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Scale-up Analysis of Continuous Cross-flow Atomic Layer Deposition Reactor Designs

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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 $\text{Zn}(\text{C}_2\text{H}_5)_2$ 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 dimen-

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

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 (Mikkulainen 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).

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

21 investigated. Such reactor designs are of major interest for the equipment used
22 to manufacture substrates of large surface area (Henn-Lecordier et al., 2011).
23 Such substrates are subject to stringent uniformity constraints (Cleveland et al.,
24 2012), where the fundamental requirement for growth uniformity is the attain-
25 ment of surface saturation. This, in turn, requires adequate precursor delivery
26 (Knoops et al., 2011; Ylilammi, 1995), optimal process operating conditions, and
27 optimal reactor design (Elers et al., 2006). Non-uniform film thickness profiles
28 in cross-flow ALD reactor designs can result from precursor depletion, which
29 can be a concern for precursors with a low vapor pressure (Granneman et al.,
30 2007).

31 Several studies on scaling up horizontal reactor designs for CVD have been
32 published, (see, for example, Dam et al. (2007) and the references cited therein).
33 However, a model-based study of dimensionless numbers with respect to scaling
34 up has never been rigorously carried out for ALD growth. The overall objective
35 of the present study, therefore, was to develop a model-based method for the ge-
36 ometrical scale up of the substrate dimension in cross-flow reactor designs that
37 use temporal precursor pulsing. The scale-up procedure provides a fixed abso-
38 lute growth rate and relative uniformity while maximizing precursor utilization.
39 This methodology was applied to an experimentally validated mechanism of the
40 ALD gas-surface reactions for the deposition of thin ZnO films from $\text{Zn}(\text{C}_2\text{H}_5)_2$
41 and H_2O precursors (Holmqvist et al., 2012, 2013a). The study presented here
42 had three main objectives:

- 43 i) To develop a structured model-based method for the geometrical scaling up
44 of the substrate dimensions in continuous cross-flow ALD reactor designs,
45 and to identify the scaling guidelines that are best suited to maintaining
46 the limit-cycle deposition rate and its relative uniformity in the scaled-up
47 system.
- 48 ii) To investigate dynamic similarity by deriving the fully coupled compress-
49 ible flow equations, along with their boundary conditions and initial con-
50 ditions, of the developed reactor model in its non-dimensional form.

51 iii) To formulate and solve a dynamic optimization problem in order to opti-
52 mize precursor utilization, subject to terminal constraints of the limit-cycle
53 deposition rate and its relative uniformity.

54 This paper is organized as follows: Section 2 outlines the mechanism of the
55 ZnO ALD gas–surface reactions. Section 3 derives the non-dimensional ALD
56 reactor model and identifies the associated non-dimensional variables that ap-
57 pear. Section 4 describes the scale-up strategies and formulates the dynamic
58 optimization problem, while Section 5 outlines the modeling and optimization
59 framework. Section 6 presents the results from the scale-up analysis, and Section
60 7 presents concluding remarks.

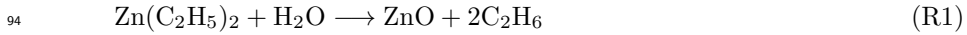
61 1.1. Previous Modeling

62 Our previous work (Holmqvist et al., 2012, 2013a,b), which presents a mech-
63 anistic model of the continuous cross-flow ALD reactor system F-120 manufac-
64 tured by ASM Microchemistry Ltd. (Suntola, 1992), is particularly relevant to
65 the present article. The work of Yanguas-Gil and Elam (2012) on what is known
66 as the “SMART” model (where “SMART” is an acronym for “Simple Model for
67 Atomic layer deposition precursor Reaction and Transport”) for the analysis
68 of transport-reaction processes in a tubular, laminar flow reactor is also highly
69 relevant. The non-dimensional model presented in the present study is founded
70 on the dimensional model that we have previously developed (Holmqvist et al.,
71 2012, 2013a,b), and the approximation of fully developed laminar channel flow
72 defined in a one-dimensional computational domain. Moreover, the model pre-
73 sented here comprises fully coupled compressible equations for the conservation
74 of mass, momentum and individual gas-phase species, while the SMART model,
75 in contrast, assumes incompressible flow. The application range of the model
76 is expanded in this way to include the region in which the pressure of the pre-
77 cursor is significant, relative to that of the carrier gas, which is necessary in the
78 scale-up analysis.

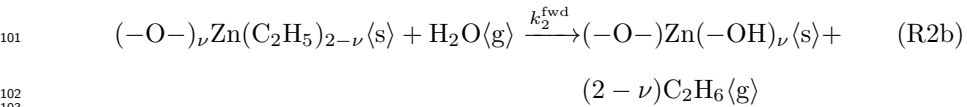
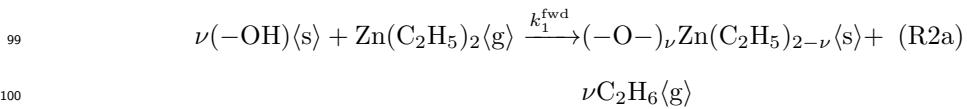
79 **2. ALD Surface Reaction Kinetics**

80 The predictive capability of the developed physically-based model to decou-
 81 ple the effects of precursor partial pressure, exposure times, process manipulated
 82 variables, and the dynamics of each exposure period on the limit-cycle spatially
 83 dependent substrate film thickness profile is essential for the purposes of this
 84 investigation. For this reason, an experimentally validated gas–surface reaction
 85 mechanism for the deposition of ZnO films from $\text{Zn}(\text{C}_2\text{H}_5)_2$ and H_2O precursors
 86 was incorporated into the model developed during the present study, in order
 87 to obtain as accurate a model as possible. The experimental investigation was
 88 conducted in the F-120 reactor system from ASM Microchemistry Ltd. (Sun-
 89 tola, 1992) and the estimated rate coefficients from *ex situ* X-ray reflectivity
 90 (XRR) thickness profile measurements are reported in Holmqvist et al. (2013a),
 91 which contains also details of the film characterization and data preprocessing.

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



95 and only encompassing the primary irreversible and sequential elementary gas–
 96 surface reactions for the $\text{Zn}(\text{C}_2\text{H}_5)_2$ and H_2O precursors on a normally hydrox-
 97 ylated surface. Such a reactions were defined in Holmqvist et al. (2013a) as:



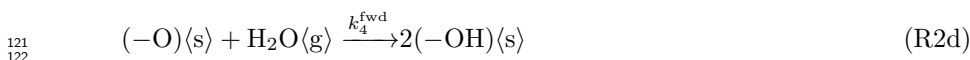
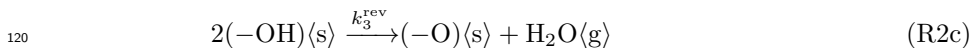
102 Here $\langle\text{s}\rangle$ and $\langle\text{g}\rangle$ denote surface and gaseous species, respectively, and $\nu =$
 103 1.37 (Elam and George, 2003) is the average number of hydroxyl groups that
 104 react with each $\text{Zn}(\text{C}_2\text{H}_5)_2$ molecule. Thus, the ZnO deposition half-reactions
 105 (Reactions (R2a and R2b)) were not broken down further into the elemental
 106
 107

Table 1: A summary of gaseous and fractional surface coverage species in Reactions (R2a–R2d), and their abbreviations.

Gaseous species ($\langle\text{g}\rangle$)	α	Surface species ($\langle\text{s}\rangle$)	κ
$\text{Zn}(\text{C}_2\text{H}_5)_2$	A	$(-\text{OH})$	A^*
H_2O	B	$(-\text{O}-)_\nu\text{Zn}(\text{C}_2\text{H}_5)_{2-\nu}$	B^*
C_2H_6	C	$(-\text{O})$	C^*
N_2	P		

108 adsorption and reaction steps during each precursor exposure (as is done in,
 109 for example, Elliott (2012); Ren (2009); Travis and Adomaitis (2013a,b,c)).
 110 Thereby, the ligand elimination was assumed to proceed without intermediate
 111 adsorption adducts or their transition states being formed, and that this is the
 112 rate-limiting step.

113 The irreversible half-reactions defined in Reaction (R2) subject to constant
 114 activation energies govern a *growth per cycle* (GPC) that increases strictly with
 115 the deposition temperature, and hence, Reaction (R2) cannot describe the sharp
 116 decrease in GPC that occurs at elevated temperatures (see, for example, Yousfi
 117 et al. (2000)). This phenomenon is generally attributed to the gradual reduction
 118 of the surface hydroxyl groups through the recombination reaction (Reaction
 119 (R2c)) (Deminsky et al., 2004; Matero et al., 2000; Rahtu et al., 2001):



123 where the hydroxyl groups may be reformed on the oxide surface during ex-
 124 posure to H_2O through the reverse reaction (Reaction (R2d)). It is, however,
 125 noteworthy that the GPC that is obtained, which is governed by the limit-
 126 cycle ZnO ALD kinetics proposed in Reactions (R2), has a convex temperature
 127 dependence. Finally, the abbreviations for the gaseous and fractional surface
 128 species in Reactions (R2a–R2d) used in this paper are listed in Table 1.

129 3. Physical Modeling

130 A one-dimensional representation of the square duct reaction chamber (with
 131 dimensions $(L \times W \times H)$ $5.0 \times 5.0 \times 0.2$ (cm)) of the reactor system constituted the
 132 spatial domain, $z \in [0, L]$, in the present study, with its z -axis coincident with
 133 the flow direction. Further details of the reactor system are given in Holmqvist
 134 et al. (2012, 2013b) and in Baunemann (2006); Yousfi et al. (2000). The original
 135 experimental configuration is denoted as the *Reactor* \mathcal{A} in the following scale-up
 136 analysis.

137 3.1. Nominal State and Algebraic Variables

138 For this paper a non-dimensionalized, physically-based model was used to
 139 calculate the spatially and temporally dependent concentration and deposition
 140 profiles for the original *Reactor* \mathcal{A} and have subsequent been applied to the
 141 scaled-up *Reactor* \mathcal{B} , while keeping certain dimensionless numbers in the dif-
 142 ferential equations and boundary conditions the same for both systems. In this
 143 way, the scale-up method strives to preserve dynamic similarity. However, in or-
 144 der to maintain constant dimensionless numbers, the underlying nominal state
 145 and algebraic variables $[\hat{\rho}, \hat{v}_\zeta, \hat{\omega}_\alpha, \hat{p}]$ must be expressed in terms of the process
 146 manipulated variables, $\mathbf{u} = [\dot{Q}_\beta, \dot{V}_{VP}, \dot{Q}_\alpha, \Delta\tau_\alpha]$ and $\forall \alpha \in \{A, B\}$. Thus, the
 147 length, $\zeta \in [\zeta_0, \zeta_{\text{end}}]$, and time, $\tau \in [\tau_0, \tau_f]$, are scaled by the nominal values L
 148 and L/\hat{v}_ζ , respectively. Additionally, the nominal mass averaged velocity, \hat{v}_ζ ,
 149 density, $\hat{\rho}$, and pressure, \hat{p} , of the carrier gas as well as the nominal precursor
 150 mass fraction, $\hat{\omega}_\alpha$, are conveniently expressed by the reactor dynamic material
 151 balances of the continuous stirred-tank reactor (CSTR) model:

$$152 \quad \left[\frac{\hat{v}_\zeta}{L} \right] \frac{d\hat{\rho}}{d\tau} = \frac{1}{V} \sum_{\forall \alpha} \dot{Q}_\alpha \rho_{\text{STP}, \alpha} \Pi_\alpha(\tau, \Delta\tau_\alpha) - \frac{\dot{V}_{VP}}{V} \hat{\rho} + \sum_{\forall \alpha} S_\alpha \quad (1a)$$

$$153 \quad \left[\frac{\hat{v}_\zeta}{L} \right] \frac{d\hat{\rho}\hat{\omega}_\alpha}{d\tau} = \frac{1}{V} \dot{Q}_\alpha \rho_{\text{STP}, \alpha} \Pi_\alpha(\tau, \Delta\tau_\alpha) - \frac{\dot{V}_{VP}}{V} \hat{\rho}\hat{\omega}_\alpha + S_\alpha \quad (1b)$$

155 where S_α denotes the net mass consumption owing to the heterogeneous gas-
 156 surface reactions (see Section 2). See Travis and Adomaitis (2013a) for further
 157 details of how the reactor dynamic material balances are derived.

158 A smooth rectangular function was used to model the non-overlapping pre-
 159 cursor injections in a cyclic time sequence. This function, $\Pi_\alpha(\tau, \Delta\tau_\alpha) \in [0, 1]$,
 160 was composed of superposed continuously differentiable logistic functions, $L(\bar{\tau})$:

$$161 \quad \Pi_\alpha(\tau, \Delta\tau_\alpha) = L(\bar{\tau} - \bar{\tau}_{0,\alpha}) - L(\bar{\tau} - \bar{\tau}_{f,\alpha}) \quad (2a)$$

$$162 \quad L(\bar{\tau}) = [1 + \exp(-\delta\tau_\alpha\bar{\tau})]^{-1} \quad (2b)$$

164 where $\bar{\tau} = N_{\Delta\tau} - \lfloor N_{\Delta\tau} \rfloor$ is the normalized cycle time, $N_{\Delta\tau} = \tau/\Delta\tau$ is the cycle
 165 number, $\Delta\tau = \Delta\tau_A + \Delta\tau_B + 2\Delta\tau_P$ denotes a complete ALD cycle, $\delta\tau_\alpha$ is a
 166 parameter that influences the maximum derivative of the function, and $\Delta\tau_\alpha =$
 167 $(\bar{\tau}_{f,\alpha} - \bar{\tau}_{0,\alpha})\Delta\tau$. Imposing stationarity on Eq. (1) under non-reactive conditions,
 168 i.e. prescribing $S_\alpha := 0$, allows to define the following explicit relationships:

$$169 \quad \hat{\rho} := \frac{\dot{Q}_\beta \rho_{\text{STP},\beta}}{\dot{V}_{\text{VP}}} \quad (3a)$$

$$170 \quad \hat{\omega}_\alpha := \frac{\dot{Q}_\alpha \rho_{\text{STP},\alpha}}{\dot{Q}_\alpha \rho_{\text{STP},\alpha} + \dot{Q}_\beta \rho_{\text{STP},\beta}} \quad (3b)$$

172 The nominal density, $\hat{\rho}$, in Eq. (3a) is defined for the carrier gas purge by
 173 prescribing $\Pi_\alpha(\tau, \Delta\tau_\alpha) := 0$, whereas the nominal gas-phase mass fraction, $\hat{\omega}_\alpha$,
 174 in Eq. (3b) is defined for the precursor pulse by prescribing $\Pi_\alpha(\tau, \Delta\tau_\alpha) := 1$
 175 and $\forall \alpha \in \{A, B\}$. Likewise, \hat{p} and \hat{v}_ζ are defined for the carrier gas purge by
 176 means of the equation of state, where:

$$177 \quad \hat{p} = \frac{\hat{\rho}}{M_\beta} RT := \frac{1}{\dot{V}_{\text{VP}}} \frac{\dot{Q}_\beta \rho_{\text{STP},\beta}}{M_\beta} RT \quad (3c)$$

$$178 \quad \hat{v}_\zeta := \frac{1}{A'} \frac{\dot{Q}_\beta \rho_{\text{STP},\beta}}{M_\beta} RT \frac{1}{\hat{p}} := \frac{\dot{V}_{\text{VP}}}{A'} \quad (3d)$$

180 where $\rho_{\text{STP},\beta}$ is the density of the carrier gas species β at standard temperature
 181 and pressure (STP).

182 It is noteworthy that the CSTR model was exploited in this study due to
 183 its inherent formalism, which describes the correlation between the mass flow of
 184 the α th precursor, \dot{Q}_α , and that of the carrier gas, \dot{Q}_β , (which are both specified
 185 upstream of the reaction chamber), and the volumetric flow rate through the
 186 vacuum pump, \dot{V}_{VP} , (which is specified downstream of the reaction chamber).

187 Accordingly, the CSTR model conveniently correlates the impact of the free
 188 design variables, \mathbf{u} , on the nominal state and algebraic variables needed to
 189 derive the equations that describe the spatially distributed reactor model in its
 190 non-dimensional form. The non-dimensionalized spatially distributed reactor
 191 model was subsequent utilized in the scale-up analysis.

192 3.2. Spatially Distributed ALD Reactor Model

193 The isothermal and variable-density gas flow in the viscous regime can be
 194 described by fully coupled, compressible (Bird et al., 1960) equations for the
 195 conservation of mass, momentum, and individual gas-phase species. This is the
 196 type of gas flow encountered in low-volume, continuous cross-flow ALD reactor
 197 designs with temporal precursor pulsing. The governing equations defined in the
 198 non-dimensionalized spatial, $\zeta \in [\zeta_0, \zeta_{\text{end}}]$, and temporal, $\tau \in [\tau_0, \tau_f]$, domains
 199 are, in an appropriate non-dimensional form:

$$200 \quad \frac{\partial \rho}{\partial \tau} = -\frac{\partial}{\partial \zeta}(\rho v_\zeta) + \sum_{\forall \alpha} \left[\frac{L}{\hat{\rho} \hat{v}_\zeta \hat{\omega}_\alpha} \right] S_\alpha \quad (4)$$

$$201 \quad \frac{\partial \rho v_\zeta}{\partial \tau} = -\frac{\partial}{\partial \zeta}(\rho v_\zeta v_\zeta + \mathcal{P}) + \left[\frac{\hat{\mu}}{\hat{\rho} \hat{v}_\zeta L} \right] \frac{4}{3} \frac{\partial}{\partial \zeta} \left(\mu \frac{\partial v_\zeta}{\partial \zeta} \right) - \left[\frac{\hat{\mu}}{\hat{\rho} \hat{v}_\zeta L} \right] \Phi_\zeta \quad (5)$$

$$202 \quad \frac{\partial \rho \omega_\alpha}{\partial \tau} = -\frac{\partial}{\partial \zeta}(\rho v_\zeta \omega_\alpha) + \left[\frac{\hat{\mathcal{D}}_{\alpha\beta}}{\hat{v}_\zeta L} \right] \frac{\partial}{\partial \zeta} \left(\rho \mathcal{D}_{\alpha\beta} \frac{\partial \omega_\alpha}{\partial \zeta} \right) + \left[\frac{L}{\hat{\rho} \hat{v}_\zeta \hat{\omega}_\alpha} \right] S_\alpha \quad (6)$$

204 where $\mathcal{P} = p \llbracket \hat{p} / (\hat{\rho} \hat{v}_\zeta \hat{v}_\zeta) \rrbracket$ denotes the characteristic modified pressure. Two
 205 dimensionless numbers dominate the gas flow and mass transfer:

$$206 \quad \text{Re} := \left[\frac{\hat{\rho} \hat{v}_\zeta L}{\hat{\mu}} \right] \quad (7)$$

$$207 \quad \text{Pe} := \left[\frac{\hat{v}_\zeta L}{\hat{\mathcal{D}}_{\alpha\beta}} \right] \quad (8)$$

209 where Re is the Reynolds number, which describes the ratio between the inertial
 210 forces and the viscous forces, and Pe is the Peclet number, which describes the
 211 ratio between the convective mass transport and the diffusive mass transport.
 212 Here, ρ and μ are the non-dimensional density and the dynamic viscosity of
 213 the gas mixture at a certain nominal pressure and temperature. The non-
 214 dimensional pressure, p , is governed by the equation of state, and (making use

215 of Eq. (3a) is given by:

$$\begin{aligned}
216 \quad p &= \left(\frac{\hat{\rho}}{\hat{p}} RT \right) \rho \sum_{\forall \alpha} \frac{\hat{\omega}_\alpha \omega_\alpha}{M_\alpha} & (9) \\
217 \quad &:= \rho \sum_{\forall \alpha} \left(\hat{\omega}_\alpha \frac{M_\beta}{M_\alpha} \right) \omega_\alpha \\
218
\end{aligned}$$

219 The non-dimensional transport coefficients, $\mathcal{D}_{\alpha\beta}$ and μ_α , in Eqs. (4–8) were de-
220 termined from the Chapman-Enskog kinetic theory of dilute gases (Hirschfelder
221 et al., 1964; Reid et al., 1988), and the non-dimensional viscosity for the mul-
222 ticomponent mixture of gases, μ , was determined from the semi-empirical mix-
223 ing formula (Wilke, 1950). The transport coefficients were converted to non-
224 dimensional forms by determining the corresponding values at the aforemen-
225 tioned nominal values determined by Eq. (3). Finally, the last term in Eq. (5)
226 is given by:

$$227 \quad \Phi_\zeta = 12(L/H)^2 \mu v_\zeta \quad (10)$$

228 and originates from the shear stress, $-\mu \partial v_\zeta(y)/\partial y$, and has been derived by
229 assuming that the flow in a square duct is fully developed and laminar, with a
230 velocity distribution given by $v_\zeta(y) = v_{\zeta,\max}(1 - [2y/H]^2)$, with $y \in (H/2)[-1, 1]$
231 and $v_{\zeta,\max} = (3/2)v_\zeta$ (Bird et al., 1960).

232 3.2.1. Boundary Conditions

233 Analogous to inlet and outlet flow rates of the CSTR model (see Eqs. (1
234 and 3)), the boundary conditions to the set of partial differential equations
235 (PDEs) (Eqs. (4–6)) prescribes the precursor and carrier gas mass flow as a
236 standard volumetric flow rate at the inlet, and the volumetric flow rate through
237 the vacuum pump, \dot{V}_{VP} , at the outlet. Thus, the inlet, $\zeta = \zeta_0$, mass fluxes for
238 each component α and for the gas mixture, along with a Neumann condition on

239 the velocity, are given by the equations:

$$240 \quad (\rho v_\zeta) \Big|_{\zeta=\zeta_0} = \frac{1}{\hat{\rho} \hat{v}_\zeta} \frac{1}{A'} \sum_{\forall \alpha} \dot{Q}_\alpha \rho_{\text{STP},\alpha} \Pi_\alpha(\tau, \Delta\tau_\alpha) \quad (11)$$

$$241 \quad \frac{\partial v_\zeta}{\partial \zeta} \Big|_{\zeta=\zeta_0} = 0 \quad (12)$$

$$242 \quad (\rho v_\zeta \omega_\alpha) \Big|_{\zeta=\zeta_0} = \frac{1}{\hat{\rho} \hat{v}_\zeta \hat{\omega}_\alpha} \frac{1}{A'} \dot{Q}_\alpha \rho_{\text{STP},\alpha} \Pi_\alpha(\tau, \Delta\tau_\alpha) \quad (13)$$

243 Further, the outlet boundary condition, $\zeta = \zeta_{\text{end}}$, prescribes that the diffusive
244 mass is zero along with a Dirichlet condition on the velocity:

$$245 \quad v_\zeta \Big|_{\zeta=\zeta_{\text{end}}} = \frac{1}{\hat{v}_\zeta} \frac{\dot{V}_{\text{VP}}}{A'} \quad (14)$$

$$246 \quad \frac{\partial \omega_\alpha}{\partial \zeta} \Big|_{\zeta=\zeta_{\text{end}}} = 0 \quad (15)$$

247 3.3. Gas-phase Species Flux at the Growth Surface

248 The heterogeneous ALD gas-surface reactions (Reaction (R2)) lead to a net
249 mass consumption at the substrate surface. The molar reaction rate of the i th
250 elementary reaction is described by the general reversible Langmuir formalism
251 (Holmqvist et al., 2012):

$$252 \quad r_i = \left[\frac{\hat{\rho} \hat{\omega}_\alpha}{M_\alpha} RT \right] \rho \omega_\alpha k_i^{\text{fwd}} \Lambda^{n_i^{\text{fwd}}} \left(1 - \sum_{\forall \ell} \theta_\ell \right)^{n_i^{\text{fwd}}} - k_i^{\text{rev}} \Lambda^{n_i^{\text{rev}}} \theta_\kappa^{n_i^{\text{rev}}} \quad (16)$$

253 where Λ is the maximum molar concentration of surface sites per unit area
254 available for deposition, the subscript ℓ represents all κ th surface species with
255 which the α th gaseous species cannot undergo a reaction, and n_i^{fwd} and n_i^{rev}
256 are the orders of the forward and reverse reactions, respectively. The partial
257 pressure, p_α , of the α th precursor in Eq. (16) can be expressed in terms of the
258 mass fraction, ω_α , and the density of the gas mixture, ρ , using the equation of
259 state, to give:

$$260 \quad \hat{p}_\alpha p_\alpha := \left[\frac{\hat{\rho} \hat{\omega}_\alpha}{M_\alpha} RT \right] \rho \omega_\alpha \quad (17)$$

261 Consequently, the source term, S_α , in the species-continuity equation (Eq. (6))
262 states that the total gas-phase mass flux of the α th species at the growth surface

263 is balanced by the net consumption or production of mass per unit area:

$$264 \quad \left[\frac{L}{\hat{\rho} \hat{v}_\zeta \hat{\omega}_\alpha} \right] S_\alpha = \left[\frac{L}{\hat{\rho} \hat{v}_\zeta \hat{\omega}_\alpha} \right] \left(\frac{A}{V} \right) M_\alpha \sum_{i=1}^{N_i} \xi_{\alpha,i} r_i \quad (18)$$

$$265 \quad := \sum_{i=1}^{N_i} \xi_{\alpha,i} \left[\left[\frac{L}{\hat{v}_\zeta} \left(\frac{A}{V} \right) RT k_i^{\text{fwd}} \Lambda^{n_i^{\text{fwd}}} \right] \rho \omega_\alpha \left(1 - \sum_{\forall \ell} \theta_\ell \right)^{n_i^{\text{fwd}}} - \right. \\ 266 \quad \left. \left[\frac{L}{\hat{v}_\zeta} \frac{M_\alpha}{\hat{\rho} \hat{\omega}_\alpha} \left(\frac{A}{V} \right) k_i^{\text{rev}} \Lambda^{n_i^{\text{rev}}} \right] \theta_\kappa^{n_i^{\text{rev}}} \right]$$

268 where $\xi_{\alpha,i}$ denotes the stoichiometric coefficient corresponding to the α th species,
269 and the appearing surface Damköhler numbers, $\text{Da}_{\alpha,i}^{\text{fwd}}$ and $\text{Da}_{\alpha,i}^{\text{rev}}$, are the ratios
270 between the molar growth rate of the ALD film at the substrate and the speed
271 of convective transport of the growth limiting species. Thus, $\text{Da}_{\alpha,i}^{\text{fwd}}$ and $\text{Da}_{\alpha,i}^{\text{rev}}$
272 are given by:

$$273 \quad \text{Da}_{\alpha,i}^{\text{fwd}} := \left[\frac{L}{\hat{v}_\zeta} \left(\frac{A}{V} \right) RT k_i^{\text{fwd}} \Lambda^{n_i^{\text{fwd}}} \right] \quad (19)$$

$$274 \quad \text{Da}_{\alpha,i}^{\text{rev}} := \left[\frac{L}{\hat{v}_\zeta} \frac{M_\alpha}{\hat{\rho} \hat{\omega}_\alpha} \left(\frac{A}{V} \right) k_i^{\text{rev}} \Lambda^{n_i^{\text{rev}}} \right] \quad (20)$$

276 3.4. Growth Surface State Dynamics

277 The characteristics of the surface reaction, in particular the probability that
278 the reaction will proceed through the formation of adsorbed species, depends
279 on the properties of the exposed adsorbent surface. The molar reaction rate
280 per unit surface area (Eq. (16)) and the non-dimensional surface Damköhler
281 numbers (Eqs. (19–20)) allow to determine the spatial and temporal fractional
282 surface coverages:

$$283 \quad \frac{\partial \theta_\kappa}{\partial \tau} = \left[\frac{L}{\Lambda \hat{v}_\zeta} \right] \sum_{i=1}^{N_i} \xi_{\kappa,i} r_i \quad (21)$$

$$284 \quad := \sum_{i=1}^{N_i} \xi_{\kappa,i} \left[\left[\frac{\hat{\rho} \hat{\omega}_\alpha}{M_\alpha} \left(\frac{V}{A} \right) \frac{1}{\Lambda} \right] \left[\text{Da}_{\alpha,i}^{\text{fwd}} \rho \omega_\alpha \left(1 - \sum_{\forall \ell} \theta_\ell \right)^{n_i^{\text{fwd}}} - \text{Da}_{\alpha,i}^{\text{rev}} \theta_\kappa^{n_i^{\text{rev}}} \right] \right. \\ 285 \quad \left. 0 = \sum_{\forall \kappa} \frac{\partial \theta_\kappa}{\partial \tau} \quad (22) \right.$$

287 where θ_κ is the fractional surface coverage of the κ th surface species, $\kappa \in$
288 $\{A^*, B^*, C^*\}$ (see Table 1). The non-dimensional term that appears in Eq.

289 (21) represents the precursor excess number and relates the maximum precursor
 290 molar density inside the reactor per unit adsorption site:

$$291 \quad \gamma_\alpha := \left\lceil \frac{\hat{\rho}\hat{\omega}_\alpha}{M_\alpha} \left(\frac{V}{A} \right) \frac{1}{\Lambda} \right\rceil \quad (23)$$

292 3.5. Model Form and Size

293 The equations of the spatially distributed ALD reactor model that describe
 294 the gas-phase and growth surface state dynamics (see Sections 3.2–3.4), constitute
 295 a system of non-linear partial differential algebraic equations (PDAEs).
 296 In this study, the PDAE system was approximated using the method-of-lines
 297 (Davis, 1984; Schiesser, 1991) and the finite volume method (FVM). The first-
 298 order spatial derivative of the non-dimensional density, ρ , in Eq. (4) and of the
 299 gas-phase mass fractions, ω_α , in Eq. (6) have been approximated using a first-
 300 order downwind discretization scheme, while a first-order upwind discretization
 301 scheme was utilized to approximate the non-dimensional mass average velocity,
 302 v_ζ , in Eq. (5). The resulting non-linear index-1 differential-algebraic equation
 303 (DAE) system can be written collectively as:

$$304 \quad \mathbf{0} = \mathbf{F}(\tau, \dot{\mathbf{x}}(\tau), \mathbf{x}(\tau), \mathbf{u}(\tau), \mathbf{w}(\tau), \boldsymbol{\beta}) \quad (24a)$$

$$305 \quad \mathbf{0} = \mathbf{F}_0(\tau_0, \dot{\mathbf{x}}(\tau_0), \mathbf{x}(\tau_0), \mathbf{u}(\tau_0), \mathbf{w}(\tau_0), \boldsymbol{\beta}) \quad (24b)$$

$$306 \quad \mathbf{0} = \mathbf{C}_{\text{eq}}(\tau_0, \tau_f, \mathbf{x}, \mathbf{u}, \mathbf{w}, \boldsymbol{\beta}) \quad (24c)$$

$$307 \quad \mathbf{x}(\tau_0) = \mathbf{x}_0 \quad (24d)$$

308 where \mathbf{F} is the DAE that represents the dynamics of the system, \mathbf{F}_0 represents
 309 the DAE augmented with additional initial conditions, \mathbf{C}_{eq} is a point
 310 equality-constraint function (see Section 3.6), and $\boldsymbol{\beta}$ is the model parameter
 311 vector. Finally, $\mathbf{x} = [\rho, v_\zeta, \omega_\alpha, \theta_\kappa]^T$, $\mathbf{w} = [p, \theta_{C^*}]^T$, and $\mathbf{u} = [\Delta\tau_\alpha, \dot{Q}_\alpha, T, \dot{V}_{\text{VP}}]^T$
 312 (where $\alpha \in \{A, B, C\}$ and $\kappa \in \{A^*, B^*\}$) describe dependent states, algebraic
 313 variables, and free design variables. Furthermore, with N_{FVM} FVM elements,
 314 the number of states, N_x , is $7N_{\text{FVM}}$ and the number of algebraic variables, N_w ,
 315 is $2N_{\text{FVM}}$. The number of FVM elements is a compromise between accuracy
 316 and computational complexity, and should be chosen such that it gives adequate

317 representation of the dispersion. In this study, the number of FVM elements
 318 was set to 25.

319 3.6. Limit-cycle Criteria

320 For the purpose of this study, substrate effects on the nucleation and ini-
 321 tial growth periods were not considered (see Section 2). For this reason, the
 322 solution strategy for the DAE system, \mathbf{F} , is to consider the limit-cycle dynamic
 323 solution that arises from the steady cyclic operation of the ALD reactor (Travis
 324 and Adomaitis, 2013a). Computation of limit-cycle solutions over the tempo-
 325 ral horizon $[\tau_0, \tau_f]$ requires one additional important criterion: that the state
 326 variables, \mathbf{x} , return to their initial conditions at the end of the cycle, $\tau = \tau_f$:

$$327 \quad \mathbf{x}(\tau_0) := \mathbf{x}(\tau_f) \quad (25a)$$

328 The following non-differentiated relationships must also be satisfied at $\tau \in$
 329 $\{\tau_0, \tau_f\}$, due to constraints that arise from the underlying assumptions on which
 330 Eqs. (4–6) and Eqs. (21–22) are based:

$$331 \quad 1 = \sum_{\forall \kappa} \theta_{\kappa}(\tau) \quad (25b)$$

$$332 \quad 1 = \sum_{\forall \alpha} \omega_{\alpha}(\tau) \quad (25c)$$

334 with $\kappa \in \{A^*, B^*, C^*\}$, and $\alpha \in \{A, B, C, P\}$. Furthermore, the limit-cycle
 335 criteria in Eq. (25) are collected in the point equality-constraint function, \mathbf{C}_{eq} .
 336 Section 5 presents numerical aspects of computing limit-cycle solutions.

337 4. Scale-up Analysis

338 In order to maintain the dynamic similarity of gas flow and deposition when
 339 scaling up an ALD reactor, the Peclet, Reynold, surface Damköhler, and pre-
 340 cursor excess numbers should be kept fixed. In this case, the flow path lines
 341 and non-dimensional distributions of concentrations will remain the same after
 342 the scale-up operation. The non-dimensional deposition rate and its relative
 343 uniformity will also remain the same. The overall objective of the scale up

344 analysis in the present study was to maintain a fixed absolute growth rate and
 345 its relative uniformity, while optimizing the precursor yield. Thus, the scale-up
 346 method can minimize individual precursor doses, while maintaining sufficiently
 347 high exposure levels, ensuring that the design specifications are not violated.
 348 The precursor yield can be expressed as:

$$349 \quad \frac{dY_\alpha}{d\tau} = - \left\| \frac{A' \hat{\rho}_\zeta \hat{\omega}_\alpha}{\dot{Q}_\alpha \rho_{\text{STP}, \alpha} \Pi_\alpha(\tau, \Delta\tau_\alpha)} \right\| (\rho v_\zeta \omega_\alpha) \Big|_{\zeta=\zeta_{\text{end}}} \quad (26)$$

350 subject to the initial value $Y_\alpha(\tau_0) = 1$. Moreover, the spatially dependent
 351 growth rate, m_s , in $\zeta \in [\zeta_0, \zeta_{\text{end}}]$ is defined by:

$$352 \quad \frac{\partial m_s}{\partial \tau} = \sum_{i=1}^{N_i} \left\| \frac{\Lambda \Delta M_i}{\hat{m}_s} \right\| \xi_{\kappa, i} \gamma_\alpha \left[\text{Da}_{\alpha, i}^{\text{fwd}} \rho \omega_\alpha \left(1 - \sum_{\forall \ell} \theta_\ell \right)^{n_i^{\text{fwd}}} - \text{Da}_{\alpha, i}^{\text{rev}} \theta_{\kappa}^{n_i^{\text{rev}}} \right] \quad (27a)$$

353 subject to the initial value $m_s(\tau_0) = 0$. Eq. (27a) uses the conversion rate
 354 of the fractional coverage of surface species (given by Eq. (21)). The scaling
 355 factor, $\hat{m}_s = M_s \Lambda$, corresponds to fully saturated ALD growth, and ΔM_i is the
 356 difference in molar mass of the outermost surface species that are governed by
 357 the i th elementary reaction (see Reaction (R2)). Eq. (27a) allows to determine
 358 the substrate spatially averaged growth rate:

$$359 \quad \frac{d\langle m_s \rangle}{d\tau} = \frac{1}{(\zeta_{\text{end}} - \zeta_0)} \int_{\zeta_0}^{\zeta_{\text{end}}} \frac{\partial m_s}{\partial \tau} d\zeta \quad (27b)$$

360 In addition, by means of Eq. (27), the growth rate uniformity, UF, was conve-
 361 niently defined as:

$$362 \quad \text{UF} = \begin{cases} 1 - \int_{\zeta_0}^{\zeta_{\text{end}}} |m_s - \langle m_s \rangle| d\zeta \left(\int_{\zeta_0}^{\zeta_{\text{end}}} m_s d\zeta \right)^{-1} & \exists \zeta \in [\zeta_0, \zeta_{\text{end}}] : m_s(\zeta) > 0 \\ 1 & \text{otherwise} \end{cases} \quad (28)$$

363 It is noteworthy that the uniformity metric defined in Eq. (28) describes the
 364 absolute deviation from the mean film mass accumulated, $\langle m_s \rangle$, at normalized
 365 time τ . However, since the ALD process is an inherently forced periodic system,
 366 it is convenient to compare the performance of the existing design with that of
 367 the scaled-up design based on absolute normalized growth per cycle, $\langle m_s \rangle(\tau_f)$,

368 where $\tau_f = (\hat{v}_\zeta/L)\Delta t$ is the end of the time horizon, $[\tau_0, \tau_f]$. The uniformity
 369 metric, $\text{UF}(\tau_f)$, is evaluated in a similar manner at the end of the pulse sequence.

370 The duration of the α th precursor pulse, $\Delta\tau_\alpha$, is not explicitly taken into
 371 account by the non-dimensional parameters defined in Eqs. (7, 8 and 19–23), but
 372 it is can, instead, be conveniently expressed by the half-cycle average substrate
 373 exposure dose for the α th adsorptive precursor:

$$374 \quad \frac{d\langle\delta_\alpha\rangle}{d\tau} = \left[\frac{L}{\hat{v}_\zeta} \frac{\hat{\rho}\hat{\omega}_\alpha}{M_\alpha} RT \Delta\tau_\alpha \right] \frac{1}{\Delta\tau_\alpha} \frac{1}{(\zeta_{\text{end}} - \zeta_0)} \int_{\zeta_0}^{\zeta_{\text{end}}} \rho\omega_\alpha d\zeta \quad (29)$$

375 subject to the initial value $\langle\delta_\alpha\rangle(\tau_0) = 0$. Moreover, the nominal α th exposure
 376 dose, ϕ_α , can be deduced from Eq. (29):

$$377 \quad \phi_\alpha := \left[\frac{L}{\hat{v}_\zeta} \frac{\hat{\rho}\hat{\omega}_\alpha}{M_\alpha} RT \Delta\tau_\alpha \right] \quad (30)$$

378 However, to capture the increase in the total mass concentration during the
 379 precursor pulse, recall that $\hat{\rho}$ has been derived with $\Pi_\alpha := 0$ in Eq. (3), the
 380 nominal exposure dose, ϕ_α , must, therefore, be scaled accordingly:

$$381 \quad \langle\hat{\delta}_\alpha\rangle = \frac{\phi_\alpha}{(1 - \hat{\omega}_\alpha)} \quad (31)$$

382 The exposure dose of the growth surface to the α th precursor defined by Eq.
 383 (29) is characterized by the time dependent, local, partial pressure (Eq. (17))
 384 during the exposure period, and during a portion of each purge period. The
 385 ALD gas–surface reactions must be coupled to the dynamic reactor transport
 386 model in order to model these features (see the systematic modeling approach
 387 described in Sections 3.2 and 3.4). Thus, there are two main ways of varying
 388 $\langle\delta_\alpha\rangle$: changing the mass flow of the precursors, \dot{Q}_α , and in this way changing
 389 the partial pressure, or changing the duration of the pulse, $\Delta\tau_\alpha$. Eq. (29) thus
 390 adds a further dimension to the scale-up analysis, incorporating the effect of
 391 the dispersion of precursor pulses along the ζ -axis, and in this way enabling the
 392 precursor exposure dose to be accurately assessed in the scale-up analysis.

393 The set of process operating parameters that can be varied for the contin-
 394 uous cross-flow ALD reactor design with temporal precursor pulsing, in order

395 to maintain a fixed absolute growth rate, $\langle m_s \rangle(\tau_f)$, and growth rate unifor-
 396 mity, $\text{UF}(\tau_f)$, is $\mathbf{u} = [\Delta\tau_\alpha, \dot{Q}_\alpha, T, \dot{V}_{\text{VP}}]^T$ and $\alpha \in \{A, B, P\}$. Table 2 lists the
 397 dimensional and non-dimensional parameters that are relevant to the scale-up
 398 methodology and the ways in which they depend on the set of manipulating
 399 variables, \mathbf{u} , and the length of the reactor.

400 4.1. Scale-up Methodology for Cross-flow ALD Reactor Designs

401 This paper analyses the implications of linearly scaling up an existing *Re-*
 402 *actor* \mathcal{A} (see Section 3) to a scaled-up *Reactor* \mathcal{B} by a geometric factor $\lambda =$
 403 $L_{\mathcal{B}}/L_{\mathcal{A}}$. In particular, the various dimensional and non-dimensional parameters
 404 presented in Table 2 and the design criteria defined in Eqs. (27–29) are consid-
 405 ered. The scale-up strategies presented here are based on a sequential method-
 406 ology in which the way in which carrier gas manipulated variables, $[\dot{Q}_\beta, \dot{V}_{\text{VP}}]$,
 407 depend on the dynamic similarity of gas flow is assessed first. The way in which
 408 the precursor pulse dose parameters, $[\dot{Q}_\alpha, \Delta\tau_\alpha]$ and $\forall \alpha \in \{A, B\}$, depend on
 409 the apparent ALD deposition rate and its relative uniformity is subsequently
 410 assessed.

411 4.1.1. Scaling Rules for the Process Operating Conditions

412 In the context of the carrier gas manipulated variables, two fundamentally
 413 different strategies (see also Table 2) were investigated when the reactor was
 414 scaled up, with $L \propto \lambda$:

- 415 i) *Scale-up strategy I* involves the reactor being scaled up without changing
 416 the carrier gas mass flow, \dot{Q}_β , or the flow rate through the vacuum pump,
 417 \dot{V}_{VP} . The nominal pressure, \hat{p} , is unchanged when this strategy is used,
 418 while $\gamma_\alpha \text{Da}_{\alpha,i}^{\text{fwd}}, \langle \hat{\delta}_\alpha \rangle \propto \dot{Q}_\alpha \lambda^2$ for the α th precursor, and the residence time,
 419 $\hat{\tau} \propto \lambda^2$, change dramatically. The resulting increase in the product of the
 420 surface Damköhler number and precursor excess number, and the nomi-
 421 nal precursor exposure dose with λ , are strictly positive, and give a higher
 422 efficiency of the deposition process in terms of precursor utilization and de-

Table 2: Scaling behavior of various dimensional and non-dimensional parameters. For the square duct that is being considered, the specific substrate surface area per unit reactor volume is $A/V = 2L^2/(L^2H)$ (m^{-1}) and the cross-sectional area is $A' = LH$ (m^2).

Variable	Dependence	Scale-up	Scale-up
	on $L, \dot{Q}_\beta,$	<i>strategy I:</i>	<i>strategy II:</i>
	$\dot{V}_{\text{VP}}, \dot{Q}_\alpha,$	$L \propto \lambda$	$L \propto \lambda$
	$\Delta\tau_\alpha$	$\dot{Q}_\beta = \text{const.}$	$\dot{Q}_\beta \propto \lambda^\vartheta$
		$\dot{V}_{\text{VP}} = \text{const.}$	$\dot{V}_{\text{VP}} \propto \lambda^\vartheta$
$\hat{v}_\zeta := \frac{\dot{V}_{\text{VP}}}{A'}$	$\propto \frac{\dot{V}_{\text{VP}}}{L}$	$\propto \lambda^{-1}$	$\propto \lambda^{\vartheta-1}$
$\hat{\rho} := \hat{p} \frac{M_\beta}{RT}$	$\propto \hat{p} \propto \frac{\dot{Q}_\beta}{\dot{V}_{\text{VP}}}$	—	—
$\hat{\omega}_\alpha := \frac{\dot{Q}_\alpha \rho_{\text{STP},\alpha}}{\dot{Q}_\alpha \rho_{\text{STP},\alpha} + \dot{Q}_\beta \rho_{\text{STP},\beta}}$	$\propto \frac{\dot{Q}_\alpha^a}{\dot{Q}_\beta}$	$\propto \dot{Q}_\alpha$	$\propto \frac{\dot{Q}_\alpha}{\lambda^\vartheta}$
$\hat{\tau} := \frac{L}{\hat{v}_\zeta}$	$\propto \frac{L^2}{\dot{V}_{\text{VP}}}$	$\propto \lambda^2$	$\propto \lambda^{2-\vartheta}$
$\hat{\mu}$	—	—	—
$\hat{\mathcal{D}}_{\alpha,\beta}$	$\propto \frac{1}{\hat{p}} \propto \frac{\dot{V}_{\text{VP}}}{\dot{Q}_\beta}$	—	—
$\text{Pe} := \frac{\hat{v}_\zeta L}{\hat{\mathcal{D}}_{\alpha,\beta}}$	$\propto \dot{Q}_\beta$	—	$\propto \lambda^\vartheta$
$\text{Re} := \frac{\hat{\rho} \hat{v}_\zeta L}{\hat{\mu}}$	$\propto \dot{Q}_\beta$	—	$\propto \lambda^\vartheta$
$\text{Da}_{\alpha,i}^{\text{fwd}} := \frac{L}{\hat{v}_\zeta} \left(\frac{A}{V}\right) RT k_i^{\text{fwd}} \Lambda^{n_i^{\text{fwd}}}$	$\propto \frac{L^2}{\dot{V}_{\text{VP}}}$	$\propto \lambda^2$	$\propto \lambda^{2-\vartheta}$
$\text{Da}_{\alpha,i}^{\text{rev}} := \frac{L}{\hat{v}_\zeta} \frac{M_\alpha}{\hat{\rho} \hat{\omega}_\alpha} \left(\frac{A}{V}\right) k_i^{\text{rev}} \Lambda^{n_i^{\text{rev}}}$	$\propto \frac{L^2}{\dot{Q}_\alpha^a}$	$\propto \frac{\lambda^2}{\dot{Q}_\alpha}$	$\propto \frac{\lambda^2}{\dot{Q}_\alpha}$
$\gamma_\alpha := \frac{\hat{\rho} \hat{\omega}_\alpha}{M_\alpha} \left(\frac{V}{A}\right) \frac{1}{\Lambda}$	$\propto \frac{\dot{Q}_\alpha}{\dot{Q}_\beta^a}$	$\propto \dot{Q}_\alpha$	$\propto \frac{\dot{Q}_\alpha}{\lambda^\vartheta}$
$\gamma_\alpha \text{Da}_{\alpha,i}^{\text{fwd}} := \frac{L}{\hat{v}_\zeta} \frac{\hat{\rho} \hat{\omega}_\alpha}{M_\alpha} RT k_i^{\text{fwd}} \Lambda^{n_i^{\text{fwd}}-1}$	$\propto \frac{\dot{Q}_\alpha L^2}{\dot{Q}_\beta \dot{V}_{\text{VP}}^a}$	$\propto \dot{Q}_\alpha \lambda^2$	$\propto \dot{Q}_\alpha \lambda^{2-2\vartheta}$
$\phi_\alpha := \frac{L}{\hat{v}_\zeta} \frac{\hat{\rho} \hat{\omega}_\alpha}{M_\alpha} RT \Delta\tau_\alpha$	$\propto \frac{\dot{Q}_\alpha \Delta\tau_\alpha L^2}{\dot{V}_{\text{VP}}^2}$	$\propto \dot{Q}_\alpha \Delta\tau_\alpha \lambda^2$	$\propto \dot{Q}_\alpha \Delta\tau_\alpha \lambda^{2-2\vartheta}$
$\langle \hat{\delta}_\alpha \rangle := \frac{L}{\hat{v}_\zeta} \frac{\hat{\rho}}{M_\alpha} \frac{\hat{\omega}_\alpha}{\hat{\omega}_\beta} RT \Delta\tau_\alpha$	$\propto \frac{\dot{Q}_\alpha \Delta\tau_\alpha L^2}{\dot{V}_{\text{VP}}^2}$	$\propto \dot{Q}_\alpha \Delta\tau_\alpha \lambda^2$	$\propto \dot{Q}_\alpha \Delta\tau_\alpha \lambda^{2-2\vartheta}$

^aOnly valid for $\dot{Q}_\alpha \rho_{\text{STP},\alpha} \ll \dot{Q}_\beta \rho_{\text{STP},\beta}$.

423 position rate. Finally, the Reynolds and Peclet numbers remain unchanged
424 in this case, and thus dynamic similarity is preserved to some extent.

425 ii) *Scale-up strategy II* strives to maintain the reactor residence time, $\hat{\tau}$, and
 426 the nominal pressure, \hat{p} , constant by scaling the carrier gas flow rate and
 427 the flow rate through the vacuum pump in parallel, as $\dot{Q}_\beta, \dot{V}_{VP} \propto \lambda^\vartheta$
 428 with $\vartheta \in (0, 2]$. The residence time from the CSTR model is constant
 429 for $\vartheta := 2$, and *Scale-up strategy I* is obtained in the case in which $\vartheta :=$
 430 0. When this strategy is used, $\gamma_\alpha \text{Da}_{\alpha,i}^{\text{fwd}}, \langle \hat{\delta}_\alpha \rangle \propto \dot{Q}_\alpha \lambda^{2-2\vartheta}$ for the α th
 431 precursor and $\text{Re}, \text{Pe} \propto \lambda^\vartheta$. The way in which the product of the surface
 432 Damköhler number and the precursor excess number, and the nominal
 433 precursor exposure dose, change, makes it clear that the efficiency of the
 434 ALD process (in terms of precursor utilization and deposition rate) falls
 435 as ϑ increases.

436 It is beneficial when using *Scale-up strategy II* to use a low value of the resi-
 437 dence time in cross-flow reactor designs, as this imposes a lower boundary onto
 438 the carrier gas purge time, $\Delta t_P \propto \hat{\tau}$ (see, for example, Jur and Parsons (2011);
 439 Mousa et al. (2012)). This is needed in the ALD sequence to ensure negligi-
 440 ble precursor interaction, and ultimately to maximize throughput in terms of
 441 the overall deposition rate per cycle time (see, for example, Holmqvist et al.
 442 (2013b)).

443 The deposition temperature, T , must be considered in a complete investiga-
 444 tion of the carrier gas manipulated variables. Aarik et al. (2006) investigated
 445 experimentally the effects of deposition temperature, while Holmqvist et al.
 446 (2013b) and Travis and Adomaitis (2013b) carried out theoretical studies. The
 447 present investigation, however, is limited to $\mathbf{u} = [\dot{Q}_\beta, \dot{V}_{VP}]$, since the tempera-
 448 ture depends on growth per cycle in a convex manner (Puurunen, 2005), which
 449 means that its optimum value could be easily determined before the scale-up
 450 analysis. The optimal deposition temperature used in this study was determined
 451 from the study by Holmqvist et al. (2013b) and set to $T = 175$ (°C). The de-
 452 sign specifications presented in Table 3 were determined in this way. The surface
 453 Damköhler number for desorption, $\text{Da}_{\alpha,i}^{\text{rev}}$ and $i = 3$, is not important at the op-
 454 timum operating temperature (though included in the model), and it is only

455 relevant in the high temperature region where extensive dehydroxylation takes
 456 place (Deminsky et al., 2004; Matero et al., 2000; Rahtu et al., 2001) (see Eqs.
 457 (R2c–R2d)). Thus, the impact of the surface Damköhler number for desorption
 458 was not considered in the scale-up analysis.

459 4.1.2. Optimal Scaling Rules for the Precursor Exposure Dose

460 High uniformity is one of the key attributes of the ALD technology (Cleve-
 461 land et al., 2012; Henn-Lecordier et al., 2011). Dynamic similarity is preserved to
 462 some extent when the scale-up strategies in Section 4.1.1 are applied. However,
 463 the growth rate, $\langle m_s \rangle(\tau_f)$, and the uniformity of the deposition rate, $UF(\tau_f)$,
 464 falls as ϑ increases unless the precursor exposure dose is properly scaled. This
 465 is, of course, not a desired result. Deposition rates and uniformities can be
 466 maintained by scaling the precursor pulse dose parameters, $\mathbf{u} = [\dot{Q}_\alpha, \Delta\tau_\alpha]$ and
 467 $\forall \alpha \in \{A, B\}$. The scaling rules deduced from Table 2 demonstrate how the
 468 free design variables depend on the metrics relevant in the scale-up strategies in
 469 a mechanistic manner, even though they are based solely on the CSTR model
 470 (see Section 3.1). The half-cycle average substrate exposure dose for the α th
 471 precursor (Eq. (29)), in particular, introduces a complex interdependency be-
 472 tween the mass flow, \dot{Q}_α , the pulse duration, $\Delta\tau_\alpha$, and the resulting local partial
 473 pressure dynamics throughout the spatial domain, $\zeta \in [\zeta_0, \zeta_{\text{end}}]$. Furthermore,
 474 the uniformity of the film thickness (Eq. (27)) is inherently spatially dependent,
 475 and thus cannot be reproduced by the CSTR model.

476 For these reasons, an optimization problem was formulated in order to dis-
 477 tinguish the proper scaling factors of $\mathbf{u} = [\dot{Q}_A, \dot{Q}_B]$. The present investigation
 478 was limited to the optimization of the precursor mass flows, since Holmqvist
 479 et al. (2013b) have recently shown that the optimal precursor pulse durations,
 480 $\Delta\tau_\alpha$ and $\forall \alpha \in \{A, B\}$, are always at the lower boundary of the assigned range
 481 when precursor utilization and overall deposition rate per cycle time are tar-
 482 geted. Therefore, the precursor pulse duration in the scaled up *Reactor B* was
 483 set to that of *Reactor A* (see Table 3). Thus, in order to penalize high values

484 of the decision variables, \mathbf{u} , the cost function was defined as:

$$485 \quad \Phi(\mathbf{y}, \mathbf{u}) = - \sum_{\alpha \in \{A, B\}} \int_{\tau_0}^{\tau_f} \frac{dY_\alpha}{d\tau} d\tau \quad (32)$$

486 and assembles the precursor yields (Eq. (26)). The cost function was optimized
 487 while fulfilling the requirements placed on deposition rate and its uniformity by
 488 incorporating the terminal inequality constraints:

$$489 \quad C_{\text{ieq}}^{\langle m_s \rangle} = \langle m_s \rangle^{\mathcal{A}}(\tau_f) - \langle m_s \rangle^{\mathcal{B}}(\tau_f) \quad (33a)$$

$$490 \quad C_{\text{ieq}}^{\text{UF}} = \text{UF}^{\mathcal{A}}(\tau_f) - \text{UF}^{\mathcal{B}}(\tau_f) \quad (33b)$$

492 which can be collectively written as $\mathbf{C}_{\text{ieq}} = [C_{\text{ieq}}^{\langle m_s \rangle}, C_{\text{ieq}}^{\text{UF}}]^T$. Table 3 lists the
 493 optimal design variables and resulting design criteria for *Reactor* \mathcal{A} used in Eq.
 494 (33). Finally, the dynamic optimization problem (DOP) in the time interval
 495 $\tau \in [\tau_0, \tau_f]$ of achieving the assigned design criteria (see Eqs. (27b–29)) in the
 496 scaled-up design *Reactor* \mathcal{B} may be stated using the cost function, Φ , as:

$$497 \quad \min_{\mathbf{u}, \mathbf{x}_0} \Phi(\mathbf{y}, \mathbf{u}) \quad (34)$$

$$498 \quad \text{s.t.} \quad \mathbf{0} = \mathbf{F}(\tau, \dot{\mathbf{x}}, \mathbf{x}, \mathbf{w}, \mathbf{u}, \boldsymbol{\beta})$$

$$499 \quad \mathbf{0} = \mathbf{F}_0(\tau_0, \dot{\mathbf{x}}(\tau_0), \mathbf{x}(\tau_0), \mathbf{u}(\tau_0), \mathbf{w}(\tau_0), \boldsymbol{\beta})$$

$$500 \quad \mathbf{y} = \mathbf{g}_y(\mathbf{x}, \mathbf{w}, \mathbf{u}, \boldsymbol{\beta})$$

$$501 \quad \mathbf{0} \geq \mathbf{C}_{\text{ieq}}(\tau_0, \tau_f, \mathbf{x}, \mathbf{u}, \mathbf{w}, \boldsymbol{\beta})$$

$$502 \quad \mathbf{0} = \mathbf{C}_{\text{eq}}(\tau_0, \tau_f, \mathbf{x}, \mathbf{u}, \mathbf{w}, \boldsymbol{\beta})$$

$$503 \quad \mathbf{x}_{\min} \leq \mathbf{x} \leq \mathbf{x}_{\max}, \quad \mathbf{w}_{\min} \leq \mathbf{w} \leq \mathbf{w}_{\max}$$

$$504 \quad \mathbf{u}_{\min} \leq \mathbf{u} \leq \mathbf{u}_{\max}, \quad \mathbf{x}(\tau_0) = \mathbf{x}_0$$

506 where \mathbf{g}_y is the response function (Eqs. (26–28)) that governs the model out-
 507 put, and where $\mathbf{y} = [\langle m_s \rangle, \text{UF}, Y_\alpha]^T$, with $\alpha \in \{A, B\}$, is used to define the cost
 508 function and terminal inequality constraints of the DOP. An important impli-
 509 cation of this formulation of the simultaneous optimization problem is that it
 510 enables the limit-cycle criteria (see Section 3.6) to be satisfied while maximizing
 511 the precursor yields (Eq. (26)). Thus, the initial values, \mathbf{x}_0 , are set to be free

Table 3: *Reactor* \mathcal{A} design specifications used in terminal inequality constraints, $\mathbf{C}_{\text{ieq}} = [\mathbf{C}_{\text{ieq}}^{\langle m_s \rangle}, \mathbf{C}_{\text{ieq}}^{\text{UF}}]^T$, and those that must be satisfied in the scaled-up *Reactor* \mathcal{B} for each geometric factor, λ .

Design variables			Design criteria		
T	$1.75 \cdot 10^2$	(°C)	$\langle m_s \rangle^{\mathcal{A}}(\tau_f)^a$	$9.00 \cdot 10^{-1}$	(cycle ⁻¹)
\dot{Q}_α	$1.83 \cdot 10^1$	(sccm)	$Y_A^{\mathcal{A}}(\tau_f)^b$	$3.59 \cdot 10^{-2}$	(cycle ⁻¹)
\dot{Q}_β	$5.00 \cdot 10^2$	(sccm)	$Y_B^{\mathcal{A}}(\tau_f)^b$	$3.53 \cdot 10^{-2}$	(cycle ⁻¹)
$\hat{\tau}\Delta\tau_\alpha$	$2.00 \cdot 10^{-2}$	(s)	$\text{UF}^{\mathcal{A}}(\tau_f)^a$	$9.50 \cdot 10^{-1}$	(cycle ⁻¹)
$\hat{\tau}\Delta\tau_\beta$	1.00	(s)	$\langle \delta_A \rangle^{\mathcal{A}}(\tau_f)^b$	2.68	(Pa s)
$p _{\zeta=\zeta_{\text{end}}}$	$3.00 \cdot 10^2$	(Pa)	$\langle \delta_B \rangle^{\mathcal{A}}(\tau_f)^b$	2.68	(Pa s)
\dot{V}_{VP}^c	$4.62 \cdot 10^{-3}$	(m ³ s ⁻¹)			

^aAssigned reference value in Eq. (33).

^bDetermined with optimized design variables from Eq. (34).

^cDetermined from Eq. (3c) and $\mathbf{u} = [T, \dot{Q}_\beta, p|_{\zeta=\zeta_{\text{end}}}]^T$.

512 when solving Eq. (34), and varied such that the equality constraint relations
513 are satisfied at $\tau \in \{\tau_0, \tau_f\}$ (Eq. (25)).

514 5. Modeling and Optimization Environment

515 Modelica (The Modelica Association, 2012) was used as the description lan-
516 guage for the dynamic ALD process model developed in this paper. Modelica
517 is an equation-based language for complex physical models, whose underlying
518 mathematical formalism is that of DAEs. The open-source platform JModel-
519 ica.org (Åkesson et al., 2010) was used for simulation and optimization of the
520 Modelica model. In the context of simulation, JModelica.org was used to com-
521 pile the Modelica model into a functional mock-up unit (FMU) (Blochwitz et al.,
522 2011), thus transforming it from a DAE form into an ordinary differential equa-
523 tion (ODE) form. JModelica.org’s interface to SUNDIALS (Hindmarsh et al.,
524 2005) was subsequently used to simulate the model. The user interacts with the
525 various components of JModelica.org using the Python scripting language.

526 *5.1. Dynamic Optimization of DAEs Using Direct Collocation with CasADi*

527 To enable the formulation of the DOP (see Eq. (34)) based on the model
528 (see Eq. (24)) described by Modelica code, the Modelica extension Optimica
529 (Åkesson, 2008) has been developed and integrated into JModelica.org. The
530 algorithm used in the work described in this paper to solve the DOP uses a di-
531 rect and local collocation method (Biegler, 2010) on finite elements, using Radau
532 points and Lagrange interpolation polynomials (Magnusson and Åkesson, 2012).
533 The algorithm has been implemented in Python in the JModelica.org framework,
534 using the computer algebra system with automatic differentiation (CasADi) op-
535 timization package (Andersson et al., 2012). Using CasADi’s symbolic syntax, it
536 is possible to transcribe the DOP into a finite dimensional non-linear program-
537 ming problem (NLP). The NLP was subsequently solved using the primal-dual
538 interior point method IPOPT v.3.10.3 (Wächter and Biegler, 2006), using MA27
539 as a linear solver. The first and second derivatives required by IPOPT are auto-
540 matically and efficiently generated by CasADi, using automatic differentiation
541 (AD) techniques.

542 The time horizon of the DOP in Eq. (34) was set to $\tau \in [0, 2.8] \cdot \hat{\tau}^{-1}$
543 (a.u.), corresponding to a single pulse sequence (see Table 3), and the collocation
544 scheme used had 50 finite elements with three Radau points in each. The state
545 and algebraic variables were approximated using Lagrange polynomials of order
546 three and two, respectively. As all trajectories over the time horizon are solved
547 for simultaneously when using a collocation method, good initial guesses of
548 the state and algebraic variables at the collocation points are crucial. For this
549 reason, the result of a simulation from the initial stationary point (through
550 imposing stationarity on Eq. (24) under non-reactive conditions (Section 3.1))
551 was used as the initial guess.

552 **6. Results and Discussion**

553 This paper describes two inherently different scale-up strategies, outlined in
554 Section 4.1.1. It is, however, vital for both strategies that the CSTR model

555 (Section 3.1) is valid, as it governs the scaling behavior of the non-dimensional
 556 parameters in Table 2. The validity of the CSTR model can be assessed by
 557 determining the discrepancy between $\hat{\tau} = L/\hat{v}_\zeta$ and the apparent spatially av-
 558 eraged reactor chamber residence time, defined as:

$$559 \quad \langle \hat{\tau} \rangle := \left\llbracket \frac{L}{\hat{v}_\zeta} \right\rrbracket (\zeta_{\text{end}} - \zeta_0) \left(\int_{\zeta_0}^{\zeta_{\text{end}}} v_\zeta d\zeta \right)^{-1} \quad (35)$$

560 where v_ζ is governed by the compressible Navier–Stokes equation (Eq. (5)). In
 561 order for the relationship $\langle \hat{\tau} \rangle := \hat{\tau}$ to be valid, the spatially averaged normalized
 562 velocity field described by Eq. (5) must be equal to one. Thus, analyzing the
 563 Navier–Stokes equation shows that this relationship is valid only if the shear
 564 stress, Φ_ζ , approaches zero. A small discrepancy between $\hat{\tau}$ and $\langle \hat{\tau} \rangle$, however,
 565 is expected for low values of Φ_ζ . The validity of the CSTR model has been
 566 assessed when calculating the results for both scale-up strategies.

567 6.1. Scale-up Strategy I

568 Fig. 1 shows the cost function entities, $Y_\alpha(\tau_f)$ and $\alpha \in \{A, B\}$, and the
 569 terminal inequality constraint entities, $\langle m_s \rangle(\tau_f)$ and $\text{UF}(\tau_f)$, as functions of the
 570 geometric factor, λ , when applying *Scale-up strategy I*. The results have been
 571 determined for the optimal precursor mass flows, $\dot{Q}_A^{\mathcal{B}} := \dot{Q}_B^{\mathcal{B}}$. Thus, the mass
 572 flows of the two precursors were set to be equal and determined from solving
 573 the DOP (Eq. (34)) for each $\lambda \in [1, 20]$. The assigned design specifications
 574 for *Reactor* \mathcal{A} , listed in Table 3, have been retained with $\lambda = 1$, and the
 575 quotient between the metrics associated with *Reactor* \mathcal{B} and those associated
 576 with *Reactor* \mathcal{A} are denoted by the superscript \mathcal{B}/\mathcal{A} . As expected from the
 577 quadratic scaling behavior of $\hat{\tau}$ with λ in Table 2, the relative apparent reactor
 578 residence time, $\langle \hat{\tau} \rangle^{\mathcal{B}/\mathcal{A}}$, depends in a linear manner on λ on a logarithmic
 579 scale with base two. By this means, the validity of the CSTR model is valid
 580 in these conditions. In contrast, the optimal relative precursor mass flows,
 581 $\dot{Q}_\alpha^{\mathcal{B}/\mathcal{A}}$, depend on λ in a weakly exponential manner, in order for the inequality
 582 constraints to be fulfilled to the specified tolerances. In addition, the relative

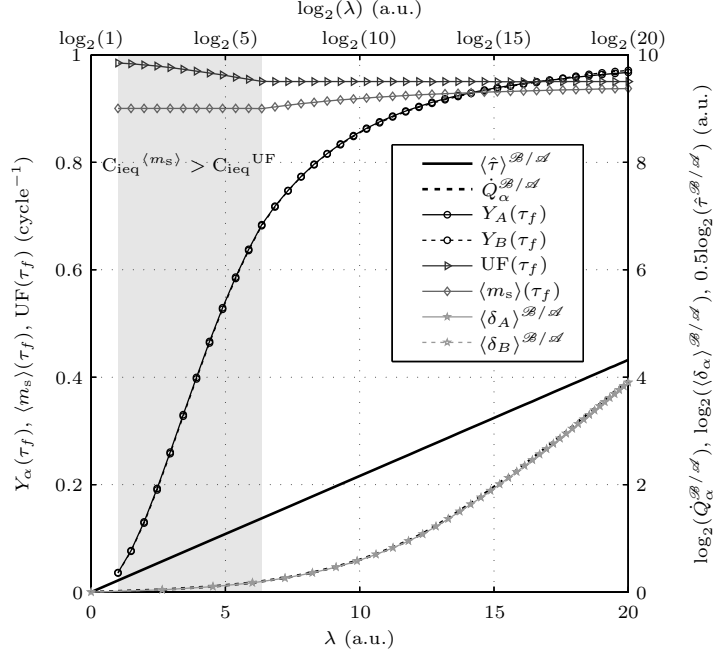


Figure 1: The effects of the geometrical factor, $\lambda \in [1, 20]$, and the optimal precursor mass flow, \dot{Q}_α and $\alpha \in \{A, B\}$, (which were set to be equal) on the cost function entities and the terminal inequality constraints when applying *Scale-up strategy I*. The shaded area represents the geometric scaling factors for which the terminal inequality constraint for $\langle m_s \rangle(\tau_f)$ is active.

583 apparent precursor exposure doses, $\langle \delta_\alpha \rangle^{\mathcal{B}/\mathcal{A}}(\tau_f)$ and $\alpha \in \{A, B\}$, determined
 584 from Eq. (29) with all gas–surface reactions switched off (i.e. $S_\alpha := 0$ and $\alpha \in$
 585 $\{A, B, C\}$), depend on λ in a similar manner as the optimal relative precursor
 586 mass flows.

587 More importantly, Fig. 1 shows that two different regimes appear, depending
 588 on the value of the geometric factor, λ , since only one of the terminal inequality
 589 constraints, $\mathbf{C}_{\text{ieq}} = [C_{\text{ieq}}^{\langle m_s \rangle}, C_{\text{ieq}}^{\text{UF}}]^T$, is active for each λ . The terminal
 590 inequality constraint for $\text{UF}(\tau_f)$ is active for $\lambda \leq 6.5$ when the reference values
 591 of *Reactor* \mathcal{A} given in Table 3 are used, whereas the constraint for $\text{UF}(\tau_f)$ is
 592 active for $\lambda > 6.5$. This implies that the film thickness uniformity constraint
 593 is more easily satisfied than the deposition rate per cycle at lower substrate di-

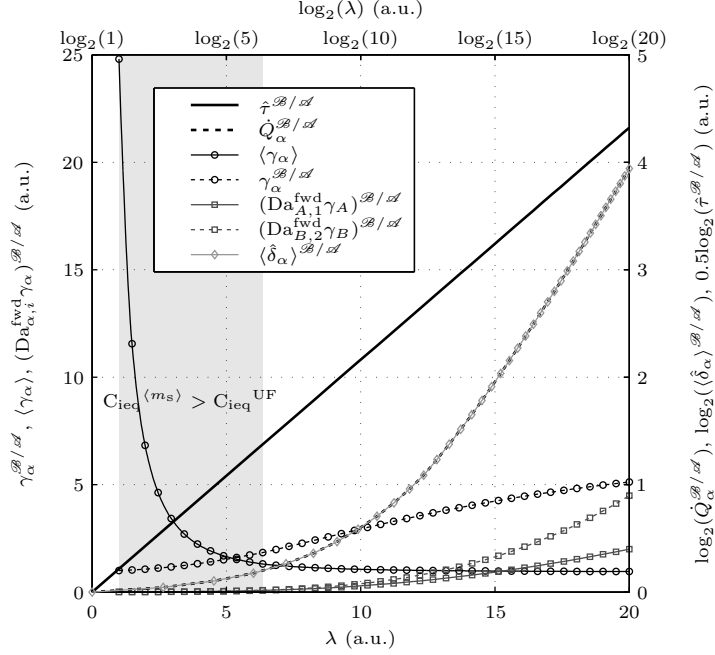


Figure 2: The effects of the geometrical factor, $\lambda \in [1, 20]$, and the optimal precursor mass flow, \dot{Q}_α and $\alpha \in \{A, B\}$, (which were set to be equal) on the non-dimensional parameters listed in Table 2 when applying *Scale-up strategy I*. The shaded area represents the geometric scaling factors for which the terminal inequality constraint for $\langle m_s \rangle(\tau_f)$ is active.

594 mensions, when optimizing precursor yields. Moreover, the extent of the region
 595 in which $C_{ieq}^{(m_s)} > C_{ieq}^{UF}$ is smaller at higher values of the assigned reference
 596 $\langle m_s \rangle^{\mathcal{A}}(\tau_f)$ of *Reactor* \mathcal{A} . The maximum growth rate per cycle, in particular,
 597 is obtained for $\langle m_s \rangle^{\mathcal{A}}(\tau_f) := 1$, at which value the film thickness uniformity is
 598 equal to one. Finally, Fig. 1 also shows that the optimal precursor yield ap-
 599 proaches unity as $\lambda \rightarrow 20$. This implies that the precursor utilization increases
 600 with scale up when applying *Scale-up strategy I*.

601 One of the conditions imposed by *Scale-up strategy I* is that the reactor
 602 is scaled up without changing any of the operating parameters, \dot{Q}_β and \dot{V}_{VP} .
 603 Further, dynamic similarity will be maintained to some extent as Re and Pe re-
 604 main unchanged, whereas the remaining dimensionless numbers in Table 2 will

605 change. Fig. 2 shows these dimensionless numbers as functions of $\lambda \in [1, 20]$.
606 The way in which the relative reactor chamber residence time, $\hat{\tau}^{\mathcal{B}/\mathcal{A}}$, and the
607 relative apparent precursor exposure doses, $\langle \hat{\delta}_\alpha \rangle^{\mathcal{B}/\mathcal{A}}(\tau_f)$ and $\alpha \in \{A, B\}$ (Eq.
608 (30)), depend on the geometrical factor resemble those of their apparent counter-
609 parts shown in Fig. 1. The product of the relative surface Damköhler number
610 and the precursor excess number, $(\text{Da}_{\alpha,1}^{\text{fwd}} \gamma_\alpha)^{\mathcal{B}/\mathcal{A}}$ and $\alpha \in \{A, B\}$, increases
611 strictly with λ when the optimal precursor mass flows are used. This metric is
612 essential since it is a major factor in determining the fractional surface coverage
613 (Eq. (21)), and the resulting deposition rate (Eq. (27a)). Thus, the increase
614 in $\text{Da}_{\alpha,1}^{\text{fwd}} \gamma_\alpha$ with λ and \dot{Q}_α causes the inherent benefits in precursor utilization
615 when the substrate dimension is scaled up, as shown in Fig. 1. The excess
616 number, γ_α , however, (as defined in Eq. (23)) is only valid for a specific time
617 instant, and thus cannot describe the entire molar amount of precursors injected
618 during a single pulse. The total molar amount of precursors injected per molar
619 unit adsorption site, $\langle \gamma_\alpha \rangle$, was defined for this reason as:

$$620 \quad \langle \gamma_\alpha \rangle := \frac{\dot{Q}_\alpha \rho_{\text{STP},\alpha} \hat{\tau} \Delta \tau_\alpha}{\Lambda A M_\alpha} \quad (36)$$

621 Fig. 2 shows that $\langle \gamma_\alpha \rangle$ decreases strictly with λ when the optimal precursor mass
622 flows are used. Moreover, approximately 25 times the saturation molar amount
623 is required for the terminal inequality constraints to be satisfied at $\lambda = 1$,
624 in these conditions. In contrast, the value of $\langle \gamma_\alpha \rangle$ asymptotically approaches
625 unity as $\lambda \rightarrow 20$, and ultimately promotes the increase in precursor utilization.
626 Finally, Eq. (36) allows to calculate the maximum theoretical precursor yield
627 from the inverse of $\langle \gamma_\alpha \rangle$, i.e. $\max Y_\alpha(\tau_f) := \langle \gamma_\alpha \rangle^{-1}$.

628 6.1.1. Film Thickness Uniformity

629 Fig. 3 shows the true implication of optimizing the precursor yields in scale-
630 up studies. It is evident that optimizing the cost function of precursor utiliza-
631 tion, subject to the inequality constraint of film thickness uniformity, creates a
632 strong coverage gradient towards the trailing edge of the substrate as $\lambda \rightarrow 20$.
633 This is a consequence of the cross-flow ALD reactor design, which means that

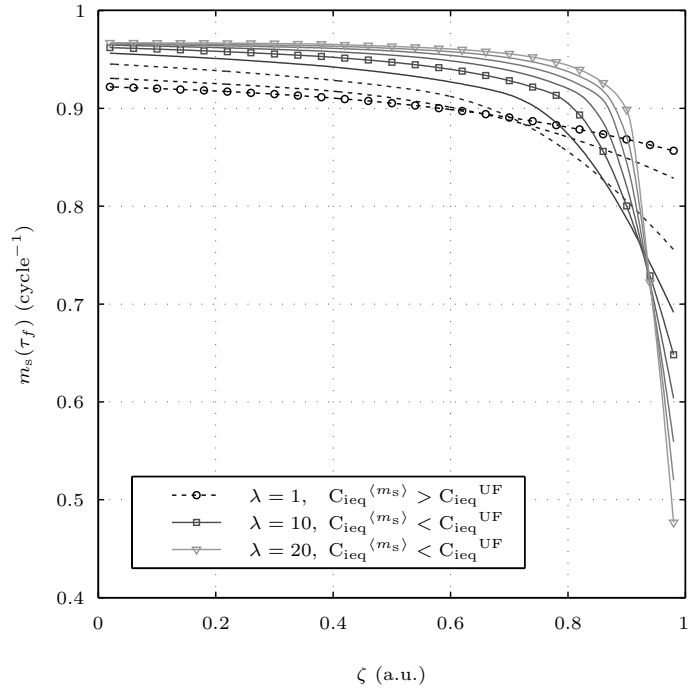


Figure 3: Film thickness profiles as functions of the non-dimensionalized spatial coordinate variable, $\zeta \in [0, 1]$, sampled for $\lambda \in [1, 20]$ when applying *Scale-up strategy I*. (--) indicates the geometric scaling factors for conditions in which the terminal inequality constraint for $\langle m_s \rangle(\tau_f)$ is active.

634 the trailing edge of the substrate is exposed to a more depleted precursor flow
635 than the leading edge, and that the cross-substrate film deposition rate is al-
636 ways inhomogeneous to some extent. Accordingly, the optimal precursor yields
637 approach unity for high values of the geometric factor (see Fig. 1), and only a
638 very small amount of the injected precursor dose is available for reaction close
639 to the trailing edge. This causes the deposition rate to approach zero rapidly in
640 this region. In contrast, the gradients in this region are significantly gentler for
641 low values of λ , such as those associated with low precursor yields and values of
642 $\langle \gamma_\alpha \rangle \gg 1$. It is, however, noteworthy that the terminal inequality constraint for
643 deposition rate uniformity is satisfied for all the profiles shown in Fig. 3. Recall
644 that the uniformity metric that was defined in Eq. (28) relates the absolute

645 deviation of the deposition rate to its spatially averaged mean value. In order
646 to enforce gentler gradients of $m_s(\tau_f)$ towards the trailing edge of the substrate,
647 it is suggested that $UF(\tau_f)$ can be redefined to describe simply the relative ac-
648 cumulated mass, $m_s|_{\zeta=\zeta_{\text{end}}}$, at $\zeta = \zeta_{\text{end}}$, since the deposition rate will always be
649 a minimum here in the cross-flow reactor design. This formulation overcomes
650 the limitation of a spatially averaged metric (Eq. (28)), while still providing the
651 physical interpretation of a perfectly uniform profile for $UF(\tau_f) := 1$.

652 6.1.2. Gas-phase Limit-cycle Dynamics

653 Fig. 4 shows the limit-cycle solution for the gas-phase state and algebraic
654 variables when using *Scale-up strategy I* and a geometric factor of $\lambda = 20$. It
655 is evident that the state and algebraic variables conform to periodic boundary
656 conditions over the time horizon $[\tau_0, \tau_f]$. The markers indicate the locations
657 of the Radau collocation points for $\zeta \in \{1/2, N_{\text{FVM}} - 1/2\} \cdot (\zeta_{\text{end}} - \zeta_0)/N_{\text{FVM}}$
658 (i.e. the centers of the first and last FVM elements). The CSTR model dynamic
659 reactor gas-phase material balances (Eq. (1)) have been extended to incorporate
660 the instantaneous formulation of the surface-state dynamics (Eq. (21)) and
661 the accumulated mass deposited (Eq. (27a)), in order to make it possible to
662 compare the results from the complete CSTR model with those obtained from
663 the spatially distributed PDAE model (Eq. (24)). Dashed lines in Fig. 4 show
664 the results from the extended CSTR model.

665 Fig. 4a shows that the nominal velocity, \hat{v}_ζ , (Eq. (3d)) is prescribed at
666 $\zeta = \zeta_{\text{end}}$ through Eq. (14). The output from the CSTR model follows that
667 of the distributed PDAE model (Eq. (24)) at the outlet, as expected, but it
668 should be remembered that the center of the last FVM element is located at
669 $\zeta = (N_{\text{FVM}} - 1/2) \cdot (\zeta_{\text{end}} - \zeta_0)/N_{\text{FVM}}$. The pressure effects propagate instan-
670 taneously throughout the spatial domain, $\zeta \in [\zeta_0, \zeta_{\text{end}}]$, during the precursor
671 exposure periods (which are indicated by shaded rectangles) (Fig. 4c), whereas
672 the density of the gas mixture propagates with the mass average velocity (Fig.
673 4b). During the subsequent purge period, the chamber pressure drops in the
674 manner of a first-order dynamical system with a single time constant given by

675 the ratio of chamber volume to pumping speed (Travis and Adomaitis, 2013a,b).
 676 The base-line pressure, \hat{p} (Eq. (3c)), is approached during the subsequent purge
 677 for $\zeta = (N_{\text{FVM}} - 1/2) \cdot (\zeta_{\text{end}} - \zeta_0)/N_{\text{FVM}}$, but it is not fully attained in the
 678 conditions studied here.

679 More importantly, the spatial distributions of v_ζ and ρ (Figs. 4a and 4b) re-
 680 sult from the pressure drop across the reactor chamber (Fig. 4c). This pressure
 681 drop is ultimately governed by the compressible formulation of the continuity
 682 equation and the Navier–Stokes equation (Eqs. (4–5)), and it is determined by
 683 the chamber dimensions and process operating parameters $[\dot{V}_{\text{VP}}, \dot{Q}_\beta, T]$. The
 684 resulting pressure drop across the reactor chamber that originates from the
 685 non-zero shear stress, Φ_ζ , in Eq. (5) implies that the cross-substrate film thick-
 686 ness deposition rate (Eq. (27a)) is always inhomogeneous despite the injected
 687 precursor exposure dose, $\langle \delta_\alpha \rangle$. Consequently, it is a combination of the degree
 688 of precursor depletion in the flow direction and the magnitude of the pressure
 689 drop across the reactor chamber that governs the extent of the deposition profile
 690 non-uniformity (see Fig. 3). Moreover, it is noteworthy that Eq. (10) governs
 691 that the pressure drop across the reactor chamber is higher for low-volume re-
 692 actor designs with high aspect ratios, $L/H \gg 1$, and for high carrier gas linear
 693 velocities.

694 Finally, the results from the distributed PDAE model (Eq. (24)) in Fig. 4d
 695 shows that the α th precursors are separated at all positions of the spatial do-
 696 main, $\zeta \in [\zeta_0, \zeta_{\text{end}}]$. Especially, the high precursor utilization at this geometric
 697 factor ensures that negligible amounts of precursor remain after each exposure
 698 period in the gas phase, at the start of the subsequent precursor exposure dose
 699 period. Undesirable CVD conditions are in this way avoided, as recently in-
 700 vestigated by Travis and Adomaitis (2013a). However, Fig. 1 shows that the
 701 number of reactor chamber volumes purged during the carrier gas purge period,
 702 $(\hat{\tau} \Delta \tau_\beta) / \langle \hat{\tau} \rangle$ (cf. Eq. (35)), decreases linearly with the apparent residence time
 703 from that of the base-case *Reactor A* when applying *Scale-up strategy I*. Thus,
 704 when the large precursor doses that are associated with lower yields are used,
 705 excess precursors remain in the gas phase and the carrier gas purge may be

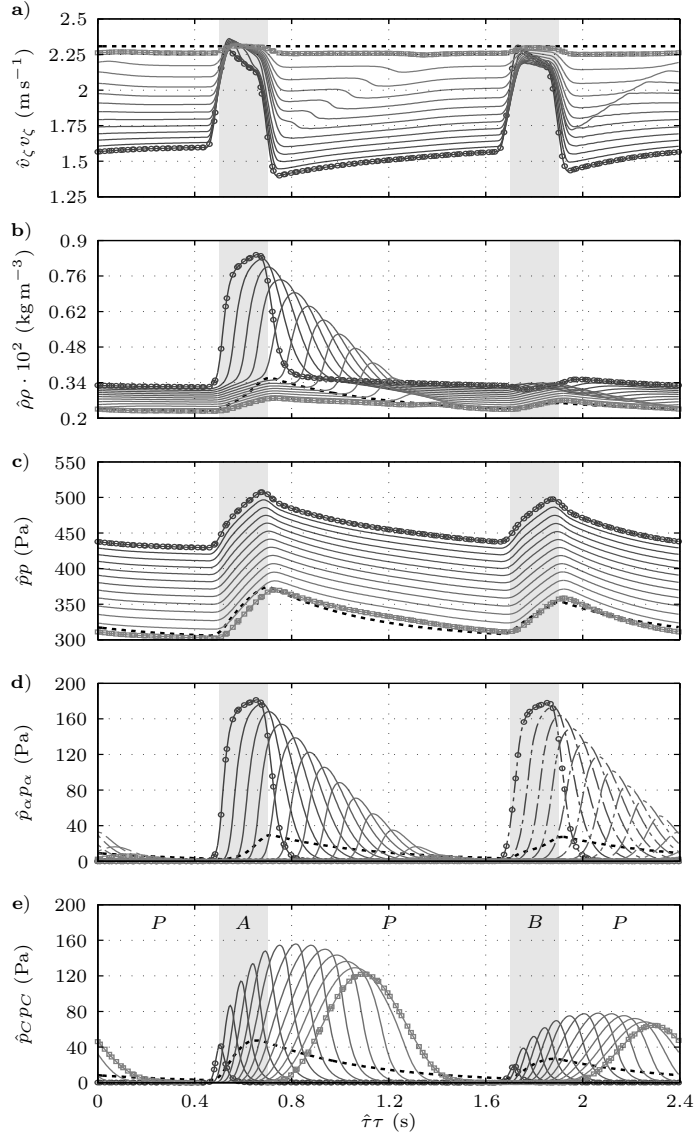


Figure 4: Scaled-up *Reactor B* gas-phase dynamics for a single-pulse horizon $\tau \in [\tau_0, \tau_f]$ and $\lambda = 20$ when using *Scale-up strategy I*. The limit-cycle solution is spatially resolved for $\zeta = (j - 1/2)(\zeta_{\text{end}} - \zeta_0)/N_{\text{FVM}}$ and $j \in \{1, 3, \dots, N_{\text{FVM}}\}$. $(-\circ-)$ indicates the state and algebraic variables for $j = 1$, while $(-\square-)$ indicates the corresponding variables for $j = N_{\text{FVM}}$. $(--)$ indicates the limit-cycle solution from the CSTR model. The shaded areas indicate the precursor pulse interval endpoints.

706 insufficient. It is expected that this phenomenon will be more pronounced at
 707 shorter purge periods. In addition, the limit-cycle solution obtained from the
 708 CSTR model depicted in Fig. 4d shows that non-negligible amounts of pre-
 709 cursors remain in the gas phase from the previous precursor exposure at the
 710 start of the subsequent precursor exposure for the given residence time. This
 711 will become more evident when examining the accumulated mass trajectory in
 712 Section 6.1.3.

713 6.1.3. Growth Surface Limit-cycle Dynamics

714 Fig. 5 shows the limit-cycle solutions for the growth surface state and al-
 715 gebraic variables obtained using *Scale-up strategy I* and a geometric factor of
 716 $\lambda = 20$. The spatially distributed mass gain trajectory (Fig. 5a) determined
 717 from Eq. (27) can be physically interpreted by means of the underlying chem-
 718 ical composition of the growth surface (Figs. 5b–5d). In particular, the net
 719 contribution from the irreversible reactions (R2a–R2b) to Eq. (27b) is the
 720 degree of saturation of the fractional surface coverage onto which the respec-
 721 tive precursors can adsorb, and the difference in molar masses, ΔM_i (where
 722 $i \in \{1, 2, \dots, 4\}$), of the adsorptive precursors and the associated number of
 723 ligands that desorb from the growth surface. Thus, the difference in molec-
 724 ular mass between the initial and terminal surface species in Reaction (R2a),
 725 $\Delta M_1 = M_{\text{Zn}(\text{C}_2\text{H}_5)_2} - \nu M_{\text{C}_2\text{H}_6}$, results in a net mass increase, whereas that of
 726 Reaction (R2b), $\Delta M_2 = M_{\text{H}_2\text{O}} - (2 - \nu)M_{\text{C}_2\text{H}_6}$, results in the net contribution
 727 to Eq. (27) from this half-reaction being less than zero, when $\nu = 1.37$. The
 728 significant difference in net mass contribution to Eq. (27) from each precursor
 729 half-reaction is reflected also in the trajectory of the deposition rate uniformity
 730 (Fig. 5a). This trajectory falls at the start of the $\text{Zn}(\text{C}_2\text{H}_5)_2$ precursor period
 731 and passes through a minimum, as the travelling wave of the precursor propa-
 732 gates across the substrate. The uniformity subsequently rises when the entire
 733 substrate has been exposed. The corresponding effect of the subsequent H_2O
 734 precursor exposure is not as pronounced, which is a consequence of the small
 735 difference in molecular mass between the initial and terminal surface species in

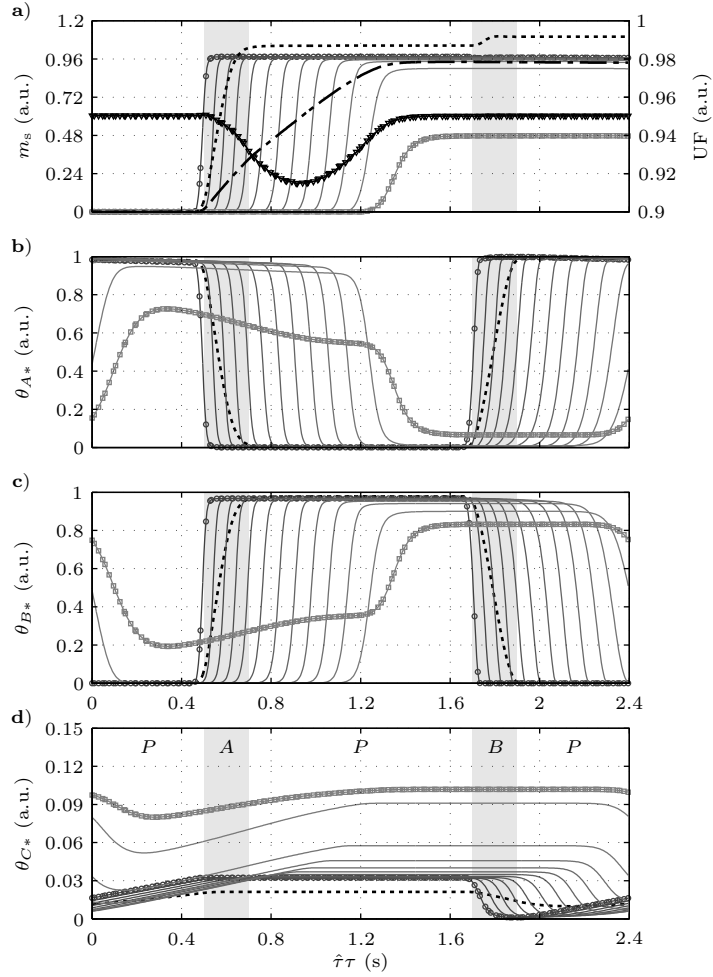


Figure 5: Scaled-up *Reactor B* film-growth dynamics for a single-pulse horizon $\tau \in [\tau_0, \tau_f]$ and $\lambda = 20$ when applying *Scale-up strategy I*. The limit-cycle solution is spatially resolved for $\zeta = (j - 1/2)(\zeta_{\text{end}} - \zeta_0)/N_{\text{FVM}}$ and $j \in \{1, 3, \dots, N_{\text{FVM}}\}$. $(-\circ-)$ indicates the state and algebraic variables for $j = 1$, while $(-\square-)$ indicates the corresponding variables for $j = N_{\text{FVM}}$. $(--)$ indicates the limit-cycle solution from the CSTR model, while $(-\cdot-)$ indicates the substrate spatially averaged deposition rate, and $(-\nabla-)$ the uniformity of the film thickness. The shaded areas indicate the precursor pulse interval endpoints.

736 Reaction (R2b). It is also evident from Fig. 5a that the terminal inequality
 737 constraints for $\langle m_s \rangle(\tau_f)$ and $\text{UF}(\tau_f)$ are satisfied.

738 As the travelling wave of the $\text{Zn}(\text{C}_2\text{H}_5)_2$ precursor propagates through the

739 reactor, the partial pressure, p_A , becomes lower in the direction of the flow (Fig.
 740 4d). As discussed in Section 6.1.1 and 6.1.2, this phenomenon originates from
 741 the pressure drop (cf. Eq. (10)) across the reactor chamber and the conver-
 742 sion of available surface OH ligands through Reaction (R2a). As this reaction
 743 continues, the coverage of $\theta_{A^*} \rightarrow 0$ as the growth surface saturates with B^* .
 744 The subsequent H_2O precursor exposure and half-reaction (see Reaction (R2b))
 745 proceed in an analogous manner, ultimately resulting in the reformation of A^* .
 746 The degree of saturation at each position in $[\zeta_0, \zeta_{\text{end}}]$ is governed by the par-
 747 tial pressure of precursors in the vicinity of the growth surface (see Eq. (16)).
 748 Thus, as $p_\alpha \rightarrow 0$ in the region close to the trailing edge of the substrate, the
 749 conversion rate of surface species falls significantly as the reaction rate $r_i \rightarrow 0$.
 750 This causes the sharp decrease in deposition rate shown in Fig. 5a and in Fig.
 751 3. Likewise, the trailing edge of the substrate is also subject to the most severe
 752 dehydroxylation (see Fig. 5d), due to the low H_2O precursor dose level in this
 753 region, which limits the rate of Reaction (R2d). The dehydroxylation reaction
 754 continues throughout the purge period following H_2O exposure, which reduces
 755 the ligand density of surface OH groups, and ultimately the overall deposition
 756 rate.

757 Fig. 5a shows that there is a clear distinction between the accumulated
 758 mass trajectory, $\langle m_s \rangle$, determined from the spatially distributed PDAE model
 759 (Eq. (24)) and that determined from the CSTR model. As expected, the CSTR
 760 model predicts an instantaneous net mass increase at the start of each precursor
 761 exposure period, whereas the PDAE model predicts a net mass increase that is
 762 related to the propagation of the travelling wave of precursors throughout the
 763 spatial domain. In addition, the mass gain trajectory from the CSTR model
 764 clearly shows the implication of the coexistence of precursors in the gas phase,
 765 as previously described in Section 6.1.2. Recall that the maximum growth rate
 766 per cycle is obtained for $\langle m_s \rangle(\tau_f) := 1$, and a net mass decrease is expected
 767 from the H_2O half-reaction (Reaction (R2b)). A net mass increase in $\langle m_s \rangle$ is,
 768 however, predicted by the CSTR model during the H_2O precursor exposure,
 769 and its terminal value exceeds one (which means that more than a single mono-

770 layer is deposited). However, the model does not describe the gas-phase CVD
771 reactions, instead this phenomenon arises from the adsorption of the remaining
772 $\text{Zn}(\text{C}_2\text{H}_5)_2$ precursor in the gas-phase onto the newly formed OH ligands on
773 the growth surface, which are, in turn, converted instantaneously throughout
774 Reaction (R2b). In contrast, the PDAE model does not predict undesirable
775 CVD conditions, and the accumulated mass trajectory that the model predicts
776 agrees with that expected to arise in true ALD conditions.

777 6.2. Scale-up Strategy II

778 Fig. 6 shows the cost function entities, $Y_\alpha(\tau_f)$ and $\alpha \in \{A, B\}$, and the
779 terminal inequality constraint entities, $\langle m_s \rangle(\tau_f)$ and $\text{UF}(\tau_f)$, as functions of
780 the geometric factor, λ , sampled for $\vartheta \in (0, 2]$ when using *Scale-up strategy*
781 *II*. The results have been calculated with the minimum precursor mass flows,
782 $\dot{Q}_A^{\mathcal{B}} := \dot{Q}_B^{\mathcal{B}}$, that satisfy the terminal inequality constraints (Eq. (33)) for
783 each value of λ and ϑ . In order to maintain the nominal mass fraction for
784 the α th precursor (Eq. (3b)) in the scaled-up *Reactor* \mathcal{B} , it is necessary that
785 $d\log_2(\dot{Q}_\alpha^{\mathcal{B}/\mathcal{A}})/(d\log_2(\lambda)) := \vartheta$ (see also Table 2). However, there is a clear
786 discrepancy between the optimal precursor mass flows, $\dot{Q}_\alpha^{\mathcal{B}/\mathcal{A}}$, and $\dot{Q}_\alpha^{\mathcal{B}/\mathcal{A}} := \lambda^\vartheta$
787 for all $\vartheta \in [0, 2]$ shown in Fig. 6d. For this reason, the scaling rule for the
788 nominal mass fraction, i.e. $\dot{Q}_\alpha^{\mathcal{B}/\mathcal{A}} := \lambda^\vartheta$, is considered not adequate to achieve
789 the assigned design criteria in the scaled-up design *Reactor* \mathcal{B} .

790 Fig. 6c shows that the highest precursor yields, $Y_\alpha(\tau_f)$, are obtained when
791 scaled-up *Reactor* \mathcal{B} is operated at the lowest possible carrier gas mass flow, \dot{Q}_β .
792 As was the case for *Scale-up strategy I*, precursor utilization increases strictly
793 with λ when using *Scale-up strategy II*. However, for $\vartheta = 2$ (which corresponds
794 to maintaining constant reactor residence time, $\hat{\tau}$, as indicated in Table 2) ap-
795 proximately the same yield is obtained for all $\lambda \in \{1, 20\}$. This is a consequence
796 of the way in which the product of the surface Damköhler number and precursor
797 excess number, $\gamma_\alpha \text{Da}_{\alpha,i}^{\text{fwd}} \propto \dot{Q}_\alpha \lambda^{2-2\vartheta}$ for the α th precursor, depends on ϑ .
798 Thus for $\vartheta = 2$, the inherent increase in this non-dimensional metric, ultimately
799 promotes the reaction rate through Eq. (21) and the resulting deposition rate

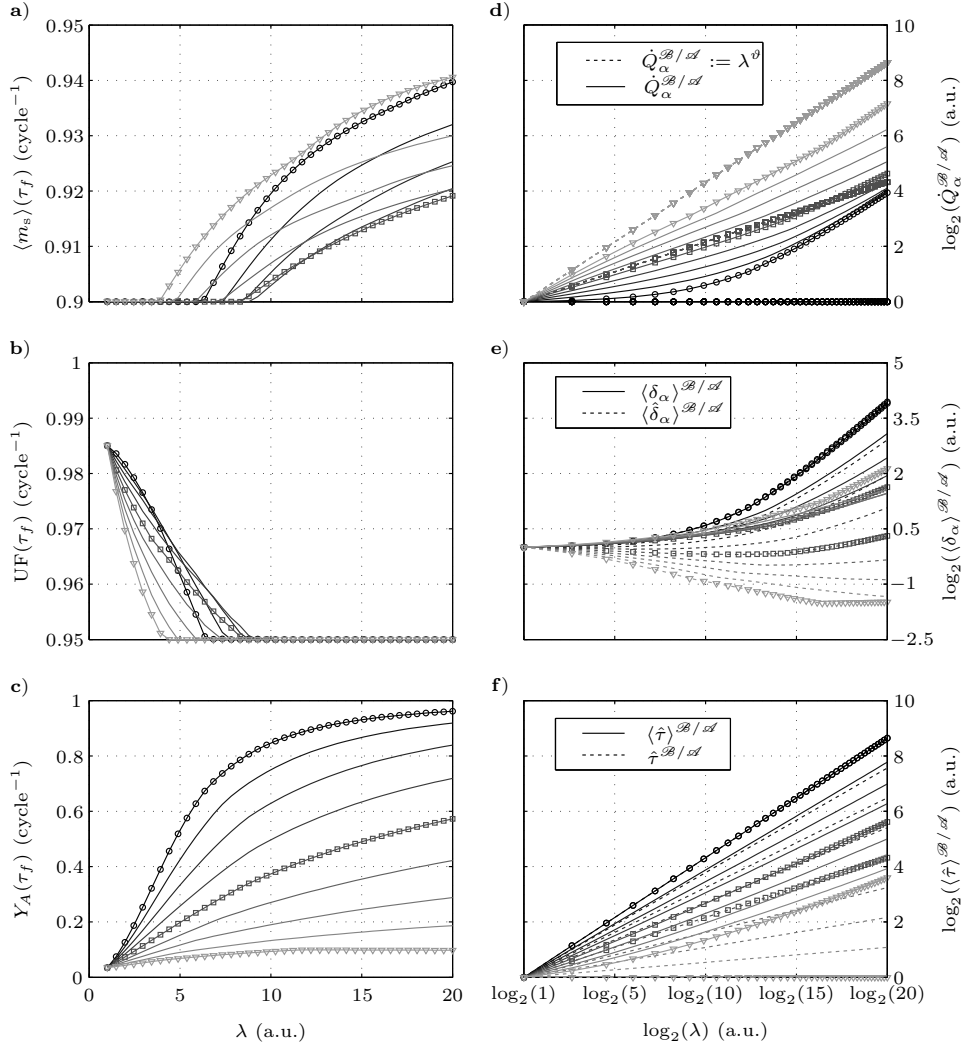


Figure 6: The effects of the geometrical factor, $\lambda \in [1, 20]$, the optimal precursor mass flow, \dot{Q}_α and $\alpha \in \{A, B\}$, (which are set to be equal) on the cost function entities and terminal inequality constraint entities when using *Scale-up strategy II*, with $\vartheta \in (0, 2]$. (\circ) indicates the solution for $\vartheta = 0.0$ (i.e. that of *Scale-up strategy I*), while (\square) indicates that for $\vartheta = 1.0$, and (∇) that for $\vartheta = 2.0$.

800 through Eq. (27), with the geometric scaling factor is lost.

801 More importantly, Figs. 6e and 6f show clearly that the discrepancies be-
802 tween the apparent reactor residence time, $\langle \hat{\tau} \rangle$, and the apparent precursor

803 exposure dose, $\langle \delta_\alpha \rangle$, from their respective non-dimensional counterparts, $\hat{\tau}$ and
 804 $\langle \hat{\delta}_\alpha \rangle$, increases as $\vartheta \rightarrow 2$. These discrepancies arise from the pressure drop
 805 across the spatial domain, $\zeta \in [\zeta_0, \zeta_{\text{end}}]$, (see Section 6.1.2 and Fig. 4c) and
 806 result in the spatial distribution of v_ζ and ρ . For this reason, a higher averaged
 807 linear flow rate, $\langle v_\zeta \rangle$ is necessary to maintain a constant residence time, $\hat{\tau}$, as
 808 $\lambda \rightarrow 20$. Thus, larger pressure drops are obtained as $\lambda \rightarrow 20$ and as the linear
 809 flow rate increases, since $\Phi_\zeta \propto v_\zeta$ in Eq. (10), subject to $\dot{Q}_\beta, \dot{V}_{\text{VP}} \propto \lambda^\vartheta$. This
 810 gives the larger discrepancies shown in Figs. 6e and 6f under these conditions.
 811 In particular, $\hat{\tau}$ is maintained for the scaled-up *Reactor B* proposed in Table 2,
 812 whereas its apparent value, $\langle \hat{\tau} \rangle$, increases strictly with the geometric factor. In
 813 contrast, these values, and those of the precursor exposure dose, coincide over
 814 the entire range of $\lambda \in [0, 20]$ when using *Scale-up strategy I*. In conclusion, the
 815 non-dimensional variables in Table 2 and the CSTR model become less valid
 816 as $\vartheta \rightarrow 2$. Thus, the results reported here clearly motivate the utility of the
 817 spatially distributed PDAE model in combination with dynamic optimization
 818 methods for maximizing the precursor utilization in the scaled-up system while
 819 maintaining fixed absolute growth rate and its relative uniformity.

820 Fig. 6a shows that $\langle m_s \rangle(\tau_f)$ depends on ϑ in a weakly convex manner for
 821 each value of $\lambda \in [10, 20]$. Fig. 7 shows this more clearly, where $\langle m_s \rangle(\tau_f)$ is
 822 plotted as a function of ϑ and sampled for $\lambda \in [10, 20]$. The terminal inequality
 823 constraint for the deposition rate uniformity is active at these geometric factors.
 824 Figs. 7a and 7c show the noteworthy result that the highest values of both
 825 $\langle m_s \rangle(\tau_f)$ and $Y_A(\tau_f)$ are obtained for $\lambda = 20$ in the entire range, $\vartheta \in (0, 2]$.
 826 The magnitude of the normalized deposition rate per cycle is governed to a
 827 large extent by the apparent precursor exposure dose, $\langle \delta_\alpha \rangle$. Thus, it can be
 828 concluded that the weak convex dependence of relative apparent exposure dose
 829 with ϑ , shown in Fig. 7b underlies the dependence of $\langle m_s \rangle(\tau_f)$ shown in Fig.
 830 7a. The magnitude of the apparent precursor exposure dose (Eq. (30)), in turn,
 831 arises from the spatially distributed pressure across the reactor and the mass
 832 fraction of the injected precursor pulse, $\hat{\omega}_\alpha$. In this context, larger pressure
 833 drops are obtained as $\vartheta \rightarrow 2$ and as the linear flow rate increases, since $\Phi_\zeta \propto v_\zeta$,

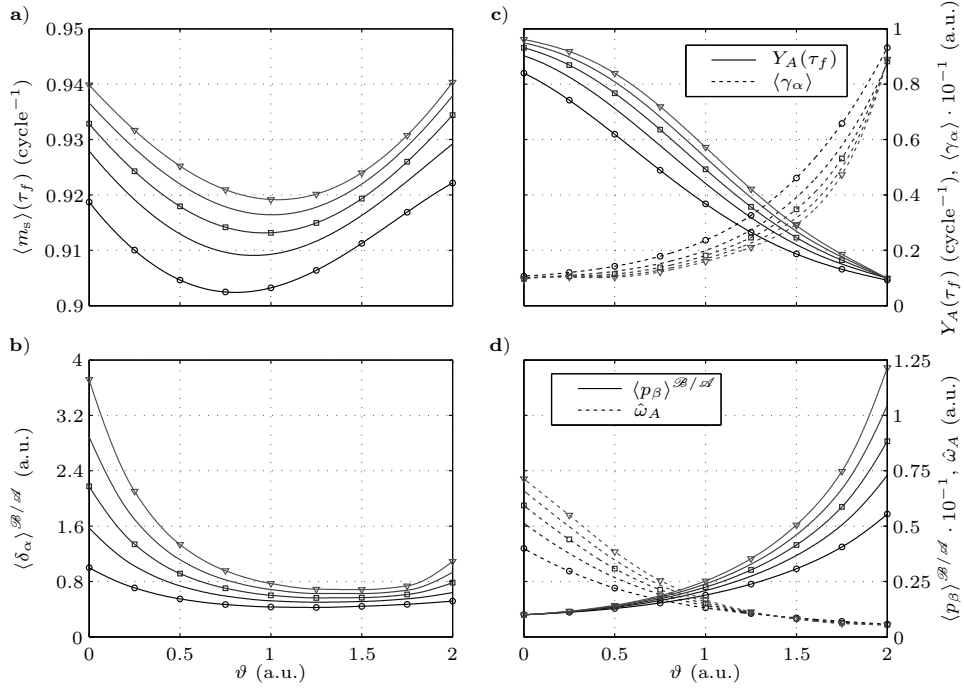


Figure 7: The effects of the geometrical factor, $\lambda \in \{10, 12.5, 15, 17.5, 20\}$, and the optimal precursor mass flow, \dot{Q}_α and $\alpha \in \{A, B\}$, (which were set to be equal) on the cost function entities and terminal inequality constraints when using *Scale-up strategy II* with $\vartheta \in (0, 2]$. (o) indicates the solution for $\lambda = 10$, (\square) for $\lambda = 15$, and (∇) for $\lambda = 20$.

834 subject to \dot{Q}_β , $\dot{V}_{VP} \propto \lambda^\vartheta$. This is clearly shown in Fig. 7d, where the spatially
835 averaged stationary carrier gas pressure, $\langle p_\beta \rangle$, is plotted as a function of ϑ . In
836 addition, the precursor mass fraction decreases with ϑ , as a consequence of the
837 minimal precursor mass flows, which must ensure that the terminal inequality
838 constraints (see Eq. (33)) are satisfied, and the assigned carrier gas mass flow,
839 $\dot{Q}_\beta \propto \lambda^\vartheta$, determined from the scaling rules in Table 2 (Fig. 7d). Therefore,
840 the compromise between the steeper pressure gradient and the lower precursor
841 mass fractions causes the observed convex dependence of $\langle \delta_\alpha \rangle$ on $\vartheta \in [0, 2]$.

842 Moreover, Fig. 7b makes it clear that significantly higher molar amounts of
843 precursors must be injected per molar unit adsorption site, $\langle \gamma_\alpha \rangle$, as $\vartheta \rightarrow 2$, and
844 the precursor yield falls accordingly. Thus, the film thickness profiles shown in

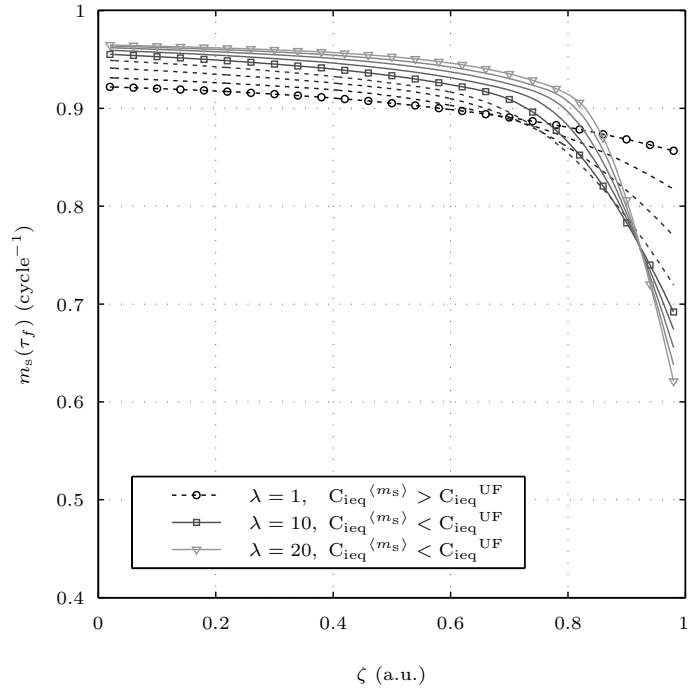


Figure 8: Film thickness profiles as functions of the non-dimensionalized spatial coordinate variable, $\zeta \in [0, 1]$, sampled for $\lambda \in [1, 20]$ when using *Scale-up strategy II* with $\vartheta = 0.5$. (--) indicates the geometric scaling factors for those profiles for which the terminal inequality constraint for $\langle m_s \rangle(\tau_f)$ is active.

845 Fig. 8 for $\vartheta = 0.5$ are more uniform for higher geometric factors than those
 846 obtained when using *Scale-up strategy I* (Fig. 3), since the overall precursor
 847 yields are lower when *Scale-up strategy II* is used. It is, however, important to
 848 remember that the negative pressure gradient in the ζ -direction (Fig. 4c) also
 849 influences the deposition rate through the precursor partial pressure: it lowers
 850 the driving force for the reaction closer to the trailing edge of the substrate, and
 851 thereby contributes to the formation of a non-uniform deposition profile.

852 6.2.1. Gas-phase and Growth Surface Limit-cycle Dynamics

853 The reason for exploring *Scale-up strategy II* was to develop a method which
 854 provides a sufficient length of the purge period to remove precursors in the gas

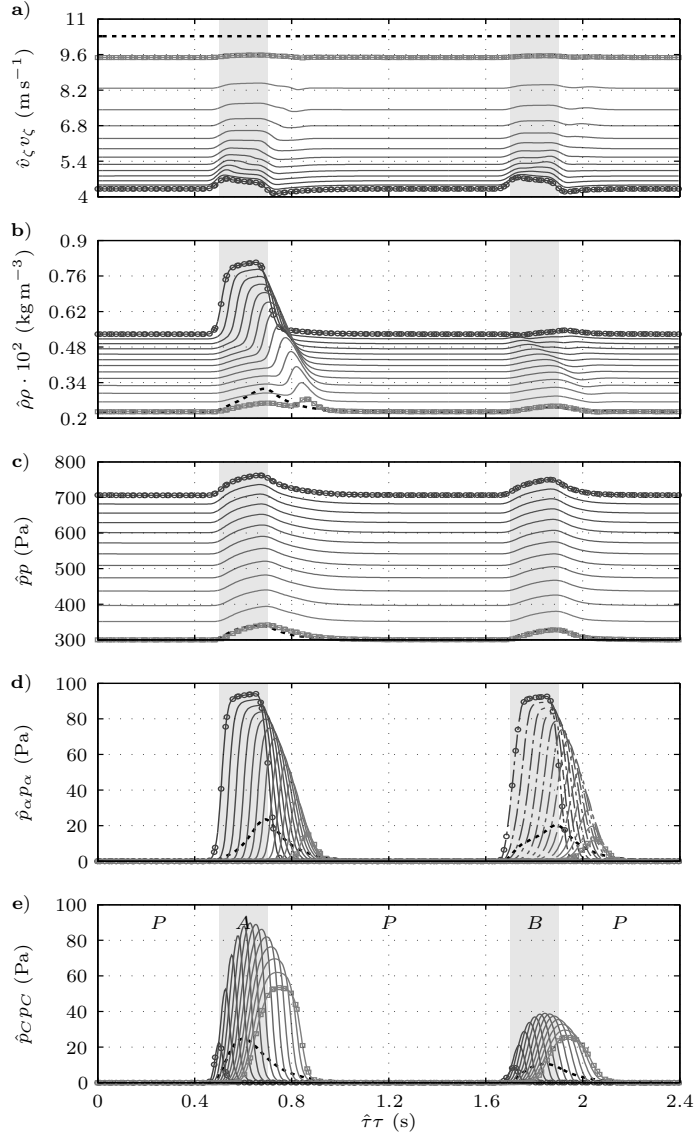


Figure 9: Scaled-up *Reactor B* gas-phase dynamics for a single-pulse horizon $\tau \in [\tau_0, \tau_f]$ and $\lambda = 20$ when using *Scale-up strategy II* with $\vartheta = 0.5$. The limit-cycle solution is spatially resolved for $\zeta = (j - 1/2)(\zeta_{\text{end}} - \zeta_0)/N_{\text{FVM}}$ and $j \in \{1, 3, \dots, N_{\text{FVM}}\}$. $(-o-)$ indicates the state and algebraic variables for $j = 1$, while $(-\square-)$ indicates the corresponding variables for $j = N_{\text{FVM}}$. $(-)$ indicates the limit-cycle solution from the CSTR model. The shaded areas indicate the precursor pulse interval endpoints.

855 phase remaining from the previous exposure period at the start of the subsequent
 856 precursor period. This was achieved by reducing the reactor chamber residence
 857 time while maintaining the nominal carrier gas pressure, \hat{p} . Fig. 9 shows the
 858 limit-cycle solution for the gas-phase state and algebraic variables when using
 859 *Scale-up strategy II*, a geometric factor $\lambda = 20$, and $\vartheta = 0.5$. The results
 860 show clearly the implications of the scaling rule for the carrier gas manipulated
 861 variables, i.e. $\dot{Q}_\beta, \dot{V}_{VP} \propto \lambda^\vartheta$, from Table 2. The travelling wave of precursors and
 862 the density of the gas mixture propagate with a significantly higher mass average
 863 velocity as expected. In addition, the overall higher mass average velocity gives
 864 rise to a significantly higher negative pressure gradient in the ζ -direction than
 865 that shown in Fig. 4. Moreover, at the start of the purge period, the total
 866 pressure relaxes to the stationary value of the carrier gas partial pressure at each
 867 position in the spatial domain, $\zeta \in [\zeta_0, \zeta_{\text{end}}]$. In particular, the total pressure at
 868 $\zeta = (N_{\text{FVM}} - 1/2) \cdot (\zeta_{\text{end}} - \zeta_0)/N_{\text{FVM}}$ relaxes to the base-line pressure, \hat{p} , and
 869 this trajectory resembles that of the CSTR model.

870 More importantly, it is evident that the reduction in residence time, which
 871 arises as a consequence of prescribing $\dot{Q}_\beta, \dot{V}_{VP} \propto \lambda^\vartheta$ with $\vartheta = 0.5$, is suffi-
 872 cient to ensure that the gas-phase precursors and the reaction by-products are
 873 transported out of the reactor chamber (at all positions) before the start of the
 874 subsequent precursor pulse period. In addition, the stationary carrier gas par-
 875 tial pressure is maintained after a fraction of the purge period, when assigned
 876 to $\hat{\tau}\Delta\tau_P := 1.0$ (s). Likewise, the appearance of the accumulated mass tra-
 877 jectory during the precursor exposures (see Fig. 10) shows that precursors do
 878 not coexist in the gas phase. These results confirm that the carrier gas pulse
 879 period can be reduced for this set of $\dot{Q}_\beta, \dot{V}_{VP} \propto \lambda^\vartheta$ and $\vartheta = 0.5$. The growth
 880 rate per cycle time, $\hat{\tau}\Delta\tau$, can in this way be significantly reduced, as previously
 881 shown in Holmqvist et al. (2013b). Alternatively, the reactor chamber residence
 882 time can be safely increased, while preventing the undesirable CVD conditions,
 883 by choosing $\vartheta < 0.5$. In any case, there is no reason to choose $\vartheta > 0.5$, since
 884 this causes a reduction in the precursor mass fractions and the partial pressures
 885 (Fig. 9d), and lowers the overall precursor yield (Figs. 6 and 7).

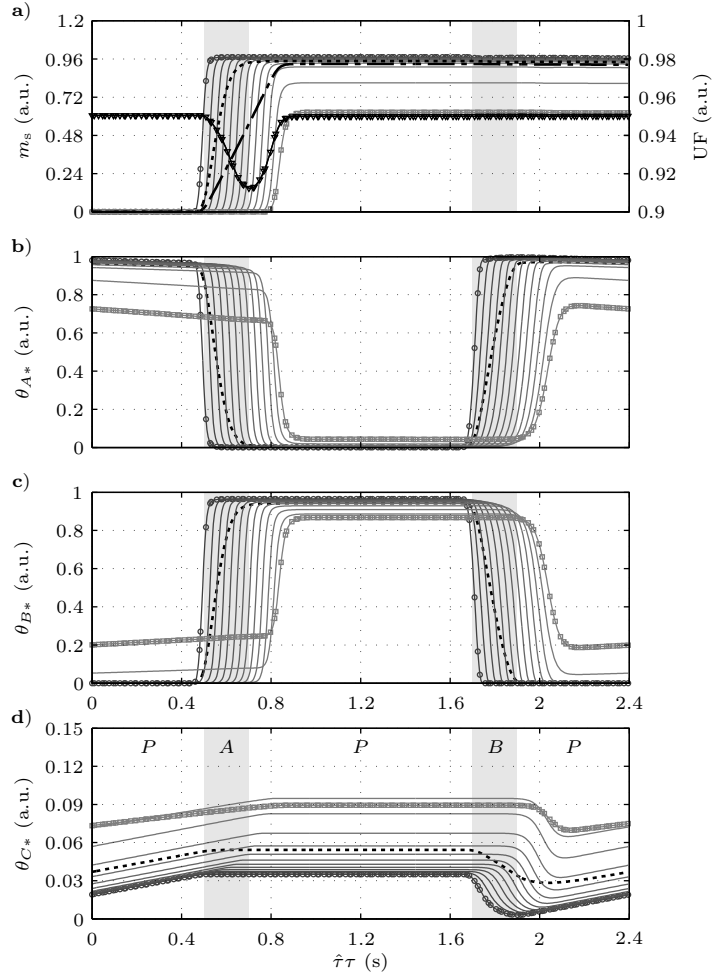


Figure 10: Scaled-up *Reactor B* film-growth dynamics for a single-pulse horizon $\tau \in [\tau_0, \tau_f]$ and $\lambda = 20$ when using *Scale-up strategy II* with $\vartheta = 0.5$. The limit-cycle solution is spatially resolved for $\zeta = (j - 1/2)(\zeta_{\text{end}} - \zeta_0)/N_{\text{FVM}}$ and $j \in \{1, 3, \dots, N_{\text{FVM}}\}$. $(-\circ-)$ indicates the state and algebraic variables for $j = 1$, while $(-\square-)$ indicates the corresponding variables for $j = N_{\text{FVM}}$. $(--)$ indicates the limit-cycle solution from the CSTR model, while (\cdots) indicates the substrate spatially averaged deposition rate and $(-\nabla-)$ its film thickness uniformity. The shaded areas indicate the precursor pulse interval endpoints.

886 7. Concluding Remarks

887 This paper presents a novel model-based methodology for scaling up contin-
888 uous cross-flow ALD reactor systems that use temporally separated precursor

889 pulsing. The overall objective of the scale-up method was to maintain dynamic
890 similarity associated with identical absolute growth rates and to maintain uni-
891 formity close to that of the base-case reactor, while maximizing precursor uti-
892 lization. A one-dimensional, physically-based process model was developed that
893 integrates components that describe the reactor-scale gas-phase dynamics and
894 surface-state dynamics with experimentally validated surface reaction kinetics
895 from previous studies (Holmqvist et al., 2012, 2013a). By this means, dynamic
896 similarity was investigated by constructing all equations that governs the gas-
897 phase and surface-state algebraic variables, together with their boundary and
898 initial conditions, in non-dimensional form. The impact of the geometric scaling
899 factor and the process manipulated variables on the non-dimensional variables
900 was subsequently thoroughly investigated.

901 The scale-up method developed comprises two steps: the carrier gas manip-
902 ulated variables are scaled in parallel to maintain various degrees of dynamic
903 similarity in the scaled-up reactor, and the mass flow of precursors is subse-
904 quently optimized to give maximum yields under the terminal constraints of
905 absolute deposition rate and its relative uniformity. To describe accurately the
906 steady cyclic operation of the ALD reactor, the limit-cycle dynamic solution
907 that arises in this way was discretized using a collocation scheme in time. The
908 optimization problem is fully discretized in the collocation method by approx-
909 imating state algebraic and control variables by Lagrange polynomials, which
910 results in one large NLP. This NLP is solved simultaneously for all state, al-
911 gebraic and control variables that describe the approximated trajectories and
912 this ensures that the limit-cycle criteria, and the terminal design criteria, are
913 fulfilled.

914 In particular, it was demonstrated that the maximum precursor yields were
915 promoted at higher substrate dimensions. Consequently, the trailing edge of
916 the substrate was exposed to a lower precursor dose, and caused in this way
917 strong deposition rate gradients in this region. Moreover, the results showed
918 that higher carrier gas linear velocities gave rise to larger pressure drops across
919 the reactor chamber, and thereby contributed significantly to the formation of a

920 non-uniform deposition profile. In conclusion, it is a combination of the degree
921 of precursor depletion in the flow direction and the magnitude of the pressure
922 drop across the reactor chamber that governs the extent of the deposition profile
923 non-uniformity. In addition, the interaction between dose and purge periods
924 was revealed by analyzing the spatially distributed limit-cycle dynamic solution
925 for the gas-phase precursor partial pressures, and the solution obtained for the
926 resulting accumulated mass gain trajectory. By this means, process regimes
927 were identified in which surface reactions occurred under CVD conditions. True
928 ALD conditions, associated with fully decoupled binary precursor doses, could
929 be retained by lowering the reactor chamber residence time at the expense of
930 lower precursor utilization.

931 The proposed scaling rules are based on nominal algebraic and state vari-
932 ables determined from the CSTR model. The validity of the CSTR model has
933 been assessed by examining the discrepancy between the nominal and the ap-
934 parent reactor chamber residence times, and between precursor exposure doses.
935 Results shown here indicate that these discrepancies are higher for low-volume
936 reactor designs with high aspect ratios, $L/H \gg 1$, and for high carrier gas linear
937 velocities. The CSTR model, however, is valid over a wider range of geometrical
938 scaling factors for reactor designs with lower aspect ratios. The results reported
939 here clearly motivate the utility of models based on PDAEs in combination with
940 dynamic optimization methods for maximizing the precursor utilization in the
941 scaled-up system while maintaining a high value of the growth rate per cycle,
942 which ensures acceptable reactor throughput. The result is a short set of opti-
943 mal scaling guidelines that can be followed to maintain deposition profiles and
944 chemistry identical when adapting a laboratory-scale thin-film process to meter-
945 scale manufacturing equipment. These guidelines allow the knowledge obtained
946 and methods developed when working with centimeter-scale substrates to be
947 directly and easily translated to larger reactors.

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952 **Nomenclature**

953 *Roman letters*

954	A	substrate surface area	m^2
955	A'	cross section area of the reaction chamber	m^2
956	$\mathbf{C}_{\text{eq}}, \mathbf{C}_{\text{ieq}}$	equality and inequality constraint vector	–
957	$\text{Da}_{\alpha,i}$	surface Damköhler number	–
958	$\hat{\mathcal{D}}_{\alpha\beta}, \mathcal{D}_{\alpha\beta}$	binary diffusivity	$\text{m}^2 \text{s}^{-1}, -$
959	\mathbf{F}	system of differential algebraic equations	–
960	\mathbf{g}	response function	–
961	H	reactor height	m
962	k_i	reaction rate constant	$(\text{mol m}^{-2})^{1-n_i} \text{Pa}^{-1} \text{s}^{-1},$ $(\text{mol m}^{-2})^{1-n_i} \text{s}^{-1}$
963			
964	L	reactor chamber length	m
965	M_α	molar mass	kg mol^{-1}
966	\hat{m}_s, m_s	film mass increment	$\text{kg m}^{-2}, -$
967	n_i	surface reaction order	–
968	Pe	Peclet number	–
969	\hat{p}, p	pressure	$\text{Pa}, -$
970	\dot{Q}_α	volumetric flow rate at STP	$\text{Nm}^3 \text{s}^{-1}$
971	R	universal gas constant	$\text{J mol}^{-1} \text{K}^{-1}$
972	Re	Reynolds number	–
973	r_i	surface reaction rate	$\text{mol m}^{-2} \text{s}^{-1}$
974	S_α	source term in the general transport equation	$\text{kg m}^{-3} \text{s}^{-1}$
975	T	temperature	K
976	t	dimensional time	s
977	UF	film thickness uniformity factor	–
978	\mathbf{u}	design variables	–
979	V	reactor chamber volume	m^3
980	\dot{V}_{VP}	volumetric flow rate of the vacuum pump	$\text{m}^3 \text{s}^{-1}$
981	\hat{v}_ζ, v_ζ	linear velocity	$\text{m s}^{-1}, -$
982	\mathbf{w}	algebraic variables	–
983	\mathbf{x}	state variables	–
984	Y_α	precursor yield	cycle^{-1}

985	\mathbf{y}	model output variables	–
986	z	dimensional spatial coordinate	m
987	<i>Greek letters</i>		
988	β	model parameter vector	–
989	γ_α	excess number	–
990	$\Delta t_\alpha, \Delta \tau_\alpha$	pulse duration	s, –
991	$\hat{\delta}_\alpha, \delta_\alpha$	half-cycle average precursor dose	Langmuir
992	ζ	non-dimensional spatial coordinate	–
993	θ_κ	fractional surface coverage of surface species	–
994	Λ	maximum molar concentration of surface sites	mol m^{-2}
995	λ	geometric scaling factor	–
996	$\hat{\mu}, \mu$	dynamic viscosity of the gas mixture	$\text{kg m}^{-1} \text{s}^{-1}$, –
997	ν	numbers of surface OH groups reacting	
998		with each $\text{Zn}(\text{C}_2\text{H}_5)_2$	–
999	ξ_i	surface reaction stoichiometric coefficient	–
1000	$\hat{\rho}, \rho$	density of the gas mixture	kg m^{-3} , –
1001	τ	non-dimensional time	–
1002	Φ_ζ	shear stress	Pa
1003	Φ	cost function	cycle^{-1}
1004	Π_α	characteristic function of τ and $\Delta \tau_\alpha$	–
1005	$\hat{\omega}_\alpha, \omega_\alpha$	mass fraction of gaseous species	–, –
1006	<i>Subscripts and superscripts</i>		
1007	$\hat{}$	nominal state and algebraic variables	
1008	0	initial value	
1009	α, β	gaseous species indices	
1010	i	surface reaction index	
1011	κ	surface species index	
1012	\mathcal{A}	state and algebraic variables in <i>Reactor A</i>	
1013	\mathcal{B}	state and algebraic variables in <i>Reactor B</i>	
1014	STP	state variable at STP	
1015	s	solid	

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