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Editorial

Chemistry and physics of metal oxide nanostructures
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Papers

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Rainer Ostermann, Sébastien Salillard and Bernd M. Smarsly, Phys. Chem. Chem. Phys., 2009
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Surprisingly high, bulk liquid-like mobility of silica-confined ionic liquids
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Fabrication of highly ordered, macroporous Na$_2$W$_4$O$_{13}$ arrays by spray pyrolysis using polystyrene colloidal crystals as templates
DOI: 10.1039/b821389p

Nanoporous Ni–Ce$_{0.8}$Gd$_{0.2}$O$_{1.9-x}$ thin film cermet SOFC anodes prepared by pulsed laser deposition
DOI: 10.1039/b821473e

Surface chemistry of carbon-templated mesoporous aluminas
Thomas Onfroy, Wen-Cui Li, Ferdi Schüth and Helmut Knözinger, Phys. Chem. Chem. Phys., 2009
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ZnO@Co hybrid nanotube arrays growth from electrochemical deposition: structural, optical, photocatalytic and magnetic properties
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Electrochemistry of LiMn$_2$O$_4$ nanoparticles made by flame spray pyrolysis
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Ligand dynamics on the surface of zirconium oxo clusters
DOI: 10.1039/b820731c
Thin-walled Er\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3} nanotubes showing up-converted fluorescence
DOI: [10.1039/b821304f](http://dx.doi.org/10.1039/b821304f)

Wettability conversion of colloidal TiO\textsubscript{2} nanocrystal thin films with UV-switchable hydrophilicity
DOI: [10.1039/b823331d](http://dx.doi.org/10.1039/b823331d)

Nucleation and growth of atomic layer deposition of HfO\textsubscript{2} gate dielectric layers on silicon oxide: a multiscale modelling investigation
DOI: [10.1039/b821502b](http://dx.doi.org/10.1039/b821502b)

Designing meso- and macropore architectures in hybrid organic–inorganic membranes by combining surfactant and breath figure templating (BFT)
DOI: [10.1039/b821506e](http://dx.doi.org/10.1039/b821506e)

The controlled deposition of metal oxides onto carbon nanotubes by atomic layer deposition: examples and a case study on the application of V,O\textsubscript{4} coated nanotubes in gas sensing
DOI: [10.1039/b821555c](http://dx.doi.org/10.1039/b821555c)

In situ investigation of molecular kinetics and particle formation of water-dispersible titania nanocrystals
DOI: [10.1039/b821973g](http://dx.doi.org/10.1039/b821973g)

Chemoresistive sensing of light alkanes with SnO\textsubscript{2} nanocrystals: a DFT-based insight
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Nucleation and growth of atomic layer deposition of HfO$_2$ gate dielectric layers on silicon oxide: a multiscale modelling investigation

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We apply our recently developed approach, combining advanced ab initio density functional theory (DFT) methods with a probabilistic kinetic Monte Carlo (KMC) scheme, to quantify the properties of mesoscopic size systems operating in real experimental conditions. The application concerns the investigation of the atomic layer deposition (ALD) of HfO$_2$ film growth on Si(100) surface. We show that the proposed models offer guidance in the optimization of the experimental deposition processes, in terms of OH density on the substrate, optimal growth temperature, pulse durations, and finally growth kinetics.

I. Introduction

The reduction of the SiO$_2$ gate oxide thickness in accordance with Moore’s law has led to unacceptable tunnelling and leakage current levels. So, the conventional SiO$_2$ gate is reaching its physical and electrical limitations. The search for suitable candidates to replace SiO$_2$ as the gate dielectric in complementary metal-oxide-semiconductor (CMOS) devices has recently received enormous attention. Of the many different materials with high dielectric constant $k$, which have been used as SiO$_2$ replacements,$^2$ hafnium oxide (HfO$_2$) is one of the most promising candidates. HfO$_2$ is attractive as it exhibits a bulk permittivity of almost 25, a wide band gap (5.68 eV) and a good thermodynamic stability in contact with silicon.$^3$ However, experimentally the EOT (equivalent oxide thickness) value of the HfO$_2$ gate stack increases, due to the growth of an interfacial layer between HfO$_2$ and the silicon substrate. Among various methods for growing high-$k$ dielectric films, atomic layer deposition (ALD) shows its unique ability in depositing ultra thin films with excellent conformity and uniformity over large areas.$^4$ ALD, which is a vapour deposition technique, is based on the cycling of self-terminating surface reactions. Indeed, each precursor is pulsed into the reaction chamber alternately, and the reaction between the incoming precursors and surface species is self-terminating. Thus atomic level control of film growth is supposed to be achieved. Experimentally, ALD has been actively investigated for depositing HfO$_2$$^{5-21}$ for which HfCl$_4$ and H$_2$O are often used as precursors.$^{22-24}$ In practice, the density of metal atoms deposited per cycle depends on the temperature, on the chemical nature of the precursors used and on the density of reactive sites available on the substrate surface. Thus, it is desired to reach full monolayer coverage at each cycle. However, Ritala et al.$^{22}$ found that only a sub-monolayer of the HfO$_2$ film is deposited during each cycle. About seven deposition cycles would be needed to entirely cover the surface$^{25}$ which then shows a non-negligible roughness. ALD growth resulting in only partial monolayer growth per cycle is due to the steric hindrance$^{26,27}$ or to the lack of reactive sites.$^{28}$ Therefore, a detailed understanding of the basic mechanisms that take place during each cycle is required if one wants to optimize the deposition. This is especially true for the few first deposited layers which are of major importance for subsequent electrical properties.

These basic atomistic mechanisms include the decomposition of HfCl$_4$ on the substrate and the further hydrolysis of the resulting SiO$_2$–O–HfCl$_3$ surface complex, but many other reactions, called “densification mechanisms” hereafter, are also involved in the process. To design optimal experimental setups in future, it is of great importance that a precise atomic level description of the basic reaction mechanisms responsible for the overall process of high-$k$ film growth, and also their relation with the thermodynamic parameters be established. Our final aim, towards this objective, is to achieve the ambitious task of elaborating a new generation of tools dedicated to atomic scale simulation of technological process. Our strategy is to combine the ab initio DFT with kinetic Monte-Carlo techniques into a multiscale approach, which will incorporate enough reaction mechanisms to be adequate for testing against experimental setups. Kinetic Monte Carlo (KMC) is a suitable procedure that can be of great help to understand mesoscopic level processes, such as deposition of high-$k$ materials.

This paper is dedicated to the application of our KMC tool, enabling the treatment of HfO$_2$ ALD from HfCl$_4$ and H$_2$O precursors at the atomic scale. In particular, we present the results concerning the following points (i) the influence of the substrate preparation on the coverage of the surface, (ii) an optimal growth temperature, since it is found experimentally that HfCl$_4$/H$_2$O ALD of HfO$_2$ has a broad process window with respect to deposition temperature, between 180 and 600 °C, (iii) surface coverage saturation and (iv) growth kinetics in different regimes.

Section II is devoted to the description of DFT and KMC theoretical approaches. Different basic mechanisms used in KMC simulations are also briefly listed in this section, with an emphasis on densification mechanisms. Section III gathers
**II. Theoretical approaches**

Recently we have developed an original approach within a multiscale strategy \(^{29}\) to simulate the growth of HfO\(_2\) on silicon. In particular, we have shown how this method provides a unique and fundamental understanding of the growth mechanism and growth kinetics. KMC is a stochastic-based model aimed at simulating film growth at the atomic scale, the final objective being to furnish alternative/new tools for replacement of the macroscopic conventional TCAD (Technology Computer Aided Design) tools used for years by engineers in microelectronics. Such a model performs virtually the explicit experimental-processing procedure, atomic-scale event by atomic-scale event. The algorithm is operated through probabilistic rules that make the overall simulation comparable with an actual experiment.\(^{30,31}\) Indeed, from the engineering point of view, the main interest is in the microstructure that is produced under specific processing conditions. This microstructure involves millions of atoms processed during periods exceeding the second. Unfortunately, the most predictive models, *i.e.* the quantum-based models, are not tractable at this scale. Two options can be further considered: molecular dynamics (MD) and kinetic Monte Carlo (KMC). MD solves the Newton equations of motion for the system of atoms under investigation. Trajectories are continuous and necessitate very short integration time steps that make the simulation cumbersome for durations that are orders of magnitude higher than nanosecond. Another drawback of the MD method is the general lack of adequate inter-atomic potentials for highly disordered and heterogeneous systems. This is particularly true for microelectronics semiconductor/oxide interfaces such as silicon/high-K gate oxides. KMC appears to be a simplification compared to MD: continuous trajectories are replaced with discrete atomic jumps. A prior knowledge of these hoppings is needed and must be listed from any other source: quantum-based models or experimental characterization. Thus, KMC methods allow the simulation of more ambitious systems in terms of size and duration of the simulated experiment, meeting the requirements of the next generation of processes in microelectronics.

Basic ingredients needed to develop what we call a lattice-based KMC model are: (i) we will define a lattice framework able to operate the desired transition between the silicon cubic structure and the oxide crystal, (ii) we detail the writing of configurations that allow the association of the lattice sites with the chemical nature of atoms occupying them, (iii) we introduce the concept of event that must describe correctly the chemistry of the process, and (iv) we finally indicate how to deal with the time evolution of the KMC, namely, the temporal dynamics of the KMC.

### II.1 Coincidence lattice model

In order to define atomic positions in our KMC model, we have to consider a two-dimensional lattice at the interface between the two materials. Different atoms are placed within the 2D lattice at different heights corresponding to the successive layers. We should emphasize that, in our KMC view, atomic positions are not defined by accurate Cartesian coordinates, but only specified approximately around an equilibrium position within a cell. This view allows displacements of atoms to satisfy elastic strain usually present in heterogeneous systems. To represent the above 2D lattice, we superimpose the conventional cubic cell of oxide and the silicon-based SiO\(_2\) surface in order to find a coincidence between the two crystallographic arrangements. The silicon (100) surface is taken as the crystal reference, an ultrathin silicon dioxide, one atomic layer thick, being able to accommodate this structure perfectly. We obtain the schematic configuration represented in Fig. 1. This resulting picture optimizes the coincidence between the two materials. The silicon part contains two layers in order to show the orientation of the bonds at the interface. Siloxanes bridges and hydroxyl functions are represented as an indication. For sake of clarity, we do not represent the dimer formation inducing Si–O–Si species: silicon atoms are schematically located at the nodes of the crystal lattice of the diamond structure, without taking into account the displacements observed usually. According to the crystallographic data,\(^{32}\) the distance separating two Si surface atoms is 3.84 Å. In addition, if one considers that the cubic lattice parameter of hafnium is approximately 5 Å, the distance separating two Hf atoms represents the half diagonal of the base of the cube, approximately 3.5 Å. It thus appears possible to match the two structures, with a tension of the cubic hafnia.

Let us imagine now that we position several HfO\(_2\) cubes in tension on the substrate, looking for an ideal match of the two 2D lattices. We see that a tilt of the cell is required to obtain a complete match of the atomic positions. It is then possible to completely cover the surface without defect: we obtain three perfectly crystalline layers of HfO\(_2\) on Si/SiO\(_2\). It is, to some extent what we would like to obtain in real experiments. Fig. 1 is a top view of this ideal configuration where the various species are represented by symbols for a better legibility. It represents a (100) silicon surface, covered by single-crystal HfO\(_2\) in its cubic phase. The square base of a conventional cubic cell is represented in dotted line: it locates five hafnium atoms: the four corners of the square and the central atom in (100) surface is taken as the crystal reference, an ultrathin silicon dioxide, one atomic layer thick, being able to accommodate this structure perfectly. We obtain the schematic configuration represented in Fig. 1. This resulting picture optimizes the coincidence between the two materials. The silicon part contains two layers in order to show the orientation of the bonds at the interface. Siloxanes bridges and hydroxyl functions are represented as an indication. For sake of clarity, we do not represent the dimer formation inducing Si–O–Si species: silicon atoms are schematically located at the nodes of the crystal lattice of the diamond structure, without taking into account the displacements observed usually. According to the crystallographic data,\(^{32}\) the distance separating two Si surface atoms is 3.84 Å. In addition, if one considers that the cubic lattice parameter of hafnium is approximately 5 Å, the distance separating two Hf atoms represents the half diagonal of the base of the cube, approximately 3.5 Å. It thus appears possible to match the two structures, with a tension of the cubic hafnia.

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lattice, on the basis of its cubic phase, on a silicon (100) surface. It contains preset sites being able to accommodate the various atoms constitutive of the system.

II.2 KMC temporal dynamics

Kinetic Monte Carlo approaches differ from static Monte Carlo techniques by the introduction of time. Most of the usual Monte Carlo procedures in condensed matter physics are static (Metropolis algorithm for instance) and their interest concern the equilibrium structure properties. In KMC, stochastic aspects are introduced through the use of random numbers, sampled according to an Arrhenius probability law, rather than using direct sampling, with uniformly distributed random numbers. The result of this procedure is that chemical

Fig. 1 Hafnia cubic lattice deposited on the Si/SiO₂ substrate, functionalized with hydroxyls groups (left side). Top view of the ideal configuration (right side). HfO₂ cubic cells are matched to the substrate through a coincidence lattice and different types of atoms are positioned in the cell.

Fig. 2 Substrate initialization with randomly distributed siloxanes.
aspects are respected, but the most probable events do not necessarily occur first. Different algorithms do exist for KMC. In the following, we suggest a procedure that becomes efficient, in comparison with the more conventional BKL (Bortz, Kalos and Lebowitz) algorithm, when dealing with many different types of events having different probabilities. This is the case of systems where local deformation energy is taken into account for the evaluation of the occurrence probabilities, or where the system exhibits a complex chemistry. It should be emphasized here that, in our KMC procedure, an event is defined as elementary mechanism occurring at a specific site.

When the software is launched, after preliminary initializations (parameters, mechanisms, neighborhood, configuration), it makes a global scan to determine which events are authorized and which are forbidden. Forbidden ones get a maximum time so that they can never occur. Authorized ones get a “specific occurrence time”: this is the time that the considered event typically takes to occur as soon as it becomes possible. The “specific occurrence time” of the event $m$ on site $(i,j,k)$ is given by

$$T_{i,j,k,m} = -\frac{\log(Z)}{\lambda_m}$$

with

$$\lambda_m = \nu \exp\left(-\frac{\Delta E_m}{k_B T}\right)$$

where $Z$ is a random number uniformly distributed between 0 and 1, $\lambda_m$ is the probability of occurrence of the mechanism per unit of time, $\nu$ is the attempt frequency, in the order of the typical lattice vibration frequency, $\Delta E_m$ the activation energy of the mechanism, $k_B$ the Boltzmann constant and $T$ the temperature. The two arrival mechanisms (1-precursor arrival and 2-water arrival) obey Maxwell–Boltzmann statistics:

$$\lambda_{1,2} = \frac{c PS}{\sqrt{M_{1,2} T}}$$

where $c$ is a constant, $P$ the pressure, $S$ the elementary 2D-cell area, $M_{1,2}$ the considered species molar mass and $T$ the temperature. Going back to the definition of events, it becomes obvious that different “specific occurrence times” are attributed to a given elementary mechanism occurring at different sites if the deposited layer. Following this procedure, we determine a huge list of “specific times”, a kind of “calendar”, just as if all events that will occur were already foreseen. Not exactly in fact, because this calendar will often be updated as the configuration evolves. As soon as the calendar is updated, the software finds the minimum “specific occurrence time” and the corresponding event occurs. As this minimum time has passed, it is withdrawn from the other times contained in the “calendar”; a new configuration is edited; pertinent events that are likely to become possible are added to the list and the forbidden ones withdrawn from the list. We then go back to the first KMC stage and search again the minimum time.

II.3 KMC application to ALD

The KMC software discussed here is built in order to simulate the ALD experimental process. ALD consists of several cycles, each one composed of four phases: precursor pulse, precursor purge, hydrolysis and water purge. Each phase has its own thermodynamic parameters and duration: some mechanisms are always possible whereas others can only occur in a typical phase. For instance, “Precursor arrival” will obviously exist during the first phase only.

The basic chemical reactions involved in ALD process are the incorporation of the precursors, followed by the formation of the HCl by product, and the hydrolysis of the chlorine terminated bonds of the incorporated precursor. Each of the above global reactions can be decomposed into several steps, called “elementary mechanisms” in our KLC approach. The thermodynamic characteristics of these “elementary mechanisms”: reaction enthalpy and activation barrier, have been determined by ab initio calculations and presented in section III. Obviously, all implemented mechanisms are assumed to be reversible, with probabilities defined by the reverse activation barriers, via the Arrhenius law.

In addition to the above basic mechanisms of ALD, we have also implemented, in our KMC model, less straightforward mechanisms, involved in the ALD of high-k materials, which we call “Densification mechanisms”. Densification is defined here as the necessary phase transition of the high-k metal oxide materials from their molecular structure in the gas-phase precursors, to their solid-state structure in the deposited film. This is particularly true in the ALD deposition of HfO2 where the metal has a covalent bonding structure in the gas phase, with a small coordination number in its precursor form, whereas the metal oxide has mainly an ionic structure, with a large coordination number, in the deposited film. This transition is mediated by the presence of oxygen atoms: densification could occur in the gas-phase in the presence of pre-oxidized precursors. We have also shown that densification can be seen as a local phenomenon where, during bridging of two metallic centres, a local re-allocation of the oxygen atoms occurs.

Therefore, densification mechanisms in the kinetic Monte Carlo account for all transitions from molecular state to ionic or crystalline states, i.e. nodes of the lattice. These include reaction between grafted molecular ligand and the surface, such as the bridging process of eqn (1), but also during bridging between two grafted molecules in tree-like positions.

$$\text{Si–O–HfCl}_3 + \text{Si–OH} \rightarrow \text{Si–O–HfCl}_2–\text{O–Si} + \text{HCl}$$

The by-product is usually HCl (when bridging a Cl-terminated tree to an OH-terminated tree) or H2O (when bridging two OH-terminated trees).

III. Results and discussion

III.1 Ab initio results

The aim of ab initio investigations is to understand the chemistry of possible reactions, during the first cycles of ALD of HfO2. The related predictive method, cluster- or periodic-based DFT, is particularly suitable for chemical mechanisms that are difficult to reach by experiments or other modelling strategies.
The reactions between the gaseous precursors HfCl₄ and H₂O with the hydroxylated SiO₂ surface are predicted to proceed via an exchange mechanism 

\[ \|\text{SiO}_2-\text{OH} + \text{HfCl}_4 \| \rightarrow \|\text{SiO}_2-\text{HfCl}_3 + \text{HCl}, \]  

This first half-cycle reaction is itself decomposed into three elementary reversible mechanisms: (i) chemisorption of the precursor molecule and its possible desorption, (ii) incorporation of the chemisorbed molecule and the formation of HCl by product, and (iii) desorption of HCl which leads to the definite incorporation of the metal atom. The decomposition of a global reaction into several elementary mechanisms allows the detailed examination of the incorporation process rather than the use of global sticking coefficients.

This second half cycle reaction [eqn (3)] is water exposure leading to the hydrolysis of Cl-terminated bonds:

\[ \|\text{SiO}_2-\text{O}-\text{Hf(OH)}_4-x-\text{Cl}_x+x-1 \| + \text{H}_2\text{O} \rightarrow \|\text{SiO}_2-\text{O}-\text{Hf(OH)}_3-x-\text{Cl}_x-x-1 \| + \text{HCl}, \]  

where \( x \) has values of 1–3.

This second half cycle reaction is also decomposed into two elementary mechanisms: (i) chemisorption of H₂O and (ii) definite hydrolysis. We have shown that the characteristics of both mechanisms depend on the value of \( x \).

We have studied these reactions in detail using DFT cluster models. Results are published in our recent papers, reported here in Table 1 and implemented in our KMC package. Values reported in Table 1 concern direct reaction characteristics: reaction enthalpies and activation barriers. The characteristics of reverse reactions can be easily deduced from the reported values.

### III.2 Kinetic Monte Carlo (KMC) results

#### A First cycle results

The starting surface is known to play a crucial role at all stages of the device development and operation. The first ALD cycle, i.e. precursor–substrate interaction, is governed by the specificity of the surface cleaning processes and subsequent presence of nucleation sites. Therefore, we start by investigating the dependence of the surface coverage on the density of OH nucleation sites on the substrate. Surfaces functionalized with hydroxyl groups can be prepared in various ways and allow a variable concentration of sites for incorporating the precursors. We thus simulated a first ALD phase with a long duration: 100 ms against 50 ms generally used in experiments, at 300 °C with different starting substrates covered with 0%, 25%, 75% and 100% OH, distributed arbitrarily (Fig. 2). Such a long time is required to overcome the poor sticking of the precursors and to saturate efficiently the reactive sites. For a fifth case, we used the option of initialization “no more than one OH by dimer” which leads to 47% hydroxyl coverage.

The resulting coverage rates are represented in Table 2. An increase in the total coverage is observed when one increases the number of reactive sites of the substrate. In the case 4, it can be noted that the total coverage amounts to approximately 55%, indicating that a majority of hafnium atoms are thus bridged consuming each one two OH: one for the incorporation and a second for the bridging process.

Experimentally, at the end of the first ALD cycle at 300 °C, a total coverage of 33% was measured, which is in good agreement with our simulations with 50% and 47% OH coverages. On the other hand, Zhuravlev’s results confirm the 50% OH coverage of SiO₂ surfaces at 300 °C (see Table 3). The excellent agreement between the simulated total coverages and those obtained experimentally confirms the great reliability of DFT results for the first mechanisms of growth and the success of their implementation at the mesoscopic scale.

An important issue in the ALD process is the growth temperature. The ALD of HfO₂ is often performed using metal chloride and water successively as precursors. Experimentally, it is found that HfCl₄/H₂O ALD of SiO₂ has a broad process window with deposition temperature between 180 °C and 600 °C. Further the metal chloride–water ALD process suffers from some disadvantages such as chlorine contaminations and slow growth rates due to submonolayer growth per cycle. As a result, high temperatures are required to minimize the contamination. Unfortunately, the film quality degrades at high temperatures. Our aim here is to optimize this temperature as a compromise between these two opposite effects, by examining KMC simulations at different temperatures. We use the Zhuravlev results for the distribution of OH groups on the substrate surface as a function of temperature (Table 3).

Fig. 3 shows the total coverage of the substrate with respect to temperature, after the first ALD cycle. The total coverage increases from 200 °C to 300 °C, then decreases until 400 °C. This confirms the existence of an optimal growth temperature at \( T = 300 \) °C, at least for the first ALD cycle. This predicted temperature is in excellent agreement with the optimal experimental temperature largely used for ALD of HfO₂ on SiO₂/Si. This result confirms again the credibility of our model.

Another important issue in the ALD process is the duration of precursor pulses. Experimentally, in the case of HfO₂

### Table 1 Reaction enthalpies and activation barriers for precursor incorporation and hydrolysis processes

<table>
<thead>
<tr>
<th>Precursor incorporation</th>
<th>Energy/eV</th>
<th>TS'</th>
<th>Energy/eV</th>
<th>TS'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si–OH–HfCl₄ complex</td>
<td>0.48</td>
<td>0.88</td>
<td>Si–O–HfCl₃–HCl complex</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HCl desorption</td>
<td>0.12</td>
</tr>
<tr>
<td>Hydrolysis processes</td>
<td></td>
<td></td>
<td>M–Cl₃–H₂O complex</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>M–OHCl₂–HCl complex</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>HCl desorption</td>
<td>0.20</td>
</tr>
</tbody>
</table>

* TS: transition state.
deposition, the pulse duration of HfCl\textsubscript{4} precursor is in the order of 50 ms. The question here is to know whether this time is sufficient or overestimated? Fig. 4 represents the evolution of the total coverage as a function of time. Simulations are performed under constant flux of HfCl\textsubscript{4}, at a pressure of 1.33 mbar, at the optimized growth temperature of 300°C. The results indicate a saturation of the coverage at 48%. At the standard duration of 50 ms, the total coverage is only of 40%. The standard experimental duration cannot thus be reduced without a strong reduction of the total coverage. Moreover, it could be, according to our simulations, slightly increased, at least for the very first phase of ALD. We should mention that the standard time of 50 ms, corresponding to the precursor pulse phase, is an experimental value, very difficult to measure in industrial ALD equipments, since their measurement threshold level is in this order of 50 ms. Therefore, this experimental value must be regarded as indicative.

Examining the results of simulation of this first cycle, we can assert the excellent validity of DFT calculations reported in ref. 29 and 36 concerning HfCl\textsubscript{4} decomposition and metal incorporation, since these mechanisms are massively used in this first cycle. A correlation is obtained between the total coverage and the preparation of the surface: distributions of siloxanes and hydroxyl groups. Further, using the Zhuravlev model to initialize the starting substrate, according to the temperature, we highlighted the existence of an optimal temperature for the incorporation of the metal precursors during the first phase of ALD. In our simulations, this optimum was a consequence of a competition between two contrary effects. However, the experimental results do not reveal this expected behaviour at low temperatures. We can therefore assume that some basic mechanisms are missing in our simulator, in order to reproduce reliably the experimental results at temperatures lower than 300°C. This does not constitute a serious drawback since the growth is generally carried out at 300°C, even higher. We finally highlighted the saturation of the substrate by the precursors, the light overestimate of the pulse phase duration and coverage limit are probably due to an overestimate of hydroxyl density obtained by the model of Zhuravlev. This model has to be adapted to the substrates used in the cases investigated here. In all these cases, the tendencies were in agreement with the experimental results.

B Kinetics of growth. In experiments, several growth modes are successively observed.\textsuperscript{37} After the first cycle consuming a large number of metal precursors, a slow rate transient mode allows reaching full coverage of the substrate. Then, a faster steady-state mode, characteristics of the deposition of HfO\textsubscript{2} on HfO\textsubscript{x}(OH)\textsubscript{y}, is established. Our aim here is to reproduce these experimental observations. In the following, we will investigate the kinetics of growth of HfO\textsubscript{2} films, for both transient and steady state regimes, up to 10 ALD cycles. Simulation results are presented, and compared with experimental data, in Fig. 5a and b, for transient and steady state regimes, respectively. Growth rates are expressed in number of metal atoms incorporated in the film rather than coverage, since some precursors are incorporated on top of already deposited metal atoms. This is a consequence of the full coverage being only reached after a large number of ALD cycles.

As we demonstrated above, Fig. 5a shows that the first cycle surface coverage is well reproduced by our simulations. This is no more the case for the second cycle where simulated growth

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Hydroxyl Density (%)</th>
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<tbody>
<tr>
<td>200</td>
<td>68</td>
</tr>
<tr>
<td>250</td>
<td>59</td>
</tr>
<tr>
<td>300</td>
<td>52</td>
</tr>
<tr>
<td>350</td>
<td>43</td>
</tr>
<tr>
<td>400</td>
<td>34</td>
</tr>
</tbody>
</table>

**Table 3** Zhuravlev model for substrate initialization. From the Monte Carlo point of view, OH density is the percentage of hydroxylated sites.
rate increases slightly, while the experimental rate shows a severe decrease. At this point, we should mention the main difference between the first and second cycles of ALD. During the first cycle, incoming precursors react only with hydroxylated SiO₂. Reactions with already deposited precursors are forbidden since the Cl-terminations have not yet been hydrolyzed. During the second cycle, some precursors react with still uncovered SiO₂ surface while others react with the already deposited and hydrolyzed Hf(OH)_x molecules. Obviously, energetic parameters are different for these two reaction pathways. This hopefully leads to lower sticking of the incoming precursors to the HfO₂ surface. In the absence of reliable data, based on DFT calculations, this difference has not been taken into account in the KMC simulations. The lower sticking of precursors to HfO₂ explains the decrease of the growth rate, observed experimentally, but not in the KMC simulations. The slight increase of the theoretical growth rate in the second ALD cycle is due to the increase of hydroxyl concentration on the hydrolyzed HfO₂ surface, with respect to the initial SiO₂ substrate.

Further, a large number of incorporations participate to the constitution of long life-time “trees”, where two precursors, on top of each other, are covalently bonded. The transition to an ionic structure, close to the bulk HfO₂ structure, can only be achieved via densification mechanisms which are expected to play an important role during ALD process. Continuing further, from cycle 3 to cycle 6, our simulations are in good agreement with experimental data, about 10¹⁴ hafnium atoms per cm² per ALD cycle. Beyond cycle 7, the simulated growth rate decreases and the growth stops at cycle 9. This corresponds to a saturation resulting from a lack of elementary mechanisms in our KMC, particularly diffusion mechanisms which allow the smoothing of the growing surface, and the inability of the densification mechanisms to be fully efficient. An examination of the final structure indicates specific sites where further densification mechanisms should occur but cannot be performed by the mechanisms already implemented in our software package. To overcome this problem, we are presently considering a revision of the algorithm in order to implement new densification mechanisms.

To complete our investigation, we have also examined the case of 100% OH concentration on the initial substrate, as an insight into the steady state regime represented by the growth of HfO₂ on fully hydrolyzed HfO₂ surface. In practice, the
simulation is performed by artificially depositing a full monolayer of HfO2 on the silicon substrate. We apply the Monte Carlo procedure only after this first step. Results are very similar to the previous case (see Fig. 5b). However, the rise of growth rate observed previously during the second is no more present, since the 100% coverage is artificially reached from the beginning. In experiments, after a slow growth to cover the substrate, a faster steady-state growth regime, around \(1.2 \times 10^{14}\) hafnium atoms per cm\(^2\) and ALD cycle, is observed. In simulations, the growth rate is again too high at the beginning, because of the inadequate parameterization model. From cycle 4, the calculations are in good agreement with experiments, but the growth stops later as it lacks mechanisms.

Our simulations correctly reproduce the two regimes of the growth observed experimentally,\(^ {37}\) at least for some ALD cycles. Results are schematically presented in Fig. 6. In the transient regime, after the first cycle leading to relatively high substrate coverage, the growth rate decreases to about 0.1 layer per cycle. Our simulator suffers from a saturation effect inherent to the method but simulations are very realistic during approximately 5 ALD cycles. The opening of the siloxanes bridges seems to be at the origin of the slow rate of this mode. Siloxane openings delay the full coverage of the surface and a more realistic functionalization. The duration of this stage is not accessible to our simulator without new optimizations.

The steady-state regime then follows (see Fig. 6). The growth rate is higher, because of the higher hydroxyl concentration on the surface. The growth rate is in agreement with experimental data,\(^ {25,44}\) about \(1.2 \times 10^{14}\) Hf per cm\(^2\) per cycle, i.e. 0.17 monolayer per cycle. It still remains very low compared to what could be expected in an “atomic layer deposition” technique where full monolayer coverage should normally be reached at each cycle.

IV. Conclusions

The purpose of the present paper is to describe a new generation of tools dedicated to the modelling of high-\(k\) material deposition on silicon substrates, providing a growth-modelling environment for atomic layer chemical vapour deposition (ALD) of the materials as HfO\(_2\). A multi-scale strategy has been chosen to achieve this investigation. The corresponding “bottom-up” approach, from quantum level calculations to macroscopic rate theory, is necessary to understand and implement the most pertinent atomic scale mechanisms in the growth models. We point out that this atomistic description is crucial to match the requirements of microelectronics and emerging nanotechnology scales. Indeed, our approaches provided interesting results concerning the substrate reactivity, growth mechanisms and the optimization of the growth temperature for HfO2 deposition. Moreover, some studies are still running to make progress towards the associated technology, in particular the calibration of activation barriers for densification mechanisms and siloxane bridge opening. These calibrations will allow us to draw a clear picture of the growth mechanisms and growth kinetics, for several deposition cycles, until a full monolayer is achieved.

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References


