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## ► To cite this version:

Nicolas Salles, Nicolas Richard, Normand Mousseau, Anne Hémerlyck. Atomic scale investigation of local strain effect on the primary stages of silicon oxidation process using a coupling between Activation Relaxation Technique and first principles calculations . 11th edition of the SiO<sub>2</sub>, Advanced Dielectrics and related Devices symposium (SiO<sub>2</sub> 2016), Jun 2016, Nice, France. 2p. hal-01407843

**HAL Id: hal-01407843**

**<https://hal.science/hal-01407843>**

Submitted on 27 Mar 2017

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# Atomic scale investigation of local strain effect on the primary stages of silicon oxidation process using a coupling between Activation Relaxation Technique and first principles calculations

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Preference : Oral

Scientific topic: Basic mechanisms and modeling

## 1. Introduction

The SiO<sub>2</sub>/Si interface is still a crucial issue in silicon-based nanotechnology [1], since the electronic properties of achieved devices are directly dependent of the quality of this interface. In the context of extreme miniaturization, the control of nanoscale structure and defects formation during the elaboration process are thus major challenges for the microelectronics industry.

Despite lot of experimental and theoretical studies dedicated to the Si oxidation, the growth process and interfacial layer formation remains elusive because of the complex oxide growth as a characteristic crystalline/amorphous transition occurs. In recent studies [2,3], the interfacial strain appears as being at the origin of the Si atom emission, creating defect and reactive site, that could enhance the oxidation process.

In this paper, we focus on how the strain evolution drives the nanoscale mechanisms of the first steps of the oxidation process thanks to an atomic scale approach coupling Density Functional Theory Calculations and Activation Relaxation Technique-nouveau [4,5]. The adsorption of oxygen molecules on a fully oxidized surface and resulting interfacial strain is described. Further activation barriers of interfacial atomic diffusion are also discussed, as primary clues of amorphisation and defects formation.

## 2. Methodology

The SiO<sub>2</sub>/Si interface is modeled as a silicon substrate composed of 14 layers of 16 atoms, covered by oxygen atoms using an alternate 4-O and 6-O rings elementary pattern as shown on Figure 1 [6-8]. Three different surface configurations have been investigated: - a medium coverage (only one oxidized dimer row, (figure 1- configuration 1), - fully oxidized surface in a symmetric scheme (figure 1- configuration 2), - fully oxidized surface with an asymmetric alternated pattern (figure 1- configuration 3). At this coverage, only 6-O rings are reactive sites for a further adsorption of O<sub>2</sub> molecule. O<sub>2</sub> adsorption process, diffusion through the oxide layer, reaction at the interface and subsequent atomic oxygen diffusion are studied.

The adsorption process is performed thanks to a relaxation using DFT calculations as implemented in the VASP package [9,10].

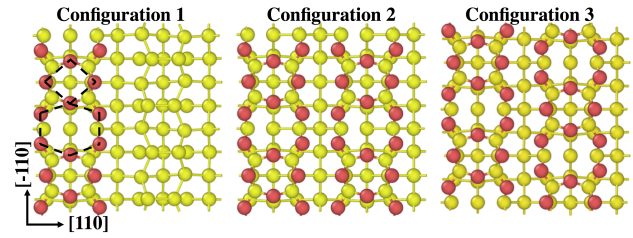


Figure 1: Three coverages of Si (001) surface by elementary pattern Si (001) surface oxidized, the medium coverage (configuration 1), symmetric coverage (configuration 2) and asymmetric coverage (configuration 3). The structure of oxide surface is formed by alternate of 4-O and 6-O rings indicate in black dashes.

For each adsorbed configuration, oxygen atomic diffusion is investigated using ARTn-VASP coupling. The Activation Relaxation Technique nouveau (ARTn) enables to explore the potential energy surface (PES) and to determine various transition states, i.e. the different possible configurations and their corresponding energy barriers. ARTn proceeds in three steps (see Figure 2) :

(1) From a local minimum energy, a sequence of random deformations is applied in order to leave the harmonic well. At each configuration, the structure is relaxed in the direction orthogonal to the deformation and the lowest eigenvalue of the Hessian matrix is calculated using Lanczos algorithm.

(2) Once a negative eigenvalue is found, the structure is pushed toward the corresponding eigenvector and relaxed in the orthogonal directions. This procedure forces the structure toward the nearest saddle point.

(3) When the saddle point is reached, the saddle configuration is pushed over the transition state and then completely relaxed to reach a new metastable configuration.

To fully exploit the efficiency of the ARTn method and to accurately take into account of the complex chemistry occurring during silicon oxidation process, the Hessian matrix construction is performed using total energy DFT calculations with VASP.

To quantify the strain energy of a given configuration, we used a simple empirical-potential model based on the formalism of Keating [11], which has been applied previously to study the SiO<sub>2</sub>/Si (001) interface [12,13]. This strain energy is estimated as:

$$E_{strain} = \frac{1}{2} \sum_i k_b (b_i - b_0)^2 + \frac{1}{2} \sum_i k_\theta (\cos \theta_{ij} - \cos \theta_0)^2 \quad (1)$$

where  $k_b$  (in eV/Å<sup>2</sup>) and  $k_\theta$  (in eV) are constants and refer to bond stretching and angle distortion respectively,  $b_i$  and  $b_0$  (in Å) are the length of  $i$ th bond and the equilibrium bond, and  $\theta_{ij}$  and  $\theta_0$  the angle between the  $i$ th and  $j$ th bonds and the equilibrium angle, respectively.

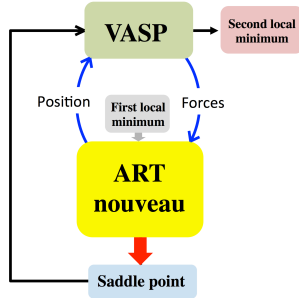


Figure 2: Algorithm of the VASP-ARTn coupling

### 3. Results

The strain in elementary pattern of oxidized surface locates on not oxidized silicon atom near the interface: silicon atoms beneath the 6-O ring are in state of tensile strain while those beneath the 4-O ring are in compressive strain. In this work, we observe that the local oxidized configuration on the surface has a deep impact on the oxygen molecule adsorption mode. This is linked to the fact that 6-O ring and 4-O ring lead to the different local strain: Indeed two facing 6-O rings in a symmetric pattern (Figure 1-conf. 2) will introduce a compressive strain in each other, while a 6-O ring facing a 4-O ring (Figure 1-conf. 3) has a tensile strain effect, in comparison with configuration 1 that has only one oxidized row. Depending on the initial strain configurations, different adsorption ways and resulting adsorbed configurations can be happened.

Even so, the first adsorption of dioxygen molecule on each surface oxidized configuration occurs in the same manner: a direct molecular penetration through the oxide layer, where molecular oxygen reaches the Si-Si bonds underneath the surface, dissociates and finally oxidizes the Si-Si bonds. This bonds oxidation permits to relax the tensile strain on Si underneath the 6-O ring and at the same time to widen the 6-O ring so that the oxidation start to impact the silicon atoms of channel. Then depending on the local oxidation and associated strain, the subsequent adsorption occurs depending on the 6-O rings adsorption site available on the surface: if oxygen molecule adsorbs in the same dimers row as in the first adsorption, the same molecular insertion adsorption process is observed. Whereas if adsorption occurs on the adjacent dimers row, here the local strain prevents penetration to occur. So we observe that as long as the oxidation progresses, the final configuration of dioxygen adsorption will depend on the strain state of reactive 6-O ring site, which are the pathways for the reactions.

In the final paper, we will also discuss the atomic oxygen diffusion mechanisms obtained with ARTn-VASP from the above adsorbed states, highlighting a great

diversity of final configurations and a wide spectrum of activation energies. For example, we observe that at this step of oxidation, atomic oxygen lateral diffusion at the interface is more favourable than deeper into the bulk. We also observe a progressive reconstruction of the silicon substrate at the SiO<sub>2</sub>/Si interface as Si-Si dimers are formed as long as the oxidation progresses, allowing to reduce the misfits at the interface. Activation barriers allow to identify kinetically favourable events for the oxidation progress.

The ARTn-VASP coupling appears as an original and powerful tool to highlight atomistic events encountered during silicon oxidation, even involving complex atomic modification appearing as key phenomenon toward silica amorphisation and defect generation at the SiO<sub>2</sub>/Si interface.

### Conclusion

Using an original atomic scale approach, we investigate the progression of the oxidation rate at the primary states of reaction with a specific focus on how strain effect affects adsorbed configurations and kinetics of local mechanisms. The compressive strain tends to prevent oxygen species penetration and favours the oxide swelling up. The tensile strain on the contrary favours the oxygen penetration in the sub-surface.

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