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Communication

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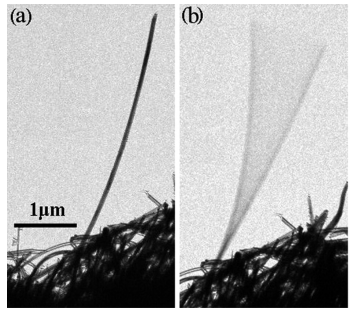

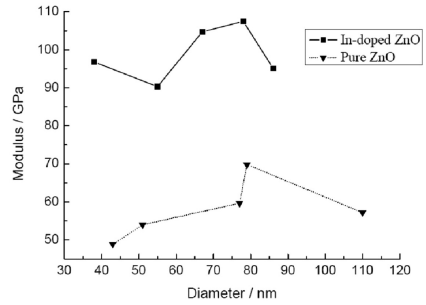

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Communications

Size Independence and Doping Dependence of Bending Modulus in ZnO Nanowires

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ABSTRACT: The bending moduli of individual pure and In-doped ZnO nanowires with different dimensions were studied in situ inside a transmission electron microscopy (TEM) using a mechanical resonance method. The results revealed that the elastic bending modulus of ZnO nanowires is dependent remarkably on doping but independent of size in the experimental nanoscaled range. Taking the structural orientation into account, doping with 17.2 at % In enhances the bending modulus of ZnO nanowires in the [$\bar{1}$010] direction by the average of 120%. The doping effect on the bending modulus of ZnO nanowires was explained by first-principles calculations.

Because of the promising applications in light-emitting diodes (LEDs), field-effect transistors (FET), ultraviolet laser diodes (LD), acousto-electrical devices, detectors and sensors, research on the controllable synthesis methods, morphologies or structures, growth mechanisms, and physical properties has attracted much attention in the area of one-dimensional (1D) zinc oxide nanomaterials.[1−12] Especially ZnO nanowires, with structurally uniform and single crystalline structure, could be directly used as nanocantilevers and nanoresonators in nanoelectromechanical systems (NEMS).[13] Nanoscale cantilever will improve sensitivity, spatial resolution, energy efficiency, and response of time,[14,15] and nanocantilever-based sensors will present more important applications in the fields of physical, chemical, and biochemical sciences.[16−18] A key phenomenon for applying nanowires in NEMS technology is their mechanical resonance behavior, and an important physical quantity for cantilever applications is their elastic bending modulus. Such potential applications have raised the interests in the mechanical properties of 1D ZnO nanostructures.[19−23] It has been reported in the literature that the elastic modulus of ZnO nanowires is 29 ± 8 GPa by using atomic force microscopy (AFM),[19] the bending modulus of ZnO nanobelt is 52 GPa, and the average bending modulus of ZnO nanowires is 58 GPa by using mechanical resonance inside a TEM.[20,21] The Young's moduli of 38−100 GPa are also reported by the similar method.[22] Meanwhile, the size effect on mechanical properties of ZnO nanowires as significant increase in Young's modulus has been reported, and the values are from about 140 to more than 220 GPa for nanowires with diameter from 550 to 17 nm.[23] However, all the modulus values measured above belong to the [0001] direction of ZnO nanowires or belts. There were few reports on Young's modulus of ZnO nanowires affected by structural anisotropy and doping.

In this communication, the mechanical resonances of individual pure ZnO nanowires in the [0001] direction and In-doped ZnO nanowire in the [$\bar{1}$010] direction, induced by an alternative electric field, were studied by the in situ TEM method. The effect of the size and doping on bending modulus of ZnO nanowires was investigated in detail, and the results of the size independence and doping dependence in the bending modulus of ZnO nanowires were obtained. Density functional calculations were applied to estimate the theoretical modulus of pure and doped ZnO nanowire in the [0001] and [$\bar{1}$010] directions. On the basis of the calculations, the underlying mechanism of the modulus enhancement after the doping was addressed, and the enhancement scale was revealed.

Experimental Section. The fabrications and characterizations of the pure and In-doped ZnO nanowires were described in our previous papers.[12,21] The products were examined by a field-emission scanning electron microscope (FESEM, LEO1530) equipped with an energy-dispersive X-ray (EDX) spectrometer and a high-resolution transmission electron microscope (HRTEM, JEOL-2010 FEG).

The mechanical property measurements of In-doped ZnO nanowires were carried out utilizing the same equipment and method as described in our previous paper.[21] A specimen holder for the HRTEM (200 kV) was built for applying a voltage across a nanowire and its counter electrode. The holder has two electrodes and a set of piezo-manipulation and translation devices. After the nanowires were attached to one of the electrodes, an oscillating voltage with tunable frequency was applied across the two

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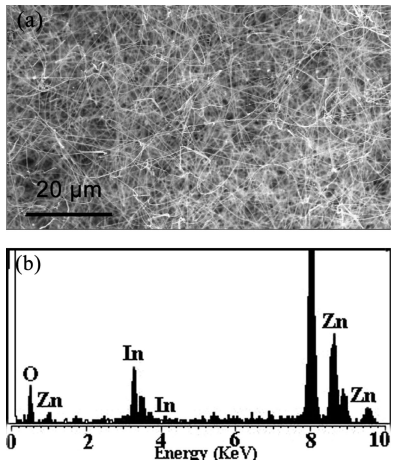

Figure 1. (a) SEM image of In-doped ZnO nanowires on a Si substrate; (b) EDX spectrum of In-doped ZnO nanowires.

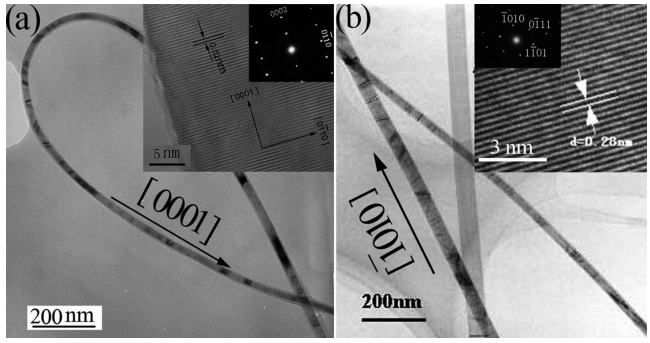

Figure 2. TEM images of nanowires (a) ZnO nanowires, (b)In doped ZnO nanowires. HRTEM images and corresponding SAED patterns shown in the inserts.

electrodes. Because 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.

Results and Discussion. Figure 1a shows that In-doped nanowires are randomly distributed on a Si substrate. The nanowires have diameters ranging from ~30 to 100 nm and length of about tens of micrometers. The corresponding EDX spectrum of the nanowires reveals that the nanowires are composed of Zn, O, and In, and the concentration of In is about 17.2 at.% (Figure 1b). Meanwhile, the pure ZnO nanowires have diameters ranging from 40 to 120 nm. The microstructures of the pure and In-doped ZnO nanowires were characterized by TEM in details. Bright-field TEM observations demonstrate that individual nanowires are single crystal (images a and b in Figure 2). Further, analyzing the HRTEM images and the patterns of selected area electron diffraction (SAED) in insets to images a and b in Figure 2, it can be found that the pure ZnO nanowires and In-doped ZnO nanowires are grown along the [0001] and [$\bar{1}$010] direction, respectively. It must be emphasized the different lengthways direction of pure and In-doped ZnO nanowires because of the remarkable anisotropy effects on bending modulus.

The bending moduli of individual pure and In-doped ZnO nanowires with different diameters were measured using a mechanical resonance method. Figure 3 showed the series of images during the oscillation and resonance of an In-doped ZnO nanowire recorded by CCD camera. The elastic bending modulus (E) can be obtained by eq 1

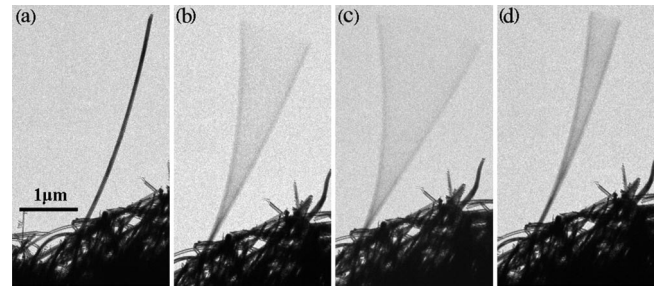

Figure 3. Images showing mechanical resonances of an In-doped ZnO nanowire (with the length of 4.0 μm and diameter of 86 nm): (a) 0, (b) 3.03, (c) 3.04, and (d) 3.05 MHz.

$$E = \rho\left[\frac{8\pi\nu_i L^2}{\beta_i^2 D}\right]^2 \quad (1)$$

where β_i is a constant for the ith harmonic: $\beta_1 = 1.875$ and $\beta_2 = 4.694$, υ_1 is fundamental resonance frequency, L is length of the nanowire, D is diameter of the nanowire, ρ is mass density.

The curves of the elastic bending moduli of pure and In-doped ZnO nanowires versus diameters were plotted in Figure 4. It can be observed that both pure and In-doped ZnO nanowires with different growth direction exhibit that the modulus is independent of the diameters among the measured samples. Also, it is unambiguous the moduli of In-doped ZnO nanowires in the [$\bar{1}$010] direction are much higher than those of pure ZnO nanowires in the [0001] direction. The average bending modulus of pure ZnO nanowires in the [0001] direction is about 58 GPa and that of In-doped ZnO nanowires in the [$\bar{1}$010] direction is 99 GPa.

Considering the anisotropy effect, the doping enhancement cannot be obtained by directly comparing the muduli of pure ZnO nanowires with that of In-doped nanowires in different directions. According to the theoretical anisotropy ratio, defined as the ratio of the modulus of pure bulk ZnO in [$\bar{1}$010] to that in [0001] direction, the modulus of pure ZnO nanowires in [$\bar{1}$010] direction can be calculated from the experimental Young's modulus of pure ZnO nanowires in [0001] direction, because of the independence of the modulus on dimensions. The value of pure ZnO nanowires in [$\bar{1}$010] can be defined as calculated experimental modulus. Then by comparing the calculated experimental modulus of pure ZnO nanowires in [$\bar{1}$010] direction with the experimental modulus of In-doped ZnO nanowires in the same direction, the doping enhancement in [$\bar{1}$010] can be deduced. To obtain the theoretical anisotropy ratio of pure ZnO, we performed the first-principles calculations.

First-principle calculations in the framework of density functional theory (DFT) were performed to study the bending modulus of pure and In-doped ZnO nanowires in order to have a insight about the origin of the doping enhancement. The calculations were realized by using the VASP code.[24] Because of the limitation of our computation capability and based on the size-independenced experimental results, bulk ZnO materials were studied and the size effects of nanowires were neglected in this work. Projector augmented-wave (PAW) method and the Perdew−Burke−Ernzerhof (PBE) type pseudopotentials are used in the calculations.[25,26] On-site Coulomb interaction (U_{eff}) were employed in the calculation by the LDA+U approach, adding an orbital-dependent term to the DFT potential, in order to deal with the strong correlation between the d electrons.[27] The effective U values were assumed to be 7.0 and 5.0 eV for Zn and In, respectively. During the calculation, the cutoff energy was 600 eV, which is 50% larger than the value suggested in the pseudopotential. K-point density was chosen to be 6 nm, resulting in an 11 × 11 × 6 Monhkorst−Pack grid in the Brillouin zone to sample the k-point.[28] In-doped ZnO was modeled by constructing 2 × 2 × 2 supercell and substituting

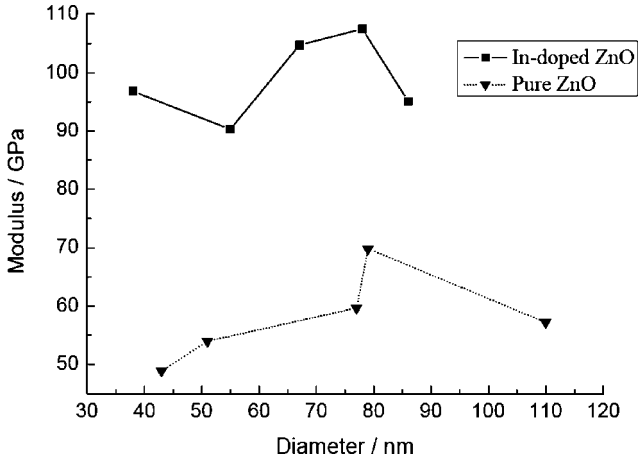

Figure 4. Curves of elastic bending modulus of pure and In-doped ZnO nanowires versus diameters.

Table 1. Calculation Results of Pure and In-Doped ZnO (GPa)

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
pure ZnO	202.9	132.4	113.0	213.6	34.19	35.24
In-doped ZnO	226.7	130.9	16.38	488.9	42.67	47.91

one Zn atom by In atom. Supercell represents a doping rate of 12.5 at %. The calculation results of pure and In-doped ZnO were shown in Table 1.

Young's modulus along [0001] and [$\bar{1}$010] direction can be expressed as

$$E_{[0001]} = c_{33} - 2c_{13}^2/(c_{11} + c_{12}) \quad (2)$$

$$E_{[\bar{1}010]} = (c_{11} - c_{12})(c_{11}c_{33} + c_{12}c_{33} - 2c_{13}^2)/(c_{11}c_{33} - c_{13}^2) \quad (3)$$

So for pure ZnO, $E_{[0001]} = 137.5$ GPa, $E_{[\bar{1}010]} = 106.3$ GPa; for 12.5 at % In-doped ZnO, $E_{[0001]} = 487.4$ GPa, $E_{[\bar{1}010]} = 151.1$ GPa.

The calculation results of pure ZnO agree well with the data in related references,[29,30] showing that the applied calculation method was feasible. On the basis of the theoretical results, for pure ZnO, the anisotropy ratio of $E_{[\bar{1}010]}/E_{[0001]}$ is determined to be 77.3% by comparing 106.3 GPa with 135.7 GPa. Thus, the modulus of calculated experimental pure ZnO nanowires along [$\bar{1}$010] can be obtained as 44.8 GPa, because the experimental modulus of pure ZnO nanowires in [0001] direction is 58 GPa. In the calculations, the anisotropy ratio was regarded as invariable in theoretical calculations and experimental measures in the same materials. Therefore, it is found that the modulus of experimental In-doped ZnO nanowires along [$\bar{1}$010] direction is 120% higher than that of pure ZnO nanowires along the same direction by comparing 99 GPa with 44.8 GPa. In other words, combining the effect of anisotropy with that of doping, the In doping with an actual concentration of 17.2 a % enhances the bending modulus of pure ZnO nanowires in [$\bar{1}$010] direction by about 120%. The tendency is in agreement with our first-principle calculations, because there is about a 42% increase in the Young's module of ZnO along the [$\bar{1}$010] direction that is due to the 12.5% In doping, 151.1 GPa compared to 106.3 GPa.

On the other hand, the enhancement of In doping with content of 17.2 at% in [0001] direction cannot be deduced, because the experimental modulus of In-doped ZnO nanowires in the [0001] direction cannot be obtained in our measurements.

As for the mechanism of doping enhancement of the Young's modulus in In-doped ZnO, let us look at the ion radii of In and Zn ions as 0.092 and 0.083 nm, respectively. Because of the large In ion radius, strain will be induced in the In-doped Zn and the ions are in the high energy strain positions. Anharmonic terms in the $E \sim \varepsilon$ curve will manifest and lead to the increase in Young's moduli.

Conclusions. In summary, mechanical behaviors of pure and In doped ZnO nanowires have been characterized by in situ TEM method. The average elastic bending modulus of pure ZnO nanowires in [0001] direction is about 58 GPa and that of In-doped ZnO nanowires in the [$\bar{1}$010] direction is 99 GPa. Meanwhile, the results indicate that both pure and doped ZnO nanowires exhibit the independence of the modulus on their diameters in the measured range, but the elastic bending modulus of ZnO nanowires is dependent on In doping. Taking account of the effects of structural orientation, the In doping with a content of 17.2 at % enhances the bending modulus of ZnO nanowires in the [$\bar{1}$010] direction by an average of 120%. The first-principle calculations suggest that the doping enhancement is associated with strain induce anharmonic terms in $E \sim \varepsilon$ curves.

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