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Quantum chemical and solution phase evaluation of metallocenes as reducing agents for the prospective atomic layer deposition of copper

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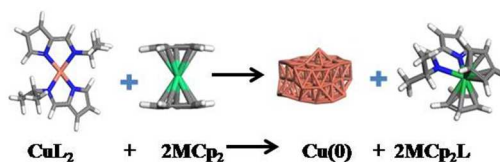
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We propose and evaluate the use of metallocene compounds as reducing agents for the chemical vapour deposition (and specifically atomic layer deposition, ALD) of the transition metal Cu from metalorganic precursors. Ten different transition metal cyclopentadienyl compounds are screened for their utility in the reduction of Cu from five different Cu precursors by evaluating model reaction energies with density functional theory (DFT) and solution phase chemistry.



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A. Introduction

The semiconductor industry is increasingly looking to deposit thin films of various materials in demanding geometries using atomic layer deposition (ALD)¹. This technique combines the control of thickness down to the monolayer level needed for nanoelectronic devices with the cross-wafer uniformity required for commercial manufacturing. It is currently used to deposit high-permittivity materials for memory and logic devices². A large number of oxides, sulfides and nitrides may be successfully deposited by ALD³. However, ALD deposition of metals has not been explored to its full potential. There is much interest in finding reliable low-temperature processes for ALD of first row transition metals such as Co, Cu and Ni, which have wide application in industry⁴. For instance, ALD of Cu has been set as a major challenge in the semiconductor industry⁵ as it is the interconnecting material in electronic chips. A seed layer of copper no more than 2 nm thick will be required to allow electrodeposition of the metal into nanoscale features. However, a uniform thin layer of Cu cannot be formed as the Cu agglomerates into small islands⁶. A deeper understanding of the reaction mechanisms would help in the development of ALD for this group of metals. In this paper, we propose new reactions that may enable deposition of Cu.

Emslie *et al.*⁷ review approaches towards metal ALD using various co-reagents and emphasize the usefulness of solution-phase studies. Knisley⁸ *et al.* give an account of different ALD techniques that have been developed to date for the transition metals. Many techniques have been explored to date for effective Cu deposition. There have been reports of using thermal ALD reactions like Cu(hfac)₂ and alcohol (hfac=1,1,1,5,5,5-hexafluoro-3,5-pentanedionate)⁹ at 300°C, CuCl and hydrogen as the reducing agent¹⁰ at $T > 360^\circ\text{C}$ and Cu(thd)₂ and hydrogen at 260°C¹¹ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate). Table 1 lists the reducing agents along with the precursors that have been used for Cu(0) deposition. The likely reaction temperatures are also reported. Along with thermal ALD, plasma ALD¹² has also been investigated.

Both Cu(II) and Cu(I) compounds have been used as precursors. The various precursor compounds differ in electronegativity of the ligands attached, intra- and intermolecular steric hindrance and flexibility¹³. In some cases Cu(I) compounds¹⁴ have been found to allow lower reaction temperature to be used and improve the quality of deposition, but in other cases the process resembles CVD rather than ALD¹⁵. Cu(I)carbene compounds have recently been proposed¹⁶ and show high promise for Cu ALD. A copper carbene hydride may itself act as the reducing agent,

thus avoiding non-copper based co-reagent and decreasing the potential for impurities^{16b}.

As seen in Table 1, some of the reducing agents for Cu ALD are metal-based compounds. Lee *et al.*¹⁷ have shown that an organometallic reagent ZnEt₂ can act as the reducing agent for Cu(dmap)₂ precursor (dmap = OCHMeCH₂-NMe₂, dialkylamino-2-propoxide). They reported the reaction temperature to be ~100°C. This was followed by the work of Vidjayacoumar *et al.*¹⁸ where other inorganic compounds (BEt₃ and AlMe₃) were tested along with ZnEt₂ in the solution phase. They reported that when BEt₃ or AlMe₃ was used as the co-reagent, there was no copper deposition. Using ZnEt₂ led to copper deposition but with Zn impurity in solution phase. In the case of ZnEt₂ the ligand Et⁻ donates an electron to copper. The -Et also forms intermediate compounds like LCuEt/LZnEt¹⁸. When explored further some aspects of the reaction pathway resemble chemical vapor deposition rather than an ALD reaction. A detailed reaction mechanism for transmetalation is presented by Dey and Elliott from a gas-phase DFT model¹³. In a more sophisticated surface model, adsorption energies for the precursors, by-products and intermediates have been explored at DFT level¹⁹. In a review article Gordon *et al.*²⁰ give a full description of ALD and CVD of Cu thin films.

These studies led us to explore other organometallic reagents that can be used for the reduction of Cu. From the literature, we found that vanadocene was used to form ultrafine magnetic iron from ferric chloride²¹. In a similar study, deposition of rhodium from [Rh(μ-Cl)(C₂H₄)₂] and vanadocene in presence of poly(vinylpyrrolidone)²² has been reported. These studies motivated us to explore the possible use of metallocenes as reducing agent for Cu ALD.

A metallocene is a compound typically consisting of two cyclopentadienyl anions (Cp, which is C₅H₅⁻) bound to a metal centre (M) in the oxidation state II, with the general formula (C₅H₅)₂M. Metallocenes are used as homogenous catalysts in organic chemistry²³. However, metallocenes are rarely used industrially.

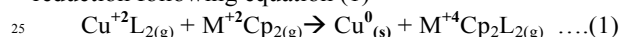
Metallocenes have been previously used as precursors in metal ALD, i.e. for the deposition of the metal in the metallocene. For example, Os was deposited from osmocene and oxygen²⁴, Co from cobaltocene^{12b} and Pt from CpPtMe₃ and oxygen²⁵. Certain metal oxides were also deposited from the respective metallocenes. For example ZrO₂ and HfO₂ were deposited from the corresponding *ansa*-metallocene precursor²⁶ and Fe₂O₃ was deposited using ferrocene and oxygen²⁷. The approach here is different, as the metallocene is intended to act as a reducing co-reagent, eliminating ligands from the surface and simultaneously supplying electrons for the reduction of Cu cations to Cu(0).

Solution phase chemistry has been widely applied for studying suitable combinations of precursor and co-reagent for effective ALD/CVD reactions^{18, 28}. This approach is rapid and straightforward, unlike time and resource intensive ALD/pulsed-CVD studies. Solution studies also allow for comparatively more facile analysis of the reaction pathways responsible for precipitation of the metal, thereby providing a starting point for consideration of the reaction pathways involved during ALD or pulsed-CVD. While the extent to which solution reaction pathways correlate with those in metal ALD has rarely been determined, solution thermolysis reactions employed in the study of CVD have in some cases provided strong evidence for mechanistic parallels between solution- and surface-based reactivity.

In our study, we initially validate the proposed chemistry by computing gas phase reaction energies and then we further explore the surface desorption energies of the by-products using DFT as a tool. Furthermore, we carry out a solution phase experimental study using vanadocene as the reducing agent and Cu(acac)₂ as the precursor.

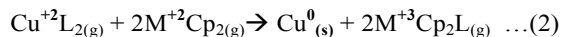
B. Proposal of new pathway to Cu ALD

In this work, we initially propose that the metal cation in the metallocene can donate two electrons to Cu(II) for its reduction following equation (1)



In the above reaction, there is complete transfer of the ligands (L) from copper precursor to metallocene, which confers oxidation state IV on M of the metallocene. Two electrons are thus transferred to Cu.

An alternative to equation (1) can be proposed as in equation (2).



A third possibility is to use the metallocene to reduce an intermediate layer of CuO or CuS. Figure 1 describes pictorially how such a three-step process may take place.

The reduction potential of some metallocenes are measured by Holloway *et al.*²⁹ using cyclic voltammetry. The trend in reduction potentials of the four metallocenes known to produce simple anions (V, Cr, Co, Ni) is that the more electron-rich the metallocene is, the easier it is to reduce. The experimental reduction potential of some of the metallocenes and copper are listed in Table 2. It shows that the Cu in oxidation state I/II has a greater tendency to be reduced to Cu(0) than for the metallocene to be reduced from oxidation state III to II.

Table 1: Co-reagents and precursors for the purpose of Cu(0) ALD. Typical temperatures at which deposition takes place have also been reported. The full name of the precursors is in the supplementary information.

Co-reagent	Precursor	Temperature (°C)	Reference
H ₂	CuCl	360	Mårtensson <i>et al.</i> ³⁰
	Cu(thd) ₂	190	Mårtensson <i>et al.</i> ³¹
	Cu(acac) ₂	250	Utriainen <i>et al.</i> ³²
	Cu ₂ (amd ^{IPr}) ₂	280	Lim <i>et al.</i> ³³
	Cu ₂ (^t Bu-Me-amd) ₂	190	Li <i>et al.</i> ³⁴
	Cu(hfac) ₂	25-100	Kang <i>et al.</i> ³⁵
	(NHC)Cu(hmde)	220-320	Pemble <i>et al.</i> ^{16c}
H ₂ SiEt	Cu(PyrIm ^{Ph}) ₂	160-170	Grushin <i>et al.</i> ³⁶
	Cu(nacnac) ₂	100	Park <i>et al.</i> ³⁷
	(nacnac)Cu(VTMS)	120	Park <i>et al.</i> ³⁷
	(nacnac ^H)Cu(VTMS)	45	Thompson <i>et al.</i> ³⁸
NH ₃ +H ₂	Cu(PyrIm ^R) ₂ (R = Me, Et)	180	Grushin <i>et al.</i> ³⁶
	Cu ₂ (amd ^{tBu}) ₂	160	Li <i>et al.</i> ³⁴
NH ₃	Cu(hfac) ₂	283	Törndahl <i>et al.</i> ³⁹
	Cu ₂ (amd ^{tBu}) ₂	280	Li <i>et al.</i> ⁴⁰
HCOOH, then N ₂ H ₄	Cu(dmap) ₂	180	Knisley <i>et al.</i> ⁴¹
HCOOH	Cu(hfac)(VTMS)	125	Norman <i>et al.</i> ⁴²
Zn	CuCl	440-550	Juppo <i>et al.</i> ⁴³
ZnEt ₂	Cu(dmap) ₂	100	Lee <i>et al.</i> ¹⁷
	Cu(PyrIm ^{Et}) ₂	130	Vidjayacoumar <i>et al.</i> ^{18a}

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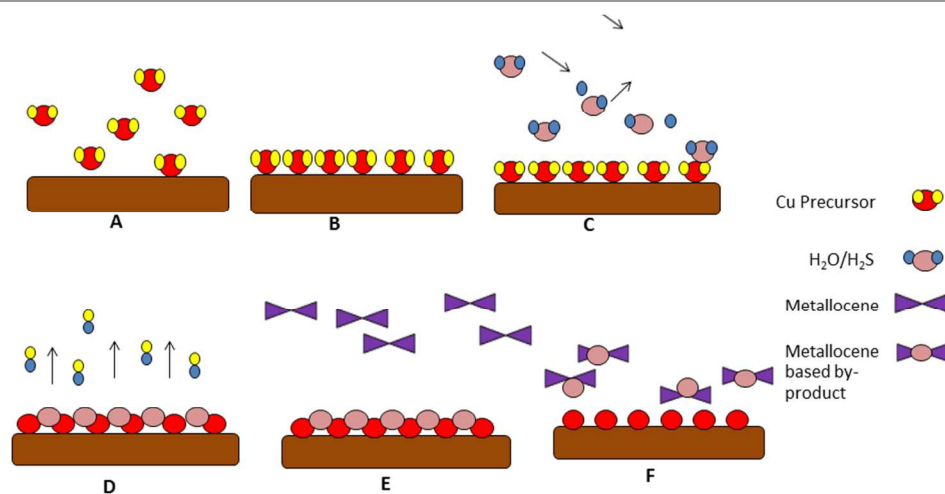


Figure 1: Scheme for the proposed deposition of copper from copper precursor with the intermediate formation of copper sulfide or copper oxide. (A) shows the precursor pulse, (B) saturation of the precursors onto the surface, (C) H₂O or H₂S pulse, (D) formation of oxide or sulfide, (E) incoming metallocene and (F) the formation of metallic copper through the desorption of substituted metallocene by-products. Steps (C) and (D) can be omitted for direct deposition of copper from the precursor.

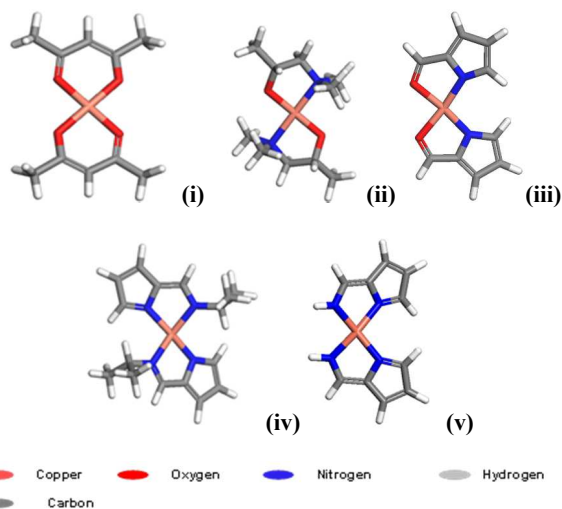


Figure 2: Stick representation of computed structures of precursors used for this study: (i) Cu(acac)₂, (ii) Cu(dmap)₂, (iii) Cu(PyrAld)₂, (iv) Cu(PyrIm^{iPr})₂, (v) Cu(PyrIm)₂. The structural features like bond lengths and bond angles can be found in another paper¹³.

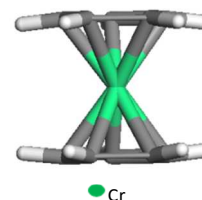


Figure 3: Stick model of structure of CrCp₂.

Five different commonly-used copper precursors are included in the initial screening, as follows:

- copper^(II)acetylacetonate, Cu(acac)₂ (Figure 2(i))
- copper^(II)dialkylamino-2-propoxide, Cu(dmap)₂ (Figure 2(ii))
- copper^(II)pyrrolyaldehyde, Cu(PyrAld)₂. (Figure 2(iii))
- copper^(II)N-isopropyl-2-pyrrolyl-aldiminate, Cu(PyrIm^{iPr})₂ (Figure 2(iv))
- copper^(II)pyrrolyl-aldiminate, Cu(PyrIm)₂ (Figure 2(v))

Most of these precursors were studied earlier and the structural properties like bond angle, torsional angle and bond length have been reported by Deyet *al.*¹³. They are pictorially represented in Figure 2. The copper precursors were screened computationally against reduction by various metallocenes represented as MCp₂ (M = Co, Ni, V, Cr and Fe, Figure 3). The theoretical energetics for reduction by other MCp₂ compounds like M = Hf, Mo, Ti, Ta, Zr are presented in the supplementary information, as they are not

experimentally known in the oxidation state II that is required here.

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Table 2: Literature values for reduction potential of some of the metallocenes in this study and of aqueous copper.

Molecule	Reduction Potential vs SCE*	Reference
$\text{CoCp}_2^+/\text{CoCp}_2$	-0.91 V	Koeppel <i>et al.</i> ⁴⁴
$\text{NiCp}_2^+/\text{NiCp}_2$	-1.74 V	Denisovichet <i>al.</i> ⁴⁵
$\text{VCp}_2^+/\text{VCp}_2$	-0.70 V	Choukrounet <i>al.</i> ²¹
$\text{CrCp}_2^+/\text{CrCp}_2$	-1.04 V	Ray <i>et al.</i> ⁴⁶
$\text{FeCp}_2^+/\text{FeCp}_2$	0.40V	Gagne <i>et al.</i> ⁴⁷
Cu^+/Cu^0	0.52 V	Samans ⁴⁸
$\text{Cu}^{+2}/\text{Cu}^0$	0.34 V	Samans ⁴⁸
$\text{Cu}^{+2}/\text{Cu}^{+1}$	-0.16 V	Samans ⁴⁸

*SATURATED CALOMEL ELECTRODE

C. Methods

C.i. Computational techniques

The Cp rings of the metallocene can be either eclipsed or staggered⁴⁹. The energy difference between the two structures is computed to be only a few kJ/mol. For simplicity we have studied only the eclipsed conformation with D_{5h} symmetry using the computational tools. We performed all electron self-consistent Kohn-Sham Density Functional Theory (DFT) calculations using the TURBOMOLE 6.4 suite of quantum chemical programs⁵⁰. The Perdew-Burke-Ernzerhof (PBE) functional⁵¹ was used with the resolution-of-identity approximation^{52,53} and valence double-zeta with polarization def-SV(P) basis set⁵⁴. A larger basis set def-TZVPP⁵⁵ and the dispersion-corrected PBE+D3 functional was used to test the accuracy in a previous study of similar molecules^{16b}, where it was seen that the reaction energies remain consistent. In this study we have tested the desorption energies of two by-products using PBE/SV(P) and PBE/TZVPP and obtained an energy difference of around 80 kJ/mol, but with the same qualitative result (i.e. that desorption of the by-products is favored). Thus, as a compromise between cost and accuracy, all reactions except the test cases in Table 4 are computed using basis set def-SV(P) and PBE without D3 correction.

In the gas phase, all the Cu precursors are open shell, as Cu is in oxidation state II. The metallocenes studied also feature the transition metal in oxidation state II, while the metallocene by-products are in oxidation states III or IV. These metallocene compounds are susceptible to having multiple spin states because of the transition metal center, and so a range of spin states was computed here. Open shell calculations are done using Unrestricted Kohn-Sham (UKS) and closed shell calculations are done through Restricted Kohn Sham (RKS). We have allowed the structures in different spin states to relax to their own equilibrium

geometry. Only the geometries and spin states with lowest total energies have been presented here.

The spin states of the most stable metallocenes and metallocene based by-products are presented in the supplementary information. They were checked using a larger basis set def-TZVPP⁵⁵ and it was found that the most stable spin states were still the ones found using def-SV(P). All the spin states are also in accordance with the findings of Swart⁵⁶, which is further justification for the choice of basis set and functional.

Spin contamination was negligible for most of the metallocene structures except vanadocene. This problem with vanadocene is well known and has been reported by Swart⁵⁶ ($\langle S^2 \rangle = 1.75$ here, instead of the value for the pure spin doublet $\langle S^2 \rangle = 0.75$). A spin projection technique has been proposed by Wittbrodt *et al.*⁵⁷ in order to deal with this problem. The energy of the pure spin doublet has been calculated using this technique for structures showing spin contamination.

The spin contamination of most of the metallocene based by-products is negligible (i.e. within the range proposed by Grenhof *et al.*⁵⁸). The exceptions are $\text{V}^{+4}\text{Cp}_2(\text{acac})_2$ ($\langle S^2 \rangle = 0.91$), $\text{Cr}^{+3}\text{Cp}_2(\text{acac})$ ($\langle S^2 \rangle = 1.69$), $\text{Cr}^{+3}\text{Cp}_2(\text{PyrIm}^{\text{ipr}})$ ($\langle S^2 \rangle = 0.99$), $\text{Fe}^{+3}\text{Cp}_2(\text{acac})$ ($\langle S^2 \rangle = 1.33$). In these cases, the spin projection technique of Wittbrodt *et al.*⁵⁷ has also been used to compute the energy of pure spin states.

An fcc Cu_{55} cluster, which is in the shape of a coin with (111) faces, was taken as a surface model. The bare cluster has C_{3v} symmetry. The copper coin is an open shell doublet system with a HOMO - LUMO energy difference of 1.8 kJ/mol. Therefore, all the calculations with adsorbate on the cluster were also open shell calculations computed within the UKS formalism. This is the same model as used by Larsson *et al.*⁵⁹ and in our previous studies^{16a, 16b}.

A reaction can either be exothermic ($\Delta E < 0$) or endothermic ($\Delta E > 0$). An exothermic reaction is thermodynamically favored and so this is the metric that we

use to assess the feasibility of overall reactions and key reaction pathways. ALD is a surface phenomenon and so one approach to ALD modelling is to consider the complex sequence of reactions that take place on a model surface⁶⁰. Clearly, such a computationally intensive approach is not appropriate for precursor screening. Instead, we note that the prerequisite for successful ALD is that the overall reaction between gas-phase precursors to produce solid film (equation 1) be strongly exothermic, even though these precursors are never admitted into the ALD chamber at the same time. This ensures a strong thermodynamic driving force for growth reactions on the surface. We therefore use the exothermicity of overall reactions such as equation (1) as a metric for the suitability of a particular precursor combination (section D i,ii,iii).

However we recognize that the actual process is of course subject to the kinetics of the individual reaction steps on the surface. In particular, certain precursor choices may lead to by-products that are not volatile, and this factor should be included in precursor screening. We therefore explicitly calculate the desorption of by-products from a model Cu surface (section D.iv).

Finally, we also use quantum chemical calculations to investigate possible complexes formed by the inner-sphere coordination and reaction of solvent molecules, neglecting other solvation effects (section E).

The entropy of the by-products $S(\text{by-product})$ has also been calculated in the gas phase from vibrational analysis using TURBOMOLE⁶¹. The entropy has been calculated at $T=393$ K as this is a typical target temperature for Cu ALD. After a by-product is desorbed from the surface, it gains translational and rotational degrees of freedom and this is probably the major contribution to the entropy change. It is therefore assumed that $S(\text{by-product}+\text{Coin}) \approx S(\text{Coin}) + S_{\text{vibr}}(\text{by-product})$ and so the entropy change is $\Delta S_{\text{des}} \approx S_{\text{trans+rot}}(\text{by-product})$. $\Delta G_{\text{des}}^{373} = \Delta E_{\text{des}} - T\Delta S_{\text{des}}$ denotes the free energy needed by the by-product to be desorbed from the surface. A lower more negative $\Delta G_{\text{des}}^{373}$ value for the by-products indicates that desorption is favored.

By employing an atom-centred basis, we are able to efficiently compute gaseous molecules and their adsorption to a cluster, but not bulk metal. Therefore, in order to calculate total energies per Cu atom of bulk Cu metal for the reaction energies, we add the adhesion energy computed for bulk $\text{Cu}_{(s)}$ using a plane-wave basis in the VASP code¹⁹ with the same functional. Here valence electron states are expanded in a plane-wave basis set with an energy cut off of 300 eV. The electron exchange and correlation were treated within the same PBE functional. For the bulk copper, k-point sampling is performed with an $8 \times 8 \times 8$ Monkhorst-Pack sampling grid. The bulk lattice constant is determined using the Murnaghan equation of state. The additional energy has been added to the reaction steps that have metallic copper formation, as reported in earlier studies^{9,20}.

C.ii. Experimental

All wet chemical tests were performed in a dry, oxygen free atmosphere of dinitrogen using Schlenk techniques and specialized glassware fitted with Young's taps. Vanadocene (95 % sublimed) was purchased from Strem Chemicals, Inc. Copper (II) acetylacetonate was purchased from Sigma Aldrich and purified via sublimation. All other solvents were bought anhydrous from Sigma Aldrich.

D. Computational results and discussion

We propose three different possible pathways for the use of metallocenes (MCp_2) as the reducing agent in ALD, described in sections D.i, D.ii and D.iii.

D.i. Reduction by abstraction of ligands from the precursor:

Cu is transferred into the ALD chamber via a pulse of precursor Cu(II)L_2 , leading to a surface covered in ligand L. The adsorption of these precursor compounds onto the surface has been described by Dey *et al.*⁶² The un-adsorbed precursor can be purged out of the system, as in standard ALD. We propose that a metallocene M(II)Cp_2 is introduced as the second pulse. It can abstract ligands from the precursor, desorbing as $\text{M(III)Cp}_2\text{L}$ or $\text{M(IV)Cp}_2\text{L}_2$ and also simultaneously donating one electron per ligand to the surface so as to yield Cu(0) . This is followed with a purge, and the cycle is repeated.

First step: $\text{surf} + \text{Cu(II)L}_2(\text{g}) \rightarrow \text{surf-Cu(II)L}_2 \dots (3)$

Second step: $\text{surf-Cu(II)L}_2 + \text{M(II)Cp}_2(\text{g}) \rightarrow \text{Cu(0)}_{(s)} + \text{M(IV)Cp}_2\text{L}_2(\text{g}) \dots (1)^*$

$\text{surf-Cu(II)L}_2 + 2\text{M(II)Cp}_2(\text{g}) \rightarrow \text{Cu(0)}_{(s)} + 2\text{M(III)Cp}_2\text{L}(\text{g}) \dots (2)^*$

We have used DFT calculations to test this proposal using five copper precursors with different metallocenes as mentioned in section 2. However, for this wide screening, we have only used gas phase molecules and corrected for bulk Cu(0) , and not explicitly considered adsorption. (The adsorption energies of the different precursors onto the surface as in equation 3 have been computed in another study¹³). This corresponds to modifying equations (1)* and (2)* to give the overall ALD equations (1) and (2) below.

$\text{Cu(II)L}_2(\text{g}) + \text{M(II)Cp}_2(\text{g}) \rightarrow \text{Cu(0)}_{(s)} + \text{M(IV)Cp}_2\text{L}_2(\text{g}) \dots (1)$

$\text{Cu(II)L}_2(\text{g}) + 2\text{M(II)Cp}_2(\text{g}) \rightarrow \text{Cu(0)}_{(s)} + 2\text{M(III)Cp}_2\text{L}(\text{g}) \dots (2)$

The computed reaction energies for equations (1) and (2) are shown in Table 3. The nature of the metallocene is the major factor dictating this energetics, with a secondary effect visible due to the copper precursor. The copper precursors used here differ in the electronegativity of the ligands attached, conjugation present and steric hindrance. The reaction energies only vary with the metallocenes that are used.

Unsurprisingly the reaction energies for equations 1 and 2 follow the same trend. If reaction 1 has an exothermic reaction energy, then reaction 2 generally shows the same.

The exception is CrCp_2 , where the reaction of equation 1 is

endothermic while reaction 2 is exothermic (Table 3), probably reflecting that the substituted metallocene oxidation state III is more stable.

Vanadocene is computed to show exothermic overall reactions with all the Cu precursors (Table 3). The same conclusion can be made for tantalocene (see supplementary information for energetics) but it is not available in oxidation state II. V(II) has d^3 configuration in the unreacted metallocene. V may donate one or two electrons to reach d^2 or d^1 configuration in the V(III) or V(IV) by-products respectively. The donation of electrons is promoted by the higher (more positive) reduction potential of Cu relative to VCp₂ as seen in Table 2. These factors show that vanadocene is a good option as the reducing agent.

Cr is in group 6 in the periodic table and has d^4 configuration in chromocene. It can in principle donate one

or two electrons to copper in order to form d^3 and d^2 configurations, but as shown in Table 3, the d^3 configuration is preferred. It has been reported that chromocene forms CrCp⁺ easily by electron transfer²⁹, which suggests that electron donation to copper may also be favored.

FeCp₂ has 18 electrons in its valence shell, which is the nearest noble gas configuration,⁶³ and it thus enjoys extra stability. Consequently reactions that remove electrons from Fe are found to be endothermic in nature. Other metallocenes like CoCp₂ and NiCp₂ that have beyond 18 electrons also show endothermic reaction energies. Although CoCp₂ is a common one electron reducing agent, it cannot follow the pathway described in equation 1 and 2 as it cannot accommodate any further ligands. Although the ideal reaction would be the transfer of two ligands to each metallocene molecule, leading to the equal molar

Table 3: Energetics of five different copper precursors interacting with different metallocene compounds to form metallic Cu following equation 1 and 2. The energies are computed using DFT as the level of calculation and def-SV(P) as the basis set. In cases like vanadocene where the computed ground state has spin contamination, the energies are corrected using the spin projection formula described by Swart⁵⁶. The energies are quoted in kJ/mol.

	Cu(acac) ₂		Cu(dmap) ₂		Cu(PyraId) ₂		Cu(Pyrim) ₂		Cu(Pyrim ^{Pr}) ₂	
	1	2	1	2	1	2	1	2	1	2
VCp ₂	-7.8	-200.9	-81.8	-157.1	-68.0	-262.2	-11.0	-256.5	-7.6	-230.7
CrCp ₂	+42.8	-142.1	+20.0	-172.2	-32.8	-242.8	+91.7	-140.9	+100.4	-257.0
FeCp ₂	+229.9	+459.2	+187.0	+347.4	+273.0	+217.8	+324.2	+200.4	+354.8	+212.3
CoCp ₂	+145.6	+339.1	+176.0	+195.0	+155.4	+84.2	+234.0	+48.2	+237.7	+67.4
NiCp ₂	+95.6	+127.6	+173.9	+63.9	+189.3	+128.5	+180.7	+13.9	+187.2	+20.8

consumption of the metallocene and precursor (equation 1), the computed reaction energies do not favor this proposal. In most of the cases described in Table 3, the reactions of equation 2 are more exothermic than those of equation 1. The reason might be an increase in the steric hindrance when both the ligands from the copper precursor are transferred to the metallocene. This might be the reason for the difference of > +150 kJ/mol for equations 1 and 2. The addition of the ligands to metallocene results in a considerable distortion of the compounds. In some cases, after addition of two ligands each new ligand is only monodentate despite being bidentate in the Cu precursor (see supplementary information for the structure).

D.ii. Reduction by abstraction of oxygen

Three-step ALD processes for Cu(0) deposition have been presented previously⁴¹ and their mechanism has been computed⁶². In this section and the next, we explore a three-step ALD cycle for Cu(0) deposition via the intermediate formation of CuO or CuS.

The first ALD pulse brings the Cu precursor to the surface, forming a surface covered with ligands L (equation 3). In the second step, H₂O is pulsed into the reactor so as to eliminate HL and form a surface layer of copper oxide. Such ALD growth of transition metal oxides is straightforward and has been tried for CVD reactions⁶⁴ as well as ALD reactions³². The metallocene M(II)Cp₂ is introduced as the third pulse and is expected to abstract oxygen from CuO. A complete reduction of the CuO layer needs a very strong reducing agent as indicated by Maimaiti *et al.*⁶⁵. If the by-product desorbs from the surface as O=M(IV)Cp₂, it will simultaneously donate two electrons to the surface so as to yield Cu(0). A strong M=O bond should ensure that O=M(IV)Cp₂ desorbs from the surface without further reaction. This reaction proposal is shown in the equations below.

First step: surf + Cu(II)L_{2(g)} → surf-Cu(II)L₂... (3)

Second step: surf-Cu(II)L₂ + O₃ → 3surf-Cu(II)O + gaseous by-products (4)*

Third step: surf-Cu(II)O + MCp_{2(g)} → Cu(0)_(s) + O=MCp_{2(g)} ... (5)*

Once again, for the purpose of computational screening, the above equations (4)* and (5)* can be modified to give the following equations (4) and (5):

Cu(II)L_{2(g)} + O₃ → 3Cu(II)O_(s) + gaseous by-products ... (4)

Cu(II)O_(s) + MCp_{2(g)} → Cu(0)_(s) + O=MCp_{2(g)} ... (5)

The formation of CuO from O₃ and oxygen plasma and common copper precursors are already known in the literature^{64, 66}. Hence, the reaction in equation 4 is feasible and will not be computed. The gas phase energetics of equation 5 is -361.2 kJ/mol where the metallocene is vanadocene. Thus it is also thermodynamically possible. Hence, this is a plausible alternative method for copper deposition. Also we compute that the metallocene by-product has high tendency to desorb (Table 4) and can be easily purged out of the system as described in section D.iv.

D.iii. Reduction by abstraction of sulfur

Like the deposition of Cu(0) via the intermediate pathway of CuO, Cu(0) can also be deposited from CuS. ALD of CuS has been reported before⁶⁷. H₂S or any sulfide containing compound can be admitted into the ALD chamber, in order to obtain a sulfide covered surface (equation 6 below). The metallocene M(II)Cp₂ can be introduced in the third pulse. We explore the energetics where the metallocene abstracts sulfur, forming S=M(IV)Cp₂ and simultaneously donating two electrons to the surface so as to yield Cu(0) as seen in equation 7. The computed reaction energy of equation (7) is nearly -200 kJ/mol. Hence, like the previous case of intermediate formation of CuO, the formation of CuS and subsequent reduction with metallocene is also a possible pathway. Our calculations show that the S=M(IV)Cp₂ by-product desorbs from the surface (Table 4). This decreases the possibility of incorporating S as an impurity during the reaction.

First step: surf + Cu(II)L_{2(g)} → surf-Cu(II)L₂... (3)

Second step: surf-Cu(II)L₂ + H₂S_(g) → surf-Cu(II)S + 2HL_(g) ... (6)

Third step: surf-Cu(II)S + MCp_{2(g)} → Cu(0)_(s) + S=MCp_{2(g)} ... (7)

D.iv. Desorption of the by-products

As discussed in previous studies, desorption of the by-products is an important aspect of ALD⁶⁵, as otherwise they will lead to impurities in the target material. In this section we use the Cu₅₅ model surface to computationally explore the desorption energies of the possible by-products occurring at the surface. A negative energy ΔG_{des} indicates that by-products are likely to desorb. The by-products produced in the above three sections are the substituted metallocenes in oxidation state IV (MCp₂L₂, MCp₂O, MCp₂S) and oxidation state II (MCp₂L). For this study we have considered vanadocene as the metallocene compound and four ligands from the Cu precursors.

Table 4 shows ΔG_{des} at 120°C for the by-products with V⁺⁴ oxidation state and Table 5 for V⁺³ oxidation state. In both the tables we can see that desorption is favored as the desorption free energy is negative because of entropy. Table 4 also shows that more sterically hindered compounds have more likelihood of desorption (e.g. VCp₂(acac)₂). In some by-products such as VCp₂(PyrIm^{iPr})₂, the ligand opens and forms a linear chain with just one ligating atom attached to the metal center. This happens predominantly in the by-products from equation 1 where there is double addition of ligands to the metal center. The structure of some of the by-products is given in the supplementary information.

Table 4 also shows desorption energies for surf-VCp₂O and surf-VCp₂S. The ΔG_{des} at T = 393 K for both the VCp₂O and VCp₂S compounds are negative. For the VCp₂O by-product, there is an alternative model that can be formed at the surface: VCp-O-surf where the O binds to both VCp₂ and the surface. The same model can occur for VCp₂S. Through our calculations we see that ΔE_{des} for VCp₂-O-surf is 57 kJ/mol greater than that for surf-VCp₂O (27 kJ/mol greater for the S analogues). Hence they can be more easily purged out of the system.

On the basis of the reaction energies we choose vanadocene as the best metallocene to be tested experimentally. The solution phase study for experimental validation is described in the following section.

Table 4: Energies (ΔE_{des}) and Gibbs free energies of desorption (ΔG_{des}) including entropy contribution (TΔS) at T = 393 K of the vanadocene by-products as discussed in section D.i, D.ii and D.iii, with the vanadium atom is in oxidation state IV. Data are computed at PBE/SV(P) level and compared to PBE/TZVPP in selected cases (in parentheses).

Molecules	ΔE _{des}	TΔS _{des}	ΔG _{des} ³⁹³
VCp ₂ O	51.1 (129.8)	483.1 (483.4)	-432.0 (-353.6)
VCp ₂ S	54.4 (135.0)	481.4 (481.7)	-427.0 (-346.7)
VCp ₂ (acac) ₂	211.6	1111.4	-899.8
VCp ₂ (dmap) ₂	110.9	1422.2	-1311.3
VCp ₂ (PyrAld) ₂	132.7	946.6	-813.9
VCp ₂ (PyrIm ^{iPr}) ₂	79.6	1470.8	-1391.2

Table 5: Energies (ΔE_{des}) and Gibbs free energies of desorption (ΔG_{des}) including entropy contribution (TΔS) at T = 393 K of the vanadocene by-products where the vanadium atom is in oxidation state III.

Molecules	ΔE _{des}	TΔS _{des}	ΔG _{des} ³⁹³
VCp ₂ (acac)	91.7	790.0	-698.3
VCp ₂ (dmap)	87.3	946.0	-858.7
VCp ₂ (PyrAld)	64.4	708.0	-643.6
VCp ₂ (PyrIm ^{iPr})	102.1	941.0	-838.9

E. Solution phase reactions

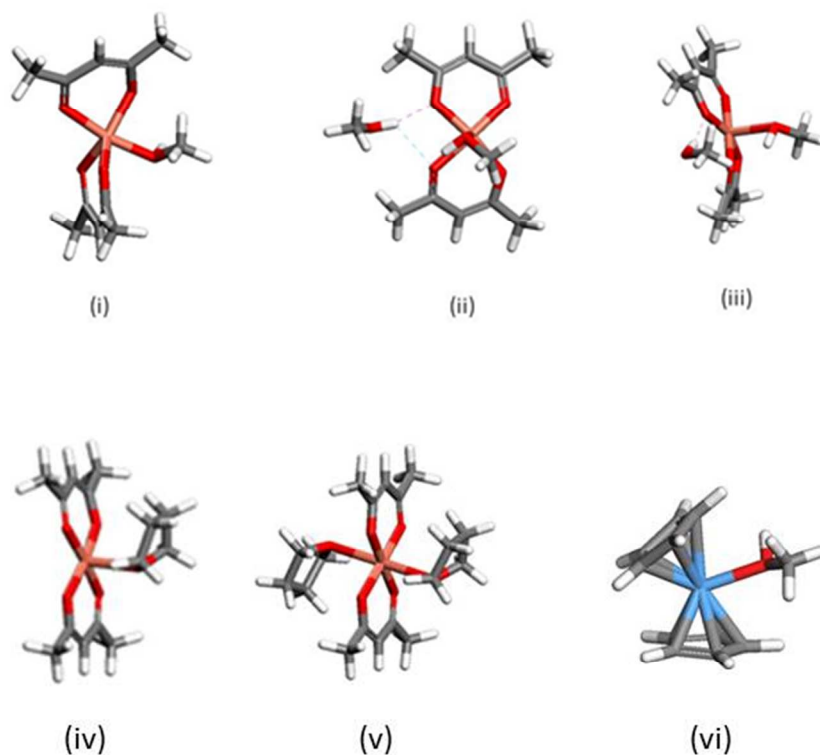
In section D.i. it is seen that vanadocene shows promise for use as the reducing agent in Cu ALD. A series of solution phase trials involving different ratios of Cu(acac)₂ to vanadocene, different solvents and reaction temperatures were performed to test the potential reduction of Cu(acac)₂ to Cu metal.

Tetrahydrofuran (THF) and methanol (MeOH) were investigated as solvents due to their difference in polarity with their dielectric constants being 7.5 and 33 respectively⁶⁸. In both cases, Cu(acac)₂ made a blue suspension in 4 ml of solvent (145 mg, 0.55 mmol). Vanadocene (100 mg, 0.55 mmol) was seen to dissolve in both solvents (8 ml) with no bubbling giving dark purple-black solutions. In all trials the vanadocene solution was added to the Cu(acac)₂ suspensions.

Using the more polar MeOH as solvent, a green solution was produced on addition of the vanadocene solution to the Cu(acac)₂ suspension in a 2:1 molar ratio, in accordance with the literature precedent that vanadocene salts of this nature appear green⁶⁹. After approximately 10 minutes of stirring, a Cu metal film began to form on the side of the

reaction flask. This delay in Cu production could be due to an effect of the MeOH, either via complexing with the vanadocene or coordinating with Cu(acac)₂ making the Cu centre and acac ligands more susceptible to interaction with the vanadocene. Kinetic barriers to the formation of such complexes might be the reason for the slow formation of the copper metal. Analysis of the supernatant using mass spectrometry showed a small peak at $m/z = 280.3$ that could correspond to the [Cp₂V(acac)]⁺ or [Cp₂V(OMe)]⁺ ion. Due to the fluxionality of the acac ligands, NMR spectroscopy proved unhelpful in determining the species present⁷⁰.

In order to see whether MeOH makes a stable coordinative bond with Cu(acac)₂ and vanadocene, 100 mg of each compound was taken and stirred separately in solution as was done at the



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Figure 5: Model structures optimized with DFT of Cu(acac)₂ complexes with inner shell solvent molecules MeOH or THF. (i) Cu(acac)₂(MeOH) with the O from MeOH coordinatively bonded to copper. (ii) Two MeOH bonded to Cu(acac)₂ in top view and (iii) side view; one MeOH is coordinatively bonded to Cu and the other is H-bonded to O from the precursor. (iv) Cu(acac)₂ coordinatively bonded to THF. (v) Cu(acac)₂ coordinatively bonded to two THF molecules. (vi) VCp₂ coordinatively bonded to one MeOH. Colour code is similar to Figure 2 with the addition of sky blue colour for Vanadium metal.

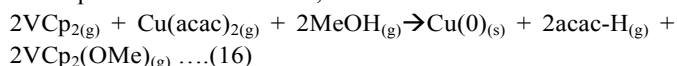
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start of the reaction. After stirring overnight at room temperature the solvent was removed from each mixture under vacuo and elemental analysis was carried out on the residue (Table 6). The elemental analysis shows that both C and H are present in compounds. Comparing both theoretical and actual results we see that only one MeOH was coordinated to VCp_2 and two to $\text{Cu}(\text{acac})_2$.

DFT structural optimization shows that MeOH can coordinate to both vanadocene and the copper precursor. The copper precursor complex can have one or more MeOH compounds attached to it. The probable structures from DFT calculations of the solvent-coordinated $\text{Cu}(\text{acac})_2$ and vanadocene are shown in Figure 5. It is seen that only one MeOH coordinates with the copper center in the precursor and distorts the planar structure. The computed bond length between the O in MeOH and the Cu in the precursor is 2.6 Å compared to typical Cu-O bond length of 1.9 Å⁷¹. (The Cu-O bond length in the acac precursor is 1.92 Å)¹³. The second MeOH forms a H-bonded compound with O in the precursor (Figure 5 ii and iii). In the case of vanadocene coordination with MeOH, DFT shows that there is only mono-coordination of MeOH with the metal center and a second MeOH does not coordinate to any part of the vanadocene. The formation energies of the MeOH coordinated complexes are quoted in equations (8-11) Table 7. The energies computed with DFT are all negative and hence inner shell coordination of MeOH is feasible. Changes in entropy and outer shell solvation are neglected in these calculations. Nevertheless, they indicate that stable MeOH adducts are formed by both the copper precursors and the vanadocene.

$\text{Cu}(\text{acac})_2$ has been reported to undergo a photolysis reaction in isopropanol to yield metallic copper as a final product⁷². This effect was not seen after stirring the copper compound in MeOH in natural light. The reduction to the metal must be an effect of the vanadocene, possibly via the coordination of a MeOH ligand.

Coordination of MeOH solvent to $\text{Cu}(\text{acac})_2$ raises the possibility of proton transfer from MeOH to acac and elimination of acacH. Based on the respective pK_a values, we expect that direct reactions resulting in $\text{Cu}(\text{acac})\text{MeO}$ or $\text{Cu}(\text{MeO})_2$ are unlikely to take place. However vanadocene could reduce Cu by abstraction of MeO. Such a reaction of vanadocene, $\text{Cu}(\text{acac})_2$ and MeOH is shown in equation 16 and is computed to be exothermic, $\Delta E = -214.3$ kJ/mol.



The formation of $\text{VCp}_2(\text{OMe})$ is more favorable than that of $\text{VCp}_2(\text{acac})$ (equation 2, $\Delta E = -200.9$ kJ/mol) due to less steric

hindrance in the former compound, and this may account for the MeOH-mediated deposition of Cu metal observed in the solution phase experiment.

In THF very little reaction was seen on addition of the vanadocene after stirring for several hours. After the application of heat up to 40°C the solution was seen to darken and decompose forming an insoluble material. Through attempting the DFT structural optimization of vanadocene attached to THF, it is seen that there is no strong coordination complex formed between these two compounds, differing in comparison with MeOH. However like MeOH, THF coordinatively bonds to the $\text{Cu}(\text{acac})_2$ precursor and coordination of two THF molecule to Cu is even possible (Figure 5 (v)). The planar structure of the acac complex is unaltered. The computed complexation energy is shown in equations 12-13, Table 7. Weak solvation of vanadocene by THF may be one reason why the reaction does not take place. In addition, THF may not transfer protons to acac and coordinate as an anion to Cu or V. These two differences probably account for the lack of Cu deposition observed in the THF experiments.

These experiments have demonstrated that under solvent dependent conditions, vanadocene can act as an effective reducing agent to give copper metal. The prospects are therefore good for vanadocene to function as an agent for reduction and ligand-removal in the gas-surface reactions of chemical vapor deposition and other thin film deposition techniques.

Table 6: Elemental Analysis of complexes with methanol adducts

Elemental Analysis	C%	H%
$(\text{C}_5\text{H}_5)_2\text{V}(\text{CH}_3\text{OH})$ (Theoretical)	61.97	6.62
$(\text{C}_5\text{H}_5)_2\text{V}(\text{CH}_3\text{OH})_2$ (Theoretical)	58.78	7.74
Actual Results	61.82	6.67
$(\text{acac})_2\text{Cu}(\text{CH}_3\text{OH})$ (Theoretical)	44.97	6.16
$(\text{acac})_2\text{Cu}(\text{CH}_3\text{OH})_2$ (Theoretical)	44.23	6.81
Actual Results	45.09	6.01

Table 7: Reaction energies for the coordination of solvents MeOH and THF to Cu(acac)₂ and vanadocene. All the energies are in kJ/mol. ‘*’ indicates that there is no optimized structure of the product.

Reaction No.	Reaction	Energy (ΔE)
8	$\text{Cu}(\text{acac})_2 + \text{MeOH} \rightarrow [\text{Cu}(\text{acac})_2(\text{MeOH})]$	-43.6
9	$\text{Cu}(\text{acac})_2 + 2\text{MeOH} \rightarrow [\text{Cu}(\text{acac})_2(\text{MeOH})_2]$	-97.7
10	$\text{VCp}_2 + \text{MeOH} \rightarrow [\text{VCp}_2(\text{MeOH})]$	-35.7
11	$\text{VCp}_2 + 2\text{MeOH} \rightarrow [\text{VCp}_2(\text{MeOH})_2]$	*
12	$\text{Cu}(\text{acac})_2 + \text{THF} \rightarrow [\text{Cu}(\text{acac})_2(\text{THF})]$	-41.6
13	$\text{Cu}(\text{acac})_2 + 2\text{THF} \rightarrow [\text{Cu}(\text{acac})_2(\text{THF})_2]$	-75.4
14	$\text{VCp}_2 + \text{THF} \rightarrow \text{VCp}_2(\text{THF})$	*
15	$\text{VCp}_2 + 2\text{THF} \rightarrow \text{VCp}_2(\text{THF})_2$	*

F. Conclusion

In this study we see how an oxidisable metal center from a metallocene compound (MCp₂) can bring about the reduction of another metal center from a precursor (CuL₂). We tested the reductive property of various metallocenes along with different copper precursors at the DFT level. We find that there are many advantages of using a metallocene as a reducing agent for Cu ALD. They are:

- Less chance of side reactions and hence less impurities compared to transmetallation.
- Vanadocene and chromocene are commercially available.
- Reactions should be possible with a wide range of Cu precursors.

Among all the metallocenes, vanadocene is proposed to be most favoured due to its availability in the market and exothermic reaction energy for reduction of Cu computed with DFT. Experiments in MeOH solution at room temperature demonstrated that Cu metal was deposited by the action of vanadocene on a Cu precursor. Vanadocene therefore shows promise as a gas-phase reducing agent in low-temperature atomic layer deposition of Cu metal.

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Notes and references

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