

Evaluation of Phosphite and Phosphane Stabilized Copper(I) Trifluoroacetates as Precursors for the Metal-Organic Chemical Vapor Deposition of Copper

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1 Introduction

Copper has become the material of choice for metallization of high-performance ULSI circuits [1]. As the feature size is continuously decreasing, metal-organic chemical vapor deposition (MOCVD) appears promising for depositing the Cu seed layer required for electroplating, as well as for filling entire interconnect structures.

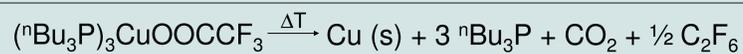
In this work, four novel Cu(I) trifluoroacetates, stabilized by organo-phosphane and organophosphite ligands, were studied as precursors for Cu MOCVD, as shown in Table 1. All substances are pale yellow to greenish liquids of oily or honey-like viscosity at room temperature. They tend to decompose upon exposure to air, but remain stable for months when stored under inert conditions.

Table 1: Cu(I) trifluoroacetates.

Precursor	Chemical structure	Solvent	Abbreviation
Tris(trimethylphosphite)-copper(I)trifluoroacetate	$[(\text{CH}_3\text{O})_3\text{P}]_3\text{Cu}-\text{O}-\text{C}(=\text{O})\text{CF}_3$	none	METFA
Tris(triethylphosphite)-copper(I)trifluoroacetate	$[(\text{CH}_3\text{CH}_2\text{O})_3\text{P}]_3\text{Cu}-\text{O}-\text{C}(=\text{O})\text{CF}_3$	Acetonitrile	ETTFA
Tris(tri(2, 2, 2-trifluoroethyl)phosphite)-copper(I)trifluoroacetate	$[(\text{CF}_3\text{CH}_2\text{O})_3\text{P}]_3\text{Cu}-\text{O}-\text{C}(=\text{O})\text{CF}_3$	Acetonitrile	CFTFA
Tris(tri- <i>n</i> -butylphosphane)-copper(I)trifluoroacetate	$[(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{P}]_3\text{Cu}-\text{O}-\text{C}(=\text{O})\text{CF}_3$	Acetonitrile or Isopropanol	BUTFA

Details are reported on CVD results obtained with BUTFA. Solutions of this precursor with acetonitrile and isopropanol were used for deposition experiments on 100 mm Si wafers sputter-coated with Cu, Cu/TiN, and Al(2 % Si)/W. Experiments were carried out in a cold-wall reactor at a pressure of 0.7 mbar, using a liquid delivery approach for precursor dosage.

Similar to respective silver(I) carboxylates [2], the precursor is assumed to decompose by decarboxylation according to the reaction:



2 Results and Discussion

2.1 Deposition on Cu seed layers

CVD on sputtered Cu seed layers resulted in continuous films, as depicted by Fig. 1. The films showed a resistivity from 2.6 to 3.3 $\mu\Omega\text{cm}$. These values are in good agreement with other results reported for thin films of CVD Cu [3]. While XPS analyses (Fig. 2) did not reveal significant impurity levels in the films, traces of oxygen and fluorine, both less than 0.1 at%, were detected by SIMS. This was particularly the case at the interface to the PVD Cu. We therefore attribute the higher resistivity values mainly to roughness effects and the influence of the film thickness.

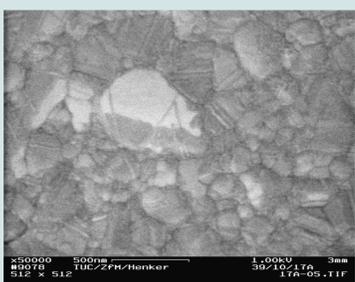


Fig. 1: SEM micrograph of CVD copper deposited by BUTFA on a sputtered Cu seed layer at 300 °C.

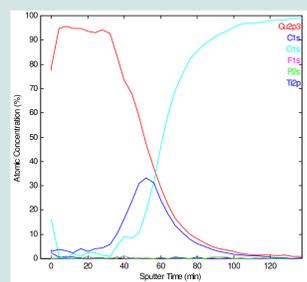


Fig. 2: XPS analysis of CVD copper deposited by BUTFA on a sputtered Cu seed layer.

The films consist of large grains with a considerable number of twins that are likely to be due to contamination effects. By EBSD, the mean grain size was determined to 278 nm, and it was found that the films are strongly (111) textured as shown in Fig. 3. At temperatures above 320 °C holes began to form in the copper films, leading to exposure of the underlying TiN (Fig. 4).

References

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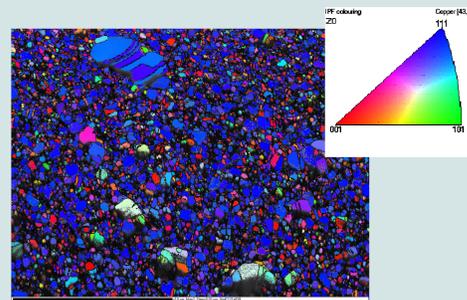


Fig. 3: EBSD grain orientation map and inverse pole figure for a sample similar to Fig. 1.

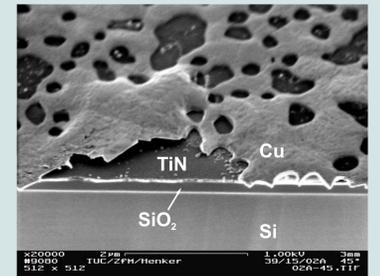


Fig. 4: Formation of holes in the Cu film after CVD at 380 °C (sample 45° tilted).

2.2 Deposition on TiN

Instead of continuous Cu films, large isolated grains were grown on TiN (Fig. 5). In addition, etch pits in the TiN formed especially at deposition temperatures above 300 °C, leading to an increase in sheet resistance. Plan-view TEM imaging and EELS analyses (Fig. 6) confirmed that the TiN was removed in these areas.

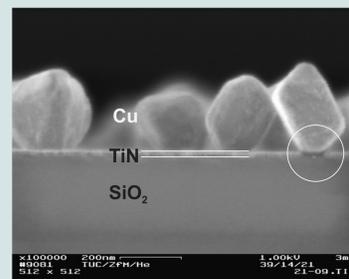


Fig. 5: Copper particles grown on TiN by MOCVD with BUTFA at 310 °C. The circled area denotes an etch pit in the TiN film, further confirmed by TEM investigations (Fig. 6).

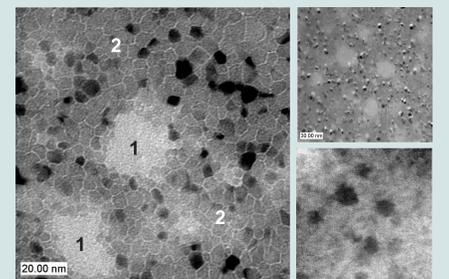


Fig. 6: Left: Plan-view TEM image of the TiN film shown in Fig. 5. Removal of the TiN is revealed in the light areas (1), where otherwise the film is intact (2). The lower right picture shows an EELS map for Ti related to the upper right TEM micrograph. The dark spots indicate a reduction of the Ti content in these areas.

2.3 Deposition on Al(Si)/W

CVD on Al(Si)/W was carried out to clarify the impact of the fluorine chemistry towards the substrate materials. Especially with Al, non-volatile reaction products may be expected that are easier to detect than volatile species probably formed in case of TiN.

The deposition experiments on Al(Si)/W resulted in grainy, disconnected Cu layers and a significant increase in sheet resistance. XPS analyses (Fig. 7) revealed fluorine and oxygen contamination. From binding energy calculations it is concluded that an isolating layer of aluminum oxyfluoride formed.

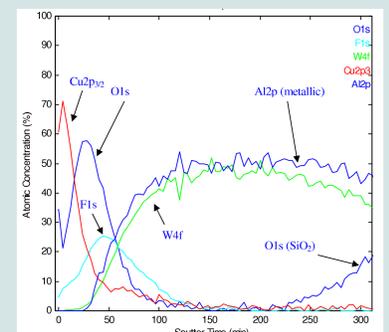


Fig. 7: XPS depth profile after CVD with BUTFA on Al(Si)/W at 340 °C.

3 Conclusions and Summary

- Phosphite and phosphane stabilized Cu(I) trifluoroacetates studied as precursors for Cu MOCVD
- Details on Cu deposition from $(\text{}^n\text{Bu}_3\text{P})_3\text{CuOOCF}_3$ ("BUTFA")
- Continuous Cu films on Cu seed layers obtained
 - Low deposition rate – insufficient vapor pressure of the precursor
 - Hole formation in Cu film at elevated temperatures
- Single Cu particles grown on TiN
- Etching of the TiN
- Isolating aluminum oxyfluoride after deposition on Al(Si)/W
 - Formation of CF_3 radicals during decarboxylation
 - No complete reaction of the CF_3 species to C_2F_6
 - Attack towards substrates during precursor decomposition

Similar results obtained with other substances (Details reported separately)

Further investigation of the precursor chemistry is required for higher volatility and elimination of the negative impact of the fluorine chemistry.

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