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LETTER TO THE EDITOR

In situ mechanical properties of individual ZnO nanowires and the mass measurement of nanoparticles

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Abstract

The mechanical properties of individual zinc oxide (ZnO) nanowires, grown by a solid–vapour phase thermal sublimation process, were studied *in situ* by transmission electron microscopy (TEM) using a home-made TEM specimen holder. The mechanical resonance is electrically induced by applying an oscillating voltage, and *in situ* imaging has been achieved simultaneously. The results indicate that the elastic bending modulus of individual ZnO nanowires were measured to be ∼58 GPa and the damping time constant of the resonance in a vacuum of 10^{-8} Torr was ∼14 ms. A nanobalance was built and the mass of the nanoparticle attached at the tip of a nanowire was measured. The ZnO nanowires are promising in potential applications as nanocantilevers and nanoresonators.

Due to their interesting properties, one-dimensional (1D) zinc oxide nanomaterials are promising for applications in light-emitting diodes (LEDs), field-effect transistors (FETs), ultraviolet laser diodes (LDs), acousto-electrical devices, detectors and sensors. Various types of 1D ZnO nanostructures, such as nanowires, nanorods, nanorings, nanobelts, and nanocombs, have been synthesized [1–8]. In the meantime, the properties of 1D ZnO, including photoluminescence, field emission, magnetism, and electric transport properties, have also been studied [3, 9–13]. Cantilever-based sensors present a wide range of applications in the field of physical, chemical, and biochemical sciences [14–16]. Nanoscale cantilevers will enable an improvement in sensitivity, spatial resolution, energy efficiency, and time of response [17, 18]. ZnO nanowires, being structurally uniform and single crystalline, could be directly used as nanocantilevers and nanoresonators in nanoelectromechanical systems (NEMS) [19]. A key phenomenon for applying nanowires in NEMS technology is their mechanical resonance

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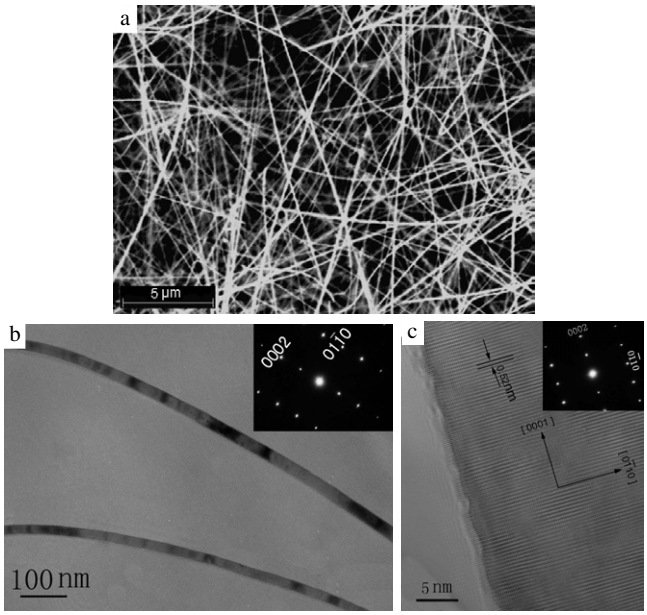

Figure 1. SEM and TEM/HRTEM images of ZnO nanowires.

behaviour, and an important physical quantity for cantilever applications is their elastic bending modulus.

Measurement of the elastic bending modulus of a nanowire object with a length of a few micrometres is rather challenging because its small size prevents the application of the established techniques for mechanical testing. Recently, a new experimental approach, based on electric-field-induced resonant excitation, has been developed for direct measurement of the mechanical properties of individual nano-objects such as carbon nanotubes, silicon nanowires, silicon carbide–silica composite nanowires, and ZnO nanobelts by *in situ* transmission electron microscopy (TEM) [20–24].

In this letter, the mechanical resonances of a single ZnO nanowire, induced by an alternative electric field, were studied by an *in situ* TEM method. The mechanical properties, including elastics and damping dissipation, have been characterized. The mass of an individual nanoparticle attached to the nanowire tip can also be measured. The mechanical behaviour of the ZnO nanowires suggests their potential for versatile applications as nanoresonators and nanocantilevers.

The ZnO nanowires were fabricated by the following procedure. The silicon substrate was placed face down on an alumina boat loaded with metal zinc powder (99.9%). The boat was inserted into the quartz tube of a tubular furnace under a constant flow of argon and oxygen. The nanowires were deposited at the total gas flow rates of ∼300 sccm, with oxygen partial pressure of ∼1%, and at 650 °C. No catalyst was utilized in the deposition process. The as-synthesized ZnO nanowires were characterized by scanning electron microscopy (SEM: Cambridge S360) and high-resolution transmission electron microscopy (HRTEM: JEOL-2010).

An SEM image of the as-synthesized ZnO nanowires is given in figure 1(a), which reveals a large quantity of nanowires with lengths over several tens to hundreds of micrometres. Figure 1(b) shows a typical TEM image of the ZnO nanowires, displaying structural uniformity. The selected area electron diffraction pattern (as shown in the insets of figures 1(b) and (c) and

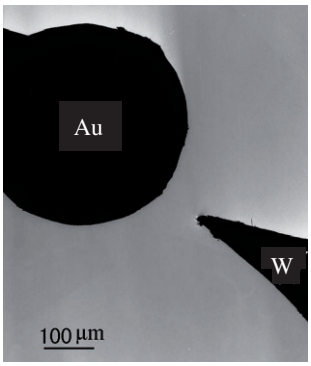

Figure 2. Set-up of the *in situ* measurement.

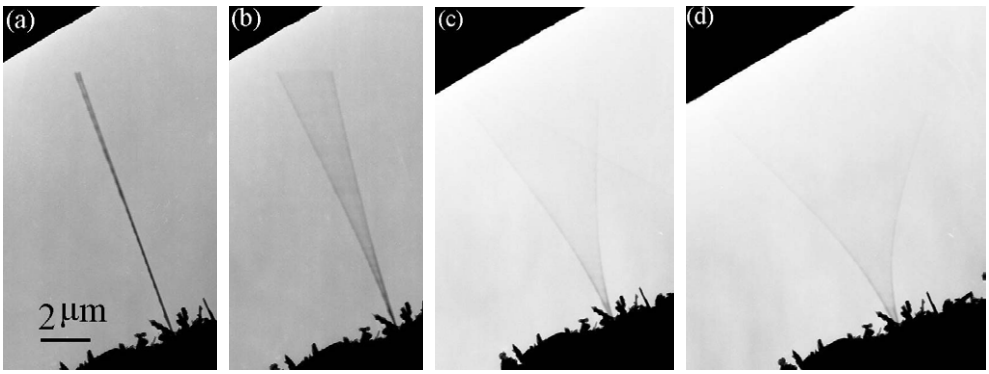

Figure 3. Images showing mechanical resonances of nanowire 1 in table 1.

the HRTEM image (as shown in figure 1(c)) indicate that the nanowires grow along the [0001] direction. The images also show that the nanowires have diameters ranging from 40 to 120 nm.

TEM is a conventional tool for characterizing the atomic-level structures of solid state materials. A novel and unique approach can be developed by integrating the structural information of a nanostructure provided by TEM with the properties measured *in situ* from the same nanostructure [19, 20]. This is a powerful technique that can provide the properties of individual nanomaterials and also can give the microstructure through electron imaging and diffraction, providing an ideal technique for understanding the one-to-one correspondence in property–structure relationships.

To carry out the mechanical property measurements of a nanowire, a specimen holder for the HRTEM (200 kV) was built for applying a voltage across a nanowire and its counter electrode. The specimen holder has two electrodes and a set of piezo-manipulation and translation devices (as shown in figure 2). The nanowires were attached to a tungsten tip; the counter electrode is a solid gold ball of 0.4 mm in diameter. An oscillating voltage with tunable frequency was applied across the two electrodes. Since the electric induced charge on the tip of the nanowire oscillates at the frequency of the applied voltage, mechanical resonance is induced if the applied frequency matches the natural vibration frequency (figure 3). The resonance is directly viewed on the TEM screen and recorded by a CCD camera.

From the classical elasticity theory for a rod or a wire, the fundamental resonance frequency is

Table 1. Systematic data for measuring elastic bending modulus of ZnO nanowires.

Nanowires	Length (μm)	Diameter (nm)	Fundamental frequency (kHz)	Bending modulus (GPa)
1	11.40	77	269	59.7
2	10.40	110	452	57.2
3	8.53	79	533	69.8
4	4.77	43	776	48.9
5	6.27	51	560	54.0

$$\nu_i = \frac{\beta_i^2 D}{8\pi L^2}\sqrt{\frac{E}{\rho}}. \tag{1}$$

Therefore, the elastic bending modulus is given by

$$E = \rho\left[\frac{8\pi\nu_i L^2}{\beta_i^2 D}\right]^2 \tag{2}$$

where β_i is a constant for the ith harmonic: $\beta_1 = 1.875$ and $\beta_2 = 4.694$, E is the elastic bending modulus, L is length of the nanowire, and ρ is the mass density.

Figure 3(a) shows a stationary selected ZnO nanowire. On changing the frequency of the applied voltage, the amplitude of vibration increases or decreases. The fundamental frequency of the nanowire was found through this process. Figure 3(d) shows the harmonic resonance of nanowire 1 in table 1. For calculating the elastic bending modulus, it is critical to measure the fundamental resonance frequency (ν_1) and the dimensional sizes (L and D) of the investigated ZnO nanowires accurately. To determine ν_1, the stability of the resonance frequency was ensured in that one end of the nanowire was tightly fixed, and the resonant excitation was carefully checked around the half value of the observed resonance frequency to ensure that it was the fundamental frequency. In contrast with the resonance frequency, it is easier to obtain the real length (L) and diameter (D) of the nanowire. Based on the experimentally measured data, the elastic bending modulus of the ZnO nanowires is calculated using equation (2).

The experimental results are summarized in table 1. The average value of elastic bending modulus of the ZnO nanowires was ~58 GPa. This value is in agreement with the elastic modulus measured by a nanoindenter for ZnO nanobelts [13], and it is slightly higher than that of ZnO nanobelts (~52 GPa) measured by the same *in situ* TEM technique [20], which may be because of the coupling effect of anisotropic elasticity, resulting from the rectangular cross section of the nanobelts, in the previous measurement [20].

The full width at half maximum (FWHM) of the resonance peak is shown in figure 4, and $\Delta\nu/\nu_1 \sim 0.7\%$. This value is independent of the vibration modes or the size of the nanowires. To explore the intrinsic meaning of the measured $\Delta\nu/\nu_1$ value, we consider a one-dimensional harmonic oscillator with a natural frequency ν_1. When a viscous (or frictional) force is acting on the particle and the force is proportional to the instantaneous speed of the particle, the damping of the vibration amplitude is given by $\exp(-t/\tau_0)$, where τ_0 is the damping time constant of the oscillator. The lifetime τ_0 is related to $\Delta\nu/\nu_1$ by the following equation for $\Delta\nu/\nu_1 \ll 1$:

$$\tau_0 = [(\Delta\nu/\nu_1)\pi\nu_1/1.732]^{-1}. \tag{3}$$

For $\Delta\nu/\nu_1 = 0.7\%$, $\nu_1 = 560$ kHz, the lifetime is $\tau_0 = 14$ ms. From the definition of τ_0, the viscosity (or friction) coefficient $\eta = 2M/\tau_0$, where M is the mass of the particle. Thus, the damping time constant depends on the viscosity coefficient of the nanowire in the medium in which the measurement was carried out.

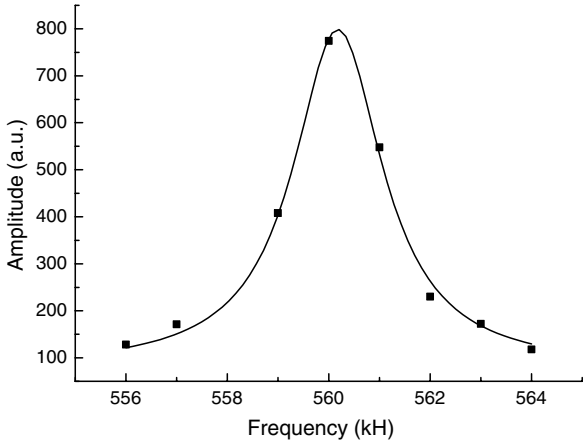

Figure 4. Frequency–amplitude curve for quality factor $\Delta\nu/\nu$ of nanowire 5 in table 1.

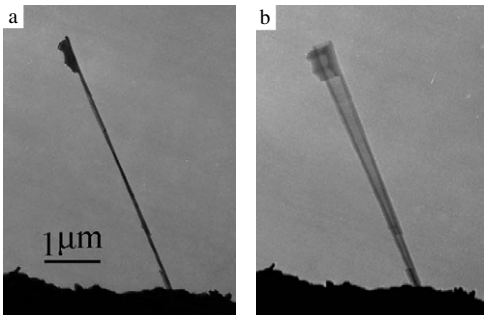

Figure 5. Nanobalance using a ZnO nanowire cantilever.

A ZnO nanowire was set on resonance for 10 min at 560 kHz and at a vibration angle of ∼30°; the shift of resonance frequency was less than 1%, and the resonance frequency and structure of the nanowire are reasonably stable under TEM electron beam irradiation at 200 kV. So the beam illumination intensity has little influence on the mechanical measurements.

Based on the resonance technique above, a ZnO nanowire as a cantilever can be used as a force sensor or a nanobalance. Figure 5 shows a ZnO cantilever with a nanoparticle attached at the tip. The mass of the nanoparticle can be calculated through measuring the resonance frequency (ν), the diameter (D) and length (L). Similar to a pendulum, the mass of particle is given by

$$\nu = D^2/16\pi L(3E/Lm_{\text{particle}})^{1/2}. \tag{4}$$

Take the nanobalance in figure 5 as an example, where ν is 149 kHz, D and L of the nanowire are 48 nm and 5.0 μm respectively, and E is 58 GPa. So the mass of the nanoparticle equals 3.3×10^{-15} g. According to the results, a nanobalance built using ZnO nanowires is feasible for applications to measure the mass of attached nanoparticles.

In summary, mechanical behaviours of ZnO nanowires have been characterized by an *in situ* TEM method. The elastic bending modulus of the ZnO nanowires was measured to be ∼58 GPa and the damping time constant of the resonance in a vacuum of 10^{-8} Torr was ∼14 ms. A nanobalance was built and the mass of the nanoparticle attached at the tip of a nanowire was measured. The single crystalline, structurally controlled nanowires could be

used as a new type of nanoresonator and nanocantilever, which is useful in NEMS and highly functional nanodevices. The ZnO nanowires could also be used as functional tips for scanning probe microscopy.

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