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Mechanical properties of individual nanorods and nanotubes in forest-like structures

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ABSTRACT

We calculated the mechanical properties of a ZnO nanorod within forest-like samples. According to the results for ZnO nanorods, we extended the calculation method to determine the mechanical properties of a TiO_2 nanotube (TN) extracted from a forest densely grown by anodization on a Ti substrate. The Euler model was adopted, and critical-load measurements were performed during vertical-compression experiments involving nanoindentation. We measured the elastic moduli of a single ZnO nanorod and a single TN as ~190 and ~27 GPa, respectively. Thus, we suggested a method for determining the mechaical properties of individual entities in one-dimensional materials grown in bundles.

In recent years, one-dimensional (1D) nanomaterials such as nanowires, nanotubes, and nanorods have attracted considerable interest for optical and chemical sensors, photocatalysts, and photoanodes in solar cells owing to their unique electrical properties [1–4]. From the viewpoint of the fabrication of electrical devices, the mechanical and functional properties of 1D nanomaterials should also be considered, because the reliability of devices is important. Furthermore, knowledge of the mechanical properties of individual 1D nanomaterials is a critical for applications in the field of nanomaterials. However, the agglomeration of 1D nanomaterials due to their high specific surface area and densely grown rods/wires on substrates has made it difficult to clarify the mechanical behavior of individual 1D nanostructures. We studied vertically grown ZnO nanorods and TiO_2 nanotubes (TNs) that were formed on GaN and Ti substrates, respectively. These nanostructured materials have been used for many electrical and optoelectronic devices [5,6].

Chen et al. reported [7] that the Young's modulus of ZnO nanowires was highly size-dependent and dramatically increased to 220 GPa as the diameter of the ZnO nanowires decreased to less than 120 nm [8]. In other studies, many different Young's moduli of ZnO were reported, depending on the size, fabrication methods, and measuring techniques [9,10]. In typical nanotube arrays, because the mechanical properties are determined by the constituent nanoelements, novel approaches are required to evaluate the strength of these discrete structures. For anodized nanoporous structures such as TNs, the modulus and hardness have been evaluated by a few research groups [11–13] using continuum mechanics [1,2,14]. Thus far, the mechanical properties of individual TNs have not been reported.

In previous studies, the mechanical properties of individual ZnO nanostructures were measured by complicated processes using microelectromechanical-systems [15,16] or *in situ* transmission electron microscopy [17,18], which are not only time-consuming and expensive but also difficult to perform. To resolve these issues, we carefully controlled the growth process to produce sparsely grown ZnO nanorods and then measured their mechanical properties. Using these data, we calculated the mechanical properties of a single ZnO nanorod within the forest-like samples. On the basis of the ZnO-nanorod example, we extended this methodology to determine the mechanical properties of an individual TN.

ZnO nanorods were grown on a 2-μm-thick GaN thin film by a wet chemical growth method using a zinc-nitrate solution. The density of the grown ZnO nanorods was controlled by seed layers, which are

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explained in detail in a previous report [19]. TNs were fabricated by the electrochemical anodization of a titanium foil. The detailed procedures for the fabrication of TNs are presented in a previous report [20]. To analyze the crystal structures of the ZnO nanorods and TNs, their X-ray diffraction patterns (Empyrean, PANalytical) were observed. The ZnO nanorods were preferentially grown along the c-axis direction [002], and the as-prepared TNs had an amorphous structure. The surface morphology of the samples and the size distribution of the nanorods and nanotubes were characterized before and after nanoindentation tests using a field-emission scanning electron microscope (FE-SEM SUPRA25, Zeiss and FE-SEM S-4700, Hitachi). Fig. 1 shows the scanning electron microscopy (SEM) images of the ZnO nanorods and TNs. Sparsely and densely grown ZnO nanorods are shown in Fig. 1(a) and (b), respectively. As shown in Fig. 1(a), the spaces between the nanorods were approximately 1–3 μm, which was large enough to allow the indentation of individual ZnO nanorods with a flat punch tip for the measurement of their mechanical properties. The diameter and height of the nanorods were approximately 500–850 nm and 3.5–4.5 μm, respectively. The diameter and height of the ZnO-nanorod bundle, which is shown in Fig. 1(b), were 150–450 and 1.8–2 μm, respectively, and the space between nanorods was ~300 nm. Using the flat punch tip, dozens of rods were simultaneously indented. Fig. 1(c) and (d) shows plane-view and side-view SEM micrographs of the TNs grown on the substrate at 50 V for up to 6 h. The average inner diameter (D_i) of the 6-h-grown TNs was ~112 nm, and the total diameter (D_e) was ~150 nm. The lengths of the 6-h-grown TNs were ~20 μm.

The mechanical properties of the ZnO nanorods and TNs were investigated using a nanoindentation system (Nanoindenter G200, Agilent Tech.). GaN and Ti metal sheets grown on 1D materials were glued onto a holder, and then an indentation test was performed with a flat diamond tip ($\phi = 2.5$ μm, Synton-MDP). Different stress states were applied to the contact region of the tip by using the flat punch shape indenter; thus, the inherent strength of the nanotubes was evaluated regardless of the loading conditions.

The indentation test was implemented with a constant strain rate of 0.05 s^{-1}, and the depth was varied from 500 to 1000 nm in order to gather complete information from the initial deformation to the final failure of the rods and tubes. Fig. 2 shows SEM images of a single ZnO nanorod and a bundle of ZnO nanorods after the indentation test (Fig. 2(a) and (b), respectively), as well as the indentation procedure for a single rod (Fig. 2(c)) and simulation data (Fig. 2(d)). Fig. 2(a) shows a representative image of the flat top tip on forest-like ZnO nanorods after the indentation experiment. With this type of failure, it is difficult to understand the mechanical properties of individual rods. We grew scanty ZnO nanorods and then indented them with the flat top tip. The spaces between the ZnO nanorods were wide enough for a single rod to be pushed through. An indented single ZnO nanorod is shown in Fig. 2(b). We presume that the ZnO nanorods broke near the interface between the GaN substrate and the nanorod. This was a commonly observed phenomenon during the study (refer to the enlarged inset in Fig. 2(b)). The reaction of the ZnO nanorod during indentation is schematically illustrated in Fig. 2(c). The ZnO nanorods were bent when the load applied to the rods reached the critical value, subsequently breaking near the interface between the GaN substrate and the nanorod. We used a computer simulation tool (COMSOL Multiphysics 4.2) to define the stress distribution in the ZnO nanorods under a load. As shown in Fig. 2(d), the stress applied to the rod was distributed from top to bottom and was highly concentrated at the edge of the bottom part, which may have caused the interfacial failure of the ZnO nanorods.

These phenomena are also observed in the load–displacement (L–D) curves shown in Fig. 3(a). A large displacement occurred when the segment was held during the indentation procedure, which is generally done for the stabilization of materials to deformation. In this procedure, the holding time was 10 s. Somehow, during the increase of the displacement, the load applied to the rods slightly decreased. Apparently, this was caused by the slip after the interfacial collapse of ZnO nanorods between the rods and substrate. Fig. 3(b) and (c) shows zoomed-in areas of the L–D curves from the initial loading to the sudden break, which is indicated by the dotted circle in Fig. 3(a). In Fig. 3(b) and (c), a few pop-ins are observed from 0 to 150 nm under displacement. Among them, it is reasonable to consider the first biggest increment in the displacement as the significant point for the critical load ($\boldsymbol{P_{cr}}$) of the nanorods, which can be used to evaluate the mechanical properties of the nanorods. Presumably, the sudden increase in the curve displacement around 60–80 nm were due to the initial buckling of the rods. This is reported in the literature as the "critical stable" zone II [21–23]. The

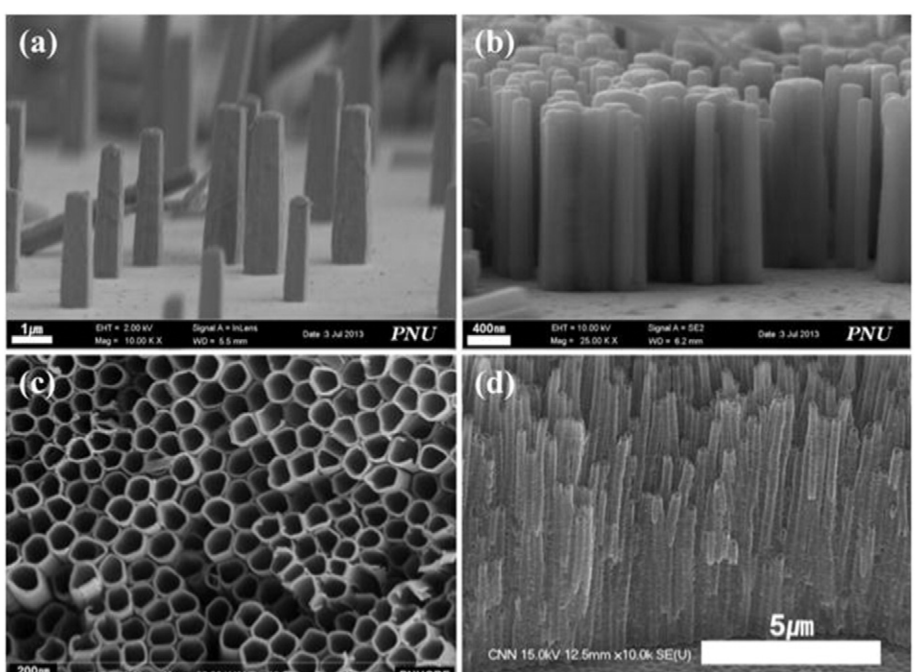

Fig. 1. SEM images of ZnO nanorods (a, b) and TNs (c, d): (a) ZnO nanorods grown sparsely with special care by a wet chemical growth method; (b) densely grown ZnO bundle; (c) top view of anodized TNs; (d) side view of (c) showing uneven heights.