Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Conformality of atomic layer deposition in microchannels: impact of process parameters on the simulated thickness profile

Authors: Jihong Yim,[1]* Emma Verkama,[1]* Jorge A. Velasco,[1] Karsten Arts,[2] and Riikka L. Puurunen[1]**

*These authors contributed equally

** Corresponding author: riikka.puurunen@aalto.fi

[1]Department of Chemical and Metallurgical Engineering, Aalto University, P.O. Box 16100 (Kemistintie 1, Espoo), FI-00076 AALTO, Finland

[2]Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

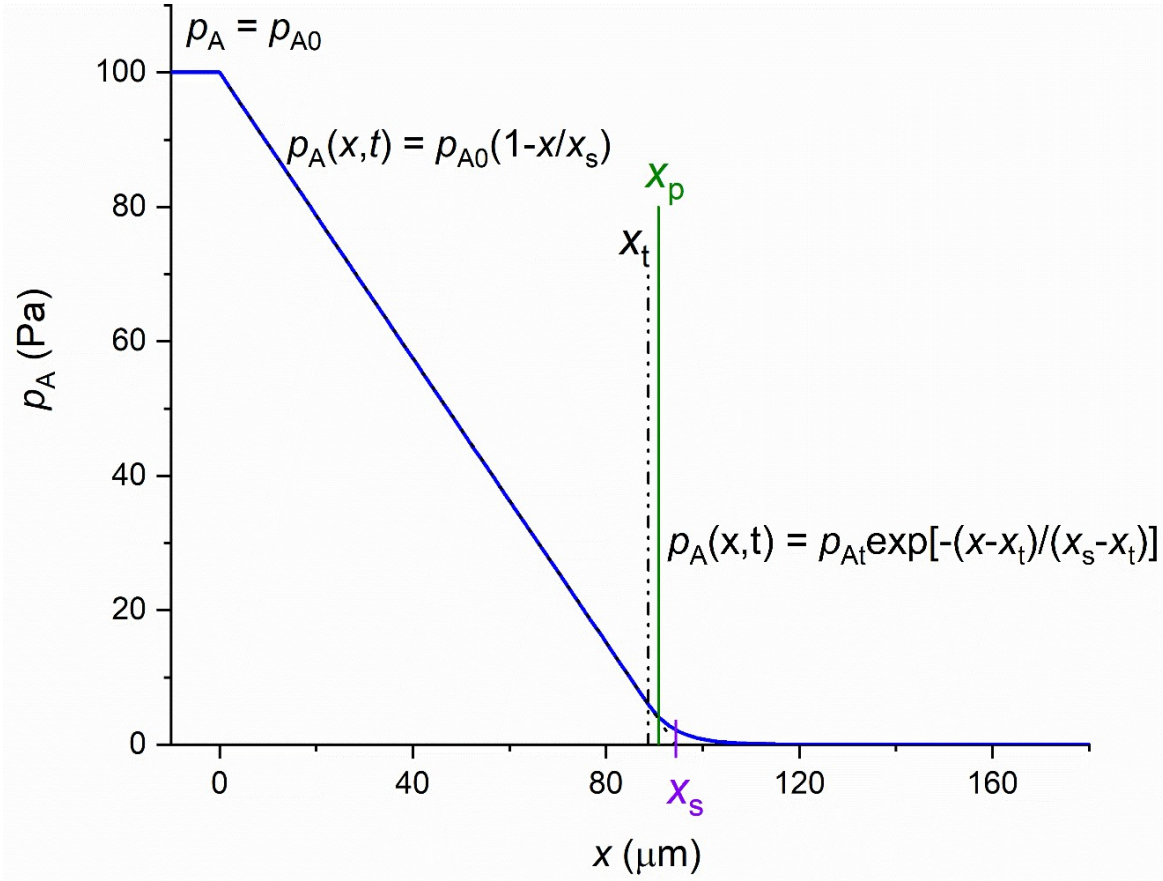

Figure S 1. Distribution of the partial pressure of Reactant A within the distance x. When $x < x_t$, partial pressure of Reactant A decreases linearly (Eq. 8). Linearly extrapolated partial pressure becomes zero at x_s (Eq. 10). When $x > x_t$, different simplification is used to describe the partial pressure (Eq. 9) within the distance. Half-thickness penetration depth is expressed as x_p.

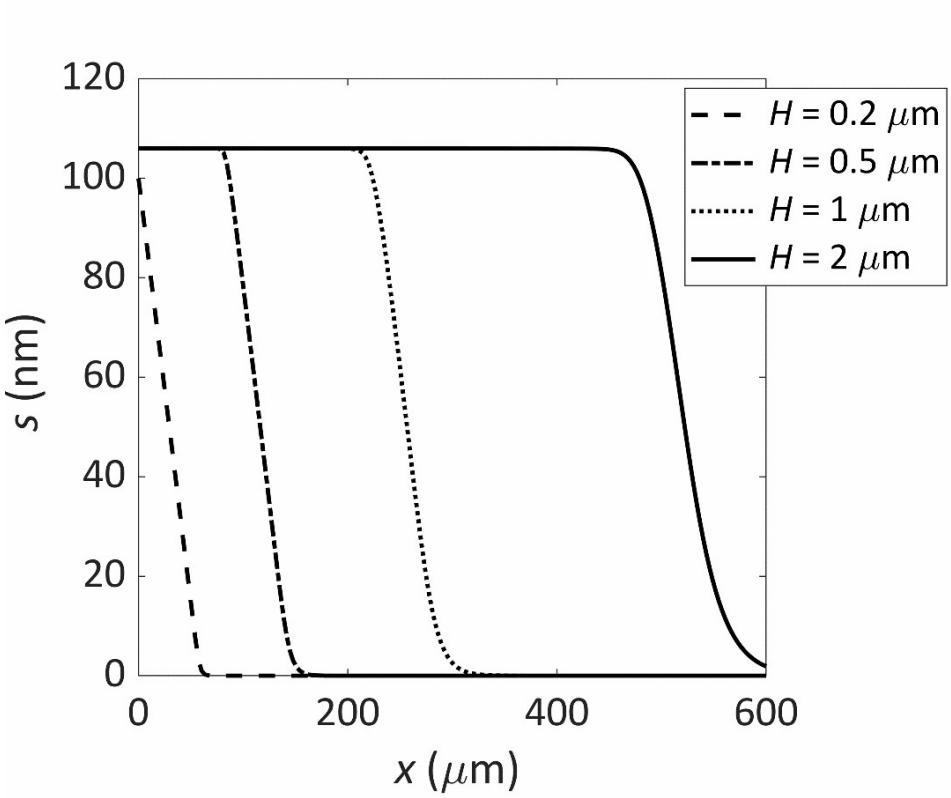

Figure S 2. Effect of channel height H on ALD thickness profile after 1000 cycles was simulated by MATLAB by using the parameter values applied to obtain Fig 4. from Ylilammi et al.[1] Parameter values used: W = 0.1 mm, p_{A0} = 100 Pa, M_A = 0.0749 kg mol^{-1}, d_A = 5.91 × 10^{-10} m, M_I = 0.028 kg mol^{-1}, d_I = 3.74 × 10^{-10} m, p_I = 300 Pa, q = 5 nm^{-2}, T = 500 K, K = 100 Pa^{-1}, c = 0.01, and gpc_{sat} = 1.06 × 10^{-10} m.

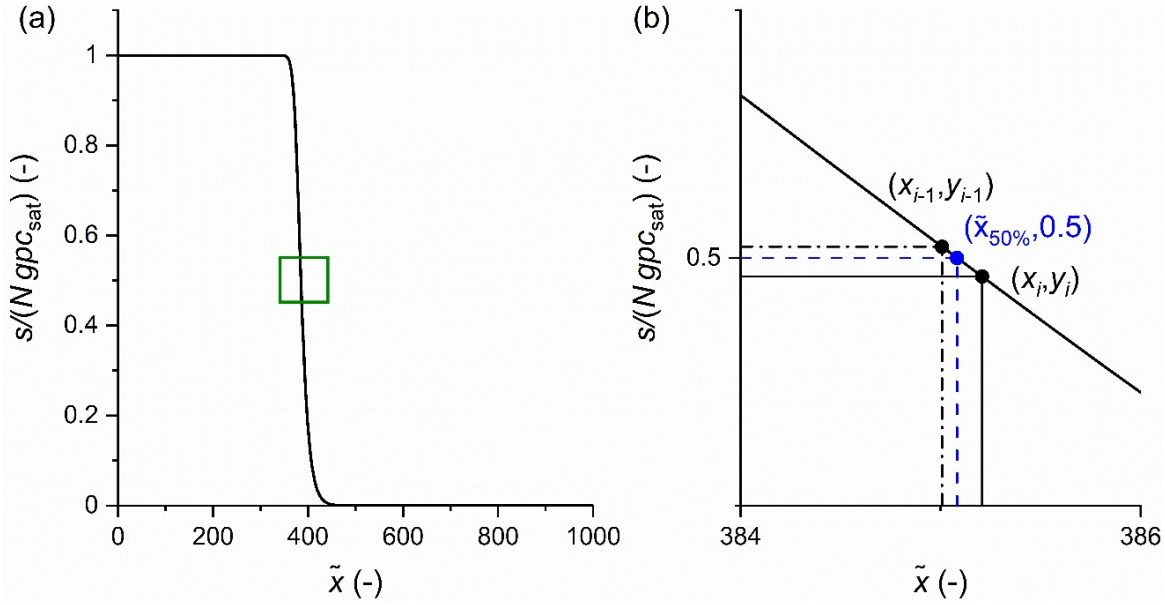

Figure S 3. (a) Example of Type 1 normalized thickness profile. (b) Details of the part of panel (a) marked with a green box. Half-thickness penetration depth $\tilde{x}_{50\%}$ and slope at half-thickness penetration depth are interpolated linearly between points (x_i,y_i), where x_i equal to or smaller than half-thickness penetration depth, and (x_{i-1},y_{i-1}).

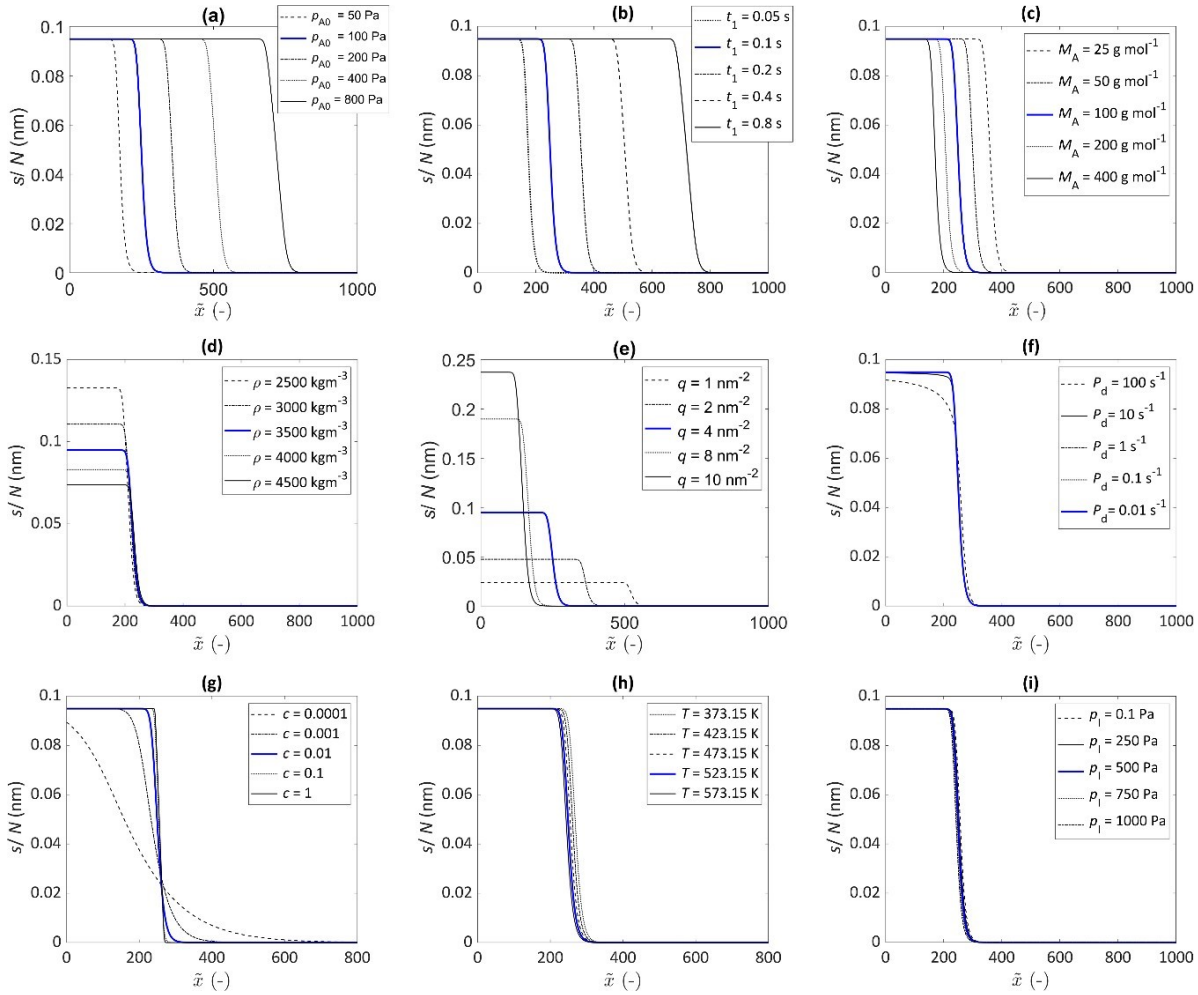

Figure S 4. Illustration of the effect of varying individual parameters on the scaled thickness profile in microchannels, simulated with the Ylilammi et al.[1] model re-implemented in this work. The parameter values used in the simulation are presented in Table 1; the simulation with the baseline values is shown as a solid blue line. The effect of (a) initial partial pressure of the Reactant A p_{A0}, (b) pulse length of Reactant A t_1, (c) molecular mass of Reactant A M_A, (d) film density □, (e) adsorption capacity q, (f) desorption probability P_d, (g) (lumped) sticking coefficient c, (h) ALD process temperature T, and (i) inert gas pressure p_I.

Table S 1. The fraction of channel filled depending on varied original channel height *H* with 250 cycles and varied number of cycles *N* within the original channel height of 500 nm, half-thickness penetration depth $\delta_{50\%}$ (-) and absolute value of the slope at $\delta_{50\%}$ (-) of scaled thickness profile.*

H **(nm)**	***N*** **(-)**	**Fraction of channel filled (-)**	$\delta_{50\%}$ **(-)**	$\left\|\frac{d(\delta/\delta)}{d\delta}\right\|_{\delta_{50\%}}$ $(-)$	***Kn*** **(-)**
100	250	0.4744	206.1	0.0007	38
200	250	0.2372	236.4	0.0015	19
500	250	0.0949	250.1	0.0026	8
1000	250	0.0474	248.8	0.0030	4
2000	250	0.0237	238.7	0.0032	2
2500	250	0.0190	233.5	0.0033	2
4000	250	0.0119	219.1	0.0035	1
500	**5**	0.0019	261.5	0.0029	8
500	**10**	0.0038	261.3	0.0029	8
500	**20**	0.0076	260.8	0.0030	8
500	**50**	0.0190	259.4	0.0029	8
500	**100**	0.0380	257.0	0.0029	8
500	**250**	0.0950	250.1	0.0026	8
500	**500**	0.1898	238.5	0.0018	8

**To satisfy the criteria of a difference between the two discretisation points in the y-axis below 3% out of the whole range, 1500 discretisation points were used for the simulation with the varied original channel height from 100 to 1000 nm and varied number of cycles. 2800 discretisation points were used for the simulation with the original channel height over 1000 nm.*

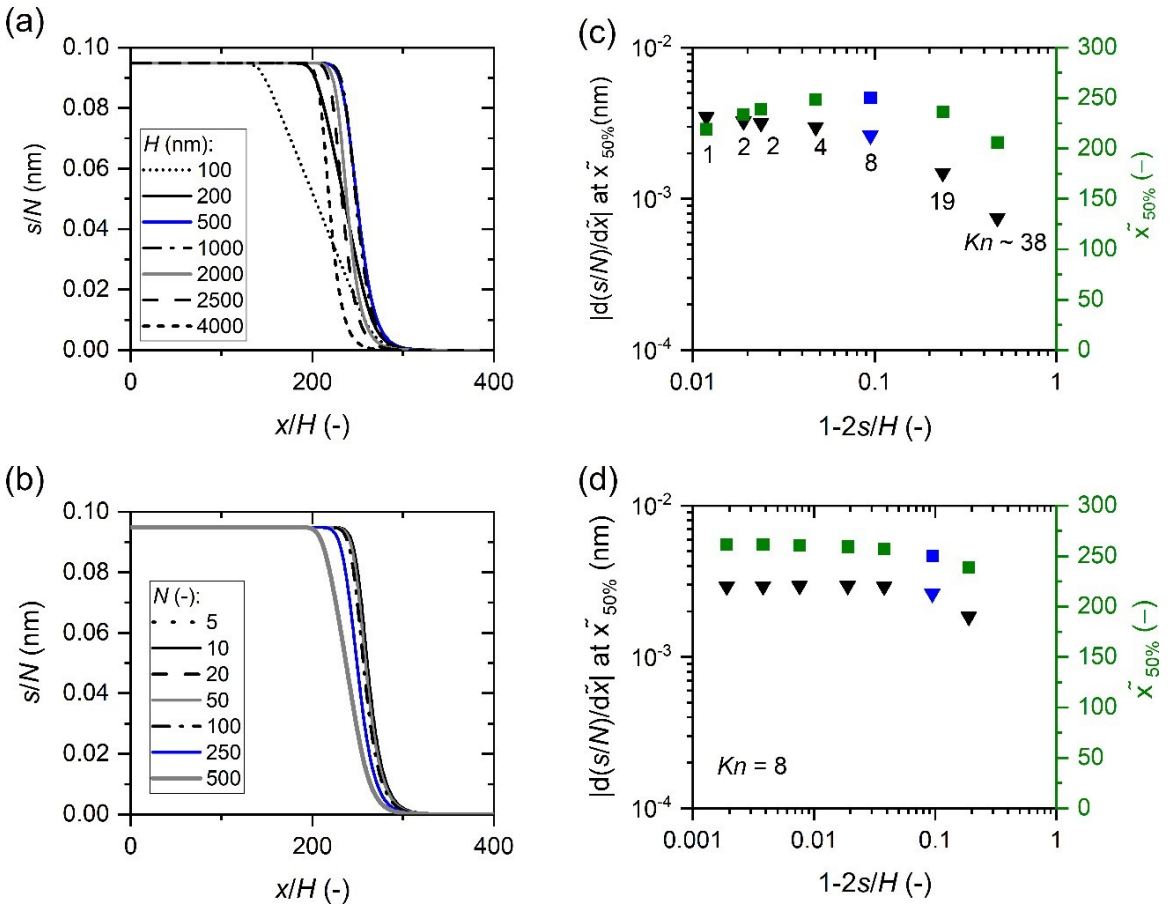

Figure S 5. Scaled thickness profile with (a) varying original channel height H with 250 cycles and (b) varying number of cycles N within the original channel height of 500 nm. (c) Half-thickness penetration depth $\tilde{x}_{50\%}$ (–) and absolute value of the slope at $\tilde{x}_{50\%}$ of the scaled thickness profile in panel (a) against the fraction of channel filled. (d) Half-thickness penetration depth $\tilde{x}_{50\%}$ (–) and absolute value of the slope at $\tilde{x}_{50\%}$ (–) of the scaled thickness profile in panel (b) against the fraction of channel filled. Knudsen number was calculated for each case. Simulation results with baseline condition is marked in blue.

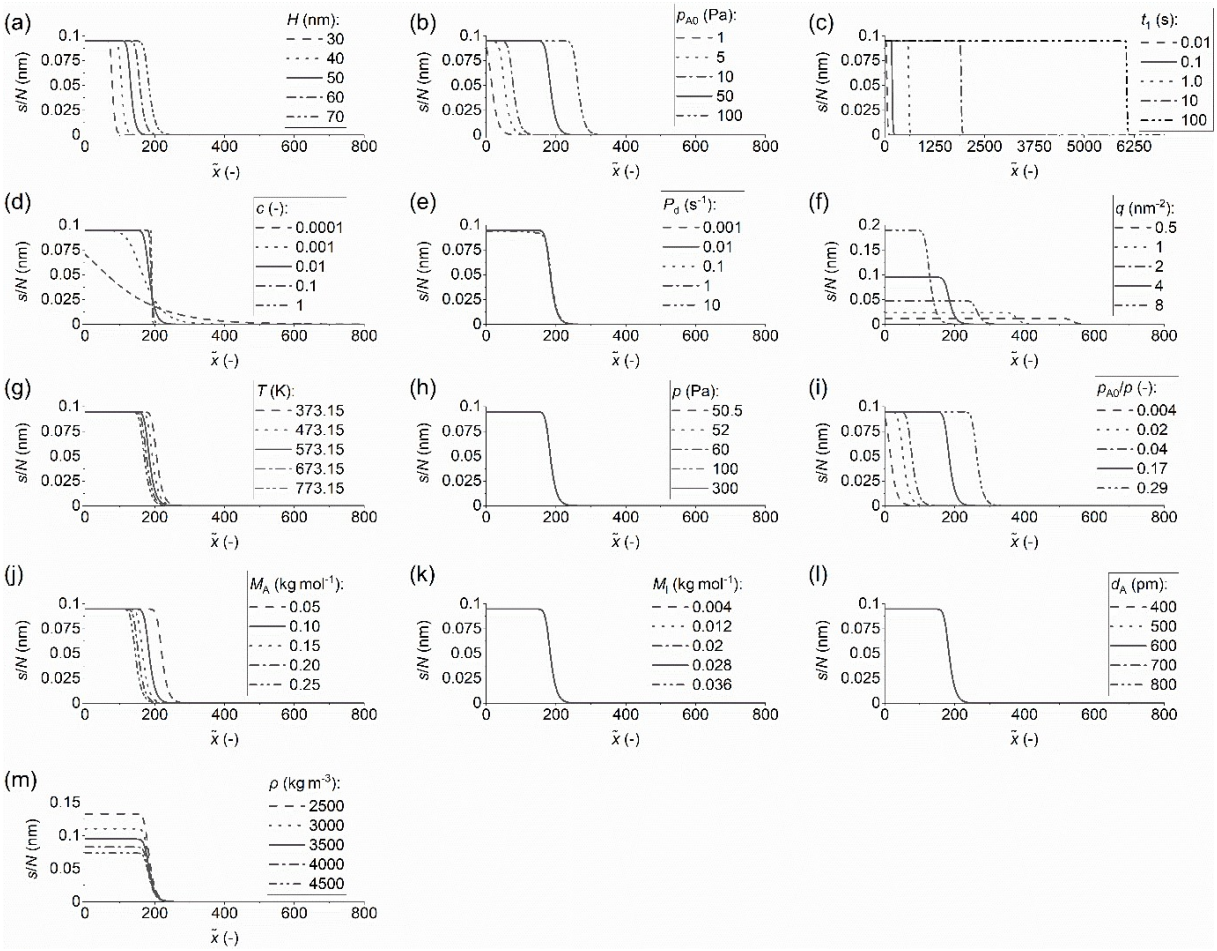

Figure S 6. Scaled thickness profiles simulated in free molecular flow regime (*Kn* >> 1) by implementing Ylilammi et al.[1] model with varying (a) original channel height, (b) initial partial pressure of Reactant A, (c) pulse length, (d) (lumped) sticking coefficient, (e) desorption probability,
(f) adsorption density, (g) temperature, (h) total pressure, (i) ratio between initial partial pressure of Reactant A to total pressure, (j) molar mass of Reactant A, (K) molar mass of inert gas, (l) diameter of Reactant A, and (m) film density. Parameter values used, if otherwise stated: $H = 5 \times 10^{-2}$ µm, $N = 1$, $t_1 = 0.1$ s, $p_{A0} = 50$ Pa, $M_A = 0.1$ kg mol^{-1}, $d_A = 6.0 \times 10^{-10}$ m, $M_I = 0.028$ kg mol^{-1}, $d_I = 4.0 \times 10^{-10}$ m, $p_I = 250$ Pa, $q = 4$ nm^{-2}, □ = 3500 kg m^{-3}, $M = 0.050$ kg mol^{-1}, $P_d = 0.01$ s^{-1}, and $c = 0.01$.

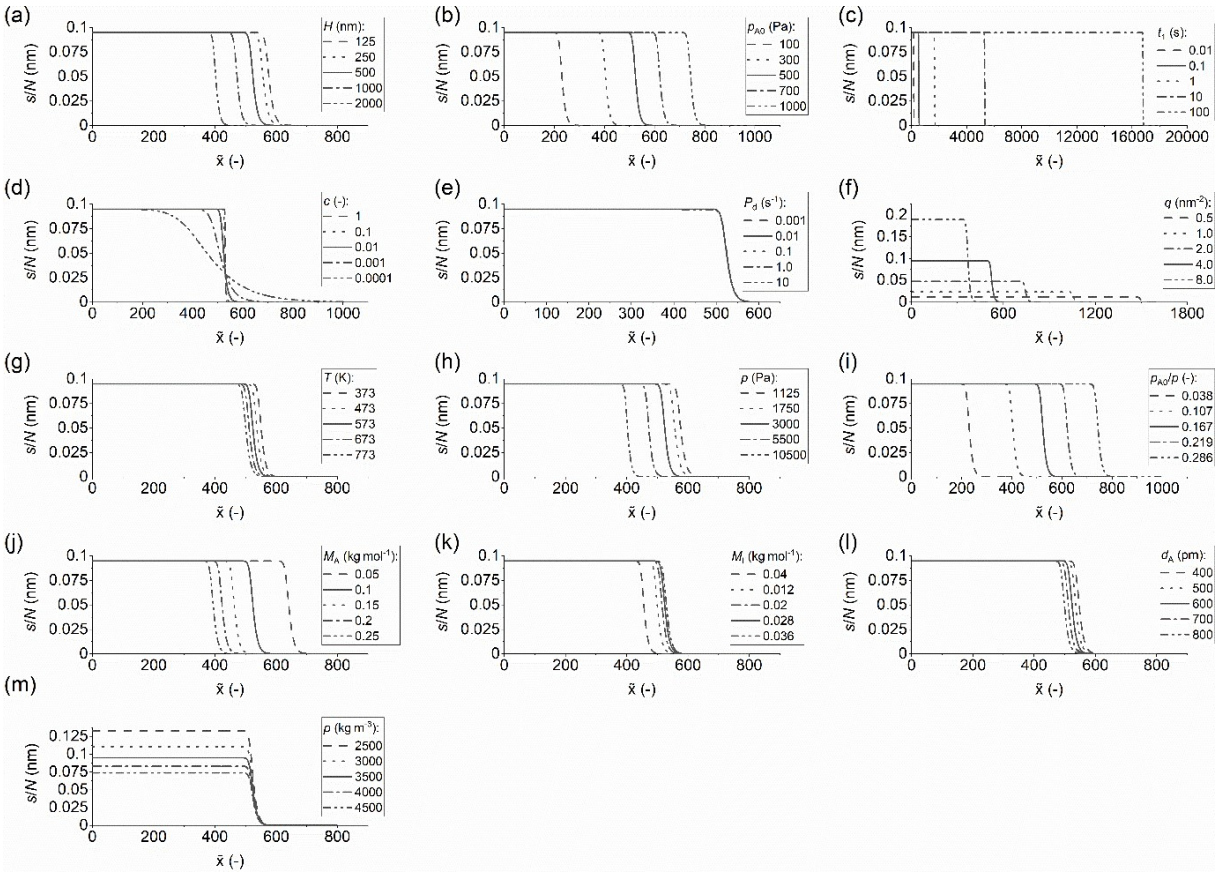

Figure S 7. Scaled thickness profiles simulated in transition flow regime ($Kn \approx 1$) by implementing Ylilammi et al.[1] model with varying (a) original channel height, (b) initial partial pressure of Reactant A, (c) pulse length, (d) (lumped) sticking coefficient, (e) desorption probability, (f) adsorption density,
(g) temperature, (h) total pressure, (i) ratio between initial partial pressure of Reactant A to total pressure, (j) molar mass of Reactant A, (K) molar mass of inert gas, (l) diameter of Reactant A, and
(m) film density. Parameter values used, if otherwise stated: H = 0.5 µm, N = 1, t_1 = 0.1 s, p_{A0} = 500 Pa, M_A = 0.1 kg mol^{-1}, d_A = 6.0 × 10^{-10} m, M_I = 0.028 kg mol^{-1}, d_I = 4.0 × 10^{-10} m, p_I = 2500 Pa, q = 4 nm^{-2}, □ = 3500 kg m^{-3}, M = 0.050 kg mol^{-1}, P_d = 0.01 s^{-1}, and c = 0.01.

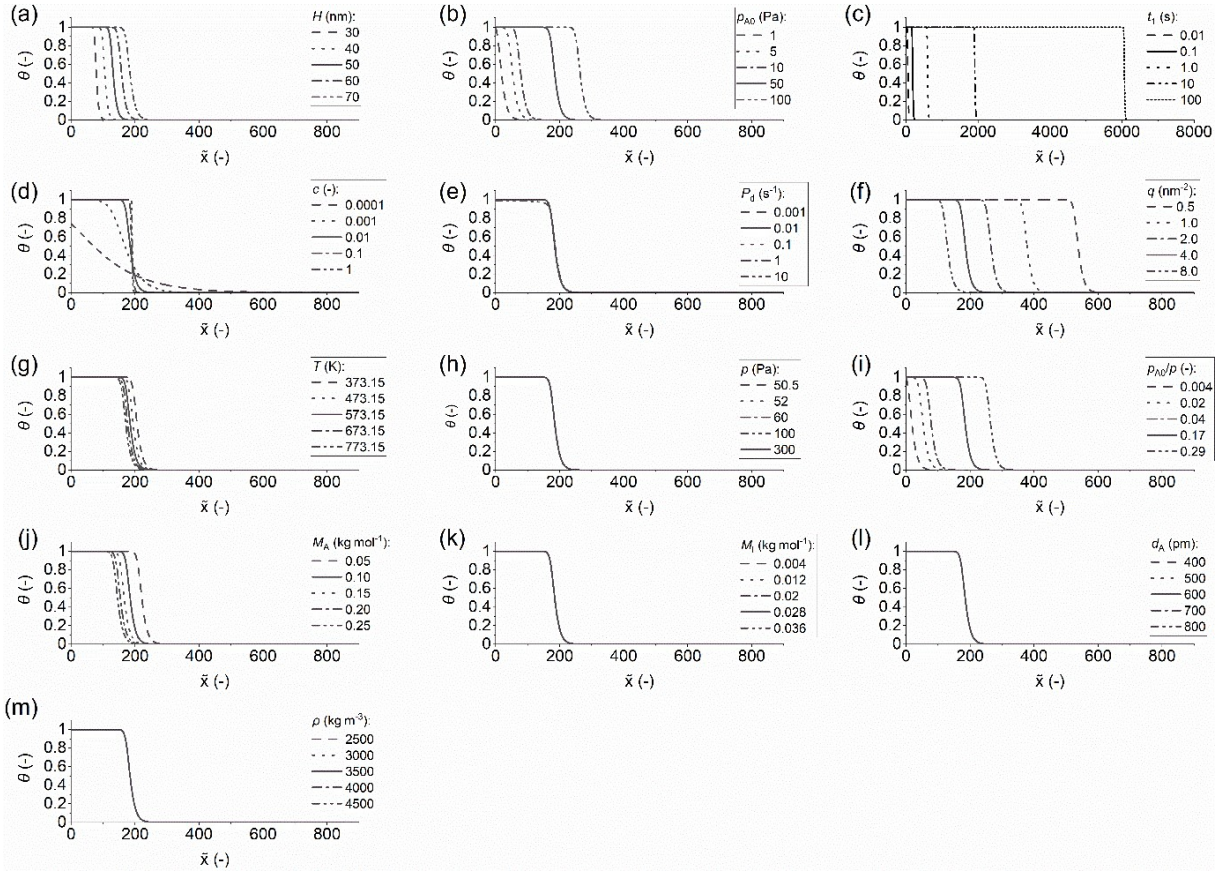

Figure S 8. Type 1 normalized thickness profiles simulated in free molecular flow regime (*Kn* >> 1) by implementing Ylilammi et al.[1] model with varying (a) original channel height, (b) initial partial pressure of Reactant A, (c) pulse length, (d) (lumped) sticking coefficient, (e) desorption probability,
(f) adsorption density, (g) temperature, (h) total pressure, (i) ratio between initial partial pressure of Reactant A to total pressure, (j) molar mass of Reactant A, (K) molar mass of inert gas, (l) diameter of Reactant A, and (m) film density. Parameter values used, if otherwise stated: $H = 5 \times 10^{-6}$ µm, $N = 1$, $t_1 = 0.1$ s, $p_{A0} = 50$ Pa, $M_A = 0.1$ kg mol^{-1}, $d_A = 6.0 \times 10^{-10}$ m, $M_I = 0.028$ kg mol^{-1}, $d_I = 4.0 \times 10^{-10}$ m, $p_I = 250$ Pa, $q = 4$ nm^{-2}, □ = 3500 kg m^{-3}, $M = 0.050$ kg mol^{-1}, $P_d = 0.01$ s^{-1}, and $c = 0.01$.

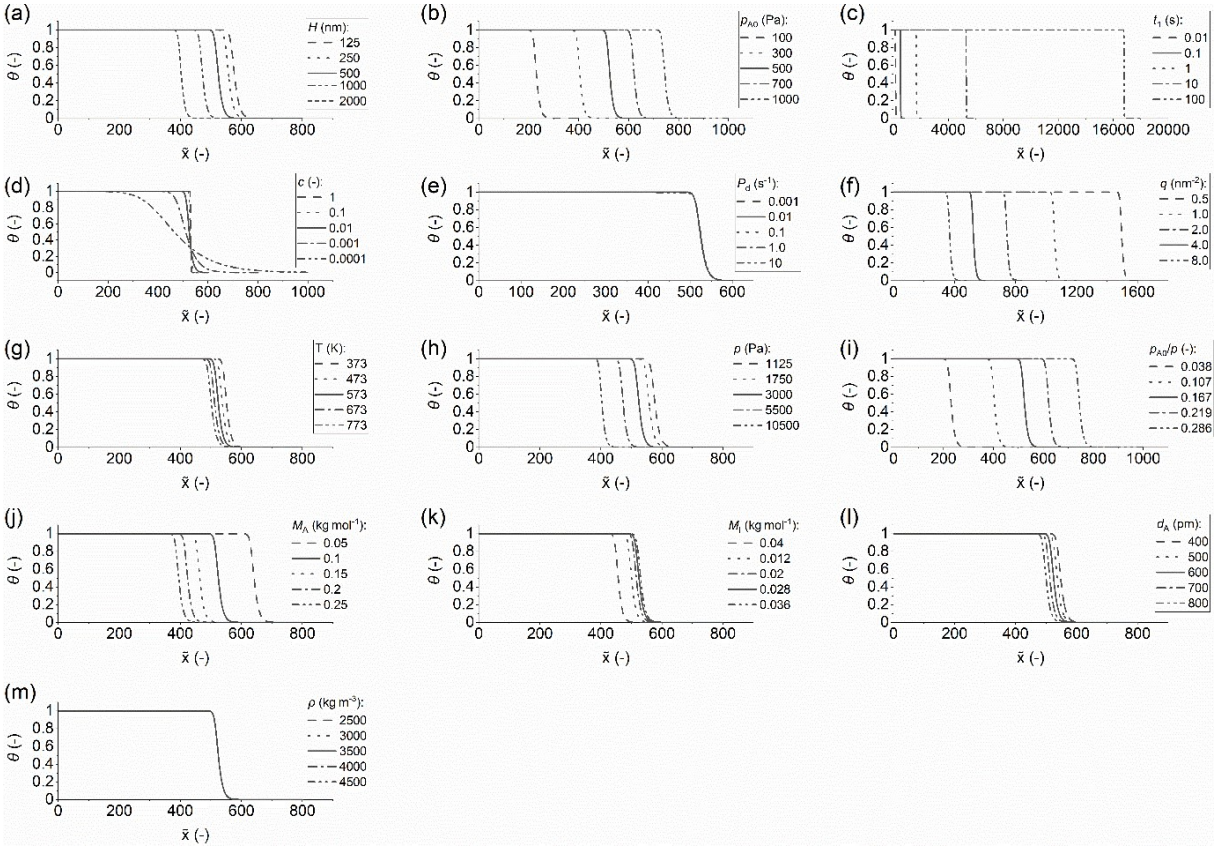

Figure S 9. Type 1 normalized thickness profiles simulated in transition flow regime (Kn ≈ 1) by implementing Ylilammi et al.[1] model with varying (a) original channel height, (b) initial partial pressure of Reactant A, (c) pulse length, (d) (lumped) sticking coefficient, (e) desorption probability,
(f) adsorption density, (g) temperature, (h) total pressure, (i) ratio between initial partial pressure of Reactant A to total pressure, (j) molar mass of Reactant A, (K) molar mass of inert gas, (l) diameter of Reactant A, and (m) film density. Parameter values used, if otherwise stated: H = 0.5 µm, N = 1, t_1 = 0.1 s, p_{A0} = 500 Pa, M_A = 0.1 kg mol^{-1}, d_A = 6.0 × 10^{-10} m, M_I = 0.028 kg mol^{-1}, d_I = 4.0 × 10^{-10} m, p_I = 2500 Pa, q = 4 nm^{-2}, □ = 3500 kg m^{-3}, M = 0.050 kg mol^{-1}, P_d = 0.01 s^{-1}, and c = 0.01.

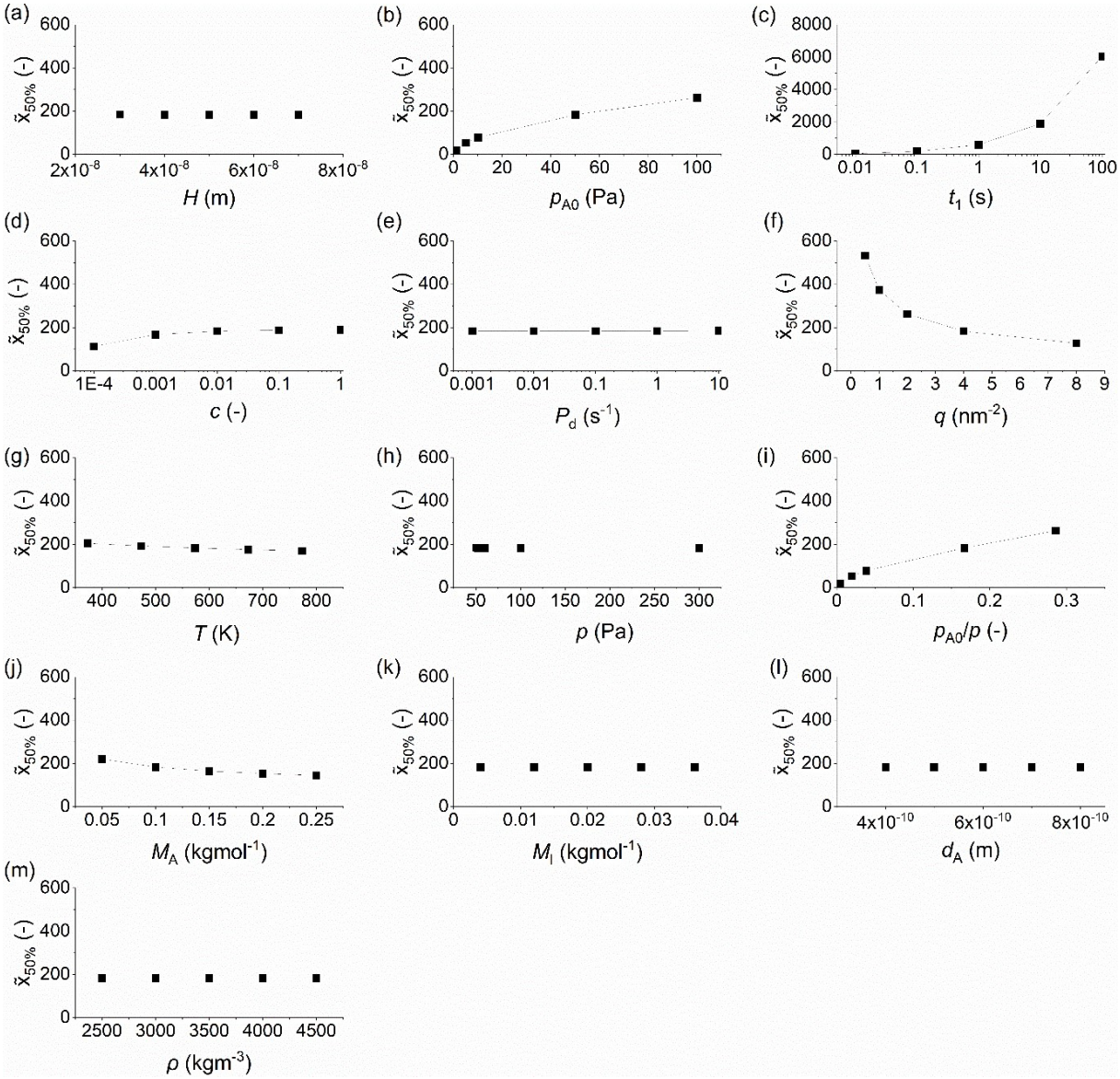

Figure S 10. Half-thickness penetration depth of scaled thickness profile simulated in free molecular flow regime (*Kn* >> 1) against varied parameters: (a) original channel height, (b) initial partial pressure of Reactant A, (c) pulse length, (d) (lumped) sticking coefficient, (e) desorption probability,
(f) adsorption density, (g) temperature, (h) total pressure, (i) ratio between initial partial pressure of Reactant A to total pressure, (j) molar mass of Reactant A, (K) molar mass of inert gas, (l) diameter of Reactant A, and (m) film density. The scaled thickness profiles, on which this data is based, are in Figure S 6.

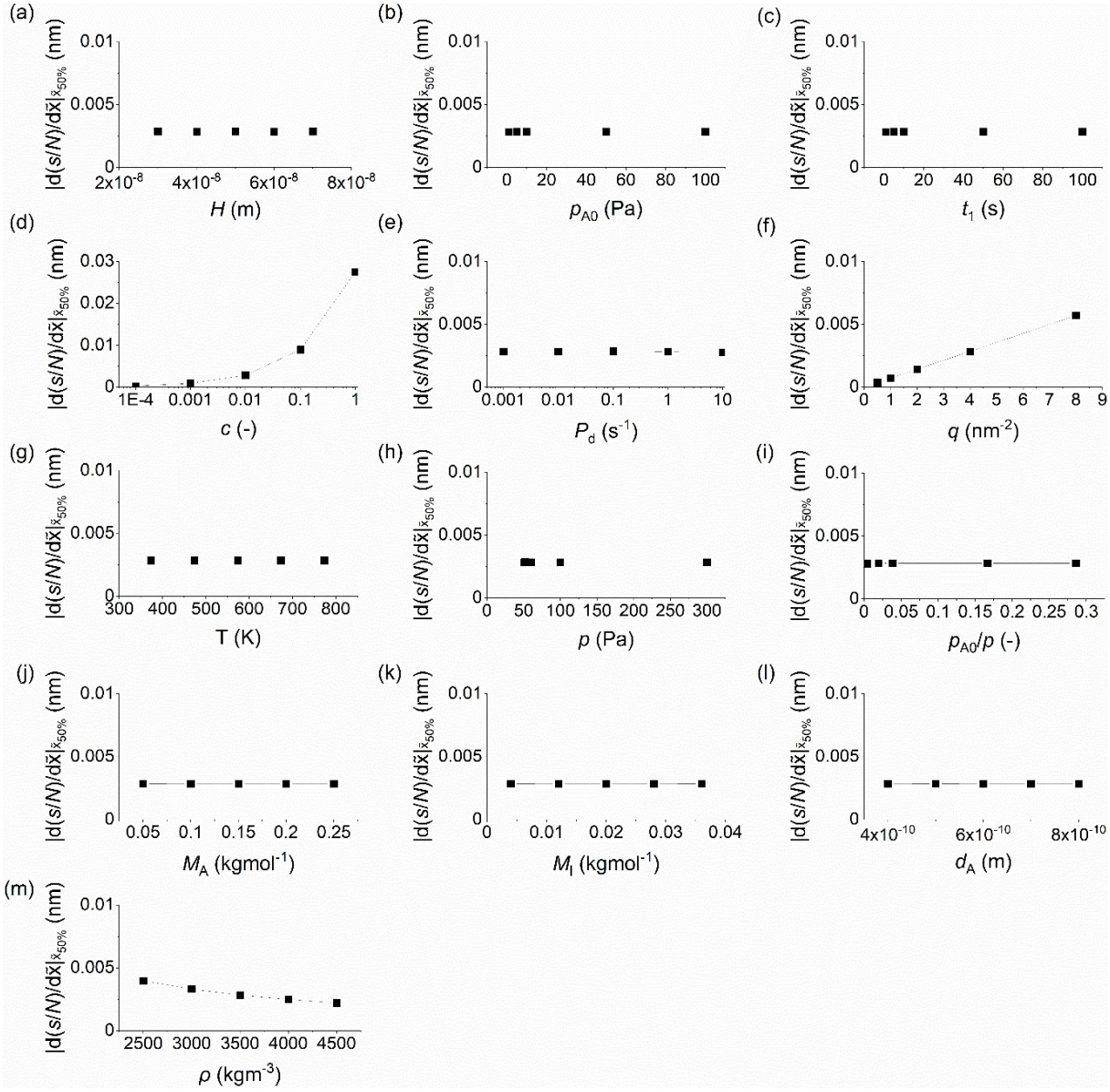

Figure S 11. Absolute value of the slope at half-thickness penetration depth of scaled thickness profile simulated in free molecular flow regime (*Kn* >> 1) against varied parameters: (a) original channel height, (b) initial partial pressure of Reactant A, (c) pulse length, (d) (lumped) sticking coefficient, (e) desorption probability, (f) adsorption density, (g) temperature, (h) total pressure, (i) ratio between initial partial pressure of Reactant A to total pressure, (j) molar mass of Reactant A,
(K) molar mass of inert gas, (l) diameter of Reactant A, and (m) film density. The scaled thickness profiles, on which this data is based, are in Figure S 6.

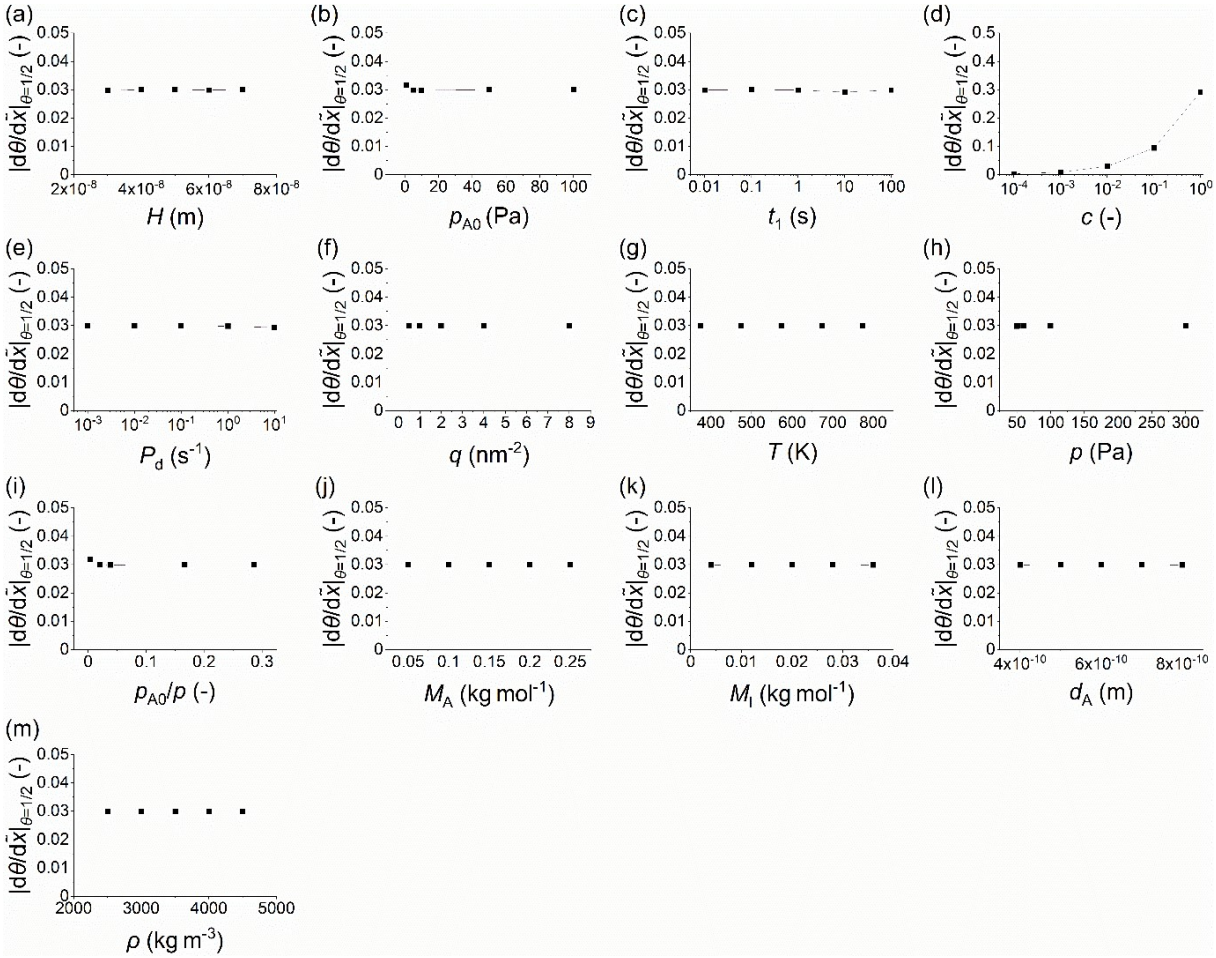

Figure S 12. Absolute value of the slope at half-thickness penetration depth of Type 1 normalized thickness profile simulated in free molecular flow regime (*Kn* >> 1) against varied parameters: (a) original channel height, (b) initial partial pressure of Reactant A, (c) pulse length, (d) (lumped) sticking coefficient, (e) desorption probability, (f) adsorption density, (g) temperature, (h) total pressure, (i) ratio between initial partial pressure of Reactant A to total pressure, (j) molar mass of Reactant A, (K) molar mass of inert gas, (l) diameter of Reactant A, and (m) film density. The Type1 normalized thickness profiles, on which this data is based, are in Figure S 8.

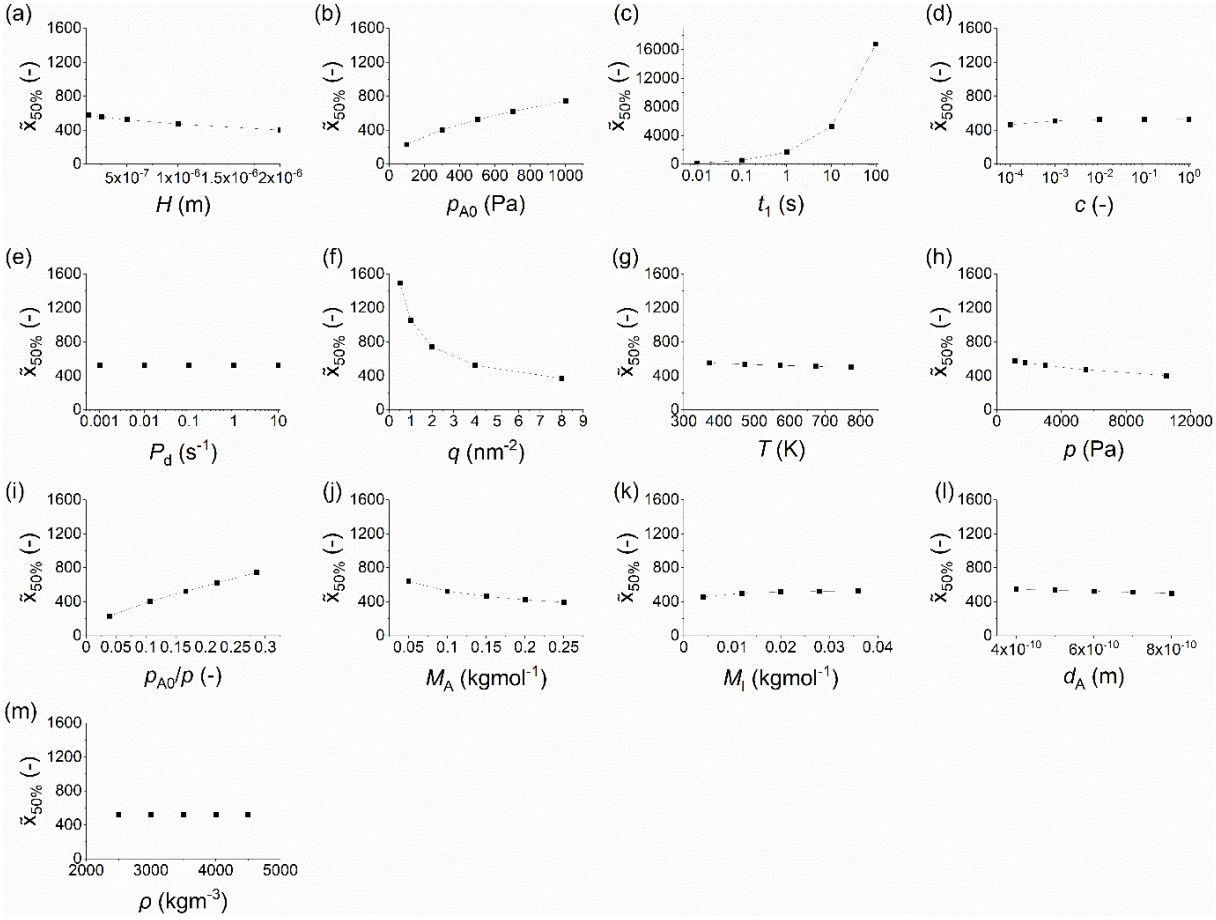

Figure S 13. Half-thickness penetration depth of scaled thickness profile simulated in transition flow regime ($Kn \approx 1$) against varied parameters: (a) original channel height, (b) initial partial pressure of Reactant A, (c) pulse length, (d) (lumped) sticking coefficient, (e) desorption probability, (f) adsorption density, (g) temperature, (h) total pressure, (i) ratio between initial partial pressure of Reactant A to total pressure, (j) molar mass of Reactant A, (K) molar mass of inert gas, (l) diameter of Reactant A, and (m) film density. The scaled thickness profiles, on which this data is based, are in Figure S 7.

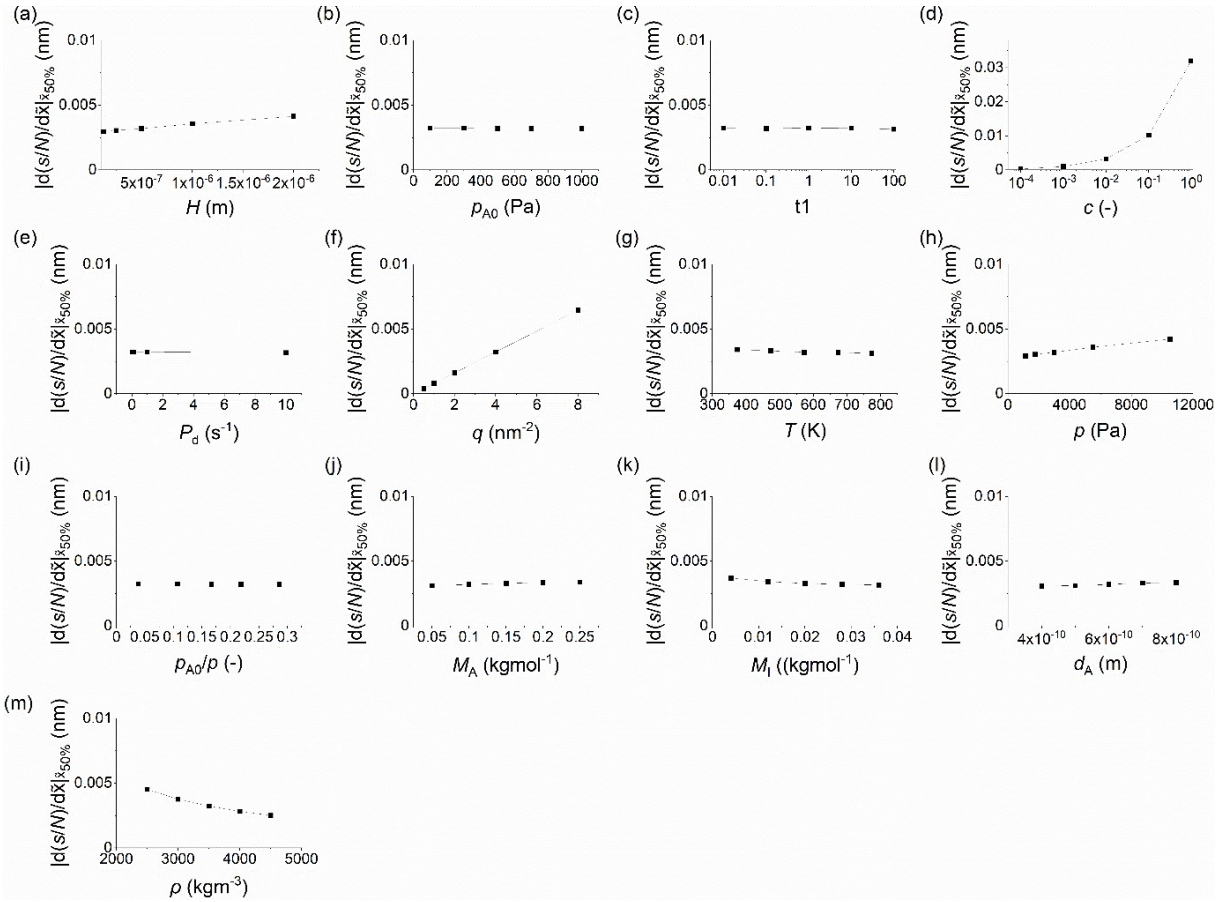

Figure S 14. Absolute value of the slope at half-thickness penetration depth of scaled thickness profile simulated in transition flow regime ($Kn \approx 1$) against varied parameters: (a) original channel height, (b) initial partial pressure of Reactant A, (c) pulse length, (d) (lumped) sticking coefficient, (e) desorption probability, (f) adsorption density, (g) temperature, (h) total pressure, (i) ratio between initial partial pressure of Reactant A to total pressure, (j) molar mass of Reactant A, (K) molar mass of inert gas, (l) diameter of Reactant A, and (m) film density. The scaled thickness profiles, on which this data is based, are in Figure S 7.

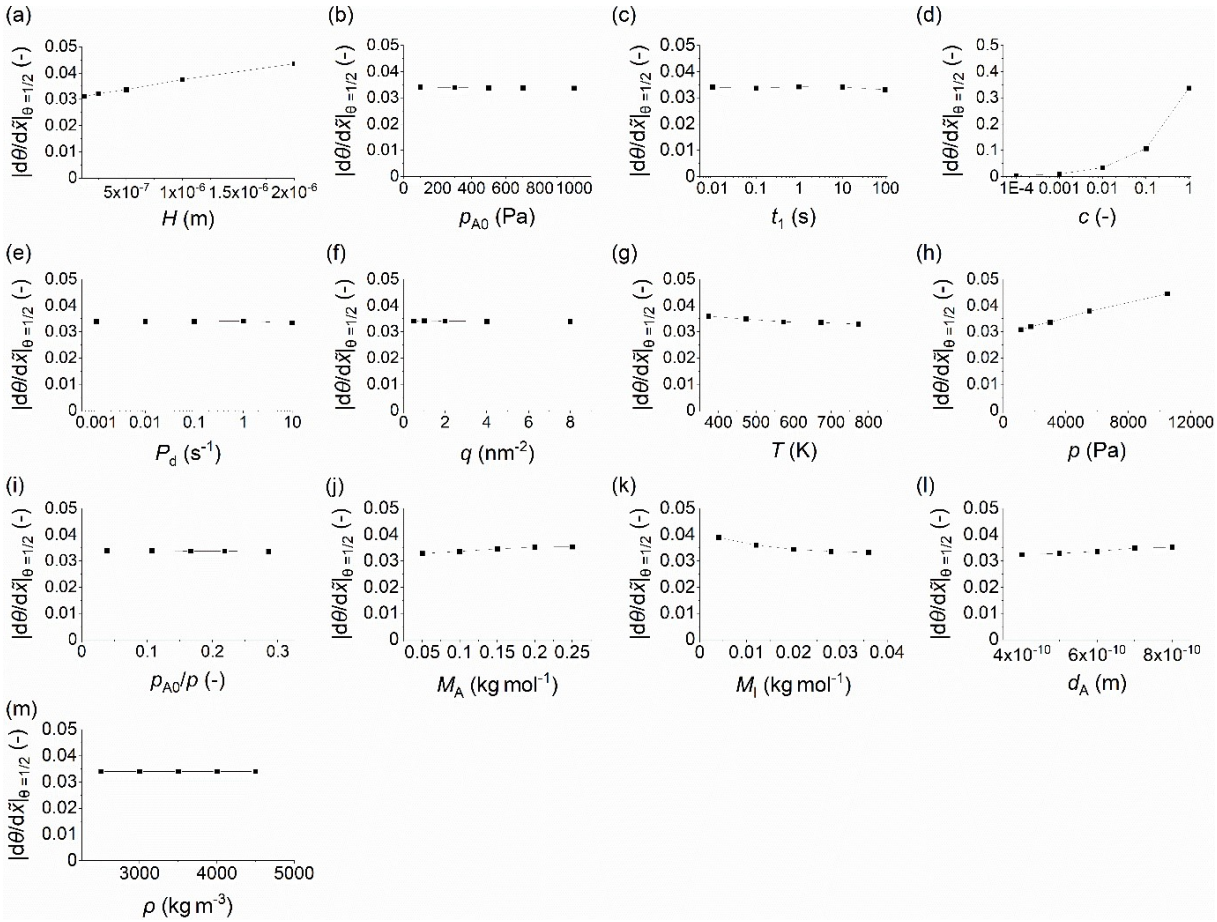

Figure S 15. Absolute value of the slope at half-thickness penetration depth of Type 1 normalized thickness profile simulated in transition flow regime ($Kn \approx 1$) against varied parameters: (a) original channel height, (b) initial partial pressure of Reactant A, (c) pulse length, (d) (lumped) sticking coefficient, (e) desorption probability, (f) adsorption density, (g) temperature, (h) total pressure, (i) ratio between initial partial pressure of Reactant A to total pressure, (j) molar mass of Reactant A,
(K) molar mass of inert gas, (l) diameter of Reactant A, and (m) film density. The Type 1 normalized thickness profiles, on which this data is based, are in Figure S 9.

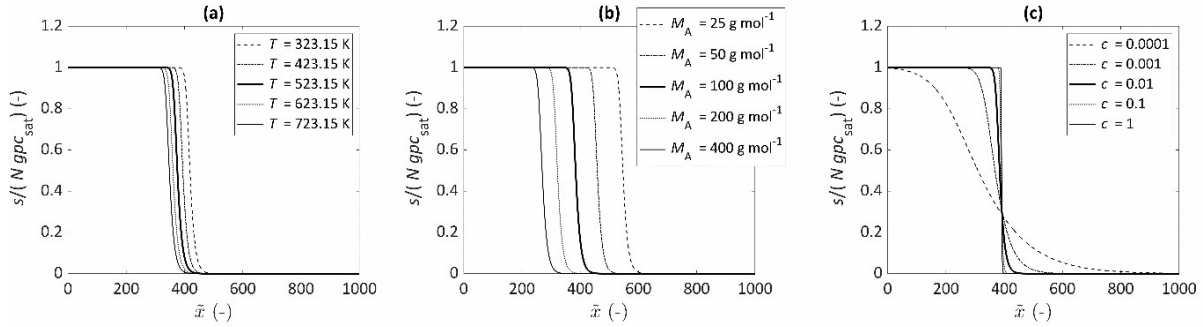

Figure S 16. Type 1 normalized thickness profiles simulated in a wide microchannel in free molecular flow with varying (a) different process temperature, (b) molar mass of reactant A, and (c) sticking coefficient. Sticking coefficient values back-extracted from these thickness profiles by the slope method[2] are listed in Table 3. Parameters used if not otherwise stated: H = 0.2 µm, N =1, W = 10 mm, T = 523.15 K, t_1 = 2 s, p_{A0} = 10 Pa, M_A = 0.1 kg mol^{-1}, d_A = 600 pm, M_I = 0.028 kg mol^{-1}, d_I = 374
pm, p_I = 50 Pa, q = 4 nm^{-2}, □ = 3500 kg m^{-3}, M = 0.050 kg mol^{-1}, P_d = 10^{-5} s^{-1}, and c = 0.01.

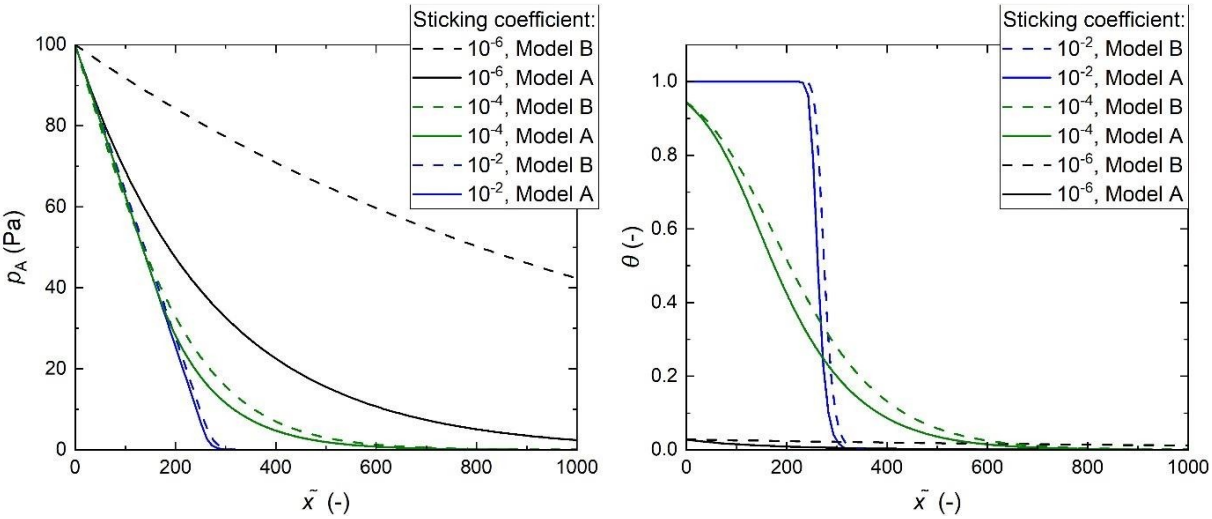

Figure S 17. Evolution of (left) partial pressure of Reactant A and (right) surface coverage in HAR was simulated by Ylilammi et al.[1] model (Model A) and by Yanguas-Gil and Elam[3] model (Model B).
Simulations were made with varied sticking coefficients and other parameters as the baseline conditions defined in Table 1 of the main manuscript. In the diffusion-limited regime (sticking coefficients 10^{-2} and 10^{-4}), the two models gave rather similar results, while in the reaction-limited case (sticking coefficient 10^{-6}) the results differed significantly. The reason behind the differences is in the specific treatment of the partial pressure p_A in Model A, which is poorly applicable for simulations in the reaction-limited regime. According to a reference,[3] the process is in reaction- limited regime when Thiele modulus $h_T << 1$. In this work, the case with the sticking coefficient of 10^{-6} was clearly in the reaction-limited regime although Thiele modulus value was not far from 1 (ca.
0.9).

References

1 M. Ylilammi, O. M. E. Ylivaara and R. L. Puurunen, Modeling growth kinetics of thin films made by atomic layer deposition in lateral high-aspect-ratio structures, *Journal of Applied Physics*, 2018, **123**, 205301.

2 K. Arts, V. Vandalon, R. L. Puurunen, M. Utriainen, F. Gao, W. M. M. Kessels and H. C. M. Knoops, Sticking probabilities of H2O and Al(CH3)3 during atomic layer deposition of Al2O3 extracted from their impact on film conformality, *Journal of Vacuum Science & Technology A*, 2019, **37**, 030908.

3 A. Yanguas-Gil and J. W. Elam, Self-limited reaction-diffusion in nanostructured substrates: Surface coverage dynamics and analytic approximations to ALD saturation times, *Chemical Vapor Deposition*, 2012, **18**, 46–52.