Species-Reaction Graphs for Reaction Network Analysis in Thin-Film Deposition Processes

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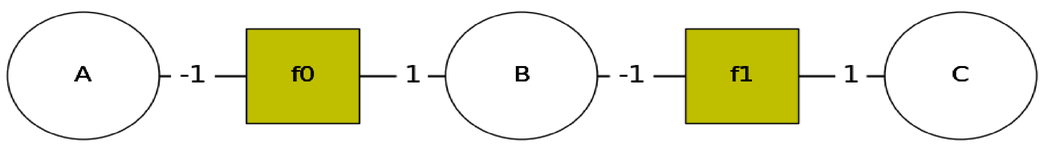
1. Motivation

Atomic Layer Deposition (ALD) is a vapor-based process for production of thin solid films in which heterogeneous and homogenous reactions with widely ranging time scales are involved. Proposing an accurate reaction mechanism that results in a well-posed species balance is among the first steps in studying these processes. A valid reaction network (RN) alongside with accurate kinetic data is vital for process modeling and optimization and forms the backbone of further engineering analysis.

In this project, we have developed an analysis method based on species reaction (SR) graphs and linear algebra which provides a mechanistic approach for identifying structurally defective RNs prior to the often time-consuming step of calculating individual reaction rates and attempt to solve the system of differential equations produced by species balances.



2. Species-Reaction Graphs

The idea of using a graph associated with a RN to study the behavior of the chemical system corresponding to that has been used before by Craciun and Feinebrg [1]. We introduce a new form of their graph where species and reactions involved form the nodes, and edges correspond to the stoichiometry of the reactions as (above example). Using our previously developed reaction factorization, we propose the following rules to extract the time independent modes in the system's dynamic (calling them RN invariants):

- 1- A terminal to terminal path can be used to formulate a RN invariant containing S_i species by using the stoichiometry $\vartheta_{p,n}$:

$$S_N - \frac{\vartheta_{p,n}}{\vartheta_{r,n}}\left[S_{N-1} - \frac{\vartheta_{p,n-1}}{\vartheta_{r,n-1}}[S_{N-2} - \cdots]\right] = constant$$

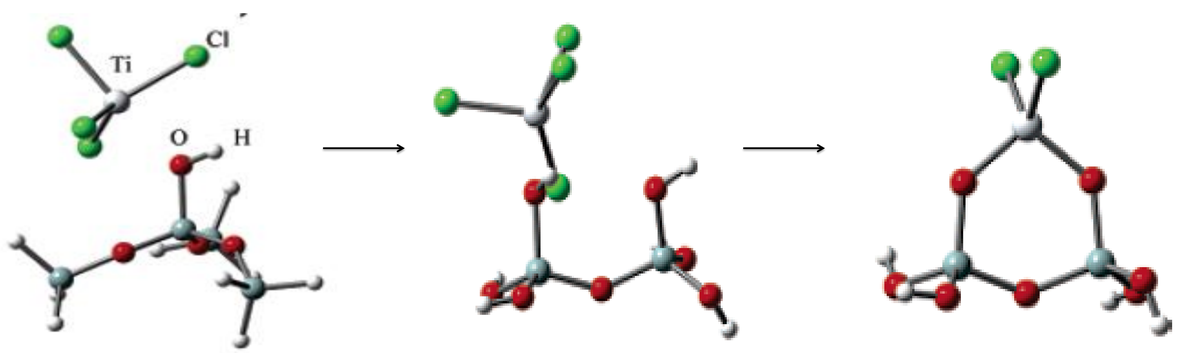
- 2- Any graphical cycle on SR graph can be broken at an arbitrary node to two virtual nodes considering them the beginning and ending nodes.

4. Conclusion and Future Works

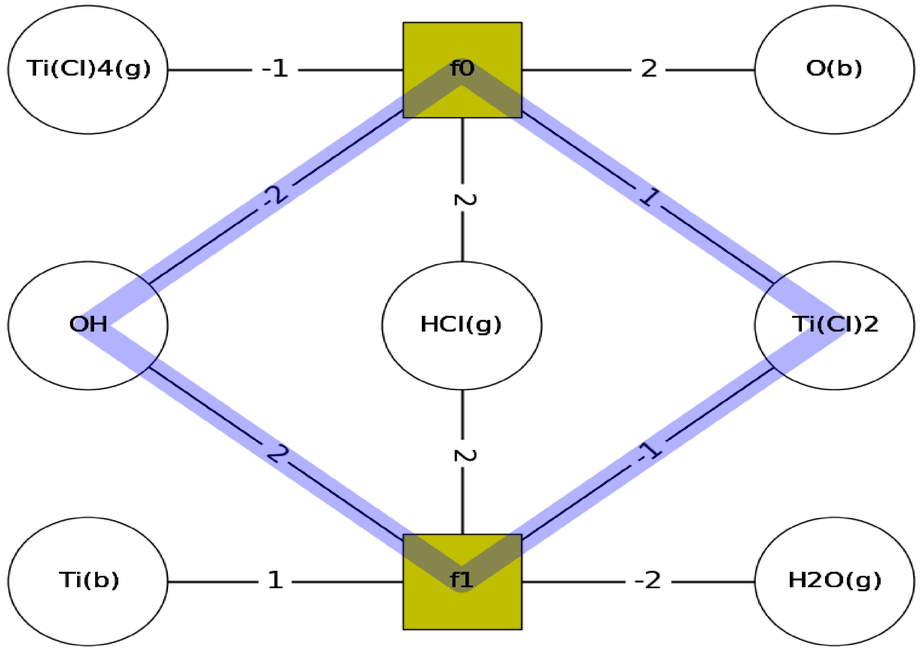
This tool enables us to come up with well-behaved and valid RNs which can later be used for modeling and optimization of the ALD process. Also new work is in progress to extend the application of SR graphs to material flux analysis for different ALD systems by incorporating available kinetic data into RN.

3. Application to Titania ALD

Thin films of titania (TiO2) have a wide variety of applications, from high dielectric layers in electronics to protective layers in sun glasses and titanium-based catalysts. One widely used precursor system for depositing titania by ALD is titanium tetrachloride TiCl4 - water. As in most of metal-oxide ALD processes the initial interaction between lone pair electrons of a surface oxygen with empty orbitals in the precursor metal atom followed by H-transfer reaction from hydroxyl groups considered to be responsible for the precursor chemisorption on the surface and eventually film growth [2].



Below shows the SR graph associated with the main reactions occurring during the titania ALD using TiCl4 and water. The blue path shows the graphical cycle which can be used to formulate time independent mode which originates from conservation of surface reactive sites (hydroxyl groups) on the deposition surface.



$$[OH] + 2 \times [TiCl(2)] = constant$$

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[1] G. Craciun, M. Feinberg, SIAM J. Appl. Math., 2006, 66(4), 1321.
[2] Z. Hu, C. H. Turner, J. Phys. Chem. B 2006, 110, 8337.