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[1]. In addition, CoSi$_2$ offers advantages 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[2]. 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 Co$_2$(CO)$_8$, (alkyl)Co(CO)$_3$, and Co(THD)$_2$ were used before with limited success[3,4]. Most recently, a cobalt amide precursor has been investigated in this study, we report the successful use of cobalt amide precursor (i.e., Co-AMD) along with several novel cobalt formamidinate precursors (i.e., Co-FAMD). The results evidently show that Co-AMD as well as Co-FAMD 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.

**References**

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

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

| Source | Delivery Temperature | Vapor Pressure | Stability | Reactivity
|--------|----------------------|----------------|-----------|------------
| Co-3   | > 90°C               | High           | High      | Air sensitive
| Co-4   | > 90°C               | High           | High      | Air sensitive
| Co-5   | > 90°C               | High           | High      | Air sensitive
| Co-6   | > 90°C               | High           | High      | Air sensitive

**Cobalt Alkyl Amides (Co-1 and Co-2)**

| Source | Delivery Temperature | Vapor Pressure | Stability | Reactivity
|--------|----------------------|----------------|-----------|------------
| Co-1   | > 90°C               | High           | High      | Air sensitive
| Co-2   | > 90°C               | High           | High      | Air sensitive

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**Vapor Pressure of 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 Co$_2$(CO)$_8$, and dissociated CO from Co$_2$(CO)$_8$ coordinated to Co-1 yielding a dark solid material.

**Reactivity of Liquid Co-1 with NH$_3$, Air, and CO$_2$(CO)$_8$**

**Accelerated Rate Calorimetry (ARC)**

Temperature/Pressure vs. Time Curves:

- For liquid Co-1, slow, non-sustaining, transient exotherms observed at 180, 210, and 219°C; a good indication showing higher surface reactivity of liquid Co-1. Some non-condensable gas generated starting at 219°C
- For solid Co-2, an exotherm onset at 240°C with pressure buildup spontaneously

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**Thin Film Processing Performance**

Liquid Co-1:
- Low temperature thermal CVD or ALD with H$_2$ or H$_2$NH$_3$, giving highly pure Co films
- Thermal CVD growth rates over 3 nm/min while thermal ALD growth rates up to 0.5 Å/cycle
- Low temperature thermal CVD/ALD with NH$_3$ giving CoN (resistivity at 102 µΩ·cm) at 180°C, further annealed to form CoSi$_2$ at 630°C (resistivity at 21 µΩ·cm near bulk value of 15-20 µΩ·cm)

**Conclusions**

- 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 CoSi$_2$ 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 CoSi$_2$ films at lower temperature, particularly for liquid Co-1.