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Defect generation during silicon oxidation: A Kinetic Monte Carlo study

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ABSTRACT

We present a synthetic review of elementary chemical mechanisms source of the oxidation of pure silicon (100) surfaces. These mechanisms are then discussed from their ability to build a mesoscale model of the Kinetic Monte Carlo type dedicated to the process simulation of silicon thermal oxidation. We show that oxidation is driven by two main processes: (i) charge transfer arising from the formation of Si – O bonds in contact to pure silicon at the interface, (ii) destructive oxidation in which SiO building blocks rearrange at the interface to form a hexagonal-based oxide network directly in contact to cubic Si layers. Based on these considerations, simulations at the process scale exhibit epitaxial behavior within the interfacial domain. The resulting oxide layers are analyzed in terms of local to more extended defects. We observe two types of defects: (i) "intra-domain defects" which are related to local distortion of the elementary hexagonal oxide pattern Si_6O_6 (ii) "inter-domain defects", which are related to global oxide structural transitions from one orientation to another.

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1. Introduction

Silicon and its oxide remain at the heart of microelectronics industry after being at the source of one major technological breakthrough enabling massive production as well as miniaturization of the Metal Oxide Semiconductor Field Effect Transistors for more than 40 years. The remarkable properties of the Si/SiO_2 interface have allowed its scaling from the submicron down to the nanoscale in the frame of the Very Large Scale Integration technologies. Despite a huge mobilization of researchers and engineers throughout the years, the basic understanding of the oxidation of silicon is still facing major contradictions and difficulties including oxidation elementary chemistry, interface growth kinetics at early oxidation stages, and finally, detailed interface atomic arrangement. To date, there is still no model at the atomic scale of the technological process of oxidation. Moreover, the formation of defects in close relation with the experimental set up has never been simulated….

From its early technological developments, silicon oxidation has been accompanied with macroscopic types of phenomenological models more or less based on chemical rate equations to unravel oxidation growth kinetics as a function of processing conditions (partial pressures, temperatures…). The most famous and invariably quoted without contest is the "linear-parabolic" model of Deal and Grove based on oxygen diffusion through the oxide followed by reactions at the silicon/silicon dioxide interface [1]. Because of the original limitation of the model to predict the growth of films below 20 nm, a number of candidate models have been proposed and pushed beyond their macroscopic conceptual limits [2,3]. In the last two decades, the goal of reaching the atomic scale information has been helpfully enriched by the use of ab initio codes, quasi exclusively of the Density Functional Theory (DFT) type [4]. Interestingly, they made it possible to investigate a number of fundamental silicon oxidation issues on the characterization of local oxide defects of interest for the device operation [5–8] and on the silicon/silicon dioxide interface structural aspects through quantum-based molecular dynamics [9,10]. In this field, a number of articles have been dedicated to the study of the oxygen adsorption [11,12], active oxidation [13–15], oxygen diffusion modes [16,17] and more interestingly, oxygen incorporation into the silicon surface [18–21]. Recently Hemeryck and coworkers have shed light into the mechanisms of oxygen incorporation exhibiting non incorporated "strand-like" oxygen precursors before oxide nucleation under nominal oxygen coverage to arrive at a crystalline semi-hexagonal pattern onto cubic silicon [21]. This theoretical observation echoed a widely discussed experimental work of the late eighties in which a local ordered silicon dioxide was observed at the interface [22].

In the following sections, we show how this basic mechanistic knowledge can be translated into elementary events allowing a description of thermal oxidation of silicon through a Kinetic Monte

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Carlo (KMC) technique. This multi-scale approach is, to the best of our knowledge, the only existing opportunity to model the oxidation technological process at the atomic scale. As suggested in previous work [23] in which only surface mechanisms, i.e. surface migrations and dimer or backbond oxygen incorporation are mixed in the KMC approach, a partial ordering of the surface oxide is found through the extension of the oxide nucleus pattern discussed above upon oxygen agglomeration. In this paper, we provide additional interface mechanisms making it possible to address the simulation of the oxide growth toward the silicon bulk as a function of the experimental conditions. In Section 2, we describe our methodological approach and we detail atomistic mechanisms which serve as ingredients in our calculations. Simulation results related to the nature of defects generated in the oxide films are then reported and discussed in Section 3.

2. Materials and methods

In many cases, the multi-scale simulation is essential for understanding the formation of mesoscopic structures, from local atomistic ordering to global layer arrangement across time scale [24]. We have performed KMC simulations of dry oxidation of silicon on a 2D periodic cell composed of (100 × 100) atoms representing a (100) oriented silicon surface. Simulations have been performed under realistic experimental conditions, namely a substrate temperature T of 993 K and an oxygen partial pressure P_{O2} of 10 Pa. For more clarity and ease of expertise, the oxidation is artificially stopped after the oxidation of three silicon layers.

As described in [24], the main ingredients for the set up of our lattice-based KMC simulator are threefold: (i) crystallographic data to account for the lattice description, (ii) events that describe the oxidation process and (iii) the temporal dynamics sequencing the microscopic events.

It has been experimentally shown that the first atomic layers of the oxide films present the crystalline structure of the tridymite lattice [22]. Based on this assumption, a coincidence between the two lattices of silicon and tridymite has been found. Here, the [001] and the [010] axes of tridymite are aligned with [011] and [01-1] axes of Si(100) substrate. In this lattice based frame, all predefine sites of our KMC can be explicitly addressed as cubic silicon or hexagonal tridymite as these two lattices are superimposed. Therefore, the local mechanisms and associated chemistry decide if a specific lattice position turns to be either silicon dioxide, silicon or interstitial (or empty site). The main concern and originality of our present investigation is the implementation of new mechanisms allowing oxidation of the deep silicon layers, beyond already investigated surface oxidation processes [23].

As already pointed out above, quantum calculations have offered a real opportunity to elucidate atomistic mechanisms of silicon oxidation [9–21,23,24]. Despite this considerable research effort, the state of the art of silicon oxidation basic mechanisms remains limited to the understanding of the initial stage of oxidation: dissociation and incorporation of the first oxygen atoms into the silicon surface to form Si–O–Si bonds. The most remarkable property derived from these results is the inability of the oxygen atoms to be systematically integrated into Si–Si bonds between first neighbors of the silicon network. This basic assumption made it possible to describe surface oxidation limited to the formation of the first oxide monolayer [23]. Nucleation is shown to occur when the surface is exposed to nominal molecular oxygen coverage and results into oxide nuclei which are semi-hexagonal [21], involving atomic structures that are strongly distorted with respect to the initial pure silicon lattice. This observation implies that the crystalline to amorphous transition, as observed in SiO_2/Si films, is initiated in the very first stages of oxidation. Further oxidation toward the bulk necessitates other basic mechanisms which have not been revealed, to date, by DFT calculations. Despite this fact, indirect interpretation of older calculations [8,15,20] including results of an oxygen atom inserted into bulk Si, in addition to the preceding conclusions on surface oxidation allows us to consider some interfacial mechanisms to be introduced in our KMC model. These new mechanisms include: (i) molecular oxygen diffusion through the oxide, (ii) active oxidation, i.e. extraction of silicon atoms from their lattice position to generate SiO molecules as building blocks for the creation of the oxide network, this process is enhanced by the local presence of inserted oxygen atoms (charge transfer), (iii) generation of Si interstitials to account for the difference in Si concentration between bulk Si and SiO_2. According to these assumptions, a typical oxidation scenario can be described in terms of the following steps. This complex scenario is pictured in Fig. 1a and b: a. Surface oxidation: accounting for the dissociation of O_2 that does form a $(SiO)_i$ interstitial molecule through extraction of a surface Si atom, the second oxygen atom then reacts with the dangling bonds left or right after $(SiO)_i$ formation. $(SiO)_i$ then reacts with either the left Si dangling bond or the Si–O surface strand to end up with the formation of a Si–O–Si surface configuration. b. Subsurface/interface oxidation: because of subsurface Si–Si bond weakening after surface oxidation, a subsurface Si atom can be more easily extracted upon O_2 dissociation. In this process, at each SiO creation, a Si interstitial atom is also created. The upper part (initial surface) rearranges to form a trydimite network. Mobile and reactive SiO and O species can then drive the tridymite network growth within the interfacial region via an epitaxial type of growth. In their side, the created silicon atoms can migrate as interstitials toward the bulk and the interface.

Another important issue to be considered in the KMC model is the charge transfer mechanism. Charge transfers occur between silicon and oxygen atoms which are always negatively charged. This ionic character of oxygen depletes the neighboring Si–Si bonds. They are responsible for the local weakening of Si–Si bonds which are then easily oxidized in the presence of oxygen molecules. These effects have been identified in DFT calculations during the investigation of surface migration and agglomeration of oxygen atoms onto silicon [17]. In our KMC model, the activation barriers of the reaction mechanism described above is assumed to be environment dependent, in order to take charge transfers and bond weakening into account. This environment dependence is implemented by reducing the activation barrier of the reaction mechanism, at a given site, by the fraction of energies Q_O and Q_{DB} taken respectively, as a function of the presence of oxygen or dangling bonds on neighboring sites. Thus, on a given site, the overall elementary oxidation activation energy for reaction mechanism is given by the following expression:

$$E_a(react) = nV_{Si-Si} - \Delta z$$

where n is the number of Si–Si bonds on a given silicon network site to be broken through oxidation (n = 2 for Si surface atoms and n = 4 for the subsurface/bulk atoms), V_{Si-Si} is set to be 2.3 eV, the Si–Si bond energy of the Si crystal. Δz is a parameter which is adjusted to modulate the activation barrier for the mechanisms of reaction, as a function of the oxidative environment. In our KMC simulation, Δz has been parameterized in terms of Q_O and Q_{DB} as follows:

$$z = Q_{DB}.N_{DB}(site) + Q_O.N_O\ (\text{1st neighb.})$$

where N_{DB} (site) is the number of created dangling bonds in a given “site” of reaction, N_O (1st neighb.) is the number of bridging oxygen connected to the four first neighbors of the given reaction site. Q_O and Q_{DB} are adjusted, in our model, to be 1.5 eV and 2.0 eV respectively, in order to reproduce the layer-by-layer oxidation mode seen experimentally. All the other activation energies of mechanisms that occur on surface or in silicon bulk, described above, are adjusted to 0.07 eV, including reconstruction mechanisms associated with tridymite growth: SiO, O adsorptions, Si–O strand recombinations.

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