with the energy axis. Figure 7 shows a Tauc plot for ML laser-deposited films yielding $E_g = 2.26 \pm 0.02$ eV. This value is slightly lower than that of 2.36 eV in thermally evaporated As_2S_3 films, most probably due to illumination of the films during the laser deposition process.

F. Nonlinear Optical Constants

Both degenerate four-wave mixing (DFWM) and the Z-scan technique[22] were used to determine the value of the nonlinear refractive index of As_2S_3 either in the bulk form or in thin films. In the case of bulk samples, the Z-scan technique was used to determine the nonlinear refractive index in the wavelength range 1200–1500 nm. The source in this case was the tunable output from a Light Conversion TOPAS traveling-wave optical parametric amplifier pumped by a Clark-MXR CPA2001 Ti:sapphire laser. A typical Z-scan for a 2-mm-thick sample is shown in Fig. 8. Note that the absence of any significant nonlinear absorption in the open-aperture scan indicates a good nonlinear figure of merit, $T = \beta\lambda/n_2$ for this material. The maximum value for T in this case was 0.1 (estimated from the small deviations in the background signal as the sample is scanned through the focus of the beam), a value well within the range required for all optical processing where $T < 1$ is generally regarded as sat-

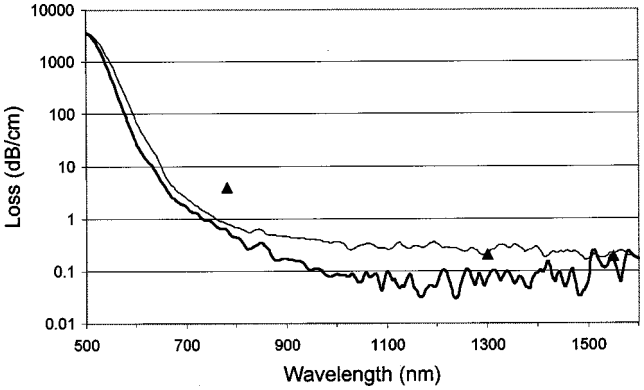

Fig. 5. Absorption losses determined from PDS measurements for as-deposited (lower) and photodarkened films (upper). The filled triangles were obtained from waveguide propagation measurements at 780 nm, 1300 nm, and 1550 nm (see text).

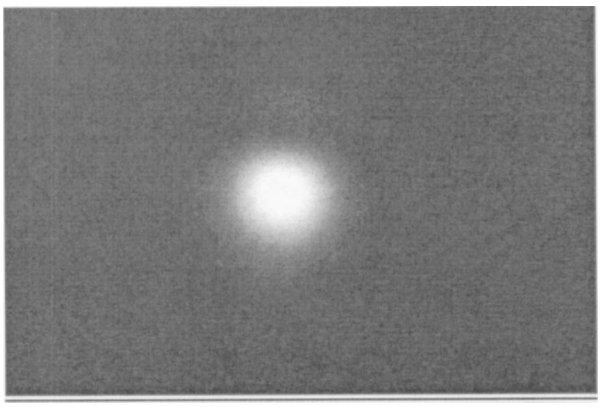

Fig. 6. Near-field image of a 800-nm single-mode output of a 3.5 μm × 2.5 μm photoinduced channel waveguide written in the ML laser-deposited films.

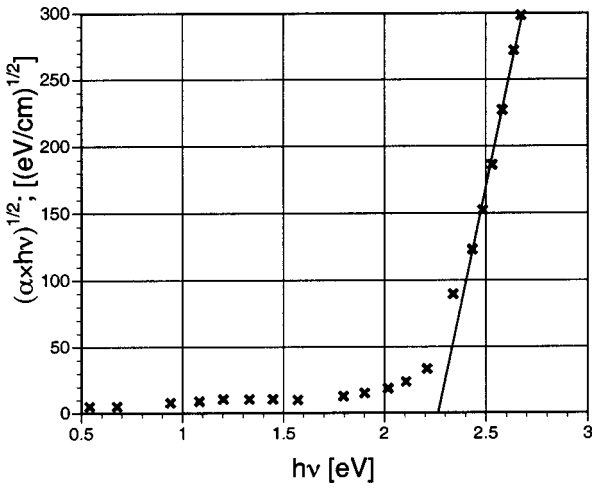

Fig. 7. Spectral dependence of $(\alpha \times h\nu)^{1/2}$ in ML laser-deposited As_2S_3 films. The solid line is linear approximation.

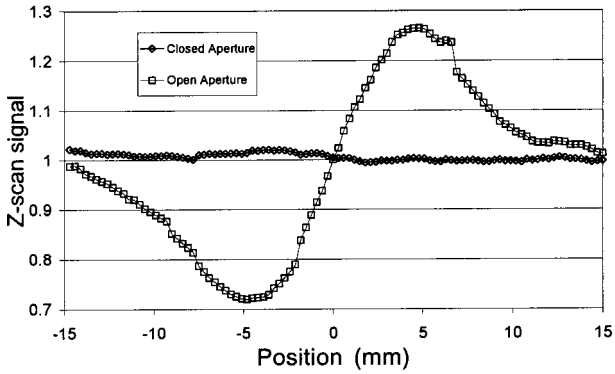

Fig. 8. Open- and closed-aperture Z-scan signals from a 2-mm-thick bulk sample of As_2S_3 glass measured at 1550 nm. Note the absence of any nonlinear absorption in the open-aperture scan.

isfactory. The results of Z-scan measurements are shown in Fig. 9. Note that to obtain these values, the amplitude of the Z-scan signal for the As_2S_3 sample was compared with that from silica for which $n_{2,\text{silica}} = 3 \times 10^{-16}\,\text{cm}^2/\text{W}$. This was necessary because the beam from the traveling-wave optical parametric amplifier of superfluorescence (TOPAS) only approximated a Gaussian and hence did not have sufficiently well-behaved focusing characteristics that are necessary to obtain the optical nonlinearity directly from the Z-scan signals. The values varied slightly with wavelength reaching a maximum for wavelengths around 1300 nm (200× silica) and decreasing to around 100× silica at 1500 nm.

The four-wave mixing experiments were performed at 800 nm using films of As_2S_3, up to 4 μm thick deposited on 1-mm-thick fused-silica substrates. The DFWM system consisted of a femtosecond Ti:sapphire laser based around a Coherent Mira-800D oscillator providing a train of 100-fs pulses that were subsequently amplified in a Ti-sapphire chirped-pulse amplifier pumped at a repetition rate of 30 Hz with 532-nm pulses from a Spectra Physics GCR30 Nd:YAG. The forward-scattering geometry was used to perform DFWM measurements.[23,24] The energy per pulse was up to 35 μJ, and the spot size on the sample was approximately 200 μm in diameter. To avoid ambiguities due to the unavoidable presence of signals, both from the silica substrate and from the chalcogenide film, two diffraction signals were monitored simultaneously. One was generated as a result of phase-matched interaction of the three incident beams, and the other was one of the non-phase-matched signals generated mostly by the arsenic trisulfide film.[24,25] For a 4-μm-thick film, the non-phase-matched signal was approximately half the phase-matched signal.

Figure 10 shows an example of a non-phase-matched DFWM signal at moderate input power (~15-μJ total energy in all three beams, corresponding to an intensity of the order of 100 GW/cm^2). The signals recorded at lower powers show essentially only the instantaneous response similar to that obtained from bare silica substrate. A very weak "tail" of the signal appears in some curves obtained at higher powers (just apparent in Fig. 10), but in this higher power range, permanent gratings are gradually formed in the material that distort the background signals.

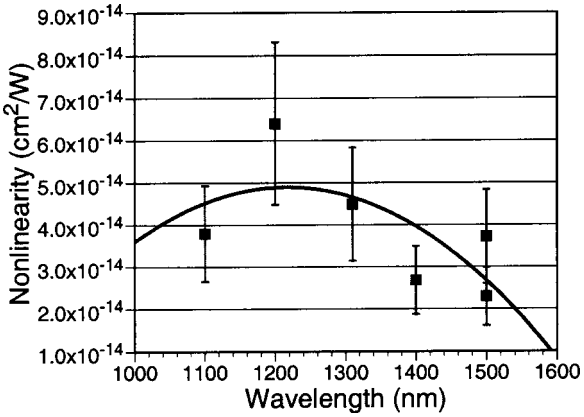

Fig. 9. Nonlinearity versus wavelength obtained from Z-scan measurements.

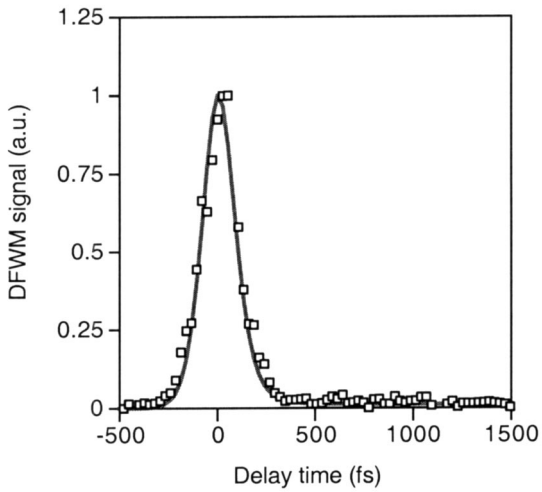

Fig. 10. An experimental non-phase-matched DFWM signal from a 4-μm-thick As_2S_3 film on silica substrate. The curve is a theoretical best-fit curve (laser pulse duration 134 fs; a small contribution of long-lived two-photon absorption induced grating was added).

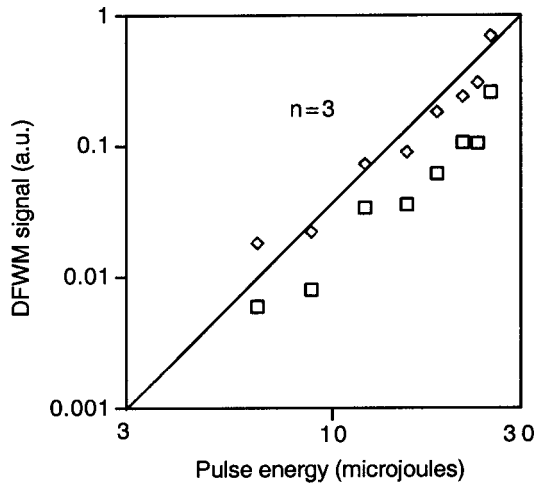

Fig. 11. Double-logarithmic plot of power dependencies of the DFWM signals (diamonds, phase matched; squares, non phase matched) from a 4-μm-thick As_2S_3 film. The line shows a theoretical cubic dependence.

At 800 nm, it became clear that photodarkening of As_2S_3 films could occur presumably due to two-photon processes in conditions similar to those needed to obtain DFWM signals. Thus it is likely that the measurements obtained here were in partially photodarkened material. Attempts to compare the nonlinearity of photodarkened and non-photodarkened regions of a film by recording the DFWM signal when scanning the beams across the film with green-light pre-exposed stripes were inconclusive but did not suggest there was a significant change in nonlinearity due to photodarkening.

Figure 11 shows a comparison of the power dependence of the phase-matched and non-phase-matched DFWM signals from a 4-μm-thick film. As expected for Kerr nonlinearity, the dependences are roughly cubic. The nonlinearity of the films, $|n_2|$, was calculated from the comparison of the DFWM signals with those for bare-silica substrates as described in Ref. 24 and assuming $n_2 = 3 \times 10^{-16}\,\mathrm{cm}^2/\mathrm{W}$ as the nonlinear refractive index of silica.

The modulus of n_2 was found from above measurements to be $2.7 \times 10^{-14}\,\mathrm{cm}^2/\mathrm{W}$. This is in a good agreement with literature data and the measurements on bulk samples of As_2S_3 performed in a wider range of wavelengths reported above. It should be mentioned that the sign of the real part of n_2 deduced from Z-scan measurements was positive also at 800 nm.

5. CONCLUSION

The results demonstrate that ultrafast pulsed laser deposition, which employs picosecond-range laser pulses at a MHz-range repetition rate, is capable of producing particulate-free films a few micrometers thick of chalcogenide glass such as As_2S_3. The deposition rate of up to 2 nm/s at 250-mm distance from the target was achieved with up to 7-W average power second-harmonic radiation from a mode-locked Nd:YAG laser. This deposition rate enables the 5-μm, films to be deposited on a 10-cm-diameter silicon wafer in less than an hour. At the same time, the *Q*-switched laser pulses with much higher peak power and lower repetition rate led to formation of particulates on the film, significantly reducing optical quality. After extensive investigation of rapid thermal annealing of the deposited films, we have concluded that, in spite of the fact that RTA bleaches the films and allows a higher change in the refractive index due to photodarkening with subsequent illumination, the RTA process applied to few micrometers-thick laser As_2S_3 film still results in cracking.

The ultrafast laser-deposited films obtained in the ML regime are quite photosensitive, though less so than thermally evaporated films, but significantly, they do not require thermal annealing before waveguide fabrication. The high optical quality and low light scattering in these films allowed us to fabricate low-loss photoinduced waveguides with losses <0.3 dB/cm at telecom wavelengths. A PMMA coating was applied to as-deposited As_2S_3 films to inhibit surface photo-decomposition, and it led to an increase of the damage threshold for more than two orders of magnitude during laser direct writing, allowing waveguides to be written rapidly at up to 16 mm/s.

The optical properties of the deposited films can be summarized as follows:

- Optical losses are down to <0.1 dB/cm for as-deposited films at 1550 nm.
- Optical losses are <0.2 dB/cm at 1550 nm for films fully photodarkened using Ar-ion 514-nm laser light or a Nd:YAG 532-nm laser.
- Optical bandgap derived from the absorption measurements is 2.26 ± 0.02 eV.
- The refractive index increases with photodarkening from 2.46 at 800 nm by up to 0.06, with an average increase 0.04–0.05.
- Nonlinear optical coefficients are determined at 800 nm through degenerative four-wave mixing using a 150-fs Ti:sapphire laser and from Z-scan measurements, indicated that the material has a moderate instantaneous third-order nonlinearity of Kerr type with $|n_2| = 3\text{–}6 \times 10^{-14}\,\mathrm{cm}^2/\mathrm{W}$ and low two-photon absorption losses.

It is possible to compare our results with the data available for the films deposited by other deposition techniques. The results on change in the refractive index as well as on photodarkening agree reasonably well with published results in Refs. 10 and 26, where a change of 0.1 in the refractive index was measured due to photodarkening in thermally evaporated arsenic sulphide films. The optical gap of 2.26 eV is slightly lower than that of 2.35–2.37 eV obtained for thermally evaporated films.[26,27] The band edge shift toward longer wavelengths in laser-deposited films is consistent with the fact that the films have been exposed to scattered laser light during the deposition. The value reported in Ref. 28 for the nonlinear refractive index for a bulk As_2S_3 glass of $2.5 \times 10^{-14}\,\mathrm{cm}^2/\mathrm{W}$ measured at 1.064 μm agrees well with the $|n_2|$ value in our laser-deposited films measured at 800 nm and with longer-wavelength Z-scan results obtained by us on bulk samples.

Various techniques have been used to measure absorption losses in chalcogenide films. Losses <0.3 dB/cm have been reported in RTA annealed sputtered films,[10]

while values of 1 dB/cm to 8 dB/cm have been measured for thermally evaporated films. PDS measurements show absorption losses below 0.1 dB/cm in as-deposited films at wavelengths beyond 1 μm. Waveguide losses measured below 0.3 dB/cm at 1550 nm are exceptionally low for this class of materials and were limited by the bulk losses of photodarkened material. This demonstrates a clear superiority of ultrafast laser-deposited films over thermally deposited and sputtered films. The results suggest that ultrafast laser-deposited As_2S_3 films are very suitable candidates for waveguide fabrication.

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