

## COUPLING THE DENSITY FUNCTIONAL THEORY AND THE ACTIVATION RELAXATION TECHNIQUE TO DEAL WITH COMPLEX ATOMISTIC EVENTS AT THE Si/SiO<sub>2</sub> INTERFACE

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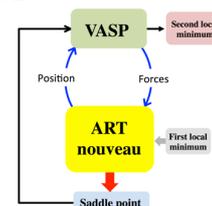
### CONTEXT

A conventional multi-levels modeling approach has been applied until then, where DFT calculations are used as input parameters for the parametrization of a kinetic Monte Carlo code developed in our team. But at our stage, i.e. from a fully oxidized surface of a silicon substrate identified in our previous studies [1], the space of atomistic configurations becomes too complex (abundance of diffusions, subjective choice due to human intervention) and consequently, DFT reaches its limits. To overcome this limitation, we use the Activation Relaxation Technique (ART) developed by Prof. Normand MOUSSEAU from Université de Montréal, Canada. This technique allows the automatized search of diffusion path in complex systems without the pre-knowledge of the arrival state [2].

### METHODOLOGICAL DEVELOPMENT: COUPLING DFT WITH ART METHOD

As ART uses traditionally empirical potentials, none empirical potential can well describe the chemistry at the Si/SiO<sub>2</sub> interface. A coupling between DFT code (here VASP) and ART was achieved, to keep the quantum precision to take into account correctly the tricky chemistry encountered in the case of the silicon oxidation, and notably to deal with specific event at the Si/SiO<sub>2</sub> interface.

Ce coupling is operational but appears to be highly expensive in terms of computational resources.



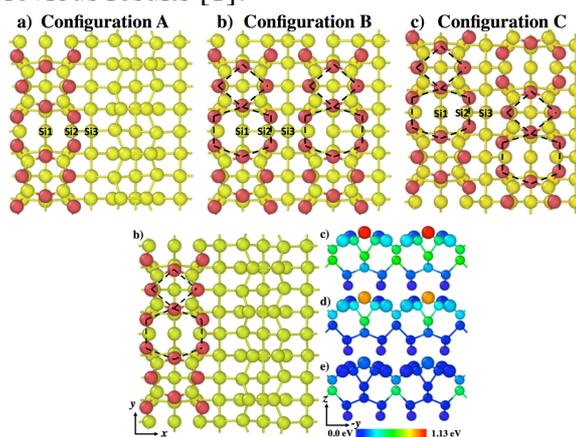
**ARTn-VASP coupling**  
doi: [10.1063/1.4996206](https://doi.org/10.1063/1.4996206)

### RESULTS

Different pre-oxidized surface structures have been considered to conduct our study. These structures have been built on the basis of our previous results [1].

We modeled partially (Configuration A) and fully (Configurations B and C) oxidized surfaces by using an elementary pattern that can be depicted as alternate 4-O atom and 6-O atom rings.

As the DFT methodology does not allow to determine the exact deformation of the electronic density around a given atom, the Keating's formalism [3] is used to evaluate the local strain associated with dioxygen adsorption and diffusion. On these modeled substrates, oxygen coverage is increasing by adsorbing one or several oxygen molecules.

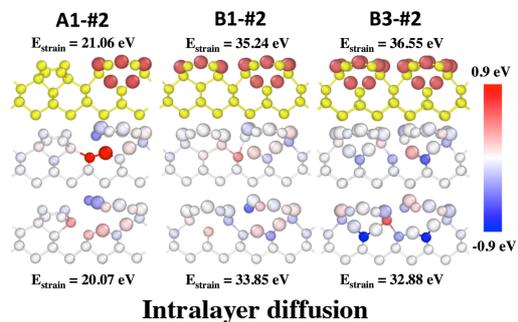


**Elementary pattern of 4-O atom and 6-O atom rings - Estimation of the strain energy using Keating's formalism.**

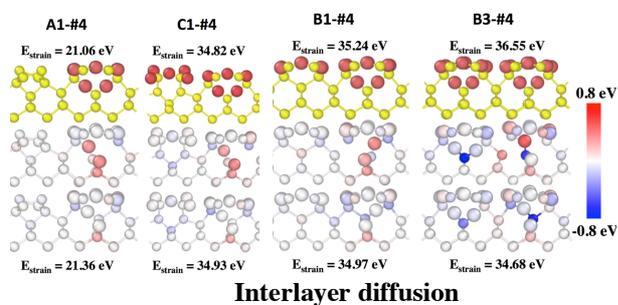
First obtained results using ARTn/DFT coupling exhibit progressive reconstructions of the Si/SiO<sub>2</sub> interface. New interesting diffusions are found enabling the propagation of the oxidation front following a layer-by-layer mode, as referred in the literature. Two diffusions are detailed below in terms of energetics as a function of the oxygen coverage:

- An oxygen diffusion below the oxidized surface as an intralayer diffusion (surface -1)
- An oxygen diffusion toward a deeper layer as an interlayer diffusion (surface -1 → surface-2)

The Figure on the right described the *intralayer diffusion* from configurations A1 and B1, with one more adsorbed oxygen molecule and B3 with three more adsorbed molecules (top = starting point). The saddle (middle), final configurations (bottom) and the strain energy are given. A progressive decrease of the activation energies for this diffusion is observed with the increasing coverage from 1.46 eV, 0.89 eV to 0.63 eV respectively.



Here, the energy gains are 0.87 eV, 0.50 eV et -0.28 eV respectively. Associated to the decrease of the activation energies, the diffusion becomes also energetically favorable, stabilizing the total energy of the system by releasing the accumulated strain energy (-1.00 eV, -1.40 eV and -3.67 eV, respectively).



The same trend is observed in the *interlayer diffusion*. When the strain energy increases from 21.06 eV in A1 to 34.29 eV, 35.24 eV and 36.55 eV in C1, B1, B3 respectively, the activation barrier decreases from 3.48 eV to 3.22 eV, 2.77 eV and 1.8 eV respectively. This favored diffusion with the growing strain energy is also accompanied by a stabilization of the final state (dE = 0.52 eV, 0.49 eV, 0.20 eV and 0.04 eV).

## CONCLUSIONS

As long as the oxygen coverage increases, the energy strain in the interfacial layer becomes so high that an atomic rearrangement becomes necessary to release the accumulated strain energy and reduce the local structural deformation. The local energy strain reduces thus the activation barriers, enhancing the diffusion and leading to a stabilization of the atomic system. The strain energy appears here as a catalyst for the atomic diffusion.

This study highlights a correlation between the energetics typical of an atomic diffusion (energy gains, and activation barriers) with the local strain energy i.e. the local atomic deformation and the oxygen coverage. This study demonstrates a logical approach of the layer-by-layer growth mode observed experimentally.

## REFERENCES

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