The Impact of Thermal- and Photo-annealing of Chalcogenide Films for Optical Waveguides

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Abstract: We applied thermal- and band-edge light annealing on an as-deposited As_2S_3 film to mitigate its phase separation and, thus to improve the propagation losses of fabricated optical waveguides. Studies of the film microstructure revealed a difference between atomic bonds and linked phases among the as-deposited, thermally-annealed, and optically-annealed films. We fabricated rib-type waveguides with 4 micron width from 0.85 μm thick films, and measured the insertion losses. Around 0.4 and 0.2 dB/cm propagation losses were obtained in the waveguides produced from as-deposited and annealed films, respectively. The waveguides produced from photo-annealed film showed almost the same propagation losses to those from thermally-annealed material. Our results, however, indicate optical-annealing provides some advantages over thermal annealing for waveguide fabrication, such as the absence of film cracking which observed at high temperature processing.

1. Introduction

Chalcogenide glasses (ChGs) have been extensively researched and demonstrated as nonlinear optical (NLO) devices for all optical signal processors, leveraging their high nonlinearities, ultrafast time response, and low linear and nonlinear losses [1]. Arsenic tri-sulphide (As_2S_3), a representative ChG, has been applied in various forms – bulk glass, optical fiber, and recently planar waveguide. Our research group, CUDOS, already reported the development of As_2S_3 planar waveguides employing thin film deposition and plasma etching [2-3], and have demonstrated several NLO devices utilizing these waveguides [1,4]. One of the issues in As_2S_3 film is that as-deposited film is known to be phase-separated in nanometre scale; that is, it consists of homo-polar bond containing phases (e.g., As_4S_4) interspersed with an orpiment-like (As_2S_3) glass backbone network.

In this work we describe the effects of thermal- and optical-annealing of As_2S_3 thin films on their microstructures and the optical propagation losses in high-index-contrast, sub-micron thick ChG waveguides. We monitor changes in the microstructure and compare optical annealed material with as-deposited and thermally-annealed films as well as the bulk glass. We find that from the perspective of microstructure and refractive index, optical annealing is a more effective in evolving an as-deposited film towards the state of the bulk glass compared with thermal treatment. However the waveguides fabricated from optical annealed material showed similar losses to those from thermally-annealed films which may indicate that side-wall scattering is the limiting loss mechanism. Other benefits of photo-annealing in the waveguide fabrication are also discussed.

2. Experimental

As_2S_3 films were deposited by thermal evaporation onto oxidized silicon wafers in a chamber evacuated to 2.5×10^{-5} Pa. Deposition occurred with a source to substrate distance of ~40 cm at a rate of ~0.2-0.3 nm/s. Prior to both annealings, ~125 nm thick SU-8 (SU-8 2 from MicroChem Corp.) layer was spin-coated and UV-cured on the film to prevent As_2S_3 evaporation at high temperature [5] and As_2O_3 crystallites formation on the surface [6]. Thermal annealing of as-deposited films were carried out at temperatures up to but below the glass transition temperature (T_g ≈ 180 °C) for 24 hours in a vacuum oven. For waveguide fabrication, however, the film was annealed at 130 °C for 24 hours in order to avoid film cracking problem [5]. For bandgap light illumination tungsten halogen lamp through a filter utilized as a light source. Its spectrum centred at 520 nm, very close to the bandgap of the film. Light intensity on the film surface was around 10 mW/cm^2. The refractive index and thickness of films were measured by a spectroscopic reflectometer (SCI Filmtek 4000). The microstructures of various As_2S_3 films and glass were probed by micro-Raman spectroscopy (Renishaw 2000 Raman microscope) in a backscattering geometry at room temperature. To minimize the photo-induced structural changes during the measurement, samples were excited with 782 nm light at intensity below 1 W/cm^2 on the surface. For waveguide fabrication, photo-resist pattern was prepared using standard contact photolithography, and then an inductively coupled plasma reactive ion etching system (Plasmalab100, Oxford) was used to etch As_2S_3 with CHF_3. The waveguides were clad with 15 μm thick

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film of UV cured inorganic polymer glass (RPO Pty Ltd, IPG™). The propagation loss of the guides was determined via standard cutback method. A tunable laser source, a polarization controller, and an InGaAs power meter were used to measure the insertion loss of waveguides.

3. Results and Discussion

We investigated the influence of each annealing process on the variation of bond content via Raman scattering (Refer to fig. 1). Here, heat treatment was done at 130 °C. Compared with the bulk glass, an as-deposited film shows several sharp peaks; in particular peaks at 150 – 250 cm^{-1} are the fingerprint of molecular species, As_4S_4, or As-As homopolar bond [7]. We can clearly see that both annealing methods diminish these peaks drastically. Considering the overall peak shape as well as the lower intensities of the molecular species, the film that has been optically annealed is closer to that of the bulk glass. The heat-treated sample still retains the peak at 220 cm^{-1}, which is assumed to come from As_4S_4 [7], that completely disappears in the optically-annealed sample. X-ray photo-electron spectroscopy also supported the effectiveness of photo-annealing in transforming the virgin film kin to bulk. In a recent paper [5] the content of As-As bonds of thermally-annealed film was obtained as a function of annealing temperature through the decomposition of As *3d* spectrum into two sub-peaks - each with and without As-As. The same measurements on the optically-annealed film showed that the fraction of arsenic atoms containing homopolar bond is much smaller than that in the film annealed at 170 °C (5 % versus 12 %)

In order to study the impact of the annealing procedure on the waveguide performance, we fabricated three sets of rib-type waveguides from 0.85 µm thick As_2S_3 films; each was as-deposited, thermal-annealed at 130 °C for 24 hours, and optically-annealed for 24 hours, respectively. Atomic force microscopy (AFM) measurement revealed that no conceivable variation was found in the morphology and roughness of etched surface among them. The inset in fig.2 shows the cross-sectional view of the waveguide. The impact of both annealings was clearly observed from the loss improvement; the propagation losses were halved over as-deposited film when it was annealed. Even though photo-annealed film is expected to contain fewer wrong bonds or absorption centres, both 4 µm wide guides had similar propagation loss (around 0.2 dB/cm). Mode calculation shows around 97% light resided inside the core [3]; hence volume scattering or absorption by the material would be a significant attenuation mechanism in such a wide guide. The above results, on the other hand, indicate that the two different annealing processes seem to result in similar losses at least in 4x0.85 µm waveguides which is likely to indicate that the losses are dominated by losses at waveguide surfaces rather than the bulk material. This is consistent with measurements of the losses of As_2S_3 optical fiber where values <1dB/m have been reported.

Nevertheless optical annealing of the film appears to have several advantages over heat treatment. Firstly, the film has properties much closer to that of the bulk glass in terms of the microstructure, atomic bonds, and the index of refraction, thereby could be produced ultimately into lower-loss waveguides. Whilst high temperature annealing might bring about the similar results, annealing near T_g is not possible due to cracking and roughening of the film surface. Secondly, optical annealing minimizes the residual photosensitivity of As_2S_3 film so that the associated issues such as the grating formation in waveguide or the resonant frequency shift in microdisk under high power CW laser [8] could be mitigated. Similarly to thermal treatment [9], the improved resistance to photo-oxidation of the film is another benefit of optical-annealing.

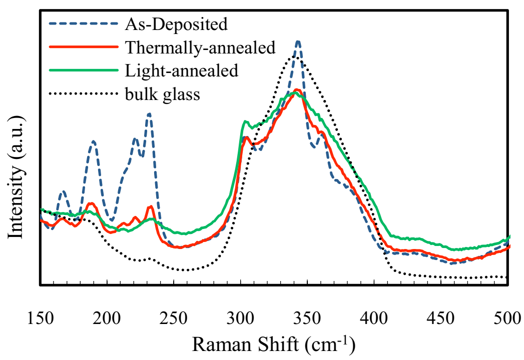

Fig. 1 Raman spectra of bulk glass, as-deposited and annealed As_2S_3 films.

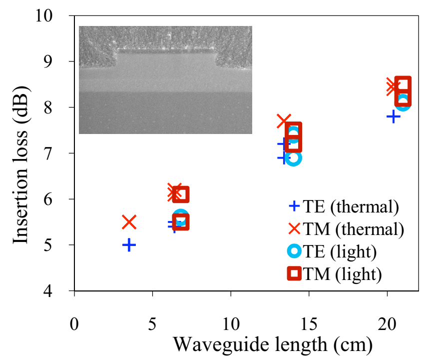

Fig. 2 Insertion losses of waveguides with their lengths when the width was 4 µm. (Inset: Cross sectional view of a waveguide)

4. Conclusion

Bandgap light illumination and heat treatment were employed to fabricate As_2S_3 thin films waveguides, and their impact on microstructural evolution and propagation losses of waveguides were compared. Polymerization in the as-deposited film were the dominant homogenization mechanism in both processes, however, photo-processing converts the film microstructure more analogous to bulk glass. Photo-annealing is superior to thermal process in As_2S_3 waveguides fabrication whist its mechanism is not yet fully understood.

5. References

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