Rapid thermal annealing of chalcogenide thin films for mid-infrared sensing and nonlinear photonics

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Abstract. The influence of rapid thermal annealing (RTA) onto chalcogenide Ge-Sb-Se thin films is reported, focusing on changes in optical properties. These materials possess broad mid-infrared transparency covering the most critical absorption bands for (bio)chemical sensing and high third-order optical nonlinearities for potential applications in nonlinear photonics. The parameters of the RTA process within this study include the annealing temperature, heating rate, and the two sample processing methods – one by placing the sample inside the graphite susceptor and the other by simply laying the sample onto the silicon wafer. Selenide thin films were found to undergo a shift of the absorption edge upon the RTA, resulting in an optical bandgap energy increase (bleaching effect) and a notable refractive index decrease. As a result of structural relaxation, such changes show a great potential of RTA in fine-tuning of optical performance of chalcogenide thin films and planar chalcogenide waveguides. The authors acknowledge the IBAIA (101092723) Horizon Europe project, the ANR AQUAE (ANR-21-CE04-0011-04) project of the French National Research Agency (ANR), and project No. 22-05179S of the Czech Science Foundation (GAČR) for financial support.

1 Introduction

Chalcogenide glasses and amorphous chalcogenide thin films possess broad mid-infrared transparency covering the most critical absorption bands for (bio)chemical sensing [1] and high third-order optical nonlinearities for potential applications in nonlinear photonics [2]. Structural modifications by thermal annealing or structural relaxation using continuous-wave lasers are particularly attractive for enhancing their optical performance for novel photonic devices, including waveguides. Additionally, rapid thermal annealing (RTA) provides an effective tool to overcome problems with cracking or film lift-off arising from relatively large thermal expansions, which may occur during conventional annealing [3].

We report the study of changes in optical properties upon RTA of ternary sputtered Ge-Sb-Se photosensitive chalcogenide thin films [4].

2 Materials and Methods

Thin films were deposited onto silicon (100) substrates by RF magnetron sputtering (13.56 MHz). The sputtering target composition was $Ge_{24}Sb_{11}Se_{66}$. The glass transition temperature of a bulk sample T_g is ~ 300 °C [4]. Thin films were annealed at different temperatures – specifically at 200, 225, 250, 275, and 300 °C for 10 seconds. Two sample processing methods were used: placing the sample inside the SiC-coated graphite susceptor and the other by simply laying the sample onto the silicon wafer. The heating rates using the susceptor were 10 °C/s and 15 °C/s, respectively, and the heating rate using the wafer was 15 °C/s. Higher heating rates, *i.e.*, 50 °C/s, 85 °C/s, and 120 °C/s were also examined for annealing at 300 °C.

Optical properties were studied by variable angle spectroscopic ellipsometry (VASE, J. A. Woollam). The refractive index dispersion $n(\lambda)$ and the optical bandgap energy E_g^{CL} were obtained by fitting the fundamental absorption edge using the Cody-Lorentz oscillator model in 300–2300 nm spectral range. The thickness of thin films was about 1 µm (± 4 %) as determined by VASE. The optical bandgap energy E_g^{CL} of as-deposited films under study was 1.65 ± 0.01 eV. The corresponding refractive index n at 1 550 nm was 2.68 ± 0.01.

The composition of thin films was determined by energy-dispersive X-ray spectroscopy (EDS analyzer Aztec X-Max 20, Oxford Instrument) coupled with a scanning electron microscope (SEM, LYRA 3, Tescan). The surface topography of samples was checked using atomic force microscopy in an amplitude-modulated

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mode (AM-AFM, Ntegra 2, NT-MDT). Finally, the potential changes in local structure upon RTA were examined by a μ-Raman spectrometer (785 nm, LabRam HR800, Horiba Jobin-Yvon) coupled with a 100× microscope (Olympus).

3 Results and Discussion

As in case of conventional annealing of $Ge_{29}Sb_8Se_{63}$ thin films under argon atmosphere, all the thin films in frame of this work exhibit the shift of the absorption edge towards higher energies (bleaching effect) upon RTA. As seen from Figure 1, the maximum magnitude of change ΔE_g^{CL} of 0.19 eV was obtained at 300 °C (bulk T_g) at a heating rate of 10 °C/s using graphite susceptor. Optical bandgap increase was accompanied by refractive index decrease Δn of −0.1 for the same sample. Changes in optical bandgap energy and the refractive index for all samples are summarized in Figure 1(a) and (b) respectively.

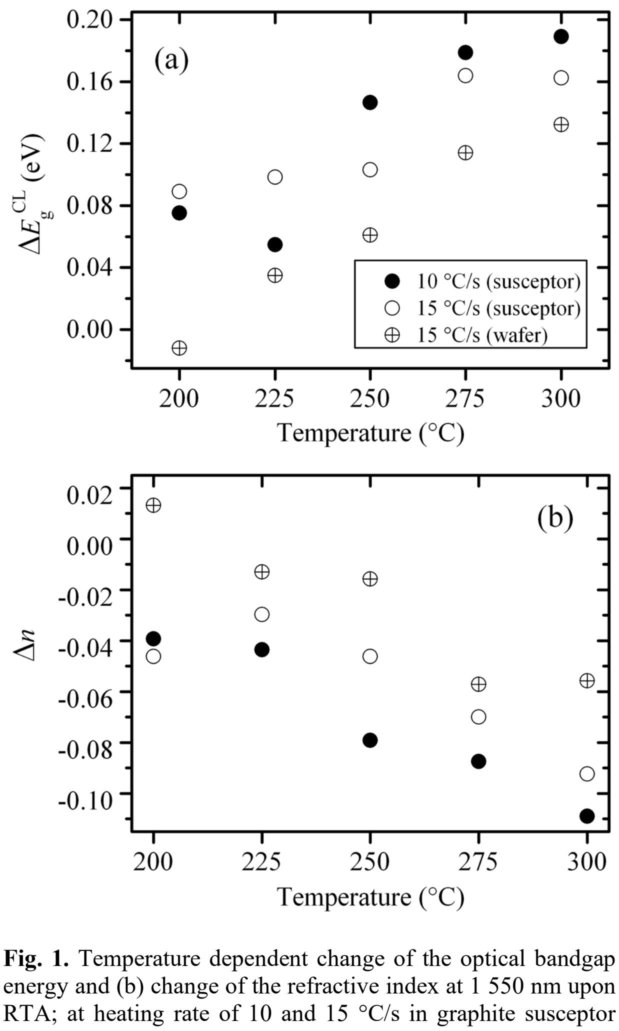

Fig. 1. Temperature dependent change of the optical bandgap energy and (b) change of the refractive index at 1 550 nm upon RTA; at heating rate of 10 and 15 °C/s in graphite susceptor (black and white circles) and 15 °C/s on silicon wafer (white circles with cross).

In spite of these high refractive index changes, the composition of the thin films remained unchanged indicating that only structural changes occurred upon annealing. However, these changes are rather small as the structural analysis by means of Raman scattering spectrometry, revealed only minor changes.

Moreover, the SEM analysis revealed the presence of dendritic crystallization in the vicinity of protrusion defects incorporated during the sputtering process upon the RTA at higher temperatures. EDS has shown that the composition of these defects is close to the composition of surrounding thin film. Despite the mentioned crystallization, the AFM scans have shown only negligible changes in overall surface topography related to annealing.

Results obtained in the frame of this study indicate that the RTA is suitable technique for the fine tuning of bandgap/refractive index of amorphous chalcogenide thin films without significant changes in their quality or composition. It was also shown that the crystallization in the vicinity of protrusion defects occurs at given conditions potentially acting as a factor increasing the optical losses.

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References

[1] M. Baillieul *et al.*, “Toward Chalcogenide Platform Infrared Sensor Dedicated to the In Situ Detection of Aromatic Hydrocarbons in Natural Waters via an Attenuated Total Reflection Spectroscopy Study,” *Sensors*, vol. 21, no. 7, 2021, doi: 10.3390/s21072449.

[2] T. Halenkovič *et al.*, “Linear and nonlinear optical properties of co-sputtered Ge-Sb-Se amorphous thin films,” *Opt. Lett.*, vol. 45, no. 6, pp. 1523–1526, Mar. 2020, doi: 10.1364/OL.386775.

[3] A. Zakery and S. R. Elliott, Eds., “An Introduction to Chalcogenide Glasses,” in *Optical Nonlinearities in Chalcogenide Glasses and their Applications*, Berlin, Heidelberg: Springer Berlin Heidelberg, 2007, pp. 1–28. doi: 10.1007/978-3-540-71068-4_1.

[4] T. Halenkovič, M. Kotrla, J. Gutwirth, V. Nazabal, and P. Nemec, “Insight into the photoinduced phenomena in ternary Ge-Sb-Se sputtered thin films,” *Photonics Research*, vol. 10, no. 9, pp. 2261–2266, 2022, doi: 10.1364/PRJ.460552.