Chemical Engineering Science 117 (2014) 301–317

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Scale-up analysis of continuous cross-flow atomic layer deposition reactor designs

A. Holmqvist [a,*], F. Magnusson [b], S. Stenström [a]

[a] Department of Chemical Engineering, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden
[b] Department of Automatic Control, Lund University, P.O. Box 118, SE-221 00 Lund, Sweden

HIGHLIGHTS

- Novel model-based methodology for scaling up cross-flow ALD reactors.
- Dynamic similarity was investigated by means of the non-dimensionalized ALD reactor model.
- ALD limit-cycle dynamic solution was numerically computed using Radau collocation schemes.
- The maximum precursor utilization was enhanced by scaling up the substrate dimensions.
- Optimal scaling rules to keep deposition profiles identical in scaled-up systems were identified.

ARTICLE INFO

Article history:
Received 13 February 2014
Received in revised form
26 June 2014
Accepted 1 July 2014
Available online 9 July 2014

Keywords:
Atomic layer deposition
Scale-up analysis
Dynamic optimization
Mathematical modeling
Limit-cycle kinetics
Numerical analysis

ABSTRACT

This paper presents the development of a non-dimensional model of a continuous cross-flow atomic layer deposition (ALD) reactor with temporally separated precursor pulsing and a structured model-based methodology for scaling up the substrate dimensions. The model incorporates an ALD gas–surface reaction kinetic mechanism for the deposition of thin ZnO films from $Zn(C_2H_5)_2$ and H_2O precursors that was experimentally validated in our previous work (Holmqvist et al., 2012, 2013a). In order to maintain dynamic similarity, a scaling analysis was applied based on the dimensionless numbers, appearing in non-dimensionalized momentum and species mass conservation equations, that describe the convective laminar flow, mass transfer and heterogeneous reaction. The impact on these dimensionless numbers and, more importantly, the impact on the limit-cycle deposition rate and its relative uniformity was thoroughly investigated when linearly scaling up the substrate dimensions. In the scale-up procedure, the limit-cycle precursor utilization was maximized by means of dynamic optimization, while ensuring that identical deposition profiles were obtained in the scaled-up system. The results presented here demonstrated that the maximum precursor yields were promoted at higher substrate dimensions. Limit-cycle dynamic solutions to the non-dimensionalized model, computed with a collocation discretization in time, revealed that it is a combination of the degree of precursor depletion in the flow direction and the magnitude of the pressure drop across the reactor chamber that governs the extent of the deposition profile non-uniformity. A key finding of this study is the identification of optimal scaling rules for maximizing precursor utilization in the scaled-up system while maintaining fixed absolute growth rate and its relative uniformity.

1. Introduction

Atomic layer deposition (ALD) is a gas-phase deposition process that can produce conformal thin films with controlled uniform thickness in the nanometer range (George, 2010). This attribute is inherent to the sequential self-terminating (Puurunen, 2005) ALD gas–surface reactions (Masel, 1996) in which the non-overlapping alternating injection of chemical precursor species separated by intermediate purge steps prevents reactions in the gas phase (Miikkulainen et al., 2013). The deposition process depends strongly on two characteristic time scales (see, for example, Adomaitis, 2010; Granneman et al., 2007): the time scale of underlying reactor-scale mass transport (Aarik et al., 2006; Jur and Parsons, 2011; Mousa et al., 2012), and the time scale of the heterogeneous gas–surface reactions (Ritala and Leskelä, 2002; Yanguas-Gil and Elam, 2014).

* Corresponding author. Tel.: +46 46 222 4925; fax: +46 46 222 4526.
E-mail addresses: anders.holmqvist@chemeng.lth.se (A. Holmqvist), fredrik.magnusson@control.lth.se (F. Magnusson), stig.stenstrom@chemeng.lth.se (S. Stenström).

http://dx.doi.org/10.1016/j.ces.2014.07.002
0009-2509/

Conventional thermal ALD is a special modification of the chemical vapor deposition (CVD) technique. One of the essential advantages of ALD is that its self-terminating nature enables uniform coating of substrates with large surface areas (Levy and Nelson, 2012; Sundaram et al., 2010), and it is thus easier to scale up the process of ALD than that of CVD (Yanguas-Gil and Elam, 2012). In this study, the geometrical scale up of the substrate dimensions in cross-flow, low-volume ALD reactor designs with temporal precursor pulsing was investigated. Such reactor designs are of major interest for the equipment used to manufacture substrates of large surface area (Henn-Lecordier et al., 2011). Such substrates are subject to stringent uniformity constraints (Cleveland et al., 2012), where the fundamental requirement for growth uniformity is the attainment of surface saturation. This, in turn, requires adequate precursor delivery (Knoops et al., 2011; Ylilammi, 1995), optimal process operating conditions, and optimal reactor design (Elers et al., 2006). Non-uniform film thickness profiles in cross-flow ALD reactor designs can result from precursor depletion, which can be a concern for precursors with a low vapor pressure (Granneman et al., 2007).

Several studies on scaling up horizontal reactor designs for CVD have been published, (see, for example, Dam et al., 2007 and the references cited therein). However, a model-based study of dimensionless numbers with respect to scaling up has never been rigorously carried out for ALD growth. The overall objective of the present study, therefore, was to develop a model-based method for the geometrical scale up of the substrate dimension in cross-flow reactor designs that use temporal precursor pulsing. The scale-up procedure provides a fixed absolute growth rate and relative uniformity while maximizing precursor utilization. This methodology was applied to an experimentally validated mechanism of the ALD gas–surface reactions for the deposition of thin ZnO films from $Zn(C_2H_5)_2$ and H_2O precursors (Holmqvist et al., 2012, 2013a). The study presented here had three main objectives:

(i) To develop a structured model-based method for the geometrical scaling up of the substrate dimensions in continuous cross-flow ALD reactor designs, and to identify the scaling guidelines that are best suited to maintaining the limit-cycle deposition rate and its relative uniformity in the scaled-up system.
(ii) To investigate dynamic similarity by deriving the fully coupled compressible flow equations, along with their boundary conditions and initial conditions, of the developed reactor model in its non-dimensional form.
(iii) To formulate and solve a dynamic optimization problem in order to optimize precursor utilization, subject to terminal constraints of the limit-cycle deposition rate and its relative uniformity.

This paper is organized as follows: Section 2 outlines the mechanism of the ZnO ALD gas–surface reactions. Section 3 derives the non-dimensional ALD reactor model and identifies the associated non-dimensional variables that appear. Section 4 describes the scale-up strategies and formulates the dynamic optimization problem, while Section 5 outlines the modeling and optimization framework. Section 6 presents the results from the scale-up analysis, and Section 7 presents the concluding remarks.

1.1. Previous modeling

Our previous work (Holmqvist et al., 2012, 2013a,b), which presents a mechanistic model of the continuous cross-flow ALD reactor system F-120 manufactured by ASM Microchemistry Ltd. (Suntola, 1992), is particularly relevant to the present article. The work of Yanguas-Gil and Elam (2012) on what is known as the "SMART" model (where "SMART" is an acronym for "Simple Model for Atomic layer deposition precursor Reaction and Transport") for the analysis of transport-reaction processes in a tubular, laminar flow reactor is also highly relevant. The non-dimensional model presented in the present study is found on the dimensional model that we have previously developed (Holmqvist et al., 2012, 2013a,b), and the approximation of fully developed laminar channel flow defined in a one-dimensional computational domain. Moreover, the model presented here comprises fully coupled compressible equations for the conservation of mass, momentum and individual gas-phase species, while the SMART model, in contrast, assumes incompressible flow. The application range of the model is expanded in this way to include the region in which the pressure of the precursor is significant, relative to that of the carrier gas, which is necessary in the scale-up analysis.

2. ALD surface reaction kinetics

The predictive capability of the developed physically based model to decouple the effects of precursor partial pressure, exposure times, process manipulated variables, and the dynamics of each exposure period on the limit-cycle spatially dependent substrate film thickness profile is essential for the purposes of this investigation. For this reason, an experimentally validated gas–surface reaction mechanism for the deposition of ZnO films from $Zn(C_2H_5)_2$ and H_2O precursors was incorporated into the model developed during the present study, in order to obtain as accurate a model as possible. The experimental investigation was conducted in the F-120 reactor system from ASM Microchemistry Ltd. (Suntola, 1992) and the estimated rate coefficients from ex situ X-ray reflectivity (XRR) thickness profile measurements are reported in Holmqvist et al. (2013a), which contains also details of the film characterization and data preprocessing.

Consider a simple ZnO ALD gas–surface reaction kinetic mechanism, with the overall reaction stoichiometry given by

$$Zn(C_2H_5)_2 + H_2O \longrightarrow ZnO + 2C_2H_6 \tag{R1}$$

and only encompassing the primary irreversible and sequential elementary gas–surface reactions for the $Zn(C_2H_5)_2$ and H_2O precursors on a normally hydroxylated surface. Such reactions were defined in Holmqvist et al. (2013a) as

$$\nu(-OH)\langle s\rangle + Zn(C_2H_5)_2\langle g\rangle \xrightarrow{k_1^{fwd}} (-O-)_\nu Zn(C_2H_5)_{2-\nu}\langle s\rangle + \nu C_2H_6\langle g\rangle \tag{R2a}$$

$$(-O-)_\nu Zn(C_2H_5)_{2-\nu}\langle s\rangle + H_2O\langle g\rangle \xrightarrow{k_2^{fwd}} (-O-)Zn(-OH)_\nu\langle s\rangle + (2-\nu)C_2H_6\langle g\rangle \tag{R2b}$$

Here $\langle s\rangle$ and $\langle g\rangle$ denote surface and gaseous species, respectively, and $\nu = 1.37$ (Elam and George, 2003) is the average number of hydroxyl groups that react with each $Zn(C_2H_5)_2$ molecule. Thus, the ZnO deposition half-reactions (Reactions (R2a) and (R2b)) were not broken down further into the elemental adsorption and reaction steps during each precursor exposure (as is done in, for example, Travis and Adomaitis, 2013a,b,c). Thereby, the ligand elimination was assumed to proceed without intermediate adsorption adducts or their transition states being formed, and that this is the rate-limiting step.

The irreversible half-reactions defined in Reaction (R2) subject to constant activation energies govern a *growth per cycle* (GPC) that increases strictly with the deposition temperature, and hence, Reaction (R2) cannot describe the sharp decrease in GPC that occurs at elevated temperatures (see, for example, Yousfi et al., 2000). This phenomenon is generally attributed to the gradual reduction of the surface hydroxyl groups through the recombination reaction (Reaction