

PHOTBLEACHING IN GeSe₂ AND SiO₂/GeSe₂ THIN FILMS

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We prepared GeSe₂ film and GeSe₂ covered by a layer of thin SiO₂ (SiO₂/GeSe₂) to examine photo-induced effects. We found, upon sub-gap light illumination, transmission edge of both the films exhibit a blue shift, but the amount of the shift in SiO₂/GeSe₂ is less than that in GeSe₂. Kinetics measurements of the photo-induced effects indicate that the both films exhibit PB behavior after more than few hundreds seconds illumination. Raman scattering measurements show that some of Ge-Ge and Se-Se bonds are broken and convert to Ge-Se bonds. All the results indicate that the change of the intrinsic structure upon illumination is dominated in the PB process.

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1. Introduction

Chalcogenide (ChG) amorphous films display a variety of remarkable photoinduced effects such as photodarkening (PD) and photobleaching (PB) when subjected to bandgap or sub-bandgap photon irradiation. PD and PB are useful for a variety of applications such as information storage, photonics, optical switching and so on [1-7]. PD in ChGs has been studied extensively over many years and is believed to originate from photoinduced structural transformations [7]. However, PB in Ge-based chalcogenide glasses is highly irreversible in nature and was thought to be originating from photo-oxidation process as well as intrinsic structural changes [7-9]. Lyubin et al[10] reported transient PD and PB in addition to metastable effects in GeSe₂ thin films. Yan et al[8] observed that oxygen enters the glass network by breaking homopolar Ge-Ge bonds and forming more stable Ge-O bonds. But the mechanism of PB in GeSe₂ thin film is still unclear.

In order to elucidate the origin of the photoinduced effect in GeSe₂ film, we prepared GeSe₂ and GeSe₂ thin films covered by a thin SiO₂ layer which can prevent the oxidation on the surface of the chalcogenide films, and thus the photo-oxidation effect can be maximally suppressed. We investigated the kinetic change of the photo-induced effect in the films and found that a slow PB behaviors in the films. We further investigated the structural change of the films before and after illumination using Raman scattering spectra and found that, the conversion of these homopolar Ge-Ge and Se-Se bonds into the heteropolar Ge-Se bonds can accounts for PB in the films.

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2. Experiments

GeSe₂ target was prepared by the melt-quench method using 5N of pure Ge and Se powders as starting materials, and SiO₂ target was purchased from commercial company. GeSe₂ and SiO₂/GeSe₂ thin films were prepared on quartz substrates and Si substrates by radio-frequency magnetron sputtering method. The base and working pressures were set to 5.0×10^{-4} Pa and 0.3 Pa, respectively. The film thickness was in-situ controlled by a thickness monitor equipped in the chamber and further ex-situ measured by Veeco Dektak 150 surface profiler. The thickness of GeSe₂ thin film was about 1 μm and the total thickness of the bilayer was around 1.1 μm containing 50 nm thick SiO₂ thin film.

We studied the photo-induced effect in the films by a pump-probe method using an experimental set up similar to that in Ref.s[11,12]. The films were illuminated by a diode laser with a wavelength 655nm (from a diode pumped solid state laser, DPSSL) at room temperature. The beam size is 2 mm in diameter and the illumination power density is 0.2 W/cm². The probe beam is a low intensity white light in a wavelength regime of 400-1000nm. During illumination, the transmission of the sample was recorded using Ocean Optics high-resolution composite grating spectrometer (HR 2000 CG-UV-NIR). The relatively weak probing white light is overlapped with the beam from the diode laser spot but its beam size is less than that of the illumination beam. It should be noted that such a small exciting laser intensity and large beam spot on the sample would result in a relatively insignificant temperature increase during illumination [13]. Therefore, the observed changes are not due to temperature rise but mainly due to photo-induced effects. In our experiments, full optical spectrum was collected in real time of 500 ms/spectrum.

Raman spectra were recorded on films using a Raman spectrometer system (Renishaw inVia, England) with a low Raman intensity, and the change of the film structure were measured before and after irradiation.

3. Results and discussion

The as-deposited films were examined by X-ray diffraction (XRD) spectra in Fig. 1, where only the broad humps from 15° to 40° were shown, confirming amorphous nature of the films. Similar XRD spectra in Fig.1 also indicated that, covering layer of SiO₂ film had no effect on the structure of GeSe₂ film.

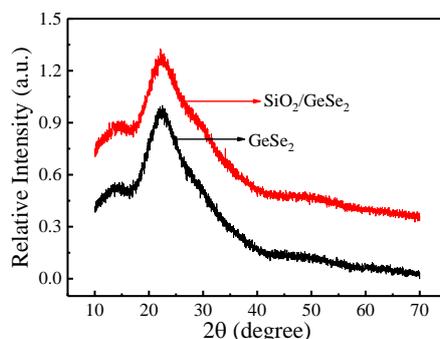


Fig. 1. XRD patterns of the as-deposited films

To examine the effect of laser illumination, the transmission spectra of the GeSe₂ and SiO₂/GeSe₂ thin films before and after illumination were measured and the results were shown in the main panel of Fig. 2. It is obvious that, while the transmission edge of the as-deposited film shifts to the shorter wavelength, such a shift is significantly decreased in the bilayer upon illumination. The inset in Fig. 2 was the Tauc plot of the optical bandgap. The optical band gap E_g of GeSe₂ thin film is increased from 1.950 eV to 2.065 eV, and that of of SiO₂/GeSe₂ thin film is increased from 1.929 eV to 1.962 eV upon illumination at the same condition.

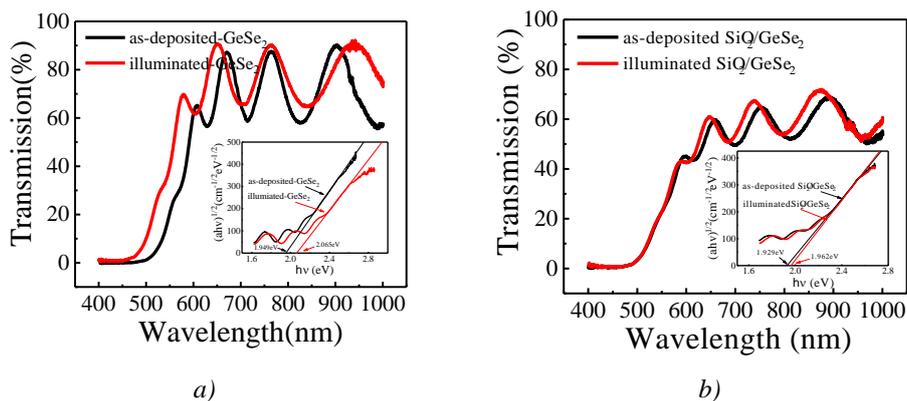


Fig. 2. Transmission spectra of the as-prepared and illuminated GeSe₂ thin film (a) and SiO₂/GeSe₂ thin film (b). The inset is their respectively $(\alpha h\nu)^{1/2}$ vs $(h\nu)$ plots.

In order to understand the kinetics behavior of PB, we recorded the transmission spectrum of the as-prepared sample in dark condition and denoted it as T_i . Then, we turned on the pump beam and simultaneously recorded the transmission spectrum as a function of time (T_f). Figs. 3 (a) and (b) show the curves of T_f/T_i at the selected wavelength, and both of them clearly show that there was no change at the initial stage without illumination. This indicates that the probe beam cannot induce any changes, probable due to its lower power. T_f/T_i in Fig. 3(a) starts to decrease almost immediately after turning on the pump beam and saturates within a few tens of seconds, and then grow before it becomes stable with few thousands second illumination. The final value of T_f/T_i is well above its initial value, indicating overall bleaching behavior. On the other hand, although Fig. 3(b) exhibits almost similar behavior to that in Fig. 3(a), the difference of T_f/T_i between the initial and final states in Fig. 3(b) is less than that in Fig. 3(a), indicating that PB is significantly suppressed by SiO₂ covering layer.

Tanaka et al. emphasized the importance of the use of various material forms, like as-prepared and annealing film and bulk glass in investigating various reversible and irreversible effect, and classified different effects in glasses [7]. Only annealed bulk and films can be used to investigate PD behaviours since it is a reversible process, while PB is irreversible and thus as-prepared film can be used to probe PB behaviours. On the other hand, illumination photo energy of 1.89eV(655nm) is less than the bandgap of all the films, no matter it is illuminated or not. Therefore, the results observed are induced by sub-bandgap light.

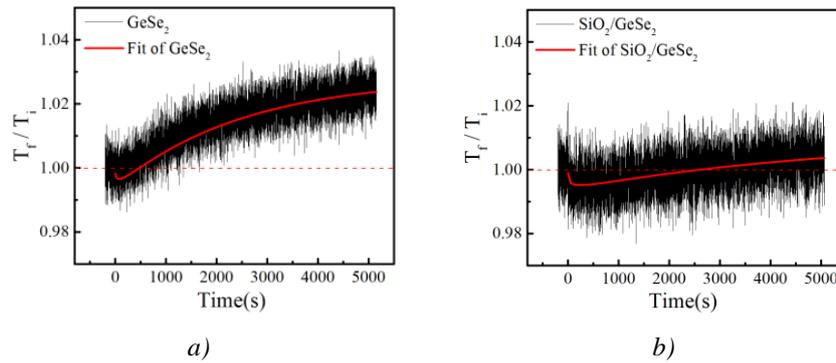


Fig. 3. Time evolution of T_f/T_i for (a) as-prepared $GeSe_2$ thin film and (b) as-prepared $SiO_2/GeSe_2$ thin film using the a 655nm pump laser irradiation with a power intensity of $0.2W/cm^2$, the black outline and red line represent the experimental data and theoretical fit.

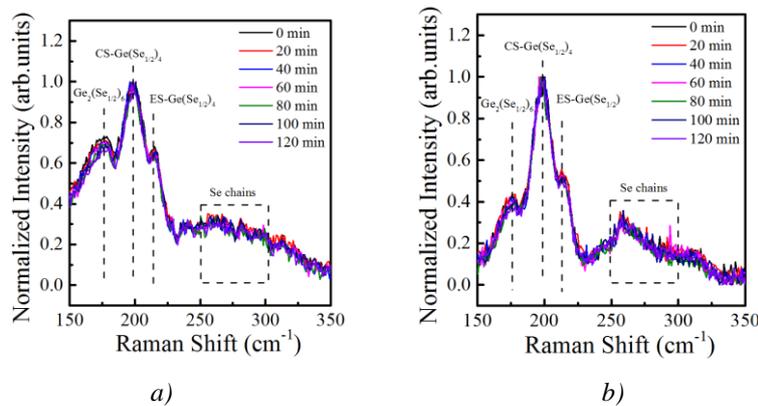


Fig. 4. Normalized Raman spectra of the as-prepared and illuminated $GeSe_2$ thin film (a) and $SiO_2/GeSe_2$ bilayer (b).

Two mechanisms have been considered for understanding PB, e.g., the photo-induced oxidation effect and photo-induced intrinsic structural change [2,7,9]. Since the illumination occurs in the atmosphere, thermal effect induced by the irradiation could accelerate surface oxidation. In this case, we use less laser irradiation power to reduce the thermal effect. Perrer et al have investigated the temperature rise induced by laser illumination with different power in chalcogenide gasses, and found that the irradiation power of 200 mW/cm^2 can cause temperature rise of $5\text{ }^\circ\text{C}$ [13], therefore in this paper, the thermal effect is negligible. On the other hand, we deposited one layer of SiO_2 on the top of $GeSe_2$ film in order to prevent the possible surface oxidation. As shown in Figs. 2 and 3, the PB effect in bilayer film is weaker than that in single layer film but it cannot be completely suppressed, suggesting that photo-oxidation is not a sole reason that can account for PB in the $GeSe_2$ films.

To examine any possible structural origin for PB effect, we measured Raman spectra of the as-deposited and irradiated films, and the results were shown in Figure 5. The Raman profiles are almost identical for all the films. It was commonly believed that the peak at 175 cm^{-1} was assigned to the $Ge_2(Se_{1/2})_6$ ethane-like units (Ge-Ge mode), and two main peaks located at 197 cm^{-1} and 213 cm^{-1} to the $Ge(Se_{1/2})_4$ corner-sharing (CS) and edge-sharing (ES) tetrahedral units,

respectively. The broad band near 257 cm^{-1} was assigned to the stretching vibrations of Se chains (Se-Se mode)[14,15]. It is well known that corner-sharing (CS) tetrahedral structure have lower free energy than the ethane-like units and edge-sharing (ES) tetrahedral structure in the glass network[14,15]. A close inspection in Fig. 5 shows that the normalized intensity of peaks representing both ES- $\text{Ge}(\text{Se}1/2)_4$ tetrahedral units and $\text{Ge}_2(\text{Se}1/2)_6$ ethane-like units decreases with increasing exposure time, we therefore conclude that some Ge-Ge and Se-Se bonds are broken and convert to Ge-Se bonds upon irradiation. The conversion is due to the glass approaching the supercooled liquid equilibrium entropy value through the change of glass structure[16]. Illumination could also cause some hybridization (mixing) of the lone-pairs and bond p-states at a top of the valence band, this could weaken the Se-Se bond. Consequently, homopolar bonds like Ge-Ge and Se-Se in the as-deposited films are not stable upon irradiation, and the conversion of these homopolar bonds into the heteropolar Ge-Se bonds.

4. Conclusions

In conclusion, we prepared the GeSe₂ to investigate photo-induced effect. For comparison, we also prepared GeSe₂ thin film covered with a SiO₂ thin protective layer in order to eliminate the effects of photo-oxidation on the surface of the film. We observed that transmission edge of both GeSe₂ and SiO₂/GeSe₂ exhibits blue shift after illumination, kinetics measurement of photo-induced effect confirms PB in the thin films, although the change of the photoinduced effect is suppressed by the protective layer of SiO₂. Raman scattering spectra demonstrated that the conversion of the homopolar Ge-Ge and Se-Se bonds into the heteropolar occurs upon illumination, and thus PB is ascribed to intrinsically structural changes in the film.

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