Mechanical Properties of ZnS Nanobelts

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ABSTRACT

Mechanical properties of ZnS nanobelts were measured at room temperature by direct nanoindentation experiments. It was found that the ZnS nanobelts achieve 79% increase in hardness but 52% decrease in elastic modulus compared to bulk ZnS. The nanobelts were found to exhibit creep under indentation. Indentation cracking was preferred along the belt growth direction. Indentation deformation behavior and fracture mechanisms of the ZnS nanobelts are discussed in conjunction with their crystalline structure, size effect, and surface-to-volume ratio.

As an important direct band gap (3.66 eV at 300 K) II–VI compound semiconductor and a luminescent material, ZnS has attracted considerable attention due to its potential applications in flat-panel displays, electroluminescent devices, infrared windows, sensors, and lasers.1,2 Recently, one-dimensional (1D) ZnS nanostructures such as nanobelts and nanowires have shown a great promise as functional and structural nanobuilding blocks in nanoelectronics, nanophotonic devices, and nanolasers.3–6 In the design and development of such nanodevices, structural integrity is of paramount importance. For instance, mechanical contacts that occur at the nanobuilding block interfaces may cause fatal damage of these devices.7–12 A precise measurement of the mechanical properties of nanostructures is therefore of great interest.

It is technically essential to measure the mechanical properties directly from these nanostructures since mechanical properties of materials must be size-dependent at some length scale. The mechanical properties of nanostructures cannot be extrapolated from results of the bulk materials. The extremely small dimensions of 1D nanostructures impose a tremendous challenge to many existing testing and measuring techniques for experimental studies of their mechanical properties. For instance, tensile testing requires that the size of the sample be sufficiently large to be clamped rigidly by the sample holder without sliding.13 This is probably impossible for most 1D nanostructures using conventional means. Furthermore, the extremely small size of nanostructures makes their manipulation rather difficult, and specialized techniques are needed for picking up and installing individual nanostructures. The methods that have been developed and used for measuring the mechanical properties of isolated individual 1D nanostructures include mechanical resonance (thermal vibration14,15 and electric-field-induced resonance13,16), atomic force microscope (AFM) bending,17–19 and axial tensile loading using a nanomanipulation stage.20–22

Clamping is a major drawback of the foregoing testing methods with which at least one end of a 1D nanostructure needs to be clamped to the sample holder or naturally cantilevered. Weak clamping condition can cause sliding, introducing uncertainty into the mechanical property measurements. The clamps fabricated by electron beam deposition or by adhesive may alter the composition and structure of the nanostructures, consequently affecting the measurement accuracy.23 Problems with clamping may be the reason. Even for measurements on the same nanostructure, different mechanical property values have been reported by different groups using the same or different methods.

A promising approach that does not require clamping is direct indentation of these nanostructures.24–26 One first has to see the nanostructures and then indent them in situ. Traditionally, AFM has been used to measure the nanometer-scale topography of surfaces while a nanoindenter has been used to measure the nanoscale mechanical properties of solid surfaces and thin films.22,27 Major questions that need to be addressed are as follows: (1) Can we extend application of traditional nanoindentation approaches to 1D nanostructures for directly measuring their mechanical properties? (2) Can one indent a nanofilament as easily as indenting a bulk material?

A recently developed nanoindenter has the capability of measuring surface morphology at the nanoscale by scanning the sample surface with the same indenter tip, which is analogous to AFM contact mode.24–26 Such a nanoindenter/AFM combination provides the “eyes”, “hands”, and “tools”
for imaging, manipulating, and testing all types of nanostructures. The hardness and Young’s modulus can be obtained directly from the nanoindentation load-displacement curves. In situ imaging of the impressions right after the indentation test together with the load-displacement curves offers a unique opportunity for studying indentation deformation behavior and fracture mechanics. In this study, using nanoindentation, we report results of mechanical properties of individual ZnS nanobelts, including their deformation behavior and fracture mechanics. We discovered that at room temperature the ZnS nanobelts exhibit significant creep under a constant load indentation.

ZnS nanobelts with the wurtzite structure used in this study were synthesized using the pulsed laser vaporization (PLV) method, as described in refs 3–5. The nanobelts of several tens to hundreds of nanometers in width and height and several micrometers in length were first dispersed into ethanol by ultrasonication. Then a few drops of this suspension were deposited onto either copper grids or Si wafers for transmission electron microscopy (TEM, Philips 420, JEOL 2010F), atomic force microscopy (AFM, Veeco, Dimension 3100), and nanoindentation (Hysitron, Triboscope nanoindenter) studies. The solvent was then vaporized under ambient conditions.

The Hysitron triboscope nanoindenter in conjunction with the Veeco Dimension 3100 AFM was used to perform imaging and nanoindentation tests. The nanoindenter monitors and records the load and displacement of the three-sided pyramidal diamond (Berkovich) indenter during indentation with a force resolution of about 1 nN and displacement resolution of about 0.2 nm.11,12 The indenter tip was used to image and locate a single ZnS nanobelt and then in situ indent the belt with the same tip. The indentation impression was also imaged with the same tip. Post-test imaging provides the ability to verify that the test was performed in the anticipated location, which maximizes the reliability of data and aids in explanation of unexpected test results. Hardness and elastic modulus were calculated from the load-displacement data obtained by nanoindentation. Before each nanoindentation test, the thermal drift was automatically tracked and recorded by means of introducing the nanoindenter in touch with the top surface of the sample with minimum contact load. All the nanoindentation tests were performed when the thermal drift or vibration induced mechanical drift dropped down to 0.01 nm/s. The load-displacement curves were obtained by subtracting the drift effect for hardness and elastic modulus analyses.

Structural and morphological information of the ZnS nanobelts was obtained from TEM and AFM images. Figure 1a is a TEM bright-field image of ZnS nanobelts showing their geometrical shape. Detailed examination of the nanobelts along their length reveals that they are uniform in width ranging from 50 to 670 nm. Figure 1b shows a TEM cross-sectional image of a single nanobelt. Most have a rectangular or square cross section. The high-resolution TEM image (Figure 1c) reveals that the ZnS nanobelts are single crystalline with the [001] growth direction and are dislocation free, as indicated by the lattice fringe and selective-area diffraction pattern (inset to Figure 1c). The measured distance between lattice fringes is 3.19 Å for the (001) planes. The AFM images with thickness analysis (Figure 1d,e) and the TEM width measurement (Figure 1a) suggest that a majority of the nanobelts have square cross section. To avoid obtaining artifacts from AFM tips, we followed the standard AFM tip calibration procedure. An AFM tapping mode etched silicon tip was employed to obtain the scan profiles of a nanobelt. The AFM tip height was 10–15 μm. The tip radius was 15 nm. A standard calibration sample from Veeco Metrology Group with the gratings (NGR-21, 200 nm depth × 10 μm pitch) was used for three-dimensional profile measurements and AFM probe calibration. The resultant angles (front, back, and side angles of the tip as well as the substrate mounting angle) were obtained from the scan line profiles. By this means, the actual line profiles of the ZnS nanobelts were precisely obtained.

A Berkovich diamond nanoindenter tip was used to image and locate a single ZnS nanobelt and then in situ to position...
the tip on the belt to perform an indentation test. Figure 2 shows the AFM images of an indentation on the nanobelt and the representative load–displacement curves. The peak nanoindentation depth can be as low as 12 nm, which is about 15% of the belt thickness. It is generally accepted that the depth of indentation should never exceed 30% of the belt thickness (film thickness).11,12 If this condition is satisfied, the substrate effect on the measurement of the hardness and elastic modulus of the belt can be ignored. The indentation impression was imaged immediately after the indentation test using the same tip. The indentation projected area obtained by the AFM was used to calibrate the hardness and elastic modulus values. Pileup (the indented material around the indenter above its original surface11) was found around the indentation impression, indicating the ductile nature of the material.

It is still unknown whether deformation can continue to take place in the indentation of ZnS nanobelts at a constant load. Such information is of ultimate importance for the performance and reliability of ZnS nanobelts and their devices. In an indentation creep test, a constant load was applied to the indenter and the change in indentation depth (size) was monitored as a function of time. The load–displacement curve of an indentation made at a 25 μN peak indentation load with a holding time period of 5 s on a ZnS nanobelt is shown in Figure 2d. Creep occurred during the holding segment. This indicates that dislocations moved during the indentation holding segment, which contributed to the increase in indentation depth.11,12 In general, for metals, ceramics, and semiconductors, time-dependent deformation occurs at elevated temperatures. Our finding indicates that for the semiconductor ZnS nanobelts, creep occurs even at room temperature. For the ZnS nanobelts, the surface-to-volume ratio is much higher than those for the micro- and macroscale structures. Surface atoms can move more easily than the atoms fully locked in the lattice.7 This makes the dislocation generation and motion easier underneath the indenter, thereby leading to the indentation displacement. The creep damage, which is first reported in this paper for the ZnS nanobelts, may occur in other nanostructure systems and should be generally taken into account in the design of nanodevices.

The nanoindentation hardness and elastic modulus values of the ZnS nanobelts were measured to be 3.4 ± 0.2 GPa and 35.9 ± 3.5 GPa, respectively. Compared with bulk ZnS with a hardness value of 1.9 GPa and an elastic modulus value of 75 GPa, the hardness of the ZnS nanobelt is increased by 79% while the elastic modulus is decreased approximately by 52%. Our previous study showed that bending strength of silicon beams exhibits a clear specimen
size effect with nanoscale numbers being twice as large as numbers reported for large-scale specimens.\textsuperscript{7} Wu et al. reported that the strength of Au nanowires is 100 times that of bulk material.\textsuperscript{28} Haque and Sai\textsuperscript{29} discovered that 1D Al and Au nanostructures exhibit reduction in Young’s modulus. The increase in hardness and decrease in elastic modulus are probably attributed to the high surface-to-volume ratio of the ZnS nanobelts.\textsuperscript{7} Unlike the atoms locked in the lattice, surface atoms are less constrained, thereby making the ZnS nanobelts easier to deform in the elastic regime, and consequently leading to a higher hardness but a lower elastic modulus.

A noteworthy phenomenon observed in the high load indentations made on the ZnS nanobelts is that cracking was preferred along the growth direction, i.e., the [001] direction of the ZnS nanobelts. Figure 3 shows a crack induced by nanoindentation, which was initiated from a triangular edge of the diamond tip. The crack formed preferentially along the [001] direction.

In summary, we have used nanoindentation to study mechanical properties of individual ZnS nanobelts micrometers in length and \( \approx 50\)–\(100\) nm in thickness. These ZnS nanobelts exhibit hardness of \(3.4 \pm 0.2\) GPa and elastic modulus of \(35.9 \pm 3.5\) GPa. Compared with bulk ZnS, the hardness of the ZnS nanobelt is increased by \(79\%\) while the elastic modulus is decreased approximately by \(52\%\). The ZnS nanobelts were also observed to exhibit significant creep under a constant load indentation at room temperature.

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\textbf{References}


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