

Nanoscale structures formed in silicon cleavage studied with large-scale electronic structure calculations; surface reconstruction, step and bending.

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The 10-nm-scale structure formed in silicon cleavage is studied by the quantum mechanical calculations of large-scale electronic structure. Cleavage process was simulated and the results show not only the elementary process of the (experimentally observed) (111)-(2×1) surface reconstruction but also several step-formation processes. These processes are studied by analyzing electronic freedom and compared with STM experiments. The stability mechanism of the (111)-(2×1) cleavage mode is presented beyond the traditional approach with surface energy. In other results, the cleavage path was bent into the experimentally observed planes, owing to the relative stability among cleavage modes. Several common aspects between cleavage and other phenomena are discussed from the viewpoints of nonequilibrium process and 10-nm-scale structure.

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I. INTRODUCTION

Cleavage is a nonequilibrium process and its dynamical mechanism is essential. In particular, the cleavage of silicon single crystals is of great interest from the multiscale viewpoint between macroscale and atomicscale pictures. In the macroscale picture, silicon shows perfect brittleness and brittle fracture is usually described by continuum mechanics.¹⁻³ On the other hand, cleaved surface shows atomicscale reconstructions, which are observed by scanning tunneling microscopy (STM)⁴ and other experiments. The multiscale feature, as discussed in this paper, appears in 10-nm-scale region near the crack tip, though such processes cannot be seen by direct (*in situ*) experimental observation.

A fundamental question is what Miller index and surface reconstruction appear at the cleavage surface. One may predict from the traditional viewpoint that the cleavage plane should be that with the smallest surface energy, or the smallest energy loss with forming surface. This prediction, however, fails to explain the following experimental facts; (i) The easiest cleavage plane of Si is a metastable (111)-(2×1) structure⁴⁻¹⁰ and will change, irreversibly, to the ground-state (7×7) structure.^{4,11} (ii) The (110) cleavage plane is also experimentally observed but less favorable (see an experimental (STM) study,¹² and a recent theoretical study¹³). (iii) The cleaved Ge(111) surface also shows the same (2×1) structure, while the ground state surface structure is the c(2×8) structure.^{4,14,15} These facts imply the importance of direct cleavage simulations with electronic structure. Although such simulations have been carried out thus far,^{8,9,13} the system size is limited to the order of 10² atoms.

In this paper, the cleavage of silicon is studied with quantum mechanical calculations of large-scale electronic structures¹⁶⁻²¹ and we use a transferable Hamiltonian²² in the Slater-Koster (tight-binding) form. The method-

ology is reviewed briefly in Appendix A. The method realizes the cleavage process with more than 10⁴ atoms or a sample length of 10 nm. This paper is organized as follows; Section II describes the important aspects discussed in this paper. The easiest cleavage mode on the (111)-(2×1) plane is discussed in Section III and Section IV. The latter section focuses on step formations. The simulation results for bending in the cleavage path are presented in Section V. Finally, in Section VI, several common aspects of nanoscale structures are discussed for cleavage and other phenomena.

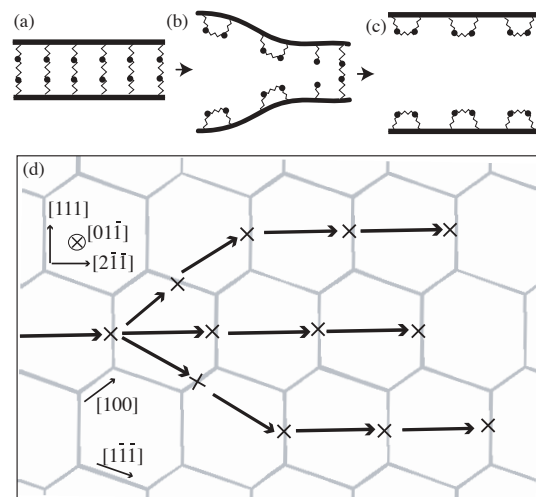


FIG. 1: (a)-(c): Toy model of cleavage, in which surface reconstruction is illustrated as dimerization. (d): Possible cleavage paths on Si(111) plane.

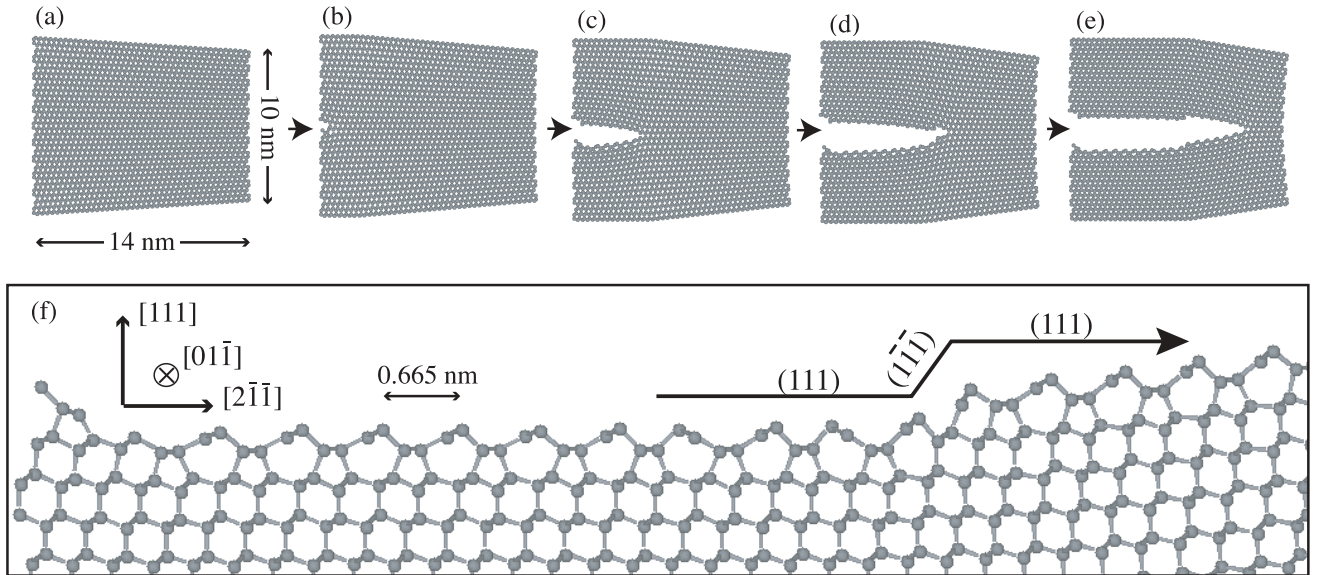


FIG. 2: Cleavage process of silicon with (111)-(2 × 1) cleaved surface. (a)-(e): Successive snapshots with a time interval of approximately 2 ps. (f): A part of the lower cleavage surface shown in the snapshot (e). A step is found and is classified into the ‘[211]-type’ or ‘via-(111)-plane type’ that can be decomposed into the successive bending of cleavage planes as (111) → (111) → (111).

II. ASPECTS OF CLEAVAGE IN REAL CRYSTAL

Several aspects of cleavage are pointed out as the foundation of the present theoretical study. The first one is the fact that cleavage, as a nonequilibrium process, has a typical time scale that is determined by the cleavage propagation velocity v_{prop} . In the continuum mechanics and many experiments, the propagation velocity v_{prop} is given on the order of, but less than, the sound velocity or the Rayleigh wave velocity ($v_R = 4.5\text{km/s} = 4.5\text{nm/ps}$ for Si).^{2,3,23} When cleavage propagates by a typical atomic length scale, say $\Delta L \approx 1\text{nm}$ for Si, it accompanies elementary processes of bond breaking and surface reconstruction in the time scale of $\Delta T = \Delta L/v_{\text{prop}}$ (less than 1 ps). Since the processes occur within this time scale, the reconstruction in cleavage should occur *locally*, unlike that in annealing. As a typical process, a surface-bound state tends to be formed between electrons in *nearest-neighbor* dangling-bond sites, as illustrated in Figs. 1(a)-(c). This nearest-neighbor reconstruction mechanism will directly give the experimentally observed (2 × 1) reconstruction (See Section III).

The second aspect comes from crystal structure. Figure 1(d) shows possible cleavage paths on the Si(111) plane, with or without step formation. Unlike the toy model of Figs. 1(a)-(c), the system does not have the mirror symmetry with the cleavage plane and the upper and lower cleaved surfaces are inequivalent in symmetry. In particular, the inequivalence between the upper and lower stepped paths in Fig. 1(d) is distinctive in experiments.

Since experiments reported only the (111) or (110)

cleavage plane, theory should explain why other surfaces *do not* appear. An interesting fact is that the calculated surface energy of the reconstructed (001) surface is *smaller* than that of the (111)-(2 × 1) surface ($\gamma_{(001)}^{4 \times 2} = 1.41\text{J/m}^2 < \gamma_{(111)}^{2 \times 1} = 1.44\text{J/m}^2$)^{14,24}. Therefore, the absence of the (001) cleavage surface is not simply predicted by surface energy.²⁵ The possibility of the (001) cleavage mode was investigated in our previous study,¹⁸ in which the (001) cleavage planes are observed for small sample sizes less than 10 nm. For larger sizes, the flat (001) cleavage surface becomes fairly unstable and many steps form. The instability of the (001) cleavage mode is helpful in understanding the stability of the (111) cleavage mode, as discussed in Section IV.

III. (111)-(2 × 1) CLEAVAGE MODE

The easiest cleavage mode in experiments is that with Si(111)-(2 × 1) surface. Pandey’s π -bonded structure⁵ is now widely accepted as the atomic structure of the cleaved surface.^{4,6-10} A surface formation process was shown in a simulation,⁸ when a *parallel* separation is introduced in a slab with the minimal periodic simulation cell for the (2 × 1) structure (See Figs. 1 and 2 of Ref.⁸).

The present cleavage simulations are performed with the [211] propagation directions (Fig. 1(d) for geometry), which are consistent with typical experiments (See Fig. 1 of Ref.²⁶, for example). An external load is imposed and its physical origin is the concentrated elastic field in the macroscale experimental sample. See Appendix B for details. A smaller sample with 416 atoms was also simulated, as shown in Appendix C, so as to confirm

