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Structural modification of swift heavy ion irradiated amorphous Ge layers

W Wesch[1], C S Schnohr[2], P Kluth[2], Z S Hussain[2], L L Araujo[2], R Giulian[2], D J Sprouster[2], A P Byrne[2] and M C Ridgway[2]

[1] Friedrich-Schiller-Universität Jena, Institute of Solid State Physics, Max-Wien-Platz 1, 07743 Jena, Germany

[2] Australian National University, Research School of Physics and Engineering, Canberra, Australia

E-mail: werner.wesch@uni-jena.de

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Abstract

Swift heavy ion (SHI) irradiation of amorphous Si (a-Si) at non-perpendicular incidence leads to non-saturable plastic flow. The positive direction of flow suggests that a liquid phase of similar density to that of the amorphous solid must exist and accordingly a-Si behaves like a conventional glass under SHI irradiation. For room-temperature irradiation of a-Si, plastic flow is accompanied by swelling due to the formation of voids and a porous structure. For this paper, we have investigated the influence of SHI irradiation at room temperature on amorphous Ge (a-Ge), the latter produced by ion implantation of crystalline Ge substrates. Like a-Si, positive plastic flow is apparent, demonstrating that liquid polymorphism is common to these two semiconductors. Porosity is also observed, again confined to the amorphous phase and the result of electronic energy deposition. Enhanced plastic flow coupled with a volume expansion is clearly responsible for the structural modification of both a-Si and a-Ge irradiated at room temperature with swift heavy ions.

1. Introduction

A swift heavy ion penetrating a solid predominantly interacts with the electrons of the substrate giving rise to the so-called electronic energy loss per path length S_e. Within 10^{-16} s, this interaction causes a high density of electronic excitation and ionization several nanometres around the ion trajectory. Depending on the degree of excitation and the specific nature of the solid, this electronic excitation may be transformed into atomic motion via different processes including Coulomb explosion, non-thermal melting and electron–phonon coupling. Growing experimental evidence now suggests that on the picosecond time scale the resulting atomic motion can be adequately described as a thermal spike [1–3].

Non-saturating anisotropic plastic deformation in glasses subjected to swift heavy ion (SHI) irradiation above a critical S_e value was first observed more than two decades ago [4–6]. With perpendicular ion incidence, thin free-standing samples shrink parallel to (and expand perpendicular to) the beam direction without a change in volume or mass density. The deformation yield, or the relative length change per unit fluence, is temperature dependent and increases with decreasing temperature. Under non-perpendicular ion incidence, a thin amorphous surface layer on a crystalline substrate exhibits non-saturable plastic flow as a consequence of this ion hammering. In conventional glasses, the corresponding surface shift and deformation yield are positive such that plastic flow occurs along the projection of the ion beam direction on the surface. The viscoelastic model for ion hammering introduced by Trinkaus and Ryazanov [7, 8] successfully describes this effect.

The positive deformation yield of glasses under SHI irradiation is a consequence of the continuous transition to their liquid phases. Amorphous Si (a-Si) was once believed to show a melting transition with a volume contraction to the dense metallic liquid Si (l-Si) phase [9]. Under such conditions, the deformation yield of a-Si should be negative and plastic flow should occur in the direction opposite to that observed for glasses. Computer simulations of supercooled l-Si did however predict a glass transition from a-Si to a low-density liquid phase followed by a liquid–liquid phase transition to the dense metallic liquid [10, 11]. If a low-density liquid phase exists, a positive deformation yield should be measurable.

Indeed, our experimental studies on SHI irradiation of a-Si at low temperatures showed plastic flow similar to that of a conventional glass [12–14] and the positive sign of the deformation yield was clear evidence for the existence of a glass transition. Irradiation at room-temperature under non-perpendicular incidence and to high ion fluences also yielded dramatic changes in the density of the a-Si layer and the formation of a porous structure was observed [14].

The effect of SHI irradiation on amorphous Ge (a-Ge) has been studied to a much lesser extent. Recently, the recrystallization of an a-Ge layer subjected to 100 MeV Ag ion irradiation ($S_e = 16.4\,\mathrm{keV\,nm^{-1}}$) has been reported and attributed to local transient melting followed by rapid solidification [15]. Local melting in c-Ge (and c-Si), however, cannot be achieved with SHI irradiation for single ions with S_e below $\approx 35\,\mathrm{keV\,nm^{-1}}$ [16–18], indicative of a significant difference in electron–phonon coupling between the amorphous and crystalline phases. For example, calculations in the framework of the extended thermal spike model yielded a maximum lattice temperature at the centre of the ion track of ≈580 K (half of that required for melting) for 200 MeV Au ion irradiation of c-Ge [18]. SHI irradiation of c-Ge to a sufficient fluence can yield a buried amorphous layer at the depth of the nuclear-energy deposition maximum. With a further increase in fluence, this layer transforms into a sponge-like structure resulting in swelling of the material [19, 20]. This effect is consistent with the well-known onset of porosity induced by low-energy ions where nuclear-energy deposition is dominant [21]. Under such conditions, vacancy production as a result of the ballistic displacement of substrate atoms is followed by vacancy agglomeration, the latter potentially enhanced under ion irradiation and by the ease with which Ge interstitials are accommodated within the amorphous phase [22]. We have previously examined the fluence-dependent atomic-scale structure of a-Ge formed by nuclear-energy deposition processes to identify the structural precursors to the onset of porosity [23]. The observed increase in the three- and five-fold coordinated atomic fraction due to nuclear energy deposition may represent a mechanism of accommodating vacancy and interstitial-like defects within the amorphous phase which under further irradiation may agglomerate and form voids. In this paper, we investigate the influence of SHI irradiation on a-Ge surface layers and determine the sign of the deformation yield. Our aim is to establish whether the liquid polymorphism observed previously in a-Si extends to a-Ge and is thus potentially a phenomenon common to tetrahedral networks.

2. Experimental

Amorphous Ge layers were produced by Ge ion implantations into (1 0 0) Ge substrates at 80 K. Based on SRIM calculations [24], multiple implantations were performed at energies ranging from 0.08 to 6.70 MeV and ion fluences between 0.49×10^{14} and $2.73 \times 10^{14}\,\mathrm{cm^{-2}}$ to yield a continuous amorphous layer extending from the surface to a depth of 3.25 μm. Prior to SHI irradiation, a Au grid of 30 nm thickness was evaporated onto the surface and a portion of the sample was masked to distinguish irradiated from unirradiated areas. SHI irradiations were then performed at room temperature with 185 MeV Au ions ($S_e = 35\,\mathrm{keV\,nm^{-1}}$ at the surface [24]) with an angle of incidence of $\Theta = 45^\circ$ relative to the surface normal. The fluence was varied between $N_I = 2.2 \times 10^{12}$ and $2.2 \times 10^{14}\,\mathrm{cm^{-2}}$, and the ion flux was kept constant at $10^{10}\,\mathrm{cm^{-2}\,s^{-1}}$. SHI irradiation at 185 MeV yields a Au ion range (∼11 μm) significantly greater than the extent of the amorphized layer. The electronic energy deposition was the maximum achievable over the latter to facilitate our study of the affects of this energy deposition process. For comparison, c-Ge was irradiated under identical conditions. Samples were then analysed by optical microscopy, surface profilometry and scanning electron microscopy (SEM), the latter in both plan-view and cross-section geometries.

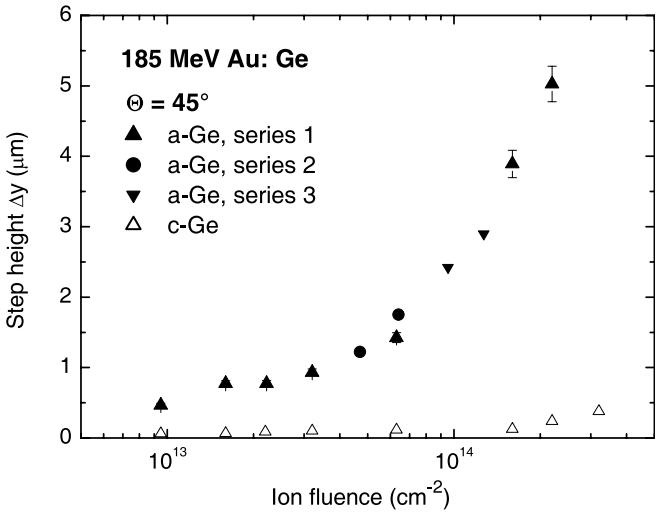

Figure 1. Swelling of irradiated regions (step height) as a function of fluence for a-Ge and c-Ge.

3. Results and discussion

The first indication of the structural modification of a-Ge under SHI irradiation was the progressive degradation of reflectivity and change in colour from light brown ($2.2 \times 10^{12}\,\mathrm{cm^{-2}}$), to dark brown, to black ($2.2 \times 10^{14}\,\mathrm{cm^{-2}}$). Surface profilometry demonstrated this colour change was accompanied by swelling of the a-Ge layer indicating a reduction in density. Figure 1 shows the step height Δy between irradiated and unirradiated areas as a function of ion fluence. For fluences less than $\approx 7 \times 10^{13}\,\mathrm{cm^{-2}}$, a linear increase is apparent which then converts to a steep superlinear increase at higher fluences. At $N_I = 2.2 \times 10^{14}\,\mathrm{cm^{-2}}$, the step height is ≈5 μm which is considerably larger than the initial thickness of the amorphous layer (3.25 μm). Irradiation of c-Ge also leads to swelling though the maximum step height amounts to only 0.38 μm at the highest fluence ($3.2 \times 10^{14}\,\mathrm{cm^{-2}}$).

Cross-section SEM analysis was performed to yield information about the micro-structure of the irradiated layers. Figure 2 shows an SEM image of a sample following irradiation to a fluence of $9.5 \times 10^{12}\,\mathrm{cm^{-2}}$. Note the presence of voids in the amorphous layer yet not in the underlying crystalline

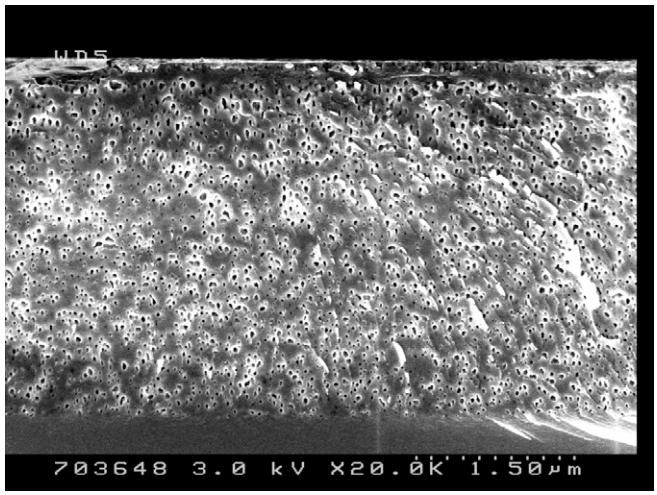

Figure 2. Cross-section SEM image of an a-Ge sample irradiated with 9.5×10^{12} cm^{-2} Au ions.

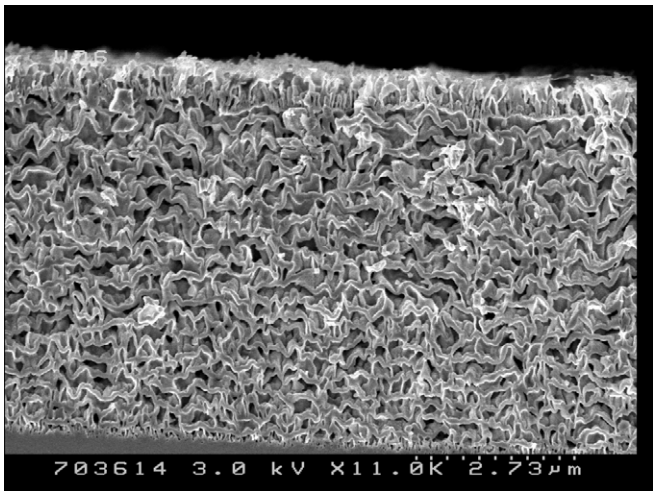

Figure 3. Cross-section SEM image of an a-Ge sample irradiated with 1.6×10^{14} cm^{-2} Au ions.

substrate. The void size and number increased with fluence giving rise to a volume expansion and the observed swelling. A further increase in fluence yields a transformation of the a-Ge layer into a porous sponge-like structure as apparent from figure 3 for irradiation to a fluence of 1.6×10^{14} cm^{-2}. In both images, the a-Ge/c-Ge interface remains planar and does not shift in depth. A lower magnification SEM image of a sample irradiated with 2.2×10^{14} cm^{-2} is shown in figure 4. A disordered layer with a high concentration of small voids is apparent at depths comparable to approximately 2/3 of the nuclear-energy deposition maximum (i.e. at depths where the ballistic displacement of substrate atoms via elastic interactions with incident ions or recoiled substrate atoms becomes more important). The small swelling observed in irradiated c-Ge (figure 1) is the result of these voids, the formation of which can be attributed to nuclear-energy deposition at this depth. Clearly the large swelling in a-Ge has to be ascribed to a large density change within the amorphous layer, obviously caused by the formation of nanopores. The fluence-dependent swelling and transformation of the a-Ge layer from continuous to porous, similar to that observed for a-Si irradiated at room temperature [14], is thus caused by electronic energy deposition processes. The planarity of the porous/crystalline interface also clearly demonstrates the underlying crystalline material is insensitive to these same electronic energy deposition processes. Only the amorphous layer is rendered porous consistent with reduced electron–phonon coupling in crystalline materials relative to their amorphous counterparts.

The SEM image in figure 4 establishes the presence of porosity at both the surface and end-of-range as a consequence of electronic- and nuclear-energy deposition, respectively. The atomistic process by which porosity is generated via nuclear-energy deposition has been described above and we now speculate on the origins of the porous structure resulting from electronic energy deposition. Recently we demonstrated that latent ion tracks in amorphous SiO_2 formed by SHI irradiation are composed of an under-dense core surrounded by an over-dense shell (relative to unirradiated material) [25]. This radial

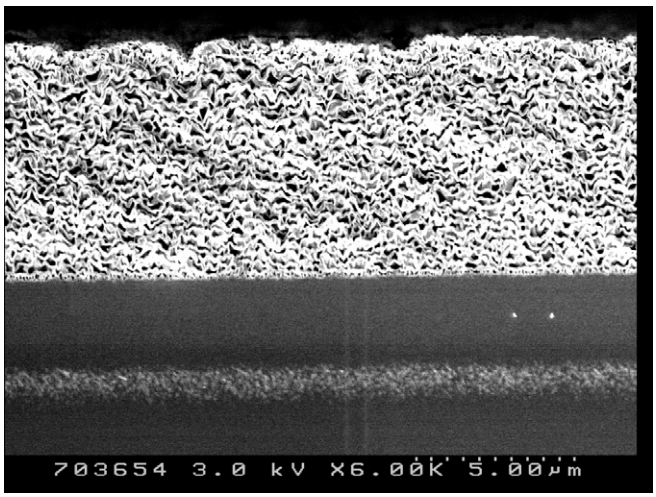

Figure 4. Cross-section SEM image of an a-Ge sample irradiated with 2.2×10^{14} cm^{-2} Au ions.

density distribution results from the rapid thermal expansion about a molten ion track subsequent to electronic energy deposition. While no comparable measurements exist for a-Ge, the under-dense core of an ion track may well serve as a source of vacancies. The lack of voids in the c-Ge substrate immediately below the a-Ge layer demonstrates this phenomenon is particular to the latter as consistent with molten track formation in a-Ge but not in c-Ge due to different electron–phonon coupling constants for the two phases. The potential influence of SHI irradiation-induced in-plane stresses on the formation of the porous structure has also been noted [6].

Using samples upon which a Au grid was evaporated, the plastic flow of a-Ge under SHI irradiation was examined. As an example, figure 5 shows an optical micrograph of a sample surface following Au irradiation to a fluence of 1.6×10^{14} cm^{-2}. The upper half was irradiated (from the right side) while the lower half was masked to completely inhibit ion penetration. The light squares are Au and the dark lines are irradiated a-Ge. Upon irradiation, a change in colour and/or reflectivity of both the a-Ge and Au in the upper half of the

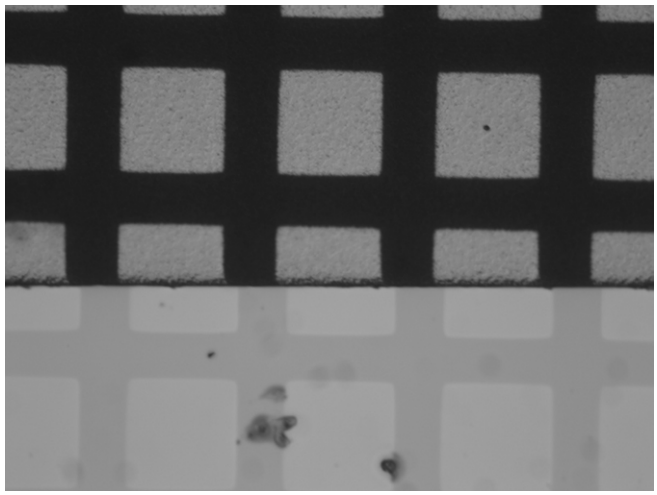

Figure 5. Optical micrograph of a masked a-Ge layer surface following Au ion irradiation to a fluence of 1.6×10^{14} cm^{-2}.

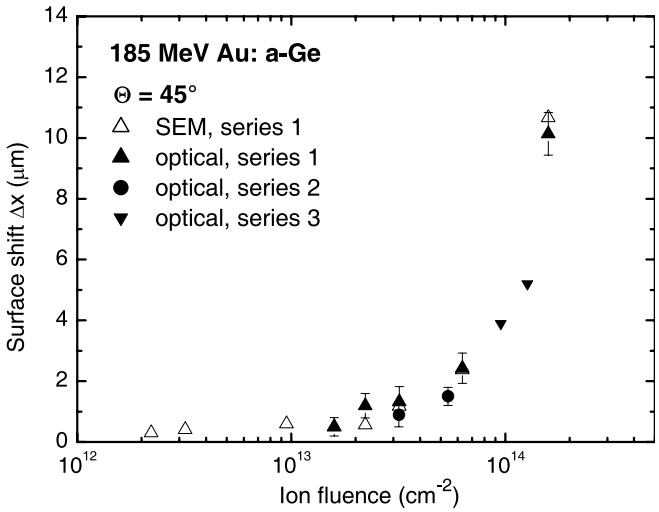

Figure 6. Surface shift Δx of a-Ge as a function of Au fluence.

figure is readily apparent. Plastic flow of the a-Ge is obvious and the surface shift Δx is positive (in the direction of the ion beam projection on the sample surface) as previously observed for glasses and a-Si. The surface shift of a-Ge is depicted in figure 6 as a function of fluence. Note the similarity with the step height evolution as shown in figure 1—a slight increase of Δx up to a fluence of $\approx 6 \times 10^{13}$ cm^{-2} is observed followed by a steep increase at higher fluences. The steep increase of Δx is thus well correlated with porous layer formation. Comparable behaviour was apparent for room-temperature irradiations of a-Si [14].

Our study of the porosity, step height, surface shift and plastic flow in a-Ge demonstrates this material behaves very much like a-Si under room-temperature SHI irradiation. Such results are consistent with the presence of a low-viscosity liquid phase induced by the extremes of electronic energy deposition and suggest liquid polymorphism is also present in a-Ge. The phase transition is connected with a non-saturating plastic deformation in combination with void and porous structure formation. Clearly, a complex mechanism coupling enhanced plastic flow and volume expansion governs the behaviour of a-Ge (and a-Si) under room-temperature SHI irradiation. Unfortunately, this volume expansion inhibits quantification of the deformation yield and complicates the applicability of the viscoelastic model [7, 8] which described well the case of a-Si irradiated at 80 K [12].

We comment that our results differ considerably from those reported recently in [15]. Therein, Som *et al* observed the complete recrystallization of an a-Ge layer ($\approx 1\ \mu$m thick) subsequent to 100 MeV Ag irradiation to a fluence of 1×10^{14} cm^{-2}, attributing such an effect to local transient melting. Though our electronic energy deposition ($S_e = 35$ keV nm^{-1}) is more than double that of [15] ($S_e = 16$ keV nm^{-1}), equating to a molten track of significantly greater diameter, we see no evidence of recrystallization at comparable fluences (both before and after the onset of porosity). Note also that porosity is not apparent in the transmission electron microscopy images presented in [15]. We speculate that the recrystallization observed by Som *et al* is not a consequence of transient melting but instead is potentially the result of thermally induced epitaxial recrystallization. Though the latter requires an elevated macroscopic temperature, the rate of epitaxial recrystallization was potentially further enhanced under the influence of ion irradiation.

4. Summary

SHI irradiation of a-Ge layers at room temperature and non-perpendicular incidence leads to fluence-dependent plastic flow in the direction of the ion beam projection on the surface. Plastic deformation is accompanied by a volume expansion due to void formation and the transformation to a sponge-like porous structure at high fluences. This porosity is the result of electronic energy deposition. Very similar behaviour has been observed following irradiation of a-Si layers under comparable conditions. The positive surface shift apparent for a-Ge and a-Si points to the existence of a low-density liquid phase and is definitive evidence for a glass transition. In both amorphous semiconductors, the coupling of enhanced plastic flow and swelling lead to the observed structural modifications.

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