Copper(I) *tert*-Butyl 3-Oxobutanoate Complexes as Precursors for Chemical Vapor Deposition of Copper

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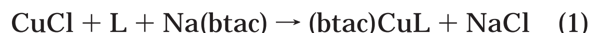
Copper(I) β-diketonate complexes, (β-diketonate)CuL, where L = Lewis base, have attracted the most attention for chemical vapor deposition (CVD) of copper since both β-diketonate and Lewis base ligands can be varied to tailor their volatility and stability.[1−6] However, 1,1,1,5,5,5-hexafluoroacetylacetonate (hfac) has been known as the only β-diketonate ligand for copper(I) complexes to exhibit sufficient thermal stability for CVD processes.[1−5] They deposit high-purity copper films via thermally induced disproportionation reactions, whereas copper(I) complexes such as (η^5-C_5H_5)$CuPMe_3$[7] or (*tert*-BuO)$CuPMe_3$[8] produce copper films via thermal decomposition. Among the (hfac)copper(I) complexes, (hfac)-Cu(TMVS), where TMVS = trimethylvinylsilane, has attracted much attention for CVD, since it is a volatile liquid. Other (hfac)copper(I) complexes, (hfac)CuL, where L = an olefin, an alkyne, or a trialkylphosphine, are either solids or low vapor pressure liquids. (Hfac)-Cu(TMVS) has been reported to deposit high-purity copper films. However, a study[9] demonstrated that (hfac)Cu(TMVS) deposited copper films contaminated with carbon and fluorine under ultrahigh vacuum conditions. Copper(I) complexes of fluorinated β-diketonates other than (hfac)CuL, such as (fod)CuL, where fod = 2,2-dimethyl-6,6,7,7,8,8-heptafluoro-3, 5-octanedionate, or (tfac)CuL, where tfac = 1,1,1-trifluoro-2,4-pentanedionate, were reported not to exhibit sufficient thermal stability to be used as CVD precursors.[10] Although (hfac)Cu(TMVS) has been the most utilized precursor due to the fact that it is a reasonably stable and volatile liquid, its stability is not satisfactory for the selective growth of copper films with reproducibility.[11] Therefore, a more stable liquid precursor is required for the CVD of copper.

Table 1. Infrared Spectroscopic Data of Ester Groups in Cu(I) *tert*-Butyl 3-Oxobutanoate Complexes

Cu(I) complex	C=O stretching (cm^{-1})	C−O stretching (cm^{-1})
(btac)Cu[P(OMe)$_3$]	1625	1153
(btac)Cu(BTMSA)	1625	1158
(btac)Cu(COD)	1637	1160
(btac)Cu(TMSP)	1620	1159
(btac)Cu(PMe$_3$)	1617	1158
(btac)Cu(2-butyne)	1623	1151
(btac)Cu(TMVS)	1624	1158
(btac)Cu(DMCOD)	1637	1160

Recently, a series of Cu(II) alkyl 3-oxobutanoates was reported as a new Cu(II) precursor system.[12] The alkyl 3-oxobutanoate compounds were the first example of Cu(II) precursors which deposited high-purity conformal copper films at temperatures below 200 °C. In this study, we synthesized Cu(I) *tert*-butyl 3-oxobutanoate complexes, (btac)CuL, where L = trimethylvinylsilane (TMVS), bistrimethylsilylacetylene (BTMSA), 1,5-cyclooctadiene (COD), 1,5-dimethyl-1,5-cyclooctadiene (DMCOD), 2-butyne, 1-trimethylsilyl-1-propyne (TMSP), and trimethyl phosphite [P(OMe)$_3$], anticipating that the alkyl 3-oxobutanoate ligands would give rise to stable Cu(I) compounds in the presence of donor ligands.

Syntheses of (btac)Cu(I) complexes were carried out by modifying the procedure reported in the literature[10] by the reaction of Na(btac) with the mixture of CuCl and the Lewis base in diethyl ether or tetrahydrofuran:



$$\mathrm{CuCl + L + Na(btac) \rightarrow (btac)CuL + NaCl} \quad (1)$$

$$\mathrm{L = TMVS,\ COD,\ BTMSA,\ 2\text{-}butyne,\ TMSP,\ DMCOD,\ PMe_3,\ and\ P(OMe)_3}$$

The (btac)CuL complexes, where L = TMVS, 2-butyne, TMSP, DMCOD, and P(OMe)$_3$, were isolated as liquids at room temperature and the (btac)CuL complexes, where L = BTMSA, PMe$_3$ and COD, were solids. Coordination of the btac ligand to copper metal in each Cu(I) *tert*-butyl 3-oxobutanoate complex was identified by IR spectroscopy (Table 1). These Cu(I) complexes produce copper metal via disproportionation reactions at elevated temperatures. The complexes showed high thermal stability.[13] Among these complexes, (btac)Cu-[P(OMe)$_3$], (btac)Cu(COD), and (btac)Cu(BTMSA) are the more stable, whereas (btac)Cu(2-butyne), (btac)Cu-(TMVS), and (btac)Cu(DMCOD) are the less stable ones. However, even the less stable Cu(I) *tert*-butyl 3-oxobutanoate complexes, e.g., (btac)Cu(2-butyne), (btac)Cu-(TMVS), and (btac)Cu(DMCOD), exhibited higher thermal stability than (hfac)Cu(TMVS). The thermal

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(13) (btac)Cu[P(OMe)$_3$], bp 33 °C/0.1 Torr, dec 120 °C; (btac)Cu-(BTMSA), mp 58 °C, dec 95 °C; (btac)Cu(COD), mp 54 °C, bp 77 °C/0.05 Torr, dec 130 °C; (btac)Cu(TMSP), dec 75 °C; (btac)Cu(PMe$_3$), dec 63 °C; (btac)Cu(2-butyne), bp 50 °C/0.1 Torr, dec 70 °C; (btac)Cu-(TMVS), bp 52 °C/0.1 Torr, dec 55 °C; (btac)Cu(DMCOD), dec 60 °C.

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Table 2. ^{1}H NMR Data[a] of (btac)Cu[(OPMe)$_3$] and (btac)Cu(BTMSA)

compound	Btac OC(CH$_3$)$_3$	Btac CH$_3$	Btac CH	P(OMe)$_3$ O−CH$_3$	BTMSA Si−CH$_3$
(Btac)CuP(OMe)$_3$	1.33(s)	1.69(s)	2.92(s)	3.36(d)	
(Btac)Cu(BTMSA)	1.44(s)	1.92(s)	2.91(s)		0.23(s)

Column headings are δ, ppm[b].

[a] Recorded in C_6D_6 at 400 MHz. [b] δ values quoted in ppm relative to Me_4Si.

stability of (btac)Cu[P(OMe)$_3$] was comparable to that of (hfac)Cu(PMe$_3$). However, (hfac)Cu[P(OMe)$_3$] was less stable than (btac)Cu[P(OMe)$_3$] and comparable to (btac)Cu(2-butyne). Another advantage is that the (btac)CuL complexes, where L = BTMSA, PMe$_3$, P(OMe)$_3$, TMVS, COD, and 2-butyne, could be handled in air with care without much decomposition, whereas (hfac)Cu(TMVS) decomposed immediately when it was exposed to air.

It is intriguing that the btac ligand could give rise to a series of stable Cu(I) complexes with various neutral ligands, while no other anionic ligands except hfac were able to produce Cu(I) complexes sufficiently stable as CVD precursors, which deposit copper via thermally induced disproportionation reaction. Copper complexes other than copper(I) hexafluoroacetylacetonates, whether they contain fluorinated ligands or not, have not been suitable as CVD precursors due to their low thermal stabilities or inability to deposit high-purity copper films. In fact, Cu(I) *tert*-butyl 3-oxobutanoates are the first examples of volatile Cu(I) complexes which are thermally stable and produce high-purity copper without employing fluorinated ligands. Among the Cu(I)−*tert*-butyl 3-oxobutanoates, (btac)Cu[P(OMe)$_3$], (btac)Cu(COD), and (btac)Cu(BTMSA) attract more attention as CVD precursors since they are highly stable liquids or low-melting solids.[13] The ^{1}H NMR spectra of (btac)Cu[(OPMe)$_3$] and (btac)Cu(BTMSA) were recorded in C_6D_6 on a Varian U400. Table 2 shows the NMR data of the coordinated ligands in (btac)Cu[(OPMe)$_3$] and (btac)Cu(BTMSA).

CVD experiments were carried out using the Cu(I) complexes as precursors in a glass cold-wall reactor onto TiN/Si wafers which were used "as received" at temperatures between 100 and 300 °C. The total pressure was maintained at 0.1−5 mmHg with or without argon carrier gas. No reducing agent such as H_2 was used for the deposition experiments. The complexes produced high-purity copper films on TiN substrates at temperatures as low as 120 °C. A typical deposition rate at 180 °C was 400 Å /min. Adhesion of the films to the substrates was good. The resistivities of the as-deposited films ranged from 1.8 to 2.5 $\mu\Omega$ cm. X-ray powder diffraction indicated that the deposited films are polycrystalline. Figure 1 shows X-ray photoelectron spectra of a deposited film obtained with (btac)CuP(OMe)$_3$ as a precursor. The peaks due to elemental copper, carbon, and oxygen were observed in the as-deposited film (Figure 1a). After etching the film with argon ion for 1.5 min, however, the carbon peak disappeared and the oxygen peaks decreased significantly (Figure 1b). No copper oxide peaks were observed in the film. This indicates that the carbon and oxygen contaminants are present only in the surface and that (btac)CuP(OMe)$_3$ produced pure elemental copper during the CVD process. Observation of (btac)$_2$Cu during the deposition process demonstrates that (btac)CuP(OMe)$_3$ deposits high-purity copper via thermally induced disproportionation. Figure 2 shows a cross-sectional SEM image of a copper film deposited with (btac)CuP(OMe)$_3$ as a precursor on a patterned TiN

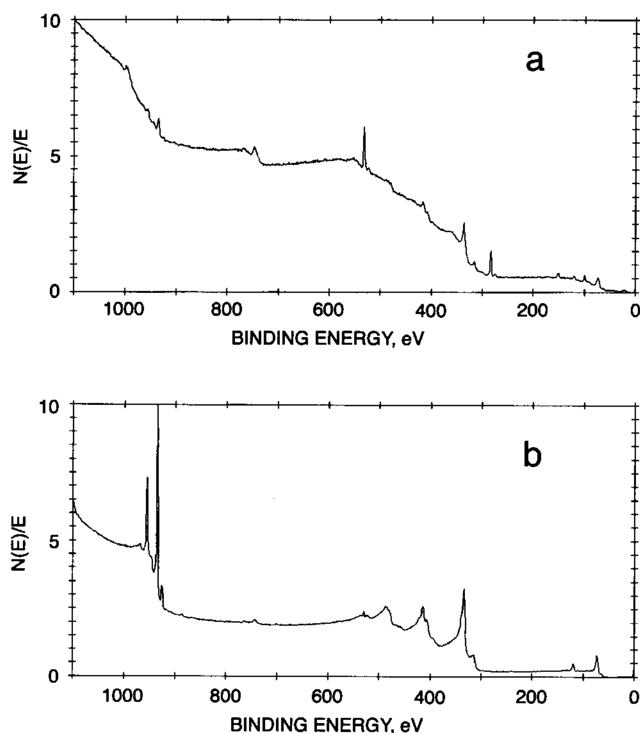

Figure 1. X-ray photoelectron spectra of a copper film deposited at 180 °C using (btac)CuP(OMe)$_3$ as a precursor on a TiN/Si wafer: (a) as deposited and (b) after etching with argon ion for 1.5 min.

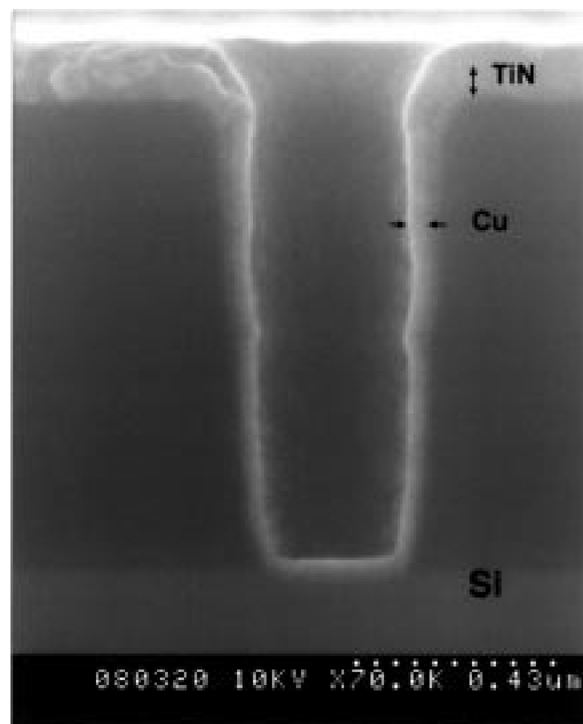

Figure 2. A cross-sectional SEM of a copper film deposited at 180 °C using (btac)CuP(OMe)$_3$ as a precursor on a patterned TiN/Si wafer with vias with a diameter of 0.35 μm and aspect ratio of 3.5.

substrate at 180 °C. The deposited film shows good step coverage on a via with diameter of 0.35 μm and aspect ratio of 3.5.

The deposition experiments were carried out on thermally grown SiO_2 substrates to evaluate the (btac)-Cu(I) complexes for selective copper deposition. No deposition of copper film was observed on SiO_2 surfaces up to 200 °C when using (btac)CuP(OMe)$_3$ as a precursor. Surprisingly, even the less stable (btac)CuPMe$_3$ did not deposit copper on SiO_2 at a temperature as high as 200 °C. With the onset of the deposition on TiN at 120 °C, the selectivity window exhibited by these precursors is wide. When the reaction was carried out using (hfac)-Cu(TMVS) under the same conditions, no selectivity was observed for TiN versus SiO_2 surfaces. The enhanced selectivity exhibited by the (btac)Cu(I) complexes demonstrates their superior thermal stability compared to (hfac)Cu(TMVS).

In summary, we have synthesized a series of stable volatile (btac)Cu(I) complexes which produce high-purity copper films via a thermally induced disproportionation reaction. Among these complexes, (btac)Cu[P(OMe)$_3$] is especially attractive as a practical CVD precursor since it is a volatile liquid with high stability. It offers the following advantages over the fluorinated Cu(I) complexes such as (hfac)Cu(TMVS): (1) no possibility of fluorine contamination in the deposited films, (2) a wide process window for the selective deposition of copper films, and (3) a longer shelf life and easier handling.

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