

Growth Inhibition to Enhance Conformal Coverage in Thin Film Chemical Vapor Deposition

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Many important technological applications depend crucially on the ability to deposit conformal (i.e., uniformly thick) films on substrates having 3-dimensional relief features. For example, in the microelectronics industry, conformal deposition processes are needed to line and fill trenches and vias as part of the fabrication of capacitors, interconnects, and other key device components.^{1,2} Physical vapor deposition (PVD) processes such as sputtering, which are widely used to grow thin films, are unfortunately unable to afford good conformality inside features with aspect ratios (ARs) above ~ 5 . For this reason, the International Technology Roadmap for Semiconductors predicts that it will be necessary to replace PVD with chemical vapor deposition (CVD) and atomic layer deposition (ALD) methods to line and fill features having the increasingly large ARs that will be characteristic of future generations of integrated circuits.^{2,3} ALD is inherently conformal, but the film growth rates are very low (typically < 0.2 nm/cycle), especially in high AR features.⁴ In contrast, CVD can routinely deposit films much more rapidly, but a key challenge is how to ensure high conformality while maintaining the high growth rates.⁵

The conformality of the growth process in a feature of given AR depends on the reactive sticking probability (β) of the gas phase precursor on the film growth surface (Supporting Information, eq 1), lower values of β giving rise to better conformality because the precursor will diffuse deeper into the feature before reacting.^{6,7} Although β depends strongly on the chemical identity of the growth species, it also can vary with deposition parameters such as pressure and temperature.⁸ For example, we have recently shown that vias of 100 nm diameter and 30:1 AR can be uniformly coated and even completely filled without voids by CVD.^{5,9} The highly conformal deposition is made possible by employing precursors that can grow useful films at low temperatures and that have relatively high vapor pressures, so that the surface can be saturated with adsorbed precursor. Saturation leads to self-blocking of surface reactive sites, which reduces β and improves conformality.⁵

In this paper, we present an alternative approach that can greatly improve the conformality of films from precursors that under normal circumstances afford poorly conformal deposits. The general idea is to decrease the value of β without changing the growth temperature or precursor partial pressure, and thereby promote greater diffusion of the precursor deep into features with high ARs. The decrease in β , and improvement in conformality, is achieved by adding a suitable second species to the growth stream that can serve as a growth inhibitor.

Here we describe the application of this idea to the CVD of titanium diboride (TiB_2) from the precursor $\text{Ti}(\text{BH}_4)_3(\text{dme})$, where $\text{dme} = 1,2$ -dimethoxyethane.^{10,11} The dme ligand is a neutral

molecule that dissociates from the precursor and desorbs without decomposition from the surface at growth temperatures of 175–200 °C. Film growth from $\text{Ti}(\text{BH}_4)_3(\text{dme})$ alone occurs with a relatively high β value of 0.30 and is therefore conformal only for features with relatively low ARs ($\sim 3:1$). The low conformality results because $\text{Ti}(\text{BH}_4)_3(\text{dme})$ is less volatile than many other precursors; under the nonequilibrium flow conditions in a low-pressure CVD deposition apparatus, the partial pressure of precursor at the film surface is well below the $\sim 10^{-3}$ Torr required for the onset of self-site-blocking effects.

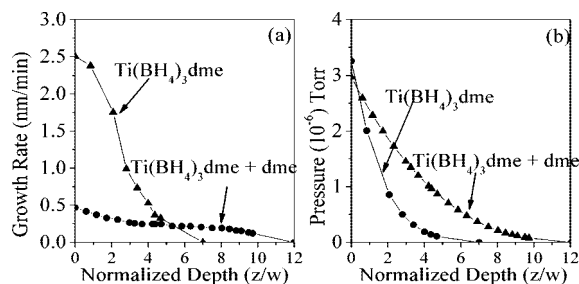


Figure 1. (a) TiB_2 film growth rate at 175 °C and (b) $\text{Ti}(\text{BH}_4)_3(\text{dme})$ precursor pressure distribution as a function of normalized depth (depth/trench width) in a macro trench in the absence of added dme (●) and in the presence of 6×10^{-4} torr added dme (▲).

Remarkably, however, when dme is added to the $\text{Ti}(\text{BH}_4)_3(\text{dme})$ growth stream, the conformality of the TiB_2 film is markedly improved. Thickness profiles for films grown under the same precursor pressure (3×10^{-6} Torr) and temperature (175 °C), one in the absence of dme and another in the presence of 6×10^{-4} Torr of dme , are dramatically different (Figure 1). We define a “conformality index” as the normalized depth within a trench at which the film thickness falls to half of the value at the top of the trench (the normalized depth is the depth divided by the aperture width of the feature). Larger values for the index correspond to greater conformality. In a macro trench with a 25 μm opening, the films fall to half their thickness at depths of 62 μm in the absence of dme and 156 μm in its presence (Figure 1a), corresponding to a nearly 3-fold increase in the conformality index from 2.5 to 6.2. Note that these depositions were conducted in a very deep trench, in which the films eventually taper to zero thickness. In a trench with a smaller aspect ratio, the boundary condition imposed by the trench bottom reduces the precursor pressure drop and causes the coating to be much more conformal. For the present TiB_2 system, adding dme can more than double the AR of a trench that can be filled conformally.

The precursor pressure along the axis of the trench, calculated from the film thickness profile using the continuity equation,⁵ falls rapidly in the absence of dme but relatively slowly in its presence (Figure

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1b). The smaller depletion of the gas phase concentration of the precursor as a function of depth is the key factor that improves the conformal coverage. The dme pressure remains relatively unchanged inside the trench, because it is not consumed in the growth reaction.

In separate experiments, we have shown that dme does in fact serve as an inhibitor of TiB_2 deposition. At a dme pressure of 6×10^{-4} Torr, the TiB_2 film growth rate from $\text{Ti}(\text{BH}_4)_3(\text{dme})$ at 175 °C is reduced by a factor of 5 (Figure 2) without any significant change in film quality and purity (see Supporting Information).

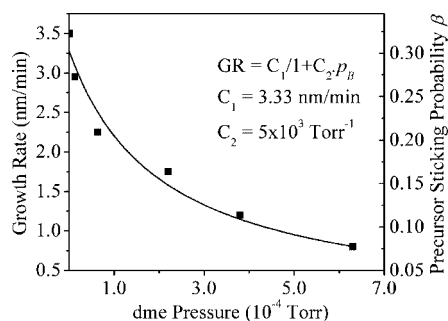


Figure 2. Growth rate (left axis) and sticking probability β (right axis) of a TiB_2 film grown at 175 °C from $\text{Ti}(\text{BH}_4)_3(\text{dme})$ as a function of dme pressure: experimental (■) and fit to theory (solid line).

At least two different but related mechanisms can be invoked to explain the reduction in a CVD growth rate upon addition of an inhibitor to the growth stream: (1) The inhibitor occupies, and therefore blocks, reactive surface sites, thus reducing the net rate of precursor adsorption and therefore the film growth rate, or (2) the inhibitor promotes the reversible desorption of adsorbed precursor, thus reducing the net rate of precursor adsorption and therefore the growth rate. The first mechanism is equivalent to reducing the rate of the forward reaction leading to film growth, whereas the second mechanism is analogous to Le Chatelier's principle, in which the addition of a reaction product increases the rate of the back reaction. As far as we are aware, there has been no previous recognition that these mechanisms are potentially relevant to CVD film growth kinetics, although it is known that recombinative desorption pathways relevant to CVD deposition processes can take place on surfaces,¹² and that film deposition from solutes dissolved in supercritical CO_2 can be slowed by addition of a reaction product.¹³

The inhibition effect can be modeled with the following steps: (i) the precursor AB_g reversibly chemisorbs on the surface to form a reactive species A_{ads} and a byproduct B_{ads} ; (ii) the adsorbed reactive species A_{ads} further reacts to afford film M_s ; and (iii) the addition of an inhibitor, in this case identical to the reaction byproduct B, raises the steady state population of B_{ads} on the surface (Supporting Information, eq 2–4). We further assume that A_{ads} and B_{ads} compete for the same surface reactive sites. Note that mechanism 1 will require a large degree of site blocking whereas mechanism 2 can take place even if the population of B_{ads} is not sufficient to block most of the adsorption sites. It is possible that other intermediate steps can occur, for example, the formation of a weakly bound (physisorbed) state preceding chemisorption, but provided that these additional steps are not rate limiting, the conclusions of the model will be unchanged.

Solving the appropriate rate equations for steady state coverage of species A_{ads} and B_{ads} under the conditions of our experiment leads to a solution for the surface coverage of A_{ads} (and therefore the growth rate) of the form $C_1/(1 + C_2 p_B)$, where p_B is the partial

pressure of the inhibitor B (see Supporting Information). The experimental growth rate data fit this functional form extremely well (Figure 2). The value of β calculated from the growth rate is given on the right abscissa in Figure 2; it falls from 0.35 to 0.07 as the dme pressure increases from 0 to 6×10^{-4} Torr. This reduction in β , which is the key effect of the inhibitor, leads to a dramatic improvement in the conformality of the CVD growth process.

Experimentally, the film growth rate at constant precursor and inhibitor pressure increases slightly as a function of temperature, corresponding to an apparent activation energy of 0.67 eV (65 kJ/mol). This increase could be due to one or both of two effects: an increase in the reaction constant k_f or an increase in the rate constant k_{des} for desorption of the inhibitor, which implies an increase in the precursor surface coverage θ_A . We have shown in our earlier work that the TiB_2 growth rate from the $\text{Ti}(\text{BH}_4)_3(\text{dme})$ precursor is very weakly activated across a wide temperature range (175–600 °C).¹¹ We believe that the increased growth rate at higher temperatures in the presence of the inhibitor is due to enhanced desorption of the dme. The apparent activation energy value compares well with the desorption activation energy of various ethers (0.4–0.6 eV) bound to metal surfaces.¹⁴ At higher growth temperatures, the partial pressure of inhibitor must be increased in order to maintain the surface coverage of B_{ads} necessary to reduce the sticking probability of the precursor and to obtain conformal coverage.

In summary, we have demonstrated that the conformality of CVD films can be increased—without changing the temperature or precursor flux—simply by adding a second component to the gas stream that reduces the precursor sticking probability. This approach should be able to enhance the conformality of many other low-temperature CVD processes.

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Supporting Information Available: Details of the deposition experiments, derivation of rate law for deposition of film as a function of precursor and inhibitor pressures, and figure of the temperature dependence of the TiB_2 growth rate deposited from $\text{Ti}(\text{BH}_4)_3(\text{dme})$ in the presence of 3×10^{-4} Torr of added dme. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Granneman, E. H. A. *Thin Solid Films* **1993**, *228*, 1–11.
- (2) International Technology Roadmap for Semiconductors. www.itrs.net, 2007.
- (3) Leskela, M.; Ritala, M. *Thin Solid Films* **2002**, *409*, 138–146.
- (4) Lim, B. S.; Rahtu, A.; Gordon, R. G. *Nat. Mater.* **2003**, *2*, 749–754.
- (5) Yang, Y.; Jayaraman, S.; Kim, D. Y.; Girolami, G. S.; Abelson, J. R. *Chem. Mater.* **2006**, *18*, 5088–5096.
- (6) Gates, S. M. *Chem. Rev.* **1996**, *96*, 1519–1532.
- (7) Hsieh, J. J. *J. Vac. Sci. Technol., A* **1993**, *11*, 78–86.
- (8) Gil, A.-Y.; Yang, Y.; Kumar, N.; Abelson, J., to be submitted.
- (9) 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.
- (10) Jensen, J. A.; Gozum, J. E.; Pollina, D. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 1643–1644.
- (11) Kumar, N.; Yang, Y.; Noh, W.; Girolami, G. S.; Abelson, J. R. *Chem. Mater.* **2007**, *19*, 3802–3807.
- (12) Chung, Y. S.; Lee, H. S.; Lee, Y. S.; Kim, S. *Surf. Sci.* **2001**, *482*, 312–317.
- (13) Zong, Y. F.; Watkins, J. J. *Chem. Mater.* **2005**, *17*, 560–565.
- (14) Sexton, B. A.; Hughes, A. E. *Surf. Sci.* **1984**, *140*, 227–248.

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