Inorg. Chem. **2006**, *45*, 8480–8482

Inorganic Chemistry

Communication

Nonfluorinated Volatile Copper(I) 1,3-Diketiminates as Precursors for Cu Metal Deposition via Atomic Layer Deposition

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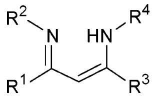
Received June 7, 2006

Novel nonfluorinated Cu(diketiminate)L complexes with L = neutral olefinic ligand have been prepared as stable, volatile Cu(I) precursors for the deposition of copper films by an atomic layer deposition (ALD) process. Among them, the complexes of **4-a** and **5-a** are the most volatile and stable at low temperature (55 °C). A clean, conformal copper film was deposited at 120 °C in an ALD process. These Cu(I) complexes are the first examples of nonfluorinated copper(I) diketiminates that can be readily applied to an industrial microelectronic fabrication process.

In this Communication, we describe the deposition of thin, conformal copper films by an atomic layer deposition (ALD) process[1] with volatile Cu(I) compounds prepared with 1,3-diketimine ligands **1**.[2,3] The target use for these compounds is the deposition of copper seed layers in the generation of copper interconnect lines on integrated circuits. A physical vapor deposition (PVD) process is currently used to deposit such layers. However, the ever-shrinking feature size on these chips suggests that an alternative to PVD will be needed.[4] ALD is recognized as a viable alternative that can generate thin, conformal films.[5]



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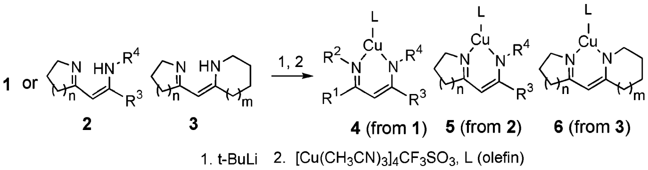
Scheme 1. Preparation of a Novel Cu(diketiminate)L from 1,3-Diketimines ($R^1-R^4 = C_1-C_4$ Alkyl)



Few copper compounds meet the conflicting requirements of an ALD precursor for this application. The compound must be volatile and stable to be vaporized and transported into the deposition chamber but reactive enough to chemisorb to the substrate in a self-limiting reaction without undergoing further reaction; generally, a low temperature is needed to avoid thermal decomposition of the metal ligands. The chemisorbed species must then be easily reducible to metal to yield a film free of component ligands or byproducts. Cu(I) and Cu(II) compounds with 1,1,1,5,5,5-hexafluoroacetylacetone have been extensively studied for use in chemical vapor deposition and ALD processes to deposit copper films because of the volatility of these compounds.[6] However, the industry has developed a “fear of fluorine” in the deposition of interconnects, which limits the usefulness of such compounds for this application.[4a]

Our Cu(I) compounds with **1** and vinyltrimethylsilane (VTMS) described here meet the industry requirements. These monomeric compounds show good volatility and stability based on thermogravimetric analysis (TGA) data without trifluoromethyl groups usually used to enhance volatility. Clean, conformal copper films are deposited in an ALD process at relatively low temperature.

We have developed a protocol to synthesize Cu(I) complexes (**4**−**6**) with both symmetrical and unsymmetrical nonfluorinated 1,3-diketimine ligands (Scheme 1). These Cu(I) precursors have been prepared in an excellent yield of over 90% from the reaction of a neutral ligand such as VTMS with their anionic 1,3-diketiminate (from compounds **1**−**3**) in the presence of tetrakis(acetonitrile)copper(I) trifluoro-

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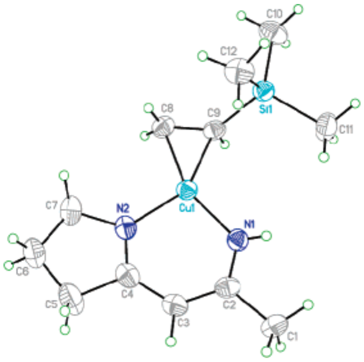

Figure 1. X-ray structure of **5-a**. Distances: Cu1−N1, 1.907(2); Cu1−N2, 1.9208(19); Cu1−C8, 1.972(2); Cu1−C9, 2.008(2); C8−C9, 1.384(3). Angles: N1−Cu1−N2, 96.95(9); N2−Cu1−C8, 107.28(10); N1−Cu1−C9, 115.12(9); C8−Cu1−C9, 40.68(10).

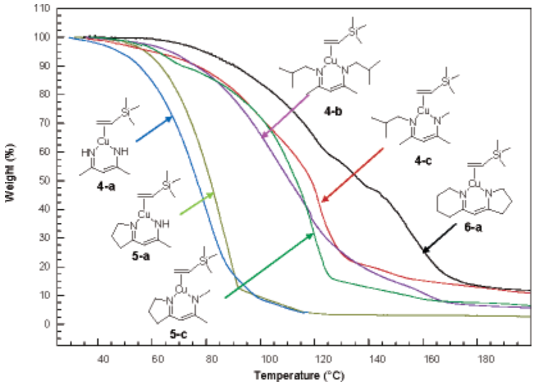

Figure 2. TGA curves for Cu(1,3-diketiminate)(VTMS) at 500 mTorr.

methanesulfonate. All of these copper(I) diketiminate complexes are air- and moisture-sensitive. Although some disproportionation occurs even at ambient temperature in a prolonged period, they are quite stable at reduced temperature under an inert atmosphere. Cold-trap collection of the copper(I) diketiminate complex also ensures the integrity of the volatilized compound.

The Cu(I) complexes are liquid or low-melting solids. Compounds **5-a** ($n = 1$, $R_3 = $ Me, $R_4 = $ H, L = VTMS) and **5-b** ($n = 1$, $R_3 = $ Me, $R_4 = $ H, L = 3,3-dimethyl-1-butene) were characterized by X-ray crystallography (Figure 1 and Supporting Information). Both complexes exhibit trigonal-planar geometry about the Cu(I) ion, characteristic of copper complexes with alkenes and alkynes.[3a]

TGA studies of these Cu(I) complexes were performed over the temperature range 25−200 °C at 500 mTorr under a nitrogen atmosphere. Representative TGA traces are given in Figure 2. Compounds **4-a** and **5-a** show good volatility and little decomposition during the volatilization of the compounds. For the remaining compounds, the TGA traces are not smooth in the high-temperature region; disproportionation of the Cu(I) complex to a Cu(II) species and copper metal is likely.

Several copper(I) diketiminate species turned out to be quite stable under prolonged heating at the vaporization temperature of 55 °C, as shown in Figure 3.

The results from isothermal TGA data provide some qualitative structure−property relationship. Thus, when the same neutral ligand (VTMS) is employed, copper(I) dicyclic diketiminate **6-a** ($n = 1$, $m = 1$, L = VTMS) is less volatile than the monocyclic analogue **5**. A Cu(I) precursor with a symmetrical diketimine, **4-b** (R_1 and $R_3 = $ Me, R_2 and $R_4 = $ isobutyl, L = VTMS), is less volatile than an unsymmetrical one **4-c** (R_1 and $R_3 = $ Me, $R_2 = $ isobutyl, $R_4 = $ Me, L = VTMS), but the former seemed to be more stable than the latter. Ligand symmetry is known to contribute to the volatility of the Cu(II) complex,[3c] but it is not as critical for Cu(I) complexes. When there are no alkyl substituents on the nitrogen atoms, copper(I) *N,N′*-dihydrodiketiminate **4-a** **(**R_1 and $R_3 = $ Me, R_2 and $R_4 = $ H, L = VTMS) is more volatile and stable than both **4-b** and **4-c**. Alkyl substituents on the nitrogen atoms can be expected to help stabilize the copper complex by pushing electrons inductively to the copper metal, which concomitantly transfers electron density via back-bonding to the antibonding orbital of the neutral ligand. However, nonbonded interactions between the neutral ligand and the substituents on the nitrogen atoms play an important role in determining the compound's stability. The same trend was observed in the cyclic system. When there is no alkyl substituent in one nitrogen atom in monocyclic copper(I) 1,3-diketiminate, monocyclic diketimine **5-a** is more volatile and stable than monocyclic copper(I) *N*-methyldiketiminate **5-c**. Thus, the Cu(I) complex having smaller molecular weight as well as less steric hindrance around the copper coordination sphere provides a volatile and stable copper complex. Among several Cu(diketiminate)(VTMS) compounds, **4-a** and **5-a** are exceptionally volatile and stable at low temperature (55 °C).

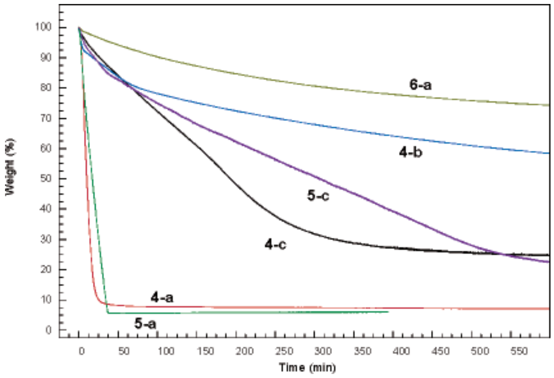

Figure 3. Isothermal TGA curves for Cu(1,3-diketiminate)(VTMS) at 55 °C and 500 mTorr.

Although there are no significant structural differences between **5-a** and **5-b**, it is noteworthy to see the effect of a silicon atom on the neutral ligand (L). The trimethylsilane (TMS) substituent seems to contribute to both the volatility and stability of these copper(I) diketiminate complexes. These physical property differences between silicon-containing copper precursors (**5-a** and **5-c**) and the analogous carbon complexes (**5-b** and **5-d**) are clearly demonstrated in Figure 4. The bulky silicon atom causes the Cu(I) complexes to be packed less compactly in the molecules, resulting in better volatility than complexes with the less bulky carbon atom.[7] Also, the lowered alkene lowest unoccupied molecular orbital energy of VTMS, interacting with the highest occupied molecular orbital ofthe d^{10} Cu(I) ion,[8] results in a more stable copper(I) diketiminate complex.[3a,99] It is also reported that

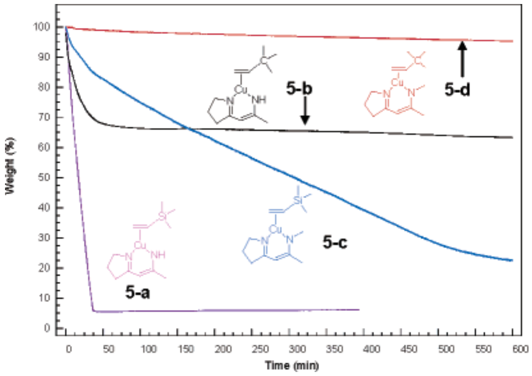

Figure 4. Isothermal TGA curves for Cu(1,3-diketiminate)(VTMS) at 55 °C and 500 mTorr.

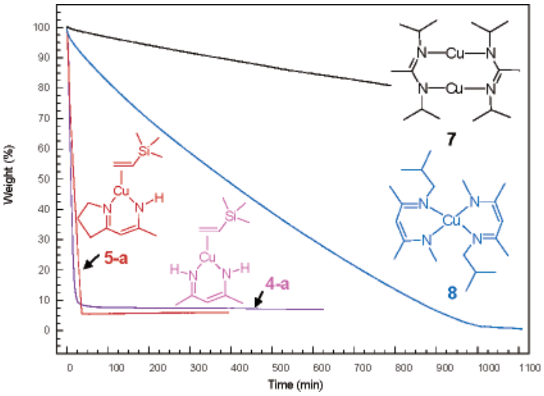

Figure 5. Comparison of isothermal TGA curves for the three different types of copper complexes at 55 °C and 500 mTorr.

the electron-donating TMS group does not donate as much electron density as a *tert*-butyl group does.[10]

A comparison of the volatility is illustrated in Figure 5. Copper(I) diketiminate complexes of both **4-a** and **5-a** are quite volatile, compared with dimeric copper(I) amidinate **7**[11] or copper(II) bis(diketiminate) **8**.[3c] All of these complexes have been suggested as copper precursors for ALD of copper films.

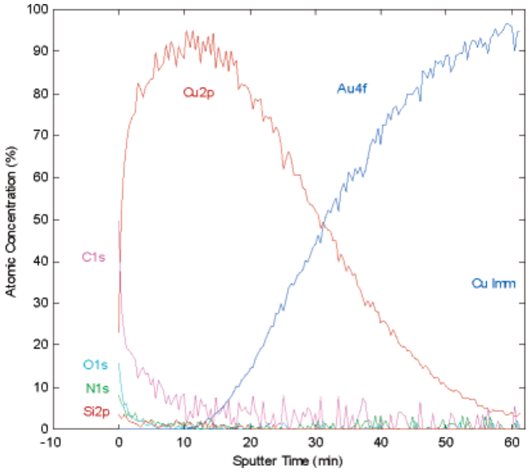

Figure 6. ESCA depth profile of a copper film deposited with **5-a**.

The copper(I) diketiminate complexes are suitable for the deposition of copper films by an ALD process. With 80 passes of the first copper precursor **5-a** and then diethylsilane as the reducing agent, a thin, clean copper film was deposited at 120 °C. Figure 6 shows an electron spectroscopy for chemical analysis (ESCA) depth profile of a copper film deposited on an Au/Si wafer. The surface contains carbon and oxygen species; however, after sputtering through the top layer and into the film, there are only background levels of these contaminants. The ESCA data show a Cu(0) film with a depth of 164 Å.

In conclusion, nonfluorinated Cu(diketiminate)(VTMS) complexes have been developed as volatile and stable copper precursors for copper metal deposition in an ALD process. A more extensive and detailed characterization of the deposited copper film from these materials is currently underway.

Acknowledgment. We thank Professor Barry M. Trost for his helpful discussion. Technical assistance from Gerald V. Glover, Linda M. Longshaw, and Timothy Bentz is acknowledged.

Supporting Information Available: Crystallographic information files (CIFs) of compounds **5-a** and **5-b**, procedure for ESCA depth profile of a copper film deposited with **5-a**, and experimental details for compounds **4-a**, **4-b**, **4-c**, **5-a**, **5-b**, **5-c**, **5-d**, and **6-a**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC061016E

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