

Numerical Simulation of Atomic Layer Oxidation of Silicon by Oxygen Gas Cluster Beams

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A gas cluster is a collection of atoms or molecules weakly bound by van der Waals forces. Gas clusters may form by the adiabatic expansion of gases. In this study, it is demonstrated by molecular dynamics simulations that a low-energy beam of oxygen gas clusters may be used to oxidize the top surface layer of silicon (Si) substrates without affecting its deeper layers. An incident oxygen gas cluster with sufficiently low incident energy may stick to the Si surface and expose a large number of oxygen molecules to the surface Si atoms for extended periods until the cluster sublimates. This may cause the formation of Si–O bonds only on the top Si surface. This is in contrast to the oxidation of Si by oxygen ion beams or plasmas, where deeper layers of the Si surface are typically oxidized by the energetic incident oxygen ions. An oxidized single Si layer may be chemically removed; therefore, this nearly single-layer oxidation process by oxygen gas cluster beams may lead to the development of a new atomic layer etching technology for Si.

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1. Introduction

As the sizes of transistors on computer chips continue to decrease, etching and deposition processes to form device structures on a chip are now required to have atomic level accuracy. Atomic layer etching (ALE) [1–16] refers to an etching process where each atomic layer of the surface of a substrate, such as crystalline Si, is etched in a single cycle. In such a process, one could specify the exact number of atomic layers to be removed from the substrate, thereby ensuring atomic level accuracy of the etched depth.

Similar to atomic layer deposition [17–23], ALE processes typically use chemical processes to modify the top single layer or a few monolayers of the substrate surface. Once the top surface is chemically modified, the subsequent step is to remove the modified monolayer(s) by a chemical or reactive ion etching process by employing the specific chemical nature of the modified layer(s).

In this study, we employ an oxygen gas cluster beam to oxidize the topmost single layer of a crystalline Si substrate. A gas cluster is an aggregation of several to tens of thousands of atoms or molecules bound by van der Waals forces [24, 25]. A beam of gas clusters is typically formed by the adiabatic expansion of a gas at room temperature in a high-vacuum chamber. When a gas is adiabatically expanded, it cools to an extremely low temperature and atoms and/or molecules of the gas may aggregate and form clusters.

Such a cluster beam may be ionized via interaction with an electron beam and accelerated by an externally ap-

plied electric field to the target substrate surface. A beam of ionized gas clusters is called a gas cluster ion beam (GCIB) [24–41]. In typical GCIB experiments, gas cluster beams are accelerated up to about 20 keV.

In such a cluster, several thousands of atoms or molecules share kinetic energy; thus, the average kinetic energy per atom or molecule of a gas cluster is typically in the range of a few eV, causing little damage to the substrate surface at impact [34, 38]. Furthermore, a number of atoms or molecules interact with the surface nearly simultaneously at impact; therefore, the atomic or molecular flux of a gas cluster beam is typically comparable with or may be even higher than that of an ordinary molecular or ion beam.

However, a possible drawback of a GCIB is that the cluster size typically has wide distribution. Every cluster of the same charge, regardless of its size, gains the same kinetic energy from the externally applied electric field for ion acceleration. Therefore, the average energy per atom or molecule may vary significantly, depending on the size of the cluster. Energetic atoms or molecules of a smaller cluster ion may cause more surface damages than less energetic atoms or molecules of a larger cluster ion when they hit the surface. Therefore, the energy control of individual atoms or molecules is important to precisely control the surface damage during the GCIB process.

As aforementioned, in most GCIB processes, the beam energy is in the range of a few eV per atom or molecule [32]. In this study, however, we focus on even lower energy ranges, which may be achieved by

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unionized gas cluster beams or gas cluster neutral beams (GCNB). Experimentally, the kinetic energy of each atom or molecule of a charge-neutral cluster generated by adiabatic expansion is in the range of the thermal energy of the original gas, regardless of the cluster size. Therefore, unlike a GCIB, the average energy per atom or molecule of a GCNB is nearly the same for all clusters of various sizes. Furthermore, the kinetic energy of a GCNB can be somewhat increased by adding lighter gas components, such as He, to the original gas (O_2 in our study) [42]. Therefore, in this study, the energy range per molecule for O_2 GCNB is from 0.025 eV to a few eV. Furthermore, we only performed numerical simulations. Experimental verification of the simulation results is the subject of a future study.

2. Numerical Method

To examine the interaction of O_2 gas clusters with the crystalline Si surface, we used molecular dynamics (MD) simulations. In earlier MD simulation studies of GCIB processes [30, 31, 36, 37, 39], a cluster of molecules with a given total kinetic energy was injected into a model substrate surface. In this study, a cluster consists of a few hundred to several thousand O_2 molecules and the substrate is the Si (100) surface. Unlike earlier studies, however, we focus on the incident energy range that is close to the thermal energy and evaluate the surface oxidation rate as a function of the cluster beam energy and cluster size. We define the surface oxidation rate as the number of O–Si bonds formed at each impact of a cluster on the Si surface.

The classical MD simulations used in this study are based on interatomic potential functions of the Stillinger–Weber-type [43–48], representing covalent bonds for the Si and O system. In addition, all atoms are assumed to interact via van der Waals forces, which are modeled by a two-body force of the Lennard–Jones-type [49, 50].

The model substrate is a rectangular box of crystalline Si whose horizontal top surface represents a Si (100) surface with a cross-section of $21.7 \times 21.7 \text{ nm}^2$. The depth of the substrate is 1.63 nm. To avoid unnecessary downward shift of the substrate by momentum transfer from incident clusters to the substrate, the bottom layer of the substrate is fixed in position as an anchor layer. With periodic boundary conditions imposed in the horizontal directions, the model substrate represents an infinitely wide horizontal surface. The initial temperature of the substrate is set to 300 K.

To form an O_2 gas cluster model in the MD simulations, we first form an oxygen molecule O_2 from two oxygen (O) atoms. Two O atoms in a single oxygen molecule are bound by a covalent bond modeled by the interatomic force function aforementioned. Then, we place a few hundred to several thousand O_2 molecules at regular intervals in a sphere of an appropriate size. In the proposed model, all atoms, including oxygen atoms, are weakly bound to each other by van der Waals forces with assumed bind-

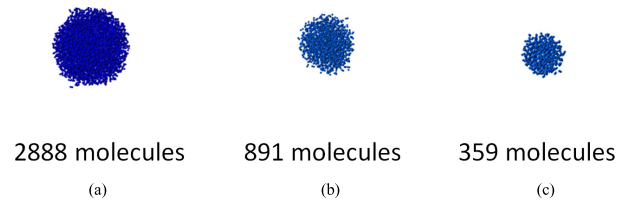


Fig. 1 Examples of the O_2 gas clusters used in the MD simulations. The clusters (a), (b), and (c) consist of 2,888, 891, and 359 O_2 molecules, respectively. Blue spheres denote O atoms. Each cluster shown here is in thermal equilibrium at 50 K.

ing energy and interaction length of 0.01 eV and about 8 \AA , respectively. Therefore, neighboring O_2 molecules are weakly bound and form clusters if their thermal energies are sufficiently low. In this study, a cluster of O_2 molecules is formed at about 10 K. Examples of such gas clusters used in our MD simulations are shown in Fig. 1.

In each MD simulation run, an O_2 gas clusters, such as those shown in Fig. 1, is launched to the Si substrate surface with a given kinetic energy. The angle of incidence is normal to the substrate surface. Each MD simulation is performed under constant total-energy (i.e., microcanonical) conditions. To obtain statistically averaged data, we repeat the simulation of the O_2 gas cluster incidence several times with a new clean Si (100) surface and the same physical parameters except for a different random number sequence to determine the impact position of the gas cluster on the substrate surface.

3. Simulation Results: Morphologies of Clusters after Impact

Figure 2 shows the morphologies obtained from the MD simulation of an O_2 gas cluster incident upon the Si (100) surface at different time instances. The cluster initially consists of 2,888 O_2 molecules, and the incident kinetic energy is 0.06 eV/molecule. The time is measured from the moment of impact, and it is seen in Fig. 2 that, at this relatively low incident energy, a gas cluster is attached to the substrate surface. The shape of the attached O_2 gas cluster barely changes after 5 ps, indicating that the initial collision process has been completed by this time. The simulation is performed up to 100 ps after impact; however, the cluster attached to the surface is expected to sublimate eventually because of the heat conduction from the substrate. At the interface between the cluster and substrate, O_2 molecules are close to the surface Si atoms for extended periods.

Similarly, Fig. 3 shows morphologies obtained from the MD simulation of an O_2 gas cluster incident upon the Si (100) surface at different time instances with higher incident energy. The initial cluster consists of 2,888 O_2 molecules, and the incident kinetic energy is

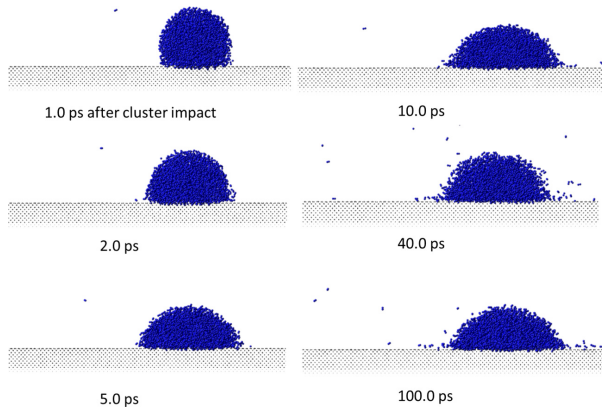


Fig. 2 Morphologies of the O_2 gas clusters incident upon the Si (100) surface at different time instances. The incident energy is 0.06 eV/molecule and the initial cluster size is 2,888 molecules. Time is measured from the moment of impact.

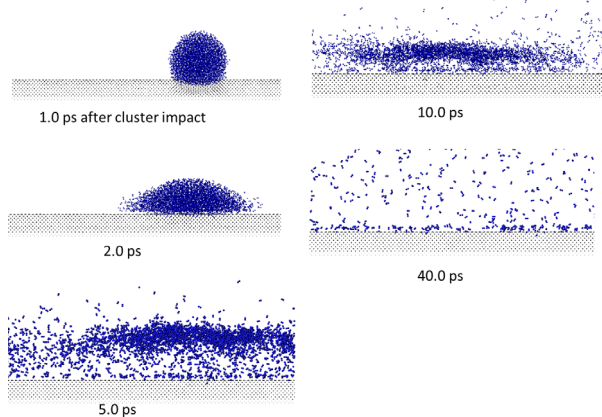


Fig. 3 Morphologies of the O_2 gas clusters incident on the Si (100) surface at different time instances. The incident energy is 0.6 eV/molecule and the initial cluster size is 2,888 molecules. Time is measured from the moment of impact.

0.6 eV/molecule. The time is measured from the moment of impact. It is seen that the cluster splits after incidence. Furthermore, the interaction time of the O_2 molecules with surface Si atoms is much shorter than that in the case of Fig. 2, because most O_2 molecules in Fig. 3 are seen to depart from the surface immediately after impact. It has been observed that, for a gas cluster of a given size, the higher the incident energy per molecule is, the more likely the splitting of the cluster occurs after impact. However, for a given incident energy per molecule, the smaller the cluster size is, the more likely the splitting of the cluster occurs after impact.

4. Simulation Results: Surface Oxidation

With cluster impact simulations, such as those described above, we evaluated the surface oxidation rate, i.e.,

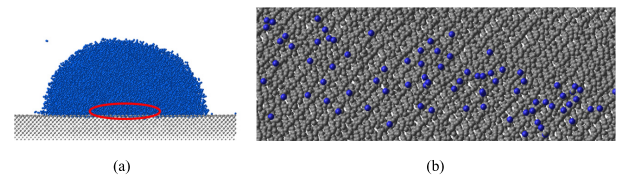


Fig. 4 (a) A side view of an O_2 gas cluster at 100 ps after its impact on the Si (100) surface. The initial cluster consists of 15,440 O_2 molecules, and the incident cluster energy is 0.06 eV/molecule. (b) A top view of the same Si surface near the center of the attached O_2 gas cluster [around the region encircled by the red ellipse in (a)], where only O atoms that are covalently bonded with Si atoms are plotted (other O atoms or O_2 molecules are not plotted for the sake of clarity).

the number of O atoms that are covalently bonded with Si atoms after cluster incidence. Figure 4(a) shows a side view of an O_2 gas cluster at 100 ps after its impact on the Si (100) surface. Here the initial cluster consists of 15,440 O_2 molecules, and the incident cluster energy is 0.06 eV/molecule. Figure 4(b) shows a top view of the same Si surface near the center of the attached O_2 gas cluster [around the region encircled by the red ellipse in (a)], where only O atoms that are covalently bonded with Si atoms are plotted (other O atoms or O_2 molecules are not plotted for the sake of clarity). The gray sphere represents a Si atom and the blue sphere represents an O atom.

Note that the average kinetic energy of the O_2 molecule before impact (0.06 eV) is far lower than the dissociation energy of the O_2 molecule (5.1 eV). Nevertheless, as shown in Fig. 4(b), the impact of the O_2 gas cluster upon the Si surface caused the formation of Si–O bonds, which suggests that dissociation of some O_2 molecules occurred during the process. In the collision process, where the incident O_2 gas cluster is brought to the Si surface, several O_2 molecules of the cluster are forced to closely approach the Si dangling bonds on the surface, forming unstable partial bonds with Si, such as Si–O–O with weakened O–O bonds. Such O_2 molecules may form Si–O bonds on the surface and release O atoms, which are again likely to form other Si–O bonds on the surface. During the collision process, part of the total kinetic energy of the incident O_2 cluster, which is more than 900 eV in the case of Fig. 4, is used to place some O_2 molecules sufficiently close to the Si atoms on the surface against the activation energy for the formation of unstable Si–O–O bonds.

Our simulations suggest that the final temperature of the O atoms in the cluster at 100 ps of Fig. 4 is approximately 630 K, including the thermal energy of the vibrations and rotations of O_2 molecules, the source of which is the conversion of the incident translational kinetic energy of the cluster to thermal energy. However, at this temperature, O_2 atoms are very unlikely to dissociate by thermal energy alone.

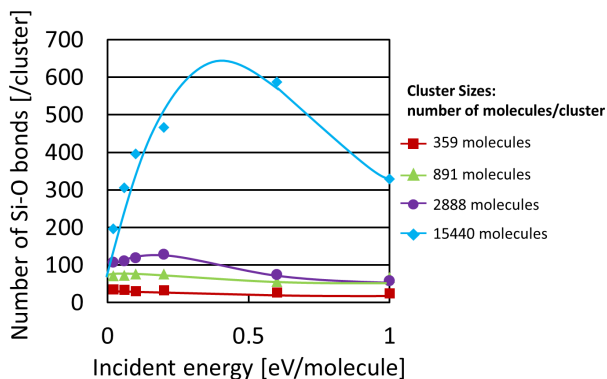


Fig. 5 The number of Si–O bonds formed per cluster incidence as functions of the incident kinetic energy per molecule for O_2 gas clusters of various sizes incident upon the Si (100) surface.

We have also confirmed by MD simulations that the incidence of a single O_2 molecule with incident kinetic energy of 0.06 eV does not cause dissociation of the molecule, thus does not oxidize the Si surface. This means that the 0.06 eV kinetic energy is not sufficient to overcome the activation energy and form unstable Si–O–O that may lead to the formation of a Si–O bond on the surface. Conversely, an O_2 molecule surrounded by a large number of O_2 molecules in the cluster may stochastically gain sufficiently large amount of kinetic energy from the momentum transfer by colliding with other O_2 molecules inside the cluster if the cluster collides with the surface at large total energy, even if the energy per molecule is small.

Figure 5 shows the number of Si–O bonds formed per cluster incidence as functions of the incident kinetic energy per O_2 molecule for O_2 gas clusters of various sizes incident upon the Si (100) surface in the normal direction, obtained from the MD simulation. The number of Si–O bonds was counted 100 ps after the cluster impact in each case. To obtain statistically averaged data, we have repeated the simulation of O_2 gas cluster incidence five times for each data with a different random number sequence.

The number of Si–O bonds formed in a single cluster incidence is lower at higher incident energy in general because the cluster tends to break apart, thus has little time to interact with the Si surface. However, in the case of relatively large clusters, if the incident energy is too low, then the number of Si–O bonds formed by a single cluster impact is also low. This is because, at such low incident energy, the cluster sticks to the surface with a relatively small interfacial area and with less momentum, which provides only a small number of O_2 molecules with sufficient energy to interact with the surface Si atoms.

It is also seen in Fig. 5 that, for a given incident energy per molecule, the rate of Si–O bond formation per single cluster impact is higher for larger clusters in general. This is mainly because a larger cluster provides more oxygen

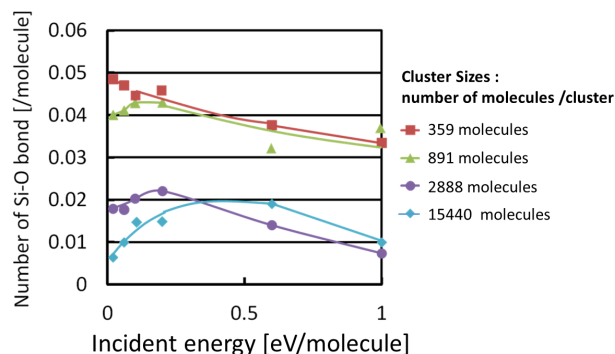


Fig. 6 The number of Si–O bonds formed per cluster incidence normalized by the number of O_2 molecules of the incident cluster. The values are plotted as functions of the incident kinetic energy per oxygen molecule for O_2 gas clusters of various sizes incident upon the Si (100) surface.

molecules to the surface at single impact. Therefore, we replotted the same data in Fig. 6 from a different perspective. Figure 6 shows the number of Si–O bonds formed by a single cluster impact, normalized by the number of O_2 molecules contained in the incident cluster. As shown in Figs. 2 and 4, if a large cluster with low incident energy sticks to the surface and forms a dorm-like structure, then many O_2 molecules in the cluster do not have the chance to interact with the surface Si atoms before they sublime. Therefore, a large cluster is in general not efficient in oxidizing the Si surface for a given number of O_2 molecules arriving at the surface. Indeed, it is clearly seen in Fig. 6 that, at a given incident energy per molecule, a smaller cluster is more efficient in using the O_2 molecules that it carries for the formation of Si–O bonds on the substrate surface.

Note that in all simulation cases discussed so far, most oxygen atoms bond with the Si atoms of the first top layer of the substrate after the cluster impact, and only a very small number of O atoms are seen to enter the second or deeper layers of the substrate. Therefore, our simulations clearly suggest that the low-energy cluster-beam incidence may be used as a process for a nearly single-layer oxidation of a crystalline Si surface.

5. Summary and Conclusions

To examine the possibility of controlling surface reactions with atomic layer level accuracy, we performed MD simulations of the dynamics of O_2 gas cluster impact on a Si (100) surface with relatively low incidence energy. Nearly all previous studies on O_2 gas cluster processes are based on ionized gas clusters accelerated by high voltage. In this study, we have examined the cases where the incident energies of the gas clusters are lower than those of typical IGCB, i.e., in the range of 1 eV/molecule or less. At such low incident energy, it has been found that the cluster-beam incidence can oxidize the top-surface atomic

layer of a Si substrate with little damage to its deeper layers. Thus, single-layer oxidation process by a low-energy O₂ gas cluster beam may be used for the ALE of Si if it is combined with a technique to remove the SiO₂ layer chemically in each etch cycle. Although the development of such an ALE technology is a subject of a future study, the present study has clearly shown that single-layer oxidation of Si by an O₂ gas cluster beam at extremely low incident energy is a feasible technology for the ALE of Si surfaces.

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