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Remarkably Volatile Copper(II) Complexes of *N,N′*-Unsymmetrically Substituted 1,3-Diketimines as Precursors for Cu Metal Deposition via CVD or ALD

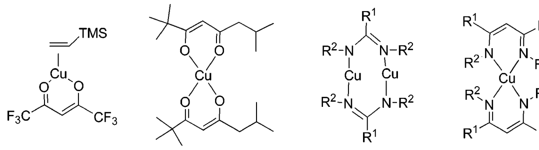
Kyung-Ho Park* and Will J. Marshall

Materials Science and Engineering, Central Research and Development, DuPont, Experimental Station, Wilmington, Delaware 19880-0328

Received February 23, 2005; E-mail: kyung-ho.park@usa.dupont.com

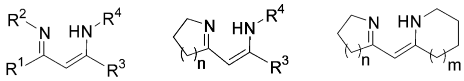
Volatile copper β-diketonates are often regarded as promising precursors for copper metal deposition via CVD and/or ALD[1] for industrial semiconductor devices of the new generation. For example, hexafluoroacetylacetonato(trimethylsilylethylene)copper (**1** in Figure 1), or Cupraselect,[2] is an important industrial candidate for copper metal deposition. Another example is 2,2,7-trimethyl-3,5-octanedionatecopper(II), **2**, which can also be used in a process using a supercritical fluid.[3] In the modern industry of microelectronics, however, it is increasingly recognized that the presence of oxygen or halogens in the precursor can be detrimental to the desired performance, including device efficiency.[4] Thus, oxygen- and halogen-free nitrogen-containing ligands are currently viewed as an alternative to 1,3-diketones, particularly with metal complex precursors for microchip interconnect layers. In this regard, Cu derivatives of 1,3-amidines and 1,3-diketimines should be the very alternative to the 1,3-diketonate complexes. Gordon et al. have recently reported[5] the synthesis of *N*,*N′*-symmetrically substituted dimeric copper(I) amidinate **3** as a copper precursor in the ALD process. However, the corresponding Cu(II) derivative cannot be obtained due to the facile reduction of $CuCl_2$ upon its treatment with the Li amidinate. Monomeric Cu(I)L(amidinate) cannot be synthesized either, due to steric factors. As for 1,3-diketimine, monomeric Cu(I)L(diketiminate) can be synthesized but is usually unstable especially when aliphatic diketimine is employed, easily undergoing disproportionation to Cu(0) and Cu(II). As a result, stable Cu(II) $(\text{diketiminate})_2$ has been focused as a potential copper precursor in ALD. Some oxygen- and halogen-free metal complexes of 1,3-diketimines have been prepared.[6] However, only metal complexes of *N*,*N′*-symmetrically substituted 1,3-diketimines (**4**) have been prepared.

To enhance the volatility of the copper precursor in the copper deposition process, it was envisioned that *N*,*N′*-unsymmetrically substituted 1,3-diketimines should be more volatile than their symmetrically substituted counterparts, possibly due to the less compacted mode of molecular stacking originating from the unsymmetrical ligand. It is also based on the assumption that the lower symmetry would change the entropy of vaporization (making it higher) and possibly making the enthalpy of sublimation lower by destabilizing the crystal lattice. When a symmetrical molecule leaves a solid lattice to the vapor (or liquid) phase, the entropy of vaporization is lowered relative to a comparable unsymmetrical molecule leaving a solid lattice to the vapor phase. A higher entropy of vaporization and a lower enthalpy of sublimation would both contribute toward a higher vapor pressure at constant temperature. The desired, individual *N*,*N′*-unsymmetrically substituted 1,3-diketimines, however, cannot be prepared by the McGeachin method.[7] We have recently developed a new strategy for the synthesis of nonhalogenated *N*,*N′*-unsymmetrically substituted aliphatic 1,3-diketimine ligands (**5**, **6**, and **7** in Figure 2) via the reaction of exocyclic enaminoketones with amines or metalloenamines with imidoyl thioethers.[8]



1 **2** **3** **4**

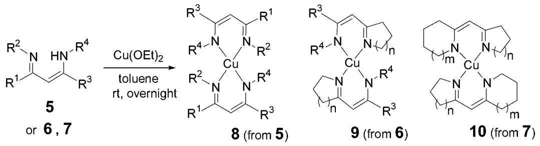
Figure 1. Cu(I) and Cu(II) precursors for CVD or ALD.



5 **6** **7**

Figure 2. *N*,*N′*-Unsymmetrically substituted 1,3-diketimines.

Scheme 1. Synthesis of Cu(II) (Unsymmetrical 1,3-Diketiminate)



Having prepared unsymmetrical ligands **5**−**7**, we synthesized their Cu(II) bischelates in up to 96% yield, as shown in Scheme 1 and Table 1.

The new Cu(II) complexes of *N*,*N′*-unsymmetrically substituted 1,3-diketimines were characterized by X-ray crystallography, and some representative structures are given in Figure 3. The structures exhibited distorted tetrahedral geometries, where dihedral angles between the two chelating NCuN planes vary in the range of 33.5−64.3°.

All unsymmetrical Cu(II) diketiminates appeared sublimable under vacuum without decomposition. As can be seen from the data in Table 1, Cu(II) complexes with aliphatic substituents are more volatile than those with aromatic groups (**8-c**, **8-d**, and **9-d**). Within the aliphatic series, unsymmetrical Cu(II) acyclicdiketiminates **8** were more volatile than mono- or dicyclic diketiminate copper(II) complexes **9** and **10**. This might be due to the tethered ring system contributing to more spatially compacted molecular stacks, thus reducing the volatility. TGA studies of these Cu(II) complexes at 500 mTorr were performed, and some representative TGA curves are given in Figure 4. Remarkably, the higher molecular weight **8-b** (*N*-*i*-Bu, *N′*-Me) was found to be more volatile than **8-a** (*N*-Et, *N′*-Me). Thus, within the comparable molecular weight range, bulkier unsymmetrical substituents seem to play a more important role to enhance the volatility of diketiminate Cu(II) complexes.

The results from isothermal TG analysis proves the effect of unsymmetry in Cu(II) complexes on their volatility (Figure 5).

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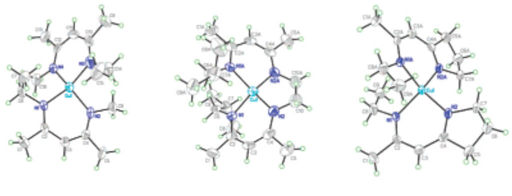
Table 1. Cu(II) (Diketiminate) and Its Vapor Pressure

compound	R^1	R^2	R^3	R^4	vapor pressure (°C/mTorr)
8-a	Me	Me	Me	Et	25/55
8-b	Me	*i*-Bu	Me	Me	25/70
8-c	Me	Me	Ph	Et	70/32
8-d	Me	*i*-Bu	Ph	Me	85/30
9-a	$n = 1$		Me	Me	50/50
9-b	$n = 1$		Me	Et	30/50
9-c	$n = 1$		Me	H	60/50
9-d	$n = 1$		Ph	Me	80/40
10-a	$n = 1$		$m = 1$		60/40
10-b[a]	$n = 1$		$m = 0$		65/40

[a] Symmetrical Cu(II) bis(diketiminate).



8-a **8-b** **9-b**

Figure 3. X-ray structures of Cu(II) (*N*,*N*′-unsymmetrically substituted 1,3-diketiminate).

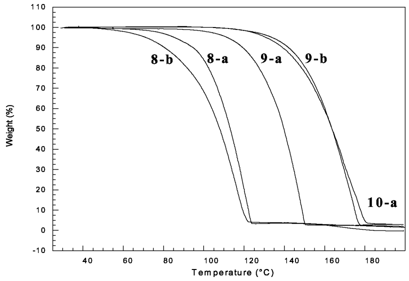


Figure 4. TG curves for unsymmetrical Cu(II) diketiminate.

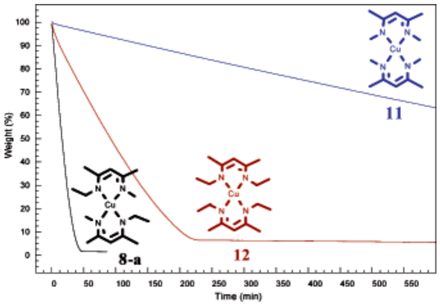
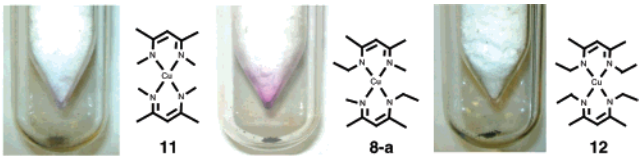


Figure 5. Comparison of TG curves between symmetrical and unsymmetrical Cu(II) diketiminates (80 °C/500 mTorr).

The symmetrical Cu(II) complex **11** is the least volatile due to the small size of the substituents (methyls) on the nitrogen atoms, followed by symmetrical Cu(II) complex **12** with the larger ethyl groups, and finally the most volatile **8-a** containing one methyl and one ethyl on the N atoms of each ligand.



11 **8-a** **12**

11 (*N*-Me, *N*′-Me) **8-a** (*N*-Me, *N*′-Et) **12** (*N*-Et, *N*′-Et)

Figure 6. Sublimation of Cu(II) diketiminate at 25 °C (55 mTorr).

The effect of asymmetry of these Cu(II) complexes on their volatility was vivid when unsymmetrical **8-a** and symmetrical **11** and **12** were tested for vacuum sublimation in a conventional glass apparatus at 55 mTorr (Figure 6). As clearly seen from Figure 6, unsymmetrical Cu(II) complex **8-a** sublimed even at room temperature, while symmetrical Cu(II) complexes **11** and **12** did not exhibit any sign of volatility under identical conditions.

Importantly, the new, highly volatile Cu(II) complexes were found to be reducible to Cu metal after vacuum deposition on a SiO_2 wafer. For example, complex **9-a** was sublimed at 50 °C under 50 mTorr, producing copper film at 100 °C upon contact with diethylsilane as a reducing agent.

In conclusion, a variety of Cu(II) (*N*,*N*′-unsymmetrically substituted 1,3-diketiminate) complexes have been synthesized and have proven qualitatively to be much more volatile than their symmetrical counterparts. We plan to disclose in a full paper more quantitative relationship data between volatility and Cu complexes' symmetry by determining its enthalpy of vaporization at several temperatures soon.

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Supporting Information Available: Experimental details (PDF) and crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

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