Area selective atomic layer deposition of molybdenum films on nanoscale metal and metal nitride patterns

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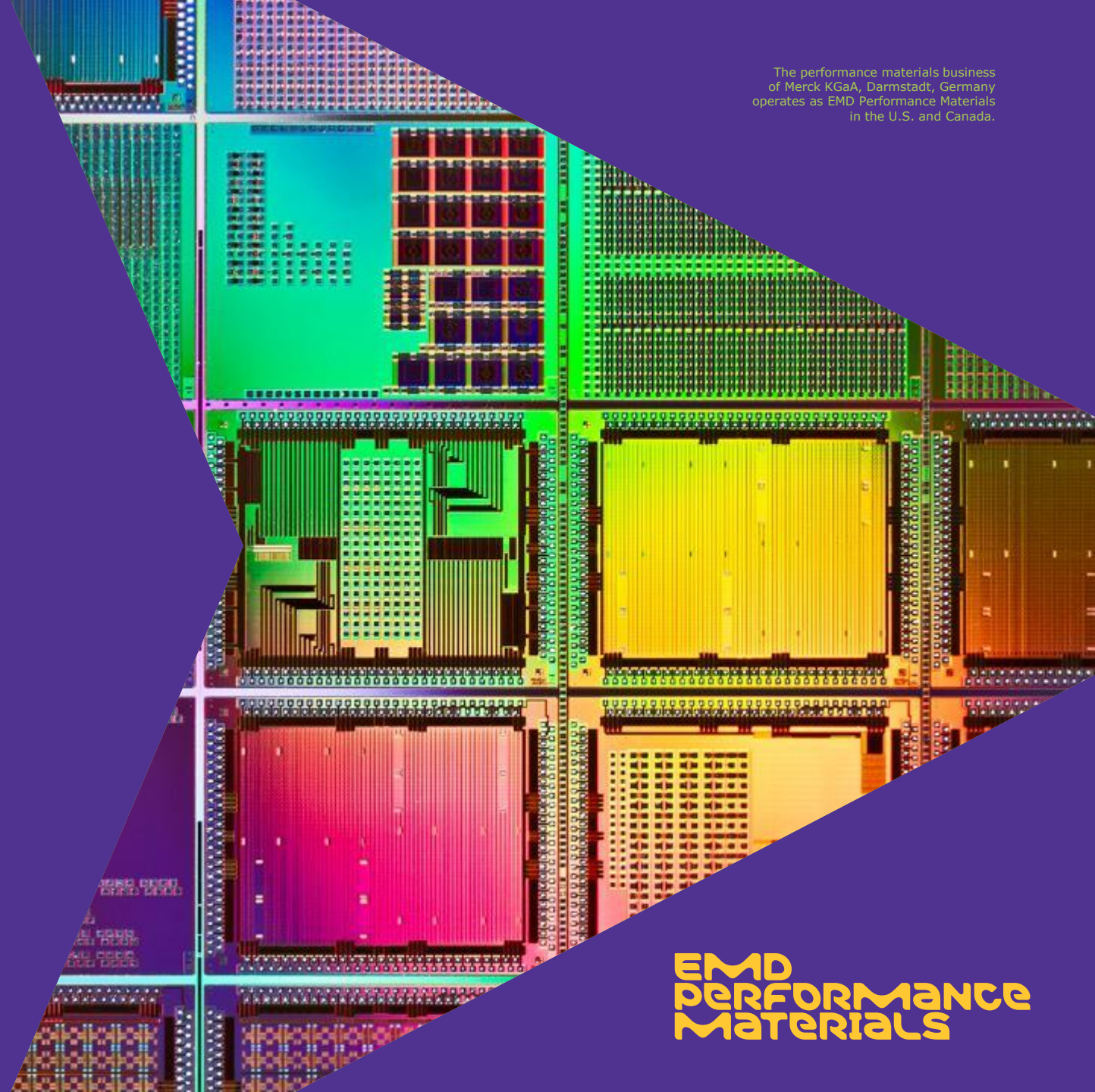
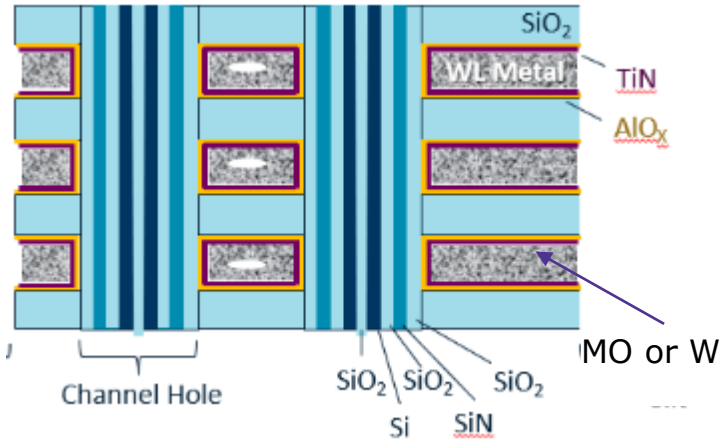


EMD Performance Materials

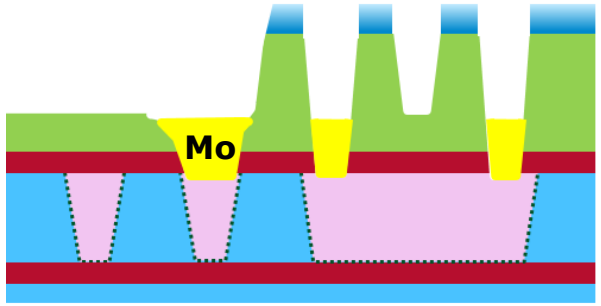
Introduction:
Needs for Selective Deposition of Molybdenum

- Molybdenum (Mo) is considered as an attractive material for future devices. Mo has almost same level of low bulk resistivity comparing to W, but it has smaller Electron Mean Free Path, so the effective resistivity is expected to be lower compared to W
- Several fluorine-free Mo precursors are available, such as MoO_2Cl_2 and $MoCl_5$
- Inherently selective deposition of Mo on metal nitride and metal films is highly attractive to reduce integration process steps in several applications

Selective Molybdenum on TiN for 3D NAND Application



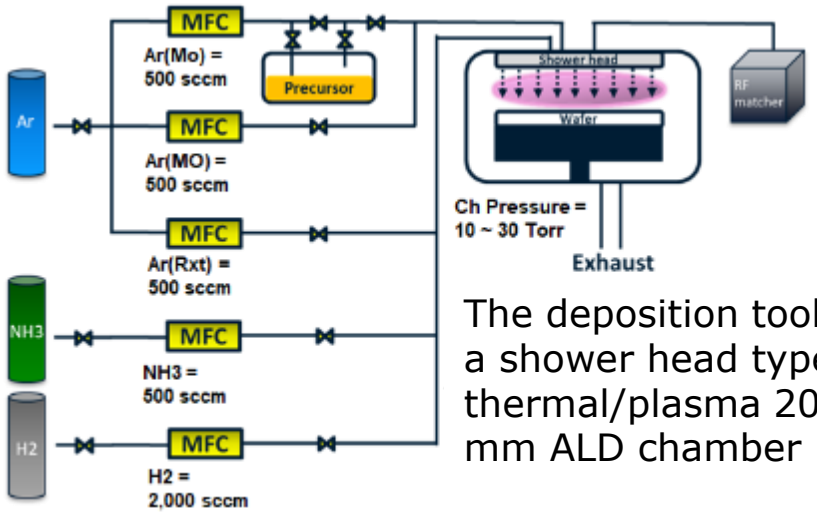
Selective Molybdenum on Ru or Co for via fill in MOL/BEOL structures



Deposition of Mo and MoN Films from $MoCl_5$ and MoO_2Cl_2: **ALD Tool Configuration and Film Metrology**

- Deposition of Mo and MoN on various substrates was investigated using two molybdenum chloride precursors: $MoCl_5$ and MoO_2Cl_2
- H_2 and NH_3 reactants were used for deposition of the Mo and MoN_x films

Tool Configuration



The deposition tool is a shower head type thermal/plasma 200 mm ALD chamber

Film Metrology

Thickness and Resistance: XRF(TEM), 4PP

Impurities in the film: XPS and AES

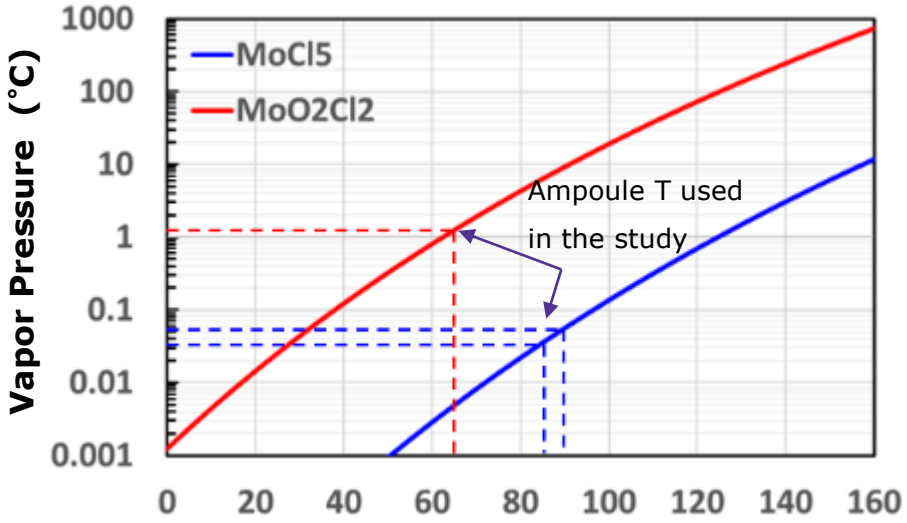
Crystallinity and Density: XRD / XRR

Surface morphology and conformality: SEM & TEM

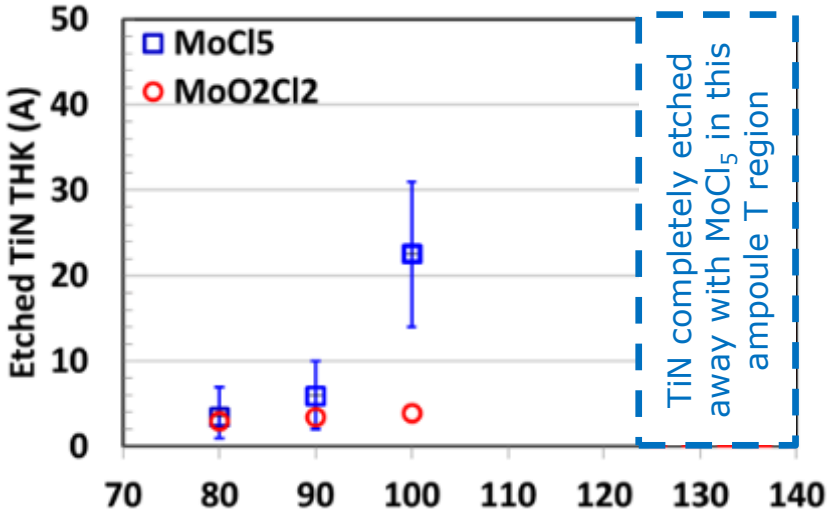
Deposition of Mo and MoN Films from $MoCl_5$ and MoO_2Cl_2: **Precursors Comparison**

- MoO_2Cl_2 has significantly higher vapor pressure compared to $MoCl_5$
- $MoCl_5$ showed strong etch of TiN substrate. The etch rate increased with ampoule temperature due to higher precursor flux and longer pulse time
- 85-90˚C ampoule temperature was selected for $MoCl_5$ process to reduce etch rate

$MoCl_5$ and MoO_2Cl_2 Vapor Pressure

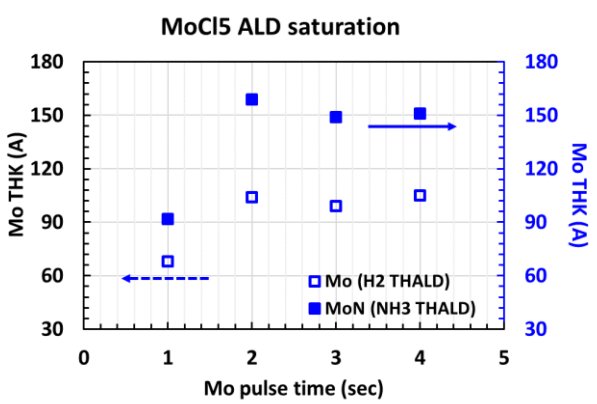


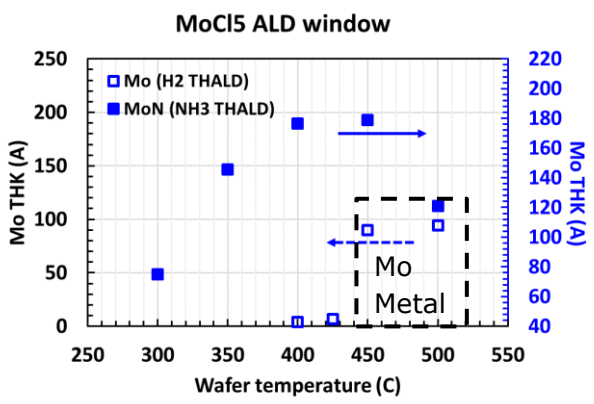
TiN Etch Thickness vs. Ampoule T

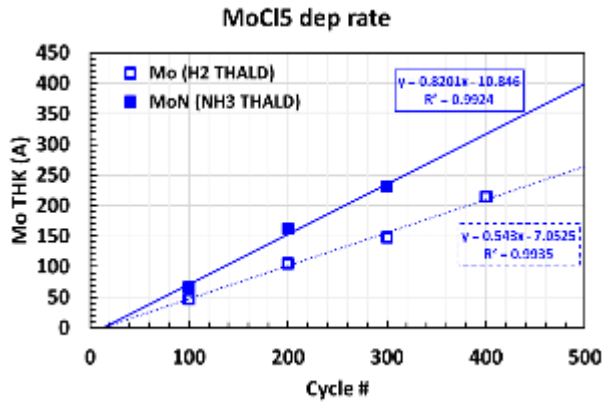


Deposition of Mo and MoN Films from $MoCl_5$ and MoO_2Cl_2: **Saturation and Growth per Cycle**

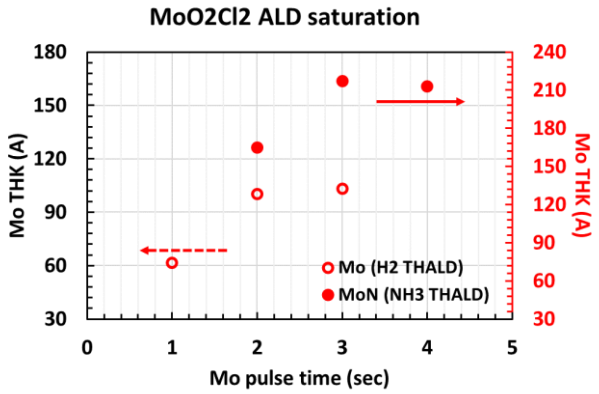
$MoCl_5$: saturation behavior but no THALD of Mo with H_2; THALD of MoN with NH_3 at 400-450˚C

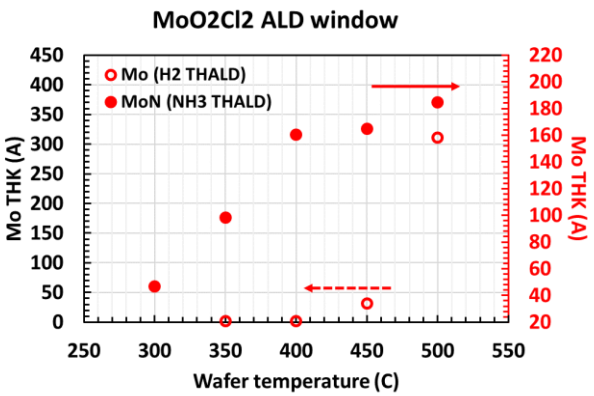


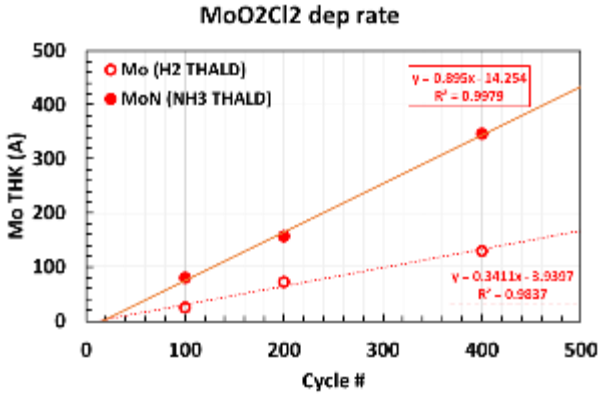




MoO_2Cl_2: no pure Mo with H_2 < 500˚C; THALD of MoN with NH_3 at 400-450˚C





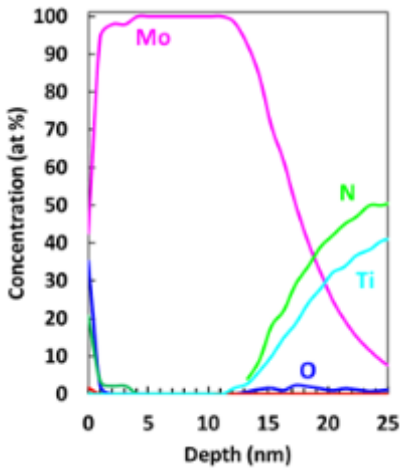


Deposition of Mo and MoN Films from $MoCl_5$ and MoO_2Cl_2: **Film Characterization by XPS and Auger (AES)**

- Mo film deposited from MoO_2Cl_2 at 500˚C contained up to 20 at % of oxygen
- $MoCl_5$ produced pure Mo films above 450˚C wafer temperature
- Both precursors produced molybdenum-rich MoN films

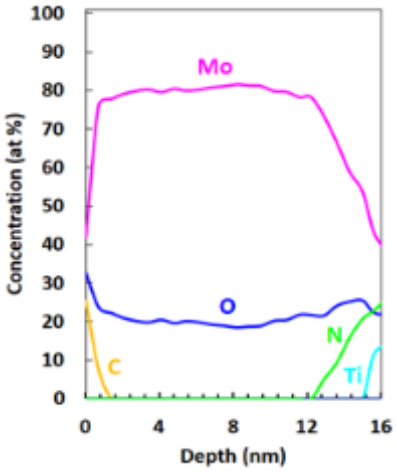
XPS Profile of Mo Films on TiN

$MoCl_5$



Wafer T = 450°C

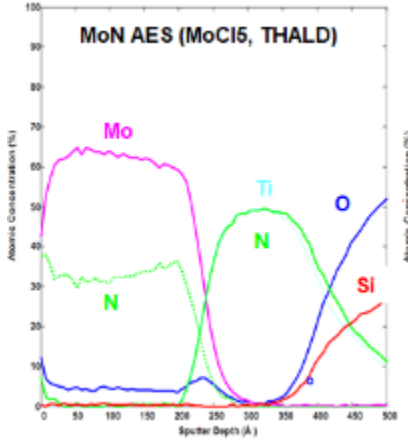
MoO_2Cl_2



Wafer T = 500°C

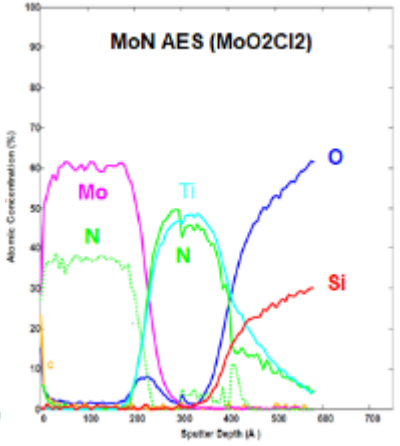
AES Profile of MoN Films on SiO_2

$MoCl_5$



Wafer T = 450°C

MoO_2Cl_2

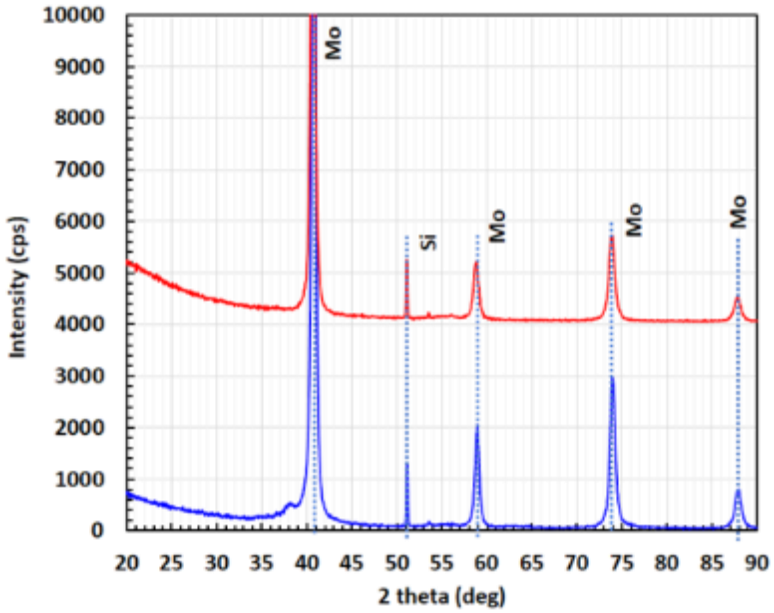


Wafer T = 450°C

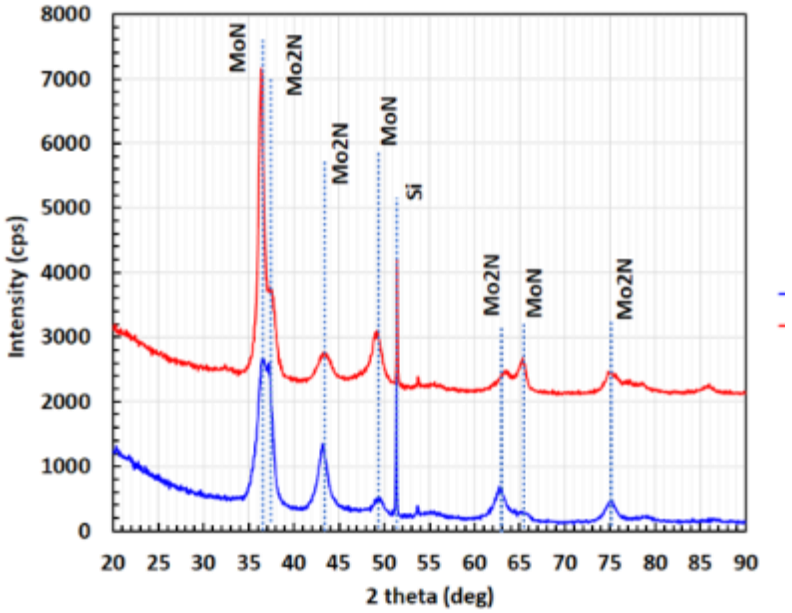
Deposition of Mo and MoN Films from $MoCl_5$ and MoO_2Cl_2: **XRD of Mo and MoN Films**

- Crystalline Mo phase was observed in films deposited from Mo and MoO_2Cl_2, even though significant amount of residual oxygen was observed in film from MoO_2Cl_2
- A mixture of MoN and Mo_2N phases was observed in molybdenum nitride films, further reduction in nitrogen content was observed upon annealing of MoN films at higher temperature

XRD of Mo Films



XRD of MoN Films

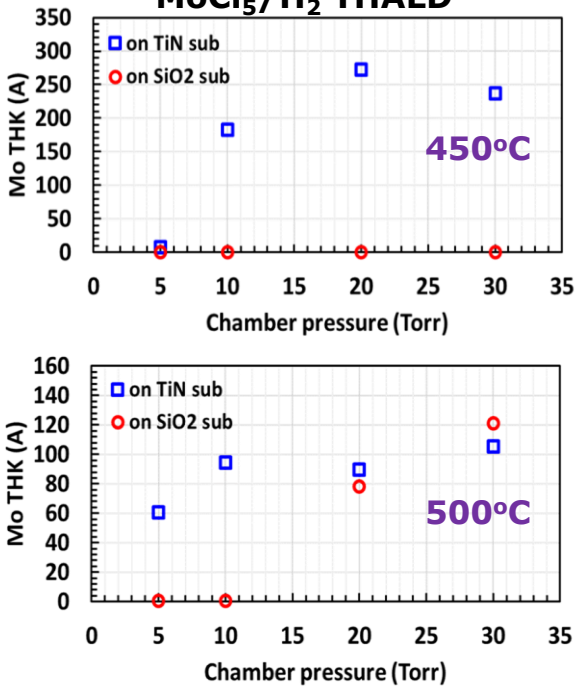


Selective Deposition of Mo Films:
The Effect of Process Conditions on Selectivity

- $MoCl_5$/Thermal H_2 process showed very high inherent selectivity toward TiN surface. Some selectivity was also observed toward AlO_x relative to SiO_2. Selectivity had strong dependence on chamber P, wafer T and $MoCl_5$ flux
- Selectivity toward TiN was also observed for MoO_2Cl_2/H_2 process, but films contained residual oxygen

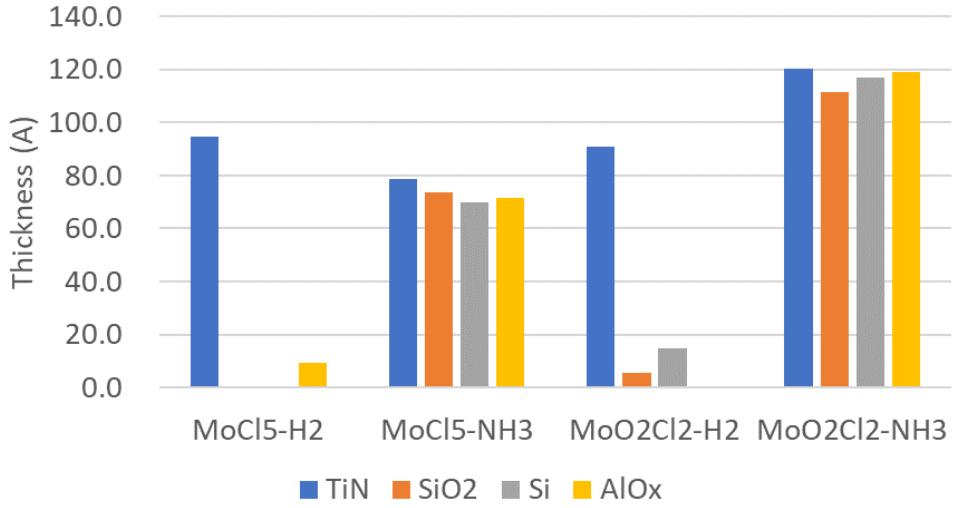
Mo Film Thickness on TiN and SiO_2

$MoCl_5/H_2$ THALD



Film Thickness on Different Substrates

Wafer T = 500°C, Chamber Pressure = 10 torr

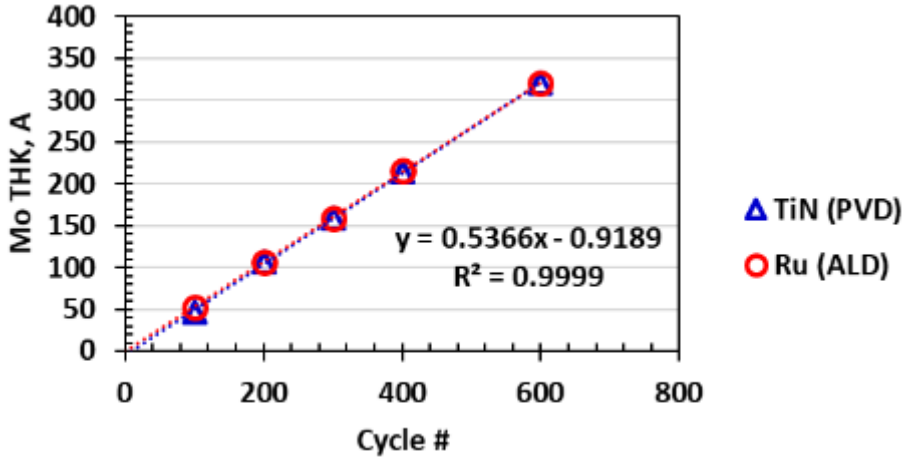


No selectivity was observed for thermal NH_3 ALD process

Selective Deposition of Mo Films:
Tuning Process Selectivity Toward Ru and TiN

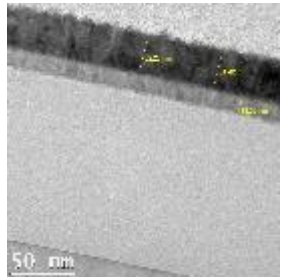
- Process conditions were optimized to demonstrate highly selective deposition of Mo films on Ru and TiN substrates

Mo Thickness vs. # of Cycles

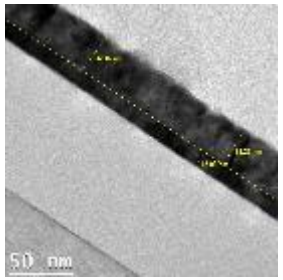


- Deposition conditions:
  - Wafer T = 450°C
  - Chamber P = 30 torr
  - H_2 Thermal ALD
  - Pulse sequence 2/20/5/20
  - # of Cycles = 100
  - GPC = 0.54A/cy on blanket wafer
- No deposition was observed on SiO_2 or LowK blanket wafers
- No detectable chloride on interface with Ru by XPS and SIMS

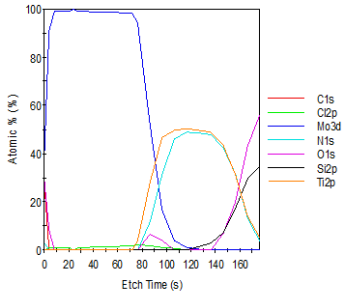
TEM of Mo Film on TiN



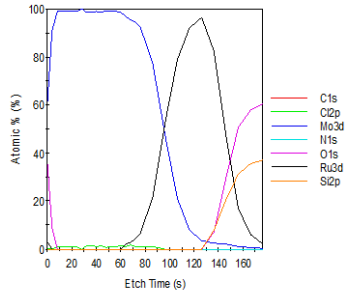
TEM of Mo Film on Ru



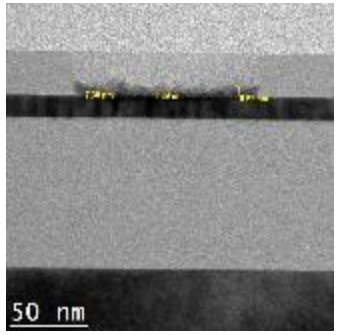
XPS of Mo Film on TiN

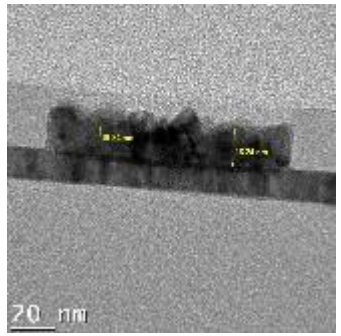


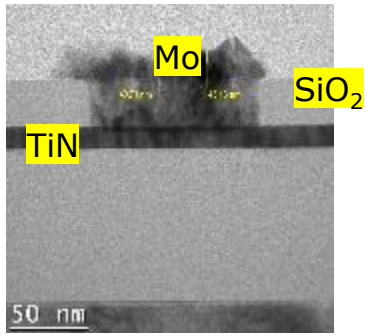
XPS of Mo Film on Ru



Selective Deposition of Mo Films:
Selective Mo on TiN/SiO_2 Pattern

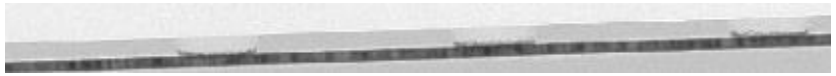




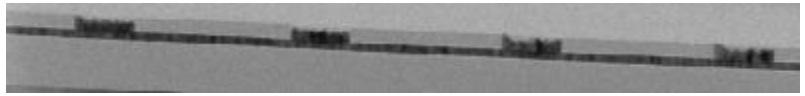


TEM of TiN/SiO_2 Patterned Wafers

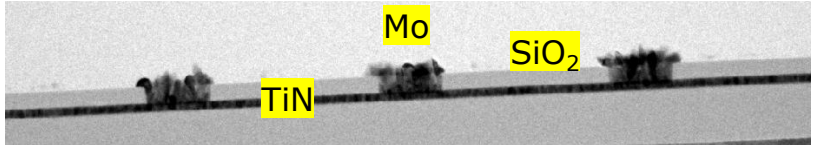
~ 6 nm Mo on TiN
No dep on SiO_2



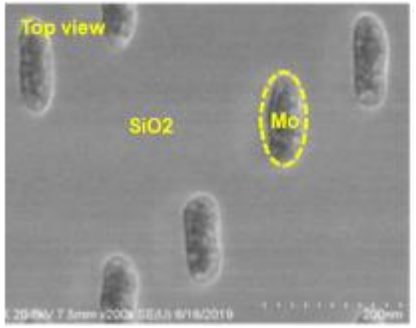
~ 20 nm Mo on TiN
No dep on SiO_2



~50 nm Mo on TiN,
Holes overfilled without
deposition on SiO_2



- **Bottom up fill of Mo on TiN surface by $MoCl_5/H_2$ thermal process**
- **Patterned wafer was provided by IMEC**

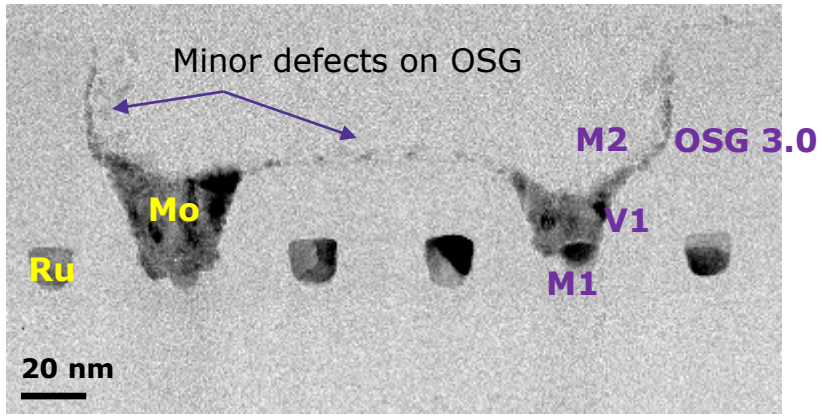


Selective Deposition of Mo Films:
Selective Mo on Ru/SiO_2 Pattern – Partial Via Fill

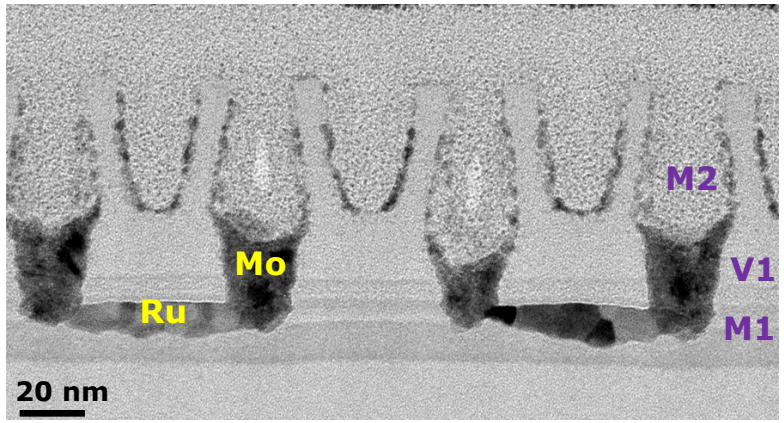
- Mo films were deposited on Ru/LowK BEOL structures provided by IMEC
- The film was deposited using the recipe for 2.5 nm Mo film on blanket Ru
- Significant enhancement in deposition rate is observed on nano-structure

XTEM on Via Chain Structure After Mo Deposition on Ru M1 Layer (2.5 nm on blanket)

Along M2 Chain



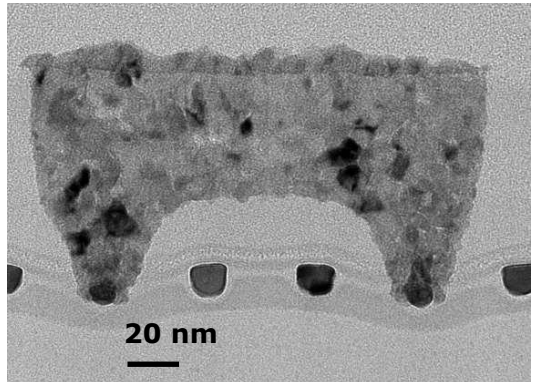
Across M2 Chain



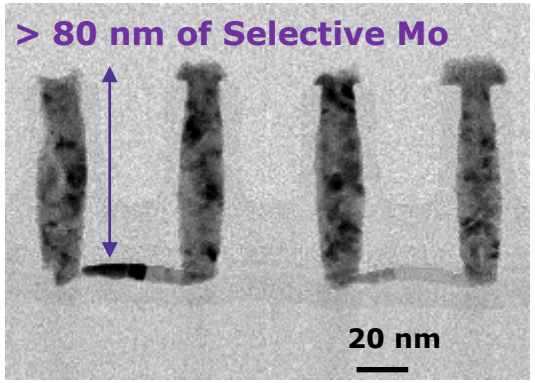
Selective Deposition of Mo Films:
Selective Mo on Ru/SiO_2 Pattern – Complete Via Fill

XTEM on Via Chain Structure After Mo Deposition on Ru M1 Layer (5.5 nm on blanket)

Along M2 Chain



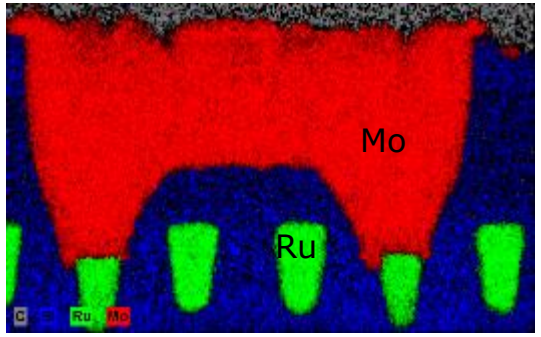
Across M2 Chain



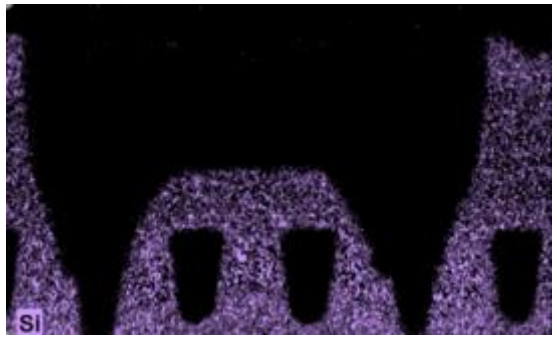
- 10 times growth enhancement inside narrow via
- No Ru and Mo intermixing

EDS Elemental Mapping Along M2 Chain

Si, C, Mo and Ru Map



Si Map



O Map

Area Selective Molybdenum Films on Nanoscale Patterns: **Summary and Conclusions**

- Thermal ALD-like of Mo and MoN films with $MoCl_5$ and MoO_2Cl_2 was demonstrated using H_2 and NH_3 as reactant gases
- Classical ALD behavior was not observed with $MoCl_5$ due to its ability to self-etch deposited Mo film
- $MoCl_5$ showed significantly higher process selectivity toward TiN and Ru surfaces relative to SiO_2/OSG 3.0 surfaces
- High resolution TEM of Mo films on patterned TiN/SiO_2 and Ru/OSG 3.0 wafers showed a seamless bottom-up molybdenum fill on highly challenging structures with CD < 30 nm and feature height > 80 nm, with very minor defects on SiO_2 and LowK dielectric
- Over 10 times enhancement of effective deposition rate was observed inside the features compared to blanket film. The result may suggest that ASD mechanism on nanoscale is different from the macroscale mechanism.

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