Growth Inhibitor To Homogenize Nucleation and Obtain Smooth HfB\textsubscript{2} Thin Films by Chemical Vapor Deposition

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ABSTRACT: We describe an example of a new phenomenon: the use of a growth inhibitor to homogenize nucleation and improve the smoothness of a thin film deposited by chemical vapor deposition. For many film–substrate combinations, the rate of nucleation on the substrate is slow relative to the growth rate, a situation that produces a broad distribution of island sizes and a rough surface morphology. We show an example in which this outcome is avoided by directing a second component onto the substrate that has little effect on the nucleation rate but significantly retards the island growth rate. The case studied is the growth of HfB\textsubscript{2} films on SiO\textsubscript{2} substrates using the chemical vapor deposition precursor Hf(BH\textsubscript{4})\textsubscript{4} with NH\textsubscript{3} as the inhibitor. The addition of the inhibitor increases the island density at coalescence by 50\% and decreases the roughness by 10\% to the subnm range. We suggest that the use of inhibitors to homogenize nucleation may be applicable to other film–substrate combinations.

KEYWORDS: chemical vapor deposition, nucleation, metals on oxide, surface morphology, ultrathin film

I. INTRODUCTION

Many nanotechnologies, especially those involved in the fabrication of integrated circuits, require low temperature deposition of extremely thin, pinhole-free, and ultrasmooth films that are conformal on high aspect ratio features such as trenches and vias.\textsuperscript{1,2} Growth processes in which the sticking coefficients of the precursor species are small, such as chemical vapor deposition (CVD) or atomic layer deposition (ALD) under surface-saturated conditions, are best suited to meet the requirement for conformality.\textsuperscript{3–7} However, if the nucleation rate on the substrate is low relative to the film growth rate, as is often the case, then the initially deposited layer will consist of a broad size distribution of islands. In this situation, coalescence to a continuous film will occur only when the total deposit is relatively thick, and the resulting surface roughness will be very large due to the peak-and-valley morphology.\textsuperscript{9–10} This outcome is unacceptable when the objective is to deposit a very smooth film only a few nm thick; furthermore, the deepest valleys may actually be pinholes. The deposition of metallic films on dielectric substrates commonly suffers from this problem; for example, in a system we have studied, the deposition HfB\textsubscript{2} on SiO\textsubscript{2} (Figure 1, top left), the film does not coalesce until its peak thickness (15–17 nm) is much larger than the desired film thickness (a few nm).

To obtain films that are conformal, thin, smooth, and pinhole-free, the lateral spacing between nuclei needs to be comparable to, or preferably smaller than, the desired film thickness, i.e., the nucleation process must occur with very high areal density on the substrate of choice and the size distribution must be narrow. It is well-known that the nucleation density in CVD and ALD processes can be increased by pretreating the substrate surface to create ‘active’ sites, such as dangling bonds, where reaction with the precursor occurs with high probability.\textsuperscript{11–14} Under favorable conditions, a large density of islands forms in a short time, and the islands then coalesce by growth to afford a smooth film. Although the reported techniques enhance nucleation, some are difficult or impossible to perform in high aspect ratio features and others may damage the substrate.

Here, we report what is potentially a new method to increase the nucleation density in low temperature CVD. We inject a growth rate inhibitor\textsuperscript{15} along with the precursor molecule. The inhibitor binds weakly enough to the bare substrate surface such that nucleation proceeds but strongly enough to the islands that their growth rate is significantly retarded. This differential change in the rates of surface processes affords a very uniform nucleation layer. No substrate pretreatment is required, and the method works equally well in very high aspect ratio features because the inhibitor, which is not consumed in steady state, will reach a uniform pressure everywhere.

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Although we have demonstrated this effect in only one system — the low-temperature CVD growth of HfB₂, from the single source precursor Hf(BH₄)₄ using NH₃ as the inhibitor — we indicate reasons to expect that growth inhibitors could improve film smoothness in other film-substrate combinations as well.

II. EXPERIMENTAL SECTION

Investigations of HfB₂ film growth from Hf(BH₄)₄ are performed in a turbo-pumped cold-wall growth chamber of ultrahigh vacuum construction. The substrates are 100 nm thick dry thermal SiO₂ on Si grown under microelectronic-grade conditions. Before loading into the chamber, the SiO₂/Si substrates are degreased successively with acetone and isopropl alcohol in an ultrasonic bath and then rinsed with DI water. During film growth the substrate temperature is 250 °C; the partial pressure of Hf(BH₄)₄ is 0.075 mTorr; and the partial pressure of the inhibitor NH₃ is either zero or 0.05 mTorr. At these pressures, gas phase collisions are negligible; all rate-limiting processes must occur on the film growth surface. The precursor and the inhibitor are injected using separate delivery lines, each of which is pointed toward the substrate surface; their mass flow rates are regulated using needle valves with no carrier gas.

In-situ spectroscopic ellipsometry (SE) experiments are performed with a fixed incident angle of 70° and a continuous spectrum of photon energies in the range 0.75–5.05 eV. SE is a sensitive and reproducible means to determine when initial islands have formed on the substrate. However, because the initial morphology can be highly anisotropic, e.g., a sparse population of tall islands, it is not physically meaningful to fit the data to an effective medium theory. To estimate the order of magnitude of the optical response, we use a multilayer optical model, consisting of a thin HfB₂ film on the SiO₂/Si substrate. Using the Woollam EASE software with the measured optical constants for thick HfB₂ films, we find that a HfB₂ thickness of 0.03 nm affords a 1% increase in the imaginary component of the complex reflectivity ρ at a photon energy of 2.4 eV. There is much less change at very low or very high photon energies due to the coherent interference effects introduced by the SiO₂ sublayer. By tracking ρ at 2.4 eV, we can detect the onset of nucleation at an earlier stage than is possible when the entire spectroscopic data set is utilized in the analysis.

Ex situ analysis of the film surface is performed by tapping mode AFM, by RBS, and by high resolution (Field Emission) SEM.

Throughout we will refer to the effective film thickness, which is defined as the areal density of Hf atoms measured by RBS divided by the volume density of Hf in crystalline HfB₂.

III. RESULTS AND DISCUSSION

The present work builds upon our past studies of the nucleation and growth of HfB₂ films using the single source precursor Hf(BH₄)₄. HfB₂ is a highly refractory conductor that is an excellent diffusion barrier, e.g., against the migration of copper.

At low growth temperature (200–300 °C), the films are essentially stoichiometric and pure, amorphous in diffraction measurements, and highly conformal on vias or trenches, e.g., the step coverage is ~0.9 on a trench of 30:1 aspect ratio. However, in situ analysis of HfB₂ growth on SiO₂ and H-terminated Si substrates reveals that there is a nucleation delay (e.g., at least 30 min at T = 200 °C and P = 10⁻³ mTorr). To achieve film growth on Si or SiO₂ at low temperatures, the precursor flux must be increased substantially (>0.1 mTorr) until nucleation occurs, or the film must be grown on a previously deposited HfB₂ film or other surface that promotes nucleation.

We recently demonstrated that the steady-state deposition rate of HfB₂ films is strongly inhibited if ammonia (NH₃) is injected into the chamber in parallel with the precursor at temperatures below 350 °C. For example, at 270 °C with a Hf(BH₄)₄ partial pressure of 0.065 mTorr, the addition of 0.05 mTorr of ammonia reduces the HfB₂ growth rate by a factor of 10. At this temperature, the addition of ammonia does not change the Hf to B stoichiometry of the film and only minor incorporation of nitrogen (<5 at. %) occurs. These findings suggest that ammonia adsorbs transiently and reversibly to the growing HfB₂ surface, where it reduces the growth rate, probably by site blocking effects.

We now show that, whereas ammonia significantly reduces the steady-state growth of HfB₂ from Hf(BH₄)₄, it does not impede the nucleation of HfB₂ on a SiO₂ substrate at T = 250 °C. This controllable decrease in the rate of island growth vs the rate of nucleation makes it possible to increase the density of nuclei and obtain coalesced films that are much smoother than in the absence of the growth inhibitor, ammonia.

Effect of Ammonia on Nucleation Density of HfB₂. We explored the early stages of HfB₂ film growth on SiO₂ both in the absence and in the presence of the inhibitor. For both cases, we interrupted film growth when im(ρ) at 2.42 eV had increased by ~7%, which is equivalent to the deposition of 0.21 nm of smooth HfB₂ (see the Experimental Section). RBS analysis reveals that the areal density of Hf atoms is very similar for these two samples: with precursor alone, growth was stopped at 12 min and the Hf density is 0.8 × 10¹⁵ atoms/cm²; with the inhibitor, growth was stopped at 35 min and the Hf density is 1.0 × 10¹⁵ atoms/cm². The equivalent film thicknesses are 0.24 and 0.30 nm, respectively. In thin film growth, the surface morphology invariably evolves as the amount of deposited material increases. Here, the fact that the deposited quantities are essentially equal provides a strong basis for comparing the morphologies. Due to the high melting point of HfB₂ (Tₘᵢₓ ~ 3200 °C), we expect that growth is an irreversible process at low growth temperature (250 °C), hence, we do not consider the possibility of island redistribution.

In the absence of the inhibitor (Figure 1, top left), the density of HfB₂ islands is small (6 × 10⁶ nuclei/cm²) and the height distribution function P(h) is broad (Figure 2, black circles). The maximum island height is 17 nm and the rms...
roughness is 2.6 nm. In contrast, in the presence of the inhibitor (Figure 1, bottom right), the surface is densely covered with islands (∼3 × 10^{12} nuclei/cm^2) with a very narrow size distribution (Figure 2, black triangles). The maximum island height is 2.5 nm and the rms roughness is 0.3 nm. For reference, the height distribution function for the bare SiO_2 substrate has a rms roughness of 0.2 nm (Figure 2, black line).

Thus, under these CVD conditions, the addition of the growth inhibitor, ammonia, results in a 50-fold increase in the number of HfB_2 nuclei, a significant narrowing of their size distribution, and a 10-fold decrease in the rms roughness.

**Evolution of Surface Roughness As a Function of Initial Nucleation Density.** The initial morphology has a very strong influence on the surface roughness at later stages of film growth. To demonstrate this point, we grew thicker films on top of two contrasting initial morphologies similar to those in Figure 1: “sparse” islands in a broad height distribution (nucleation in the absence of the growth inhibitor, top left) and “dense” islands in a narrow height distribution (nucleation in the presence of the growth inhibitor, bottom right). On top of each initial morphology, we grew HfB_2 films at a rate of ∼2 nm/min using the precursor alone or at a rate of ∼0.12 nm/min using both the inhibitor and precursor. The lower growth rate of the latter is due to a reduction in the effective sticking coefficient of the precursor.

First, let us consider growth on the sparse nucleation layer. A 7.8 nm thick film grown using the precursor alone has a rms roughness of 6.5 nm and ∼4 × 10^{10} cm^{-2} of mounds in a broad height distribution (Figure 3, black filled circles). For comparison, a 6.5 nm thick film grown in the presence of the inhibitor not only exhibits very smooth areas on the surface but also has ∼2 × 10^{10} cm^{-2} of mounds and a relatively large rms roughness of ∼5.2 nm (Figure 3, black open circles). Thus, the sparse nucleation layer creates enough initial roughness to prevent the growth of a smooth thick film, irrespective of whether the additional film is grown in the presence or absence of an inhibitor.

The latter result is at first somewhat surprising, because it is known that lowering the sticking coefficient of a CVD precursor generally favors higher conformality (less depletion in recesses) and also favors the growth of smooth surfaces.24

Therefore, it might have been expected that the initial rough morphology of a sparsely nucleated layer could be eliminated by the growth of a sufficiently thick film on top, especially if the sticking coefficient of the precursor is lowered by the presence of an inhibitor. Consistent with earlier studies, however, the present results confirm that CVD is unable to smooth out initial surface roughness on long lateral length scales, even under highly conformal growth conditions.25 This result is principally due to the instability against roughening caused by peak shadowing.24

Second, let us consider growth on the dense nucleation layer. A 5.7 nm thick film grown on this nucleation layer in the presence of the inhibitor has a rms roughness of only 0.9 nm and a very narrow height distribution (Figure 4, black empty triangles). This is an excellent result; the only drawback is that the film growth rate is relatively slow, ∼0.12 nm/min. However, a 15.2 nm thick film grown on the dense nucleation layer using the precursor alone has a similarly small rms roughness of 1.1 nm and a narrow height distribution (Figure 4, black filled triangles). This excellent result shows that, when the initial nucleation morphology is extremely smooth, very smooth and fully coalesced films can be grown even when the precursor has a relatively high sticking coefficient.

These results suggest a technologically attractive new method to grow very smooth thin films, one in which a growth inhibitor is added only during the nucleation stage. In this way, i.e., slow nucleation followed by rapid film growth, the total deposition time can be kept acceptably short. In high aspect ratio features, however, it might be advantageous to continue adding inhibitor during the steady-state growth so as to minimize precursor depletion effects and improve the conformality.

**Microscopic Mechanism of Improved Nucleation.** The findings above show that the nucleation of a CVD-deposited
HfB$_2$ film can be greatly improved by addition of ammonia, which we know from previous studies is an inhibitor of steady-state growth. The microscopic mechanism(s) responsible for growth inhibition in the present study will be probed in future experiments, but two important aspects of the mechanism can be inferred from the results at hand (Figure 5). First, the fact that nucleation continues on the substrate surface in the presence of NH$_3$ indicates that the inhibitor has only a small (if any) direct effect on the population and reaction of growth species. This conclusion is consistent with previous studies of the adsorption of NH$_3$ on hydroxylated SiO$_2$ surfaces: the first layer of ammonia has a small adsorption energy of 0.41 eV and a desorption prefactor of $1.0 \times 10^{12}$ s$^{-1}$. For the substrate temperature and NH$_3$ pressure (flux) used in our experiments, these studies predict a negligible NH$_3$ surface coverage ($\theta \sim 0$). Similar conclusions were reached in other studies of the adsorption of ammonia on silicon dioxide as well as hydrogen terminated Si(100). In contrast, NH$_3$ evidently binds with a higher coverage on the surface of the HfB$_2$ nuclei, where it reduces the growth rate, probably by a site blocking effect that inhibits precursor adsorption. It is known that the HfB$_2$ surface is terminated by hafnium atoms. This surface should show a high relative affinity for ammonia, as it does for other adsorbates.

We investigated how strongly ammonia binds to our HfB$_2$ films by measuring the reduction in HfB$_2$ growth rate as a function of ammonia partial pressure. The growth rate depends quantitatively on the ammonia flux (pressure) via the form

$$GR = \frac{GR_0}{1 + CP_i}$$

where $P_i$ is the inhibitor pressure. For a precursor pressure of 0.065 mTorr and temperature of 270 °C, the fitting constant $C = 250$ mTorr$^{-1}$ (Figure 6: experimental data, filled and empty squares; fit, solid curve).

Both the precursor and inhibitor undergo reversible adsorption on the growth surface. The film growth rate must therefore result from a process of competitive adsorption, in which adsorbed inhibitor molecules may block the adsorption of incident precursor molecules and thus lower the reaction (growth) rate. We have elsewhere derived the rate formalism under the assumption that both the precursor and inhibitor obey first-order Langmuirian kinetics. In the present case, the effect of ammonia adsorption dominates the kinetic competition, and the fitting constant asymptotically approaches the
value $C = (k_{ads}/k_{des})_{NH3}$ with increasing inhibitor pressure. This relationship can be used to estimate the desorption activation energy of ammonia from the HfB$_2$ growth surface as $\sim$1.3 eV. In $k_{ads}$ we assume that the microscopic sticking coefficient is 0.5; in $k_{des}$ we assume that the desorption attempt frequency $\nu = 10^{13}/s$ and that the density of surface sites $N_s = 10^{15}/cm^2$. (Note that the values of these constants influence the desorption activation energy only as $kT$ times their natural logarithm, hence, even a factor of 10 uncertainty in the constants would change the estimated adsorption energy by only 0.1 eV.) As our microscopic mechanism requires, this binding energy is $\sim$0.9 eV larger than for binding of ammonia to SiO$_2$ cited above. To test the estimate for the binding energy on HfB$_2$, we performed selected growth experiments at 288 °C (not shown). The suppression in growth rate was predicted by recalculating C using the above parameters. Experimental results agreed with the predictions.

The parameters can also be used to plot the fractional steady-state coverage of the surface by adsorbed ammonia as a function of the ammonia partial pressure and the substrate temperature (Figure 7). For all the temperatures and pressures we have investigated, the enhanced nucleation density, resulting in ultrasmooth films, corresponds to a fractional coverage of ammonia $\geq$0.85. This coverage can be maintained at higher growth temperatures by increasing the ammonia pressure as indicated by the adsorption isotherm.

In this proposed mechanism, NH$_3$ adsorbs reversibly, returning to the gas phase without decomposition or consumption. As a result, the partial pressure of NH$_3$ will, following an initial time delay due to transport by diffusion, equilibrate to the same value everywhere in a deep feature no matter how high its aspect ratio. This behavior implies that the increase in nucleation density due to the inhibitor will occur equally well on all surfaces. We have specifically verified this assertion using macrotrenches$^{23}$ of 500:1 aspect ratio ($T = 275$ °C, precursor pressure = 0.1 mTorr, inhibitor pressure = 0.7 mTorr, and $T_{growth} = 90$ min). AFM analysis as a function of depth shows that surface morphology is variable for growth without inhibitor (Figure 8). However, in the presence of the inhibitor the morphology is remarkably smooth and similarly everywhere on the trench walls (Figure 9). This behavior is in sharp contrast to plasma or ion beam treatments, which are unable to afford uniform fluxes on the inner surfaces of high aspect ratio features.

**Possible Generality of Mechanism for Improved Nucleation.** In this concluding section, we make a few comments about the applicability of the inhibitor approach for improving nucleation to other CVD processes. It will not always be possible to discover a substance that acts like ammonia does in the present system, but we can propose some general guidelines about how to identify potential candidates for such a substance. The first step is to identify a reagent that inhibits film growth, preferably without changing the film composition. This issue, which is essentially a chemical one, centers on the identification of molecular species that bind to the growth surface strongly, so that it can block surface sites necessary for deposition to occur. Lewis acid/Lewis base and hard/soft donor/acceptor properties can serve to identify possible candidates for growth inhibitors. As mentioned above, the HfB$_2$ surface is terminated by hafnium atoms, which are Lewis acids (electron acceptors) that should bind Lewis bases such as ammonia (Figure 5a). Our previous experimental work confirmed that ammonia does in fact serve as a growth inhibitor, with the additional attribute of not becoming incorporated into the film and changing the film composition.$^{20}$

Second, the inhibitor should bind relatively weakly to the substrate surface so that, at appropriate inhibitor partial pressure and temperature, the steady-state coverage on the substrate surface is low relative to the inhibitor coverage on the islands (Figure 5b top and bottom, respectively). Under these conditions, initial nuclei form but then become covered with inhibitor and cannot grow very quickly. Subsequent nuclei develop on bare areas of the substrate but likewise are unable to
grow rapidly. Ultimately the surface becomes densely populated with very small nuclei that slowly grow and coalesce to form a smooth and continuous film. As discussed above, it is known that silicon dioxide surfaces do not bind ammonia at temperatures above about 250 °C. This fact is consistent with the absence of electron acceptor sites on such surfaces (the hydroxyl coverage is low at these temperatures) and the thermodynamic unfavorability of adding a N–H bond across a Si–O bond.

Preliminary results in our laboratory indicate that the inhibition method does in fact work with other precursor-inhibitor combinations. Detailed results and analyses will be the subject of future publications.

IV. CONCLUSIONS
We have demonstrated a new method to increase the areal density of nuclei during low-temperature CVD and to enhance the smoothness of coalesced thin films, by adding a molecular growth inhibitor. This method has been demonstrated for the growth of HfB films on SiO substrates using NH as the inhibitor. NH greatly reduces the film growth rate on already established HfB nuclei but allows the nucleation process to proceed largely unimpeded on bare areas of the substrate. As a result, the surface becomes covered with a large density of fine nuclei with a narrow height distribution. In the presence of the inhibitor, the precursor affords fully coalesced films at a thickness of only ~0.3 nm with a remarkably low rms roughness of 0.3 nm. The presence of the inhibitor does not change the film stoichiometry or introduce nitrogen in significant concentrations.

The ability to grow very smooth and very thin pinhole-free films of HfB has at least one potential application: such films may be superior to those presently used as diffusion barriers against copper diffusion in microelectronic circuits. More generally, however, the use of growth inhibitors has the potential to enable the controllable formation of ultrathin films on a wide variety of high aspect ratio, porous, or reentrant features for nanotechnology applications.

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