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The role of oxide formation on insulating versus metallic substrates during Co and Ru selective ALD

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ABSTRACT

Advanced interconnect materials replacing Cu include Co and Ru, particularly at early metallization steps in small vias where Cu resistivity increases due to grain boundary scattering. In this study, hyper-selective Co ALD was performed from Bis(1,4-di-tert-butyl-1,3-diazadienyl) cobalt [Co(dad)\textsubscript{2}] and two co-reactants (formic acid [HCOOH] and tert-butylamine [TBA]). Utilizing HCOOH, \textit{in situ} XPS showed no deposition on an insulator (SiO\textsubscript{2}) and thick films on metallic substrates (Pt) consistent with infinite selectivity; however, Cu etching was observed. By switching to TBA, similar thick Co films were achieved on Cu with no evidence of etching; while only 4\% CoO\textsubscript{x} on SiO\textsubscript{2} was observed consistent with Co scavenging weakly bound oxygen from under-coordinated sites. This scavenging produced to an unreactive reactive particulate. These co-reactants were also employed with a Ru precursor, \(\eta^2-2,3\)-dimethylbutadiene ruthenium tricarbonyl [RuDMBD(CO)\textsubscript{3}]. Selective deposition on metals vs. SiO\textsubscript{2} with sub-1 nm roughness in AFM was achieved; however, the formation of sub-stoichiometric RuO\textsubscript{x} on SiO\textsubscript{2} was unable to inhibit further deposition due to the low valency of the RuDMBD(CO)\textsubscript{3} precursor and Ru not oxidizing as easily as Co. The results revealed a robust type of passivant-free metal ALD that can be self-limiting on oxides if the metal is able to fully oxidize.

1. Introduction

As the scaling of transistors continues, so does the need for depositing conductive interconnect metal in shrinking vias. It is desired to have selective metal deposition on metals against insulators for bottom-up fill for both middle-of-line (MOL or BEOL) and back end-of-line (BEOL) processing. This would induce the formation and growth of larger grains, which are expected to decrease via interconnect resistance by reducing grain boundaries and decreasing surface roughness (see Fig. 1). This scattering has been well documented and simulated for current Cu interconnects [1–3]. In addition, bottom-up atomic layer deposition (ALD) growth is the preferred deposition method since it should prevent keyhole and seam formation in tight geometries and high aspect ratio features. The key advanced metals for bottom-up growth include cobalt [4] and ruthenium [5]. Cobalt is particularly important since it used as both a capping layer on Cu to protect it from oxidation [6], and in sub-10 nm vias, where Cu is considered to be a better conductor than Cu due to Co having a smaller electron mean free path. Additionally, there are problems with Cu electroplating in sub-10 nm vias [7,8].

Conductive Co has previously been reported by the Winter group and was grown via ALD using Bis(1,4-di-tert-butyl-1,3-diazadienyl) cobalt [Co(dad)\textsubscript{2}] and either formic acid (HCOOH) or tert-butylamine (TBA) at temperatures near 180 °C with high selectivity on metals versus insulators but were not studied with \textit{in situ} XPS [9,10]. Additionally, the mechanism of selectivity was presumed to be precursor decomposition by catalysis on metallic surfaces. Other recent work involving Co(dad)\textsubscript{2} was performed by Kim et al who used ozone as a co-reactant, but was only able to achieve cobalt oxide films at 120 °C [11]. Ozone as a co-reactant is corrosive to Cu interconnects [12,13]; therefore, exploring and discovering co-reactants that are not caustic to Cu are crucial. This study seeks to understand the mechanism for ALD Co and Ru selectivity on metals versus insulators using \textit{in situ} XPS, and ultimately determine the role of oxide formation on insulators that results in infinite selectivity.

Additionally, the co-reactants TBA and HCOOH were applied to ALD with a Ru precursor, \(\eta^2\)-2,3-dimethylbutadiene ruthenium tricarbonyl [RuDMBD(CO)\textsubscript{3}]. Previous reports show that this precursor can react with O\textsubscript{2} and plasma O\textsubscript{2} at elevated temperatures (>220 °C) to form ruthenium metal or ruthenium oxide depending on the temperature and amount of oxygen dosed per cycle [14]. Additionally, resistivities of these films were reported as low as 13.7 \textmu\textOmega\textcdot\text{cm} after a post-deposition anneal [15]. More recent work has also seen ALD using RuDMBD(CO)\textsubscript{3} with H\textsubscript{2}O at lower temperatures [16], but no reference to selective deposition has been reported. Khan et al have used dicarbonyl-bis(5-methyl-2,4-hexanediuronate)Ru and O\textsubscript{2} at 283 °C to selec-
Fig. 1. Selective bottom-up Co. By depositing Co selectively on metals vs. low-k materials during via fill, bottom-up growth can induce the formation of larger grains that provide lower electrical resistance.

2. Experimental methodology

ALD cobalt metal was explored using a metal-organic cobalt precursor, [Co(dad)$_2$], and either a co-reactant of HCOOH or TBA at 180 °C on Cu, Pt, and SiO$_2$ substrates. Similarly, Ru films were deposited at temperatures between 100 °C and 325 °C with HCOOH and TBA to determine the selectivity window. The deposited Co films were studied using in situ x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Cross-sectional scanning electron microscopy (SEM) was used to check the film thicknesses to estimate a growth per cycle.

Cu and Pt samples used in this study were deposited by DC magnetron sputtering on SiO$_2$ substrates consisting of 300 nm of thermal SiO$_2$ on Si(0 0 1) (University Wafer). Samples underwent an ex situ degrease involving rinses in acetone, methanol, and water before being rapidly loaded into the vacuum chamber (<5 min). Once loaded into the load lock chamber, the samples were transferred into the UHV XPS chamber and typically heated to 350 °C for 30 min to produce clean starting substrates. Precursor exposures were performed in a deposition chamber, as shown in Fig. 2. The deposition chamber and dosing lines were pumped with a turbomolecular pump producing a base pressure of ~5 x 10$^{-7}$ Torr. The chamber was heated ~125 °C, and dosing lines were kept ~10–20 °C warmer than precursor containers to ensure precursors would not condense in the lines. The Co(dad)$_2$ precursor was heated to 150 °C and was used with ultrahigh purity N$_2$ that was passed through a purifier to act as a push gas for the delivery of the Co(dad)$_2$ to the samples. RuDMBD(CO)$_3$ was supplied by EMD and gently heated to 30 °C. TBA and HCOOH (Sigma Aldrich) were used as received and dosed at room temperature. No purge gas was employed to reduce any surface contamination/oxygen incorporation into the films. Before moving samples into the deposition chamber, they were preheated in the UHV chamber via a pyrolytic boron nitride heater. For the ALD, samples were heated via an enclosed cartridge heater to eliminate hot wire reactions and minimize CVD, which would lead to improved selectivity. After deposition, samples were transferred back to the UHV chamber where in situ x-ray photoelectron spectroscopy (XPS) was performed without breaking vacuum. A monochromatic XPS system (Al kα hν = 1486.7 eV) was employed to collect surface-sensitive spectra at an angle of 30° with respect to the surface parallel. An electron pass energy of 50 eV and a line width of 0.1 eV were used for collection, and CASA XPS v.2.3 utilizing Shirley background subtractions was used for analysis. Relative sensitivity factors (Schofield) were used to correct raw peak areas before normalization to the sum of all compo-

![Chamber schematic](image-url) Fig. 2. Chamber schematic. An ALD chamber connected in situ to the XPS system allows for chemical composition characterization without exposure to ambient conditions. Additionally, a second chamber with an RF downstream plasma source can be used to clean samples with atomic hydrogen.
ments present during the collected scan. In addition to XPS, surface topography was characterized with AFM and samples thick enough were analyzed with cross-sectional SEM.

3. Hyper-selective Co ALD

3.1. Deposition with HCOOH

Nearly infinite selective deposition of Co on a conductor and not an SiO$_2$ was observed for 180 °C ALD with Co(dad)$_2$ and HCOOH. Fig. 3 plots the XPS corrected peak areas normalized to the sum of all components after 100 ALD cycles followed by an additional 100 cycles on UHV annealed Pt vs SiO$_2$. Note all raw XPS data can be found in the supplemental materials. Pt was employed since it is not etched by HCOOH. On Pt, a thick (>10 nm) Co enriched film was deposited while virtually no deposition occurred on SiO$_2$. The raw binding energy peaks of the Co spectra on Pt and SiO$_2$ are plotted in Fig. 3C and 3D, respectively. The metallic Co 2p$_{3/2}$ signal on Pt had a binding energy of ~778 eV consistent with previous reports for metallic Co [18,19], while there was no detectable Co 2p signal on SiO$_2$ after deposition.

AFM images showed no change on SiO$_2$ before and after Co ALD cycles consistent with no nuclei formation, while the Co on Pt surface roughness remains below 1.8 nm (Fig. 4). The brighter white-colored dots observed on SiO$_2$ before and after deposition did not significantly change and can be attributed to hydrocarbon contamination from ambient exposure; these features were ~2-3 nm tall before and after deposition. On Pt, the imaging indicated a low density of pits consistent with depositing Co on a significant carbon component as seen in XPS; plasma pre-clean should eliminate these features by reducing the carbon on the starting surface allowing for better nucleation and growth.

To verify self-limiting precursor exposures consistent with ALD, a saturation study was performed and monitored with XPS; Fig. 5A highlights the effect of individual half cycle amounts that resulted in self-limiting Co(dad)$_2$ and HCOOH exposures confirming ALD behavior. Essentially, 1 pulse (1 s exposure) of each precursor was followed by 2 additional pulses of the same precursor (2 s) to confirm self-limiting behavior in XPS peak areas. Additionally, this study revealed a novel mechanism about the reaction. Previously it was thought that the HCOOH dissociatively chemisorbed to produce atomic H which removed the ligands from Co(dad)$_2$. Instead, XPS indicated that HCOOH did not remove the ligands but instead induced a ligand-exchange process. Fig. 5B shows the Co 2p peaks that indicated the HCOOH induced a higher binding energy component consistent with a formate on the surface that was subsequently removed upon exposure to Co(dad)$_2$. The Co 2p$_{3/2}$ and the Co 2p$_{1/2}$ shifted components appear at about 786 eV and 797 eV, respectively. Note that the Co 2p$_{1/2}$ component is slightly less distinguishable due to electron scattering on the high intensity peak. Fig. 5C verifies the presence of the formate on the surface; a higher BE C 1 s peak forms after HCOOH deposition at ~288.5 eV. Similarly, this peak is removed upon exposure to Co(dad)$_2$.

3.2. Selective Co from TBA

Deposition with HCOOH was attempted on Cu substrates (Fig. 6A); however, the Cu substrate signal never decreased to zero, consistent with either etching of the substrate [20,21] or etching of the depositing Co film by HCOOH. Both etching mechanisms would prevent full attenuation of the underlying Cu substrate by an overlayer Co film. Therefore, an alkyl amine co-reactant (TBA) was also studied (Fig. 6B). For Co(dad)$_2$ + TBA ALD at 180 °C, reduced Co metal films were deposited on Cu and Pt substrates with hyper-selectivity against SiO$_2$. Films as thick as 30 nm were grown on the conductors while completely attenuating the substrate Cu 2p peaks consistent with zero etching of Cu. On SiO$_2$, only 4% Co$_x$ was deposited after an initial 50 ALD cycles. After an additional 250 ALD cycles, there was still only 4% Co$_x$ indicative of saturation and hyper-selectivity due to a self-limiting growth on the oxide (Fig. 7B). The Co 2p$_{3/2}$ signal on SiO$_2$ was highly shifted in comparison to the signal on Cu (Fig. 7C and D). This shifted signal on SiO$_2$ had a peak position at ~782 eV, corresponding to a very oxygen rich, and likely stoichiometric Co$_2$O$_3$ or Co$_3$O$_4$ [22,23]. It should be noted that the SiO$_2$ substrate can charge slightly in XPS, resulting in all peak positions being shifted including the overlayer Co peaks. Therefore correcting the peak positions of the Co 2p peaks relative to known Si and O$_2$ peak positions is necessary, which still results in a shifted Co peak. Additionally, after 300 total ALD cycles, there is no evidence of a metallic component allowing for the justification that Co$_x$ is being deposited on SiO$_2$. A similar saturation study for Co grown with TBA can be found in the supplemental materials.

AFM imaging and corresponding line trace data from 300 cycles of ALD with TBA confirmed smooth films with low surface roughness on Pt and Cu. After deposition on SiO$_2$, small (~5 nm tall and ~5–10

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Fig. 3. XPS of UHV annealed substrates that underwent 100 + 100 additional ALD cycles of Co(dad)$_2$ + HCOOH at 180 °C. (A) On Pt, a completely buried Pt signal was consistent with a film ~10 nm thick. The rapid decrease in the Pt signal (grey) was consistent with a conformal film. (B) On SiO$_2$, the constant Si signal and lack of a Co signal indicated no Co consistent with infinite selectivity. Raw XPS Co 2p spectra showed a strong metallic component on (C) Pt, while no observable spectra is observed on (D) SiO$_2$. 

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Fig. 4. AFM imaging before and after ALD cycles on SiO₂ and Pt. On SiO₂, (A) before a degrease and (C) after cycles, no significant change was observed, while on Pt (B) before and (D) after deposition surface roughness increased from 0.30 nm to 1.77 nm. Note there was carbon on the starting Pt surface; therefore, plasma cleaning Pt should allow for a more uniform Co film.

Fig. 5. Saturation study of Co(dad)₂ and HCOOH at 180 °C. (A) The self-limiting exposures were consistent with ALD. The C (black arrows) and O (red arrows) increased after HCOOH dosing suggested a formate was deposited on the surface. The decrease in C and O, and increase in Co₂ after Co(dad)₂ dosing indicated a ligand exchange mechanism for the reaction. After HCOOH dosing higher BE components in the (B) Co 2p spectrum and (C) C 1s spectrum are consistent with a formate deposited on the Co surface. The formate was removed after Co(dad)₂ dosing. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

nm wide) CoOₓ particles were present on SiO₂ (Fig. 8), which corresponds to the CoOₓ observed in the Co 2p XPS spectra.

To check for the bottom-up fill nature of Co using the TBA process, 3000 cycles of ALD was performed on a patterned sample from Applied Materials consisting of SiCOH/SiN sidewalls with Cu at the bottom of vias (Fig. 9). The patterned sample underwent a 300 °C atomic H clean to ensure maximum cleanliness without damaging the low-k material. The amount of Cu on the patterned sample was < 1% (Fig. 9A) even by performing XPS analysis at 90°; however, the oxidation state was consistent with metallic Cu (shifted due to the effect of surface charging) after the H clean (Fig. 9B). The 3000 cycles of ALD was infinitely selective to the insulating SiCOH and SiN. Moreover, the cobalt began growing up from the metallic Cu. Approximately 12 nm of Co was grown bottom-up; however, the expected thickness was on the order of 100 nm. It was hypothesized that the porous SiCOH can poison the growth by allowing oxygen/water to diffuse out and oxidize the cobalt. Once oxidation occurs, further deposition was inhibited; therefore, metallic Co must be restored prior to additional deposition with
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Fig. 6. Co ALD with Co(dad)$_2$ along with HCOOH vs TBA on Cu. (A) No attenuation of the substrate Cu signal (green arrow) with HCOOH was consistent with etching of Cu/Cu$_{2}$O. (B) When ALD was performed with TBA, the Cu fully attenuation (green arrow) consistent with no etching. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 7. Co ALD with Co(dad)$_2$ + TBA on Pt and SiO$_2$. (A) Attenuation of the substrate Pt signal (grey arrow) with TBA was consistent with growing a metallic film on Co from 300 cycles. (B) When ALD was performed with TBA on SiO$_2$, the SiO$_2$ showed a saturated amount of 4% CoO$_x$ on the surface independent of the number of cycles (blue arrow). The Co 2p raw XPS spectra for growth on (C) Pt and (D) SiO$_2$ resulted in an ~4 eV difference in binding energy corresponding to metallic vs. oxidized Co deposition, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

this process. It should be noted that the atomic hydrogen clean was proven not to damage the SiCOH so it can be employed for the in situ clean.

4. Ru ALD

Ru metal ALD was performed with RuDMBD(CO)$_3$ and either HCOOH or TBA. It was observed that at a sample temperature of 325 °C, unselective growth of Ru was achieved on all surfaces. Likewise, when the sample temperature was set to 100 °C and the Ru ALD performed, there was no deposition. However, ALD at 215 °C resulted in selectivity of about 1.8 nm on Cu to 0.2 nm on SiO$_2$ when using TBA as a co-reactant. Further dropping the temperature to 200 °C resulted in slightly better selectivity, but decreased the growth rate by nearly a factor of four (Fig. 10). Similar selectivity was observed for HCOOH; however, similar to the Co ALD with HCOOH, AFM imaging after RuDMBD(CO)$_3$ and HCOOH showed rough films on Cu with an RMS surface roughness of nearly 10 nm consistent with etching. By using the more-gentle TBA, the deposited films in AFM were very flat with a surface roughness of less than 1 nm consistent with the absence of etching (Fig. 11).

To understand the nature of the selectivity, the raw elemental Ru 3d peaks are plotted in Fig. 12. Fig. 12A shows the Ru 3d peak for deposition on SiO$_2$, while Fig. 12B shows the deposition on the conduc-
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**Fig. 8.** Co AFM imaging and line traces of 300 cycles of ALD with Co(dad)$_2$ along with TBA on Pt, Cu, and SiO$_2$. (A) Pt and (B) Cu AFM imaging showed smooth films with low surface roughness. (C) Small nuclei consistent with the 4% CoO in XPS were detected on SiO$_2$. The nuclei on SiO$_2$ were about 2–5 nm tall and about 5–10 nm wide.

**Fig. 9.** Co XPS and TEM of 3000 cycles of ALD with TBA on patterned sample. (A) Normalized XPS data indicated Co grew after 500 cycles (blue arrow), but saturated after running additional cycles. (B) The Cu 2p peaks became metallic after plasma cleaning and buried after deposition. (C) ALD was selective for 3000 cycles against SiCOH and SiN. (D) Zoomed-in TEM highlighting ~12 nm Co grown on Cu surface.

tors. It was observed that the Ru 3d$_{3/2}$ peak had a position of ~280.3 eV for Ru grown on the oxide, whereas the peak position for growth on Pt and Cu was ~279.8 eV. These binding energies differ by only 0.5 eV; in the literature metallic Ru has been reported at values most commonly ranging from 279.9 eV to about 280.1 eV [24–26]. As for ruthenium oxides, values as high as ~283 eV have been reported for ruthenium in +3 and +4 oxidation states [26,27]. Observing a peak position nearly 2.5 eV lower than reported values for RuO$_4$ is more consistent with a metallic-like sub-stoichiometric RuO$_x$ [27].

This very small shift coupled with the inability to achieve as high of a selectivity as observed with the Co ALD process allows for the conclusion that more oxidized Ru ultimately would need to be deposited on SiO$_2$ to gain additional selectivity. It should also be noted that there is a small C 1s overlap with the Ru 3d$_{3/2}$ component.

**5. Discussion and conclusion**

The mechanism of selectivity between the Co and Ru processes has been studied with XPS. For Co ALD, XPS saturation studies
Two of etch 4 in by weakly us There Ru from process, and HCOOH va HCOOH, was on by has The HCOOH was with TBA, se Ru:O The pumped low oxy (green of in the web due re byprod 10. com lig of low Min away. tem and SiO ex a co AFM SiO are bu as HCOOH ar pro SiO dif and (A) re of (D) lim per BEOL When was and de a [30] a on of sur RuO 1.8 (C) the weakly Ru com to TBA an metal for be of and of SiO the ° the of reader more self the dif mech co of com kJ/ im ALD on as the the sur AFM the nearly was In man Co re sur be Ru ex to TBA of TBA of metal has Cu, kJ/ Co to sub needed xxx-xxx films pre vs Co(dad) sur RuO, al cor volatile Ru on eV. de Sim the the sur RuO 5 was BE Low com con the of RuO to Co Cu re hy with Co with TBA of metal has Cu. with HCOOH hy SiO as dri 0.2 in and again con ox Co with TBA [17] CO of such sim the va Cu higher im was on C, HCOOH for HCOOH. amine hy SiO as dri leaves the leaves the surface terminated with metallic Ru (Fig. 14).

The Co process is inherently more selective than the Ru process because of the formation of a very oxygen-rich CoO. The peak position between metallic Co grown on Pt/Cu and the oxidized Co grown on SiO2 was nearly 4 eV with TBA. With HCOOH grown Co ALD, no CoO nuclei are hypothesized to have formed on SiO2 due to likely etching by the HCOOH. In comparison, the Ru grown on Pt/Cu vs. SiO2 was only 0.5 eV. This small difference means the sub-oxide of Ru is likely still conductive and able to continue the ALD reaction. Two factors are hypothesized to result in the lack of more oxygen-rich RuO formation: (a) The Ru precursor is low valent and (b) RuO4 and even RuO2 have heats of formation of −239 kJ/mol [28] and −315 kJ/mol [29], respectively, per Ru atom. CoO is a heat of formation of −910 kJ/mol [30] that corresponds to −455 kJ/mol per Co atom. Therefore Co has a much stronger tendency to react with more weakly bound, under-coordinated oxygen on SiO2. In order to achieve better selectivity, formation of a more oxygen-rich RuO4 is necessary consistent with the higher selectivity observed when using a Ru precursor, which has a Ru:C ratio of 4 such as dicarboxyl-bis(5-methyl-2,4-hexanediketonato)Ru [17]. Similarly, RuO4, as fairly recently used by Minjauw et al. [31], may display improved selectivity.

The novel Ru ALD selectivity was limited due to the formation of a sub-stoichiometric RuOx that was not as inhibitive to further deposition. To further improve the selectivity on Cu, use of oxygen-rich Ru precursor is needed since an oxidizing co-reactant must be avoided for interconnects. Hyper-selective Co metal deposition was produced from Co(dad)2 and both co-reactants (HCOOH and TBA). Utilizing HCOOH, no deposition was seen on SiO2 consistent with infinite deposition, however HCOOH was observed to etch Cu. By switching to TBA, no Cu etching was observed, a crucial restraint to be compatible with existing MEOL and BEOL processing, and similar metallic Co films were deposited with only 4% CoO on SiO2 independent of the number of Co ALD cycles. The self-limiting deposition on SiO2 is a novel mechanism of selectivity through the formation of an oxidic particulate, which results in hyper-selectivity.

Fig. 10. Ru XPS on Cu vs SiO2. At 215 °C, the selectivity of Ru ALD was 1.8 nm on (A) Cu (green arrows) vs. 0.2 nm on (B) SiO2 (yellow arrows). Lowering the temperature slightly to 200 °C improved the selectivity on (C) Cu vs (D) SiO2, but decreased the growth rate almost a factor of four. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 11. Ru AFM on Cu with HCOOH and TBA. Much higher RMS surface roughness was observed from Ru ALD grown with (A) HCOOH compared to (B) TBA on Cu. Corresponding AFM of Ru grown on SiO2 using (C) HCOOH and (D) TBA indicated the RMS surface roughness improved on Cu and SiO2 by switching to TBA as a co-reactant.

with HCOOH and TBA indicate a ligand exchange mechanism. As shown in Fig. 5 dosing HCOOH clearly increased the C, O, and shifted higher BE components of C and O on the surface. Ending with a Co(dad)2 pulse removes the higher BE formate on the surface inducing the formation of a volatile reaction byproduct. This was consistent with Co(dad)2 promoting the dissociation of the formate ligand from the surface and ultimately driving the formation of a volatile specie(s) that are pumped away. In a similar manner, when TBA was used as a co-reactant, the C and N increase after TBA dosing, and were reduced after Co(dad)2 dosing (supplemental material). This reaction was again consistent with a ligand exchange reaction occurring on the surface (Fig. 13).

As for the Ru ALD process, a slightly different mechanism is thought to occur due to inherent differences with the precursor being low va- lent and processing dissimilar ligands. When the RuDMBD(CO)3 is introduced to the surface, the CO termination remains intact, but the weakly bound butadiene is able to dissociate and pump away. When the TBA is then introduced to the surface, the amine can react with the carbonyls inducing the formation of a volatile reaction byproduct that leaves the surface terminated with metallic Ru (Fig. 14).
Fig. 12. Ru 3d raw XPS peaks. XPS peaks from the as loaded surfaces, after a UHV anneal, and after Ru ALD. The chemical shift of Ru grown on (A) SiO₂ vs (B) metallic substrates was only about 0.5 eV. This was consistent with a sub-stoichiometric RuOₓ depositing on the surface unable to fully inhibit further Ru deposition. Note the small C 1s overlap.

Fig. 13. Proposed mechanism for Co(dad)₂ + TBA ALD. When Co(dad)₂ is exposed to the surface, dad ligands terminate the surface. Following a dose with TBA, the dad ligands are replaced with the amine. The XPS data is consistent with ligand exchange.

Fig. 14. Proposed mechanism for RuDMBD(CO)₃ + TBA ALD. When RuDMBD(CO)₃ was exposed to the surface the weakly bound butadiene was able to dissociate and volatilize. Following a dose with TBA, the CO ligands were able to react and induce a favorable reaction byproduct leaving metallic Ru on the surface.

CRediT authorship contribution statement


Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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