Structural relaxation and optical properties in amorphous $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ films

R.P. Wang^{*}, A.V. Rode, S.J. Madden, C.J. Zha, R.A. Jarvis, B. Luther-Davies

*Centre for Ultrahigh Bandwidth Device for Optical Systems, Laser Physics Centre, Research School of Physical Sciences and Engineering,
Australian National University, Canberra, ACT 0200, Australia*

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Abstract

Amorphous $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ films prepared by ultra fast pulsed laser deposition (PLD) have been vacuum annealed over a range of different temperatures. Raman scattering measurements indicated that the features corresponding to Ge–Se and As–Se clusters increase in intensity with increasing annealing temperature (T_a) up to their respective glass transition temperature, and then decrease with further increasing T_a up to 300 °C. Optical property measurements showed that the refractive index decreases but the optical band gap increases with increasing T_a , and both of them could be fitted by the exponential function. The corresponding characteristic time extracted was found not to obey Arrhenius behavior, which is consistent with the existence of a broken network cut by cross-linking bonds and different clusters in films.

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1. Introduction

Chalcogenide glasses have been considered as promising candidates for integrated non-linear optical components because they exhibit many attractive optical properties including high refractive index, large non-linearities, as well as low optical loss [1–3]. However, the stability of the material hampers further applications in optoelectronics devices. For example, illuminating amorphous chalcogenide with near band gap light can induce a change of the optical absorption edge and refractive index (RI). While this so-called photo-darkening effect has been widely investigated, there have been few attempts to investigate thermal-annealing induced change in the optical properties of the chalcogenide films, especially pulsed laser deposited (PLD) films.

Here we focus on $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ which exhibits a high glass transition temperature T_g of 362 °C, as well as excellent non-linearity that is several hundreds times higher than that of silica at 1540 nm [4]. Since our as-grown PLD film has a different RI from the target, which is believed due to that all the films are deposited in the non-equilibrium conditions, annealing is necessary to release the excess internal energy stored in films and relax the glass structure back to the thermal equilibrium state [5,6]. We therefore vacuum annealed our high quality $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ films, and studied their structural relaxation and optical properties by measuring Raman spectra and some optical properties parameters such as optical bandgap and RI.

2. Experiments

AMTIR-1 glass from Amorphous Material Co. was used as target. All high quality AMTIR-1 films were deposited by our unique ultrafast laser ablation method. The laser ablation system and the deposition conditions are

^{*} Corresponding author. Tel.: +61 2 6125 1591; fax: +61 2 6249 0029.
E-mail address: rpw111@rsphysse.anu.edu.au (R.P. Wang).

similar to those in our previous work [7]. A 1.7 μm thick sample was deposited on a silicon wafer, cut into smaller pieces, and then annealed in a Heraeus Vacutherm oven. Raman scattering spectra were measured at room temperature using a Renishaw spectrometer. To minimize the photo-induced structural and/or compositional changes during the experiments, the samples were excited with the 782 nm line at a power of 0.02 mW and each spectrum was recorded within 60 s. An SCI FilmTek 4000 was used to *ex situ* evaluate a series of parameters such as film thickness, refractive index, and band gap.

3. Results and discussion

Raman spectra of the target, as-grown and annealed films are shown in Fig. 1. The target displays a strong Raman feature at 200 cm^{-1} which can be assigned to Ge–Se vibrations in the corner-shared $\text{GeSe}_{4/2}$ tetrahedrons, and a broad band from 258 to 308 cm^{-1} . The former is separated into several peaks at 179 cm^{-1} (assigned to Ge–Se vibrations in the corner-shared $\text{Se}_3\text{Ge–GeSe}_3$ units), 196 cm^{-1} (to Ge–Se vibrations in the corner-shared $\text{GeSe}_{4/2}$ tetrahedrons) and $214\text{–}217\text{ cm}^{-1}$ which are related to edge-shared Ge tetrahedrons. The latter is shifted to low wavenumber with several weak features at 240, 252, 302 cm^{-1} in the as-grown films, which are possibly related to As_2Se_3 and GeSe_2 clusters [8–12]. These results suggest that the uniform structural units in the bulk glass have been separated into various clusters during the laser ablation process. The spectral shapes of the annealed films are almost identical to those of the as-grown film except for the change of the relative intensity of the respective features and the increasing photoluminescence background with increasing T_a in the higher wavenumber region. In combination with Refs. [8–12], the change of the Raman spectra of the annealed films and its substantial hints to the structural evolution could be summarized as follows: (1) the amplitudes of 179, 196, 302 cm^{-1} peaks appeared in the as-grown film increased in the 250°C annealed film but

Fig. 1. Raman spectra of the as-grown and annealed films.

finally decreased in the 300°C annealed film [8,9]. This indicates that the Ge clusters initially formed in the as-grown film seem to grow with increasing T_a . Since the GeSe_2 clusters will be melted and coalesced with As when T_a is more than T_g of the GeSe_2 at 265°C , further increasing T_a will lead to decreasing Raman scattering intensities of these peaks; (2) the bands from 239 to 300 cm^{-1} with several weak features at 239, 250, and 305 cm^{-1} , corresponding to As_2Se_3 clusters with T_g around 205°C [10–12], have a similar evolution with increasing T_a , and thus are supposed due to similar physical origins; (3) at high T_a of 300°C , clusters were melted and rebonded, and thus the high temperature annealed film has a tendency to change its structure closer to the material.

Fig. 2(a) and (b) shows the annealing time dependence of the refractive index at 1550 nm and the optical bandgap, respectively. During thermal annealing, RI rapidly decreases but the optical bandgap increases with increasing annealing time up to 100 min, and then both of them keep almost constants with further increasing annealing times. On the other hand, it seems that both RI and optical bandgap can be relaxed into different values depending on the annealing temperature. All the relaxation processes can be fitted by the exponential function; however, the characteristic times extracted from both Fig. 2(a) and (b) seem not to obey the Arrhenius behavior. This is consistent with the existence of a substantial number of the separated clusters in as-grown and annealed films. Although part of these separated clusters are coalesced by thermal annealing, the remaining ones with high T_g made it difficult to cross-link all structural units forming unbroken glass network, leading to non-Arrhenius behavior [13,14].

Fig. 2. The annealing time dependence of refractive index at 1550 nm (a), and; optical bandgap (b).

4. Conclusions

In summary, amorphous $\text{Ge}_{33}\text{As}_{12}\text{S}_{55}$ films prepared by PLD have been vacuum annealed over a range of different temperatures. Raman scattering measurements indicated that a substantial amount of separated As_2Se_3 and GeSe_2 clusters may be formed during the laser ablation process. The features corresponding to Ge–Se and As–Se clusters increase in intensity with increasing T_a up to their respective T_g , and then decrease with further increasing T_a to 300 °C. Optical properties measurement showed that the refractive index decreases but the optical band gap increases with increasing T_a . The corresponding characteristic time extracted from the relaxation of the refractive index and optical band gap was found not to obey the Arrhenius behavior, consistent with the existence of the broken network cut by the cross-linking bonds and different clusters in films.

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