New functionality of chalcogenide glasses for radiation sensing of nuclear wastes

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HIGHLIGHTS

- Study of thin film chalcogenide glasses under gamma radiation and a proposed radiation sensor design.  
- Structural changes were observed at various radiation doses.  
- Formation of Ag2Se in Se depleted glasses with sufficient radiation dose.  
- In conventional semiconductor chip environment, the proposed sensor has a linear current vs. dose behavior up to 600 J/cm².

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ABSTRACT

Data about gamma radiation induced effects in Ge40Se60 chalcogenide thin films and radiation induced silver diffusion within these are presented. Blanket films and devices were created to study the structural changes, diffusion products, and device performance. Raman spectroscopy, X-ray diffraction, current vs. voltage (I–V) and impedance measurements expound the behavior of Ge40Se60 glass and silver diffusion within this glass under radiation. Raman study shows that there is a decrease in the area ratio between edge shared and corner shared structural units revealing structural reorganization occurring in the glasses as a result of gamma radiation. X-ray diffraction studies revealed that with sufficiently radiation dose it is also possible to create Ag2Se in selenium-depleted systems. Oxidation of the Ge enriched chalcogenide backbone is confirmed through the electrical performance of the sensing elements based on these films. Combination of these structural and diffusion products influences the device performance. The I–V behavior is characterized by increase in current and then stabilization as a function of radiation dose. Additionally, device modeling is also presented using Silvaco software and analytical methods to shed light on the device behavior. This type of sensor design and material characterizations facilitate in improving the radiation sensing capabilities of silver containing chalcogenide glass thin films.

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1. Introduction

The advantage that arises from the use of nuclear power plants to generate clean power also comes with one responsibility, to securely contain and monitor the generated radioactive wastes to ensure that radiation generated from these wastes does not affect the ground water or other living beings. To monitor these storage sites there is a need to create small, portable and inexpensive radiation sensing detectors with a capability to be included in integrated circuits for remotely sensing the radiation activity. There exists many types of solid-state micro-dosimeters, among the most common are p-intrinsic-n (PIN) dosimeters and radiation sensing field effect transistors (RADFETs). The PIN device is a reverse-biased diode consisting of a large intrinsic silicon region sandwiched between p-type and n-type silicon layers [1]. Charges generated in the intrinsic layer by incident ionizing radiation enable real-time readout of the radiation fluence level [1]. However, the operation of the PIN device requires a static reverse bias; therefore, it will dissipate power during exposure. Besides, as a transient current mode dosimeter, the PIN device is better suited for measuring dose rate than cumulative dose over time. While on the other hand, the RADFET is by design a non-volatile dosimeter. It is fabricated in a standard CMOS flow with a radiation sensitive thermally grown or
deposited oxide layer (typically SiO₂) between a crystalline silicon substrate and a degenerately doped polysilicon gate [2]. However, it has several drawbacks: (1) poor resolution at low total dose levels; (2) a large static gate bias requirement during exposure to reduce response fading; (3) significant temperature sensitivity; and (4) once radiation activated, it cannot be recalibrated to its initial condition. All the above-mentioned disadvantages can be eliminated by using dosimetric systems based on chalcogenide glasses. The introduction of new systems for radiation control based on the application of chalcogenide glasses will enable the design of safety systems with “go”/“no-go” response, requiring no operator intervention in the event of a major malfunction at very low technological costs.

Thin film chalcogenide glasses have promising effects that can perform similar functions as larger conventional dosimeters [3]. Chalcogenide glasses have various structural coordination ranging from floppy to rigid structures [4]. This flexible nature of the glasses allows for the generation of defects and structural modifications in the presence of radiation, which can be measured by electrical and optical methods.

Studies have shown that in the presence of γ-ray radiation, structural changes occur by creating homopolar bonds from heteropolar bonds, which produce localized charges in addition to molecular rearrangements [5]. These localized charges have also been observed in the presence of X-rays; Kasap and Rowlands have stated ionizing radiation generates electrons and holes, which upon transport in the glass film create localized electric fields [6]. The combination of molecular rearrangements along with the presence of localized fields aid in the diffusion of mobile ions, i.e. silver (Ag). The introduction of a small amount of Ag into the chalcogenide glass structure results in a drastic increase in the conductivity of the glasses [7]. A similar result has been achieved by Kolobov and Elliot through photodoping Ag into the chalcogenide glass structure [8].

The photodoping phenomenon has been researched for viable and UV exposure [9], but this effect has not been studied extensively for shorter wavelengths. These short wavelengths can generate more defects due to the high energy transferred to material, resulting in a larger number of electron–hole pairs and more structure reorganization, which enhances the ability for Ag diffusion. As silver diffuses into the structure, the conductivity increases [10], because of the diffusion products that are generated due to reaction of Ag with the glassy medium, therefore it is important to study the types of reaction products and their contribution toward the change in conductivity. Clearly, a need exists for studying the gamma ray induced defect formation assisting in silver diffusion, and the combination of these effects on the device performance.

In this work, structural changes in the Ge₄₀Se₆₀ chalcogenide glasses were studied under γ-ray irradiation using Raman Spectroscopy along with the utilization of X-ray diffraction (XRD) to study the Ag diffusion products occurring after radiation in the chalcogenide glass films. Electrical performance of a specific sensor structure is given using I–V and impedance measurements. Simulations on device performance are presented using Silvaco software, which is applied to model the device structure. The study of the structure and the structural alterations caused by radiation exposure allows the ability to design a sensor and enhance its performance through material optimization.

2. Materials and methods

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 × 10⁻⁶ mbar pressure, on oxidized silicon wafer using thermal evaporation (PVD) with the aid of a Cressington 308R evaporation system with 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 nm of Ge₄₀Se₆₀ film was deposited followed by a 50 nm continuous film of Ag, after which a 300 nm film Ge₉₀Ag₁₀ 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 final device with 2 mm diameter circles with 1 mm spacing, whose cross section is shown in Fig. 1.

![Fig. 1. Radiation sensing device cross section.](image)

Devices and films were irradiated with 60Co gamma rays using a GammaCell 220 irradiator, with a dose of 10.5 rad/s. Films and devices were retrieved and measured at discrete doses. Raman spectroscopy on the surface of the Ge–Se films was measured 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 ~1 μm diameter. Laser power was 250 μW for 600 s and the samples were measured at room temperature.

X-ray diffraction patterns were obtained using a Bruker AXS DB Discover X-Ray Diffractometer equipped with a Hi-Star area detector. Beam conditions included a Cu anode at 40 kV and 40 mA to produce Cu Kα₁ radiation (λ = 1.5406 Å) through a Göbel mirror producing a collimated beam. Further experimental details are given in [11].

Energy Dispersive X-ray Spectroscopy (EDS) has been conducted with a Hitachi S-3400N-II. A beam of electrons was generated from a tungsten filament, and the electrons are accelerated with 20 kV 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 vs. voltage (I–V) curves have been measured using an Agilent 4156C 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. This specific voltage has been thoroughly investigated to ensure that the applied voltage bias does not alter the device performance from sweep to sweep. Further details about the IV measurements and gamma source explanations are given in [12].

3. Results

Energy Dispersive X-ray Spectroscopy has been performed on five locations on each sample such that 25 points were used to determine the uniformity of the film composition. Measured composition shows that the films composition were Ge₃₇.₆₅±₀.₉₅Se₆₂.₃₅±₀.₉₃. Raman spectra of the films, mode assignments and corresponding structural units for characteristic films of Ge₃₈Se₆₂ compositions are shown in Fig. 2a. Development of the
spectra as a function of the applied γ radiation shows an increase in the intensity of the peaks relating to the ethane-like (ETH) and the corner-shared (CS) modes when compared to the edge-shared (ES) mode. The spectra show the peaks located at 178 cm⁻¹, 195 cm⁻¹, 219 cm⁻¹ corresponding to ETH, CS and ES respectively [13]. A close observation of the area ratio between ES and CS modes demonstrates a constant decrease in the ratio as shown in Fig. 2b.

X-ray diffraction spectra for four radiation doses are shown in Fig. 3 and respective peaks have been assigned for the formation of various diffusion products. 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, Ag₆GeSe₂ and β-Ag₂Se respectively.

Several devices were irradiated and direct current (DC) I-V measurements were performed after discrete radiation dose steps, which are presented in Fig. 4a. An I-V curve of one such device is also presented in Fig. 4b. The trend observed from the various devices shows an immediate increase in the current from the pre radiation measurement to the first radiation dose. Then after this sharp increase, the current stabilizes with increasing radiation dose and then the current begins to decrease with additional radiation dose.

The next step in the study of these devices was to simulate their performance. Impedance measurements were performed on the devices and then the spectra was compared with analytical models as well as simulated results from Silvaco Atlas device simulator. The motivation for pursuing these simulations is mimic the impedance behavior of the device using basic electrical components (resistors, capacitors and inductors) in order to substitute this novel device as a small portion of a larger radiation sensing circuit. Device has been modeled using the same thicknesses and parameters as the fabricated devices and the material parameters are shown in Table 1.

In order to verify the Silvaco model, mixed mode electrical simulations were performed on the device structure. The simulations entail simulating the frequency response of the device with a constant 10 mV amplitude ac voltage applied between the Al electrodes. From these results, the magnitude and phase of the device impedance can be extracted and compared to an equivalent circuit model as well as experimentally measured data. The equivalent circuit model proposed is a 1-pole network, composed of a resistor (R1) in series with a second resistor (R2) in parallel with a capacitor (C). The resistor R1 corresponds to the contact resistance comprising of both of the Al electrodes and the chalcogenide glass film consisting of R and C component. Modeling the device with this 1-pole circuit and using the materials parameters for the Silvaco software correlates very well with the measured data, which suggests that this device can be replaced with this simple circuit model. The impedance measurement data and comparison with the simulated results are depicted in Fig. 5. This is a good validation of the methodology used for these device simulations.

### Table 1

<table>
<thead>
<tr>
<th>Material property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum workfunction</td>
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</tr>
<tr>
<td>Silver workfunction</td>
<td>4.6 eV</td>
</tr>
<tr>
<td>Ge₂Se₃ parameters</td>
<td></td>
</tr>
<tr>
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<td>Bandgap</td>
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<td>Dielectric constant</td>
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<tr>
<td>Carrier mobility</td>
<td>100 cm²/V</td>
</tr>
<tr>
<td>Density of states</td>
<td>10¹⁰ cm⁻³</td>
</tr>
</tbody>
</table>

4. Discussion

There are two processes that we have to consider when discussing the performance of the studied devices: on one hand,
chalcogenide film is affected by the radiation and reacts in a specific way, and on the other hand, Ag diffusion is in effect due to the radiation. The former is elucidated through Raman spectroscopy study of the bare films and the latter can be explained through XRD investigation of the sandwich structures.

Analysis of the Raman spectra using the area ratio between the Edge shared (ES) structural units corresponding to the peak located at 218 cm\(^{-1}\) and corner shared (CS) structural units corresponding to the peak at 202 cm\(^{-1}\), demonstrates an increased destruction of ES structures and subsequent increase in the CS structures at low radiation dose. This suggests that gamma radiation affects mainly the bonding sites between Ge–Se atoms. Due to the decreased availability of CS structural units in Ge-rich films, this bond is likely associated with an ES unit. Annihilation of the Ge–Se bond causes the destruction of the ES unit, creating a negative charge on the Se atom. In the presence of ionized silver atoms (Ag\(^+\)), the Ag\(^+\) ions become attracted to the defect site associated with the Se atom and bond with Se\(^-\) atom. This new molecule is Raman silent and thus cannot be detected using Raman spectroscopy. In this manner, the previously detectable ES structural unit is removed from the system and their intensity in the Raman spectra decreases. The maximum change in the area ratios described so far corresponds to the change observed in the device measurement in Fig. 4. Increase in the conductivity occurs at the same radiation dose range as the drastic reduction in the ES/CS ratio, suggesting that the change in the structure has a contribution toward the increase in the conductivity. After the very large change in the ES/CS ratio up to 3.19 Mrad, the ratio stabilizes and concurrently the device conductivity begins to decline from this point onwards.

It is also important to consider the role of silver within the backbone structure of the film. Since silver containing molecules are Raman silent, another method is required to detect the manner

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Fig. 4. (a) Current vs. radiation dose measurements showing the development of the current as a function of exposure dose. (b) Current vs. voltage curves of one of the radiated devices, measured at discrete radiation doses.

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Fig. 5. (a) Magnitude of impedance vs. frequency and (b) phase of impedance vs. frequency for analytical model (Zmod, theta mod), device simulations (Zsim; Theta sim), and experimental data (Zdat; theta dat) for prerad impedance characteristics of one of the investigated devices.
in which silver is reacting with the chalcogenide structure. These reaction products are illustrated by the XRD study of the films. The original film and device structure contains a pure layer of silver underneath the chalcogenide film, explaining the origins for the peak at 34°. With low doses of radiation, the films contain the ternary form (Ag₈GeSe₆) occurring at angle θ = 44°, and this result corresponds to the decrease in the ES structural units in the Raman spectra. After sufficient radiation dose (>7.59 Mrad) other peaks corresponding to Ag₈GeSe₆ begin to form at angles θ = 28° and 46°, which are associated with different orientation of the ternary molecule. The most important result from the XRD spectra occurs beginning in the 7.59 Mrad radiation dose spectra; where there is a distinct peak corresponding to the formation of β-Ag₈Se₆. This is an interesting find, since the original structure is significantly depleted of Se to a point that the structure is forced to form Ethane-like bonding as shown by the presence of the peak at 179 cm⁻¹ in the Raman spectra. In this type of bonding, Ge forms a sigma bond with another Ge, which is a weak bond (1.92 eV) compared to a Ge–Se bond (2.38 eV) and Ge–Ge bond is not as preferential, but only forms due to the shortage of Se atoms. Even after the formation of Ethane-like bonding, the formation of Ag₈Se₆ further depletes the original structure of Selenium atoms.

The measured current of the devices does not continue to increase which should be the case with the generation of Ag₈Se₆ and the other Ag₈GeSe₆ peaks. The reason behind this reverts to the destruction of the ES bond, where along with the creation of a negatively charged Se atom, a positively charged defect is generated on the Ge atom. Since these films are rich in germanium and the radiation has been performed in ambient environment in the presence of oxygen, photo oxidation can occur as described by Sagaguchi et al. [14]. In this manner, Germanium oxide (GeO₂) could be formed, which is a dielectric that can decrease the conductivity of the film hence impeding the effect of Ag₈Se₆ and Ag₈GeSe₆ on the device.

This has been confirmed by performing current vs. irradiation time measurements under vacuum and in ambient conditions. A strict care has been taken to use only the devices with the same fabrication processes and other environmental conditions to ensure the results were comparable. A 1.5 W/cm² UV lamp provided the source of radiation and a Keithley picoammeter was used to measure the current, while simultaneously placing a 100 mV voltage bias across the device. This constant voltage bias was placed on each device and the performance of each device was monitored for 15 min before the start of the experiment to ensure that the constant voltage bias did not affect the device behavior. Some devices were placed in ambient room temperature inside a closed chamber to prevent the introduction of additional light sources, while other devices were placed inside a cryostat at a pressure of 1 x 10⁻⁵ mbar in the same dark conditions. After assuring the stability of the experiment at dark conditions, illumination with the UV lamp was performed. The results for this experiment are presented in Fig. 6 where it was observed that devices in ambient behaved in a similar manner as the γ-irradiated devices, where there was an initial increase in the current followed by stabilization and a subsequent decrease in the current.

Devices under vacuum on the other hand, showed a linear increase in the current as a function of radiation dose without any decrease in the current even up to a total energy absorption density of 1000J/cm². From this result, it can be suggested that oxygen does play a major role on the performance of the device performance.

5. Conclusion

In this study, we showed the effect of gamma radiation on the Ge rich films from the Ge–Se system with the presence of silver. In addition, data about the performance of radiation sensing devices based on these films as well as radiation induced silver diffusion has been presented. Structural consideration showed a decrease in the ES/CS ratio with low radiation and concurrent incorporation of silver within the backbone structure, which has been expounded, by Raman and XRD studies of the films. Device performance confirms the change in the film structure proving that structural changes as well as the incorporation of silver will result in the electrically measured change in the conductivity. It has been proved that oxidation occurs when all these processes are carried out in oxygen containing environment. This type of device is highly applicable for sensing different ranges of radiation doses with a linear response of current as a function of irradiation time. However, oxidation of the films should be avoided during preparation and normal functionality to harness the full sensing capability of these devices.

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