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RESEARCH ARTICLE

A Molecular Dynamics Simulation Study on the Initial Stage of Si(001) Oxidation Under Biaxial Strain

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We have studied the very early stage of the room temperature oxidation of the externally-strained Si(001) surface using molecular dynamics simulation. It was found that the different treatment history of the sample under the same strain resulted in the difference in the number density of dimer. The as-prepared samples of different treatment history with 12.15% strain were used to investigate the initial oxidation behavior of Si(001). 500 times of independent deposition of single oxygen molecule onto the random position of clean Si(001) surface was simulated. Oxidation behavior was statistically analyzed for various dimer density of the surface which is dependent on strain-treatment history. Oxygen uptake and penetration depth profile showed an important role of dimers on the surface oxidation behavior.

Keywords: Molecular Dynamics Simulation (MD), Si(001) Oxidation, Strain, Stress, Dimer.

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1. INTRODUCTION

During the past decades, silicon served as a widely used semiconductor material and one of its advantages is that it can form stable adhering insulating oxide that can be used for isolation and protection.[1,2] The oxidation behaviors of silicon surfaces has been a topic of interest in both experimental and theory.[3] Strain effect is also an important issue when silicon device scaling down to nano-regime.[4] Strain can be introduced by growing silicon epitaxially on a relaxed silicon germanium (SiGe) layer. The mismatch between lattices causes the tensile strain in the Si layer, which enhances the channel mobility and thus improves the performance of the device. In another study, $Si/SiO_2/SiN_4$ heterozygote was devised as a novel electro-optic material.[5]

Many researchers focused on the externally applied stress effect on the thermal oxidation of silicon.[6–16] Noma et al. found that the biaxial compress strain suppresses the oxidation rate.[6] Yen et al. found that the tensile stress strongly enhanced the oxidation rate of silicon. It was explained by using $Si–SiO_2$ model that the tensile stress in the silicon will enlarge the atom spacing of silicon and resulting in faster and easier oxidation.[7] Yata focused on the external tensile stress's effect on the dissociation of O_2 on the Si(001) surface and the systemic research had provided an insight into the mechanism.[10–12] However, in-depth understanding of the oxidation reaction on the strained surface is required for the systematic control of the oxidation behavior.

In the present work, we studied the very early stage of Si(001) surface oxidation with externally applied strain by using the classic molecular dynamics simulation. (2×1) dimer structure over Si(001) surface is an effective way to reduce the dangling bond density of surface. The dimer structure influences the chemical activity of Si(001), particularly at the early stage of adsorption and film growth.[17] Recently, externally applied strain is used to tailor the Si(111) surface reactivity to realize anisotropic oxidation.[18] We focused on the effect of the dimer structure on the oxidation behavior of Si(001) surface. We could control the dimer density of strained Si(001) surface by the relaxation process of the surface before applying strain. In the surface with smaller number density of dimer, oxygen molecules have higher probability to be absorbed. The possible mechanism was discussed herein and the results were compared with another work by our group.[19]

2. COMPUTATIONAL DETAILS

The effects of strain on the silicon oxidation was studied by using Large-scale Atomic/Molecular Massively Parallel

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Simulator (LAMMPS) code developed by Sandia National Laboratories.[20] The interactions between Si, O atoms were described by a many-body reactive force field (ReaxFF).[21] In ReaxFF, the total potential energy contains bond-order terms that are updated at each time step, allowing for breaking and formation of bonds during the MD simulation. Also, long-range interaction terms are included and atomic charges is computed dynamically to indicate polarization effects. In the previous publication, we benchmarked the potential for amorphous silica and silicon crystals.[19]

Figure 1 shows the simulation box used in the present work. The size of Si substrate was $10a_0 \times 10a_0 \times 15a_0$ which consisted of 12000 Si atoms and 60 atomic layers with 200 Si on each layer. Here, a_0 is the equilibrium lattice constant for crystal Si, 5.315 Å, which was determined by the minimum potential energy of the system. The simulation box was periodic along the x and y, i.e., [100] and [010] directions and was free in the z direction. The (001) surface of the crystal was exposed to the vacuum region where the oxygen molecules were generated. Along z axis, the substrate was divided into three parts. The bottom layer of Si atoms was held fixed in bulk lattice sites. The middle part containing 49 layers of Si atoms was at a constant temperature 300 K through the every individual simulation acting as the thermo bath. The temperature of the topmost 10 layers is set to be 300 K initially and, then, no any constraint was applied any more. The system was thermalized in the NVE ensemble. The time step of MD simulation was 1 fs.

Biaxial tensile strain was applied by increasing the dimension of the simulation box at a constant strain rate $1.0 \times 10^{-4}\% \cdot \mathrm{fs}^{-1}$. A series of strain can be realized: 3.15%, 5.15%, 7.15% and 12.15%. After reaching the target strain levels, all the samples were relaxed for 30 ps. In order to control the dimer density of the surface, different pre-treatment was applied before applying the strain. Relaxation of the sample for 40 ps before applying the strain induces the dimer structure of the surface that is maintained during applying strain. On the other hand, when the sample was not relaxed before applying strain, dimer structure of much lower density was obtained during post-relaxation process.

For the purpose of investigation of reactivity of Si(001), statistical analysis was carried on. The single oxygen molecule was supplied on a randomly chosen position on the Si(001) surface of various dimer densities at the tensile strain 12.15%. Independent 500 events of oxidation at 300 K were simulated for the statistical analysis. Each oxidation reaction was simulated for 10 ps. The sticking property of oxygen was examined in terms of the fraction of adsorbed oxygen and the penetration depth profile which oxygen atom can reach.

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3. RESULTS AND DISCUSSION

Stress–strain curve of Si substrate with linear fitting plot are shown in Figure 2. Biaxial elastic modulus was obtained by the slope of the curve: 151.5 GPa. This value is a little smaller than the experimental data of 180 GPa.[22] This discrepancy is presumably due to very high strain rate of the present simulation. Surface morphology of a series of Si(001) surface are shown in Figure 3. Figures 3(a)–(d) indicate the top-view of the Si(001) surface which were relaxed for 40 ps before applying strain. The dimer

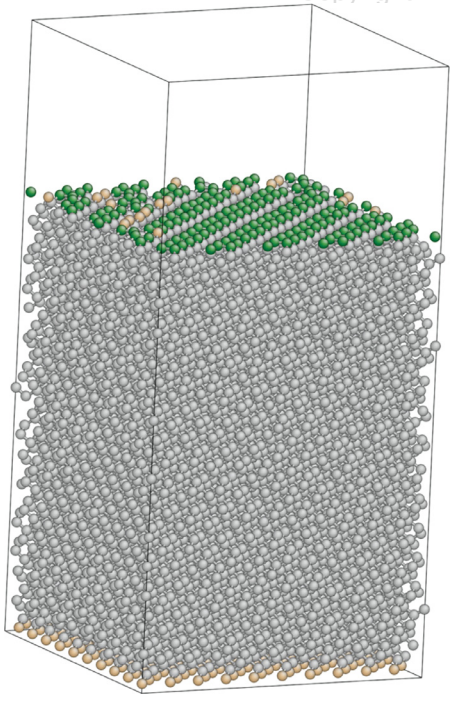

Fig. 1. The simulation box with the size $(10 \times 10 \times 15)a_0$. It consists of fixed bottom layer, the thermostat and the surface layer. Above the Si(001) surface is the vacuum region. The green atoms are dimmers.

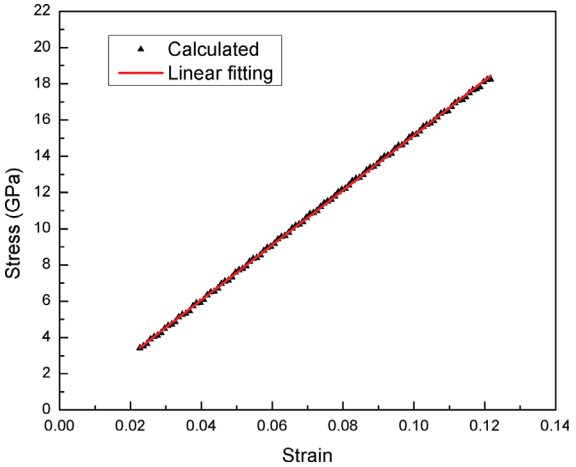

Fig. 2. The linear fitting of strain–stress curve of Si(001).

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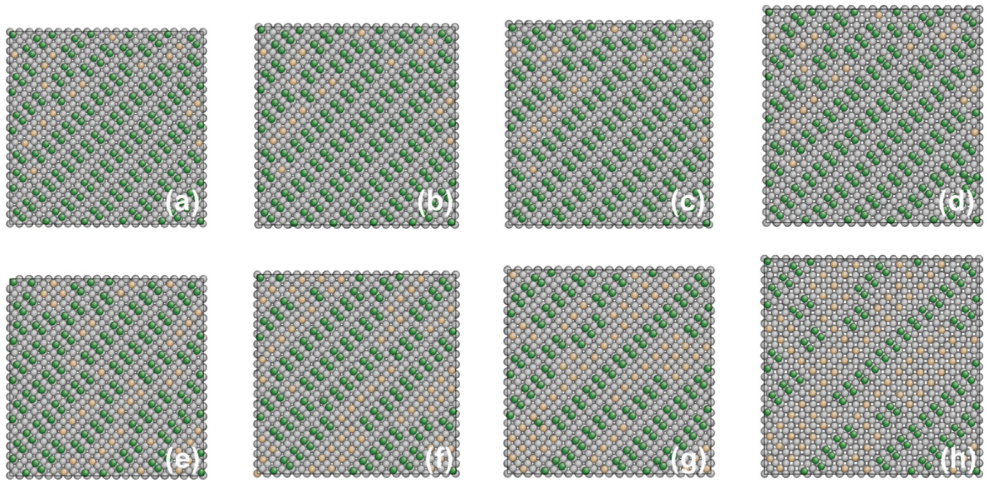

Fig. 3. Top view of Si(001) surface obtained from different pre-treatment under various strain. Green balls indicate the three coordinated silicon atoms, i.e., the dimer atoms. (a)–(d) are relaxed for 40 ps before applying different strains: 3.15%, 5.15%, 7.15% and 12.15%, respectively. (e)–(h) are obtained without relaxation before applying series of strains: : 3.15%, 5.15%, 7.15% and 12.15%, respectively.

numbers within each Si(001) area were counted to be 91, 91, 91 and 92 pairs, respectively. This result shows that the dimer structure was maintained during applying strain once the dimer was formed. Figures 3(e)–(h) exhibit the top-view of the Si(001) surface which were not relaxed before the strain were applied. The dimer numbers within each Si(001) area were counted to be 81, 71, 69 and 57, respectively. The number of dimer decreased as the tensile strain increased.

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It is widely accepted that the dimerization over the Si(001) surface can effectively saturate the dangling bonds after cleaving the Si crystal and exposing Si(001) surface. The neighboring two Si atoms in the surface with two dangling bonds on each prefer to form new Si–Si bond and, as a result, one dangling bond of each Si is eliminated. This effect of dimer formation can reduce the surface energy and stabilize the surface. In all the samples, silicon atoms in (001) surface tend to form three coordinated structure and dimerize. Dimers were aligned row by row along [110] direction which is perpendicular to that of the dimer bonds. However, there are distinct contrasts between the surfaces with and without relaxation before applying strain. In the latter case, less dimers formed and the number density of dimer are smaller than that in the case of relaxation. In experiment, the dimers come into being at room temperature without energy barrier, just similar to the case with relaxation. In the present work, the strain prevented the formation of dimers when there is no relaxation. This can be ascribed to the increasing distance between Si atoms. To certain extent, the distance between Si atoms in Si(001) can considered as one factor which has influence on the dimerization process.

In the present work, we compared the oxidation behavior of the Si(001) surfaces with different number density of dimer under the same strain. The surface with less dimer means that it is more unstable and more reactive. Table I shows the statistical analysis result of the oxidation behavior on two different Si(001) surface. The oxidation behavior was presented in terms of the penetration depth profile of oxygen and the total fraction of oxygen uptake. Total fraction of the oxygen uptake was 76.4% for the Si surface with relaxation before applying strain, whereas that of the Si surface without relaxation before applying strain was 79.8%. It is clear that the surface with smaller number of dimers tends to absorb more oxygen into its oxide layer with the possibility of 3.4% higher than that with higher number of dimers. This result reveals the contribution of the dimer structure to the oxidation behavior of the strained Si surface.

The effect of the dimer was also observed in the penetration depth of oxygen atoms as shown in Figure 4. In both cases, the deepest depth that the oxygen atom can reach

Table I. The statistic results from 500 times of independent single oxygen molecule deposition onto the Si(001) surface with and without relaxation under the strain of 12.15%.

	Oxygen depth in Si oxide (Å)	Sample with relaxation before applying strain (%)	Sample without relaxation before applying strain (%)
Fractions of oxygen atoms reach different depth among the absorbed ones	0.0–1.5	8.24607	6.14035
	1.5–3.0	53.53403	48.74687
	3.0–4.5	27.48691	35.46366
	4.5–6.0	8.37696	7.39348
	6.0–7.5	2.09424	1.75439
	7.5–9.0	0.26178	0.50125
Fraction of adsorbed oxygen over total 500 times of independent single O_2 deposition		76.4	79.8

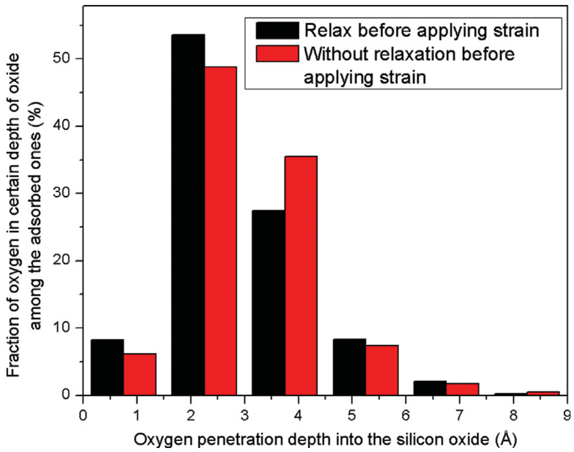

Fig. 4. The plot of statistic analysis of 500 times independent oxygen molecule deposition onto the Si(001) surfaces with and without relaxation before applying the strain of 12.15%.

is 8.54 Å. This value is similar to the previous results.[19] Interestingly, oxygen atoms tend to stay in the shallow outer layers from 0 to 3.0 Å in the case with relaxation before applying strain. On the other hand, oxygen atom can penetrate deeper in the case without relaxation before applying strain. Because the simulation time is just for 10 ps, the penetration should be considered to occur in a ballistic manner.[19] The enhanced ballistic penetration on the surface of smaller number of dimers presumably result from the kinetic energy of oxygen that can be obtained during reaction with Si surface atoms of higher number of dangling bond. The further investigation is still going on in our group to clarify the mechanism of the enhanced penetration.

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4. CONCLUSIONS

Very early stage of the room temperature oxidation of the externally-strained Si(001) surface was studied by using reactive molecular dynamics simulation. The treatment history of the sample under the same strain was found to affect the number density of dimer. The distance between Si was considered as one of the factors which are related to the dimerization process. Oxidation behavior of the surface with different number of surface dimers was statistically analyzed by simulating 500 independent oxidation events. Fraction of total oxygen uptake and the penetration depth profile revealed that the dimer plays an important role in the surface oxidation reaction.

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