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.

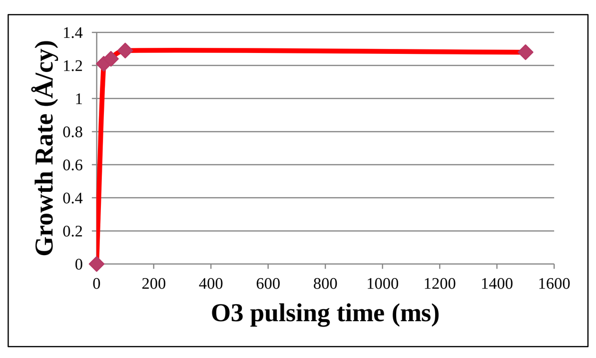
Typically thermal Pt ALD has been achieved using molecular oxygen or air and methylcyclopentadienyltrimethylplatinum (MeCpPtMe3) as the reactant gases at deposition temperatures in the range of 250−300 °C. The Pt/O_2 process exhibited Volmer-Weber island growth, followed by island coalescence and the formation of a continuous thin film on substrate surfaces such as SiO_2 and Al_2O_3. So a 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 (O_3) as a reactant, pure metallic Pt film had been deposited temperatures as low as 100 °C. In this work, the low temperature Pt/O_3 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.

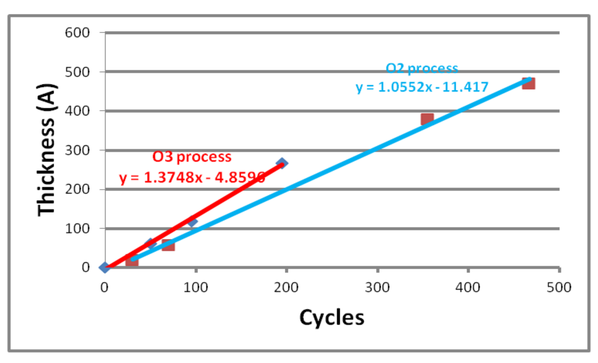
Precursors used and Instrumentation

- MeCpPtMe3 was used as Pt source.
- 8% Ozone was generated by a qualified Pacific Ozone generator (bottom right) and used as second reagent in Pt/O_3.
- TMA (98%) was used as Al source and DI water was used as oxidizer in Al_2O_3 nucleation layer in Pt/O_2 process.
- O2 (99.993%) was used as oxidizer in ALD Pt/O_2 process.
- All films were deposited on a GEMStar ALD system.
  - MeCpPtMe3 held at 75C
  - TMA precursor held at room temperature,
  - H_2O precursor held at room temperature,
  - 8% Ozone was generated by a qualified ozone generator (bottom right),
  - All films grown at a temperature range of 100℃ to 280℃.

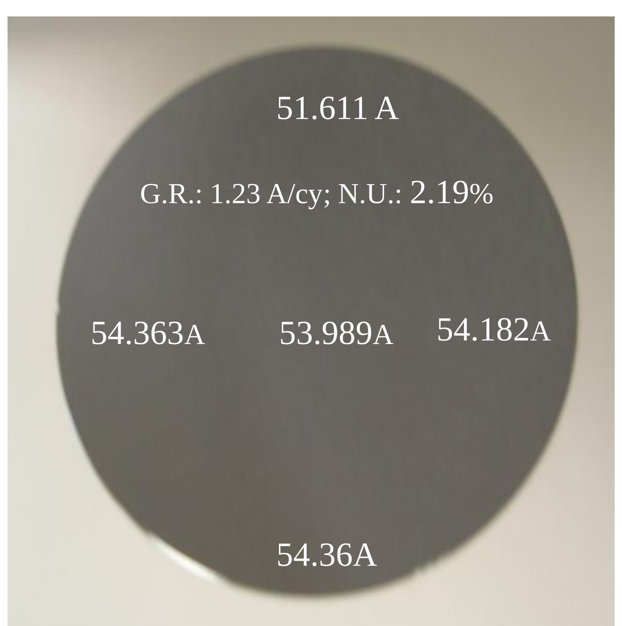
Growth Characteristics



The left chart shows the saturated growth of Pt films versus pulsing of O_3 gas at 150℃ . Saturation curve shows that platinum growth saturates at 150ms O_3 pulse time. At dose lower than 40 ms, the growth rate is lower. The saturated growth is around 1.24 Å/cy. At this temperature there is very little Pt growth using pure oxygen.

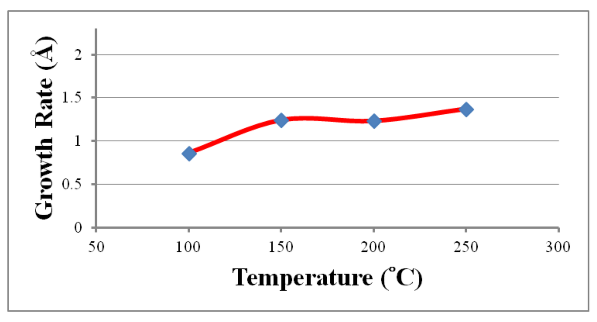


The chart shows the growth rate of ALD Pt/O_3 process and ALD Pt/O_2 with Al_2O_3 as the nucleation layer at 250℃ . ALD Pt/O_3 process shows very little nucleation delay while ALD Pt/O_2 process shows 11 cycles of nucleation delay. The ALD Pt/O_3 process shows the grow rate of 1.37 Å/cy while the O_2 process shows the growth rate of 1.03 Å/cy.



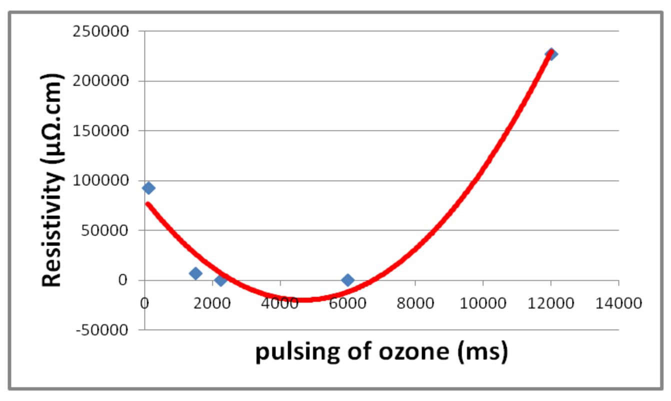
ALD Pt by O_3 process at 150℃ on 200mm (8") bare Si wafer through exposure mode. The non-uniformity is around 2%.

Growth Characteristics

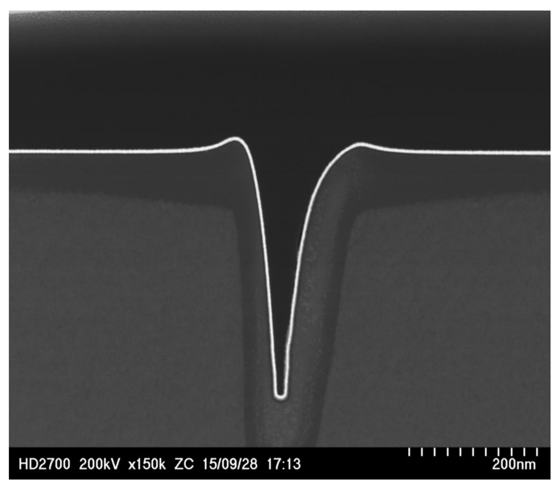


The picture depicts the variation of Platinum growth rate with process temperature for the O_3 process. As evident from the graph, the process shows ALD characteristics by exhibiting a constant growth rate across a wide range of temperatures.

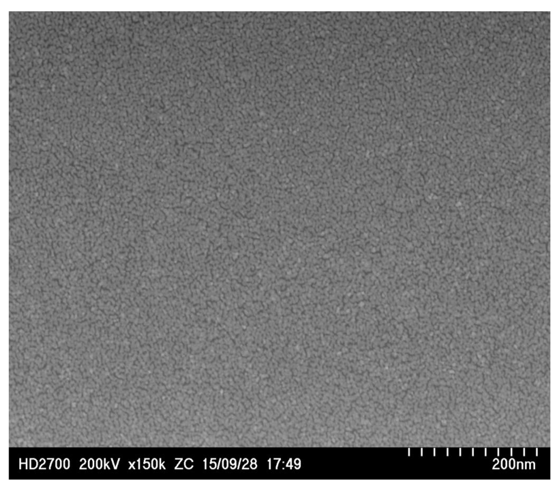
Performance of Pt films by Pt/O3 process



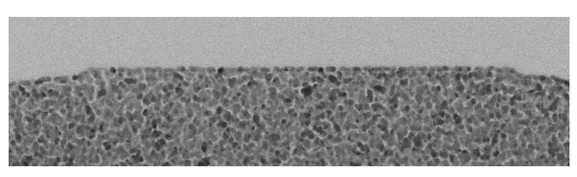
To study the effect of ozone on the resistivity of Platinum, the ozone dose was varied for the Pt deposition at 150C. It was seen that the resistivity first decreases and then increases with increasing O_3 dose. At lower doses, there is not enough activity between O3 and MeCpPtMe3. So the resultant Pt film contains some impurities and exhibits high resistivity. While at higher does, the ozone has a great oxidation power and part of the Pt film converts to non conductive PtO2. The optimum condition is at 5000ms of ozone dose for the Pt deposition at 150C. We also tried 100 C deposition. However, the film was non conductive and presumably PtO2 film was formed.



Pt films deposited at 150℃ inside an aspect ratio 5:1 trench structure showing excellent conformality of ALD Pt/O_3 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 inside UV/ozone treated Si holes, the film thickness at the top of the holes is found to be 5.6 nm, while the thickness at the middle and bottom of the holes is around 5.5 nm. This gives a step coverage of close to 100%.



By STEM image of ALD Pt films on top of UV/ozone treated Si substrate, the Pt film is very smooth and the grain size is very small. It indicated that at a low temperature of 150℃ ALD Pt/O_3 has very good nucleation on SiO_2/Si surface. In contrast, ALD Pt/O_2 process has a very long nucleation delay on SiO_2/Si surface. The white bar on the bottom of each image represents 200 nm.



For comparison, the 2.5 nm of Pt by Pt/O_2 process with 2 nm of Al_2O_3 at 250℃ is very rough with larger grain of Pt crystallites.

Summary

- **ALD Pt was done using MeCpPtMe3 and a qualified O_3 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 unitform Pt with low impurity level was achieved at temperature as low as 150 °C.**
- **Below 150 °C, a non-conductive PtO_2 films were achieved.**
- **The Pt process has zero nucleation delay and did not need a Al_2O_3 nucleation layer.**
- **The resultant Pt film was smooth and had very small grain of Pt crystallite by SEM.**
- **Good conformality of the low-temperature ALD process by Pt deposition was demonstrated using a trench of aspect ratio of 5:1.**

References

- D. R. Beaulieu et al "*Nano-engineered ultra high gain microchannel plates*", Nucl. Instr. Meth. A 607 (**2009**) pp. 81-84.
- D.R. Beaulieu et al "*Plastic microchannel plates with nano-engineered films*", Nucl. Instr. Meth. A 633 (**2011**) pp. S59-S61
- T. Aaltone, M. Ritala, T. Sajavaara, J. Keinonen, M. Leskela; "*Atomic Layer Deposition of Platinum Thin Films*"; Chem. Mater. 2003, 15, 1924−1928.
- P. de Rouffignac et al; "*Platinum Thin Film Properties in High Aspect Ratio Structures and Correlation to Process Conditions*"; ALD 2011, Cambridge, MA.
- Jolien Dendooven et al; "*Low-Temperature Atomic Layer Deposition of Platinum Using (Methylcyclopentadienyl)trimethylplatinum and Ozone*"; J. Phys. Chem. C 2013, 117, 20557−20561.
- J. Hamalainen, F. Munnik, M. Ritala, M. Leskela; "*Atomic Layer Deposition of Platinum Oxide and Metallic Platinum Thin Films from Pt(acac)2 and Ozone*"; Chem. Mater. 2008, 20, 6840−6846.
- H. C. M. Knoops et al; "*Remote Plasma ALD of Platinum and Platinum Oxide Films*"; Electrochem. Solid-State Lett. 2009, 12, G34−G36
- H. Li et al; "*Low Temperature (LT) Thermal ALD Silicon Dioxide Using Ozone Process*"; ALD 2014, Kyoto, Japan.
- D. Gorelikov, H. Li, J. Narayanamoorthy, N. Sullivan; "*High surface area /high aspect ratio ALD process optimization using anodic aluminum oxide*"; ALD 2013, San Diego, CA, July 28–31.
- J. Narayanamoorthy, D. Gorelikov, H. Li, , N. Sullivan; "*Large Area MCPs Coating by ALD*"; C-ALD 2014, Shanghai, China;
- H. Li, J. Narayanamoorthy, N. Sullivan, D. Gorelikov; "*Characterization of ALD Undoped and Doped ZnO Films*"; ALD 2015, Portland, OR.