Area-selective chemical vapor deposition of cobalt from dicobalt octacarbonyl: Enhancement of dielectric-dielectric selectivity by adding a coflow of NH₃

The authors describe the enhancement of the area-selective chemical vapor deposition of cobalt films on one oxide surface over another from the precursor Co₂(CO)₈ by addition of the nucleation inhibitor ammonia (NH₃). In the absence of an NH₃ coflow, the Co₂(CO)₈ precursor exhibits a weak intrinsic selectivity: at 70 °C, Co nucleates quickly on Al₂O₃ but more slowly on SiO₂. The addition of an NH₃ coflow, however, greatly amplifies the selectivity between different oxide surfaces. Thus, NH₃ significantly inhibits nucleation on acidic oxides such as SiO₂ and WO₃ but has little effect on more basic oxides such as Al₂O₃, HfO₂, and MgO. Comparison of growth on fully hydroxylated and dehydroxylated SiO₂ suggests that hydroxyl groups are the nucleation sites that are affected by the addition of NH₃. The mechanism of nucleation appears to be disproportionation of Co₂(CO)₈ to Co²⁺ (the intermediate that leads to nucleation) and Co(CO)₄⁻: this disproportionation occurs readily on basic oxides but not on acidic oxides. The addition of NH₃ has little effect on Co nucleation on basic oxides, probably because ammonia binds poorly to such surfaces, but NH₃ greatly retards nucleation on acidic oxides such as SiO₂; the authors propose that the latter result is either a site blocking effect or the result of conversion of Co²⁺ to inactive Co(NH₃)ₓ²⁺ species.

Nucleation of cobalt is facile on gold (a very unreactive metal) even in the presence of NH₃. The authors have found, however, that the deposition of Co on tungsten can be inhibited by exposing the surface briefly to ozone; no deposition occurs on the resulting thin tungsten oxide overlayer from Co₂(CO)₈ in the presence of NH₃. In other words, this thin oxide overlayer affords the same selective inhibition behavior as seen on bulk WO₃. In this way, both metal-on-metal and metal-on-oxide selectivity can be achieved. Cobalt films grown in the absence and presence of ammonia have resistivities of 11–20 and 15–25 μΩ cm, respectively.

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I. INTRODUCTION

Many nanoscale electronic devices are fabricated by a top-down approach involving blanket thin film deposition followed by photolithographic patterning and etching steps. However, as feature sizes shrink toward or below 10 nm, edge placement errors in photolithography make it difficult to avoid unacceptable misalignments between layers. For this reason, bottom-up patterning methods that automatically result in pattern registry are becoming increasingly attractive. One such bottom-up method is area-selective deposition (ASD) in which, for example, growth occurs on metallic surfaces but not on dielectric surfaces. As a result, ASD reduces production costs by obviating the need for additional patterning and etching steps. Another potential application of ASD is dual damascene metallization, which requires void-free filling of vias with a high aspect ratio. ASD can meet this need by bottom-up growth, which occurs when a film nucleates on the bottom of the feature but not on the sidewalls. Most area-selective deposition
processes developed so far concern selective deposition of a metal on metal or an oxide on oxide; only a few studies have dealt with selective deposition of other material combinations, such as metal on oxide or metal on one oxide but not on another.

No deposition process is area-selective indefinitely; even on the most unreceptive surfaces, nucleation and growth will eventually occur. Therefore, given a pair of surfaces, a deposition can be considered as "more selective" if there is a larger difference in the nucleation delay. But if steady-state growth after nucleation is slow, then a relatively little film can be grown selectively even if the nucleation delay times differ significantly. As a result, a better metric for selectivity for a particular deposition process is not the difference in nucleation delay but how thick a film can be grown on one surface versus another.

Accordingly, a useful metric for selectivity is the parameter $S$, which is defined as

$$S = \frac{n_{GS} - n_{NG}}{n_{GS} + n_{NG}},$$

where $n_{GS}$ and $n_{NG}$ are the number of atoms deposited per unit area on the growth surface and the nongrowth surface, respectively. The $n$ values are equivalent to film thickness under the assumption of constant atomic density. If $S = 1$, then the deposition is perfectly selective and there is no deposition on the nongrowth substrate; if $S = 0$, then the deposition is nonselective. It is sometimes possible to increase $S$ by employing a cyclic deposition process in which a light etching step on each cycle is used to remove stray nuclei or metal atoms from the nongrowth surface.

There is significant and growing interest in cobalt, especially in the context of applications in interconnects (ICs) at <10 nm node. The reason for this interest is that cobalt has a low bulk resistivity (≈6 μΩ cm), adheres strongly to Cu,6 and has a low solubility in Cu. A Co capping layer significantly improves the lifetime of the copper lines in modern ICs by reducing Cu electromigration without unduly increasing the RC delay. Also, Co requires less or no diffusion barrier when used alone as an interconnect material, thus avoiding the increased interconnect resistivity associated with scaling down the sizes of vias in ICs.

Area-selective deposition of cobalt films has been carried out by electrodeposition14 and electroless deposition15 methods and also by atomic layer deposition (ALD)16 and CVD.17,18 Most of these studies involve selective Co deposition on a metal versus a neighboring oxide.

In the present work, we investigate the ASD of cobalt on different oxides from dicobalt octacarbonyl, Co₂(CO)₈, and investigate the effect of ammonia on the selectivity. The choice of ammonia as a selectivity enhancer was made because we have recently shown that this molecule enhances metal versus oxide ASD from Mo (CO)₆.19 As we will show, Co₂(CO)₈ behaves quite differently from Mo(CO)₆. For example, nucleation from Co₂(CO)₈ in the absence of ammonia is somewhat faster on basic oxides such as Al₂O₃ than on acidic oxides such as SiO₂, whereas in other systems, the exact opposite behavior is seen. In addition, for Co₂(CO)₈, a cfollow of ammonia has a negligible effect on the nucleation rate for deposition on Al₂O₃, but it strongly inhibits nucleation and growth on SiO₂, whereas for other metal carbonyls, ammonia slows growth on all oxide surfaces.

The net result is that ammonia enables highly selective ASD of Co from Co₂(CO)₈ on some oxide surfaces over others. In addition, the cobalt deposition process can in some cases be tuned to enable nucleation of Co on the metal but not on the oxide, or Co on the oxide but not on the metal, by taking advantage of native oxides or ozone-generated oxide overlayers.

II. EXPERIMENT

CVD experiments are performed in a cold wall high vacuum chamber described elsewhere. The precursor Co₂(CO)₈ is purchased from Sigma-Aldrich and used as received. This precursor is supplied by the vendor as a mixture with 1%–10% hexane to improve shelf life; the hexane is removed by evacuation before the first use of the precursor. The precursor is maintained in a glass container immersed in a water bath at 20 °C and delivered to the chamber without a carrier gas through a 0.4 cm i.d. stainless steel tube aimed at the substrate. These conditions supply a precursor partial pressure of 0.018 mTorr as measured in the chamber background, but the local fluxes delivered to the substrate by the effusive flow from the dosing tube are higher than those suggested by the isotropic background pressure. At higher flow rates, the local fluxes are also affected by gas scattering when the mean free path becomes smaller than the distance from the injection tube to the substrate. To maintain a nearly constant effect of gas scattering on the effusing flux of the precursor, Ar is added to maintain a total chamber pressure of 4 mTorr. Research grade ammonia (99.992%) and Ar (99.999%) are delivered into the chamber via separate mass flow controllers and delivery lines. Substrates are radiatively heated to 70 °C, as measured by a K-type thermocouple attached to the sample holder.

All substrates are degreased by washing successively with acetone, isopropyl alcohol, and de-ionized water and are then cleaned by a UV ozone treatment for 10 min before being loaded into the chamber, unless noted otherwise. In control experiments (supplementary material), we determined that UV ozone treatment can remove organic contamination due to exposure to atmosphere, which otherwise may increase the nucleation delay. The UV ozone treatment also restores hydrophilicity (Fig. S2), which is not the case when using acetone, IPA, and de-ionized water cleaning alone.22,23 The following substrates have been studied: (a) 300 nm thermal SiO₂ (microelectronic grade) on Si, (b) 10 nm ALD Al₂O₃ on Si deposited from trimethylaluminum and water; a patterned Al₂O₃/SiO₂ substrate is also fabricated by ALD of Al₂O₃ on SiO₂ that had been masked using a standard photolithography process, followed by lift-off. (c) 10 nm ALD HfO₂ on Si deposited from tetraakis(dimethylamido)hafnium and water. (d) 300 nm CVD MgO on Si deposited from magnesium NN-dimethylamidoborate and water.24 (e) 10 nm ALD TiO₂ on Si deposited from tetraakis(dimethylamido)tinanium and water. (f) 50 nm thermal WO₃ on Si fabricated by annealing an e-beam evaporated tungsten film at 400 °C in O₂ for 3 h.25 (g) Dehydroxylated SiO₂, which is obtained by annealing sample (a) at 900 °C for 2 h and cooling to room temperature in dry oxygen; the resulting substrate is immediately loaded into the CVD chamber, without further cleaning. Unlike some metal oxides, the rehydroxylation process on dehydroxylated SiO₂ is very slow in air at room temperature (typically weeks to months).27–30 so the SiO₂ surface does not rehydroxylate significantly during the few
minutes required to transfer the sample from the annealing furnace to the CVD chamber. For resistivity and growth rate measurements, the SiO2 substrates are predosed in situ with tetrakis(dimethylamino) vanadium (TDMAV) (Sigma-Aldrich) for 2 min to create a nucleation layer that minimizes the nucleation delay. The self-limiting TDMAV layer is thin (~1 monolayer), and the contribution to electrical conductivity is negligible.

Real-time spectroscopic ellipsometry (SE) is used during growth to monitor the onset of nucleation. We report the change in the ellipsometric angle $\Psi$ at a single energy, 2.65 eV, which provides the greatest sensitivity to the onset of nucleation, as discussed previously. Co2(CO)$_8$ molecules start to flow at time $t = 0$. The start of the nucleation is defined by the time at which $\Psi$ starts to change. Note that $\Psi$ is the amplitude component of the complex reflectance ratio between p and s components, which includes all interference effects between layers. Hence, for different substrates, the slope of the curve does not correspond in an intuitive way to the growth rate, i.e., the curve can have a descending or ascending slope, and may change the trend as the deposition proceeds. The area density of metal atoms is measured by X-ray fluorescence (XRF) (Shimadzu EDX7000); we report an equivalent film thickness under the assumption that the deposited cobalt has bulk density. Measurement by XRF is quite accurate with 10% random error for a film of thickness 1.5 nm. The average growth rate is determined by dividing film thickness with growth time after subtracting the nucleation delay time indicated by SE. Elemental mapping is carried out by XPS (Kratos AXIS XPS). Depth profiling of the composition is also performed by XPS (PHI 5400). Film roughness is measured by AFM (Asylum cypher). Resistivity is measured by the four-point probe method (thicknesses of films for resistivity are measured by SEM).

III. RESULTS AND DISCUSSION

Sections III A–III G will describe our studies of the area-selective deposition of cobalt from the precursor dicobalt octacarbonyl. As we previously discussed, the phenomenon of area-selective deposition is sensitive to the history of the surfaces being studied. The use of UV ozone cleaning appears to eliminate the effect of contamination due to atmosphere. Other experimental factors, such as the duration of exposure to air during sample transfer, the temperature to which a surface is heated, and how long it is kept at that temperature before deposition, are kept constant. Below, we report that the state of hydroxilation of the oxide surface is an important variable in ASD. The results below pertain to growth of cobalt on surfaces prepared as described in the experiment section; substrates pretreated in other ways may show different behavior.

A. Area-selective growth of cobalt on oxides in the absence of ammonia

We find that deposition of cobalt from Co2(CO)$_8$ at 0.018 mTorr and 70 °C on Al2O3 exhibits a short (<1 min) nucleation delay as observed by SE, followed by an increasing growth rate for 5–9 min, which is attributed to the progressive increase in surface coverage up to coalescence (Fig. 1). For longer times, the growth rate is stable at ~1.5 nm/min. In these experiments (and those conducted in the presence of ammonia to be described later), we keep the gas scattering rate approximately constant by adding a coflow of Ar such that the total chamber pressure is always 4 mTorr. In the absence of Ar, the growth rates with 0.018 mTorr of precursor flow alone are a little higher (1.7–1.8 nm/min), indicating that gas scattering effects have only a slight effect on the growth rate.

By contrast, on SiO2, no change is observed by SE during the first ~4 min, but after this time, deposition commences. Thus, at 70 °C, the deposition of cobalt from Co2(CO)$_8$ is inherently selective on SiO2 versus Al2O3 although the selectivity is lost after only ~4 min.

AFM data show that the film roughness is ~0.8 nm on Al2O3 and ~2.2 nm on SiO2 for the same film thickness of ~1.5 nm (Fig. 2). This result is consistent with the nucleation results

![FIG. 1.](image-url)
obtained by SE: the rate of nucleation relative to the rate of steady-state growth is higher on Al2O3 than on SiO2, so that, at coalescence, there is a higher density of smaller islands on Al2O3 and the resulting coalesced film is less rough.32 When the precursor pressure is 0.018 mTorr, the steady-state growth rate of cobalt is ∼1.5 nm/min (Fig. 3). The electrical resistivity of 11–20 μΩ cm for films of 40 nm thick matches the results from other groups.33,34 XPS depth profiling shows that carbon and oxygen contents of cobalt films is below the detection limit (Fig. 4).

B. Effect of ammonia on steady-state growth of cobalt

We now describe the effect of adding a coflow of ammonia on the growth of cobalt from Co2(CO)8 at 0.018 mTorr and 70 °C. Before we consider the effect on nucleation delays, we first describe the effect on the steady-state growth rate and other properties. The steady-state growth rate of 1.5 nm/min seen in the absence of NH3 slows to 0.8–1.1 nm/min at a coflow of 0.1 mTorr of NH3 and becomes constant at 0.4–0.5 nm/min for an NH3 coflow of ∼0.5 mTorr and above (Fig. 3). Thus, NH3 acts as a growth inhibitor; in several other CVD systems, we have seen similar behavior in which the growth rate is significantly slowed but not reduced to zero at high inhibitor pressures.

Films grown in the presence of ammonia have a resistivity of 15–25 μΩ cm that is marginally higher than 11–20 μΩ cm values seen in the absence of ammonia. Films grown at both conditions are XRD amorphous (Fig. S3).35 The films contain no detectable carbon and nitrogen, but there is ∼5 at. % oxygen (Fig. 4), which may account for the slightly higher resistivity seen for samples grown in the presence of NH3. The oxygen may come from the background of the chamber (10−7 Torr) during the longer growth time (slower growth rate) or from postgrowth air exposure. The absence of detectable carbon rules out the possibility that the oxygen arises by cracking of CO.

At a small coflow of NH3 (∼0.1 mTorr), the film roughness is reduced on SiO2 (Fig. S4).58 Such smoothing could arise if NH3 reduces the precursor surface diffusion rate on the bare surface, therefore preventing the formation of large islands. Alternatively, the growth rate could be more sensitive to NH3 pressure (up to the rate saturation, Fig. 3) than the nucleation rate.

C. Area-selective growth of cobalt on oxides in the presence of ammonia

When cobalt is deposited from 0.018 mTorr Co2(CO)8 at 70 °C in the presence of 4 mTorr of NH3, the nucleation delay on Al2O3 is lengthened from <1 to ∼7 min, and the nucleation delay on SiO2 is lengthened from ∼4 to 35 min [Fig. 5(a)]. Higher pressure of ammonia (∼8 mTorr) does not lengthen the delay further. This inhibition effect greatly expands the process window for selective growth on a patterned Al2O3/SiO2 substrate. When such a patterned substrate is exposed at 70 °C for 30 min to a Co2(CO)8 pressure of 0.018 mTorr and an ammonia pressure of 4 mTorr, XPS elemental mapping shows that significant cobalt deposition occurs on the Al2O3 surface but essentially none on SiO2; a clear boundary separates the two regions [Fig. 5(b)]. An XPS survey scan on the SiO2 side reveals that only a trace of cobalt (equivalent to a film of 0.05 nm thick, according to a detailed fit36) can be detected on the surface [Fig. 5(c)]. The Co film deposited on Al2O3 has a thickness of ∼9.5 nm as judged by AFM (Fig. S5).58
FIG. 4. XPS sputter depth profiles of cobalt films grown from Co2(CO)8 at 70 °C with Ar (left) and ammonia (right). Thicknesses are 52 nm and 41 nm, respectively. The difference in sputtering time is due to different ion beam settings. Insets: SEM images of the samples.

FIG. 5. (a) In situ ellipsometry parameter γ at a photon energy of 2.65 eV vs time for Co film growth from Co2(CO)8 at 70 °C on SiO2 and Al2O3 in the presence of NH3 (curves are shifted vertically to facilitate comparison). (b) XPS elemental map of cobalt (bright contrast) on a patterned substrate: lower left is Al2O3 and upper right is SiO2. Precursor pressure is 0.018 mTorr, ammonia pressure is 4 mTorr, temperature is 70 °C, and growth time is 30 min. (c) XPS survey spectrum of the SiO2 surface for the same sample as in (b).
The ability of ammonia to enhance the selectivity for nucleation and growth of Co on Al₂O₃ over SiO₂ is also seen for surfaces prepared in alternative ways: in the presence of NH₃, nucleation is strongly inhibited on SiO₂ deposited by magnetron sputtering (SiO₂ target), but nucleation occurs readily on Al₂O₃ formed by thermal oxidation of Al (Fig. S6).58

To further investigate selective nucleation on Al₂O₃ versus SiO₂, we deposited cobalt films from 0.018 mTorr of precursor and 4 mTorr of ammonia for periods of 10–40 min; the thickness is measured by XRF [Fig. 6(a)]. On Al₂O₃, growth has already started after 10 min, and the steady-state growth rate is ~0.5 nm/min; after 40 min, 15 nm of cobalt is deposited. In contrast, on SiO₂, growth begins only after 40 min.

Taken together, these results show that, for 14 nm of Co grown on Al₂O₃ under conditions above, the selectivity S (defined in the introduction) of Al₂O₃ over SiO₂ is 0.97 in the presence of NH₃ but <0.5 in the absence of NH₃ [Fig. 6(b)], i.e., selectivity is improved significantly by coflowing with NH₃.

D. Nucleation delay as a function of the oxide surface

In order to extend the observations above, we investigated the effect of an NH₃ coflow on the deposition of Co films from Co₂(CO)₈ on a variety of oxide surfaces [Figs. (5)–(7)]. For growth at 70 °C from 0.018 mTorr of Co₂(CO)₈ in the presence of 4 mTorr of NH₃, the nucleation delays decrease in the following order (as determined by ellipsometry): WO₃ (>30 min), SiO₂ (>30 min), TiO₂ (15 min), HfO₂ (10 min), Al₂O₃ (10 min), and MgO (10 min). Notably, for these oxide surfaces, there is an excellent correlation between the nucleation delay and the acidity of the surface: as judged by their isoelectric points (IEP values given in parentheses), the oxide surfaces we investigated decrease in acidity in the order: WO₃ (IEP = 1.5–2), SiO₂ (2.2), TiO₂ (4–6), HfO₂ (7.5), Al₂O₃ (8–9), and MgO (12).37 XRF studies confirm that no deposition of Co occurs before the times indicated by ellipsometry (Fig. 7).

For comparison, nucleation occurs with short delays (1–2 min) on WO₃ when deposition is conducted in the absence of NH₃ (Fig. S7).58

E. Mechanistic role of hydroxyl groups in the enhancement of cobalt deposition selectivity by ammonia

To explore the role of hydroxyl groups in the nucleation process, SiO₂ surfaces were treated in ways that are known to subtract or add hydroxyl sites. As described above, our reference

FIG. 6. (a) Film thickness vs total growth time for deposition of Co from Co₂(CO)₈ at 70 °C on Al₂O₃ and SiO₂ substrates in the presence of NH₃. (b) Selectivity S for preferential growth on Al₂O₃ over SiO₂ substrates vs Co film thickness on Al₂O₃, both with and without a coflow of NH₃.

FIG. 7. In situ ellipsometry parameter Ψ, at a photon energy of 2.65 eV, vs time for Co film growth on acidic oxides (WO₃ and SiO₂) and on basic oxides (TiO₂, HfO₂, Al₂O₃, and MgO) in the presence of NH₃. Growth temperature is 70 °C and NH₃ pressure is 4 mTorr. The thicknesses are measured by XRF.
surface, a 300 nm thermal SiO2/Si substrate that is prewashed and cleaned by UV ozone treatment, shows a nucleation delay of ∼4 min in the absence of ammonia and ∼35 min in its presence.

First, a fully dehydroxylated SiO2 surface was prepared by heating a previously prepared SiO2/Si sample to 900 °C in dry oxygen. On this surface, Co nucleation is rapid:38 in the absence of NH3, it occurs after ∼2 min (and the film is 3.9 nm thick after 5 min); in the presence of NH3, nucleation is delayed and begins after ∼10 min (and the film is 6 nm thick after 30 min) (Fig. 8). Second, a dehydroxylated surface was rehydroxylated by dipping it in a piranha solution at 80 °C for 10 min. This process is reported to afford a higher density of hydroxyl groups compared to the original SiO2 surface (before dehydroxylation).39 On the rehydroxylated surface, nucleation is suppressed by NH3 to an even greater degree than on the original surface, and no cobalt is deposited even after 60 min (Fig. 8). An AFM image (Fig. 8, inset) shows no difference between this exposed surface and a fresh substrate.

These results indicate that (1) the chemically reactive strained siloxane rings, which are present on highly dehydroxylated SiO2 surfaces,39 are good nucleation sites for Co2(CO)8; (2) nucleation at such strained siloxane rings is not strongly inhibited by added NH3; and (3) hydroxyl groups on SiO2 are the target of the inhibition of cobalt deposition from Co2(CO)8.

F. Selectivity between oxides and metals

In the absence of NH3, the nucleation delay for deposition of Co on gold (Fig. S7)38 and vanadium nitride (deposition by CVD40) is negligible, so that there is little intrinsic selectivity between gold and SiO2 (which also has a short nucleation delay in the absence of NH3, as shown above). Interestingly, although NH3 can significantly inhibit nucleation on SiO2, it has a negligible effect on gold and vanadium nitride, and nucleation still takes place readily [Fig. 9(a)]. Therefore, we conclude that the area-selective deposition of cobalt on gold or vanadium nitride, and not on SiO2, should be possible by carrying the deposition in the presence of NH3.

Selective deposition of Co on oxide but not on the metal can also be achieved using NH3 as an inhibitor when the oxide (intended growth surface) is basic and the metal (intended non-growth surface) can form an acidic oxide overlayer. Nucleation on tungsten with a UV/ozone-grown oxide [Fig. 9(b)] behaves similarly to that on thermal WO3 and can be significantly retarded by using ammonia. When cobalt is desired on Al2O3 but not on tungsten, the whole substrate can be treated with ozone to oxidize W and form a thin WO3 layer, followed by selective deposition from Co2(CO)8 in the presence of NH3 (As noted above, all Al2O3
surfaces used in this work are cleaned by UV/ozone; hence, the treatment required to oxidize W will have no further effect on the Al2O3 surface.). After cobalt deposition on Al2O3, the tungsten oxide could then be reduced, for example, by a H2 plasma or etched to restore a metallic surface.

C. Mechanistic interpretation

We previously demonstrated ASD of metallic films on metal substrates in preference to oxide substrates from the carbonyl precursor Mo(CO)6 and showed that the selectivity was greatly enhanced by adding a coflow of ammonia during CVD.16 We now find that there are some interesting differences between the behavior of Co2(CO)8 and Mo(CO)6:

- For Mo(CO)6 in the absence of ammonia, the nucleation delay is longer on the basic oxides Al2O3 and MgO and is shorter on the acidic oxides SiO2, TiO2, and RuO2. In contrast, for Co2(CO)8 in the absence of ammonia, the nucleation delay is shorter on basic oxides such as Al2O3 and longer on acidic oxides such as SiO2.
- For Mo(CO)6, the addition of ammonia results in long nucleation delays on all oxide surfaces; the net effect is to decrease selectivity for growth on one oxide over another (although the selectivity for growth on the metal over oxide is greatly improved). For Co2(CO)8, a coflow of ammonia has a negligible effect on the nucleation rate on basic oxides such as Al2O3 (the nucleation delay remains short), but it greatly lengthens the nucleation delay on acidic oxides such as SiO2; the net result is that the selectivity for growth on one oxide over another is greatly enhanced.

In our earlier work, we proposed that the effect of ammonia in ASD from Mo(CO)6 can be understood as follows.19 On basic oxides such as Al2O3, the intermediate Mo(CO)5 is stable up to 400 °C and as a result, the decarbonylation of Mo(CO)6 stops at this stage and the nucleation delay is long. Addition of NH3 has little effect on this result. On acidic oxides such as SiO2, however, the intermediate Mo(CO)5 is intrinsically unstable and the nucleation delay is therefore short. The addition of NH3 lengthens the nucleation delay in one of two ways: either it acts as a site blocker that prevents adsorption of the Mo(CO)5 precursor, or it increases the basicity of the surface, which then stabilizes the Mo(CO)5 subcarbonyl intermediate. In either case, nucleation is delayed.

Here, we discuss possible reasons for different behavior of cobalt, which is grounded in experimental and theoretical studies of the chemistry of Co2(CO)8 on various oxide surfaces.38–44 Basic oxide surfaces such as Al2O3 promote the disproportionation of Co2(CO)8 to Co2+ and Co(CO)4, in which the Co2+ species are bound to the basic sites.38,55 This surface reaction is analogous to the well-known disproportionation that takes place when Lewis bases are added to Co2(CO)8 in solution.54 We hypothesize that the surface-bound Co2+ species serve as nucleation sites for growth of Co; this hypothesis accounts for why the nucleation delay is short on basic oxides. In contrast, on acidic oxide surfaces such as SiO2, the low basicity of the surface means that the disproportionation of Co2(CO)8 to Co2+ and Co(CO)4 is unfavorable, which leads to a long nucleation delay.55

The above mechanism explains why, in the absence of ammonia, Co2(CO)8 nucleates with a shorter delay on basic oxides but a longer delay on acidic oxides. We now turn to the question of why ammonia further lengthens the nucleation delay on acidic oxides (but has little effect on basic oxides). The adsorption of NH3 should make acidic oxides more basic and thus induce the disproportionation of Co2(CO)8 in the absence of other factors, the net result should be to shorten the nucleation delay, instead of the lengthening actually observed.

One possible way to explain the observed behavior is that, on acidic oxides, NH3 acts as a site blocker, which prevents adsorption of the Co2(CO)8 precursor. Another possibility is that NH3 converts the active adsorbed cobalt species [Co2(CO)8 and Co2+] to an inert form such as Co(NH3)42+; the reaction of Co2+ with ammonia to form Co(NH3)42+ species is known to occur on oxide surfaces at room temperature in the presence of >2 Torr pressures of NH3.38,46

But if NH3 renders the Co2+ species inert on acidic oxides, why is this same effect not seen on basic oxides? It is known that SiO2 and other acidic oxides have surface sites with a very high binding affinity for ammonia, so that ammonia remains on the surface even at temperatures much higher than 70 °C; in contrast, basic oxides such as Al2O3 do not bind ammonia strongly at these temperatures.57 Therefore, when a Co2+ ion is formed on an acidic oxide (which has a high concentration of adsorbed NH3), it is rapidly trapped and deactivated by the reaction with surface-bound NH3, whereas when a Co2+ ion is formed on a basic oxide (which has a low concentration of adsorbed NH3), it is not rapidly trapped and instead can serve as a nucleation site for growth of Co.

Thus, the difference in nucleation behavior between Mo(CO)6 and Co2(CO)8 on acidic versus basic oxide surfaces (and the effect of added ammonia) is attributed to the different nature of the reaction intermediates that are formed and their relative kinetic stabilities.

IV. SUMMARY AND CONCLUSIONS

Area-selective CVD of cobalt from Co2(CO)8 on one oxide surface but not on another is demonstrated: a coflow of ammonia can inhibit nucleation on acidic oxides, such as SiO2 and WO3, whereas it has a negligible effect on more basic oxides, such as Al2O3, HfO2, and MgO. Thus, 15 nm of Co can be grown on Al2O3 in 40 min, whereas the Co thickness on SiO2 is less than 0.1 nm. The effect of NH3 on nucleation delay is seen not only for bulk oxide surfaces but also for metal surfaces on which a thin oxide has been grown.

Acidic hydroxyl groups on the oxide surface appear to play an important role in inhibition because ammonia will not inhibit nucleation on dehydroxylated SiO2. In contrast, on rehydroxylated SiO2 surfaces, nucleation in the presence of ammonia is completely suppressed in experiments lasting 1 h.

The mechanism of nucleation appears to be disproportionation of Co2(CO)8 to Co2+ (which promotes nucleation) and Co(CO)4. This disproportionation occurs readily on basic oxides but is unfavorable on acidic oxides such as SiO2. The addition of NH3 has little effect on basic oxides (probably because such surfaces do not bind NH3 well), whereas NH3 further retards the formation of nucleation centers on SiO2 [probably because such surfaces bind NH3, which either acts as a site blocker or converts Co2+ to inactive Co(NH3)42+ species].
The results of this study open up new possibilities for selective growth on one metal over another, on an oxide over metal, and on a metal over oxide, in some cases by taking advantage of the different effect of ammonia on the nucleation delay seen for the native metal surface versus the same metal surface covered with a thin oxide overlayer.

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40. See supplementary material at https://doi.org/10.1116/1.5144501 for effect of oxide treatment on nucleation and contact angle; XRD patterns; film roughnesses; AFM images of patterned substrate before and after deposition; and ellipsometry studies for various conditions.