In situ TEM observation of preferential amorphization in single crystal Si nanowire

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Abstract

The nanoinstability of a single crystal Si nanowire under electron beam irradiation was in situ investigated at room temperature by the transmission electron microscopy technique. It was observed that the Si nanowire amorphized preferentially from the surface towards the center, with the increasing of the electron dose. In contrast, in the center of the Si nanowire the amorphization seemed much more difficult, being accompanied by the rotation of crystal grains and the compression of d-spacing. Such a preferential amorphization, which is athermally induced by the electron beam irradiation, can be well accounted for by our proposed concepts of the nanocurvature effect and the energetic beam-induced athermal activation effect, while the classical knock-on mechanism and the electron beam heating effect seem inadequate to explain these processes. Furthermore, the findings revealed the difference of amorphization between a Si nanowire and a Si film under electron beam irradiation. Also, the findings have important implications for the nanoinstability and nanoprocessing of future Si nanowire-based devices.

Supplementary material for this article is available online

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(Some figures may appear in colour only in the online journal)

1. Introduction

It has been reported that semiconductor Si nanowires have potential applications in nanodevices owing to their special electronic and optical properties [1, 2]. However, the intrinsic nanostructural instability of Si nanowires due to their nanosize effect, especially due to their nanocurvature effect, may have negative effects on their performance and lifetime in service. Thus, it becomes imperative and crucial to study the nanostructural instability (called nanoinstability or nanoprocessing, in general) of Si nanowires especially under external excitation such as energetic beam irradiation. In this sense, the delicate, energetic field emission focused electron beam in a transmission electron microscope (TEM) has been proven to be uniquely versatile and powerful [3–5]. Up until now, the focused electron beam in a TEM has been mainly applied to create holes, gaps and other patterns on an individual Si nanowires, or to weld an individual Si nanowire with metal nanowires to form semiconductor-metal junctions [6]. In addition, Dai et al [7, 8] have reported the crystalline-amorphous transition of Si nanowires and the subsequent plastic bending, as induced by electron beam irradiation; Han et al [9, 10] have studied the axially-extending and bending of Si nanowires and the related amorphization process, which is induced by an external tension force along with electron beam irradiation; He et al [11] have realized the shear-driven dynamic amorphization process in silicon crystals using an in situ high-resolution TEM. In spite of these, the existing studies on the electron beam-induced amorphization of Si nanowires are complicated by external deformation such as bending, extending or shearing. Moreover, the amorphization of Si nanowires with a unique nanocurved wire surface is
expected to be greatly different from that of Si films with a flat planar surface [12–15]. However, in previous studies, such a difference between the electron beam-induced amorphization of Si nanowires and Si films [12–15] has not been revealed. Thus, the fundamental nanoscience, such as the nanocurvature effect [16, 17] and the energetic beam-induced athermal activation effect [16, 18] underlying the amorphization process, especially the preferential amorphization of Si nanowires during electron beam irradiation, has not been explored yet.

With the above considerations, in this paper we particularly study the amorphization of a single crystal Si nanowire under electron beam irradiation without any external mechanical force assistance. We report an intriguing preferential amorphization from the nanowire surface, which is athermally induced purely by the focused electron beam irradiation. In contrast, in the center of the Si nanowire, the amorphization that was induced during the irradiation seemed non-uniform and much more difficult, being accompanied by the rotation of crystal grains and the compression of d-spacing. These findings have important implications for nanoinstability or nanoprocessing of future Si nanowire-based devices. More importantly, the findings demonstrate that the current knock-on mechanism [19] and the electron beam heating effect [6, 20, 21] are inadequate to explain these processes, but our proposed nanocurvature effect and energetic beam-induced athermal activation effect obviously dominate the processes.

2. Experimental

Single crystal Si nanowires synthesized by the chemical vapor deposition method were firstly treated in 5% hydrofluoric acid for 10 min, then dispersed and diluted in 99.7% ethanol, and finally collected on holey carbon grids (with large holes in the electron-transparent film) to prepare TEM specimens. With such a treatment, it is expected that the oxide layer on the surface of the wires was fully removed. An in situ irradiation on the treated wire was subsequently carried out at room temperature in a field emission TEM (FEI Tecnai F30), operating at 300 kV with a focused beam of about 90 nm in beam spot diameter and a beam current density of about $1.5 \times 10^2 \text{A cm}^{-2}$. The beam was perpendicular to the wire axis and focused on the center of the wire. Also, the irradiation was performed on a settled segment of an individual nanowire protruding into the open space of the holes in the carbon film, so that local structure transformation or deformation of the wire is not hindered by any support within the holes. It is estimated that the penetration depth of such electrons exceeded the TEM sample thickness or nanowire diameter and the energy deposition rate would be uniform over all the materials in the sample [22]. During the observation or when taking a picture, the beam was spread to an around 100 times weaker intensity so that the corresponding irradiation effect could be minimized to a negligible degree and at the same time the image contrast could also be improved. In the experiment, several characterization techniques such as TEM, high-resolution TEM (HRTEM), fast Fourier transformation (FFT) and energy-dispersed x-ray spectroscopy (EDX) were applied for a detailed analysis of the shape, structure and composition of the wires.

3. Results and discussion

As shown in figure 1(a), both HRTEM and FFT images illustrated that the Si nanowire we used here was almost of a well-defined (111) single crystal structure (as indicated by Area A) before irradiation, except for a very thin amorphous layer of 3–4 nm in thickness enveloped on the surface of the wire (as indicated by Area B). Since the surfaces of the Si nanowire specimens have been fully treated via hydrofluoric acid, any possible original oxide layers on the wire surface formed during its high temperature growth should be completely removed. Thus, the observed amorphous layer here on the surface could only be a newly and preferentially formed amorphous Si layer after the chemical etching. Indeed, our further quantitative EDX analysis indicated this tendency. As is further addressed in the following discussion, with a positive activation volume [16], the amorphization
transformation can preferentially occur from the surface of a solid, where the surrounding open space can be provided for volume expansion during the amorphization. In particular for the nanowire here, its high surface energy associated with its high surface nanocurvature [16] can provide an additional driving force for such a preferential amorphization.

After irradiation for 308 s, as shown in figure 1(b), both HRTEM and FFT images demonstrated that the central part of the Si nanowire amorphized non-uniformly, for example, with an increase of amorphization degree from Area C to E. If we regard the less-amorphized areas (such as Area C and D) as crystal grains, the sizes of them are different, from several nanometers to ten nanometers or more. More intriguingly, such grain fragments are still (111)-orientated but their directions are different, Areas C and D for example. We further measured the angle between the directions of Areas C and D and got the value of 48.7 degree. This value is greatly inconsistent with that determined by crystallographic symmetry, in which the angles between any two of (111), (-1-1 1) and (1-1 1) orientations should be 109.5 or 70.5 degrees. So, it indicates that there was an adjustment or rotation of the (111) grains under electron beam irradiation. This is probably due to the surrounding space change or stress unbalance caused during the above non-uniform amorphization. Furthermore, the d-spacing values of the (111) grains in the central part of the Si nanowire were also a little different, all of which were slightly smaller than before irradiation, as shown in figure 1(a). It is expected that the amorphization in the center of the Si nanowire, accompanied by an at least 1.8% [23] volume expansion, would slightly contract or compress the d-spacing of the grains. Therefore, the amorphization in the center of the Si nanowire is incomplete and non-uniform and thus seems to be difficult. Note that the volume expansion of 1.8% is an ideal status that there is no void or vacancy in the amorphized material with a continuous network structure. However, the real volume expansion should be larger or even much larger than 1.8% due to the existence of voids or vacancies in amorphous material. In this work, the volume expansion is roughly estimated to be about 6%, which is much larger than the ideal value, probably due to a further production of voids or vacancies (see the red arrows in figure 1(b)) in the amorphous Si as caused by electron beam irradiation.

While on the surface of the wire, as shown in figure 1(c), there were three layers that could be differentiated clearly (i.e., Layers F, G and H) according to their crystal structures or image contrast. In detail, Layer F was a nearly amorphized layer and still had a crystalline structure (see the HRTEM and FFT images). Layers G and H, however, were almost amorphous with an obviously different image contrast (see the corresponding HRTEM and FFT images). Further EDX analysis shown in figure 2 illustrated that the main components of Layer G (also covered by Layer H right above) and H were silicon and carbon, respectively. The amorphous carbon layer (Layer H) probably came from the residual organic gas in the TEM chamber or the supporting organic films, which decomposed under focused electron beam irradiation and further deposited onto the surface of the Si nanowire [24]. The Layer G of amorphous Si was about 8 nm, which was much thicker than the initial amorphous Si layer in figure 1(a). It was the result of a further and complete amorphization from the wire surface during the irradiation. In contrast to the incomplete and non-uniform amorphization in the center of the Si nanowire, the amorphization on or near the wire surface seems to be much easier, preferential and uniform. Note that the near-surface Layer F of crystalline structure seems larger than the crystal grains in the wire center. This can be attributed to the different amorphization behaviors in the wire center and on the wire surface. For the specified Layer F, the side close to Layer G is suffering from a uniform amorphization from the surface toward the center and thus presents a continuous interface. Although Layer F is getting thinner and thinner, it still needs more time to get amorphized fully. Hence, we can see a long strip-like or thin layer of crystalline Si close to the amorphous Si shell at an intermediate time, such as at 308 s, as shown in figure 1(c). In contrast, for the central part of wire, it is suffering from a non-uniform and random amorphization and thus the as-formed non-amorphized areas or crystal grains exhibit a fragments-like shape. In this way, the long strip-like Layer F near the wire surface seems larger than the fragment-like grains in the wire center.

According to the conventional views, the main mechanisms of interaction between an energetic electron beam and solid materials are the knock-on mechanism [19] and the electron beam heating effect [6, 20, 21]. However, the knock-on mechanism and related simulations are neither fully consistent with, nor can offer a full explanation for the experimental observed wire structure changes, especially the above preferential
amorphization on the surface and formation of a local coaxial structure during the irradiation. This is because the electron irradiation energy for the knock-on displacement of Si atoms is about 440 keV [10], which largely exceeds the value of 300 keV applied in this work. More importantly, the existing theories such as the knock-on mechanism and related simulations were built in the first place on the consideration of the nature of equilibrium, symmetry, periodicity and linearity of a bulk crystalline structure or its approximation, whereas the energetic beam-induced nanophenomena are intrinsically of non-equilibrium, amorphous and non-linear nature. Moreover, the simulations are of roughness and the atomic movements on the scale of atomic bond lengths are difficult to be observed with current TEM techniques, and thus a direct comparison of the simulated atomic structure changes of the wires with the experimental results is impossible. On the other hand, due to the extremely high ratio of surface to volume of a nanowire at the nanoscale, the electron beam irradiation is expected to heat the specimen by no more than a few degrees [7, 19, 22, 25–27] and thus the dominant irradiation effect should be athermal, although a direct and precise measurement of the temperature of a nanoscaled TEM specimen has been rather difficult so far.

In fact, our previous work on the energetic beam, irradiation-induced structural instability and processing of low dimensional nanostructures (LDNs), such as nanocavities in Si [16, 28–31], carbon nanotubes [32, 33] and amorphous SiOx nanowires [22, 34], has proven that our proposed nanocurvature effect [16, 17] and energetic beam-induced athermal activation effect [16, 18] are universal concepts and applicable in the prediction or explanation of energetic beam irradiation-induced nanophenomena, including the amorphization of LDNs. For the amorphization of a solid, the open space which can act as the positive activation volume [16] is firstly required for the volume expansion during the amorphization. In particular, for a nanowire there is sufficient open space surrounding the wire surface, but little open space in the center of the nanowire. It is thus expected that the amorphization on the nanowire surface should be much easier and preferential. Besides, as demonstrated in the following, an additional driving force on the nanowire surface, which is a result of the nanocurvature effect, would further dominantly contribute to the preferential amorphization.

For the nanocurvature effect on a nanowire, we can suppose that, similar to the particle case [16, 17], when the radius of a nanowire reduces down to nanoscale and can be comparable to its atomic bond length, a positive nanocurvature on the highly curved wire surface will become appreciable, as shown in figure 3(a). Such a positive nanocurvature would cause an additional tensile stress on the electron cloud structure of surface atoms, which would lead to a dramatic increase in surface energy. This dramatically increased surface energy could provide a driving force for the atoms to migrate or escape thermodynamically and thus cause a strong tendency of amorphization transformation for a crystalline nanowire, especially on the wire surface. In this sense, the intrinsic nanocurvature effect of a Si nanowire is thus regarded as one of the key factors contributing to the preferential amorphization on the wire surface. Also note that the existence of an amorphous Si shell may somewhat reduce the surface energy of crystalline Si core due to the decrease of dangling bonds. However, the nanocurvature effect is accounted for by the deviation of the atom position of a nanoscale structure from its thermodynamic equilibrium position, with respect to its bulk counterpart. This deviation dramatically increases from the inner core to the surface of a nanostructure, not just on the surface. What is more, the formation of an amorphous Si shell would smooth the possible surface-faceted structure of a crystalline Si core and thus enhance the nanocurvature effect. In this regard, we believe that the nanocurvature effect would exist during the whole amorphization process, although the thickness of the amorphous shell is increasing with irradiation time. Our previous work has demonstrated that amorphous carbon particles attached on the surface of a single-walled carbon nanotube (SWCNT) would cause little passivation effect on the structure changes of a SWCNT [32]. This is because the amorphous carbon particle is much more unstable than the SWCNT. Similarly, it is expected that the much more unstable amorphous Si shell would also cause little passivation effect on the amorphization of the Si nanowire.

Although the positive nanocurvature can provide the driving force for the atoms to migrate or escape thermodynamically, further assistance from external excitation such as energetic beam irradiation is still needed to lower the energy barrier and kinetically realize the amorphization. In the case of energetic electron beam irradiation in TEM, we can assume that, when the beam energy deposition rate of the incident energetic beam becomes so fast that there is not enough time for the deposited energy to transfer to thermal vibration energy of the atoms within a single period of the vibration and thus the vibration of atoms would lose stability or the mode of atomic vibration would be softened [16, 18].
athlonally activate the structure transformations, such as the amorphization of the Si nanowire, not only on its surface but also in its center, as illustrated in figure 3(a). In this way, as driven by the effects of nanocurvature and beam-induced athermal activation, the Si nanowire amorphized preferentially on the wire surface (see figures 1 and 3).

Note that the electrons of 300 keV can penetrate the TEM sample thickness or the Si nanowire diameter easily, with a typical energy loss of only several keV. The influence of sample thickness on the uniformity of beam energy deposition rate should thus be negligible. Furthermore, as schematically illustrated in figure 3, the diameter of the focused electron beam is much larger than that of the Si nanowire (90 nm vs. 67 nm). Although a focused electron beam often exhibits a Gaussian-like intensity profile, the intensity is regarded to be uniform within the central zone of the beam, which can fully cover the wire diameter (see figure 3). Therefore, the beam energy deposition rate would be uniform over all the materials in the nanowire sample. In this sense, the preferential amorphization on the surface of the Si nanowire is only attributed to the high nanocurvature on the wire surface along with a large positive activation volume. In contrast, as reported in [12–15], it was found that the Si film amorphized preferentially in the central zone of the focused beam. As illustrated in figure 3(b), the Si film is flat without detectable nanocurvature on the film surface. Accordingly, there is no nanocurvature effect working on the preferential amorphization. Instead, the focused electron beam has a higher flux or beam energy deposition rate in the central zone of the beam, relative to that at the edges of the beam (see figure 3). As a result, the effect of such a Gaussian-like intensity profile of the incident energetic beam determines the amorphization process of the Si film. That is, the Si film would amorphize preferentially and quickly in the central zone of the beam, but difficulty and slowly at the edges of the beam. In this sense, the nanocurvature- or intensity-dependent preferential amorphization behavior is probably the greatest difference of amorphization between the Si nanowire and the Si film under focused electron beam irradiation.

4. Conclusions

In this work, the focused electron beam irradiation-induced athermal amorphization of single crystal Si nanowires was investigated at room temperature in a field emission TEM. With the beam spot diameter larger than that of the Si nanowire, the local wire segment within the irradiated area demonstrated a preferential amorphization on the surface during the irradiation. Such an amorphization can be well accounted for by our proposed concepts of the nanocurvature effect and the energetic beam-induced athermal activation effect, whereas the classical knock-on mechanism and the electron beam heating effect seem inadequate to explain these processes. Furthermore, the findings revealed the differences between the amorphization of a Si nanowire and that of a Si film under focused electron beam irradiation. Also, the findings have important implications for nanoinstability and nanofabrication of future Si nanowire-based devices.

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