Investigation of Thermal Stability and Delivery of Cobalt Amidinates and Novel Cobalt Formamidinates for Metallic Cobalt by ALD/CVD

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Introduction

There is growing interest in cobalt metal and cobalt silicide films in logic and memory devices, especially for Co capping layer application. It is now well established that the Co capping layer formed on the Cu interconnect (as opposed to the low-k dielectric) significantly improves the top interface of the Cu lines for electromigration (EM) resistance. Co offers the advantage of substantially lower resistance and physical and electrical compatibilities with Si so that it could be potentially used in CMOS for source and drain contact metals and other Si nanowire devices. The Co precursor selection for CVD and ALD is primarily based on good thermal stability, high reactivity, the ease of deposition of Co, and precursor delivery technique including Direct Liquid injection process (DLI).

For CVD and ALD of cobalt, various sources such as Co2(CO)8, (allyl)Co(CO)3, and Co(THD)2 were used before with limited success [1-3]. Most recently, a cobalt amidinate precursor (i.e., Co-AMD) along with several novel cobalt formamidinate precursors (i.e., Co-FAMD) was investigated. In this study, we report the successful use of cobalt amidinate precursor (i.e., Co-FAMD) along with several novel cobalt formamidinate precursors (i.e., Co-FAMD) that offer significant advantages over conventional precursors in terms of their higher vapor pressures and greater thermal stabilities.

The physical properties of these sources, such as solubility, volatility, thermal stability, chemical compatibility, and viscosity will be discussed. Results showing the high purity of the sources based on ICP-MS and FT-NMR analyses will be reported, along with the characterization of the thermal stabilities with supporting TGA, ARC, and FT-NMR analysis. Preliminary ALD and CVD results of Co metal deposition using the new sources will be discussed, using Vapor-Draw process.

Cobalt Alkyl Amidinates (Co-1 and Co-2)

- High thermal stability up to 250°C
- Highly thermally stable liquid Co-1
- High vapor pressure
- A dark greenish solid precursor at room temperature

Cobalt Alkyl Formamidinates (Co-3, Co-4, Co-5 and Co-6)

- Highly reactive towards ammonia, air and moisture
- Co-2:
  - A deep greenish liquid precursor at room temperature with high vapor pressure
  - Vapor cobalt source < 80°C
  - Thermally stable liquid cobalt source at delivery temperature
  - Highly reactive towards ammonia, air and moisture
- Co-3:
  - A dark greenish solid precursor at room temperature with high vapor pressure
  - Melted at 84°C giving a liquid cobalt source at delivery temperature of > 90°C
  - Highly thermally stable up to 250°C

Thermal Stress Test on Liquid Co-1 and Co-2

- Liquid Co-1:
  - Ammonia coordinated with Co-1 spontaneously and turned liquid Co-1 into a dark solid material at room temperature.
  - Oxygen reacted with Co-1 spontaneously and turned liquid Co-1 into a black solid material immediately followed by fully oxidizing process forming a dark brownish solid material.
  - Liquid Co-1 was not chemically compatible with Co2(CO)8 and dissociated CO from Co2(CO)8 coordinated to Co-1 yielding a dark solid material.

Reactivity of Liquid Co-1 with NH3, Air, and Co2(CO)8

Thin Film Processing Performance

- New cobalt sources (liquid Co-1, Co-2, Co-3, Co-4, Co-5, and Co-6) were successfully developed as the choices of Co precursors for deposition of Co and CoSi2 thin-films by ALD and CVD.
- Those Cobalt precursors were also designed to be Co sources for direct liquid injection delivery for ALD and CVD.
- The new cobalt precursors were successfully demonstrated to grow metallic Co and CoSi2 films at lower temperature, particularly for liquid Co-1.