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Photo-induced effects in Ge-Ga-Se films

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We investigated photo-induced effects in Ge-Ga-Se films. It was found that, thermal annealing causes the increase of the bandgap in the as-prepared films, and all three annealed films show photodarkening (PD) behavior with light illumination but the change of optical bandgap is minimum in Ge25 film. Such PD behavior can be recovered by reannealing of the film. The kinetic process of T_f/T_i exhibits part recovering of PD during the cycle of laser on and off. Moreover, no obvious structural change can be observed in the Raman spectra of the films at different states, especially in that of Ge25 film.

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1. Introduction

Chalcogenide glasses are kinds of important optical materials in the midinfrared because of their broad transparent window, low phonon energy and high linear and nonlinear refractive index[1-3]. Among various chalcogenide glass compositions, Ga-contained glasses are especially interesting since Ga is considered to promote the solubility of rare earth ions in the glasses and thus they are potentially in various active applications like optical amplifiers and midinfrared lasers[4-6]. However, due to their covalent bonding nature, the glasses usually exhibit strong photo-induced effects, typically photodarkening and photobleaching, which would lead to red- or blue-shift of absorption edge. When chalcogenide glasses-based optical devices are exposed to light illumination or are used to deliver the light from the laser, those effects would induce extra optical losses and deteriorate the performance of the devices via producing the defects or forming weak middle states between the conduction and valence band of the glass[1,7]. Therefore it is important to investigate the photo-induced effects in chalcogenide glasses.

Photo-induced effects in As-S[8,9], As-Se[10,11], Ge-Se[12-14], GeAsSe[15-20] films have been widely investigated. Here we need to emphasize the conceptional difference of photo-induced effects in the chalcogenide films with the different states. Compared with the as-prepared film, the annealed film has relatively small disorder and free energy which is comparable to the bulk glasses. The photodarkening behavior represents red-shift of the band gap and is strictly defined to occur in the annealed film or bulk glasses, being a reversible process, which means the "darkening state" can be erased by the further thermal annealing. On the other hand, photobleaching is blue shift of absorbed edge that could occur in the as-deposited film but could not be recovered by thermal annealing, e.g., an irreversible process[1]. In binary AsS and AsSe an GeSe film, PD and PB behaviors have been reported in the as-deposited and annealed films, which is sensitive to illumination power, photon energy and illumination duration[8-14]. In ternary chalcogenide Ge-As-Se films, it was found that, by increasing the ratio of Ge/Se, the original photodarkening effect occurring in low ratio of Ge/Se would increasingly be replaced by simultaneous existence of photodarkening and photobleaching effect, and the photostable composition could be obtained by appropriated ratio of Ge/Se[15-20].

In terms of the physical origin of PD and PB, the red shift of the absorption edge is due to broadening of the valence, top of which is formed mainly by states of lone pair electrons of the chalcogen atoms. Based on the "slip motion" model, while exposed to the light illumination, the photoexcited electrons are captured, and the repulsive force are built between the layers. The

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forces cause enlargement of the interlayer distance and slip motion along the layers[1,21]. In some cases, some literatures reported the change of Raman spectra of the films before and after illumination, and thus suggesting that photo-induced structural change is the main reason for PD[13,19,20]. On the other hand, PB is considered a local structural reordering stimulated by light, e.g., breaking Ge-Ge and Se-Se homopolar bonds into Ge-Se heteropolar bonds, or induced by possible photo-oxidation in the film[11]. However, a general physical model that can account for PD and PB is still absent currently.

Here we investigated the photo-induced effects in GeGaSe films. We deposited the films with three different compositions, being $Ge_{21.1}Ga_{6.1}Se_{72.8}$(Ge21), $Ge_{25.2}Ga_{5.9}Se_{68.9}$(Ge25) and $Ge_{32.1}Ga_{6.1}Se_{61.8}$(Ge32), respectively. We investigated the photo-induced effects in the films with different states, e.g. as-deposited, annealed, illuminated and annealed-illuminated states to understand the correlation between photo-induced effects and chemical compositions of the films. We also investigated the kinetic process of the photoinduced effect in the annealed films to extract the evolution of the kinetic parameters upon illumination. Moreover, we employed Raman scattering spectra to detect the possible structural changes related to photoinduced effects.

2. Experiments

Ge-Ga-Se glasses were prepared by the melt-quenching method as described in the previous literature. The glass rod with a diameter of 50 mm was cut into a tablet with a thickness of 4 mm as a target for film deposition. The films were deposited onto silica and thermally-oxidized-Silicon substrates by the magnetron sputtering deposition technique. The thicknesses of these films were in-situ controlled by a thickness monitor equipped in the chamber and further checked by a Veeco Dektak 150 surface profiler. The chemical compositions of the films were determined by an Energy Dispersive X-ray Spectrometer (EDS) installed in a Tescan VEGA3 Scanning Electron Microscope (SEM).

Photo-induced effects in the films were investigated by the pump-probe method, and the experimental set-up was as same as what we used in the previous experiments[11,13]. We investigated the photo-induced effect in the films with various physical states including the as-prepared, annealed, illuminated, annealed-illuminated states. The films were annealed in vacuum furnace about 3 hours at a temperature below their respective glass transition temperature (T_g). For the illumination, they were illuminated with different power density of 10 mW/cm^2,122 mW/cm^2,244 mW/cm^2, and 400 mW/cm^2, respectively. Raman spectra of the films with 4 different states (as-prepared, annealed, illuminated, annealed-illuminated) were measured by an InVia spectroscope (Renishaw) coupled to a Leica DM 2500 M microscope with a 785 nm laser excitation.

3. Results and discussion

The thickness and the chemical compositions of each film were listed in Table 1. It can be seen that all the film thickness is close to the typical penetration depth of the chalcogenide film around 1 μm. On the other hand, Ga content in three films is almost same at 6%. Therefore they can be comparatively investigated to understand the effect of Ge content on the photoinduced effect.

Table 1. The thicknesses and compositions of these films and their corresponding value of MCN.

Sample	Composition (±0.1 at. %)			Thickness (±50nm)
	Ge	Ga	Se	
Ge21	21.1	6.1	72.8	850
Ge25	25.2	5.9	68.9	850
Ge32	32.1	6.1	61.8	875

The absorption spectra of these samples in 4 different states were measured, and the optical bandgap of the films were calculated using the Tauc plots as shown in Figs. 1(a), (b) and (c), for Ge21, Ge25 and Ge32 samples, respectively. The corresponding value of the optical bandgap is listed in Table 2. All the black solid lines in Fig.1 represent the Tauc plots for the as-deposited films. And the other colorful lines like red, blue and green represent annealed, annealed-illuminated, and re-annealed-illuminated-annealed films, respectively. It can be seen that, in all cases, thermal annealing leads to blue shift of the bandgap, and the degree of the change in optical bandgap increases with increasing Ge content in the films. On the other hand, the illumination of the annealed film with a power density of 400 mW/cm^2 induce a red shift of the bandgap, exhibiting a PD behavior for Ge21 and Ge32 films, but this is not a case in Ge25 where illumination almost has no effect on the bandgap of the annealed film. Such a red shift can be recovered by re-annealing of the illuminated film to its original annealing state, indicated that PD is a reversible process. It should be emphasized that, thermal effect induced by the illumination can be neglected in the cases, since the temperature change of the film irradiated by the 655 nm laser with a power density of 400 mW/cm^2 is less than 3K recorded by infrared thermal image[11,16].

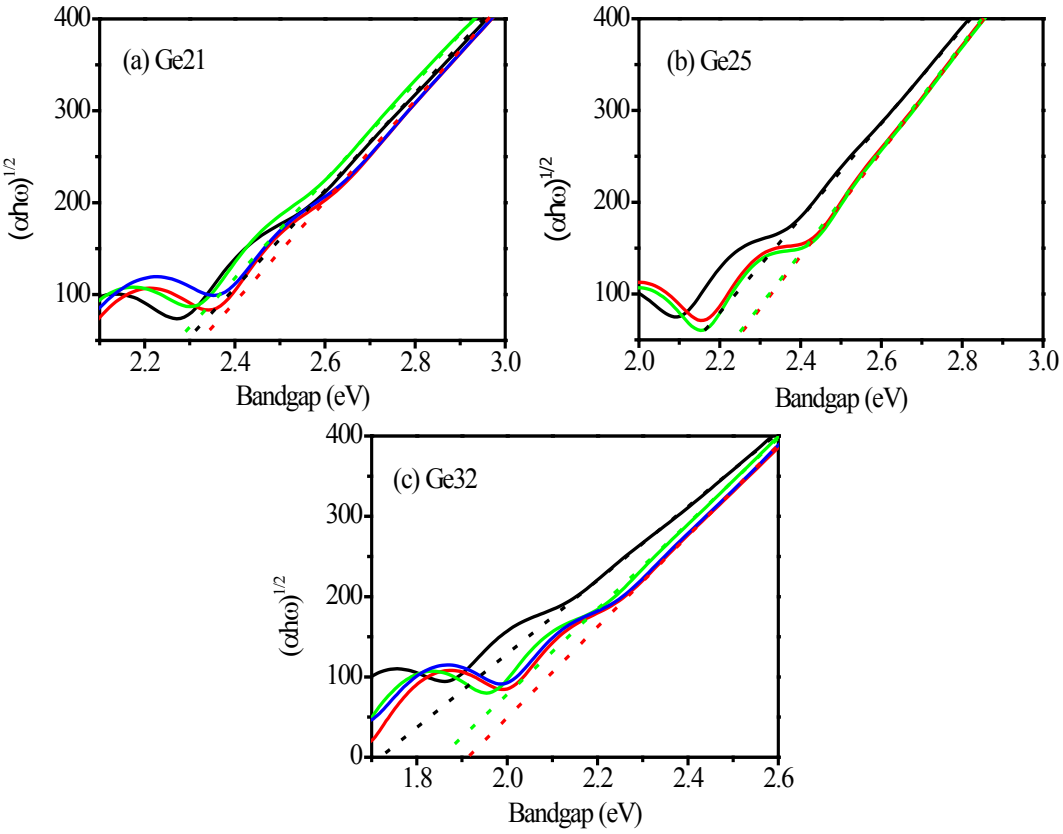

Fig. 1. The transmission spectra of different samples: (a)Ge21, (b)Ge25, (c)Ge32 in 4 states. The black solid line represents the as-prepared state, the red, blue, green dash line is the illuminated, annealed, annealed-illuminated states, respectively.

Table 2. Bandgap values of three films at in as-prepared, annealed, illuminated, and annealed-illuminated state, respectively.

State	Bandgap (eV)		
	Ge21	Ge25	Ge32
As-deposited	2.29	2.05	1.72
Annealed	2.32	2.14	1.85
Illuminated	2.27	2.13	1.83
Reannealed	2.32	2.14	1.85

Since there is a difference in the as-prepared and annealed films in terms of quasi-stability and structural disorder, it is important to investigate photo-induced effect in the annealed films or bulk glasses due to their relatively low free energy and small disorder [1,21]. Therefore, in the next part of the paper, we concentrated on the annealed films and investigated their kinetic PD process.

Following the previous literatures[11,13,14], we recorded the transmission spectra of the annealed samples without any illumination, and expressed it as T_i. Then, we turned on the pump beam and recorded the transmission spectrum as T_f. Finally, T_f/T_i at a certain wavelength was used to investigate the kinetic process of photo-induced effects in those films. We took a wavelength where the sample has a transmittance of 30% in the dark in the annealed state.

Fig.s 2 (a), (b) and (c) show T_f/T_i vs. illumination time in annealed Ge21, Ge25 and Ge32 samples with different illumination power densities, respectively. All the films show same PD behavior, although the time required to reach themselves to their respectively saturated states is different. We use the stretching exponential functions to simulate the reaction kinetics of PD effect as:

$$\Delta T = A\left[\exp\left\{-(t/\tau_d)^{\beta_d}\right\}\right] + \Delta T_{sd} \tag{1}$$

where the subscript d corresponds to PD. ΔT_{sd} is the metastable part, τ_d is the time constant, β_d is the dimensionless parameter, t is the illumination time, A is a temperature dependent quantity that is equal to the maximum transient changes. The value between the initial and final process of T_f/T_i, which is determined by the fitting stretched exponential function, is defined as ΔT.

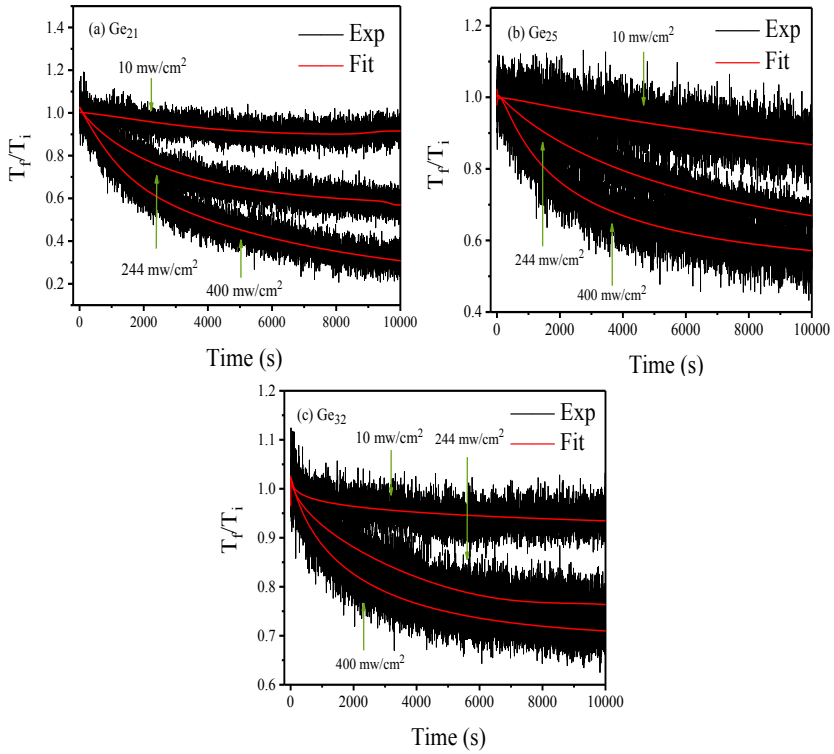

Fig. 2. Time evolution of T_f/T_i at 10, 244 and 400 mW/cm^2 in annealed Ge21 (a), Ge25 (b), and Ge32 (c) respectively. The black lines are the experimental results, while the red lines are the fitting based on the equation (1).

Table 3. The fitting parameters of photo-induced effects in annealed Ge21, Ge25 and Ge32 samples at different power densities.

Sample	Power Density(mW/cm^2)	τ_d(s)	β_d	ΔT_{sd}
Ge21	10	9122	0.89	0.96
	244	5090	0.84	0.61
	400	4045	0.69	0.29
Ge25	10	12476	0.91	0.97
	244	6324	0.79	0.71
	400	4270	0.75	0.54
Ge32	10	14426	0.88	0.94
	244	3040	0.79	0.75
	400	2159	0.81	0.69

Each curve in Fig.2 is fitted by Eq.(1) and all the fitting parameters are listed in Table 3. For all annealed samples, T_f/T_i exhibits a tendency to decrease with prolonged illumination, corresponding to a PD process. At the same time, with the increase of laser power density, the degree of photodarkening of the three groups of annealed films also increases. As shown in the Table 5, When the illumination power density increases from 10 to 400 mW/cm^2, τ_d decreases from 9122 s to 4045 s, but ΔT_{sd} decreases from 0.96 to 0.29 for the Ge21. On the other hand, when the illumination power density increases from 10 to 400 mW/cm^2, τ_d decreases from 12476 s to 4270 s, but ΔT_{sd} decreases from 0.97 to 0.54 for the Ge25. For the Ge32, τ_d decreases from 14426 s to 2159 s, but ΔT_{sd} decreases from 0.94 to 0.69.

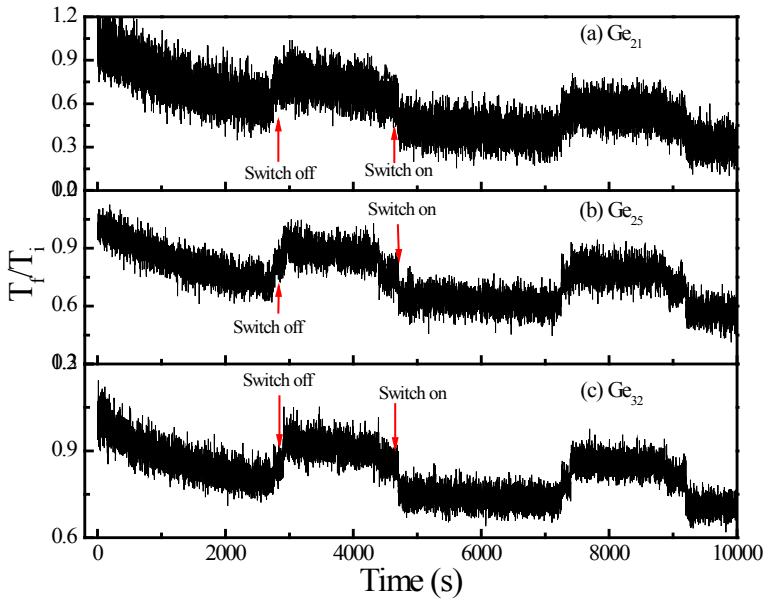

Fig. 3. Photoinduced effects in annealed Ge21 (a), Ge25 (b) and Ge32 (c) under different illumination power densities.

We further investigated the sensitivity of PD to switching-on and -off illumination light under different illumination power. It was found that, in all cases, switching-off the light can induce an increase of T_f/T_i and such an increase becomes larger with increasing illumination power. Re-switching-on light can recover T_f/T_i to its initial value. The typical results for the annealed Ge21, Ge25 and Ge32 films under 400 mW/cm^2 illumination are shown in Figs. 3(a), (b) and (c), respectively.

To explore possible structural origin of photoinduced effects in the films, we measured Raman spectra of the as-deposited, illuminated, annealed and annealed-illuminated films, and the Raman spectra are shown in Fig.4, where all the Raman intensity are normalized at 200 cm^{-1} peak. Following the previous literatures, the Raman band near 201 cm^{-1} is assigned to the vibration of $GeSe_{4/2}$ tetrahedron. The shoulder at 216 cm^{-1} can be connected with the vibration of the edge sharing $Ge_2Se_{8/2}$ tetrahedron[13,15]. The Raman peak at 180 cm^{-1} may be caused by Ge-Ge, Ga-Ga or Ge-Ga bonds in $Ge_2Se_{6/2}$, $Ga_2Se_{6/2}$ or $GeGaSe_{6/2}$ structural units[23]. The broad Raman band at around 235-330 cm^{-1} with lower intensity is composed of the overlapping of Se-Se bond (245-265 cm^{-1}) and $GeSe_4$ structural unit (300 cm^{-1})[13,15].

In all cases in Fig.4, the main features of the Raman profiles have almost no change, but slight changes in Raman spectra can be found. For example, Se-Se related vibrations in Fig.4(a) for Ge21 reduces the intensity in annealed and annealed-illuminated films, while there is a change in vibration bands below 140 cm^{-1} and from 250-300 cm^{-1} in Fig.4(c) for Ge32. Obviously, these changes in Raman spectra are due to external energy input by thermal annealing or light illumination. While the assignment of these bands and their changes can be found in number of literatures, here we emphasized a fact that Raman spectra in Fig.4(b) for Ge 25 is almost identical. Since both three annealing films exhibit PD as shown in Fig.2, we thus argue whether the PD originates from the change of the glass structure induced by illumination as suggested in literature.

It is widely accepted that, thermal annealing or light illumination can trigger the conversion of chemical bonds for example from Ge-Ge and Se-Se to Ge-Se. However, if the number of the change of the bonds is negligible beyond the probing limit of Raman spectra, saying less than 0.5%, such a structural change would not be observed. This could be a case in Fig.4(b) for Ge25 film where no change in Raman spectra can be found.

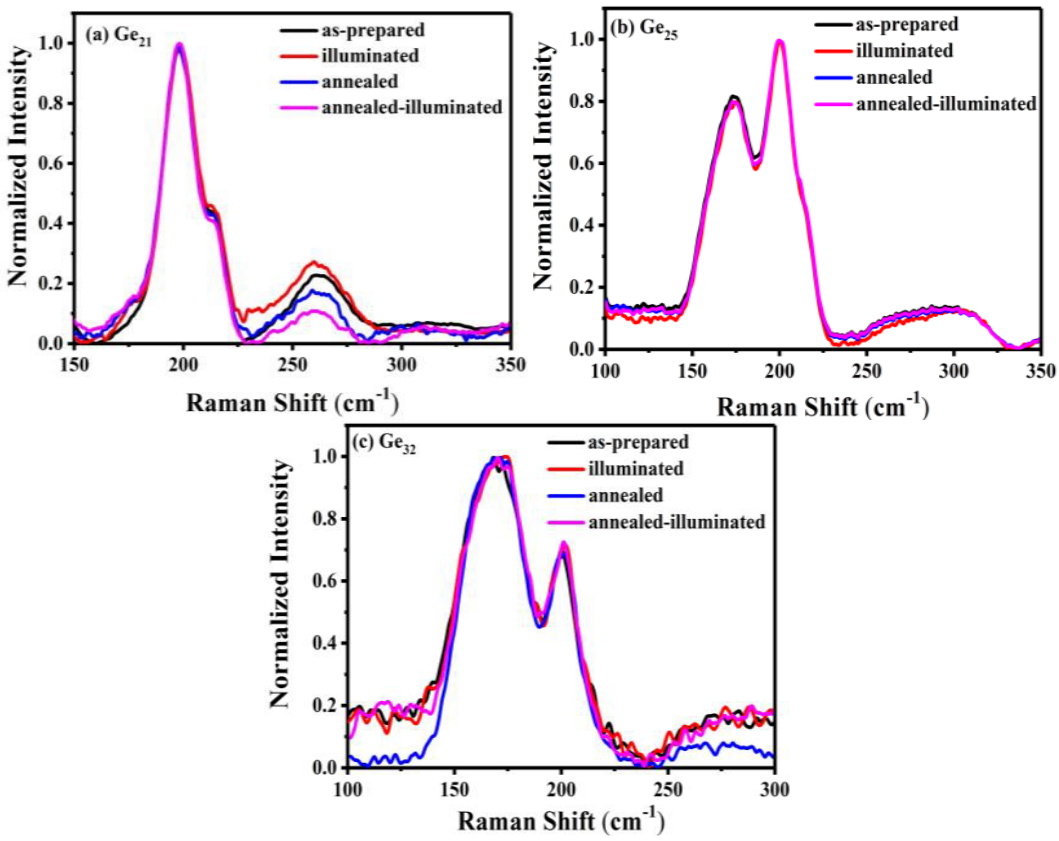

Fig. 4. The Raman spectra of three groups of samples in different states. (a)Ge21, (b)Ge25, (c)Ge32. The black, red, blue, and pink solid lines represent films in as-prepared, illuminated, annealed, and annealed-illuminated states, respectively.

On the other hand, if PD is correlated with the change of glass structure, the intensity of the PD should be proportional to the change of glass structure. In Fig.4, we can find, for the films with same illumination power of 400mW/cm^2 and 10000s illumination duration, the change of PD is 0.7, 0.5, 0.3 for Ge21, Ge25 and Ge32, respectively. In another word, Ge21 exhibit maximum PD effect while it is minimum in Ge32. This is in contradicted with the results from Raman spectra where minimum change of glass structure appears in Ge25. Therefore, the present results suggest that the change of the glass structure that can be probed by Raman spectra is not a requisite to observe PD effect. Instead, the change of the band structure may play an important role in photo-induced effect in GeGaSe films. Multiple capture of carriers are continuously distributed in the optical gap in the local states [24]. Several processes, including the capture of carriers in the trap, the subsequent thermal activation and the repeated capture process, can modify the distribution of localized states of trapped carriers in the gap. The illumination excites non-bonded electronic states and injects excess carriers into the conduction band. Then the electrons are captured by the band tail state, which is proportional to their density.

In Ge-Ga-Se system, Ge, Ga and Se is four-, three- and two-coordinated, respectively, in the glasses [1,2]. Ideally, each Ge needs two Se and each Ga needs one and half Se, therefore if Ga content is fixed at 6%, Ge21 and Ge25 films are Se-rich and -poor, respectively, only Ge25 is close to chemical stoichiometric composition. This means the minimum number of the defective bonds in the Ge25 compared with those in Ge21 and Ge25. This is why minimum change of the bandgap in the annealing film and almost identical Raman profiles of Ge25 film can be observed. Such a less photosensitive composition could be useful in the applications since it can reduce extra optical loss in the glasses induced by light illumination.

4. Conclusion

In this paper, Ge-Ga-Se films with almost similar Ga content of 6% were prepared by RF magnetron sputtering. These films in different four states (as-prepared, annealed, illuminated, and reannealed-illuminated) were researched to understand the photoinduced effects. The optical band gap value of the films after illumination under different conditions was calculated using the Tauc plot. While thermal annealing causes the increase of the bandgap, PD behaviors are observed in all three films with minimum change of bandgap in Ge25 film. Such PD behaviors can be recovered by reannealing of the film. The cycle of laser on and off can cause the part recovering of PD from the investigation of the kinetic process of T_f/T_i. On the other hand, Raman spectra of the films at different states show no obvious structural change, especially in Ge25 film. This indicates that chemically stoichiometric composition of Ge25 can be potentially used for rare earth element doping for active applications such as optical amplifiers and lasers.

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