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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.

Cobalt offers an advantage of substantially lower resistance and physical and electrical compatibilities with Si so that it could be potentially used in CMOS 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 (alkyl acetylene), Co3(CO)9 (allyl), and Co2(CO)8 (allyl) were used before with limited success. Most recently, a cobalt amidinate precursor (i.e., Co-AMD) along with several novel cobalt formamidinate precursors (i.e., Co-FAMD) has been investigated. In this study, we report the successful use of cobalt amidinate precursor (i.e., Co-AMD) along with several novel cobalt formamidinate precursors (i.e., Co-FAMD) for Co deposition using the new sources will be discussed, using Vapor-Draw process.

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

- Co-1: 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-2: 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

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

- Co-3 and Co-4 were surprisingly air stable while Co-5 and Co-6 were air sensitive but at a much lesser degree than Co-1 and Co-2.
- Soluble in organic solvents, very good cobalt source for DLI.
- Highly thermally stable with high volatility

Vapor Pressure of Co-1 and Co-2

- Liquid Co-1: Slow, non-sustaining, transient pressure buildup spontaneously starting at 219°C
- Some non-condensable gas generated
- Exotherms observed at 180, 210, and 219°C, a good indication showing higher surface reactivity of liquid Co-1; Some non-condensable gas generated

Thermal Stress Test of Liquid Co-AMD at 120°C for 60 hours

- 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 dark solid material immediately followed by fully oxidizing process forming a dark brownish solid material.
- Liquid Co-1 was not chemically compatible with Co-1(CO)4 and dissociated CO from Co2(CO)8 coordinated to Co-1 yielding a dark solid material.

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.

References

4. H.-B.-R. Lee, G.H. Gu, C.G. Park, H. Kim, 216th ECS meeting, October 4-9, 2009, Vienna, Austria

Conclusions