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Direct atomistic simulation of brittle-to-ductile transition in silicon single crystals

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ABSTRACT

Silicon is an important material not only for semiconductor applications, but also for the development of novel bioinspired and biomimicking materials and structures or drug delivery systems in the context of nanomedicine. For these applications, a thorough understanding of the fracture behavior of the material is critical. In this paper we address this issue by investigating a fundamental issue of the mechanical properties of silicon, its behavior under extreme mechanical loading. Earlier experimental work has shown that at low temperatures, silicon is a brittle material that fractures catastrophically like glass once the applied load exceeds a threshold value. At elevated temperatures, however, the behavior of silicon is ductile. This brittle-to-ductile transition (BDT) has been observed in many experimental studies of single crystals of silicon. However, the mechanisms that lead to this change in behavior remain questionable, and the atomic-scale phenomena are unknown. Here we report for the first time the direct atomistic simulation of the nucleation of dislocations from a crack tip in silicon only due to an increase of the temperature, using large-scale atomistic simulation with the first principles based ReaxFF force field. By raising the temperature in a computational experiment with otherwise identical boundary conditions, we show that the material response changes from brittle cracking to emission of a dislocation at the crack tip, representing evidence for a potential mechanisms of dislocation mediated ductility in silicon.

INTRODUCTION

The mechanical response of solids subject to extreme applied stress is controlled by atomistic mechanisms in the vicinity of stress concentrations such as crack tips (Figure 1(a)) [1-3]. Crack tips represent mathematical singularities for the stress distribution, providing local large interatomic forces that form the seeds for macroscopic failure [1, 3-6]. In brittle materials, the

material responds by further extension and resulting growth of cracks, leading to a catastrophic failure through fragmentation. In ductile materials, the repeated shear of lattice planes through dislocations leads to macroscopic permanent change of the shape of the material without catastrophic failure [1, 3, 4, 7]. These two extreme cases of brittle and ductile material response are summarized schematically in Figure 1(b). Whether a material is ductile or brittle depends on the competition of intrinsic material parameters (such as the energy required to create new surfaces, versus the energy required to initiate shearing of a lattice to form a dislocation). Alternatively, it has been shown that the type of failure response can be controlled by the temperature. Low temperatures tend to lead to more brittle, and higher temperature to a more ductile material response [8, 9]. In silicon, experimental studies of single crystals with a crack have shown that the material response can be either brittle or ductile, depending on the temperature [10]. At temperatures below ≈ 800 K silicon tends to be extremely brittle, while it exhibits ductile behaviour above ≈ 800 K [10]. This surprising phenomenon has been studied experimentally and theoretically for more than 20 years. Several explanations have been proposed. Rice's criteria for dislocation nucleation at crack tips [4] describe BDT as a dislocation nucleation-controlled event [11]. Others describe the BDT in terms of dislocation mobility-controlled events [12, 13], along with changes in the density of dislocations emitted [14].

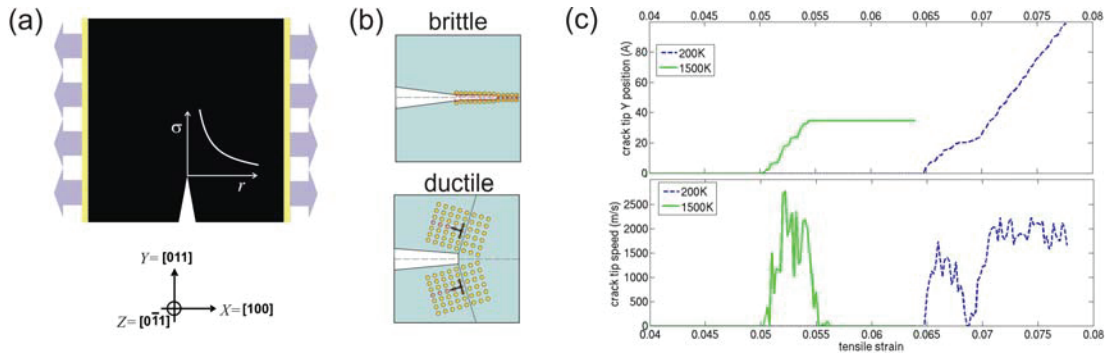


Figure 1: Subplot (a): Silicon single crystal under mode I loading with edge crack of $\{100\} \langle 110 \rangle$ character. Subplot (b): Schematic illustration of brittle (crack extension) versus ductile material (dislocation nucleation) behaviour. Subplot (c): Crack tip position and velocity for low (200 K) and high (1500 K) temperatures, as a function of engineering strain $\varepsilon = \Delta L_X / L_{0,X}$. Crack blunting and stopping accompanied by dislocation emission is observed at higher temperature, whereas at 200 K brittle cleavage fracture is observed. An equilibrium crack speed of $\approx 2,000$ m/s is achieved at 200 K. The 200 K simulation results show a temporary slowdown of the crack due to a sessile 5-7 defect in the crack pathway [15] (at approximately 6.9% strain or 34.5 ps). The formation of the 5-7 defect lowers the stress intensity at the crack tip by bond-rotations, and slows the crack to an arrest, before the increasing loading allows the crack to proceed again. Several more such arrest phenomena occurrences may be expected in longer simulations over larger crack paths due to the thermally-activated nature of these defects.

The development of atomistic level understanding of BDT has been hindered partly due to the lack of atomistic models that enable the simulation of sufficiently large systems to accurately describe the fracture processes associated with fracture at a range of temperatures. For silicon, these processes involve several tens of thousands of atoms surrounding a crack tip for time periods of fractions of nanoseconds. Describing bond breaking processes in silicon has

required quantum mechanical (QM) methods to properly describe the complex electronic rearrangements that determine the barriers and hence the rates, where large changes in bond angles and coordination can affect the interatomic forces [15-18]. However, accurate QM calculations for large system sizes that would be required to describe the complex details of bond rearrangements under large stresses are currently impractical. An alternative approach has been to apply relatively simple empirical relationships between bond stretch and force [6, 19, 20], but earlier results suggested that fracture in silicon cannot be modelled with such force fields [17].

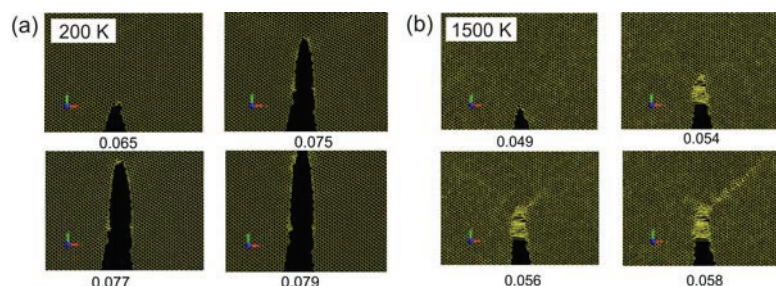


Figure 2: Subplot (a): Crack motion at 200 K. The numbers indicate engineering strain values at the particular snapshots. Brittle cleavage fracture with smooth surfaces is observed. Subplot (b): Crack motion at 1500 K. Slight crack opening followed by sudden

crack blunting with emission of a dislocation is observed. (Note; in subplot (b) we use a different visualization scheme than in subplot (a). To better visualize the shear of atomic planes, we keep the initial bond connectivity, which leads to the plotting of overstretched bonds that easily indicate the slip plane. In subplot (a) we use dynamic bond redrawing in VMD.)

METHODS

We apply the first principles based ReaxFF reactive force field, which retains nearly the accuracy of QM, even for bond breaking events. The ReaxFF parameters are determined solely by fitting to QM-data on silicon and silicon oxide chemistry [21]. The ReaxFF computational costs are only one magnitude higher than ordinary force fields, enabling parallelized applications to systems larger than 1,000,000 atoms at nanosecond time-scales [22]. ReaxFF therefore allows us to directly simulate the BDT without any fitting against experimental results or fracture properties. Earlier studies with the ReaxFF force field have shown that it reproduces key experimental observations of purely brittle fracture of silicon [15, 18]. Figure 1(a) shows the simulation geometry, a single crystal of silicon with a surface crack under mode I tensile loading. We carry out two simulations, one at 200 K and one at 1500 K, with exactly the same initial and boundary conditions (other than the temperature) and the same constant loading rate throughout the simulation (increase of loading is never stopped). We use the GRASP simulation code (General Reactive Atomistic Simulation Program), a new code developed to carry out the large-scale molecular dynamics simulations of crack growth using reactive force fields. GRASP was developed at Sandia National Laboratories, Albuquerque, New Mexico. GRASP uses a spatial decomposition algorithm [23] in order to distribute the calculation of atom positions, velocities and forces over a large number of processors. The ReaxFF charge equilibration equations are solved every time step using a sparse parallel conjugate gradient algorithm [24]. This approach provides excellent parallel scaling on general-purpose computing clusters. Typical MD simulations using the ReaxFF force field using GRASP can be run efficiently on up to $N/200$ processors, where N is the number of atoms. Beyond this point, the parallel efficiency drops below 50%. One MD time step with the ReaxFF force field requires about 10^{-3} processor-seconds per atom, making it considerably more expensive than conventional force fields such as

Tersoff and Stillinger-Weber. We consider a perfect silicon crystal oriented so that the x - y - z directions are $(1,0,0) \times (0,1,1) \times (0,\bar{1},1)$, with an initial crack on a (100) fracture plane with initial [011] fracture direction. The slab geometry used is approximately 20 nm by 18 nm, with an initial crack length of 4 nm. We use periodic boundary conditions in the out-of-plane direction, imposing purely in-plane strain in a plane-strain setup. The thickness of the systems is 15 Å, and the system consists of $\sim 27,500$ atoms. To apply load, we continuously strain the system according to mode I by displacing the boundaries [6, 19] at a strain rate of $2 \times 10^9 \text{ s}^{-1}$ (see Figure 1(a)). The system evolution is under a canonical ensemble, with temperature being controlled by a Berendsen thermostat. Loading is initiated after a system equilibration of 50,000 MD steps at the target temperature. Runs at each temperature are repeated two times.

RESULTS AND DISCUSSION

Figure 1(c) shows the results of the crack tip history and the crack tip velocity history, respectively, for both temperatures. A significant difference in the behaviour can be observed. In the 200 K case, fracture initiates at approximately 6.5% applied strain (or 32.5 ps) and the crack speed quickly approaches 2 km/sec, in agreement with earlier simulations [15, 17] and experimental results [25]. For the 1500 K case, a small regime of crack extension initiates at 5% applied strain (or 25 ps), but the crack arrests quickly and does not propagate any further. The initial load of 5% is slightly smaller than the load for the low temperature, which is attributed to thermal activation effects. The high-temperature discontinuation of crack propagation, despite the increase of applied loading, suggests that an alternative mechanism is activated that is responsible for dissipating the energy supplied through continued elastic loading at the boundary of the slab.

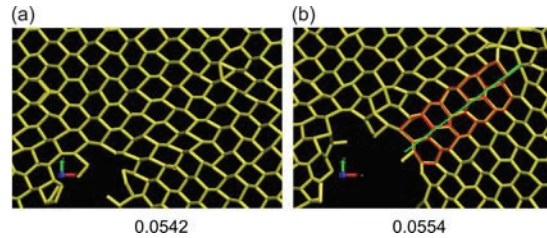


Figure 3: Subplot (a-b): Details of atomic structure close to crack tip around the time of dislocation emission in the 1500 K simulation. (a), viewing into the $\langle 110 \rangle$ direction shows the crack just before partial emission, with distorted hexagonal silicon cages (numbers indicate engineering strain values). (b) shows the characteristic atomic structure of a stacking fault on the glide plane (outlined in red) showing that a partial dislocation has passed.

The analysis of the atomistic structure during the deformation process explains this observation. Figure 2(a) displays snapshots of crack dynamics at 200 K, showing clean brittle fracture through generation of almost perfectly flat atomic surfaces. The analysis at 1500 K shown in Figure 2(b) reveals a drastically different behaviour, showing the nucleation of a partial dislocation from the crack tip. This observation demonstrates clearly the change of the response of silicon from brittle to ductile, solely due to a rise in the temperature, and confirms that the BDT is associated with a distinct change in the atomistic deformation mechanism. Immediately preceding either crack extension or dislocation nucleation, both systems behave virtually identically, showing no signature of either response. Figure 3 provides further detailed views into the region at the crack tip for the case of 1500 K. Figure 3(b) displays the crack tip configuration with a nucleated dislocation, showing the existence of a small stacking fault region and the dislocation core. The resistance to crack extension is determined by the fracture surface energy, describing the amount of energy needed to create new material surfaces during crack

growth [4, 5, 26]. The resistance to nucleation of dislocations is described by a similar parameter, the unstable stacking fault energy (USF), describing the energy barrier associated with creating a dislocation in a crystal. There are two possible slip planes, the “shuffle plane” and the “glide plane” [27, 28]. The USF value for the shuffle plane is lower than that of a glide-plane partial. However, our simulation results show that a partial dislocation is emitted despite the higher energy barrier. This observation agrees with results from experimental studies of this phenomenon [29]. Figure 4(a) shows another snapshot of the region close to the crack tip after the dislocation has been nucleated at 1500 K. We find that a 90° partial dislocation is emitted on a $(\bar{1}11)$ glide plane, with the slip direction $[211]$. Figure 4(b) shows the structure of the incipient dislocation, where the incipient dislocation is highlighted by a red ellipse. The incipient dislocation appears extended and its size extends over 4 hexagonal silicon rings, viewed along the $\langle 110 \rangle$ direction. The formation of this wide incipient dislocation, which evolves into a glissile partial, requires a large activation energy, and it could be that it is only favoured at high temperatures. Notably, at all temperature, sessile 5-7 crystal defect formation is observed at the crack tip [15]. However, whereas at low temperature this defect remains sessile (and can lead to crack tip deflection and instability; see [15]), at higher temperature this defect provides a seed for formation of the incipient stage of the glissile partial dislocation.

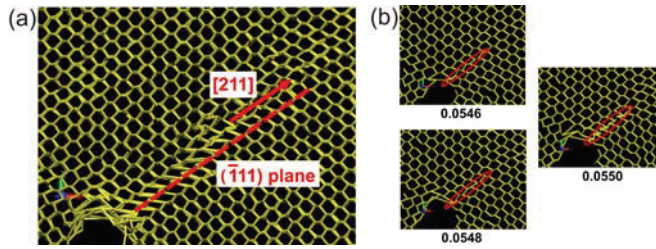


Figure 4: Subplot (a): Dislocation emission at crack tip at 1500 K. A 90° partial dislocation is emitted on a $(\bar{1}11)$ glide plane and the crack stops growing (slip direction $[211]$). Subplot (b): Structure of the incipient dislocation at 1500 K (position outlined in a red ellipse).

The numbers below each snapshot indicate engineering strain. Dislocation emission occurs at approximately 5.46% strain, or 27.3 ps.

The results reported here provide the first atomistic-scale view of the BDT in silicon. The use of a full chemistry full physics, first principles based atomistic model in the simulations is essential to directly simulate BDT. In earlier simulation models we used a hybrid formulation [15, 18] that involved only up to 3,000 reactive ReaxFF atoms in the crack tip vicinity. We observe that whereas this smaller reactive region is sufficient to describe brittle fracture of silicon, it is too small to capture the formation of dislocations from the crack tip at elevated temperatures. This is explained by the observations shown in Figures 3 and 4 that reveal extended disordered regions. A reactive description of these domains, which requires more than 20,000 atoms, is crucial in order to reflect the transition to ductile behaviour. After the success of phenomenological dislocation models in describing BDT [4, 14, 26, 30], progress has been somewhat limited. This may have been partly due to the absence of an atomistic simulation model that was capable of capturing the chemistry of silicon bond breaking and thus the atomistic mechanisms of BDT. Our results may enable the development of first principles based dislocation mechanics models. Since ReaxFF is capable of describing a diverse range of materials, the approach used here for silicon as a brittle “model material”, provides a practical means to studying the coupling of chemical reactions to mechanical properties in other brittle materials. The results reported here leave many questions open, including a more detailed analysis of the mechanisms that result in the transition from brittle cracking to dislocation

emission, the study of a more gradual increase of the temperature (and the investigation of the transition occurs suddenly as observed in experiment, with an identification of the actual transition temperature), and a careful analysis of the rate dependence of the transition temperature. An enhanced understanding of the mechanical properties of silicon could enable us to utilize silicon in the development of novel bioinspired functional nanomaterials, as the large-scale manufacture of silicon nanostructures is possible with current technology derived from semiconductor manufacturing. These and other issues could be addressed in future work.

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