Elastic Property of Vertically Aligned Nanowires

Jinhui Song,[†] Xudong Wang,[†] Elisa Riedo,*,[‡] and Zhong L. Wang*,[†]

School of Materials Science and Engineering and School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0245

ABSTRACT

An atomic force microscopy (AFM) based technique is demonstrated for measuring the elastic modulus of individual nanowires/nanotubes aligned on a solid substrate without destructing or manipulating the sample. By simultaneously acquiring the topography and lateral force image of the aligned nanowires in the AFM contacting mode, the elastic modulus of the individual nanowires in the image has been derived. The measurement is based on quantifying the lateral force required to induce the maximal deflection of the nanowire where the AFM tip was scanning over the surface in contact mode. For the [0001] ZnO nanowires/nanorods grown on a sapphire surface with an average diameter of 45 nm, the elastic modulus is measured to be 29 ± 8 GPa.

Characterizing the mechanical properties of nanowiress/nanotubes/nanorods (NWs/NTs/NRs) is of great importance for their applications in electronics, optoelectronics, sensors, and actuators. There are several techniques that have been developed for measuring the elastic properties of individual NTs. The technique demonstrated by Lieber et al.[1] was based on quantifying the deflection of a carbon NT that was affixed at one end and the other end was free to be deflected by an atomic force microscope tip. The NT was laid in parallel to a solid substrate, and the elastic modulus of a carbon NT was calculated from the force−deflection curve. A technique by Wang et al. [2,3] relied on the electromechanical resonance of a NT/NW by in situ transmission electron microscopy (TEM). The resonance was stimulated by applying ac voltage across two electrodes, one of which was a carbon NT that was glued to a metal tip affixed on a specimen holder. The resonance frequency together with the geometrical parameters of the NT provided by TEM yielded the elastic modulus. The technique of Yu et al.[4] used two atomic force microscope tips to stretch a carbon NT that was glued at both ends to the two tips, respectively; the stretching force−displacement curve gave tensile strength and elastic modulus. A technique developed by Salvetat et al.[5,6] used an atomic force microscope tip to bend a NT or a bundle of single-walled NTs lying across a hole in a solid substrate. Quantifying the thermal vibration amplitude of a NT in TEM also yielded its elastic modulus.[7] Atomic force microscopy (AFM) has also been applied to study the transversal elasticity of NTs.[8] For all of these techniques, the NTs have to be removed from the substrate used in the growth and are manipulated for the measurements.

Growth of aligned NTs/NWs is of great importance for many technological applications. Elastic properties of densely aligned carbon NTs have been measured by an "indentation" method,[9] in which a tip was pushed downward against the aligned NTs so that many NTs are in contact with the tip and its side surface. By measurment of the force−displacement curve, and the average number of NTs that were in contact with the tip and the contacting area of the NTs with the tip, an average elastic modulus of the NTs was received. This method requires that the density of the nanotubes is high and all of the nanotubes have the same size and length, and the measured result is a statistical average of all the NTs.

In this paper, we demonstrate an alternative AFM based technique for measuring the elastic properties of individual aligned ZnO NWs in scanning area. By simultaneously recording the topography and lateral force image in AFM contact mode when the AFM tip scans across the aligned nanowire arrays, the elastic modulus of individual NWs is determined. This technique allows a measurement of the mechanical properties of individual NWs of different lengths in an aligned array without destructing or manipulating the sample.

The aligned ZnO NW arrays were grown using gold as catalyst by a vapor−liquid−solid method (VLS) process, as reported previously.[10] By choice of an appropriate substrate, the epitaxial growth of ZnO on the single-crystal substrate, such as α-Al_2O_3, GaN, AlN, or $Al_{0.5}Ga_{0.5}N$,[11] yields aligned ZnO nanowires. Figure 1a shows a scanning electron microscopy (SEM) image of the as-grown ZnO nanowires on an α-Al_2O_3 substrate, showing well-aligned distribution

* Corresponding authors. E-mail: zhong.wang@mse.gatech.edu (Z.L.W.); elisa.riedo@physics.gatech.edu (E.R.).
† School of Materials Science and Engineering.
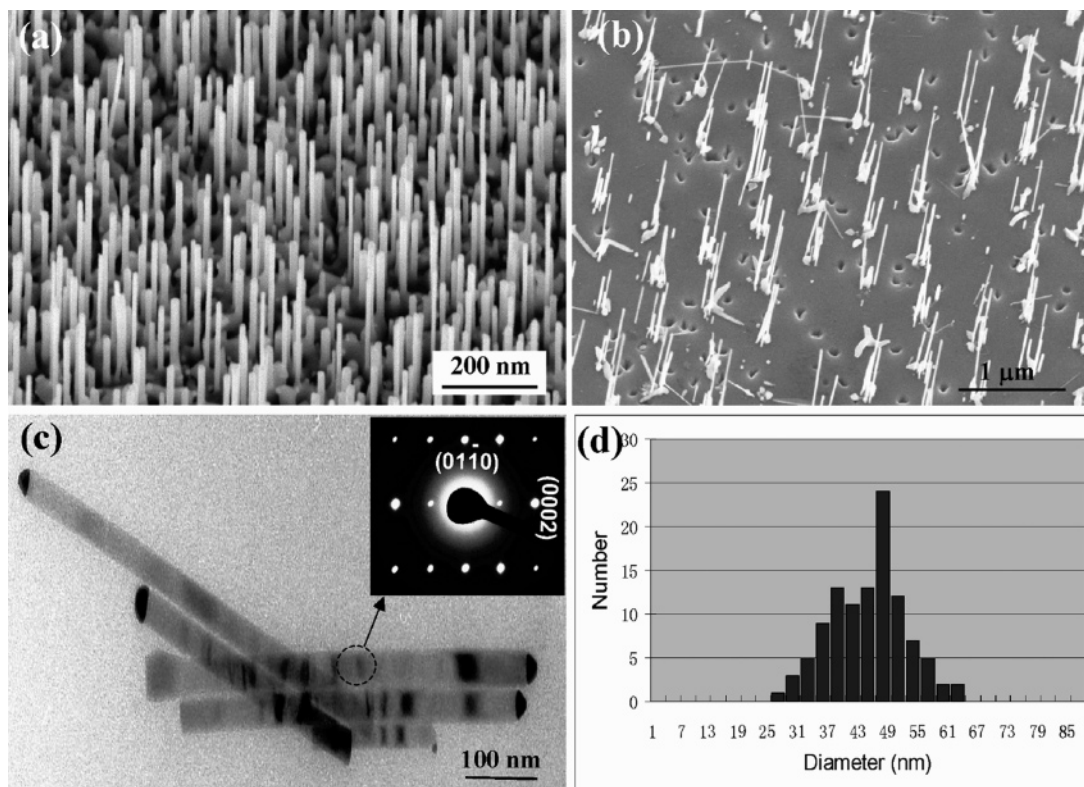‡ School of Physics.

Figure 1. (a, b) SEM images of ZnO nanowire arrays grown on sapphire surfaces. (c) TEM image of the nanowires with gold catalyst at their tips. Inset is an electron diffraction pattern recorded from a nanowire. (d) Statistical distribution in nanowire diameter measured from TEM images.

but a large variation in height/length. If the density of the NWs is too high and/or the NW is too long, the AFM tip is probably too big to reach the surface of the substrate without simultaneously touching two nanowires. For the purpose of our measurements, we have grown a NW array that has relatively less density or shorter length (Figure 1b), so that the AFM tip can exclusively reach one NW and the growth substrate without touching another nanowire; thus, our calculation can be carried out with considering only one nanowire. Each NW is a single crystal and grows along [0001] and is enclosed by six {01$\bar{1}$0} sides facets (Figure 1c). The NWs exhibit a uniform shape, and their size is measured from the TEM image to have an average diameter of 45 nm (Figure 1d).

The elastic measurements were performed by an AFM (PicoPlus from Molecular Imaging) operated in contact mode. A Si tip with 20° cone angle (from Nanosensors) was used for the measurements. The rectangular cantilever had a calibrated normal spring constant of 4.5 N/m and a lateral spring constant of 1378.1 N/m.[12] The set point (constant normal force) was 21 nN. The scanning velocity was 7.8 μm/s.

The principle for the AFM measurement is illustrated in Figure 2. In AFM contact mode, a constant normal force is kept between the tip and sample surface. The tip scans over the top of the ZnO NW and the tip's height is adjusted according to the surface morphology and local contacting force. Before the tip meets a NW, a small lateral force is observed (Figure 2a). When the tip comes in contact with a NW, the lateral force increases almost linearly as the NW is
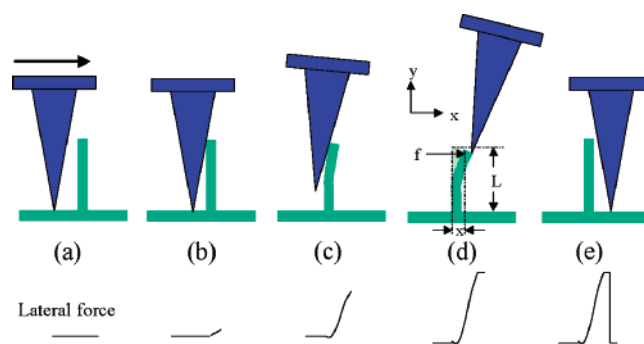

Figure 2. Procedures for measuring the elastic modulus of a nanowire in the AFM contacting mode (see text).

elastically bent from its equilibrium position (Figure 2b,c). At the largest bending position, as illustrated in Figure 2d, the tip crosses the top of the NW, then the NW is released; the lateral force drops suddenly and reaches the ordinary level (Figure 2e). Considering the size of the NW, the thermal vibration of the NW at room temperature can be ignored.[7]

During this scanning process, the AFM works in the following way: When the tip contacts the NW, the scanner (or cantilever) retracts at the same time in order to maintain a constant normal force, the cantilever is twisted, and a rapid change in lateral signal is detected by the photodetector. At the largest bending position, the scanner retracts to the highest position and the lateral signal reaches the maximal value. As the tip keeps moving at a low scanning speed, the bent NW is released by the tip, then the scanner extends quickly to touch the substrate, and the twisted cantilever
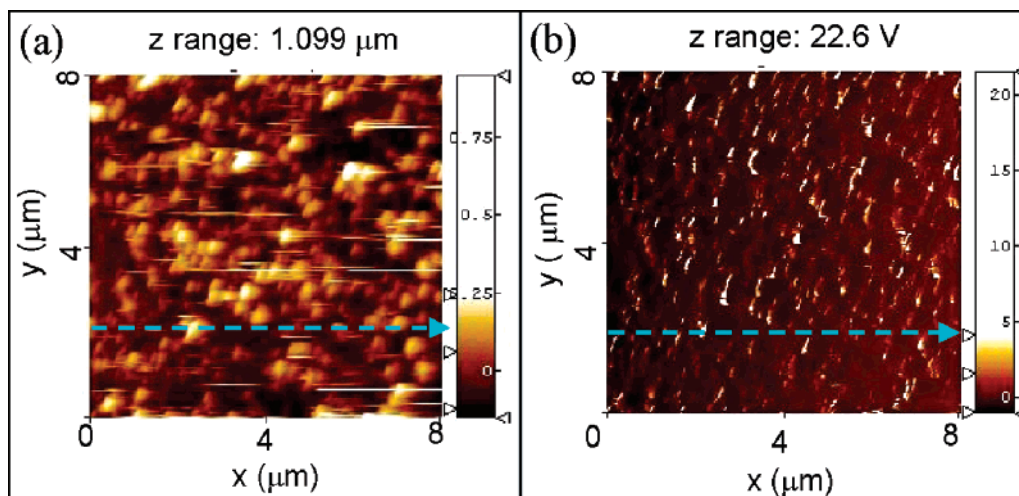
Figure 3. (a) Topography image and (b) lateral force image of the aligned ZnO nanowire arrays received in AFM contacting mode. The elastic modulus of each nanowire in the scanning range can be derived from these images.

immediately recovers to its equilibrium position. From the torsion of the cantilever, the lateral force is measured.

Experimentally, the as-synthesized sample was loaded upward on a specimen holder, and the tip of the AFM was scanned across the aligned NW arrays. Both the topography image (feed back signal from the scanner) and the lateral force image were recorded simultaneously. The scanning area varies from 25 to 100 μm^2. In contact mode, the AFM tip keeps in touch with the sample surface at a constant force (set point). In contact mode, as the tip scans over the vertically aligned NWs, the NWs are bent consecutively if their density is reasonably low. The bending force is captured in the lateral force image (Figure 3b), and the bending distance is directly recorded in the topography image (Figure 3a). The elastic modulus will be derived from the relationship between maximal lateral force and maximal bending distance.

The elastic modulus is derived based on the following calculation. As the AFM tip swipes over the NW with its side and top surfaces in contact with the NW, a lateral force is applied on the top of the NW. At the largest bending position (Figure 2d), the applied lateral force reaches the maximum, so does the bending distance. The lateral force can be directly read out from the lateral friction force image, and the corresponding bending distance is read from the topography image. From the geometrical relationship illustrated in Figure 2d, when a vertical NW experiences a lateral force f parallel to the scanning direction, the displacement of the NW under the small deflection approximation can be expressed as[13]

$$EI\frac{d^4x}{dy^4} = (f_0 + f)\delta(y - L) \quad (1)$$

where f_0 is the projected component of the friction force between the tip and the NW in parallel to the tip scanning direction, E and I are the elastic modulus and momentum of inertia of the NW, x is the lateral displacement perpendicular to the NW, y is the height from the fixed end (root) of the NW to the point where the lateral force is applied, which is

approximately the tip of the NW ($y = L$), and the contact is assumed to be a point, and L is the length of the NW. f_0 is much smaller than the bending force f especially when the scanning speed is low; it thus can be dropped out in eq 1. The applied lateral force f is expressed as

$$f = 3EI\frac{x}{L^3} \quad (2)$$

From Hook's law, the spring constant is $K = f/x$; thus, the elastic modulus can be expressed as a function of the spring constant K, the length of the NW, and the momentum of inertia: $E = KL^3/3I$. The ZnO nanowire growing along [0001] usually has a hexagonal cross section with side length of a (a is the radius of the NW), for which the momentum of inertia is $I = (5(3^{1/2})/16)a^4$. From the SEM and TEM images, the aligned ZnO NWs have a uniform diameter of 45 nm (Figure 1d) and heights varying from 200 to 800 nm (Figure 1b). The elastic modulus is given by

$$E = \frac{16L^3K}{15(3^{1/2})a^4} \quad (3)$$

From the topography image (Figure 3a), the bright spots with tails are from the NWs, and the tails are due to the deflection of the NWs along the scanning direction of the tip. The line scan speed of the tip was 7.8 $\mu m/s$, and the gain was set at a medium range. At the same points in the corresponding lateral force image (Figure 3b), there are also spots. To ensure that the center of the conical tip touches the center of the NW as assumed in theoretical calculation, both curves were read from the center of the NW as indicated in the images by dashed lines. Taking a line scan across the middle point of a spot in the topography image, a curve for the scanner retracting distance verses the NW lateral displacement is obtained, as shown in Figure 4a. A sudden change in the profile occurs when the tip scans over the NW; the relatively flat part is when the tip scans on the substrate
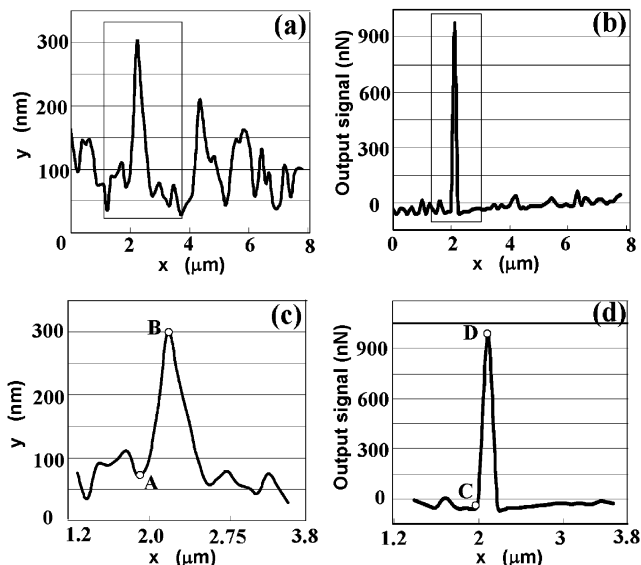
Figure 4. (a, b) Line profiles along the dashed lines in Figure 3 (a, b) showing the curves of scanner retracting distance versus the nanowire lateral displacement and the lateral force versus the lateral displacement, respectively. (c, d) Enlarged portions of the areas enclosed by rectangles in (a, b), respectively. The set point of the AFM was 0.15 V, while the photodetector output was ∼6 V at the maximum lateral force.

Figure 5. Tip−nanowire geometry for calculating the length/height of the nanowire.

where there are no NWs. Taking a scanning profile at the corresponding line in the lateral force image (as indicated in Figure 3b), the maximal lateral force for bending the NW is measured. A sudden change in the curve occurs when the tip meets the NW and the friction force increases rapidly. Parts c and d of Figure 4 are the enlarged portions of the curves enclosed by rectangles in parts a and b of Figure 4, respectively. As in Figure 4c, the scanner retracting distance and the corresponding lateral displacement are the differences in y and x coordinates, respectively, between points A and B. In the corresponding lateral force curve in Figure 4d, the difference in heights between points C and D is the maximum bending force of the NW. It is noticed that the profile of lateral force is not as asymmetric as schematically shown in Figure 2. This is because the gain of the AFM has to be set very high to observe the ideal profile, but a high gain would result in an ultrasensitivity of the measurement to system noise. A choice of medium gain produces a lateral force profile that is not as asymmetric as expected. In addition, the nanowire can vibrate after being released by the tip, and a subsequent contact of the vibrating tip with the body of the cone-shape tip also reduces the asymmetry of the profile.

The length of the nanowire can be derived from the AFM image, as demonstrated in Figure 5. When the tip meets a NW, the scanner/cantilever retracts and at the same time the tip is deflected. From the point at which the scanner begins to retract to the largest retracting position, the vertical and lateral displacements are represented by h and d, respectively, which are measured from the topography image (Figure 4a). The true lateral displacement of the NW has to consider the bending of the cantilever. For the same force applying to the cantilever and the NW, the lateral displacement of the cantilever is 4 orders of magnitude smaller than that of the
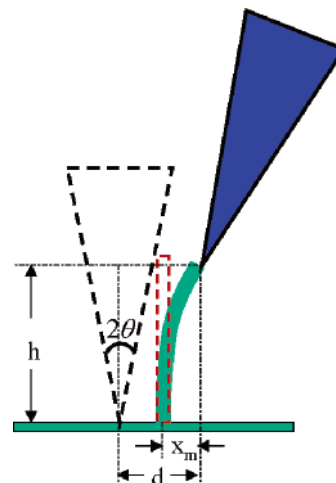
Table 1. Measured Elastic Modulus of Aligned ZnO Nanowires

nanowire	length (μm)	elastic modulus (GPa)
1	0.277	20
2	0.281	22
3	0.452	20
4	0.211	36
5	0.301	42
6	0.640	36
7	0.683	47
8	0.209	35
9	0.168	15
10	0.209	35
11	0.194	22
12	0.285	28
13	0.631	21
14	0.328	31
15	0.641	20

NW; thus, it can be ignored in the calculation. Therefore, the length of a NW is given by $L \approx (h^2 + x_m^2)^{1/2}$, and the bending displacement of the NW is given by $x_m = d - h \tan\theta$, where 2θ is the apex angle of the AFM tip ($2\theta = 20°$). From the same position in the lateral force image, we can get the lateral force f_m that caused the maximal NW bending.[14] Combining the measured x_m and f_m from the two line profiles, the spring constant $K = f_m/x_m$ is obtained.

The elastic modulus of several well aligned ZnO NWs is presented in Table 1. The lengths of the nanowires vary from 167.9 to 683.4 nm, the corresponding elastic modulus varies from 15 to 47 GPa. The averaged elastic modulus of ZnO NW is 29 GPa. This is consistent with the results measured by in situ TEM.[15] From eq 3, the estimated error in E measurement is

$$\Delta E/E = 3|\Delta L/L| + 4|\Delta a/a| + |\Delta f/f| + |\Delta x/x| \quad (4)$$

For typical values of $\Delta L = 10$ nm, $L = 300$ nm, $\Delta a = 0.5$ nm, $a = 22.5$ nm, $\Delta f/f = 3\%$ and $\Delta x/x = 3\%$, eq 4 yields $\Delta E/E = 26\%$, which gives $E = 29 \pm 8$ GPa. The spread of

data in Table 1 cannot be totally attributed to experimental error because the elastic modulus may depend on the size and length of the NWs. It must be pointed out that the variation in diameter as presented in Figure 1d is one of the major errors in this type of measurement because the size of the nanowire cannot be accurately measured by AFM without destroying the sample.

In summary, we have presented a general method for measuring the elastic modulus of individual nanowires aligned on a solid substrate using AFM. The technique has two advantages. One, it is feasible to measure the elastic modulus of an as-grown nanowire without destroying or manipulating the sample. Second, the measurements are carried out individually, systematically, and almost simultaneously for all of the nanowires aligned in the scanning area. The lengths of the NWs can be different. The topography image and the lateral force image simultaneously capture the geometrical profile and mechanical properties of all the nanowires in the area. An analysis of the images gives the elastic modulus of individual nanowires. The disadvantage of the technique is its inaccuracy in evaluating the size of individual nanowires without destroying the sample. For the ZnO nanowires grown on sapphire surfaces with an average diameter of 45 nm, the elastic modulus is measured to be 29 ± 8 GPa. This technique can be applied to one-dimensional nanostructures of any material as long as they are aligned on a solid substrate and their density is relatively low and/or heights are relatively short.

References

(1) Wong, E. W,; Sheehan, P. E.; Lieber, C. M. *Science* **1997**, *277*, 1971.
(2) Gao, R. P.; Wang, Z. L.; Bai, Z. G.; de Heer, W. A.; Dai, L. M.; Gao, M. *Phys. Rev. Lett.* **2000**, *85*, 622.
(3) Poncharal, P.; Wang, Z. L.; Ugarte, D.; de Heer, W. A. *Science* **1999**, *283*, 1513.
(4) Yu, M. F.; Lourie, O.; Dyer, M. J.; Moloni, K.; Kelly, T. F.; Ruoff, R. S. *Science* **2000**, *287*, 637.
(5) Salvetat, J. P.; Kulik, A. J.; Bonard, J. M.; Andrew, G.; Briggs, D.; Stöckli, T.; Méténier, K.; Bonnamy, S.; Béguin, F.; Burnham, N. A.; Forró, L. *Adv. Mater.* **1999**, *11*, 161.
(6) Salvetat, J. P.; Andrew, G.; Briggs, D.; Bonard, J. M.; Bacsa, R. R.; Kulik, A. J.; Stöckli, T.; Burnham, N. A.; Forró, Lásló. *Phys. Rev. Lett.* **1999**, *82*, 944.
(7) Treacy, M. M. J.; Ebbesen, T. W.; Gibson, J. M. *Nature* **1996**, *381*, 678.
(8) Palaci, I.; Fedrigo, S.; Brune, H.; Klinke, C.; Chen, M.; Riedo, E. *Phys. Rev. Lett.* **2005**, *94*, 175502.
(9) Qi, H. J.; Teo, K. B. K.; Lau, K. K. S. *J. Mech. Phys. Solids* **2003**, *51*, 2213.
(10) Wang, X. D.; Summers, C. J.; Wang, Z. L. *Nano Lett.* **2004**, *3*, 423.
(11) Wang, X. D.; Song, J. H.; Li, P.; Ryou, J. H.; Dupuis, R. D.; Summers, C. J.; Wang, Z. L. *J. Am. Chem. Soc.* **2005**, *127*, 7920.
(12) We calculated the lateral spring constant by $K_l = W^2 K_n/T^2$, where K_n is the normal spring constant and W and T are the width and thickness of the cantilever determined from SEM images.
(13) Landau, L. D.; Lifshitz, E. M. *Theory of Elasticity*; Addison-Wesley Publishing Company, Inc.: Reading, MA, 1959,
(14) The lateral sensitivity was determined from the curve of lateral force vs distance when the tip was scanned in contact mode on a flat surface area of the GaN substrate, which was used for growing the nanowires.
(15) Bai, X. D.; Gao, P. X.; Wang, Z. L.; Wang, E. G. *Appl. Phys. Lett.* **2003**, *82*, 4806.

NL051334V