Influence of co-reagent on the atomic layer deposition of copper thin films

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ABSTRACT

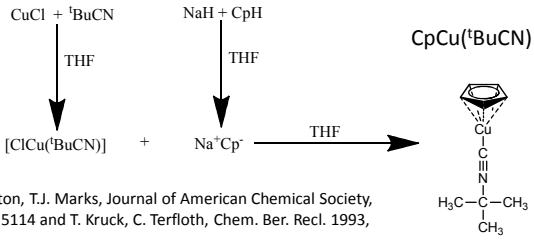
The superlative electrical conductivities of copper (5.96×10^7S/m) and silver (6.30×10^7S/m) make them attractive candidates for interconnects in electronic devices, such as CMOS circuits, solar cells and plastic electronics. These factors have stimulated research to identify precursors for the ALD of copper thin films. The cyclopentadienyl copper tertiarybutyl isocyanide precursor, [CpCu(tBuCN)] has been reported previously for Cu deposition by chemical vapor deposition[1].

This poster investigated the use of [CpCu(tBuCN)] in an ALD regime and compares the influence of a hydrogen plasma as a co-reagent with direct thermal decomposition in a pulsed delivery mode. Using ALD the low temperature growth of electrically conductive copper films is achieved.

[1] D. Blessman, A Grafe, R. Heinen, F.Jansen, Th. Kruck, C. Terfloth, Materials Science and Engineering, B17 (1993) 104-107

EXPERIMENTAL

The synthesis route for CpCu^{t}BuCN is shown below [2]. It exploits the formation of a copper-chloro-ligand adduct, followed by a salt metathesis reaction to yield the copper complex.



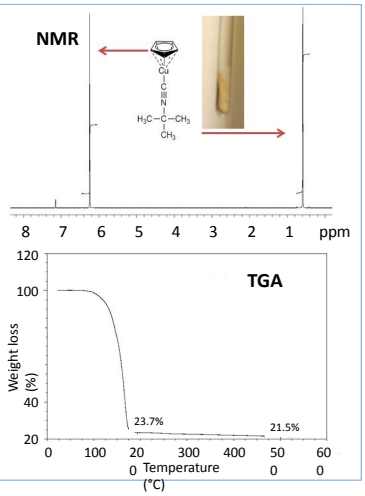
[2] F. A. Cotton, T.J. Marks, Journal of American Chemical Society, 1970, 92, 5114 and T. Kruck, C. Terfloth, Chem. Ber. Recl. 1993, 126, 1101

The atomic layer deposition experiments were performed in an Oxford Instruments OpaL™ plasma system. The precursor was delivered by vapor draw at a source temperature of 100°C.

THE PRECURSOR

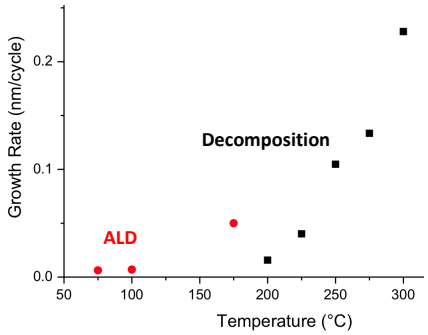
The ^{1}H NMR indicates singlet resonances at δ= 0.5ppm and δ= 6.2 ppm and a proton ratio of 9:5, indicating an η^5-coordination mode of Cp to copper in the solution phase at room temperature.

Thermogravimetric analysis shows a mass drop from 100°C to 175°C relating to precursor volatilisation. Above 200°C the mass loss plateau of 21.5% is less than expected (34%) correlated with copper metal formation.



DEPOSITION

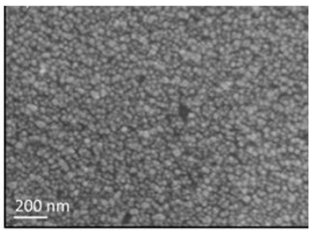
Thermal decomposition was investigated using 2s doses and 3s purges. An Arrhenius – type increase in growth rate occurs with increasing substrate temperature.
ALD experiments were performed with additional cycles of 300W H_2 plasma 2s doses and 3s purges.



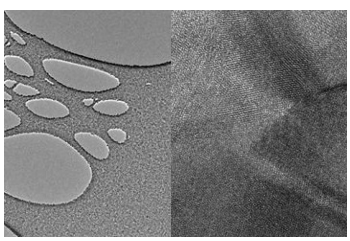
The H_2 plasma co-reagent enables deposition at lower temperatures down to 75°C, which is 100°C lower than thermal decomposition. This allowed films to be deposited on Melinex™ plastic, glass, titanium nitride and silicon.

FILM MORPHOLOGY

Scanning electron microscopy (right) reveals that the copper film deposited at 75°C onto Melinex™ is continous and free of pin-holes. consisted of small equiaxed grains.



To explore the nano-scale morphology a holey carbon grid was coated using the same conditions and examined using transmission electron microscopy. At a magnification of 250k atomic lattice imaging the the copper crystallites exhibit twinning.

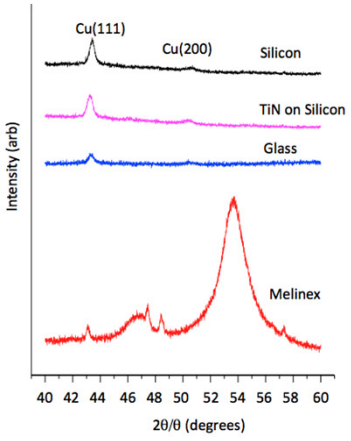


DIFFRACTION STUDIES

X-ray diffraction analysis of copper films deposited on silicon, titanium nitride, glass, and Mellinex® 505 plastic substrates was made.

The diffraction patterns exhibit the Cu(111) and (200) with intensity ratios consistent with a randomly oriented crystalline habit.

The electrical sheet resistance of a 30nm thick copper film deposited on glass at 75°C was measured. 4 – point probe analysis yielded a resistance of 0.55Ω/□.



DISCUSSION AND CONCLUSIONS

The precursor Cyclopentadienyl copper tertiarybutyl Isocyanide (CpCu^{t}BuCN) has been investigated for the ALD deposition of copper films using vapour draw approach. A hydrogen plasma was used as a co-reagent and compared with direct thermal decomposition of the precursor alone. The hydrogen plasma co-reagent has a significant influence on the deposition process, enabling copper films to be deposited at temperatures as low as 75°C on silicon, titanium nitride, glass and Mellinex® 505 plastic substrates. Continuous copper films could be deposited at thicknesses of 30nm on glass with a sheet resistance of 0.55Ω/□.