Direct femtosecond laser writing of waveguides in As_2S_3 thin films

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Single-channel waveguides and Y couplers were fabricated in chalcogenide thin films by use of femtosecond laser pulses from a 25-MHz repetition rate Ti:sapphire laser. Refractive-index differentials ($\Delta n > 10^{-2}$) were measured through interferometric microscopy and are higher than the typical values reported for oxide glasses. The dependence of the index differential on the peak intensity reveals the nonlinear nature of the photosensitivity in arsenic trisulfide below its bandgap energy, and the refractive-index change is correlated to the photoinduced structural changes inferred by Raman spectroscopy data. A free-electron model to predict the parametric dependence of Δn is proposed. © 2004 Optical Society of America

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The use of focused femtosecond laser pulses to produce structural modification in optical glasses is now well known.[1–5] Many of the advantages of femtosecond lasers compared with conventional lasers, and their potential for use in the fabrication of photonic devices,[1] stem from their highly localized and deterministic energy deposition. In this regime the focused intensity within the material must reach a certain minimum value, depending on the material, for a structural change to occur. Initially these intensities could be achieved with only ~100-fs Ti:sapphire lasers employing chirped-pulse amplification in conjunction with a regenerative or multipass amplifier, producing pulses at kilohertz repetition rates with microjoule energies.[1,2] However, if the required intensities can be achieved, there are advantages to be gained from operating at higher repetition rates with lower pulse energies. Recent studies have reported the fabrication of photonic devices by use of simple megahertz femtosecond laser oscillators,[3–5] decreasing the complexity of the laser scheme and allowing for greater processing speeds.

Most studies that use femtosecond direct laser writing have investigated waveguide fabrication in oxide glasses.[2,3,5] However, the chalcogenide glass (ChG) family exhibits several interesting properties that can be exploited for the fabrication of photonic devices. In particular, their excellent infrared transparency, large nonlinear refractive indices, and low phonon energies make ChG films good candidates for use in the fabrication of all-optical switches[6] and as integrated optical elements.[7] Optical waveguides in As–S–Se-based ChG have been fabricated by several techniques, including photolithography, ion implantation, and laser beam writing.[8] The material investigated in this study is arsenic trisulfide (As_2S_3), which, like other ChGs, has a semiconductor band structure. Despite its optical bandgap E_g at 2.35 eV ($\lambda \sim 517$ nm), photosensitive properties have been demonstrated over a broad energy range, from γ radiation down to infrared, below the bandgap energy. Subbandgap irradiation has already been successfully exploited to write holographic gratings and self-written channel waveguides through two-photon-induced processes at 800 nm.[7] Here we describe the fabrication of two-dimensional waveguide structures in As_2S_3 thin films with a simple femtosecond oscillator laser. Measurements were made of the refractive-index change produced within the waveguide; the index differential is shown to be much larger than photoinduced index changes in other materials.[2,3] From the parametric dependence of this refractive-index modification, and from Raman spectroscopic studies, insight into the nature of the physical mechanisms that occur in the material is given.

The laser oscillator used for writing was an extended cavity Ti:sapphire laser with a repetition rate reduced to 25 MHz and an ~40-nm spectral bandwidth centered at 800 nm and produced 20-nJ pulses of 30-fs duration with 4.5% pulse-to-pulse stability. The Gaussian laser output beam (M^2 of ~2.6) was focused to a 10-μm-diameter spot with a 0.28-N.A. Schwarzschild microscope objective. The writing studies described here were made with 1.6-μm-thick films of As_2S_3 thermally evaporated from bulk glass starting materials onto Si/SiO_2 wafers. Details of the thin-film deposition are described elsewhere.[8] Waveguides were written in the As_2S_3 films by translation of the film transversally with respect to the focused laser beam by use of a three-dimensional motorized translation stage. The translation speed could be varied from 0.1 to 20 mm/s, allowing the number of pulses incident upon the laser focal spot area to be varied for different laser intensities. The laser intensity was adjusted with a variable metallic neutral-density filter placed before the microscope objective. The experiment was performed with a pulse rate of 10^4–10^6 pulses per focal spot and intensities

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in the range of 0–0.3 GW/cm^2. Waveguides as long as 2 cm have been fabricated, limited only by the range of the translation stage and the sample size. The waveguides were displayed by a differential interference contrast microscope with a magnification of 20× that identified the photoinduced change [Figs. 1(a)–1(c)].

Characterization of the optical properties of the waveguides produced was made by butt coupling a 785-nm single-mode pigtailed laser diode to the cleaved waveguides. The near-field pattern of the coupled modes was then imaged onto a CCD [Figs. 1(d)–1(f)]. Coupling into As_2S_3 thin films was limited by the high refractive index of the material ($n = 2.45$), which produced high Fresnel losses at both ends of the waveguide. However, more than 70% of the light exiting the film end face (channel and film) was confined in the channel waveguide. Only a small fraction of the light either did not couple because of mode mismatch, or was decoupled owing to scattering, and appeared on either side of the coupled mode, as shown in Fig. 1(e). The measured ratio of power coupled in the two output branches of the Y coupler was near 50%/50%. Refractive-index change Δn induced inside the waveguide was measured with a Zygo (NewView5000) interference microscope. Measurements were made of the dependence of Δn on the laser's irradiating intensity and the integrated absorbed laser flux density. The latter is shown in Fig. 2(a). The value of Δn increased approximately logarithmically when the integrated laser flux density was increased by a decrease in the translation speed. The Δn value showed a much sharper dependence on the pulse intensity for a constant translation speed, as shown in Fig. 2(b). Because the exposure photon energy was well below the absorption edge of the material, this result strongly suggests that the mechanisms that are responsible for the photoinduced index change rely on nonlinear optical processes.

Many of the results described above can be explained by a model based on free-electron generation by multiphoton ionization, joule heating, and avalanche ionization that was previously proposed to describe optical ablation by high-power ultrashort pulses.[9] The electron kinetics is described by the rate equation

$$\frac{\partial n_e}{\partial t} = \alpha I(t) n_e + \sigma_k I(t)^k, \qquad (1)$$

where the first and second terms on the right-hand side describe avalanche ionization and multiphoton ionization, respectively. Here n_e is the electron density, α is the avalanche coefficient, $I(t)$ is the time-dependent intensity of the laser, and σ_k is the k-photon absorption cross section; the smallest k satisfies $khv \geq E_g$. Under the assumption that multiphoton ionization is the dominant mechanism for pulses of <150-fs duration,[10] the first term on the right-hand side of the equation can be ignored. This assumption is supported by the fact that a better fit to our experimental results was obtained when α was set to 0. Previous studies showed that n_e is expected to increase as the laser intensity is increased, until it reaches a critical value that corresponds to the onset of ablation. The experiments described here were well below ablation threshold. At these intensities, nonetheless, a permanent structural change in the glass matrix is created, accompanied by a change in the index of refraction. The magnitude of refractive-index change Δn depends on both the irradiation conditions and the material. In As_2S_3, Δn induced at these intensities is positive, and it saturates before ablation occurs, as shown in Fig. 2. We therefore introduced a semiempirical parameter N_0, a saturation parameter that represents the maximum number of electrons available to participate in the mechanism of

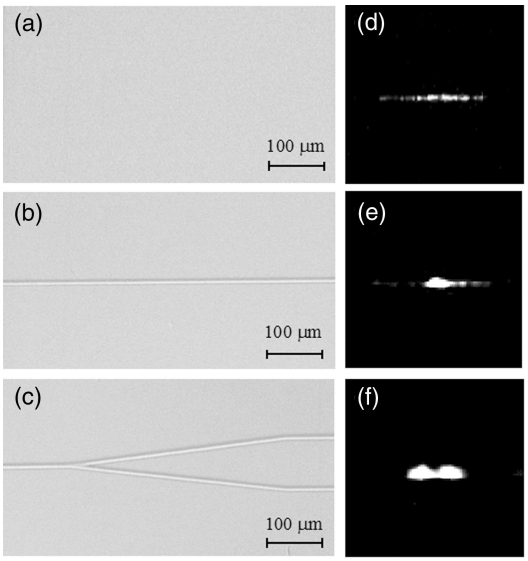

Fig. 1. Optical microscope images of (a) the unexposed film, (b) a single-channel waveguide, and (c) a Y coupler. (d)–(f) CCD images of the near-field pattern of the coupled modes.

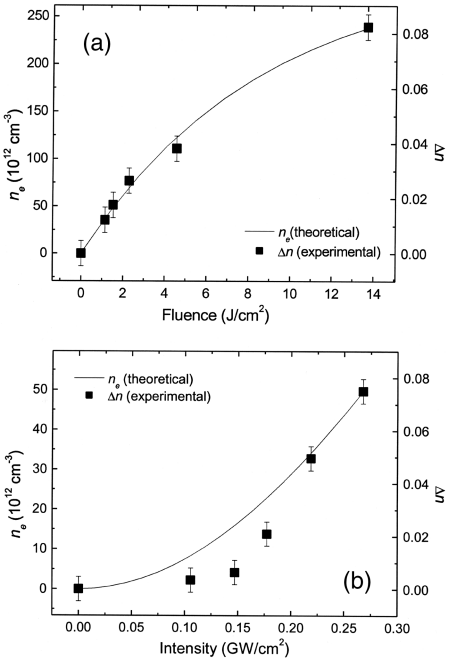

Fig. 2. Measured Δn and calculated electron density versus (a) the integrated fluence (pulse intensity was set to 0.25 GW/cm^2) and (b) the pulse intensity.

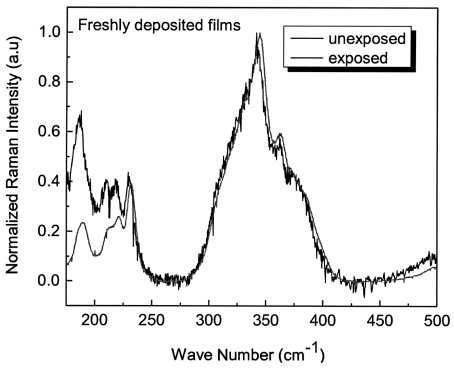

Fig. 3. Raman spectra of an as-deposited As_2S_3 film (unexposed) and of a written waveguide (exposed).

electron generation. Equation (1) then became

$$\frac{\partial n_e}{\partial t} = \sigma_k I(t)^k \frac{N_0 - n_e}{N_0} . \quad (2)$$

The results of the simulation are plotted in Fig. 2 with the experimental data. A comparison with the experimental evolution of Δn shows that the model is able to predict the general trend of Δn, as the laser intensity and the number of pulses are separately varied. In the calculation, two-photon cross section σ_k was calculated from the two-photon absorption coefficient given in Ref. 11. The best fit was obtained for saturation parameter $N_0 = 3 \times 10^{14}$ cm^{-3}.

Raman spectroscopy has proved to be a valuable tool to reveal the photoinduced structural changes that occur in a glass matrix after its exposure to femtosecond pulses. In fused silica, an increase in the concentration of four- and three-member ring structures in the silica network was measured by Raman spectroscopy.[2] Figure 3 illustrates the normalized Raman spectra of two freshly deposited As_2S_3 films that we obtained with an excitation wavelength of 840 nm by employing a waveguide Raman geometry, as described in Ref. 12. The main Raman feature is the broad band at 345 cm^{-1}, attributed to the symmetric As–S–As stretching vibration in the $As(S)_{3/2}$ pyramidal units of the glass network. The low-frequency vibrations from 175 to 250 cm^{-1} are attributed to the As_4S_4 molecular clusters and the As–As homopolar bonds that are present in the freshly deposited films.[12] Moreover, the weak Raman band at 494 cm^{-1} is correlated to the presence of S–S homopolar bonds.[13,14]

Changes in the Raman spectra suggest that subbandgap femtosecond irradiation had an effect on the structure of the freshly deposited films, inducing apparent modifications in the molecular arrangement. As more As_4S_4 molecular clusters reorganize to form part of the glass network, the number of homopolar bonds decreases. As a result, the intensity of the low-frequency Raman bands is noticeably smaller for the exposed film than for the as-deposited film. This result is consistent with Raman spectral changes observed in As_2S_3 films exposed to bandgap energy radiation.[13] It is interesting to note that in bulk As_2S_3, in which no As_4S_4 units were present,[12] subbandgap illumination produced an increase in the bands at 236 and 494 cm^{-1}, corresponding to the creation of homopolar bonds.[14] In both bulk and film As_2S_3, exposure to femtosecond radiation at 800 nm resulted in a positive change in the refractive index through photodarkening.[4,14]

In summary, we have demonstrated the fabrication of two-dimensional waveguiding structures in arsenic trisulfide thin films by using a simple Ti:sapphire laser oscillator. Large refractive-index changes were induced and light coupling in the waveguides was achieved in both the single-channel waveguide and the Y coupler, with a near 50%/50% splitting ratio in the Y coupler. A semiempirical model has been proposed for a quantitative estimate of the generated electron density on femtosecond irradiation that will successfully predict the dependence of the index differential on the irradiation parameters. Finally, the photoinduced structural changes have been inferred from waveguide Raman spectroscopy data.

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