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Dynamic fatigue studies of ZnO nanowires by in-situ transmission electron microscopy

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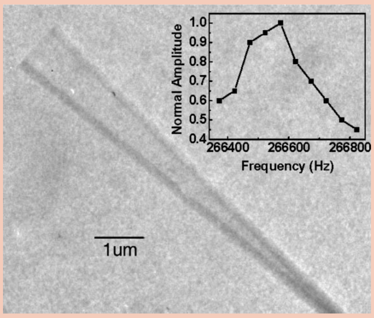
The fatigue behavior of ceramic ZnO nanowires (NWs) has been investigated under resonance cyclic loading conditions using in-situ transmission electron microscopy (TEM). After mechanical deformation at the resonance frequency at a vibration angle of 5.2° for 35 billion cycles, no failure or any defect generations have been found. We believe that the dislocation-free nature of NWs and the large surface-to-volume ratio contribute to the NWs' ability to undergo deformation without fatigue or fracture, proving their durability and toughness for nanogenerators and nanopiezotronics.



1 Introduction Nanopiezotronics, a newly developed field in nanotechnology, utilizes the coupled piezoelectric and semiconducting properties of nanowires (NWs) and nanobelts for designing and fabricating electronic devices such as transistors and diodes [1]. It is anticipated to have a wide range of applications in electromechanical coupled sensors and devices [2], nanoscale energy conversion for self-powered nanosystems [3], and harvesting energy from environment [4]. Mechanical reliability of NWs is an important issue for such applications that involve dynamic deformation processes. Fatigue, or the delayed failure of a material under cyclic loading conditions, is a commonly encountered mode of failure in materials that determines its device stability and lifetime. Although there are several cases of fatigue studies on nanoscale structures for micro/nanoelectromechanical system (MEMS/NEMS) applications [5–8], fatigue observations on one-dimensional (1D) nanomaterials, especially those for nanopiezotronic applications, have not been reported yet. The current understanding of material fatigue is, to a large extent, for metals. Fatigue of metals is associated with the generation and motions of dislocations and accumulation of plastic deformation. However, a common characteristic of ceramic-type ZnO NWs is that they are mostly dislocation free [9, 10]. In this letter, we present a fatigue test of ZnO NWs under cyclic loading conditions using in-situ transmission electron microscopy (TEM) measurements. Fatigue-free NWs were observed after being deformed for over 10^{10} cycles.

2 Experimental The ZnO NWs used here were synthesized in a horizontal furnace with a quartz tube at a pressure around 2200 Pa for 20 min, with lengths in the range of 6–11 µm, and widths in the range of 100–200 nm. Fatigue test was performed by means of the in-situ TEM technique [11]. Load cycles were applied to the NW by a periodic electrostatic force driven at the NW's resonance frequency. A TEM specimen holder was specially built for applying an AC voltage across the NW and its counter electrode. One end of the NW was fixed at the holder by silver paste. The other end was set free and pointing to the counter electrode. Fatigue behavior can be directly monitored under TEM so that fracture or any incipient dislocation formation can be immediately captured. The resonance frequency was determined from the frequency–amplitude relation. When the frequency of the driving voltage matches to the resonant frequency, the NW vibrates with large amplitude. And the numbers of loading cycles were determined from the resonance frequency times the elapsed time. It should be mentioned that the resonance frequency may shift under continuous electron beam illumination, possibly due to the carbon deposition induced by electron beam on the NW and possible structure damage by the beam (200 kV) [12], which changed the mass of the NW. During loading process, we just took a quick view to see if the NW had been resonating at the maximum amplitude and if fracture had occurred, and then quickly moved the NW out of the electron illumination circle. Then, it was brought back under the beam to examine if it is still in resonance within about 5 min. This procedure was repeatedly taken during the entire observation of fatigue to ensure that the NW was continuously at resonance status. For most of the cases, each time we checked it, the NW was keeping the same resonance frequency. Hence in this way, we can make sure that the NW can oscillate for a long time under the same frequency. Then after high loading cycles, we would be able to examine the NW carefully. A small tuning adjustment was made to bring the NW back to resonance if it drifted off. Nevertheless, the frequency will not shift too much, typically less than 100 Hz. The number of cycles was determined from the sum of the respective frequency times the elapsed time at that frequency. We kept the electron beam illumination to low current density as long as we can see it, but the important point is that the intensity of the illuminating electron beam did not affect in any visible way the resonance status of the NW.

3 Results and discussion Figure 1 shows a TEM image of a NW vibrating at its resonance frequency of 266.6 kHz. The resonance amplitude is about 1 μm, corresponding to a vibration angle of 5.2°. The structure of the NW was examined before and after many cycles of fatigue testing. Figure 2 shows the TEM images taken before and right after 3.5×10^{10} loading cycles for comparison. Figure 2(a) is a low magnification image showing the whole structure of the NW before dynamic loading. There is no diffraction contrast other than some thickness contour appearing in the TEM image [10]. It is distinguished from the defect contrast as its contrast is not that sharp. Figure 2(b) and (c) are two high magnification images taken at two different segments of the NW, as denoted by the dashed line in Fig. 1(a). The estimated axis strain amplitude is 0.74% near the top region and 1.81% near the root region, which is below the yield strain (5%) of ZnO nanowire [13]. After applying 3.5×10^{10} cycles of loading, no change in structure has taken place as shown in Fig. 2(d), except that some thickness–mass contrast may have changed very slightly. The local enlarged images of Fig. 2(e) and (f) look quite the same like those before loading in Fig. 2(b) and (c). The diffraction contrast is uniform, showing that the NW is free of dislocations after fatigue loading. This agrees with the high stability of the resonance frequency during the entire observation. We have tested six NWs, and all of them have survived well after loading cycles at least up to 3×10^9, without any fatigue damage.

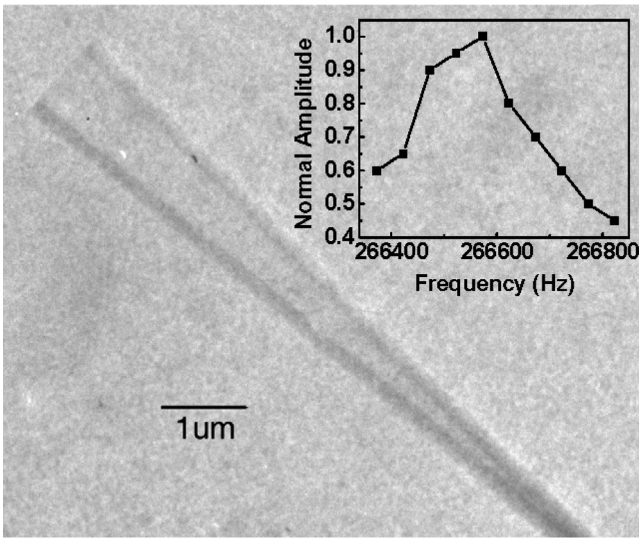


Figure 1 TEM image of a NW (200 nm in width and 11 μm in length) that is cyclically deformed by resonance load at a frequency of 266.6 kHz. Inset shows the amplitude–frequency relation, from which the quality factor is 1344.

Two mechanisms are supposed to give rise to this fatigue-free feature of the ZnO nanowire. The first one should be attributed to the defect-free nature of the 1D nanostructure. Dislocations cannot be pinned in the volume of the 1D nanostructure, and they can easily migrate if any to the surfaces and finally disappear [9]. As a result, most of the 1D nanostructure is dislocation-free. Hence the traditional dislocation multiplication mechanism as proposed in metals is not applicable below a critical diameter, and dislocations pass the sample freely to pop out of the volume without leaving any residual in the volume of the NW. Continuing plastic deformation is only possible if the applied stress is large enough to nucleate new dislocations [14]. Fortunately, however, such case hardly happens for single crystalline NWs.

The large surface-to-volume ratio of 1D nanostructures also contributes to the NW's ability to undergo deformation without fracture. Several studies have revealed that mechanical properties of materials are size-dependent [15–17]. Our hypothesis is that as the surface-to-volume ratio increases, the number of surface atoms increases as well, thereby resulting in more unbalanced surface atoms than the atoms locked in the lattice. The surface unsaturated atom states are believed to affect the dislocation generation

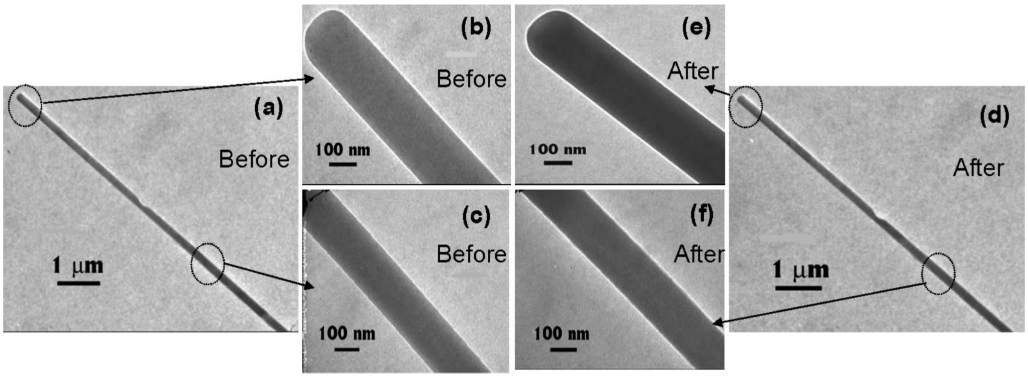


Figure 2 Low and high magnification TEM images of the same NW as in figure. Images (a), (b), (c) are taken before cyclic loading, and (d), (e), (f) are taken right after 3.5×10^{10} loading cycles. No dislocations can be observed.

and motion in a different way to the locked atoms inside the lattice, thus affecting the mechanical behavior of 1D nanomaterials [16]. Another study also suggests that a large surface-to-volume ratio will enhance the atomic mobility, thus preventing defect formation when the material undergoes deformation [17]. As a result, dislocations are difficult to be introduced at the nanoscale level during dynamic loading.

4 Conclusions Fatigue tests have been performed on ZnO nanowires using resonance cyclic loading by means of in-situ TEM. Our experimental evidence suggests that the ZnO nanowire is free of fatigue after high loading circles up to 10^{10} cycles, proving the durability and toughness of ZnO NWs for nanopiezotronic devices.

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