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LETTER

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Self-Healing of Fractured GaAs Nanowires

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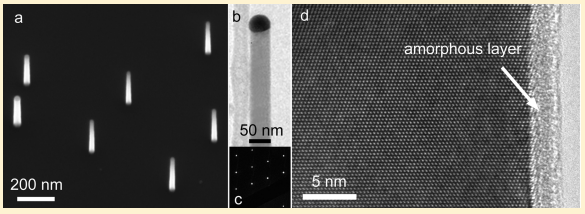
Supporting Information

ABSTRACT: In-situ deformation experiments were carried out in a transmission electron microscope to investigate the structural response of single crystal GaAs nanowires (NWs) under compression. A repeatable self-healing process was discovered in which a partially fractured GaAs NW restored its original single crystal structure immediately after an external compressive force was removed. Possible mechanisms of the self-healing process are discussed.



KEYWORDS: Semiconductor, nanowire, self-healing, transmission electron microscopy, in situ deformation

One-dimensional nanostructures such as nanowires (NWs), nanotubes, and nanobelts have significant applications as nanoscale interconnects and active components of electronic, optoelectronic, and electromechanical devices.[1−3] These materials are susceptible to microcracks and fracture when subjected to repeated thermal or mechanical loading. These defects limit the performance of materials, including mechanical stability, electrical, and optical properties. One common strategy for repairing such damages involves the application of various welding techniques that take advantage of high-intensity electron-beam or laser beam irradiation,[4−8] voltage/current,[6,9,10] electron beam chemical vapor deposition,[11] or Joule-heating induced joining.[12−15] These techniques not only induce local heating from high-energy electron/ion beams, which subsequently alters the properties of the materials, but are also generally time-consuming and complicated.

Recently, self-healing, which is an autonomous process of healing and restoring damaged materials to their original set of properties, has drawn significant attention because it is more efficient in repairing fractured materials than the welding techniques and has also the potential of extending the lifetime and increasing the reliability of materials. Self-healing was explored in some materials such as polymers[16−19] and ceramics.[20−22] Several self-healing methods have been proposed that take advantage of a microencapsulated healing agent,[17,23] a thermally reversible reaction that allows remending upon heating,[24] or a thermoplastic phase dissolving in an epoxy matrix.[25] After self-healing, the strength and fracture toughness of polymeric materials remain about the same as those of the original materials.[26] Heat treatment-induced crack healing in SiC ceramic with additive SiO_2 showed that the strength of SiC after crack healing becomes even stronger than that of the original SiC.[21] Nevertheless, all self-healing processes reported in the literature require some form of external intervention (temperature, heat, manual fluid injection, etc.).

In this Letter, we report a truly spontaneous self-healing process in GaAs NWs. GaAs NWs were successively fractured and self-healed in a transmission electron microscope (TEM) at room temperature when a compressive force was applied and then released repeatedly. We propose that factors including nanoscale sample dimensions, surface attraction, atomistic diffusion, and oriented attachment contribute to the self-healing process.

GaAs NWs were synthesized using a gold nanoparticle-catalyzed metalorganic chemical vapor deposition method. Single crystal GaAs NWs were epitaxially grown on a GaAs (111)B substrate using Au nanoparticles as catalyst with trimethylgallium and AsH_3 as the precursors. Details on the growth of GaAs NWs have been reported elsewhere.[27] To obtain NWs with very small diameters and short lengths, very small Au particles and a short growth time were used for the growth of the NWs. Structural characterisations were carried out using a Zeiss ULTRA scanning electron microscope (SEM) and a JEM-3000F TEM. In situ compression experiments were conducted using Hysitron PI 95 TEM PicoIndenter[28,29] with a flat diamond punch in a JEM-2100 TEM. A sample consisting of GaAs NWs attached to the substrate was pasted onto a mount, which was held in the PicoIndenter. A compression test was applied along the axial direction of NWs.

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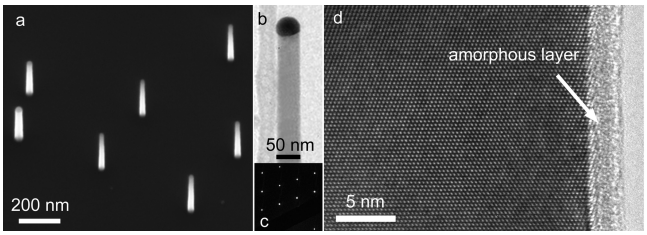

Figure 1. NWs of GaAs. (a) An SEM image of GaAs NWs. (b) A TEM image of a NW. (c) A ⟨110⟩ selected-area electron diffraction pattern obtained from a NW. (d) A high-resolution TEM image of a NW showing a perfect crystalline core and an amorphous shell of ∼2 nm.

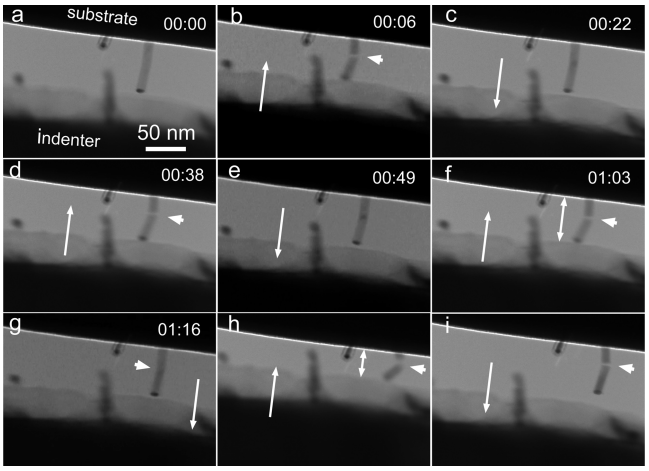

Figure 2. (a−g) A series of in situ TEM micrographs extracted from Movie 1 in the Supporting Information showing the fracture and self-healing processes of a GaAs NW when a compression force was applied and retracted repeatedly. (h,i) Two in situ TEM micrographs taken after Movie 1. The moving direction of a flat punch, the distance between the punch and the substrate, and the breaking sites are marked by an arrow, a double arrow, and an arrowhead, respectively.

The compression process was recorded by TEM images and real-time video at the speed of 30 frames per second.

Figure 1 shows a typical SEM image of the GaAs NWs (a), a low-magnification TEM image of a single NW (b), a selected-area electron diffraction pattern recorded along a ⟨110⟩ zone axis of a NW (c), and a high-resolution TEM image of a NW (d). Structural characterization confirmed that each individual GaAs NW was a single crystal, grown epitaxially along the [111] direction, which is perpendicular to the GaAs substrate. The cross-sectional diameters, measured from a middle length position, of the NWs are in the range of several nanometers to less than 100 nm while the lengths are less than 300 nm. An amorphous oxide layer with a thickness of ∼2 nm is seen on the surface of each NW (Figure 1d), which was formed after the NW was exposed to the air.[30]

Figure 2 presents a series of in situ TEM micrographs extracted from the video Movie 1 in the Supporting Information (note that the blackouts that occur several times in the movies in the Supporting Information were caused by imaging using the CCD camera in the TEM during the video recording processes), revealing the structural evolution of a GaAs NW with a diameter of ∼12 nm during repeated compression using a flat punch. The flat punch first touched the NW at 0 s (Figure 2a). At ∼ 6 s, a crack was initiated and propagated approximately perpendicular

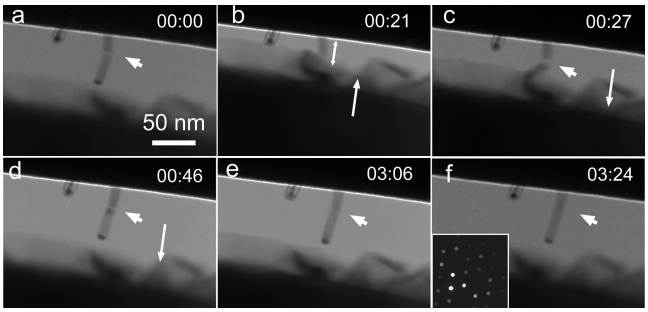

Figure 3. A series of in situ TEM micrographs extracted from Movie 2 in the Supporting Information showing that the time needed for self-healing to complete increases with increasing the crack size. The inset in panel f is a nanobeam electron diffraction pattern taken from an area that includes the self-healing site.

to the axial direction at a middle point of the NW, which is indicated with a white arrowhead in Figure 2b. The crack site in Figure 2b is identified by its contrast, which is the same as that of the surrounding empty area in the figure. At this stage of the deformation, the crack did not penetrate across the entire diameter of the NW but stopped somewhere on the left part of the NW because the NW did not completely separate into two parts. Therefore, the left part of the NW (the area with compressive strain) was still attached to the rest of the NW. The unbroken part presented in Figure 2b should comprise only the amorphous layer because of its contrast that is consistent with the light contrast of the amorphous layer on the surface of a NW shown in Figure 1d. Interestingly, when the punch was retracted from this point along the direction indicated by the arrow shown in Figure 2c until it was fully separated from the NW, the NW promptly restored its original shape and the crack was self-healed. The uniform image contrast across the self-healed site in Figure 2c (and also Figure 3f shown later) confirms that the two fractured parts have completely healed, rather than a simple mechanical contact. The self-healing process was completed within a short time (∼16 s). The crack and self-healing processes were successfully repeated several times by applying and then retracting the compression force (Figure 2d−g). By pushing the flat punch to a longer displacement distance than the previous compression tests (the distance between the punch and the substrate of the sample is indicated using a double-arrow in Figure 2f,h), the crack size increased, as shown in Figure 2h in which the two parts of the NW at the two sides of the crack form a near 90° angle. After the punch was retracted, the NW did not immediately restore its original shape but left a little crack as indicated by an arrowhead in Figure 2i. The two parts in Figure 2i must still connect to each other by the amorphous layer. Otherwise, the part close to the indenter would have fallen into the TEM column. With the healing time increase, the width of this crack gradually reduced. As a result of this larger crack, the self-healing process completed in a longer time frame than in previous processes, indicating that the time needed for self-healing was a function of the crack size.

To confirm the crack size effect on the time needed for self-healing, one compression test with an even larger compressive displacement distance was carried out on the same NW after a few more repeated compression tests with displacements similar to that shown in Figure 2. Figure 3 shows snapshot images extracted from Movie 2 in the online Supporting Information. Note that a small crack (marked by arrowhead in Figure 3a) was

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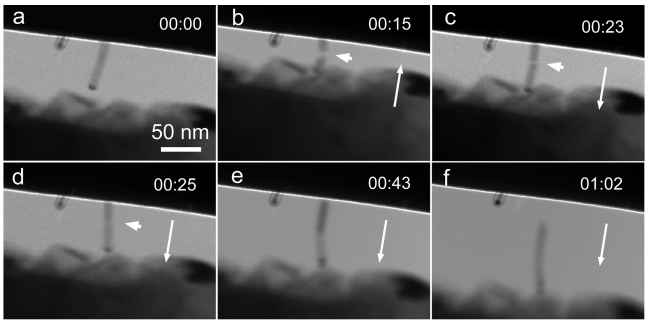

Figure 4. A series of in situ TEM micrographs extracted from Movie 3 in the Supporting Information showing that the self-healed site is strong enough to sustain a tensile force that pulled the whole NW out from the GaAs substrate.

still seen because there was not enough time to complete the self-healing process from the last compression. The following compressive displacement was so large that the NW was almost completely broken (it was evidenced from Movie 2 that the two parts of the NW still connected to each other) and one part of the NW laid on the surface of the punch (Figure 3b). When the punch was partially retracted, the NW was also partly restored but a crack remained, as indicated by an arrowhead in Figure 3c. After full retraction of the punch, the self-healing process continued (Figure 3d,e) and completed at 03:24 (Figure 3f). It took ~3 min and 3 s to complete the whole self-healing process (Figure 3c−f). Note that weak adhesion between the punch and the fractured NW may help the broken part of the NW return to close to its original position when retracting the punch. A nanobeam electron diffraction pattern (the inset in Figure 3f) taken at the self-healing site reveals that the whole NW remained as a single crystal without any misorientation after several cycles of fracture and healing.

The crack self-healed site was strong enough to sustain some tensile force as evidence by the last compression-retraction test of the same NW shown in Figure 4. The restored original NW (Figure 4a) was again compressed to break (Figure 4b) followed by the retraction of the flat punch to allow a partial completion of another self-healing process (Figure 4c,d). For some reason, the NW tip was stuck to the flat punch and further retraction of the punch detached the NW from the substrate (Figure 4e,f). Interestingly, the breakage point was not the place where the previous crack occurred but near or at the NW/substrate interface. This phenomenon suggests that the strength of the self-healing site was strong that it even survived from being pulled apart by a tensile force. The new breakage point may already have a small crack or damage during previous compression experiments and therefore became a weak point under the tensile force. Figure 4 is strong evidence of self-healing as a simple mechanical contact would not be able to sustain a tensile force.

Surface attraction is considered an important factor in a self-healing process.[16,19,20] Obviously, the two parts of the fractured NW spontaneously approached each other in our experiments (e.g., Figure 2c,e,g) due to the electrostatic force between the two fractured surfaces[31,32] and the release of the elastic strain energy imposed on the unbroken amorphous layer. Electrostatic attractive force has been reported to play an important role in the bonding between ZnO−ZnO,[31,32] where the two fractured surfaces have opposite charges. Such an attractive force in the near-field region led to the rebonding of two fractured parts.[5,31,32] Our recent investigation suggested that a GaAs NW with an amorphous surface layer can be elastically deformed to a strain of ~11% and that the Young's modulus of a GaAs NW increases with reducing the diameter of the NWs;[33] this can be explained using a core−shell model[34,35] in which the shell layer has a very high Young's modulus. Therefore, with the high strain and high Young's modulus the elastic deformation of the amorphous layer is expected to store a relatively large amount of elastic energy, which helps the two fractured parts of the NW return to their original shape by releasing the elastic energy after the compressive force was retracted.

Atomistic diffusion or rearrangement is another important factor for self-healing.[16,19,20] As the atomic arrangements on the surface and the internal part of a solid are different, atomistic diffusion and rearrangement occurs when the two surfaces are in contact with each other. Previous investigations showed that surface and grain boundary diffusion increases significantly as the grain size is decreased to the nanometer scale.[36] Therefore, atomistic diffusion and rearrangement on the fractured surfaces, even at room temperature, could finish instantly when the two fractured surfaces meet. The driving force of this atomistic rearrangement is the reduction of the system energy by reducing surface area and therefore surface energy. The occurrence of the atomistic rearrangement at room temperature indicates that even at this temperature there is enough activation energy for the surface atomic diffusion to occur. Rebonding induced by atomistic diffusion has been reported in many nanomateirals.[4−15,37]

The oriented-attachment mechanism, as reported for PdSe nanocrystal[12,38] and Au NWs,[39] should also play an important role during the self-healing process of GaAs NWs at room temperature. In the present experiments, a single crystal NW was fractured to two segments under a compressive force. It is expected that slight grain rotation relative to the axial direction occurred and the angle of the rotation increased with increasing the crack size. As a result, a longer time for reorientation to complete is needed for a larger crack during its subsequent self-healing process to restore the original single crystal structure of the NW. The vacuum environment in TEM is beneficial to the self-healing of GaAs NWs as this provides clean fractured surfaces, making the rebonding on the fractured surfaces possible. As the experiments were carried out in a TEM, the effect of electron irradiation on the self-healing cannot be ruled out. However, because the electron beam intensity used in this investigation was only ~1×10^{-3} A/cm^2, which was so weak that it was almost not detectable by eyes on the fluorescence screen in the TEM and was several orders of magnitude lower than that used in previous investigations.[8,40] It is expected that the effect of electron irradiation on the self-healing phenomenon should not be significant.

In summary, self-healing in GaAs NWs was discovered during in situ compression and subsequent release experiments in a TEM at room temperature. It is believed that nanoscale sample dimensions, surface attraction, atomistic diffusion, and oriented attachment contribute to the self-healing process. It has the potential to extend the lifetime and increase the reliability of NW-based devices.

■ ASSOCIATED CONTENT

Supporting Information. Movies 1−3 from which the snapshot images in Figure 2, Figure 3, and Figure 4, respectively, were obtained. This material is available free of charge via the Internet at http://pubs.acs.org.

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