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Ozone Recombination Impact on Conformality of Pt ALD

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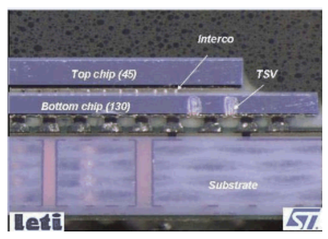
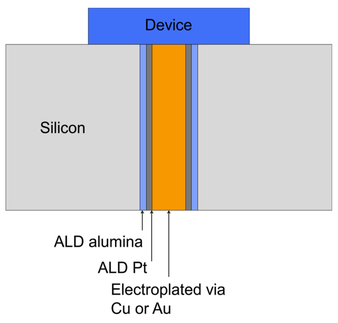
Pt deposition by Atomic Layer Deposition (ALD) is commonly used to uniformly create a conductive metal layer on high aspect ratio features. We have used this technique to create a conformal coating, which served as a conductive seed layer for electro-chemical deposition. These technologies have been combined to enable deep micro-structured transmission gratings used as optical elements in X-ray phase contrast imaging and electrically conductive paths in through silicon vias. ALD deposition using precursors of methylcyclopentadienyl(trimethyl)platinum or MeCpPtMe3 and oxygen requires a reactor processing temperature in excess of 250°C for reasonable deposition rates. Using ozone as the reactant enables a reduction of this processing temperature to 150°C for metal deposition. However, ozone has a high recombination rate on Pt surfaces which significantly reduces the conformal deposition on high aspect ratio features as the ozone doesn't survive very far down a via. The aspect ratio coverage limitations with this low temperature ozone process have been explored to provide design guidance for device fabrication.

Through-Silicon Via (TSV) for Backside Electrical Connections

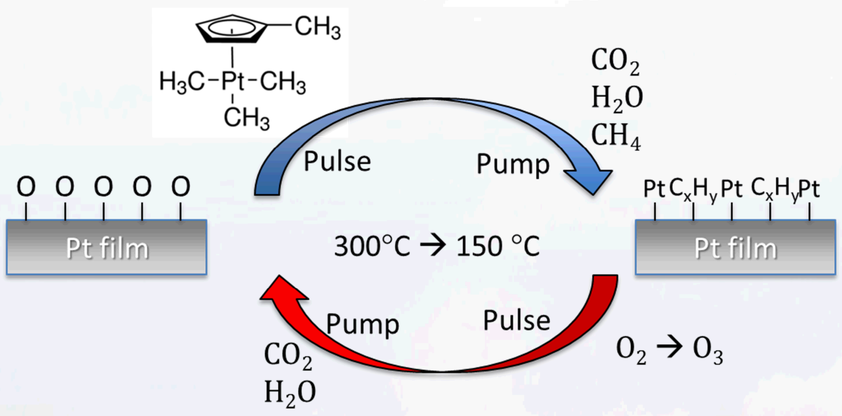
- **TSV**: Electrical connection passing through the wafer significantly shortens conductor path and increases packing density. This 3D approach is becoming the standard approach to manage the shrinking area demands.
- **High aspect ratio**: Vias formed by deep reactive ion etch (DRIE) in Si can achieve > 50:1 Aspect Ratios. ALD was used to passivate the via and to deposit a conductive seed layer for electroplating.
- **Post process via fill**: For custom device fabrication prefilled TSVs may not be possible, so a post process via metallization process is required and may have temperature restriction for device protection. To avoid reflowing SnPb solder (mp ~180C), Pt ALD process temperature of 150°C was selected requiring the use of ozone as the secondary reactant.



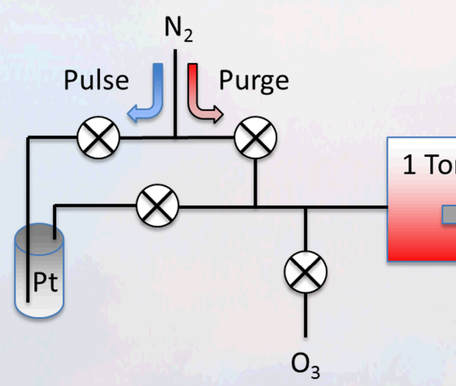
Source: CTI Leti/ST Micro



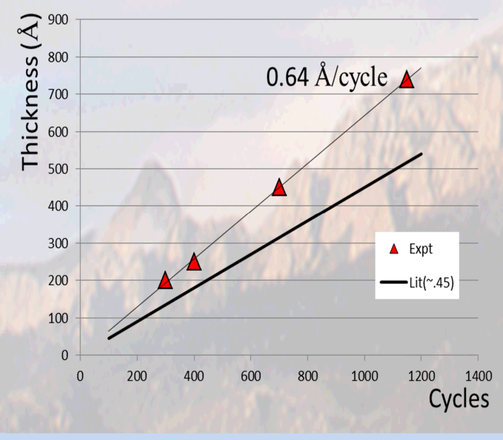
ALD Deposition of Conductive Pt Seed Layer

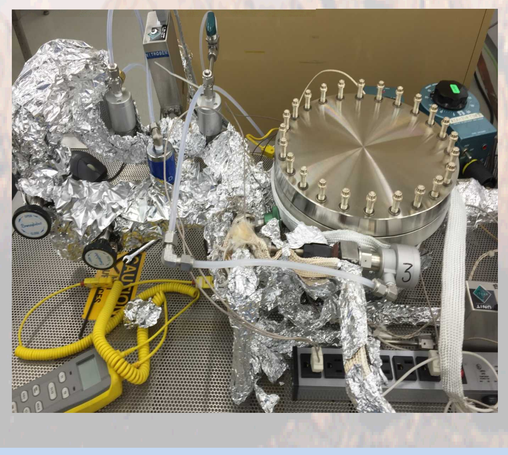


Thermal ALD was processed in a custom built flow reactor with warm walls and hot wafer stage. Pt precursor was heated to 75°C and delivered by flow through bubbler.

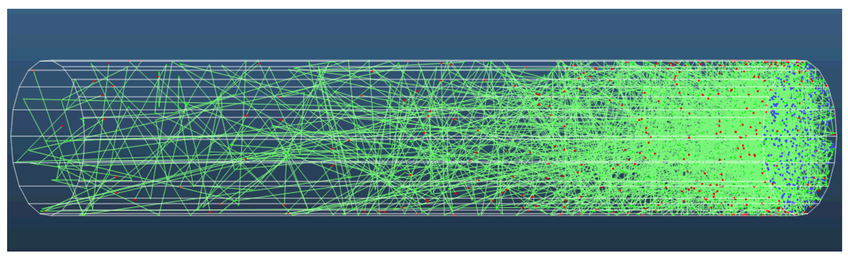


- Pt pulse 3s with 20s purge
- O_3 pulse 3s with 20s purge





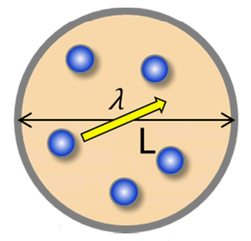
Monte Carlo Simulation



Monte Carlo simulation conducted using **Molflow**. Gas flow inside pores with less than 100 μm diameter is molecular flow with chamber pressure of 1 torr.

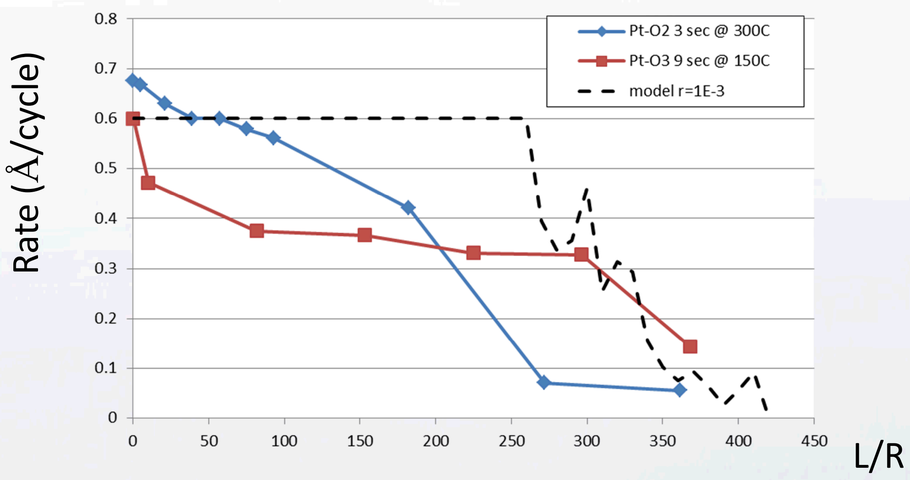
$$Kn = \lambda/L \qquad \lambda = 100\ \mu m\ @\ P = 1\ torr \qquad \lambda = \frac{\sqrt{2}k_B T}{2\pi d^2 P}$$

- If ***Kn* < 0.01**, pressure is high, the flow is viscous.
- ✓If ***Kn* > 1**, pressure is low, gas flow is molecular

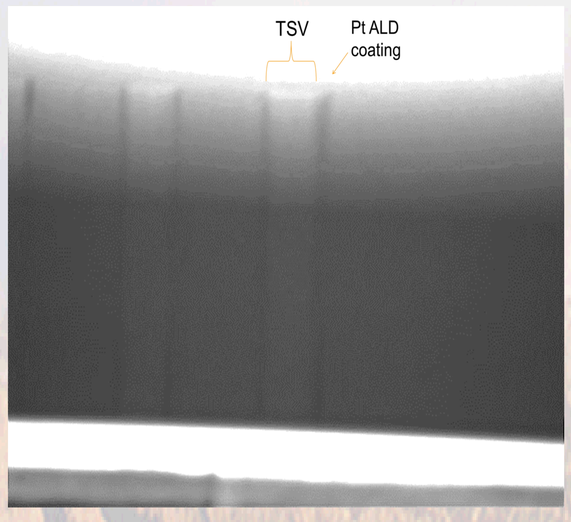


Using a ozone recombination probability of r = 10^{-3} resulted in good agreement with experimental results. Also good agreement with paper by Knoops, Elam et.al. Chemistry of Materials, 2011.

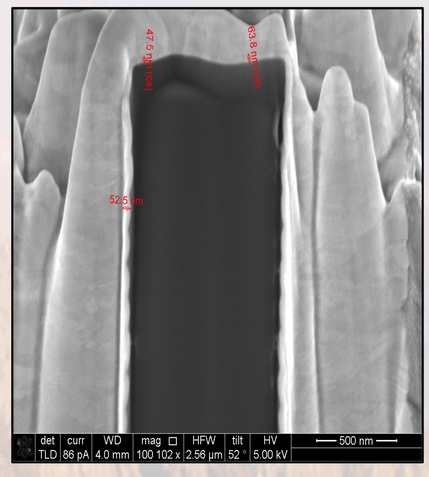
Results



Ozone recombination rate of r=10^{-3} was used to model the aspect ratio coverage for 50 micron diameter TSV.



Plated Au on 50nm ALD Pt



Pt – O_3 ALD uniformly coated 12:1 aspect ratio via with 9 sec exposures at 150C . Coating was electroplated with Au.

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