

Diffusion-Reaction Model of ALD in Nanostructured Substrates: Analytic Approximations to Dose Times as a Function of the Surface Reaction Probability

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We have developed a transport model for Atomic Layer Deposition (ALD) in nanostructured substrates. The model comprises a non-linear advection-diffusion–reaction equation coupled to a surface kinetic equation that incorporates the self-limiting nature of ALD. In their nondimensional forms, these equations show that coverage dynamics in ALD depend only on two parameters: the Damkoeler number and the precursor excess number. These parameters depend on the surface chemistry and experimental conditions and can be readily calculated for a wide range of substrate geometries including trenches and vias, anodized alumina, and powders.

Introduction

One of the advantages of Atomic Layer Deposition (ALD) is that, due to its self-limiting nature, it is possible to coat large area substrate and nanostructured materials. This eases the constraints in reactor design compared to CVD where the need to minimize concentration gradients is much more important. However, precursor transport still plays a fundamental role in ALD in determining the processing times and throughput both at the substrate and reactor scales. Dose times and purge times are dictated by the need to achieve precursor saturation everywhere inside nanostructured substrates and, as shown in the literature, it is important to optimize dose times to avoid undersaturation and maximize throughput.

One of the better known approximations to the problem of determining saturation dose times in nanostructured substrates is the model of Gordon et al.¹ Assuming a step-function coverage profile and a growth front that propagates towards the bottom of the feature at a rate dictated by the precursor flow, the model yields dose times as a function of the aspect-ratio for circular vias. One of the limitations of this model is that it does not take surface kinetics into account. As other authors have shown, reaction probability has a strong influence on coverage profiles in high aspect ratio features.²⁻³ Also, it is well known that more complex surface processes, such as poisoning by reaction byproducts or surface recombination for one of the reactants, can strongly influence both the coverage profiles and the saturation dose times required inside nanostructured features.⁴ Finally, the studies mentioned above are limited to the particular case of trenches and vias. The dynamics of ALD saturation on other nanostructured substrates, such as nanoparticle films, catalysts supports, and other porous materials have not yet been modeled.⁵

This manuscript describes a general model that provides a framework for understanding the reaction-diffusion problem in nanostructured substrates during ALD.

This model is equivalent to previous kinetic Monte Carlo simulations, but with the advantages that it provides analytic expressions for computing saturating exposure times for different structures and that it generalizes the circular via to any nanostructured substrate.

Model Equations

The model is composed of two equations: a precursor mass balance equation that takes the form of a time-dependent diffusion equation and a surface kinetics equation that tracks the surface coverage at every surface point of the nanostructure as a function of time. As shown elsewhere,⁶ if the equations are transformed into their non-dimensional form, the transport-diffusion problem can be shown to depend on just two parameters that govern the coverage profile and the dynamics of infiltration. These non-dimensional equations are:

$$\frac{\partial x}{\partial \tau} - \frac{\partial^2 x}{\partial \xi^2} = -\alpha \theta x \quad [1]$$

$$\frac{d\theta}{d\tau} = -\alpha \gamma \theta n \quad [2]$$

Where the normalized density is $x = n/n_0$ with n the precursor density along the feature and n_0 the precursor density at $\xi = z/L$ and $\tau = tD/L^2$ are the position normalized to the depth of the feature L and D is the diffusion coefficient inside the nanostructure.

The two parameters, α and γ , are the Damkoeler number (diffusion time/reaction time ratio), and the precursor excess number (precursor molecules in the nanostructure per surface site), respectively. These two parameters are given by:⁶

$$\alpha = \frac{1}{4} L^2 \bar{s} \frac{v_{th}}{D} \beta_0 = \frac{t_{diff}}{t_{reac}} \quad [3]$$

$$\gamma = \frac{V n_0 s_0}{S} = \frac{N_V}{N_S} \quad [4]$$

where V and S are the nanostructure volume and surface, respectively, v_{th} is the thermal velocity, β_0 is the reaction probability, \bar{s} is the specific surface area of the nanostructure (area per unit volume) and s_0 is the average surface site area.

Model Results and Discussion

Analytic expression for dose times

Solving Eqs [1] and [2] with the appropriate boundary conditions, it can be shown that the time required to coat a high aspect ratio feature is given by:

$$t_c = \frac{L^2}{D} \frac{1}{\gamma} \left(1 - \frac{\log(1-c)}{\alpha} \right) \quad [5]$$

where c is the coverage fraction at the bottom of the feature. In the particular case of a circular pore, this expression becomes:

$$t_c = \frac{\sqrt{2\pi mkT}}{s_0 p} \frac{3}{2} (AR)^2 \left(1 - \frac{2 \log(1-c)}{3\beta(AR)^2} \right) \quad [6]$$

Note that when the reaction probability is high enough, the expression derived by Gordon et al is obtained.¹ Conversely, when the reaction probability is low enough, we reach the reaction limited regime where the dose time becomes independent of the aspect ratio.

Eq. [6] can be brought into a simpler form by expressing the time to dose as a function of the dose time required to achieve saturation on a flat substrate. Keeping the assumption of a first order Langmuir dependence used for developing Eq. [6], the time required to achieve a certain coverage on a planar surface is given by:

$$t_s = -\frac{\sqrt{2\pi mkT}}{s_0 p} \frac{\log(1-c)}{\beta} \quad [7]$$

Then the time to coat a feature is given by:

$$t_c = t_s + \frac{\sqrt{2\pi mkT}}{s_0 p} \frac{3}{2} (AR)^2 \quad [8]$$

We should emphasize that t_s is not necessarily the saturation time observed in any given reactor since transport effects might be significant. However, Eq. [7] can be used as a lower bound for the estimate.

In Fig. 1 we present the additional dose time ($t_c - t_s$) required as a function of the aspect ratio and the precursor pressure (mTorr) for the case of TMA.

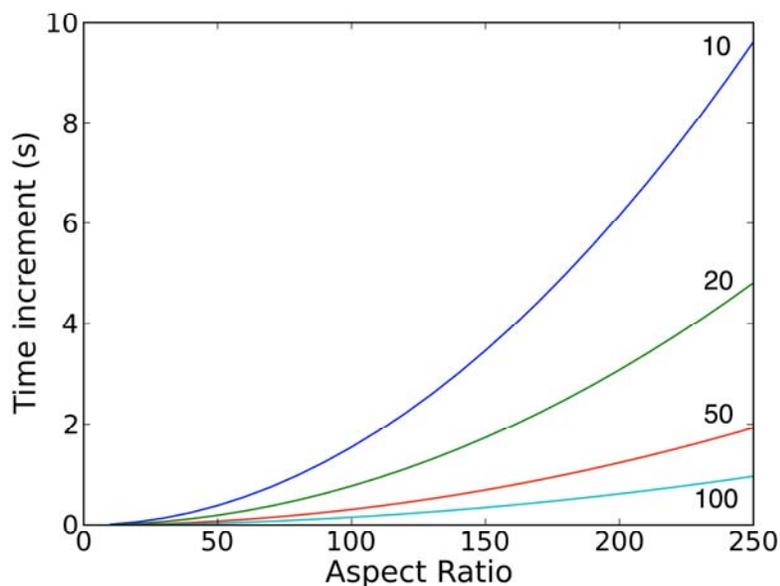


Figure 1. Influence of aspect ratio and pressure on the additional dose time required to achieve saturation in a circular pore. Pressure values are in mTorr.

Influence of reaction probability on coverage profiles

The influence of the reaction probability on step coverage is shown in Fig. 2 for an aspect ratio of 100 and different values of the reaction probability, β . Gordon's model assumed a step profile for the coverage in their dose time expression.¹ As shown in Fig. 2, this approximation is valid when the reaction probability is sufficiently high ($\beta \geq 0.01$), but the profiles become flattened with decreasing reaction probability.

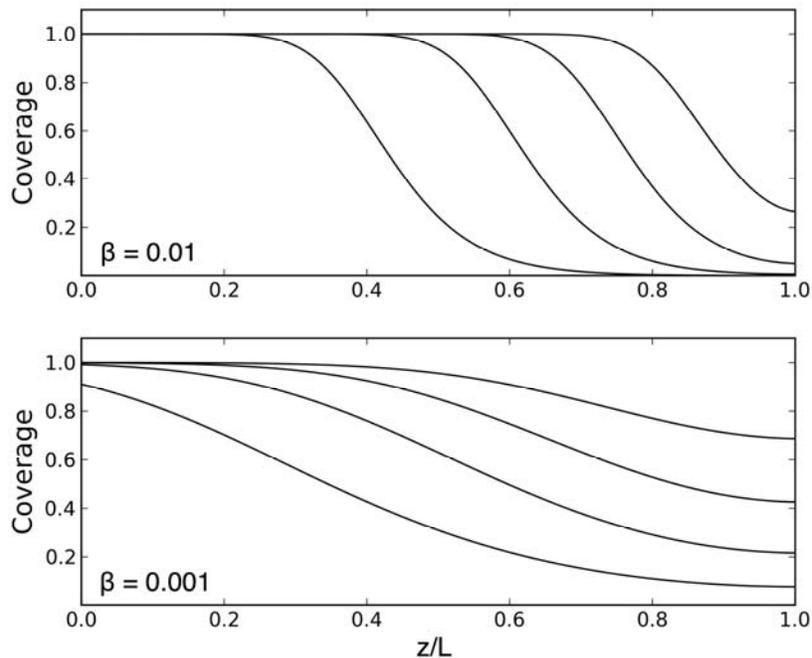


Figure 2. Influence of precursor reaction probability on the growth profiles for a circular via of aspect ratio 100.

Influence of wall recombination: the PEALD case

One advantage of our model is that it can be adapted to include any arbitrarily complex chemistry. For instance, it is common in ALD to have an additional, self-limited reaction pathway such as the surface recombination of ozone or atomic hydrogen precursors.^{7,8} In this case we can simply modify Eq. [1] to include an additional loss term:

$$\frac{\partial x}{\partial \tau} - \frac{\partial^2 x}{\partial \xi^2} = -\alpha \theta x - \nu x^n \quad [8]$$

In this expression n corresponds to the reaction order and ν is given by:

$$\nu = \frac{1}{4} L^2 \bar{s} \frac{\nu_{th}}{D} \beta_{rec} \quad [9]$$

Where β_{rec} is the wall recombination probability.

Solving Eqs [8] and [2] we can simulate profiles along the trench. The results are presented in Fig. 3 for an aspect ratio of 100 and a reaction probability for the self-limited reaction of 10^{-2} .

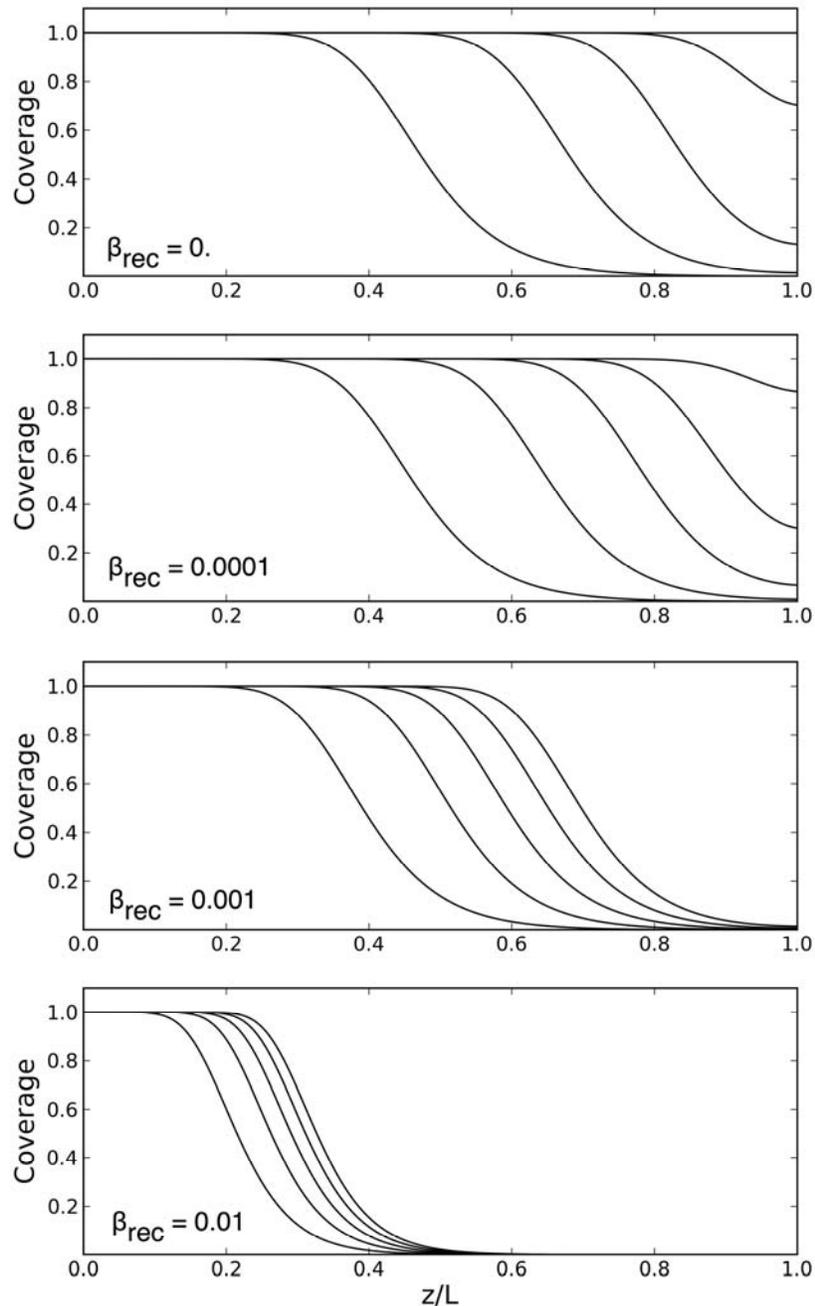


Figure 3. Influence of wall recombination with probability β_{rec} on the coverage profiles along a circular via of aspect ratio 100. A reaction probability of 10^{-2} is assumed.

As the wall recombination becomes more important, it takes longer for the system to reach saturation, and the dose times increase almost exponentially with time. The profiles

obtained in Fig. 3 are in good agreement with kinetic Monte Carlo simulations carried out by Knoops et al.⁷

Discussions and Conclusions

We have developed a model for precursor transport and surface coverage during ALD in nanostructured substrates. Our model reobtains Gordon's expression for dose times in the diffusion limited regime¹ and offers a more general expression where the dose time is the sum of two times, one corresponding to the saturation time on a flat surface and the second that takes diffusion into account. As we have shown previously,⁶ the agreement between this analytic approximation to full numerical solution is excellent. The coverage profiles in the case of circular pores are in good agreement with previous Monte Carlo simulations.^{2,3} This is not surprising, since the kinetic Monte Carlo simulations and this model are mathematically related and constitute two representations of the same physical model. Two advantages of the model are that it can be easily generalized to different geometries by choosing the right specific volume and diffusion coefficient.

Acknowledgments

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