# PREPARATION OF CU THIN FILMS BY MOCVD USING NOVEL ORGANOMETALLIC CU(II) PRECURSORS

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Copper metal has attracted interest considerably as an alternative interconnecting metal to Al alloys for multilevel metallization applications in ULSI technology (1-3) because of its excellent electrical conductivity and high resistance to electromigration.

Novel Cu(DMAMP)$_2$ (I) and Cu(DEAMP)$_2$ (II) precursors were synthesized by the alcohol exchange reaction (4) of copper (II) methoxide with the corresponding aminoalcohols {dimethylamino-2-methyl-2-propanol (dmampH) and diethylamino-2-methyl-2-propanol (deampH)} in toluene. The ligands, DMAMP and DEAMP have been employed for the synthesis of the volatile precursors to reduce intermolecular interaction by shielding a Cu atom from the O and N atoms of the neighbor molecule. Indeed, our "fluoride free" precursors are volatile enough to be employed for Cu MOCVD. Both of the precursors I and II were highly soluble in organic solvents such as toluene and THF. Thermogravimetric data collected under an Ar atmosphere (100 sccm) with a 10 °C/min heating rate, show that the precursors are sufficiently volatile. Upon heating under argon atmosphere, the precursor I and II undergo rapid weight loss in the temperature range of 100-200 °C and 60-170 °C respectively.

MOCVD of Cu thin films was carried out on Si (100) substrates using a stainless steel vacuum chamber. The base pressure of CVD reactor was maintained at 4 mTorr. An inert Ar gas (99.999%) was used as a carrier gas with a flow rate of 5.5 sccm. During the deposition, working pressure was maintained at 55 mTorr. The precursor was maintained at RT and the substrate temperature was varied in the range of 180-300℃ for 3 hours. Figure 1 shows the XRD pattern of the copper films deposited on a Si(100) substrate at 250 $^{o}$C by using the precursor I. The Cu (111) and Cu (200) peaks were observed at $2\theta = 43.2°$ and 50.5°, respectively. XPS data of the Cu thin films also show that Cu LVV Auger transition peak and Cu 2p$_{3/2}$ peak are observed at 918.5 and 932.8 eV, respectively, indicating that the deposited copper film consists of only metallic copper.

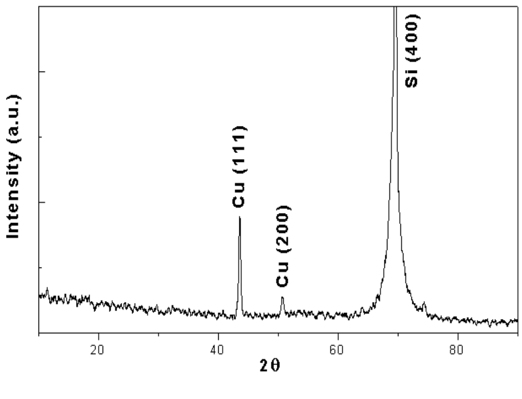

Figure 1. XRD pattern of copper film deposited at 250 $^{o}$C

The SEM image in Figure 2 shows that the deposited copper film has a dense structure with roughly surfaced spherical islands in 0.2 μm diameter. At this stage, the growth rate of the Cu films is about 60 nm/hr without heating the precursor I. The growth rate of the Cu thin films could be increased with heating the precursor and increasing the flow rate of Ar gas.

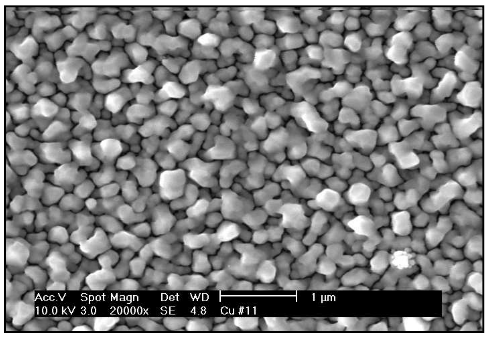

Figure 2. SEM image of copper film deposited at 250 $^{o}$C.

The GC/MS and $^1$H NMR studies of by-products collected in liquid N$_2$ during MOCVD process revealed that the precursor I thermally decomposes into Cu metal, $HOC(CH_3)_2CH_2N(CH_3)_2$, $(CH_3)_2NCHCHN(CH_3)_2$ and acetone. As discussed in the paper of Chi's group (5), the aminoalkoxide ligand of the precursor I could be decomposed through a C(α)-C(β) bond fission reaction to produce acetone and an unstable dimethylaminocarbanion which further undergoes hydrogen transfer to second aminoalkoxide and dimerization to produce Cu metal, $HOC(CH_3)_2CH_2N(CH_3)_2$, and $(CH_3)_2NCHCHN(CH_3)_2$.

In summary The "fluoride free" copper precursors I and II are synthesized in good yields and are quite volatile by shielding intermolecular interaction of Cu atom and electron donor O and N atoms of aminoalkoxide ligands. The precursors are suitable for the deposition of copper thin films without reactive carrier gas by self-reduction. The decomposition studies of the precursor I by GC/MS and $^1$H NMR show that our precursors thermally decompose below 200 $^{o}$C to produce metallic copper, aminoalcohol, acetone and bis(dimethylamino)ethene. Further modification of the precursors using tertiaryaminoalkoxide is under study.

## REFERENCES

1. J. Li, T.E. Seidel, and J. W. Mayer, *MRS Bull.*, **19**, 15 (1994)
2. J. Torres, J. L. Mermer, R. Madar, G. Crean, T. Gessner, A. Bertz, W. Hasse, M. Plotner, F. Binder, D. Save, *Microelectronic Engineering*, **34**, 119 (1996)
3. T. T. Kodas, M. J. Hampden-Smith, *The Chemistry of Metal CVD*, Vol. 1; VCH, Weinheim (1994)
4. J. V. Singh, B. P. Baranwal, R. C. Mehrotra, *Z. Anorg. Allg. Chem.*, **477**, 235 (1981)
5. P. F. Hsu, Y. Chi, T. W. Lin, C. S. Liu, A. J. Carty, S. M. Peng, *Chem. Vap. Deposition*, **7** 28 (2001)