On the *c*-Sil*a*-SiO₂ Interface in Hyperthermal Si Oxidation at Room Temperature

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ABSTRACT: The exact structure and properties of the SilSiO₂ interface are very important in microelectronics and photovoltaic devices such as metal-oxide-semiconductor field-effect transistors (MOSFETs) and solar cells. Whereas SilSiO₂ structures are traditionally produced by thermal oxidation, hyperthermal oxidation shows a number of promising advantages. However, the SilSiO₂ interface induced in hyperthermal Si oxidation has not been properly investigated yet. Therefore, in this work, the interface morphology and interfacial stresses during hyperthermal oxidation at room temperature are studied using reactive molecular dynamics simulations based on the ReaxFF potential. Interface thickness and roughness, as well as the bond length and bond angle distributions in the interface are discussed and compared with other models developed for the interfaces induced by traditional thermal oxidation. The formation of a compressive stress is observed. This compressive stress, which at the interface amounts about 2 GPa, significantly slows down the inward silica growth. This value is close to the experimental value in the SilSiO₂ interface obtained in traditional thermal oxidation.



1. INTRODUCTION

As gate insulator films in metal-oxide-semiconductor (MOS) devices are becoming as thin as a few nanometers or less, atomic scale understanding of the interface geometry as well as the electronic structure becomes increasingly important, specifically in relation to the required properties, such as high reliability, high resistivity, excellent dielectric strength, low interface defect density, and large band gap.^{1,2} The SilSiO₂ interface obtained by traditional thermal Si oxidation³ is therefore a very important interface, both from an economical as well as a technological viewpoint.⁴ This interface has been investigated in detail through the years and various models have been put forward.³⁻¹²

Although the physics and chemistry of the SilSiO₂ interface as formed in traditional thermal oxidation has already been intensively studied,^{1,4,6,13} we still do not have a basic understanding of the interface obtained in hyperthermal Si oxidation.¹⁴ Nevertheless, interest in hyperthermal oxidation of Si surfaces as an alternative to thermal oxidation has been rapidly increasing, and this process can be envisaged for semiconductor applications as well.^{15–25} The reaction of hyperthermal oxygen species (O, O₂; i.e., with energies of 1– 5 eV) with Si surfaces at low temperature has unique properties compared to ordinary high temperature thermal oxidation. Specifically, using hyperthermal oxidation, ultrathin oxide films can be formed even at room temperature.^{14–20} Furthermore, the possibility to accurately control^{14,18,20} the oxide thickness at low temperatures (i.e., less than 500 K²⁶) potentially provides new opportunities in the development of integrated nanoelectronic technologies.

Atomic scale investigations could elucidate several fundamental aspects of the hyperthermal oxidation of Si at low temperatures. Although several works [e.g., refs 27 and 28], which can be considered as modifications of the Deal-Grove model,²⁹ describe thermal oxidation kinetics well even at low temperatures, they fail to describe the formation of ultrathin oxide with a thickness lower than 2 nm.³⁰ Such ultrathin oxide films can be obtained by hyperthermal oxidation of Si at room temperature.²⁰ In this oxidation process, the nature of the selflimiting oxidation behavior is still unclear. Recently, we investigated silicon oxidation on the atomic level, suggesting a SiO₂ growth mechanism.²⁶ We found that the oxide growth is controlled by direct oxidation and that diffusion does not play a significant role in this process at low temperature.²⁶ These aspects can affect the SilSiO₂ interface quality in the hyperthermal oxidation regime and distinguish it from thermal oxidation. Therefore, a set of questions regarding the interface remains open: How does the interface affect the growth process? What is a chemical composition of the transition layer compared to nonstoichiometric oxide layers as obtained in thermal oxidation? Indeed, investigation of the oxidation or of the defect formation processes near the SilSiO₂ interface is also important to clarify various phenomena, such as the generation of defects and the interface degradation due to interfacial stresses.

This work is focused on the c-Si(100)|a-SiO₂ interface as formed in hyperthermal Si oxidation. We carried out reactive

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molecular dynamics (MD) calculations in order to investigate the quality and oxide-limiting behavior of the interface on the atomic scale during the oxidation of the (2×1) reconstructed Si(100) surface, which is the most important surface facet for MOS device fabrication at room temperature.

2. COMPUTATIONAL DETAILS

The SilSiO₂ interface, as formed during hyperthermal Si oxidation, is investigated at the atomic scale by reactive MD simulations, employing the Reactive Force Field (ReaxFF).³¹

The ReaxFF potential uses the concept of partial bond orders to accurately model bond breaking and bond formation and is based on the bond length—bond order/bond order—bond energy relationship formally introduced by Abell.³² A detailed description of the force field as developed for SilSiO₂ can be found elsewhere.^{20,25,26,31,33} ReaxFF can currently describe tens of elements and their compounds, including hydrocarbons, silicon/silicon oxide,^{34,35} metals and metal-catalyzed reactions,^{36–38} metal oxides,³⁹ metal hydrides,⁴⁰ biochemical systems,⁴¹ and others.

In this work, we use the force field parameters employed by Buehler et al.⁴² for crack propagation in silicon. This force field was trained extensively against both Si and SiO₂ phases. Although SiO_x (x < 2.0) suboxide phases were not included explicitly in this training, our previous results on planar SilSiO₂ interfaces including these Si suboxide species were in agreement with both experimental and DFT results.²⁰ Our choice for ReaxFF is based on the fact that it has been parametrized to describe deformations and strains^{42,43} including bond breaking and formation and its ability to accurately describe the expansion of the crystal during the oxide formation process.

For the simulation, a Si(100){ 2×1 } reconstructed surface is chosen, with dimensions $21.7 \times 21.7 \times 27.1$ Å. The simulation bulk initially contains 640 Si atoms. Periodic boundary conditions are applied to the (*x*,*y*) plane, to mimic a laterally infinite surface. Our calculations are based on the mass center position of Si layer planes⁴⁴ and show that the average thickness of each (mono)layer is equal to 1.296 Å, corresponding to the thickness of one-half oxide layer (one oxide layer thickness is 2.6 Å¹⁹). In our calculations, 1 ML (monolayer) corresponds to 32 atoms, which equal the amount of Si atoms per layer.

Prior to the oxidation process, the (2×1) reconstructed Si(100) surface is prepared as follows. First, the surface is equilibrated at 300 K using the Berendsen heat bath (NVT dynamics)⁴⁵ for 20 ps with a damping constant of 0.1 ps. Next, the obtained structure is relaxed in the microcanonical ensemble (NVE dynamics) for 10 ps. Energetic oxygen impacts are subsequently performed as follows. The incident particle (oxygen atom or oxygen molecule) is positioned at a z-position of 10 Å above the uppermost Si-atom of the crystal. The $\{x,y\}$ coordinates of the incident particle are chosen randomly. In the case of molecular oxygen, the O_2 molecule is rotated randomly prior to impact. The impinging particle is directed normal to the surface, corresponding to laser detonation experiments.^{15,21} Every impact is followed for 3 ps. The initial kinetic energies of the oxygen species (O, O_2) were set to 5 eV. At the end of each impact, the excess energy is allowed to dissipate, and the temperature is allowed to decrease to 300 K applying canonical (NVT) ensemble prior to the next impact.

Cauchy atomic stresses were calculated using the approach proposed by Daruka et al.⁴⁶ for structures obtained by O and O_2 oxidation, as well as for the pristine Si crystal. For all stress

calculations, the structures were first equilibrated at 0.01 K using NpT dynamics, to remove the kinetic energy part from the stress calculation, and subsequently, the total energy was minimized using the steepest descent and conjugate gradient techniques.

3. RESULTS AND DISCUSSION

3.1. Partially Oxidized and Transition Oxide Layers during Oxidation. Corresponding to experimental^{14,16} and MD studies,^{20,26} the oxidation process in hyperthermal Si oxidation at room temperature can be divided in two stages: (I) the initial fast (or direct) oxidation stage and (II) the subsequent slow oxidation stage. In Figure 1, two representative



Figure 1. Oxidized Si structures induced by hyperthermal (5 eV) oxygen impacts in the first (a) and second (b) oxidation stages, respectively. Here, the light gray, gray, and white Si atoms are components of silicon (Si), nonstoichiometric oxide layers (SiO_x, 0 < x < 2), and silica (SiO₂) regions, respectively. The oxygen atoms are colored in red. Every structure is analyzed by means of the Si-(sub)oxide (Siⁱ⁺) components; 0 Å corresponds to the topmost layer of the original pristine Si lattice.

oxygenated Si structures are shown for both stages, corresponding to the atomic oxidation with initial incident energy of 5 eV. The oxide growth process and the chemical structure of the obtained oxide can be easily analyzed by means of the Si-(sub)oxide components.^{15–20} The Si¹⁺, Si²⁺, Si³⁺, and Si⁴⁺ components arise from interfacial silicon atoms, which bind to one, two, three and four nearest-neighbor oxygen atoms, respectively, and thus correspond to Si₂O, SiO, Si₂O₃, and SiO₂, respectively.⁴⁷ The notation used corresponds to formal charge states and not to the actual atomic charges. The nomenclature "SiO₂" is used for fully oxidized silicon (i.e., silica). The term "SiO_x" is used to indicate the partially oxidized or nonstoichiometric oxide region (0 < x < 2), instead of Si₂O, SiO, and Si₂O₃. As this work is devoted to the understanding of the SilSiO₂ interface, we focus on the nonstoichiometric oxide (SiO_r) region as formed during hyperthermal oxidation. We found that the nonstoichiometric oxide layers mostly consist of three Si suboxide species (i.e., Si^{1+} , Si^{2+} , and Si^{3+}), albeit some Si⁴⁺ atoms, which is the unique component of amorphous stoichiometric oxide $(a-SiO_2)$, can also be found in low concentration.⁴⁸

Figure 2 shows the spatial distribution of the Si-oxide components in the oxygenated Si region during both atomic (A) and molecular (M) oxidation at an impact energy of 5 eV.



Figure 2. Distribution of Si-(sub)oxide components during atomic (A) and molecular (M) oxidation using 5 eV impacts. Here, Si¹⁺ (light gray), Si²⁺ (gray), and Si³⁺ (dark gray) species are components of the SiO_x region. Most Si⁰ (black dash) and Si⁴⁺ (black solid) atoms are located in the *c*-Si and *a*-SiO₂ regions, respectively; 0 Å corresponds to the topmost layer of the original pristine Si lattice. Note that 1 ML corresponds to 32 atoms.

As mentioned before, 1 ML (monolayer) corresponds to 32 atoms. In the first stage, the oxygen content increases rapidly due to the high adsorption probability of the oxygen species on the pure silicon surface.²⁰ As shown in the figure, the Si¹⁺ component dominates in the first three MLs of oxygen fluence for both oxidation cases. This is due to the direct oxidation of the silicon surface and subsurface layers by hyperthermal oxygen atoms.^{15,19,20,26,49} In this stage, penetrating oxygen atoms can directly oxidize up to the second subsurface layer^{19,23,26} at room temperature. This is a marked difference with thermal oxidation at the same temperature.^{27,28} Because of the relatively high impact energy, the chemisorption of O2 molecules is found to be dissociative in all cases.²⁵ Therefore, in both oxidation cases (O as well as O_2), the only penetrating particle is an O atom. Our previous results^{20,25,26} also showed that the final penetration depth per impact is found to be determined in the first ps, and essentially remains constant afterward, thereby validating our impingement rate of 1 impact every 3 ps. At low temperatures, however, the deposited oxygen atoms cannot move deeper into the crystal due to the high energy barrier.⁵⁰ As a result, the Si¹⁺ gradually converts to Si²⁺ and Si^{3+15–20} forming a nonstoichiometric oxide layer, which consists of oxygen atoms with relatively high oxidation states. Consequently, the oxygenated Si region (i.e., partially oxidized layers) consists of three suboxide components, which are consecutively dominating in the SiO_x oxide formation process.²⁰ Namely, the entire oxygenated Si region is nonstoichiometric in this stage, while some initial silica molecules (SiO_2) appear on the oxygenated Si surface after 4 ML. Consequently, in the period from 4 to 8 ML, the surface becomes fully covered by one silica layer.

When the second oxidation stage starts, a SiO₂ monolayer completely covers the SiO_x surface. Therefore, in stage II, the oxygenated Si is divided into a stoichiometric (SiO₂) oxide region and a nonstoichiometric (SiO_x) oxide one. This nonstoichiometric oxide region therefore forms a transition layer between crystalline silicon (*c*-Si) and amorphous silica (*a*-SiO₂).^{14–20,26} We refer to the nonstoichiometric oxide region as a partially oxidized layer (Figure 1a) in stage I and as the *c*-Sil *a*-SiO₂ interface or transition oxide layer (Figure 1b) in stage II. Thus, as shown in Figure 2, the partially oxidized layer (A, 1 ML) becomes the transition oxide layer (A, 20 ML), which corresponds to the c-Sila-SiO₂ interface after about 8 ML for both atomic and molecular oxidation. This value constitutes the transition between the first and second oxidation stages.

In stage II, all Si oxide components are found in the transition oxide layers as shown in the figure. In the transition layers, the spatial distribution of the suboxide species indicates that Si¹⁺, Si²⁺, and Si³⁺ species are concentrated in a region of 4.5, 5.0, and 5.5 Å between the nonoxidized Si layer and the *a*-SiO₂, respectively. The Si²⁺ species are localized between Si¹⁺ and Si³⁺ states in the transition oxide region. The interval of the distribution peaks is about 1.0 Å.

The percentages of Si-oxide components in the SiO_x and SiO₂ regions are 45% and 55%, respectively, in molecular oxidation in the second stage. In the atomic oxidation case, they are 26% and 74%, respectively. However, Tagawa and coworkers¹⁴ reported that the oxide formed by 5 eV O atoms at room temperature consisted mainly of Si⁴⁺ with only 6% suboxide components, based on an analysis of X-ray photoelectron spectroscopy (XPS), which plots the number of detected electrons versus their binding energy. This difference can be explained by considering that this percentage of Si-oxide components depends on the oxide thickness, which, in turn, also strongly depends on the fluence of the energetic oxygen species even at the same temperatures.²³ It has been reported that the oxide thickness decreases from 4.5 to 1.75 nm when the oxygen fluence is reduced from 1×10^{19} to 1×10^{17} O atoms \cdot cm⁻², at almost the same conditions^{14,16} as those for the hyperthermal oxidation process. In our calculations, the O fluence is 2.1×10^{17} O atoms·cm⁻², and the obtained oxide thickness is 1.85 nm for the atomic oxidation. This is fairly close to the experimental oxide thickness of 1.75 nm obtained using a fluence of 1×10^{17} O atoms·cm⁻², as determined from XPS measurements.¹⁶ Further, our simulations show that the percentage of Si-oxide components in the partial (SiO_r) and fully oxidized Si (SiO₂) regions is almost constant during the relatively long second oxidation stage.

An important quantity is the number of Si atoms displaying an intermediate oxidation state (per unit area), which we denote by $N_{\rm SiOx}$. In the second stage, after 20 ML of O fluence, the total density in the interface is about 5.5 MLs or 3.7×10^{15} atoms cm⁻², which is somewhat larger than the experimental estimates for the thermal oxidation.^{8,51,52} However, we point



Figure 3. Distribution of the Si-(sub)oxide species, i.e., Si¹⁺ (black), Si²⁺ (gray), and Si³⁺ (light gray) in the nonstoichiometric oxide region, i.e., the partially oxidized layers (0-8 ML) and transition oxide layers (8-152 ML) during atomic (A) and molecular (M) oxidation at an impact energy of 5 eV.

out that the distribution character of suboxide species in the transition region, as shown in Figure 2, agrees with the XPS and photoemission spectroscopy (i.e., PES, measurement of the energy of photoelectrons emitted from target) reports.^{8,52} In Figure 3, the distribution of the Si-(sub)oxide species versus the oxidation progression is shown.

With respect to the nominal population ratio of Si¹⁺, Si²⁺, and Si^{3+} species in the SiO_x oxide region in the first stage, we find that the density of the intermediate oxidation states evolves as $N(Si^{1+}) > N(Si^{2+}) > N(Si^{3+})$ for both the atomic and molecular oxidation (Figure 3). However, this distribution changes in this case. The intensity distribution of intermediate oxidation states in the second stage is $N(\text{Si}^{1+}) < N(\text{Si}^{2+}) \leq N(\text{Si}^{3+})$ for the atomic oxidation, suggesting that this is a universal property of the SilSiO₂ interface during a thermal oxidation process.⁸ In the molecular case, the distribution is $N(\text{Si}^{1+}) < N(\text{Si}^{3+}) \le N(\text{Si}^{2+})$. Indeed, the number of the Si²⁺ components is greater than the number of Si³⁺ components in the last 100 MLs. Therefore, the oxygen deficiency is somewhat larger in the interface induced during molecular oxidation. Furthermore, our calculations show that the silicon density in the transition region is slightly higher than in the a-SiO₂ region, while the oxygen density is lower, corresponding to experimental evidence obtained by Gusev et al.⁵³

3.2. Thickness of the Nonstoichiometric Oxide Region. Figure 4 illustrates the evolution of the thickness of the oxygenated Si and its nonstoichiometric oxide layers for oxidation by both atomic (A) and molecular (M) oxygen, at an impact energy of 5 eV. The thickness is calculated based on the distribution of the Si-(sub)oxide species as shown in Figure 2, and its resolution is 1.296 Å, which corresponds to the thickness of one-half oxide layer (OL).¹⁹



Figure 4. Thickness of (a) the oxygenated Si and (b) its nonstoichiometric oxide layers as a function of the oxygen fluence, for both atomic (A) and molecular (M) impacts of 5 eV.

In stage I, the thickness of the oxygenated Si region (a) and its nonstoichiometric oxide layers (b) rapidly increases up to 11.7 Å (4.5 OLs) for both atomic and molecular oxidation, as shown in the figure. At the beginning of stage II, the thickness of the nonstoichiometric oxide region starts decreasing due to partial conversion of this region to silica, reducing the thickness of the transition oxide layers (or a c-Sila-SiO₂ interface) to 5.3 Å (2.0 OLs) for atomic oxidation and to 6.5 Å (2.5 OLs) for molecular oxidation. These c-Sila-SiO₂ interface thicknesses correspond to the lower limit of several experimental measurements⁵⁴ and ab initio results⁵⁵ in which the one of the nonstoichiometric oxides was reported to range from 4 to 50 Å in thermal Si oxidation. However, because of the immediate breakup upon impact of the O2 molecules, the change in the oxygenated silicon thickness as a function of the incident energy is smaller for the molecular oxidation than for the atomic oxidation process, and the final thickness is equal to 24.7 Å in the atomic oxidation case and to 14.3 Å in the molecular oxidation one. Indeed, as the impinging molecules are given the same initial kinetic energy as the impinging atoms, the individual atoms obtained after molecule dissociation have less momentum and hence a lower velocity. As a result, oxygen molecules do not penetrate as deep in the surface as the oxygen atoms.²⁵

Although the thickness of the ultrathin interface remains constant and almost the same for both atomic and molecular oxidation, the morphology of the interface structure might be different. This is discussed in the next sections.

3.3. Roughness of the *c***-Si***la***-SiO**₂ **Interface.** The morphology of the transition oxide region (or the *c*-Si*la*-SiO₂ interface) is characterized in terms of its root-mean-square (RMS) roughness. Figure 5 presents the variation of the RMS roughness versus the oxygen fluence for both atomic and molecular oxidation using 5 eV impacts. The RMS roughness δ^{56} is obtained as

$$\delta = \sqrt{\langle (h - \overline{h})^2 \rangle} \tag{1}$$

where *h* is the top *z*-coordinate of a Si atom, which has no O neighbors in the *c*-Sil*a*-SiO₂ interface, and \overline{h} is the average over all *h* values. Prior to oxidation, the roughness of the (2×1) reconstructed Si(100) surface is 1.03 Å. The figure demonstrates a roughening of the initially smooth surface in the first oxidation stage and subsequently a smoothening of the rough surface during the second stage, as was previously also proposed by Irene.¹¹ In stage I, the surface roughness linearly increases up to approximately 3 Å in both oxidation cases. In this stage, some surface restructuring occurs, resulting in higher



Figure 5. Root-mean-square (RMS) roughness of the c-Sila-SiO₂ interface versus the oxygen fluence, for both atomic (A) and molecular (M) impacts of 5 eV.

Si oxidation states. In the second stage, the *c*-Sil*a*-SiO₂ interface roughness decreases again due to the appearance of a stoichiometric oxide layer on top of the SiO_x region. In atomic oxidation, the roughness of the interface is constant at about 1.5 Å, which is close to the RMS value (~ 1.3 Å) of the c-Sila-SiO₂ interface as obtained in thermal oxidation.⁵⁷ Molecular oxidation, however, enhances the surface roughness: The average value is somewhat larger (~ 2.1 Å) than in the atomic oxidation case, and the interface is therefore less abrupt. In addition, such behavior is also experimentally observed in thermal oxidation. In typical industrial oxides, the roughness of the SilSiO₂ interface increases with decreasing oxide layer thickness.58 Furthermore, stress in the interface region may change the interface roughness as well, which is discussed in section 3.6. Discussion of the interface morphology is continued in the next sections.

3.4. Bond Length and Bond Angle Distributions in the c-Sila-SiO₂ Interface. The bond length and bond angle distributions for the interface structures as generated during the oxidation are shown in Figure 6.



Figure 6. (a) Bond length and (b) bond angle distributions in the *c*-Sil a-SiO₂ interface during atomic (A) and molecular (M) oxidation with impact energy of 5 eV after 150 MLs of oxygen fluence.

During the second oxidation stage, the bond length distributions are very similar in both atomic and molecular oxidation (see Figure 6a). Indeed, the peaks of the Si–O and Si–Si bond length distributions correspond to 1.58 and 2.35 Å in the atomic case, respectively, and to 1.59 and 2.4 Å in the molecular case. These values are fairly close to the results reported in interface models.^{9,12} However, we also observe an unusual tail in the Si–Si bond length distribution in the range 2.5–2.9 Å, which has not been reported in the thermal models (see the section 3.5). Although O–O peroxyl-bridge bonds are not found in this structure,²⁰ the interface is not free from coordination defects, that is, some 3-fold oxygen atoms (O^{3–}) are found in the interface, albeit in very low concentration.

In Figure 6b, the Si–Si–Si, O–Si–O, Si–O–Si, and Si–Si– O bond angle distributions in the second oxidation stage (after 150 ML) for only the atomic oxidation case are shown. We found that these distributions are almost the same for the molecular oxidation case, and therefore, only the picture for the atomic oxidation case is shown. The bond angle is about 110° for both the Si–Si–Si and O–Si–O angle distributions, which is fairly close to the experimental value, while the O–Si–O distribution is somewhat wider in our structures (i.e., 75–165°) than the distribution usually cited for amorphous silica (i.e., $109^{\circ} \pm 10^{\circ}$).^{35,59,60} Also, two main peaks are observed for both the Si–O–Si and Si–Si–O cases. The peaks are located at about 103° and 152° for the Si–O–Si angle distribution and at 38° and 100° for the Si–Si–O angle distribution.

For the vitreous (amorphous) silica structure as generated by thermal O_2 oxidation, Mozzi and Warren⁵⁹ obtained a wide distribution of Si–O–Si angles varying between 120° and 180°, with a main peak found at 144°. However, Da Silva et al.⁶¹ suggested that the most probable Si–O–Si bond angle of vitreous silica is 152° instead of 144°. Mauri et al.⁶⁰ also found a slightly higher mean value of 151° ± 11° and a relatively narrow distribution (120–170°) in the Si–O–Si angular distribution of vitreous silica. In our model, a second peak in the Si–O–Si angle distribution is in the range of 120–180°, peaking at about 152°. These values are in good agreement with the results of Silva et al.⁶¹ and Mauri et al.⁶⁰ and indicate that some part of the transition region is similar to *a*-SiO₂.

Although the interface morphology is close to interface models proposed for thermal oxidation, some unexpected SiO (defect) structures are found in our interface model induced by hyperthermal oxidation, which is discussed in the next section.

3.5. Si Epoxide Linkages in the *c*-Sil*a*-SiO₂ Interface. The first peak of the Si–O–Si and Si–Si–O bond angle distributions indicates that some defects, i.e., Si–O–Si triangular configurations (indicated by blue circles in Figure 7a) exist in the interface. Stefanov et al.⁶² also observed such three-membered Si–O–Si rings in high temperature annealing of the water-exposed Si(100)-{2 × 1} surface using infrared absorption spectroscopy and density functional cluster calculations to identify the intermediate oxide structures. They termed this unexpected defect "Si epoxide linkage" and



Figure 7. (a) Top view of the SilSiO₂ interface and some Si–O–Si triangular configurations (or Si epoxide linkages) in the interface (in blue circles). (b) Evolution of the Si epoxide concentration during oxidation. (c) Physical stress-enhanced bond breaking mechanism, proposed by Yang et al.⁶³

The Journal of Physical Chemistry C

denoted it by SiØSi, by reference to the analogous structure in carbon chemistry. They demonstrated that this structure is the thermodynamically favored product and should be preferentially formed at silica interfaces. In our calculations, the Si–Si bond length of this configuration is in the range 2.5–2.9 Å (see Figure 6a), which is somewhat longer than the Si–Si bond length of 2.16 Å suggested by Stefanov et al.⁶² Figure 7b shows that the concentration of these triangular structures significantly increases in the initial oxidation stage. In this stage, the entire oxygenated Si region is nonstoichiometric and the Si epoxide linkages can be found in this entire region. However, these epoxide structures are only found in the interface when the silica formation begins. Therefore, their concentration remains constant during the second oxidation stage.

Formation of such structures may also be explained by a physical stress-enhanced bond breaking mechanism as proposed by Yang and Saraswat,⁶³ which is schematically represented in Figure 7c. For the oxide breakdown to occur, the Si-O-Si bonds in SiO₂ (panel 1) break and are replaced by the Si-Si bonds, ultimately pushing away the O atom (panel 2). It was proposed that the Si–O–Si (α) angle decreases when the stress increases. They concluded that this mechanism is strongly dependent on the physical stress in the thin oxide films. This conclusion was also in agreement with the previous Fourier transform infrared spectroscopy results of Tagawa et al.,¹⁴ which revealed that smaller Si-O-Si bond angles exist in oxide films as created by hyperthermal atomic oxygen, compared to the Si-O-Si angles in alpha-quartz, implying that compressive stresses exist in the SiO₂ film. We propose that the SiØSi structures (Figure 7a) in our c-Sila-SiO₂ interface may constitute a transition state between two states (panels 1 and 2 in Figure 7c) in the bond breaking mechanism due to interfacial stresses.⁶⁴ It is also known that a high stress is associated with low temperature oxidation while a low stress is associated with high temperature oxidation.^{14,63,64} Therefore, the interfacial stresses may significantly enhance the concentration of Si-O-Si triangular structures in our interface as obtained at room temperature. This behavior will be explained by the stress calculation, as presented in section 3.6. Hence, the study of the interfacial stress gives useful information on the interface properties in hyperthermal oxidation at low temperatures.14

3.6. Interfacial Stresses during Oxidation. The interfacial stress, which can be thought as a combination of chemical and mechanical (physical) stresses,⁶⁵ plays an important role in the reliability of gate oxides with its ultrathin interface.⁶³ The chemical stress at the interface is associated with Si atoms that have an intermediate oxidation state between 0 (in Si) and 4+ (in SiO₂). Mechanical stress appears from the mismatch of unit cells and local bonding mismatch in the bulk construction between the Si and SiO₂ parts. Mechanical stress causes the deformation of bonds and bond angles at the interface. Korkin et al.⁶⁵ suggested that the chemical and the mechanical stress make comparable contributions to the total SilSiO₂ interface stress.

We calculated stresses as the symmetric per-atom stress tensor for each Si atom in the *c*-Si, SiO_x, and *a*-SiO₂ regions using the approach proposed in ref 46. The tensor has 6 components for each atom and is stored as a 6-element vector in rectangular Cartesian coordinates: normal, σ_{xx} , σ_{yy} , σ_{zz} , and shear, σ_{yz} , σ_{zx} , σ_{xy} . The stress components in all directions are averaged per unit thickness of 1.296 Å, corresponding to the distance between two neighbor layers in the *c*-Si(100) along the *z*-axis or equal to half of the thickness of the oxide layer.¹⁹

The calculations show that all stress components in the nonoxidized c-Si(100)-{2 × 1} surface are very small and compressive, i.e., $\sigma_{xx} \approx 0.1$ GPa, $\sigma_{yy} \approx 0.1$ GPa, and $\sigma_{zz} \approx 0.2$ GPa. We believe that the oxidation reaction rate coefficient is not lowered by the stress in the initial oxidation stage as suggested Kao and co-workers.⁶⁶ Consequently, the initial oxidation rate coefficient rather than on stress and temperature. In the c-Sila-SiO₂ interface, as formed during the oxidation, however, σ_{xx} and σ_{yy} are somewhat higher than the σ_{zz} and are in the range 6–8.5 GPa. The applied periodic boundary conditions (PBC) in x and y directions increases the mechanical stress in those directions.^{44,66} We suggest that the inward oxide growth²⁶ depends on the σ_{zz} rather than σ_{xx} and σ_{yy} stresses.

Figure 8 shows the evolution of stress along the z-axis (σ_{zz}) versus the oxygen fluence for both atomic and molecular



Figure 8. Evolution of the in-plane (x-y plane) averaged stress along the *z*-axis in the *c*-Sil*a*-SiO₂ interface during atomic (A) and molecular (M) oxidation with 5 eV impacts.

oxidation. Note that positive and negative values correspond to compressive and tensile stresses, respectively. In the first oxidation stage, the σ_{zz} stress significantly increases due to the quick expansion of the *c*-Si. In this stage, the Si¹⁺ \rightarrow Si²⁺ \rightarrow Si³⁺ conversion occurs relatively fast as mentioned in the previous sections, and it leads to an increase in both the chemical as well as the mechanical stresses. As a result, the average value of the σ_{zz} stress increases up to 8 GPa in the partially oxidized Si layers. In the second oxidation stage, however, the average stress value at the c-Sila-SiO₂ interface decreases to about 2.0 and 2.5 GPa for atomic and molecular oxidation, respectively, and subsequently remains almost constant. These obtained stress values are in good agreement with experimental data in which the SilSiO₂ interface was investigated using highresolution transmission electron microscopy (HRTEM) analysis and a compressive stress was found of approximately 2 GPa.⁶⁷ While this value is not very high, it is strong enough for significantly reducing the oxygen diffusivity in the SilSiO₂ interface during the second oxidation stage. Such a self-limiting effect, which increases with decreasing growth temperature,¹ was previously also observed in Si nanowire oxidation.^{64,68-71} This effect may also significantly influence the flat interface thickness and roughness, which were discussed in previous sections. Because of both the high impact energy and the compressive interfacial stresses, the resulting interface thickness is different in atomic and molecular oxidation.

In summary, we investigated the formation and properties of the $Si|SiO_2$ interface in hyperthermal oxidation, in comparison

The Journal of Physical Chemistry C

with existing thermal models. Although no attempt was made to determine the statistical variation in the obtained results, the general conclusions are found to correspond to experimental results. As reported in several experimental studies,^{14–19} the interface plays a significant role in controlling the hyperthermal oxide thickness. The high reactivity of hyperthermal oxygen reduces the mobility of atomic oxygen at the SilSiO₂ interface at the low (room) oxidation temperature and leads to micro roughness, suboxides, and a high stress at the interface. In these low temperature experiments, the hyperthermal oxygen species (atoms and molecules) (with energies in the range of 1–10 eV) were generated by a laser-detonation source developed by Physical Science Inc.⁷² These experimental outcomes corroborate our conclusions.

4. CONCLUSIONS

The *c*-Sil*a*-SiO₂ interface as obtained by hyperthermal oxidation of Si(100)- $\{2 \times 1\}$ surfaces by oxygen atoms and molecules was studied using reactive molecular dynamics simulations.

We analyzed the formation of the nonstoichiometric oxide region and found two oxidation regimes: First, a fast oxidation stage lasting for about 8 monolayers (MLs) of oxygen fluence (stage I), followed by a subsequent slow oxidation stage (stage II). Distribution of Si-(sub)oxide components show that the oxygen deficiency is somewhat higher in the interface induced by molecular oxidation compared to atomic oxidation. The distribution of the suboxide species in the transition region agrees with several interface models. Calculations show that the thickness of the oxygenated Si region rapidly increases up to 11.7 Å in the initial oxidation stage. The thickness of the nonstoichiometric oxide region decreases again in the second oxidation stage due to a partial conversion to silica. The interface reaches a constant thickness of about 6.0 Å, which corresponds to the lower limit in experimental results. We also observe that molecular oxidation increases the surface roughness. A root-mean-square (RMS) roughness value of about 2.1 Å was found, whereas it was about 1.5 Å in the atomic oxidation case. This indicates that the interface is less abrupt in the molecular oxidation case. The Si-Si-Si and O-Si-O angle distributions show a peak at 110°, which is close to the experimental value. However, the Si-O-Si and Si-Si-O bond angle distributions indicate some defects, e.g., Si-O-Si triangular configurations (or Si epoxide linkages) exist in the c-Sila-SiO₂ interface, which can be explained by a physical stress-enhanced bond breaking mechanism. Finally, the interfacial stresses during oxidation were also investigated. In the interface, a compressive stress of about 2 GPa was found, which is in agreement with experimental evidence.

These results are of importance for the fabrication of silicabased devices with their ultrathin interface induced by hyperthermal oxidation at low temperatures in the micro- and nanoelectronics industry.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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The Journal of Physical Chemistry C

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