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DFT modeling of atomic layer deposition of Ru interconnect metal for EUV scaling

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Abstract

Density functional theory (DFT) simulations have been applied to understand the surface reaction mechanisms for the selective deposition of Ru metal for use in vias or interconnects. Ruthenium-ALD with bis-(ethylcyclopentadienyl)-ruthenium [Ru(EtCp)₂] and O₂ as reactants shows promising surface selectivity but necessitates activation steps for desorption of ligands to complete each ALD cycle. DFT modeling of Ru(EtCp)₂ on Ru surfaces reveals that ALD processes are limited by the strong aromatic-ring interaction with the metallic surface. Introduction of atomic H as a nonoxidizing co-reactant gas in place of O₂ can overcome these barriers by saturation of the Cp π -bonds, weakening the bonds to the metallic Ru surface. This study aims to provide a comprehensive understanding of leveraging ligand–surface, surface–hydrogen, and ligand–hydrogen interactions to achieve oxygen-free ALD with the Ru(EtCp)₂ precursor at moderate to low temperatures.

Introduction

As goals for computational and memory resources continue to grow, the need to consistently reach critical dimensions (CDs) below 10 nm is rapidly approaching. The use of Cu in advanced semiconductor devices has been prevalent since the early 2000s for its reliability and low resistivity, but in such downscaled interconnects, increased surface scattering gives rise to higher effective resistivity [1]. An additional constraint to CDs for Cu is the use of liners to improve adhesion and prevent Cu diffusion into dielectric surroundings, because the added thickness exacerbates reductions to the metal cross-sectional area and conductivity. Preliminary replacement criteria include short-electron mean-free path and low resistivity in bulk, as well as a high melting temperature. Metals with a lower product of mean-free path and resistivity than copper should better maintain conductivity during scaling [1]. A higher melting temperature implies higher cohesive energy, mitigating electromigration and drift into dielectrics thereby sometimes obviating the need for liners and allowing a large effective cross section for the

Kyeongjae Cho KJCho@utdallas.edu materials in scaled vias. Correspondingly, platinum group metals (Pt, Pd, Rh, Ir, and Ru) have emerged as candidates [1, 2], where Ru has received particular attention [3, 4] owing to low bulk resistivity (~ $7.1 \ \mu\Omega$ cm) and high melting point (2334 °C) for barrierless integration.

Additional considerations must include available techniques, film quality, and control in depositing the material. Reaching beyond 20 nm critical dimension features has driven the advancement of patterning techniques. Implementation of extreme ultraviolet lithography (EUVL) has enabled decreased feature sizes for sub-10 nm nodes with a single-mask exposure rather than multi-exposure processes [5]. As CDs further shrink, the alignment of components in multilayer device stacks becomes more challenging. When edge placement error (EPE) must remain small, bottom-up fabrication with self-aligning fabrication schemes relying on area-selective atomic layer deposition (AS-ALD) [6] is attractive. Growth on the intended surface while delaying or preventing growth on the non-growth area with atomic control relies on the surface chemistry and interactions with the precursor and co-reactants in emerging AS-ALD processes for nanopatterning [5]. Many works have investigated growth characteristics of Ru precursors and co-reactants in search of highly selective deposition of quality metal interconnects, compatible with back-end-of-line (BEOL) processes.

Many noble metal ALD routes rely on the reaction of volatile organometallic or metal–organic precursors with O_2 or ozone at temperatures of 200 °C or higher [7]. One

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widely studied and applied group of Ru precursors consists of ruthenocenes and their derivatives, e.g., RuCp₂, [8] Ru(EtCp)₂, [9] (MeCp)Ru(EtCp) [10], Ru(DMPD)₂, [11] where Me = methyl, Cp = cyclopentadienyl, Et = ethyl, and DMPD = dimethylpentadienyl. Such oxygen-assisted processes for Ru growth yield pure thin films with excellent conformality on high aspect ratio structures, with resistivities from 40 down to 8.1 $\mu\Omega$ cm [3, 9].

Ru thermal ALD processes operating around 200 °C without oxidizing co-reactants are of interest, to mitigate Cu diffusion for mixed Ru-Cu via interconnects and reaction of oxygen with other material surfaces. Recent experimental works report ALD processes for the growth of Ru films with (η^4 -2,3-dimethylbutadiene)(tricarbonyl)ruthenium [Ru(DMBD)(CO)₃], co-reacted with water [12] and with oxygen-free 1,1-dimethylhydrazine (DMH) [13] or tertiary butyl amine (TBA) at 180 °C [3]. Deposition of a seed layer with DMBD, and subsequent deposition with high selectivity by Ru(EtCp)₂ may be possible, but permeation of oxygen-free processes.

Previous modeling works by Delabie et al. [14] and Nolan et al. [15] have studied relevant co-reactants via density functional theory (DFT), by modeling the surface–precursor and surface–ligand interactions for the RuCp₂ precursor. Herein, the study of Ru(EtCp)₂ and the EtCp ligand chemisorption character is expanded to Ru surface oxides (RuO_x), surface hydrided (RuH_x), and compared to reactions on clean Ru.

Theoretical methodology

First-principle density functional theory (DFT) calculations as implemented in the Vienna *ab initio* Simulation Package (VASP) [16, 17] were employed. Full details for the calculations are presented in the Supporting Information (SI).

The formation energy of each reaction step is calculated by Eq. 1, subtracting the substrate (E^s) and gas phase reactants (E_i) from the reacted supercell (E^r) . Note that negative formation energy means a favorable reaction and positive indicates endothermic reaction steps:

$$\Delta E^{\rm f} = E^{\rm r} - E^{\rm s} - \sum_{i} E_{i}.$$
 (1)

Results and discussion

The area selectivity of $Ru(EtCp)_2$ was considered first by comparing the formation energy of Ru atom deposition on various surfaces. Up to seven Ru atoms were clustered on preferably stable surfaces of Ru, Cu, Si, and SiO₂ with energies to nucleate Ru on surfaces 2–4 eV smaller than the enthalpy to dissociate gas phase $Ru(EtCp)_2$ (8.8 eV to dissociate to Ru + 2EtCp (g)), as shown in SI Figure S1. This indicates ligand–surface interactions and mechanisms for decomposition or desorption are critical to predict and achieve growth of Ru films.

Fundamental growth properties follow from the unsaturated π -orbital electron density of the X-Cp aromatic ring and steric hindrances. The inductive effect of ethyl substitution on the Cp ring increases the Ru-L bond energy of Ru(EtCp)₂ (- 4.4 eV/bond) relative to RuCp₂ (- 3.0 eV/ bond) [15, 18, 19]. Selectivity is induced by the relative net energy including exothermic surface and co-reactant interactions to compensate for breaking the ~ 4–5 eV RuEtCp bonds.

Figure 1 summarizes relative formation energies for dissociation of the precursor accounting for ligand-surface interactions (solid lines) and ligand removal directly to the gas phase (dashed line). Surfaces presented here include a clean Ru surface, as well as Ru with a surface oxide and surface hydride; SiO_2 -OH is compared in SI Fig. S2 as a non-growth example. Step 0 is referenced to the bare surface and gaseous precursor. Step 1 follows adsorption of the precursor to the surface. Step 2 is adsorbed RuEtCp and adsorbed (or combusted) EtCp (solid line) or an adsorbed RuEtCp and gaseous EtCp (dashed line). Step 3 is a Ru adatom, and both EtCp ligands adsorbed (or combusted) (solid line) or desorbed (dashed line), with relative energies calculated as Eq. 1.

For sustained growth mechanisms, the pristine Ru(001) surface (lowest surface energy of 2.62 J/m² and density of 15.6 atoms/nm²) is considered as well as Ru with a monolayer (1 oxygen or hydrogen atom per Ru, i.e., coverage $\Theta = 1$) surface oxide and surface hydride to reflect metal precursor pulse reaction mechanisms with O₂ and H correactants, respectively. More details of the surface models and coverage can be found in Supplementary Information.

On clean Ru(001), dissociation of ligands from the precursor is facilitated by preferable chemisorption to the surface, as shown by the solid gray line of Fig. 1a. Returning to a clean surface for subsequent ALD cycles necessitates removing the ligands and is (very) endothermic (dashed





Fig. 1 Formation energy for reaction steps of precursor dissociation on a Ru(001), b RuO_{x1} and c RuH_x surfaces. Solid lines and full symbols correspond to EtCp ligands interacting with the surface, while dashed lines and half-symbols reflect ligands dissociating from the precursor to gas phase

gray line of Fig. 1a), thus, preventing CVD-like growth. The solid purple line in Fig. 1b indicates the energetically favorable route to combusting the EtCp ligand with oxygen, with the CO₂ and H₂O products adsorbed with energies less than 0.7 eV, compared to desorbing EtCp (dashed purple RuO_x line). Equation 2a describes the complete combustion of each EtCp (C₅H₄CH₂CH₃) by surface-bound oxygen, and vacancies are compensated by subsequent co-reactant ALD steps, per Eq. 2b.

$$2C_7H_9^* + 37O^* \to 14CO_2^* + 9H_2O^*,$$
 (2a)

$$\frac{37}{2}O_2(g) + 37V_0^* \to 370^*.$$
 (2b)

Catalytic surfaces, such as platinum group metals, have been known to decompose hydrocarbons, leaving carbon adatoms and evolving H₂ gas. As such, residual carbide in Ru ALD films has necessitated post-deposition techniques to achieve metallic films [3]. Delabie et al. have modeled dehydrogenation of RuCp2 and RuCpPy on clean and hydrogenated surfaces, finding unfavorable adsorption on hydrogenated surfaces except by the Py ligand [14]. Nolan, et al. modeled instead ligand hydrogenation via NH_v terminated Ru [15]. Without chemical interaction with the surface hydrogen, Fig. 1c indicates a similar RuEtCp-terminated surface. Desorption of the first physisorbed ligand is energy neutral, but adsorbing (solid line) and/or desorbing (dashed line) the second ligand is endothermic. Hydrogenation of the ligands via weaker bound surface H can make the overall reaction more exothermic, discussed below.

To elucidate the surface chemistry, the charge density difference isosurfaces are displayed in Fig. 2. The yellow isosurfaces of Fig. 2a and b indicate the shift in charge density as the Cp ring's π -bonding electrons interact strongly with the metallic Ru. This gives each EtCp threefold bonding with strong adsorption energy of 3.8 eV, as in Table 1. The C–C and C–H bond angles shift away from the plane as charge density is drawn toward the metallic surface.

Figure 2c and d indicates the same molecule on the surface saturated with a monolayer of hydrogen. Minimal charge density is displayed, consistent with the physisorbed character by van der Waals interaction, and binding energy of less than 1 eV for the EtCp on $\Theta \sim 1 \text{ RuH}_x$ surface. The ligand–surface interaction is sufficiently reduced that the ligand may be driven off thermally at moderate temperatures and incidentally removes the mechanism for ligand exchange, correspondingly poisoning the surface against subsequent ALD cycles (see Fig. 1c).

In the presence of molecular hydrogen, reactions with the unsaturated carbon atoms of a gaseous EtCp ligand are exothermic, forming ethylcyclopentadiene (C_7H_{10}), ethylcyclopentene (C_7H_{12}), and ethylcyclopentane (C_7H_{14}), as shown in SI Fig. S3. On the Ru surface with low surface hydrogen coverage, the bonding of partially saturated EtCp-H_x species is significantly lessened.

The metastable 2H-EtCp, resultant of two hydrogen attacking neighboring C atoms, partially deactivates the ring. Figure 2e and f shows EtCp-2H chemisorbed only by a single-carbon atom, due to steric effects of the ethyl group.



Fig. 2 Top and side views of charge density difference \blacktriangleright $(\Delta \rho = \rho_{\text{total}} - \rho_{\text{Ru-surface}} - \rho_{\text{ligand}})$ isosurface (charge density of 0.0075 eV/Å³) for an EtCp ligand chemisorbed on Ru before from above (**a**, **b**); EtCp bonded to two H saturating two carbon ions (**c**, **d**); EtCp physisorbed on RuH_x ($\Theta = 1$) (**e**, **f**)

Table 1 shows the binding energies of $EtCp-H_x$ molecules to the clean Ru(001), half-coverage ($\Theta = 0.5$) RuH_x surfaces, and full-monolayer RuH_x. Saturating just two of the carbons greatly reduces the molecule's binding energy by disrupting the aromatic ring. Direct interaction of surface-bound EtCp with gaseous H₂ shows kinetic barriers ~3 eV via nudged elastic band (neb) calculations, shown in SI Fig. S4.

Interactions between adsorbed EtCp and adsorbed atomic hydrogen may provide an alternative, with two 0.8–0.9 eV kinetic barriers, estimated by nudged elastic band calculations. Figure 3 indicates the full precursor dissociation and ligand desorption pathways on Ru(001) with hydrogen $\Theta < 0.5$. The gray line indicates dissociation, and ligand desorption without hydrogen is endothermic by 4 eV. The blue line shows the effect of a small exposure of molecular hydrogen, catalyzed by Ru surface to dissociate into two adsorbed H* species, and saturating EtCp. Sufficient thermal energy for migration of hydrogen and EtCp is essential to interrupting the bond between EtCp and the Ru surface. The favorable red curve presumes that sufficient atomic hydrogen is present to react with the dissociated EtCp resulting in EtCp-H_x species, such as ethylcyclopentene to readily volatilize from the surface.

Limiting hydrogen exposure to prevent poisoning of the surface is a significant challenge. The exact temperature dependence of surface coverage by hydrogen currently is undetermined, though cluster expansion, molecular dynamics, and Monte-Carlo (e.g., Metropolis) approaches would be the best method to estimate the optimal surface temperature. To clean the surface through direct means, organic species with unsaturated carbons may be of interest.

Conclusion

To realize the intrinsic area selectivity of $\text{Ru}(\text{EtCp})_2$ for backend-of-line and via fill processes, oxygen-free, low-temperature methods are being explored. The high binding energy of the ligands from the organometallic complex necessitates continued study of ligand–surface and ligand–co-reactant interactions. In modeling of hydrogen as a reducing coreactant, the EtCp ligand could become volatilized through surface-catalyzed hydrogenation. The risk of poisoning by hydrogen saturation of the surface must be studied further, for example, cleaning the Ru surface via unsaturated carbons, e.g., of ^{tBu}Ethylene or electron-enhanced ALD is worth further consideration.



 Table 1
 Binding energies of H, EtCp, partially and fully saturated Cp carbon atoms, interrupting aromatic ring's interaction with surfaces

	Binding energy (eV)		
	Ru(001)	RuH _{x/2}	RuH _x
Н	- 0.65	- 0.6	- 0.57
EtCp	- 3.8	- 2.1	- 0.9
EtCp-2H	- 1.6	- 0.96	- 0.73
EtCp-5H	- 1.3	- 1.2	-



Fig. 3 Beyond dissociation of the ligands from the adsorbed molecule onto the Ru(001) surface desorption is necessary for subsequent ALD cycles, but significantly endothermic with no additional reactions (gray), or relying on molecular H_2 to react directly with the adsorbed ligand (blue). Interaction with temporarily adsorbed atomic H can weaken ligand binding to enable thermally driven desorption (red)

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Data availability Data will be made available upon reasonable request.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

- 1. D. Gall, J. Appl. Phys. (2020). https://doi.org/10.1063/1.5133671
- C. Adelmann, L.G. Wen, A.P. Peter, Y.K. Siew, K. Croes, J. Swerts, M. Popovici, K. Sankaran, G. Pourtois, S. Van Elshocht, J. Bommels, Z. Tokei, 2014 IEEE International Interconnect Technology Conference/Advanced Metallization Conference, IITC/ AMC 2014 (2014), pp. 173–176
- 3. M. Breeden, J. Woodruff, A. Kummel, IITC 1, 4-6 (2022)
- L.G. Wen, C. Adelmann, O.V. Pedreira, S. Dutta, M. Popovici, B. Briggs, N. Heylen, K. Vanstreels, C.J. Wilson, S. van Elshocht, K. Croes, J. Bommels, Z. Tokei, 2016 IEEE International Interconnect Technology Conference/Advanced Metallization Conference, IITC/AMC 2016 (2016), pp. 34–36
- A.J.M. Mackus, A.A. Bol, W.M.M. Kessels, Nanoscale 6, 10941– 10960 (2014)
- A.J.M. Mackus, M.J.M. Merkx, W.M.M. Kessels, Chem. Mater. 31, 2–12 (2019)
- J. Hämäläinen, M. Ritala, M. Leskelä, Chem. Mater. 26, 786–801 (2014)
- B.T. Aaltonen, P. Aløn, M. Ritala, M. Leskelä, Chem. Vap. Depos. 9, 45–49 (2003)
- O.-K. Kwon, J.-H. Kim, H.-S. Park, S.-W. Kang, J. Electrochem. Soc. 151, G109 (2004)
- K. Kukli, J. Aarik, A. Aidla, T. Uustare, I. Jgi, J. Lu, M. Tallarida, M. Kemell, A.A. Kiisler, M. Ritala, M. Leskel, J. Cryst. Growth 312, 2025–2032 (2010)
- O. van der Straten, S.M. Rossnagel, J.P. Doyle, K.P. Rodbell, ECS Trans. 1, 51–56 (2006)
- Z. Gao, D. Le, A. Khaniya, C.L. Dezelah, J. Woodruff, R.K. Kanjolia, W.E. Kaden, T.S. Rahman, P. Banerjee, Chem. Mater. 31, 1304–1317 (2019)
- S. Cwik, K.N. Woods, M.J. Saly, T.J. Knisley, C.H. Winter, J. Vac. Sci. Technol. A 38, 012402 (2020)
- Q.M. Phung, G. Pourtois, J. Swerts, K. Pierloot, A. Delabie, J. Phys. Chem. C 119, 6592–6603 (2015)
- J. Liu, H. Lu, D.W. Zhang, M. Nolan, J. Mater. Chem. C Mater. 9, 2919–2932 (2021)
- G. Kresse, J. Furthmüller, Phys. Rev. B Condens. Matter Mater. Phys. 54, 11169–11186 (1996)
- D. Joubert, Phys. Rev. B Condens. Matter Mater. Phys. 59, 1758– 1775 (1999)
- M. Johnson, S. Graul, M. Bowers, B. Hase, D. Truhlar, J. Brauman, M. Flenchman, D.E. Richardson, M.F. Ryan, N.I. Khan, K.A. Maxwell, J. Am. Chem. Soc. 114, 10482–10485 (1992)
- 19. M. Swart, Inorg. Chim. Acta 360, 179–189 (2007)

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