PLATINUM THIN FILM PROPERTIES IN HIGH ASPECT RATIO STRUCTURES AND CORRELATION TO PROCESS CONDITIONS

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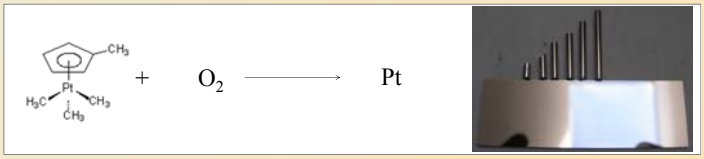
INTRODUCTION

High conformality in high aspect ratio structures is the hallmark of ALD processes, however, achieving good conformality for metal films can be challenging. In this presentation, the process conditions for thermal ALD required to achieve highly conformal Platinum (Pt) films with uniform electrical properties will be presented. In addition, several simple methods for quantifying conformality of both thickness and electrical properties of thin films will be provided. Platinum is an important metal for catalytic devices as well as for applications that take advantage of high conductivity. The ALD of Pt has been reported in many publications, but the treatment of uniformity, composition, and conductivity as a function of aspect ratio and process conditions is limited. This work will demonstrate, for the first time, conformal deposition of Pt on substrates with aspect ratios ranging from 10:1 to 150:1.

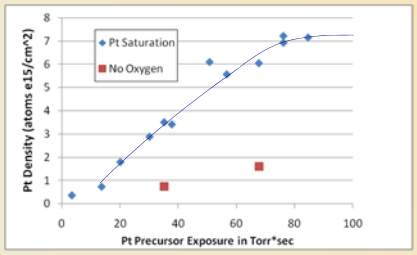
Precursor Used

The Me_3CpMe platinum precursor is readily obtained commercially . In this work , the precursor bottles were filled at Strem chemical with (Trimethyl)methylcyclopentadienylplatinum(IV), of 99% purity. Oxygen was used as the oxidant and was dosed directly into the ALD system.

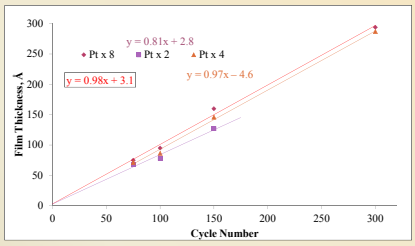


- All film depositions performed in an Arradiance GemStar Desktop ALD system
- Films grown in a temperature range of 200 – 275 °C
- Me_3CpMe was used in a temperature range of 60-75°C and was directly dosed from a 150cc precursor delivery bottle
- O_2 was used as the oxidant at room temperature and was directly dosed to process chamber

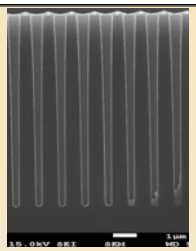
ALD Growth Characteristics



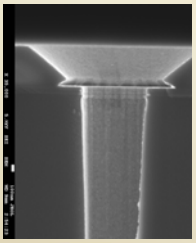
- Exposure was changed by either increasing the Pt bottle temperature or multipulsing the Pt precursor (see saturation to the left)
- Multipulsing is exposing PtCp to the surface, evacuating the chamber, and then exposing the PtCp again
- In the rest of the work three Pt exposure levels using multipulsing were used (Pt at 70 C)
  - Pt pulsed 2 times
  - Pt pulsed 4 times
  - Pt pulsed 8 times



Film thickness determined using spectroscopic ellipsometer for thin Pt films and high resolution SEM for films over 25nm.
Extrapolated growth rate = 0.98Å/cycle Pt x8; 0.97Å/cycle Pt x4; = 0.81Å/cycle Pt x 2; ZERO inhibition on Al_2O_3 surface



Pt film can easily penetrate a 40:1 hole

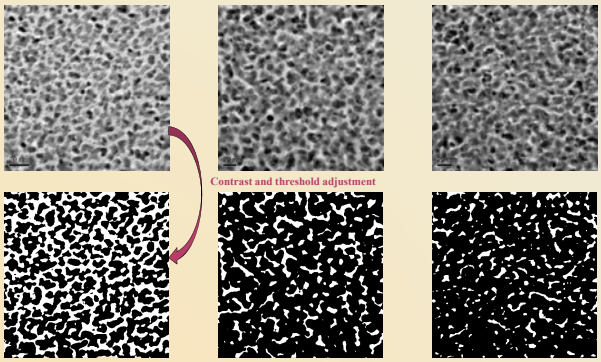


300 Pt x 2

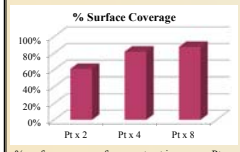
300 Pt x 8

Nucleation

- 30 cycles of Pt + O_2
- All films grown at 250 °C with a source temperature of 70 °C
- Starting surface is 1nm Al_2O_3 on Si_3N_4 TEM membranes
- TEM images analyzed using Image J

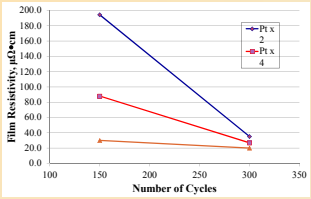


- Using a different threshold level, the nucleation rate after 2 x Pt pulses is ≈ 1e12/cm²
- Increasing the number of Pt pulses increases the island size, either through preferential growth on Pt centers or through agglomeration.
- Nucleation rate may have also increased with increasing Pt doses, however, this experiment would need to be repeated using fewer overall cycles to be certain.
- % surface coverage reaches 88% for 8xPt on a flat surface
- The % coverage is likely influenced by the aspect ratio



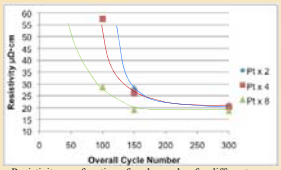
% surface coverage from contrast images vs Pt pulse #; coverage is close to saturated after 4 cycles

2D Resistivity 4pt.Probe– Deposition Temperature



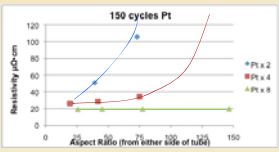
Using the four point probe instrument, the resistivity of films grown on alumina coated glass slides was measured with various Pt pulse multiples. Utilizing 8 Pt pulses yields a film resistivity of ~30 µΩ-cm after only 150 cycles while fewer multiples yields much higher resistivities. By 300 cycles the resistivities start to converge. By 500 cycles it is expected that the resistivities will all reach the bulk value, although the higher the Pt pulse multiple, the sooner it reaches bulk properties.

Resistivity and Conformality – Pt Exposure



Resistivity as a function of cycle number for different Pt pulses all at 70 °C – AR ~ 25:1

Electrical measurements made using Ag contacts on tube ends. IV measurements using a Keithley 2410 and Micromanipulator Probe station



Resistivity vs aspect ratio for different Pt pulse multiples

Increasing the exposure moves the resistivity vs. cycle curve to the left. It also extends the penetration depth where the resistivity is constant. So, a recipe with a double pulse of Pt will yield fairly conductive (<20µΩ•cm) Pt films after 150cycles, but the resistivity will increase significantly as the AR goes over 50:1. A recipe where the Pt is exposed to the feature for 3s x 8 pulses yields a film with bulk resistivity after only 150 cycles (~7.5nm) and uniform physically and electrically to AR >150:1

Conclusions

- Saturation of Pt film thickness does not perfectly correspond to saturation of film properties such as resistivity
- TEM analysis of Pt after 30 cycles shows that the surface is almost completely covered in Pt for the highest Pt pulse multiple, though the height of the islands is similar for all pulse multiples
- Pt multi pulsing yields higher nucleation rates over just increasing Pt exposure time (not shown)
- Pt film resistivities converge as the overall cycle number goes up.
  - If high conductivity is required at low cycle number you would use a high Pt exposure.
- Pt properties as a function of aspect ratio are strongly dependent on Pt multi pulsing
  - After 150 cycles, Pt film is visually present in high aspect ratio structures, but resistivity is high for films grown with the low multiples
- A hybrid pulsing recipe (high pulse multiples at first then less for the bulk) may yield the best combination of film properties and efficient precursor usage

Acknowledgements

Professor Meni Wanunu at Northeastern University provided the TEM and Gregory McMahon from the Boston College Nanofabrication Center provided the SEM images.