Oxygen-assisted photoinduced structural transformation in amorphous Ge–S films

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We report our results of continuous illumination of Ge46S54 chalcogenide glass films with bandgap light in air. The outcome of this process is the formation of Ge–S backbone depleted in germanium. We relate this to consumption of some of the germanium available in the initial material due to the occurrence of a photoinduced oxidation. This is proved using energy dispersion spectroscopy which shows the presence of 17.68 at.% oxygen in the glass post-radiation. Raman spectra demonstrate that the initial material shows breathing modes, characteristic for Ge46S54 glass. After prolonged illumination Raman spectra reveal structure characteristic for the composition of the Ge–S backbone close to Ge33S67. The oxide forms a film on the surface and this changes the surface relief, studied by atomic force microscopy, but the oxidation is not surface-limited. The oxidation process in these glasses is discussed and the higher priority of germanium oxidation compared to the oxidation of sulphur is stated.

1 Introduction

Photoinduced changes in chalcogenide glasses are among their most important features that stimulate active investigations in this field in the search for new phenomena and novel applications. The photoinduced effects arise from the changes that occur in a glass structure after its electrons are excited by radiation [1]. These cause–effect relationships are very complex and manifest in many seemingly unrelated properties. In broad terms, a given effect results from the changes in physical (atom positions and periodicity, etc.), chemical (composition, bonding among the atoms, etc.), electronic (density of states in the valence and conduction bands) and vibrational (modes of vibrations of structural units) structures [2–5]. The reason why the chalcogenide glasses exhibit many kinds of radiation-induced phenomena can be ascribed to their unique electronic and atomic structures and lack of periodicity [6–8]. Electronically, these glasses are semiconductors with an energy gap of 1–3 eV. However, a unique feature is the availability of states in the band gap due to the lone pair of electrons located at the chalcogen atoms [6]. Accordingly, they can be excited by a wide range of wavelengths which contribute to different structural effects [9–11]. In addition, excited carriers are effectively localized in disordered and defective glass structures, and they undergo strong electron–lattice interactions which have been modelled [12, 13].

Historically, the photoinduced effects have been studied in air. Later Tanaka et al. discovered that oxidation accompanies the already well-described electron-related effects [14]. Photoinduced oxidation has always been a subject of discussion because it is quite difficult to be analysed in a short-term experiment related to photoinduced effects. Spence and Elliott [15] have found that in air oxidation occurs, increasing with increase of the irradiation dose. The key information about photo-oxidation remains fragmented at best. Tichy et al. [16, 17] have observed three bands in the infrared spectra at 870, 820 and 800 cm−1. The first of these corresponds to the dominant mode of GeO2 glass. The other features, according to the authors, could be related to the Ge–O stretches of Sx−1O−Ge–O–Ge–O–Sx clusters. When increasing the amount of oxygen, a shift occurs towards smaller wavenumber because of increasing local electronegativity. In quite controversial work, Harshavardhan and coworkers [18, 19] have reported
weight and thickness losses in obliquely deposited films, which they connect to the formation of volatile chalcogenide oxides. The lack of these effects in normally deposited films and the difference in the behaviour of sulphur- and selenium-containing films have been, however, very vaguely explained. While these interpretations could be accepted in the cases of photocontraction, there is no way to explain the photoinduced losses due to the formation of oxides. One interpretation of the effect related to photo-oxidation suggests that the oxide film is located on the surface, thus producing strain on the interface, which creates states into the bandgap. In a broader sense this contradicts the general view that oxidation can be identified with bleaching of the glasses [20].

In this work, we report our results of continuous illumination of Ge$_{44}$S$_{56}$ chalcogenide glass film with bandgap light in air. This results in changes of the structure of the Ge–S backbone, which we relate to depletion of germanium available to participate in it due to oxidation.

2 Experimental Ge–S films were prepared by thermal evaporation on a silicon substrate in a Cresington 308R desktop coating system from previously synthesized glasses with composition Ge$_{40}$S$_{60}$. This method of film formation results in a relaxed medium which makes it possible to compare the films’ structure to that of bulk materials with the same composition. The thickness of the films was 300 nm.

The composition of the original films was measured with an electron probe microanalyzer in a scanning electron microscope system (LEO 1430VP) using energy dispersive X-ray spectroscopy (EDS). Raman spectra were recorded in backscattering geometry at room temperature using a Jobin Yvon T64000 triple spectrometer equipped with a liquid-nitrogen-cooled multichannel coupled-charge-device detector. The spectra were recorded every minute to follow the evolution of the spectra in time with continuous laser irradiation. The 441.6 nm laser line of a He–Cd continuous wave laser (Kimmon Koha Co. Ltd, IK5752 I-G) with a power of ∼80 mW at the sample surface was used for the excitation and long-term illumination for the formation of oxides. Microscopic images were obtained using a optical microscope (Nikon ECLIPSE LV150) and digital camera (Canon PC1049). Atomic force microscopy (AFM) studies were conducted with a Veeco automated AFM Vx200/300 atomic force profiler.

3 Results The compositional studies of the films show that the actual composition of the films is Ge$_{40}$S$_{60}$. Curve a of Fig. 1 shows the result obtained from EDS analysis. The repeatability in composition is very good and the produced films are free of oxygen. The time evolution of the Raman spectrum is shown in Fig. 2. The top spectrum was measured at the first minute. The laser illumination started from the first measurement. The spectrum taken after 1 min irradiation is comparable to those of Ge$_{40}$S$_{60}$ bulk, Ge$_{45}$S$_{55}$ bulk and Ge$_{46}$S$_{54}$ film, measured by other researchers [21, 22] as plotted in Fig. 2. Among these spectra, the spectrum after 1 min irradiation is very similar to the spectrum of bulk Ge$_{40}$S$_{60}$.

This indicates that the structure of the present film is close to that of the bulk material. In the spectrum of bulk Ge$_{40}$S$_{60}$, the broad peak in the range from 190 to 310 cm$^{-1}$ is composed of the peak at 220 cm$^{-1}$ and the peak at 255 cm$^{-1}$. These peaks are attributed to the vibration of the double-layer units and the vibration of the ethane-like units, respectively [23]. The broad peak in the range from 320 to 450 cm$^{-1}$ is composed of the peaks at 340, 370 and 410 cm$^{-1}$. The peaks at 340 and 370 cm$^{-1}$ are attributed to the vibrational modes of the ethane-like units [24]. The peak at 410 cm$^{-1}$ is assigned to the stretching mode of single Ge–S chains, which are made by the failure in forming a double-layer structure [23].

The (H, H)-horizontal polarized Raman spectrum in Fig. 3 indicates that the peak at 340 cm$^{-1}$ is polarized vibration. This is consistent with the results obtained by Lucovsky et al. [24]. The peak is assigned to the totally symmetric vibration of sulphur atoms along the z-axis and out-of-phase germanium motions of the ethane-like unit. Overall, in Ge$_{40}$S$_{55}$ film, there are ethane-like units, double-layer-type units and, possibly, single Ge–S chains. Within 7 min, these broad peaks do not change much.

However, the intensity of the phonon peak from the silicon substrate at 520 cm$^{-1}$ increases with time, as shown in Fig. 4. This indicates decreased absorption by the Ge–S film, which becomes optically ‘thinner’. Such an increase in the substrate signal has not been observed as long as the same measurements were carried out in vacuum. In the initial short period of time from 8 to 10 min, the spectrum drastically changes. The peak positions completely change, as shown in
Fig. 2 (see the Raman shapes indicated by the arrows). The peaks at 250 and 350 cm\(^{-1}\) become well pronounced in the spectrum obtained after 21 min. In addition, the background intensity abruptly decreases during this period, as shown in Fig. 4. This is usually related to an increase in the surface smoothness and we will discuss this in more detail later.

We have also found a compositional difference in the films after long-term illumination. Their EDS spectra obtained from the illumination spot show a distinct presence of oxygen (about 17.68 at.\%), as shown by curve b of Fig. 1b. We tried to study the X-ray diffraction spectra of these films to understand the molecular character of the oxygen-containing phases but although we aligned the X-ray...
equipment to the area of the illuminated spot, we could not detect oxygen-containing phases, possibly because they occur in amorphous structure or the size of eventually occurring oxide crystals was below the sensitivity of the instrument.

One other method to determine the structures containing oxygen could be Raman spectroscopy, but since the Raman intensity of the GeO$_2$ peaks is about 10 times weaker than that of GeS$_2$ [25] the breathing modes of GeO$_2$ remain undetected. At the time of this study, we did not have a chance to conduct infrared studies, which would be the most informative method as regards the presence of Ge–O bonds.

Figure 5 shows optical microscope images of the illuminated spots recorded after different times of irradiation.

The illuminated area can be easily recognized because the spot has a different colour. The colour becomes greenish with illumination time.

4 Discussion When one considers the oxygen-containing environment in which the photoinduced changes of the chalcogenide glasses take place, the occurrence of oxidation is usually accepted as a fact. However, the oxidation products are the subject of discussion. The reason for the contradictions is that in some cases shrinking of the films has been observed [19], while other authors [16, 17] reported direct evidence for the appearance of Ge–O bonds. Indeed, the problem persists, since there has not been a direct proof for the formation of chalcogenide oxides, and because of this, secondary data like film shrinking and weight loss have been used in support of the formation of gaseous products leaving the system. However, in these cases the changes in density or bond lengths, which could also cause the effects observed, have not been discussed.

Considering the standard potential data for the formation of the particular bivalent oxides $E_0/E^{n-2}$, it turns out that germanium is much easier to oxidize with potential $V_{Ge} = 0.23$ compared to that for sulphur ($V_S = 0.54$). Consequently, after the reaction to light illumination and formation of defects on germanium and sulphur sites, germanium will be oxidized first. As a result of this, one can expect that oxygen will replace part of the chalcogen atoms in the structure of the films studied. This will increase the number of sulphur atoms ready to build structural units with germanium. In other words, the Ge:S ratio will decrease giving rise to the formation of units, characteristic for compositions richer in sulphur.

Comparing the Raman spectra of the films after illumination to those of Ge–S films and bulks with different compositions, we have found out that the spectrum taken after 21 min is quite similar to that of Ge$_{33}$S$_{67}$ film. In the spectrum of Ge$_{33}$S$_{67}$ film, the peak at 250 cm$^{-1}$ is assigned...
to the vibration of the ethane-like units. The superposed peak in the range from 310 to 460 cm\(^{-1}\) is composed of the peaks at 340, 370 and 430 cm\(^{-1}\). The peak at 340 cm\(^{-1}\) is assigned to the breathing mode of the corner-sharing Ge(S\(_{1/2}\))\(_4\) tetrahedral units [24]. The peak at 370 cm\(^{-1}\) is the companion peak. It is assigned to the vibration of the edge-sharing tetrahedral units [26] or the stretching mode of a S–S dimmer, which is located on the edge of the outrigger raft cluster [27, 28]. This assignment is still a subject of controversy. The peak at 430 cm\(^{-1}\) is attributed to the stretching mode of dimerized S–S atoms on the edge of the outrigger raft [29]. The positions of the peaks at 340 and 370 cm\(^{-1}\) are the same as those of the vibrational modes of the ethane-like units, which appear in the spectrum of Ge\(_{33}\)S\(_{67}\) bulk. However, in the spectra of Ge\(_{33}\)S\(_{67}\) film and bulk, the main contribution to the peaks is supposed to come from the tetrahedral units according to the results of Mössbauer spectroscopy [30]. The polarized Raman spectra obtained after illumination for 20 min (see Fig. 3) indicate that the peaks at 250 and 340 cm\(^{-1}\) are related to the polarized vibration. The peak at 250 cm\(^{-1}\) is attributed to the vibrational mode of the ethane-like units. The peak at 340 cm\(^{-1}\) is attributed mainly to the breathing mode of the corner-sharing tetrahedral units, and partially to the vibrational mode of the ethane-like units. These results prove that there are ethane-like units and tetrahedral units in the film after 20 min of illumination in air. This situation is exactly the same for thin-film and bulk Ge\(_{33}\)S\(_{67}\). This suggests (1) that the vibrational spectra of films after 20 min of laser illumination in air change from those characteristic for films containing 46 at.% germanium to those for films containing 33 at.% germanium, and (2) that the structural organization totally changes from double-layer to tetrahedral units building the films. In a previous study, we proposed a model for Ge\(_{40}\)S\(_{60}\) glasses in which a structural transition in the constitutional organization is envisaged when germanium composition changes from 33 to 50% and the nature of bonding fundamentally changes [22]. At 33% germanium, the chains are composed of a sequence of tetrahedral Ge(S\(_{1/2}\))\(_4\) units. Two chains are connected with the edge-sharing tetrahedral units and the ethane-like units. Germanium atoms have four-fold coordination by sp\(^3\) hybridization, as shown in Fig. 6a. On the other hand, at a germanium concentration of 46 at.% or close to 50 at.%, the chains are composed of Ge–S chains with two-fold coordinated germanium and sulphur atoms. The chains are connected to each other with a coordinate bond, which is formed only between heteropolar atoms on the chains. At a germanium atom side, two p electrons are used to form two covalent bonds without forming hybridization and one empty p orbital is used to form a coordinate bond (Fig. 6b). At a sulphur atom side, two p electrons are used to form two covalent bonds and two lone-pair p electrons are used to form the coordinate bond (Fig. 6c).

The Raman peak position of the breathing mode of the corner-sharing tetrahedral units for films illuminated for 21 min is shifted from 347 to 350 cm\(^{-1}\) in this spectrum. This may be because there is a partial substitution of oxygen for sulphur in the tetrahedral units, or there is a different environment for the tetrahedral units in the reorganized networks that are formed after laser illumination. In Raman spectra of glassy GeO\(_2\), there are two characteristic features: an intense peak at 400 cm\(^{-1}\) and its broad tail extending to 650 cm\(^{-1}\) [31]. In the spectrum at 21 min in Fig. 2, such peaks are not clearly observed. Therefore, the change in the spectrum is mainly attributed to the compositional change in the Ge–S film. However, oxygen should be involved in the change and its presence in the films was proved by the EDS studies (Fig. 1).

According to Kawaguchi et al. [20], the optical gap of amorphous Ge–S rapidly increases with decreasing germanium composition from 42 to 33%, which means that the absorption edge shifts to shorter wavelength with decreasing germanium composition. The observed colour change (Fig. 5) is consistent with the shift of the absorption edge. In addition, this is also consistent with the increase in the silicon peak at 520 cm\(^{-1}\). By shifting the absorption edge to the shorter wavelength side, the 441.6 nm laser light can penetrate deeper through the film and the intensity of scattering from the silicon substrate increases. There are fringes in the coloured area. They must be Newton rings, caused by the presence of a thin layer with a different refractive index. Although not clearly seen in the images in Fig. 5, the coloured part looks to be below the surface in the actual microscopic images. For that reason, we assume that there is a transparent layer composed of germanium dioxide (GeO\(_2\)) on the surface, and a Ge–S film with a different colour is positioned below this layer. This assumption can explain why the GeO\(_2\) features have not been detected in Raman spectra. The non-illuminated portion has a rough surface (Fig. 7a). When the film is illuminated with the laser in air, we observe that the surface becomes smoother (Fig. 7b). This smoothing of the surface is a likely reason for the decreased background in Raman spectra. The formation of the transparent GeO\(_2\) layer is also consistent with the increase in the silicon peak at 520 cm\(^{-1}\). The transparent layer, which replaces a part of Ge\(_{46}\)S\(_{54}\) layer, would make the laser penetration deeper, and the scattered intensity from the silicon substrate would be expected to increase.
From an analysis of the spectra and the images, it is suggested that the oxidation does not stop at the surface of the film. There would be (1) a progression of the front of the GeO$_2$ layer and (2) a compositional change in the Ge–S layer. Since the GeO$_2$ layer is transparent to the blue laser, the laser can affect the Ge–S bond at the interface between GeO$_2$ and Ge–S layers and cause dangling germanium atoms. In order to achieve the progression of the front, reorganization of the Ge–O network is required by supplying the oxygen to the other open side, which is opposite to the interface. For the Ge–S layer, it would be possible that the reaction stops just at the interface, making two layers in the Ge–S film: a sulphur-rich Ge–S layer and the original Ge$_{46}$S$_{54}$ layer. In such a case, the spectrum should be a mixture of the spectra of the sulphur-rich Ge–S film and the original Ge$_{46}$S$_{54}$ layer. If there is a sulphur-rich Ge–S layer, sharp peaks should appear at 218 and 470 cm$^{-1}$, which are attributed to the bending mode of $S_8$ ring molecules and the stretching mode of $S_8$ chains, respectively. In addition, if the reaction is blocked at the sulphur-rich Ge–S layer, the spectrum component of the Ge$_{46}$S$_{54}$ film should remain. However, the spectral change in Fig. 1 is not like that. Therefore, the reaction is not blocked at the interface, but the whole Ge–S layer is involved in the reaction, in which a reorganization of the Ge–S network takes place. Hence, the phenomenon can be regarded as a ‘structural transition’, although the change is initiated by reaction with oxygen.

5 Summary We have found that a strong laser illumination of continuous blue light in air induces a compositional and a structural transition change in the Ge–S film. This is a result of the development of an oxidation process in the glass film which predominantly affects germanium atoms in it, and contributes towards the formation of a new type of structure due to the phase separation of the oxidized product. Although there is evidence for the concentration of the oxidized product at the surface of the films, this does not stop the process which also occurs within the volume of the films. The compositional change has been achieved within 10 min of illumination. This provides a large advantage for the development of a dynamic change, which cannot easily be obtained by other methods. It can be applied to in situ formation of materials with a new structural organization.

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