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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY C · OCTOBER 2011

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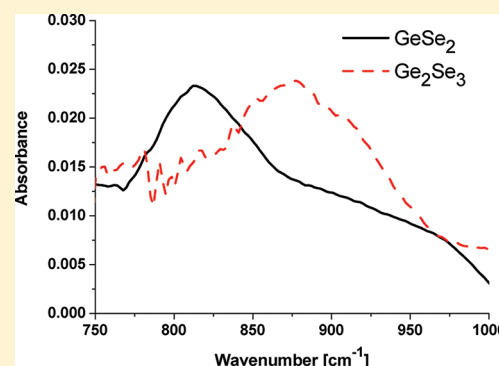
# Effect of Photo-Oxidation on Photobleaching of GeSe<sub>2</sub> and Ge<sub>2</sub>Se<sub>3</sub> Films

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**ABSTRACT:** Photoinduced effects of GeSe<sub>2</sub> and Ge<sub>2</sub>Se<sub>3</sub> films illuminated in air and in vacuum are investigated by in situ transmission spectra measurements. Both compositions exhibit photobleaching (PB) when exposed to bandgap laser for a prolonged time in air. By comparing with the photoinduced effects in vacuum, we conclude that PB in Ge<sub>2</sub>Se<sub>3</sub> film results from surface photo-oxidation, whereas intrinsic structural changes dominate the PB in GeSe<sub>2</sub> film.



## INTRODUCTION

Photoinduced effects such as photodarkening (PD) and photobleaching (PB) are among the most explored properties of chalcogenide thin films because of the high potential in a variety of applications in information storage, photonics, optomechanical transducers, and so on.<sup>1,2</sup> PB, that is, the irreversible blue shift of the absorption edge, occurs mostly in Ge-based chalcogenide films, such as Ge–S films, when illuminated with the band gap or superband-gap light.<sup>3–5</sup> Despite intensive studies, the origin of PB is not yet fully understood and its mechanisms remain controversial. The favored explanation for PB occurring in air is photo-oxidation, which has been established in Ge–S films by the appearance of Ge–O vibrational bands around 800 cm<sup>–1</sup> in the infrared (IR) transmission and Raman spectra.<sup>6–8</sup> On the basis of the far-IR and X-ray diffraction spectra, it has been proposed that the intrinsic structural changes viz. an increase in the Ge–S bond density and a subsequent increase in the ordering of the local structures are responsible for PB occurring in the same type of films in vacuum.<sup>9</sup> A number of investigations also showed that for some Ge–S films illuminated in air PB was caused by both the intrinsic structural changes as well as photo-oxidation,<sup>9,10</sup> but the relative contribution of the two processes was not established.

In this Article, we focus on the PB of GeSe<sub>2</sub> and Ge<sub>2</sub>Se<sub>3</sub> films observed in air and in vacuum, which have been much less investigated than their sulfide analogs. Although sulfide compounds are cheaper and easier to obtain, their IR transparent windows are limited to no larger than 8  $\mu$ m wavelength, which excludes their being the material choice for thermal imaging applications, especially in outdoor uses based on the second atmospheric window of 8–14  $\mu$ m in the IR region. GeSe<sub>2</sub>-based glasses/films show low attenuation in the 8–14  $\mu$ m window and much

reduced cost as compared with Ge single crystals.<sup>11</sup> At present, these glasses have become commercially available and extended to civilian applications.<sup>12</sup> They also exhibit excellent optical limiting behavior owing to their larger optical nonlinearities than sulfide analogs. Therefore, they are used to protect expensive optical sensors from being destroyed by the powerful laser beam.<sup>13</sup> A very recent application also based on selenide glasses relies on their transmission of CO<sub>2</sub> laser beams at 10.6  $\mu$ m for laser surgery and material processing.<sup>14</sup> It is important to know the interaction of GeSe<sub>2</sub>-based glass films with laser beams from both academic and practical points of view.

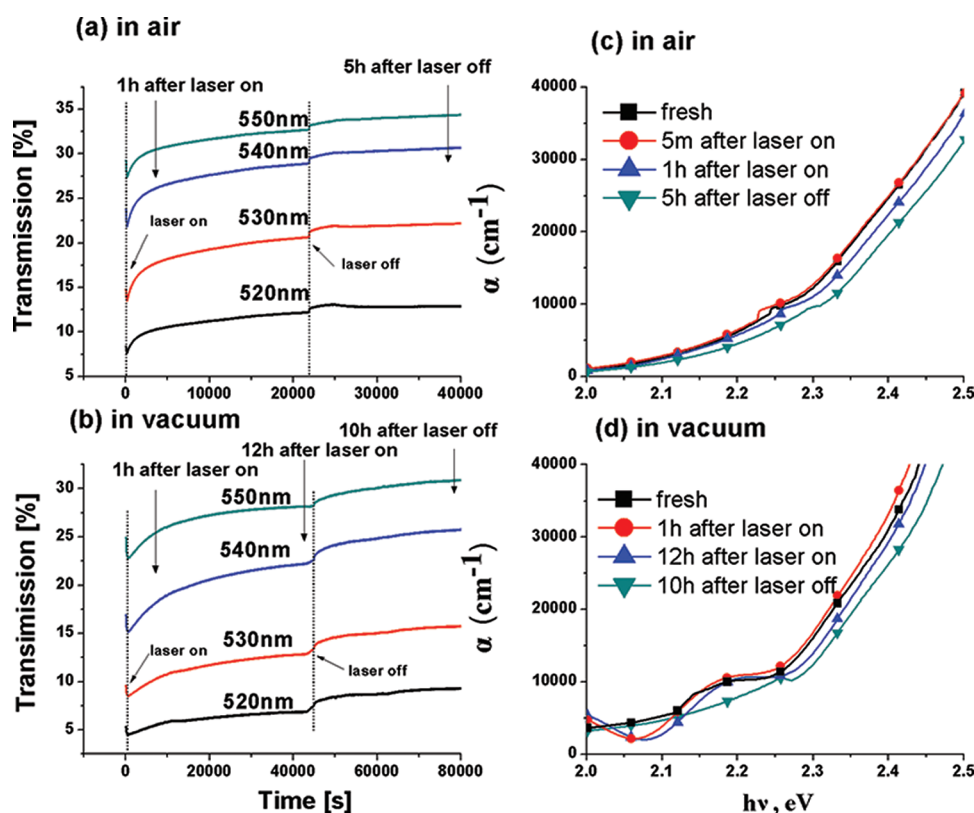
## EXPERIMENTAL SECTION

Bulk glass samples GeSe<sub>2</sub> were prepared by the melt-quenching method using 99.999% pure germanium and selenium. The elemental powders were vacuum-sealed in quartz ampules and gradually heated to 850 °C and rocked for 10 h. The melt was then quenched in ice water to form bulk glass. It was used as the source material for depositing thin film (thickness:  $\sim$ 1.0  $\mu$ m) on microscope glass slide substrate by thermal vacuum evaporation using a conventional coating unit (Edwards Coating System E306A) and vacuum of  $\sim$ 1  $\times$  10<sup>–6</sup> Torr. The deposition rate was  $\sim$ 10 Å/s, which was continuously monitored using a quartz crystal monitor (Sigma Instruments SQM-160). It is well known that such a low deposition rate produces film composition that is very close to the starting bulk materials.<sup>15</sup> The total thickness of

**Received:** April 18, 2011

**Revised:** September 20, 2011

**Published:** September 21, 2011



**Figure 1.** Time variation of transmission for as-deposited GeSe<sub>2</sub> films illuminated in air (a) versus in vacuum (b) and the changes in absorption coefficient observed before, during, and after illumination in air (c) or in vacuum (d). The spectra (c) and (d) are taken at different times, as indicated by the arrows in (a) and (b).

the film was 1.0  $\mu\text{m}$ , which is approximately the penetration depth of the band gap light for the selected compositions.

Photoinduced optical changes in the samples were determined as a function of time by in situ optical transmission spectroscopy, as described elsewhere.<sup>16</sup> The thin film samples were illuminated at room temperature by a diode laser with the pump light of wavelength,  $\lambda = 488$  or  $660$  nm. The laser beam was focused into a spot of 5 mm in diameter resulting in intensity 22.5 and 150  $\text{mW}/\text{cm}^2$ , respectively. The diameter of the relatively weak probing white light from the spectrometer was 2 mm. The two beams were directed such that they crossed each other at the sample surface with the pumping light completely overlapping the probing light. The data before, during, and after laser illumination were collected every 10 ms. It should be noted that such a small intensity and large spot size of the pumping lights would result in a relatively insignificant temperature rise during illumination.<sup>17</sup> Therefore, the observed changes are mainly due to photoinduced effects. Our interest was in the changes of the absorption at wavelengths near the band gap, where photoinduced effects were expected to be the largest. Accordingly, simultaneously with the full spectrum, transmission signals were also recorded at four fixed wavelengths (520, 530, 540, and 550 nm) by using different channels of the spectrometer. The IR spectra were obtained with a Varian 7000e FT-IR spectrometer.

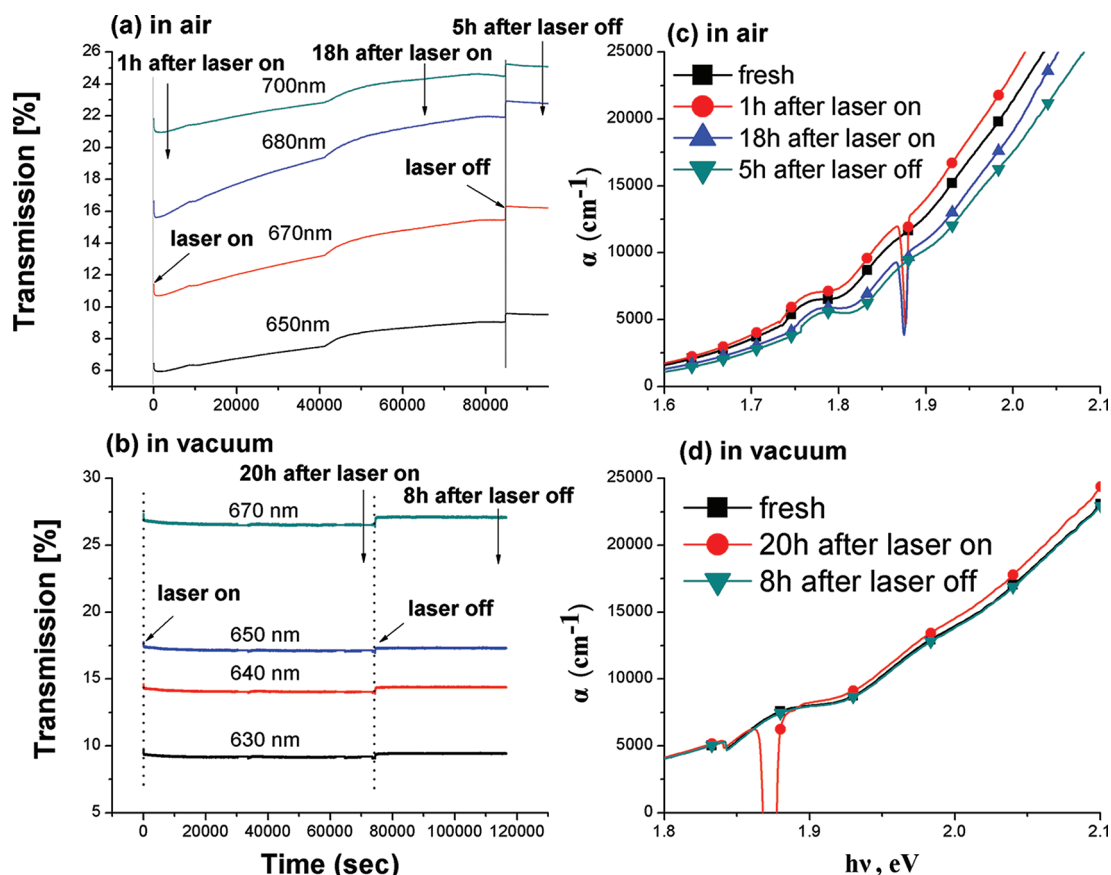
## RESULTS

Figure 1 shows the time variation of the transmissions at four fixed wavelengths for as-deposited GeSe<sub>2</sub> films illuminated in air

(a) or in vacuum (b). To assess the effect of the probing light, the spectra are first recorded under the “dark condition”, that is, without the pumping laser. No visible change in the spectra is observed until the pumping laser is turned on; therefore, the probing light has no impact on the photoinduced changes. It is seen from Figure 1a,b that when the pumping laser (488 nm, Ar<sup>+</sup> laser) is switched on, the transmission at each wavelength begins to decrease within only a few minutes and then gradually increases, approaching a plateau lying above the initial value. When the laser is switched off, the transmission increases further and reaches a constant value very quickly. Our results are in good accord with the observation of Lyubin et al., who also reported transient darkening and irreversible bleaching in glassy GeSe<sub>2</sub> films (refer to<sup>18</sup> for a detailed study on the changes in the transmissions of GeSe<sub>2</sub> films as a function of illumination time).

Figure 1 shows further the changes in absorption coefficient observed before, during, and after the illumination of as-deposited GeSe<sub>2</sub> films in air (c) or in vacuum (d). The spectra are taken at different times, as indicated by the arrows in Figure 1a,b. As soon as the pump laser is turned on, the absorption edge first shifts to a lower photon energy and then to a higher photon energy as time lapses, which is a clear evidence of PB. After the laser is switched off, the absorption edge continues shifting to higher photon energies. This observation again indicates the existence of a reversible transient PD component, which decays and vanishes when the illumination is switched off.

Figure 2 shows the time variation of the transmission at four fixed wavelengths for Ge<sub>2</sub>Se<sub>3</sub> films illuminated in air (a) or in vacuum (b). When Ge<sub>2</sub>Se<sub>3</sub> films are exposed in air (Figure 2a),



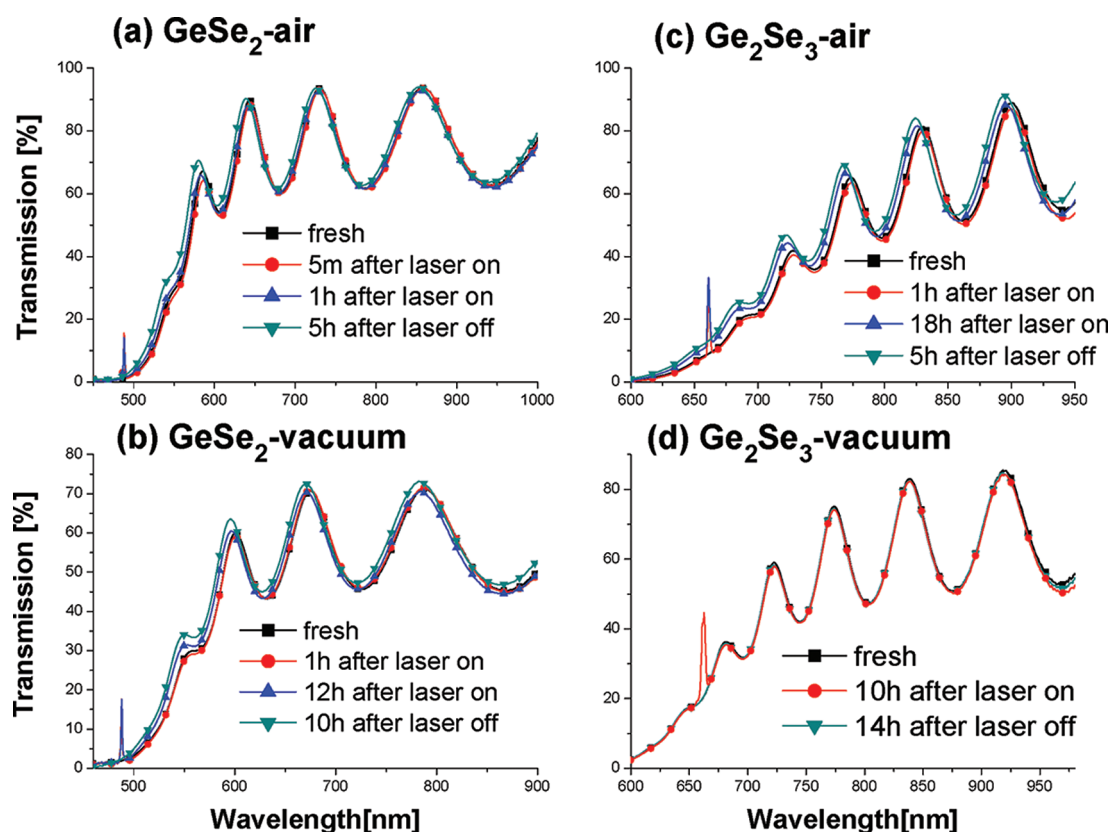
**Figure 2.** Time variation of transmission through as-deposited  $\text{Ge}_2\text{Se}_3$  films illuminated in air (a) and in vacuum (b) and the changes in absorption coefficient observed before, during, and after the illumination in air (c) and in vacuum (d). The spectra (c) and (d) are taken at different times as indicated by the arrows in (a) and (b).

the transmission first decreases very sharply (in a few minutes) and then increases gradually to a constant value upon prolonged exposure. Further increase to a greater final value in the transmission is observed after the illumination is turned off. However, only very slight changes in the transmission can be detected when the films are exposed in vacuum (Figure 2b). As seen again from Figure 2b, the transmission decreases abruptly in the beginning of exposure and stays at the lower values for a very long time. Only when the exposure is stopped for a certain period of time, the transmission recovers to the initial values.

Figure 2c,d describes the changes in absorption coefficient observed before, during, and after the illumination in air (c) or in vacuum (d) for  $\text{Ge}_2\text{Se}_3$  films. The spectra were taken at different times, as indicated by the arrows in Figures 2a,b. The absorption edge of  $\text{Ge}_2\text{Se}_3$  films shifts to longer wavelength (red shift) upon illumination by a 660 nm diode laser in the first 1 h and then to shorter wavelengths (blue shift) upon prolonged illumination in air (Figure 2c). Note that the spike observed at  $\sim 660$  nm is the signal from the pumping laser. When the laser is turned off, the blue shift of the transmission spectra continues. However, when the  $\text{Ge}_2\text{Se}_3$  film is illuminated in vacuum, the results are quite different, as seen in Figure 2d. The transmission spectra still show the red shift even after the laser is turned on for 20 h. However, the transmission spectrum recovers (blue shifts) almost to the original value when the laser is switched off. Only transient PD is occurring in this case.

The changes in the full transmission spectra for  $\text{GeSe}_2$  and  $\text{Ge}_2\text{Se}_3$  films upon exposure in air versus in vacuum are compared in Figure 3. The changes in the short wavelength absorption edge have been described above. The shift of the interference interval arises because of the change in the film thickness, refractive index, or both. We calculated the film thickness by fitting the transmission  $T(\lambda)$  curve according to the Swanepoel model by using the computer program "PARAV".<sup>19</sup> The fitted values are listed in Table 1. All spectra have been fitted with the best accuracy. The relative changes in the film thickness ( $\Delta d/d$ ,  $< 0.6\%$ ) are small as compared with the 5% giant photoexpansion observed in  $\text{As}_2\text{S}_3$  film<sup>20</sup> or 4.8% in  $\text{GeS}_2$  film<sup>5</sup> when exposed to sub-bandgap light. A possible reason for this difference in the magnitude of photoexpansion is that the  $\text{GeSe}_2$  films and the  $\text{Ge}_2\text{Se}_3$  films belong to the so-called "over-constrained" glasses with average coordination number bigger than 2.67, and hence these glasses do not allow significant structural relaxations.<sup>21</sup>

Generally speaking, an increase in the band gap (blue shift in the absorption edge) is accompanied by a decrease in the refractive index according to Moss's rule ( $E_g n^4 \approx \text{constant}$ ).<sup>5</sup> The refractive index  $n$  can be obtained by fitting the transmission  $T(\lambda)$  curve according to the Swanepoel theory by using the computer program "PARAV".<sup>19</sup> The dispersion of refractive index of as-deposited and laser exposed  $\text{GeSe}_2$  and  $\text{Ge}_2\text{Se}_3$  films is shown in Figure 4. Indeed, the refractive index decreases after laser irradiation (Figure 4a–c) except for the laser-exposed  $\text{Ge}_2\text{Se}_3$  film in vacuum (d) for which only negligible changes in the refractive index can



**Figure 3.** Changes in the full transmission spectra for GeSe<sub>2</sub> and Ge<sub>2</sub>Se<sub>3</sub> films upon exposure in air versus in vacuum. (a) GeSe<sub>2</sub> film exposed in air, (b) GeSe<sub>2</sub> film exposed in vacuum, (c) Ge<sub>2</sub>Se<sub>3</sub> film exposed in air, and (d) Ge<sub>2</sub>Se<sub>3</sub> film exposed in vacuum.

**Table 1.** Calculated Film Thickness of Samples in Air and Vacuum

thickness ( $\mu\text{m}$ )	GeSe <sub>2</sub> (air)	GeSe <sub>2</sub> (vacuum)	Ge <sub>2</sub> Se <sub>3</sub> (air)	Ge <sub>2</sub> Se <sub>3</sub> (vacuum)
as-deposited	0.980	0.935	1.606	1.532
laser exposed	0.986	0.938	1.608	1.532
$\Delta d/d$ (%)	0.6	0.3	0.1	0

be detected. The photoinduced polymerization that is accompanied by an increase in the film thickness (photoexpansion, Table 1) and thus a decrease in the density of the exposed region is responsible for the observed decrease in the refractive index.<sup>5</sup>

To characterize photoinduced chemical changes, IR absorption spectra of the present GeSe<sub>2</sub> and Ge<sub>2</sub>Se<sub>3</sub> films were recorded after the laser illumination, as shown in Figure 5. Here we present only the difference IR absorption spectra (after–before illumination) for GeSe<sub>2</sub> (solid line) and Ge<sub>2</sub>Se<sub>3</sub> (dashed line) films. We refer to Spence and Elliott who also used the IR difference spectra to characterize the chemical changes in the thermally evaporated films of germanium chalcogenide glasses.<sup>22</sup>

## DISCUSSION

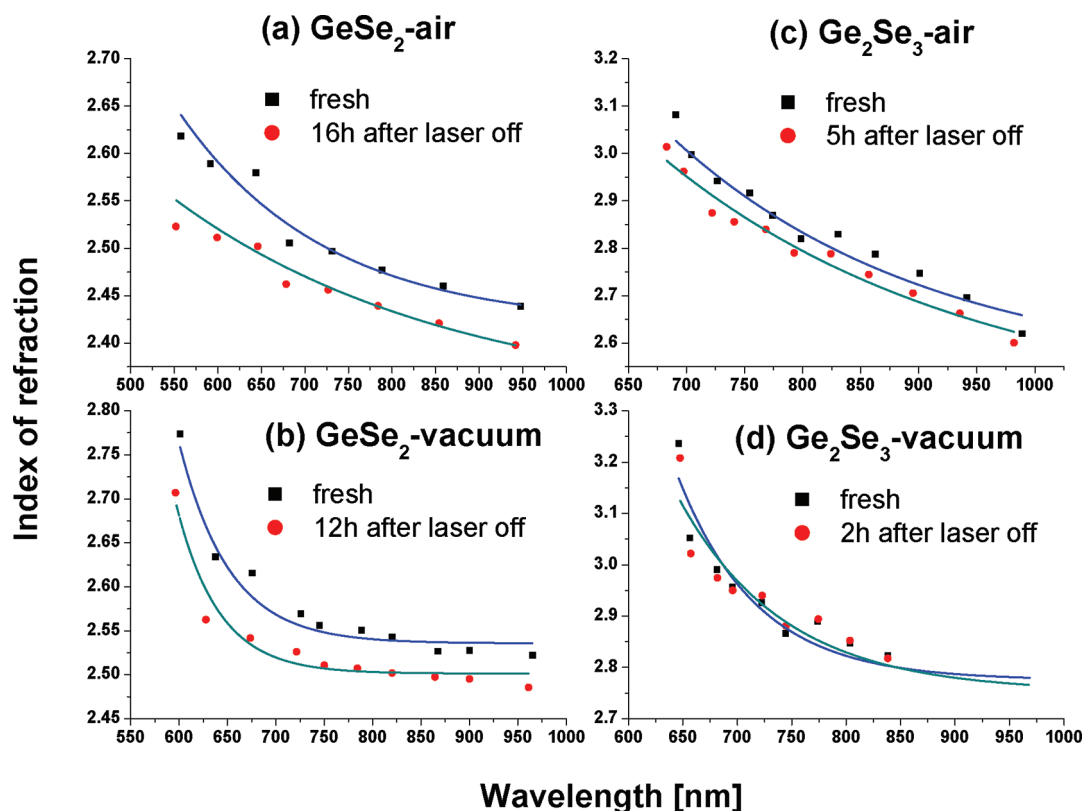
The important finding of the experiments reported here is the presence of both the metastable and the transient photoinduced changes but of different kinds in glassy Ge<sub>2</sub>Se<sub>3</sub> and GeSe<sub>2</sub> films. Transient PD in Ge<sub>2</sub>Se<sub>3</sub> and GeSe<sub>2</sub> films is probably of the same nature as in As chalcogenide films and results from photoinduced bond switching and atom movement.<sup>23</sup> The transient nature of

PD can be explained by assuming the existence of an intermediate (transient) state of electron transitions between the ground and photoexcited states.<sup>24</sup>

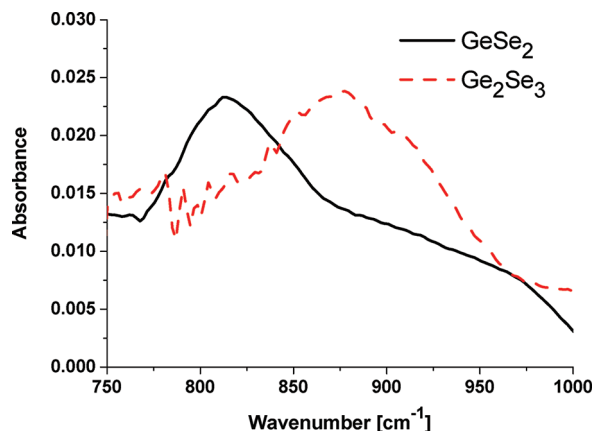
There are two popular mechanisms for understanding PB, viz. structural ordering and photo-oxidation. It is known that the disorder in the local structure may create localized states at the edge of the conduction band. A decrease in the density of such localized states may enlarge the band gap leading to the blue shift of the electronic absorption edge.<sup>25</sup> The disorder in the as-deposited Ge–Se film is mainly due to the wrong Ge–Ge (or Se–Se) homopolar bonds and Ge (Se) dangling bonds.<sup>10</sup> Therefore, the intrinsic structural change in the PB processes has been proposed as the increase in the Ge–Se bond density and subsequent increase in the structural ordering in the short and medium range. On the basis of in situ extended X-ray absorption fine structure (EXAFS) analysis, Ganjoo et al.<sup>26</sup> suggested that illumination created local ordering in the GeSe<sub>2</sub> films with homopolar Ge–Ge and Se–Se bonds being converted into heteropolar Ge–Se bonds. This observation is in agreement with the fact that the latter bonds are stronger than the former bonds and are favored as the glass tries to reach the thermal equilibrium of the lowest free energy.

In contrast with ordering mechanism, photo-oxidation is believed to be responsible for the PB occurring in air. Tichy et al.<sup>27,28</sup> report that three bands in the IR spectra of Ge–S glasses at 870, 820, and 800 cm<sup>−1</sup> are found after the illumination in air. The first band is assigned to the dominant mode of GeO<sub>2</sub> structure, whereas the other features are related to the Ge–O stretching within S<sub>3−x</sub>–O<sub>x</sub>–Ge–O–Ge–O<sub>x</sub>–S<sub>3−x</sub> clusters. The reaction of the films is considered to be partially dependent on the





**Figure 4.** Dispersion of refractive index of as-deposited and laser exposed  $\text{GeSe}_2$  and  $\text{Ge}_2\text{Se}_3$  films. (a)  $\text{GeSe}_2$  film exposed in air, (b)  $\text{GeSe}_2$  film exposed in vacuum, (c)  $\text{Ge}_2\text{Se}_3$  film exposed in air, and (d)  $\text{Ge}_2\text{Se}_3$  film exposed in vacuum.



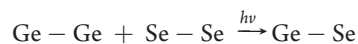
**Figure 5.** IR difference absorption spectra (after-before illumination) for  $\text{GeSe}_2$  (solid line) and  $\text{Ge}_2\text{Se}_3$  (dashed line) films.

densities of the Ge–Ge bonds because Ge–O bonds presumably form after the Ge–Ge bonds are broken by illumination. For the present films, we readily find peaks around 820 and 870  $\text{cm}^{-1}$  in the IR spectrum, which are assigned to the Ge–O bonds in Figure 5. Photo-oxidation occurs in  $\text{GeSe}_2$  and  $\text{Ge}_2\text{Se}_3$  films but to a different stage, as seen from Figure 5. As more Ge–Ge bonds are expected to be present in as-deposited  $\text{Ge}_2\text{Se}_3$  film, it is plausible that the photo-oxidation should occur to a greater degree, forming predominantly the  $\text{GeO}_2$  structural units (870  $\text{cm}^{-1}$ ). In as-deposited  $\text{GeSe}_2$  film, however, the oxygen atoms encounter fewer Ge–Ge bonds and therefore may prefer to replace partially selenium atoms, forming  $\text{Se}_{3-x}\text{O}_x\text{–Ge–O–Ge–O}_x\text{–Se}_{3-x}$

clusters (820  $\text{cm}^{-1}$ ) in the exposed region. Tichý et al.<sup>8</sup> also find that the Ge–O–Ge stretching band shifts from 820 to 870  $\text{cm}^{-1}$  with exposure time in the IR spectra of  $\text{Ge}_{30}\text{S}_{70}$  film, which may be connected to an increased degree of photo-oxidation.

Because PB in  $\text{Ge}_2\text{Se}_3$  is observed only when the film is illuminated in air but not in vacuum, the surface photo-oxidation should be the sole cause of PB. The photo-oxidation of  $\text{Ge}_2\text{Se}_3$  film illuminated in air has been proved by X-ray photoelectron spectroscopy (XPS).<sup>29</sup> In this work, it has been verified by the presence of the Ge–O absorption peak in FTIR spectra (Figure 5, dashed line).

For  $\text{GeSe}_2$  film, PB is observed irrespective of whether if it has been illuminated in air or in vacuum. So, in principle, both photo-oxidation and intrinsic structural changes could be responsible for the PB observed in the  $\text{GeSe}_2$  film. Surface photo-oxidation is verified also for this case by FTIR, as shown in Figure 5 (solid line). The intrinsic structural changes are ascribed to the following photoreaction



We calculated the band gap energy ( $E_g$ ) of the  $\text{GeSe}_2$  films before and after the laser illumination in air and in vacuum by the computer program PARAV.<sup>19</sup> Table 2 presents the calculated data, which indicate that  $E_g$  is almost the same for different as-deposited  $\text{GeSe}_2$  films, indicating good reproducibility of the film fabrication procedure. After illumination, the band gap energy increases, representing PB. The relative contribution of photo-oxidation versus intrinsic structural changes to PB is analyzed by comparing the difference of the band gap energy ( $\Delta E_g$ ) before and after the illumination in air versus in vacuum. It is not new to

**Table 2.** Calculated Energy Band Gap of GeSe<sub>2</sub> Films under Different Conditions

	GeSe <sub>2</sub> (illuminated in air) (eV)	GeSe <sub>2</sub> (illuminated in vacuum) (eV)
$E_g$ (fresh)	$2.0665 \pm 0.0015$	$2.0649 \pm 0.0022$
$E_g$ (12 h after illumination)	$2.1170 \pm 0.0018$	$2.1012 \pm 0.0020$
$\Delta E_g$	$0.0505 \pm 0.0003$	$0.0363 \pm 0.0002$

characterize the magnitude of PD/PB in terms of the changes in the band gap energy. For example, Vatera<sup>30</sup> compared the magnitude of PD and PB in a variety of binary and ternary chalcogenide films in terms of the fractional change in the band gap energy defined as  $\Delta E_g/E_g$ . Tichy et al. also studied the magnitude of PB induced by bandgap photons in terms of the relative changes in the bandgap energy.<sup>5</sup> For GeSe<sub>2</sub> films, the  $\Delta E_g$  in vacuum equals  $\sim 70\%$  of  $\Delta E_g$  in air, so we conclude that the intrinsic structural changes dominate the PB observed in GeSe<sub>2</sub> films.

PB is irreversible because the glass network is transferred to a more ordered state. In terms of energy equilibrium, the glass is reaching a more stable stage. The degree of disorder of the prepared films can be analyzed according to the following equation<sup>31</sup>

$$\alpha(\omega) \propto \alpha_0 \exp[-\Gamma(E_0 - \hbar\omega)]$$

where  $\alpha$  is the absorption coefficient at frequency ( $\omega$ ),  $E_0$  is an energy comparable to the optical gap  $E_g$ , and  $\Gamma$  is a temperature-dependent constant (above  $\sim 77$  K), typically having values in the range  $10$ – $25$  eV<sup>−1</sup>. The greater the disorder, the smaller the  $\Gamma$ . It should be noted that the equation describes well the absorption of amorphous materials in the frequency range where  $10^0 < \alpha < 10^4$  cm<sup>−1</sup>.<sup>31</sup> By plotting  $\ln \alpha$  against photon energy  $\hbar\omega$ , we obtained the value of  $\Gamma$  for GeSe<sub>2</sub> and Ge<sub>2</sub>Se<sub>3</sub> films as 1.87 and 1.37, respectively. As expected, the Ge<sub>2</sub>Se<sub>3</sub> film of nonstoichiometric composition has a more disordered glass network than GeSe<sub>2</sub>, probably due to the larger concentration of Ge–Ge wrong bonds. When attacked by O<sup>2−</sup>, the Ge–Ge bonds tend to break and form more stable Ge–O bonds. Therefore, we can understand why the photo-oxidation dominates the PB observed in Ge<sub>2</sub>Se<sub>3</sub> films illuminated in air, whereas only the intrinsic structural changes dominate the PB observed in GeSe<sub>2</sub> films illuminated in air.

## CONCLUSIONS

The PB phenomenon of GeSe<sub>2</sub> and Ge<sub>2</sub>Se<sub>3</sub> films illuminated in air versus in vacuum has been studied. The results show that Ge<sub>2</sub>Se<sub>3</sub> film exhibits PB in air but not in vacuum after prolonged bandgap illumination (660 nm diode laser). The PB is ascribed to photo-oxidation. GeSe<sub>2</sub> film exhibits PB both in air and in vacuum upon super bandgap illumination (488 nm Ar<sup>+</sup> laser). For this case, PB is ascribed to intrinsic structural changes (Ge–Ge + Se–Se  $\rightarrow$   $h\nu$  Ge–Se) as well as surface photo-oxidation.

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## ACKNOWLEDGMENT

This study is supported by Shanghai Leading Academic Discipline Project (no. B502), Shanghai Key Laboratory Project (08DZ2230500), National Natural Science Foundation of China (NSFC 51072052), and the U.S. National Science Foundation for initiating and supporting our international collaboration through the International Materials Institute for New Functionality in Glass (grant no. DMR-0844014).

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