Phase Transition and Compressibility in Silicon Nanowires

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Received June 10, 2008

ABSTRACT

Silicon nanowires (Si NWs), one-dimensional single crystalline, have recently drawn extensive attention, thanks to their robust applications in electrical and optical devices as well as in the strengthening of diamond/SiC superhard composites. Here, we conducted high-pressure synchrotron diffraction experiments in a diamond anvil cell to study phase transitions and compressibility of Si NWs. Our results revealed that the onset pressure for the Si I–II transformation in Si NWs is approximately 2.0 GPa lower than previously determined values for bulk Si, a trend that is consistent with the analysis of misfit in strain energy. The bulk modulus of Si I NWs derived from the pressure–volume measurements is 123 GPa, which is comparable to that of Si V NWs but 25% larger than the reported values for bulk silicon. The reduced compressibility in Si NWs indicates that the unique wire-like structure in nanoscale plays vital roles in the elastic behavior of condensed matter.

The mechanical properties and phase stability of nanometer-sized inorganic materials such as dots, wires, and belts strongly depend on their grain size, shape, and structure. High-pressure synchrotron X-ray diffraction demonstrated that wurtzite ZnS nanobelts have a wide field of structural stability up to 6.8 GPa, remarkably different from the bulk and monodisperse spherical nanoparticles which transform to the sphalerite structure at ambient conditions.1 Under static compression in a diamond anvil cell, a superhard phase has been made from carbon nanotubes, which exhibits bulk modulus and hardness comparable to diamond.3 Recently, studies showed that yield strength of nano-Ni measured under triaxial compression is more than three times higher than that of micrometer-Ni.3 All of these results demonstrate that nanostructures lead to distinct, usually enhanced, properties compared with conventional bulk polycrystalline materials.

One-dimensional (1-D) nanocrystalline semiconductor Si has been under extensive investigation because of its unique electronic, electric-mechanical, and optical properties associated with their wire-like geometry.4–6 It is known that electronic properties in nanoscale materials can be strongly altered because of the reduced mobility of the electron/hole pairs. These one-dimensional, nanoscale structures are also expected to offer practical routes for the strengthening of nanostructured composites, functioning in a way similar to the steel-bar reinforcement of concretes. However, investigations of nanowires or nanorods under high pressure are almost a virgin field. Application of 1-D structures for materials strengthening through high-pressure (P)/high-temperature (T) sintering, for example, requires the knowledge of materials’ mechanical properties and phase stability under the relevant P–T conditions. In this work, we conducted synchrotron X-ray diffraction experiments to study high-pressure behavior of Si NWs, with particular focuses on pressure-induced phase transformations and equation of state (EOS). The results are compared with those reported for bulk Si to elucidate the impacts of 1-D nanostructures on materials’ elastic properties and phase stability.

Si nanowires were prepared using a vapor–liquid–solid (VLS) synthetic route with sputtered thin Au films as catalysts, and the experimental setup is shown in Figure 1. To fabricate Si nanowires, the Si(100) wafer coated with 20 nm thick Au film was loaded into an alumina boat, which was then placed in the center of a quartz tube reactor heated by a 6 in. long oven. After 1 h annealing at 600 °C, 30 sccm (standard cubic centimeters per minute) SiH4 was then introduced into the system (0.5% in UHP grade He), which was further diluted with an additional 3000 sccm helium. The Si nanowire growth was carried out at 600 °C for 10 min. The silane gas flow was then turned off, and the reactor was cooled down to room temperature naturally. Brown and fluffy films of Si nanowires were produced on the Si wafer.
Figure 2a shows the morphology of Si NWs obtained from scanning electron microscopy (SEM), which consists of interwoven nanowires. Energy-dispersive X-ray analysis (EDX; Figure 2b) reveals that the nanowires are composed purely of Si. Typical transmission electron microscopy (TEM) image (Figure 21c) demonstrates that Si NWs possess smooth and clean surface with diameters of 60–80 nm and lengths up to several tens of micrometers. Both selected-area electron diffraction (SAED) and high resolution TEM (HRTEM) images (Figure 2d) show that the nanowire is single-crystal growing along the [111] direction. The lattice parameters were measured from the HRTEM image (Figure 1d) under ambient condition, which shows an fcc diamond phase with $a_0 = 5.423(2)$ Å, $V_0 = 159.48(9)$ Å³, and a volumetric contraction compared with the reported values for the bulk Si with $a_0 = 5.435$ or 5.43075 Å (Table 1). In a previous study, AlN NWs with an average diameter of 45 nm show an expanded unit cell at ambient conditions. These authors attributed such expansion to the specific shape and morphology of AlN NWs.

In the case of spherical nano materials, previous studies revealed a volumetric expansion with grain size less than 15 nm and volumetric contraction with grain size larger than this critical value. The different behaviors in unit-cell parameters of NWs can be reconciled if there also exists a critical diameter for NWs, which is possibly located between 45 and 60 nm based on the current study on Si NWs and previous work on AlN NWs. Along this line of speculation, both the unique 1-D structure and its diameter size have effects on the unit cell configuration of NWs at ambient conditions.

The high-pressure synchrotron X-ray diffraction experiments were performed by employing a gasketed diamond anvil cell at Sector 16-IDB of HPCAT, Advanced Photon Source (APS) of Argonne National Laboratory. The incident monochromatic X-ray beam with wavelength of 0.36806 Å was focused down to 5–10 μm in diameter. The Si NWs and liquid pressure transmission medium (4:1 methanol/ethanol) were loaded into a rhenium gasket hole of 130 μm diameter and ∼45 μm depth. Several ruby crystals and gold chips were also mounted inside the gasket hole to serve as internal pressure standards. The use of ruby allowed us to quickly estimate the pressure and thus to plan the experimental runs. Furthermore, from the comparison between the Au and ruby measurements, we can determine the pressures more accurately inside the sample. Our analysis shows that below 11 GPa the sample pressures measured from ruby and Au are essentially identical. At higher pressures, we used Au as pressure marker to determine the sample pressures. The diffraction data were collected on a MAR345 image plate, 350.3597 mm away from the sample, and were integrated and converted to regular two-dimensional (2-D) patterns using the software package FIT2D.

Figure 3 shows the XRD patterns of Si NWs under high pressure up to 41.0 GPa. Si NWs remain stable in Si—I (diamond-cubic) in the pressure range of 0 to 8.5 GPa, as illustrated in Figure 3a. Upon compression to 9.9 GPa, a new diffraction peak started to emerge, which can be indexed to the 200 peak of Si—II ($\beta$-Sn). With further compression to 11.4 GPa, the Si—II became the dominant phase, whereas the peak intensity of Si—I phase weakened significantly, as

| Table 1. Transition Pressure, Unit-Cell Parameters, and Equations of State for Si—I of Different Morphology |
|---|---|---|---|---|
| Si morphology | transition pressure (GPa) | lattice parameter $a_0$ (Å) | $B_o$ (GPa) | $B$ ref |
| bulk | 11.3 | 98 | 4.24 | 12 |
| bulk | 11.2 | 98 | 4.16 | 13 |
| bulk | 11.7 | 5.43 | 100 | 3.84 | 14 |
| bulk | 5.435 | 15 |
| bulk | 5.43075 | 16 |
| nanowires | 8.5−9.9 | 5.4231 | 123(5) | 4.24 | this study |
| 122(5) | 4.16 |

2892 Nano Lett., Vol. 8, No. 9, 2008
The bracketed onset pressure of 8.5–9.9 GPa for the Si–I → Si–II transition is lower than the reported values of 11.3–11.7 GPa for microcrystalline Si studied using essentially identical experimental techniques (Table 1). For experiments performed under nonhydrostatic conditions, the stress concentration at grain contacts of polycrystalline materials will typically enhance the transition to lower pressures. For example, depending on the pressure medium used in diamond anvil cell experiments, the onset pressure of the α–ω phase transformation in Ti metal varied from 4.9 GPa (no pressure medium) to 10.5 GPa (argon pressure medium). The pressure medium used in the present experiment, however, typically allows experiments to be conducted under hydrostatic conditions up to 13 GPa. In addition, with increasing pressure, no peak width broadening was detected in Si NWs at pressures up to 10 GPa, which confirms that the measurements in this pressure range were indeed conducted under hydrostatic conditions.

For a solid-state phase transformation under high pressure, the new phase usually has a different density. This misfit creates elastic stresses around nuclei and also consumes some energy. As a result, the phase transformation cannot start immediately at the equilibrium phase boundary but only after some metastable overshoot in pressure, which provides a sufficiently large driving force to overcome a nucleation barrier for transformation to occur. The misfit strain energy can be expressed as $\Delta G = \frac{3E\Delta V^2}{2\rho\gamma}$, where $E$ is Young’s modulus, $\Delta V$ is the volume change of the phase transformation, $\gamma$ is Poisson’s ratio, and $\rho$ is density of the Si–II phase. Previous theoretical studies indicated that the Young’s modulus of Si NWs decreases monotonously with the diameter size, varying from 150 GPa for microcrystalline
Si to 77 GPa for Si NWs with a diameter of 70 nm.\textsuperscript{19,20} Furthermore, the volume change (19\%) during the Si I–II phase transformation in Si NWs is smaller than that (22\%) in bulk Si.\textsuperscript{12} For most of the materials, the Poisson’s ratio is around 1/3; if we presume that density of Si–II is insensitive to the shape as well as grain/diameter size, the misfit strain energy for the Si I–II transformation in Si NWs would be smaller than that in bulk Si. This tends to lower the energy barrier and thus enhance the phase transformation in Si NWs to a lower pressure. The lower activation energy of dislocation and the larger dislocation velocity as well as the expanded surface area may be the other factors contributing to the lower transition pressure in Si NWs.\textsuperscript{19}

At 13.4 GPa, Si–II in Si NWs was transformed to Si–XI (Figure 3b). A further increase in pressure to 14.3 GPa resulted in the transformation to the Si–V phase, which was stable up to 33.4 GPa, as shown in Figure 3c. The Si–V phase has a simple hexagonal crystal structure (space group \textit{P63mm}) with lattice parameters of \(a = 2.533 \text{ Å}\) and \(c = 2.399 \text{ Å}\), and a \(c/a\) ratio of 0.947 at 15.1 GPa. The observed onset pressure of the Si XI–V phase transformation, 14.3 GPa, is comparable to the reported value of 15.4 for bulk Si.\textsuperscript{14} This suggests that under high pressure NWs would gradually lose their nanoscale, wire-like structure and therefore their effect on the material’s behavior. Upon further compression, as illustrated in Figure 3d, Si–VI and Si–VII phases were observed simultaneously at two experimental pressures of 37.7 and 41.0 GPa. Also, the observed pressures for the Si–V to Si–VI/VII transformation are comparable to those observed for the bulk Si. This again demonstrates a diminishing distinction between NWs and bulk crystalline Si and provides evidence of a pressure-induced collapse of wire-like structure under a certain high pressure.

A third-order Birch–Murnaghan equation of state (EOS)\textsuperscript{21} was used to derive EOS parameters from the measured pressure–volume data, as shown in Figure 4. Because of the very limited stability fields for phases II, VI, VII, and XI, we only derive the bulk modulus \((B_0)\) for phases I and V, which are stable in relatively large pressure ranges (Figure 4). With the pressure derivative of the bulk modulus, \(B’\), fixed at previously reported values of 4.24 and 4.16, the least-squares fitting for phase Si–I yields \(B_0 = 123 \pm 5\) GPa, which is approximately 25\% larger than the bulk moduli (98–100 GPa) determined for the phase I of microcrystalline Si (see also Table 1).\textsuperscript{12–14} The bulk modulus can be formulated by Young’s modulus \((E)\) and Poisson’s ratio \((\gamma)\) according to the equation: \(B = E/\{3(1 - 2\gamma)\}\). Recently, Han et al.\textsuperscript{19} studied the relationship between Young’s modulus and the diameter of Si NWs and they revealed a monotonous correlation between these two parameters. Based on this work, the Young’s modulus corresponding to the diameter of our Si NWs (~70 nm) is approximately 77 GPa. The Poisson ratio of diamond type Si (Si–I) NWs was reported to be 0.35;\textsuperscript{22} substitution of these two values into the above equation results in a bulk modulus value of 128 GPa for Si NWs, which is in good agreement with the present experimental result. Therefore, both experiments and theoretical calculations reveal a reduced compressibility in Si–I NWs, indicating that the unique wire-like shape in the nanoscale plays vital roles in the observed elastic strengthening. Furthermore, the least-squares fitting of our \(P–V\) data yields an ambient unit-cell volume of \(V_o = 159.99 (\pm 0.33) \text{ Å}^3\), which is consistent with the value measured from our TEM study. For Si–V NWs, the least-squares fitting of the \(P–V\) data results in \(B_0 = 119 (7)\) GPa, also with \(B’\) fixed at \(B’ = 4.24\). Within the experimental uncertainty, this value is comparable to the bulk modulus of 123 (5) GPa determined for Si–I. From the same fitting procedure, we obtained \(V_o = 14.817 \text{ Å}^3\) for Si–V NWs.

In summary, phase transition and bulk modulus of Si NWs with diameter of 60–80 nm were investigated at pressures up to 41 GPa under hydrostatic and quasi-hydrostatic conditions by using synchrotron X-ray diffraction in a diamond anvil cell. Si NWs exhibit a noticeable volumetric contraction at ambient conditions. Under high pressure, Si NWs start to transform to \(\beta\)-Sn structure at a pressure between 8.5 and 9.9 GPa, which is approximately 2 GPa lower than that observed in the Si microcrystals. This discrepancy can be explained from the misfit in strain energy, in the sense that the smaller misfit in Si NWs would stimulate the phase transformation to a lower pressure. The bulk modulus of Si–I NWs derived from the \(P–V\) measurements is 123 GPa, which is comparable to that of Si–V NWs but 25\% larger than the reported values for bulk silicon. The reduced compressibility in Si NWs indicates that the unique wire-like structure in nanoscale plays vital roles in the elastic behavior of condensed matter.

Acknowledgment. This research is supported by the Los Alamos National Laboratory, which is operated by Los Alamos National Security LLC under DOE Contract No. DE-AC52-06NA25396. The experimental work was performed at HPCAT (Sector 16), Advanced Photon Source (APS), Argonne National Laboratory. HPCAT is supported by DOE-BES, DOE-NSNSA, NSF, and the W.M. Keck Foundation.
APS is supported by DOE-BES, under Contract No. DE-AC02-06CH11357, and JLC by the Robert A. Welch Foundation.

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NL8016576