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Positron annihilation lifetime spectroscopy (PALS) studies of gamma irradiated As_2Se_3 films used in MIR integrated photonics

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ABSTRACT

Chalcogenide glass (ChG) materials are increasingly being utilized in infrared planar photonic devices due to their tailorable refractive indices and compatibility with other on-chip materials and manufacturing methodologies. The performance and reliability of such integrated photonic components in land or space-based environments where radiation impact structure and properties is important to their ultimate deployment. Bulk glasses and thermally evaporated thin films of As_2Se_3 were subjected to a gamma exposure of 229 Mrad to compare bulk/film material response and the impact of film thickness on such response. Positron annihilation lifetime (PAL) spectroscopy was employed to compare the effect of gamma irradiation on the different forms of the glass. The average positron lifetime was found to be longer for the films than the bulk glass in unirradiated specimens, and the films showed more significant increases in lifetimes with gamma exposure. This effect was more pronounced for thinner films, which showed, for example, an increase in positron lifetime. Positron lifetime was measured over the course of 20 days after exposure, over which the effect of the gamma radiation was found to relax at room temperature. Long-term or incomplete relaxation of the gamma-induced changes were observed in the films, while the bulk glass positron lifetime returned to pre-exposed values. A proposed mechanism for these observations based on coordination topological defects (CTD) is presented to explain the initial and longer term response, and the possible consequence when such films are integrated in device geometries.

1. Introduction

Due to their unique optical properties including broad infrared transparency, high nonlinearity and photosensitivity, chalcogenide glasses (ChGs) are important materials in emerging applications such as sensing, communications, imaging, and radiation dosimetry [1,2]. As these devices are being considered for deployment in areas of high radiation, such as space or dosimetry applications, it is crucial to understand the effects of radiation on the performance of the device to establish operational limits and thresholds for component degradation. How such mechanisms previously studied in bulk glasses extend to the same materials in thin film form has not been well studied, especially consideration of film thickness effects on scales relevant to those found in photonic devices, and as a function of time following radiation exposure where transient performance stability may be tolerated if devices cannot be readily repaired or replaced, such as in space.

At present, three different mechanisms have been proposed to explain the γ-induced effects in bulk ChG [3]. The first of these involves simultaneous switching of two heteropolar covalent bonds into two homopolar bonds (or vice versa) without any changes in the local coordination of all bond-forming atoms. The second model involves breaking a covalent chemical bond to form a transient D^+-D^- coordination topological defect (CTD) pair. These charged diamagnetic defects then immediately annihilate, producing the final state (Fig. 1). The third model is similar to the second, consisting of the production of a CTD pair which is then stabilized, as in Fig. 1, to an intermediate stage. Stabilization can be achieved through additional bond switching, which increases the spatial separation between created CTDs and preserves

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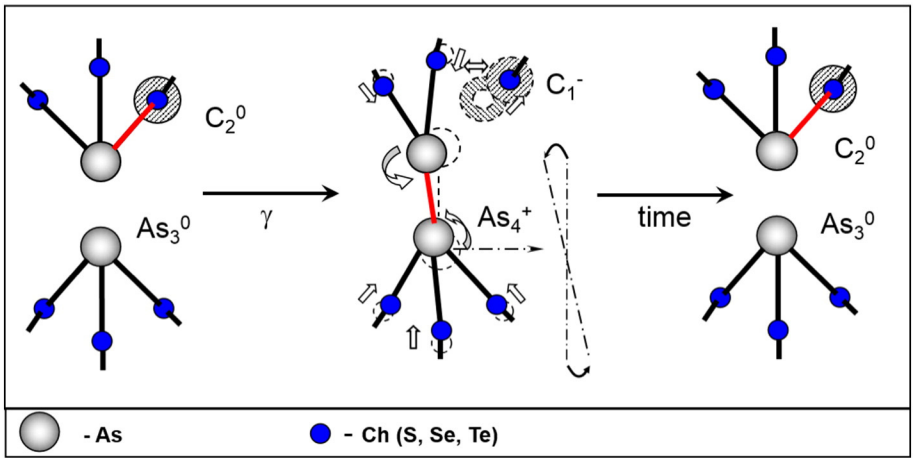

Fig. 1. Coordination topological defects formed by gamma radiation in As-Ch material (subscript means coordination, superscript means charge state).

them from spontaneous annihilation. This mechanism is believed to be the most promising as it can explain the wide variety of the observed gamma-induced effects [4].

For example, the observed darkening effect, or long-wave shift of the fundamental optical absorption edge, in vitreous As_2S_3 can be explained by switching of the heteropolar As—S covalent bonds into homopolar As—As bonds, accompanied by charged D^+-D^- CTD formation [5]. Here, these CTDs enhance the intrinsic electrical fields within the glass network, leading to the observed decrease in the slope of the fundamental optical absorption edge [6]. Destruction-polymerization transformations shown in Fig. 1 together with CTD formation can also explain the changes in the refractive index and density of various As—S compositions with gamma-irradiation to doses up to 400 Mrad, as reported by Sundaram et al. [7] Annealing of radiation-induced CTDs at room or elevated temperatures is responsible for the observed complete or partial restoration of ChGs initial physical properties with time [6,8]. The time constant of this process is assumed to depend significantly on the nature of the chalcogen atom (S, Se or Te), being the largest for sulfides [4,9,10]. This ability to fully recover with time could be especially important in film-based photonic devices where long-term stability may be needed in adverse environments.

As noted, coordination topological defects (CTDs) are a central part of these mechanisms and warrants a brief review. The concept of CTDs exploits Anderson's idea [11] based on strong electron-phonon coupling in amorphous semiconductors, which results in a negative spin-pairing correlation energy and pinning of the Fermi level in the absence of paramagnetism. The corresponding electronic states models were developed by Mott, Davis, Street [12] and expanded by Kastner, Adler, Fritzshe [13], which allowed explanation, in part, of the unique physical properties of amorphous semiconductors and chalcogenide glasses. Early theoretical calculations of correlation energies supported the possibility of CTD formation in vitreous As_2Se_3, but their equilibrium concentration in as-prepared glass was predicted to be at the level of only ~10^{18} cm^{-3} [14,15]. More recent calculations [16,17] suggest higher concentration of CTDs, especially as a result of external influences, such as photoexposure or radiation treatment [5,18,19]. Nevertheless, to date, there is no confirmed experimental evidence of CTD formation in *as-prepared* ChGs or ChG thin films because of their diamagnetic nature and, most likely, their very low concentrations.

Conversely, direct evidence of the presence of *induced* CTDs has been obtained through X-ray photoelectron spectroscopy and extended X-ray absorption fine structure analyses [20,21], or indirect measurements using vibrational spectroscopies such as Raman and Fourier transform infrared spectroscopy [3–5,10,22]. These observations made in glasses upon exposure to various forms of radiation suggest a threshold for formation. However, these techniques can only provide information on CTDs from a structural standpoint, which is insufficient to fully characterize the presence, concentration and stability of such defects under all 'exposure' conditions.

Complementary information to that realized in the above techniques can be obtained through the investigation of electron deficient sub-system of glass network voids, which can be achieved by using positron annihilation lifetime (PAL) spectroscopy. PAL spectroscopy is believed to be one of the best techniques capable of characterizing the local free volume, such as open-volume defects or pores in materials on a subnanometer scale. Because of the reduced coordination and negative charge of under-coordinated CTDs such as seen for one-fold coordinated chalcogen atoms in Fig. 1, this provides free volume with an associated negative effective charge, where a positron can be trapped before annihilation. This process should lead to an increase in the average positron lifetime in such a material [23,24], which can be measured with PAL spectroscopy.

As noted above, while many studies have investigated the effects of gamma radiation on various compositions of bulk ChG, only a few studies have been done to understand gamma-induced effects in the thin film form of these materials [25–28]. Because thermally evaporated As_2Se_3 thin films have been proposed for microphotonic applications [29], the effect of gamma exposure on thermally evaporated, glassy As_2Se_3 films is therefore studied in this paper by PAL spectroscopy. Thin films of varying thickness are compared to bulk As_2Se_3 glass and the post-irradiation stability of the radiation-induced modification of glass network is examined.

2. Experimental

Bulk As_2Se_3 was made by conventional ChG fabrication methods, beginning by batching elemental starting materials into a fused SiO_2 ampoule inside of a nitrogen-purged glovebox [30]. The tube was sealed under vacuum with a methane-oxygen torch, and melted for 16 h at 750 °C in a rocking furnace, air quenched, and annealed at 150 °C for 24 h. The bulk glass was cut into discs with thickness of approximately 3 mm, and optically polished. The bulk glass was also broken into pieces about 2–5 mm in size using a mortar and pestle, which were used for film deposition by thermal evaporation. Films were deposited on a Si wafer maintained at 25 °C, at a rate of 18 $Å s^{-1}$, by heating the glass pieces in a tantalum boat, using protocols optimized for fabrication of low loss optical waveguides and resonators [31]. Here, blanket As_2Se_3 films with thicknesses of 0.4, 0.8, and 2.0 μm were prepared.

Gamma exposure was done inside of evacuated glass ampoules at a rate of approximately 400 krad/h to a total dose of 229 Mrad. The PAL spectra of unexposed and gamma-exposed bulk and film samples were recorded with fast coincidence system (ORTEC) of 230 ps

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resolution. FWHM of a single Gaussian was determined by measuring ^{60}Co isotope at a temperature of 22 °C and relative humidity of 45%. Each PAL spectrum was recorded with a statistics $2.5 \cdot 10^5$ coincidence to balance reasonable time of measurements and quality of lifetime spectrum. The channel width of 6.15 ps allows 8000 total channels. The source of positrons was a ^{22}Na isotope of low ~50 kBq activity prepared from aqueous solution of ^{22}NaCl, and wrapped by Kapton foil of 7 μm thickness and sealed. This source was sandwiched between two identical thin film samples. The raw PAL spectra of the investigated glasses were processed with LT 9.0 program [32]. For the case of the film samples, PAL spectra were taken of the irradiated and unirradiated Si substrates, with no significant differences detected. Calibration of the instrument and source contribution were checked by routine measurement of standards.

PAL spectra for thin films were treated by subtracting contributions from source and substrate, following the regular well-approbated procedure in LT 9.0 [32]. Despite the fact that the fraction of positrons annihilated in thin film is smaller than in the substrate, the developed algorithm allowed us to unambiguously register the changes produced by gamma-irradiation. Irradiated and non-irradiated substrates and thin films of different thicknesses (on substrates) were measured with the same conditions, which additionally increased the confidence in PAL data. Fig. 2 shows an example positron decay data for the unirradiated 2.0 μm As_2Se_3 film, employing the above protocol.

Accepting the two-state positron trapping model validated for ChG [33,34], which assumes only one kind of positron trapping centers exist and no positronium formation takes place, the experimental PAL spectra were fitted with two lifetime components (τ_1 I_1) and (τ_2, I_2), where τ_i stands for the lifetime and I_i for the intensity of i-component. Then, the average positron lifetime (τ_{av}), defect-free bulk positron lifetime (τ_b) and positron trapping rate in defects (κ_d) can be calculated as follows:

$$\tau_{av} = \frac{\tau_1 I_1 + \tau_2 I_2}{I_1 + I_2} \quad (1)$$

$$\tau_b = \frac{I_1 + I_2}{\frac{I_1}{\tau_1} + \frac{I_2}{\tau_2}} \quad (2)$$

$$k_d = \frac{I_2}{I_1}\left(\frac{1}{\tau_b} - \frac{1}{\tau_2}\right) \quad (3)$$

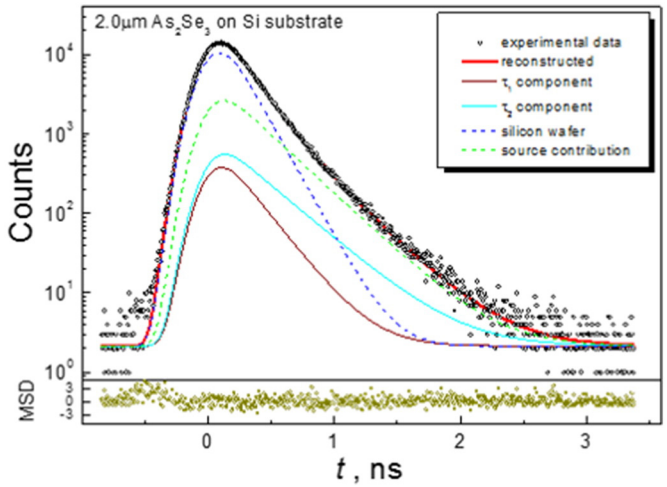

Fig. 2. Sample positron decays of 2.0 μm As_2Se_3 film, τ_1 and τ_2 components, the reconstructed fit, uncoated Si wafer, and the source contribution.

3. Results and discussion

The positron decay behavior of the bulk As_2Se_3 glass samples were fit using two exponential terms, τ_1 and τ_2, which were allowed to vary freely along with their relative weights, I_1 and I_2. In the case of the films, τ_1 was fixed to the value of the bulk glass, 0.215 ns, while τ_2, I_1 and I_2 were allowed to vary freely. Table 1 shows the measured PAL parameters post-irradiation, including calculated τ_{av}, the weighted average positron lifetime, and k_d, the positron trapping rate of the defect.

According to the adopted two-state positron trapping model, the first component (τ_1, I_1) includes free annihilation of positrons and is also related to the positron bulk lifetime (τ_b) as discussed in measurements made for bulk As_2Se_3 in prior work [23,35]. The second component (τ_2, I_2) is usually caused by positrons which are trapped before annihilation in open-volume defects, such as vacancies and their agglomerations in crystals, grain boundaries in ceramics and glass-ceramics, shallow positron traps, and precipitates and inclusions, such as in crystals and some disordered materials where positronium is not formed [23,24,35]. In the non-irradiated bulk As—Se glasses, the most efficient positron traps contributing to the second component (τ_2, I_2) are identified as bond free solid angle sub-nanovoids, including their agglomeration with each other or different sub-nanometer open volumes, near the chalcogen atoms within heteropolar As—Se bonds [36]. Size of these open volume entities in bulk As_2Se_3 glass can be estimated using bond free solid angle concept [36,37], and τ_2 values within Jensen's approach [38]. The concentration of these trapping centers can be roughly estimated through the intensity, I_2, of the second component in the fit. By comparing the I_2 values in Table 1, it can be concluded that thinner non-irradiated films have a more defective structure. Simultaneously, the value of τ_2 has a tendency to increase with decreasing thickness, indicating a higher degree of voids agglomeration at the nanoscale, meaning more geometric free volume, like vacancies or their clusters, present in thin films compared to bulk.

The dramatic increase in k_d seen for the thin films as shown in Table 1, suggests either formation of CTDs in significant concentrations during thermal evaporation or more significant contrast in charge distribution (charging of the open-volume entities), that leads to more efficient trapping of positrons in geometric free volume defects as compared to bulk As_2Se_3 glass. Indeed, it is known that the structure of As-Ch evaporated films differs from that of the bulk glass, as the films can contain higher concentrations of homopolar As—As and Se—Se bonds, in addition to As_4Se_4 and As_4Se_3 molecular units and Se_8 rings [39]. The interface between film and substrate can also contribute to positron trapping, but it is not possible to resolve this contribution. PAL experiment using moderated positron source is required in that case.

The weighted average lifetime, τ_{av}, increases post-gamma exposure, which is apparent in all samples tested, including bulk and thin film forms. The magnitude of the gamma-induced increase in τ_{av} is greater as the sample becomes thinner, with the bulk glass exhibiting the smallest increase and the 0.4 μm film showing the largest increase. In bulk As_2Se_3 glass the observed increase in τ_{av} can be explained by the two-state positron trapping model. Indeed, a ~7% increase in I_2 after gamma-irradiation can be associated with the increase in the concentration of trapping centers responsible for the τ_2 and I_2 component. Since the value of τ_2 did not change significantly after gamma-irradiation of bulk As_2Se_3 glass, we do not expect changes in geometric dimensions of corresponding open-volume entities, but increase in k_d may indicate a negative effective charging of the voids. This is consistent with the CTD concept, particularly with the formation of negatively charged Ch_1^- defects in Fig. 1. These gamma-induced changes are unstable and decay completely after about two weeks of storage at room temperature, as shown in Figs. 3a and 4a. During the decay process, τ_2 values were found to be constant, while τ_{av}, I_2 and k_d gradually decreased to their values for the non-irradiated bulk As_2Se_3 glass. It is noteworthy that the observed changes in PAL parameters cannot be

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Table 1
PAL parameters measured before and post-irradiation. Error on the lifetimes (τ) is ± 0.02 ns, and error on the weight (I) is ±5%.

Sample	τ_1 (ns)	I_1 (a.u.)	τ_2 (ns)	I_2 (a.u.)	τ_{av} (ns)	τ_b (ns)	k_d
As_2Se_3 bulk Non-irradiated	0.215	0.64	0.351	0.36	0.262	0.250	0.65
As_2Se_3 bulk Irradiated	0.215	0.56	0.343	0.43	0.270	0.256	0.75
0.4 μm Non-irradiated	0.215	0.01	0.425	0.99	0.425	0.424	2.29
0.4 μm Irradiated	0.215	0.01	0.687	0.99	0.684	0.678	3.18
0.8 μm Non-irradiated	0.215	0.04	0.358	0.96	0.352	0.348	1.78
0.8 μm Irradiated	0.215	0.01	0.468	0.99	0.465	0.461	2.48
2.0 μm Non-irradiated	0.215	0.06	0.301	0.94	0.296	0.294	1.26
2.0 μm Irradiated	0.215	0.02	0.318	0.98	0.317	0.316	1.49

explained by gamma-induced structural relaxation, which is known to be negligible for bulk glass As_2Se_3 composition which possesses an optimally-constrained network [40].

In thin film samples, an increase in τ_{av}, I_2 and k_d parameters of two-component fits is also observed, but changes are more pronounced in magnitude. Additionally, an increase in τ_2 after gamma-irradiation is noticeable. The latter circumstance indicates that the mechanism of radiation-induced effects in thin films include additional processes not characteristic of the processes seen in bulk glass. For example, the observed changes here may be attributed to more complicated structural transformations like agglomeration of free-volume entities due to the destruction-polymerization transformations, non-defect switching of covalent bonds, and radiation-induced shrinkage/expansion of the films. Some of these changes may be permanent, since as shown in Figs. 3b–d and 4b–d, the τ_{av}, τ_2, I_2 and k_d parameters do not restore to the initial values seen prior to irradiation. The time dependent relaxation PAL studies in thin films reveal a somewhat faster decaying component, on the order of one week. Following this initial recovery, no appreciable change in PAL parameters are subsequently observed over the remaining duration of the long-term experiment.

4. Conclusions

In summary, these results illustrate a difference in the effect of gamma irradiation on thermally evaporated ChG films of device-relevant thicknesses as compared to behavior seen in the same material in bulk glass form. In the case of the bulk form, complete relaxation of the defects is observed over time, whereas in the case of the films, long term changes to the structure are observed and remain, as quantified by an increase in the positron annihilation lifetime. The magnitude and impact of this long(er) term lifetime in defects in film structures on photonic device performance is not yet known. Future work will consist of efforts to identify the types and concentrations of the defects that are induced in film as compared to bulk, and, ultimately, to characterize device performance as a function of gamma radiation dose.

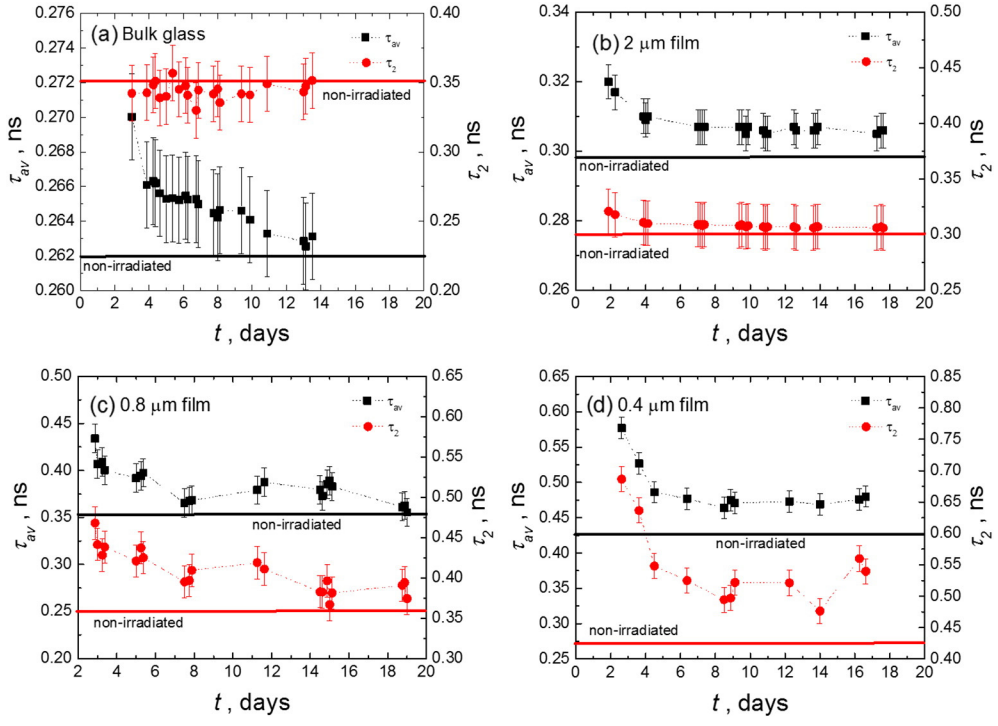

Fig. 3. τ_{av} and τ_2 of bulk and film ChG samples measured periodically after gamma exposure.

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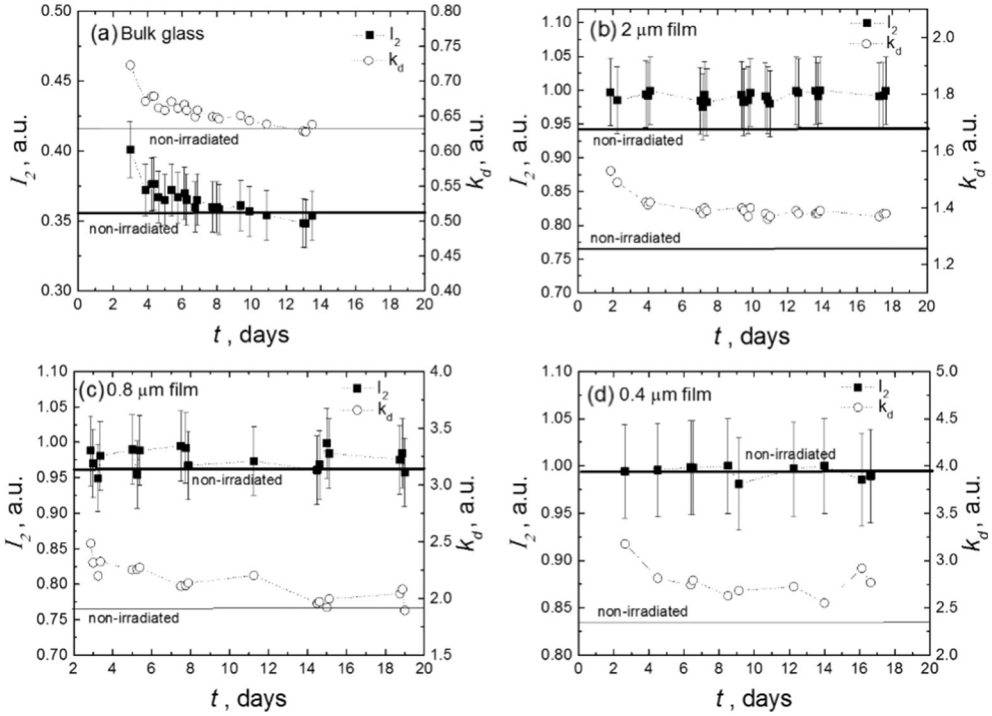

Fig. 4. I_2 and k_d determined from periodic measurements after gamma exposure. In all samples τ_1 is fixed at 215 ps, and for the bulk sample only, τ_2 is fixed at 351 ps.

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