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Atomistic-mesoscopic modeling of area-selective thermal atomic layer deposition



Sungil Yun^a, Feiyang Ou^a, Henrik Wang^a, Matthew Tom^a, Gerassimos Orkoulas^c, Panagiotis D. Christofides^{*a,b,**}

^a Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, CA 90095-1592, USA

^b Department of Electrical and Computer Engineering, University of California, Los Angeles, CA 90095-1592, USA

^c Department of Chemical Engineering, Widener University, Chester, PA 19013, USA

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ABSTRACT

There has been growing interest in area-selective atomic layer deposition (ASALD) with the integration of small-molecule inhibitors (SMIs) to improve the regioselectivity of thinlayer deposition on growth areas. ASALD offers an alternative solution to the challenges for the nanofabrication of transistors: difficulty of achieving self-alignment and imprecise thickness control. In this work, atomistic simulations are performed using density functional theory (DFT) and a mesoscopic model for ASALD is developed on a SiO₂/Al₂O₃ surface based on a kinetic Monte Carlo (kMC) method, which simulates the deposition and reaction processes that take place on the surface. The ASALD process comprises the SMI, acetylacetone, for Step A, precursor, bis(diethylamino)silane (BDEAS), for Step B, and oxidant, ozone, for Step C. The simulation results comprehensively characterize the surface kinetics of ASALD implemented with steric effects that are produced by the SMI and BDEAS and are comparable to the results from experimental findings.

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1. Introduction

Currently, nanofabrication is highly dependent on top-down fabrication processes that consist of deposition, photolithography, and etching steps that are repeated to produce nanoscale devices. This conventional top-down fabrication approach, based on atomic layer deposition (ALD) and atomic layer etching (ALE), is conducive to highly conformal and ultra-thin film deposition, allowing for the construction of three-dimensional (3D) architectures in fin field-effect transistors (FinFETs) (Leskelä and Ritala, 2002; George, 2010). Therefore, there has been a growing interest in improving and optimizing ALD processes with a plethora of research focused on this topic. ALD inherently relies on surface chemistry and ambient fluid conditions to exhibit selflimiting behavior, which is achieved by repeating two or three reaction steps sequentially with an extended purge time between the reaction steps. ALD is a deposition process with precise thickness control capabilities over various materials, including metals, metal oxides, and organic molecules. Therefore, ALD is able to produce exceptionally uniform thin films with high-aspect ratios for a variety of materials such as hafnium oxide, HfO_2 , titanium oxide, TiO_2 , and aluminum oxide, Al_2O_3 .

Despite the widely regarded capabilities of ALD, the semiconductor industry is facing many challenges with the continued down-scaling of nano-electronics. The primary bottleneck of the miniaturization process is the misalignment of features in the 3D architectures of the substrate while fabricating stacked, integrated circuits, which are

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^{*} Corresponding author at: Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, CA 90095-1592, USA.

E-mail address: pdc@seas.ucla.edu (P.D. Christofides).

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Nomenclature

Acronyms	
ALD	Atomic layer deposition.
ALE	Atomic layer etching.
ASALD	Area-selective atomic layer deposition.
BDEAS	Bis(diethylamino)silane.
CT	Collision theory.
DEA	Diethylamine.
DFT	Density functional theory.
EPEs	Edge placement errors.
FinFETs	Fin field-effect transistors.
GA	Growth area.
GUI	Graphical user interface.
Hacac	Acetylacetone.
kMC	Kinetic Monte Carlo.
MC	Monte Carlo.
NEB	Nudged elastic band.
NGA	Non-growth area.
PAW	Projector augmented-wave.
PWscf	Plane-wave self-consistent field.
QE	Quantum ESPRESSO.
SAM	Self-assembled monomer.
SCF	Self-consistent field.
SMI	Small-molecule inhibitor.
TST	Transition state theory.
VSSM	Variable step size method.

known as edge placement errors (EPEs) (Mameli et al., 2017; Mackus et al., 2019). The conventional top-down fabrication process of the sub-5 nm channel uses a series of deposition, photolithography, and etching processes. During these processes, discrepancies between the targeted position and the actual position emerge, causing ALD growth in undesirable areas (Merkx et al., 2020b). Therefore, EPEs restrict how many well-aligned 3D structural layers can be stacked due to the misplacement between the top and the bottom layers. To address alignment challenges, area-selective atomic layer deposition (ASALD), as a bottom-up fabrication technique, has been proposed due to its potential to facilitate nanoelectronic production in high-volume manufacturing (Fang and Ho, 2015; Parsons and Clark, 2020). ASALD consists of an additional procedure that deactivates a target area, the socalled non-growth area (NGA), to prevent ALD growth on the NGA of the substrate surface while a subsequent process selectively deposits materials on the growth area (GA). This feature is achieved by chemically modifying the top surface of the NGA with inhibitors. In such a scenario, ASALD strongly depends on the chemical interactions between the substrate and of the precursors; specifically, there must be no interaction between the passivated NGA area and the deposited reagents intended for the GA. ASALD has emerged as a possible remedy to the aforementioned issues associated with conventional ALD processes. Firstly, ASALD is able to reduce the need for additional, subsequent processing steps such as photolithography and etching applied in conventional ALD processes, which extensively reduces the overall manufacturing time and is capable of sustaining the growing demand for semiconductors, resulting in cost-effective fabrication while minimizing the toxic reagents used in photolithography and etching processes (Fang and Ho, 2015; Seo et al., 2017). However, the most attractive characteristic of ASALD to the industry allows for higher stacks on transistors to be produced and the potential to fabricate self-aligned nanoscale devices as mentioned above (Mackus et al., 2019).

There are several approaches to creating a protective layer that allow for selective deposition. The most popular approach is to use self-assembled monomers (SAMs) as inhibitors to produce effective barriers. SAMs, such as alkylsilanes, have large aliphatic chains on their tails that block or delay ALD nucleation on the NGA while the head groups of the SAMs are connected to the NGA. Thus, SAMs act as growth inhibitors and allow film deposition to occur only on the GA of the substrate surface. The applications of ASALD using various SAMs have been investigated in several works (Chen et al., 2005; Sinha et al., 2006; Huang et al., 2014; Minaye Hashemi et al., 2015; Haider et al., 2016). Another advantage is that SAMs are readily removed by acetone and demineralized water after the ALD process is completed. Despite the aforementioned benefits of the SAMs, the ALD growth selectivity is limited to just a few nanometers of thickness due to potential defects in the SAMs. Furthermore, it is difficult and time-consuming to prepare defect-free SAMs (Fang and Ho, 2015). In addition, most SAMs, which are based on wet chemistry, are difficult to integrate into vapor phase processes such as ALD. These issues make it challenging for SAM-based ASALD to yield high-aspect-ratio dielectric films.

To overcome the drawbacks of SAM-based ASALD, smallmolecule inhibitors (SMIs) have been proposed. Unlike SAMs, which use a large inert functional group to physically block ALD growth, the reactive moieties of SMIs play a paramount role in preventing precursor adsorption onto the NGA (Yarbrough et al., 2021). ASALD based on SMIs effectively blocks precursors through a combination of chemical passivation and steric shielding (Merkx et al., 2022). The degradation of the blocking layer created by SMIs during the deposition processes is insignificant in contrast to that of the polymeric blocking layer of SAMs (Merkx et al., 2020a). Since SMIs can be delivered through the vapor phase by adding a fixing step, the application of SMIs can be easily implemented to further improve selectivity. The protective layer formed via SMI-based ASALD allows surface destructive co-reactants such as oxygen plasma and ozone to be applicable as oxidants. An ABC-type area-selective ALD process (Mameli et al., 2017) has been developed based on this motivation and is also integrated into this work as discussed below.

The reaction mechanism for ASALD is composed of three sequential steps designated by Steps A, B, and C. In Step A, inhibitors selectively adsorb onto the NGA and form a blocking layer to prevent precursors from adsorbing onto the NGA during the entire ALD process. In Step B, precursors restrictively adsorb onto the GA due to the deactivation of the top layer of the NGA. Lastly, an oxidant oxidizes the top layer of the GA to complete a cycle of the deposition process. During the dosing of the precursor and oxidant, there is the possibility that some inhibitor molecules might desorb from the NGA, which contributes to a loss in selectivity. Thus, the correction step (Step A) is repeatedly introduced into the entire reaction cycle to re-saturate the protective layer. The ABC-type ASALD is schematically illustrated in Fig. 1.

Despite the merits mentioned above, there is little computational or experimental research on the mesoscopic behavior of SMI-based ASALD. In particular, prior research (Mameli et al., 2017; Merkx et al., 2020a) demonstrated the



Figure 1 – Schematic illustration of the ABC-type SMI-based ASALD. The molecules A, B, and C correspond to the inhibitor, precursor, and oxidant, respectively.

technical viability of ASALD using SMIs, which was mainly performed from an experimental perspective. However, these previous works have not studied the surface kinetics for the entire cycle at the atomistic level in great detail. Thus, it is necessary to study how inhibitors selectively prohibit film growth on the NGA substrate with SMI-based ASALD in great detail. In this work, a kinetic Monte Carlo (kMC) study is performed to characterize ASALD of a SiO₂ (GA) and Al₂O₃ (NGA) substrate using small-molecule inhibitors (SMIs). Past studies have successfully employed the kMC method to simulate atomic layer etching processes (Yun et al., 2022a, 2022b, 2022c, 2022d) to express the stochastic behavior of thin-film surface kinetics, which will similarly be integrated into this work. Acetylacetone (Hacac), bis(diethylamino)silane (BDEAS), and ozone (O_3) are selected as a SMI, precursor, and oxidant, respectively. Density functional theory (DFT) calculations are carried out to conduct an investigation into the atomistic behavior of all reaction steps. In addition, to visualize the steric effects of Hacac, a model that simulates the surface coverage for Hacac is developed. The structure of this work is as follows: Section 2 describes the methodology of mesoscopic modeling, Section 2.1 illustrates the ASALD process in detail, Section 2.2 describes the calculations to define the atomistic behavior via DFT, Section 2.3 discusses the steric effects, Section 3 describes the results of the kMC study and its validation, and Section 4 provides a summary of this work.

2. Atomistic-mesoscopic modeling

2.1. Surface kinetics

The purpose of the ASALD process is to achieve a selective thin-film metal-oxide deposition that occurs solely on the growth area (GA) of β -SiO₂ (1 0 1) by integrating a protective surface of the non-growth area (NGA) of α -Al₂O₃ (0 0 0 1). The ASALD process consists of three sequential reactions (Steps A, B, and C) that are situated between purging steps, which are conducted in a cyclical manner. This work will also assume that all reactions are of bimolecular type, which only occur in elementary steps; thus, the reactions will proceed sequentially. Step A is composed of an inhibition-adsorption reaction in which the inhibitor selectively binds to Al₂O₃. Step B is a precursor modification reaction that uses bis (diethylamino)silane (BDEAS) to produce a modified surface layer on SiO₂, which possesses a self-limiting nature. Step C is an oxidation process that introduces ozone (O₃) onto the modified surface layer, thereby depositing a monolayer. These three sequential reactions are components of the so-called ABC-type reaction cycle, which is elucidated in this section.

Inhibitors are designed to reduce the occurrence of a reaction, which makes inhibitor selection an issue of great importance for ASALD processes. Ideally, the inhibitor for an ASALD process must be chosen such that the inhibitor selectively reacts with the NGA; thus, this implies that there needs to be a substantial difference in the magnitude of the activation energy barriers between the NGA and GA, which is characterized by chemoselective behavior. Inhibitors must also have a low decay rate so that the protective layer can sustain cycles of Steps B and C without requiring numerous doses of inhibition treatment between the deposition steps (Steps B and C). Thus, this work employs a small molecule inhibitor (SMI) with acetylacetone (Hacac) to fabricate an inhibition layer on the NGA of Al₂O₃, which exploits the conjugated structure of the tautomerized enol isomer to deprive the active oxygen sites on the NGA of subsequent adsorption reactions (Steps B and C). Hacac can exist in a keto isomer that can undergo a tautomerization process to produce a stable enol isomer composed of conjugated π bonds, which are the driving force that allows Hacac to bind to an Al atom on the NGA.



The keto and enol structural isomers that are formed through resonance allow the two resonance structures to coexist in basic and acidic forms, respectively. However, the stability of the enol form is more preferential and stable than the keto structure in the gas phase (Folkendt et al., 1985). This work first characterizes the surface of Al_2O_3 as being uniformly composed of hydroxyl-terminated ligands (Al-OH) in a vicinal diol structure. This hydroxylation of the Al_2O_3 surface promotes basicity and interacts with the acidic Hacac, giving rise to a thermodynamically feasible neutralization reaction (Mameli et al., 2017). The reaction between the hydroxyl-terminated Al and Hacac molecule produces H_2O vapor as a byproduct, which is defined in the following reaction:



In Step A-1, an enol Hacac molecule withdraws its acidic hydrogen proton from the hydroxyl group, which is donated to the hydroxyl-terminated Al atom to produce a H₂O leaving group. The deprotonated enol Hacac molecule adsorbs onto the Al site to form a monodentate structure. Then, in Step A-2, the deprotonated Hacac adsorbate forms a protective sixmember cyclic ring, also called its chelate form, through a chelation process by adsorbing onto the surface Al atom with the nonadsorbed keto group. The delocalized electrons in the conjugated π bonds of the chelate ring is illustrated with a dotted line (Gamekkanda et al., 2017). Also, note that the wavy bonds from the Al atoms do not necessarily imply that the terminal is a single bond as shown in the reaction mechanisms; instead, they are used to represent the ligand structure that is unimportant to the mechanism and to illustrate that the reactions are occurring on the surface of the substrate. Although Hacac is intended to selectively adsorb only to Al-OH active sites, there is also potential for Hacac to adsorb onto Si-OH active sites that may be generated during the hydroxylation step.



This undesirable reaction is the main source for nonuniform deposition in the SiO_2 growth region and can impede substrate quality and conformity by deflecting precursor adsorbates in Steps B and C of the ASALD process.

Precursors are intended to undergo surface reactions on the GA while having inherent properties that prevent further permeation beyond the substrate surface. Typically, bulky precursors are integrated into this modification step to ensure that a transport-limited boundary is established. The precursor, bis(diethylamino)silane (BDEAS), is used as an adsorbate on SiO₂ to produce Si lattice sites. The adsorption of BDEAS on the GA exemplifies self-limiting behavior such that single atomic monolayers of Si are deposited and byproducts are easily volatized. This Step B reaction mechanism is simplified by the following overall reaction:



In Step B-1, BDEAS first adsorbs to an active hydroxyl surface site while simultaneously withdrawing a molecule of diethylamine (DEA). It is assumed that the hydroxylated SiO₂ surface consists of a homogeneous composition of vicinal hydroxyl ligands. Following the initial adsorption of BDEAS in Step B-2, the adsorbate binds to an adjacent hydroxyl surface site while simultaneously removing an additional DEA molecule, which results in a deposited monolayer of silicon atoms.

Following Step B, an oxidant, ozone, is introduced into the ASALD process to convert the hydride-terminated ligands of the newly deposited Si surface to hydroxyl-terminated ligands through an oxidation process. Ozone, which exhibits both electronegative and electropositive characteristics, performs a simultaneous and spontaneous ligand-exchange mechanism that substitutes a hydroxyl group for the hydride-terminated group while producing a leaving group of O_2 , oxygen gas. This oxidation step is incredibly spontaneous to the point where the reaction can occur simultaneously for both hydride-terminated groups on the Si atom. The result completes the final monolayer of SiO₂ deposition and concludes the cycle of the ASALD process. The overall reaction for Step C is described as follows:





The resulting surface layer becomes composed of a homogeneous array of geminal hydroxylated ligands that can be recrystallized through an annealing cycle after the ASALD process (Hughes et al., 2012) to reform the initial vicinal diol surface structure. It is, however, worth mentioning that after each step (Steps A, B, and C) in the ASALD process, a purging cycle is introduced with an inert gas such as nitrogen gas, N₂, to ensure that the reagent species (Hacac, BDEAS, and O_3) do not intermix and disrupt the self-limiting behavior, which is essential to ensuring high surface uniformity.

2.2. DFT calculation

2.2.1. Electronic structure calculation framework

With the reactions defined in Section 2.1, kinetic rate constants for each reaction must be defined for these elementary reaction steps. Mesoscopic simulation requires the knowledge of important reaction parameters to compute such reaction rate constants including the activation energies, the pre-exponential factors, vibrational frequencies, and sticking coefficients. These parameters may be difficult to measure experimentally and generally require various computation methods that combine ab initio molecular dynamics, first principles quantum mechanics, and statistical chemistry. The open-source software for materials modeling, Quantum ESPRESSO (QE), is used in this work to calculate such kinetic parameters, which are needed to define the mesoscopic model. QE uses theoretical concepts including density functional theory (DFT), which computes the energy of phononic interactions using pseudopotential data that define each element by wavelengths to facilitate the computations (Baroni et al., 2011; Giannozzi, 2009). Previous works have employed QE for computing electronic structure optimization as well as for performing computations of kinetic parameters (Pitriana et al., 2018; Yun et al., 2022a, 2022c). This work will integrate DFT computations via QE to compute an optimal (minimal electronic energy) electronic structure for each species produced in each step of the ASALD process.

The initial stage of the electronic structure optimization process consists of modeling the atomic structures using an open-source, graphical user interface (GUI) program that supports QE called BURAI. The surface crystal structures of α - $\rm Al_2O_3$ and $\beta \mbox{-}SiO_2$ are constructed by defining a Bravais lattice of (0 0 0 1) (Mameli et al., 2017) with a trigonal crystal and vicinal (1 0 1) (Roh et al., 2022) with a triclinic crystal structure, respectively. Also, lattice model unit cells for α -Al₂O₃ and β -SiO₂ are constrained within a 2×2×2 supercell. Precursor and byproduct species including BDEAS, DEA, H₂O, O₃, and O₂ are developed using a free crystal lattice that is selfdetermined using a unit cell size that contains the entirety of the molecular structure. This method prevents divergence by defining boundary conditions for the "particle-in-a-box" model. Projector Augmented-Wave (PAW) pseudopotential data are used in conjunction with the Plane-Wave Self-Consistent Field (PWscf) package. In the program, the "relaxed" calculation method is utilized to optimize electronic forces that allow the translation of atoms in space to generate an electronic structure of minimum electronic energy. The use of the aforementioned pseudopotential data facilitates the solving of the position-dependent and time-independent Schrödinger equation, which is defined by the following expression:

$$\hat{H}\psi(\vec{x}) = E\psi(\vec{x}) \quad \text{where } \hat{H} = \frac{\hbar}{2m_e}\nabla^2 + \hat{V}(\vec{x})$$
 (1)

where \hat{H} is the Hamiltonian operator, which is a function of the sum of the kinetic and potential energies that are defined by the reduced Planck constant, \hbar , the particle mass, m_e , the Laplacian operator, ∇ , and the potential energy, \hat{V} , respectively. Also, E refers to the total electronic energy of the

variable	Delimition
A _{site}	Surface area of an active reaction site
D	Dimension size of a $D \times D$ 2D grid
E	Total electronic energy
Ea	Activation energy
h	Planck constant
ħ	Reduced Planck constant
Ĥ	Hamiltonian operator
k	Reaction rate constant
k _{ads}	Reaction rate constant of adsorption reaction
k _{nonad}	Reaction rate constant of nonadsorption reaction
k _B	Boltzmann constant
k _{sum}	Sum of the reaction constants
т	Atomic mass of adsorption species
me	Atomic mass of particle
n	Number of molecules
Р	Adsorption species partial pressure
Q	Partition function for the reactant
Q [‡]	Partition function for the transition state
R	Universal gas constant
S	Distance between two adjacent active sites
t	Reaction time progress
Т	Operating temperature (absolute)
Ŷ	Potential energy
х	Horizontal distance between two active sites
\overrightarrow{x}	Displacement vector
Z	Coordination number of adsorption species
Δt	Time interval
γ1, γ2	Random numbers where $\gamma_1, \gamma_2 \in (0, 1]$
ν	Pre-exponential factor
ρ	Molecule density
σ	Sticking coefficient for adsorption species
Ψ	Time-independent and position-dependent wave
	function

Table 1 - Summary and description of variables.

Table 2 – Self-determined parameters for DFT calculations.					
Material	Variable	Value			
SiO ₂ Al ₂ O ₃	degauss ecutwfc [†] ecutrho [‡] k-points degauss ecutwfc [†] ecutrho [‡] k-points	0.02 50 Ry 200 Ry 2 2 2 0.01 50 Ry 200 Ry 3 3 2			
[†] Kinetic energy cuto for charge density a	off for wave functions. [‡] Kir nd potential	netic energy cutoff			

system, and $\psi(\vec{x})$ is the wave function that depends on the displacement vector, \vec{x} . A complete summary of the variables and their definitions used throughout this work is provided in Table 1. Self-determined parameters including the *degauss*, the kinetic energy cutoff for wave functions (*ecutufc*), the kinetic energy cutoff for charge density and potential (*ecutrho*), and the *k*-points are determined through the SCF (self-consistent field) computation in QE and summarized in Table 2. The optimized electronic structures exported from QE and compiled in BURAI are visualized in Fig. 2.

2.2.2. Computation of kinetic parameters

Various first principles theoretical concepts derived from quantum mechanics and chemistry are integrated into this



Figure 2 – Minimum energy paths from the DFT calculations for the Hacac adsorption on (a) Al_2O_3 and (b) SiO_2 , for the BDEAS adsorption on (c) SiO_2 , and for the O_3 adsorption on (d) SiO_2 . Color code for atoms: aluminum, dark gray; silicon, light brown; oxygen, red; hydrogen, white; nitrogen, dark blue; carbon, gray. The paths for the Hacac adsorption from A1 to A3 was sourced from Mameli et al. (2017). Specifically, A2, V2, V5 and V7, and V9 indicate the physisorption reactions for Hacac on the NGA, BDEAS on the GA, ozone on the GA, and Hacac on the GA, respectively.

work to compute reaction rate parameters that include the reaction rate constant, activation energy, and pre-exponential factor. The aforementioned parameters are fundamental for the mesoscopic modeling via the kinetic Monte Carlo method, which is discussed in Section 2.4. This section examines the methodological approaches to computing these kinetic parameters for adsorption and nonadsorption reactions that are described in Section 2.1.

Adsorption reactions occur during the initial bombardment of the inhibitor (Step A), precursor (Step B), and oxidant (Step C) on the surfaces of the substrate. These adsorption reactions can be modeled as bimolecular reactions through Maxwell-Boltzmann statistics and Collision Theory (CT). The probability of a successful adsorption reaction is modeled based on a sticking coefficient factor, σ , which is deduced from experimental works. The following equation provides the definition of CT: where k_{ads} is the reaction rate constant for the adsorption reaction, P is the pressure of the gaseous reagent (Hacac, BDEAS, or O₃), A_{site} is the surface area of a single active site, Z is the coordination number of the gas, *m* is the atomic mass of the gas, k_B is the Boltzmann constant, and T is the absolute temperature of the ambient environment. This work defines a sticking coefficient, σ , for Hacac as 1.0×10^{-4} (George, 2010), BDEAS as 2.0×10^{-5} (Schwille et al., 2017), and O₃ as 4.5×10^{-5} (Lee et al., 2009). It is noteworthy that the sticking coefficient of Hacac was determined from surface adsorption using precursor species for ALD and was assumed to be similar in magnitude to that of Hacac adsorption onto Al₂O₃.

A majority of reactions discussed in this work involve chemisorption, desorption, and other surface reactions that cannot be computed via CT. Nonadsorption reaction rate constants can be calculated using the Arrhenius equation, which is defined by the following equation:

Table 3 – Geometry description for reaction paths.					
Substrate	Step	Number	Description		
Al_2O_3	Step A	A1	OH-terminated Al ₂ O ₃		
		A2	Hacac physisorption on Al ₂ O ₃		
		A3	Monodentate configuration (deprotonated Hacac on Al ₂ O ₃)		
		A4	Chelate configuration (deprotonated Hacac on Al ₂ O ₃)		
SiO ₂	Step A	V1	OH-terminated SiO ₂		
		V9	Hacac physisorption on SiO ₂		
		V10	Monodentate configuration (deprotonated Hacac on SiO ₂)		
	Step B	V2	BDEAS physisorption on SiO ₂		
		V3	DEA-deprived BDEAS adsorbate on SiO ₂		
		V4	SiH ₂ adsorbate on SiO ₂		
	Step C	V5	O ₃ physisorption on SiH ₂		
		V6	H-Si-OH on SiO ₂		
		V7	O₃ physisorption on H-Si-OH		
		V8	Final configuration (Si(OH) ₂)		

where k_{nonad} is the reaction rate constant for the nonadsorption reaction, ν is the pre-exponential factor, E_A is the activation energy, R is the universal gas constant, and T is the absolute temperature of the reaction. One challenge arises with the computation of the pre-exponential factor term, which is modeled on the frequency of collisions where the reactants overcome the activation energy barrier. Thus, Transition State Theory (TST) is often employed to reduce the computational requirements to collect such frequency data and is described by the following expression that computes the pre-exponential factor:

$$\nu = \frac{k_{\rm B}T}{h} \frac{Q^{\ddagger}}{Q} \tag{4}$$

where *h* is the Planck constant and Q^{\ddagger} and *Q* are the products of the electronic, rotational, translational, and vibrational partition functions for the transition state species and reactant, respectively. To reduce the computational requirements for evaluating the partition functions, the ratios between the transition state and reactant partition functions are often simplified to unity (Jansen, 2012). Thus, the preexponential factor is largely dependent on the temperature of the reaction. Lastly, the activation energy of the reactions should also be established in Eq. (3), which are computed using the nudged elastic band (NEB) method in this work. QE contains a NEB package that is designed to carry out such computations by essentially constructing a minimum energy path between reactants and products. The NEB method requires optimized structures, which are obtained from the PWscf package described in Section 2.2. With the optimized structure data, the NEB computation requests a self-determined number of electronic steps that computes an energy for each step to ultimately determine the activation energy barrier. This work defines seven electronic steps to reduce the computational demand while establishing a robust procedure for computing an accurate activation energy barrier to establish the reaction rate constants. Fig. 2 illustrates the results produced from the application of ab initio and first principles modeling concepts as well as simulation results generated from QE. The activation energies essential for the mesoscopic model are shown in Fig. 2. It is notable that the energy on the y-axis does not denote an absolute energy, but rather the energy difference between the starting structure and the ending structure in each step. Geometries for the reaction paths on Al₂O₃ and on SiO₂ are numbered as A1 through A4 and V1 through V10, respectively, and they are summarized in Table 3.

2.3. Steric hindrance

2.3.1. Fundamentals of steric effects

Steric effects play a substantial role in the frequency of adsorption reactions discussed above by blocking other molecules from approaching the surface, thus hindering specific surface reactions. The regioselective adsorption of the SMI, Hacac, and bulky precursor, BDEAS, depends on how much space is available for these reactions to occur. In other words, Hacac and BDEAS cannot be densely packed on the surface due to their large molecular size, and the bulky adsorbates that have already bonded to the surface can prevent surrounding molecules from interacting with the substrate surface because of steric effects. Thus, the repulsive effect that results from the steric hindrance of the bulky reagents used in ASALD must be investigated and accounted for to accurately depict the kinetic behavior of the surface reactions. The computational methods used to simulate the steric effects in conjunction with the kinetic Monte Carlo model are elucidated in this section.

There are several studies that have reproduced the repulsive effects of steric hindrance in surface adsorption reactions through computational approaches (Hu et al., 2018; Jin et al., 2018; Weckman et al., 2018; Kim et al., 2020). For example, Hu et al. (2018) considered the molecular interactions of Si-S, Si-Se, and Si-Te bonds between the substrate and bulky organic functional ligands in adsorption reactions, which were simulated in a two-dimensional (2D) stochastic model. In this model, the adsorbates were represented by disks defined by their van der Waals radii, which are defined as the minimum approach distance between two atoms that are represented as solid spheres. The van der Waals radii of some organic functional groups are presented in Richards (1973), which are applied in the simulation for Step A and summarized in Table 4. This section will discuss the steric hindrance involved in the Hacac adsorption on Al_2O_3 in Step A and the BDEAS adsorption on SiO2 in Step B (due to the small van der Waals radius of ozone, steric hindrance effects are not expected in Step C). In regard to the BDEAS adsorption, a detailed review of the open literature indicates that it is difficult to find either experimental or simulation studies that discuss the steric hindrance effects taking place in the ALD process with BDEAS as precursor. Prior work presented

Table 4 – Van der Waals radii of functional groups in Hacac molecule.				
Functional group	Van der Waals radius (Å)			
$-CH_3$	2.0			
$-CH_2-$	2.0			
C = O	1.7			
Sourced from Richards (1973)				



Figure 3 – The intervals between two functional groups of the chelate and the monodentate are 4.8 and 3.8 Å, respectively. For the monodentate configuration, the CO group is considered as the group that is potentially able to hinder neighboring adsorption reactions. It is assumed that the CH₃ group at the far right of the monodentate product does not contribute to steric effects on adjacent reaction sites. Color code for atoms: aluminum, large dark gray; oxygen, red; hydrogen, white; carbon, small light gray.

important results from macroscopic measurements and observations (Roh et al., 2022; Mameli et al., 2017), but there is no mesoscopic explanation for the phenomena from a steric hindrance perspective. Thus, this surface modeling work accounting for steric effects provides a potential approach to reveal how steric hindrance influences the ALD nucleation of BDEAS.

2.3.2. Hacac adsorption on Al_2O_3

Hacac is a bulky molecule compared to the active reaction sites on α -Al₂O₃, which are defined as OH ligands. Thus, the deprotonated Hacac adsorbates on the Al_2O_3 surface can block other Hacac molecules from adsorbing onto neighboring reaction sites. There are two molecular configurations for deprotonated Hacac that can adsorb onto Al₂O₃: monodentate (A3) and chelate (A4), as shown in Fig. 2a and described in Table 3. The reaction Step A-2 from the monodentate to the chelate configuration is exothermic and has a low activation energy barrier as illustrated in Fig. 2a, which implies that the monodentate ligand can easily overcome the activation energy barrier of 0.173 eV and transform into the chelate molecule through a chelation process. As a result, the monodentate structure spontaneously converts to the chelate structure from a kinetics perspective, which is in agreement with Mameli et al. (2017). However, Merkx et al. (2020a) reported that part of deprotonated Hacac exists as monodentates on the Al₂O₃ surface through IR inspection.

To investigate the Hacac adsorption process in greater detail, this work constructs a 2D model with a 100×100 surface grid, which has been proposed by Hu et al. (2018). In the grid, all active sites, denoted by small black dots in Fig. 7,

are randomly searched to determine their possibility for Hacac adsorption. In the simulation, the chelate adsorption is performed first and then followed by the monodentate adsorption due to the difference in magnitude between the sizes of the two molecules. A horizontal chelate adsorbate exists on the surface as revealed in Fig. 3. The chelate structure has two methyl, CH₃, functional groups with a van der Waals radius of 2.0 Å and a spacing of 4.8 Å between the two functional groups, which is denoted as an empty capsule with two circles in Fig. 7. Conversely, a monodentate adsorbate is placed diagonally on the surface as shown in Fig. 3. To simulate the adsorption of deprotonated Hacac monodentates onto the 2D grid, it is assumed that the CH₃ functional group does not affect other adsorption reactions at adjacent reaction sites due to its high position. Instead, the free CO functional group is solely responsible for the steric repulsions of other molecules. Therefore, in the 2D model, monodentate structures have CH₃ and CO functional groups with van der Waals radii of 2.0 and 1.7 Å, respectively, and a spacing of 3.8 Å; they are depicted as two conjoined circles in blue in Fig. 7. The simulation procedure is as follows:

- 1. The chelate adsorbate is placed on the site throughout the grid if there is no steric hindrance. The orientation of the adsorbate is stochastically selected from 360° with intervals of 10°.
- 2. Next, the monodentate adsorption selection is performed, filling the empty sites with adsorbates in viable orientations in the same manner with the chelate adsorption.

Even after Step 1 (chelate adsorption) is performed, vacant active sites still exist due to the steric hindrance of the chelate configurations. Thus, Hacac molecules can nonetheless still adsorb onto the surface in the monodentate configuration. To reduce large deviations attributable to the stochastic nature of the algorithm, 100 simulations are carried out, and the surface densities are averaged. In addition, the standard deviation is calculated from the set of computations to evaluate the developed model for steric effects.

A prior study developed a 2D surface model to investigate the effects of steric hindrance on Hacac adsorption on Al₂O₃ (Merkx et al., 2020a). The surface model simulated chelate and physisorbed monodentate configurations; however, the model lacked chemisorbed monodentate products on the active reaction sites. To advance the model proposed by (Merkx et al., 2020a) and to obtain the final surface structure, both chemisorbed chelate and monodentate molecules are considered in this research. This improvement enables the model to obtain more precise and realistic surface information, which provides a deeper explanation of the hinderance effect. The approach of this paper, which is adopted from Hu et al. (2018) and advanced from Merkx et al. (2020a), can be extended to other surface kinetics in which the surface can be approximated into a 2D lattice model simply with the calculations of van der Waals radii of adsorbed molecules. The simulation results from the surface model of the Step A (Hacac) cycle are discussed in Section 3.1. After the simulation, the molecular density on the surface is calculated by Eq. (5).

$$\rho = \frac{n}{D^2 \cdot \mathbf{s} \cdot \mathbf{x}} \tag{5}$$

where ρ is the molecular density in molecules/nm², n is the number of molecules on the 100 × 100 grid, D is the



Figure 4 – Top view of (a) Case 1 for Geometry V2, (b) Case 2 for Geometry V2, and (c) Geometry V3. The blue circled reaction sites are hindered and deactivated by the current reaction site in yellow. Color code for atoms: silicon, light brown; oxygen, red; hydrogen, white; nitrogen, dark blue; carbon, gray.



Figure 5 – Top view of a OH terminated SiO_2 surface, expressed by Geometry V1 in Table 3. Sites 2 through 5 are numbered with Site 1 as the center. Color code for atoms: silicon, light brown; oxygen, red; hydrogen, white.

dimension of the grid, which is 100 in this simulation, s is the distance between two adjacent sites, and x is the distance between two sites in the horizontal direction, which is calculated by the following equation:

$$\mathbf{x} = \frac{\sqrt{3}}{2}\mathbf{s} \tag{6}$$

2.3.3. BDEAS adsorption on SiO₂

A BDEAS adsorbate is capable of preventing other BDEAS molecules from adsorbing on the GA, SiO₂. Fig. 5 illustrates the top view of the GA surface, which is expressed by Geometry V1 in Table 3, and it consists of 8 active reaction sites, which are shown as OH functional groups. If a BDEAS molecule adsorbs onto one of these sites (Geometry V2), the two functional groups of diethylamine (DEA) may protect the two neighboring reaction sites from the physisorption of other

BDEAS molecules as shown in Figs. 4a and 4b. When the physisorbed BDEAS reacts with the OH group by releasing H₂O, the BDEAS molecule turns into a DEA-deprived BDEAS (Geometry V3) on the GA as illustrated in Fig. 4c. However, the remaining DEA group may block an adjacent site so that additional BDEAS physisorptions on the blocked site are hindered. When forming SiH_2 (Geometry V4 in Table 3) by discharging the DEA group from Geometry V3, the adsorbate must bind to two adjacent sites on the surface. There are 5 potential reaction sites from which SiH₂ can be formed on the GA. In Fig. 5, the distances between Sites 1 and the 4 adjacent reaction sites, denoted as Sites 2 through 5, are calculated from the optimized structure computed through electronic structure calculations. The distances between Sites 1 and 2, Sites 1 and 3, Sites 1 and 4, and Sites 1 and 5 are 5.03, 4.01, 4.02, 6.00, and 5.92 Å, respectively. It is reasonable to assume that Site 1 preferentially binds with Sites 3 and 4 to deposit SiH₂ films (Geometry V4) due to these sites being the closest, leading to those binding reactions to have the lowest activation energy. Therefore, the reactions between Sites 1 and 2, Sites 1 and 5, and Sites 1 and 6 can be reasonably ignored in the kinetic Monte Carlo (kMC) simulation. According to the periodical and symmetrical nature of the surface grid, Site 3 can only react with Sites 1 or 2. In other words, the reactions are constrained in the "bicolumn" system from a modeling perspective.

In addition to the steric effects, another issue to consider is that some reaction sites can be deactivated through isolation effects when two adjoining sites are already occupied. As a result, it is nearly impossible to reach full coverage for Step B (BDEAS cycle on the GA). In the experimental data of the BDEAS adsorption from Roh et al. (2022), coverages of 94% and 86% were observed both within and outside the studied ALD window, respectively. In this mesoscopic model, the



Figure 6 – Conversion of the mesoscopic surface kinetics into a matrix of identifiable numbers. The blue and red circles in the lattice, corresponding to 1 and 2 in the matrix, indicate different reaction statuses.

deactivated sites are ignored when calculating the surface coverage in the kMC simulation so that the simulation stops appropriately. With this modification, the computational model can reach 100% coverage by disabling the deactivated sites. On the basis of these steric and kinetic constraints, the kinetic Monte Carlo (kMC) model is built to simulate the surface kinetics, including the blocking effect of adsorbed molecules and the interactions between reaction sites. The detailed description of the kMC model is discussed in Section 2.4 in depth.

2.4. Kinetic Monte Carlo simulation

The conformity of the substrate is dictated by various quality specifications including the uniformity and the amount of deposition on the growth area (GA). However, the latter presents a challenge for modeling in the mesoscopic surface domain due to the disorganization of the reaction kinetics. While it is theoretically possible to simulate the complete reaction mechanism on the surface of a 200 or 300 mm substrate, such a task is extremely computationally demanding to the point of infeasibility. As a popular approach to simulate surface kinetics at the mesoscopic level, statistical Monte Carlo (MC) methods use random sampling in a constrained domain to accurately estimate the effects of a much larger stochastic system. Such atomistic-mesoscopic simulation using MC methods is applicable to nanoscale material systems and minimizes the variability of timescale prediction as described by Maroudas (2000). These algorithms are the most reliable when applied to complex simulations that maintain their probability distribution. Additionally, the kinetics of multiple reaction systems will evolve as the system progresses; thus, there must also be a temporal element to the algorithm. The reaction systems occur at predetermined reaction sites on the surface of the wafer substrate, which indicates that the kinetic Monte Carlo (kMC) simulation method is an appropriate algorithm to integrate into this work (Jansen, 2012). There are various kinetic Monte Carlo (kMC) algorithms that have been investigated; however, this work applies the variable step size method (VSSM), also called the Gillespie algorithm, which was advanced by Bortz, Kalos, and Lebowitz (Bortz et al., 1975). This algorithm is ideal because it is more computationally efficient when there are numerous reaction pathways (Shirazi and Elliott, 2014), which is exactly the case for the ASALD reactions. The VSSM method converts the surface structure of the substrate into a matrix of identifiable numbers, which is illustrated in Fig. 6. The basic formulation of the VSSM algorithm can be separated into 5 steps as described in (Yun et al., 2022a; Shirazi and Elliott, 2014): 1) identification of possible reactions, 2) rate constant summation, 3) reaction selection, 4) time step evolution, and 5) process continuation.

The first step of the VSSM algorithm is to identify all possible reactions for each active site, which is determined by conditions in the simulation. Next, all the possible reaction rate constants are summed, which establishes the bounded conditions for the kMC simulation and is calculated from the following equation:

$$k_{\text{total}} = \sum_{i=1}^{N} k_i \tag{7}$$

where k_{total} is the sum of all reaction rate constants, k_i is the reaction rate constant for the potential reaction i, which was evaluated in Section 2.2.2, and N is the total number of possible reaction pathways. Secondly, the algorithm employs a randomly generated number, $\gamma_1 \in (0, 1]$, to stochastically select a reaction, *j*, that fulfills the following criterion:

$$\sum_{i=1}^{j-1} k_i \le \gamma_1 k_{\text{total}} \le \sum_{i=1}^j k_i \tag{8}$$

where *j* is the index of the reaction in N that satisfies the equation. As a reaction path is determined depending on the product of γ_1 and k_{total} , it is observed that the larger the individual rate constant, the more likely it is to be chosen. Of note, the random number is computed using the Python "*random*()" function from the *random* package. Then, the following algorithm is used to determine a time interval in which no reactions occur (Jansen, 2012).

$$\Delta t = \frac{-\ln \gamma_2}{k_{\text{total}}} \tag{9}$$

where Δt is the aforementioned time interval and $\gamma_2 \in (0, 1]$ is another randomly generated number between 0 and 1 that is independent of γ_1 . Finally, the simulation is conditionalized with an ending criterion to determine the continuation or termination of the simulation. If the former is chosen, the algorithm is repeated starting from the first step of the VSSM algorithm as the time progresses from $t_{old} \rightarrow t_{new} = t_{old} + \Delta t$. In addition, k_{total} is recalculated with each iteration of the algorithm since the possible reaction pathways across the substrate surface change as the system evolves. For the simulation of ASALD, the kMC simulation is used to estimate the time necessary for the surface of the wafer substrate to reach complete, 100%, coverage; thus, the terminal condition for the simulation is defined for the latter. The simulation is conducted using Python scripting language in serial processing and various packages dedicated to the randomization of the simulation and for carrying out numerical computations.

For generality, the procedural steps of the atomistic *ab initio* quantum mechanics and mesoscopic simulations are summarized as follows:



Figure 7 – The adsorption pattern of Hacac chelate (represented by unfilled geometry) and monodentate (represented by filled geometry) configurations on Al₂O₃ sites (blue dots) from the 2D stochastic simulation model.

- 1. Elementary reaction pathways are defined and limited to rate-determining reactions from the electronic structure calculations of the surface structures.
- 2. Ab initio quantum mechanics simulations are simulated via Quantum ESPRESSO for individual species generated for surface reactions.
- 3. Reaction rate constants are calculated using CT and the Arrhenius Equation for adsorption and nonadsorption reactions, respectively.
- 4. The kMC method considering hinderance effects is exploited following the characterization of the kinetics parameters.

3. Simulation results and discussion

In this work, surface modeling results for the simulation of Hacac adsorption on the NGA, described in Section 2.3.2, are discussed. In addition to the surface modeling, the temperature and pressure dependence of the area-selective atomic layer deposition (ALD) of SiO₂/Al₂O₃ are investigated in a pressure range of 10 to 500 Pa with a temperature range of 423 to 573 K. As mentioned above, SiO_2 is defined as the growth area (GA); on the other hand, Al_2O_3 is considered to be the non-growth area (NGA) where the film deposition is not required. It is also noted that the ALD process has a selflimiting behavior in that only a single layer of SiO₂ is deposited on the top layer of the surface. Thus, the kinetic Monte Carlo (kMC) simulations considering steric effects are performed until each step in the ABC cycle reaches full coverage. It is noted that the kinetic interaction between SiO_2 and Al_2O_3 on the boundary is ignored in this study as described in Section 2.4. Thus, two separate lattices for SiO₂ and Al_2O_3 of 100×100 are simulated for surface kinetics. A



Figure 8 – Hacac coverage versus time at T = 423 K and P = 400 Pa. The red and blue solid lines denote the Hacac adsorption on Al₂O₃ and SiO₂, respectively.

number of simulations with a lattice size of 100 through 900 were performed to explore size-dependence of the kMC simulation. It was observed that there was no significant effect of the lattice size on the simulation results while requiring higher computing power with increasing lattice size, which is also supported by previous studies (Huang et al., 2010; Yun et al., 2022a). To minimize the effect of stochastic sampling, 100 kMC computations are performed and averaged to obtain a data point for the process time under the operating conditions. To provide a benchmark, the computation time for the entire cycle is about 30 *min* for 100 trials using a constant temperature of 523 K and pressure of 300 *Pa*, while simulated using similar computational resources.

3.1. Surface modeling for protective layer

Fig. 7 visualizes the surface of Al_2O_3 where chelate and monodentate products are randomly distributed at different angles. Due to the small molecular size, chelate molecules occupy the space between monodentate molecules. The surface density of each chelate and monodentate adsorbate is 1.45 ± 0.02 molecules/nm² and 0.35 ± 0.03 molecules/nm², respectively. 1.80 \pm 0.01 molecules/nm² is thus calculated to be the combined surface density from the simulation. The fraction of monodentate configurations on the surface is 19.37 ± 1.40%. The reported experimental value of the monodentate fraction on the surface by IR inspection is $20 \pm 5\%$ (Merkx et al., 2020a), and thus, the simulation result conforms with the experimental value. However, the molecular density simulated from the model developed in this work is lower than the density from Merkx et al. (2020a) for the chelate configuration, which is 1.7 ± 0.1 molecules/nm². The deviation of the molecular density is attributed to differences in the atomic distances calculated in Section 2.2 using Quantum ESPRESSO and the atomic distances evaluated by Merkx et al. (2020a) who reported a lower atomic distance.



Figure 9 – Scatter charts for process time collected from kMC simulations under the operating window ($423 \le T \le 573$ K and $10 \le P \le 500$ Pa) in (a) Step A, (b) Step B, and (c) Step C, respectively.

3.2. Selectivity of ASALD

Fig. 8 illustrates the selectivity of Hacac adsorption on Al₂O₃ (NGA) as opposed to SiO_2 (GA) in Step A (Hacac cycle) at T = 423 K and P = 400 Pa. No Hacac adsorption is observed on the NGA, which is also detected throughout the entire operating window, which is in agreement with the experimental results (Mameli et al., 2017; Merkx et al., 2020a). The selective Hacac adsorption forms a protective layer on the NGA, leading to SiO₂ being deposited on the GA in a selective manner. The selectivity of ASALD can be influenced by two factors: chemical passivation and steric hindrance. In contrast to the GA, the NGA is chemically deactivated through the adsorption of Hacac as a result of the difference in the magnitude of the activation energies of the adsorption. This chemoselectivity is supported by the DFT calculations as discussed in Section 2.2. As shown in Figs. 2a and 2b, the Hacac adsorption on SiO₂ is endothermic and has a high activation energy barrier of 0.831 eV. Meanwhile, the Hacac adsorption on Al_2O_3 is exothermic and has a low activation energy of 0.25 eV. Therefore, the adsorption predominantly occurs on Al_2O_3 , resulting in the localized formation of a protective layer on the NGA. In addition to the chemoselective deposition behavior, the regioselective behavior is accounted for by the inclusion of steric repulsion effects. As discussed in Sections 2.3 and 3.1, complete Hacac coverage is not possible on the NGA since some reaction sites are sterically hindered by neighboring deprotonated Hacac adsorbates. As a result, the blocked reaction sites are physically deactivated. In conclusion, the NGA is deactivated both chemically and sterically, leading to high effective selectivity for ASALD.

3.3. Impact of operating conditions

The simulation results in the studied operating window (423 $K \le T \le 573$ K and 10 Pa \le P \le 500 Pa) from the mesoscopic model based on the kMC simulation with steric hindrance are shown in Fig. 9. 800 data points are collected with a temperature and pressure interval of 10 K and 10 Pa, respectively. Depending on the operating temperature and pressure, the overall process time significantly varies. Specifically, a Hacac dose of more than 3 s is calculated for saturation at a pressure of below 100 Pa. Hacac pulse times from the kMC simulations are comparable to the experiment results, where the Hacac pulse of 5 s per cycle was reported to be used to reach saturation (Mameli et al., 2017). In the BDEAS cycle, a BDEAS dosage time of 2.3 s at P = 400 Pa is computed to reach full coverage, which is consistent with prior experimental research from Merkx et al. (2020a). In addition, Roh et al. (2022) reported that dosing BDEAS for around 2 s was required for saturation on SiO2 in a typical ALD operating window.

Fig. 10 shows the process time dependence on the operating temperature and pressure on 2D graphs by presenting isobaric lines produced from Fig. 9. As expected, a



Figure 10 – 2D plots of process time as a function of temperature with different pressures in (a) Step A, (b) Step B, and (c) Step C, respectively.

higher operating pressure causes a shorter process time for all steps due to the higher pressure accelerating the physisorption reactions, which can be explained by the kMC algorithm. Surface reactions and desorption reactions, which are based on the Arrhenius equation, are mostly dependent on temperature. On the contrary, the pressure only affects physisorption reactions. Therefore, high pressure solely has a substantial impact on the physisorption step. Specifically, when pressure is increased from 100 to 500 *Pa*, the process time decreases by a factor of 5.03 for Step A, 4.89 for Step B, and 5.01 for Step C throughout the temperature window. Therefore, the operating pressure linearly affects the process time for all steps, which indicates that the physisorption step is the key component in determining the process time.

As shown in Fig. 10, changing the temperature does not cause any significant impact on the process time in the aforementioned range. Due to the randomness, the process time slightly fluctuates with increasing temperature. Although an increase in temperature accelerates all surface reactions based on the simulation algorithm, Fig. 10 reveals that the process time is rarely reliant on temperature. Prior research reported that the deposition of BDEAS was nearly constant (Roh et al., 2022). With regard to the kMC algorithm, the reaction rate constants of the surface reactions are based on the Arrhenius equation in Eq. (3) increase with increasing temperature. However, increasing temperature decelerates the physisorption reaction rate. With the independence of temperature in the ALD growth process, the reduction in the physisorption reaction rates and the increase in the surface reaction rates with increasing temperature offset each other.

The stochastic behavior of the kMC algorithm may present a variation in dosage times for reaching full coverage. Thus, 100 simulations of the same condition were simulated and averaged to compensate for the randomness and deviation in the dosage times. Histograms depicting the distribution of the dosage times for Steps A, B, and C, are presented in Fig. 11 and illustrate that most dosage times computed were within a single standard deviation, σ , from the average, μ , dosage time. Therefore, the stochastic behavior has a moderate impact on the precision of the dosage times, which is the reason why averaging the dosage time is an effective method for producing consistent results.



Figure 11 – Histograms depicting the distribution of dosage times for 100 iterations while at constant operating conditions for (a) Step A (T = 523 K, P = 100 Pa), (b) Step B (T = 523 K, P = 350 Pa), and (c) Step C (T = 523 K, P = 200 Pa).

4. Conclusion

In this work, a combined atomistic and mesoscopic model considering the effects of chemoselectivity and regioselectivity (steric hindrance) based on a kinetic Monte Carlo (kMC) simulation was developed to investigate the surface kinetics of area-selective atomic layer deposition (ASALD) of SiO₂/ Acetylacetone (Hacac), bis(diethylamino)silane Al_2O_3 . (BDEAS), and ozone were used for Steps A through C as small molecule inhibitors (SMI), precursors, and oxidants, respectively. Density functional theory (DFT) calculations including the nudged elastic band (NEB) method were performed to obtain kinetic parameters for the basis of the kinetic mechanisms. This study revealed that the inhibitor forms a protective layer on the non-growth area (NGA), Al₂O₃, as a preferential reaction path as opposed to the growth area (GA), SiO₂, by visualizing the surface coverage of Hacac, demonstrating the chemoselectivity of the Hacac adsorption. Additionally, the regioselective behavior of bulky species, Hacac and BDEAS, was simulated, which determined the preference for particular configurations (chelate configuration) that would provide the least steric hindrance to maximize the surface coverage. It was also observed that regioselective dependence of BDEAS adsorption prevented the precursor from adsorbing onto the Hacac protective layer as a consequence of steric repulsion effects. In addition, the temperature and pressure dependence on the ALD growth on the GA was discussed. The ALD growth was linearly dependent on pressure, while there was no impact of temperature on the ALD growth on the GA. This simulation work was supported and demonstrated by several experimental studies as discussed in Section 3. Therefore, the developed mesoscopic model greatly exemplifies the surface kinetics at the atomic level, providing insight into ASALD as a brandnew technology for bottom-up nanofabrication. This research can be integrated with not only other experimental research, but also a computational fluid dynamics model to optimize the industrial reactor design and the operating conditions of the ASALD process in future research.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Baroni, S., Giannozzi, P., Isaev, E., 2011. Thermal properties of materials from ab initio quasi-harmonic phonons. arXiv preprint arXiv:1112.4977.
- Bortz, A., Kalos, M.H., Lebowitz, J.L., 1975. A new algorithm for monte carlo simulation of ising spin systems. J. Comput. Phys. 17, 10–18.
- Chen, R., Kim, H., McIntyre, P.C., Porter, D.W., Bent, S.F., 2005. Achieving area-selective atomic layer deposition on patterned substrates by selective surface modification. Appl. Phys. Lett. 86, 191910.
- Fang, M., Ho, J.C., 2015. Area-selective atomic layer deposition: conformal coating, subnanometer thickness control, and smart positioning. ACS Nano 9, 8651–8654.
- Folkendt, M.M., Weiss-Lopez Jr., B.E., True,N.S, J.P.C., 1985. Gasphase proton nmr studies of keto-enol tautomerism of acetylacetone, methyl acetoacetate, and ethyl acetoacetate. J. Phys. Chem. 89, 3347–3352.
- Gamekkanda, J.C., Sinha, A.S., Desper, J., Đaković, M., Aakeröy, C.B., 2017. The role of halogen bonding in controlling assembly and organization of Cu(II)-Acac based coordination complexes. Crystals 7, 226.
- George, S.M., 2010. Atomic layer deposition: an overview. Chem. Rev. 110, 111–131.
- Giannozzi, P., 2009. QUANTUM ESPRESSO: a modular and opensource software project for quantum simulations of materials. J. Phys. Condens. Matter 21, 395502.
- Haider, A., Yilmaz, M., Deminskyi, P., Eren, H., Biyikli, N., 2016. Nanoscale selective area atomic layer deposition of TiO_2 using e-beam patterned polymers. RSC Adv. 6, 106109–106119.
- Hu, M., Hauger, T.C., Olsen, B.C., Luber, E.J., Buriak, J.M., 2018. UVinitiated Si-S, Si-Se, and Si-Te bond formation on Si(111): Coverage, mechanism, and electronics. J. Phys. Chem. C 122, 13803–13814.
- Huang, J., Hu, G., Orkoulas, G., Christofides, P.D., 2010. Dynamics and lattice-size dependence of surface mean slope in thinfilm deposition. Ind. Eng. Chem. Res. 50, 1219–1230.
- Huang, J., Lee, M., Lucero, A., Cheng, L., Kim, J., 2014. Area-selective ald of TiO_2 nanolines with electron-beam lithography. J. Phys. Chem. C 118, 23306–23312.
- Hughes, K.J., Dube, A., Sharma, M., Engstrom, J.R., 2012. Initial stages of atomic layer deposition of tantalum nitride on SiO_2 and porous low- κ substrates modified by a branched interfacial organic layer: chemisorption and the transition to steady-state growth. J. Phys. Chem. C 116, 21948–21960.
- Jansen, A.P.J., 2012. An Introduction to Kinetic Monte Carlo Simulations of Surface Reactions. vol. 1 Academic Press.
- Jin, L., Li, Y., Hu, Z., Chu, J., 2018. Full three-dimensional morphology evolution of amorphous thin films for atomic layer deposition. AIP Adv. 8, 045304.
- Kim, H.G., Kim, M., Gu, B., Khan, M.R., Ko, B.G., Yasmeen, S., Kim, C.S., Kwon, S.H., Kim, J., Kwon, J., Jin, K., Cho, B., Chun, J.S., Shong, B., Lee, H.B.R., 2020. Effects of Al precursors on deposition selectivity of atomic layer deposition of Al₂ O₃ using ethanethiol inhibitor. Chem. Mater. 32, 8921–8929.
- Lee, G., Lee, B., Kim, J., Cho, K., 2009. Ozone adsorption on graphene: Ab initio study and experimental validation. J. Phys. Chem. C 113, 14225–14229.

- Leskelä, M., Ritala, M., 2002. Atomic layer deposition (ALD): from precursors to thin film structures. Thin Solid Films 409, 138–146.
- Mackus, A.J.M., Merkx, M.J.M., Kessels, W.M.M., 2019. From the bottom-up: toward area-selective atomic layer deposition with high selectivity. Chem. Mater. 31, 2–12.
- Mameli, A., Merkx, M.J.M., Karasulu, B., Roozeboom, F., Kessels, W.E.M.M., Mackus, A.J.M., 2017. Area-selective atomic layer deposition of SiO₂ using acetylacetone as a chemoselective inhibitor in an ABC-type cycle. ACS Nano 11, 9303–9311.
- Maroudas, D., 2000. Multiscale modeling of hard materials: challenges and opportunities for chemical engineering. AIChE J. 46, 878–882.
- Merkx, M.J.M., Angelidis, A., Mameli, A., Li, J., Lemaire, P.C., Sharma, K., Hausmann, D.M., Kessels, W.M.M., Sandoval, T.E., Mackus, A.J.M., 2022. Relation between reactive surface sites and precursor choice for area-selective atomic layer deposition using small molecule inhibitors. J. Phys. Chem. C 126, 4845–4853.
- Merkx, M.J.M., Sandoval, T.E., Hausmann, D.M., Kessels, W.M.M., Mackus, A.J.M., 2020a. Mechanism of precursor blocking by acetylacetone inhibitor molecules during areaselective atomic layer deposition of SiO₂. Chem. Mater. 32, 3335–3345.
- Merkx, M.J.M., Vlaanderen, S., Faraz, T., Verheijen, M.A., Kessels, W.M.M., Mackus, A.J.M., 2020b. Area-selective atomic layer deposition of TiN using aromatic inhibitor molecules for metal/dielectric selectivity. Chem. Mater. 32, 7788–7795.
- MinayeHashemi, F.S., Prasittichai, C., Bent, S.F., 2015. Self-correcting process for high quality patterning by atomic layer deposition. ACS Nano 9, 8710–8717.
- Parsons, G.N., Clark, R.D., 2020. Area-selective deposition: fundamentals, applications, and future outlook. Chem. Mater. 32, 4920–4953.
- Pitriana, P., Wungu, T.D.K., Herman, H., Hidayat, R., 2018. The computation parameters optimizations for electronic structure calculation of LiPbI₃ perovskite by the density functional theory method. IOP Conf. Ser. Mater. Sci. Eng. 434, 012026.
- Richards, F.M., 1973. The interpretation of protein structures: total volume, group volume distributions and packing density.J. Mol. Biol. 82, 1–14.
- Roh, H., Kim, H.L., Khumaini, K., Son, H., Shin, D., Lee, W.J., 2022. Effect of deposition temperature and surface reactions in atomic layer deposition of silicon oxide using bis(diethylamino)silane and ozone. Appl. Surf. Sci. 571, 151231.
- Schwille, M.C., Schössler, T., Schön, F., Oettel, M., Bartha, J.W., 2017. Temperature dependence of the sticking coefficients of bis-diethyl aminosilane and trimethylaluminum in atomic layer deposition. J. Vac. Sci. Technol. A 35, 01B119.
- Seo, S., Yeo, B.C., Han, S.S., Yoon, C.M., Yang, J.Y., Yoon, J., Yoo, C., jin Kim, H., baek Lee, Y., Lee, S.J., Myoung, J.M., Lee, H.B.R., Kim, W.H., Oh, I.K., Kim, H., 2017. Reaction mechanism of area-selective atomic layer deposition for Al₂ O₃ nanopatterns. ACS Appl. Mater. Interfaces 9, 41607–41617.
- Shirazi, M., Elliott, S.D., 2014. Atomistic kinetic monte carlo study of atomic layer deposition derived from density functional theory. J. Comput. Chem. 35, 244–259.
- Sinha, A., Hess, D.W., Henderson, C.L., 2006. Area selective atomic layer deposition of titanium dioxide: effect of precursor chemistry. J. Vac. Sci. Technol. B Microelectron. Nanometer Struct. Process. Meas. Phenom. 24, 2523–2532.
- Weckman, T., Shirazi, M., Elliott, S.D., Laasonen, K., 2018. Kinetic monte carlo study of the atomic layer deposition of zinc oxide. J. Phys. Chem. C 122, 27044–27058.
- Yarbrough, J., Shearer, A.B., Bent, S.F., 2021. Next generation nanopatterning using small molecule inhibitors for area-selective atomic layer deposition. J. Vac. Sci. Technol. A 39, 021002.

- Yun, S., Tom, M., Luo, J., Orkoulas, G., Christofides, P.D., 2022a. Microscopic and data-driven modeling and operation of thermal atomic layer etching of aluminum oxide thin films. Chem. Eng. Res. Des. 177, 96–107.
- Yun, S., Tom, M., Orkoulas, G., Christofides, P.D., 2022b. Multiscale computational fluid dynamics modeling of spatial thermal atomic layer etching. Comput. Chem. Eng. 163, 107861.
- Yun, S., Tom, M., Ou, F., Orkoulas, G., Christofides, P.D., 2022c. Multiscale computational fluid dynamics modeling of thermal atomic layer etching: application to chamber configuration design. Comput. Chem. Eng. 161, 107757.
- Yun, S., Tom, M., Ou, F., Orkoulas, G., Christofides, P.D., 2022d. Multivariable run-to-run control of thermal atomic layer etching of aluminum oxide thin films. Chem. Eng. Res. Des. 182, 1–12.