Nanoindentation Test of Radiation-Modified As$_2$S$_3$ Glass After $^{60}$Co Gamma-Irradiation

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Abstract: The results of the surface mechanical properties (i.e., hardness and elastic modulus) in the unmodified and radiation-modified As$_2$S$_3$ glass measured about 10 years after $^{60}$Co $\gamma$-irradiation, using a nanoindentation test with an ultra nano hardness tester (UNHT) were reported. It is indicated that the $\gamma$-irradiated g-As$_2$S$_3$ (g- for glassy) with the average energy of $^{60}$Co $\gamma$-quanta of 1.25 MeV and the accumulated dose of 2.41 MGy exhibits the increased surface hardness and elastic modulus values, compared to the unirradiated material, in the range of 200–1 600 nm indentation depth. In the long-term radiation-induced improvement of the surface mechanical properties in g-As$_2$S$_3$, the broader distribution of the experimental data was detected for the irradiated sample with radiation-induced oxidized layer, compared to the clean sample without the layer that was removed by washing and polishing.

Keywords: chalcogenide glass; mechanical properties; nanoindentation; radiation modification

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applications. Some studies also dealt with silica glass with copper nanoparticles[7], polarizing oxide glasses with silver nanorods[8] and ZnO film with silver nanoparticles[9]. Recently, Stronski et al.[10] reported some interesting results on photoluminescence in g-As2S3 doped by rare-earth elements. Therefore, the g-As2S3 remains still a modern object of ChGs.

However, g-As2S3 has a disadvantage regarding γ-irradiation-induced effects for structural investigations and optical observations due to its surface radiation-induced oxidation process[11–12]. Wet investigations and optical observations due to its surface oxidized layer[13]. We could do it in laboratory for 1 h. 

456–465 K[2,19]) for 1 h.

Recently, Stronski established 60Co radioisotope capsules[20]. No special cylindrical cavity by a number of concentrically condition of stationary radiation field, created in a sealed, with other chalcogenides like Ge–As–S glasses without the surface radiation-induced oxidized layer[11–12].

g-As2S3 has a long-term radiation-induced optical darkening effect for the sample (~2 mm thick) measured about 10 years after γ-irradiation (2.41 MGy accumulated dose)[16], which is comparable well with that reported in literature[17] for γ-irradiated (~3 MgY accumulated dose) g-As2S3 (1.5 mm thick), measured just after γ-irradiation.

The aim of this work is to investigate the surface mechanical properties (i.e., hardness and elastic modulus) in the unmodified and the radiation-modified g-As2S3, measured about 10 years after 60Co γ-irradiation, with and without radiation-induced oxidized layer using nanoindentation technique with an ultra nano hardness tester (UNHT).

2 Experimental

The investigated g-As2S3 bulk samples were prepared by conventional melt-quenching technique[18–19]. In order to remove the mechanical strains, formed during the synthesis procedure, the samples were annealed at (433±1) K (below the glass transition temperature Tg = 456–465 K[2,19]) for 1 h.

Radiation treatment of the samples by γ-quanta with average energy (E = 1.25 MeV) and accumulated dose (ϕ = 2.41 MGy) was performed under the normal condition of stationary radiation field, created in a closed cylindrical cavity by a number of concentrically established 60Co radioisotope capsules[20]. No special measures were taken to prevent uncontrolled thermal annealing of the samples, but maximum temperature in the irradiating camera did not exceed 320–330 K during prolonged γ-irradiation (more than 30 days), providing an absorbed dose power P of < 5 Gy/s[20–21].

The nanoindentation test of the investigated materials (i.e., measurements of the surface mechanical properties, i.e., hardness and elastic modulus, on the nanoscale level) was carried out using the UNHT in progressive multicycle mode with a diamond Berkovich indenter at the Lublin University of Technology (Poland). The main improvements of the UNHT compared to the conventional nano indenter (or NHT) design, both developed by the CSM Instruments Co., Switzerland[22,23], are a new tip and reference fixing system introduced in the ultra indenter head and the use of active top referring (very low loads applied by the reference, less than 1 g), the possibility of depth and load measurements, one order less noise level, etc., which allow us to make the measurements using the UNHT with high performance. The hardness and elastic modulus (with the Poisson ratio of the specimen of 0.29 for g-As2S3[23]) values were calculated in the load-depth measurements by the method of Oliver and Pharr[24–25] with the software of CSM Instruments Co. for the UNHT.

The surface morphology of the investigated γ-irradiated sample due to radiation-induced oxidation effect connected with appearance of As2O3 (arsenolite) crystals and S phases on the surface of g-As2S3, forming a white oxidized layer visible to the eye[11], was examined using MIRA (Tescan) field emission scanning electron microscope (SEM) with an EDS detector.

3 Results and discussion

The theory and models of nanoindentation tests of materials are well described in literature. Typical load-depth and load/depth-time curves obtained with the UNHT used in progressive multicycle mode are reported elsewhere[20]. Figure 1 shows the obtained indentation hardness (H) and elastic modulus (E) values versus penetration depth (Pd) for the unirradiated g-As2S3 in the three crossed ranges of indenter displacement, i.e., 200–1 000, 500–1 500, and 1 000–1 500 nm. The nanoindentation characterization indicates that, in all the tests performed, the indentation hardness and elastic modulus of the unirradiated sample linearly decrease from the maximum values (Hmax ≈ 2 250 MPa and Emax ≈ 23 GPa) to the minimum values (Hmin ≈ 900 MPa and Emin ≈ 11 GPa) as the penetration depth increases up to 1 600 nm. Figure 2 shows a typical indentation imprint for the unirradiated g-As2S3.

Figure 3 shows the indentation hardness and elastic modulus versus the penetration depth for the γ-irradiated g-As2S3, measured about 10 years after γ-irradiation, with radiation-induced oxidized layer in the three crossed ranges of indenter displacement, i.e., 200–1 000, 500–1 500, and 1 000–1 500 nm. Similarly to the unirradiated sample, as the penetration depth increases up to 1 600 nm the indentation hardness and elastic modulus of the γ-irradiated sample also decrease from the maximum values (Hmax ≈ 2 200 MPa and Emax ≈ 22 GPa) to the
minimum values ($H_{\text{min}} \approx 1\,100\, \text{MPa}$ and $E_{\text{min}} \approx 9\, \text{GPa}$), but the observed $H(P_d)$ and $E(P_d)$ are rather nonlinear with some plateau in the indentation depth range of 200–1\,000 nm. Clearly, this plateau is caused by the larger distributions between $H_{\text{max}}$ and $H_{\text{min}}$, and $E_{\text{max}}$ and $E_{\text{min}}$ in the near-surface region up to 1\,000 nm indentation depth. This effect is plausibly connected with the existence of radiation-induced oxidized layer covering the sample surface in nano-scale. Comparing γ-irradiated sample with radiation-induced oxidized layer with the unirradiated one, we found some improvements of the surface hardness in the direction of bulk material (i.e., $H_{\text{min}} \approx 1\,100\, \text{MPa}$ for the γ-irradiated sample and $H_{\text{min}} \approx 900\, \text{MPa}$ for the unirradiated sample) and a narrower distribution of the elastic modulus values for the γ-irradiated sample nearby 1\,500 nm indentation depth. Figure 4 shows a typical indentation imprint for the γ-irradiated g-As$_2$S$_3$ with radiation-induced oxidized layer. There is an impact of radiation-induced oxidation on the indentation imprint, forming a local region of ‘damaged oxidation products’ around the imprint upon nanoindentation.

Figure 5 shows the SEM image of the γ-irradiated g-As$_2$S$_3$ surface with radiation-induced oxidized layer. Clearly, the radiation-induced oxidation is due to appearance of As$_2$O$_3$ (arsenolite) crystals and S phases.

In order to remove that layer, washing and polishing procedures were applied and then the γ-irradiated g-As$_2$S$_3$ was measured again.
Fig. 4 Indentation imprint for the γ-irradiated g-As₂S₃ with radiation-induced oxidized layer

Figure 6 shows the indentation hardness and elastic modulus versus the penetration depth for the γ-irradiated g-As₂S₃ without radiation-induced oxidized layer in the three crossed ranges of indenter displacement, i.e., 200–1 000, 500–1 500, and 1 000–1 500 nm. As the penetration depth increases up to 1 600 nm, the indentation hardness and elastic modulus of the γ-irradiated sample decrease from the maximum values ($H_{\text{max}} \approx 2600$ MPa and $E_{\text{max}} \approx 25$ GPa) to the minimum values ($H_{\text{min}} \approx 1100$ MPa and $E_{\text{min}} \approx 14$ GPa) and the observed $H(P_d)$ and $E(P_d)$ are linear likely to those of the unirradiated sample (see Fig. 1).

Fig. 5 SEM image of the γ-irradiated g-As₂S₃ surface with radiation-induced oxidized layer

Fig. 6 Hardness and elastic modulus versus penetration depth for the γ-irradiated g-As₂S₃ without radiation-induced oxidized layer in three crossed ranges of indenter displacement

Figure 7 shows a typical indentation imprint for the γ-irradiated g-As₂S₃ without radiation-induced oxidized layer. Clearly, there is a clean surface of the γ-irradiated sample after removing the radiation-induced oxidized layer using washing and polishing, and the indentation imprint is similar to that for the unirradiated one (see Figs. 2, 4 and 7). The comparison of the nanoindentation characterization for the γ-irradiated sample without radiation-induced oxidized layer with the unirradiated sample demonstrates that (i) the surface hardness and elastic modulus of the γ-irradiated sample without radiation-induced oxidized layer increase in the indentation depth range of 200–1 600 nm, compared to the unirradiated material; and (ii) in the long-term radiation-induced improvement of the surface mechanical properties in g-As₂S₃, the broader distribution of the experimental data is detected for the irradiated sample with radiation-induced oxidized layer, compared to the clean sample without that layer.

Fig. 7 Indentation imprint for the γ-irradiated g-As₂S₃ without radiation-induced oxidized layer
4 Conclusions

The surface mechanical properties (i.e., hardness and elastic modulus) in the unmodified and radiation-modified g-As$_2$S$_3$, measured about 10 years after $^{60}$Co $\gamma$-irradiation, using nanoindentation technique with UNHT were investigated. The surface hardness and elastic modulus of the radiation-modified g-As$_2$S$_3$ increased in the indentation depth range of 200–1 600 nm, compared to the unirradiated material. In the long-term radiation-induced improvement of the surface mechanical properties in g-As$_2$S$_3$, the broader distribution of the experimental data was detected for the irradiated sample with radiation-induced oxidized layer, compared to the clean sample without the layer that was removed by washing and polishing. The results obtained should be taken into account for the practical use of g-As$_2$S$_3$, e.g. for the fabrication of long-term chalcogenide glass based dosimetric systems.

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