A study on the Metal Organic Chemical Vapor Deposition of Pure Copper Films from Low Cost Copper(II) Dialkylamino-2-propoxides:
Tuning the Thermal Properties of the Precursor by Small Variations of the Ligand.

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Abstract

Pure copper metal thin films were grown on SiO₂/Si(100) substrates by metal-organic chemical vapor deposition (MOCVD) in a horizontal cold wall CVD reactor employing the two different metal organic compounds Cu(OCHMeCH₂NR₂)₂, where R = Et (1) and R = Me (2) as precursors. Thermogravimetric analyses proved them to be convenient compounds for the deposition of copper without any reducing agent. Depositions were carried out at substrate temperatures varied in the range 230 to 350 °C. The resulting films were highly crystalline according to their X-ray diffraction pattern and show a strong (111) preferred orientation,
which increases with increasing deposition temperature. Photoelectron spectroscopy (XPS) revealed, that copper films deposited at 230 and 260 °C solely consist of metallic copper, without any detectable carbon, nitrogen or oxygen contaminations. Copper films obtained from 1 at 260 °C had a resistivity of 2.16 μO-cm.

Introduction

Metal organic chemical vapor deposition (MOCVD) of copper metal thin films has been of great interest for more than one decade\(^1\) because of its potential in microelectronic industry to substitute aluminium as the conducting material in device manufacture. This is mainly due to the greater conductivity of copper metal and the better resistance against electromigration and stress migration compared to aluminium\(^2\). The deposition of copper metal via a MOCVD process is achieved by the usage of metal organic Cu\(^{II}\) or Cu\(^{I}\) compounds as precursors with the general formula Cu\(^{II}\)(hfac)\(_2\) (A) or (hfac)Cu\(^{I}\)L (B), where hfac = hexafluoroacetylacetonato and L = neutral soft donor, such as PMe\(_3\), vinyltrimethylsilane (vtms) or other alkenes or alkynes\(^{3,4}\).

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\text{Cu(hfac)}_2 + \text{H}_2 \rightarrow \text{Cu} + 2\text{Hhfac}
\]

Scheme 1. Copper deposition from Cu(hfac)\(_2\) with H\(_2\) as reducing agent.

In the cases of Cu\(^{II}\) precursors of type A, it is necessary to use an external reducing agent such as H\(_2\) to get good quality thin films of copper metal without significant carbon or oxygen contaminations. The deposition reaction of the Cu\(^{I}\) precursors of type B involves the disproportionation into Cu\(^{II}\)(hfac)\(_2\), the free donor ligand and copper metal.