



Introducing densification mechanisms into the modelling of HfO₂ atomic layer deposition

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ABSTRACT

Density functional theory calculations are used to highlight some basics of the densification mechanisms arising during atomic layer deposition of HfO₂ onto silicon dioxide. The obtained results are discussed at the light of a multi-model approach that enables process simulation at the atomic scale via Kinetic Monte Carlo simulations. The impact of the proposed densification mechanisms on the growth is demonstrated. We show that a complete coverage is possible thanks to these mechanisms at a slow rate after that all surface reactive sites (OH sites) have been consumed by precursor molecules.

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1. Introduction

Nowadays, chemical vapor deposition processes are well-established techniques in which Atomic Layer Deposition (ALD) is found to be suitable for the slow and controlled growth of ultrathin, conformal films for the microelectronics industry [1,2]. Leaving the detailed processing conditions aside, a general but fundamental question that arises during growth is the necessary phase transition of the interesting materials from their molecular structure in the gas phase to their solid state structure in the deposited film. This is particularly true for metallic compounds such as metallic oxides. Indeed, in these cases, the metal has a covalent bonding structure, with a small coordination number when considered as a precursor in the gas phase, while at its end deposited ionic structure, it exhibits a large coordination number. The origin of these findings, which has been referred to as densification in the study by Dkhissi et al. [3] lies in the above structural phase transition. The case of HfO₂ layers, intended to be used in the first generation of high-k-based gate oxides in the future generation of MOS (Metal Oxide Semiconductor) transistors, constitutes a relevant example. It is worth noting that while an abundant literature is dedicated to precursor/surface physico-chemistry, particularly in the frame of ALD deposition techniques [4–12], the detailed understanding of

the densification mechanisms remains elusive and poorly treated [13]. The present paper aims at giving insight into the densification processes based on gas phase DFT calculations. The ALD process consists in trying to atomically control the growth by separating each of its steps. The film growth proceeds through self-terminating reactions on surfaces. The ALD process can be separated into two half-reactions; the first half-cycle reaction concerns the precursor gas exposure and the second half cycle is the oxidant precursor exposure. In the case of the ALD of HfO₂, the precursor molecules considered in the present study are HfCl₄ and water molecules respectively for the metallic and oxidant precursors. As compared to CVD, this technique prevents from gas phase reaction/densification since there is no contact between water and precursor molecules. So the densification is expected only in the specific context of each ALD cycle. Each exposure phase is separated by a purge phase using an inert gas to remove the remaining unreacted precursor molecules and unwanted reaction products. Actually, it has been experimentally observed that under usual ALD growth conditions, approximately ten cycles are needed to obtain the complete coverage of the initial substrate, suggesting a partial monolayer growth per cycle. Moreover, the density and the coordination number of the deposited oxide near the substrate surface are much lower than those in the bulk oxide, but increase with increasing the film thickness. In more general terms, growth of such an oxide on silicon is still not well understood for two main reasons: ALD growth is associated with complex physico-chemical mechanisms and it is strongly dependent on the deposition procedure, temperature conditions or preparation conditions of the substrate. In principle, a multiscale modelling strategy can provide

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the necessary link for answering questions associating local physico-chemical investigations and the deposition process. In this spirit, we have recently developed an approach combining DFT calculations for depicting local physico-chemical mechanisms, with a kinetic Monte-Carlo algorithm to simulate at the mesoscale the ALD experimental process of the growth of HfO_2 on silicon. To date, DFT investigations have been limited to simple precursor decomposition onto surfaces without any specific consideration of densification mechanisms. An empirical attempt to introduce such mechanisms have been proposed leading to some bottlenecks [14], notably in predicting the coordination increase during growth and the coverage versus ALD deposition cycles (resulting in a saturation of the coverage limited to 73% and the crystallinity limited to 62% after 10 ALD cycles). In the following, we perform gas phase DFT calculations to open a preliminary window into densification mechanisms. From these results, densification mechanisms are implemented, discussed at the KMC level and their impact is evaluated on the coverage versus ALD cycles results. We demonstrate that densification mechanisms allow to predict basic experimental observations.

2. Computational details

All the calculations are performed using the Gaussian03 package [15] within the frame of the density functional theory, using the gradient corrected PBE functional [16]. Oxygen, hydrogen and silicon are described with the triple zeta augmented with a polarization function, respectively d and p, TZVP basis set [17]. Hafnium [Kr], 4d10,4f14 core is replaced with a pseudo-potential [18] and valence electrons were described with a (8s, 7p, 6d)/[6s, 5p, 3d] basis set [19]. All the stationary points are checked to be real minima thanks to the determination of the vibration frequencies; this allows us to correct the binding energies of the zero point vibrational energy. Finally, the Basis Set Superposition Error (BSSE) is corrected by the Boys and Bernardi counterpoise scheme [20]. All Kinetic Monte Carlo calculations are performed with the HIKAD code developed in our team [3,21]. Basic KMC simulations here presented are performed on 20×20 atoms for the substrate modelling with periodic boundary conditions in order to mimic an infinite substrate.

3. Results and discussion

3.1. DFT investigation

In order to get further insights into the densification mechanisms, we propose a preliminary approach in which surface densification mechanisms are extrapolated from gas phase reactions. The idea is to extract the local chemical part of these mechanisms from their intrinsic collective behavior. Such an approximation has already been proposed and validated for more conventional mechanisms of the ALD. Hydroxylated metal $\text{M}(\text{OH})_x$ has been used to study the chemical reactions within deposition of metal oxide and the energetic oscillations induced by the size effect. For the deposition of $\text{Al}(\text{CH}_3)_3$ on $\text{Al}(\text{OH})$ site, an oscillation of around ~ 0.1 eV with the cluster size has been observed by Widjaja [23] and Heyman [24]. In addition, many studies for the deposition of molecules on silicon oxide have examined the size effect of the cluster and showed that oscillations are negligible [25–28].

In this frame, $\text{M}(\text{OH})_3\text{-OH}$ cluster is seen as a surface model after hydrolysis. Two reacting species are considered on this model surface: HfCl_4 and $\text{Hf}(\text{OH})_4$. These two systems allow us to address densification in each ALD cycle, respectively during precursor and oxidant exposures. The energy diagrams along the reaction path are presented in Fig. 1. Nevertheless, once validated through the complete multi-scale methodology, a more precise view of these mechanisms will be reassessed using more advanced DFT calculations. In this spirit, we have studied for a future publication, the adsorption mechanism of HfCl_4 on HfOH

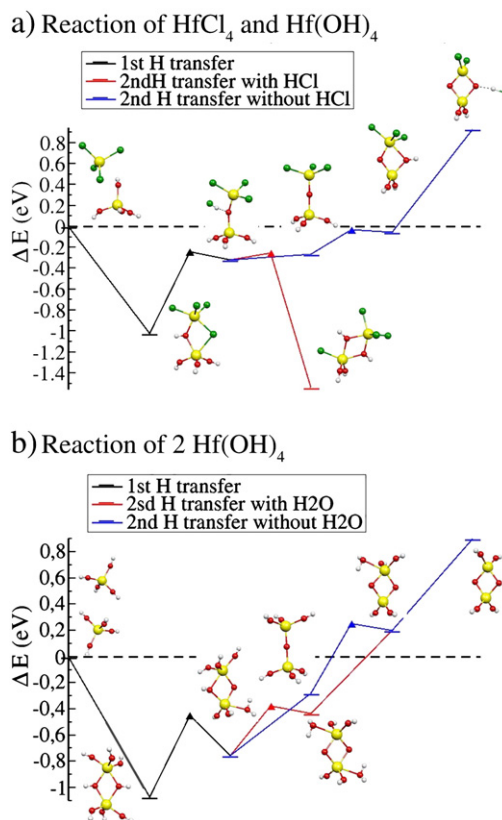


Fig. 1. Precursor dimerization, including H transfer from OH bridges. Black curve is 1st H transfer, blue curve is 2nd H transfer with HCl physisorbed and red curve is 2nd H transfer without HCl physisorbed. Hf is yellow balls, Chlorine green balls, oxygen red balls and hydrogen white balls.

substrate by using a bigger cluster ($\text{Si}_9\text{O}_6\text{H}_{12}\text{Hf}(\text{OH})_2$). These initial calculations confirm an oscillation for the adsorption energy of 0.1 eV (calculations not shown). We can then, consider $\text{M}(\text{OH})_3\text{-OH}$ acceptable in a first approximation.

First of all, we consider a typical precursor surface interaction through $\text{HfCl}_4/\text{Hf}(\text{OH})_4$ as pictured in Fig. 1a. The initial deposition step is endothermic and leads to the formation of a strand or tree like complex on the surface (see black curve) as already known from the literature. Then, densifying this complex can be operated in two different ways. The red curve indicates an exothermic path in which a Cl atom is exchanged between the precursor molecule and the model surface. This almost barrierless exothermic path can be seen as a source for Chlorine contamination of the substrate. However, the endothermic path indicated in blue where a hydroxyl group of the surface can be bonded to the precursor leading to a double bridging oxygen of the deposited Hafnium atom. This process is characterized by two activation barriers (0.24 and 0.99 eV) to arrive at the de-hydrogenation of the bridging oxygen.

Along the same line, we now investigate the interaction of $\text{Hf}(\text{OH})_4$ (Fig. 1b). Our calculation that demonstrates a barrierless pathways is responsible for a spontaneous dimerization (<0.05 eV activation) giving rise to two bridging oxygen atoms having both one hydrogen atom. This process is exothermic (-1.07 eV), similarly to the case of the dimerisation reaction of HfCl_4 and $\text{Hf}(\text{OH})_4$ (-1.01 eV). In these two dimerization cases, we observe 2 ligands bridging the 2Hf atoms leading to pentacoordinated metal centers. This can be viewed as a first step toward the cubic HfO_2 crystalline structure since the same symmetries can be found in crystalline oxide as previously defined as a densification process [22]. This observation is of technological

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