Nanoindentation of vertical ZnO nanowires

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Abstract

We report the experimental observations of buckling instabilities of vertical well-aligned single-crystal ZnO nanowires prepared on ZnO:Ga/glass templates. It was found that critical buckling load and buckling energy of the ZnO nanowires were 215\,μN and 3.69\,μJ, respectively. It was also found that Young’s modulus of the ZnO nanowires were 232 and 454\,GPa while critical buckling strains were 0.35% and 0.18% when fixed–fixed column mode and fixed–pinned column mode were used, respectively.

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1. Introduction

One-dimensional (1D) materials such as nanowires, nanobelts and nanorods have attracted considerable interest in recent years. They present the utmost challenge to semiconductor technology, making fascinating novel devices possible. It has been demonstrated that these 1D materials exhibit superior electrical, optical, mechanical and thermal properties. It has also been shown that these materials are potential useful for nanoscale interconnects, active components of optical electronic devices and nanoelectromechanical systems. However, it is important to understand mechanical characteristics of these nanowires prior to any feasible applications\cite{1–3}. For example, mechanical properties of carbon nanotubes have been extensively studied by tensile loading, bending and buckling\cite{22–29}. To our knowledge, mechanical properties of various Si and III–V semiconductor-based nanowires have also been reported\cite{4–7}.

1D oxide systems such as SnO\textsubscript{2} \cite{8}, tungsten oxide (W\textsubscript{18}O\textsubscript{49}) \cite{9}, GeO\textsubscript{2} \cite{10}, indium tin oxide (ITO) \cite{11}, Al\textsubscript{2}O\textsubscript{3} \cite{12} and ZnO \cite{1–3,13,14} nanowires have also attracted much attention in recent years. Among them, ZnO is an n-type direct-gap semiconductor with a large exciton binding energy of 60\,meV and wide bandgap energy of 3.37\,eV at room temperature. Hence, ZnO is regarded as a promising photonic material\cite{15–19}. However, only few reports on the mechanical properties of ZnO nanowires can be found in the literature\cite{1–3,20,21,31}. In this work, we selectively deposited vertically well-aligned ZnO nanowires on ZnO:Ga/glass templates and performed nanoindentation tests to study the buckling instabilities of these nanowires. Based on Euler buckling model, we also estimated Young’s modulus (elastic modulus) of the ZnO nanowire.

2. Experiments

The ZnO nanowires used in this study were grown on ZnO:Ga/glass templates. Detailed growth procedures can be found elsewhere\cite{10–14}. During the growth of ZnO nanowires, the pressure inside the quartz tube, growth temperature and growth time were kept at 10\,Torr, 600\,\degree C and 60\,min, respectively. A Philips PW3710 X-ray diffractometer was used to characterize the crystallographic property of the as-grown ZnO nanowires. After ZnO
nanowire growth, we used a Hysitron triboscope nanoindentation system from Hysitron Inc. to investigate buckling behavior of the nanowires. As shown in Fig. 1, we applied a uniaxial compression onto the ZnO nanowires a diamond indenter diameter of 2 μm. During nanoindentation tests, we applied various prescribed forces onto the vertical ZnO nanowires. Surface morphologies of the samples and size distribution of the nanowires before and after the nanoindentation tests were characterized by a JEOL JSM-6500 F field emission scanning electron microscope (FESEM), operated at 5 KeV.

3. Results and discussion

Fig. 2 shows cross-sectional FESEM image with 30° title angle of the as-grown ZnO nanowires. It can be seen clearly that high-density well-aligned ZnO nanowires with uniform length and diameter were selectively grown. It was found that typical diameter, length and density of these nanowires were 30, 800 nm and 1.2 \times 10^{10} \text{cm}^{-2}, respectively. It was also found that these ZnO nanowires were distributed uniformly while tops of these nanowires were hexagonal with the c-axis perpendicular to the substrate surface [14]. From X-ray diffraction and photoluminescence measurements, it was found that the ZnO nanowires were preferred oriented in the (002) c-axis direction with good crystal quality. Fig. 3 shows top-view SEM micrograph of the nanowires after the nanoindentation test. It can be seen that these nanowires were severely distorted. Since these tests were destructive, we performed several tests for each prescribed force and found that the results were reproducible.

Fig. 4 shows load–displacement curve of our ZnO nanowires. This curve represents a loading–unloading cycle. The loading portion consists of three stages: an initial increase, followed by a sudden drop in the slop and the curve became flat, and a third stage comprising an increasing load. Inset of Fig. 4 shows an enlarged
load–displacement curve. As shown in this enlarged curve, it can be seen that collapse force or the critical buckling load for these ZnO nanowires was around 215 μN. The corresponding buckling energy was around 3.69 × 10^-11 J.

From top-view FESEM images of the buckled ZnO nanowires, we can easily estimate that average critical buckling load, $P_{cr}$, of each individual ZnO nanowire was around 0.57 μN. This value is important in determining Young’s modulus of a single ZnO nanowire. It is well known that the behavior of an ideal column and/or nanowire compressed by an axial load $P$ can be summarized as follows: (1) if $P < P_{cr}$, the column is in stable equilibrium in the straight position; (2) if $P = P_{cr}$, the column is in a neutral equilibrium in either the straight or a slightly bent position; (3) if $P > P_{cr}$, the column is in unstable equilibrium in the straight position will buckle under the slightest disturbance [30]. The critical loads for column with various supports can be related to the critical load of a pinned-end column through the concept of an effective length, $L_e$. The critical load can be derived from buckling equation as follows [30]:

$$P_{cr} = \frac{\pi^2 EI}{L_e^2},$$

where $E$ is the Young’s modulus and $I = \pi R^4 / 4$ is the moment of inertia for the column (i.e., vertical ZnO nanowire). Note that such buckling is called Euler buckling and the critical load for an ideal elastic column is often called Euler load. The effective length is expressed in term of an effective-length factor $K$

$$L_e = KL,$$

where $L$ is the actual length of the column. Thus, the critical load is given by

$$P_{cr} = \frac{\pi^2 EI}{(KL)^2}.$$

The buckling behavior of ZnO nanowires in this work can be approached by two possible conditions as follows: (1) Mode 1: $K = 0.5$, i.e. $L_e = 0.5L$, a nanocolumn with both ends fixed against rotation (i.e., fixed–fixed column), where $P_{cr} = 4\pi^2 EI / L^2$ (or $E = P_{cr}L^2 / 4\pi^2 I$); (2) Mode 2: $K = 0.7$, i.e. $L_e = 0.7L$, a nanocolumn fixed at the base and pinned at the top (i.e., fixed–pinned column), where $P_{cr} = 2.046\pi^2 EI / L^2$ (or $E = P_{cr}L^2 / 2.046\pi^2 I$). For a Euler buckling column, the critical buckling strain is given by: 

$$\varepsilon_{cr} = \frac{\sigma_{cr}}{E},$$

where critical buckling stress $\sigma_{cr} = P_{cr}/A$ [30].

As shown in Table 1, we can estimate the critical stress ($\sigma_{cr}$), critical buckling strain ($\varepsilon_{cr}$) and Young’s modulus ($E$) of the ZnO nanowires from the critical buckling load of an individual ZnO nanowire. It was found that the calculated Young’s modulus were 232 and 454 GPa while critical buckling strain was 0.35% and 0.18% when modes 1 and 2 were used, respectively. For comparison, the results of ZnO nanowires prepared on GaAs (0 0 2) [32] and ZnO thin film [2,33] were also listed in the same table. Based on Euler buckling, it was found that Young’s modulus of the ZnO nanowires increases with decreasing diameters for both fixed–fixed column mode ($K = 0.5$) and fixed–pinned column mode ($K = 0.7$) mode. These results agree well with the molecular dynamics simulation reported by Kulkarni et al. [31], and with the experimental results reported by Chen et al. [2]. For high-quality nanowires, Young’s modulus is determined mainly by surface modification of the nanowires. Thus, these agreements should be attributed to the high compressive internal stress levels resulting from the surface stress and the high surface-to-volume ratio of our ZnO nanowires [2,31]. These agreements also suggest that crystal quality of our ZnO nanowires is good.

### 4. Conclusion

In summary, we report the experimental observations of buckling instabilities of vertical well-aligned single-crystal ZnO nanowires prepared on ZnO:Ga/glass templates. It was found that critical buckling load and buckling energy of the ZnO nanowires were 215 μN and 3.69 × 10^-11 J, respectively. It was also found that Young’s modulus of the ZnO nanowires were 232 and 454 GPa while critical buckling strains were 0.35% and 0.18% when fixed–fixed column mode and fixed–pinned column mode were used, respectively.

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Reference