New copper(I) precursors for the deposition of copper films

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Copper deposition has become an important and rapidly growing area in integrated circuit manufacturing in microelectronic industry. Regarding copper(I) precursors, Lewis base stabilized fluorine-containing (ß-diketonate) copper(I) complexes receive the most attention.[1] However, fluorine-free copper(I) precursors have recently attracted interest as a result of adhesion problems of the deposited copper layer onto TiN when using fluorine-containing copper precursors.

Therefore, a new type of fluorine-free copper(I) precursor, Lewis base stabilized copper(I) oxalate complexes, has been developed (Figure 1).[2] The X-ray single crystal structure of $(Me_3SiC{\equiv}CSiMe_3)_2Cu^I_2(C_2O_4)$ (**1**) shows that two (alkyne)Cu^I building blocks are bridged by an oxalate ligand.

In contrast to most other copper(I) precursors, the new compounds show excellent thermal behaviour and air stability. TGA and DSC measurements indicate a thermal stability up to 100 °C followed by a 2 step decomposition that is completed at 300 °C (Figure 2). The two step decomposition corresponds to ligand dissociation followed by an internal redox reaction (Figure 3).

The decomposition mechanism ensures a 100 % yield of copper(0). The byproducts CO_2 and the neutral Lewis base are non-toxic, thus enabling a safe and environmentally friendly process. A comparison of the new fluorine-free copper(I) precursor with the presently available fluorine-containing precursor CupraSelect® (VTMS)Cu^I(hfac) will be given.

[1] see for example: IBM Corporation **1992**, US5220044; CNRS Paris **1999**, US6130345; ATM Inc. **1999**, WO0071550; Chem. Mater. **1992**, *4*, 365 and 577; Chem. Mater. **2001**, *13*, 3993.

[2] Merck Patent GmbH, **2002**, DE 10228050.

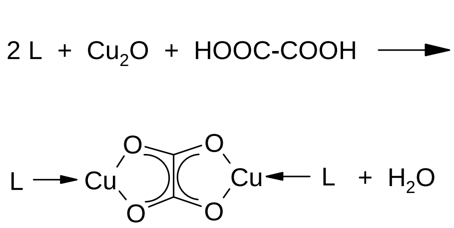

Fig. 1: Synthesis of L_2Cu_2(oxalate), L = alkyne, alkene.

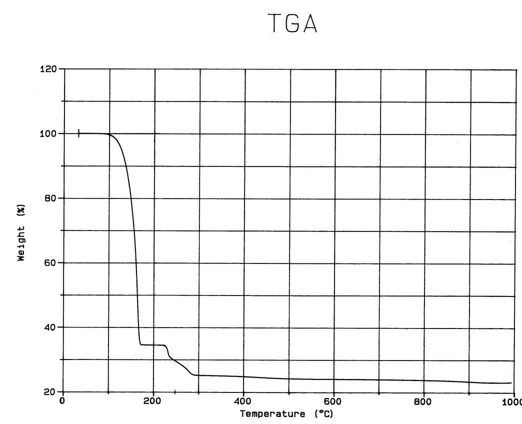

Fig. 2: Thermal analysis (TGA) of **1**.

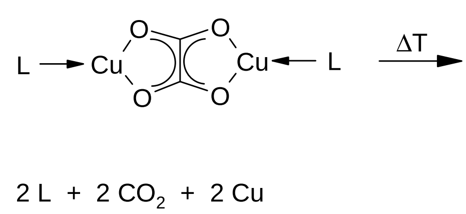

Fig. 3: Decomposition reaction of L_2Cu_2(oxalate), L = alkyne, alkene.