Stress-driven oxidation chemistry of wet silicon surfaces

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Abstract

The formation of a hydroxylated native oxide layer on Si(001) under wet conditions is studied by means of first principles molecular dynamics simulations. Water molecules are found to adsorb and dissociate on the oxidised surface leading to rupture of Si-O bonds and producing reactive sites for attack by dissolved dioxygen or hydrogen peroxide molecules. Tensile strain is found to enhance the driving force for the dissociative adsorption of water, suggesting that similar reactions could be responsible for environmentally-driven subcritical crack propagation in silicon.

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The chemistry at the interface between silicon and a wet environment is of great importance for the processing, the function and the failure of microelectromechanical systems (MEMS). In particular, the behaviour of MEMS for biomedical applications [1] is governed by the adhesion of extracellular matrix proteins to the oxidised surface [2] and by dissolution of Si(OH)$_4$ molecules from the surface [3]. Similar dissolution processes occur during the release of MEMS via etching of sacrificial oxides. During this processing stage, dissolved oxygen in the etching solution may lead to pronounced surface roughness [4, 5], which may later promote crack initiation and failure of the device under mechanical load [6]. Moreover, when mobile devices operate in a humid atmosphere, the crack-propagation rate under fatigue loading is substantially accelerated and the device’s life-time reduced with respect to vacuum conditions [7–10].

Conclusive atomic-level interpretations for the origin of all these processes are lacking, due to the complexity of phenomena which include a combination of surface oxidation, reaction of the native oxide layer with water molecules, and the presence of mechanical stresses in the silicon structure [11]. To gain an atomistic insight into these mechanisms we have studied the oxidation of a Si(001) surface, the reactions of the oxidised surface with liquid water and dissolved oxidising chemical species, as well as the effect of mechanical stresses on the reactivity of the surface by means of first-principles molecular dynamics (FPMD) simulations [12–14].

Under dry conditions, we have found that oxygen molecules spontaneously react with the bare surface and a native oxide layer quickly grows until the oxygen coverage reaches about 1.5 monolayer (ML) [16]. At higher coverages, further oxide growth is limited by the thermally activated diffusion of dioxygen molecules through the oxide layer to the chemically active Si/SiO$_x$ interface [17]. Namely, several attempts at placing O$_2$ molecules close to putative adsorption sites all resulted in repulsion of the added molecule away from the oxide layer. Moreover, no changes in the topology of the Si-O network have been observed upon annealing of the structure at 600 K in a 0.6 ps FPMD simulation. These results indicate a considerable chemical stability of the oxide model, which has a Si:O ratio of about 1:1 and contains partially oxidised Si species in proportions roughly consistent with medium-energy ion scattering experiments [18] (details on the composition obtained are reported in Refs. [16] and [19]).
Oxide layers of very similar structure and composition form also when B and P impurities are initially present in the bare surface layers. In this case the oxidation proceeds while the impurities remain trapped at the Si/SiO$_x$ interface and an oxide layer gradually builds up above them [19]. This indicates that dopants should not substantially influence the interactions between the oxide layer and an outer wet environment and are thus not considered in the simulations presented here.

Interestingly, the formation of a thin oxide layer on Si(001) is accompanied by development of surface tensile stress [19], as previously measured experimentally [20]. In our simulations, the surface stress initially decreases from the value of 0.81 N/m for the bare p-2x2 reconstructed Si(001) surface to a minimum of 0.05 N/m at an oxygen coverage of 0.75 ML, then it rapidly increases at higher coverages, reaching a maximum of 2.92 N/m at 1.5 ML. The fact that a tensile stress is present in the amorphous SiO$_x$ layer which spontaneously forms on the silicon surface in contact with the atmosphere suggests that the surface could readily react with water molecules, as in the case of mechanically stressed silicate glasses [21]. In silicate glasses, attack by water is thought to be due to polarisation of a strained Si-O bond, which promotes the adsorption of water on the Si atom accompanied by proton transfer to a neighbouring O atom, eventually resulting in the cleavage of the bond [22].

To test whether similar reactions may take place on the native oxide grown on Si surfaces, we have performed a FPMD simulation of the model previously obtained for the dry oxidised Si(001) surface in contact with liquid water (Fig. 1). The atomic coordinates of the oxidised models were directly taken from the output of the calculations described in Ref. [16], while the positions of the water molecules were initially randomised. As noted above, in spite of the presence of exposed Si$^{2+}$ and Si$^{3+}$ species, the oxidised surface did not present any reactive sites for further reactions with O$_2$ molecules [16]. However, in the present case, soon after starting the simulation we observe two water molecules adsorbing on the surface. The first molecule binds with its O atom to a twofold-coordinated Si atom donating a proton to a neighbouring water molecule. This proton then stays in solution for the remainder of the simulation, indicating an active role of the water hydrogen-bond network in the reaction mechanism [23]. The second molecule binds to a fourfold-coordinated Si atom, initially forming a fivefold-coordinated reaction intermediate
(Fig. 1a). This adsorbed molecule later dissociates donating a proton to a nearby oxygen atom, which was originally bridging two Si atoms of the oxide structure. As a consequence, one of the Si-O bonds breaks with formation of a hydroxyl group bound to a Si atom on one side and of a threefold-coordinated Si atom on the other side (Fig. 1b).

The creation of this newly exposed reactive site opens up the possibility of further reactions with water molecules or other chemical species which may be dissolved in solution, such as hydrogen peroxide or oxygen. Indeed, continuing the simulation, a third water molecule spontaneously adsorbs on this site (Fig. 1c) and in turn dissociates donating a proton to the Si atom which was originally twofold-coordinated in the dry oxide model (Fig. 1d). Moreover, in further FPMD simulations we replaced this third water molecule with an H$_2$O$_2$ molecule prior to the adsorption event (with an initial Si-O distance of 2.8 Å between the molecule and the newly created threefold-coordinated Si site). As for the case of H$_2$O, the H$_2$O$_2$ molecule quickly binds to the surface and dissociates (Fig. 2a-d). Unexpectedly, not only does cleavage of the O-O bond of H$_2$O$_2$ occur upon chemisorption but also proton transfer from the dissociating molecule to the originally twofold-coordinated Si atom, just as was observed in the case of water adsorption (cf. Fig. 2b with Fig. 1d). This suggests that concerted electrophilic/nucleophilic attacks could also take place during the stress corrosion of silicate glass induced by H$_2$O$_2$, and provides an alternative mechanism to the proposed simple cleavage of the peroxide molecule leading to the creation of two OH radicals [24].

Finally, when an O$_2$ molecule instead of an H$_2$O$_2$ molecule is placed near the same reactive site, spontaneous chemisorption and dissociation again take place (Fig. 2e-h). During the reaction, which is driven by the donation of electrons from the surface to the antibonding molecular orbitals of O$_2$ [16], a proton is donated to the dissociating molecule from a hydroxyl group nearby (Fig. 2f). Later, the O$^-$ atom produced receives, from the solution, a dissolved proton which had been released previously by a water molecule after adsorption on the twofold-coordinated Si surface site (Fig. 2f,h). After the dissociation, the second O atom binds to the originally twofold-coordinated Si atom, revealing in particular the ability of the latter to be both reduced (i.e. to accept protons) and oxidised (cf. Fig. 2d and Fig. 2h).

At the end of the simulation the hydroxylated oxide layer is composed of 13 oxidised Si
species with formal valences ranging from +1 to +4, 12 O atoms twofold coordinated by Si atoms, and 4 adsorbed OH groups. It is worth noting that, despite the limited size of the model and the short simulation time, the obtained concentration of 4 hydroxyl groups on a surface of 1.2 nm$^2$ agrees well with the values between 2.6 and 4.6 OH/nm$^2$ measured experimentally on amorphous silica surfaces [25, 26].

In order to check whether the presence of stress in the native oxide structure has a direct influence on the dissociative adsorption of water and the creation of exposed reactive Si sites, we have repeated the simulation shown in Fig. 1 in the presence of -7.5 % compressive plane strain. Strain was applied via a uniform rescaling of the cell vectors and of the atomic coordinates of the oxidised Si model in the directions parallel to the surface. After relaxing the atomic positions, the height of the simulation cell was adjusted to obtain a free volume equal to the case of zero-strain, which was filled with the same number of water molecules as before. In this case, two water molecules are again observed to adsorb on Si atoms of the surface, one of which donates a proton into the bulk water. However, whereas in the absence of external strain (Fig. 1) protons were transferred to O atoms of the surface and Si-O bonds broken, in this case neither processes are observed during the entire simulation, which was stopped after 3.3 ps. In addition, we performed a further FPMD simulation starting from the final structure obtained in Fig. 1(d) and applying an external tensile plane strain of 7.5 % [27]. In this case, after about 0.6 ps, a third water molecule was observed to attack a strained Si-Si bond, adsorbing onto one of the two atoms, dissociating and donating a proton to the second atom, irreversibly breaking the bond. These combined results suggest that the driving force for water attack of surface bonds may be reduced by the presence of compressive and enhanced by the presence of tensile externally applied stress.

We would like to note here that the simulations performed above are only indicative of the possible chemical processes that occur, and cannot provide any quantitative conclusions regarding reaction times and reaction rates. Moreover, in all cases we started from randomized positions of water molecules, which may in principle influence the chemical mechanisms that are observed here. Nevertheless, it is interesting that, both in the simulation in the presence of compressive strain and in the simulation in the absence of strain, a water molecule adsorbs on the same Si surface site, although at a later simulation time.
when compression is present (about 1.0 ps vs. 0.3 ps, respectively). However, only in the absence of compressive strain does the molecule dissociate causing the rupture of a Si-O bond, suggesting a strong influence of the strain field on the behavior of the system.

To substantiate this hypothesis we have performed FPMD simulations of a system composed of the oxidised surface and a single water molecule initially placed at a distance of 2.8 Å from the fourfold-coordinated Si atom which first reacted with water in the simulation described above (labelled 5 in Figure 1a). In the absence of externally applied strain or in the presence of tensile strain, the water molecule adsorbs spontaneously immediately after starting the simulation. Remarkably, when the surface slab is put under compressive strain, no spontaneous adsorption takes place and the molecule diffuses away from the surface.

To understand the reasons behind this observation, we have computed the atomic point charges which best fit the electrostatic potential obtained \textit{ab initio} in a 1 Å thick region outside the Van der Waals radius of the atoms of the oxidised surface (ESP charges [29]). The positive ESP charge on the Si atom is found to increase from a value of 0.06 $e$ under compressive strain to 0.13 $e$ in the absence of strain and to 0.20 $e$ in the case of tensile strain, indicating progressively increasing electrophilicity of the Si site. Consistently, the charges on neighbouring O atoms are more negative by about 0.1 $e$, enhancing the electrostatic driving force toward proton acception. Analysis of the local density of states (LDOS) projected on the Si atom of the surface and on the O atom of the water molecule immediately after formation of the penta-coordinated complex (see Fig. 1a) shows that the Si-O chemical bond initially forms via hybridisation of the p orbitals of O with d-type orbitals of Si (Fig. 3a). The associated d-type LDOS peak moves to higher energy and increases in intensity when the externally applied strain moves from compression to tension (Fig. 3b), indicating increased chemical reactivity of the Si atom with increasing tensile strain. In summary, the presence of tensile stress has the effect of both enhancing the electrostatic driving force for the approach of water molecules to Si sites and facilitating the hybridisation of Si and O orbitals. This leads to water chemisorption, subsequent deprotonation and breaking of existing Si-O bonds, thus exposing reactive Si sites to the solution environment.

The results of our simulations suggest that further oxidation reactions of previously
oxidised Si surfaces which are inert under dry conditions can take place in the combined presence of tensile stress and humid air. The enhanced oxidation reactivity of silicon in the presence of a humid environment is consistent with the fact that even the very low concentrations of dissolved oxygen molecules present in conventional etching solutions can significantly affect the morphology of the resulting surfaces, in particular leading to pronounced surface roughness [4, 5].

Our results seem to support a mechanism for the observed premature failure of single-crystal silicon MEMS under fatigue loading in humid environments based on sequential steps of oxide formation and stress-driven corrosion cracking of the oxide layer at the tip of a stable crack [8, 9, 30, 31]. Historically, this “reaction-layer” mechanism had been questioned since it was thought that a relatively thick (~20 nm) oxide layer was necessary to activate stress-corrosion, and the time-scale of the fatigue process is too short to allow such thick oxide growth [10, 32]. However, as we have now demonstrated, ultrathin oxide layers on the Si(001) surface are under tensile stress at coverages of about 1 ML of oxygen, and are subjected to virtually barrierless stress-driven water attack leading to breaking of Si-O bonds. Whether or not such mechanisms are active in silicon MEMS may depend on the crystallographic directions of the propagating crack. Indeed, while both our calculations and experimental evidence [20] show that tensile stress is naturally present on the oxidised (001) surface, only compressive stress was found to develop at all oxygen coverages upon oxidation of the (111) surface at room temperature [20]. Finally, we note that more complex mechanisms involving grain boundaries may be active during sub-critical crack propagation in polycrystalline silicon structures, where fatigue is found to occur irrespective of the presence of a corrosive environment [33, 34].

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[14] Our density-functional theory simulations were performed using norm-conserving pseudopotentials and the PW91 xc potential. The wave functions were expanded in plane waves at the (0.25,0.25,0.0) point of the Brillouin zone up to a kinetic energy cut-off of 60 Ry, applying a smearing of $k_B T=0.1$ eV to the electronic occupancies. A convergence test of the forces and the MD trajectory during the adsorption of a water molecule on the oxidised Si(100) surface has been performed using a larger cut-off of
80 Ry. Differences between forces are limited to a few meV/Å and differences between atom-atom distances to about 0.01 Å indicating that 60 Ry is an acceptable cut-off for the simulation of the adsorption reactions investigated here. All dynamical simulations were performed with the Car-Parrinello method [12] using a time-step of 5.0 au, a fictitious electronic orbital mass of 300 au and a hydrogen mass of 2.0 amu. Using a deuterium mass for H atoms is usual in Car-Parrinello simulations including water, and ensures that adiabatic conditions for the electrons are maintained throughout the dynamics [15]. The Si(001) surface was modelled with a periodically repeated slab of 8 Si layers separated by 8 corresponding layers of vacuum, using a 2x2 surface unit cell with surface area of 10.91x10.91 Å². In the simulations including water the space between the slabs was filled with 29 water molecules (corresponding to a density of about 1 g/cm³) and the bottom surface was passivated with H atoms. All simulations were performed without temperature constraint, the simulation temperature never exceeding 350 K.

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Figures

Figure 1: Snapshots from a FPMD simulation of a Si(001) surface covered by its native oxide layer in contact with water. Si atoms are grey, O red, H white. (a) adsorption of a water molecule on a Si atom (labelled 5) forming a penta-coordinate reaction intermediate (simulation time \( t = 0.5 \) ps). (b) dissociation of the water molecule (see arrow) resulting in breaking of a Si-O bond nearby, formation of two Si-OH groups, and exposure of a threefold-coordinated Si atom to the solution medium (labelled 3) \( (t = 1.1 \) ps). (c) adsorption of a further water molecule (black arrow) on the newly exposed reactive site \( (t = 1.4 \) ps). (d) dissociation of the latter water molecule causing protonation (black arrow) of a Si atom nearby (labelled 2) \( (t = 2.9 \) ps).

Figure 2: Snapshots from two FPMD simulations of the reaction of \( \text{H}_2\text{O}_2 \) (a-d) and \( \text{O}_2 \) (e-h) with an electrophilic Si site of the oxidised Si(001) surface (labelled 3) exposed upon chemical attack of a Si-O bond by water (see Fig. 1a,b). Color code and labels are as in Fig. 1. The O atoms of the reacting molecules are indicated with asterisks, and proton transfer processes are indicated with black arrows (see text).

Figure 3: (a) Local density of states (LDOS) projected on the d orbitals of a surface Si atom and on the p orbitals of the O atom of a water molecule chemisorbing on it. (b) Shift to higher energy and increase of intensity of the d-type LDOS peak of the same Si atom in the presence of applied strain.
L. Colombi Ciacchi et al., Figure 1
L. Colombi Ciacchi et al., Figure 2
L. Colombi Ciacchi et al., Figure 3
