Title: Modeling silane deposition in nanoporous carbon for high-capacity Si/C composite anode.

Abstract:

This study aims to optimize the operating conditions in a silane tube reactor to achieve uniform deposition on carbon particles. Various parameters such as temperature, pressure, tube length, flow rate, and pore size were investigated to determine their effects on deposition uniformity and filling portion along the tube. Mathematical models were developed to describe the dynamics in the tube and within the particles, considering diffusion, consumption, and advection as driving forces. The governing equations were solved using numerical methods. Our simulation results demonstrated that lower temperature, lower pressure, smaller pore size, and smaller carbon amount led to more uniform deposition inside the carbon particles. Additionally, higher flow rate and shorter tube length were identified as critical factors for achieving uniformity. This work provides valuable insights for optimizing the operating conditions in silane tube reactors and can contribute to the advancement of deposition processes.

1. Introduction

- Explanation of the objective and significance of the research
- Overview of the parameters investigated and their impact on deposition uniformity

2. Mathematical Model

As shown in Fig. 1, the as-developed models take three key transport process into accounts: 1) transport of silane (c) in a tube furnace, including both gas flow and diffusion, 2) diffusion of silane inside micron-sized nanoporous carbon particles, and 3) decomposition of silane to form solid silicon inside nanoporous carbon particles.

In the tube furnace, the governing transport equations are

$$J = -D(T,P)\frac{\partial c}{\partial x} + cv$$

$$\frac{\partial c}{\partial t} = -\nabla \cdot J - \rho(x,t)$$

Where J is the silane flux, D is the diffusion coefficient, v is the velocity of silane, ρ is the consumption rate of silane. The velocity is controlled by the gas flow. The temperature (T) and pressure (P)-dependent D is taken into account, which is expressed as $D = 0.2 \times \frac{\left(\frac{T}{298.15}\right)^{\frac{3}{2}}}{\frac{P}{P_0}} \times 10^{-4}$

where P_0 is one standard atmosphere. The boundary condition is $c(0,t) = c_0$, $\left.\frac{\partial c}{\partial x}\right|_{x=L} = 0$ and initial condition is $c(x,0) = c_0$ where L is the deposition zone length and c_0 can be adjusted based on experiments.

Inside a microparticle, as the pore size is nanoscale, there is no convection and the only process is diffusion in pores. So, the governing equation is

$$\frac{\partial c}{\partial t}(x,r,t) = \nabla \cdot \left(D_i(x,r,t)\nabla c(x,r,t)\right) - k_i S(x,r,t)c(x,r,t)$$

Boundary conditions are $\left.\dfrac{\partial c}{\partial r}\right|_{r=0} = 0$, $c(x, r_0, t) = c(x, t)$ and initial condition is $c(x, r, 0) = c_0$

where D_i is the diffusion coefficient inside the particle, k_i is the consumption rate of silane, S is the surface area per volume of porous carbon and r_0 is the radius of the particle. At target deposition temperature and pressure, the mean free path (λ_0) of silane gas is ~ 10-100 nm. Since the pore size is much smaller than the mean free path, so Knudsen diffusion theory is applied to correct the diffusivity. Moreover, as silane diffuses in a porous matrix, we applied the buggerman theory to take porosity and tortuosity into account, which yields

$$D_i(x, r, t) = \varepsilon^{\frac{3}{2}} \frac{D}{\lambda_0} w \left(\frac{w}{w_0}\right)^4$$

Where ε is the porosity of carbon particle, w is the pore diameter of carbon particle and the governing equation is

$$w = w_0 - 2H$$

Where H is the thickness of deposited silicon and w_0 is the initial pore diameter.

The transport in the tube furnace and inside particles are coupled through the silane concentration at the surface of nanoporous particles and the silane deposition rates. For concentration coupling,

$$c(x, r_0, t) = c(x, t)$$

Which is the boundary condition for the dynamic system inside the microparticle.

For coupling of silane reaction rate, the reaction rate in the tube furnace (ρ) equals to Si deposition in particles in all local particles, which is

$$\rho_i(x, t) = p \int k_i S(x, r, t) c(x, r, t) dV / V_{par}$$

$$\rho_o(x, t) = 3 p k_o c(x, r_0, t) / r_0$$

respectively

Where p is the volume fraction of carbon particles to the reaction volume, k_i and k_o is the deposition rate inside and on the surface of the particle respectively, V_{par} is the volume of a particle.

In total, the consumption rate is

$$\rho(x, t) = \rho_i(x, t) + \rho_o(x, t)$$
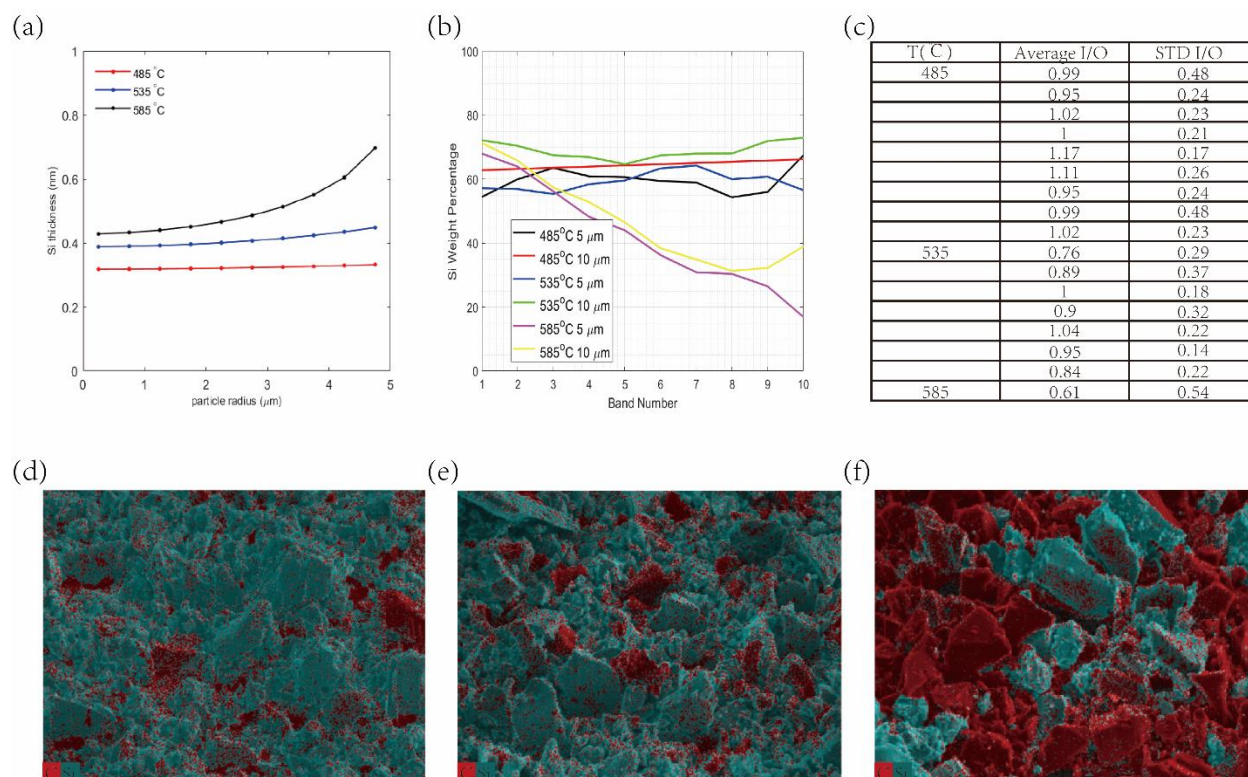
3. Simulation Results

To validate that the model can describe experimental results semi-quantitatively, we first use temperature-dependent radial uniformity inside a nanoporous particle, and tubing position-dependent Si deposition percentage as validation of intraparticle and interparticle processes. We simulated the experiment situation where the mixing gas with 2% silane is pumped into the tube with uniform distributed carbon particles of 0.2 g along the tube.

Baseline for the simulation: 0.03 m, 150 sccm, 0.8 atm, 485 °C, 0.2 g

In studying the temperature-dependent radial uniformity inside a nanoporous particle, we tested three temperatures of 485, 535 and 585 °C. As shown in Fig. 2a, when Si wt% reaches 40% inside a particle, the Si deposition is highly uniform inside both 10 µm and 20 µm-size particles at 485 °C, with an I/O ratio of 0.96 and 0.84, respectively. When the temperature increases to 535 °C, slight non-uniformity was observed, and I/O ratios are 0.87 and 0.62, respectively. When the temperature further increases to 585 °C, the deposition concentrates at the outer part of the particle, and I/O ratios are as low as 0.61 and 0.30 for 10 µm and 20 µm-size particles, respectively.

Such results are consistent with experimental observations by cross-sectional EDS of FIB-cut Si/C particles after silane deposition. First, EDS mapping results clearly show uniform Si deposition inside most particles at 485 and 535 °C, but obvious gradient at 585 °C (Fig. 2 d-f). Moreover, quantified EDS mapping results (Fig. 2 b-c) also show the same trend of inhomogeneity as modeling results. For example, I/O ratios of 1.03/1.05 and 1.06/1.02 for particles with size of 10-20 µm at 485 and 535 °C, and this value decreases to 0.26 and 0.41 at 585 °C.

Comment: The data from Joe doesn't seem right, need to check.

(a)

(b)

(c)

T(C)	Average I/O	STD I/O
485	0.99	0.48
	0.95	0.24
	1.02	0.23
	1	0.21
	1.17	0.17
	1.11	0.26
	0.95	0.24
	0.99	0.48
	1.02	0.23
535	0.76	0.29
	0.89	0.37
	1	0.18
	0.9	0.32
	1.04	0.22
	0.95	0.14
	0.84	0.22
585	0.61	0.54

(d)

(e)

(f)

Comment: Need ruler

Fig. 2 (a) Simulated deposition thickness vs. radius at 485, 535 and 585 °C. (b) Silicon Weight portion vs particle position with 5 µm and 10 µm particle size. (c) I/O ratio from EDS results. (d)-(f) EDS cross sectional images at 485, 535 and 585 °C.

Joe's Comment: the std for particle size is too big.

The model also captures the zone position-dependent silicon deposition. At 585 °C and a deposition zone length of 3 cm, when the average Si wt% reaches 40%, it is predicted that the top 1/3 has a Si wt% of 59.3%, and the bottom 1/3 only has a Si wt% of 36.5%. This is because the majority of silane is consumed at the upstream, so the silane concentration is reduced at downstream and thus there is less deposition at downstream.

Such results align with experimental observation. As shown in Fig. 3, Si deposition is clearly observed on the inner surface of a quartz tube at upstream, while no or little deposition is observed downstream. Further EDS analysis of powders collected upstream and downstream shows …………… (10 μm matchup is good)
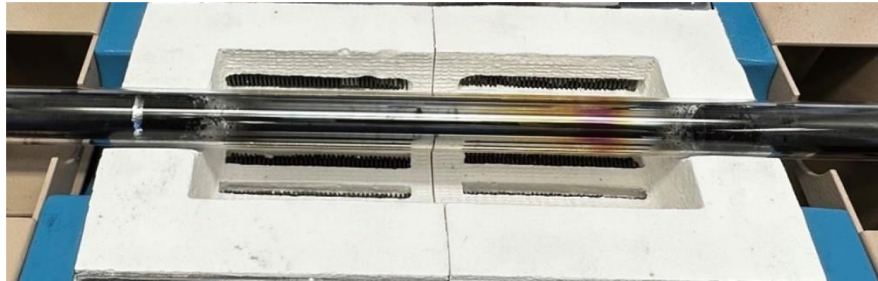
Fig. 3 Weight portion vs tube length at 585 °C(500 now), flowing from right to left.

After checking the validity of our model as above, we carry out more simulations to understand effects of various parameters on Si depositions, including pressure, flow rate, carbon loading, and deposition zone length. We find that lower pressure, higher flow rate and higher carbon loading and shorter deposition zone length favor the deposition uniformity. The details are as follows.

(Finish the pressure first then other parameters are basically the same)

We first study pressure in the range of 0.5-5 atm, which are practical for industrial applications. As shown in Fig. 4, when Si wt% reaches 40% inside a particle, the Si deposition is highly uniform along the tube at 0.5 atm. When the pressure increases to 5 atm, the range of wt% is from 39.6% to 38.7%. This is because lower pressure helps with the uniform distribution of silane along the tube which achieves uniformity.
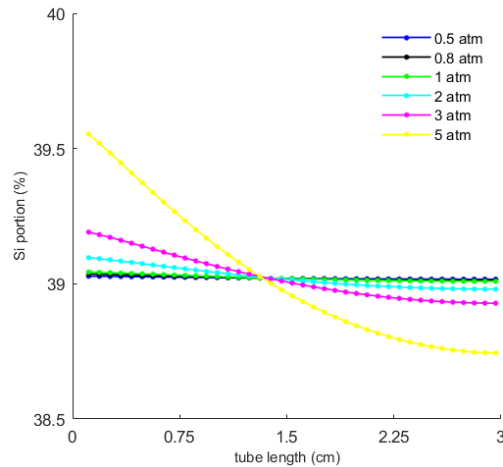
Fig. 4 Simulated Si portion vs. tube length at 0.5, 0.8, 1, 2, 3, 5 atm.

(May disregard below parameters and jump to large model)

For flow rate…

For carbon loading ……

For carbon properties…

For zone length…

After understanding these factors, we further carry out modeling for a large deposition system which can be used for pilot production (1-5 kg per batch).

Baseline for the simulation: 0.1 m, 300 sccm, 0.8 atm, 485 ℃, 300 g

Due to the scale of the system, the impact of different parameters become more visible while the analysis remains the same as the previous model. We can conclude that the crucial factor is to reduce reaction rate and diminish the effect caused by different position in the tube, hence lower pressure, shorter deposition zone length, more carbon loading and higher flowrate is favorable.

We developed two version of codes to tackle 2D and 3D scenarios respectively.

- Presentation of experimental setup and results, confirming uniform deposition at certain conditions

3.1 Deposition Rate Analysis on temperature and pressure

First, we set up a baseline for effect of parameters in terms of deposition rate.
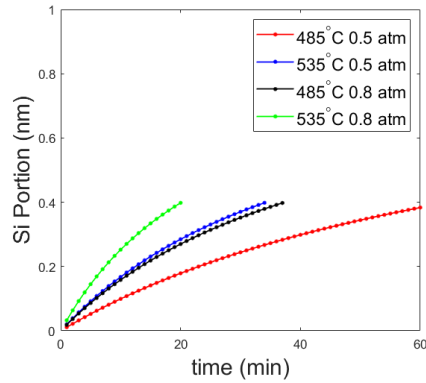
According to the graph, higher temperature and higher pressure lead to higher deposition rate.

3.2 Uniformity Analysis on different parameters (inside carbon particle)

- Evaluation of different conditions and their impact on deposition uniformity inside carbon particles

We consider the effect of temperature, pressure, particle size, zone length, flowrate. As shown in Fig. 2a, the deposition is highly uniform at 485 ℃ and 535 ℃ with I/O ratio 0.96 and 0.87 respectively, while at 585 ℃, the I/O ratio is 0.61. In Fig. XXX (a), the I/O ratio is bigger at 5 µm than at 10 µm, indicating more uniformity. From Fig XXX (b-d), we can conclude that pressure, zone length and flowrate doesn't affect the deposition uniformity inside the particle. (I think this conclusion is trivial so maybe we can explain it more technically?)
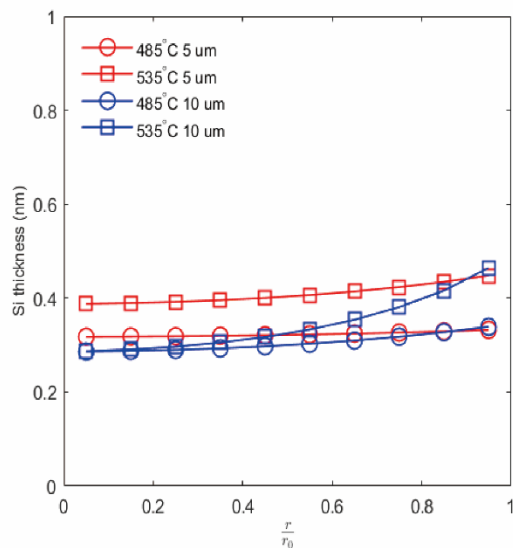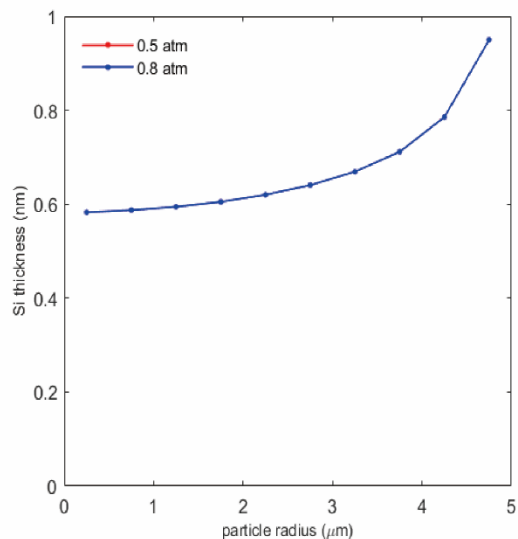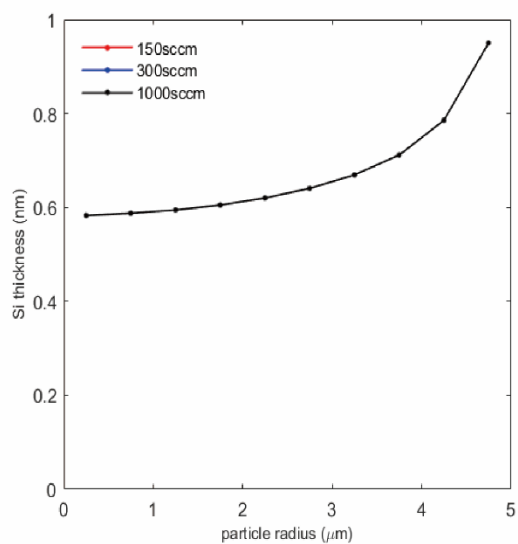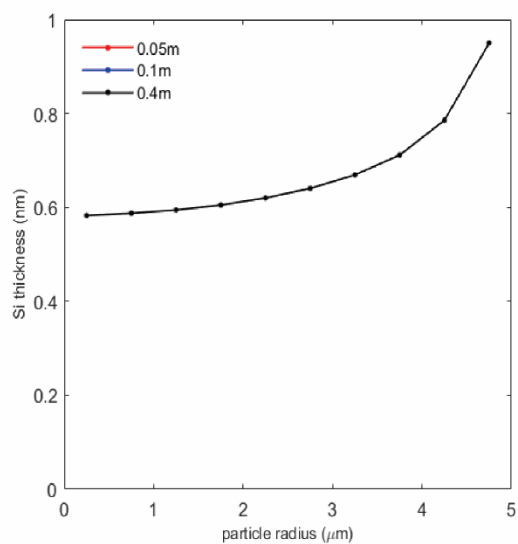
Fig. XXX (a) Simulated deposition thickness vs. radius at 485, 535 ℃ with particle size 5 and 10 μm. (b) Simulated deposition thickness vs. radius at 0.5 and 0.8 atm. (c) Simulated deposition thickness vs. radius at 150, 300 and 1000 sccm. (d) Simulated deposition thickness vs. radius with zone length of 0.05, 0.1 and 0.4 m.

3.3 Uniformity Analysis on different parameters (vs zone position)

We evaluate the same parameters on the effect of deposition distribution along the tube. In Fig XXXX (a), std for Si weight portion is 0.1830 (0.18) and 0.1734 (0.17) at 485 and 535 ℃ respectively, concluding that higher temperature achieves slightly more uniformity along the tube. In Fig XXXX (b), std for Si weight portion is 0.1711 and 0.1830 at 0.5 and 0.8 atm respectively, concluding that lower pressure achieves more uniformity. In Fig XXXX (c), std for Si weight portion is 0.1759, 0.1830 and 0.2291 with 0.05, 0.1 and 0.4 m respectively, concluding that shorter tube achieves more uniformity. In Fig XXXX (d), std for Si weight portion is 0.2024, 0.1830 and 0.1711 with 150, 300 and 1000 sccm respectively, concluding that higher flowrate achieves more uniformity.
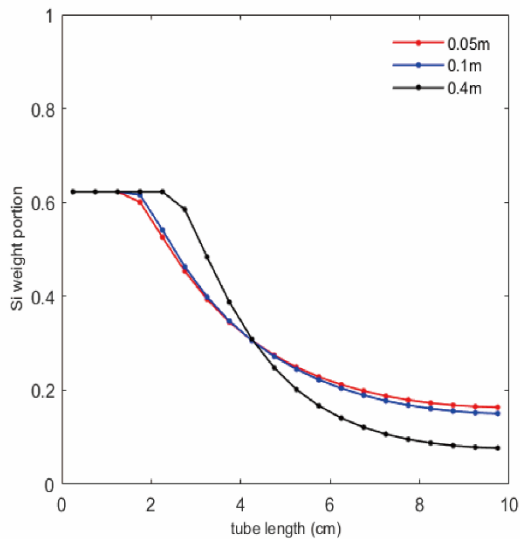
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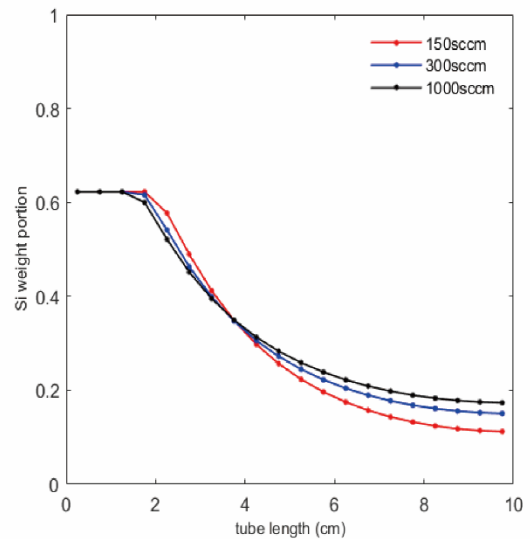
(a)
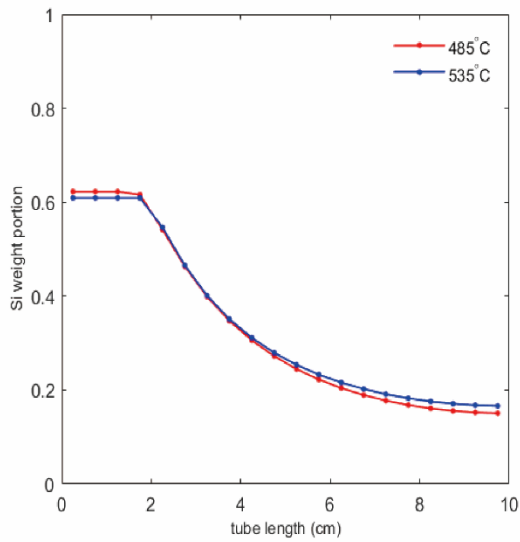
(b)
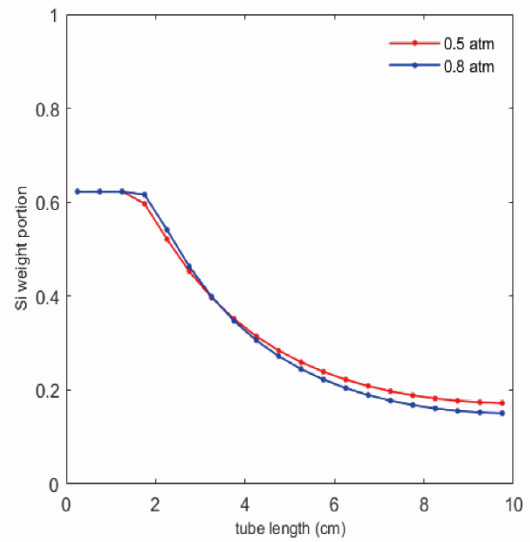
(c)

(d)

Fig XXXX (a-d): Silicon weight portion vs zone position at different temperature, pressure, zone length and flowrate respectively.

Comment: Std $=(\frac{\sum_{i=1}^{N}(w_i-\widetilde{w})^2}{N-1})^{\frac{1}{2}}$

4. Conclusion

Based on the results, we can conclude that the most important factors to achieve uniformity are higher flowrate and shorter tube, while lower temperature, lower pressure, smaller pore size, less carbon could also be beneficial.
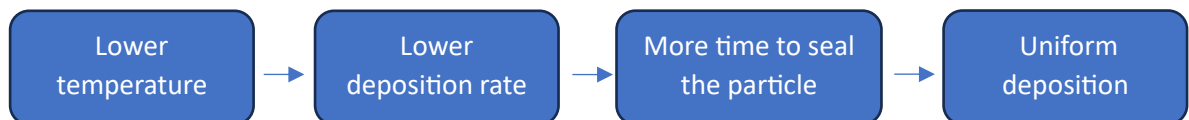
5. Discussion

In the simulation, we haven't considered the effect of H_2 released from the reaction as it would disturb the diffusion of the silane. Right now, we assume H_2 doesn't affect the dynamics of silane since the proportion of silane in the mixing gas is low.

Also, we haven't considered the turbulence of the gas flow when the flowrate is too big.

Appendix

Flow Diagram of Effects

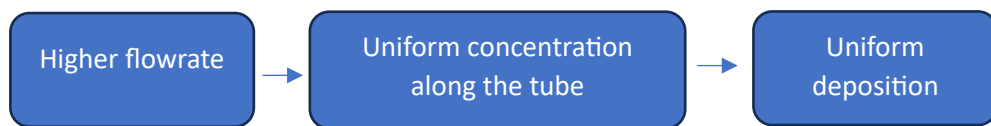1. Temperature

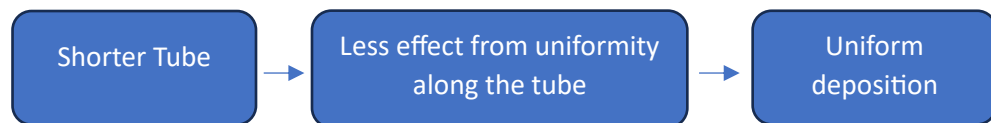| Lower temperature | → | Lower deposition rate | → | More time to seal the particle | → | Uniform deposition |

2. Pressure

| Lower pressure | → | Lower concentration | → | More time to seal the particle | → | Uniform deposition |

3. Flowrate

```
┌──────────────────┐     ┌──────────────────────┐     ┌──────────────────┐
│                  │ →   │ Uniform concentration│ →   │ Uniform          │
│  Higher flowrate │     │    along the tube    │     │ deposition       │
└──────────────────┘     └──────────────────────┘     └──────────────────┘
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4. Tube length

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┌──────────────────┐     ┌──────────────────────┐     ┌──────────────────┐
│                  │ →   │ Less effect from     │ →   │ Uniform          │
│  Shorter Tube    │     │ uniformity along the │     │ deposition       │
│                  │     │        tube          │     │                  │
└──────────────────┘     └──────────────────────┘     └──────────────────┘
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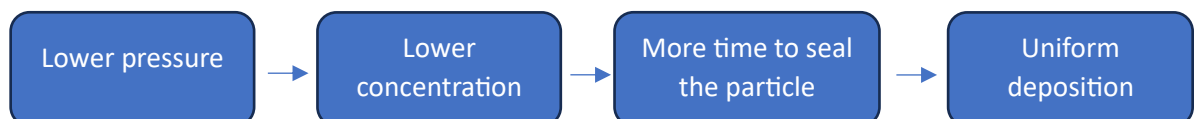
Data Availability

Declaration of competing interest

Acknowledgments

Author contributions