Wall-thickness-dependent strength of nanotubular ZnO

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We fabricate nanotubular ZnO with wall thickness of 45, 92, 123 nm using nanoporous gold (np-Au) with ligament diameter at necks of 1.43 μm as sacrificial template. Through micro-tensile and micro-compressive testing of nanotubular ZnO structures, we find that the exponent $m$ in $\bar{\sigma} \propto \bar{p}^m$, where $\bar{\sigma}$ is the relative strength and $\bar{p}$ is the relative density, for tension is 1.09 and for compression is 0.63. Both exponents are lower than the value of 1.5 in the Gibson-Ashby model that describes the relation between relative strength and relative density where the strength of constituent material is independent of external size, which indicates that strength of constituent ZnO increases as wall thickness decreases. We find, based on hole-nanoindentation and glazing incidence X-ray diffraction, that this wall-thickness-dependent strength of nanotubular ZnO is not caused by strengthening of constituent ZnO by size reduction at the nanoscale. Finite element analysis suggests that the wall-thickness-dependent strength of nanotubular ZnO originates from nanotubular structures formed on ligaments of np-Au.

Functional metal oxides such as ZnO have been widely used for sensor, energy conversion, and catalyst materials⁴⁻⁷. Because of its excellent piezoelectric properties, ZnO has been widely studied for applications in nano-generators that convert mechanical energy to electrical energy, and various ZnO structures have been suggested to achieve high conversion efficiency and mechanical reliability⁸⁻¹⁰. Nano-accordion structures of ZnO and Al-doped ZnO have been fabricated by using interference lithography and atomic layer deposition (ALD), and its stretchability attains 51%, i.e. two orders of magnitude greater than the planar film structure⁸. ZnO nano-sheet structures proposed as nano-generators provide highly enhanced stretchability by using elastic buckling of the structure with high aspect ratio⁹, 10. The reliability of these devices relies on the mechanical properties of bulk structure and constituent materials.

Recently, three-dimensional micro-architectures with superior mechanical properties have been suggested¹¹⁻¹⁷. Meza et al. fabricated three-dimensional nano-structural metamaterials by ALD coating of metal oxide on a polymer nano-lattice patterned by direct laser writing followed by selective etching of the polymer template using oxygen plasma etching⁰¹. They are ultralight and so energy-absorbent that they can recover their original shape after compression to greater than 50% strain. During compression in the thin-walled structure, brittle fracture in the constituent solid can be suppressed by optimizing the wall thickness-to-tube radius ratio, resulting in ductile-like behavior by dominant elastic shell buckling. Various hollow nano-lattices with low density and high elastic deformation limit have been suggested, and the relation between the structure of the nano-lattice and wall thickness has been studied. Schaedler et al. suggested metal micro-lattices prepared by electroless plating of Ni on three-dimensional polymer templates; these materials show complete recovery after compression to greater than 50% strain, and degradation in compressive strength is lower than 10% after repeatable compressions¹⁶. Biener et al. introduced nanotubular TiO₂ and Al₂O₃, with ultralow density¹⁶. They synthesized ultralow-density bulk materials with interconnected nanotubular morphology using nanoporous gold (np-Au) as template. These nanotubular materials provide superior mechanical properties in terms of hardness-to-weight ratio, as investigated by nanoindentation. These three-dimensional micro-architectures with hollow and/or lattice structures have excellent mechanical performance such as high energy absorption and high strength-to-weight ratio, overcoming brittle nature of constituent materials.

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Here we fabricate nanotubular ZnO using ALD on np-Au followed by selective etching of the np-Au template, and perform micro-tensile and micro-compressive testing. We compare tensile and compressive behavior of nanotubular ZnO structure. The strength of the constituent ZnO, as evaluated by the Gibson-Ashby model looking at the strength of a cellular structure as a function of relative density, is found to increase with decreasing wall thickness. We propose that the wall-thickness-dependent strength of nanotubular ZnO comes from material or structural properties and investigate this proposition with hole-nanoindentation, grazing incidence X-ray diffraction (XRD), and finite element analysis (FEA).

Results and Discussion

Tensile and compressive behavior of nanotubular ZnO. Nanotubular micro-tensile and micro-compressive ZnO samples with wall thickness, $t$, of 45 ($\pm$3), 92 ($\pm$4), and 123 ($\pm$6) nm are shown in Fig. 1 (see Methods and Supplementary Fig. S1). Hereafter, these nanotubular ZnO samples with wall thickness of 45, 92, and 123 nm are referred to as $t = 45$, 92, 123 nm, respectively. We measured the volume and weight of bulk nanotubular ZnO samples at millimeter scale, from which relative density, ratio of volume occupied by constituent solid to total volume of nanotubular ZnO, was measured with density of solid ZnO, 5.61 g/cm$^3$. As shown in Fig. 1g, relative density is 1.4% ($\pm$0.10%) for $t = 45$ nm, 2.8% ($\pm$0.16%) for $t = 92$ nm, and 3.5% ($\pm$0.24%) for $t = 123$ nm. Figure 2a shows typical tensile stress-strain curves for nanotubular ZnO, indicating brittle behavior in tension, linear elastic deformation and catastrophic failure (see Supplementary Movie 1 for $t = 123$ nm). Fracture strain is 0.91% ($\pm$0.05%) for $t = 45$ nm, 0.61% ($\pm$0.06%) for $t = 92$ nm, and 0.18% ($\pm$0.01%) for $t = 123$ nm. They show negligible plasticity in tension, so these fracture strains are almost identical to tensile elastic limit of nanotubular ZnO samples. Measurement of the tensile elastic limit is critical since this property determines the critical bending radius of flexible devices and maximum tensile strains of stretchable device where nanotubular materials are used. Compared with fracture strain of 0.03% for bulk ZnO$^{18}$, tensile elastic limits of nanotubular ZnO structures are greatly improved values. Fracture strength is 131 ($\pm$10) kPa for $t = 45$ nm, 289 ($\pm$7) kPa for $t = 92$ nm, and 363 ($\pm$8) kPa for $t = 123$ nm. All nanotubular ZnO samples were made with identical np-Au templates, and hence the nanotubular structures are identical and differences in mechanical behavior probably come from different wall thicknesses of constituent ZnO.

Figure 2b shows typical compressive stress-strain curves for $t = 45$, 92, 123 nm. They show similar trends as compressive strain increases regardless of wall thickness: stage (i) linear elastic deformation, (ii) nonlinear increase in stress between onset of nonlinearity and highest stress, followed by (iii) gradual decrease in stress, and (iv) wavy plateau (see Supplementary Movie 2 for $t = 123$ nm). The onset of nonlinearity as indicated by arrows in Fig. 2b, boundary between stages (i) and (ii), is attributed to elastic shell buckling and/or local fracture. As shown in Fig. 2c, we performed interrupted unloading during stage (ii) for $t = 45$ nm. Unloading curve shows anelastic loop-type recovery rather than reversible elastic recovery, and the sample does not recover its original shape; instead, about 2% plastic deformation remains after unloading. This indicates that during stage (ii), elastically recoverable shell buckling and local fracture leading to plastic deformation occur simultaneously. The critical
ratio of wall thickness \( t \) to tube radius \( a \) for elastic shell buckling of straight tubes in three-dimensional architectures \(^{14,19} \) is given by

\[
\left( \frac{t}{a} \right)_{\text{crit}} = \frac{\sigma_f E}{3(1 - \nu^2)},
\]

(1)

where \( \sigma_f \), \( E \), and \( \nu \) are respectively the fracture strength, elastic modulus, and Poisson's ratio of the constituent solid. The critical ratio of wall thickness to radius for nanotubular ZnO is estimated to be 0.063 for \( t = 45 \) nm, 0.128 for \( t = 92 \) nm, and 0.172 for \( t = 123 \) nm where a tube radius of 715 nm, the average radius of ligament necks in np-Au, is used. The right-hand term in Equation (1) is 0.0859 when \( \sigma_f = 3.9 \) GPa, \( E = 77 \) GPa, and \( \nu = 0.2 \) \(^{21} \) are used. \( \sigma_f \) and \( E \) are measured by hole-nanoindentation, as described below. The critical ratio in the left term for \( t = 45 \) nm is smaller than right term, 0.0859 and left terms are greater than right term for other two samples, \( t = 92 \) nm and \( t = 123 \) nm. If the nanotubular ZnO is composed of long and straight tubes \(^{14} \), this may mean that the \( t = 45 \) nm sample could show ductile-like behavior by dominant shell buckling while the \( t = 92 \) nm and \( t = 123 \) nm samples could show brittle-like behavior by dominant local fracture. However, no transition in deformation mode depending on wall thickness was observed, and the three samples showed similar behavior in tension and compression. Unlike three-dimensional architectures composed of long, straight, and hollow struts, the nanotubular ZnO in this study was formed on np-Au ligaments with mostly saddle-shape and convex-shape surfaces \(^{22}\); this results in curved shells, np-Au ligament diameter at necks that is thinnest inner diameter of tubes is somewhat distributed, connectivity between ligaments is irregular, and tubes are randomly distributed \(^{23,24} \). Due to these structural features, a mixed mode of elastic shell buckling and local fracture is likely to operate widely simultaneously after onset of nonlinearity.

Compressive yield strain at boundary between stages (i) and (ii), is 7.5% (±1.9%) for \( t = 45 \) nm, 5.3% (±0.7%) for \( t = 92 \) nm, and 3.8% (±1.0%) for \( t = 123 \) nm. These values are approximately one order of magnitude greater than the elastic limits in tension. During stage (iii), local fractures are observed widely, as indicated in Fig. 2b inset. Locally-fractured shells can hardly support external force until densification stage at extremely high strain, suggesting that any decrease in stress is caused by extensive local fractures. In previous reports on compression of hollow-tube lattice of NiP with relative densities ranging from 0.01% to 0.54% \(^{15} \), hollow-tube lattice structures

Figure 2. (a) Tensile behavior of nanotubular ZnO. Inset: OM images before and after micro-tensile testing (scale bars, 500 μm). (b) Compressive behavior of nanotubular ZnO. Insets: OM images of compressed nanotubular ZnO at points 1 through 4 in compressive stress-strain curve for \( t = 123 \) nm (scale bars, 500 μm). (c) Interrupted unloading testing for \( t = 45 \) nm. Insets: OM images of nanotubular ZnO at points 1 through 3 in stress-strain curve (scale bars, 500 μm). (d) Relative yield strength, ratio of yield strength of nanotubular ZnO structure to strength of constituent ZnO measured by hole-nanoindentation, 3.9 GPa as a function of relative density.
with high relative density showing brittle-like behavior by dominant local fracture have a stress-drop region similar to ours while those with low relative density do not. One feature of the stress drop in stage (iii) is that discrete strain bursts are not observed, implying that fine local fractures occur gradually. Stage (iv) (Fig. 2b inset) shows severe collapse of the nanotubular ZnO structure.

Figure 2d shows the relation between relative yield strength, ratio of yield strength of nanotubular ZnO structure to fracture strength of the constituent solid, (3.9 GPa is used for the fracture strength of the constituent solid, ZnO nanotubular walls, which is measured by hole-nanoindentation as described below), and relative density in log-log scales. The linear slope for tension is found to be 1.09 and that for compression is 0.63. By Gibson and Ashby\(^2\), the ratio of brittle-crushing strength for open-cell foams with a box-like central tubular void size \(t_i\) within struts of thickness \(t_s\) to the fracture strength of the constituent solid is

\[
\frac{\sigma_c}{\sigma_f} = \frac{1 + \left(\frac{t_i}{t_s}\right)^2}{1 - \left(\frac{t_i}{t_s}\right)^2} C^{1.5},
\]

where \(C\) is the proportional constant. This equation suggests that linear slope is 1.5 in Fig. 2d if the fracture strength of the constituent solid is independent of wall thickness. Linear slopes in Fig. 2d, 1.09 in tension and 0.63 in compression, are smaller than 1.5 as in Equation (2), which means that the fracture strength of the constituent solid increases as wall thickness decreases. In other words, if yield strengths of nanotubular ZnO structures in tension and compression in Fig. 2d are converted to fracture strength of constituent ZnO as a function of wall thickness using the Gibson-Ashby model with exponent 1.5, the fracture strength of constituent ZnO tends to increase with decreasing wall thickness.

**Thickness-independent fracture strength and grain size of ZnO film.** To investigate whether this apparent wall-thickness effect comes from material and/or structural properties, we performed hole-nanoindentation tests on suspended ZnO thin films (see Supplementary Movie 3) and grazing incidence XRD for ZnO thin films on Au film/Si substrates. Here, ‘material property’ means that the inherent strength of the constituent ZnO increases as wall thickness decreases, i.e. the thickness-dependent strength of ZnO\(^1\), and ‘structural property’ indicates features caused by the nanotubular structures formed on np-Au described above, based on the thickness-independent strength of ZnO. Figure 3a shows scanning electron microscope (SEM) images of hole-nanoindentation. From indentation force-displacement curves, the fracture strength and elastic modulus of ZnO films are measured using

\[
F = \sigma_0 \left(\frac{\pi a}{2}ight) \left(\frac{\delta}{a}\right) + E \left(\frac{q_0 a}{\delta}\right)^3,
\]
surface energy and atomic strain. This surface stress is very important and critical in understanding mechanical properties of nanostructures. Such size-dependent elasticity is significant when at least one of the dimensions of interest is smaller than 10 nm. This size-dependent surface energy might contribute to increase in deduced strength of constituent materials with decreasing wall thickness seen in Fig. 5a and b. Also, surface stress is calculated from yield strength of nanotubular structure (simplified in FEA) since wall thickness-independent strength of constituent ZnO were used as input value in the FEA.

The Gibson-Ashby model is widely used to correlate relative strength, defined by the ratio of the strength of cellular materials to that of the constituent solid, and relative density, \( \rho \), given by \( \rho = \frac{\sigma}{\sigma_0} \), where \( \sigma_0 \) is a proportional constant depending on the specific structure of a cellular material. Figure 5a and b show the deduced strengths of constituent ZnO calculated with yield strength of nanotubular structure measured in FEA (Fig. 4c) and experiments (Fig. 2a and b), respectively, by applying the Gibson-Ashby model. The value of \( \sigma_0 \) of 0.3 for open-cell foams is used for simplicity. Deduced strengths of constituent ZnO calculated with yield strength of nanotubular structure measured in FEA, in Fig. 5a, are greater than input strength of constituent ZnO, 3.9 GPa in FEA, and tend to increase as wall thickness decreases. This indicates that the wall-thickness effect in strength of constituent materials with decreasing wall thickness seen in Fig. 5a and b. Also, surface stress is calculated from the size-dependent surface energy by using the Shuttleworth equation and the relationship between surface energy and atomic strain. This size-dependent surface energy might contribute to increase in deduced strength of constituent materials with decreasing wall thickness seen in Fig. 5a and b. Also, surface stress is calculated from the size-dependent surface energy by using the Shuttleworth equation and the relationship between surface energy and atomic strain.
In our study, nanotubular ZnO are formed on np-Au with average ligament size of 1.43 μm and wall thicknesses are 45, 92, 123 nm, thus effects of surface energy on mechanical properties may not be remarkable.

Strength of constituent ZnO in nanotubular structure, evaluated from yield strength of nanotubular structure measured in experiments (Fig. 2d) by applying general Gibson-Ashby model $\sigma = 0.3\rho^{0.5}$, also tends to increase with decreasing wall thickness, as shown in Fig. 5b. The strengths of constituent ZnO evaluated from FEA (Fig. 5a) are about 30–50 times greater than those from experiments (Fig. 5b). One possible cause for this difference is a loss of connectivity in np-Au, as appears on the fracture surface of nanotubular ZnO of $t = 92$ nm by micro-tensile testing in Fig. 5c. About 14% of the tubes are broken (red circles in Fig. 5b) when comparing with all tubes are interconnected periodically along x, y, and z directions in the FEA simulations. Recently, Ling et al. introduced a concept of effective relative density, $\rho_{eff}$ in np-Au which is much lower than relative density in terms of the nanostructures is smaller than 10 nm.

Figure 4. FEA simulations for nanotubular ZnO structure. (a) Unit cells of octahedral structure in which three tubes are interconnected normal to one another with curved surfaces are connected with periodic boundary conditions along x, y, and z directions. Representative loading directions are chosen as [100], [110], and [111]. (b) Distribution of von Mises stress when local von Mises stress attains a critical value in compression and tension for representative three loading directions. (c) Relation between yield strength of nanotubular ZnO structure evaluated by FEA simulations and wall thickness.
of volume fraction because np-Au contains many broken or dangling ligaments that do not support external force. They showed strength of constituent ligament is described accurately when strength of np-Au is analyzed by the Gibson-Ashby model combining with the effective relative density. Following this method taking into account effective relative density, we evaluated strength of constituent ZnO corrected for effective relative density as 14% of relative density in terms of volume fraction (right y-axis). These values are presented on the basis of right y-axis in Fig. 5b, which become much closer to those from FEA (Fig. 5a) by

Figure 5. Strength of constituent ZnO evaluated by the Gibson-Ashby model as a function of wall thickness. (a) Strength of constituent ZnO in nanotubular structure evaluated from yield strengths evaluated by FEA simulations, by applying general Gibson-Ashby model \( \sigma = 0.3 \sigma_{el}^{1.5} \). (b) Strength of constituent ZnO evaluated from yield strengths measured by experiments by general Gibson-Ashby model (left y-axis), and those corrected for effective relative density as 14% of relative density in terms of volume fraction (right y-axis). (c) Fracture surface of nanotubular ZnO by micro-tensile testing (scale bar, 10 \( \mu \)m).
were chosen as three-dimensional deformable solids; their elements are presented in templates for nanotubular ZnO. Au films were etched by Au etchant, which makes ZnO film float on the solution, and ZnO films were transferred onto hole-patterned Si substrates with hole diameters 5, 10, and 15 μm. Hole-nanoindentations on suspended ZnO films were carried out using in-situ nanoindenter (Hysitron PI 87) in SEM. Hole-nanoindentation was performed with cube corner tip with tip radius 90 nm (see Supplementary Fig. S2) at the center of the hole. The microstructure of ZnO thin films were measured by grazing incidence XRD (Bruker, D8 Advance) with Cu Kα radiation (Fig. S2). The microstructure of ZnO thin films were measured by grazing incidence XRD (Bruker, D8 Advance) with Cu Kα radiation (Fig. S2).

Micro-tensile and compressive testing. Micro-tensile tests for nanotubular ZnO were performed with a custom-built nano-tensile tester with load cell capacity of 500 mN and piezoactuator with displacement resolution of 1 nm. Tensile strain was analyzed by digital image correlation (DIC, VIC-2D by Correlated Solutions, Columbia, SC, USA). Compression tests for nanotubular ZnO were carried out using a micro-universal testing machine (Instron, Instron 5948). Displacement-controlled tensile and compressive testing were carried out. Wall thicknesses of 45, 92, 123 nm and inner diameter of tube necks of 1.43 μm were used. FEA simulations for linear elasticity with elastic modulus 77 GPa and fracture strength 3.9 GPa that are measured by hole-nanoindentation and Poisson’s ratio of 0.2 were used. Models were chosen as three-dimensional deformable solids; their elements are presented in Supplementary Table 1.

Methods
Fabrication of nanotubular ZnO. Np-Au was used as the sacrificial template for nanotubular ZnO. Au30Ag70 in at. % precursor alloys were made by arc melting under N2 environment from pure Au (99.99%) and Ag (99.99%) pellets, and homogenization was carried out under N2 environment at 800 °C for 72 hours. The Au30Ag70 precursor alloys were compressed to the desired disk shape using a Universal Testing Machine (Instron, Instron 5982), and both sides were gently polished using 1 μm diamond suspension. Dog-bone-shape Au30Ag70 precursor alloys for micro-tensile testing with gauge width 500 μm and gauge length 2 mm and cuboids for micro-compressive testing with dimension 0.8 mm width × 0.8 mm length × 1.6 mm height were machined using an ultra-precision nano-machine (Fanuc, Robonano α-0iβ). Machined precursor alloys were annealed at 800 °C for 24 hours to release residual stress introduced during mechanical polishing and machining. Samples were immersed in 35% nitric acid solution at 80 °C for 72 hours with stirring, producing np-Au with ligament size of 130 nm.
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Author Contributions

N.-R.K. and J.-Y.K. designed the process and experiments. N.-R.K. performed all experiments. S.K.K. designed the ALD process. H.J., Y.-C.K., J.-i.J., and H.N.H. performed FEA simulations. N.-R.K. and J.-Y.K. wrote the initial manuscript. All authors contributed to discussion of the results, provided input and approved the final manuscript.
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