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 damages to introduce a thermal or mechanical load that promotes the formation of defects.4,5 These welding techniques have been used to repair microcracks in 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 epoxied to a GaAs (111)B substrate using Au nanoparticles as catalyst with trimethylgallium and AsH3 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 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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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
After full retraction of the punch, the self-healing process but a crack remained, as indicated by an arrowhead in Figure 3c. When the punch was partially retracted, the NW was also partly restored 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 compressive displacement was so large that the NW was almost completely broken (it was evidenced from Movie 2 that 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 nanomaterials.1-15,37

The oriented-attachment mechanism, as reported for PdSe nanocrystal31,32 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/cm², 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.3,40 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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