

Supporting Material

For

Growth inhibition to enhance conformal coverage in thin film chemical vapor deposition

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Experimental

The growth experiments have been carried out in a UHV chamber under low pressure CVD conditions.¹ The substrate used for all the growth runs is thermally grown SiO₂; we have shown that TiB₂ nucleates remarkably well on this surface.² The conformal coverage is evaluated by the macro-trench method. Accurate measurements of the film thickness profile are analyzed, using the continuity equation under molecular flow conditions in the trench, to afford the precursor pressure as a function of depth and the variation of β with pressure (depth).^{3,4} The growth rate on planar substrates is measured during growth by *in-situ* ellipsometry, and post-growth from SEM cross-sections. The Ti atomic density in the film, ρ_{Ti} , is measured *ex-situ* using RBS. Post-growth AES reveals that the carbon and oxygen contents in the film are 8 and 5 at.%, respectively, in the presence of dme and 5 at % each without it. This small increase is consistent with increased incorporation of impurities from the vacuum background at the lower

film growth rate. Because the pressure of added dme is 200 times that of the precursor, it is clear that the dme undergoes little or no decomposition under these growth conditions.

Conformality Index

We define a conformality index as a quantitative measure of conformality for a thin film deposition profile in a high aspect ratio feature. In Figure S1, z is the depth along the macro-trench, b is the width of the trench and $t(z)$ is the film thickness at different depths. The conformality index, C , is defined as the ratio z_1/b , where z_1 is the depth at which $t(z_1) = 1/2 t(z=0)$.

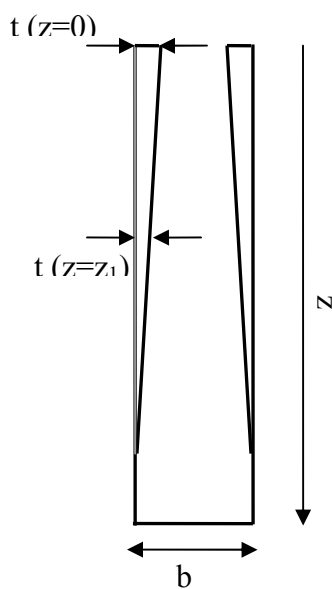
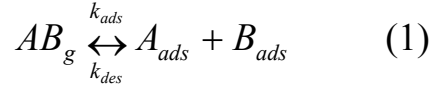


Figure S1. Diagram of a macro-trench with a film profile and quantities needed to calculate conformality index.

Kinetic Model and Derivation of Rate Law for Film Growth

The mechanistic scheme proposed in the text corresponds to the following individual kinetic steps:



Equation 2 may involve the release of additional byproducts (for example BH_x in this case), but we assume that their effect on the kinetics is small compared with that of B_{ads} . The steady state coverage of A and B (θ_A , θ_B) are solutions of the following equations:

$$\frac{\partial \theta_A}{\partial t} = k_{ads} p_{AB} (1 - \theta_A - \theta_B) - k_{des} \theta_A \theta_B - k_r \theta_A = 0 \quad (4)$$

$$\frac{\partial \theta_B}{\partial t} = k'_{ads} p_B (1 - \theta_A - \theta_B) + k_{ads} p_{AB} (1 - \theta_A - \theta_B) - k_{des} \theta_A \theta_B - k'_{des} \theta_B = 0 \quad (5)$$

Rearranging equation 4 provides insight into the role of B in inhibiting the growth rate:

$$\theta_A = \frac{k_{ads} p_{AB} (1 - \theta_B)}{k_r + k_{des} \theta_B + k_{ads} p_{AB}} \quad (6)$$

The term $(1 - \theta_B)$ in the numerator is the site blocking effect by which adsorbed B inhibits the adsorption of AB and hence reduces θ_A . The term $k_{des} \theta_B$ in the denominator accounts for the reduction of θ_A through associative desorption of the precursor AB. These two terms correspond

to mechanisms a and b, respectively. No matter which term dominates, increasing the partial pressure of B will increase θ_B and therefore decrease the GR.

Equations 5 and 6 can be solved for the dependence of θ_A on P_B , giving an exact solution that involves a quadratic term. We can simplify the analysis, however, by taking advantage of the conditions under which our experiments are conducted. For a high pressure of inhibitor as compared to precursor, we can assume that $k'_{ads}P_B \gg k_{ads}P_{AB}$ and $k'_{ads}P_B \gg k_r$. These inequalities, which are equivalent to postulating that the rate of inhibitor adsorption dominates the rates of precursor adsorption and of precursor reaction on the growth surface, lead to a solution for θ_A (and therefore the growth rate) of the form $C_1 / (1 + C_2 p_B)$, where

$$C_1 = \frac{2k_{ads}k'_{des}P_{AB}}{k_r k'_{des} + p_{AB}k_{ads}(k_r + k_{des})}, \quad C_2 = \frac{k'_{ads}(k_r + k'_{des})}{k_r k'_{des} + p_{AB}k_{ads}(k_r + k_{des})} \quad (7)$$

The film growth rate GR is obtained by multiplying θ_A by the reaction rate constant k_r and the area density of surface sites B_o , $GR = \theta_A k_r B_o$.

The sticking coefficient β is related to the film growth rate GR by the following expression:

$$\beta = \frac{\text{flux sticking}}{\text{incident flux}} = \frac{GR / \rho_M}{p / \sqrt{2\pi mkT}} \quad (8)$$

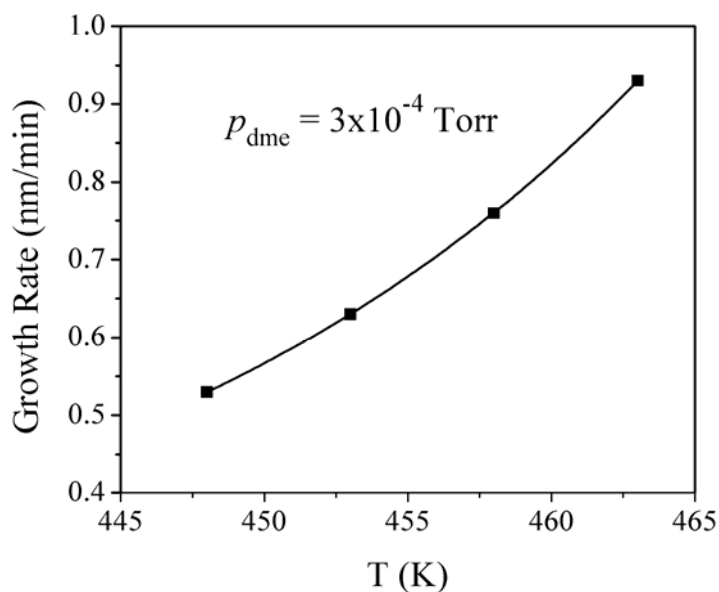


Figure S2. Temperature dependence of the growth rate of a TiB_2 film deposited from $\text{Ti}(\text{BH}_4)_3(\text{dme})$ in the presence of 3×10^{-4} Torr of added dme: experimental (■) and exponential fit (solid line).

References:

- (1) Jayaraman, S.; Klein, E. J.; Yang, Y.; Kim, D. Y.; Girolami, G. S.; Abelson, J. R. *J. Vac. Sci. Technol. A* **2005**, *23*, 631-633.
- (2) Kumar, N.; Yang, Y.; Noh, W.; Girolami, G. S.; Abelson, J. R. *Chem. Mat.* **2007**, *19*, 3802-3807.
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