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Copper(I) carbene hydride complexes acting both as a reducing agent and precursor for Cu ALD - A study through Density Functional Theory

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Abstract We propose dual functional copper complexes that may act both as reducing agents and as Cu sources for prospective Cu Atomic Layer Deposition (ALD). Here we see a CuH carbene complex, which can donate the H^- anion to another Cu precursor forming neutral by-products and metallic Cu(0). We compute that such a reaction is thermodynamically possible because the Cu-H bond strength is weaker than that of Cu-C (from the carbene). For most other neutral ligands like PPh_3, BEt_3 etc. the order of bond strengths is vice versa. We also find that substitution in the carbene by electronegative groups reduces the Cu-H bond strength. This further facilitates the donation of H^- to the surface. The most promising copper carbene precursor is computed to be 1,3-diphenyl-4,5-imidazolidinedithione copper hydride (S-NHC)-CuH.

Keywords ALD · Carbene Hydride · DFT · Cu

1 Introduction

The atomic layer deposition (ALD) of copper is a challenge to the scientific community due to the need for conformal thin films of Cu in the electronics industry, where it is used as an interconnect material. A decrease in size of the Cu seed layer will permit further decrease

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in the size of the electronic devices. However, the formation of copper islands rather than a uniform layer during ALD is preventing such scaling of the seed layer. This problem has been highlighted by the International Technology Roadmap for Semiconductors as one of their key targets [1].

The usual approach to Cu ALD is to try reducing agents like hydrogen [2–5], alcohols [6] or like hydrazine [7] along with Chemical Vapour Deposition (CVD) type Cu precursors. Problems remain with the island formation and the impurities that come into the system from the reducing agents. In 2009, Lee *et al.* [8] proposed the use of an organometallic reagent $ZnEt_2$ as the reducing agent. But a subsequent study by Vidjayacoumar *et al.* [9,10] showed that there is Zn contamination in the system. We have studied this transmetallation reaction mechanism using Density Functional Theory (DFT) [11]. We suggest that metals close to Cu in the electrochemical series, like Zn, have a high chance of co-deposition along with copper. Thus, the use of an organometallic reagent as a reducing agent is limited by the choice of the metal.

Hydrogen (H_2) can be viewed formally as a proton donor and hydride donor and so can be used in various different ways for copper formation. First, it can be used to protonate the ligand (L) that is attached to the copper center and reduce copper to metallic form.

$$CuL_{2(g)} + H_{2(g)} \rightarrow Cu_{(s)} + 2HL_{(g)} \tag{1}$$

Alternatively, if there is a sulfide or nitride covered surface, it can combine to form H_2S or NH_3 respectively, leaving elemental Cu on the surface.

$$surf - CuS + H_{2(g)} \rightarrow surf - Cu + H_2S_{(g)} \uparrow \tag{2}$$

There have been similar attempts to convert other copper binary compounds like Cu_3N [12] into copper metal by using molecular hydrogen. However in order to crack the H-H bond, energy in excess of 400 kJ/mol is required [13]. Providing this as thermal energy means a high deposition temperature, which has been considered responsible for copper agglomeration. As an alternative H plasma has often been used for the reduction [14]. The narrow and deep interconnect features where the Cu is to be coated increases the probability of reformation of a H_2 molecule rather than a reactive H radical. Thus a thermal ALD technique is being targetted deposition of Cu in these applications.

If a new hydride source can be found with the following criteria, then it can be regarded as a good alternative hydride source rather than molecular hydrogen.

- **Weakly bound hydride** - Hydride should be easily donated by the compound without needing high thermal energy to break the bond.
- **Exothermic reaction** - The overall ALD reaction between the reagents producing Cu(0) should be exothermic in nature.
- **Precursors adsorb readily** - The precursors that are used in the ALD reaction should have strong adsorption onto the growing copper surface.
- **By-products desorb readily** - By-products that remain adsorbed onto the surface may lead to impurities. Thus by-products that can be easily desorbed should be favored.
- **Free of foreign metals** - Metals which are close to copper in the electrochemical surface have a high chance of co-deposition along with copper. Thus a non-copper organometallic reducing agent should be avoided even if it has other desirable properties.
- **Commercially available** - Being easily available in the market and cheap would be an added advantage.
- **Volatile and stable during delivery** - The hydride source should be volatile at low temperature and stable during delivery into the reactor in the gas phase.

Ritala *et al.* have proposed in 2004 [15] a technique to deposit Al_2O_3 with two Al compounds AlR_3 and $Al(OR)_3$. The use of only Al in the two reagents helps to reduce the changes of impurity and improve the quality of deposition. In this paper our main target is to achieve a similar deposition technique for Cu.

Recently Cu carbenes have been considered as a new family of precursor compounds [16,17]. A carbene is a neutral molecule containing carbon with two bonds and two unshared electrons, i.e. R_2C :. Carbenes are thus strong Lewis bases and candidates as neutral ligands in metal complexes. The first persistent carbene was prepared by Wanzlick's group in 1970's. They formed imidazol-2-ylidene carbene by the deprotonation of an imidazolium salt. It was believed that these imidazole-based carbenes, with a 4n+2 π-electron ring system, should be more stable than the 4,5-dihydro analogues, due to Hückel-type aromaticity. The carbene molecule is not isolated, but obtained as a coordination compound with e.g. mercury, copper and isothiocyanate [18–20]. Copper carbene complexes have a number of uses in organic chemistry. For instance a copper carbene complex with Cl has been widely studied for possible use in alkylation, allylation and reduction in organic chemistry [21–23]. A copper(I) carbene OH complex has been used for C-H bond activation [24]. Copper(I)

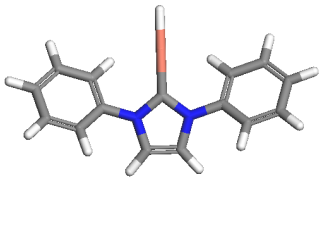


Fig. 1 N-heterocyclic-Cu hydride. Color code: brown=copper, white=hydrogen, blue=nitrogen, grey=carbon

hydride complexes like $CuH(PPh_3)$ are known to be mild reducing agents [25] and intermediates during catalysis reactions.

In this work we are proposing a modified 1,3-diphenyl-imidazolin-2-ylidene copper hydride complex that has been synthesized by Mankand *et al.* [26], as a suitable hydride donor and as a source of Cu (as seen in figure 1). Donation of hydride as a reducing agent broadens the chemistry of its use as the resulting proton can bond with various anion ligands from other copper precursors and form neutral by-products that can be readily purged out of the system. Related copper carbene compounds N-heterocyclic copper hexamethyldisilazide $(NHC)Cu(Si(NMe)_2)_2$ have been studied by Coyle *et al.* [27]. In this work we examine the quality of the copper carbene hydride complex to be used for possible Cu ALD using Density Functional Theory (DFT) as a tool.

2 Method Used

To evaluate certain aspects like the reaction energies and the adsorption of the precursors and desorption of the by-products of the copper carbene complexes, we have used Density Functional Theory (DFT) as implemented in the TURBOMOLE code [28]. As a level of calculation we have taken Perdew-Burke-Ernzerhof (PBE) [29] functional, which is suitable for organometallic systems and an all electron double zeta with polarization basis set def-SV(P) [30]. The level of calculation has been chosen as a compromise between computational cost and accuracy. Unconstrained geometry optimisation was carried out on all systems. A 55-copper atom cluster of C_{3v} geometry has been chosen as a model for the Cu(111) surface

during growth. All the Cu complexes studied are closed shell. An error may arise in the gas phase calculations for isolated Cu(0) atoms.

To calculate reaction energies for Cu ALD, we require the total energy per Cu atom of bulk copper metal. However, TURBOMOLE is limited to gas-phase atoms or clusters. We therefore correct the computed energy of a gas-phase $Cu_{(g)}$ atom using the adhesion energy computed for bulk $Cu_{(s)}$ with the periodic code VASP [31].

The entropy of the molecules (both precursors and by-products) has also been calculated in the gas phase from vibrational analysis using TURBOMOLE [32]. $\Delta G_{ad} = \Delta E_{ad} - T\Delta S_{ad}$ denotes the free energy needed by the molecules to be adsorbed onto the surface. The entropy has been calculated at T = 373 K as this is a typical target temperature for Cu ALD. It is assumed that the entropy of the molecules adsorbed onto the bare copper surface is primarily vibrational entropy. This is because after being adsorbed onto the surface, the molecule loses its translational and rotational degrees of freedom These are therefore the major contributions to ΔS_{ad}.

3 Results and Discussion - Evaluation of the copper carbene as a new precursor and reducing agent

We use the criteria in section 1 to evaluate the copper carbene complexes as new alternative sources of both hydride and copper.

3.1 Weakly bound hydride source

We seek a Cu-H bond that is sufficiently weak to break during ALD, but stable during delivery. Through quantum chemical calculations we have explored bond energies in the copper carbene complexes via equations 3 and 4. Equation 3 shows the homolytic dissociation of the complex to form XCu and neutral H (X = ligand) while 4 refers to homolytic dissociation of the same into CuH and X. These bond dissociation energies may be modified by adsorption and by the presence of co-reagents. We have taken neutral ligands (X) like PPh_3, BF_3 etc to understand the chemistry of bond breaking.

$$XCuH \rightarrow XCu + H \tag{3}$$

$$XCuH \rightarrow CuH + X \tag{4}$$

Table 1 Bond dissociation energy for copper ligand complexes XCuH according to equation 3 and 4 with the copper-ligating atom bond length shown as Cu-X

		ΔE (kJ/mol)	
Ligand	Cu-X (Å)	equation 3	equation 4
PPh_3	2.21	216.30	169.79
$P(OEt)_3$	2.19	228.53	167.32
BEt_3	2.13	165.18	106.60
BF_3	2.20	139.64	57.89
N-heterocyclic carbene (NHC)	1.91	231.06	241.48
sulfur substituted N-heterocyclic carbene (S-NHC)	1.90	200.09	247.03
methyl substituted N-heterocyclic carbene (CH_3-NHC)	1.90	248.84	239.65
oxo substituted N-heterocyclic carbene (O-NHC)	1.89	269.15	280.97
chloro substituted N-heterocyclic carbene (Cl-NHC)	1.90	231.34	236.17

The computed ΔE values for these reactions at $T = 0$ K are presented in Table 1 along with the bond length of Cu to the ligating atom in the ligand. The Cu-H bond length remains almost constant (1.5 Å) in all the cases regardless of ΔE for equation 3.

From Table 1 we can see that the P and B based ligands give complexes with stronger Cu-H bonding (equation 3) than Cu-X (equation 4), assuming that there is no chemical effect at the surface that changes the energetics of Cu-H vs. Cu-X dissociation. We find that the NHC complex (Figure 1) shows a difference between ΔE values of $<$12 kJ/mol. However, when we substitute two hydrogen atoms at 4,5 positions on the heterocycle with sulfur atoms as in Figure 2, the difference is around 47 kJ/mol. This substituted ligand in the compound is called 1,3-diphenyl-4,5-imidazolidinedithione copper hydride (S-NHC)CuH. This lower bond strength for Cu-H than Cu-X enables the Cu-H bond to break first and liberate H radical (homolytic fission) or anion (heteroleptic fission) which can act as the electron donor to the Cu metal centers. The difference is very little if we

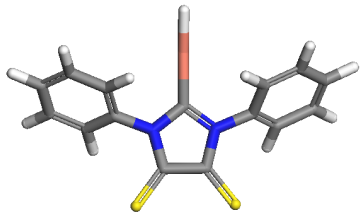


Fig. 2 (S-NHC)CuH showing S substituted for H at 4 and 5 positions. Color code: brown=copper, white=hydrogen, blue=nitrogen, grey=carbon, sulfur=yellow

Table 2 Reaction energies for deposition of copper in ideal ALD (eq. 5) and a competing side reaction (eq. 6) using (S-NHC)CuH and two different copper precursors CuL_2 as co-reagents

	ΔE) (kJ/mol)	
Ligand L	Equation 5	Equation 6
dmap	-22.1	55.1
acac	-28.0	37.9

substitute with other electron withdrawing groups (-I inductive effect) like Cl^-. If we substitute with positive inductive effect (electron donating) groups like $-CH_3$, then the energy difference is reversed. We conclude that an electron withdrawing group on the heterocycle is favorable for making the hydride accessible. Hence our first condition is fulfilled with the copper carbene complex (S-NHC)CuH.

3.2 **Exothermic reaction energy**

The next metric that we computed to asses the suitability of the copper carbene, both as a precursor and also as a reducing agent is the reaction energy of the proposed ALD reaction. Deposition of copper from the single source copper carbene might be possible via a CVD type reaction at elevated temperatures rather than ALD. However, our interest is in ALD and so at least two reagents are necessary.

One ALD reaction in which we propose using the carbene as a reducing agent is:

$$2(\mathrm{S-NHC})\mathrm{CuH}_{(g)} + \mathrm{CuL}_{2(g)} \rightarrow 3\mathrm{Cu}(0)_{(s)} + 2\mathrm{LH}_{(g)} + 2(\mathrm{S-NHC})_{(g)} \quad (5)$$

Here L is the ligand from the second precursor. We can also write a competing side reaction where S-NHC does not desorb, which would hinder ALD.

$$2(\mathrm{S-NHC})\mathrm{CuH}_{(g)} + \mathrm{CuL}_{2(g)} \rightarrow \mathrm{Cu}(0)_{(s)} + 2\mathrm{LH}_{(g)} + 2(\mathrm{S-NHC})\mathrm{Cu}(0)_{(g)} \quad (6)$$

In (S-NHC)CuH, the S-NHC is a spectator ligand that does not have any specific role. The H has the dual role of delivering electrons to Cu(I)/Cu(II) and also ligating with the ligand L in order to form neutral by-products. The copper precursor $\mathrm{CuL}_{2(g)}$ has dual role of delivering the copper atom and also provide ligands to saturate the surface and later bond with the H from the copper carbene complex. CuL_2 represents the copper precursors where the ligand (L) can be dmap (diphenylamine-2-propoxide), acac (acetylacetonate) or any other commonly used ligand [11]. Table 2 shows the computed reaction energies for equations 5 and 6 using dmap and acac precursors. The two ligands studied here differ in the π conjugation (present in the acac ligand) and also in the electronegativity of the ligating atom. Both the precursors have exothermic reaction energies of similar magnitude for equation 5. This shows that the reaction is feasible for different copper precursors, with only a weak dependence on the precursor used. The reaction energies are little endothermic for the competing reaction of equation 6. The low endothermicity for the latter reaction can be overcome by entropy due to the formation of gaseous compounds like LH. Nevertheless, it is encouraging that the desired ALD reaction is more thermodynamically favored

Cu can also be deposited by a three step ALD process. A thin layer of CuS or else $\mathrm{Cu_3N}$ can be deposited in the first two ALD steps. The sulfide or the nitride layer can then be reduced by (S-NHC)CuH in the third step, resulting in the deposition of $\mathrm{Cu}_{(s)}$. ALD of CuS [33] is known in the literature and deposition of Cu with $\mathrm{Cu_3N}$ has also been tried before [12]. The different steps are shown in Figure 3. For the reduction of copper sulfide, the probable reactions are presented in equations 7 and 8 and those for copper nitride are presented in equations 9 and 10, where again the second reactions in each case are unwanted side-reactions that poison the surface. If $\mathrm{H_2S}$ or $\mathrm{NH_3}$ are used to generate CuS or $\mathrm{Cu_3N}$ respectively from $\mathrm{CuL_2}$, then the ALD reaction energies for

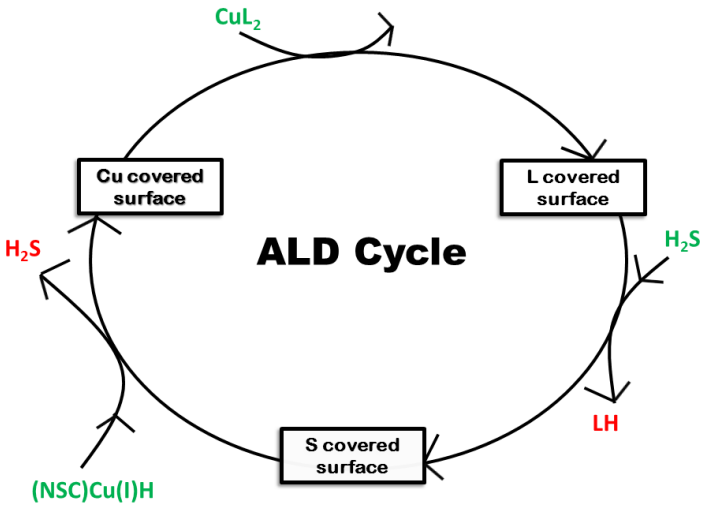


Fig. 3 Flowchart showing the three-step ALD cycle for the deposition of Cu with the intermediate formation of CuS layer. L = ligand and S = sulfide.

these three-step process are identical to the two-step ones (eq. 5 and eq. 6, Table 2).

$$2(\mathrm{S-NHC})\mathrm{CuH}_{(g)} + \mathrm{CuS}_{(s)} \rightarrow 3\mathrm{Cu}(0)_{(s)} + \mathrm{H_2S} + 2(\mathrm{S-NHC})_{(g)} \quad (7)$$

$$2(\mathrm{S-NHC})\mathrm{CuH}_{(g)} + \mathrm{CuS}_{(s)} \rightarrow \mathrm{Cu}(0)_{(s)} + \mathrm{H_2S}_{(g)} + 2(\mathrm{S-NHC})\mathrm{Cu}(0)_{(s)} \quad (8)$$

$$3(\mathrm{S-NHC})\mathrm{CuH}_{(g)} + \mathrm{Cu_3N}_{(s)} \rightarrow 6\mathrm{Cu}(0)_{(s)} + \mathrm{NH_3}_{(g)} + 3(\mathrm{S-NHC})_{(g)} \quad (9)$$

$$3(\mathrm{S-NHC})\mathrm{CuH}_{(g)} + \mathrm{Cu_3N}_{(s)} \rightarrow 3\mathrm{Cu}(0)_{(s)} + \mathrm{NH_3}_{(g)} + 3(\mathrm{S-NHC})\mathrm{Cu}(0)_{(s)} \quad (10)$$

The same conclusion therefore apply as in the two-step case, i.e. the ALD reaction is moderately favored relative to the side reaction.

3.3 **Precursors should adsorb and by-products should desorb readily**

Another metric is the free energy of adsorption or desorption onto the bare copper surface, modelled by a Cu(111) facet on a 55-atom Cu cluster. It is a criterion for successful ALD that the reactants adsorb but the by-products desorb from the surface, even at low temperatures. As shown in 3, we find that $\Delta G > 0$ at T = 120°C for all reactants (except the CuL_2 precursors) and by-products, indicating that desorption is always favored.

Table 3 Energy of adsorption of the molecules onto a Cu(111) model surface computed by DFT. Negative energy shows that adsorption of the molecule is favorable. The entropy contribution of the molecules has been calculated at $T = 120°C$. All the energy values are in kJ/mol.

Molecules	ΔE_{ad}	$T\Delta S$	ΔG^{120}
(S-NHC)CuH	-518.4	638.2	119.8
(NHC)CuH	-296.6	677.6	381.0
$Cu(acac)_2$	-258.4	179.2	-79.2
$Cu(dmap)_2$	-249.0	184.0	-64.9
NH_3	-47.1	95.8	48.7
H_2S	-43.8	47.7	3.8
S-NHC	-284.8	608.4	397.8
NHC	-210.6	648.4	437.8
acacH	-91.5	339.8	248.3
dmapH	-102.1	497.4	395.3

There is molecular adsorption for all the compounds listed in Table 3. NH_3, H_2S, acacH and dmapH show physisorption on the bare copper surface. The (S-NHC)CuH precursor adsorbs strongly onto the copper surface through bonds between the under coordinated Cu surface and the S atoms. However there are significant differences in the ΔG values.

We can see that the (S-NHC)CuH compound will adsorb more strongly than the corresponding compound without any sulfur substitution. Thus the sulfur containing compound will be a better choice as a precursor. The by-products S-NHC and NHC will desorb readily as the free energy values are >0. The by-product NH_3 has low adsorption energy and hence can be easily desorbed. However H_2S has a free energy of adsorption approximately equal to zero and therefore is less likely to desorb. Free ligands like acacH and dmapH also have poor adsorption energies and hence can be readily desorbed. We can also use the data in Table 3 to assess the viability of the proposed two step (eq. 5) and three-step (eq. 7 and 9) ALD process. A two step process without intermediate formation of the binary compound might be a better choice because the protonated ligands

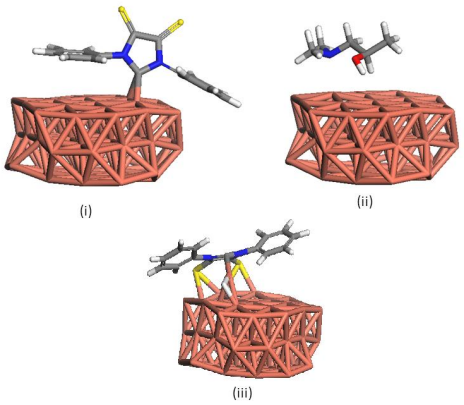


Fig. 4 (i) shows the S-NHC carbene chemisorbed onto the bare copper surface via C. (ii) shows the acacH ligand physisorbed onto the surface. (iii) shows the (S-NHC)CuH adsorbed onto the surface via Cu and S.

(LH) desorb more readily from the surface than NH_3 and H_2S. A three step process might therefore increase the chances of impurities.

To summarise this section, we see that the proposed new precursors (S-NHC)CuH adsorb strongly and the by-products desorb readily, thus fulfilling an important factor for a good ALD reaction to take place.

3.4 **Free of foreign metals**

There is no foreign metal present in the proposed system and hence there is no chance of any impurity coming from the co-deposition of another metal as happens for the reaction with $ZnEt_2$ [8]. C, N and O impurities are expected from the possible thermal decomposition of the ligands.

3.5 **Synthesisable and Commercially available**

Although copper carbene compounds have not been functionalised yet with S in this way, a Pd carbene has been functionalised at 4, 5 carbons with ester groups by Hara *et al.* [34]. The Pd carbene is shown in Figure 5.

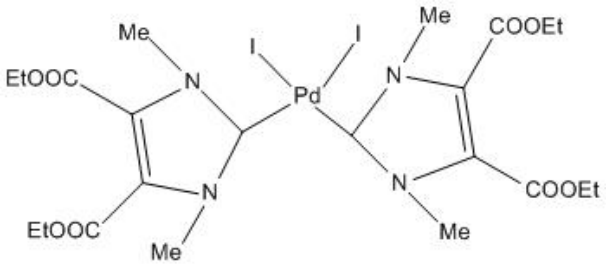


Fig. 5 Ester-functionalised carbene coordinated to Pd [34].

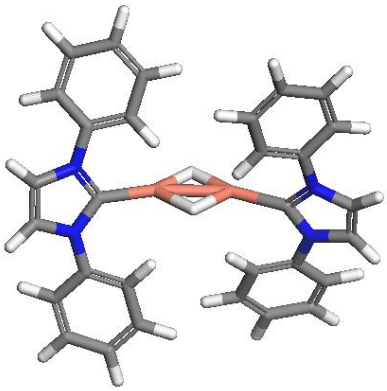


Fig. 6 N-heterocyclic-Cu hydride dimer. Color code: brown=copper, white=hydrogen, blue=nitrogen, grey=carbon. The dihedral angle between C-Cu-Cu-C where the C is from the liagted carbene molecule is 16°.

3.6 **Volatile and Stable during delivery**

Since the -I electron-withdrawing (inductive effect) substituted copper compounds have not been synthesized yet, we cannot comment about stability during delivery. However, (NHC)CuH complexes have a tendency to be in dimer form as mentioned by Mankand *et al.*. The probable dimer structure optimised with DFT is presented in Figure 6. The dimer is computed to be nearly isoenergetic with a pair of monomers (dimerization costs +5kJ/mol). However the monomer structure is favored by entropy. Coyle *et al.* mentions in their work [19] that the copper carbene compounds synthesized by them have low volatility as seen from the thermogravimetric analysis (TGA).

4 Conclusion

We propose -I (electron-withdrawing inductive) group substituted (NHC)CuH complex 4,5 imidazolidinedithione-N-heterocyclic copper carbene (S-NHC)CuH as a new precursor for Cu ALD. Due to the weak bond strength between the copper and the hydrogen in (S-NHC)CuH, the hydride anion is readily available as a reducing agent for copper, either from precursors or binary compounds. Thus low temperature ALD can perhaps be carried out and the problem of islanding can perhaps be alleviated in this manner. As the ALD reaction energies are either exothermic or slightly endothermic (overcome with the help of entropy as in eq.6) for all our test cases, we can conclude that the proposed ALD reactions are feasible.

When using an organometallic reagent as a reducing agent, there is always the danger of reduction of the metal center, which may lead to unwanted co-deposition of that metal. Here, we propose a Cu based reducing agent, so that co-deposition is desirable. We find that such co-deposition of copper from the copper carbene complex is always favored. We can also see that the reactant is more adsorbent to the surface than the corresponding by-products like the protonated acac ligand. This indicates that the by-products can be desorbed from the surface in a clean ALD process. A current disadvantage of the process is that the precursor is not commercially available.

Thus, we propose a S substituted copper(I) carbene hydride functioning both as a reducing agent and as a copper source for the ALD of copper metal.

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References

1. *International Technology Roadmap for Semiconductors*. http://www.itrs.net, 2011.
2. Per Mårtensson, Karin Larsson, and Jan-Otto Carlsson. Atomic layer epitaxy of copper: an ab initio investigation of the $CuCl/H_2$ process:II.reaction energies. *Applied surface science*, 148(1):9–16, 1999.
3. Per Mårtensson, Karin Larsson, and Jan-Otto Carlsson. Atomic layer epitaxy of copper: an ab initio investigation of the $CuCl/H_2$ process:I.adsorption of cucl on cu (111). *Applied surface science*, 136(1):137–146, 1998.
4. Per Mårtensson, Karin Larsson, and Jan-Otto Carlsson. Atomic layer epitaxy of copper: an ab initio investigation of the $CuCl/H_2$ process:III.reaction barriers. *Applied surface science*, 157(1):92–100, 2000.
5. Irene J. Hsu, Brian E. McCandless, Conan Weiland, and Brian G. Willis. Characterization of ald copper thin films on palladium seed layers. *Journal of Vacuum Science Technology A:Vacuum, Surfaces, and Films*, 27(4):660–667, 2009.
6. Balu Pathangey Raj Solankia. Atomic layer deposition of copper seed layers. *Electrochemical and solid state letters*, 3:479, 2000.
7. Thomas J Knisley, Thiloka C Ariyasena, Timo Sajavaara, Mark J Saly, and Charles H Winter. Low temperature growth of high purity, low resistivity copper films by atomic layer deposition. *Chemistry of Materials*, 23(20):4417–4419, 2011.
8. Byoung H. Lee, Jae K. Hwang, Jae W. Nam, Song U. Lee, Jun T. Kim, Sang-M. Koo, A. Baunemann, Roland. A. Fischer, and MyungM. Sung. Low-temperature atomic layer deposition of copper metal thin films: Self-limiting surface reaction of copper dimethylamino-2-propoxide with diethylzinc. *Angewandte Chemie International Edition*, 48(25):4536–4539, 2009.
9. Balamurugan Vidjayacoumar, David J. H. Emslie, Scott B. Clendenning, James M. Blackwell, James F. Britten, and Arnold Rheingold. Investigation of $AlMe_3$, BEt_3, and $ZnEt_2$ as co-reagents for low-temperature copper metal ald/pulsed-cvd. *Chemistry of Materials*, 22(17):4844–4853, 2010.
10. Balamurugan Vidjayacoumar, David JH Emslie, James M Blackwell, Scott B Clendenning, and James F Britten. Solution reactions of a bis (pyrrolylaldiminate) copper (ii) complex with peralkyl zinc, aluminum, and boron reagents: Investigation of the pathways responsible for copper metal deposition. *Chemistry of Materials*, 22(17):4854–4866, 2010.
11. Gangotri Dey and Simon D. Elliott. Mechanism for the atomic layer deposition of copper using diethylzinc as the reducing agent: A density functional theory study using gas-phase molecules as a model. *The Journal of Physical Chemistry A*, 116(35):8893–8901, 2012.
12. Z. Li and R.G. Gordon. Thin, continuous, and conformal copper films by reduction of atomic layer deposited copper nitride. *Chemical Vapor Deposition*, 12(7):435–441, 2006.
13. T.L. Cottrell. *The Strengths of Chemical Bonds*. Butterworths Scientific Publications, 2nd edition edition, 1958.
14. L Wu and E Eisenbraun. Effects of hydrogen plasma treatments on the atomic layer deposition of copper. *Electrochemical and Solid-State Letters*, 11(5):H107–H110, 2008.
15. Mikko Ritala, Kaupo Kukli, Antti Rahtu, Petri I. Räisänen, Markku Leskelä, Timo Sajavaara, and Juhani Keinonen. Atomic layer deposition of oxide thin films with metal alkoxides as oxygen sources. *Science*, 288(5464):319–321, 2000.

16. Alexander M Willcocks, Thomas Pugh, Jeff A Hamilton, Andrew L Johnson, Stephen P Richards, and Andrew J Kingsley. Cvd of pure copper films from novel iso-ureate complexes. *Dalton Transactions*, 42:5554–5565, 2013.
17. Qiang Ma, Hansheng Guo, Roy G Gordon, and Francisco Zaera. Surface chemistry of copper (i) acetamidinates in connection with atomic layer deposition (ald) processes. *Chemistry of Materials*, 23(14):3325–3334, 2011.
18. Hans-Jürgen Schönherr and Hans-Werner Wanzlick. Chemie nucleophiler carbene, xviii1) 1.3.4.5-tetraphenyl-imidazoliumperchlorat. *Justus Liebigs Annalen der Chemie*, 731(1):176–179, 1970.
19. Jason P. Coyle, Agnieszka Kurek, Peter J. Pallister, Eric R. Sirianni, Glenn P. A. Yap, and Sean T. Barry. Preventing thermolysis: precursor design for volatile copper compounds. *Chem. Commun.*, 48:10440–10442, 2012.
20. H. W. Wanzlick. Aspects of nucleophilic carbene chemistry. *Angewandte Chemie International Edition in English*, 1(2):75–80, 1962.
21. Andrejs Pels, Esa T. T. Kumpulainen, and Ari M. P. Koskinen. Highly chemoselective copper-catalyzed conjugate reduction of stereochemically labile unsaturated amino ketones. *The Journal of Organic Chemistry*, 74(19):7598–7601, 2009.
22. Satoshi Tominaga, Yukinao Oi, Toshio Kato, Duk Keun An, and Sentaro Okamoto. Selective allylic substitution reaction with grignard reagents catalyzed by copper n-heterocyclic carbene complexes and its application to enantioselective synthesis. *Tetrahedron Letters*, 45(29):5585 – 5588, 2004.
23. Valdas Jurkauskas, Joseph P. Sadighi, and Stephen L. Buchwald. Conjugate reduction of unsaturated carbonyl compounds catalyzed by a copper carbene complex. *Organic Letters*, 5(14):2417–2420, 2003.
24. Ine I F Boogaerts and Steven P Nolan. Carboxylation of c-h bonds using n-heterocyclic carbene gold(i) complexes. *Journal of the American Chemical Society*, 132(26):8858–8859, 2010.
25. Thomas M. Koenig, John F. Daeuble, Donna M. Brestensky, and Jeffrey M. Stryker. Conjugate reduction of polyfunctional $\alpha\beta$ unsaturated carbonyl compounds using $[(Ph_3P)CuH]_6$. compatibility with halogen, sulfonate, and γ oxygen and sulfur substituents. *Tetrahedron Letters*, 31(23):3237 – 3240, 1990.
26. Neal P. Mankad, David S. Laitar, and Joseph P. Sadighi. Synthesis, structure, and alkyne reactivity of a dimeric (carbene)copper(i) hydride. *Organometallics*, 23(14):3369–3371, 2004.
27. Jason P. Coyle, Gangotri Dey, Eric R. Sirianni, Marianna L. Kemell, Glenn P. A. Yap, Mikko Ritala, Markku Leskela, Simon D. Elliott, and Sean T. Barry. Deposition of copper by plasma-enhanced atomic layer deposition using a novel n-heterocyclic carbene precursor. *Chemistry of Materials*, 25(7):1132–1138, 2013.
28. Ansgar Schäfer, Christian Huber, and Reinhart Ahlrichs. Fully optimized contracted gaussian basis sets of triple zeta valence quality for atoms Li to Kr. *The Journal of chemical physics*, 100:5829, 1994.
29. John P Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized gradient approximation made simple. *Physical review letters*, 77(18):3865–3868, 1996.
30. Karin Eichkorn, Florian Weigend, Oliver Treutler, and Reinhart Ahlrichs. Auxiliary basis sets for main row atoms and transition metals and their use to approximate coulomb potentials. *Theoretical Chemistry Accounts: Theory, Computation, and Modeling (Theoretica Chimica Acta)*, 97(1):119–124, 1997.
31. G. Kresse and J. Hafner. *Ab initio* molecular-dynamics simulation of the liquid-metal˘amorphous-semiconductor transition in germanium. *Phys. Rev. B*, 49:14251–14269, May 1994.

32. Peter Deglmann, Klaus May, Filipp Furche, and Reinhart Ahlrichs. Nuclear second analytical derivative calculations using auxiliary basis set expansions. *Chemical Physics Letters*, 384:103 – 107, 2004.
33. Johanna Johansson, Juhana Kostamo, Maarit Karppinen, and Lauri Niinisto. Growth of conductive copper sulfide thin films by atomic layer deposition. *J. Mater. Chem.*, 12:1022–1026, 2002.
34. Kenji Hara, Yoshikazu Kanamori, and Masaya Sawamura. Ring carbon functionalization of *N-heterocyclic carbene ligand with ester groups. electronic effect of ester groups on coordination properties.* Bulletin of the Chemical Society of Japan*, 79(11):1781–1786, 2006.*