Nanostructuring Germanium Nanowires by In Situ TEM Ion Irradiation

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1. Introduction

Modifying the features of materials at the nanoscale may significantly affect their properties. This may include the direct building of nanoscale objects such as nanowires,[1] or the alteration of materials at the nanoscale by, for instance, engineering nanoholes in thin films.[3,4] By using these processes, materials can be functionalized to gain new properties or have existing ones enhanced.[3,5-8] Understanding the fundamental aspects of such modifications is necessary in order to be able to fully exploit material properties for applications in areas such as biomedicine,[9] electrochemistry,[10] and electronics.[11]

One example of a polyvalent nanostructure is the semiconductor germanium nanowire. Many attempts have been made to grow high-quality germanium nanowires as they can be deployed in a wide range of devices such as batteries,[12,13] field-effect transistors,[14] and optoelectronic devices.[15] Furthermore, there is a relevant interest in germanium due to, for example, the relatively high-charge-carrier mobility.[16] Germanium nanowires are considered particularly interesting as they can bring additional advantages such as a better resistance to tensile stress,[17,18] a higher adaptability to the cyclic volume changes occurring when they are being used as the anode in batteries,[19,20] and an easier propensity to quantum confinement compared to silicon nanowires (owing to their larger exciton Bohr radius).[20] The surface to volume ratio then allows germanium nanowires to efficiently partake in chemical or physical reactions at their surfaces.[21]

On the other hand, as stated above, instead of making nanomaterials, another route is to modify the surface of bulk materials to form nanostructures. For this purpose, it has been proposed in the literature to use ion beams to nanostructure several semiconductor materials such as gallium antimonide, indium antimonide, gallium nitride, and germanium.[22-29] Indeed, it is reported that these materials can become nanoporous when subjected to ion bombardment.[22-29] The use of ion beams to induce nanopores in germanium is attractive as nanoporous germanium is interesting for integration in photovoltaic cells, batteries, microelectromechanical systems or gas and bio sensors.[22,30,31]

Whilst the exact characteristics of the mechanisms are still being investigated, it is generally accepted that the nanoporosity is the result of void formation by the agglomeration of vacancies.[22-29] The voids are first observed in germanium...
when the fluence is above $10^{15}$ ions cm$^{-2}$ as the irradiated material gradually takes on a nanoporous form (also referred to as a honeycomb or foam-like structure).\[22,32\] The vacancies which may form the nanopores are induced during ion irradiation in the collision cascade. Consequently, the thickness of the nano-structured layer is related to the ion beam energy and is thus restricted by the penetration depth of the ions.

At the crossroad between the two nanoengineering methods mentioned above (i.e., growth of nanowires and engineering nanoporous materials), we propose to combine the two approaches as a way to also combine their advantages, by using the ion beam as a means of inducing nanopores in germanium nanowires. Furthermore, using such a method might also overcome one of the limitations of this nanostructuring technique. Indeed, various authors including Rudawski et al. have shown that in thicker target materials the porous structures were not formed in all the volume of the materials, but were restricted to the surface and subsurface, even at high fluences.\[22,29\]

In this work, germanium nanowires were synthesized via the vapor–liquid–solid (VLS) growth mechanism and were irradiated in situ within a transmission electron microscope (TEM). As will be shown, the use of in situ TEM tomography, high resolution microscopy as well as ion irradiation performed at elevated temperatures will allow both the unravelling of the characteristics of the nanostructuring technique and the exploration of the consequences of using such methods on nanowires.

2. Results and Discussion

2.1. Morphology of the Nanostructured Nanowires

Germanium nanowires were irradiated by 300 keV xenon ions in situ within a TEM. A bright field TEM (BF-TEM) image of a germanium nanowire before and after irradiation at room temperature (RT) to a fluence of $3.2 \times 10^{15}$ ions cm$^{-2}$ is shown in Figure 1a,b, respectively. The figure confirms that the nanowire is nanoporous after the irradiation. Whilst contamination can be considered minimum during an irradiation performed within the TEM chamber, the ions used for irradiation may impact the experiments as they can accumulate and form gas bubbles.\[33\] However, the typical Fresnel fringes typically observed around gas bubbles when recorded out of focus in a TEM were not detected in this work, thus, indicating that the nanopores were not xenon gas bubbles.\[33\]

To overcome the TEM limitations in terms of spatial information, a tilt series was performed allowing the 3D reconstruction of the nanowire. The tilt series and the 3D reconstruction of a section of the nanowire is shown in Figure 2a,b, respectively. It is worth noting that whilst artifacts can occur in tomographic reconstructions based BF-TEM images of crystalline materials (due to diffraction contrast being interpreted as thickness variations); here this issue is avoided as the nanostructured nanowire is fully amorphous after irradiation at such high fluences with the heavy ions. These figures reveal that the nanostructures are present in all the volume of the nanowire and not just on the ion-beam facing side of the nanowire. This contrasts with other works in the literature where the nanostructuring is limited to the surface of the target material when the irradiation is performed on thicker specimens.\[22,29\] However, this should be expected, as in the current work the ion beam is able to penetrate the whole target material due to the relatively small thickness (i.e., diameter) of the germanium nanowires. Therefore, whilst in bulk material the efficiency of this nanostructuring technique may be limited and depends on
the ratio between the porous layer and the non-porous layer, the use of ion beams to induce nanopores is particularly suitable for nanowires.

The 3D reconstruction and the tilt series confirmed that the nanopores were cylindrical or spherical. In fact, as it will be shown later, the diameters of the nanopores were observed to increase as a function of fluence. This is in contrast to previous works in the literature in which the nanopores diameter did not increase continuously with the fluence. [22,26] For example, Alkhadi et al. [26] during self-ion irradiation of bulk germanium, did not observe an increase of the pore diameters but, instead, an evolution of the nanostructures from spherical, when they emerged, to nanopores of relatively small radius (10–20 nm), although elongated in the direction of the ion beam at higher fluences.

Typically, the elongated nanopores in germanium can be several hundred nm long. [22,26,29] In this work, as such elongation was limited due to the reduced dimension of the target material such long cylindrical nanopores were not formed and the nanostructuring has instead led to an increase of the nanopores diameter as a function of fluence. The tilt series as well as the BF images and the in situ high resolution TEM (HR-TEM) video (Video S1, Supporting Information) showed that the nanovoids grew whilst remaining relatively circular. It was observed that their diameters could reach more than 90 nm as their volume growth was only limited by the surface of the nanowire or by adjacent pores. In this latter case, the spherical pores were smaller and were superimposed on top of each other. This can be more clearly seen in Video S2, Supporting Information revealing more details of the 3D reconstruction. Whilst the nanowire shown in Figures 1 and 2 demonstrates that the ion beam can be used to induce nanostructures which are more spherical than in the bulk, it will be shown that the shape of the nanostructures can become more complex at higher fluences, exhibiting novel features. An example of such features, increasingly observed at higher fluences, is shown in Figure 2: these are 2D sections referred as planar nanobands, which will be described below.

When observing the nanowire in Figures 1 and 2, one can notice that the wall between nanopores is more or less the same thickness. In fact, walls between nanopores also shared the same thickness during irradiation even though their thickness decreased during nanostructuring. This behavior was similarly reported in the literature during irradiation of bulk germanium as the thickness of the walls was shown to decrease until it becomes small enough to allow the passage of vacancies between nanopores. [26]

As shown in Figures 1 and 2, the nanowire’s outer layer (i.e., the side walls) also changed during irradiation. As nanopores have either reached the surface or are only a few nm away from it, the shape of the nanowires’ side wall is defined by that of the nanopores. After nanostructuring, both the roughness of the nanowires’ side walls and the walls between adjacent nanopores can be of technological interest. For instance, using ion beams to induce nanopores in germanium, Cavalcoti et al. showed that the presence of the walls between nanopores was beneficial as their reduced dimension could lead to quantum confinement and light trapping. [31] Similarly, engineering the roughness of the nanowire via ion beams may also be of practical use, as it was shown in the literature that the presence of ripples on the surface of ion bombarded germanium could induce light trapping. [34,35]

The BF-TEM images in Figure 3 show the evolution of another germanium nanowire during the in situ ion irradiation (the nanowire evolution can also be seen in Video S3, Supporting Information). The BF-TEM image in Figure 3a shows the nanowire before irradiation whilst Figure 3b shows the nanowire when the morphological changes just start to be evident (i.e., at a fluence of $1.3 \times 10^{15}$ ions cm$^{-2}$). At this fluence, the mean damage dose is 14 displacement per atom (dpa). [16] Hence, at $1.3 \times 10^{15}$ ions cm$^{-2}$ the nanowire is completely amorphous due to the damage caused by the xenon ions. In the BF-TEM images, the regions where the electron beam encounters less material are brighter and correspond to voids in the nanostructured nanowire. As the fluence increases to $4.2 \times 10^{15}$ ions cm$^{-2}$ in Figure 3a–e, it becomes clear that more regions with voids appear and/or occupy a larger volume of the nanowire.

Figure 3 shows that the nanowire’s surface becomes progressively rougher as a result of the nanostructuring. Whilst surface roughening has been previously reported on the ion beam facing side of bulk specimens, [22] here the roughening occurs all around the nanowires (this was also confirmed by the tilt series and the 3D reconstruction). Another consequence of the irradiation was the change of shape of the nanowires. Indeed, the nanowire shown in Figure 3d–i is bent and has a zigzag shape. It might be argued that the deformation of the nanowire’s shape is due to the ion-induced bending (IIB) effect. [37–39] However, here, the bending seems to occur as a result of the nanostructuring: it is observed only when the sample becomes nanoporous and only if the fluence is relatively high (i.e., at $3.3 \times 10^{15}$ ions cm$^{-2}$). On the other hand, when IIB is observed on germanium nanowires, the shape modification occurs almost immediately after the irradiation starts and leads to a bending either toward or away from the ion beam and not to the weave-like shape displayed in Figure 3. [37,40] It must be noted that in the previous work, where the target material was thicker, the bending was not reported during nanostructuring. [41–43] This is probably due to the fact that the irradiated layer was supported by a non-porous layer which limited the deformation of the film during nanostructuring.

The thickness of the germanium nanowires changed during the irradiation as a function of fluence. As with previous authors, who observed an out-of-plane swelling of the irradiated films during nanostructuring, [29] the nanowires irradiated in the present work also swelled during irradiation.

However, it could also be seen that once the irradiation reached a threshold fluence ($4.2 \times 10^{15}$ ions cm$^{-2}$) the trend was reversed as the nanowires started to shrink. Figure 3a–i illustrates such diameter change as the nanowire which has been irradiated to a relatively high fluence (i.e., $8.4 \times 10^{15}$ ions cm$^{-2}$) was observed to first swell and then shrink. To quantitatively characterize the swelling and shrinking of the nanowire, the evolution of its diameter had to be monitored. However, because the diameter of the nanowire is not uniform along its length during irradiation, the graph displayed in Figure 3j shows diameters which have been measured at several locations along the nanowire as a function of ion fluence.
The graph reveals that the change of thickness of the nanowire really becomes apparent above $10^{15}$ ions cm$^{-2}$, which is also the fluence at which the nanostructures become evident. This observation confirms that together with the aforementioned bending of the nanowire, swelling is a direct consequence of the nanostructuring.

The swelling during nanostructuring is expected to be proportional to the volume occupied by the pores within the irradiated material. Yet, this assumption is only reasonable at the first stages of the irradiation, as long as the irradiation induces the formation of mostly 3D nanopores. However, at high fluences (i.e., above $4.2 \times 10^{15}$ ions cm$^{-2}$), it will be shown below that more and more sections within the nanowires must be thin planar regions (i.e., planar nanobands such as the one shown in Figure 2) instead of nanopores. For instance, a few of these regions are indicated in Figure 4a which shows the nanowire after irradiation to a fluence of $8.4 \times 10^{15}$ ions cm$^{-2}$. It should be noted that whilst the two nanobands indicated in Figure 2 were induced within areas which are not supported by the carbon films, in general nanobands were formed regardless of the presence of the carbon film.

Such areas of the nanowire have a brightness as intense as the brightness given by the carbon film, meaning that the electron beam could only have encountered, at most, a very thin layer of germanium atoms. Furthermore whilst it might be difficult to interpret images captured using a TEM (as they are the result of transmitted electrons), the tilt series and the 3D reconstruction shown in Figure 2 have also confirmed the existence of such thin regions. The formation of these nanobands should be facilitated by both the sputtering (which may remove layers of germanium atoms), and by the possibility of nanopores to reach the surface of the nanowires. As the planar nanobands become more prevalent during irradiation, it must be noted that even though in this work we use the terms “diameters” and “nanowires” to talk about the target material, at relatively high fluences these structures cannot really be considered as having a wire-like shape anymore, as they become complex nanostructures encompassing large planar nanobands. The properties and applications of these nanostructured “nanowires” might merit further investigations in the future. For instance, charge carriers in these planar nanobands may be subject to quantum confinement due to the reduced thickness of such sections.
2.2. Formation and Stability of the Nanostructures at High Temperatures

In situ ion irradiation experiments have been carried out under the same conditions (i.e., ion beam species, energy, target material, and flux) but at elevated temperatures. Using the SADPs to monitor the microstructure of the nanowires after irradiation, it was determined that even at high fluences (above $3.4 \times 10^{15}$ ions cm$^{-2}$) the nanowires remained crystalline when the irradiation was performed at 500, 450, 400, and 350 °C. As shown in Figure S1, Supporting Information, even at such high fluences nanopores were not formed and the overall shape of the nanowire did not change even though some moderate sputtering was observed on the nanowire outer layer (i.e., the side walls) which also became smoother after irradiation. However, when the xenon irradiation was performed at 300 °C, the nanowires became fully amorphous after just a fluence of $8 \times 10^{14}$ ions cm$^{-2}$. Likewise, the ion beam was unable to nanostructure the nanowires when the irradiation was performed at 500, 450, 400, and 350 °C but made the nanowires nanoporous when irradiated at 300 °C. At 300 °C, the nanostructures became evident at a fluence $=0.6 \times 10^{15}$ ions cm$^{-2}$, which is significantly lower than the fluence at which the nanoporous structures were also observed when the irradiation was performed at RT. When ion irradiation is performed at elevated temperatures, the competition between damage accumulation and damage annealing is the determining factor as to whether the material amorphizes, thus, amorphization can be prevented if the temperature is high enough. The inability of the xenon ions to induce the formation of nanopores above a threshold temperature is in agreement with the literature as the nanostructuring is always reported to occur after the material has become amorphous. However, this threshold temperature varies in the literature as the tipping point at which the damage accumulation rate is greater than the damage annealing depends on the experimental conditions (e.g., mass of the accelerated ions, flux, etc.).

After irradiation, the nanowire shown in Figure 3 was annealed for 5 min at 530 °C. Figure 4a,b show the BF-TEM image of the nanowire and its SADP before and after annealing, respectively. As revealed by the figures, the nanowire structure changed from amorphous prior to annealing to polycrystalline as a result of random nucleation and growth. The nanostructuring formed during the irradiation remained mostly stable during the annealing, whereas a few morphological alterations occurred. As shown in Figure 4, the nanowire became slightly thinner whilst several other morphological features, such as the ones indicated by the large black arrows in Figure 4b, were also altered. It is worth noting that mass transport and morphological changes are facilitated during crystallization and it was observed in a previous work that the shape of irradiated germanium nanowires can evolve during recrystallization. In fact as the amorphous phase of germanium is less dense than its crystalline phase, the aforementioned shrinking is to be expected as the density of germanium will change during recrystallization. In the literature, it was for instance shown that after annealing of amorphous nanoporous germanium, the thickness of the wall between nanopores decreased of approximately 20%.

As stated in the introduction, the formation of the nanopores is considered to be the result of an agglomeration of vacancies induced by irradiation. Here, even at high fluences, amorphization was not observed above a threshold temperature (i.e., 300 °C), suggesting that the thermal energy was high enough to readily allow a recombination of point defects (i.e., vacancies and interstitials) and consequently prevent the agglomeration of vacancies. Under these conditions, the formation of nanopores was thus prevented. Furthermore, the fact that the nanoporous structures were only observed in the amorphous phase is expected. Indeed, the formation of nanopores must require bond rearrangements, mass transport, and deformation of the target material, and these phenomena occur more readily in the amorphous phase. Interestingly, Holland et al. showed that germanium specimens irradiated below $-196$ °C did not exhibit nanoporosity. At such low temperatures, the reduced mobility of the vacancies may prevent their agglomeration and thus the formation of the nanoporous structure.

2.3. Impact of Temperature and Fluence on the Nanopores Size

As stated above, the thickness of the nanowire varies with the ion beam fluence (and thus to the number of vacancies). However, to have a better correlation between the growth of the nanopores and the fluence, HR-TEM was performed, allowing the observation of the evolution of a nanopore during irradiation (see Video S1, Supporting Information). As HR-TEM imaging was performed, a reduced field of view was imaged, meaning that the quantitative analysis was thus restricted to two nanopores. A video frame showing these two nanopores and the corresponding plots of their volumes as a function of ion beam fluences is displayed in Figure 5. It is evident that the volume of the nanopores did not increase linearly, as the growth rate increased during the irradiation. If the growth of the nanopores is caused by agglomeration of vacancies, it should be proportional to the probability of absorbing a vacancy. Consequently, if the probability of a pore to absorb a vacancy was constant during irradiation, the growth of the pore as a function of fluence would be linear. However, as the volume of the pore

Figure 4. a) BF-TEM images and selected area diffraction pattern (SADP) of a germanium nanowire after irradiation at RT with a 300 keV xenon ion beam to a fluence of $8.4 \times 10^{15}$ ions cm$^{-2}$ and b) after annealing at 530 °C for 5 min. The SADP in (a) reveals that the nanowire is amorphous and the SADP in (b) shows that the nanowire has crystalized and is polycrystalline. The scale bar in (a) also applies to (b).
is increasing, so does its surface. If vacancies are induced in the vicinity of the nanopore’s surface, they are more likely to be absorbed into the nanopore. Consequently, with growing surface area, more surface is available for vacancy absorption, and hence the growth rate of the pore must also increase during irradiation. The growth of the nanopores monitored during irradiation is therefore in agreement with a vacancy-based mechanism.

Above a fluence of $2 \times 10^{15}$ ions cm$^{-1}$, the shapes of the two nanopores shown in Figure 5 diverge from the ideal spherical form as their projections appear as ellipses in the HR-TEM images. Furthermore, the relatively high magnification used to follow the evolution of these nanopores only allowed a limited section of the nanowire to be monitored. Consequently, to better grasp the nanopores’ overall shapes and sizes, a larger section of this nanowire was analyzed after irradiation. For the quantitative analysis, only the nanostructures which appeared in the TEM images as pores were considered; meaning that the porosities open toward what is viewed as the side of the nanowires in the micrographs were excluded. The mean area of the nanopores ($A$) as seen in projection in the TEM image plane and the mean aspect ratio ($r$) of the nanopores were determined following the irradiation (i.e., at a fluence of $3.2 \times 10^{15}$ ions cm$^{-1}$ at RT) as shown in Figure 6a,b, respectively. Likewise, Figure 6a,b also shows $A$ and $r$ for a nanowire (shown in Figure S2, Supporting Information) which was irradiated at an equivalent fluence but at 300 °C, thus allowing comparisons to be made between the two irradiation conditions.

The results shown in Figure 6a indicate that the pores induced at 300 °C are much larger than those formed at RT ($A$ is measured to be more than 3 times larger after the 300 °C irradiation). Furthermore (as detailed in Table S1, Supporting Information), it must be noted that on the nanowire irradiated at RT most pores had a value $A$ below 500 nm$^2$ whilst at 300 °C most pores measured between 500 and 1000 nm$^2$. However, even though both at RT and at 300 °C, the size distribution of the nanopores is rather large as the standard deviation is 526 nm and 1400 nm, respectively, it is substantially larger at 300 °C. Similarly the standard deviation of the aspect ratio is larger at 300 °C than at RT (0.6 and 0.4, respectively). As it will be shown below, the larger standard deviations at 300 °C may be due to the formation of a few particularly large and elongated

![Figure 5.](image-url)
nanopores. Furthermore, as illustrated in Figure 6c,d, showing the two largest nanopores induced at RT and 300 °C, respectively, the irradiation performed at elevated temperatures were able to induce much larger pores than the RT irradiation. Interestingly, this means that whilst the literature shows that performing the irradiation at an elevated temperature may inhibit the formation of the nanopores (as also confirmed in this work), it can also facilitate the growth of larger nanopores. Yet, even though in the current work the nanopores are larger after the elevated temperature irradiation, a loss of circularity was induced as the average aspect ratio of the nanopores is 13% higher at 300 °C than at RT. Furthermore, as illustrated in Figure 6d, large nanopores induced at 300 °C were particularly elongated in the direction of the nanowires’ axis, as their growth was limited by the outer surface of the nanowire. Upon irradiation, nanopores may grow by merging with adjacent nanopores or via assimilation of the vacancies generated by the ion beams. As observed during the in situ irradiation (Figure S3, Supporting Information), nanopores were monitored merging along the nanowire axis resulting in the formation of particularly elongated nanopores. As atomic transport is increased at elevated temperatures, such merging arose more readily at 300 °C. On the other hand, the growth of nanopores via assimilation of the vacancies (or via merging of nanopores distributed across the nanowire diameter) can induce the formation of planar nanobands. Indeed, large spherical nanopores (e.g., Figure 6b) may grow and reach as far as the nanowire surface. In this case, either a planar surface will be formed or the nanowire will break depending on how many of the nanopores have broken through the nanowire surface.

Whilst future work relative to the effect of temperature may help to determine at which temperature the nanopores’ growth rate is the fastest as well as how the characteristics of the nanopores and the nanostructures precisely evolve as a function of temperature, the differences shown in Figure 6 can already be interpreted in terms of the increased defect mobility at 300 °C. Indeed, as vacancies are more mobile at elevated temperatures, their agglomeration into larger nanopores is facilitated. Similarly, as stated above, the elevated temperatures will also facilitate the merging of adjacent nanopores. This contrasts with the two situations described above where the formation of nanopores is inhibited because the temperature is either too low and the point defects are not mobile, or the temperature is too high and dynamic annealing prevent amorphization.

Typically, ion beams are reported to induce in germanium the formation of a porous layer at RT at a minimum fluence of approximately 10^{15} ions cm^{-2}\textsuperscript{[22]}. In this work, at RT, nanostructuring has been evident at similar fluences. However, it is critical to consider the fact that the experiments reported in the literature were carried out ex situ or in situ within a FIB-SEM.

Figure 6. a) The mean projected area, A, and b) the mean aspect ratio, r, are shown for the two irradiation conditions. As indicated in the figure, the nanowires were irradiated at RT and at 300 °C. In both cases the nanowires were irradiated by the 300 keV xenon ion beam at a fluence of \textasciitilde3.2 \times 10^{15} ions cm\textsuperscript{-2}. c) BF-TEM images showing the two largest nanopores induced by the irradiation at RT and d) the irradiation at 300 °C. For each of these nanowires, the value A and r are indicated in the figures. A perfectly equiaxed nanopore is indicated by r = 1. The yellow arrows within the nanopores serve as a way of identifying the nanopores of interest and are a guide to the eye illustrating their aspect ratio. The scale bar in (c) also applies to (d).
thus, generally not providing insights into the early stages of the nanostructuring. In the current work, the HR-TEM performed on the nanowire shown in Figure 5 have shown that the nanostructuring starts at a much earlier stage (i.e., almost immediately after the nanowires become amorphous). For instance, when the region containing the two nanopores shown in Figure 5 was first imaged, the nanopores had already started to develop even though the fluence was as low as \(2.2 \times 10^{15}\) ions cm\(^{-2}\). Whilst the presence of these two nanopores was detected at such low fluences, the formation of these or other nanopores at an earlier stage cannot be excluded. Indeed, because imaging smaller pores during in situ ion irradiation might be challenging, the possibility that regardless of the temperature the nanostructuring starts as soon as the target material is amorphous must be considered.

3. Conclusion

The ion irradiation of germanium nanowires has led to nanostructuring and the impact of the nanostructuring technique has been revealed for the first time on a nanowire. As compared with the more conventional use of ion beams to induce nanostructures on thicker material, it was shown that the ion beam could cause more drastic changes in a nanowire. For instance, the ion beam induced the nanoporous structures in all the volume of the nanowires (and not just at the surface of the target material), thus making such nanostructured nanowires promising materials for applications where a large surface to bulk ratio is required. It also induced bending of the nanowires, formation of large spherical nanopores, and a swelling which represents a considerable proportion of the nanowire’s initial diameter. It was also shown that above \(4.2 \times 10^{15}\) ions cm\(^{-2}\) other nanostructures appear, the nanowire diameter decreases, and its wire-like shape is lost. Furthermore, because the in situ experiments have also demonstrated that such changes happen gradually during irradiation and start at very low fluence, this work demonstrates that ion beams can allow the transformation of nanowires to various levels of nanostructuring just by varying the ion beam fluence or the temperature of irradiation.

4. Experimental Section

Single crystalline germanium nanowires were grown on a germanium substrate via the VLS growth process at the Institute of Materials for Electronics and Magnetism from the National Research Council (IMEM-CNR). More details about the growth technique and the properties of these germanium nanowires can be found in refs. \cite{1,45}. The nanowires chosen for irradiation had diameters ranging from 80 to 90 nm and lengths up to 30 µm. To remove the nanowires from the substrate, ultrasonication was performed in ethanol at RT for 5 min. After dispersion of the nanowires in the ethanol, a drop of the solution was deposited onto a molybdenum TEM grid covered by a holey carbon film.

The irradiations were carried out at the Microscopes and Ion Accelerators for Materials Investigations (MIAMI-2) facility which allowed in situ TEM ion irradiation. \cite{46} The nanowires were irradiated at normal incidence with a 300 keV xenon ion beam at a flux of \(\approx 10^{13}\) ions cm\(^{-2}\) s\(^{-1}\) within a Hitachi H-9500 TEM. The ion beam energy was such that the average damage range (\(\approx 80\) nm), was equal to the nanowire diameter, meaning that the radiation damage was induced in the entire nanowire. The damage range was determined via the software package, Stopping and Range of ions in Matter (SRIM) which simulates the interaction between the ions and the target material using Monte-Carlo calculations. \cite{47} SRIM calculations were made using a displacement energy of 21 eV for germanium atoms, and the dpa was determined using SRIM in “detailed calculation with full damage cascades” mode. \cite{48}

The experiments were performed using a Gatan double-tint TEM heating holder (model 652). The TEM holder allows the heating of the sample to temperatures high enough to prevent amorphization during irradiation at elevated temperatures. Furthermore, when the irradiation was performed at RT (conditions under which amorphization is possible), the heating holder was used to crystallize the germanium nanowires. To induce crystallization of amorphous nanowires, they were heated to a temperature of 530 °C for a duration of 5 min. Afterward, SADPs were acquired to monitor the microstructure of the nanowires and thus confirm that crystallization had occurred. Furthermore, SADPs were also used to monitor whether amorphization was induced during the irradiations performed at temperatures ranging from 500 °C to RT (i.e., at 500 °C, 400 °C, 300 °C, and at RT). To confirm the reproducibility of the nanostructuring, the same ion irradiation experiments were repeated on two additional germanium nanowires at RT and one at 300 °C.

Video recordings acquired during in situ experiments (see Videos S1 and S3, Supporting Information) were used to obtain qualitative and quantitative information related to the evolution of the nanowires’ nanostructures, diameter, and shape during irradiation via the still video frames. BF-TEM image mode was used to monitor a relatively large section of the nanowires during irradiation. In addition, in order to resolve relatively small nanopores, HR-TEM was used to better observe nanopores at an early stage and monitor their growth.

For further, quantitative analysis, in-house MATLAB script was used. Majority of nanopores could be segmented automatically by adaptive threshold, \cite{49} whilst the outlines of overlapping ones were created manually. The script was then used to determine the area of the nanopores as seen in the TEM images and their aspect ratios. The aspect ratio was used as a basic shape descriptor where a value of 1 illustrates equiaxed nanopores (which appear more circular on the TEM images) and higher values were attributed to elongated ones. The quantitative analysis was carried out on one nanowire irradiated at RT and on another irradiated at 300 °C on a \(\approx 2.5\) µm long section. The aim of the analysis was to compare the characteristics of nanopores induced at different temperatures of irradiation but under otherwise similar conditions (i.e., ion beam energy, fluence, material, etc.).

After ion irradiation of a nanowire at RT, a series of BF-TEM images was captured at tilt angles ranging from 0° to 112° with 2° increments. The 57 BF-TEM images acquired during the tilt series were then used to reconstruct a 3D picture of the irradiated nanowire and provide detailed information about its nanostructures. However, since only a limited data-set was available due to limited angular sampling, the Simultaneous Iterative Reconstruction Technique (SIRT) method was used, as implemented in. \cite{50} It does not overcome the missing wedge problem, however it approximates to the authentic solution while decreasing the error caused by the angular step.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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germanium, in situ transmission electron microscopy, ion beam, nanopores, nanostructuring, nanowires, radiation damage

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