Dislocation glide-controlled room-temperature plasticity in 6H-SiC single crystals

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Abstract

In situ transmission electron microscopy observations of uniaxial compression of sub-300 nm diameter, cylindrical, single-crystalline 6H-SiC pillars oriented along $\langle 0001 \rangle$ and at 45° with respect to $\langle 0001 \rangle$ reveal that plastic slip occurs at room-temperature on the basal $\{0001\}$ planes at stresses above 7.8 GPa. Using a combination of aberration-corrected electron microscopy, molecular dynamics simulations and density functional theory calculations, we attribute the observed phenomenon to basal slip on the shuffle set along $\langle 1\overline{1}00 \rangle$. By comparing the experimentally measured yield stresses with the calculated values required for dislocation nucleation, we suggest that room-temperature plastic deformation in 6H-SiC crystals is controlled by glide rather than nucleation of dislocations.

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1. Introduction

The critical load-bearing components of many modern structures are often constructed from metallic alloys having lower strengths than their ceramic counterparts. This design compromise is often driven by the need for component reliability, a trait that is generally superior in metallic alloys due to their ability to deform plastically at room-temperature. The availability of higher-strength materials with enhanced ductility would significantly boost the performance and enable next-generation advanced technologies. This, however, is a challenge and requires fundamental understanding of the factors influencing mechanical properties of materials. In the case of metals, recent investigations have helped to identify the role of crystal size and microstructure on their mechanical properties [1,2]. For higher-strength refractory materials such as SiC, a covalently bonded structural ceramic and a semiconductor, most of the existing literature is focused on the mechanical behavior of bulk crystals at elevated temperatures ($T > 673$ K) [3–7] as they are expected to be brittle at room-temperature. For example, high-temperature compression and bending of bulk 4H-SiC crystals revealed the existence of partial dislocations on the basal $\{0001\}$ planes, full dislocations out of the basal planes, and stacking faults due to the 4H to 3C transformation [8,9]. Room-temperature measurements of indentation hardness [10–12] of bulk single-crystalline SiC and fracture strengths [13,14]...
of SiC nanorods and nanowires have helped identify the role of indenter geometry, crystal size and crystal orientation on the mechanical properties of SiC. Room-temperature plasticity, although not common, has been observed in crystalline \(\beta\)-SiC nanowires under tension and is attributed to the formation and motion of dislocations followed by transition to an amorphous state [15,16]. Here, we focus on understanding the room-temperature mechanical behavior of single-crystalline 6H-SiC (a polytype of \(\alpha\)-SiC), a hard (>25 GPa), stiff (elastic modulus >415 GPa), and high melting point \((T_m \approx 3000 \text{ K})\) solid subjected to uniaxial compression [17–19]. We show that small \(<300 \text{ nm in diameter}\) 6H-SiC single crystals deform plastically at room-temperature under a compressive load, exhibiting a long-sought combination of mechanical properties, high yield strength (>7.8 GPa), and considerable \((\sim 10\% \text{ strain})\) plastic flow before failure, indicative of ductility. By combining in situ transmission electron microscopy (TEM)-based nanomechanical testing with aberration-corrected TEM, molecular dynamics (MD) simulations and density functional theory (DFT) calculations, we identify the mechanism leading to plastic flow in single-crystalline 6H-SiC.

2. Methods

2.1. Experimental details

All the in situ compression experiments were conducted on cylindrical SiC pillars prepared from 5 mm \(\times\) 5 mm \(\times\) 0.33 mm 6H-SiC(0001) single crystals purchased from MTI Corporation. A combination of mechanical polishing and focused ion beam (FIB) milling was used to prepare \(\Phi_{0}\) and \(\Phi_{45}\) pillars oriented along \(\langle 0001 \rangle\) and at 45° with respect to \(\langle 0001 \rangle\), respectively.

In order to prepare \(\Phi_{0}\) pillars, which are uniaxially compressed in the direction normal to the basal plane, a 1 mm \(\times\) 1 mm \(\times\) 0.33 mm piece was first cut out of the larger crystal with a diamond saw and mechanically thinned to sub-100 \(\mu\text{m}\) thickness using a Multiprep auto-polisher (Allied High Tech Products, Inc.). The sample was then mounted on a copper half-grid using M-bond 610 adhesive (Micro-Measurements) and cured at 160 °C for 1.5 h. This process ensures that the thinned sample was permanently bonded to the half-grid. The grid-sample was attached to a copper sample mount (from Hysitron Inc.) using Crystalbond TM 509 adhesive (Ted Pella, Inc.) and transferred to a FEI 235 dual-beam FIB system for milling. (Supplementary Fig. S1 shows a schematic of the sample assembly used for milling.) The whole assembly \((\text{sample} + \text{copper-half-grid} + \text{copper sample mount})\) was attached to a 45° stub using Pelco colloidal graphite paste (Ted Pella, Inc.) to maximize electrical conductivity and to minimize drift during FIB milling. FIB milling was carried out using 30 kV Ga\(^+\) beams in two steps: initial coarse milling at an ion beam current of 7 nA, followed by finer milling with 30 pA current. The final step involved a low-voltage (6 kV) milling to minimize Ga\(^+\) implantation in, and the formation of amorphous layers on, the pillars. The resulting pillar diameters \((D)\) were between 170 and 280 nm, with aspect ratios chosen to be less than 3.5 to minimize buckling.

We followed a similar procedure to prepare \(\Phi_{45}\) pillars, whose loading direction is 45° with respect to \(\langle 0001 \rangle\). The key difference is that the 1 mm \(\times\) 1 mm \(\times\) 0.33 mm piece cut out from the bulk crystal was mounted on a 45° stub and mechanically polished using the Multiprep auto-polisher to create a 45°-cut surface. Then the sample was remounted on one side and mechanically thinned from 0.33 mm thickness to sub-100 \(\mu\text{m}\) using the Multiprep auto-polisher. All the other pillar fabrication steps were as described in the previous section.

The copper sample mount was then loaded into a Hysitron PicoIndenter 95 with a flat 3 \(\mu\text{m}\) wide diamond punch for in situ uniaxial compression at room-temperature inside a JEOL 3010 TEM operated at 300 kV. The applied load was gradually increased such that the displacement changes at a rate of 4 nm s\(^{-1}\). During compression of each pillar, load vs. displacement data, video-rate (30 frames s\(^{-1}\)) TEM images and selected-area electron diffraction (SAED) patterns were acquired. The engineering stress and strain values were calculated from the load–displacement data using the lengths and diameters of the undeformed pillars.

2.2. Molecular dynamics (MD) simulations and density functional theory (DFT) calculations

The MD simulations were performed using the LAMMPS package [20] with Devanathan et al. [21] potential for SiC. This potential reliably reproduces the equilibrium properties of the crystal including lattice parameters, elastic constants, cohesive energy and point defect formation energy. In the simulation, cylindrical and defect-free 6H-SiC single crystals with diameter \(D = 8.4 \text{ nm}\) and a height of 24 nm, consisting of 133,690 atoms, are oriented such that the direction of the applied load is 45° with respect to \(\langle 0001 \rangle\). The simulation cell is first thermalized for 10 ps at 300 K to release surface stresses in all directions and to initialize atomic positions and velocities. The cell temperature is controlled by a Langevin thermostat [22]. A canonical (NVT) ensemble, where \(N\) is the number of particles in a system of volume \(V\) held at an absolute temperature \(T\), is employed with an integration time step of 1 fs for the velocity-Verlet integration scheme [23]. Uniaxial compression is simulated by imposing deformation on the cell at a strain rate of \(5.7 \times 10^{10} \text{ s}^{-1}\). Stresses are computed with the virial theorem [24] and strains are determined from the changes in the crystal height. The Atomeye package is used for atomistic visualization of the crystal [25].

The DFT simulation cell is a fully periodic 6H-SiC crystal with both its lateral dimensions equal to one crystallographic period length \((= 0.31 \times 0.53 \text{ nm})\) and 12 layers of atoms \((= 2.94 \text{ nm})\) with a 1.75 nm vacuum layer along
the vertical dimension. Electronic structure calculations are performed using the Kohn–Sham DFT approach with the Vienna Ab initio Simulation Package (VASP) [26]. Core electrons of each atom are assumed fixed using an ultrasoft pseudopotential model. The exchange and correlation interactions of the electrons are approximated with the generalized gradient approximation (GGA). The simulation cell is discretized with a plane-wave basis set having a plane-wave cutoff energy of 240 eV. A Brillouin zone integration scheme having an $8 \times 8 \times 1$ k-point grid is employed. These parameters, the simulation cell height, and vacuum layer thickness are varied and tested to ensure energy convergence. The generalized stacking fault (GSF) energies $E_{GSF}$ are calculated as a function of normalized displacement $(x/b)$ by rigidly shifting the atomic layers in the top part of the cell against the fixed bottom layers. The simulation cell is subsequently relaxed perpendicular to the slip plane to attain the minimum energy configuration.

3. Results

3.1. In situ TEM uniaxial compression test

From the mechanical responses of uniaxially compressed SiC pillars oriented along $(0001)$ and along $45^\circ$ with respect to $(0001)$, referred to as $\Phi_0$ and $\Phi_{45}$ respectively, we show that plastic flow in SiC is due to slip on the basal planes. These findings are consistent with ab initio theoretical analysis, which suggests that plastic slip at room-temperature is energetically most favorable on the basal plane and will occur by full dislocation glide on the shuffle set. In our experiments, we measure yield strengths $\sigma_y$ as high as 14.3 GPa. Both MD and DFT calculations suggest that these values are significantly below what is required to nucleate dislocations. Based upon our experimental, MD simulation and DFT calculation results, we conclude that sustained plastic flow in SiC crystals at room-temperature is governed by dislocation glide.

Figs. 1a–g show representative bright-field TEM images (extracted from the “6H-SiC $\Phi_{45}$ pillar” movie), a selected-area electron diffraction (SAED) pattern, and stress-displacement data recorded during uniaxial compression of a ~600 nm long, $\Phi_{45}$-oriented 6H-SiC pillar with diameter $D = 180$ nm. In this experiment, the pillar is compressed until a nominal displacement of 100 nm after which the load is released. During compression, the initial stress-displacement response is linear, characteristic of elastic deformation, up to a point beyond which the displacement increases non-linearly with applied stress indicative of plastic flow as shown in Fig. 1g. The TEM images, e.g. Fig. 1b, corresponding to this transition reveal the generation of dislocations from the point of contact between the pillar and the diamond punch. After this initial event, additional bursts of dislocations are observed in the specimen. These events, highlighted by arrows labeled 1 and 2 in Figs. 1c, 1d and 1g correspond to abrupt changes in the stress–displacement behavior. Fig. 1e is an image of the pillar obtained after compression. Clearly, the pillar is intact, without any visible cracks, and is ~10% shorter in length, all characteristic of plastic deformation. The SAED pattern (Fig. 1f) acquired from the pillar indicates that its crystallinity and crystal structure are not affected by the compression process. All of these results are typical of six $\Phi_{45}$ pillars with $D$ between 170 and 280 nm. Although the stress–displacement responses of these pillars are qualitatively similar, the extent of plastic hardening, the elastic to plastic transition point (i.e. the yield point, $\sigma_y$), and the loading-unloading curve slopes vary from pillar to pillar due to differences in alignment of the pillars (see Supplementary Fig. S2). We measure $\sigma_y$ values between ~7.8 and 14.3 GPa for the different pillars, but $\sigma_y$ did not vary systematically with $D$ in our experiments.

In comparison, $\Phi_0$-pillars, i.e. 6H-SiC(0001) pillars compressed uniaxially along $(0001)$, do not undergo plastic deformation but fail catastrophically via brittle fracture (see “6H-SiC $\Phi_0$ pillar” movie and Supplementary Fig. S3). In these $\Phi_0$-pillars, the displacement increases linearly with applied stress up to the point of failure, which occurs at stresses between 15 and 22 GPa. The lack of any contrast changes in the TEM images acquired during the test suggest that dislocation motion is either limited or absent in $\Phi_0$ pillars, as expected for the brittle fracture. We observe a similar mechanical response in all the six $\Phi_0$ pillars with $D$ between 180 and 300 nm. We attribute the ductility (brittleness) of $\Phi_{45}$ ($\Phi_0$) pillars to the activation (suppression) of slip on the basal planes at room-temperature and to the higher critical resolved shear stresses required to activate non-basal prismatic or pyramidal slip planes.

We note that the unloading portion of the stress–displacement curve in Fig. 1g is nonlinear. Such a deviation from linearity in the unloading curve, referred to as knee or elbow, has been observed during indentation of silicon and attributed to reversible pressure-induced phase transformation [27–29].

In order to check for any such phase transformations occurring within the 6H-SiC pillars, we carried out detailed TEM characterization of the deformed pillars. Fig. 2a is a low-magnification TEM image obtained after further thinning of the compressed pillar shown in Fig. 1. In this image, several dislocation lines are visible near the bottom of the pillar and slip traces at the top of the pillar are highlighted with a circle. Fig. 2b is a higher-magnification scanning TEM (STEM) image obtained from the area around a slip trace within the circle. Figs. 2c and 2d are high-resolution STEM images from the areas outlined by blue and red lines above and below the slip trace, respectively. In both these images, we observe alternate zigzag symmetry, characteristic of 6H-SiC [30,31]. We did not find any stacking faults or evidence of structural phase transformation in this deformed region, consistent with the assertion that the observed plastic flow is due to dislocation glide. During STEM characterization (see Supplementary Fig. S4 for details) of this pillar, we found an interesting phenomenon:
rotation of the crystal lattice near the slipped regions of the sample, a consequence of plastic flow during compression. Similar behavior has been observed in mechanically deformed single-crystalline metallic materials subjected to tensile loading [32].

In order to determine the mechanisms underlying the sustained plastic flow in the 6H-SiC \( \Phi_{45} \) pillars, we performed MD simulations of uniaxial compression and calculated the energies associated with slip using DFT. This combination of MD and DFT calculations enabled prediction of the most probable slip system and the corresponding critical stress.

### 3.2. MD simulations

Figs. 3a–d are typical MD simulation images (see the “6H-SiC \( \Phi_{45} \) pillar MD simulations” movie for an animated version) obtained during uniaxial compression of a 6H-SiC \( \Phi_{45} \) pillar with \( D = 8.4 \) nm. Fig. 3e is a plot of the stress as a function of strain obtained from the simulations. The pillar deforms elastically up to a strain of \( \sim 8\% \), corresponding to an applied stress of \( \sim 20 \) GPa. At higher stress, the pillar exhibits non-uniform, elastic shear deformation; this behavior, which occurred in the form of slip bands on the more easily-shearable atomic planes, depicted in Fig. 3c by higher von Mises strain, is followed by nucleation of a dislocation with full Burgers vector \( b = (11 \overline{2} 0) \) on the shuffle set of a \{0001\} plane, consistent with the literature [33]. Our MD simulations predict that the critical compressive stress required for dislocation nucleation is 31 GPa. Following nucleation, the dislocation eventually glides to the surface and forms an atomic step as shown in Fig. 3d. Based on these results, we suggest that 6H-SiC \( \Phi_{45} \) pillars, subjected to uniaxial compression, can undergo plastic deformation via slip by dislocation nucleation and glide on the shuffle set of basal planes.

We realize that the accuracy of empirical potential used in our MD simulations can be limited. Therefore, we have also carried out electronic structure calculations with DFT to determine the most energetically favorable pathways for dislocation glide.

### 3.3. DFT calculations

While theoretical predictions of plastic deformation in covalent materials are still a developing research area, the resistance to dislocation glide is often strongly correlated with the maxima in the generalized stacking fault energy...
and the gradient (dE_{GSF}/dx) of E_{GSF} vs. rigid displacement (x) curves. For a given slip system, the maximum value in the dE_{GSF}/dx vs. (x/b) curve is the ideal shear stress (τ₀) required to destabilize a perfect crystal when sheared on that particular slip plane and slip direction. τ₀ is a measure of the critical stress at which a dislocation nucleates from a free surface in a pure crystal [34].

We calculated E_{GSF} vs. x/b for four different possible slip systems involving two sets of basal planes, the shuffle and the glide sets, and two slip directions, ⟨1120⟩ and ⟨1100⟩ using a crystal with periodic boundary conditions in the in-plane directions and the basal planes as the top and bottom surfaces. Figs. 4a–d show schematics of the simulation cells used. The calculated E_{GSF} and dE_{GSF}/dx data are plotted vs. (x/b) in Figs. 4e and 4f, respectively. For all the four slip systems, the E_{GSF} increases monotonically with x and the maxima is obtained at x = b/2, and the maxima in dE_{GSF}/dx (i.e. τ₀) are observed at x = b/4. From the data, we find that energetically the most favorable (lowest τ₀) and unfavorable (highest τ₀) slip systems are the basal slip on the shuffle set along ⟨1100⟩ (the dashed curves in Figs. 4e and 4f) and basal slip on the glide set along ⟨1120⟩ (the data is off scale on both Figs. 4e and 4f), respectively. While the basal slip on the shuffle set along ⟨1100⟩ consists of two distinct directions, with shearing first along 1/3⟨1100⟩ and then along 1/3⟨1010⟩, the lack of an intermediate energy minimum along this path suggests that the dislocation does not dissociate into partials separated by a stacking fault. The second most favorable slip path, i.e. the path with the second lowest τ₀, is on the shuffle set along ⟨1120⟩ corresponding to the solid curve in Fig. 4f. The third possible basal slip is on the glide set along ⟨1100⟩ that involves dissociation of the dislocation into two partials along 1/3⟨1100⟩ + 1/3⟨1010⟩ separated by a stable stacking fault. This slip mechanism is considered to be active at high temperatures [35,36]. Although E_{GSF} is the lowest for this process, shown by the dotted curve in Fig. 4e, τ₀ is higher than those required for basal slip on the shuffle sets along ⟨1100⟩ and ⟨1120⟩ because the magnitude of the Burgers vector, |b| = 1/√6, is shorter compared to both 2/√6 along ⟨1100⟩ and 1/√2 along ⟨1120⟩. Based upon our calculations, we conclude that the plastic deformation of single-crystalline, defect-free, 6H-SiC Φ_{45} pillars occurs via glide of full dislocations on the shuffle set of the basal plane at room-temperature. Our TEM analysis (see Supplementary Fig. S5) suggests that dislocations with b = [1120] are present in the deformed sample. While our results are qualitatively consistent with TEM observations of post-indented microstructures of 4H- and 3C-SiC samples [33], we cannot rule out the possibility of operation of other pathways because the sample geometry and in situ TEM experimental setup has limited our ability to detect other dislocations. Additional detailed TEM characterization is necessary to help better understand the observed mechanical behavior.

We now focus on whether the experimentally observed plastic flow in 6H-SiC is controlled by nucleation or glide of dislocations. Under compression, the dislocations are likely to nucleate at the surface of pillars in contact with the diamond tip. However, due to the limited resolution of the in situ TEM, the onset of nucleation and the exact nucleation sites are difficult to determine in our experiments. Our DFT calculations of dE_{GSF}/dx vs. (x/b) (Fig. 4f) predict that the ideal shear stress (the lowest τ₀) associated with nucleation of a dislocation on the shuffle set along ⟨1100⟩ of the basal plane surface is ~33 GPa. The corresponding uniaxial compressive stress is ~66 GPa (since the Schmid factor is ½ for this slip system) and is more than twice the stresses obtained from MD simulations. Nevertheless, both MD- and DFT-calculated stresses for dislocation nucleation are up to an order of magnitude higher than the experimentally determined σ_y. Therefore, we suggest that the observed plastic deformation in 6H-SiC is due to existing dislocations rather than the nucleation of new dislocations. This assertion is...
consistent with the stresses expected for dislocation glide at room-temperature in 6H-SiC [37].

4. Conclusions

In summary, we have directly observed sustained plastic flow in 6H-SiC pillars at room-temperature. Using TEM along with ab initio modeling, we determined that the glide of full dislocations on shuffle set of basal planes leads to the observed plastic deformation. Based on our electronic structure calculations, we identify dislocation propagation along $\frac{1}{3}\{1100\}/2 + \frac{1}{3}\{1010\}/3$ for (a, e), $\{1100\}/6 + (1100)/6$ for (d). Plots of (e) $E_{GSF}$ and (f) $dE_{GSF}/dx$ vs. position ($x/b$), where $b$ is the Burgers vector. The solid, dashed and dotted curves represent dislocation glide depicted in (a), (b) and (d) respectively. $E_{GSF}$ and $dE_{GSF}/dx$ values for path (c) are over 2× higher than those of the other paths and hence are not shown in these plots.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.actamat.2014.07.066.

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