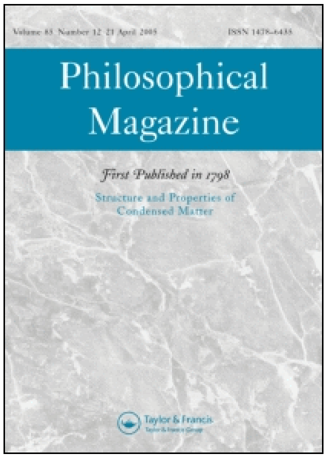

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Size dependence of the mechanical properties of ZnO nanobelts

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The Young's modulus of ZnO nanobelts was measured using an atomic force microscope following the modulated nanoindentation method. The nanobelts have a rectangular cross-section, with width-to-thickness ratios ranging 1–10 and lengths up to a few millimetres. The Young's modulus of two nanobelts with width-to-thickness ratio of 2.2 and 1.3 was measured at 55 and 108 GPa, respectively, indicating a size dependence of the elastic properties of the nanobelts.

1. Introduction

The semiconductor zinc oxide (ZnO) has drawn considerable interest due to its piezoelectric properties [1], band gap in the ultraviolet and wide range of applications [2]. Various ZnO nanostructures, such as nanocombs, nanorings, nanosprings, nanobelts, nanowires and nanocages have been synthesized [3]. These nanomaterials exhibit structure-dependent physical and chemical properties, which are different from those of bulk materials [4] and make ideal building blocks for future electronic components, gas sensors [5], field-emission displays [6] and nanoelectromechanical systems (NEMS) [7].

Among this rich variety of nanostructures, ZnO nanobelts are characterized by a rectangular cross-section and well-defined growth directions, with widths ranging from 30 nm to 2 μm, width-to-thickness ratios ranging 1–10 and lengths of up to a few millimetres [8]. Determining their elastic properties and understanding the size dependence of these properties are essential to the development of ZnO-based NEMS.

The elastic properties of ZnO single-crystals and polycrystalline films were previously studied by ultrasonic measurement and nanoindentation [2, 9, 10]. Nanoindentation on (0001)-oriented bulk wurtzite ZnO crystals yielded a Young's

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modulus value of 111 GPa, which was relatively constant over the indenter penetration depth range of 10–400 nm [10]. A wide range of Young's moduli between 40 and 120 GPa has been reported for polycrystalline ZnO films, depending on their preparation method [2].

Recent attempts to determine the elastic properties of ZnO nanostructures have been made using two main techniques. In the first approach, the mechanical response of a nanostructure, fixed at one end and free at the other, to an oscillating electric field is observed in an electron microscope. The bending modulus is then determined from the resonance frequency and the physical dimensions of the nanostructure [11–13]. Using this technique, Bai *et al.* [11] obtained an average value of 52 GPa for the Young's modulus of ZnO nanobelts. Four nanobelts of width-to-thickness ratio ranging from 1.1 to 1.7 were studied and no clear size-dependence of the bending modulus was observed. Yum *et al.* [12] measured the resonance frequency of four ZnO nanobelts used as mechanical beam resonators, with width-to-thickness ratio ranging from 1.4 to 4.4. The Young's moduli in the thickness direction, calculated from the resonant frequencies, were between 38 and 85 GPa with the maximum value corresponding to the nanobelt with the lowest width-to-thickness ratio of 1.4. Chen *et al.* [13] reported an increase of the Young's modulus of ZnO nanowires from 139 GPa (close to the bulk value of 140 GPa) to over 220 GPa as their diameter decreases from 550 to 17 nm. The size dependence was explained by the surface-stiffening effect related to bond length contraction near the free surfaces.

Another approach is to use an atomic force microscope (AFM) to measure the force and the corresponding deformation of the nanostructure [14–17]. The hardness on ZnO nanobelts was measured by AFM and the values between 2 and 8 GPa are consistent with the value of 5 GPa from the ZnO single-crystal [14]. Song *et al.* [15] reported an average value of 29 GPa for the elastic modulus of vertically aligned ZnO nanowires with an average diameter of 45 nm. The bending modulus of three individual ZnO nanobelts deposited over trenches (widths around 100 nm) was measured by collecting AFM images in contact mode of the nanobelt under different forces. The values obtained for the nanobelts of width-to-thickness ratio 1.1, 1.2, and 1.3 were 118, 105 and 162 GPa, respectively [16]. The bending modulus of individual ZnO nanobelts was also measured with an AFM tip in a three-point bending configuration. Ni *et al.* [17] concluded that the bending modulus does not depend on the surface-to-volume ratio in the range from 0.017 to 0.035 nm^2/nm^3 or the width-to-thickness ratio from 2 to 9. They admit, however, that the size dependence of the bending modulus may be obvious only for nanobelts with a width and a thickness smaller than 10 nm [17].

Molecular dynamics simulations on the elastic properties of ZnO nanobelts indicate that the elastic modulus of nanobelts with width and thickness smaller than 4 nm increases with decreasing lateral dimensions, with predicted values that are higher than the bulk value [18].

In this study, the Young's modulus of ZnO nanobelts with a width-to-thickness ratio between 1 and 2 and width of $\sim$1 μm was measured using an AFM following the modulated nanoindentation method.

2. Material and experiment

The elastic properties of the ZnO nanobelts were studied using the modulated nanoindentation method. This technique was previously applied on carbon nanotubes [19] and carbon fibres embedded in an epoxy matrix [20]. Modulated nanoindentation consists in indenting an AFM tip in a sample while normally (perpendicularly to the substrate) oscillating the sample supported by the AFM scanner. The oscillations have to be small, about 1 Å, so that the tip sticks on the nanostructure. During the stick regime, the normal force F necessary to vertically move the nanostructure by d_{tot} with respect to the cantilever support coincides with the force needed to elastically stretch two springs in series [21, 22]: the cantilever, with normal stiffness k_{lever}, and the tip-sample contact with normal stiffness $k_{contact}$. The total stiffness k_{total} is given by:

$$\frac{\partial F}{\partial d_{tot}} = k_{total} = \left(\frac{1}{k_{lever}} + \frac{1}{k_{contact}}\right)^{-1} \tag{1}$$

d_{tot} is the sum of the contact deformation and the cantilever bending. Since k_{lever} is known, a measure of $\partial F/\partial d_{tot}$ at different normal loads F_0 would yield k_{total} as a function of F_0.

During the experiment, the value of $\partial F/\partial d_{tot}$ is measured by means of a lock-in amplifier. The lock-in amplifier vertically modulates the sample position by Δd_{tot} by exciting the piezo-tube of the AFM scanner with a sinusoidal signal of given amplitude and frequency, and it simultaneously measures the signal ΔF extracted from the AFM photodiode (PSD) via a signal-access module (figure 1).

The elastic modulus is deduced from the k_{total} as a function of F_0 by modelling the contact between the AFM tip and the nanobelt with the Hertz model. Since the nanobelt width is generally much larger than the AFM tip radius, the system is modelled as a sphere (tip) indenting a flat surface, in which case, the normal contact stiffness is proportional to the contact radius a [23]:

$$k_{contact} = 2E^* a \tag{2}$$

where E^* is the reduced modulus of elasticity defined by $E^* = [(1-\nu_1^2)/E_1 + (1-\nu_2^2)/E_2]^{-1}$ with ν_i and E_i the Poisson's ratio and Young's modulus of the indenter ($i=1$) and sample ($i=2$). Following the continuum contact mechanics

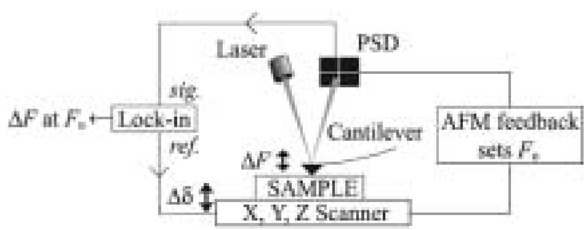

Figure 1. Experimental setup for the modulated nanoindentation method.

theories, for small normal forces, the contact radius a for a sphere indenting a flat surface is given by [21, 22]:

$$a^3 = \frac{3}{4}\frac{R \cdot (F + F_{\mathrm{adh}})}{E^*} \tag{3}$$

where R is the tip radius and F_{adh} is the tip-sample adhesion force. Combining equations (1)–(3), the data k_{total} against F are fitted with:

$$k_{\mathrm{total}} = \left\{\frac{1}{k_{\mathrm{lever}}} + \frac{1}{2E^*[3/4 \cdot R \cdot (F + F_{\mathrm{adh}})/E^*]^{1/3}}\right\}^{-1} \tag{4}$$

where E^* is the only unknown fit parameter.

The ZnO nanobelts used for this study were prepared by vapour deposition, following the procedure described by Pan *et al.* [8], and deposited on a flat silicon substrate. The nanobelt samples were characterized by scanning electron microscopy and AFM (Veeco CP-II) operating in non-contact mode in air. The same silicon tip (PointProbe NCHR from Nanoworld), of radius ~60 nm, was used for the images and the modulated nanoindentation experiments. The normal cantilever spring constant, 48 N/m, was calibrated using the method of Sader *et al.* [24]. The amplitude of the oscillations for the modulated nanoindentation was 1.5 Å and the frequency was set at 14.018 kHz. This technique was previously tested with a tip of similar spring constant on the silicon substrate and other nanostructures. Typically, the experimental error for the reduced modulus E^* is below 10%. The relation between E^* and the nanobelt Young's modulus E increases the error to 16% for E values around 100 GPa.

3. Results

Scanning electron microscopy and AFM images show that the nanobelts have a rectangular cross-section, with lateral dimensions of several tens of nanometres to a few microns and lengths up to a few millimetres (figure 2). In this study, two different nanobelts were studied: one nanobelt is 450 nm thick and 1000 nm wide (labelled NB1), and the other is 820 nm thick and 1100 nm wide (NB2). Both are several hundreds of microns long.

Figure 3 plots total stiffness against normal indentation force for NB1 (figure 3a) and NB2 (figure 3b). Using $\nu_1 = 0.27$, $E_1 = 169$ GPa for the silicon tip, and $\nu_2 = 0.3$, an average value calculated using the elastic constants tabulated in [2], the data fit gives Young's modulus values of 55 and 108 GPa for NB1 and NB2, respectively. These values are consistent with those reported in the literature, obtained from the mechanical resonance technique or other AFM methods.

The significant difference in Young's modulus between the two nanobelts of distinct width-to-thickness ratio in the range 1–2 indicates that there is a size dependence of the elastic properties of the ZnO nanobelts. The trend is similar to that from the data compiled from [11, 12, 16, 17], where the highest Young's moduli were measured on the nanobelts with the smallest width-to-thickness ratio, usually

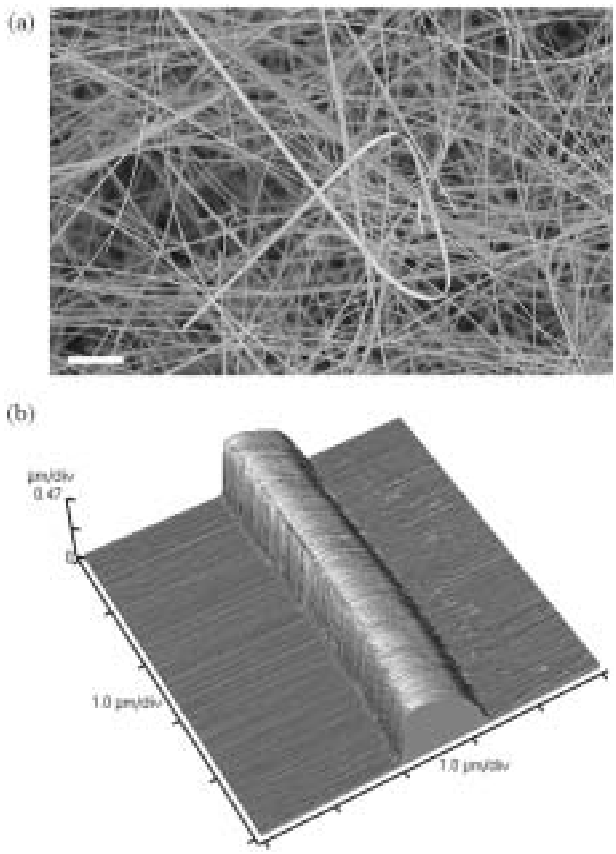

Figure 2. (a) SEM image of the ZnO nanobelts. The scale bar is 20 μm. (b) AFM image (5 × 5 μm) of a ZnO nanobelt.

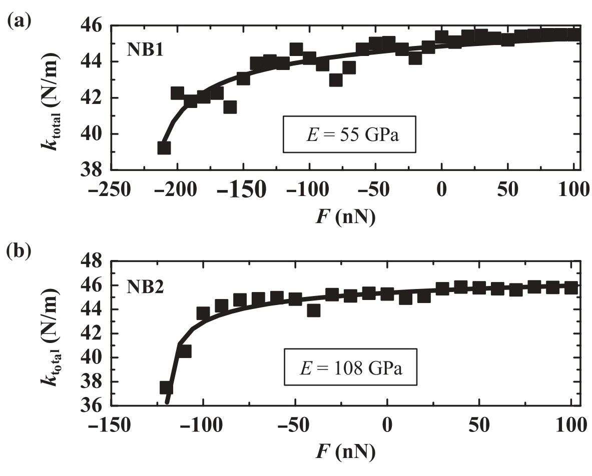

Figure 3. Total stiffness versus normal indentation force for (a) 1000 × 450 nm NB1, (b) 1100 × 820 nm NB2.

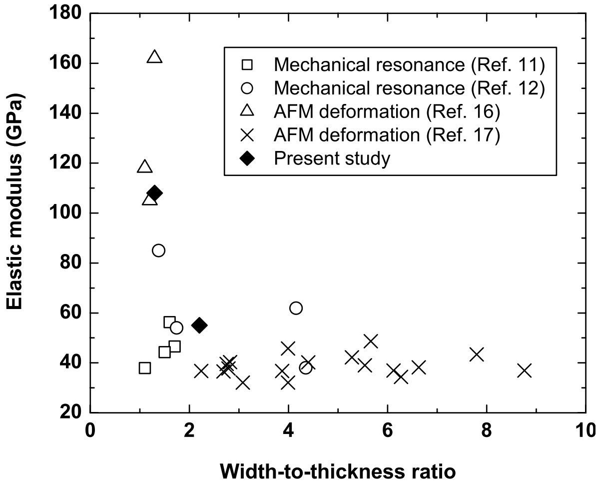

Figure 4. Elastic modulus of ZnO nanobelts as a function of the width-to-thickness ratio.

lower than 1.5 (figure 4). This result is also consistent with the conclusion of Ni *et al.* [17] that the modulus does not depend on the width-to-thickness ratio of 2–9. Additional theoretical studies and further experiments are underway to understand the origin of the size dependence of the mechanical properties of ZnO nanobelts.

4. Conclusion

Using the modulated nanoindentation method, the Young's modulus of two nanobelts with width-to-thickness ratio of 2.2 and 1.3 was measured at 55 and 108 GPa, respectively, indicating a size dependence of the elastic properties of the nanobelts. The two values are consistent with those obtained with other techniques and indicate a width-to-thickness ratio dependence of the Young's modulus for ratios between 1 and 2. The origin of this size dependence requires further investigation.

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