

Theory of large-scale electronic structure calculation and nanostructures formed in silicon cleavage simulation: surface reconstruction, step and bending

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ABSTRACT

Several methodologies are developed for large-scale atomistic simulations with fully quantum mechanical description of electron systems. The important methodological concepts are (i) generalized Wannier state and (ii) Krylov subspace. Test calculations are done with upto 10^6 atoms using a standard workstation. As a practical nanoscale calculation, the 10 nm scale structure in cleavage process of silicon is investigated. Discussions are focused mainly on the stable (experimentally observed) (111)-(2 × 1) cleavage process. Surface reconstruction and step formation are observed and compared with experiments. These processes are analyzed by the quantum mechanical freedoms of electron system, such as the local density of states (LDOS). We also observed the bending of cleavage plane into the (111) plane from other planes, which is a direct evidence of the stability of the (111) cleavage mode. Finally, several common aspects between cleavage and other phenomena are discussed from a general viewpoint of 10 nm scale structure.

INTRODUCTION

Brittle fracture or cleavage is a non-equilibrium process and the dynamics is essential. Especially, the cleavage of silicon single crystal is of great interest from the multiscale viewpoint between macroscale and atomscale pictures; In the macroscale picture, silicon shows perfect brittleness. In general, brittle fracture is mainly described by the continuum mechanics. [1, 2, 3] In the atomscale picture, on the other hand, a cleaved surface contains areas with well-defined reconstructions. Nowadays, these atomscale structures are observed by scanning tunneling microscopy (STM) [4] and other experiments. The multiscale feature of the phenomenon appears, as discussed later, in atomistic processes within a nanoscale (or 10 nm scale) region near the crack tip, though such processes cannot be seen by a direct (*in situ*) experimental observation.

A simple but fundamental question is what Miller index and surface reconstruction appear as cleavage surface in semiconductor? A naive prediction is that the cleavage plane should be that with the smallest surface energy, or the smallest energy loss with forming surface. The naive prediction, however, is not always satisfactory, since cleavage is a non-equilibrium process. For example, the easiest cleavage surface of silicon is the (111)-(2 × 1) structure, [4, 5, 7, 6, 8, 9, 10, 11] though the calculated surface energy of the (2 × 1) structure is larger than that of the ground state (7 × 7) structure. [12] The (2 × 1) structure is metastable and will change, irreversibly, to the (7 × 7) structure at finite temperatures. [13, 4] Several

related experimental facts [14, 15] may be important, when we try to understand the cleavage mechanism of silicon.

Using the theory of large-scale electronic structure calculation, [16, 17, 18, 19, 20, 21, 22] the cleavage process was simulated in our recent works [18, 21]. In the present paper, we review the methodology and show the result of silicon cleavage simulations.

METHOD

For recent years, we have developed theories and program codes for large-scale electronic structure calculations. [16, 17, 18, 19, 20, 21, 22] Their common mathematical foundation is to calculate the one-body density matrix $\hat{\rho}$, in stead of one-electron eigen states $\{\phi_k^{(\text{eig})}\}$. The density matrix $\hat{\rho}$ is defined, formally, as

$$\hat{\rho} \equiv \sum_k^{\text{occ.}} |\phi_k^{(\text{eig})}\rangle \langle \phi_k^{(\text{eig})}|. \quad (1)$$

Any physical quantity $\langle \hat{X} \rangle$ is described as

$$\langle \hat{X} \rangle \equiv \sum_k^{\text{occ.}} \langle \phi_k^{(\text{eig})} | \hat{X} | \phi_k^{(\text{eig})} \rangle = \text{Tr}[\hat{\rho} \hat{X}]. \quad (2)$$

Among the methods, the present cleavage simulations are carried out by the method with generalized Wannier state, [16, 17, 18, 21] which is suitable for covalent materials. The generalized Wannier states are formally defined as the unitary transformation of occupied eigen states. The pioneering works were done by Walter Kohn, [23, 24] in the context of large-scale calculations. In a qualitative picture, the Wannier state is well-defined localized ‘chemical’ wavefunctions in condensed matters, such as a bonding state or a lone-pair state, with a slight spatial extension. [25] The suffix i of the Wannier state $\phi_i^{(\text{WS})}$ denotes its localization center. The practical algorithm is constructed, when an exact equation of Wannier states is solved by the perturbation or variational procedure. [16] Test calculations were done with up to 1.4 million atoms using a standard workstation (Fig. 1(a)). Parallel computations with the OpenMP technique (www.openmp.org) are tested with up to more than ten million atoms. [21] In these results, the computational time of our calculations is ‘order- N ’, or proportional to the system size (N).

The Krylov subspace [26], a mathematical concept, is focused as another important concept for large-scale calculations. The Krylov subspace gives the foundation of many linear algebraic algorithms, such as the standard conjugate gradient method [26]. Recently, we developed two practical Krylov subspace methods and applied them to semiconductor (silicon surface) and metal (fcc Cu). [20, 22] In the present paper, the Krylov subspace method is used to calculate the local density of states (LDOS) for each atom. In the actual algorithm, the Green function G_{ij} is calculated by an iterative solver algorithm, called shifted conjugate orthogonal conjugate gradient method, for the linear equation [22]

$$(z - H)|x_j\rangle = |j\rangle, \quad (3)$$

where $z \equiv \varepsilon + i\gamma$ is a given energy point with a tiny imaginary part (γ). The Green function is given by

$$G_{ij} \equiv \langle i | (z - H)^{-1} | j \rangle = \langle i | x_j \rangle. \quad (4)$$

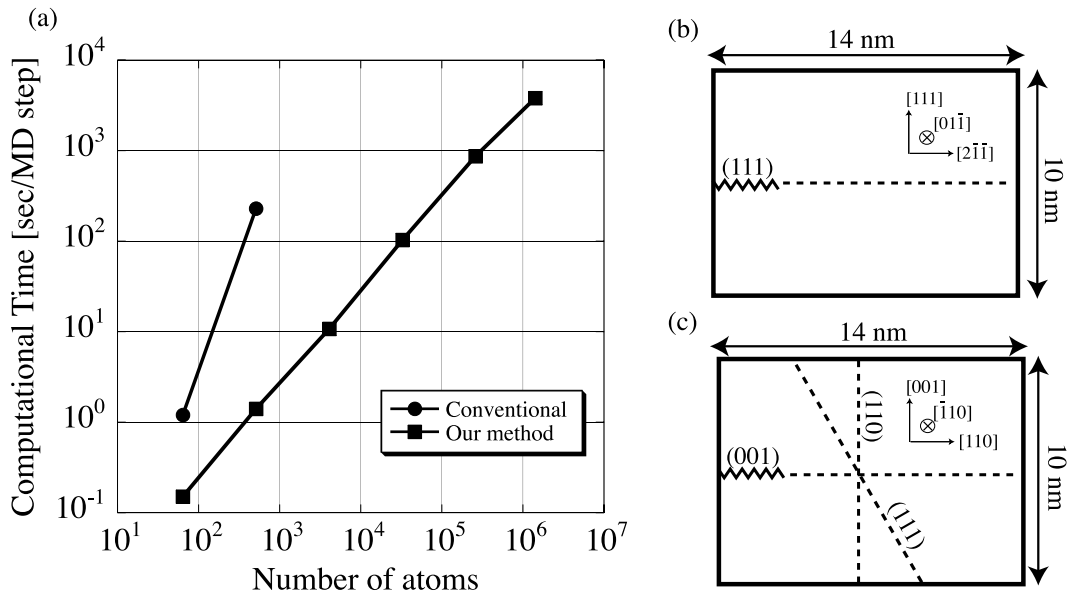


Figure 1: (a) The computational time with up to 1,423,909 atoms of bulk silicon. [18] Our calculation in the perturbation procedure for Wannier states is compared to the conventional method with calculating eigen states. The computational time is measured for one time step in the molecular dynamics (MD) simulation with a standard workstation. (b)(c) Typical sample geometries used in the silicon cleavage simulations. The zigzag lines indicate initial crack ‘seeds’, schematically. Several atomic planes are shown as dashed lines. In the cleaved Si(111)-(2 × 1) surface, the unit length in the $[2\bar{1}\bar{1}]$ direction is twice as large as in the ideal Si(111) surface. The nearest neighbor atomic distance of crystalline silicon is $d = 0.24$ nm.

Since the basis, $|i\rangle$ or $|j\rangle$, is an atomic orbital in the present calculation, the LDOS is obtained as the summation of the diagonal elements of the Green function (G_{jj}) over the bases of a given atom.

RESULTS OF SILICON CLEAVAGE SIMULATION

Using the large-scale electronic structure calculations, the cleavage process of silicon is simulated with a transferable Hamiltonian in the Slater-Koster (tight-binding) form [18, 21]. The simulations are carried out with the sample size of up to more than 10 nm (or 10^4 atoms). External loads are imposed for the motive force of cleavage. The physical origin of the external loads is the concentrated strain field at the crack tip. Discussions are mainly focused on the following points.

(I) As a non-equilibrium process, cleavage phenomenon has a typical time scale determined by the cleavage propagation velocity. In the continuum mechanics and many experiments, the propagation velocity 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] Therefore, the elementary atomistic process occurs within the time scale. These processes are ‘fast’ and almost free from thermal equilibration. Due to the limited time scale, the reconstruction process

in cleavage should occur *locally*. As the most typical process, *nearest neighbor* dangling bonds tend to form a surface bound state. In other words, the elementary cleavage process should contain *two* successive bond breakings, *not one*. This nearest neighbor reconstruction mechanism gives directly the experimentally observed (2×1) reconstruction of cleaved Si or Ge(111) surface. [15] The ‘fast’ reconstruction with forming the (111) - (2×1) structure can be found also in other non-equilibrium processes (See references in Ref. [21]).

(II) The (111) cleavage processes are investigated. [21] A typical sample geometry is shown in Fig. 1(b). The formation of the π -bonded (2×1) structure is commonly observed, as expected. [4, 5, 6, 7, 8, 9, 10, 11] Several step formations are observed and compared to experiments [27, 28, 29] or the pioneering theoretical work [30]. Two types of step formations are obtained, known as ‘ $[2\bar{1}\bar{1}]$ type’ and ‘ $[\bar{2}11]$ type’.

(III) In several calculations, the initial crack is artificially prepared on (001) plane, *not* experimentally observed cleavage plane. Such simulations are carried out, so as to discuss the (relative) stability of the cleavage modes on different planes. [21] A typical sample geometry is shown in Fig. 1(c). In result, the cleavage path is bent into the (111) or (110) plane, if the sample size is larger than 10 nm. This result is consistent to the experimental preference of the (111) and (110) cleavage planes. [14]

(IV) For the resultant (111) - (2×1) cleaved surfaces, the local density of states (LDOS) is calculated using Eqs. (3) and (4). The present LDOS calculation on the flat (not stepped) region reproduces the following facts established by *ab initio* calculations [6, 8, 11] and/or by bias-dependent STM experiments; [7] (i) the (111) - (2×1) cleaved surface has *tilted zigzag* π -bonded chains, (ii) the upper tilted atom has an *occupied* surface state and the lower tilted atom has an *unoccupied* surface state. As an important application of large-scale calculations, the LDOS is calculated also in the step edge region of the resultant $[\bar{2}11]$ -type step. The calculated LDOS contains sharp peaks of surface states, which is placed at almost the same energy positions as in the flat region. This result can be understood, because the step edge is a six-membered ring that has an tilted π -bonded zigzag chain as on the flat region.

GENERAL DISCUSSION ON 10 NM SCALE STRUCTURES

Apart from the cleavage phenomenon, the present investigation is discussed from the general viewpoints of nanomechanics. [21] Since the fundamental theory is given by the competition between the volume energy and the surface energy, the general dimensional analysis gives a crossover in length scale. In the case of silicon, the above energy competition is reduced to that between the sp^3 (bulk) term and the non- sp^3 (surface) term. We speculate that the scale of the crossover is universal, because the surface energy is always on the same order, 1 J/m² or 1 eV per surface atom, among different planes and reconstructions. As a geometrical discussion of the crossover, a well-defined reconstructed surface appears, only when the system size is much larger than the unit length of the reconstructed surface. In the present investigations of cleavage, the crossover at the scale of 10 nm is found in the formation of step or bending in cleavage path. Another example of the crossover may be seen in the shape of self-organized Si islands [31]; an island with the size of 10 nm or less has a semispherical shape and an island in larger sizes has a pyramidal shape that has facets with well-defined indices.

The present method of the large-scale electronic structure calculation is widely applicable,

not specific for cleavage. The expected crossover at the scale of 10 nm is of general importance and can be a future work of the present simulation method.

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