

Theoretical Study of Stress Corrosion Cracking in Si

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This article presents simulation results of effects of water on cracked-Si model under tension (mode-I opening) using a recently developed hybrid quantum-mechanical/molecular-dynamics simulation code for parallel computers. Our purpose is to clarify a controversial statement about existence of stress corrosion cracking in a sub-micron Si-system. We investigate effects of both saturation of dangling bonds of Si crack surfaces with hydrogen atoms, and environment molecules on the fracture initiation. Our results demonstrate existence of both attractive and repulsive forces around the crack tip depending on settings. The H₂O molecule reacts with Si-Si bond at the crack tip and causes the breakage of the bond by chemical reaction. The oxygen atom dissociated from H₂O molecule and inserts between a Si-Si bond, which results in increasing bond-distance with time. The bond breaks when the distance reaches a critical value.

Key words: Hybrid quantum mechanical molecular dynamics simulation, stress corrosion cracking, environment effects on fracture, parallel computing.

1. INTRODUCTION

Silicon material plays an important role in manufacturing very small (nanometer size) electro-mechanical components [1]. Reliable operations of small devices are essential. One of the unresolved problems of Si-based nano-devices is the stress corrosion in harsh environment [2]. The nano-components have relatively large surface-to-volume ratios. Their large fractions of surface make these components sensitive and vulnerable to corrosive environment, and hence may shorten their lifetimes. Environmentally enhanced crack growths have been observed in silicate glasses [3]. Theoretical studies have shown that reactive molecules such as water promote slow crack growth by attacking the strained inter-atomic bonds at the crack tip [3].

Stress corrosion cracking in bulk silicon is not observed in experiments. However, an evidence of corrosion cracking was reported in sub-micron-size Si-systems at high strains [4]. There are no explicit explanations on its mechanisms. Stress fields in materials depend on the size and the overall shape of the system since the fields are long-ranged. Understanding combined effects of tensile stress and environmental molecules in such nano-sized systems requires a dynamic simulation of realistic systems with chemical reactions.

In a previous theoretical work, Wong-Ng et al. addressed the environment effects of H₂O on fracture of Si by using the molecular-orbital (MO) method [5]. Their computation used a small hydrogen and OH terminated Si cluster (Si₈H₁₇OH) to mimic an atomic structure near the crack tip.

Dangling bonds on the crack surfaces of Si were saturated with hydrogen and OH. They found that moisture does not enhance crack-growth via chemical reactions in strained Si. They concluded that a water molecule cannot reach the Si-Si crack tip bonds because of the steric repulsion between saturation-hydrogen and OH in water [5]. Understanding chemical reactions of the environmental H₂O molecules with the crack-tip atoms under stress, however, requires to use more realistic atomic-structure model than the one in Ref. 5, and to take into account transfer of the reaction energy.

Theoretical investigation of the effects of moisture on Si fracture requires a quantum-mechanical method with reasonable accuracy such as the density-functional theory (DFT) [6]. However, DFT-based simulations are currently limited to systems containing less than or equal to a few hundred atoms due to long computation times [7,8]. Recently Ogata et al. [9,10] developed a hybrid quantum-mechanical/molecular-dynamics (QMMD) code for parallel computers to overcome this limitation. They performed hybrid simulation of model cracked-Si without saturating dangling bonds of the crack surfaces [11]. In the hybrid QMMD method, chemically reacting regions are treated by DFT, which are embedded in a classical atomic system of molecular dynamics (MD) with an empirical inter-atomic potential. In this paper, we present QMMD simulation results for a cracked-Si system with dangling bonds of Si atoms on the crack surfaces saturated by hydrogen atoms, to study effects of both water and the saturation on the stress corrosion cracking.

2. CALCULATION METHOD

Chemical reactions in materials are often complex and require a robust simulation methodology. The hybrid method couples QM and MD methodologies in a seamless way for efficient simulation of various material processes in a large-scale atomic system. In the simulation model, we partition the total atomic system into a selected set of QM atoms, which are involved in chemical reactions, and the rest of MD atoms described by molecular dynamics. The validity of such a partitioning of the system is based on the fact that the reaction often involves a small number of atoms. The electronic structure calculations are significant only for those atoms.

Figure 1 shows the atomic classification for the present simulation. Atoms in the total system are classified into three types: (i) QM atoms forming an atomic cluster to which QM calculations apply, (ii) MD atoms described by empirical inter-atomic potential, and (iii) handshake (HS) classical atoms bonding to QM atoms at the QM/MD boundary. The coupling between the QM and MD region is done by constructing an explicit Hamiltonian for the total system, H , given as:

$$H = H_{MD} + \sum_{\text{cluster}} [E_{QM}^{\text{cluster}}(\{\vec{r}_{QM}\}, \{\vec{r}_{HS}\}) - E_{MD}^{\text{cluster}}(\{\vec{r}_{QM}\}, \{\vec{r}_{HS}\})] \quad (1)$$

where

$$H_{MD} = \sum_i m |\dot{\vec{r}}_i|^2 / 2 + \sum_{i < j} V_2(\vec{r}_i, \vec{r}_j) + \sum_{i < j < k} V_3(\vec{r}_i, \vec{r}_j, \vec{r}_k).$$

The dynamic of the system is determined by H , which includes MD and QM regions. Handshake atoms are used to couple the QM and MD atoms dynamically based on the scaled position method [9]. In the equation, the last two terms on the right hand side represent the QM correction to the MD potential energy for each cluster of QM atoms. The $\{\vec{r}_{QM}\}$ and $\{\vec{r}_{HS}\}$ in Eq. (1) are the positions of the QM atoms and the positions of the HS atoms,

respectively. E_{QM}^{cluster} is the total energy of a QM

atoms cluster calculated using DFT. E_{MD}^{cluster} is the classical potential energy of the atomic cluster. The H_{MD} is the MD hamiltonian composed of the atomic kinetic energy and the Stillinger-Weber [12] potential energy defined as a sum over pairs of atoms, V_2 , plus a sum over triplets of atoms, V_3 , as defined in Eq. (1). Details about Eq. (1) and the hybrid method are explained in Refs. 9 and 10.

For the QM calculations, we use the real-space multigrid-based DFT [13], in which electronic wave functions are represented on a uniform real-space mesh in Cartesian coordinates. Stabilizing atomic configuration of the cluster requires termination of its dangling bonds by hydrogen atoms. The position of the termination atoms are obtained using scaled-position method [10]. Electronic eigenstates are determined

band-by-band using the conjugate gradient method [7]. The DFT calculations of the terminated-hydrogen atomic cluster are performed with free

boundary condition to obtain E_{QM}^{cluster} and the corresponding forces on both the QM and HS atoms. For efficient implementation of DFT on parallel computers, data on the mesh-points are spatially decomposed and stored in parallel compute-nodes [9,10]. Numerical accuracy of the calculations is controlled by varying the point density. The gradient of H with respect to the position of the i^{th} atom gives the total atomic force on the i^{th} atom, which is a sum of forces from H_{MD} , E_{QM}^{cluster} , and

E_{MD}^{cluster} . The calculated total forces are used for time integration of the equations of motion using the velocity-Verlet algorithm [14].

The hybrid QM/MD scheme is implemented on parallel computers using the message passing interface standard. In the scheme MD and QM are treated separately on parallel compute nodes. In the hybrid simulation, the total hamiltonian, H , is conserved during the simulation run. Thermal energies produced at the chemical reaction in the QM regions are transferred to the surrounding MD region.

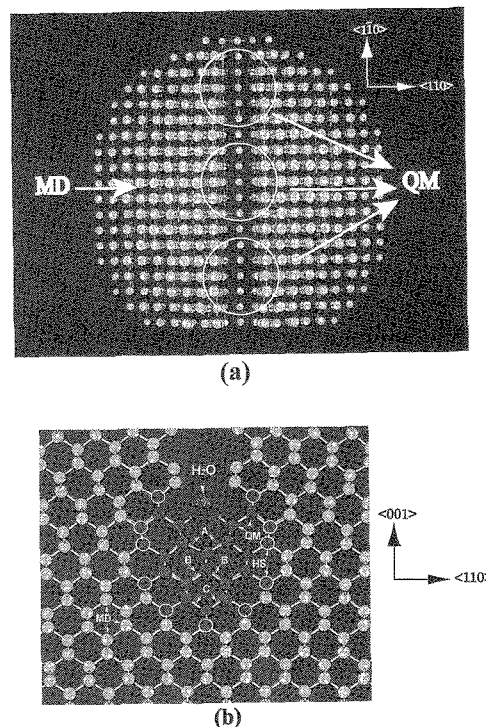


Fig. 1. (a) Decomposition of the total hybrid system into MD and QM regions. For better view, only central region is shown. (b) Close-up view of the QM region for the initial configuration in the simulation around the crack tip. HS atoms couple between QM atoms and MD atoms. Bonds A, B, and C are located in order along crack extension direction.

We consider strained silicon with (110) planes for the crack surfaces. Figure 1 shows the geometrical decomposition of silicon slab into MD and QM regions in the simulation. In the present hybrid simulation, neighboring three atomic QM clusters of the same size containing atoms around the crack-front are selected from the MD atoms, as shown in Fig. 1(a). The centers of the QM clusters are aligned along the crack-front line, which points to the $\langle 1\bar{1}0 \rangle$ -direction.

3. RESULTS AND DISCUSSION

Previous hybrid simulation results of model cracked-Si with dangling bonds of Si on crack surfaces [11], found that strain affects fracture mechanisms significantly.

In experiments, crack surfaces can be partially saturated by hydrogen or other elements depending on preparation procedure [15]. To investigate effects of hydrogen saturation of the dangling bonds on the cracked surface, we use the same configuration of model cracked-Si with the one in Ref. 11, and saturate the dangling bonds in the present simulation. Figure 2 shows the dimensions of cracked-Si model. In the simulation, we consider the crack-front line parallel to $\langle 1\bar{1}0 \rangle$. To mimic straight-edged crack, a half of the atomic layer parallel to (110) from the center, $(x,z)=(L_x/2,L_z/2)$, of the slab is removed, see Fig. 2. Free boundary conditions are imposed at the slab in z direction, and the periodic boundary conditions in the x and y -directions. As in Ref. 11, the system is stretched uniformly by 3% along the x -direction, and it is relaxed to zero temperature by scaling the atomic velocities.

To investigate possible effects of H_2O molecules on fracture initiation we add an H_2O molecule to each QM cluster (see Fig. 1(b)), with zero velocity and random orientation, at a position separated by about 5.5 Å in $\langle 001 \rangle$ -direction from the central Si atom at the crack-front. In this simulation the total number of QM atoms is 249 (108 Si atoms, 120 termination-hydrogen atoms, 12 saturation-hydrogen atoms and 3 H_2O molecules). The simulation run is performed for 130 fs. Figure 3 shows the close-up around the crack-front region, which describes the results at 80 fs.

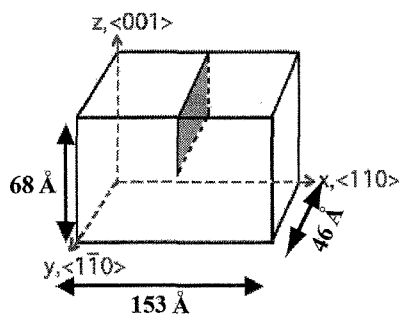


Fig. 2. Geometry description of the cracked-Si model in the simulation.

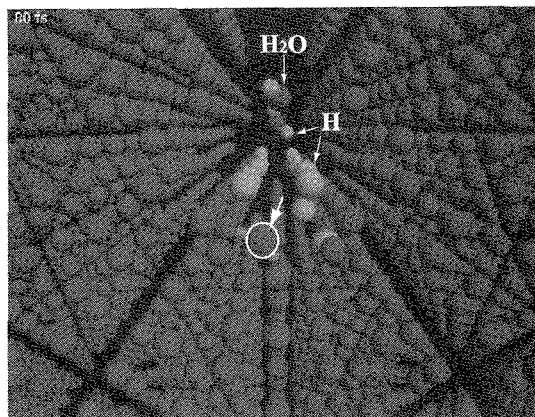


Fig. 3. Snapshot at 80 fs in the hybrid simulation. The arrow mark shows the insertion of O between Si-Si bond. In the figure, H indicates both the hydrogen saturation of the Si dangling bonds and hydrogen atoms in H_2O molecules.

During the simulation run, chemical reactions occur only for one H_2O molecule. The other two H_2O molecules feel repulsive forces from saturation hydrogen atoms on Si crack surfaces, which prevent the water molecule to access to the Si-Si bonds. However, a path exists for a H_2O molecule to react with the Si-Si bond at the crack tip as illustrated in Fig. 4. There appears to exist attractive forces on H_2O molecule going toward Si crack surface, as shown in the Fig. 3. In this case, the H_2O molecule dissociates into 2H and O and then the O atom is inserted between a Si-Si pair at the crack-front at 80 fs to initiate the bond breakage. Further simulation run up to 130 fs indicates the breakage of Si-Si bond at the crack tip. We define three types (A, B, and C) of Si-Si pairs as shown in Fig. 1(b) to characterize the strain relaxation at the crack-front. The value of A-type pair is extended to about 3.3 Å at 80 fs, which represents the insertion of O between two Si atoms before the bond breakage. At this stage, the fracture initiates by chemical reaction and the A-type bond breaks at 130 fs; the bond distance is about 5.2 Å at 130 fs. The other bonds at the crack front are less affected and they oscillate around their equilibrium values due to their thermal motions. The fact that the bond breakage initiated when the Si-Si distance in Si-O-Si reached a critical value of 3.3 Å, is reasonable since the distance exceeds substantially the value of 3.1 Å in quartz (SiO_2).

The released energy from the reaction affects O and H atoms by increasing their kinetic energies. In the present simulation, there is no dangling bond and the electronic structure of the system may be more similar to the bulk silicon than the one without hydrogen-saturation. The origin of the attractive forces responsible of the chemical reaction may be related to a kind of electronic polarization of the Si-Si bond due to the strain.

The previous MO analyses [5] considered a simple model with a water molecule in vacuum (i.e.,

$\text{Si}_8\text{H}_{17}\text{OH}+\text{H}_2\text{O}$). In the analyses, energy optimization of the molecule was performed to study moisture effects on Si-Si bonds at the crack tip. In the analyses, dynamics of atoms around the crack tip were ignored. The present hybrid method is suited to study such a problem than the one in Ref. 5 since atoms which surround the crack tip region are also considered; the QM atoms are coupled dynamically to the surrounding atoms. The surrounding atoms may play important roles to absorb heat produced from chemical reactions. The MO results showed both lack of driving forces and existence of steric barrier due to the saturation hydrogen atoms, which may hinder insertion of an H_2O molecule toward the crack front. Our hybrid results demonstrate clearly, in Fig. 3, existence of a path for an H_2O molecule to reach a Si-Si bond and react with it.

The effects of strain are not negligible as found in the previous hybrid simulation [11]. However, in the present study the strain effect was not considered and we chose only 3%-extension case along the $\langle 110 \rangle$ -direction for (110) crack surface of Si with surface saturation. Further studies are in progress to understand effects of stresses and crack plane orientations on corrosion cracking in Si. We believe that our simulation studies will contribute significantly to understanding stress corrosion in Si.

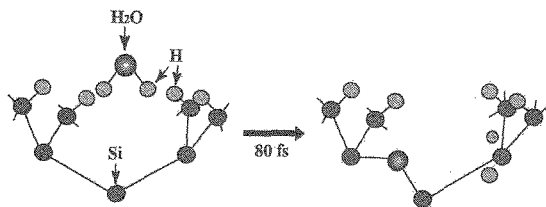


Fig.4. Schematic illustration of reaction mechanisms at 80 fs.

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