Copper is used in many advanced nanoscale technologies due to its high electrical and thermal conductivity, and its strong surface plasmon resonance when in the form of nanoparticles.1–5 For continuous films, such as those used as the seed layer for electrodeposition in integrated circuits, the film must be less than 10 nm thick, pinhole-free, and extremely smooth, with an rms roughness of less than 1 nm. For optical devices based on copper nanoparticles, it is important to control the nanoparticle size and morphology.4,6 Rigorous control of copper growth can be difficult: the surface energy of copper is high and the atomic diffusion rate is significant, so that dewetting often occurs during growth or subsequent annealing.3–12

Thin films of copper can be deposited by a wide variety of techniques including wet chemical growth, physical vapor deposition, chemical vapor deposition (CVD) and atomic layer deposition (ALD). To deposit copper conformally in substrate architectures such as trenches and vias that have re-entrant or high aspect ratio features, ALD and CVD are preferred techniques because of the ability of the precursor molecules to diffuse throughout the structure.13–17 A general difficulty arises when the substrate is relatively unreactive, such as an oxide surface: the resulting films tend to be rough owing to a combination of sparse nucleation and the tendency of the deposited material to agglomerate.18 Once surface roughness on the length scale of the island separation is formed, it cannot be eliminated by the overgrowth of more material.18

The use of additives to enhance film smoothness is well established in the electrochemical deposition of copper19,20 but is not common in CVD. For CVD, the morphology of copper films can sometimes be improved by adding a second component to the growth gas. For example, addition of H₂O to a flux of Cu(hfac)VTMS (hfac = hexafluoroacetone) results in the deposition of smoother copper films.21–25 Unfortunately, the addition of water tends to increase the resistivity of the film because copper oxides are also deposited.21,22,26 Thus, this approach is not suitable for applications that require very thin (≤10 nm) copper films with high electrical conductivities, although it can be useful for making thicker films by employing water only during the nucleation stage.27 Addition of iodine to a flux of Cu(hfac)VTMS enables bottom-up filling of deep features due to the surface segregation and catalytic effects of iodine.28–33

Improved nucleation density and morphology of copper films can also be achieved by employing process variations such as plasma enhanced CVD (or ALD) and pulsed CVD. For example, a surface rms roughness as low as 1.1 nm has been reported by using plasma enhanced ALD.34 Alternatively, the morphology can be improved by depositing a Cu phase that wets the substrate, such as CuON, and then chemically converting the phase to Cu metal.35,36

Thin films with ∼1 nm surface roughness have been reported by this method. In high aspect ratio or convoluted structures, however, pulsed processes are limited by the time constant for gas diffusion, and plasma-enhanced processes are limited by the rapid consumption of active species during wall collisions.

As a result, it would be desirable to develop morphology-controlling additives for copper growth that operate in steady-state and that do not change the film composition. Such additives would enable the uniform coating of any feature. Here, we report such a method to control copper film morphology – ranging from uniformly islanded to extremely smooth – by co-flowing a growth inhibitor molecule along with the well-known copper precursor Cu(hfac)VTMS.

Selection of Growth Inhibitor

This work builds on our previous finding that the conformality of other materials, such as metal diborides, grown by low temperature CVD can be improved by adding a molecular inhibitor to the flux of precursor species.14,18 We have been able to identify inhibitors able to control the morphology of copper thin films by taking into account the following considerations:

1. The inhibitor should be able to bind strongly enough to the surface to affect the rate of film nucleation and/or the rate of film growth on itself, often by a site blocking mechanism. The film morphology will be modified according to the relative effect on the kinetic rates of nucleation vs. growth. If the growth rate can be reduced relative to the nucleation rate, as in the deposition of HfB₂ on SiO₂ substrates, then the surface will “fill in” with a large density of small nuclei and will coalesce with extremely low surface roughness. Conversely, if the nucleation rate is suppressed relative to the growth rate, then the film will consist of a lower density of larger nuclei (islands).

2. After coalescence of the nuclei has occurred, the inhibitor should bind to the film surface well enough to reduce the sticking coefficient of the precursor, and thus reduce the rate at which the film roughens with increasing thickness. This result derives from the known effect that reducing the effective sticking coefficient of the precursor tends to homogenize the arrival rate of precursor on all surfaces.15,18 That reduces the instability of the surface morphology to perturbations such as high spots, which would otherwise “shadow” the precursor flux from neighboring areas and grow at a faster rate. A reduction in the sticking coefficient of the precursor also enhances the conformality (step coverage) of the film on high aspect ratio or convoluted structures.

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We report a method to control the surface morphology of thin copper films during growth by chemical vapor deposition from the precursor Cu(hfac)VTMS. A molecular inhibitor – an additive that modifies the surface attachment kinetics but does not decompose and contribute impurity atoms to the film – is added during the nucleation and/or growth stages of the film. Here we show that the reaction by-product VTMS can serve as such an inhibitor. If the inhibitor is added during the nucleation stage, when bare substrate surface is still exposed, the inhibitor greatly reduces the rate of coalescence and promotes the formation of a large density of uniformly-sized copper islands. Alternatively, if the film is allowed to nucleate in the absence of the inhibitor, subsequent addition of the inhibitor leads to a continuous copper film that is remarkably smooth on the nm scale.

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3. The inhibitor should desorb back to the gas phase without decomposition on the surface, such that all possible growth sites are ultimately made available and the surface is not contaminated (or rendered unreactive) by the inhibitor or its fragments. An attractive choice as inhibitor is a neutral byproduct of the CVD process: if high purity thin films can be deposited from the precursor then the decomposition rate of byproducts on the surface must be slow relative to their desorption rate. For example, we have previously shown that the addition of dme (1,2-dimethoxyethane) to a flux of Ti(BH4)3(dme) slows the growth rate of TiB2 without changing the composition of the deposited film. An alternative approach is to employ an inhibitor that is chemically unrelated to the precursor. An example of this approach is the addition of NH3 to the precursor Hf(BH4)4 for the deposition of HfB2. Mechanistically, an unrelated inhibitor probably acts by blocking surface reactive sites.

We identify the by-product VTMS as an excellent choice as the inhibitor (and thus smoothing agent) for copper deposition from the precursor Cu(hfac)VTMS. VTMS is known to bind to Cu with reasonable energies (criteria 1 & 2) and to desorb without decomposition (criterion 3). The use of VTMS in Cu CVD has previously been reported in two respects. First, it enhances the lifetime of the Cu(hfac)VTMS precursor, which tends to decompose when stored, depositing Cu on the container walls and generating both VTMS and Cu(hfac)2, which accumulate in the container. Presumably, this decomposition is why commercial sources of Cu(hfac)VTMS intentionally contain 10–20% copper(II) and likely contain significant amounts of free VTMS. An earlier means to suppress the decomposition rate was to add excess VTMS to the source (e.g., Schumacher “Blend 2504”). Secondly, there is one phenomenological report that adding 5 wt% VTMS to Cu(hfac)VTMS produced deposits with a particulate morphology on TiN surfaces, but relatively smooth films on a copper substrate. However, those films were much thicker (about a micron thick), and no attempt was made to explain the origin of the results. Here, we show that VTMS modifies surface kinetics and can afford control of morphology. The use of VTMS as a stabilizer implies that other results may have been influenced by the surface kinetics.

**Experimental** — All films are deposited in a custom-built turbopumped high vacuum chamber described in detail previously. The substrate is heated radiatively with a tungsten filament; the substrate temperature is measured with a K-type thermocouple clamped on top of the mounting platen. A reference thermocouple at the back of the heating stage is also used to monitor the temperature. Optical properties are measured by in-situ ellipsometry performed with fixed incident angle of 70° and continuous spectrum of photon energies in the range of 0.75–5.05 eV.

The growth of copper films from Cu(hfac)VTMS is carried out on air-exposed E-beam evaporated Ru, a candidate diffusion barrier material which shows good Cu wettabiity. Growth is done without any pretreatment of the substrate surface. The growth temperature is 100°C, partial pressure of Ar carrier gas is 1 mTorr, and the partial pressure of the Cu(hfac)VTMS precursor is 0.1 mTorr. At these pressures, gas phase collisions are negligible: all processes must occur at the film growth surface. In the present experiments, the precursor is purified so that it is free of excess VTMS as judged by 1H NMR spectroscopy (further details on the substrate surface and precursor composition are given in the supplementary document).

**Results and Discussion**

**Formation of islands** — After the RuOx substrate is exposed for 1 min to the Cu(hfac)VTMS precursor in the absence of added VTMS, the density of initial copper nuclei determined by AFM is somewhat sparse, N ≈ 4.7 × 1010 cm−2 (not shown). The initial rms surface roughness due to the nuclei, 0.6 nm, is large enough to promote roughening when additional copper is deposited. For example, for a 75 nm thick copper film the rms surface roughness is 5.7 nm (Figure 1).

Significantly different behavior is seen if growth from Cu(hfac)VTMS is carried out with a co-flow of VTMS. Notably, the incubation time for nucleation increases from ~25 sec using the precursor alone to 5 min with co-flowing VTMS (supplementary information, Figure S1). The total amount of deposited Cu, measured by RBS, is reduced by a factor of six compared with growth without inhibitor for the same growth times. These results indicate clearly that VTMS is serving as an inhibitor.

After being grown for 30 min in the presence of VTMS, the copper deposit consists of islands with an areal density N ∼ 5 × 1010 cm−2, essentially identical to the density of nuclei in the absence of VTMS (supplementary information, Figure S2). The height distribution is narrow and the rms roughness is 2 nm (Figure 2a). A similar morphology was obtained under the same conditions for a 45 min growth time; thus, although this morphology is not in steady state, it is easy to reproduce experimentally. Similar results are also obtained

**Figure 1.** Cross sectional SEM image of Cu film grown on RuOx with precursor only. Mean thickness 75 nm (measured by RBS), rms roughness 5.7 nm (measured by AFM), sheet resistance 0.1 Ω/□. Tsub = 100°C and f_growth = 30 min. The scale bar represents 100 nm.

**Figure 2.** Cross sectional SEM image of copper growth on RuOx at T_sub = 100°C and f_growth = 30 min: (a) 8.2 nm effective thickness (measured by RBS), deposited in a co-flow of precursor and 2 mTorr of VTMS inhibitor; (b) 13.5 nm thick Cu film grown with a co-flow of 1 mTorr VTMS only after the nucleation stage, sheet resistance 1.9 Ω/□. The faintly visible under-layer at the interface is the Ru seed layer. The scale bar represents 100 nm.
for precursor pressures within the range 0.05–0.10 mTorr, and growth temperatures between 100 and 120 °C. The morphology degrades at higher temperatures: e.g., for T = 150 °C and a growth time of 10 min, the density of nuclei has lowered to ∼ 1.3 × 10^10 cm^-2, the height distribution is broader, and the rms surface roughness has more than doubled to 4.4 nm.

We cannot deduce from the present data what factor(s) control the absolute density of Cu islands on the air-exposed Ru surface, but it is possible that a pre-existing density of surface defects, which may be a function of the surface preparation, accounts for the observed island density.27,44–46 The effect of the VTMS inhibitor on copper growth is very distinct from that of NH₃ on growth of HfB₂ on SiO₂ from Hf(BH₄)₃, in which the density of nuclei increased continuously with time.18 Evidently, in the latter system, nucleation is not directed by surface defects.

Additional factors may influence the Cu island morphology, including the surface diffusion of Cu atoms, which ultimately leads to dewetting; and the degree to which added VTMS affects the surface transport and reaction rate of Cu(hfac)ads.47 Similar film morphologies and rate suppressions are seen when 2-methyl-1-hexyn-3-ylne (MHY) is employed as the inhibitor instead of VTMS (supplementary information, Figure S.6 and 7). Both MHY and VTMS can bind to copper; the analogous compound Cu(hfac)(MHY) is a known CVD precursor for copper thin films.47

The lengthening of the incubation time, the factor of six slowing of the net deposition rate, and the slow change in surface morphology with growth time suggest that VTMS is inhibiting both Cu nucleation on RuOₓ, and Cu deposition on Cu. Consistent with this view, we have separately measured the effect of VTMS on the steady state growth of copper on copper films, and find that the rate is reduced by a factor of four.

Formation of ultra-smooth films.— Alternatively, VTMS can promote the growth of copper films that are much smoother than those grown in the absence of VTMS. This result can be achieved by first initiating growth using the precursor alone for 1 minute to deposit nuclei with an areal density of ∼ 4.7 × 10^10 cm^-2 and a rms roughness of ∼ 0.6 nm. Additional copper is then deposited in the presence of 1 mTorr of VTMS. A 13.5 nm thick film produced in this manner has a rms surface roughness of only 1.4 nm (Figure 2b). Four-point probe measurements (after exposure to air) indicate a sheet resistance of 1.9 Ω/□, which is sufficient to serve as the seed layer for copper electroplating in microelectronics fabrication. For comparison, growth of similarly thick film without the inhibitor has a significantly larger rms surface roughness, 2.8 nm, and a similar sheet resistance (Figure 3).

Rate model of inhibition effect.— As mentioned earlier, the steady state growth rate of copper decreases as a function of VTMS pressure, Figure 4. Interestingly, the rate does not fall toward zero, but tends toward a saturated rate of ∼ 0.3 nm/min for VTMS pressures above 1 mTorr. Similar behavior was found48 for the growth of TiB₂ using the inhibitor dme, a component of the precursor Ti(BH₄)₃(dme).

The incomplete inhibition can be explained in a kinetic model that takes into account the competitive adsorption equilibria for precursor and for VTMS together with the saturation of available surface sites (Figure 4).

The pre-equilibrium approximation for Cu growth from Cu(hfac)VTMS considers that the local equilibria corresponding to Eq. 1, 2, 3, and 5 are fast but that the disproportionation reaction (Cu deposition) corresponding to Eq. 4 is slow, which is consistent with the reported literature for metallization from Cu(hfac)VTMS. Desorption of VTMS and of Cu(hfac)₂ is known to be facile.57,58

\[
\text{Cu(hfac)}_\text{Lg} \leftrightarrow \text{Cu(hfac)}_\text{ads} \\
\text{L}_\text{g} \leftrightarrow \text{L}_\text{ads}. \\
\text{Cu(hfac)}_\text{ads} \leftrightarrow \text{Cu(hfac)}_\text{ads} + \text{L}_\text{ads} \\
\text{Cu(hfac)}_\text{ads} \leftrightarrow \text{Cu(hfac)}_\text{ads} + \text{L}_\text{ads}
\]

\[
2\text{Cu(hfac)}_\text{ads} \leftrightarrow \text{Cu} + \text{Cu(hfac)}_\text{ads}.
\]

\[
\text{Cu(hfac)}_\text{ads} \leftrightarrow \text{Cu(hfac)}_\text{ads} + \text{L}_\text{ads}
\]

The functional form of the Cu growth rate vs. inhibitor pressure can be obtained by adding the assumption that the inhibitor coverage is limited to a maximum surface concentration \([\text{VTMS}]_{\text{max}}\). This in turn limits the inhibitor effect, such that the growth rate is finite at high inhibitor pressure. We signal that this is certainly not the only possible model that is capable of fitting the data; however, it is the simplest and most physically obvious model we are aware of that rationalizes the experimental observations and requires no additional mechanisms. The fitting parameters \(\alpha\) and \(\beta\) correspond to the desorption activation energy of VTMS from the Cu growth surface and the saturated growth rate, respectively.

**Figure 3.** The height distribution functions, derived from AFM data, for films in which the VTMS inhibitor is used only during the growth stage (black curve) and film in which precursor only is used during both the nucleation and growth stages (red curve). For the latter, the substrate temperature and precursor pressure are the same as for Figure 2; \(t_{\text{growth}} = 9\) min, thickness 20 nm. \(R_q\) is the rms surface roughness.

**Figure 4.** Comparison of experimental growth rate vs. VTMS pressure (squares) with model calculations (solid line) using the parameters given in the text.
A first estimate of $\beta$ can be made from the ratio of experimentally measured $GR_{\text{max}}$ to $GR_{\text{Sat}}$. Using $\alpha = 1.4$ from the fit, $\delta = 0.05$ from the experiment, and assuming $N_s = 10^{19} \text{ m}^{-2}$ and $v = 10^{12} \text{ Hz}$, the VTMS desorption energy $E_d \sim 0.75 \text{ eV}$ is estimated. The reported values for VTMS desorption are 0.61 to 0.65 eV. This is comparable to the estimate considering that the values of the constants influence the desorption activation energy as $kT$ times their natural logarithm, hence, a factor of 10 uncertainty in the constants would change the estimate by 0.1 eV.

Conclusions
We have demonstrated that VTMS serves as a growth inhibitor for copper CVD from the Cu(hfac)VTMS precursor. On air-exposed Ru substrates, the VTMS affects the rates of nucleation and of steady state growth. Use of the VTMS inhibitor during the nucleation stage leads to the growth of discrete Cu islands with a relatively uniform size distribution. By contrast, nucleation in the absence of inhibitor, followed by growth with a co-flow of the inhibitor, affords continuous films with a rms roughness of $<1.5 \text{ nm}$. The former could be of interest in the production of textured films for photonic applications; the latter could be useful for the deposition of very thin and very smooth copper films for use in the microelectronics industry.

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