Novel Volatile Precursors of Palladium For ALD and CVD

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Introduction

➢ There is growing interest in palladium films and palladium-containing metal films for the applications as electrical contacts in logic and memory devices. For example, palladium and platinum are applied as doping agents in nickel silicide (NiSi) in source, drain, and gate of CMOS devices to increase thermal stability of NiSi by preventing $NiSi_2$ formation. So far, the preparation of suitable palladium precursors for ALD and/or CVD has long been a challenge, and no ideal Pd sources have been developed to meet the requirement for volatility, thermal stability, as well as high purity of palladium films. The Pd precursor selection for CVD and ALD is primarily based on good volatility, thermal stability, high reactivity, the ease of deposition of Pd, and precursor delivery technique including Direct Liquid Injection process (DLI).

➢ For CVD and ALD of Palladium, various sources such as (η^3-allyl)$_2$Pd, (η^3-allyl)CpPd, cis-$PdMe_2(PR_3)_2$ (R = Me, Et), $Pd(hfac)_2$, and $Pd(THD)_2$ were used before with limited success[1-3]. In this study, for the first time, we report use of several amidinate and formamidinate precursors of Palladium (*i.e.*, Pd-AMD and Pd-FAMD). These Palladium sources are either homoleptic amidinate or heteroleptic formamidinates containing strategic alkenyl ligand[4]. These novel sources exhibit high vapor pressures and greater thermal stability, and importantly, they do not contain any undesirable oxygen or fluorine or chlorine atoms. Our results show that Pd-AMD as well as heteroleptic Pd-FAMD offer significant advantages over conventional sources in terms of ease of vapor transportation and their reactivity. Formamidine ligands have previously been leveraged for new enabling metalorganic sources of lanthanum, zirconium, and hafnium with excellent thermal stabilities and high vapor pressures [5].

➢ The physical properties of these sources, such as solubility, volatility, and thermal stability will be discussed. Results confirming the high purity of the sources and the characterization of their thermal stabilities by (TGA and ARC analysis) will be reported along with preliminary ALD results.

References

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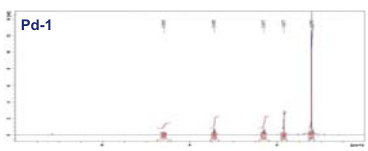
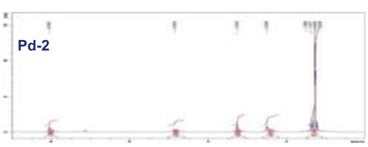
Heteroleptic Palladium Amidinate and Formamidinate (Pd-1 and Pd-2)

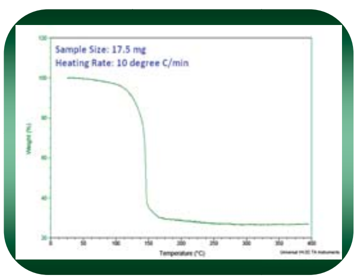
Heteroleptic Palladium Amidinate (Pd-1) and Formamidinate (Pd-2) containing strategic alkenyl ligand:

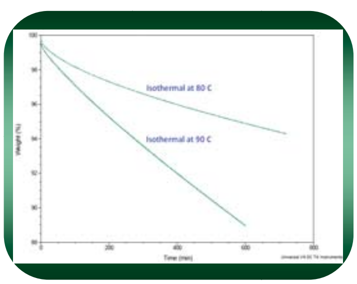
- Both Pd-1 and Pd-2 are yellowish crystalline materials with high volatility
- Very soluble in organic solvents, a very good palladium source for DLI
- Highly reactive towards air and moisture
- Thermally labile with slow degradation at > 60°C





TGA and isothermal TGA of Pd-3

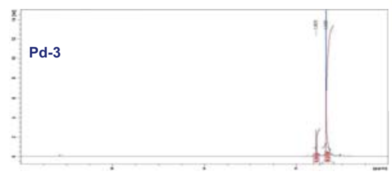




Homoleptic Palladium Amidinate (Pd-3)

Homoleptic Palladium Amidinate (Pd-3):

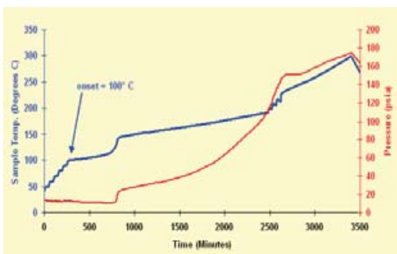
- Pd-3 is a brownish crystalline materials with high volatility and mp at 138°C
- Very soluble in organic solvents, a very good palladium source for DLI
- Highly reactive towards air and moisture
- Thermally stable with no degradation up to 100°C



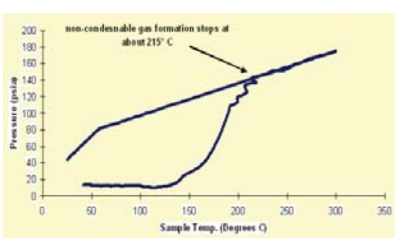
Accelerated Rate Calorimetry (ARC) Study on Pd-3

Temperature/Pressure vs. Time Curves:

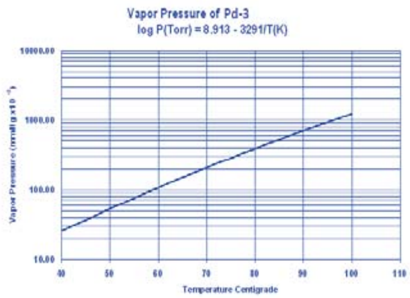
- An exotherm onset at 100°C with a typical runaway temperature profile ending at 150°C as well as the corresponding pressure spike at the same temperature
- After 150°C, a slow and linear exotherm took place, accompanied by a steadily increasing pressure up to 190°C
- Another exotherm onset at 230°C with the ARC test terminating at 300°C



Pressure vs. Temperature Hysteresis Curve:



Vapor Pressure of Pd-3

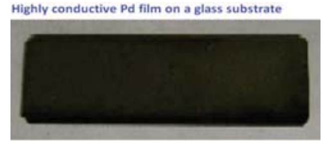


Deposition of Palladium Thin Films

Homoleptic Palladium Amidinate (Pd-3):

- Lower temperature thermal ALD with H_2 giving pure metallic Pd films
- ALD process condition:
  - ➢ Bubbler Temperatures: 80, 90, 95°C
  - ➢ Substrate Temperature: 150 – 250°C
  - ➢ ALD Pulse sequence: 2 s of H_2/3 s of Pd-3
  - ➢ Number of cycles: 1000
- Thermal ALD with H_2 giving highly conductive Pd films at 200°C as deposited
- No films or very thin Pd films were obtained with H_2/NH_3 as co-reactants.

Highly conductive Pd film on a glass substrate



Conclusions

- New heteroleptic and homoleptic palladium sources (Pd-1, Pd-2, and Pd-3) were successfully developed as the choices of Pd precursors for deposition of Pd thin-films by ALD and CVD.
- Those palladium precursors were also designed to be Pd sources for direct liquid injection delivery for ALD and CVD
- The new palladium precursors were successfully demonstrated to grow metallic Pd films at lower temperature.

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