Structural comparison between Cu(hfac)(VTMS) and Cu(hfac)(MHY) : An answer to differences in copper film deposition

M. JOULAUD [a, b, c, *], L. OMNES [b, c], T. MOURIER [a], D. MAYER [c], P. DOPPELT [b]

[a] Cea-Leti DTS/STME/LDCM Grenoble (FRANCE)
[b] ESPCI, Centre d'Etudes de Chimie Métallurgique, CNRS UPR 2801 (FRANCE)
[c] Merck KgaA - EC/GE - Darmstadt, (GERMANY)

[*] **Corresponding author** *:* Cea-Leti DTS/STME/LDCM - 17 rue des Martyrs - 38054 Grenoble CEDEX 9 (FRANCE)
Phone : 00-33-4-38-78-9971
Fax : 00-33-4-38-78-5459
E-mail : joulaudmi@chartreuse.cea.fr

Because of its low resistivity, high thermal conductivity and resistance to electromigration, copper became the successor of Al alloys for interconnection metallization [1, 2]. Among all deposition techniques, CVD appears to be the best to deposit element like copper with a conformal film growth in high aspect ratio features (8:1 for dual damascene process on 0.1 μm) [3].

Here we present recent studies on Cu Chemical Vapor Deposition using a promising β-diketonate Cu^{I} (L) precursor : Cu(hfac)(MHY) [4] trade name Giga Copper®. This precursor was compared to Cu(hfac)(VTMS), trade name Cupraselect® [5] (by far the mostly used precursor for the copper CVD), in terms of molecular structure, deposition rate and film resistivity.

On the ground of observations made on X-ray structures of Cu(pfac)(VTMS) [6] and Cu(pfac)(MHY), higher intermolecular interactions were highlighted for Cu(pfac)(VTMS). Since these interactions are not directly linked to (pfac) ligands, these observations were extended to a structural comparison of Cu(hfac)(VTMS) and Cu(hfac)(MHY). The influence of these interactions on the deposition process was also discussed.

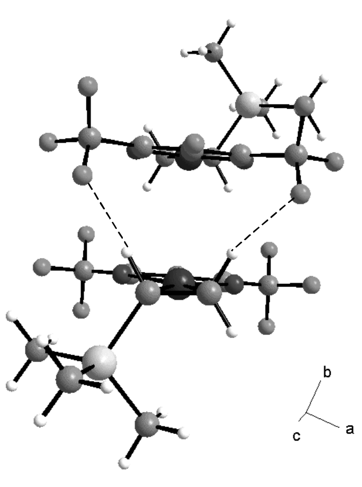


Figure 1. Intermolecular interactions between two hydrogen atoms of the vinyl group and two fluorine atoms of the CF_3 groups in Cu(pfac)(VTMS).

Copper depositions were performed with those two precursors in an industrial equipment on 200 mm wafers priory coated with CVD TiN barriers.
We observed a higher deposition rate using Giga Copper® than Cupraselect® for short and long deposition times. This phenomenon was associated to lower intermolecular interactions giving a more homogenous gas phase and, by the way, a higher reaction yield at the wafer surface (disproportionation). The disproportionation yield is also increased because of a better adsorption due to the free double bond of MHY (See Figure 2).

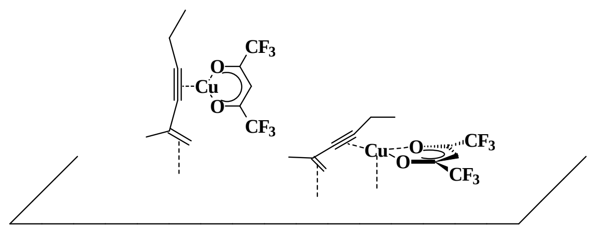
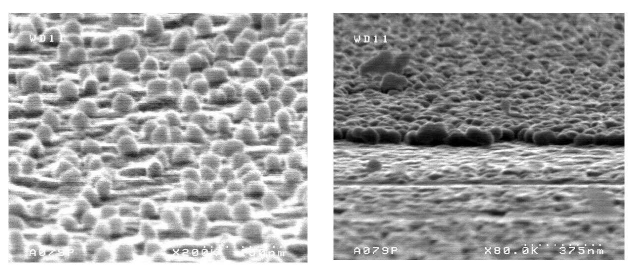


Figure 2. Different possibilities for the adsorption of Cu(hfac)(MHY) at the substrate surface

We also measured a lower resistivity for films deposited using Giga Copper® (without anneal). Since a better reaction at the wafer surface decreases the number of trapped atoms due to precursor decomposition, a lower resistivity is in agreement with a higher reaction yield with Giga Copper®.

Finally, we looked at the copper film growth. As we can see on Picture 1 (a) and (b), Giga Copper® seems to enhance lateral growth of copper nuclei. This hypothesis has to be confirmed with further investigations and related to the specific molecular structure of Giga Copper®.



Picture 1 (a) SEM picture of the nucleation phase with Giga Copper®
(b) SEM picture of a 70 nm thick film deposited with Giga Copper®

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