In Situ Nano-thermomechanical Experiment Reveals Brittle to Ductile Transition in Silicon Nanowires

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ABSTRACT: Silicon (Si) nanostructures are widely used in microelectronics and nanotechnology. Brittle to ductile transition in nanoscale Si is of great scientific and technological interest but this phenomenon and its underlying mechanism remain elusive. By conducting in situ temperature-controlled nanomechanical testing inside a transmission electron microscope (TEM), here we show that the crystalline Si nanowires under tension are brittle at room temperature but exhibit ductile behavior with dislocation-mediated plasticity at elevated temperatures. We find that reducing the nanowire diameter promotes the dislocation-mediated responses, as shown by 78 Si nanowires tested between room temperature and 600 K. In situ high-resolution TEM imaging and atomistic reaction pathway modeling reveal that the unconventional $1/2\langle110\rangle\langle001\rangle$ dislocations become highly active with increasing temperature and thus play a critical role in the formation of deformation bands, leading to transition from brittle fracture to dislocation-mediated failure in Si nanowires at elevated temperatures. This study provides quantitative characterization and mechanistic insight for the brittle to ductile transition in Si nanostructures.

KEYWORDS: Brittle to ductile transition, dislocation, plasticity, silicon nanowire, in situ TEM

Silicon nanostructures have been used extensively in modern microelectronics. The ever-increasing integration density in microelectronic chips inevitably leads to a marked temperature rise of Si nanostructures, which are required to withstand large thermal stresses for maintaining their proper functions. Si nanostructures are also the building blocks for many novel nanotechnology applications, including energy harvesting and storage, flexible and stretchable electronics, sensors, and nanoelectromechanical systems.\(^1\)\textsuperscript{−}\textsuperscript{5} The reliability concerns of these applications call for a fundamental understanding of the mechanical behavior of Si nanostructures at elevated temperatures.

Brittle to ductile transition (BDT) in Si has been of great scientific and technological interest for a long time.\(^6\) For bulk Si crystals, BDT was observed in the temperature range from 0.32 to 0.70 $T_m$ (with $T_m$ being the Si melting temperature of 1414 °C) under different loading conditions such as tension, indentation, compression, and bending.\(^7\)\textsuperscript{−}\textsuperscript{15} The BDT phenomenon was understood in terms of the change of dislocation nucleation rate or dislocation mobility with loading rate and temperature.\(^16\)\textsuperscript{−}\textsuperscript{19} For nanoscale Si, experimental studies on BDT have been scarce. Evidence of BDT at room temperature (RT) was found during indentation/compression of Si nano-

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conducting the nano-thermomechanical testing inside a transmission electron microscope (TEM) (see Materials and Methods). This platform allows stress−strain measurement with simultaneous TEM imaging of atomic-scale deformation at different temperatures.\textsuperscript{37−39} An on-chip heater is built into the MEMS-based platform, allowing the controlled heating of the specimen. Our results show that the Si NWs tested at elevated temperatures exhibit pronounced dislocation-mediated plastic deformation followed by fracture, which stands in contrast to brittle cleavage fracture in the Si NWs tested at RT. Our in situ high-resolution TEM imaging and atomistic reaction pathway modeling\textsuperscript{40,41} reveal the critical role of unconventional 1/2⟨110⟩{001} dislocations in the plastic deformation of Si NWs at elevated temperatures. We tested 78 Si NWs to systematically investigate the effects of size and temperature on dislocation-mediated plasticity and fracture.

**Results.** Single crystal Si NWs were synthesized by chemical evaporation deposition through the vapor−liquid−solid mechanism. These NWs grow uniformly in the axial direction (Figure 1a) and have diameters ranging from 24 to 160 nm (Figure 1b). All Si NWs used for mechanical testing are ⟨112⟩-oriented and have a central {111} twin boundary running parallel to the axial direction of the NW (Figure 1c). Figure 1d shows a typical cross section of the ⟨112⟩-oriented NW.

In situ TEM tensile testing of individual Si NWs was performed at temperatures ranging from 295 to 600 K. In Figure 2, we compare the brittle response at RT (295 K) with the moderate ductile behavior at 600 K for Si NWs with similar diameters. Figure 2a shows the stress−strain curve of a Si NW with a diameter of 61 nm at 295 K. This NW initially exhibited a linear elastic response. As the tensile strain increased to 7.4% and the corresponding tensile stress to 11.5 GPa, brittle fracture occurred. The inset in Figure 2a shows a TEM image of the sharp {111} cleavage surfaces (see more details in Figures S2 and S3 and Movie 1), which are known to have the lowest surface energy and also typically observed during brittle fracture of bulk Si crystals.\textsuperscript{42} The two fracture surfaces in the upper and lower twin variants are symmetric and tilted at ∼70° with respect to the axial direction.

In contrast, the Si NW with a diameter of 66 nm at 600 K exhibited moderate ductile behavior. As shown in Figure 2b, the tensile stress−strain curve was initially linear and became slightly nonlinear with increasing stress until the maximum stress of 5.8 GPa was reached at the critical strain of 4.0%. Subsequently, the stress decreased with increasing strain, and this softening response continued until fracture occurred at the strain of 4.7%. The inset in Figure 2b shows the TEM image of fracture surfaces, which exhibit the features of ductile failure such as localized necking, deformation bands and rough fracture planes (Figure S4 and Movie 2). Figure 2c shows the TEM snapshots during in situ tensile testing at 600 K, and the corresponding stress/strain for each snapshot is marked in Figure 2b. It is seen that the maximum stress and ensuing softening response can be associated with surface nucleation and migration of dislocations as well as dislocation interactions with the twin boundary, as marked by blue arrows in Figure 2cii−iv.
These continued dislocation processes resulted in large plastic strains in Si NWs at elevated temperatures. Overall, Figure 2 and Figures S2–S4 reveal that the Si NWs under tension are brittle at RT but exhibit pronounced plastic deformation followed by fracture at elevated temperatures (e.g., 600 K).

We found that a decrease in the NW diameter can lead to enhanced plastic deformation. Figure 2b also includes the tensile stress–strain curve of a thinner Si NW with a diameter of 24 nm at 600 K, which is qualitatively similar to the Si NW with a diameter of 66 nm at 600 K. However, in this thinner NW, a lower maximum stress of 5.1 GPa was attained at a smaller critical strain of 4.3%, signifying a stronger tendency to plastic deformation. Moreover, the subsequent softening response was sustained over a strain range of 1.6% until the fracture strain $\epsilon_f$ of 5.9%; this strain range is defined as plastic strain $\epsilon_p$. Hence, both $\epsilon_p$ and $\epsilon_f$ measured for the thinner Si NW are larger than the corresponding $\epsilon_p$ of 0.7% and $\epsilon_f$ of 4.7% for the thicker Si NW (Figure 2b).

The more extensive plasticity in the thinner Si NW was manifested by the formation of a number of deformation bands that are uniformly distributed throughout the entire NW (Figure 3a,b), which contrasts with fewer deformation bands in the thicker NW (Figure 2c).

We performed in situ high-resolution TEM (HRTEM) imaging to characterize the deformation bands in the Si NW with a diameter of 24 nm at 600 K. As shown in Figure 3d (corresponding to the boxed area in Figure 3b), the deformation bands first initiated from the free surface (marked by arrows for both twin variants) and then propagated along the inclined plane close to $\{100\}$ in the direction close to $\langle 112 \rangle$. Figure 3d further reveals the atomic structures within the deformation bands, which consist of 1/2$\langle 110 \rangle${001} dislocations, disordered regions (marked by a solid oval), and reoriented grains (marked by dashed square B). The disordered structures can evolve into a new Si phase with the diamond hexagonal (dh) lattice structure (marked by solid square A), which is a 2H polypeptide of diamond cubic Si with the stacking sequence $\cdots$AaBbAaBb$\cdots$ along the $\langle 111 \rangle$ direction (known as wurtzite Si$^{43}$). Both the reoriented grains and new Si phases were verified by selected area diffraction maps in Figure 3c.

Our in situ HRTEM experiments at elevated temperatures indicated that the formation of deformation bands originates from the dominant operation of 1/2$\langle 110 \rangle${001} full dislocations, which were observed in all Si NWs tested at elevated temperatures, irrespective of existence of a central twin boundary (see testing of single crystalline Si in Figure S6 and atomistic simulations showing the effect of twin boundary in Figure S11). This stands in contrast with the dominant activities of 1/2$\langle 110 \rangle$\{111\} full dislocations or 1/6$\langle 112 \rangle$\{111\} partials during plastic deformation of bulk Si structures.44 Interestingly, the HRTEM image in Figure 3d reveals three parallel deformation bands at different stages, which clearly reveal the impact of the 1/2$\langle 110 \rangle$\{100\} dislocations. The three stages correspond to the band formation (stage I), growth (stage II), and crossing through the twin boundary (stage III), as schematically illustrated in Figure 3e. During stage I, 1/2$\langle 110 \rangle${001} dislocations nucleate from the NW surface and propagate into the upper twin variant. Gliding of 1/2$\langle 110 \rangle${001} dislocations led to band extension, while climbing of 1/2$\langle 110 \rangle${001} dislocations appears necessary for band

Figure 2. In situ MEMS-based measurement and TEM observation of mechanical behavior of individual Si NWs under uniaxial tension at room and elevated temperatures. (a,b) Stress–strain curves of Si NWs tested at 295 and 600 K, respectively. Insets in (a,b) are the corresponding fracture morphologies of the tested NWs with diameters of 61 and 66 nm, respectively. Scale bar, 20 nm. (c) Snapshots of microstructure evolution corresponding to (b). Each snapshot corresponds to a data point marked in (b). Blue arrows indicate the dislocation activities, including (ii) surface nucleation, (iii) obstruction by twin boundary and (iv) slip transmission across twin boundary. Scale bar, 100 nm.
HRTEM observation showing three stages (marked by I) of deformation band, leading to crack nucleation and fracture in the structure in stage I is marked by a solid oval. Green arrows indicate the formation of deformation bands in the boxed area in (b). Disordered bands is dictated by the slip-plane orientation of $\langle 110 \rangle$ provide direct evidence that the orientation of deformation orientation from the $\{100\}$ plane (Figure 3d,e-ii). These results indicate that expansion of a nucleating loop has to overcome a series of energy barriers to dislocation glide can be substantial, such that expansion of a nucleating loop has to overcome a series of primary nucleation barriers. Increasing the applied stress usually has a pronounced effect on reducing primary barriers, but is less effective on reducing secondary barriers.

From FENE calculations, we obtained the minimum energy path (MEP) of surface nucleation of a $1/2\langle 110 \rangle\{001\}$ loop (Figure 4c,d), when the Si NW is subjected to an applied tensile stress of 13.2 GPa. It is seen that the MEP is substantially leaned forward due to the high stress applied, indicating the vanishing primary nucleation barrier on an envelope curve (not drawn) connecting local minima. Moreover, this MEP is highly rugged, featuring a series of small secondary barriers on the order of 1–1.2 eV. These secondary barriers can lead to sluggish dislocation motion at RT according to the aforementioned 25$^\circ/k_B T$ rule, thus effectively suppressing the nucleation of the $1/2\langle 110 \rangle\{001\}$ dislocations at RT. However, the dislocation mobility can be markedly increased, as the temperature is elevated to 600 K. This is because an increase of thermal energy enables the frequent crossing of energy barriers on the order of about 1.2 eV, thereby promoting the surface nucleation and migration of the $1/2\langle 110 \rangle\{001\}$ dislocations in strained Si NWs, as observed during our in situ TEM experiments. In contrast, Figure 4e,f shows the MEP of surface nucleation of a $1/2\langle 110 \rangle\{111\}$ loop, which was also obtained under the applied tensile stress of 13.2 GPa. This smooth MEP only exhibits a single primary energy barrier with a high value of 4.87 eV. Hence the surface nucleation of $1/2\langle 110 \rangle\{111\}$ dislocations is less favorable than $1/2\langle 110 \rangle\{001\}$ dislocations in $\{112\}$-oriented Si NWs under tension at elevated temperatures. The higher primary barrier of surface nucleation of the $1/2\langle 110 \rangle\{111\}$ loop can be partly attributed to the relatively small Schmid factor of 0.41 under axial loading, as opposed to 0.47 for the $1/2\langle 110 \rangle\{001\}$ loop. In addition, differences in surface ledge energy and dislocation line tension can also affect the primary energy barriers for the two competing modes of surface nucleation of a $1/2\langle 110 \rangle\{001\}$ loop (Supporting Information).
dislocation modes. It should be noted that the lack of (or substantially weaker) secondary barriers for nucleation of a 1/2⟨110⟩⟨111⟩ loop can be attributed to the close-packed ⟨111⟩ slip planes in diamond cubic Si, which facilitate dislocation glide by eliminating (or largely reducing) the secondary barriers at high loads. Hence, 1/2⟨110⟩⟨111⟩ dislocations could become active at RT, when the primary energy barrier is sufficiently reduced by increasing load (Figure S10), provided that the tensile stress component on the potential cleavage planes is sufficiently low for averting brittle fracture.

To further understand the size and temperature dependence of dislocation-mediated plasticity and fracture, we tested 78 Si NWs.

Figure 4. Atomistic reaction pathway modeling results of surface nucleation of a 1/2⟨110⟩⟨001⟩ versus a 1/2⟨110⟩⟨111⟩ dislocation in a ⟨112⟩-oriented Si NW from FENE calculations. (a,b) Atomic configuration showing a fully nucleated 1/2⟨110⟩⟨001⟩ and 1/2⟨110⟩⟨111⟩ dislocation loop from the side surface of Si NW, respectively. (c) MEP of surface nucleation of a 1/2⟨110⟩⟨001⟩ dislocation; (d) corresponding atomic configurations along the MEP, as marked in (c). (e) MEP of surface nucleation of a 1/2⟨110⟩⟨111⟩ dislocation, (f1–f4) corresponding atomic configurations along the MEP, as marked in (e). Atoms are colored according to coordination number, so as to display atoms on the NW surface and in the dislocation core. The reaction coordinate in (c,e) is defined as the normalized path length along the MEP.

Figure 5. Size and temperature dependence of brittle versus ductile behaviors of 78 Si NWs tested in the temperature range of 295 to 600 K. (a) Measured plastic strain $\epsilon_p$ as a function of NW diameter at different temperatures. (b) BDT map in the parameter space of temperature and NW diameter. The ductile NWs ($\epsilon_p > 0.1\%$) are marked by green solid circles, whereas the brittle ones by black solid squares.
NWs with the diameter range of 24–160 nm and in the temperature range of 295–600 K. As shown in Figure 5a, the plastic strain $\epsilon_p$ increases with decreasing NW diameter. For example, at 600 K $\epsilon_p$ increases from 0.27 to 1.6%, as the NW diameter decreases from 160 to 24 nm. For the same diameter, $\epsilon_p$ increases with temperature. The results of the 78 Si NWs tested are summarized in a deformation mechanism map of Figure S5b. In this map, green circles represent Si NWs with dislocation-mediated failure, whereas black squares Si NWs with brittle cleavage fracture. A transition line, as defined by a critical $\epsilon_p$ of 0.1%, is drawn to separate the regimes of brittle and dislocation-mediated responses. The map also reveals that as the NW diameter decreases, the critical temperature associated with dislocation-mediated plastic deformation decreases. For example, the Si NW with diameter of 110 nm showed brittle fracture at 398 K, while the NW with diameter of 30 nm exhibited plastic deformation with dislocation activities even at 362 K (Figure S8). Hence, Figure 5b indicates that both the increase of temperature and the decrease of NW diameter can promote plastic deformation in Si NWs, leading to dislocation-mediated failure (Figures S7–S9).

**Discussions.** Plastic deformation with extensive dislocation activities is critical for the BDT in both bulk and nanoscale Si crystals. Full dislocations of 1/2$\langle 110\rangle\{111\}$, which can dissociate into 1/6$\langle 112\rangle\{111\}$ partials, are responsible for most of the reported plastic deformation in bulk Si crystals, similar to face-centered cubic metals. Dislocation activities on $\{111\}$ slip planes have also been reported in Si nanostructures (such as nanocubes and nanopillars) under compression at RT to serve as experimental evidence of size-dependent BDT. Overall, the onset of plastic deformation, including activities of dislocation nucleation and propagation, in Si crystals is deemed to have a strong dependence on loading condition, stress state, strain rate, temperature, and sample size. In this study, we focused on the uniaxial tension of Si NWs but we did not observe any twinning during plastic deformation between 300 and 600 K. This can be well related to the lack of 1/6$\langle 112\rangle\{111\}$ partials in the present experimental conditions. We showed that the unconventional 1/2$\langle 110\rangle\{001\}$ dislocations can become highly active in $\langle 112\rangle$-oriented Si NWs at elevated temperatures. This is attributed to the following possible factors: the high Schmid factor (0.47) that favors the 1/2$\langle 110\rangle\{001\}$ slip system (see Table S1), the high stress attainable in Si NWs, and the assistance of elevated temperatures for overcoming the secondary energy barriers of 1/2$\langle 110\rangle\{001\}$ dislocation glide.

In bulk Si, the BDT typically involves a transition from cleavage fracture to extensive plastic deformation that might end up with ductile tearing. In contrast, what we observed from Si NWs at elevated temperatures is the initial ductile response associated with dislocation plasticity (as evidenced by the necking deformation in Figure 2b and Figures S4 and S7–S9) followed by “brittle fracture” (i.e., cracks grew along the cleavage planes), at least for the temperature and NW diameter ranges studied in this work. These results represent a BDT mode in Si NWs different from that in bulk Si, which arises presumably due to the small volume, large surface area, and high stress associated with Si NWs that collectively limit the extent of plastic deformation before the tensile failure of Si NWs. Taking into account the size effect, the transition temperature for BDT might go over 600 K as the NW diameter increases to hundreds of nanometer. In addition to sample size, the BDT temperature would depend on crystal orientation, microstructure, loading mode (tension, compression, or bending), with or without precracks, and so forth.

The twin boundary in the center of the Si NW plays an important role in obstructing the propagation of both individual dislocations (Figure S11) and deformation bands. This obstruction will result in back stresses that impede the continued operation of the same surface dislocation sources. As a result, plastic deformation becomes delocalized, an effect known to enhance the tensile ductility. As the NW diameter is reduced, the thickness of the twin variant is decreased. Hence the twin boundary can further promote the delocalized plastic deformation, thereby enhancing the tensile ductility, as shown in Figure 5. This reinforces the notion of harnessing internal interfaces for enhancing the tensile ductility of nanostructured materials.

Finally, we note the formidable role that quantitative in situ nanomechanical testing at elevated temperatures can play in our understanding of the nano-thermomechanical behavior of materials. Not only can they provide quantitative characterization and critical insight for the brittle and ductile responses of Si nanostructures but also can be extended for other studies of mechanical behavior of nanoscale materials at elevated temperatures.

**Materials and Methods.** Sample Synthesis and Characterization. Si NWs were synthesized by chemical vapor deposition (CVD) using gold nanoclusters as catalysts and silane ($\text{SiH}_4$) as a vapor-phase reactant, following the method developed by Wu et al. Gold nanoclusters with diameters ranging from 10 to 50 nm were deposited on Si substrates capped with a 600 nm thick layer of thermal silicon dioxide. The substrates were placed in a quartz tube furnace (EasyTube 3000, First Nano). After a 30 min purge in $\text{H}_2$ ambient at 50 Torr, VLS growth of Si NWs was carried out at 480 °C, 15 Torr for 10 min with the flow of $\text{SiH}_4$ (20 sccm) and $\text{H}_2$ (200 sccm).

High-resolution TEM observations were performed on JEOL 2010F with a Schottky field emission gun (FEG) operated at 200 kV.

**In Situ SEM/TEM Mechanical Testing.** The mechanical testing was carried out in situ inside a TEM using a MEMS-based material testing stage, which consists of an electrostatic (comb-drive) actuator, a capacitive load sensor and an on-chip heater (Figure S1a). The stage was fabricated out of one layer of single crystalline silicon with thickness of 25 μm. The on-chip heater is based on Joule heating of the single crystalline silicon structure itself (i.e., no additional heating layer) (Figure S1b). The temperature (from RT to 600 K) on the sample area is controllable by changing the applied voltage on the on-chip heater. A key feature of this testing stage is the symmetry of the overall structure (i.e., the electrostatic actuator and the capacitive load sensor are identical). Details on the testing stage has been reported previously.

The temperature is uniformly distributed along the Si NW, which was verified by the Raman spectroscopy measurement. Figure S1c shows the Stokes-shifted Raman spectra of the gap edge of the device (dark line) and the middle of a Si NW (red line) under 8 V heating voltage in air, respectively. Note that the NW is clamped across a gap between the actuator and the load sensor. The difference in temperature between the two locations was less than 2 K. The peak shift in Figure S1c reflects the temperature change following a linear relationship. The large difference in the spectra amplitude is because the probe areas in the middle of the Si NW is much smaller than that in the gap edge of the device.
Si NWs were mounted on the testing stage using a nanomanipulator (Klocke Nanotechnik, Germany) inside a FEI Quanta 3D FEG dual beam. An individual Si NW was welded to the nanomanipulator probe, then mounted to the MEMS stage and clamped by electron-beam-induced Pt deposition at the two free ends. Two local markers were deposited on the NWs for displacement (and strain) measurement. Displacement (and strain) is measured by digital image correlation of TEM images of two local markers on the specimen (Figure S1d), giving rise to a strain resolution of 0.01% (gage length 2 μm). The stress resolution depends on the NW diameter (e.g., 1.4 MPa for a NW diameter of 104 nm). In situ TEM mechanical testing was performed in JEOL 2010F. The current density of incident e-beam was <0.1 A/cm² and its loading and unloading strain rates were ~0.003%/s. Low-magnification images were recorded at a fixed condense (the second condense lens) current to minimize the focus change. The current density of incident e-beam was ~0.1 A/cm² and its effect on the mechanical behavior of the NWs under tensile testing can be neglected.

Atomistic Modeling. The free-end nudged elastic band (FENEB) calculation is performed using the Stillinger–Weber (SW) Si potential with an in-house code. The (112)-oriented Si NW has a circular cross section with the diameter of ~9 nm. It contains 39 616 Si atoms. The periodic boundary condition is applied along the axial direction of the Si NW. The lateral side of the NW is freely relaxed. After relaxation by conjugate gradient energy minimization, the supercell along the NW direction has a length of 10.6 nm. Following a similar dislocation embedding scheme in our previous study, a surface dislocation loop in the NW is created by the following operations using LAMMPS: (i) define a surface dislocation loop by selecting a patch of Si atoms on the two adjacent [111] or [100] planes; (ii) impose a relative shear displacement of δs/2[110] (where δs is the lattice constant) between the two layers of atoms in the patch; specifically, the shear displacement is increased incrementally in 10 steps and the atomic structure is partially relaxed after shearing in each step while holding the atoms in the patch fixed; (iii) partially relax the entire NW to obtain a sufficiently large dislocation loop that can be used as the free-end state of the FENEB calculation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.9b01789.

Description of MEMS device, post-mortem characterization of the fracture morphology, in situ mechanical testing of Si NWs at 362, 399, and 450 K, atomistic reaction pathway modeling results and molecular statics simulation snapshots, Schmid factors of typical slip systems in Si (PDF)

Mechanical response and microstructure evolution of a Si NW with diameter of 61 nm (corresponding to the one in Figure 2a) under in situ TEM tensile testing at room temperature; NW shows brittle fracture (AVI)

Mechanical response and microstructure evolution of a Si NW with diameter of 66 nm (corresponding to the one in Figure 2b) under in situ TEM tensile testing at 600 K; NW shows dislocation-mediated plastic deformation followed by fracture (AVI)

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Notes

The authors declare no competing financial interest.

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