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A Theoretical Study Of Dislocation Formation At Surfaces In Covalent Materials: Effect Of Step Geometry And Reactivity

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Abstract. Atomistic simulations using both semi-empirical potential and first principles calculation have been performed to study the initiation of plasticity near surface steps in silicon. A comparison of both techniques on a prototypic case shows qualitative and quantitative agreement. Then each method has been used to analyze in detail some characteristics of the surface step: the step geometry thanks to semi-empirical potential calculations, and the step reactivity with *ab initio* techniques.

Introduction

As a prototype of semi-conductor material used in microelectronic devices, silicon is a good candidate for the study of dislocation formation under stress. During the fabrication of such devices, very large stresses may be introduced. Stress can be relaxed through dislocations formation, which can damage the electronic properties of these systems. It is then important to understand the dislocation formation in these materials. Now because of the reduced dimensions and / or the absence of pre-existing dislocation, the Frank-Read sources mechanism of dislocation multiplication can not operate. In this context, surface or interface defects, such as surface steps, can act as dislocation sources. This assumption is supported by experimental evidence of dislocation nucleation from or near surface defects in silicon [1,2].

Because of the reduced dimensions and time scale involved in the initiation of plasticity near surfaces, atomic scale simulations are expected to bring useful information. We have realized such simulations using two complementary techniques: semi-empirical potential and first principles calculations. The former has a low computational cost compared to the latter, so that it allows many tests to be done, with quite large systems. In return, first principles calculations are more accurate; in particular they allow the determination of the electronic structure of the system, so that the chemical structure is accurately modeled.

In the following section, the methodology is explained. Then we compare the results obtained with both techniques for a typical step configuration, for which a perfect dislocation is nucleated. Finally, we show how step height, structure and reactivity affect the onset of plasticity and the process of dislocation nucleation.

Methodology

Computational methods. Both semi-empirical potentials and first principles calculations have been used in this work. Both methods have advantages and drawbacks, but for the particular

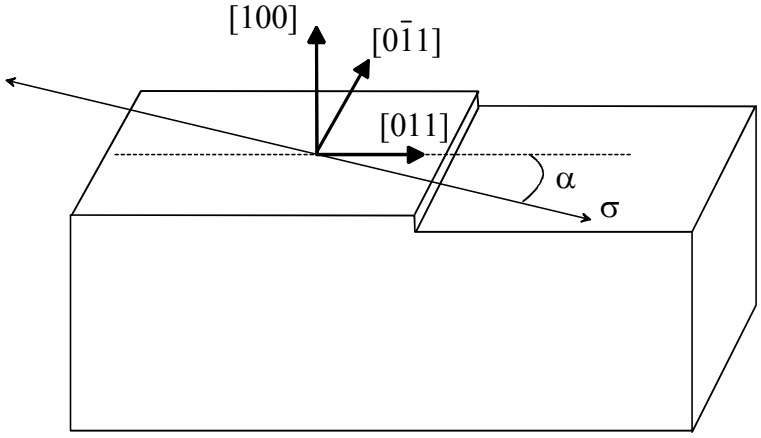
problem we are interested in, that is the formation of plastic defects from surface steps, they both give insight in the mechanisms involved, as will be seen in the next sections.

In a previous study [3], it has been shown that under the large strains considered, the best semi-empirical potential to model silicon is the potential of Stillinger and Weber (SW) [4]. With this potential, simulations at 0K have been done, using a conjugate gradient algorithm for the energy minimization. The convergence has been reached when the resulting force on every atom was less than 10^{-3} eV/Å.

The *ab initio* calculations are based on the density-functional theory [5] within local density approximation for exchange and correlation contributions [6,7]. The SIESTA method [8,9] has been used to calculate the energy and atomic forces, with separable norm-conserving Troullier-Martins pseudopotentials [10], and valence wave functions expanded on pseudoatomic orbitals. More details on the parameters employed can be found in [11]. The atomic positions have been relaxed with a conjugate gradient algorithm until the atomic forces were lower than 0.04 eV/Å.

Structure and geometry. The geometry chosen for the simulations is shown in Fig. 1: on a (100) free surface, the step line lies along a $[0\ \bar{1}1]$ direction, intersection of a {111} glide plane and the surface. The (100) surface of silicon is reconstructed (2×1) [12]. Depending if a single or a double step is considered, four different steps can result from this orientation [13]. A single step S can be formed by the emergence at the surface of a Shockley partial dislocation, while a double step D corresponds to the emergence of a perfect dislocation. In this study, we have focused on the most stable steps, that is, using Chadi's notations, S_A and D_B (rebonded and non rebonded). We have also considered a cleavage ledge corresponding to 5 D_B steps and forming a {111} facet (Fig. 2).

Fig. 1: Geometry of the system.

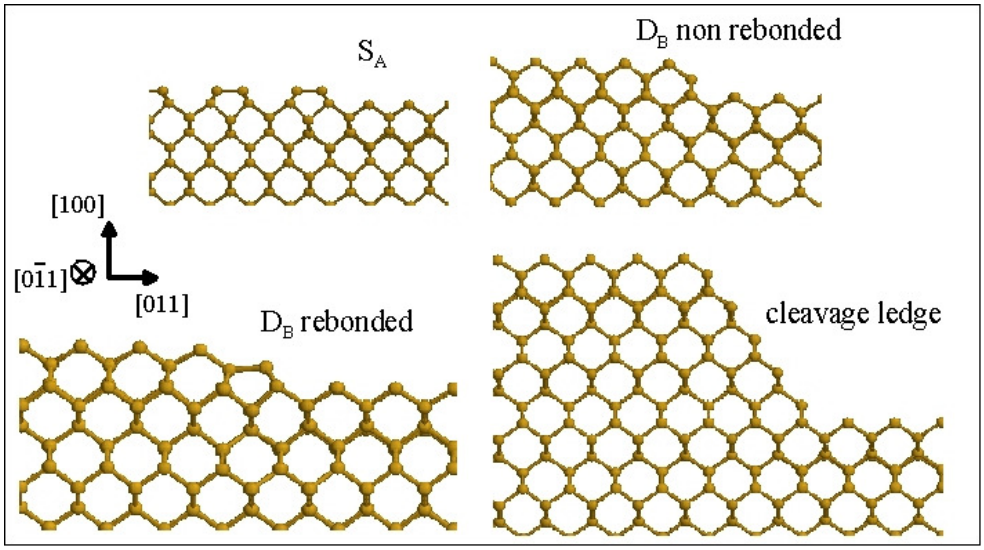


To simulate the effect of an uniaxial stress σ, the corresponding strains calculated using linear anisotropic elasticity are applied to the system. Different stress orientations have been studied, all contained in the surface plane. The stress direction is denoted by the angle α, which is the angle between the stress direction and the normal to the step line (see Fig. 1). The stress on the system is gradually increased, and the atomic positions are relaxed with the conjugate gradient method between each stress increment.

Because of the reduced dimensions of the simulated systems compared to a real sample, specific boundary conditions must be used. Along the $[0\ \bar{1}1]$ step line direction, periodic boundary conditions are applied, with enough thickness to allow the (2×1) reconstruction (at least 4 atomic planes). However, the thickness along this direction is too small to allow the formation of a dislocation half-loop: the nucleated dislocation are always straight, parallel to the step line direction. Along the [011] direction (normal to the step line), periodic boundary conditions are employed. Finally, in order to model a bulk crystal, four atomic layers at the bottom of the slab, opposite to the free surface, are frozen for simulations with the SW potential. For the *ab initio*

calculations, because of the huge computational cost, smaller systems must be considered. In such small systems, a frozen bottom would rigidify too much the system for the plastic defect formation to occur. So we have used a slab with two opposite free surfaces, each of them containing one step. With such boundary conditions, the typical systems we have considered include 120 (respectively 18) atomic layers along the surface normal [100] and 160 (respectively 6) along [011], which corresponds to about 80000 atoms (respectively 196 atoms) for the SW potential (respectively *ab initio*) calculation.

Fig. 2: Steps studied on the (100) surface.



60° dislocation nucleation.

In silicon, the Burgers vector of a perfect dislocation is 1/2 <1 $\bar{1}$ 0>, which can be at 60° or parallel to the dislocation line <0 $\bar{1}$ 1> in the {111} glide plane. In the following, the former will be called 60° dislocation, and the latter screw dislocation. The dissociation of a perfect dislocation into two Shockley partial dislocations is possible through the formation of a stable stacking fault in the glide set, that is, the narrowly spaced set of {111} planes of the diamond-like structure. However, all the dislocations formed during our simulations are perfect dislocations in a shuffle set plane (the widely spaced set of {111} planes) [14], probably because of the low temperature regime we are studying, and in agreement with experimental observations at low temperatures [15]. Here we have chosen an orientation of the stress that favors the formation of 60° perfect dislocations, that is, following a Schmid factor analysis, an angle α equal to 22.5°. A D_B non-rebonded step, which can be formed by the emergence of a perfect dislocation at the surface, has been used. In Table 1, a summary of the plastic events obtained and the corresponding strains is presented.

Table 1: Plastic events obtained and corresponding strains for a stress orientation at 22.5° from the step normal, with an *ab initio* calculation (SIESTA method) and with the SW potential.

	strain		**plastic events observed**	
	ab initio	**SW potential**	***ab initio***	**SW potential**
tension	21.9%	18.7%	60° perfect dislocation nucleated near the step after the formation of a locally disordered crystal near the step	60° perfect dislocation nucleated from the step
compression	-13.6%	-10.0%	60° perfect dislocation nucleated from the step	plastic deformations in {111} planes (no dislocations)

A good agreement concerning the critical strains for plastic defects formation (considered as the elastic limit in the following) is found. Although the values are not exactly the same, which is not surprising considering the so different backgrounds of the two methods used, the same trend is observed. As a matter of fact, the elastic limit is about half in compression than in tension. It must be pointed out that for all the stress orientations studied at 0K with the SW potential, the plastic defects have been formed more easily in compression than in tension, in the sense of lower critical deformations [14] (see also Table 2). Although the particular crystal structure and potential may be important, it must be noted that at the very large stresses involved here, it is possible that the solid undergo some buckling instability in compression, instability which can help dislocation formation.

As for the plastic events observed, the main discrepancy between the two techniques is obtained for the compression case. But it can be put forward that when a MD simulation with a temperature of 300K is performed with the same system, a perfect 60° dislocation nucleated from the surface step is also observed with the SW potential calculation [14] (for 7.5% strain).

In summary, in spite of the already mentioned very different theoretical backgrounds of the two simulation techniques used, and the different systems geometries, the results are very similar, both qualitatively (type of defect formed) and quantitatively (elastic limit). Consequently, one can be confident in using the advantages of each method to study some particular step effects.

Step role

The presence of the step localizes the initiation of the plastic deformation near or at the surface step, as can be seen in Table 1. A comparison of a bulk system, a system with a perfect surface and a system with a surface step (Table 2) also clearly shows a reduction of the elastic limit due to the presence of the step [16]. But depending on the geometric and chemical structure of the step, some differences in the elastic – plastic transition can be observed. We have been able to analyze the step geometry effect with the SW potential simulations, and the step reactivity effect with the first principles calculations, on the elastic – plastic transition.

Table 2: Elastic limits for a stress orientation normal to the step line, obtained with the SW potential.

crystal geometry	bulk	perfect surface	S_A step	D_B step		cleavage ledge
				rebonded	non-rebonded	
tension	35.9%	28.3%	24.7%	24.1%	22.9%	17.0%
compression	—	-11.0%	—	-7.7%	-7.6%	-4.4%

Step height and geometry. A quite exhaustive study of the step geometry influence on the elastic limit can be performed thanks to SW potential simulations. For this study, we have favored a stress direction normal to the step line. Thus, we have been able to compare the elastic limits for the different step geometries, for a bulk system and for a system with a perfect surface. These values are given in Table 2 for both tension and compression stresses.

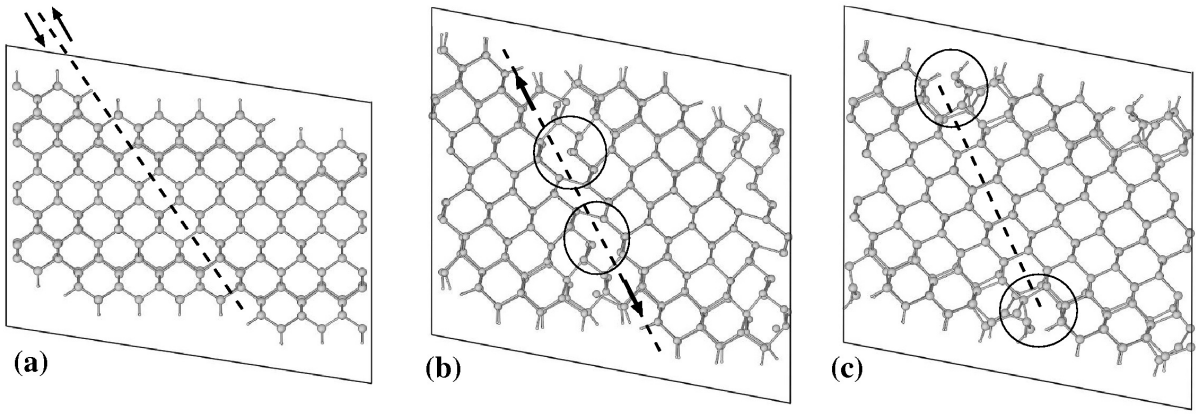
For the system containing a perfect surface without step, in tension, the initiation of plasticity occurs near the frozen zone at the bottom of the slab. It is due to a non physical discontinuity between the frozen zone, where linear elasticity is applied, and the free zone, where, for so large stresses, the behavior of the system is no more linear. For the bulk system, there is no frozen zone (periodic boundary conditions are applied in all directions), and the calculated elastic limit is larger. The value of –11.0% obtained in compression with a perfect surface does not result from technical constrains. Indeed, in this case, plasticity starts at the free surface with surface bulges.

As said above, the presence of the step on the surface decreases significantly the elastic limit compared to a system without step, for all configurations. The plastic deformations observed are quite similar for the different steps, with no dislocation nucleated [16,17] (this is particular with the stress orientation studied here). Apart for the cleavage ledge, the elastic limits are little modified

when the step geometry changes. However, one can note that the elastic limit is slightly decreased when the defect height is greater (compare S_A and D_B steps), or when the step front is more abrupt (compare D_B non rebonded and rebonded steps). For the D_B rebonded step, there is a supplementary atom which links the upper and lower terraces (see Fig. 2), allowing a repartition of the stress on a larger crystal zone. This is probably why the elastic limit is slightly larger than for the D_B non rebonded step. Finally, the influence of the step height is clearly evidenced with the cleavage ledge for which the elastic limit is significantly decreased compared to single or double steps.

Step reactivity. It has been observed that, in compression, the nucleation of the 60° dislocation described in the previous section is preceded by the formation of bonds between the upper and lower terraces, across the step. It can then be assumed that surface and step terminations will play a key role in the process of dislocation formation, and, more generally, initiation of plasticity. This is particularly true for the (100) reconstructed surface of silicon where one dangling bond remains for each silicon atom of the surface. To determine the role of the surface and step terminations during the dislocation nucleation, we have saturated all the dangling bonds of the free surface by an hydrogen atom (Fig. 3). Unlike in the previous section, the steps on each free surface are placed so that they cut the same glide plane, in order to facilitate dislocation nucleation. In that case, the compressive strain must be increased up to –16.7% before any plastic event is observed. Besides, plasticity first occurs inside the slab, with the formation of a dipole of perfect dislocations in the shuffle set plane going through the steps. Then, each dislocation moves progressively towards one surface (Fig. 3). During this process, no bond is formed near the surface step. Consequently, the surface and step terminations clearly influence the plastic relaxation mechanisms, but slightly the corresponding critical strain.

Fig. 3: System studied with the surfaces passivated with hydrogen atoms (represented by the lower spheres). (a) Unstrained system. (b-c) –16.7% of strain. The {111} shuffle set plane passing through the steps is indicated by a dashed line. The nucleated dislocation cores are encircled in (b-c), and their glide direction is indicated by arrows. The crystallographic directions are the same as in Fig. 2.



Conclusion

Thanks to atomistic simulations, the role of steps in the process of dislocation nucleation from surfaces in a model covalent material, silicon, has been analyzed. Two complementary methods have been used: semi-empirical potential and *ab initio* calculations. A comparison of both techniques on a prototypic case has ensured that they provide reliable results. Each one has brought useful information on the mechanisms involved. It has been shown that the main step effect is to localize the plastic deformation, the step geometry and reactivity playing an important role.

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