Tracks and voids in amorphous Ge induced by swift heavy ion irradiation

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Ion tracks formed in amorphous Ge by swift heavy-ion irradiation have been identified with experiment and modelling to yield unambiguous evidence of tracks in an amorphous semiconductor. Their under-dense core/over-dense shell results from quenched-in radially-outward material flow. Following a solid-to-liquid phase transformation, the volume contraction necessary to accommodate the high-density molten phase produces voids, potentially the precursors to porosity, along the ion direction. Their bow-tie shape, reproduced by simulation, results from radially inward resolidification.
Swift heavy-ion irradiation (SHII) has many applications, spanning geochronological dating [1] to nanostructure fabrication [2]. Though this approach has found industrial application [3], the fundamental nature of ion-solid interactions at very-high ion energies remains poorly understood. Such interactions are dominated by inelastic processes (electronic stopping) resulting in the excitation and ionisation of substrate atoms while, in contrast, the elastic processes (nuclear stopping) that lead to ballistic atomic displacements at much lower energies are negligible in the SHII regime. The efficiency with which energy deposited in the electronic subsystem is subsequently transferred to the lattice is governed by the electron-phonon coupling parameter $g$ where typically $g_{\text{amorphous}} > g_{\text{crystalline}}$ due to a reduced electron mean free path in the former. When the lattice temperature exceeds that required for melting, a narrow cylinder of molten material is formed along the ion path. The ensuing rapid resolidification of this transient liquid phase can yield remnant structural modifications within the substrate in the form of an ion track.

*Crystalline* Ge (c-Ge) is relatively insensitive to SHII such that ion-track production necessitates very-high electronic stopping $S_e$ values. Discontinuous tracks follow single-ion irradiation ($S_e = 35$ keV/nm) [4,5] while cluster-ion irradiation ($S_e = 37-51$ keV/nm) yields tracks of diameter 5-15 nm [5]. In contrast, *amorphous* Ge (a-Ge) is rendered porous under SHII with $S_e > \sim 10$ keV/nm [6] while ion hammering results for $S_e > \sim 12$ keV/nm [6], the latter manifested as a non-zero deformation yield [7]. These observations are consistent with $g_{\text{amorphous}} > g_{\text{crystalline}}$ and ion-track formation has been suggested as the origin of these two phenomena [6,7]. A recent molecular dynamics (MD) study of irradiated a-Ge [8] suggested voids originate from outgoing shock waves resulting from rapid heating and expansion of the ion-track core. The sole report of ion tracks in a-Ge is that of Furuno *et al.* [9] who reported recrystallisation of tracks in a 5-nm a-Ge layer.
following SHII in a grazing-incidence orientation, a geometry that can lead to significant reductions in threshold $S_e$ values for ion-track formation [10]. The proximity of the surface could also perturb resolidification and enable recrystallization given the molten ion track is no longer completely surrounded by an amorphous matrix.

An unambiguous identification of ion tracks in amorphous semiconductors has significant implications. The pioneering report of Hedler et al. [11] demonstrating a glass transition in amorphous Si was predicated on ion-track formation yet the latter remains unverified. The lack of direct evidence stems from difficulties in detection. For example, TEM identification of amorphous ion tracks in an amorphous matrix is impeded by the lack of diffraction and absorption contrast. In contrast, small-angle x-ray scattering (SAXS) is an effective means of characterising ion tracks under such conditions, as we have demonstrated for amorphous SiO$_2$ [12]. For this report, we now combine physical characterisation using SAXS and TEM with a multi-time-scale theoretical approach including an Asymptotical Trajectory Monte Carlo (MC) calculation of the electron dynamics, a Two-Temperature Model (TTM) description of the heat dissipation and a MD simulation of the atom dynamics for ion tracks in a-Ge. With this novel approach, we characterise ion-track creation and evolution theoretically and ion-track structure experimentally.

An a–Ge layer of thickness 2.5 µm was formed on crystalline Si then irradiated with 185-MeV Au$^{13+}$ ions ($S_e = \sim 22$ keV/nm [13]). Samples were subsequently characterised with SAXS and cross-section TEM (XTEM). For experimental details, see Supplementary Information.

The simulation of ion tracks in a-Ge induced by SHII was achieved via three interconnected stages. The first included the excitation of electrons due to the ion energy deposition. The electron dynamics were then followed by combining a MC approach [14]
and TTM [15-17]. While the MC method is a kinetic means of modelling the initial electron excitation and the non-equilibrium electron dynamics, the TTM describes the energy transport within the electronic and lattice subsystems. Using the MC-TTM approach, the rate of energy transfer between the electronic and lattice subsystems \( (g_{\text{amorphous}}) \) was extracted so fitting this parameter was unnecessary. Instead, the electron-phonon coupling and specific heat capacity were calculated explicitly as a function of electron temperature (see Supplementary Information). Here we do not consider ultrafast phase transformations like athermal melting [18] because the particular timescale of the relevant phase transformation is of minor importance. The calculation of the lattice temperature is used here to judge whether the localised energy is sufficient to induce and maintain the molten state on a timescale of several picoseconds.

The evolution of the lattice temperature is mirrored in the MD simulation where the spatially varying, time-dependent energy transfer between the two subsystems from the MC-TTM calculation was used as input for continuously depositing kinetic energy in a random direction on the lattice atoms until the two subsystems were in equilibrium at 3 ps. MD simulations were performed with the PARCAS code [19] using the Stillinger-Weber (SW) and Tersoff potentials [20,21]. The choice of potential was governed by the most accurate description of the solid-to-liquid and liquid-to-solid phase transformations. The simulation cell volume was 61 x 41 x 41 nm\(^3\). Note that MD simulations with fixed cell dimensions (mechanically rigid boundaries) coupled with a volume contraction within the ion track (demonstrated below) could potentially over-estimate the resultant tensile stress compared to that for elastically-responding boundaries. The initial a-Ge cell was constructed from c-Ge using the WWW approach [22] (see Supplementary Information). Using the MC-TTM result as input, the molten track width deduced from MD was half that
measured experimentally, an extraordinary result given the absence of fitted parameters. To better enable the comparison of calculation, simulation and experiment, the MC-TTM input was then scaled so the width of the molten ion track extracted from MD was consistent with that determined from SAXS.

SAXS detector images (Figure 1(a) and (b) insets) were comprised of two anisotropic scattering components separable by tilting the sample relative to the x-ray direction. The scattering intensity $I$ as a function of the scattering vector $Q$, isolated and background subtracted, is shown in Figure 1 for two orientations. In both spectra, the scattering contributions from ion tracks and voids are apparent as horizontal streaks and mirrored hemispheres, respectively. Long, parallel cylindrical-like features (ion tracks) yield the streaks which are compressed in the detector image upon tilting. The voids responsible for the second scattering component were identifiable with TEM.

In Figure 1(a), $I$ increases as a function of fluence consistent with an increase in the number of scattering centres, in this case ion tracks. As the fluence exceeds $10^{11} \text{ /cm}^2$, the well-defined oscillations wash out as ion-track overlap becomes more probable. Fitting the two lower fluences with a core-shell model yields the ion-track parameters given in Table I including a total track radius of $11.1 \pm 0.2 \text{ nm}$. (The measured radius of an ion track is considered indicative of the maximum melt radius [12,23].) A negative value of the core-to-shell density ratio ($\Delta \rho_{\text{core}} / \Delta \rho_{\text{shell}}$ where $\Delta \rho_{\text{core}}$ and $\Delta \rho_{\text{shell}}$ are the change in density of the core and shell relative to the unirradiated matrix, respectively) indicates core and shell have a density lower and higher, respectively, than the surrounding matrix (or vice versa). We suggest the shell is over-dense, consistent with frozen-in radially-outward material flow from the ion-track core following a thermal spike. The relative radial density distribution across the ion track derived from SAXS measurements is shown in the Figure 1(a) inset.
This distribution, corroborated by simulations presented below, yields a net volume contraction which is accommodated by the creation of open volume.

Figure 1(b) shows the scattering contribution from the second component, fitted with the bow-tie shape shown in the inset. This choice of shape was governed by TEM observations shown in Figure 2 which depict a void. TEM through-focus analysis confirmed these features are less dense than the matrix. The parallel sides of the void are aligned with the incident ion direction, suggesting their formation mechanisms are correlated. Table II lists the void parameters derived from SAXS and TEM measurements.

Insight into the ion-track and void formation processes was garnered from MD simulations (see Supplementary Information animation). Using the SW potential, the solid-to-liquid phase transformation along the ion track was apparent with MD. The density of the six-fold coordinated molten Ge exceeded that of the four-fold coordinated amorphous solid, as expected [24]. Within the molten material, spherical voids appeared at ~10 ps followed by void agglomeration for surface-area minimisation. Prior to resolidification, the void shape was prolate ellipsoid with the major axis aligned with the incident ion direction. The minor axis equalled ~60% of the molten ion-track width. For our ion energy deposition parameters, void formation was not apparent using the Tersoff potential.

While the SW potential effectively yielded the high-density liquid phase upon melting, this density was retained upon resolidification for the simulation of the ion track and a bulk cell of liquid Ge quenched at $3 \times 10^{13} \text{K/s}$, a rate comparable to that for the ion track. In contrast, the Tersoff potential reproduced the low-density amorphous solid upon quenching of the bulk cell of liquid Ge. We thus implemented the Tersoff potential at 100 ps for the MD simulation of ion-track formation, following which the transformation from high-density liquid to low-density solid was observable upon cooling.
The validity of changing potentials mid-simulation is demonstrated with Figure 2 which shows the MD simulation of the void after resolidification of the molten ion track (300 ps total). The similarity between experiment and simulation is remarkable. While spherical voids form as a consequence of the volume contraction induced by the low-density solid to high-density liquid phase transformation, the peculiar shape of the voids upon resolidification is the result of radially-inward cooling. As the molten ion track progressively solidifies from the maximum melt radius toward the ion-track core, the expanding volume of the solidified material compresses the residual molten material necessitating axial motion toward the void. The innermost volume experiences the greatest effect and a bow-tie shaped void results.

Figure 3 shows time-dependent MD results of the relative radial density across (a) an ion track (between voids) and (b) a void, respectively. Across the ion track, the development of the core-shell structure is rapid with the greatest density ratio achieved ~4 ps after the ion energy deposition. At the same time, the maximum temperature was achieved within the ion track (~4600K), a temperature beyond that required for boiling (3093K) [25].) The maximum melt radius (~11 nm) was reached at 100 ps and the presence of the high-density liquid phase spanning the ion track is readily apparent. Thereafter, the ion-track density distribution relaxes toward the pre-irradiation, low-density amorphous phase. MD yielded no evidence of crystallisation within the ion track upon resolidification, consistent with XTEM observations. Both results contradict those of Furuno et al. [9] potentially due to the influence of the free surface in reference 9. Across the void, formation begins in the vapour phase (10 ps) but evolves fully in the liquid phase (> 25 ps). The maximum radii of the void and molten track (~6.5 and ~11 nm, respectively) are achieved at the same time (100 ps) again suggesting their formation is correlated.
Relaxation yields a slight narrowing of the void with the radial density distribution constant for $\geq 200$ ps. The entire cell has cooled to below the melting point of a-Ge (965 K [26]) by 300 ps.

We propose the following scenario for ion-track and void formation in a-Ge. For our irradiation conditions, the energy transferred from the electronic to lattice subsystems is sufficient to induce melting and the formation of a molten cylinder of radius $\sim11$ nm. For elemental Ge, the liquid-phase density exceeds that of the solid and this increase in density necessitates a volume contraction within the ion track upon melting. Void formation begins in the vapour phase but clearly evolves in the liquid phase as shown from our MD simulations. As the lattice cools, our SAXS results show remnants of a core-shell structure are quenched into the ion track and radially-inward resolidification yields bow-tie shaped voids.

We now calculate the number of voids per unit track length using two approaches. For the first, we estimate an ion track contains $2.8 \pm 0.5$ voids/$\mu$m based on the amplitude of the SAXS spectrum. For the second, we approximate the void as a cylinder (13-nm wide and 15-nm long from XTEM) and calculate 99% surface coverage is achieved with a fluence of $\sim3.5 \times 10^{12}$ /cm$^2$ (using an exponential overlap model (fractional coverage $= 1 – \exp(-nR_v^2\phi)$ with $R_v$ the void radius and $\phi$ the fluence). Using a void length of 15 nm as above and the irradiation-induced swelling data for a-Ge from Steinbach et al. [6] (derived with conditions identical to those in this report), yields a second, independent estimate of $\sim2.1$ voids/$\mu$m in an ion track.$^1$ This leads us to suggest that the bow-tie shaped features apparent in our XTEM image of Figure 2 not only result from the contraction of the molten voids.

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$^1$ A third estimate from the MD simulation would clearly yield an erroneously high value given the limited length (61 nm) of the simulation cell. Our use of MD was to identify radial density distributions and the void formation mechanism.
volume within an ion track but, furthermore, they represent the embryonic precursors to
the porous structure induced in a-Ge by SHII.

In summary, we have identified and characterised ion tracks and voids in a-Ge, thus
demonstrating ion-track formation in an amorphous semiconductor. SAXS measurements
showed the ion track was comprised of a core-shell structure consistent with quenched-in
material flow, the latter resulting from a thermal spike and emanating radially outwards.
MD simulations, using a MC-TTM approach as input, showed not only that a core-shell
structure is present in the early stages of ion-track formation but remarkably reproduced
the void geometry apparent from XTEM observations. The evolution of the void size and
shape was a natural consequence of the density difference between solid and liquid Ge.

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measurements.
REFERENCES

FIGURE CAPTIONS

Figure 1: (a) Background-subtracted SAXS intensity as a function of scattering vector for ion tracks including the detector image recorded with the surface normal at 10° to the x-ray direction (bottom-left) and the calculated radial density distribution (top-right). (b) Background-subtracted SAXS intensity as a function of scattering vector for voids including the detector image recorded with the surface normal at 5° to the x-ray direction (bottom-left). The void geometry used for fitting (top-right) was 10.6, 7.4 and 6.6 nm for L, R₁ and R₂, respectively.

Figure 2: XTEM image from a-Ge irradiated to a fluence of 6x10^{10} /cm² (left) and MD simulation of the void geometry following resolidification (300 ps) (right).

Figure 3: MD simulation of the time-dependent radial density distribution across an (a) ion track and (b) void. In (a), the reduction in density at ~10 nm radial distance for times 100-130 ps is an artifact from changing the potential at 100 ps.
TABLE CAPTIONS

Table I: Ion-track structural parameters determined with SAXS. $R_{\text{core}}$, $R_{\text{shell}}$ and $R_{\text{total}}$ are the core radius, shell thickness and total radius, respectively; $\sigma_{\text{core}}$, $\sigma_{\text{shell}}$ and $\sigma_{\text{total}}$ are the standard deviation of the Gaussian distributions used to account for the polydispersity of the core, shell and total radii, respectively; $\Delta \rho_{\text{core}}$ and $\Delta \rho_{\text{shell}}$ are the change in density of the core and shell relative to the unirradiated matrix, respectively.

Table II: Void structural parameters determined with SAXS, XTEM and MD. XTEM and MD values are estimated from very few occurrences.
Table I

<table>
<thead>
<tr>
<th>$R_{\text{core}}$ (nm)</th>
<th>$\sigma_{\text{core}}$ (nm)</th>
<th>$R_{\text{shell}}$ (nm)</th>
<th>$\sigma_{\text{shell}}$ (nm)</th>
<th>$R_{\text{total}}$ (nm)</th>
<th>$\sigma_{\text{total}}$ (nm)</th>
<th>$\Delta \rho_{\text{core}}/\Delta \rho_{\text{shell}}$</th>
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<td>6.5±0.1</td>
<td>1.01</td>
<td>11.1±0.2</td>
<td>1.69</td>
<td>-0.91±0.14</td>
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Table II

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<th>Radial Width (nm)</th>
<th>Length (nm)</th>
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<tbody>
<tr>
<td>SAXS</td>
<td>~7</td>
<td>~24</td>
</tr>
<tr>
<td>XTEM</td>
<td>~7</td>
<td>~10-20</td>
</tr>
<tr>
<td>MD</td>
<td>~6</td>
<td>~10</td>
</tr>
</tbody>
</table>
scattering intensity [a.u.]

scattering vector $q$ [Å$^{-1}$]

$10^{-4}$ $10^{-3}$ $10^{-2}$ $10^{-1}$ $10^{0}$ $10^{1}$

$6 	imes 10^{10}$ cm$^{-2}$ $10^{11}$ cm$^{-2}$ $3 	imes 10^{11}$ cm$^{-2}$ $5 	imes 10^{11}$ cm$^{-2}$

fit of $6 	imes 10^{10}$ cm$^{-2}$

fit of $10^{11}$ cm$^{-2}$
Supplementary Information SI1: The Asymptotical Trajectory Monte Carlo – Two-Temperature Model

To determine the effects of an ion’s electronic stopping power on a dielectric substrate, one must account for several different processes. The energy loss experienced by the penetrating ion is expended ionising target atoms, thus creating excited electrons in the conduction band. These free electrons, referred to as first generation electrons or δ–electrons, may have energies up to tens of eV. The excitation of electrons is accompanied by the creation of holes in the valence band. The δ–electrons traverse through the dielectric substrate and scatter with lattice atoms. These electron–atom collisions may transfer sufficient energy to excite additional electrons into the conduction band (impact ionisation). On the other hand, electron–hole pairs recombine via Auger processes, further changing the energy and number–density of electrons in the conduction band. Also, low-energy electrons may emit phonons via the electron-phonon coupling mechanism, effectively heating the lattice. Eventually, the lattice temperature may exceed that required for melting or vaporisation and lead to permanent, observable modifications on the surface [s1] or, as in this work, within the bulk.

While the electron–phonon coupling is conveniently described using thermodynamic equations, the strong perturbation of the electrons induced by the ions discourages their use. To overcome this problem, a model was recently proposed [s2] which utilizes kinetic equations on the basis of the Asymptotical Trajectory Monte Carlo (MC) method [s3] to describe the generation and dynamics of the δ–electrons, including impact ionisation and Auger recombination of electron–hole pairs. Based on the spatial and temporal energy distributions and the number–density of the conduction band electrons, we determine at what time after ion impact the definition of an electron temperature is meaningful [s4].
Once an electron temperature is established, the subsequent electron transport and electron–phonon coupling are described by the two-temperature model (TTM) [s5] using the MC method as input. This so called MC–TTM model has been successfully used to describe modifications in SiO$_2$ induced by swift heavy ions [s2].

For this work we have adapted our model to the particular density of states of a-Ge given in reference [s6]. Therein, a vanishing bandgap is reported, in contrast to that of reference [s7]. For both the vanishing and small bandgaps, a small energy is sufficient to excite electrons into the conduction band. As a consequence, the number of electrons to be treated with the MC method is significantly larger than compared to the case of SiO$_2$ and the required computation time increases accordingly. More importantly, low-energy electrons will be created even at early time scales. As mentioned above, these low-energy electrons induce phonon emission, which is not accounted for with the MC method. To account for both the emission of phonons as well as the increased number of particles, the following distinction is made: First, electrons excited with $\geq 5$ eV of kinetic energy are treated using the MC method. These electrons traverse ballistically through the substrate and participate in impact ionisation and Auger recombination processes. Electrons with energies $< 5$ eV are treated within the TTM where they are considered as diffusive and participate in the electron–phonon coupling process. By doing so, all electrons are treated with the appropriate model.

Both models are applied with synchronised time steps which is necessary since high-energy electrons may lose energy due to impact ionisation and fall below the 5 eV cut-off. In that case, they are removed from the MC calculation and their energy is added to the ensemble of low-energy electrons which are treated with the TTM. Therefore, the MC and TTM calculations can no longer be performed sequentially. Details of the input parameters
and numerical implementations of the MC simulation are given in [s4] where, in particular, the source term $S = S(r,t)$ accounting for the space- and time-dependent heating of the electron system in the TTM framework is provided. The latter describes the temporal and spatial evolution of the electron and phonon temperatures $T_e = T_e(r,t)$ and $T_p = T_p(r,t)$, respectively:

$$C_e \frac{\partial T_e}{\partial t} = \nabla \cdot (\kappa_e \nabla T_e) - g \cdot (T_e - T_p) + S \quad (s1)$$

$$C_p \frac{\partial T_p}{\partial t} = \nabla \cdot (\kappa_p \nabla T_p) + g \cdot (T_e - T_p) \quad (s2)$$

Here, $\kappa_e$ and $\kappa_p$ denote the heat conductivity and $C_e$ and $C_p$ denote the specific heat capacity of the electrons and lattice, respectively, and $g$ is the electron–phonon coupling term. All material parameters potentially depend on the electron and lattice temperatures. Empirical expressions for the lattice heat conductivity and heat capacity are from [s8], while an expression for the electron heat conductivity was taken from [s9]. The electron heat capacity was obtained exploiting moments of the Fermi distribution [s2]. The electron-phonon coupling term $g$ is determined through the energy loss of hot electrons $\frac{\partial u_e}{\partial t}$ due to collisions with cold phonons (here assumed at room temperature):

$$g = \frac{1}{(T_e - T_p)} \int_0^\infty \frac{\partial u_e}{\partial t} \left| \frac{\partial u_e}{\partial t} \right| dt \quad (s3)$$

where $\frac{\partial u_e}{\partial t}$ is calculated through the second moment of the electron–phonon collision integral given in equation (6) of [s10]. The density of states in a-Ge was taken into account to calculate the internal energy $u_e$. Since we sum over all electrons in the valence and conduction bands, we apply for the evaluation of equation (s3) the same matrix element as in [s10] for the self-screened interaction of free and degenerate electrons with phonons in crystalline metals.
We end with $g$ in the range $3 \times 10^{14}$ to $2 \times 10^{17}$ W/m$^3$/K depending on the electron temperature. A strong increase is found in the low-temperature range due to the rapidly changing electron density in the conduction band of a-Ge. For temperatures $> \sim 5000$ K, the dependence and magnitude of $g$ resembles that of Au (for example, see [s11]). The synchronised MC-TTM approach is applied up to 30 ps after the ion impact and, finally, the electron–phonon energy exchange rates obtained from equations (s1) and (s2) are passed to the Molecular dynamics simulation (see SI2).

**Supplementary Information SI2: Molecular dynamics simulations**

Molecular dynamics (MD) simulations provided insight into the physics governing the formation of the bow-tie shaped voids. The remarkable agreement between experiment and simulation shown in Figure 2 was the result of following the experimental density changes at phase transformations in the MD simulation.

The simulation of ion tracks in MD utilizes data from the MC-TTM model, as described above, as input for the energy deposition from the electronic to lattice subsystems. The energy deposition at each time step between the two subsystems in TTM was multiplied by 1.45 and the width of the deposition by 1.50 for the MD simulations to align the simulated and experimental values of molten track diameter and produce a minimal void size. The energy deposition to the simulation cell was 8 keV/nm.

The simulation cell encompassed $\sim 4.5M$ atoms with boundary cooling in the x and y directions, with a 0.6 nm wide border region cooled towards 300 K by Berendsen temperature control [s12]. We have previously demonstrated this approach cools down the sound/heat wave emanating from heat spikes sufficiently well not to affect disorder in the
center of the simulation cell [s13]. In the current simulations, time-dependent analysis of the density evolution showed that there is no noticeable reflection of the density wave.

During the MD simulation, the Posselt Stillinger-Weber (SW) potential [s14] effectively reproduced the high-density liquid phase [s15] upon melting and produced voids within the molten track. This high density was, however, retained upon re-solidification. To examine whether this was related to the special geometry of the ion track or an artifact of the potential, a test simulation with a bulk cell of liquid Ge was quenched isobarically at $3 \times 10^{13}$ K/s (or equivalently 3000 K in 100 ps), a rate comparable to that for the ion track. The high density was again retained after cooling, demonstrating this potential does not correctly reproduce the high-density liquid to low-density amorphous phase transformation [s15, s16]. As a consequence, the void shape does not change upon re-solidification from that of the prolate ellipsoid formed inside the molten ion track. In contrast, a second test simulation using the Tersoff potential [s17] adequately reproduced the low-density amorphous solid upon quenching of a bulk cell of liquid Ge at the same rate as above. However, the formation of voids within the ion track was not apparent, even for clearly larger energy deposition, most probably related to the too-high melting point associated with the Tersoff potential ($\sim 2400$ K as determined using the liquid-solid equilibrium approach similar to that utilized in [s18]).

We suggest these density changes, low-to-high upon melting and high-to-low upon re-solidification, are essential to understanding the underlying physics of the void shape. Given no single Ge potential would show both void formation within the molten track and the subsequent return to the amorphous-solid density upon cooling, we used a two-step simulation to study the effect: in the first stage, ion track formation was simulated for 100 ps using the Posselt SW potential, and thereafter, in the second stage, the cell containing
the void and molten track was cooled using the Tersoff potential. In this manner, the correct transformations in density during both melting and re-solidification were achieved. The result was bow-tie shaped voids and thus we conclude that a simulation approach that reproduces the known density changes leads to the experimentally-observed void shape. This was demonstrated in Figure 2 which showed the MD simulation of the void shape at 300 ps (total) or equivalently after re-solidification of the molten ion track. The evolution of the void shape is readily apparent in the animation that follows (SI3).

**Supplementary Information SI3: Molecular dynamics animation**

The animation MDSIM.wmv shows the formation of a bow-tie shaped void subsequent to 185-MeV Au-ion irradiation. Each sphere shows the position of a Ge atom in an 0.8 nm thick cross-section of the simulation cell. The Au ion (which is not explicitly shown) travels horizontally from left to right and the energy deposition to the Ge atoms is determined with the MC-TTM model as described above.

The movie format is *.wmv and can be viewed with Windows Media Player and Powerpoint for a Windows operating system or using the free mplayer software in MacIntosh and Linux operating systems.

**Supplementary Information SI4: Sample preparation and characterisation**

A 2.5-µm c-Ge layer was deposited on a crystalline Si (c-Si) substrate by molecular-beam epitaxy. The c-Ge layer was then implanted with a multiple-energy, multiple-fluence Ge-ion sequence at ~196°C to amorphise the Ge layer to a depth of ~2.5 µm without inducing the well-known amorphous-to-porous transformation due to nuclear stopping [s19 and references therein]. Samples were subsequently irradiated at normal incidence and
room temperature with 185-MeV Au\textsuperscript{13+} ions, yielding an $S_e$ value of $\sim$22 keV/nm over the a-Ge layer. For our irradiation conditions, no disorder was measurable in c-Si or c-Ge control samples over the first $\sim$3 $\mu$m.

SAXS measurements were performed in transmission geometry at the Australian Synchrotron using 12-keV photons, camera lengths of 722 and 7047 mm and a CCD detector to collect scattering spectra. A goniometer was utilised to orient the sample surface normal with respect to the incident x-ray direction. To reduce scattering and diffraction from the c-Si substrate, the latter was thinned to $\sim$40 $\mu$m before measurement. Samples were also characterised with cross-section TEM (XTEM) using a Phillips CM300 microscope operating at 300 kV with samples prepared by the small-angle cleavage technique \cite{s20} to minimise exposure to elevated temperatures.

**Supplementary Information SIS5: SAXS data analysis**

Both voids and tracks contribute to the SAXS scattering images that were shown as insets in Figures 1(a) and (b). Due to their anisotropic nature, both components can be separated by tilting the sample with respect to the x-ray beam. The streaks of high intensity are caused by the high aspect ratio of the ion tracks whereas the hemispheres of increased scattering intensity on either side of the streaks originate from the non-spherical voids that were shown in the XTEM image of Figure 2.

**Analysis of ion tracks**

A SAXS spectrum of an unirradiated sample was utilised for background subtraction. Following reference s21, discrete sectors of the detector images were analysed separately to extract structural information for the two scattering components. To analyse the ion tracks, the intensity of the corresponding streaks was isolated. Since both scattering
features are overlapping, the low intensity area next to the streaks was isolated for background subtraction taking into account the effect of the underlying void scattering. Figure 1(a) showed the background subtracted SAXS spectra of ion tracks as a function of ion fluence (open symbols). The solid lines are fits to the spectra using a core-shell model as described in \[s22\]. The scattering amplitude equates to:

\[
f(q_r) = \frac{2\pi L}{q_r} [(d - 1) r_c f_1(r_c q_r) + (r_c + r_s) f_1(r_c + r_s) q_r]
\]

with the core radius \(r_c\), the shell thickness \(r_s\), the first order Bessel function \(f_1\), the track length \(L\), and the ratio of the density contrast in core and shell \(d = \frac{\rho_c}{\rho_s}\). Assuming a narrow Gaussian distribution of \(r_c\) with a mean value of \(R_c\) \([s22]\), the scattering intensity can be written as:

\[
I(q_r) \propto \int \frac{1}{\sqrt{2\pi} \sigma_r} \exp \left\{ -\frac{(r_c - R_c)^2}{2 \sigma_r^2} \right\} |f(q_r, r_c)|^2 dr_c.
\]

The distribution of the shell thickness \(r_s\) with mean value \(R_s\) was adjusted by rescaling the Gaussian distribution in \(r_c\).

The overlap of the ion track and void scattering features becomes more dominant at low \(q\) values. Hence, both signals are less separable in this \(q\) range which distorts the extracted scattering spectra of the ion tracks. This can be incorporated by convoluting the formfactor with a narrow Gaussian distribution in \(q\). The scattering intensity follows as:

\[
I(q_r) \propto \int \frac{1}{\sqrt{2\pi} \sigma_r} \exp \left\{ -\frac{(r_c - R_c)^2}{2 \sigma_r^2} \right\} |f(q_r, r_c)|^2 dr_c \otimes \frac{1}{\sqrt{2\pi} \sigma_q} \exp \left\{ -\frac{(q_r - q)^2}{2 \sigma_q^2} \right\}.
\]

Fitting of the spectra was performed in three stages. First, the SAXS spectra were fitted excluding the polydisperse radius distribution and \(q\)-convolution to obtain the basic ion-track properties. Parameters determining the ion track morphology, such as \(r_c\), \(r_s\), and \(d\), were then kept constant at the fitted values. Second, the width of the Gaussian distribution in \(r_c\) was fitted to obtain the polydispersity of the radii still excluding the \(q\)-
convolution. Finally, the width of the Gaussian distribution for the $q$-convolution was fitted with all other fitting parameters being fixed at values determined previously.

**Analysis of voids**

The void scattering was extracted by masking an area perpendicular to the streaks and the background subtracted was that from an unirradiated sample. A cylindrical density distribution with ellipsoidal concavities at either end (shown schematically in the inset of Figure 1(b)) was assumed (based on the XTEM observations of Figure 2):

$$
\rho(r) = \begin{cases} 
\rho_v & 0 \leq r \leq R_1, |z| \leq \frac{L_v}{2} + R_2 \left(1 - \sqrt{1 - \left(\frac{r}{R_1}\right)^2}\right) \\
0 & \text{else}
\end{cases} \tag{s7}
$$

where $\rho_v$ is the electron density contrast, $L_v$ the minimum distance between the ellipsoidal dents, and $R_1$ and $R_2$ the major and minor radii of the ellipsoid, respectively. The scattering amplitude then equates to:

$$
f(q_r) = 4\pi\rho_v \int_0^{R_1} \left[\frac{L_v}{2} + R_2 \left(1 - \sqrt{1 - \left(\frac{r}{R_1}\right)^2}\right)\right] r J_0(rq_r) \, dr \tag{s8}
$$

where $J_0$ is the Bessel function of zeroth order. Fitting this scattering amplitude to the SAXS spectra in Figure 2 results in $L_v = 10.6$ nm, $R_1 = 7.4$ nm, and $R_2 = 6.6$ nm, in good agreement with XTEM and MD results. A Gaussian distribution in $R_1$ was assumed as in equation (s5) which was rescaled for $L_v$ and $R_2$ to take into account a realistic size variation for the voids. The SAXS spectrum was recalculated with the fit parameters assuming a width of the Gaussian distribution of 10% of $R_1$. The result is shown as the solid line in Figure 2.
Supplementary Information References:


