Electrochemical Atomic Layer Deposition of Cobalt Enabled by the Surface-Limited Redox Replacement of Underpotentially Deposited Zinc

Kailash Venkatraman, a Yezdi Dordi, b,* and Rohan Akolkara b,E

a Department of Chemical and Biomolecular Engineering, Case Western Reserve University, Cleveland, Ohio 44106, USA
b Lam Research Corporation, Fremont, California 94538, USA

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High-performance integrated circuits utilize nano-scale, current-carrying copper (Cu) interconnects. In accordance with the Moore’s law,1 miniaturized interconnects are required in modern devices to obtain superior device performance. The continued shrinkage in the size (cross-sectional area) of each interconnect leads to an increase in its electrical resistance. This detrimentally impacts the electrical performance of the integrated circuit.2 Furthermore, aggressive interconnect size scaling below the 10 nm node poses challenges to void-free interconnect fabrication. State-of-the-art interconnects are fabricated of Cu metal due to its low electrical resistivity and superior electromigration resistance.3 The interconnect signal delay (τ) is given by τ = RC, where R is the interconnect resistance and C is the capacitance of the surrounding inter-layer dielectric. The interconnect resistance R increases dramatically for Cu interconnect dimensions below 40 nm due to the substantial increase in the electrical resistivity of Cu at such narrow dimensions. The resistivity increase is typically attributed to electron scattering processes at grain boundaries and at interfaces within the Cu interconnect structure. Such scattering processes become dominant when the interconnect dimension approaches the electron mean free path (EMFP = 39 nm at room temperature) in Cu.4 As a consequence, the interconnect signal delay increases. To overcome this critical issue, an interconnect material which exhibits lower electrical resistivity at narrow (sub 10 nm) dimensions is required. Cobalt (Co) is considered as a promising alternative interconnect material to replace the conventionally used Cu.5,6 At narrow dimensions, i.e., below 10 nm, Co exhibits comparable or lower electrical resistivity compared to Cu, largely attributed to the lower electron mean free path in Co (EMFP = 7–12 nm at room temperature).7 Co thin-films can be fabricated using a variety of techniques, e.g., physical vapor deposition (PVD),8,9 chemical vapor deposition (CVD),10–13 vapor-phase atomic layer deposition (ALD),14–17 and electrosless deposition,18–22 PVD, CVD, and ALD processes have several drawbacks including the use of expensive targets or unstable metal-organic precursors. Electrosless Co deposition too has drawbacks such as the use of toxic reductants, e.g., formaldehyde or hydrazine. If electrosless Co deposition is performed using relatively benign reductants such as dimethylamine borane or sodium hydrosulfide, incorporation of boron or phosphorus impurity during deposition renders the Co deposits amorphous and with high electrical resistivity. In the present work, an electrochemical technique for Co deposition called electrochemical atomic layer deposition is developed. This technique employs low-cost, benign liquid-phase precursors that allow Co deposition with precise atomic-level control over thickness and deposit morphology, enabling the fabrication of nano- and atom-scale Co films for potential applications in interconnect metallization.

Over the last two decades, electrochemical ALD (or e-ALD) has been utilized for deposition of a variety of metals,3,4 including Pt,25–28 Cu,29–31 Pd,32 Ru,33 Ag,34–36 Au,37 Ge,38 and semiconductor compounds.39–41 In the following introductory discussion, the process of e-ALD of Cu is described as a representative example. The conventional Cu e-ALD process begins with the deposition of a sacrificial lead (Pb) monolayer onto a foreign substrate via underpotential deposition (UPD) in a Pb–2-containing electrolyte. Since UPD leverages the energetically favorable interactions between the depositing metal and the substrate, it facilitates the self-limiting growth of a single atomic layer of the UPD metal (Pb) onto the substrate. On a gold (Au) substrate, Pbupd adlayer formation proceeds via:

\[
Pb^{2+} + 2e^- \rightarrow Pb_{upd}
\]

After Pbupd formation, the electrode is immersed in a Cu2+–containing electrolyte, which triggers the spontaneous (ΔG < 0) surface-limited redox replacement (SLRR) of Pbupd by nobler Cu:

\[
Pb_{upd} + Cu^{2+} \rightarrow Cu_{upd} + Pb^{2+}, \Delta G^0 = -91 kJ/mol
\]

Pbupd (Reaction 1) followed by its SLRR (Reaction 2) constitutes one cycle of Cu e-ALD. The thermodynamic feasibility of e-ALD is governed by the Gibbs free energy change (ΔG) of Reaction 2. While e-ALD of Cu is favored, the e-ALD of Co, i.e., Pbupd followed by its redox replacement by Co, is thermodynamically unfavorable because ΔG > 0 for the redox replacement reaction:

\[
Pb_{upd} + Co^{2+} \rightarrow Co_{upd} + Pb^{2+}, \Delta G^0 = 29 kJ/mol
\]

Thus, conventional e-ALD approaches (using Pbupd) do not provide the necessary driving force required for e-ALD of Co and other such active metals. Clearly, an alternative e-ALD approach is required. In a previous publication from our research group, the underpotential deposition of zinc (Znupd) on Cu and Ru substrates was reported (in an alkaline medium) at electrode potentials close to −1.1 V vs. Ag/AgCl.42 Zn is a highly active metal and thus it can be substituted
AgCl. Following the Znupd adlayer formation, the substrate was subjected to spontaneous surface-limited redox replacement (SLRR) of Znupd by Ag at a pH of 6.5. This facilitated, under open circuit conditions, the 

\[
\Delta G^0 = -92 \text{ kJ/mol}
\]

for all electroanalytical measurements. All potentials reported below are referenced to the open circuit potential (OCP) to –1.2 V (vs. AgCl). The working electrode potential was scanned from the open circuit potential to –1.2 V vs. AgCl and the current response was recorded. Since Znupd proceeds at different onset potentials on Ru and Co, the position of the peak current on the potential axis during LSV is an indicator of the surface composition after various e-ALD cycles. After e-ALD for various cycles was performed using the procedure described above, the substrate was transferred to the alkaline ZnSO4 electrolyte for LSV-based characterization. Air exposure during transfer was minimized to less than 60s.

Anodic stripping coulometry of e-ALD Co.—Anodic stripping coulometry was utilized to quantify the e-ALD Co deposit mass. Co deposits using e-ALD was electrochemically stripped under potentiostatic conditions (0.1 V vs. Ag/AgCl) in an electrolyte containing 100 mM CoSO4. The electrolyte pH was adjusted to 5 by H2SO4. The stripping charge density provided (via Faraday’s law) the mass of Co deposited after various number of e-ALD cycles.

Deposit roughness characterization.—The surface roughness of the deposited e-ALD Co films could not be characterized via ex situ microscopy due to the propensity of Co to rapidly develop surface oxides upon exposure to ambient. Thus, we resorted to an in situ electrochemical technique based on coulometry during Zn underpotential deposition. Co deposits fabricated using e-ALD were subjected to anodic stripping coulometry in an electrolyte containing 1 mM ZnSO4 and 100 mM NH4OH (pH = 11.2). This electrolyte has the same composition as that used for the potentiostatic Znupd step during e-ALD growth. The electrode potential was scanned from OCP to –1.1 V vs. Ag/AgCl (at a scan rate of 20 mV/s) and the corresponding charge density was recorded. This charge density corresponds to Znupd as well as some parasitic hydrogen co-evolution. Nonetheless, the charge density is proportional to the electrochemically active surface area, which enabled quantitative characterization of the surface roughness evolution during Co e-ALD.

Results and Discussion

In this section, we first discuss the characteristics of Zn underpotential deposition on two relevant substrates (Co and Ru). We then leverage the Znupd behavior for developing an electrochemical ALD (e-ALD) sequence for growing Co nano-layers. Finally, we characterize the e-ALD Co deposit properties (surface coverage, roughness) as a function of the number of e-ALD cycles.

Volummetry studies of Znupd on Co and Ru substrates.—Zn is known to exhibit underpotential deposition on Cu,42,44,45 Ni,46 Pt,47,48 and Au.49 In our work, LSV measurements of Znupd were performed on PVD-Ru and PVD-Co substrates. The electrolyte employed for LSV studies consisted of 1 mM ZnSO4 supported by 100 mM NH4OH (pH = 11.2). The scan rate was 20 mV/s. Following observations are evident in the volummograms (Fig. 1 and Fig. 2):

(i) Znupd on Co (Fig. 1): The substrate potential was scanned from OCP to –1.2 V vs. Ag/AgCl. During the cathodic potential scan, a reduction peak was observed at a potential of about –0.97 V vs. Ag/AgCl. This peak corresponds to Znupd on a PVD-Co substrate. A background volummogram (i.e., in the absence of Zn2+ in solution) is also shown for reference. The peak around –0.97 V was absent in this background scan. Also, at potentials cathodic to –1.0 V vs. Ag/AgCl, a sharp increase in current was recorded in the background scan. This was attributed to hydrogen co-evolution, which is moderately catalyzed by the Co substrate. In a similar potential range, the hydrogen co-evolution current in the scan with Zn2+ present in the electrolyte was relatively small. We believe this is due to the presence of a Znupd adlayer (formed on Co at potential close to –0.97 V) which is known to suppress the hydrogen evolution reaction.9,50
underpotential deposition from a de-aerated electrolyte with 1 mM ZnSO₄ supported by 100 mM NH₄OH

Zn_{upd} peak position on Co, i.e., –0.97 V, is quite similar to that observed previously on a Cu substrate.42

Zn_{upd} on Ru (Fig. 2): On a PVD-Ru substrate, in the presence of Zn²⁺ in the electrolyte, a broad cathodic current peak was observed at a potential of –0.82 V vs. Ag/AgCl. This peak can be attributed to Zn_{upd} on Ru. During the anodic scan (not shown), an oxidation peak was observed at a potential of about –0.55 V vs. Ag/AgCl corresponding to stripping of the Zn_{upd} layer. Since the onset potential for electrodeposition of Zn is –1.32 V vs. Ag/AgCl, the potential window scanned in Fig. 2 does not correspond to the bulk electrodeposition of Zn. It is noteworthy that the peak positions for Zn_{upd} on Co (–0.97 V, Fig. 1) and that on Ru (–0.82 V, Fig. 2) are separated by about 150 mV. This surface sensitive nature of the Zn_{upd} allows characterization of the surface coverage of Co deposited during the early stages of e-ALD Co as discussed later.

Based on LSV investigations reported above, a potential of –1.15 V vs. Ag/AgCl is guaranteed to facilitate Zn_{upd} layer formation on PVD-Co and PVD-Ru substrates while avoiding bulk Zn electrodeposition.

**Electrochemical ALD of Co.**—PVD-Ru substrates were employed for the growth of atomic layers of Co via e-ALD. The two-step protocol used for Co e-ALD is illustrated in Fig. 3. STEP-1 involved Zn underpotential deposition from a de-aerated electrolyte with 1 mM ZnSO₄ supported by 100 mM NH₄OH (pH = 11.2). STEP-2 involved surface-limited redox replacement (SLRR) of Zn by nobler Co from a de-aerated electrolyte containing 100 mM CoSO₄ (pH = 6.5). The growth protocol for e-ALD Co consisted of STEP-1 and STEP-2 repeated cyclically:

(i)  (STEP-1) Sacrificial Zn_{upd} layer formation: Zn was underpotentially deposited onto Ru at an applied potential of $E_{\text{upd}} = –1.15$ V vs. Ag/AgCl. The choice of this potential is based on findings in Figs. 1 and 2 which concluded that this potential facilitates Zn_{upd} on Ru and Co surfaces without allowing bulk Zn electrodeposition. Zn_{upd} adlayer formation was performed potentiostatically for 20 s.

(ii)  (STEP-2) Spontaneous SLRR of sacrificial Zn_{upd} layer by a monolayer of Co: Following the growth of sacrificial Zn_{upd} layer in STEP-1, the substrate was removed from the Zn_{upd} electrolyte, dried under a stream of N₂ and then transferred to the SLRR electrolyte. Under open-circuit conditions, spontaneous redox replacement of the Zn_{upd} layer by a noble Co monolayer was facilitated. The relatively large Co²⁺ concentration employed in STEP-2, i.e., 100 mM, accelerated the SLRR electrolyte mass transfer. The relatively large Co²⁺ concentration employed in STEP-2, i.e., 100 mM, accelerated the SLRR electrolyte mass transfer. Open-circuit potential for hydrogen evolution on the exposed Ru substrate which is not completed covered by Co during the first few cycles of e-ALD. After about 3 cycles, when the Ru substrate is completely covered by Co, the integrated charge density during Zn_{upd} on Co remains constant.

During e-ALD of Co using the two-step protocol outlined above, the current and electrode potential transients were recorded. These are shown in Figs. 4 and 5, respectively. The following observations were made:

(i)  During potentiostatic Zn_{upd} adlayer formation (STEP-1), the current density changes dramatically over the 20 s UPD time period. The current density is large (~500 $\mu$A/cm²) at short times and rapidly decreases over 20 s (Fig. 4). This decrease is consistent with the self-terminating properties of the Zn_{upd} deposition process. It is noted that the charge density measured by integrating the current trace over time is larger during the first few cycles, and then decreases to a constant cycle-independent value after about 2–3 cycles. The rationale for this is the increased propensity for hydrogen evolution on the exposed Ru substrate which is completed covered by Co during the first few cycles of e-ALD. After about 3 cycles, when the Ru substrate is completely covered by Co, the integrated charge density during Zn_{upd} on Co remains constant.

(ii)  During the subsequent SLRR step (STEP-2), a gradual anodic drift in the open circuit potential was noticed (Fig. 5). This indicates that the sacrificial Zn_{upd} layer (which is less noble) is gradually replaced by a more noble Co layer. The steady-state OCP of a pure PVD-Co substrate in the SLRR electrolyte was independently measured to be about –0.5 V vs. Ag/AgCl. Thus, the SLRR process step (STEP-2) was terminated after 60 s when the surface potential reaches close to –0.5 V (Fig. 5) indicative of the near complete redox replacement reaction.

Not shown in Fig. 5 is the measurement of the substrate OCP after varying number of e-ALD cycles. As the number of e-ALD Co cycles increased, the OCP of the substrate (measured just before the Zn_{upd} step) was potentiostatically triggered drifted in the negative (cathodic)
Figure 3. Schematic representation of the electrochemical ALD process for deposition of Co. Sacrificial Zn upd (STEP-1) is carried out at an applied potential of $E_{\text{upd}} = -1.15 \text{ V vs. Ag} | \text{AgCl}$. Spontaneous surface-limited redox replacement (STEP-2: SLRR) of Zn upd by nobler Co is performed at open circuit conditions in an electrolyte with 100 mM CoSO$_4$ at pH = 6.5.

direction. This too suggested that the noble Ru substrate was gradually covered with Co as the number of e-ALD cycles increased.

Characterization of e-ALD Co coverage on Ru using Zn underpotential deposition.—The onset potential for Zn upd depends on the substrate. This is seen in Fig. 2. The peak current associated with Zn upd on Co corresponds to a potential of –0.97 V vs. Ag|AgCl, whereas the peak current associated with Zn upd on Ru corresponds to –0.82 V vs. Ag|AgCl, i.e., a 150 mV difference in the potentials for Zn upd on Co vs. Ru. This suggests that linear sweep voltammetry (in a Zn upd electrolyte) of a Ru substrate coated with e-ALD Co deposit can discern exposed Ru from Co-covered Ru. Such a technique, developed in greater depth elsewhere, was implemented to characterize the evolution of e-ALD Co coverage on Ru.

Electrochemical ALD of Co was performed on a PVD-Ru substrate for various cycles following the protocol described above. After e-ALD Co deposition, the substrate was rinsed with de-oxygenated DI water, dried under a stream of N$_2$ gas, and immersed in a Zn upd electrolyte containing 1 mM ZnSO$_4$ and 100 mM NH$_4$OH. The electrode potential was scanned in the cathodic direction from the OCP to $-1.2 \text{ V vs. Ag} | \text{AgCl}$ at a scan rate of 20 mV/s. Fig. 6 displays LSV scans collected on a PVD-Ru substrate which was covered with varying number of cycles ($n$) of e-ALD Co. The voltammogram collected on a blank PVD-Ru substrate ($n = 0$) served as the baseline. For $n = 0$, the peak in the LSV scan at –0.82 V represents Zn upd on Ru as also seen earlier in Fig. 2. As the number of e-ALD Co cycles increases ($n = 3, 5, 10$), a cathodic shift in the OCP was observed, consistent

Figure 4. Transient response of the current density during underpotential deposition of Zn measured in STEP-1 of each electrochemical ALD cycle. Response is shown for e-ALD cycles $n = 1, 2, 5$ and 6.

Figure 5. Transient response of the electrode potential during electrochemical ALD of Co mediated by the surface-limited redox replacement of sacrificial Zn upd. Response is shown for e-ALD cycles $n = 1, 2, 5$ and 6.
with the transformation of the surface from Ru (more noble) to Co (comparatively less noble). After 3 cycles of e-ALD Co deposited on Ru, the broad peak around –0.82 V was still observed indicative of the fact that Ru was not completely covered by the e-ALD Co deposit. A small peak around –1.05 V began to form after \( n = 3 \) cycles suggesting that Co deposition had commenced, thereby providing sites for Znupd deposition on Co in the LSV scan. This observation suggests that the Ru substrate is not completely covered by Co in the first few cycles of e-ALD. This could be due to various factors such as corrosion of the Znupd adlayer due to small quantities of dissolved oxygen (even after rigorous de-aeration) or surface oxidation during sample transfer in air. Increasing the cycle number further decreased the current associated with Znupd on Ru. After 5 cycles of e-ALD Co, the Znupd peak on Ru completely disappeared and a well-defined Znupd peak on e-ALD deposited Co appeared at –1.05 V vs. Ag|AgCl. This indicates that, after \( n = 5 \) cycles, the Ru substrate was completely covered by Co. After \( n = 10 \) cycles, the voltammograms essentially resembled the one after \( n = 5 \) cycles indicating no active surface area increases (i.e., no roughness evolution) between 5 and 10 cycles of e-ALD. This is further discussed in the coulometry measurements provided below.

**Anodic stripping coulometry of e-ALD Co deposits on Ru.**—To determine the mass of e-ALD Co deposited as a function of the e-ALD cycle number \( n \), anodic stripping coulometry was performed. After e-ALD Co deposition (using the protocol described above), anodic stripping coulometry was performed in a 100 mM CoSO\(_4\) electrolyte with pH adjusted to \( \sim 5 \). Stripping was performed potentiostatically at 0.1 V vs. Ag|AgCl. At this potential, hydrogen co-evolution is not thermodynamically permitted. Thus, the only feasible reaction is Co dissolution. The current density transients during stripping of 3 cycles of e-ALD Co (on Ru substrate) is shown in Fig. 7a. During anodic stripping, the current eventually decays to zero after \( \sim 30 \) s indicating complete stripping of the Co layer from the Ru substrate. The Co stripping charge density was plotted as a function of the number of e-ALD Co cycles. This is shown in Fig. 7b. A linear increase in charge density was observed, indicating the constant growth rate of Co e-ALD on Ru. From Fig. 7b, a growth rate corresponding to 172 \( \mu \)C/cm\(^2\) per e-ALD cycle (or \( 0.54 \times 10^{15} \) atoms/cm\(^2\)/cycle) was computed. This surface atom density is lower than that expected for complete Co monolayer coverage in each cycle, suggesting that the deposition rate is likely to provide sub-monolayer growth per deposition cycle. The likely cause of this is the surface oxidation of the Zn upd layer during sample transfer (exposure to ambient) between the UPD and SLRR steps. In analogous two-step e-ALD experiments for Cu deposition, we also observed low average mass densities per deposition cycle.
This indirectly supports the Zn oxidation induced loss of deposition efficiency in a two-cell e-ALD configuration as employed herein.

**Roughness evolution during e-ALD Co deposition.**—The surface morphology of the deposited e-ALD Co films was characterized using an electrochemical technique based on coulometry during Znupd formation. Coulometry during UPD formation has been used previously to characterize the electrochemically active surface area and thus the evolution of roughness during deposition.\(^5\)\(^-\)\(^3\) The fabricated e-ALD Co films were transferred to an electrolyte containing 1 mM ZnSO\(_4\) and 100 mM NH\(_4\)OH. In this electrolyte, the substrate potential was scanned from OCP to \(-1.1\) V vs. Ag/AgCl at a scan rate of 20 mV/s and the charge was recorded. This facilitates Znupd as confirmed earlier in Figs. 1 and 2. For coulometry-based roughness characterization, the first few cycles of e-ALD were neglected as these do not provide coalesced films (discussed above). Coulometry data beyond 5 cycles was obtained because the Ru substrate was completely covered by e-ALD Co after 5 cycles (Fig. 6). The charge density for Znupd on e-ALD Co was estimated by integrating the area under the curve from OCP to \(-1.1\) V vs. Ag/AgCl. We note that the charge density measured in the first 10 cycles of e-ALD Co did not occur during the first 10 cycles of e-ALD. This is suggestive of the true layer-by-layer growth mode of e-ALD. For further roughness characterization, we plan to access in situ AFM or STM.

**Conclusions**

We demonstrate an electrochemical ALD process, which utilizes sacrificial Znupd instead of conventionally used Pbupd, for enabling the deposition of Co films on a Ru substrate. A two-step process, involving Znupd followed by its redox replacement by Co, allows layer-by-layer growth of Co. Process characteristics, i.e., deposition rate, coverage evolution and roughness, were studied using electrochemical methods. These characteristics were found to be favorable for potential application of e-ALD for nano-fabrication of Co films. Future work must focus on studying and optimizing the composition, purity, and crystallinity of deposited Co films and their electrical properties. Such investigations will prove critical in scale-up and implementation of the proposed e-ALD process for advanced interconnect fabrication. While the present Co e-ALD approach utilizes a two-step process to demonstrate basic feasibility, work on one-pot e-ALD of Co is planned as future work.

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| Number of Co e-ALD cycles (n) | Net Charge Density Measured (μC/cm\(^2\)) |
|-----------------------------|------------------------------------------|
| 0                          | 600                                      |
| 5                          | 560                                      |
| 7                          | 595                                      |
| 8                          | 581                                      |
| 10                         | 616                                      |

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