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Copper CVD Precursors Containing Alkyl 3-Oxobutanoate Ligands

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The need for high-performance interconnetion materials increases as the design rules for intergrated circuits shrink below 0.5 μm. Copper film has attracted much attention due to its high conductivity as well as high electromigration resistance.[1] Conventional processing has been reported to be problematic to fill features with aspect ratios even as low as 1.0 without creating internal voids.[2] The chemical vapor deposition (CVD) method is one of the techniques under investigation to effectively fill high-aspect ratio holes of sub-half-micron scale.

Copper CVD precursors are divided into two groups, i.e., Cu(I) and Cu(II) complexes. The precursors in the former group are quite volatile and show low deposition temperatures but are highly unstable. The latter precursors are rather stable but show low volatility and high deposition temperatures. The most promising choice would be a copper compound with high vapor pressure and stability as well as low deposition temperature. The strategy is either to enhance the thermal stability of a Cu(I) complex or to increase the volatility and lower the deposition temperature of a Cu(II) complex. We focused our study on developing Cu(II) precursors with these properties.

Fluorinated ligands have been employed to increase the volatility of Cu(II) complexes for the CVD process. Bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)copper(II),[3−14] Cu(hfac)$_2$, has been the most extensively studied Cu(II) complex. A perfluorinated β-ketoiminato copper(II) complex[15] and an amine adduct of copper(II) hexafluoroisopropoxide[16] were also reported to be used as CVD precursors. Most of these fluorinated Cu(II) compounds deposited copper films at higher temperatures than 300 °C. Some of the results showed that thermally induced decomposition of ligands occurred due to high deposition temperatures, which could produce carbon- and fluorine-containing species. A study[13] on the chemical vapor deposition reactions of Cu(hfac)$_2$ and Cu(hfac)(vtms), where vtms = vinyltrimethylsilane, under ultrahigh-vacuum conditions demonstrated contamination by those species in the deposited films.

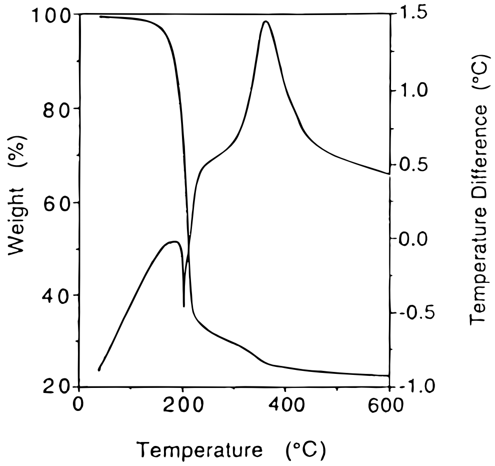

Figure 1. TG/DTA plot of Cu(etac)$_2$.

In our studies, we employed bis(alkyl 3-oxobutanoato)copper(II) as CVD precursors, where alkyl 3-oxobutanoate (CH_3COCH_2COOR, where $R = CH_3$, C_2H_5, $C_2H_2OCH_3$, t-C_4H_9, and $CH_2C_6H_5$) = methyl 3-oxobutanoate (mtacH), ethyl 3-oxobutanoate (etacH), 2-methoxyethyl 3-oxobutanoate (metaH), *tert*-butyl 3-oxobutanoate (btacH), and benzyl 3-oxobutanoate (beacH), to deposit copper films for ULSI applications.

Syntheses of bis(methyl 3-oxobutanoato)copper(II), Cu(mtac)$_2$, bis(ethyl 3-oxobutanoato)copper(II), Cu(etac)$_2$, bis(2-methoxyethyl 3-oxobutanoato)copper(II), Cu(meta)$_2$, bis(*tert*-butyl 3-oxobutanoato)copper(II), Cu(btac)$_2$, and bis(benzyl 3-oxobutanoato)copper(II), Cu(beac)$_2$, were carried out by modifying the reported literature procedures.[17−19] Thermogravimetry and differential thermal analysis (TG/DTA) were employed to evaluate the thermal transitions and decomposition patterns. Figure 1 shows a typical TG/DTA diagram of Cu(etac)$_2$ in air. A melting endotherm was observed around 200 °C. The TGA curve indicated that a large portion of the compound sublimed below 200 °C. A DTA peak around 370 °C was attributed to the decomposition of the ligand. Table 1 summarizes melting and sublimation temperatures of the Cu(II) precursors. Cu(meta)$_2$, Cu(btac)$_2$, and Cu(beac)$_2$ could be obtained as either hydrated or anhydrous forms depending on the reaction conditions used. The anhydrous forms showed lower melting points than the hydrates. Cu(btac)$_2$, which exhibited the lowest melting point and sublima-

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Table 1. Physical Properties of Copper(II) Precursors[a]

Cu(II) precursor	melting point (°C)	subl temp (°C/0.16 Torr)
$\mathrm{Cu(mtac)_2}$	194	112
$\mathrm{Cu(etac)_2}$	192	108
$\mathrm{Cu(meta)_2}$	117	97
$\mathrm{Cu(meta)_2 \cdot }x\mathrm{H_2O}$	200	97
$\mathrm{Cu(btac)_2}$	92	88
$\mathrm{Cu(btac)_2 \cdot EtOH}$	95	78
$\mathrm{Cu(btac)_2 \cdot EtOH \cdot }x\mathrm{H_2O}$	110	80
$\mathrm{Cu(btac)_2 \cdot }y\mathrm{H_2O}$	195	98
$\mathrm{Cu(beac)_2}$	125	108
$\mathrm{Cu(beac)_2 \cdot }x\mathrm{H_2O}$	189	113
$\mathrm{Cu(hfac)_2 \cdot }x\mathrm{H_2O}$	130	67

[a] $x < y$; $\mathrm{Cu(mtac)_2}$ = bis(methyl 3-oxobutanoato)copper, $\mathrm{Cu(etac)_2}$ = bis(ethyl 3-oxobutanoato)copper, $\mathrm{Cu(meta)_2}$ = bis(2-methoxyethyl 3-oxobutanoato)copper, $\mathrm{Cu(btac)_2}$ = bis(*tert*-butyl 3-oxobutanoato)copper, $\mathrm{Cu(beac)_2}$ = bis(benzyl 3-oxobutanoato)copper, $\mathrm{Cu(hfac)_2}$ = bis(1,1,1,5,5,5,-hexafluoropentane-2,4-dionato)copper.

Table 2. Infrared Spectroscopic Data of Ester Groups in Bis(alkyl 3-oxobutanoato)copper Precursors[a]

Cu(II) precursor	C=O stretching ($\mathrm{cm^{-1}}$)	C−O stretching ($\mathrm{cm^{-1}}$)
$\mathrm{Cu(mtac)_2}$	1601, 1540	1180
$\mathrm{Cu(etac)_2}$	1604, 1538	1180
$\mathrm{Cu(meta)_2}$	1605, 1545	1184
$\mathrm{Cu(btac)_2}$	1064, 1538	1179
$\mathrm{Cu(beac)_2}$	1606, 1538	1179

[a] $\mathrm{Cu(mtac)_2}$ = bis(methyl 3-oxobutanoato)copper, $\mathrm{Cu(etac)_2}$ = bis(ethyl 3-oxobutanoato)copper, $\mathrm{Cu(meta)_2}$ = bis(2-methoxyethyl 3-oxobutanoato)copper, $\mathrm{Cu(btac)_2}$ = bis(*tert*-butyl 3-oxobutanoato)copper, $\mathrm{Cu(beac)_2}$ = bis(benzyl 3-oxobutanoato)copper.

tion temperature among these precursors, was obtained as an ethanol adduct as well when anhydrous ethanol solvent was used during the synthesis. Coordination of the ligands to copper metal was identified by ir spectroscopy (Table 2). Elemental analysis data for C, H, O, and Cu in these compounds matched well with the calculated values.

All CVD experiments were carried out using the Cu(II) precursors in a glass warm-wall reactor with substrate temperatures at 160−330 °C and feed temperatures at 90−130 °C using H_2 flowing at 30−150 sccm. Working pressure during deposition was maintained at 0.1−1 Torr with a typical base pressure of 1×10^{-4} Torr. No additional gas other than H_2 was used. High-purity copper films were deposited on Si, TiN sputtered on Si (TiN/Si), and TiW sputtered on Si substrates (TiW/Si). No deposition of copper was observed on the reactor wall even at elevated temperatures, i.e., higher than 200 °C. Adhesion of films on the substrates was good. Deposition rates ranged from 5 to 200 Å/min. Resistivities of the as-deposited films ranged from 1.8 to 2.5 $\mu\Omega$ cm. Films deposited at temperatures higher than 300 °C exhibited relatively higher resistivities (>2.0 $\mu\Omega$ cm). AES analysis indicated no detectable impurities such as C or O.

The main advantage of the alkyl 3-oxobutanoate precursors is their low deposition temperatures compared with other copper(II) precursors. The present precursors deposited high-purity copper films at substrate temperatures as low as 160 °C which is substantially lower than the lowest deposition temperature of $\mathrm{Cu(hfac)_2}$, which was reported to be 310 °C.[9,14] The deposition temperatures lower than the thermal decomposition temperatures (>300 °C) of the precursors are beneficial for them to liberate free ligands without further decomposition, which is important to obtain high-purity copper films by CVD. The exhaust gas from the reaction of $\mathrm{Cu(etac)_2}$ at 230 °C was analyzed by GC/MS and was shown to be solely the ethyl 3-oxobutanoate liberated from the precursor intact during the deposition process. In addition, the hydrated precursors required lower deposition temperatures than the anhydrous forms. These results suggest a deposition mechanism similar to that of copper(II) bishexafluoroacetylacetonate[10−14] which would be that the Cu(II) ion was reduced by the substrate surface to form a Cu(I) intermediate and further reduced by H_2 to form adsorbed Cu(0) and desorbed ligand. H_2O would accelerate the protonation of the coordinated or adsorbed ligand.

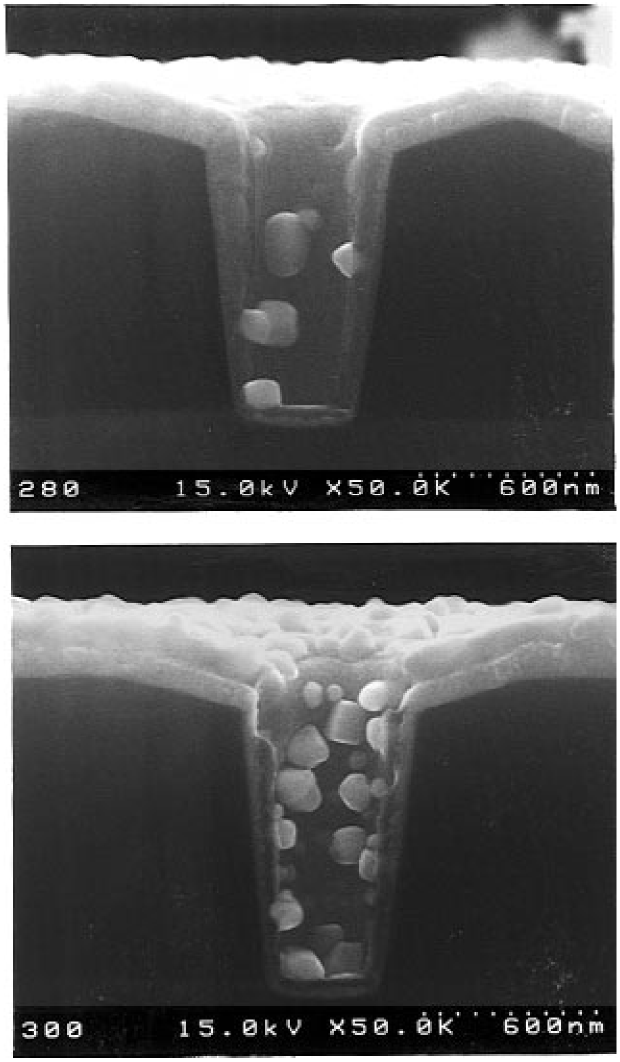

Figure 2. Scanning electron micrographs of copper films deposited using $\mathrm{Cu(meta)_2}$ as a precursor on TiN/Si substrates with holes with diameter of 0.35 μm and aspect ratio of 3 at deposition temperatures of (a, top) 230 °C and (b, bottom) 250 °C.

The morphology of the deposited films depended on the substrate temperature and the deposition time. Large-grained films were produced at high deposition temperatures. For instance, the average grain size of the copper films grown on TiN/Si substrates at 270 °C was about 0.5 μm after 1 h and increased up to 4 μm after 10 h of deposition. The copper films grown on Si or TiW substrates displayed similar behavior.

Figure 3. Scanning electron micrographs of copper films deposited at 180 °C on TiN/Si substrates with holes with diameter of 0.67 μm and aspect ratio of 1 using (a, top) Cu(etac)$_2$ and (b, bottom) Cu(meta)$_2$ as precursors.

Figure 2 illustrates the grain growth of the copper films deposited with Cu(meta)$_2$ precursor on TiN/Si at temperatures of 230 and 250 °C. Large grains were observed on top of a fine-grained copper layer at these temperatures. The deposition of the films appeared to occur via two different rates and mechanisms to form an under layer which was grown directly on TiN and a top layer in which the grain growth took place. Figure 3 shows two scanning electron microscopy (SEM) pictures of the copper films which were deposited at 180 °C using Cu(meta)$_2$ and Cu(etac)$_2$. No grain growth was observed with either Cu(meta)$_2$ or Cu(etac)$_2$ at this temperature. However, layer separation seemed to be taking place with Cu(etac)$_2$ precursor, which also suggests that the deposition rate of the top layer would be quite different from that of the under layer or the rate of nucleation. With Cu(meta)$_2$, bilayer formation did not occur or was, at least, not obvious. This suggests that the dependence of the growth rate and mechanism of the copper films on the deposition temperature could be varied with the precursor used and that Cu(meta)$_2$ could be a better CVD precursor than Cu(etac)$_2$ since it exhibited higher vapor pressure and produced better morphology of the deposited films. A further study is needed to understand the growth mechanism of the copper films with these precursors.

Conformality of the deposited copper films was excellent contrary to the poor step coverages of the underlying TiN layers. The aspect ratios of the holes in these pictures were approximately 3 and 1 with diameters of 0.35 and 0.67 μm, respectively.

These results suggest that it is possible to control the morphology of the deposited copper films using a proper precursor under appropriate deposition conditions, demonstrating the potential of copper CVD for the metallization of ULSI devices.

In this study, we have introduced bis(alkyl 3-oxobutanoato)copper(II) as new CVD precursors which do not require fluorine substitution to improve the volatility and exhibited good thermal characteristics, thus producing high-quality copper films at low deposition temperatures.

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