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PHOTOINDUCED CHANGES IN VACUUM EVAPORATED AMORPHOUS GESE$_2$ FILMS

Qiming Liu*, XiuJian Zhao, Fuxi Gan[a]

Key Laboratory of Silicate Materials Science and Engneering (Wuhan University of Technology), Ministry of Education, 122 Luoshi Road, Hongshan District, Wuhan, Hubei 430070, P. R. China
[a]Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences，P.O. Box 800-211, Shanghai, 201800, P. R. China School of Information Sciences and Engineering, Fudan University, Shanghai 200433, P. R. China

With light illumination from an Ar ion laser, the photoinduced changes in vacuum evaporated amorphous GeSe$_2$ films were investigated with the X-ray diffraction (XRD), infrared absorption (IR), scanning electron microscope (SEM), transmitting electron microscope (TEM) and transmittance spectra analysis. It was observed that the optical transmittance edges of films shifted to shorter wavelength according to annealing and light illumination and the shift in well-annealed films could be recovered by annealing at 200 °C for 1 h in Ar air. The magnitude of shift increased with the increase of the intensity of illumination light and the illumination time. By sides, photoinduced crystallization was also observed in the exposed regions of GeSe$_2$ films and more of it was observed with stronger intensity of illumination light.

Keywords: Amorphous GeSe$_2$ films, Photobleaching, Photoinduced crystallization

1. Introduction

It is well known that amorphous chalcogenides exhibit a wide variety of photoinduced phenomena, which are connected with photoinduced structural transformations, defects creation and diffusion of metallic atoms in the films [1-5]. These photoinduced effects in amorphous chalcogenides have been extensively studied, partly as an interesting subject for fundamental research in the field of disordered materials and partly due to potential application of these effects in optoelectronics (photoresists, optical memories, optoelectronic circuits, etc.) [6-8]. The illumination by band gap light of many amorphous chalcogenides changes their internal and/or surface structure and the optical absorption edge will have a red or blue shift [9]. Another interesting photoinduced phenomenon is the photocrystallization, which was first observed by Dresner and Stringfellow in amorphous Se films [10]. The microscopic origin of these photoinduced phenomena, despite extensive studies for more than twenty years, are not clear up to now. To get a detailed insight into the photoinduced changes process in amorphous GeSe$_2$ films, in the present paper, we have studied extensively the photoinduced shift of optical transmittance edge as well as the photoinduced crystallization.

2. Experimental

The bulk GeSe$_2$ glasses were prepared by standard thermal synthesis from 5N purity (99.999%) Ge and Se elements, heated in an evacuated quartz ampoules (10^{-3} pa), at a temperature of ~1000 °C, for about 48h. After the synthesis the melt was water-quenched,

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* Corresponding author: qmliu@mail.whut.edu.cn

resulting in a bulk glass of the desired chemical composition. The $GeSe_2$ thin films with the thickness of ~500 nm were prepared from bulk $GeSe_2$ glass powder by the conventional vacuum evaporation technique using a double-covered tantalum boat onto K_9 substrates at a rate of 15 Å/s in a 1×10^{-3} Pa vacuum. The thermal evaporation process was carried out in a coating system, at a pressure of ~10^{-3} pa. The films were annealed at 200 ^{o}C for 1 h in Ar air. The X-ray diffraction, using Cu/40 kV/300 mA K_α radiation (Rigaku D/max-2550 V), was used to examine the amorphous or crystalline nature of $GeSe_2$ films. The IR spectra were measured by the method of KBr in the Perkin Elmer Landa-1600 IR absorption spectrophotometer, the measure range was 400~4000 cm^{-1}. The films were illuminated by light from an argon ion laser at 514.5 nm. The transmittance spectra of freshly evaporated, illuminated and annealed films were performed in Perkin Elmer Landa 900UV/VIS/NIR spectrophotometer, the measure range was 400 ~ 900 nm. The SEM pictures were obtained from the SEM (Rigaku EPMA-8705QH2) and the film samples were aurum-plated in the vacuum before measurements. The $GeSe_2$ films were deposited into copper nets and were measured in the TEM (Hitachi, H-800).

3. Results and discussion

It is shown from Fig. 1 that $GeSe_2$ bulk obtained by water-quenched method and film prepared from bulk $GeSe_2$ glass powder by the conventional vacuum evaporation technique are amorphous. No diffraction peaks occurs except two wide diffraction peaks occur in the X-ray diffraction spectrum of $GeSe_2$ film due to the effect of K_9 glass substrate.

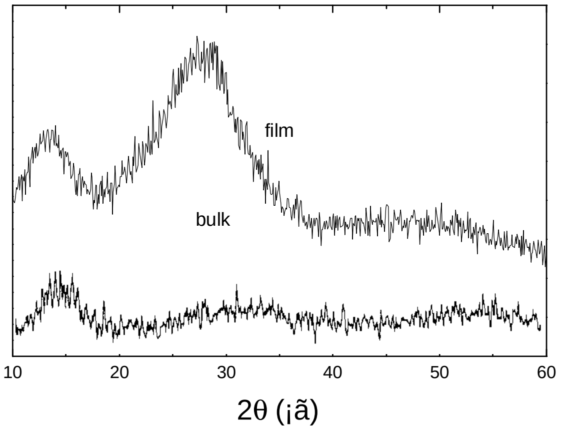


Fig. 1. The XRD spectrum of $GeSe_2$ bulk and film.

Fig. 2 is the IR spectra of $GeSe_2$ bulk and film by the method of KBr. It is seen from Fig. 2 that few absorption bands occur in the IR spectra due to highly pure Ge and Se elements in our experiments, which means that the impurities in the $GeSe_2$ bulk and film are few. –OH (3454.1 cm^{-}1 and the wavelength is 2.895 μm) and H-O-H (1636.3 cm^{-1} and the wavelength is 6.111μm) are observed in the IR spectra according to the water-absorption of KBr. Another absorption band in 1384.1 cm^{-1} (the wavelength is 7.225 μm) is As_4O_6 impurity [11]. It is also seen from Fig. 2 that the IR spectra of $GeSe_2$ bulk and film are similar except there is little different in the transmittance of them. So the composition of the $GeSe_2$ film is the same as the $GeSe_2$ bulk.

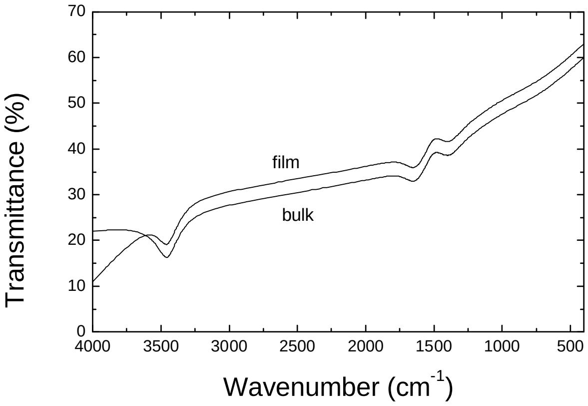


Fig. 2. The IR curves of a-GeSe$_2$ bulk and film.

The transmittance spectra of GeSe$_2$ films are shown in Fig. 3. With band gap light illumination from an argon ion laser at room temperature and annealing at 200 ^{o}C, we can see from Fig. 3 that the optical transmittance edges of GeSe$_2$ films shift to shorter wavelength. This photoinduced effect is the so-called photobleaching [9], which has been studied by many researchers in the past twenty years, but the mechanism of it is still unknown. As is shown from Fig. 3, with band gap light illumination, the as-deposited state (a) shifts to the illuminated sate (b), but it will shift to the annealed state (c) if the as-deposited films are thermally annealed at 200 ^{o}C in Ar air. The annealed state (c) will shift to the state (d) if the films are illuminated, but the illuminated state (d) will restore to the annealed state (c) if the films are annealed again. The shifts between the illuminated state (d) and the annealed state (c) can be repeated by annealing and illuminating, but the shift from the as-deposited state (a) to the annealed state (c) or to the illuminated (b) is irreversible. So the shift of optical transmittance edges from (a) to (c) or (a) to (b) and between (c) and (d) are denoted as the irreversible and reversible photobleaching process, respectively. With band gap light illumination, photobleaching is observed in a-GeSe$_2$ films. The occurrence of photobleaching is strongly related to the intensity of illumination light and the illumination time. The dependence of the shift $\Delta\lambda$ of photobleaching on the intensity of illumination light and the illumination time are shown in Fig. 4. Trends are seen from Fig. 4 that the magnitude of shift $\Delta\lambda$ increases with the increase of the intensity of illumination light and the illumination time. With further intensity of illumination light and illumination time, the magnitude of shift $\Delta\lambda$ will be saturated finally.

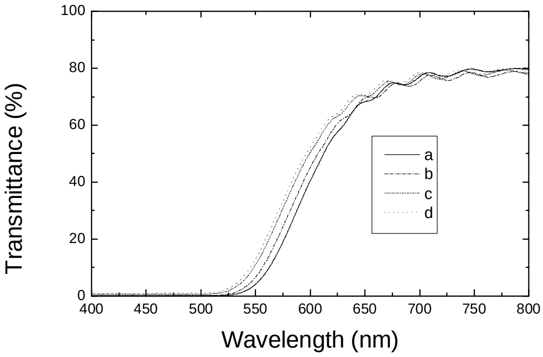


Fig. 3. The transmittance spectra of a-GeSe$_2$ film. The intensity of illumination light was 100 mW and the illumination time was 5 min. (a) as-deposited film, (b) illuminated film, (c) annealed film, (d) illuminated after annealing.

The optical transmittance edge of a-$GeSe_2$ films shifts to lower energy by the band gap light illumination. This photoinduced phenomenon (i.e. photobleaching) is interesting and has been studied many years, but the mechanism of it is still obscure. Researchers only posed different viewpoints according to different system and different structure, which are limited to qualitative explanation and are far from quantitative explanation. Because a-$GeSe_2$ films are structural flexibility, they are susceptible to light-induced changes [12]. In a-$GeSe_2$ films, the Se atoms are only two-fold coordinated and possess a lone pair of electrons which are normally non-bonding but which can undergo light-induced reactions to produce structural defects of threefold or singly coordinated Se atoms. The states associated with the non-bonding electrons lie at the top of the valence band and hence are preferentially excited by illumination. It is known that the valence band is formed by the interaction of the lone pair orbits in chalcogenide glasses and the conduction band is formed by the anti-bonding orbits. Therefore, the lone pair electrons play an important role in the photobleaching induced by band gap light illumination. In the case of band gap illumination, it is believed that the photobleaching is caused by changes of atomic configurations and positions resulting from exciting lone pair electrons. In the case of band gap light illumination, inner core electrons can be excited, i.e. generation of inner core holes. The inner core holes can be immediately filled by outer electrons with auger processes which could induce more holes in upper states (bonding and lone-pair states), since one auger process creates two holes (vacancy cascade process). In this situation, bond-breaking or ionization of atoms is easy to occur, leading to a change in local structural order in the amorphous network and a blue shift of optical transmittance edge.

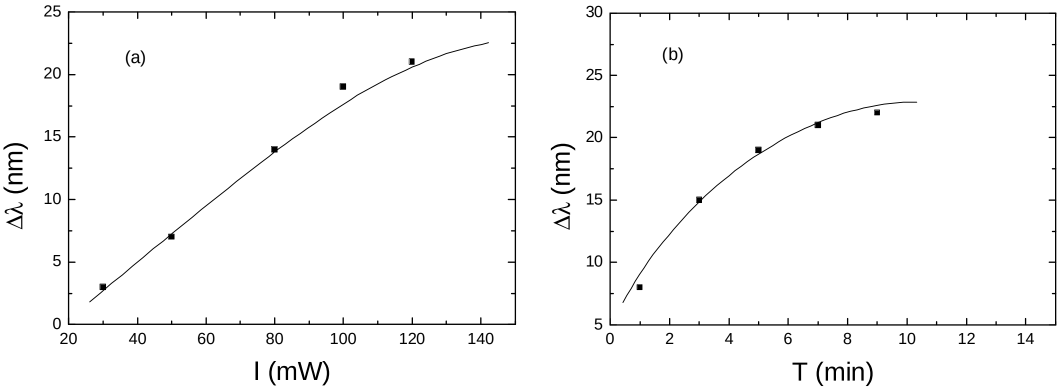


Fig. 4. The magnitude of photobleaching Δλ versus（a）the intensity of illumination light and (the illumination time is 5 min),（b）the illumination time（the intensity of illumination light was100 mW）in the a- $GeSe_2$ films.

Amorphous $GeSe_2$ films, prepared by rapid depositing from the vapor phase, usually have a more or less disordered network, containing a substantial density of wrong chemical bonds. So the amorphous $GeSe_2$ films are metastable and could be changed easily by the band gap light illumination or annealing. Upon thermal annealing or illumination with band gap light, bonds rearrangements can take place and the film can relaxationally restore to its stable state, leading to irreversible changes in many physical properties, e.g. optical transmittance edge blue shift. So we can see the irreversible shifts between the (a) to (b) and (a) to (c) in Fig. 3. However, some bonds would be transformed if the well-annealed a-$GeSe_2$ films were illuminated according to the interaction between the photons and some atoms in the network of a-$GeSe_2$ films, such as Se-Se to Ge-Se, which induces the photoinduced structural changes and a further blue shift of optical transmittance edge. But it would relaxationally restore to the well-annealed state when the films were annealed again, i.e. the process between (c) and (d) is reversible. Reversibility of photobleaching in a-$GeSe_2$ films can be applied in optical memories.

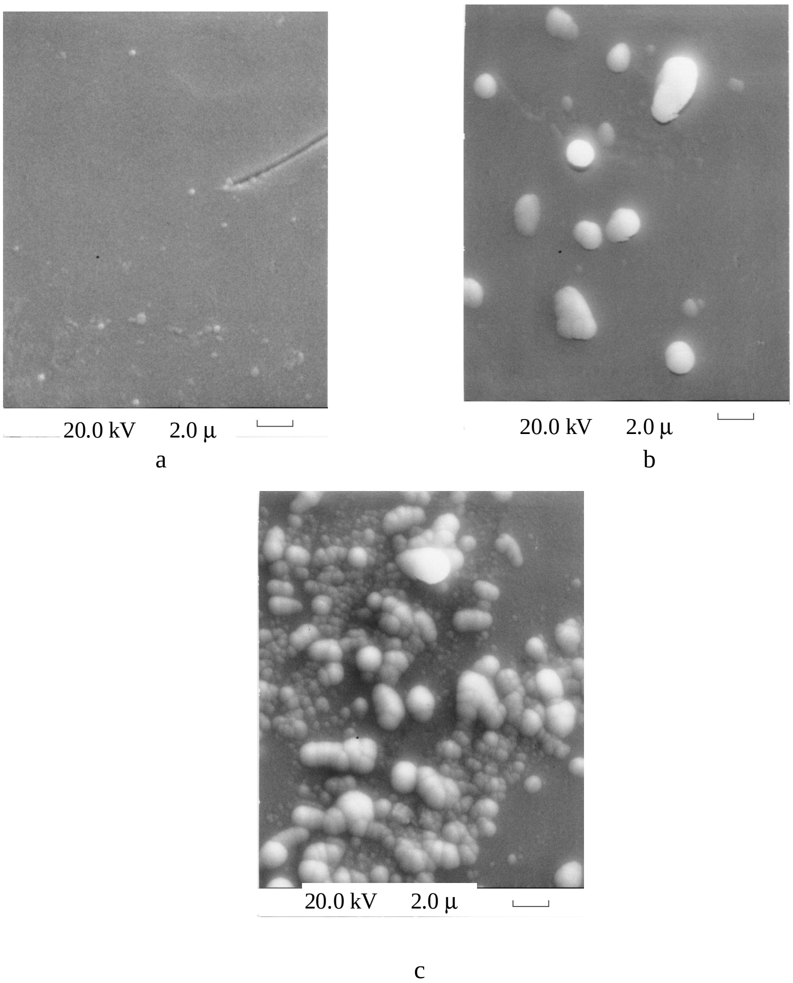
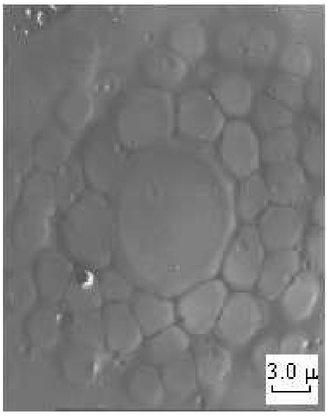


Fig. 5. The SEM pictures of a-GeSe$_2$ films. （a）0 mW，（b）20 mW, 5 min，（c）100 mW, 5 min.

The occurrence of photobleaching in a-GeSe$_2$ films is due to photoinduced structural change. The SEM pictures of a-GeSe$_2$ films illuminated by the intensity of 0 mW, 20 mW and 100 mW light (the illumination time is 3 min) are shown in Fig. 5. The surface of a-GeSe$_2$ film with no illumination is smooth and no crystallization occurs. But it occurs upon illumination of 20 mW light. With higher intensity of 100 mW light illumination, more crystallization appears. For a-GeSe$_2$ chalcogenide semiconductors, with band gap light illumination, electronic excitation by photon absorption is assumed to be capable of achieving bonds switching and rearrangement in order, such as Se-Se, Ge-Ge to Ge-Se, which is the origin of the photoinduced structural changes. The same kind of bonds switching and rearrangement mechanism should also be involved in the photoinduced crystallization process. On the other hand, a spatially wide-spread excitation should also be required to produce a long-range order, which induces photoinduced crystallization. The crystal-to-amorphous will take place when GeSe$_2$ film with crystallization is melt by illumination of high intensity or shorter pulse light and cooled quickly, which is the origin of the phase-change optical storage materials. Fig. 6 shows the TEM pictures of GeSe$_2$ film with illumination of 50 mW(3 min). The diffraction patterns of (a) as-deposited amorphous region and (b) crystallized region are indicated that the amorphous-to-crystal can be realized by illumination of band gap light.



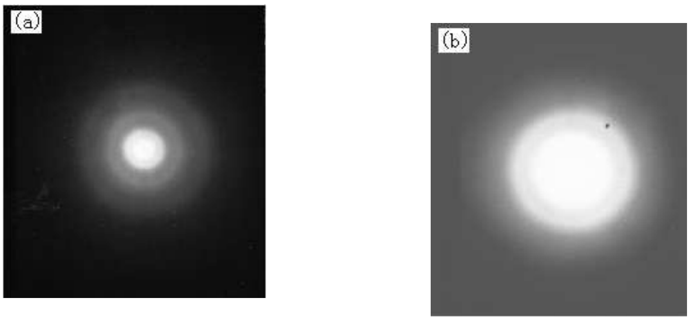


Fig. 6. The TEM pictures of a-$GeSe_2$ films. The intensity of illumination light was 100 mW and the illumination time was 5 min. (a) the crystallized region and (b) as-deposited amorphous region.

4. Conclusion

The changes of properties and structure in $GeSe_2$ amorphous semiconductor films by light illumination from Ar ion laser were studied with the XRD, IR, SEM, TEM and transmission spectra analysis. It was indicated that the optical transmittance edges of films shifted to shorter wavelength according to annealing and light illumination and the shift in well-annealed films was reversible. The magnitude of shift increased with the increase of the intensity of illumination light and the illumination time. Photoinduced crystallization was also observed in the exposed films by SEM and TEM imagines. By sides, more crystalline was occurred with higher intensity of illumination light.

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