Area selective CVD of metallic films from molybdenum, iron, and ruthenium carbonyl precursors: Use of ammonia to inhibit nucleation on oxide surfaces

Elham Mohimi and Zhejun V. Zhang
Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, 1304 W. Green St., Urbana, Illinois 61801

Sumeng Liu
Department of Chemistry, University of Illinois at Urbana Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801

Justin L. Mallek
MIT Lincoln Laboratory, 244 Wood Street, Lexington, Massachusetts 02420

Gregory S. Girolami
Department of Chemistry, University of Illinois at Urbana Champaign, 600 South Mathews Avenue, Urbana, Illinois 61801

John R. Abelson
Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, 1304 W. Green St., Urbana, Illinois 61801

(Received 22 January 2018; accepted 18 June 2018; published 5 July 2018)

The authors demonstrate that the addition of an ammonia coflow during the chemical vapor deposition of MoCxNy, Fe, or Ru thin films at $200^\circ C$ from the metal carbonyl precursors Mo(CO)$_6$, Fe(CO)$_5$, or Ru$_3$(CO)$_{12}$ affords area-selective growth: film grows readily on titanium metal or vanadium nitride substrate surfaces, but no nucleation occurs on air-exposed SiO$_2$, TiO$_2$, Al$_2$O$_3$, or MgO within the investigated times of 1–2 h. By contrast, in the absence of ammonia, nucleation and deposition on these oxide surfaces can either be slow or rapid, depending strongly on the oxide surface preparation. NH$_3$ is also the source of N in MoCxNy, which has a resistivity of $\rho = 200 \mu\Omega$ cm and becomes superconducting at a critical temperature of 4 K. The authors hypothesize that the passivating effect of NH$_3$ on oxide surfaces involves site blocking to prevent precursor adsorption, or an acid–base interaction to stabilize surface-bound metal subcarbonyl intermediates, or a combination of these mechanisms. A key finding is that surface selective growth is often crucially dependent on the sample history of the substrate, which must be specified in detail if reproducible results are to be obtained. Published by the AVS. https://doi.org/10.1116/1.5023236

I. INTRODUCTION

Many nanoscale electronic devices are fabricated by top–down approaches involving blanket film deposition, lithographic patterning, and etching steps. However, as feature sizes shrink toward 10 nm, pattern registry becomes very difficult. One bottom–up method that in principal can guarantee pattern registry is area selective deposition (ASD), in which a thin film grows selectively, for example, on metallic but not on dielectric surfaces. ASD builds upon the previously established pattern on the substrate and obviates the need for additional patterning and etching steps. In chemical vapor deposition (CVD) or atomic layer deposition (ALD) processes, selective growth occurs when film nucleation is inherently difficult on some surfaces (usually, oxides) but not on others, or when a surface is rendered passive by chemical termination such as by the deposition of a dense self-assembled monolayer.

In ASD processes, selectivity is lost when nucleation commences on the intended nongrowth surface, which often occurs at defects in the surface or in the passivation treatments. One way to achieve a robust ASD process is to ensure that no nucleation occurs on the oxide over the total time needed to deposit the desired film thickness on the metal. In CVD, we have previously demonstrated that in some systems this outcome can be accomplished by continuously injecting a suitable neutral molecular inhibitor along with the precursor: the inhibitor allows film growth to occur on metal surfaces, but reduces the nucleation rate on oxide surfaces essentially to zero. Specifically, we showed that Cu growth from the hexafluoroacetylacetonate, vinyltrimethylsilane [Cu(hfac)VTMS] precursor on oxide surfaces can be inhibited by coinjecting additional VTMS. On both metal and dielectric surfaces, the effect of added VTMS is to promote the associative desorption of Cu(hfac) intermediates in the form of the Cu(hfac)VTMS precursor on oxide surfaces can be inhibited by coinjecting additional VTMS. On both metal and dielectric surfaces, the effect of added VTMS is to promote the associative desorption of Cu(hfac) intermediates in the form of the Cu(hfac)VTMS precursor.

Here, we report a different example of the inhibitor approach to ASD, in which CVD film growth from molybdenum, iron, and ruthenium carbonyl precursors can be

---

*Electronic mail: abelson@illinois.edu*
completely suppressed on many oxide surfaces by injecting NH$_3$, a strong Lewis base, along with the precursor. In the absence of ammonia, selective deposition from these carbonyl precursors on metal substrates but not on oxides can sometimes be achieved, but the selectivity depends capriciously on the oxide substrate history; furthermore, even when selectivity is seen, it is often quickly lost as deposition is continued. We show that the presence of NH$_3$ completely eliminates the nucleation of metal on many oxide surfaces for the 1–2 h duration of the experiments performed. At the same time, film nucleation and growth occur readily on metallic seed layers despite the presence of NH$_3$ in the feed gas, i.e., the approach affords perfect selectivity. Ammonia thus lengthens the nucleation delay on oxide surfaces, and makes the delay far less dependent on the substrate history.

We hypothesize that the mechanism by which ammonia promotes ASD from these metal carbonyl precursors is quite different than in the Cu(hfac)$_2$(VTMS) system: instead of promoting redesorption of the precursor, ammonia changes the surface in such a way to prevent the precursor from converting to film. The mechanistic possibilities are that: (1) NH$_3$ adsors to an aerial coverage that is sufficient to site block the process of precursor adsorption; or (2) the adsorption of NH$_3$ stabilizes surface-bound M(CO)$_x$ intermediates with respect to further loss of CO ligands and thus prevents them from converting to a metallic film. A combination of these mechanisms could also be operative. In Sec. IV, we interpret our results in the context of relevant studies of oxide surfaces from the heterogeneous catalysis literature.

An important lesson of our studies is that the ability to carry out ASD reproducibly often requires that one use substrates with identical sample histories. This must be, because ASD depends on the control of phenomena such as precursor adsorption, precursor activation, nucleation that are intrinsically surface-sensitive.

II. EXPERIMENT

CVD experiments are performed in a cold wall high vacuum chamber described elsewhere. We explore the behavior of carbonyl precursors of Mo, Fe, and Ru in the presence of NH$_3$. The pressure of Mo(CO)$_6$ is controlled by setting the temperature of the precursor reservoir in the range of 20–40°C; this precursor flows under its own vapor pressure (i.e., with no carrier gas) through the delivery tube, which is heated to 55°C to avoid condensation of sublimed precursor. The precursor pressure in the chamber is 0.01–0.03 mTorr. The Fe(CO)$_5$ precursor is cooled to 0°C in an ice bath, and the precursor pressure is controlled by a needle valve to establish a partial pressure in the chamber of 0.01 mTorr. The Ru$_3$(CO)$_{12}$ precursor is heated in the reservoir to 85°C and is delivered to the chamber by means of 50 sccm of Ar as a carrier gas. Research grade ammonia (99.9992%) is delivered through a separate gas line, regulated by a mass flow controller to establish a partial pressure of 1–20 mTorr in the chamber. All the gas delivery lines are pointed toward the substrate; hence, the local fluxes are higher than those suggested by the isotropic background pressure.

The substrate is heated radiatively to a temperature of 130–225°C, as measured by a K-type thermocouple attached to the sample holder. The following substrates are used with no cleaning or other pretreatment following their preparation in other facilities on our campus (all samples have been exposed to lab air for a period of days to weeks, except as noted): (1) 300 nm thermal SiO$_2$ (microelectronic grade)/Si; (2) 10 nm e-beam Ru/SiO$_2$/Si; (3) 50 nm CVD MgO/Si; (4) 8 nm ALD Al$_2$O$_3$ (doped with 5% TiO$_2$/Si (precursors are trimethylaluminum and tetrakis(dimethylamido)titanium and water); (4) TiO$_2$/Ti/Si prepared by e-beam depositing 20 nm Ti and then oxidizing under ozone in air for 1 h; (5) 60 nm of e-beam Ti/Si; and (6) 1–2 nm vanadium nitride (VN)/thermal SiO$_2$ grown by CVD from tetrakis(dimethylamido)vanadium and ammonia at 200°C. The Ru and Ti films are exposed to air before use and thus are surface-oxidized; for example, XPS confirms the presence of RuO$_2$ on the surface of the Ru films. For Ti, freshly prepared samples are exposed to air as briefly as possible and promptly transferred from the e-beam system to the CVD system (“fresh Ti”); we find that Ti films that have been exposed to lab air for several days to form a thicker oxide overlayer (“aged Ti”) behave quite differently. We note here that our results pertain only to substrates prepared as described above; samples of these same oxides prepared by following other protocols or with different sample histories may not give identical results. For example, nucleation on SiO$_2$ annealed in O$_2$ at 900°C for 1 h cannot be stopped by NH$_3$.

Film thickness and microstructure are determined from cross-sectional and top-view SEM images. Compositional depth profiles are obtained by AES with sputtering. The onset of nucleation and the growth are monitored by real-time spectroscopic ellipsometry; for each substrate-film combination, we report change in the ellipsometric angle delta at a single energy, 2.65 eV, which provides the greatest sensitivity to the onset of nucleation, as discussed previously. Ex situ AFM (2 × 2 μm scan area), RBS, TOF-SIMS, and high resolution XPS are used to detect the formation of nuclei on the nongrowth surfaces.

To rule out the effect of gas scattering, i.e., that the partial pressure of NH$_3$ reduces the flux of precursor to the growth surface, a screening experiment is performed by replacing NH$_3$ by Ar. (Because the mass of Ar is greater than that of NH$_3$, we expect that the effect, if any, will be slightly stronger than that of NH$_3$.) The steady state growth rate of the MoC$_x$ films decreases by approximately 20% upon addition of Ar. In this work, we will assume that the modest reduction in precursor flux due to gas scattering is not the explanation for the dramatic increase in nucleation time upon addition of NH$_3$.

III. RESULTS

A. Control studies of deposition from Mo(CO)$_6$ on metal oxide surfaces

We initially investigated the chemical vapor deposition of molybdenum-containing films from the carbonyl precursor

Mo(CO)$_6$ on different oxide substrates in the absence of any coreactant.\textsuperscript{18,19} The onset temperature for Mo(CO)$_6$ thermolysis is 150°C. For growth at 200°C from 0.010 mTorr of precursor, there is a relatively short nucleation delay of 5 min on SiO$_2$, after which growth reaches a steady-state rate of roughly 8 nm/min (Fig. 1). Growth at 200°C affords a molybdenum carbide film with 15 at. % oxygen content. When a film is grown under identical conditions and capped \textit{in situ} with HfB$_2$ (which protects against postgrowth oxidation in air), the oxygen content is only slightly less, 13 at. %; this result indicates that the oxygen in the film originates mostly from carbonyl decomposition and not from postgrowth air exposure, in agreement with previous studies.\textsuperscript{18,20,21} The film surface is rough, which is indicative of sparse nucleation [Fig. 2(b)].\textsuperscript{22,23}

Under the same experimental conditions, except that the surface is changed from SiO$_2$ to MgO or Al$_2$O$_3$, no change in the ellipsometry signal occurs, i.e., no nucleation takes place, for growth times of 22 and 35 min, respectively, after which a small deviation indicates the onset of nucleation (Fig. 1 inset). After 20 min of attempted growth, high-resolution XPS and RBS measurements do not detect Mo on the MgO or Al$_2$O$_3$ substrates; and the surface roughness of the Al$_2$O$_3$ substrate is identical to that of the bare substrate.

In contrast to the short nucleation delay seen on SiO$_2$ and the longer delays seen on MgO and Al$_2$O$_3$, there is no nucleation delay on RuO$_2$ or TiO$_2$ surfaces; a 70 nm thick film grows within 9 min, with a growth rate of 8 nm/min. Thus, MoCx growth occurs promptly on RuO$_2$ and TiO$_2$; and after a short delay on SiO$_2$, but there is a significant nucleation delay (barrier) on Al$_2$O$_3$ and MgO surfaces, when prepared as described in Sec. II.

We briefly note here that the results above are for substrates prepared exactly as described in the Experimental section; substrates with different sample histories may behave differently. This caveat implicitly applies to the results given in the rest of this paper.

**B. Inhibition of nucleation and growth from Mo(CO)$_6$ on oxide surfaces by ammonia**

The short nucleation delay on SiO$_2$ substrates at 200°C is dramatically lengthened when ammonia is coflowed with the Mo(CO)$_6$ precursor. For example, at 0.01 mTorr of precursor and 1.8 mTorr of ammonia on SiO$_2$ at 200°C, no nucleation is detected even after 120 min, as compared with deposition of nearly 200 nm after 30 min in the absence of ammonia [Figs. 2(a) and 2(b)]. AFM images of samples exposed to Mo(CO)$_6$ and ammonia for 0.5, 1, and 2 h of exposure to the flow of precursor and ammonia as in part (a).

When the ammonia coflow experiment is repeated at a higher precursor pressure, 0.025 mTorr, while keeping the ammonia pressure at 1.8 mTorr, some nucleation can be detected after 15 min. But nucleation at the higher precursor pressure can be inhibited simply by increasing the pressure...
of ammonia: in a third experiment at a precursor pressure of 0.025 mTorr and an ammonia pressure of 3.7 mTorr, no nucleation occurs after 60 min. AFM detects no nuclei, and XPS shows no molybdenum.

Similar results are seen on TiO2 at 200 °C: in contrast to the rapid nucleation and growth that take place on TiO2 from 0.020 mTorr of Mo(CO)6 in the absence of ammonia, there is no nucleation when 3.5 mTorr of ammonia is coflowed under these conditions, even after 30 min. On RuO2, coflow of ammonia considerably slows nucleation from Mo(CO)6 but does not completely suppress it: after a RuO2 surface is exposed to 200 °C to 0.025 mTorr precursor and 3.7 mTorr ammonia for 30 min, AFM detects about 10 nuclei/μm².

We also investigated the effect of ammonia on MgO and Al2O3, two surfaces for which there is a significant nucleation delay (intrinsic selectivity) when exposed to Mo(CO)6 at 200 °C in the absence of ammonia. On these two surfaces, coflow of ammonia significantly extended the nucleation delay: even after 40 and 65 min of exposure, AFM and ellipsometry (Fig. 3) show the absence of any nuclei.

AES depth profiles show that the films deposited from Mo(CO)6 in the presence of ammonia (both in this section and later in this paper) contain 20 at. % nitrogen and 21 at. % carbon: the oxygen content is 3–4 at. % after air exposure. Thus, the film composition is best described as MoC0.36N0.35. The significant nitrogen content is consistent with the known ability of molybdenum carbide and molybdenum nitride surfaces to promote ammonia decomposition at this deposition temperature.24-26 The MoC0.36N0.35 samples in this study are metallic and have room temperature resistivities of 200–300 μΩcm. This material is also superconducting, with a critical temperature of 4 K; detailed studies of this property are described elsewhere.27

C. Nucleation and growth from Mo(CO)6 on metal and metal nitride surfaces in the presence of ammonia

In contrast to the above results—and highly significant in the context of surface-selective deposition—we find that ammonia does not stop nucleation and growth from Mo(CO)6 on in situ grown vanadium nitride and a freshly e-beam deposited titanium film bearing a thin oxide overlayer. When these substrates are exposed to 0.025 mTorr of Mo(CO)6 at 200 °C, film grows with no detectable nucleation delay at a rate of 12 nm/min. Under the same conditions but with coflow of 3.7 mTorr of NH3, there is also no nucleation delay on VN but the film grows more slowly: 19 nm of film deposits during a 20 min growth time. On a freshly prepared Ti substrate bearing only a thin oxide overlayer, there is a short nucleation delay of 5 to 20 min in the presence of a coflow of 3.7 mTorr of NH3, but after that film grows steadily.

The ability of Mo(CO)6 to nucleate and grow on some surfaces but not on others in the presence of NH3 suggests these differences can be exploited to achieve surface-selective growth, a topic to which we now turn.

D. Area-selective growth on patterned substrates and bottom-up filling

On a patterned substrate of fresh Ti/SiO2, growth from 0.025 mTorr Mo(CO)6 and 3.7 mTorr ammonia at 200 °C affords film only on the metallic areas of the pattern, with no deposition on oxide as evidenced by Auger elemental mapping (Fig. 4). This perfectly selective growth process can also be used to affect the bottom-up filling of trenches and vias. When a pattern of vias consisting of SiO2 sidewalls and a Nb film on the via bottoms is exposed to the same growth conditions as above, growth occurs only at the base of the via with no nucleation on the sidewalls or top surface (Fig. 5).

E. Inhibition of nucleation and growth from Mo(CO)6 on native oxide surfaces by ammonia

Many nonoxide surfaces form native oxide overlayers when exposed to air; for example, silicon nitride forms a silicon-rich and nitrogen-depleted native oxide that is terminated by Si-OH sites, similar to those present on SiO2 surfaces.28 Consistent with this finding, Si, SiN, Ti, and TiN substrates covered with a sufficiently thick overlayer of their native oxides respond to ammonia as other oxide surfaces do: thus, 3.7 mTorr ammonia completely inhibits nucleation.

Fig. 4. (Color online) (a) SEM image of patterned substrate with fresh Ti on the upper left and SiO2 on lower right; (b) Auger elemental map of Mo (upper left). The substrate had been exposed to 0.025 mTorr of Mo(CO)6 and 3.7 mTorr of NH3 at 200 °C. Growth time is 60 min.
from 0.025 mTorr of Mo(CO)6 at 200°C. For example, whereas Mo(CO)6 deposits onto freshly prepared Ti surfaces in the presence of ammonia (as described above), we find that deposition is strongly inhibited on a Ti surface that has been left in air for several days.

This result raises the possibility that selective inhibition of growth from a carbonyl precursor on Si, SiN, Ti, TiN, and potentially other nonoxide substrates, can be achieved by first forming a coat of native oxide. After selective deposition on other surfaces in the presence of ammonia, the native oxide can be etched off or chemically reduced to return the surface to its original state.

F. Process window and reversibility of inhibition on oxide surfaces by ammonia

We find that the temperature window for inhibition of CVD from Mo(CO)6 on thermal SiO2 is approximately 150–210°C for ammonia pressures within the mTorr range. At 150°C and 0.02 mTorr Mo(CO)6 pressure, a relatively small ammonia pressure of 1.5 mTorr is enough to inhibit growth on SiO2 altogether. In contrast, at 225°C using 0.02 mTorr precursor and a higher ammonia pressure of 9 mTorr, nucleation occurs after a 13 min delay. We have not investigated whether even higher NH3 pressures can again inhibit growth.

Interestingly, when the ammonia flow to the growth chamber is stopped during a CVD experiment, nucleation occurs within a few seconds on the substrates such as RuO2, TiO2, and SiO2 which exhibit little intrinsic nucleation delay. This result suggests that ammonia inhibition is a reversible process. The mean residence time of ammonia on SiO2, as estimated from the desorption energy of 0.43 eV, is \( \sim 1.3 \times 10^{-8} \) s at 150°C; thus, the finding that the surface becomes active for nucleation upon interruption of the ammonia coflow is consistent with the known ammonia desorption energy.

G. Selective growth of Fe from Fe(CO)5 and of Ru from Ru3(CO)12 in the presence of ammonia

We have briefly investigated whether ammonia can inhibit nucleation and growth on metal oxide surfaces from other metal carbonyl precursors. On thermal SiO2, 0.01 mTorr of Fe(CO)5 alone affords a high coverage of islands >100 nm tall after 9 min at 130–150°C (Fig. 6); under the same conditions except with a coflow of 10–18 mTorr of ammonia, AFM indicates that no nucleation occurs at all at 130 and 150°C during a 20 min experiment (supplementary material, Fig. S1). High resolution XPS detects no iron on the substrate.

On MgO substrates, growth from 0.01 mTorr Fe(CO)5 in the absence of ammonia is characterized by a long nucleation delay, over 40 min at 150°C, as evidenced by in situ ellipsometry and ex situ high resolution XPS. The longer nucleation delay on MgO versus SiO2 in the absence of ammonia is consistent with the results reported above for Mo(CO)6.

In contrast, Fe deposits rapidly from Fe(CO)5 on titanium metal and vanadium nitride surfaces, even in the presence of ammonia. For example, a 50 nm thick Fe film grows in 20 min on a VN seed layer or on fresh Ti at 130°C using 0.01 and 10 mTorr of precursor and ammonia, respectively. An Auger depth profile indicates incorporation of 3 at. % nitrogen in the Fe film, along with 2 at. % carbon and 1 at. % oxygen. On a SiO2 substrate onto which Ti has been pattern deposited, Fe growth occurs only on Ti, with no Fe detected on the bare SiO2 regions by AES.

Ru CVD from Ru3(CO)12 behaves in the same manner as Fe(CO)5. At 150°C in the absence of ammonia, nucleation and growth occur readily on SiO2 [Fig. 7(a)]. A coflow of 10 mTorr ammonia completely shuts down nucleation [Fig. 7(b)], whereas Ru nucleation and growth in the presence of ammonia occur easily on the fresh Ti and VN surfaces.

Finally, RBS studies of the SiO2, TiO2, MgO, and Al2O3 surfaces exposed to Mo(CO)6, Fe(CO)5, and Ru3(CO)12 in the presence of ammonia under the above conditions confirm the absence of detectable amounts of metal. Selected samples were also analyzed by TOF-SIMS to determine how much Mo, Fe, or Ru metal (if any) had been deposited on SiO2 substrates in the presence of ammonia, and in the absence of ammonia. The metal/substrate count ratios in all cases were less than 0.001, confirming the highly effective inhibition process investigated here (details in the supplementary material, Table S1).
We find that the reaction of Mo(CO)$_6$ on acidic oxide surfaces in the absence of ammonia leads to rapid nucleation and growth of MoO$_x$C$_y$ films. Consistent with this finding, Mo(CO)$_6$ dissociatively adsorbs on the (100) face of hydroxylated TiO$_2$ above $-50^\circ$C. The latter study reported that no stable subcarbonyls were detected at this temperature, and that the deposit consisted of molybdenum particles; however, the XPS binding energy is also consistent with the presence of a variety of molybdenum carbide phases, whose presence is far more likely on chemical grounds. In contrast, on basic surfaces, TPD experiments suggest that stable subcarbonyls are formed which do not further react until much higher temperatures. For example, on Al$_2$O$_3$, Mo(CO)$_6$ reacts to form film only above $400^\circ$C. TPD experiments show that Mo(CO)$_6$ loses CO in two steps, each step involving desorption of three CO molecules per precursor molecule; this result suggests that stable adsorbed Mo(CO)$_3$ species are formed after the first step, which lose the remaining three CO groups only in the second step at $400^\circ$C, a higher temperature than those in the present study.

On acidic oxides such as SiO$_2$, Ru$_3$(CO)$_{12}$ reacts with surface OH groups to form the grafted cluster H$_2$Ru$_3$(CO)$_{11}$(SiO$_3$), which decarbonylates completely upon being heated to $200^\circ$C. On strongly basic oxides such as MgO, Ru$_3$(CO)$_{12}$ reacts with OH groups to form the stable anionic carbonyl-ruthenate species [$H]$Ru$_3$(CO)$_{11}$$^-$, which decarbonylates completely only at temperatures above $350^\circ$C. On the mildly basic oxide La$_2$O$_3$, adsorption of Ru$_3$(CO)$_{12}$ generates mononuclear (dicarbonyl) ruthenium species, which decarbonylate only above $250^\circ$C. Similar results are reported for Fe(CO)$_5$, which generates the thermally robust anionic cluster [HFe$_3$(CO)$_{11}$]$^-$ on basic oxides.

According to the heterogeneous catalysis literature, the reaction pathway of metal-carbonyl precursors such as Cr(CO)$_6$, W(CO)$_6$, Co$_2$(CO)$_8$, and Re$_2$(CO)$_{10}$ depends strongly on the degree of hydroxylation of the oxide surface and on the acid-base character of the oxide. The temperature at which these precursors completely decarbonylate is lower on acidic oxides than on basic oxides.

**IV. DISCUSSION**

**A. Reactivity of metal carbonyls on oxide surfaces**

We have shown that, at relatively low temperatures in the absence of ammonia, CVD from metal carbonyls shows little or no nucleation delay on some oxides (such as SiO$_2$, TiO$_2$, and RuO$_2$) but longer nucleation delays on other oxides (such as MgO and Al$_2$O$_3$), when these oxide surfaces are prepared as described in the Experimental section. Our findings are consistent with studies of the formation of metal nanoparticle catalysts on oxide supports from metal carbonyl precursors at similar temperatures. Molybdenum and its compounds constitute a well-known group of heterogeneous catalysts for the dehydrogenation and metathesis of alkenes; compounds constitute a well-known group of heterogeneous catalysts for the dehydrogenation and metathesis of alkenes; the chemistry and kinetics of catalyst formation have been studied extensively.

Oxide surfaces, unless vacuum annealed at high temperature, are always hydroxylated because the -OH termination lowers the surface energy. The character of the -OH groups can, however, be either acidic or basic; a hydroxyl group becomes more acidic with an increase in the covalency (especially the pi bonding) of the bulk metal-oxygen bond or with an increase in the charge/radius ratio of the cation to which the hydroxyl group is bound. The average acidity can be characterized by the isoelectric point (IEP), which is the pH value of an aqueous solution needed to establish zero net charge on the oxide surface. Acidic hydroxyl groups have a negative surface charge in liquid water at neutral pH, so that the pH has to be lowered to obtain a neutral surface charge, and conversely for basic hydroxyls. The oxides SiO$_2$, RuO$_2$, and TiO$_2$ have acidic hydroxyl groups with IEPs of 2.2, 4.2, and 4–6, respectively; MgO and Al$_2$O$_3$ have basic hydroxyl groups with IEPs of 12 and 8–9, respectively. IEP values decrease slightly with increasing temperature, but in general higher temperatures will not convert basic hydroxyl groups to acidic ones.

![Fig. 7. AFM scans of Ru growth using the Ru$_3$(CO)$_{12}$ precursor on SiO$_2$ substrate: (a) at 150°C using precursor only; and (b) at 150°C with a coflow of 10 mTorr ammonia.](image-url)
only a small fraction of the total number of surface sites. In a study of Ru CVD from Ru3(CO)12 on SiO2,52 the nucleation density (~1013 sites/cm2) was 3 orders of magnitude smaller than the hydroxyl density (~1014 sites/cm2) and the temperature dependence of the nucleation density followed the same temperature dependence as the density of isolated OH groups.

A second and possibly synergistic mechanistic explanation of the effect of ammonia is that it creates conditions that disfavor the complete decarbonylation of metal carbonyl intermediates, thus preventing them from converting to metal nuclei. Ammonia could cause such an outcome in several ways: by reducing the acidity (increasing the basicity) of oxide surfaces by hydrogen bonding to the surface hydroxyl groups, or by bonding directly to the metal centers of subcarbonyl intermediates. All these factors will increase the electron richness of the metal subcarbonyl intermediates and stabilize them against decarbonylation by increasing the M-CO backbonding.

One distinction between the two mechanisms is that site blocking should prevent precursor from adsorbing to the surface, whereas the stabilization of subcarbonyl intermediates would permit some (i.e., submonolayer) precursor adsorption. Our SIMS studies show that the metal coverages in the presence of ammonia in all cases are less than 0.001, which is certainly consistent with site blocking as the main inhibition mechanism. But it may also be consistent with suppression of decarbonylation, if adsorption of precursor occurs only at a small subset (i.e., the most reactive) surface sites.

Finally, a related issue is why growth occurs on titanium metal and vanadium nitride surfaces. One possibility is that low energy empty states in the band structure could oxidize the electron-rich metal carbonyl species, thereby promoting loss of CO. It has been suggested previously that dissociation of carbonyl groups from adsorbed metal carbonyl species could be enhanced by charge transfer: thermally activated decomposition of metal carbonyls happens on Ni(100), but little dissociation has been observed on Si and Ag(110) surfaces.53 An alternative possibility is that, on surfaces that bind CO groups well,54 migration of CO ligands to the metallic surface could destabilize otherwise stable metal carbonyl species, thus initiating nucleation events. Investigations on a larger variety of metallic surfaces will be necessary to test these hypotheses.

V. SUMMARY AND CONCLUSIONS

Area selective CVD from Mo(CO)6, Fe(CO)5, and Ru3(CO)12 precursors is reported: nucleation and growth on air-exposed SiO2, TiO2, Al2O3, and MgO substrates can be inhibited by the addition of a coflow of ammonia. In all cases, we have found it possible to inhibit growth on these oxide substrates for periods of up to an hour, whereas metal film grows on conductive surfaces such as freshly deposited Ti and vanadium nitride (and to some extent on RuO2). The hypothesized mechanisms are either site blocking by NH3, or inhibition of the complete reaction (decarbonylation) of adsorbed metal carbonyl intermediate groups. This selective growth method also affords a means to achieve the bottom-up fill of deep structures, such as trenches and vias, when the sidewalls are dielectric and the bottom bears a metal nucleation layer. Finally, it is important to note that ASD is often crucially dependent on the sample history of the substrate, which must be specified in detail if reproducible results are to be obtained.

ACKNOWLEDGMENTS

The financial support from MIT-Lincoln Laboratories is gratefully acknowledged. G.S.G. acknowledges support from the National Science Foundation under Grant Nos. CHE 1362931 and CHE 1665191. J.R.A. acknowledges support from the National Science Foundation under Grant No. 1410209. Ex situ materials characterization was carried out in the Center for Microanalysis of Materials at the Frederick Seitz Materials Research Laboratory, University of Illinois.


JVST A - Vacuum, Surfaces, and Films
33. Y. Liu et al., Chem. Commun. 52, 5030 (2016).
34. Y. Ma, G. Guan, X. Hao, J. Cao, and A. Abudula, Renewable Sustainable Energy Rev. 75, 1101 (2017).
55. See supplementary material at https://doi.org/10.1116/1.5023236 for AFM image of Fe nucleation and TOF-SIMS data for metal/substrate ratio.