Thin Ge–Se films as a sensing material for radiation doses

Mahesh S. Ailavajhala¹, Tyler Nichol¹, Yago Gonzalez-Velo², Christian D. Poweleit³, Hugh J. Barnaby², Michael N. Kozicki², Darryl P. Butt², and Maria Mitkova*¹

¹ Department of Electrical and Computer Engineering, Boise State University, Boise, ID 83725, USA
² School of Electrical, Computer and Energy Engineering, Arizona State University, Tempe, AZ 85287-5706, USA
³ Department of Physics, Arizona State University, Tempe, AZ 85287-5706, USA
⁴ Department of Materials Science and Engineering, Boise State University, Boise, ID 83725, USA

Received 10 September 2013, revised 13 November 2013, accepted 26 November 2013
Published online 27 December 2013

Keywords chalcogenide glasses, radiation-induced Ag diffusion, radiation-induced effects

*Corresponding author: e-mail mariamitkova@boisestate.edu, Phone: +1 208 426 1319, Fax +1 208 426 2470

This work focuses on the study of Ge rich phases in the Ge–Se chalcogenide glass system. Radiation induced effects particularly related to Ag diffusion in the glasses under the influence of different doses of γ radiation are investigated and documented. Raman spectroscopy, X-ray diffraction, energy dispersive X-ray spectroscopy, scanning electron microscopy, and atom force microscopy confirmed the occurrence of radiation-induced Ag diffusion and oxidation of the hosting chalcogenide thin films. This causes Ag surface deposition and structural reorganization of the hosting backbone, and affects the electrical performance of the films. It is suggested that the sensing ability of the thin films can be substantially influenced by the encapsulating the sensing elements to avoid the oxidation of the chalcogenide film.

1 Introduction The research on chalcogenide glasses has made substantial progress in identifying their properties and relevance for various applications. One part of the chalcogenide glass exploration, that is thoroughly studied is related to photoinduced effects within these materials [1]. In the process of understanding these effects, the importance of the lone pair electrons associated with the chalcogen atoms was revealed. They are usually non-bonding electrons whose function is not obvious. Since the states related to these electrons are situated on the top of the valence band, when the glasses are illuminated by a light source, the lone pair electrons can be easily excited producing photoinduced effects. These photoinduced effects could be restricted to the formation of electron hole pairs or contribute to a change of the chalcogenide atoms’ coordination and play a role in the formation of onefold or threefold coordinated chalcogens (defects). In accordance with all these changes, two specific effects have been reported: photo bleaching [2] or photo darkening [3]. The light illumination can even have a dual effect, contributing to a transition from one effect to another [4, 5]. Furthermore, chalcogenide glasses have various structural coordination ranging from floppy to rigid structure [6], which allows for the generation of a variety of defects and structural modifications in the presence of radiation with visible light [7, 8] or shorter wavelength electromagnetic waves. This created interest in studying the influence of the X-rays over the chalcogenide glasses [9, 10] as well as the effects caused by γ radiation [11, 12].

One other effect, closely related to the above-mentioned effects and depending upon the radiation-induced changes, corresponds to the photo induced Ag diffusion within the glasses [13]. Kluge [14] considered the process of photo-diffusion of metals in chalcogenides as an intercalation reaction. The main reason this can be realized in chalcogenide glasses is the fact that they possess relatively rigid covalent bonds, mixed with soft Van der Waals interconnections. This type of structure ensures the formation of voids and channels where the diffusing ions can migrate and can reside [15]. The reaction can be efficient when the reversible transport of ions and electrons can be achieved, accompanied by formation of bonds with the host matrix, according to the reaction:

\[ C_2^0 + e^- + M^+ \rightarrow C_1^- M^+ \]  (1)

This reaction describes the transition of an initially twofold covalently bonded chalcogenide atom (C₂⁰) into a C₁⁻...
charged unit possessing only a single covalent bond and an excess electron that can establish an ionic bond with \( \text{Ag}^+ \) (M\(^+\)). Equation (1) shows the importance of the potential in forming the new \( \text{C}_2\text{M}^+ \) bonds of another compound – the intercalation product. The possible number of these bond-units is fairly high as the chalcogenide glasses are able to form a significant number of single \( \text{C}_2 \) centers under light illumination. Indeed, this capability is a unique property of the chalcogenides and thus explains the occurrence of number of illumination-induced effects within these materials. One can expect that similar effects will also occur under X-ray and \( \gamma \) radiation, which however have not been studied so far.

In this work, we study the effect of Ag diffusion in \( \text{Ge}_{40}\text{Se}_{60} \) based on a device structure, which allows investigating the influence of various radiation doses on the material properties through the measurement of the electrical performance of the devices. Our research focuses on Ge rich glasses, since our previous studies on both Ge–Se and Ge–S systems show that this type of material undergoes structural changes under \( \gamma \) radiation, which stabilize the radiation-induced effects within them [16, 17]. Raman spectroscopy, X-ray diffraction (XRD), atom force microscopy (AFM), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS) were used to collect data about the effects occurring in the films after being exposed to different radiation doses. Analysis of these data was used to create understanding about the nature of effects and provide an insight into the device performance.

2 Experimental The source material for film deposition was synthesized by using the conventional melt quench technique to obtain bulk chalcogenide glasses. Thin films were deposited at \( 1 \times 10^{-4} \text{Pa} \) pressure, on oxidized silicon wafer using thermal evaporation (PVD) with the aid of a Cressington 308R evaporation system from a semi Knudsen cell crucible. Multiple layers were deposited onto the substrate without breaking vacuum to protect against the introduction of contaminants between the films. Initially, \( 100 \text{nm} \) of \( \text{Ge}_{40}\text{Se}_{60} \) film was deposited followed by a \( 50 \text{nm} \) continuous film of Ag, after which a \( 300 \text{nm} \) film \( \text{Ge}_{40}\text{Se}_{60} \) was evaporated. Part of the wafer was set aside after this step to be used for the film study, while on the remaining portion of the wafer radiation-sensing devices were created by placing of non-diffusive aluminum (Al) electrodes. These electrodes were thermally evaporated and selectively deposited in specific regions of the wafer with the aid of a circular mask. This mask generated a final device with 2 mm diameter circles used as contacting electrodes with 1 mm spacing. The cross-section of these devices is shown in Fig. 1.

Devices and films were simultaneously irradiated by \( \text{Co} \gamma \) rays by a Gammacell 220 irradiator, with a dose rate of \( 10.5 \text{rad s}^{-1} \). Films and devices were retrieved as measured at discrete doses.

Raman spectroscopy was performed using an Acton 275 spectrometer with an Andor CCD back thinned detector. For excitation, a 514.5 nm line laser was focused into a circular spot of \( \sim 1 \mu \text{m} \) diameter. To avoid photo-induced changes in the studied film, a laser power of \( 250 \mu \text{W} \) was used with an accumulation time of \( 600 \text{s} \). These measurements were conducted at room temperature.

XRD patterns were obtained using a Bruker AXS D8 Discover X-Ray Diffracrometer equipped with a Hi-Star area detector. Beam conditions included a Cu anode at 40 kV and 40 mA to produce Cu Kα1 radiation (\( \lambda = 1.5406 \text{Å} \)) through a Göbel mirror producing a collimated beam. Further experimental details are given in Ref. [18].

EDS has been conducted with a Hitachi S-3400N-II. A beam of electrons was generated from a tungsten filament, and the electrons were accelerated using a 20 kV bias, which were then directed onto the sample. Interaction between the electrons and the sample generates characteristic X-rays corresponding to the elemental composition across the sample, which were analyzed using INCA software.

Current versus voltage (\( I–V \)) curves have been measured using an Agilent 4156C signal analyzer using two source measuring units (SMU) connected to the device. A voltage sweep was applied from 0 V to 200 mV with a step size of 5 mV and the current was measured simultaneously. These experiments were similar to our previous studies where the IV measurements and \( \gamma \) source radiation are explained in more details [17].

The surface characterization of the bare films was studied using Bruker Dimensions 3100 AFM system. These measurements were verified using a Hitachi field emission scanning electron microscope (FESEM) capable of 5 nm resolution with backscattering detector and Quartz imaging capture software.

3 Results EDS has been performed on five locations on each sample such that 25 points were used to determine the uniformity of the film composition. The average deposited film composition was \( \text{Ge}_{37.65}\text{Se}_{62.35} \) with a standard deviation of 0.93, which suggests that the overall film composition is uniform.

Raman spectra of the sandwich structure (chalcogenide glass/silver/chalcogenide glass), mode assignments and corresponding structural units for characterized studied
structures are shown in Fig. 2a. Development of the spectra as a function of the applied radiation shows a decrease in the intensity of the peaks relating to the ethane-like (ETH) and the edge-shared (ES) modes when compared to the corner-shared (CS) mode. The spectra show the peaks located at 178, 195, and 219 cm\(^{-1}\) which correspond to ETH, CS, and ES structural units, respectively [19]. A close observation of the area ratio between ES and CS modes demonstrates a non-monotonous decrease in the ratio as shown in Fig. 2b. The comparison of the areas of the fitted ETH structure shows a continued decrease with increase in the radiation dose up to 7.58 Mrad, after which the areal intensity of this mode increases as shown in Fig. 2c.

XRD spectra for four radiation doses are shown in Fig. 3 and respective peaks have been assigned for the formation of various diffusion products. The XRD data obtained at very low radiation dose reflects a spectrum of an amorphous film, as was also the non-radiated film, while the higher radiation doses affirm the notion of silver diffusion and the formation of Ag-containing compositions within the chalcogenide film. There are three main peaks that are evident from the spectra, which have been identified with JCPDS cards 04-0783, 71-190, 24-1041, corresponding to pure Ag, Ag\(_8\)GeSe\(_6\), and \(\beta\)Ag\(_2\)Se respectively.

The electrical performances of the devices were characterized by current versus voltage (I–V) measurements obtained after discrete radiation dose steps. Data for one of the irradiated and analyzed devices is represented in Fig. 4. The trend observed from the device measurement reveals that for low radiation doses (<7.59 Mrad), there is a consistent increase in the current through the device with increasing radiation dose, while over 7.59 Mrad, the current through the device is significantly lower.

Analysis of the SEM images shows that silver surface deposition occurs as a result of the Ag diffusion in the chalcogenide film and Ag-containing clusters are visible. The radius of the silver deposits and the distribution density of the deposits are inversely related. Increasing the radiation dose caused an increase in the silver surface deposits and concurrently, a decrease in the density of nucleation of the silver islands per unit area up to 7.59 Mrad. Above this radiation dose, the radius of the deposits decreases while the density increases. Simultaneously, a second phase with a smaller size is also formed in the higher radiation doses. The SEM images are shown in

![Figure 2](https://example.com/figure2.png)

**Figure 2** (a) Raman data and the corresponding mode assignment. (b) Scattering strength ratio between edge-shared and corner-shared modes. (c) Area analysis of the scattering strength for the ethane-like structural units.

![Figure 3](https://example.com/figure3.png)

**Figure 3** XRD spectra of the films after discrete radiation doses, depicting the formation of Ag\(_2\)Se and Ag\(_8\)GeSe\(_6\) phases.
Fig. 5 and the analysis of these images is summarized in Fig. 6.

The AFM study revealed that the height of these deposits decreases with increasing radiation doses. This trend is opposite to the mean radius of the deposits as illustrated through the SEM analysis mentioned above. Another aspect that was studied using AFM was the topological roughness. The surface roughness of the films was measured by excluding the areas occupied by the deposits to study roughness of the film attributed to the presence of smaller silver deposits and the radiation-induced changes due to structural reorganization. The AFM scans were performed on the same areas where the SEM images were taken to maintain consistency between the two types of studies. Analysis of the AFM films is presented in Fig. 7.

Detailed inspection of the EDS spectra revealed the presence of oxygen within the films. Based on this analysis, it was revealed that the oxygen content in the films increases with radiation dose (Fig. 8).

4 Discussion First, it is important to distinguish the type of films that were characterized in these studies. This...
distinction can be made through XRD, EDS, and Raman inspections. Based on the XRD spectra, it can be stated that the films are amorphous in nature. Additionally, the EDS analysis revealed that the films consisted of 37.65% Ge content, categorizing them to be germanium rich when comparison to GeSe2 composition. The peak at 178 cm\(^{-1}\) in the Raman spectra corresponding to the ETH structure, also affirms the claim that these films are germanium rich [20, 21]. This structure arises due to lack of bonding sites on neighboring chalcogen atoms and the bond between two germanium atoms forms the ETH structure. This bond is indeed the weakest in the system. One can expect that radiation will cause a destruction of these bonds and consequently the areal intensity of the ETH structures will decrease. The destruction of the Ge–Ge bonding creates defect sites located on the germanium atom, which can be influenced by the presence of oxygen. Since the radiation experiments have been carried out at ambient environment, oxidation can easily occur as revealed by the EDS data presented in Fig. 8. Even though the presence of oxygen in the Ge rich glasses is well documented, there are plenty of discussions as how exactly it reacts with them. Indeed, the problem persists, since there is not easy to give 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 chalcogen-oxide products leaving the system. In some cases, shrinking of the films has been observed [22] in support of the idea that the chalcogen atoms are oxidizing, while other authors [23, 24] reported direct evidence, studying the infrared spectra, for the appearance of Ge–O bonds. 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 selenium \( V_{Se} = 0.35 \). Consequently, after the radiation and formation of defects on germanium sites, even if Se defect sites exist, germanium will be oxidized first. As a result of this, one can expect that the oxygen atoms will replace part of the chalcogen atoms bonded to Ge. In this manner, the number of selenium atoms ready to build structural units with germanium increases and formation of CS units, which consume the highest number of chalcogen atoms grows. In other words, the Ge:Se ratio will decrease giving rise to the formation of units, characteristic for compositions richer in selenium. It is for this reason that there is increase of the areal intensity of the CS units in the system, which otherwise are not expected to appear with such intensity in the initially regarded system. One other evidence of this fact is the light shift of the CS peak to lower wave numbers from 202.82 to 201.86 cm\(^{-1}\). We have to point out that due to its low intensity, the Ge–O bonding is not detectable by Raman scattering.

Bonding strength of Ge–O is 6.83 eV, which is significantly greater than the Ge–Se 2.38 eV and Ge–Ge 1.92 eV and this stabilizes the presence of oxygen in the
The nucleation and growth of Ag clusters on the surface of the film up to a radiation dose of 7.59 Mrad coincides with the data discussed by Kawaguchi and Maruno [25] for the Ag surface deposition in Ag–As–S glasses and can be related to the increased Ag diffusion with increase of the radiation. This brings about the further growth and agglomeration of the existing nuclei, which reduces the number of the Ag-containing sites. However, the radius of these clusters increases. One could ask about the reason behind the lack of continuation of these processes with increased radiation over 7.59 Mrad, i.e., why does the radius of the deposits decreases beyond this radiation dose? We believe the reason is that at that point, the majority of Ag is reacting to form βAg2Se, which depletes the formation of Ag5GeSe6 clusters. The resolution of our EDS system does not allow distinguishing the elements embedded in the big and small crystals visible on the SEM image but we suggest that the small crystals that appear at radiation with 3.19 Mrad and higher, are those of βAg2Se. Their nucleation is restricted at lower radiation doses and therefore these crystals have not been registered by the XRD system. At radiation with a dose of 7.59 Mrad and over, their appearance is obvious with the high number of nucleation sites increasing with radiation, which suppresses the growth of the Ag5GeSe6 clusters. In accordance to the βAg2Se nucleation on the surface, its roughness increases as shown on Fig. 7. The formation of βAg2Se contributes to a new depletion of the hosting film of Se and because of this a new increase of the aerial intensity of the ETH units occurs at radiation of 14.82 Mrad. We suggest that it is also the reason behind the occurrence of the ES/CS ratio saturation and even a small increase in the areal intensity of the ES units. We noticed that plenty of effects go through an inflection point at a radiation dose of 7.59 Mrad. It seems that this dose is a threshold one, for many of the studied processes.

The last and indeed the most important, from the application point of view, is how to understand the device performance. The largest increase in the conductivity occurs between pre-radiation condition and 2 Mrad radiation, where the structural changes (observed by the Raman spectroscopy) and silver incorporation (as exhibited by the XRD) are dominant. After 2 Mrad, the oxygen-induced effects begin to dominate the device performance. To reduce the consequences of oxygen on the device performance, the radiation sensor can be encapsulated in a vacuum environment and in this manner; the silver and structural dominant region of the device performance can be enhanced creating a sensor that can sense large spectrum of radiation doses. However, there could be another hypothesis. Considering the chalcogenide film, there is published data about the dual role of light within the chalcogenide systems [26]. These effects are related to changes in the band gap of the glasses and thus would contribute to an initial increase followed by a decrease of the conductivity. In the studied case, Ag and oxygen are introduced in the system, which considerably change the situation and we suggest that their influence is stronger than this of the effects, intrinsic to the chalcogenide glasses. To check which influence (the one of the effects, occurring in the chalcogenide films or the presence of Ag) will prevail, studies in completely encapsulated devices are in progress. Their data will confirm or reject the applicability of the structure presented in this work for radiation sensing.

5 Conclusions Sandwich structures of Ge37.65Se62.35 glass–silver–Ge37.65Se62.35 glass with Al electrodes on top of them are studied in order to understand the nature of the effects occurring in them under radiation with different doses of γ radiation. It is shown that under radiation, the chalcogenide films undergo structural changes related to increase of the CS structural units and decrease of the ETH and ES structural units up to radiation dose of ~7 Mrad. This effect is connected to the reaction of the chalcogenide matrix with Ag diffusing within the films and the oxidation from the environment in which the experiments have been conducted. The diffusion product of the reaction of Ag with the chalcogenide matrix is initially Ag5GeSe6 with development of a second phase – βAg2Se once the amount of oxygen, reacting with the chalcogenide matrix, increases due to radiation. The Ag diffusion in the chalcogenide matrix results in silver surface deposits, which are built initially by clusters from Ag5GeSe6 whose growth at high radiation doses is retarded due to formation of a new phase – βAg2Se surface nucleates. The introduction of Ag and the intrinsic radiation-induced effects in the chalcogenide matrix lead initially to increasing of the conductivity of the structures, which later due to the dominant role of the oxidation decreases.

Acknowledgements This work has been funded by the Defense Threat Reduction Agency under grant no: HDTRA1-11-1-0055. The authors would like to thank Dr. James Reed of DTRA for his support. The authors would also like to acknowledge the Surface Science Lab at Boise State University for AFM use and Dr. Paul Davis for assistance in performing AFM and Muhammad Rizwan Latif for his help with the SEM and the AFM studies.

References