Low-Temperature Atomic Layer Deposition of Platinum Using (Methylcyclopentadienyl)trimethylplatinum and Ozone

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Abstract

Due to excellent electric and catalytic properties, Platinum (Pt) has attracted considerable attention for applications in nanoelectronics, electrochemistry, catalysis, and sensing. Since Pt is very expensive, it is desirable to use it in the form of fine particles or very thin films for large volume applications. Atomic layer deposition (ALD) is capable of controlled deposition of ultra-small amounts of Pt in a conformal and uniform nanofilm due to the self-limiting nature. Typically thermal Pt ALD has been achieved using molecular oxygen or air and methylcyclopentadienyltrimethylplatinum (MeCpPtMe3) as the reactant gases at deposition temperatures in the range of 250–300 °C. The Pt/O2 process exhibited Volmer-Weber island growth, followed by island coalescence and the formation of a continuous thin film on substrate surfaces such as SiO2, Al2O3, and ZnO surfaces. So no nucleation delay of platinum growth has been reported for SiO2, Al2O3 and ZnO surfaces. And no Pt growth has been observed at temperatures lower than 150 °C due to the lack of reactivity between MeCpPtMe3 and O2. Some novel chemistry is needed to get a low temperature ALD Pt deposition and no nucleation delay process.

It was reported that using ozone (O3) as a reactant, pure metallic Pt film had been deposited at temperatures as low as 100 °C. In this work, the low temperature Pt/O3 ALD process using GEMStar ALD tool and qualified ozone kit has been studied. Reported herein: growth rate at different temperatures, resistivity at the low temperature of 150 °C and conformality with special attention to the nucleation of the Pt films.

Precursors used and Instrumentation

- MeCpPtMe3 was used as Pt source.
- 8% Ozone was generated by a qualified PacifOx generator (bottom right) and used as second reagent in Pt/O3.
- TMA (98%) was used as Al source and DI water was used as oxidizer in Al2O3 nucleation layer in PtO2 process.
- O2 (99.999%) was used as oxidizer in ALD PtO2 process.
- All films were deposited on a GEMStar ALD system.
- MeCpPtMe3 held at 75°C
- TMA precursor held at room temperature,
- H2O oxidizer held at room temperature,
- 8% Ozone was generated by a qualified ozone generator (bottom right),
- All films grown at a temperature range of 100°C to 280°C.

Growth Characteristics

The picture depicts the variation of Platinum growth rate with process temperature for the O2 process. As evident from the graph, the process shows ALD characteristics by exhibiting a constant growth rate across a wide range of temperatures.

The left chart shows the saturated growth of Pt films versus pulsing of O2 gas at 150°C. Saturation curve shows that platinum growth saturates at 100Å pulse time. At this temperature, the growth rate is lower. The saturated growth is around 1.2 Å/cycle. At this temperature there is very little Pt growth using pure oxygen.

The chart shows the growth rate of ALD PtO2, process and ALD PtO2 with Al2O3 as the nucleation layer at 250°C. ALD PtO2 process shows very little nucleation delay while ALD PtO2 process shows 15 cycles of nucleation delay. The ALD PtO2 process shows the growth rate of 1.3 Å/cycle while the O2 process shows the growth rate of 1.03 Å/cycle.

Summary

- ALD Pt was done using MeCpPtMe3 and a qualified O3 kit.
- The novel process is characterized by a constant growth rate of 1.2 Å per cycle within the 100–250 °C temperature window.
- Conductive and uniform Pt with low impurity level was achieved at temperature as low as 150 °C.
- Below 150 °C, a non-conductive PtO2 films were achieved.
- The Pt process has zero nucleation delay and did not need a Al2O3 nucleation layer.
- The resultant Pt film was smooth and had very small grain size of platinum crystallites by SEM.
- Good conformality of the low-temperature ALD process by Pt deposition was demonstrated using a trench aspect ratio of 5:1.

Performance of Pt films by Pt/O3 process

Pt films deposited at 150°C inside an aspect ratio 5:1 trench structures showing excellent conformality of the Pt/O3 process with ALD PtO2 process. The white bar on the bottom of the image represents 200 nm. By the scanning transmission electron microscopy STEM image of cross sections of ALD Pt films, the Pt growth is smooth and the grain size is very small. It indicated that at a low temperature of 150°C ALD PtO2 has very good nucleation on SiO2/Si surface. In contrast, ALD PtO2 process has a very long nucleation delay on SiO2/Si surface. The white bar on the bottom of each image represents 200 nm.

For comparison, the 2.5 nm of Pt by Pt/O3 process with 2 Å of Al2O3 at 250°C is very rough with larger grain of Pt crystallites.

References

- D. Breitkreutz et al; “Platinum thin film properties in high stress geometric structures and corrosion to Process Conditions,” ALD 2011, Cambridge, MA.
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