Free Energies of Generalized Stacking Faults in Si and Implications for the Brittle-Ductile Transition

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The generalized stacking fault energy and entropy have been calculated from first principles for two {111} planar cuts in Si separating widely spaced (shuffle plane) and narrowly spaced (glide plane) atomic layers. Energy considerations predict that the preferred fault is the shuffle plane. When the entropy is taken into account, it is found that for tensile stresses there is a critical temperature above which the preferred mode changes from shuffle to glide. We suggest that this change in preferred fault mode may be related to the brittle-ductile transition.

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The change of state in which crystalline solids convert from brittle, easily fractured substances into ductile, tough materials has been recognized as vital to technology for many years, but has eluded explanation by modern physics. Understanding of the nucleation and motion of extended defects, particularly dislocations, is crucial to the physical description of this important transition. To this end, classical elasticity theory is useful for length scales beyond a few lattice spacings [1], but cannot account for the wide discrepancies observed in materials with different structures and binding properties [2]. Atomistic computations based on effective potentials have met with considerable success for metals, but are inadequate for nonmetals, where the ionic and electronic components of the energy cannot be readily decoupled [2]. A first-principles quantum mechanical description appears to be necessary to capture the rich behavior of extended defect nucleation and motion in solids.

Here we present such a study for a prototypical covalent solid, silicon. This choice was inspired by a regenerated interest in the behavior of dislocations in this solid, which may serve as a paradigm for studying the brittle-to-ductile transition (BDT) [3]. We relate our results on the zero-temperature and zero-pressure energetics of generalized stacking faults in Si to crucial solid state parameters that control dislocation nucleation and propagation. We also develop a formal, yet simple way of extending these results to finite temperature and pressure, thus allowing in principle a complete thermodynamic description of the processes under consideration. We discuss how this picture provides valuable insight to longstanding controversies regarding the properties of dislocations in Si.

Recent theoretical work by Rice [4] on the BDT has shown that a solid state parameter called the unstable stacking energy γ_{us} can be used to characterize dislocation nucleation at, and motion away from a crack tip. γ_{us} is defined as the lowest energy barrier that needs to be crossed when one part of a perfect crystal slips, on a particular reference plane, relative to the other part to complete a total displacement equal to a lattice repeat vector (the slip path does *not* necessarily lie along the lattice vector). The unstable stacking energy is an extremum of the generalized stacking fault energy surface $\gamma(\mathbf{f})$ [5], which measures the excess energy for relative displacement $\mathbf{f}$ spanning a complete cell on the reference plane. In Si, the relevant reference plane is the {111} slip and cleavage plane. The crystal structure of Si, the diamond cubic lattice, allows for two distinct placements of the slip plane: (a) Between atomic planes that are separated by a distance equal to the nearest neighbor distance (slip on this plane breaks one covalent bond per pair of atoms lying on either side of the plane). (b) Between atomic planes that are separated by one third of a nearest neighbor distance (slip in this case severs three covalent bonds per pair of atoms lying on either side of the plane). The positions of the two planes are illustrated in Figs. 1(a) and 1(b). These two slip planes between (a) widely spaced and (b) narrowly spaced atomic layers are referred to as "shuffle" and "glide" planes in the context of dislocation motion [1]. We adopt this terminology in the present wider context of dislocation nucleation and motion for convenience and brevity.

We have calculated the generalized stacking fault energy $\gamma(\mathbf{f})$ for both shuffle and glide planes, for a dense grid of 33 points in the irreducible part of the slip plane (which is 1/12 of the area shown in Fig. 1). Our calculations are based on the local density approximation (LDA) to density functional theory (DFT) [6], a first-principles quantum-mechanical approach which has proven very reliable in studying the energetics of bulk and surface structures of Si. The energy surfaces $\gamma(\mathbf{f})$ for the shuffle and glide planes, before allowing for atomic relaxation, are shown in Figs. 1(a) and 1(b), respectively [7]. Two interesting points emerge from this comparison. First, the energy scales are vastly different for the shuffle and glide

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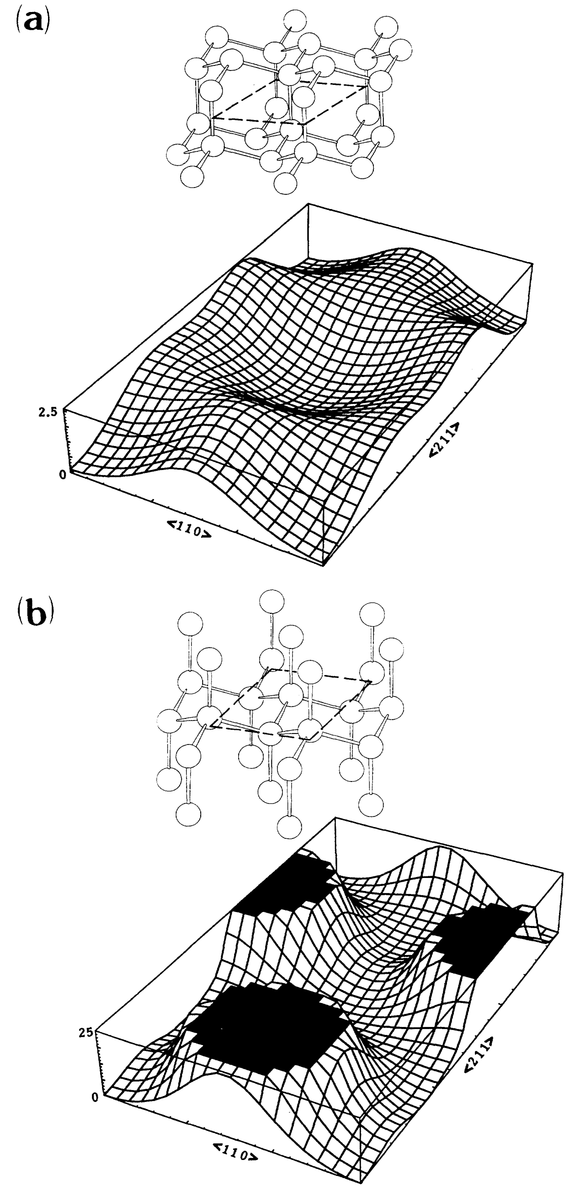

FIG. 1. (a) Energy surface $\gamma(\mathbf{f})$ for displacement along the shuffle plane in J/m^2. The corners of the box and its center correspond to identical equilibrium configurations, i.e., the ideal Si crystal. The inset shows a portion of the crystal with the shuffle cut indicated by dashed lines. (b) Same as in (a) for the glide plane. Notice the different energy scale (dark areas correspond to values of the energy that are higher than 25 J/m^2).

planes, differing by almost 2 orders of magnitude (see Fig. 1). Nevertheless, the lowest energy barriers ($\gamma_{\rm us}$) are comparable in magnitude (differing by only 25% before relaxation, see Table I). Second, the lowest-energy displacement paths corresponding to the shuffle and glide planes are also very different. In order to clarify this point we present in Fig. 2 a schematic representation of the lowest-energy displacement paths on the two planes.

We next discuss the specifics of the lowest-energy displacement paths since they are related to the mechanisms of dislocation nucleation and motion. On the glide plane there is a metastable energy minimum for a displacement vector $\frac{1}{6}[1\bar{2}1]$ (displacements are given in units of the lattice constant of Si). The lowest-energy path follows this route, completing a $\frac{1}{2}[0\bar{1}1]$ repeat translation with a displacement of $\frac{1}{6}[\bar{1}\bar{1}2]$. The metastable minimum corresponds to the intrinsic stacking fault encountered in the well-known dissociation of the total dislocation into a pair of Shockley partial dislocations [8]. For dislocation nucleation or propagation on the glide plane, displacement through a repeat distance will take place by successive translations along $\langle 211\rangle$ directions. The unstable stacking energy occurs for a displacement vector of $\frac{1}{12}[1\bar{2}1]$; the energy at this saddle point is an order of magnitude smaller than that of the corresponding saddle point in the $\langle\bar{1}01\rangle$ direction [see Fig. 1(b)]. For the shuffle plane there are no secondary minima in the energy surface. The preferred slip path lies parallel to the $\langle 110\rangle$ directions and the unstable stacking energy occurs for a displacement vector of $\frac{1}{4}[110]$. Dissociation could take place on this plane also [9], but since it has to be accompanied by rows of point defects (vacancies or interstitials) this possibility is generally dismissed as energetically unfavorable [1,10].

The calculations discussed so far did not include atomic relaxations. Using the DFT-LDA approach, it is feasible, though computationally demanding, to account fully for atomic relaxations by minimizing the magnitude of the calculated Hellmann-Feynman forces through steepest descent. We have calculated the atomic relaxations only for the configurations that correspond to the lowest-energy barrier ($\gamma_{\rm us}$) of the shuffle and glide planes. The relaxation was performed in two stages: first the volume was fixed and the atoms adjacent to the slippage plane were allowed to relax [7]. Then this procedure was repeated at several volumes, spanning values below and above the ideal volume of bulk Si. In this manner, the full relaxation associated with the distortion is taken into

TABLE I. Energy of unstable stacking, $\gamma_{\rm us}$, at various levels of relaxation, for the shiffle and glide planes (in J/m^2).

	No Relaxation	Atomic relaxation at ideal volume	Atomic relaxation and volume relaxation
(a) Shuffle	1.84	1.81	1.67
(b) Glide	2.51	2.02	1.91

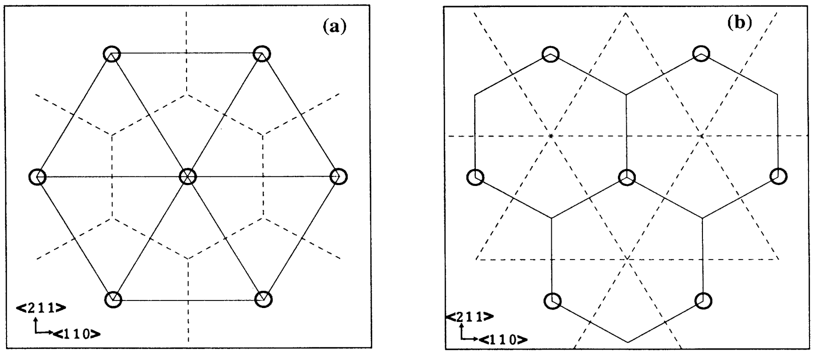

FIG. 2. (a) The lowest energy paths (solid lines) for slippage on the shuffle plane, which are along equivalent ⟨110⟩ directions. The circles denote the equilibrium configurations (ideal Si crystal). The dashed lines indicate the saddle-point surfaces. The intersection of dashed and solid lines determine the position of the γ_{us} configurations. (b) Same as in (a) for the glide plane. Here all the slippage paths (solid lines) are along equivalent ⟨211⟩ directions.

account. We find that in the lowest-energy configuration the the slab contracts by 0.24 a.u. in the direction perpendicular to the slip for the shuffle plane, and expands by 0.24 a.u. for the glide plane. This relaxation is the result of bond dilation (characteristic of the shuffle) or bond compression (characteristic of the glide) in the unrelaxed configurations. The results of the energy comparisons are summarized in Table I. Direct comparison of γ_{us} for shuffle and glide planes suggests that nucleation on the shuffle plane will be preferred.

The implications for dislocation motion are more subtle. The shape and magnitude of the $\gamma(\mathrm{f})$ surface determine the distribution of misfit in the dislocation. For the misfit confined to a plane, as is expected for Si, a connection to dislocation motion is given by the Peierls model [11]: The resistance to dislocation motion (the Peierls stress) is determined by the variation of the energy of the misfit distribution with position in the lattice. The Peierls stress is lower for a wider dislocation, and this width increases as the maximum gradient of the $\gamma(\mathrm{f})$ surface along the displacement path decreases [12]. Recent calculations of the Peierls stress in Si [13] show that the stress is lowest for glide partials, intermediate for the shuffle total and highest for the glide total dislocations, indicating that motion on the glide plane is favored.

We next discuss the extension of these zero-temperature and zero-pressure results to include the effect of finite temperature and pressure. This will prove important in obtaining insight to which plane (shuffle or glide) is dominant for dislocation nucleation and motion, an issue that has been the subject of controversy [10,14–16]. The extension of our results to finite temperature is based on the transition-state theory of Vineyard [17], which is used to describe diffusion. First, we note that having calculated the entire quantum-mechanical $\gamma(\mathbf{f})$ surface for slip, we can formally map this process to the problem of a classical particle moving on a two-dimensional potential energy surface. This mapping involves folding all the degrees of freedom of the original many-atom system to two collective degrees of freedom, which represent motion in the plane spanned by the $[\bar{1}01]$ and $[1\bar{2}1]$ vectors (see Figs. 1 and 2). In principle, full relaxation of the energy surface with respect to all the other degrees of freedom should be included in the energy surface (we return to this point below). With this mapping, we can borrow directly from transition state theory the formulas for calculating the entropy associated with the diffusion of a particle. The entropy is the logarithm of the ratio of two Boltzman integrals [18], the first over a $(d-1)$-dimensional surface around the saddle point (γ_{us}) configuration and the second over a d-dimensional volume at the equilibrium configuration (d is the dimensionality of space, in the present case $d = 2$).

Our results indicate that, although the glide plane has a higher γ_{us} value, it also has higher entropy. Since the entropy term enters in the free energy with a negative sign, it is possible that under the proper conditions the free energy of the glide plane can become *lower* than that of the shuffle plane. It is a reasonable assumption to replace the energy of the fault in the Peierls model by the free energy at finite temperature [19] (the same applies to the relative Peierls stresses). One can also take into account the effect of pressure in the free energy, by considering the volume difference between the ideal crystal and the saddle point configuration for the two modes of slippage. This leads to the following expression for the pressure at which the free energies for the two modes become equal:

$$P = \frac{(S_{\mathrm{glide}} - S_{\mathrm{shuffle}})T - (\gamma_{\mathrm{us\text{-}glide}} - \gamma_{\mathrm{us\text{-}shuffle}})}{(\Delta z_{\mathrm{glide}} - \Delta z_{\mathrm{shuffle}})}, \qquad (1)$$

where energies (γ_{us}) and entropies (S) are given per unit area along the slip plane and Δz is the relaxation in the direction perpendicular to the slip plane. The solid line in the (P,T) plane of Fig. 3 corresponds to points at which the equality in Eq. (1) holds. For (P,T) values above the equality line, the free energy favors the shuffle plane, whereas for values below the line the glide plane is preferred. This clearly indicates the importance of temperature and pressure in discussing the nature of dislocation nucleation and motion in Si. Two remarks are in order. First, as seen from Fig. 3, the glide plane becomes important only at relatively large tensile pressures (such an environment may be encountered at the tip of a crack, for instance). Second, the values of γ_{us} and Δz in Eq. (1) include full relaxation, whereas the

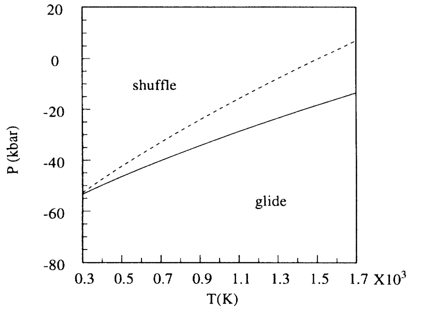

FIG. 3. Phase diagram on the (P,T) plane. The equality in Eq. (1) determines the (P,T) transition (solid) line. Below (above) the line, slippage on the glide (shuffle) plane is preferred. The solid line is from the calculation which does not include the effect of relaxation on the entropy. The dashed line includes an estimate of the correction to the entropy due to relaxation (see text).

entropy values were obtained from the energy surfaces of Fig. 1, which do not include relaxation. Atomic relaxation will increase the entropy since it lowers the energy significantly at the saddle point configuration but only marginally at the equilibrium configuration (see [20]). This effect will be more pronounced for the glide plane as Table I shows. To obtain an order-of-magnitude estimate of this effect, we assume an increase in the entropy difference in Eq. (1) due to relaxation equal to that for point defects in Si ($\sim 50\%$). This moves the equality line to the dashed position in Fig. 3 but does not affect the qualitative features of the transition. The transition from the shuffle to the glide mode indicated by the (P,T) phase diagram may be related to the sharp BDT observed in Si at $T_c \sim 873$ K [3]. Dislocations nucleate more easily on the shuffle plane, but as experiments suggest [14–16], they become mobile on the glide plane. The phase diagram of Fig. 3 shows that a tensile stress of order 10 kbar is necessary to induce a transition to glide plane dominance at a critical temperature of order 10^3 K (at the present level of accuracy in the entropy calculation only such order-of-magnitude comparisons are meaningful).

In conclusion, we have calculated the generalized stacking fault energy surface $\gamma(\mathrm{f})$, entropy, and volume relaxation for faulting on the shuffle and glide planes in Si. Our results, based on a first-principles computational scheme, provide for the first time a clear picture of the relative importance of the two different modes of dislocation nucleation and motion in Si. We have shown that either mode can be dominant, depending on the temperature and pressure conditions, and that under tensile deformation, a transition from the sessile shuffle mode to the glissile glide mode can occur as the temperature increases beyond a critical value. We suggest that this change of modes could be related to the brittle-ductile transition in Si.

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