

Multi-scale modeling of oxygen molecule adsorption on a Si(100)- $p(2 \times 2)$ surface

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Abstract

The first steps of molecular oxygen adsorption and further incorporation on a Si(100)- $p(2 \times 2)$ surface are described here using density functional theory for the atomistic mechanisms. In this study, our aim is to combine this approach with kinetic Monte Carlo simulations to get an insight into the description of the oxide growth on silicon surface. We detail the reaction paths and corresponding energy barriers for the atomistic mechanisms: oxygen dissociation, adsorption and migration. We then explain how these data emanating from first principle calculations can be implemented in our kinetic Monte Carlo code OXCAD.

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1. Introduction

With the constant miniaturization of microelectronic devices in the integrated circuit industry, the silicon technology will reach its physical limitations within a few years. For instance, to obey the Moore's law, which is still a topical reference, the transistor gets close to the atomic scale, having the gate oxide layer below 2 nm thick. It has been proven that the gate thickness cannot be thinner than five atomic silicon layers which should be reached by 2012 without generating basic problems such as the leakage current, reliability, tunneling. Despite a large amount of experimental and theoretical studies [1–6], the oxide growth mechanisms are still unknown or subject to much controversy. Understanding the first steps of silicon oxidation remains essential to control the oxide growth and to anticipate the addition of further materials such as high- k materials. Recently, advanced characterization techniques –

infrared spectroscopy and scanning tunneling microscopy [7,8] – have demonstrated new insight into the atomic scale understanding of the early stage of the silicon oxidation. In particular, the presence of a specific transition state has been underlined and referred to as 'on-top position'.

In this paper, we present a theoretical attempt to simulate the early stage of silicon oxidation based on a multi-scale approach combining *ab initio* and kinetic Monte Carlo simulations. In the two following sections, we present fundamental *ab initio* calculation details and results used to investigate the energetic of oxygen molecule on (100) silicon substrates. The local properties of one oxygen molecule adsorption process, such as activation energies and atomic structures, are shown. Non-dissociative and dissociative chemisorption are discussed. Further, we introduce the 'on-top bond' incorporation process that is seen as an intermediate step for the dimer bond configuration formation. In Section 4, we discuss a list of events aimed at being implemented into the kinetic Monte Carlo (KMC) simulator code (OXCAD) allowing the complete simulation of the technological process under realistic

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experimental conditions. The way these data are filtered and implemented in the KMC code is detailed.

2. Calculation details

All *ab initio* calculations are performed with the program package VASP [9,10] within the density functional theory (DFT) using the generalized gradient approximation (GGA) and a plane wave basis sets expansion with an associated cutoff fixed at 475 eV, ultrasoft pseudopotentials [11]. Spin-polarization is taken into account to describe the triplet-to-singlet transition of the O₂ molecule during dissociation. All the atomic relaxations are performed using the conjugate gradient method. The Brillouin zone is sampled at the Γ point.

The Si(100)- $p(2 \times 2)$ surface is modeled as a Si₄₈H₁₆ periodic slab. The slab consists in six layers of eight silicon atoms exhibiting four dimer units on its surface, i.e. a $p(2 \times 2)$ reconstruction with a buckling along the dimer row and the buckling alternates along those rows [12,13]. This kind of silicon surface is one of the most stable reconstructed silicon surface and it is shown to be a realistic model of the clean Si(100) surface. The periodic supercell is defined with an inter-slab vacuum spacing of 10 Å. The lower surface atoms in the slab are saturated with 16 frozen hydrogen atoms. The two lowest silicon layers are kept fixed in order to simulate the bulk. All other layers, as well as the oxygen atoms, are allowed to relax. The energy barriers are calculated with the Nudged Elastic Band method [14,15].

3. Ab initio results

3.1. Oxidation reaction investigation

The driving idea of these calculations is to obtain a statistical landscape of the structural properties of the oxygen molecule adsorption reaction on a Si(100)- $p(2 \times 2)$ surface. To do so, we put the oxygen molecule above the different sites of the surface at the height of 4 Å. At this height, we verified that the interactions with the surface and the bottom of the cell are negligible. For the first step, the O₂ molecular axis is kept parallel to the surface. Then, we let the system relax. We bring down the molecule by step of 0.5 Å until the adsorption is performed. So, we test various initial positions and orientations of the oxygen molecule above the silicon surface to picture the favorable reaction sites. We have actually tested 16 different initial configurations, the characteristics of which are summarized in Table 1. The initial and final configurations, the energy gains and activation barriers are represented in Table 1. Among the 16 initial configurations of O₂ tested, we find mostly barrierless dissociative chemisorption processes with direct insertion into dimer bonds, or with non-inserted ‘on-top’ positions as referred in literature. In fact, only five negligible energetic barriers ranging from 0.02 eV to 0.1 eV have been obtained for five configurations out of 16 (see Table 1 – #5, 6, 7, 10, 15). The triplet state of the oxygen molecule is taken as reference for the calculation of adsorption energy. The adsorption energy of the different configurations, depending on the initial position and orientation of oxygen molecules, range from around 2 eV (non-fully

Table 1

Barriers and energy gains for each configuration during the adsorption process: adsorption above the dimer row (#1–2), above a single dimer (#3–7), between two dimers (#8–9), near a dimer silicon atom (#10–12) and in the channel (#13–16)

#	1	2	3	4	5	6	7	8
<i>E</i> Barrier (eV)	0	0	0	0	0.1	0.04	0.03	0
<i>E</i> Gain	1.72	6.67	3.22	3.23	3.23	2.07	2.21	2.08
Starting position								
Final position								
#	9	10	11	12	13	14	15	16
<i>E</i> Barrier (eV)	0	0.06	0	0	0	0	0.02	0
<i>E</i> Gain	4.9	1.95	2.23	2.13	2.26	2.3	2.15	2.11
Starting position								
Final position								

The size of the grey and black circles indicates the layer to which the silicon atoms belongs and the empty circles represent the oxygen atoms.

dissociative chemisorption such as #6,7 for example) to around 7 eV (dissociative chemisorption #2). In all tested configurations, we observe the spin conversion from the spin-triplet state to spin-singlet state as observed by Kato et al. [1] and by Fan et al. [6]. Among all the tested adsorption sites, we observe that the energy gain is larger when the molecule is completely dissociated on two different silicon sites and directly integrated into the surface, i.e. creation of Si–O–Si bonds: the most stable configuration corresponds to the two oxygen atoms in two adjacent dimers (#2). The preferential energetic position of the oxygen atom on a silicon surface is in a dimer bond. In fifteen configurations out of 16, we obtain a local minimum energy exhibiting on-top configurations (all except #2). However, this type of position is metastable since the dimer position is found to be the most stable one. This local minimum can be qualitatively explained by the presence of two dangling bonds per silicon atom on a (100) silicon surface. The $p(2 \times 2)$ surface reconstruction reduces the number of dangling bonds to one per silicon atom. Those remaining dangling bonds offer favorable adsorption sites to oxygen well above the (100) surface, i.e. well above the final dimer position. For a more quantitative explanation, we tried to evaluate the cross section for the reaction pathway through the on-top position. For this purpose, the oxygen molecule is slightly shifted from its original symmetrical position. An example of a such situation is shown in Fig. 1. Here, three shifted positions out of a total of 10 positions actually tested around the symmetrical position (#2) are shown. While the initial position (#2) leads to both oxygen atoms in dimer positions, the shifted initial configurations (see Fig. 1(i) #2a, #2b, #2c) lead to at least one oxygen atom in on-top position (see Fig. 1(ii) #2a', #2b', #2c'). The energy gains are 6 eV for #2a' and #2b', and 4.9 eV for #2c' all three reactions being barrierless.

The on-top configuration seems to be the most kinetically probable configuration but, energetically, it is only a metastable intermediate state during the oxidation. Therefore, the atoms in on-top positions would migrate towards more energetically favorable sites: dimers or backbonds.

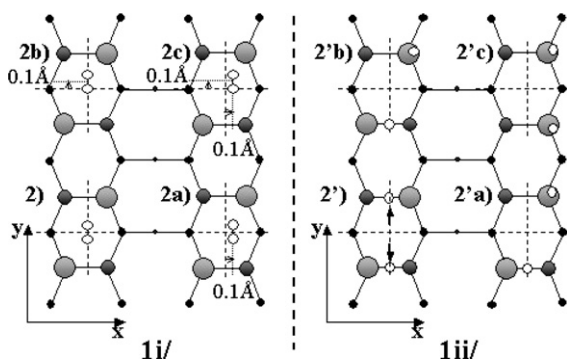


Fig. 1. Influence of a 0.1 Å displacement of the oxygen molecule away from the configuration #2 referred in Table 1 in any direction above the Si(100)- $p(2 \times 2)$ silicon surface. (i) represents the starting point, and (ii) the final configurations.

So, the whole adsorption reaction proceeds in two steps via this intermediate.

3.2. First oxygen atom diffusion into Si–Si bonds

A thorough examination of the energetic landscape around the local minimum, corresponding to the on-top oxygen atom, shows that the oxygen atom can diffuse towards three configurations inserted in dimer bond, in backbond, and in ‘bridge position’ as Si–O–Si between two adjacent dimers, perpendicularly to the dimer row.

The oxygen atom in the on-top position can be easily incorporated in the dimer bond with an activation energy of 0.11 eV and an energy gain of 1 eV. During the incorporation, the Si–Si dimer bond is broken in a first step, the oxygen atom being still in an on-top position, but weakly bond to a silicon atom. The oxygen atom moves to a ‘bridge position’ without forming real bonds with the silicon atoms. The gain in energy, during this step, is of 0.34 eV. In a second step, the Si–Si dimer bond is formed again, the oxygen atom remains quite far from both Si atoms (at 1.7 Å) and the Si–O–Si angle is small (84°). The gain is of 0.66 eV during this second step. The reaction path is shown in Fig. 2(a). The incorporation into a backbond has a higher activation energy of 0.38 eV compared to the dimer incorporation, whereas the energy gain is roughly the same (around 1 eV) (see Fig. 2(b)). The bridge structure is shown in Fig. 2(c). We can notice at first in Fig. 2(c), that the bridge structure is less stable than the on-top configuration, with a large activation barrier of 0.79 eV. That is why the bridge incorporation seems to be less probable compared to the dimer or backbond incorporations. Despite this fact, this position offers the best path for inter-dimer migration along the dimer rows.

These calculations show that the thermodynamically favorable incorporation of one oxygen atom occurs in Si–Si bond. Even if the incorporation of the on-top oxygen atom in the dimer seems easier than into the backbond, both mechanisms are frequent since the calculated barriers are small compared to the 2 eV obtained during the dissociative chemisorption (see Table 1). To conclude, we can assume that the incorporation occurs as well in the dimer row as in the backbond. Indeed, we point out the fact that the incorporation process is performed through two steps where an on-top intermediate is observed: we believe that this intermediate is one key issue to understand the formation of various species observed experimentally [8].

While the *ab initio* calculations are the most reliable ones for describing the complex system chemistry, direct comparison with experiments is limited by the time scale and the size of systems. Therefore, in the following, we suggest a kinetic Monte Carlo simulator as close as possible to the precision of quantum results as these results are used as input parameters to determine transition probabilities. The full set of *ab initio* data established above should allow us to get a satisfactory statistical description for the kinetic Monte Carlo events.

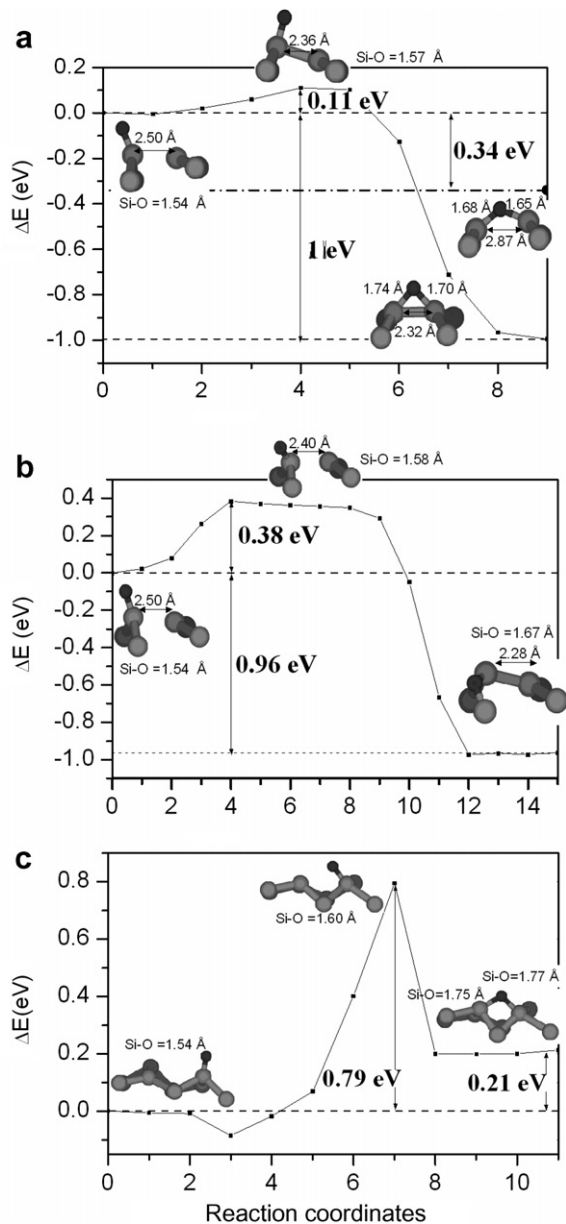


Fig. 2. On-top incorporation pathway in dimer bond (a), in backbond (b) and in the bridge position (c); black spheres correspond to O atoms and grey spheres indicate Si atoms.

4. Monte Carlo procedure

4.1. Introduction to OXCAD

Thus, another aspect of our work is to provide new tools for the simulation of the silicon oxidation process in realistic conditions in order to understand the kinetics of oxygen atom incorporation into the silicon substrate during the silicon oxide growth as a function of the experimental parameters (temperature, pressure). For this purpose, we have developed the OXCAD software package. This software is based on a time continuous kinetic Monte Carlo (KMC) technique: the events random drawing is governed by a minimum time having a realistic evolution. Therefore

the events occur one after the other. In the following, we describe the key points that need to be established to performed KMC, namely the lattice description, the temporal dynamics and the mechanisms implementation. The results obtained with OXCAD are not presented here and will be the subject of a future publication.

4.2. Lattice site description

The lattice description is necessary to allow an efficient treatment of the atomic movements as compared to traditional continuous trajectory (for instance through cartesian coordinates). In our case, as we restrict our study to the surface oxidation, our lattice corresponds to the silicon cubic lattice. Therefore, we build a grid to help us to locate the atoms following the *FCC-diamond* structure in which the bulk silicon crystallizes. In a systematic way, each silicon atom is defined on one crystal site. To investigate the oxygen atoms migrations on the surface, we should accurately know the local atomic arrangement. This is crucial if one wants to know which mechanisms: dissociation, adsorption or migration, are possible or not at each site. In order to determine if a chemical reaction is possible or not for a given site, we define its neighborhood. In our kinetic Monte Carlo simulator, the first, second, third and fourth neighbors of the silicon crystal structure are explicitly defined. Thus, each atom moves discretely from one predefined sites to another according to the transition probabilities.

4.3. Temporal dynamics

The general procedure is schematically described in Fig. 4. Starting from a clean silicon surface, reconstructed or not, a global surface scan (step 1 in Fig. 3) is run in order to establish which events are authorized at each site, following the landscape of the site and the nature of its bonds. Possible tested chemical reactions are selected among the list of events established from *ab initio* calculations with assistance of filters. The kinetic Monte Carlo simulator is able to check the required conditions for each mechanism to occur.

Each authorized event gets a probability according to the Arrhenius law, using activation barriers evaluated from

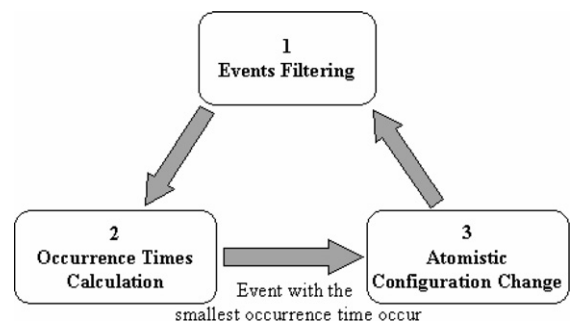


Fig. 3. Kinetic Monte Carlo master plan.

ab initio calculations, which serve as input parameters in the KMC package. Each event can also get a ‘typical time’ t (step 2 in Fig. 3) sampled with a random number to allow the simulations to be close to actual experiments.

As soon as the calendar of events is updated, the software finds the minimum ‘typical time’ among all authorized events and the corresponding event occurs. Then, the configuration changes (step 3 in Fig. 3) and another cycle can start again from this new configuration.

The kinetic Monte Carlo simulator should be able to treat events on the surface with millions of atoms, during few seconds of experiments.

4.4. Mechanisms implementation

The elementary mechanisms in any kinetic Monte Carlo procedure generally comes from literature data, *ab initio* results or the kinetic Monte Carlo itself. In the first version of our kinetic Monte Carlo simulator, we intend to restrict the choice of mechanisms to the field of our DFT results because the position of each surface or bulk atom had to be continuously known. Also, this KMC method can treat the oxygen atoms diffusions into the silicon substrate and study the charge transfer deduced from our previous *ab initio* calculations.

From the previous *ab initio* results described in Section 3, the barrierless dissociative chemisorption is adopted: the oxygen molecular bond is broken and the two oxygen atoms are dissociated onto one or two adjacent dimers in a on-top positions (see Fig. 4). This is the first event considered by our simulator: it simulates the arrival of oxygen molecules above the silicon surface and is driven by the Maxwell–Boltzmann statistics. The second mechanism is the incorporation of these ‘on-top bonds’ into the silicon substrate. The *ab initio* calculated energy barriers allow us to obtain the acceptance and the occurrence time of each incorporation into the dimer bond, in the backbond or in a bridge positioning based on the Arrhenius law. In this case, the input parameters for ΔE are the values of the above three activation barriers, respectively 0.11 eV, 0.38 eV and 0.79 eV. The back-reactions to return to the on-top position is also implemented in our simulator with a ΔE of

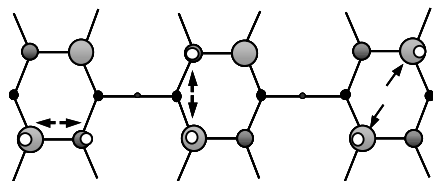


Fig. 4. Dissociative chemisorption taken into account in the kinetic Monte Carlo simulator OXCAD.

1.11 eV, 1.34 eV and 0.58 eV respectively from the dimer, the backbond and the bridge positions.

5. Conclusion

The DFT method is used to theoretically investigate the first steps of silicon oxide growth on the Si(100)- $p(2 \times 2)$ surface. From the *ab initio* calculations, we can assert that the adsorption processes occur via a dissociative chemisorption, even at low temperatures and on a clean Si surface without defects showing that the non-bridged oxygen is a stable structure and an intermediate during the silicon oxidation process. The on-top configuration is shown to be a metastable state configuration for oxygen migration and further incorporation into the silicon network. It is therefore a key precursor in the silicon oxidation process.

Ongoing research effort is dedicated to the oxygen incorporation process as well as the formation of the experimentally observed species. We show how these *ab initio* data can be further introduced into an atomic scale kinetic Monte Carlo level theory. Simulations on larger systems and over larger times scales will be performed with the help of the OXCAD package.

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