Higher-order harmonic resonances and mechanical properties of individual cadmium sulphide nanowires measured by...

Article in Journal of electron microscopy · February 2010
DOI: 10.1093/jmicro/dfq004 · Source: PubMed

10 authors, including:

Peng Gao
Brookhaven National Laboratory
38 PUBLICATIONS 987 CITATIONS

Lei Liu
Shenzhen children hospital.china
216 PUBLICATIONS 4,095 CITATIONS

Zhi Xu
Chinese Academy of Sciences
72 PUBLICATIONS 1,879 CITATIONS

Some of the authors of this publication are also working on these related projects:

Advanced Scanning Transmission Electron Microscopy View project

Microscopy of functional materials View project

All content following this page was uploaded by Zhi Xu on 02 July 2014.
The user has requested enhancement of the downloaded file. All in-text references underlined in blue are added to the original document and are linked to publications on ResearchGate, letting you access and read them immediately.
Higher-order harmonic resonances and mechanical properties of individual cadmium sulphide nanowires measured by in situ transmission electron microscopy

Peng Gao¹, Kaihui Liu¹, Lei Liu¹, Zhenzhong Wang¹, Zhaoliao Liao¹, Zhi Xu¹, Wenlong Wang¹, Xuedong Bai¹,* Enge Wang¹,* and Yanqing Li²

¹Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China and ²Functional Nano & Soft Materials Laboratory (FUNSOM), Soochow University, Suzhou 215123, China

*To whom correspondence should be addressed. E-mail: xdbai@aphy.iphy.ac.cn; egwang@aphy.iphy.ac.cn.

Abstract

The higher-order harmonic resonances, including second and third harmonic modes, were induced by applying alternative current signals inside a high-resolution transmission electron microscope (HRTEM), which have been used to study the mechanical properties of individual cadmium sulphide (CdS) nanowires. Young’s moduli (E) and mechanical quality factors (Q) of individual CdS nanowires with diameters in the range of 50–350 nm were measured with the assistance of the mechanical resonances. The results indicate that the smooth nanowires have larger E and Q in comparison with the rough nanowires, and for the rough nanowires, E and Q increase with increasing diameters. The morphology- and size-dependent mechanical properties of CdS nanowires are directly correlated with their structure, as imaged by in situ TEM.

Keywords

in situ TEM, higher-order harmonic resonances, mechanical properties nanowires

Received 2 November 2009, accepted 22 January 2010, online 24 February 2010

Due to its extremely small size and enhanced physical properties, one-dimensional nanostructure materials are promising for nanoelectromechanical systems, electronics and energy conversion applications, such as high-frequency nanowire electromechanical resonators [1–3], single-atom sensitivity carbon nanotube mass sensors [4–6] and nanowire piezoelectric nanogenerator [7]. It is of significance to understand the unique mechanical properties of nanomaterials based on their morphology, size and atomic-level structure. So far, several methods for measuring the mechanical properties of nanomaterials, for example, bending test by atomic force microscope (AFM) [8,9], electrostatic pull-in approach [10], axial tensile loading [11], instrumented indentation [12] and contact-resonance AFM [13], have been developed. With the assistance of electric-induced mechanical resonance, an in situ transmission electron microscopy (TEM) method has been invented to directly measure the Young’s modulus of individual nanotubes [14,15], nanowires [16,17] and nanobelts [18]. The most important advantage of the in situ TEM approach is that it allows the properties of the nano-object to be directly correlated with its structure, providing a powerful technique for investigating the structure-dependent mechanical properties of individual nano-objects [19,20].

Here, we report the morphology- and size-dependent mechanical behaviours of individual cadmium sulphide (CdS) nanowires studied by in situ TEM where the higher-order harmonic resonances
of individual nanowires were excited by the applied alternative current (AC) signals. With the assistance of the electric-induced mechanical resonances, Young’s moduli \((E)\) and mechanical quality factors \((Q)\) of individual CdS nanowires have been measured, which are directly linked with their structure characterized by \textit{in situ} TEM.

The CdS nanowires were synthesized by the chemical vapour deposition method with diameters from tens of nanometres to hundreds of nanometres, as reported elsewhere [21]. To carry out the mechanical property measurements, nanowires were attached to the tungsten scanning tunnelling microscopy (STM) tip with graphite paste. The STM tip was loaded into a home-made specimen holder, and then it was inserted inside a TEM (JEOL 2010 FEG TEM under the vacuum of \(10^{-7}\) Torr at room temperature) [22]. The selected nanowire was driven to approach its counter electrode (Pt) by a three-directional nanomanipulator. Using an AC signal generator (Stanford Research System DS345), an oscillating voltage \([V(t) = V_\text{ac}\cos(2\pi ft)]\) ranging from 0.1 to 10 V was applied across the CdS nanowire and its counter electrode, and the mechanical resonance was induced by tuning the frequency of the AC signal.

A stationary selected CdS nanowire is given in Fig. 1a, which can be regarded as a vibration cantilever clamped at one end. By adjusting the frequency of the applied voltage, the natural resonance was achieved at \(f_1 = 15.3\) kHz, as shown in Fig. 1b. The enlarged TEM image (inset of Fig. 1a) indicates that the nanowire is cylindrical. The amplitude at resonance was maintained below \(\text{length}/10\) to minimize the bending curvature, thus it fits the assumptions of the Euler–Bernoulli equation [23]. Under this condition, resonance frequency can be expressed by the following equation:

\[
f_j = \frac{\rho_j^2}{8\pi L^2} \sqrt{\frac{E}{\rho}}
\]

(1)

where \(D, L, E\) and \(\rho\) are the diameter, length, Young’s modulus and mass density of the nanowires, respectively, and \(\rho_j\) is a constant for the \(j\)th harmonic: \(\rho_1 = 1.875, \rho_2 = 4.694\) and \(\rho_3 = 7.855\), such that Young’s modulus can be obtained from the length \(L\) and diameter \(D\) measured by \textit{in situ} TEM. For the CdS nanowire with \(L = 120\) \(\mu\)m and \(D = 317\) nm given in Fig. 1a, \(E\) is measured as \(\sim 119\) GPa. The second and third harmonic of the same nanowire were also observed, as shown in Fig. 1c and d. Their resonance frequencies are \(f_2 = 91.0\) kHz = \(5.95 f_1\) and \(f_3 = 281.5\) kHz = \(18.4 f_1\), respectively. They are very close to the theoretical ratios that are \(f_2/f_1 = \beta_2^2/\beta_1^2 = 6.2\) and \(f_3/f_1 = \beta_3^2/\beta_1^2 = 17.5\), respectively [23]. The node position of the second harmonic is 0.73 \(L\), in good agreement with the theoretical value 0.78 \(L\). For the \(f_3\) mode, there are two nodes, 0.45 \(L\) and 0.85 \(L\) (Fig. 1d), well fitting the theoretical ratios 0.5 \(L\) and 0.87 \(L\) [23]. The consistency of the observed frequency ratios and node positions with the theoretical data are solid evidences that the true fundamental natural frequency has been found, which is crucial for this study.

The mechanical quality factor \(Q\) can be obtained from the full width at half maximum of the resonance peak, i.e. \(Q = f_j/\Delta f\). Fig. 1e shows that \(Q\) is \(\sim 1000\) when a resonance occurred at 835.2 kHz.

![Fig. 1. (a) A stationary CdS nanowire with the length of 120 \(\mu\)m and diameter of 317 nm, respectively. Inset, low-magnification image shows that the nanowire has a smooth surface. Inset scale bar = 200 nm. (b) The first harmonic mode \(f_1 = 15.3\) kHz. (c) The second harmonic mode \(f_2 = 91.0\) kHz. (d) The third harmonic mode \(f_3 = 281.5\) kHz. (e) The vibration amplitude versus frequency is fitted to a Lorentzian curve where \(Q = 1000\) is measured for a smooth CdS nanowire, whose resonance occurred at 835.2 kHz.](image-url)
Fig. 2a gives another stationary selected CdS nanowire with $L = 9.5$ μm and $D = 159$ nm. The natural resonance was excited at the frequency of 696.7 kHz, as shown in Fig. 2b. Young’s modulus was measured as ~38 GPa and the quality factor $Q$ of this nanowire is ~360, as displayed in Fig. 2d, both are smaller than those of the nanowire in Fig. 1a. The TEM image (Fig. 2c) shows that this nanowire has a rough surface, which is different from the nanowire having a smooth surface in Fig. 1a (inset).

In this study, 19 nanowires in total have been measured, whose diameters are in the range of 64–317.5 nm, including smooth nanowires and rough nanowires. The experimental results are summarized in Fig. 3. The Young’s modulus $E$ for the eight nanowires with smooth surfaces vary in the range of 95–196 GPa, and the mechanical quality factors $Q$ vary in the range of 400–1000. For the 11 rough nanowires, the $E$ are measured as 11–90 GPa and the $Q$ are in the range of 100–600. As given in Fig. 3, the rough nanowires show a size-dependent Young’s modulus, i.e. the rough nanowire with larger diameter tends to have a higher $E$, and the $E$ of smooth nanowires are larger than those of the rough nanowires. The Young’s modulus of bulk CdS is about 62 GPa [24], which is equivalent to our data for the nanowires with rough surface, and the measured Young’s modulus of nanowires with the smooth surface is 1.5–3 times as large as that of bulk CdS, which could be attributed to the surface effect as reported elsewhere [17].

To explore the origin of the morphology- and size-dependent mechanical behaviours of CdS nanowires, microstructure characterization of nanowires were carried out using high-resolution transmission electron microscopy.
electron microscopy (HRTEM) images and electron diffraction (ED) patterns. Fig. 4a–c shows a low-magnification TEM image, a HRTEM image and an ED pattern, respectively, of a typical smooth surface nanowire with 95 nm in diameter and growth direction along [0001]. The HRTEM image shows its high-quality single crystal, which is also confirmed by the ED pattern recorded from the same nanowire. Fig. 4d–f shows the TEM characterization of a typical rough surface nanowire with 115 nm in diameter and growth direction along [10–10]. The HRTEM image (Fig. 4e) shows the presence of planar defects. The ED pattern (Fig. 4f) also shows the non-uniform crystal structure with polycrystalline reflection spots. Such planar defects were observed for all the nanowires with rough surfaces. For the rough nanowires with larger diameters, the crystal quality is improved and defect density is reduced, as shown in Fig. 4g–i, whose diameter is 290 nm.

Furthermore, the mechanical quality factors $Q$ also show the morphology and size dependence. The nanowires with smooth surfaces have larger $Q$ in comparison with the nanowires with rough surfaces, and for the rough nanowires, the nanowires with larger diameters have larger $Q$ than those with smaller diameters. It is known that the inverse factor $1/Q$ is related to the energy dissipation, which is determined by the intrinsic properties of “internal friction” involving surface and defect effects. Since the air damping can be neglected in TEM ($10^{-7}$ Torr) [19], the high defect density and grain boundary ‘friction’ in the rough nanowires could result in much more energy dissipation.

In summary, the higher-order harmonic resonances have been observed by the excitation of AC signals inside TEM. Young’s moduli and mechanical quality factor of CdS nanowires with different morphology, size and growth orientation were measured with the assistance of the electric-induced mechanical resonances. It is found that Young’s moduli and mechanical quality factor are dependent on the morphology and size of the nanowires, which are directly linked with the nanowire structure obtained through in situ TEM. The morphology and size-dependent mechanical properties of CdS nanowires with known structure have implications for their nanoelectromechanical applications.

**Funding**

National Science Foundation (grant nos. 50725209 and 10874218); Ministry of Science and Technology (grant nos. 2009DFA01290, 2007CB936203 and 2007AA03Z353); Chinese Academy of Sciences of China.

**References**


