

Shape Modification of Germanium Nanowires During Ion Irradiation and Subsequent Solid-phase Epitaxial Growth

Osmane Camara*, Imran Hanif, Matheus Tunes, Robert Harrison, Graeme Greaves, Stephen Donnelly and Jonathan Hinks

School of Computing and Engineering, University of Huddersfield, Queensgate,
Huddersfield, HD1 3DH, United Kingdom

Abstract

During ion irradiation which is often used for the purposes of band gap engineering, nanostructures can experience a phenomenon known as ion-induced bending (IIB). The mechanisms behind this permanent deformation are the subject of debate. In this work, germanium nanowires are irradiated with 30 or 70 keV xenon ions to induce bending either away from or towards the ion beam. By comparing experimental results with Monte-Carlo calculations, the direction of the bending is found to depend on the damage profile over the cross-section of the nanowire. After irradiation, the nanowires are annealed at temperatures up to 440°C triggering solid-phase epitaxial growth (SPEG) causing further modification to the deformed nanowires. After IIB, it is observed that nanowires which had bent away from the ion beam then straighten during SPEG whilst those which had bent towards the ion beam bend even more. This is attributed to differences in the mechanisms responsible for the ion-beam-induced bending in opposite directions. Thus, the results reported here give insights into the mechanisms causing the IIB of nanowires and demonstrate how to predict the evolution of nanowires under irradiation and annealing. Finally, they show that, under certain conditions, the bending can even be removed via SPEG.

Keywords: radiation damage; nanomanipulation; germanium nanowires; *in situ* transmission electron microscopy; ion-induced bending

1.0 Introduction

New materials are required to overcome the technological challenges faced in keeping pace with Moore's law.[1] In this context, one-dimensional semiconductor nanostructures have rapidly become accepted as potential building blocks for the next generation of devices.[2], [3] Of the various semiconductor nanostructures under consideration, germanium nanowires are one of the most-promising candidates.[3], [4] Compared to silicon, germanium has a larger exciton Bohr radius meaning that charge carriers are more-readily subject to quantum confinement.[5] Germanium also offers the advantage of reduced thermal budgets for device fabrication as it can be recrystallised at 300°C compared to silicon at 470°C.[6], [7] More importantly, the mobility of its charge carriers is higher making it an excellent material for nanowire-based field-effect transistors (NWFETs).[4] Furthermore, germanium has also attracted attention due to the potential to alter the nature of its indirect band gap by subjecting it to heavy doping and/or strain.[8]–[10]

It is common to incorporate impurities acting as dopants to modify the electronic properties of semiconductors.[11] In order to incorporate the dopants in a precise manner, techniques are required to control their distribution within the host material. A standard technique to achieve this is ion implantation.[5], [6], [11] However, ion irradiation can also induce damage in the target material such as the creation of point defects (e.g. interstitials and vacancies), larger defect structures (e.g. dislocation loops and cavities) and even amorphisation of the material.[6] To repair the crystal and to electrically activate the chemical dopants, an annealing step is often required.[6], [11] However, if an implanted single-crystal suffers amorphisation due to the ion irradiation then a residual crystalline seed is required to enable its recovery via solid-phase epitaxial growth (SPEG).[6], [12]–[14] Although ion implantation and subsequent recrystallisation via SPEG are well-established techniques in the processing of silicon, when studied in nanostructures significant differences have been observed compared to the bulk.[5], [6], [11], [12], [14] For instance, different SPEG recrystallisation activation energies and/or altered damage profiles have been reported.[12], [15]

The phenomenon of ion-induced bending (IIB) has been observed where nanostructures such as cantilevers,[16], [17] nanotubes[18] or nanowires[19]–[25] suffer plastic deformation under irradiation. In the case of nanowires, different bending behaviour has been reported as they bend either away or towards the ion beam depending on the ion species, target material, nanowire diameter and incident angle of irradiation.[19], [23], [24] Although such bending can be a deleterious consequence of ion beam doping, IIB offers tremendous opportunities for the manipulation and engineering of nanostructures.[12], [23] The possibility of aligning an array of nanowires has drawn interest from the microelectronic industry including a patent deposited in 2001 and currently owned by Samsung Ltd.[26] The authors of the patent described the alignment of nanowires using inert gas ion beams. The use of inert gas ions to achieve IIB offers the advantage of minimizing unwanted alteration to the electronic properties of the nanostructures during the nanoscale manipulation.[24] Furthermore, during processing of semiconductor devices, a pre-amorphisation step is often performed using ion irradiation with self or inert gas ions (such as xenon) to prevent channelling effects in subsequent ion beam manufacturing steps.[27]–[29] As IIB can be induced using either dopant or inert-gas ion beams, the bending can therefore occur in the processing of nanostructured semiconductors during both the pre-amorphisation step and the subsequent doping .[20], [25] As well as showing potential for future transistor technologies, IIB has also been used by Yoshida *et al.*[30] to create waveguides by bending silicon wires using self-ion irradiation. [30] Furthermore, as straining of germanium nanowires is being investigated as a way of optically activating germanium, IIB might modify the optoelectronics properties of germanium as residual strain is expected to be present in bent nanowires .[8], [20], [23], [31]

Currently, there is much debate and no consensus regarding the nature of the precise mechanisms which drive the IIB phenomenon.[17], [19]–[21], [23] Various theories presented in the literature include models based on a viscoelastic flow process occurring in amorphous materials,[21]–[23], [32] density changes due to damage accumulation,[19], [24] surface rearrangement of atoms[16], [31], [33] and unequal thermal expansion induced by thermal gradients within the nanostructure.[17] However, mechanisms based on thermal gradients as suggested in [17] would work only for materials with a

negative thermal coefficient. Instead, germanium exhibits positive thermal expansion over a large range of temperatures.[34]–[37]

In our previous work, single-crystal germanium nanowires were irradiated *in situ* in a transmission electron microscope (TEM) with 30 keV xenon ions at 400°C.[25] At this temperature, defect mobility prevented any major damage accumulation and amorphisation but the nanowires were still observed to bend towards the ion beam. However, the germanium nanowires never bent away from the ion beam when irradiated at elevated temperature. Conversely, it was shown that irradiation performed under the same conditions (i.e. ion species, energy, flux, nanowire diameter and angle of incidence) but at room temperature could induce the nanowires to either bend away or bend towards the ion beam. From these observations, it was inferred that inhibition of major damage accumulation and amorphisation prevented bending away from the ion beam at 400°C. Moreover, for such conditions, proposed mechanisms based on viscoelastic flow in amorphous material and density changes due to damage accumulation causing bending could be discounted as amorphisation and damage accumulation were suppressed at elevated temperature.[25] Consequently, out of the proposed theories only those based on surface rearrangement could explain the bending of nanowires towards the ion beam at elevated temperatures.[25] It was therefore concluded that while bending away from the ion beam must be the result of damage accumulation, surface effects (such as surface rearrangement of atoms) could lead a nanowire to bend towards the ion beam. However, the question remains as to whether mechanisms based on surface rearrangement are also responsible for bending of nanowires towards the ion beam under irradiation at room temperature.

Whilst our former work gave valuable insights into the mechanisms behind IIB,[25] the exact irradiation conditions which induce either bending direction at room temperature need to be determined if IIB is to be used as a predictable tool. Additionally, as damage accumulates during irradiation, semiconductors are routinely subject to an annealing step. Therefore, the influence of such annealing on ion beam bent nanowires also needs to be investigated.

The current paper reports on a study of xenon ion irradiation of germanium nanowires using *in situ* TEM at room temperature. The experimental results are compared to calculations performed using the *Stopping and Range of Ions in Matter* (SRIM) Monte-Carlo code adapted to better model the cylindrical shape of the nanowires in order to help understand the conditions which lead to bending in different directions. The behaviour of the nanowires post-irradiation is then studied by *in situ* annealing experiments. It will be shown that, during annealing, the bent nanowires experience further shape modification when epitaxial recrystallisation occurs, giving further valuable insights into the underlying mechanism behind IIB.

2.0 Result and discussion

2.1 Effect of damage distribution on bending behaviour

Since the nanowires were irradiated with xenon ions at either 30 keV or 70 keV and as both the incidence angle α and the diameters of the nanowires varied, damage profiles for a range of experimental conditions were computed using IDRAGON. The average damage depth normalised to the nanowire diameter, Ω , allows comparison of irradiation of nanowires with different dimensions. Equation 1 was used to calculate Ω , where $a_{m,n}$ is the number of atomic displacements calculated by SRIM in slice n at depth x_m in the IDRAGON multislice model and \emptyset is the nanowire average diameter. The depth x is defined such that at $\Omega = 0.5$ the average depth of an atomic displacement is in the middle of the nanowire (i.e where $x_m = \frac{\emptyset}{2}$).

$$\Omega = \frac{\sum_{n=1}^{100} \left(\frac{\sum_{m=1}^{100} (a_{m,n} x_{m,n})}{\sum_{m=1}^{100} a_{m,n}} \right)}{100 \times \emptyset} \quad \text{Equation 1}$$

Figures 1(a–d) show Bright-field TEM (BF-TEM) images and selected area diffraction patterns (SADPs) with the calculated Ω values for two cases of IIB of germanium nanowires both irradiated with 30 keV xenon ions at room temperature. The nanowire shown in figures 1(a–b) bent away from the ion beam whilst the nanowire shown in figures 1(c–d) bent towards the ion beam during irradiation. Due to the different nanowire average diameters, \varnothing , and ion beam incidence angles, α , the normalised damage distribution, Ω , for the situation depicted in figure 1(a) is smaller ($\Omega = 0.28$) than that depicted in figure 1(c) ($\Omega = 0.36$).

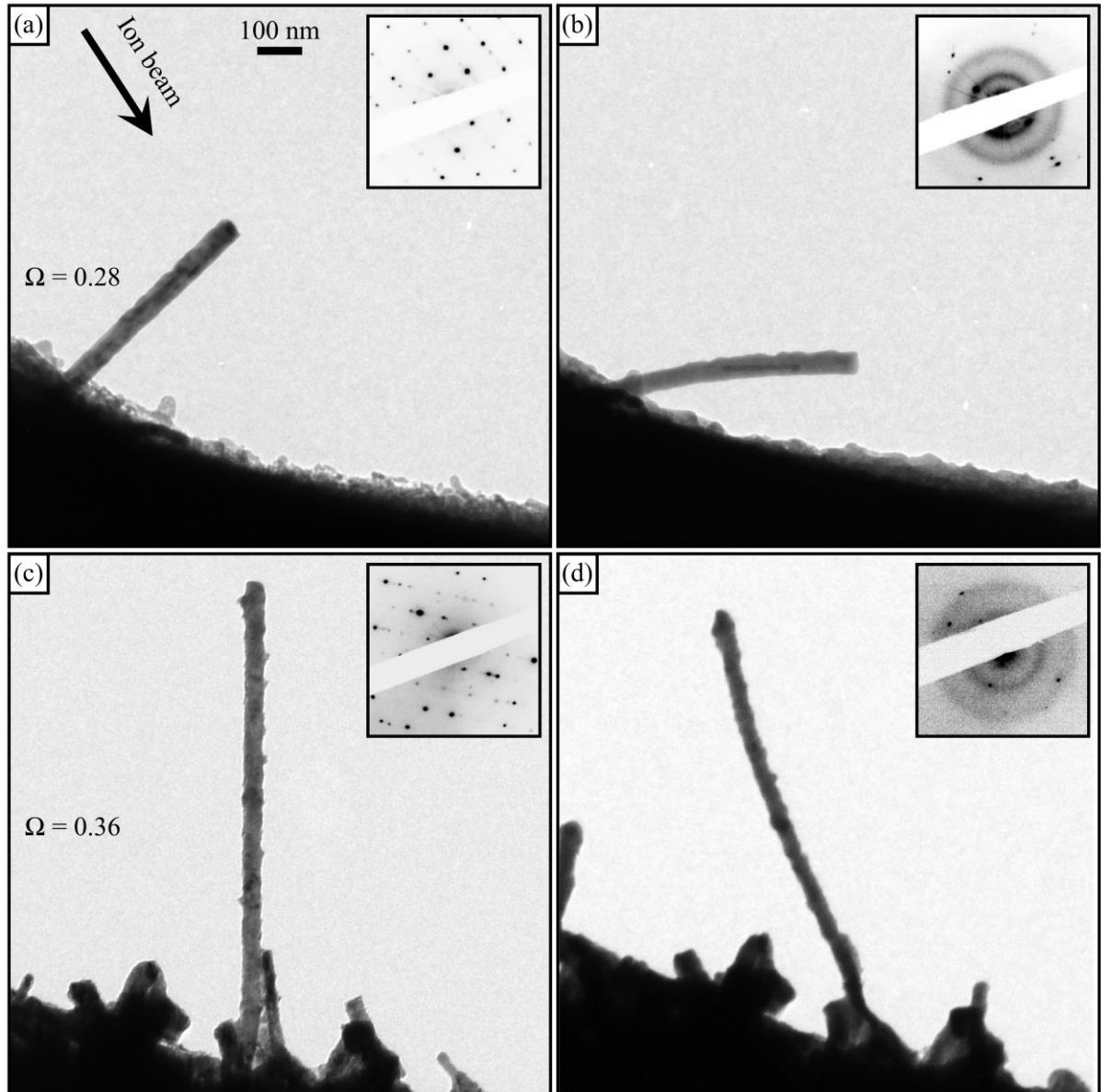
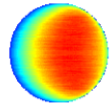
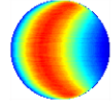
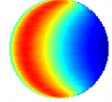
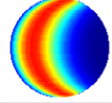
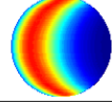
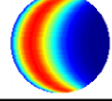
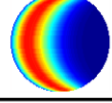
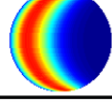
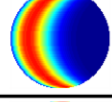
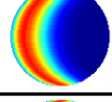
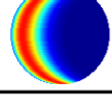



Figure 1. BF-TEM images and SADPs of nanowires undergoing IIB: (a) a $\Phi = 52$ nm nanowire before irradiation; (b) the same nanowire after irradiation with 30 keV xenon ions to a fluence of 3.3×10^{14} ions. cm^{-2} which caused bending away from the ion beam and partial amorphisation as indicated by the SADP; (c) a different $\Phi = 39$ nm nanowire before irradiation; and (d) after irradiation with 30 keV xenon ion irradiation to a fluence of 3.9×10^{14} ions. cm^{-2} which caused bending and alignment towards the ion beam and partial amorphisation as indicated by the SADP. The projection of the ion beam onto the image plane is represented by the arrow in (a). The scale bar in (a) applies to all the images in the figure.

Table 1 shows the nanowire diameters, xenon ion energy, calculated values of Ω , direction of bending and IDRAGON damage profiles for eleven germanium nanowires irradiated for the current work. With one exception, it can be seen from table 1 that nanowires with a lower Ω will bend away, those with a higher value will bend towards and that there is a tipping point around $0.34 < \Omega < 0.36$.

	\varnothing (nm)	α ($^{\circ}$)	Energy (keV)	Ω	Bending direction	IDRAGON
i	18	37	70	0.54	Towards	
ii	43	26	70	0.46	Away	
iii	27	67	70	0.39	Towards	
iv	37	10	30	0.38	Towards	
v	51	42	70	0.38	Towards	
vi	39	20	30	0.36	Towards	
vii	40	31	30	0.34	Away	
viii	43	29	30	0.33	Away	
ix	48	1	30	0.33	Away	
x	40	44	30	0.31	Away	
xi	52	37	30	0.28	Away	



0 Maximum

Table 1. Table summarising the results of irradiation experiments on individual nanowires including details of the diameters, \varnothing , incident angle of the ion irradiation, α , xenon ion energy, calculated values of Ω , direction of bending and IDRAGON damage profiles for eleven germanium nanowires irradiated for the current work. The results are presented in descending values of Ω and the damage in the IDRAGON profiles is indicated using a colour scale in which red represents the maximum damage experienced by a particular nanowire.

In the works by Romano *et al.*[23] and Pecora *et al.*[21], [22] a viscoelastic flow known as ion hammering was considered as a possible mechanism to drive the bending of silicon and germanium nanowires towards the ion beam. This mechanism was considered to operate only under conditions in which the nanowires were fully amorphous along their cross-section. In the current work, nanowires were observed to begin bending towards the ion beam at room temperature immediately from the beginning of the irradiation (i.e. at very low fluences) before any major degree of amorphisation could transpire. In such cases, the viscoelastic flow processes invoked to explain the bending of nanowires towards the ion beam would not be possible as it occurs only in amorphous material.

The case of nanowires which bend towards the ion beam with most of the radiation damage located near the irradiated side (i.e. $\Omega < 0.5$) is discussed below. It will be shown that, according to proposed mechanisms based on density changes, such nanowires should have bent away from the ion beam. To illustrate this inconsistency, the nanowire in figure 1(d) and table 1(vi) is taken as an example. A density change could potentially lead this nanowire to bend if there were a sufficient density difference between its highly damaged side and its relatively undamaged side. Bending of nanowire (vi) towards the ion beam was observed as soon as the *in situ* irradiation started and before major amorphisation could occur. If the presence of the Frenkel pairs generated during irradiation were to cause a density change, it would be expected that these would induce an overall expansion of the material as swelling around interstitials is greater than contraction around vacancies.[38], [39] As damage is concentrated on the side facing the ion beam, the stress between the swollen region and the rear-side of the nanowire would cause the nanowire to bend away. The same arguments hold true if damage accumulation leads to amorphisation at higher fluences. As amorphous germanium is less dense than the crystalline phase,[23] the stress generated between the expanded ion-beam-facing side and the unirradiated part of the nanowire should also make the nanowire bend away from the ion beam as previously suggested by Romano *et al.*[23] Furthermore, it is worth noting that TEM observations in previous experiments on the irradiation of silicon with inert gases have shown that their distribution remained close to the expected initial stopping range at room temperature.[40] Therefore, as out-diffusion is unlikely, the role of internal stresses due to the implantation of xenon must be taken into account. According to the

IDRAGON calculation shown in the figure S1 in the Supporting Information, the implanted ions should be located in the ion-beam-facing side of the nanowire. Therefore, if the xenon ions were to play a role in the bending of the nanowire, one should expect that the heavy ion would have caused internal stresses causing the nanowire to bend away from the ion beam.

Borschel *et al.*[19], [24] have invoked the distribution of self-interstitials and vacancies during irradiation as being responsible for density changes within nanowires which could cause both bending away and towards the ion beam.[19], [24] They calculated the difference between the distributions of the interstitials and vacancies due to ion irradiation in zinc oxide nanowires; the idea being that when a nanowire bends towards the beam there is an excess of interstitials deeper in the nanowire and an excess of vacancies closer to the part of the nanowire facing the ion beam. The excess of interstitials would lead to a volume expansion and the excess of vacancies to a volume contraction. The resulting bending moment would therefore make the nanowire bend towards the ion beam. It should be noted that according to the Monte Carlo simulations presented in their work on ZnO, the nanowires that bent towards the ion beam were damaged through their entire thickness. The situation is very different in most of the germanium nanowires presented here. For instance, nanowire (vi) in table 1 bent towards the ion beam with relatively little damage in its rear side. When germanium is irradiated, amorphisation occurs after the displacements per atom (dpa) reach a threshold value (0.3 dpa under self-irradiation at room temperature and even lower when irradiated by heavier ions).[41], [42] At fluences when bending towards occurs, calculating the dpa in two halves of the nanowire (vi), it could be expected that the ion-beam-facing side of the nanowire must have rapidly suffered amorphisation whilst due to the relatively small value of Ω whilst the opposite side remained crystalline. For instance, after an irradiation of 4 seconds to a fluence $\approx 5 \times 10^{13}$ ions.cm⁻² the average dpa value in the ion-beam-facing side of the nanowire was calculated to be ≈ 0.45 while the average dpa value in the opposite half was only ≈ 0.05 . Under these conditions, as the range of the ion is approximately only 14 nm and $\Omega = 0.36$, most of the interstitials and vacancies would have been generated within the highly damaged part of the nanowires which should become amorphous due to damage accumulation. Therefore, instead of density changes caused by the separation of self-interstitials and vacancies during irradiation, the stress generated

between the swollen amorphous side and the denser crystalline side of the nanowire should lead it to bend away from the ion beam as described above and by Romano *et al.*[23]

Consequently, as mechanisms based on density changes due to damage accumulation are more likely to cause bending away from the ion beam when $\Omega < 0.5$, mechanisms based on surface effects proposed in the literature are the most likely to have caused the bending of the germanium nanowire towards the ion beam by out-competing density-change-based mechanisms. Whilst previous experiments on germanium nanowires irradiated at elevated temperature to prevent damage accumulation and thus inhibit bending away due to density-change-based mechanisms,[25] the results presented here are different as mechanisms based on density changes due to damage accumulation and those based on surface rearrangement can both occur. Typically, it can be inferred that as a result of the competition between these mechanisms, at low values of Ω (< 0.34) the nanowires bend away from the ion beam and at higher Ω values (> 0.36) they bend towards. Furthermore, this competition can be directly observed using TEM with *in situ* ion irradiation for instances in which Ω is between 0.31 and 0.36. Under such conditions, nanowires have been observed to react by bending slightly one way and then the other as a “struggle” occurs before one mechanism appears to win out and comes to dominate (see the figure S2 in Supporting Information).

At low values of Ω (< 0.34), some of the structural changes leading to bending away from the ion beam can be seen in the TEM. For instance, the presence of an amorphous phase on the ion-beam-facing side of the bent nanowire shown in figure 1(d) has been evidenced by electron diffraction and dark-field TEM (DF-TEM) (see also figure S3 in the Supporting Information). To quantify this driving force, equations based on the Stoney formula can be used.[43] The Stoney formula is typically applied to determine the driving force causing bending of a thin film but also to other geometries such as cantilevers and nanowires.[44], [45] However, during IIB such a calculation would depend on variables which change throughout the bending such as the Young’s modulus in the damaged part of the nanowire. Indeed, the properties of the swollen damaged part of the nanowire are expected to undergo complex dynamic changes during irradiation. The swollen damaged part of the nanowire will be made of a mix of continuous amorphous material (which becomes more and more porous during

irradiation),[46]–[48] point defects, extended defects and isolated amorphous pockets when irradiated by an heavy ion irradiation such as xenon.[42], [49], [50] Therefore, this would require computer simulations which could be the subject of further study.

In this work, at the tipping point in bending behaviour when Ω is between 0.31 and 0.36 the forces driving the nanowire towards the ion beam and those driving it away from it are balanced. However, because of the complexity regarding the state of the damaged region, the ratio Ω at which the bending direction of a germanium nanowire is reversed cannot be expected to remain the same if irradiations are performed with significantly different combinations of ion and energy (even if these achieved the same value of Ω) as the type of defects generated would vary.[42], [49], [50] A clear example of this can be found when comparing the work performed by Romano *et al.*[23] on single crystalline germanium nanowires irradiated with 30 keV gallium and the present work. According to our IDRAGON calculations, their nanowires irradiated under conditions corresponding to $\Omega = 0.32$. If irradiated with xenon, such a value would result in the nanowire permanently bending away from the ion beam. However, under gallium irradiation the germanium nanowires permanently bend towards the ion beam. Furthermore, as the reversal of the bending direction depends on surface rearrangement, the nature of the bombarded surface can also play a role on the tipping point value Ω . It has been reported that both build up and release of stress at surfaces during ion irradiation can be greatly influenced by even minor surface contamination or surface roughness and thus also influencing bending behaviour.[51]–[54] This may be the explanation for the contrary behaviour exhibited by nanowire (ii) in table 1.

2.2 Annealing of fully-amorphous bent germanium nanowires after IIB

Images and SADPs of a germanium nanowire before and after 30 keV xenon ion irradiation to a fluence of 7.3×10^{13} ions.cm⁻² are shown in figures 2(a–b). After irradiation, the nanowire was permanently bent towards the ion beam and the inset SADPs indicate that the nanowire was fully amorphous as a result of the damage induced by the irradiation. Figure 2(c) shows an image and SAPD of the bent nanowire after annealing at 440°C for 25 minutes; the diffraction data indicate that the nanowire remained bent

and fully amorphous after annealing. This annealing temperature is well above the 300°C minimum temperature at which SPEG from a crystalline seed is reported to be activated in germanium.[6] As SPEG did not occur during annealing, it suggests that the nanowire was fully amorphous with no crystalline seeds present after the irradiation. Recrystallisation can also occur via random nucleation and growth (RNG) for which no crystal seed is required as crystallites randomly nucleate within the amorphous phase leading to a polycrystalline material.[5], [55] However, fully amorphous nanowires such as the one represented in figure 2 remained amorphous after annealing indicating that a temperature of 440°C was insufficient to induce RNG.

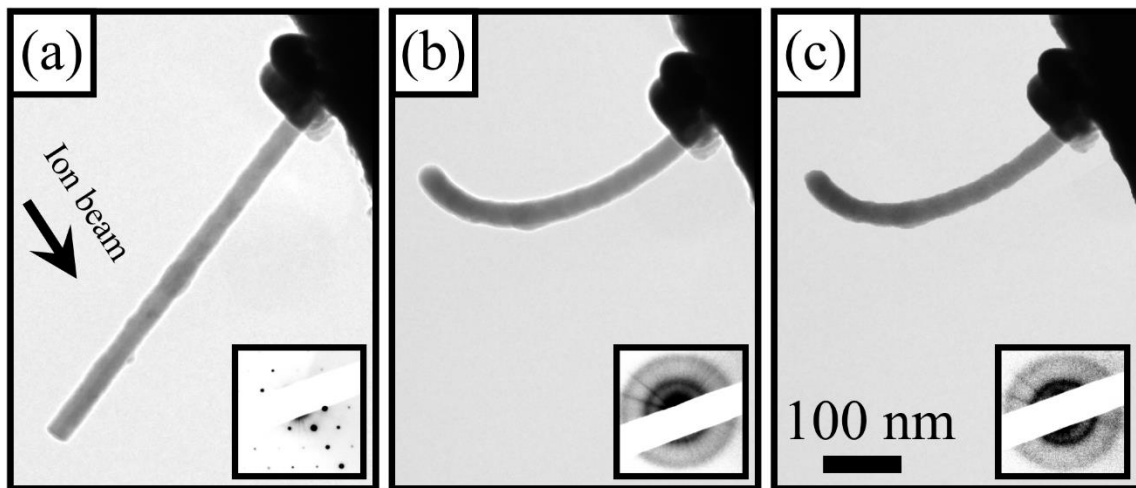


Figure 2. *BF-TEM images and SADPs of a $\varnothing = 28$ nm germanium nanowire: (a) before irradiation; (b) after irradiation with 30 keV xenon to a fluence of 7.3×10^{13} ions.cm⁻² at room temperature; and (c) BF-TEM images and SADP after subsequent annealing at 440°C for 25 minutes. The BF-TEM image and the SAPD in (b) show that the nanowire bent towards the ion beam and that no remaining crystal was detected within the nanowire after irradiation. After annealing, no improvement of the crystal structure is detected in the SAPD and no further significant shape modification occurred. The scale bar in (c) applies to all the images in the figure. The projection of the direction of the ion beam onto the image plane is represented by the arrow in (a).*

2.3 Annealing of partially-amorphous bent germanium nanowires

Following xenon ion irradiation, annealing of bent germanium nanowires which were only partially amorphous induced further morphological changes. Shape changes during annealing of silicon nanowires which were bent due to IIB has been reported in [22]. In the work presented here, the behaviour of partially-amorphous bent nanowires during annealing was found to be dependent on their initial bending direction resulting in two distinct cases as discussed below.

In the first scenario, nanowires that had bent away from the ion beam under irradiation underwent shape modification during recrystallisation via SPEG. The evolution of a nanowire undergoing this process during annealing is presented in figures 3(a–c). Figures 3(a–b) show that the nanowire became partially amorphous after irradiation and bent away from the ion beam. Figure 3(c) shows that the nanowire regained its original shape and the SADP reveals that it also recovered its single-crystal nature after 5 minutes of annealing at 440°C. Likewise, all other partially amorphous nanowires that were bent away from the ion beam tended to straighten during SPEG. Furthermore, it was found that the straightening of the nanowires during annealing can be driven to a sufficient degree for complete recovery of the original straight shape observed prior to irradiation.

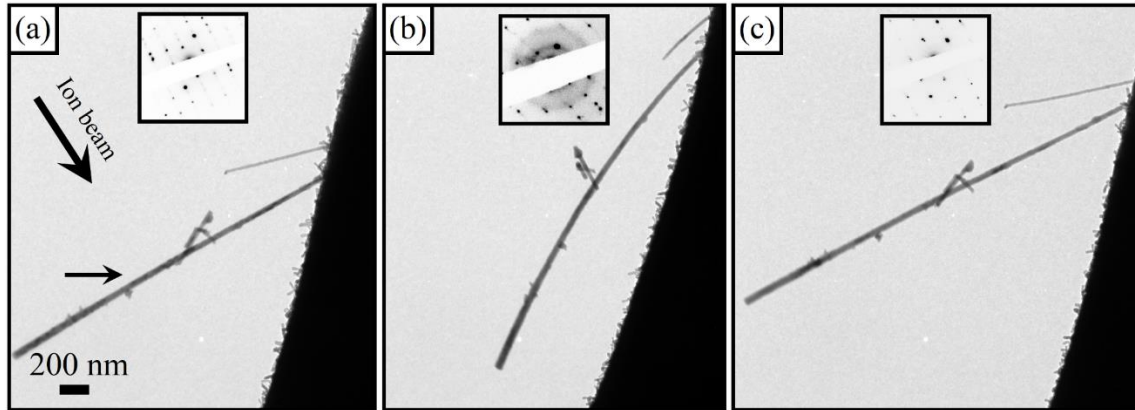


Figure 3. BF-TEM images and SADPs showing the evolution of a $\varnothing = 30$ nm germanium nanowire: (a) before irradiation; (b) after irradiation with 30 keV xenon to a fluence of 9.1×10^{13} ions.cm⁻² at room temperature resulting in the nanowire bending away from the ion beam and becoming partially amorphous; and (c) after annealing at 440°C for 5 minutes showing that the nanowire has nearly regained its original shape and crystallinity. The projection of the direction of the ion beam onto the image plane is represented by the large arrow in (a). The nanowire of interest is indicated by the small arrow in (a). The scale bar in (a) applies to all the images in the figure.

As discussed in this work and previously,[19], [23]–[25] bending away from the ion beam could be caused by density changes of the ion-beam-facing side of the nanowire due to displacement damage (i.e. point defect accumulation and/or amorphisation). However, during annealing the damage is repaired and the amorphous phase is replaced by the crystalline phase via SPEG. Thus, this density change from the damaged region of the nanowires is removed, causing the nanowires to unbend and recover their original shape.

In the opposite scenario to bending away from the ion beam, nanowires which were bent towards the ion beam also underwent shape modification during SPEG. However, unlike in the first scenario, these nanowires did not straighten during annealing but rather bent even more. An example of this, is presented in figures 4(a–c) which show images and SADPs of a nanowire before irradiation, after irradiation and after a subsequent annealing step, respectively. In figure 4(b) the nanowire is bent

towards the ion beam and its SADP indicates that the nanowire became partially amorphous as a result of the irradiation. After 18 minutes of annealing at 440°C, the SADP and the image in figure 4(c) show that the nanowire underwent recrystallisation while its curvature increased as it bent even further.

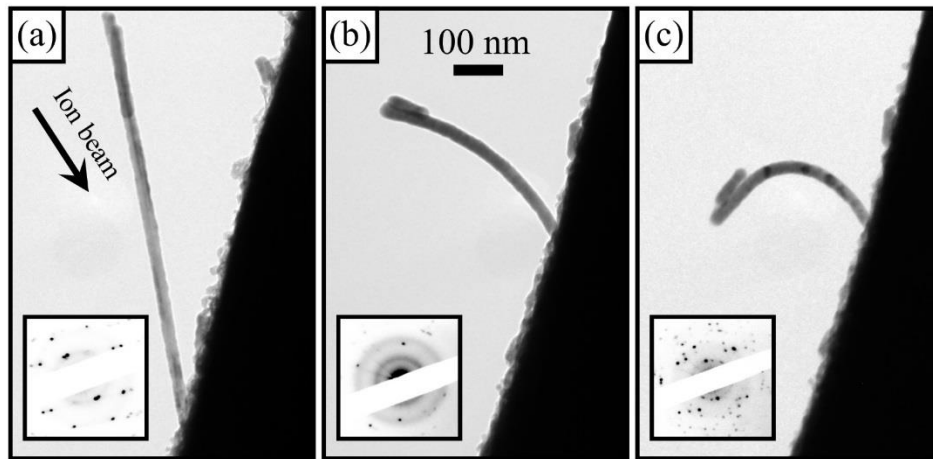


Figure 4. BF-TEM images and SADPs showing the evolution of a $\varnothing = 26$ nm germanium nanowire: (a) before irradiation; (b) after irradiation with 30 keV xenon to a fluence of 7.3×10^{13} ions.cm⁻² at room temperature resulting in the nanowire bending towards the ion beam and becoming partially amorphous; and (c) after annealing at 440°C for 18 minutes showing that the nanowire has undergone recrystallisation to a polycrystalline state and that the bending curvature has increased. The projection of the direction of the ion beam onto the image plane is represented by the arrow in (a). The scale bar in (b) applies to all the images in the figure.

As discussed above, RNG did not occur at an annealing temperature of 440°C. For this reason, the polycrystallinity observed in the SADP in figure 4(c) cannot be the result of RNG. In the event of epitaxial regrowth from several differently-orientated crystalline seeds within a partially amorphous material the structure can, after recrystallisation, be composed of as many crystals as it had crystalline seeds before SPEG. Thus, the polycrystallinity observed in this nanowire after regrowth could be the result of such a process. Moreover, the relative misorientation between crystalline seeds distributed

along the length of the nanowire could have been amplified by the increase in bending observed during annealing.

Furthermore, in the case of nanowires which bent towards the ion beam, the increase in curvature during annealing seems to indicate that these nanowires did not bend towards the ion beam due to damage induced density changes during irradiation. If the nanowires did indeed bend towards the ion beam due to such mechanisms then, unless significant irreversible mass transport has occurred, the post-irradiation annealing should have helped damage recovery and consequently result in re-straightening as was the case for nanowires which bent away from the ion beam. However, as discussed below, mechanisms based on surface rearrangement seem to be in line with the increase of curvature during annealing. Rajput *et al.* [16], [20], [33] and Bettge *et al.*[31] reported that IIB of nanowires and cantilevers has been observed in various materials with different crystalline structures, and that shrinkage of the irradiated surface must be the cause of the bending of all these nanostructures and that one of the sources of energy needed to reorganise the damaged surface is the heat provided during irradiation.[16], [31], [33], [56] Molecular dynamic simulations of polycrystalline silicon nanowires irradiated with 16 keV gallium ions showed that after the thermal spike phase of an atomic collision cascade, a lower temperature of a few hundred °C remains for about 140 ps.[56] According to the simulations, this temperature anneals out most of the defects generated during irradiation and allows rearrangement of the damaged surface. In the experiments presented here, the germanium nanowires are concluded to have bent towards the ion beam due to surface rearrangement, similarly taking advantage of the heat provided during irradiation. As each incoming ion generates defects and induces dynamic annealing processes, once the irradiation stops and the last ion has interacted with the nanowire the surface remains damaged but no more thermal energy is provided above the ambient conditions. During annealing the elevated temperature can reactivate the rearrangement of the disturbed surface, thus causing the curvature to increase as the surface reconstruction continues.[15]

3.0 Conclusions

Germanium nanowires have been observed to undergo IIB under irradiation with xenon ions at room temperature. The nanowires showed a preference for either bending away or towards the ion beam depending on the normalised damage distribution, Ω . It was observed that nanowires with $\Omega \leq 0.34$ bent away from the ion beam whilst nanowires with $\Omega \geq 0.36$ bent towards it. The normalised damage distribution, Ω , can therefore be used to predict the bending direction of the nanowires. When the driving mechanisms were close to balancing at $\Omega \approx 0.35$, the nanowires were observed to alternate between bending slightly away or towards the ion beam at the start of the irradiation before continuously bending in a definite direction as irradiation continued.

The annealing of bent ion-irradiated germanium nanowires at 440°C has been performed in order to recover crystalline nanowires. Shape modification of the bent nanowires was observed during SPEG and the nature of the shape changes was found to depend on the initial bending direction. Nanowires that bent towards the ion beam (concluded to be due to surface rearrangement) bent further during annealing. This is attributed to the reactivation of surface rearrangement by the thermal energy provided during annealing. Conversely, nanowires which bent away from the ion beam subsequently straightened during recrystallisation. As damage accumulation is thought to induce the bending away of nanowires, it is reasonable to assume that annealing of the defects during recrystallisation similarly caused the nanowires to straighten.

In conclusion, annealing can be used as a way to reverse bending after ion irradiation for conditions under which a nanowire bends away from the ion beam – i.e. with $\Omega \leq 0.34$ in the present work. For higher values of $\Omega \geq 0.36$, the nanowire cannot be straightened by annealing as the curvature of bending actually increases when SPEG is induced.

As a tool to modify the structure and geometry of nanomaterials, ion irradiation can be an efficient technique if it is predictable, reproducible and if any deleterious effects can be repaired. The experimental work and IDRAGON calculations reported here have shown that the behaviour of the nanowires during IIB and annealing can be forecast based on the normalised damage distribution, Ω .

Furthermore, the bending can be reversed by annealing but only for a certain range of values of Ω which correspond to bending away from the ion beam.

Experimental details

Single-crystal intrinsic germanium nanowires were synthesized on silicon wafers using chemical vapour deposition (CVD) via the vapour-liquid-solid (VLS) method by Nanowire Tech Ltd (product number GNWsI15). To remove the nanowires, the wafer was placed in an ultrasonic bath of ethanol at room temperature. The solution was then dispersed onto molybdenum TEM grids and allowed to dry under ambient conditions.

The angle, α , between the ion beam and the plane normal to the nanowire axis is defined such that an angle of 0° indicates that the irradiation is incident normal to the nanowire axis. As the nanowires were dispersed randomly on the grid, α could potentially vary between 0° and 90° . The sample preparation method was designed to produce isolated nanowires which were not agglomerated into entangled clusters as this could prevent, limit or otherwise perturb bending during irradiation. The nanowires were found to be between 15 and 60 nm in diameter and from 100 nm to 2 μm in projected length from the TEM grid bar into free space.

Irradiations were performed at the Microscopes and Ion Accelerators for Materials Investigation (MIAMI-1) facility. MIAMI-1 is equipped with a JEOL JEM-2000FX TEM which was operated at 200 kV and is coupled with an ion accelerator capable of delivering ions with energies up to 100 keV at an angle of 30° to the electron beam.[57] Irradiations were achieved using 30 or 70 keV xenon ions to explore the effects of the damage range on the bending direction. The typical ion flux was 10^{13} ions. $\text{cm}^{-2}.\text{s}^{-1}$ and the irradiations were performed at room temperature. To calculate the range of the induced damage and implanted ions in the germanium nanowires, the open-source *Ion Damage and Range in the Geometry Of Nanowires* (IDRAGON) code was used. IDRAGON is a Matlab-based implementation of the *Stopping and Range of Ions in Matter* (SRIM) Monte Carlo computer code.[58] Natively, SRIM considers only the interaction of ions with a flat target. IDRAGON divides the nanowire into 100 slices

which when put together represent the circular cross section of the nanowire. Version 2013 of SRIM was run in the “Detailed calculation with full damage cascades” mode for 1000 ions per slice using a displacement energy of 21 eV.[59] The resulting atomic displacement events determined by SRIM were used to calculate the displacements per atom (dpa).

Pre- and post-irradiation tilt-series were captured in order to determine α and the direction of the induced bending. A schematic of the tilting procedure is shown in figure 5. This was necessary as it is possible for a nanowire to appear straight when viewed in projection in the TEM but actually to be bent in the direction of the optical axis of the microscope (z-axis). Similarly, as a nanowire can be inclined out of the xy-plane of the TEM, using the tilting procedure allows α to be correctly determined.

After irradiation, to induce SPEG the nanowires were annealed at 440°C using a Gatan 652 double-tilt heating holder which allows both the tilting procedure and control of the temperature. BF-TEM and DF-TEM images were taken to follow the morphological and structural evolution of the nanowires during irradiation and annealing. SADPs were captured to characterise crystallographic changes.

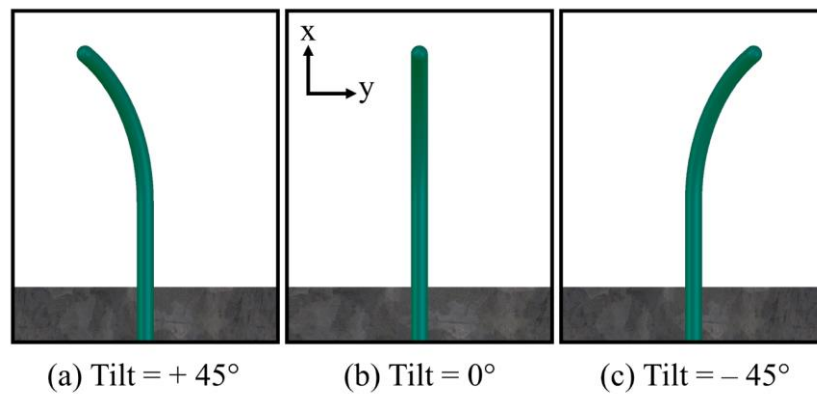


Figure 5. Schematic diagram showing an example of changes in appearance of a nanowire when viewed in the TEM (i.e. the TEM image plane) during tilting from +45° to -45°: (a) the bent nanowire appears bent to the left when it is tilted to +45°; (b) appears straight when observed at a 0° tilt angle; and (c) appears bent to the right when tilted to -45°. Tilting with the goniometer x-tilt to +45° and -45° reveals that, in this case, the nanowire is bent upward. An unbent nanowire would remain straight in projection when tilted whilst the image of a nanowire bent downwards in the TEM would appear reversed in (a) and (c).

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Supporting Information

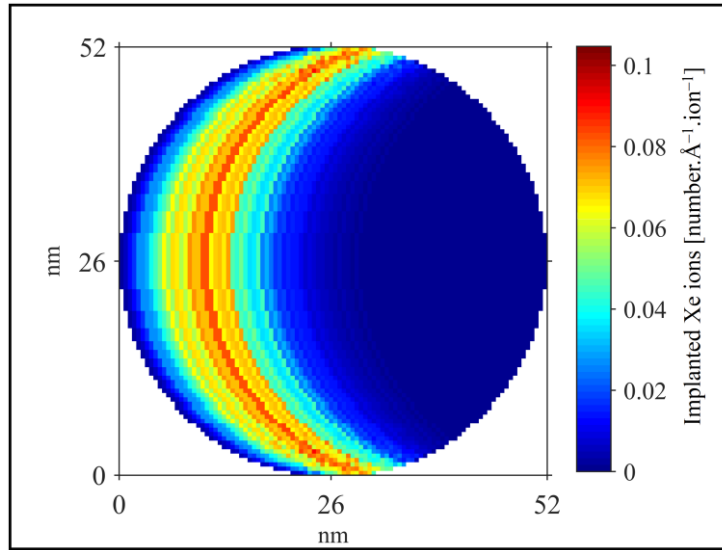


Figure S1. Calculated implantation profile using IDRAGON on the nanowire displayed in figure 1(b) under 30 keV xenon irradiation at $\alpha = 37^\circ$.

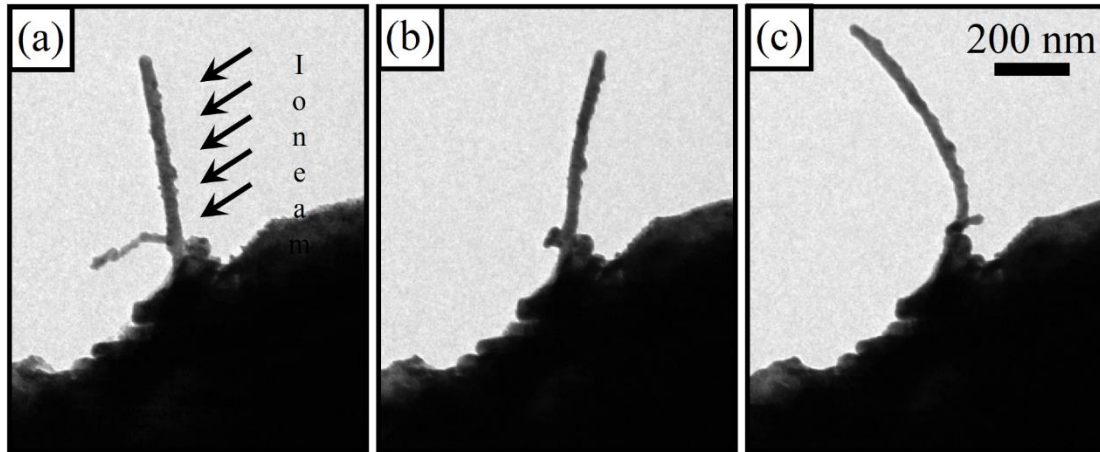


Figure S2. BF-TEM images showing the evolution of a $\varnothing = 40$ nm germanium nanowire at room temperature under conditions where $\Omega=0.35$: (a) before irradiation; (b) after irradiation with 30 keV xenon to a fluence of 1×10^{14} ions.cm $^{-2}$ resulting in the nanowire bending slightly towards the ion beam; and (c) after irradiation to a fluence of 3×10^{14} ions.cm $^{-2}$ resulting in the nanowire bending away from the ion beam. The projection of the direction of the ion beam onto the image plane is represented by the arrows in (a). The scale bar in (c) applies to all the images in the figure.

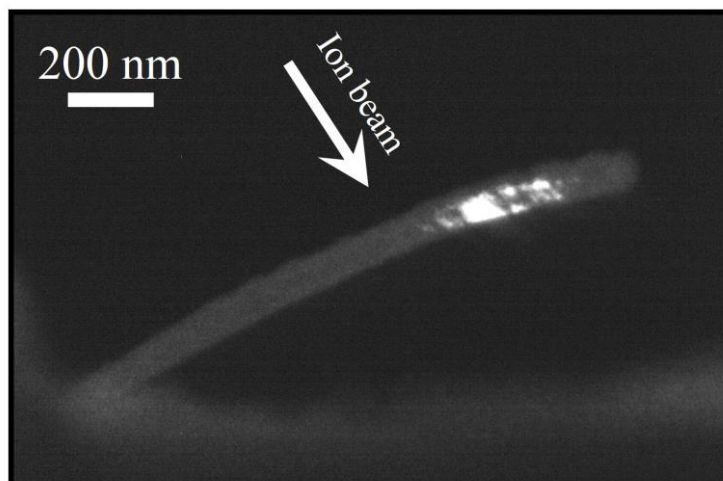


Figure S3. DF-TEM image showing the nanowire featured in figure 1(b) formed with a {220} reflection. The bright part in the DF image confirms the presence of a crystal in the rear-side of the nanowire directly adjacent to a darker region in the ion-beam-facing side of the nanowire. As the nanowire is bent, the crystalline regions of the nanowire do not satisfy the Bragg condition all along the deformed nanowire. The projection of the direction of the ion beam onto the image plane is represented by the arrow.