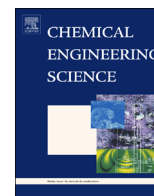




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Reaction factorization for the dynamic analysis of atomic layer deposition kinetics



Elizabeth M. Remmers, Curtisha D. Travis, Raymond A. Adomaitis*

Department of Chemical & Biomolecular Engineering, Institute for Systems Research, University of Maryland, College Park, MD, United States

HIGHLIGHTS

- Model reduction approach for surface reaction dynamics.
- Based on a reaction model factorization procedure.
- Applicable to atomic layer deposition (ALD) and other thin-film processes.
- Provides insight into the structure of differential-algebraic equation models describing thin-film deposition processes.
- Presents a new dynamic model for alumina ALD.

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ABSTRACT

We develop a Gauss–Jordan factorization procedure to explicitly separate the slow (deposition), fast (equilibrium), and instantaneous (conserved) modes of thin-film deposition models describing the dynamics of the precursor, surface, and deposition chemical species, focusing primarily on the dynamics of atomic layer deposition (ALD) processes. Our reaction factorization procedure provides an unambiguous means of translating sequences of equilibrium and irreversible reactions characterizing a deposition system into a low-dimensional DAE system when the reaction kinetics are predicted using transition-state theory. The factorization eliminates redundant dynamic modes; an implicit Euler procedure then is used to solve the singular-perturbation problem describing the time-evolution of the reaction species on the manifold defined by the combination of the equilibrium relationships and conserved quantities. An alumina ALD process based on the TMA/water precursor system serves as the example used in this work; despite the intense study of this ALD process, several new observations regarding this reaction system are made and a number of new questions are raised.

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1. Introduction

Atomic layer deposition (ALD) is a thin film deposition process used to create highly conformal films with precise control of thickness and composition. ALD utilizes a cycle of sequential, self-limiting surface reactions to deposit the desired film one monolayer or sub-monolayer during each cycle. Typically, a binary sequence of gaseous precursors is used, with purge periods in between to prevent gas phase reactions. The self-limiting nature of the deposition half-reactions arises from surface saturation due to a finite density of surface reaction sites, or steric hindrance when precursor ligands remain after the chemisorption reactions.

ALD has a contested history; many trace its origin to Finland the 1970s, when in fact this process had already been developed by another group in the Soviet Union in the 1960s (Puurunen, 2005). ALD was, and still is, used in the manufacture of electroluminescent flat panel displays but experienced a resurgence in interest in the 1990s for use in microelectronics processing (Leskelä and Ritala, 2003). The advantages of ALD over other thin film deposition techniques are precise thickness control, good conformality over high aspect ratio structures, and low process temperature. These advantages make ALD a desirable process for microelectronics applications including high-k gate oxide deposition for MOSFETs, DRAM trench capacitor dielectrics, 3D multi-gate field effect transistors, and nonvolatile memory devices (Leskelä and Ritala, 2003; Kim et al., 2009). Photovoltaic applications include surface passivation layers on crystalline-Si cells

* Corresponding author.

E-mail address: adomaiti@umd.edu (R.A. Adomaitis).

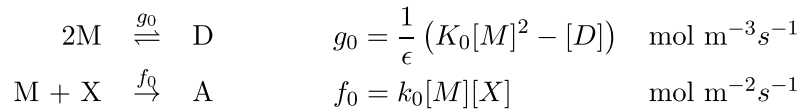
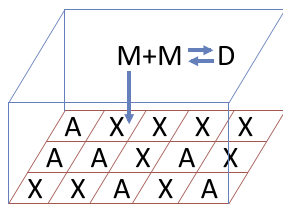
(Werner et al., 2011), as well as buffer and barrier layers in CIGS cells (Pimenoff, 2012; Holmqvist, 2013). ALD also finds use in numerous other applications such as nanostructured self-cleaning surfaces (Ng et al., 2008), protective coatings for spacecraft surfaces (Cooper et al., 2008) and glass displays (Pimenoff, 2012), as well as solid lubricant oxides used in various devices including MEMS (Kim et al., 2009) and automotive components (Doll et al., 2009).

ALD modeling work falls into two main categories: empirical methods which require fitting parameters based on experiments (such as Holmqvist et al., 2012, 2013), and first principles (or *ab initio*) methods which do not. First principles methods allow for the exploration of novel processes, and can provide information about reaction pathways, substrate effects, and precursor decomposition (Elliott, 2012). First principles ALD studies frequently utilize density functional theory (DFT) calculations to determine reaction pathways and energetics that in turn can be incorporated in reaction rate expressions, such as those derived from transition state theory (TST), to determine reaction kinetics. This kinetics information is used to compare the effect of different surface functional groups on reaction rates (Xu and Musgrave, 2004; Xu and Ye, 2010), or to explain experimentally observed differences in growth rate due to different precursor pulsing sequences in the deposition of $\text{HfO}_2/\text{Al}_2\text{O}_3$ mixtures (Nyns et al., 2010). Kinetics information can further be fed into a reactor model or kinetic Monte Carlo (kMC) simulation to determine the mechanism behind experimentally observed behavior such as the temperature dependency of growth rate (Deminsky et al., 2004), or to predict desirable operating conditions (Travis and Adomaitis, 2013b).

Despite these extensive efforts into understanding the fundamental aspects of ALD surface reaction mechanisms and integration of surface reaction models with reactor-scale precursor transport models (see Holmqvist, 2013 for an excellent review), a fundamental understanding of how one models the surface species dynamics during the different phases of an ALD processing cycle is lacking. Likewise, an understanding of how these models connect to the more extensively studied chemical vapor deposition (CVD) processes requires further study. The objective of this paper is to take the first step in decomposing the ALD surface reaction dynamics into those processes which take place relatively slowly (the deposition modes), those that are fast (the equilibrium reactions), and those processes which are governed by conservation principles, and so constitute instantaneous processes. Our contribution is the development of a reaction factorization technique which rigorously determines if the deposition process time scales can be separated and whether the singular perturbation problem that results from the factorization process results in a well-posed DAE system. We claim that the new approach we present to modeling ALD kinetics provides a rational path to model development that signals when reaction networks are structurally incorrect, along with providing other insights into the deposition reaction chemistry.

2. A simple deposition reaction scheme

To begin, consider a simplified deposition reaction where we define a gas-phase monomer M and dimer D precursor species and the equilibrium relationship between the two. In the context of thin-film deposition processes, each precursor molecule M can be thought of as containing a single atom of the material (species A) to be deposited. An irreversible monomer reaction with surface site X produces the deposited film species A :



where g_0 and f_0 are the net-forward equilibrium and deposition reaction rates, respectively. In our analysis, the rates associated with the equilibrium reactions are assumed to be much greater than that of deposition and so scaling the time appropriately, $g_0 = \mathcal{O}(1/\epsilon)$ with $\epsilon \ll 1$ and $f_0 = \mathcal{O}(1)$. By-products of the surface reactions are omitted in this simplified analysis. Writing the material balances for each species give the four ODEs in time:

$$\frac{d\mathbf{c}^{n_c \times 1}}{dt} = \mathbf{S}^{n_c \times n_r} \mathbf{r}^{n_r \times 1} \implies \frac{d}{dt} \begin{bmatrix} [M] \\ [D] \\ \sigma[X] \\ \sigma[A] \end{bmatrix} = \begin{bmatrix} -2 & -1 \\ 1 & 0 \\ 0 & -1 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} g_0 \\ \sigma f_0 \end{bmatrix} \quad (1)$$

where σ = deposition surface area/reactant gas volume with units m^{-1} . The matrices \mathbf{c} , \mathbf{S} , and \mathbf{r} contain the species concentrations, stoichiometric coefficients, and reaction rates respectively. n_c and n_r refer to the number of components and reactions.

Clearly, two issues arise at this point: (i) we have a higher-dimensional set of ODEs (four) relative to the single rate-limiting deposition step, and (ii) the monomer concentration dynamic behavior $[M](t)$ is governed by reaction rates of different orders of magnitude. Reducing (1) to its minimal dynamic dimension is straightforward using the QR factorization or the singular value decomposition. However, because array \mathbf{S} represents reaction stoichiometry, not reaction rates, these decomposition methods will not provide guidance on separating time scales for the system. Therefore, the approach we pursue is based on the Gauss–Jordan factorization of \mathbf{S} (see Vora and Daoutidis, 2001 for a comparable approach). In (1), both dynamic dimension reduction and timescale separation can be accomplished if there exists a transformation $\mathbf{y} = \mathbf{U}\mathbf{c}$ in which the objective is to determine a new reactant coordinate system \mathbf{y} such that to the greatest extent possible, each reaction becomes associated with a single new reactant $y_i \in \mathcal{R}^{n_c}$, i.e.,

$$\mathbf{U}^{n_c \times n_c} \mathbf{S}^{n_c \times n_r} \approx \begin{bmatrix} \mathbf{I}^{n_r \times n_r} \\ \mathbf{0}^{(n_c - n_r) \times n_r} \end{bmatrix}$$

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