The PE-ALD of Ta Based Metals/Nitrides: The Growth, Materials Properties, and Applications to Future Device Fabrications

TFUG/PEUG
Northern California Chapter
AVS

Hyungjun Kim and Steve M. Rossnagel

12/12/02

Thomas J. Watson Research Center
IBM Research Division

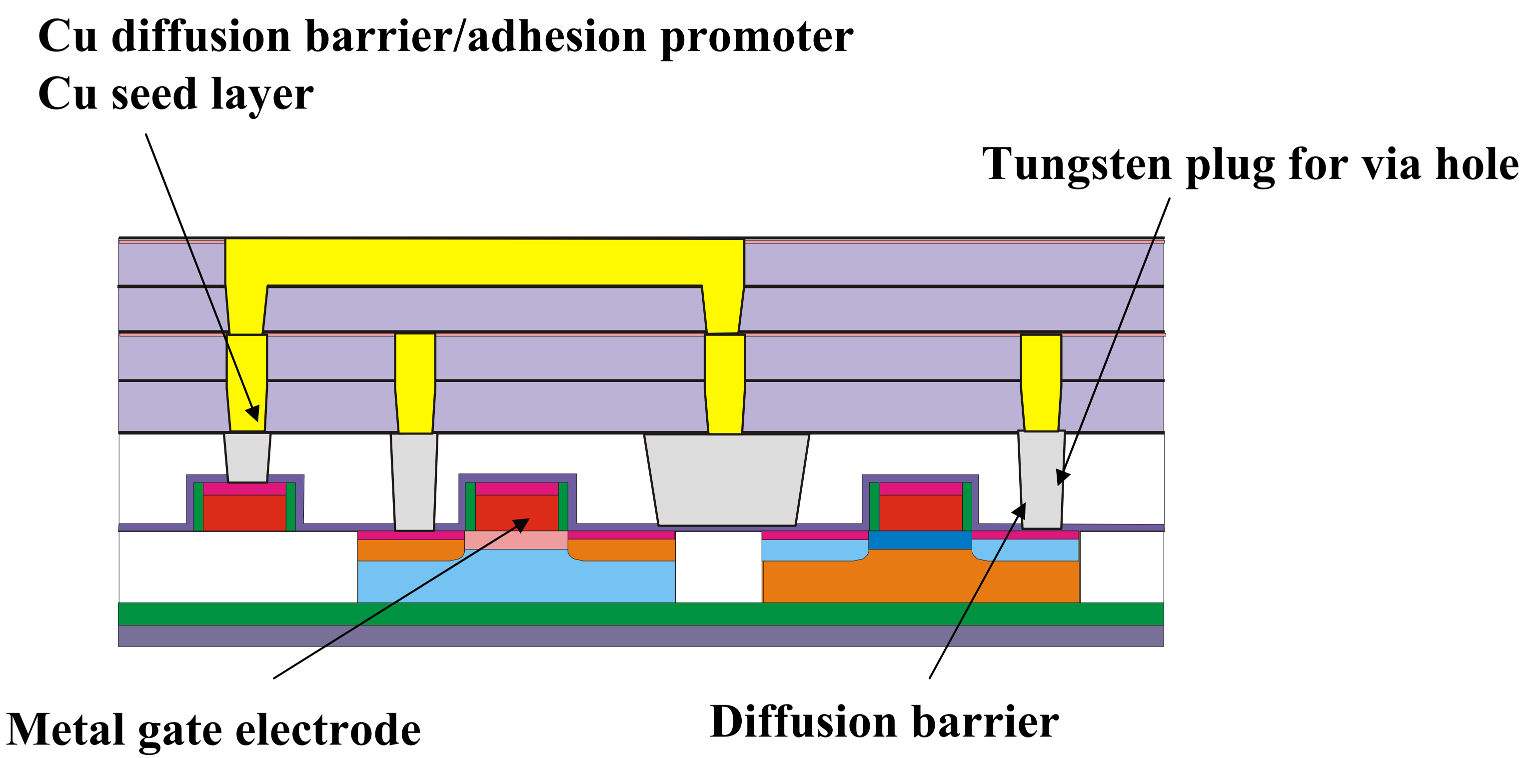
Atomic Layer Deposition

- **ALD (Atomic Layer Deposition):** Self-limiting film growth method by alternate exposure of chemical species in layer-by-layer manner.
    - Good conformality
    - Easily controlled thickness at the atomic scale
    - Atomic level composition control
    - Large area uniformity
    - Low impurity at low growth temperature

- **For sub-100 nm node with Cu interconnect,**
    - Ultra thin/highly conformal diffusion barrier.

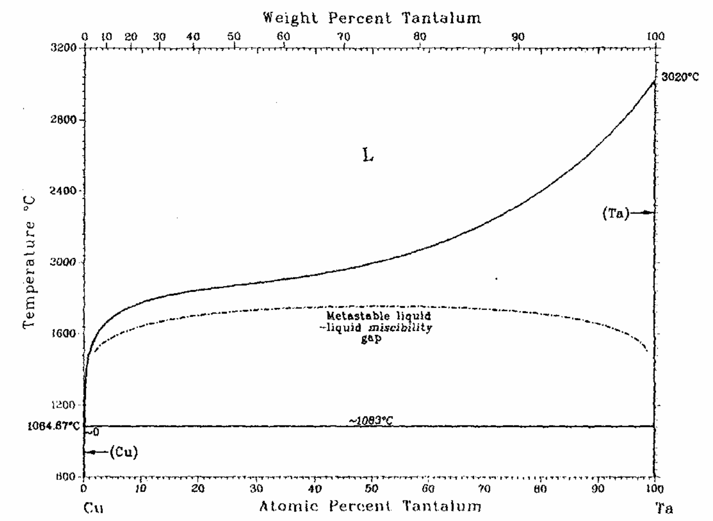
→ **ALD is a promising technique.**

Potential Applications of ALD Metals/Nitrides in Nanoscale Devices



Ta and TaN Thin Films

- **Ta**
  - Good resistivity
    α phase (bcc): 15-60 μΩ cm
    (β phase (tetragonal): 170-210 μΩ cm)
  - High thermal stability (T_m = 2669 °C)
  - No intermetallic compound with Cu
  - Cu has very low lattice diffusivity in Ta.



Binary Alloy Phase diagrams, ASM International, 1990

- **TaN**
  - High chemical, mechanical, and thermal stability
  - Various phase: solid-solution α phase Ta, hexagonal Ta_2N, hexagonal TaN, cubic TaN, hexagonal Ta_5N_6, tetragonal Ta_4N_5, orthorhombic Ta_3N_5

Ta and TaN layer for Cu interconnect

♦ TaN/Ta bilayer liner

Both Ta and TaN have good DB property. Why bilayer liner?

- Good adhesion: resisting delamination during process or thermal processing, high EM resistance
- Liner/ILD and Cu/liner adhesion have conflicting dependencies on N content for TaN_x
  - Ta adhesion on SiO_2 (low k) is poor: TaN on SiO_2 (low k) is require.
  - Cu adhesion on TaN is poor: Cu on Ta is required.

→ TaN/Ta bilayer is the only viable option so far.
  - TiN/Ta causes corrosion for some CMP process
  - alpha Ta formation on TaN: low in-plane resistivity

Currently PVD is used, but if we want to implement ALD liner process…

Need ALD process for both Ta and TaN liners!

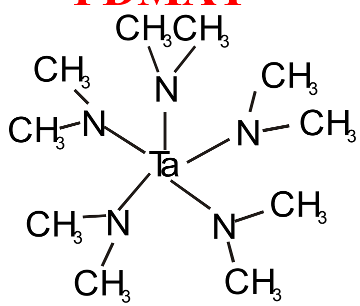
Ref) D. Edelstein et al, Proc. 2001 IITC, 9 (2001).

Ta/TaN ALD : Precursors

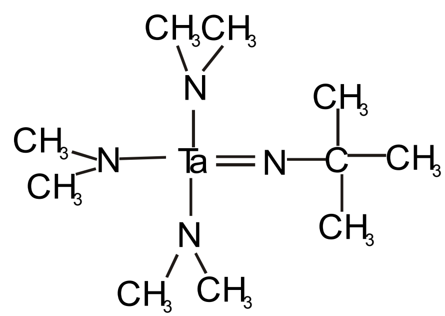
♦ Ta metal precursor

- Halides: $TaCl_5$, $TaBr_5$, TaI_5, all solid source
- MO source: N is contained

PDMAT



TBTDET



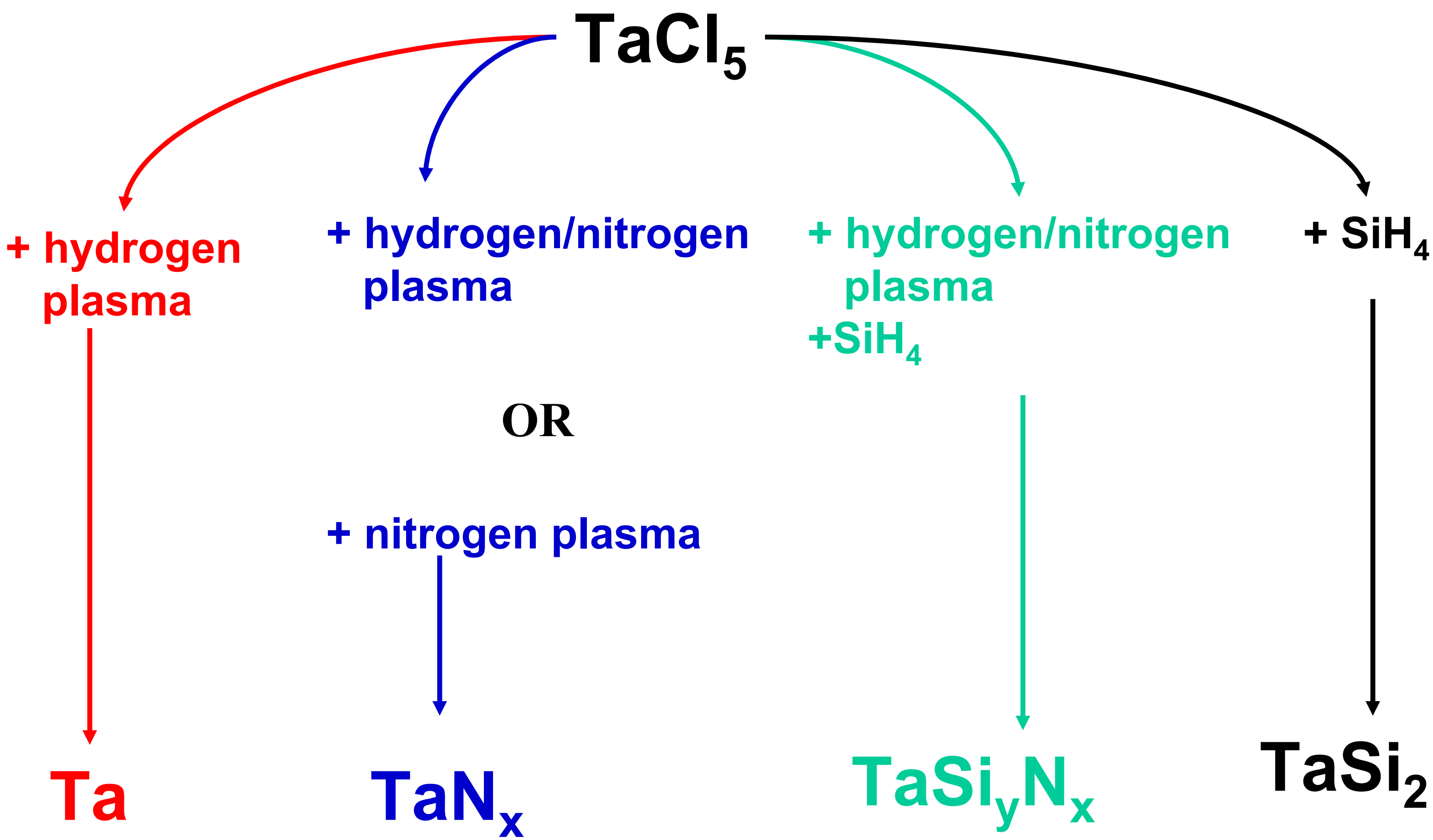
♦ Ta ALD: Ta halides + reducing agents

- Molecular H_2: require above 700 °C

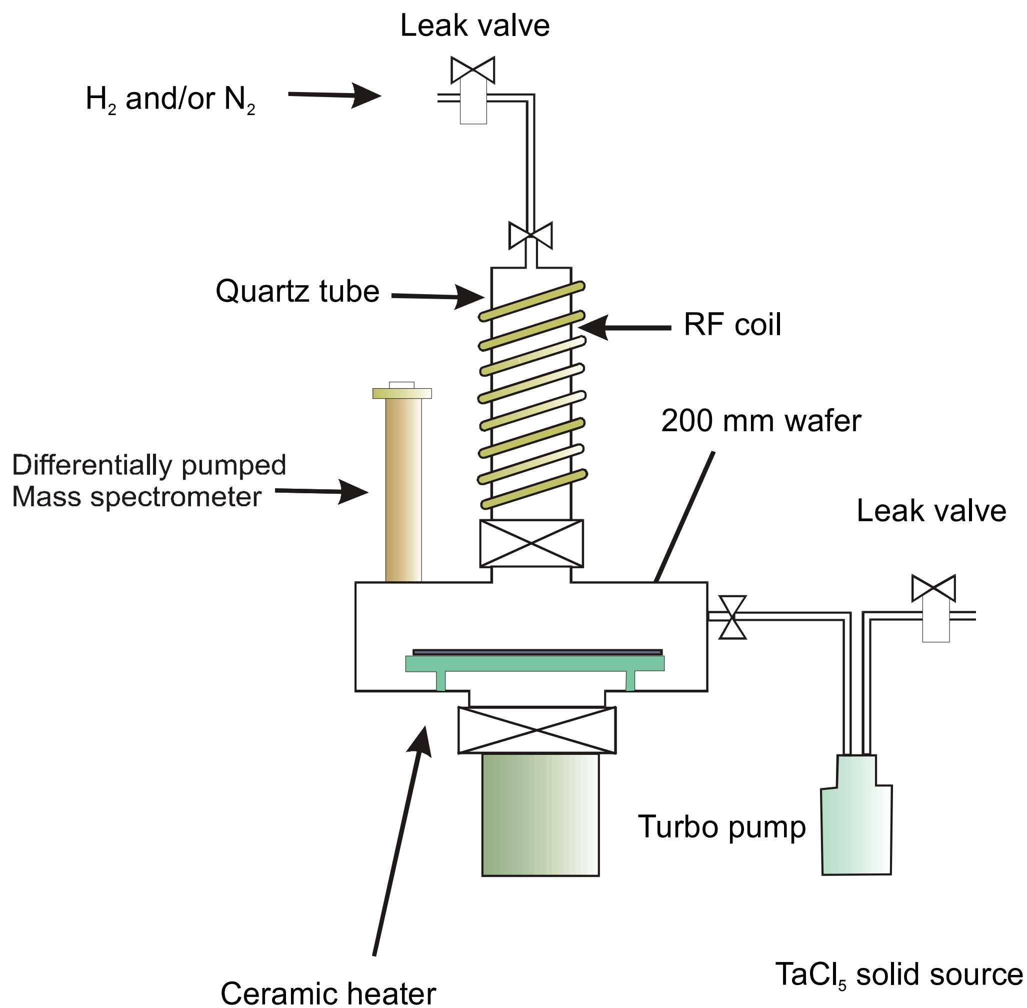
♦ TaN ALD

- Halides + NH_3 : high resistivity Ta_3N_5
- MO sources: high C content

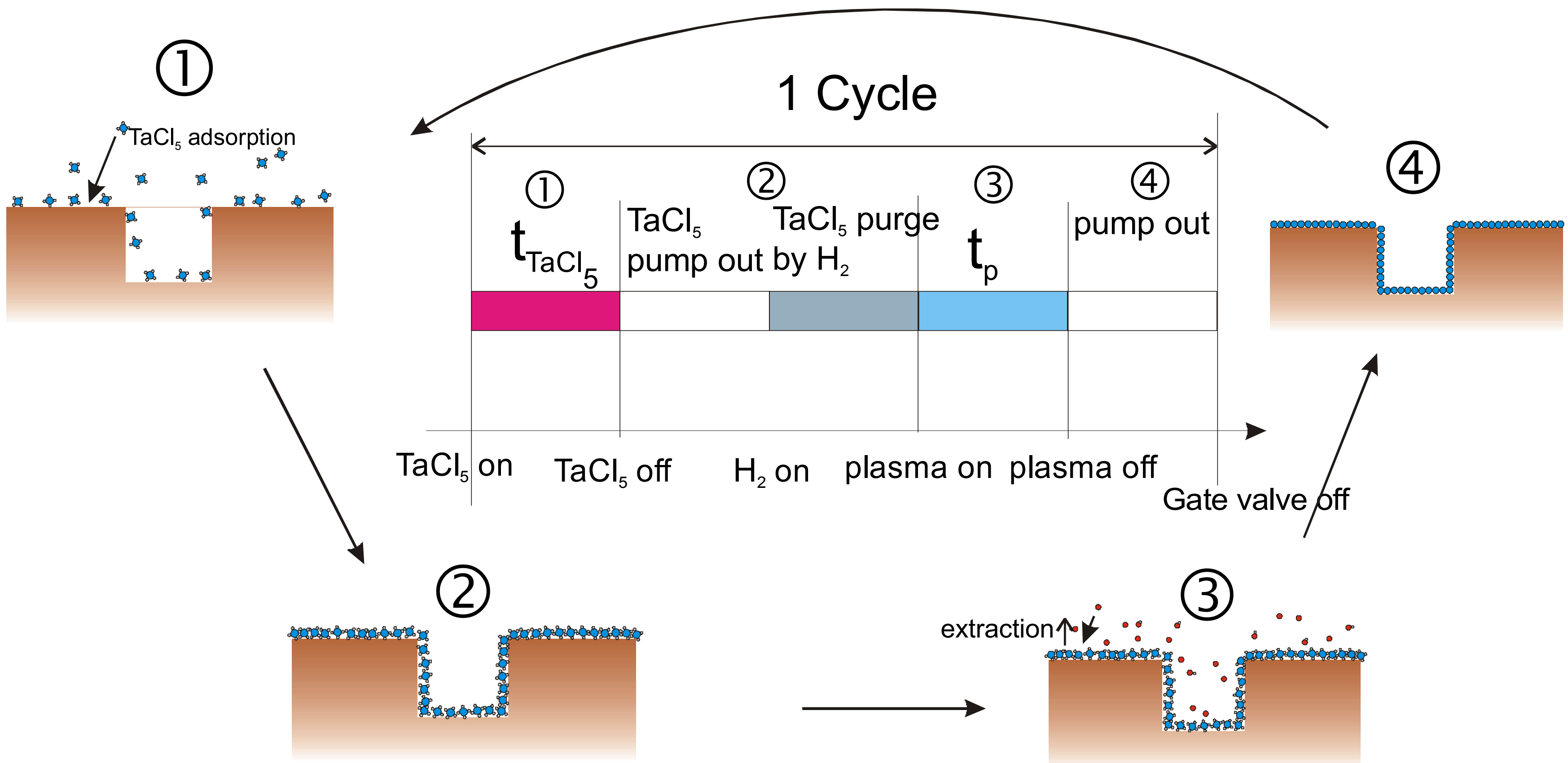
Strategy for Ta based metals/nitrides ALD



Experimental Setup for PE-ALD

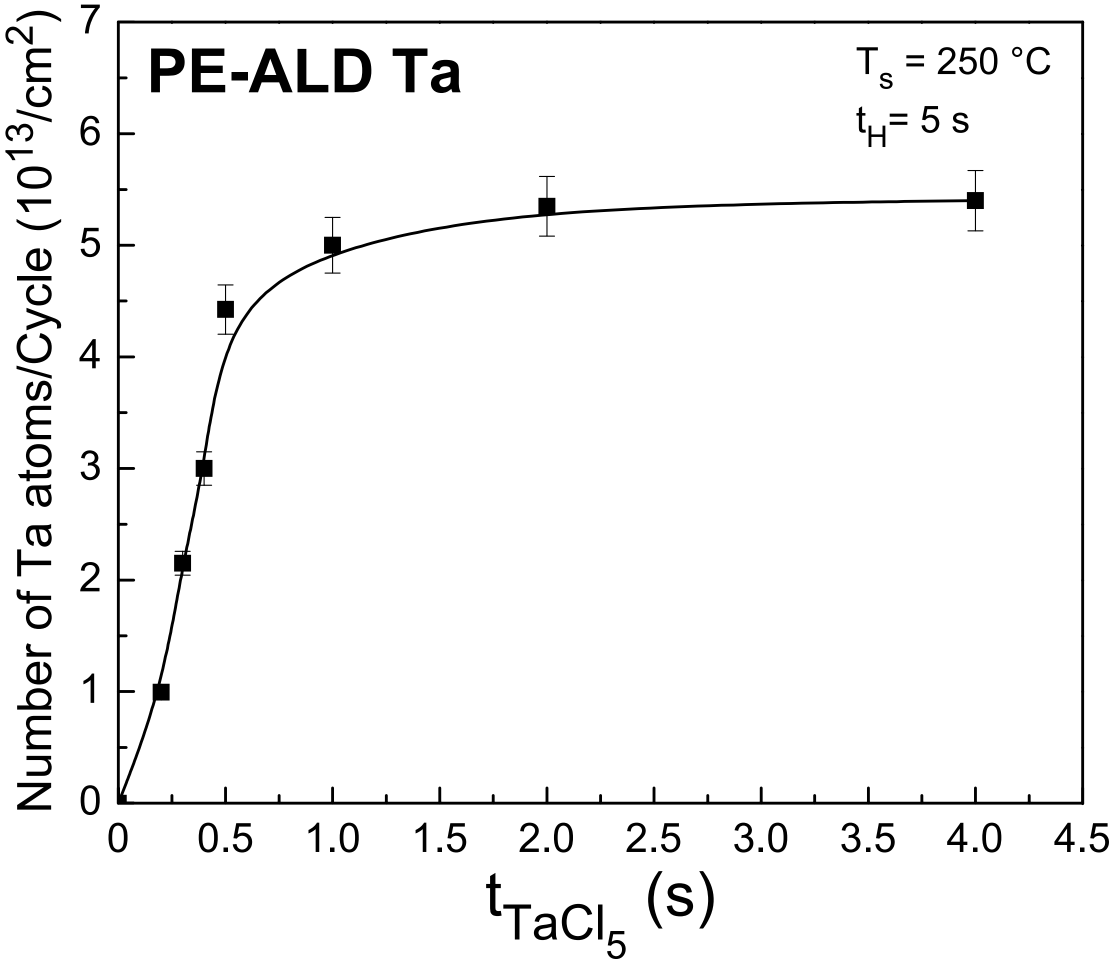


Growth Procedure



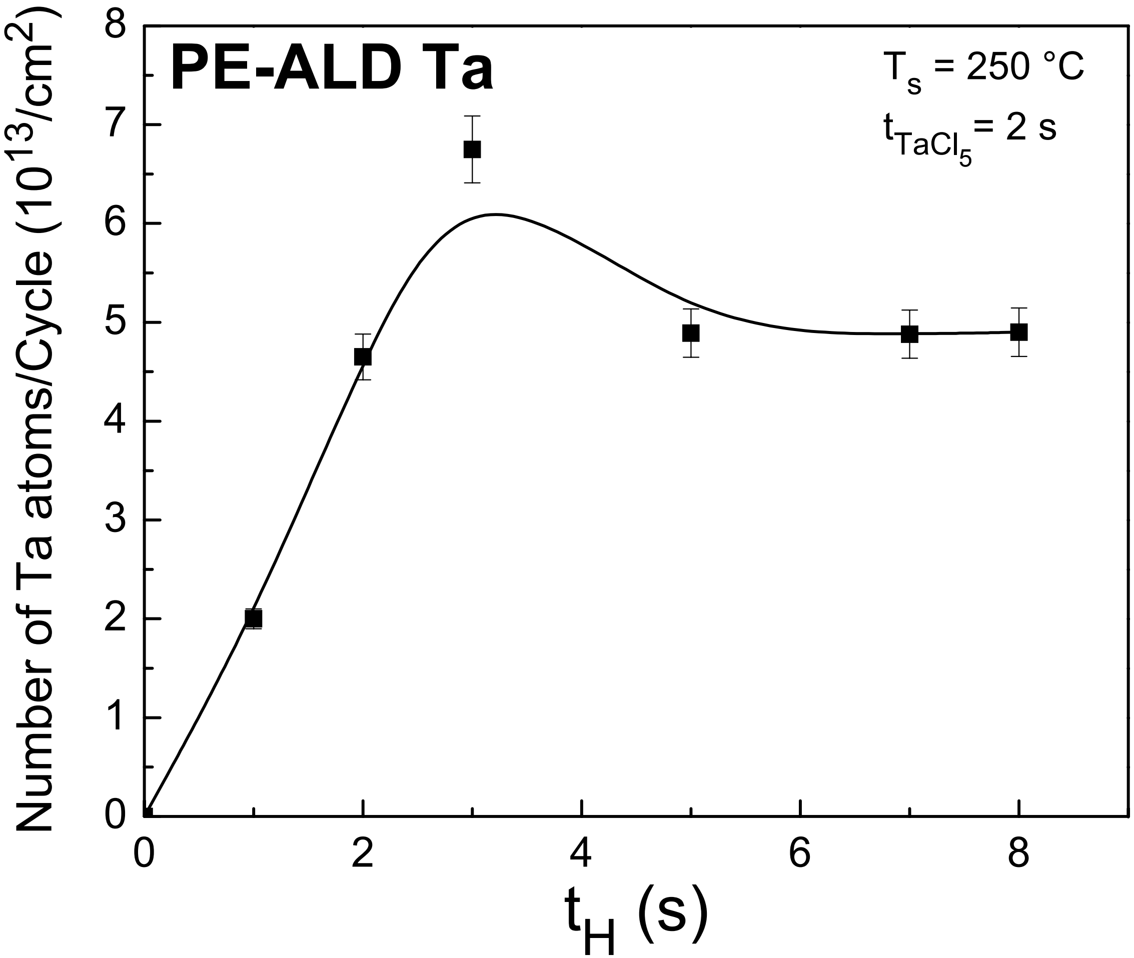
$$TaCl_5\ (a) + 5H\ (g) \rightarrow Ta(a) + 5HCl\ (g)\uparrow$$

PE-ALD Ta: Self-limited Adsorption



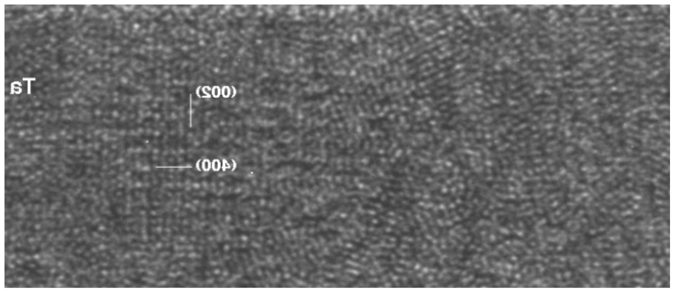
- **Saturation condition:** $t_H > 4$ s, $t_{TaCl_5} > 1$ s
- **Saturated growth rate:** 5.3x10^{13} /cm^2 (0.08 Å/cycle)

PE-ALD Ta: Plasma Exposure Time

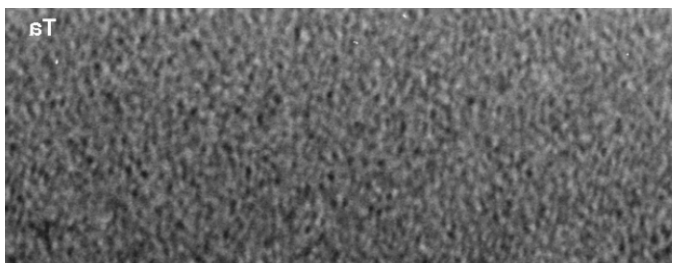


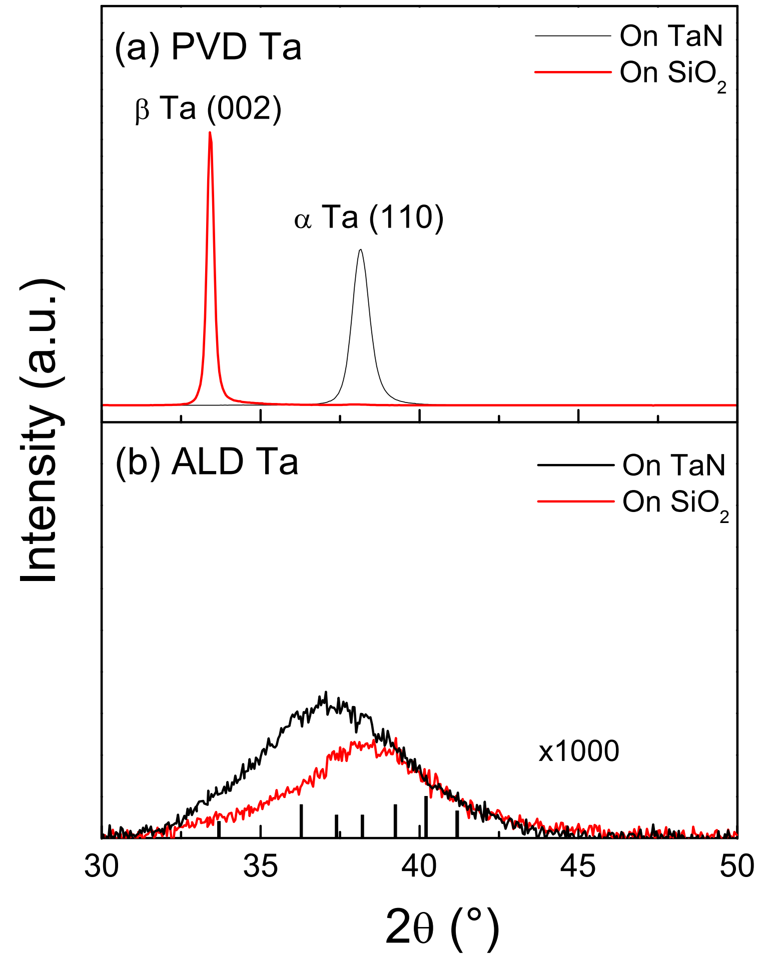
PE-ALD Ta: Microstructure

PVD Ta



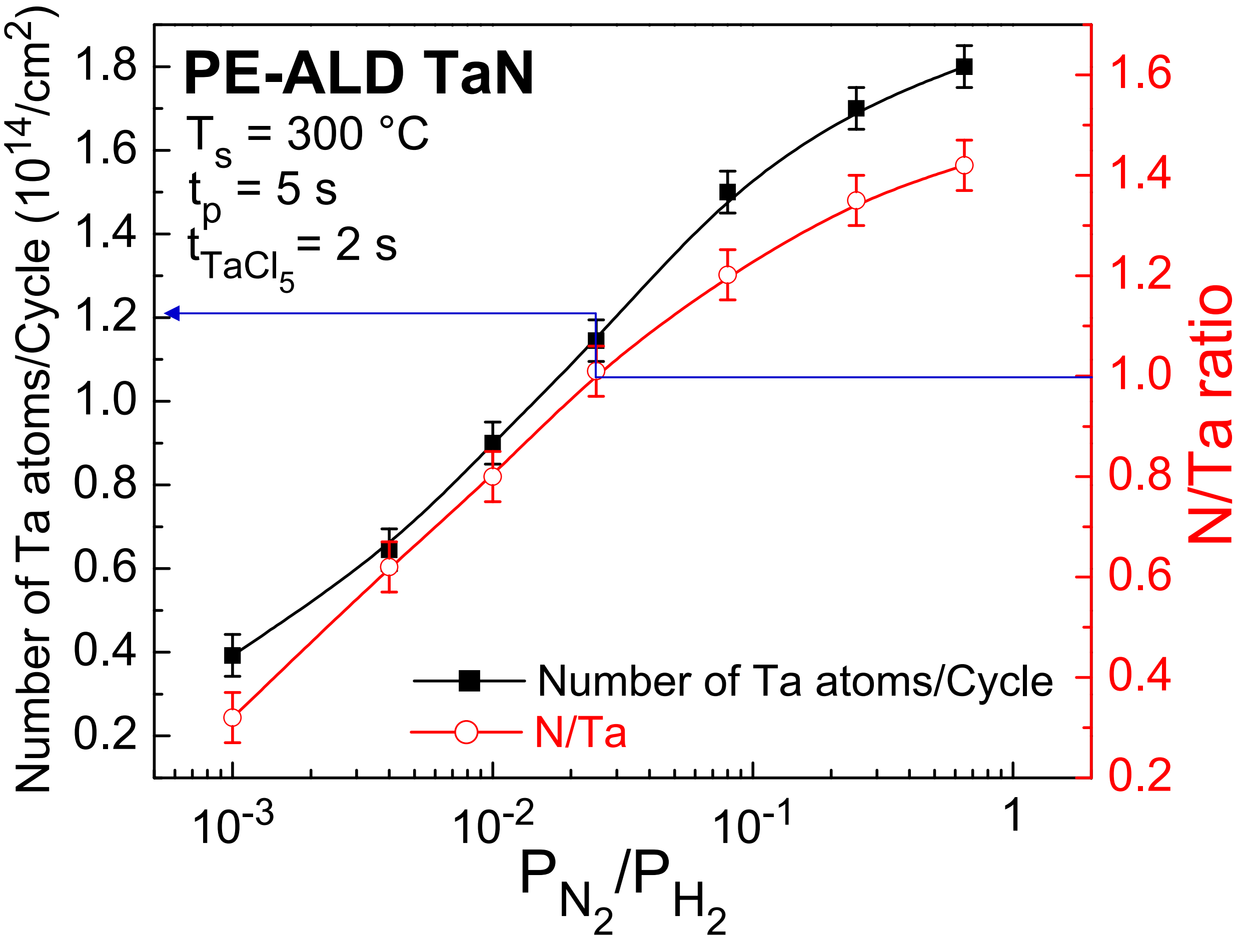
ALD Ta





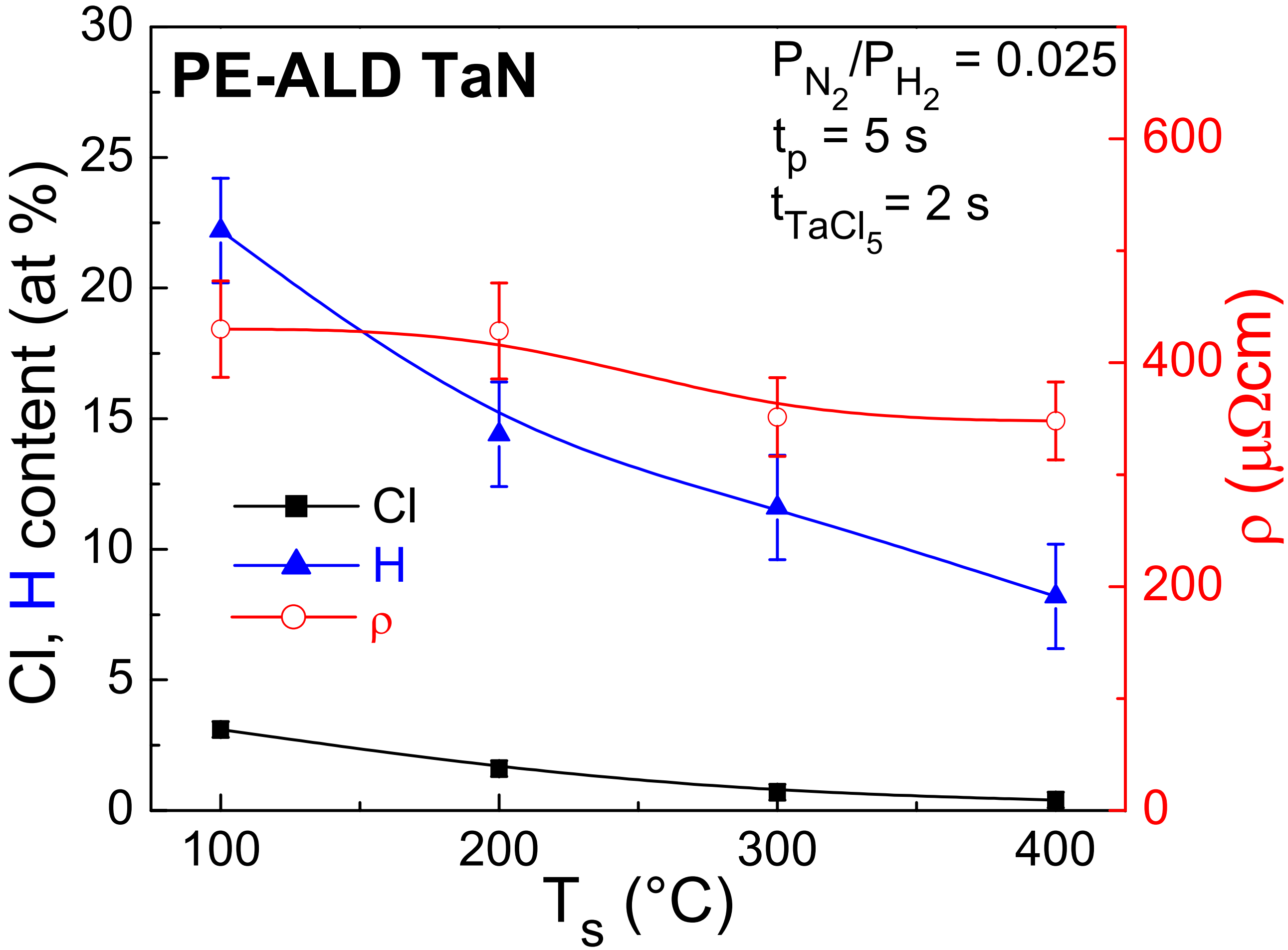
- **Resistivity:** ρ = 150-180 μΩcm → close to β-Ta phase
- **RBS:** Cl concentration = 0.5-2 at% at T_s < 300 °C

PE-ALD TaN_x : Mixture of N and H

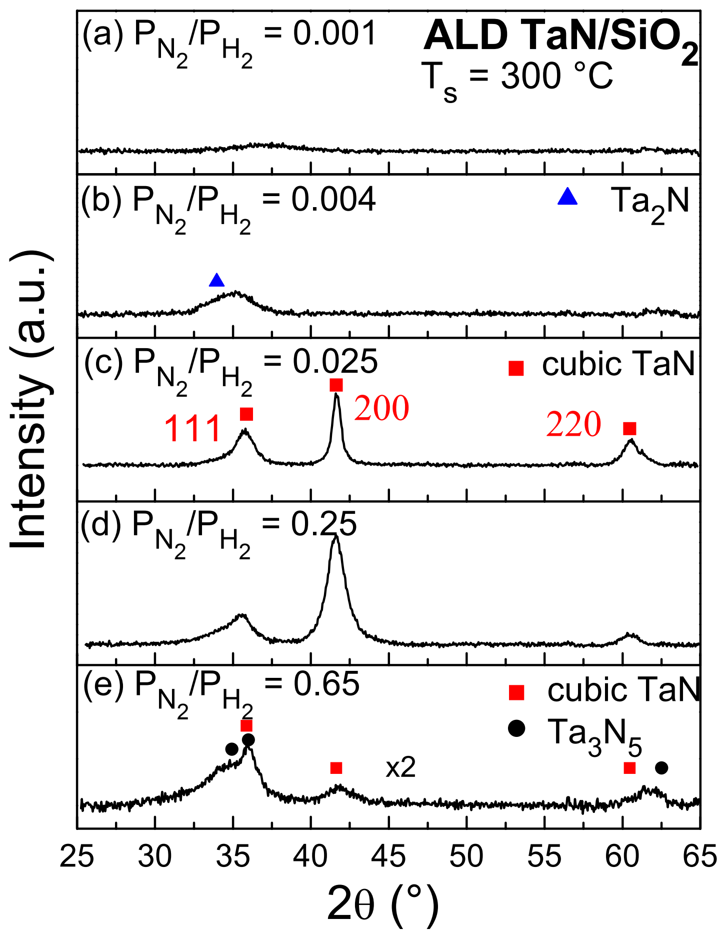


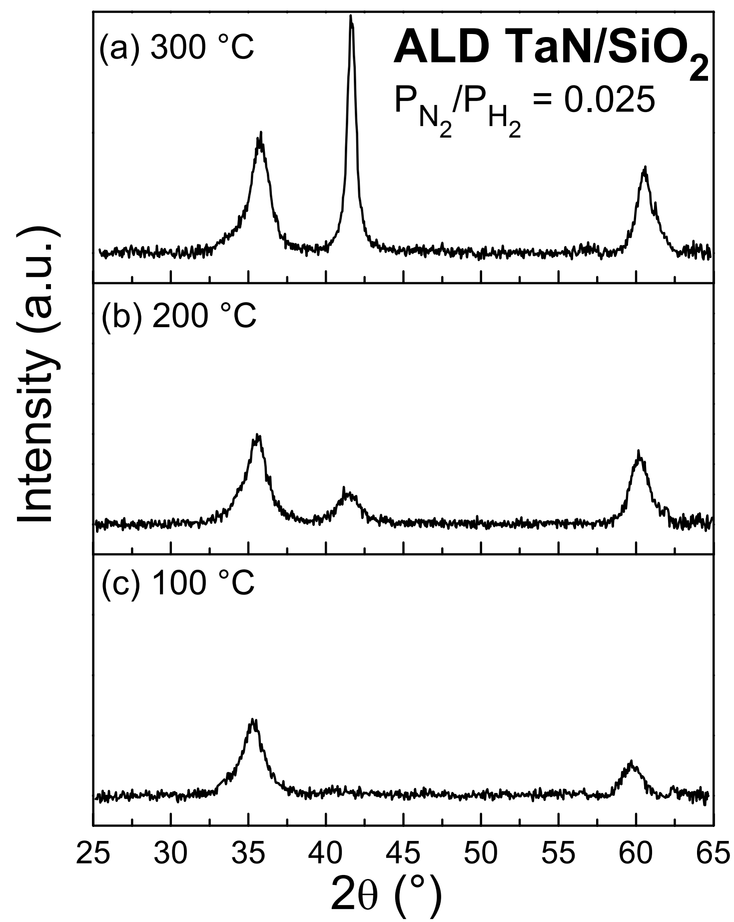
- **Growth rate (for N/Ta = 1):** 1.2×10^{14} /cm^2 (0.24 Å/cycle)
- **Easy control of N content**

PE-ALD TaN: Growth Temperature

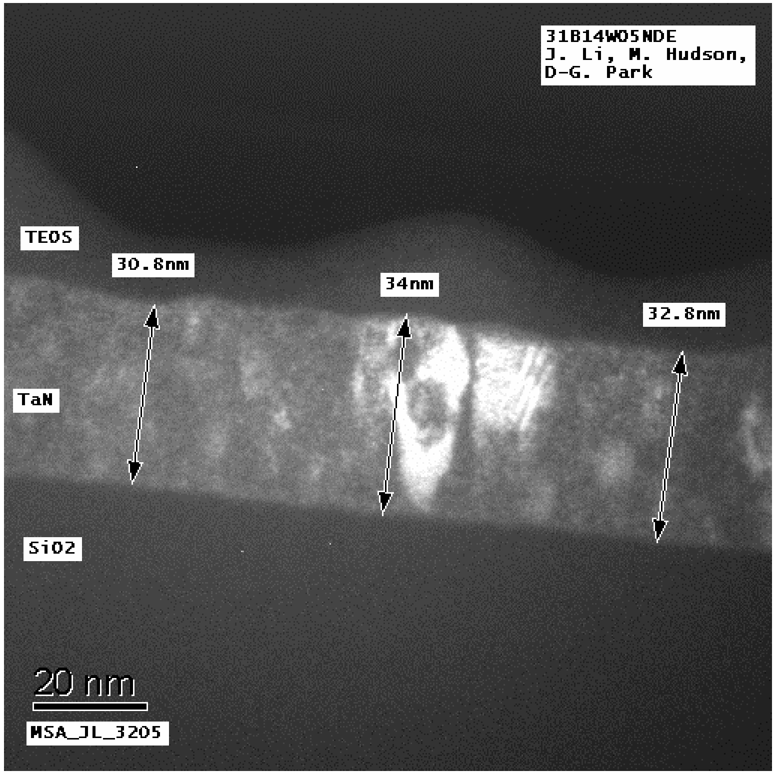


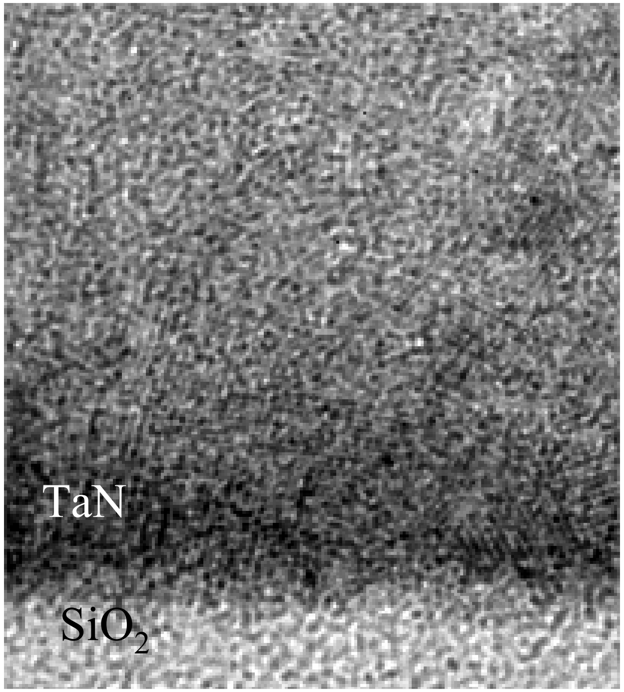
PE-ALD TaN: XRD



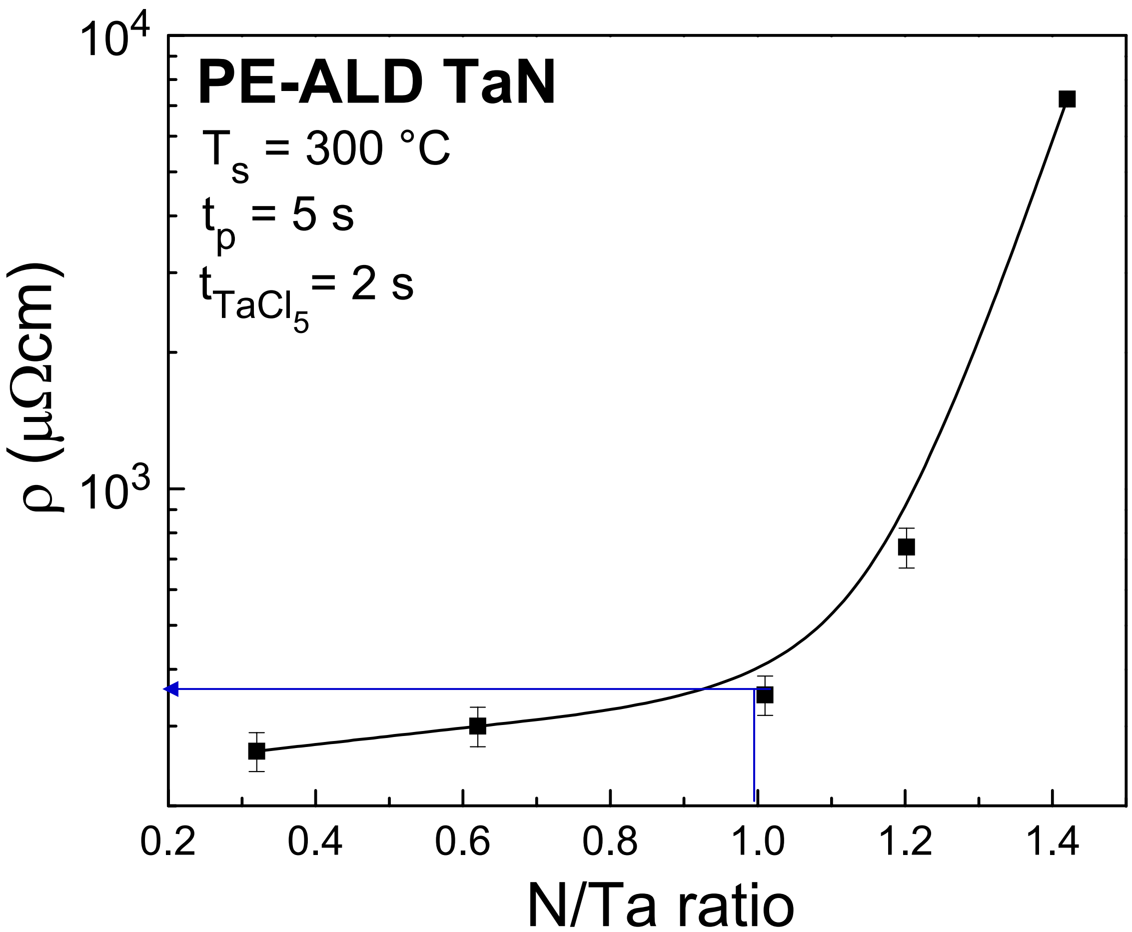


PE-ALD TaN: TEM



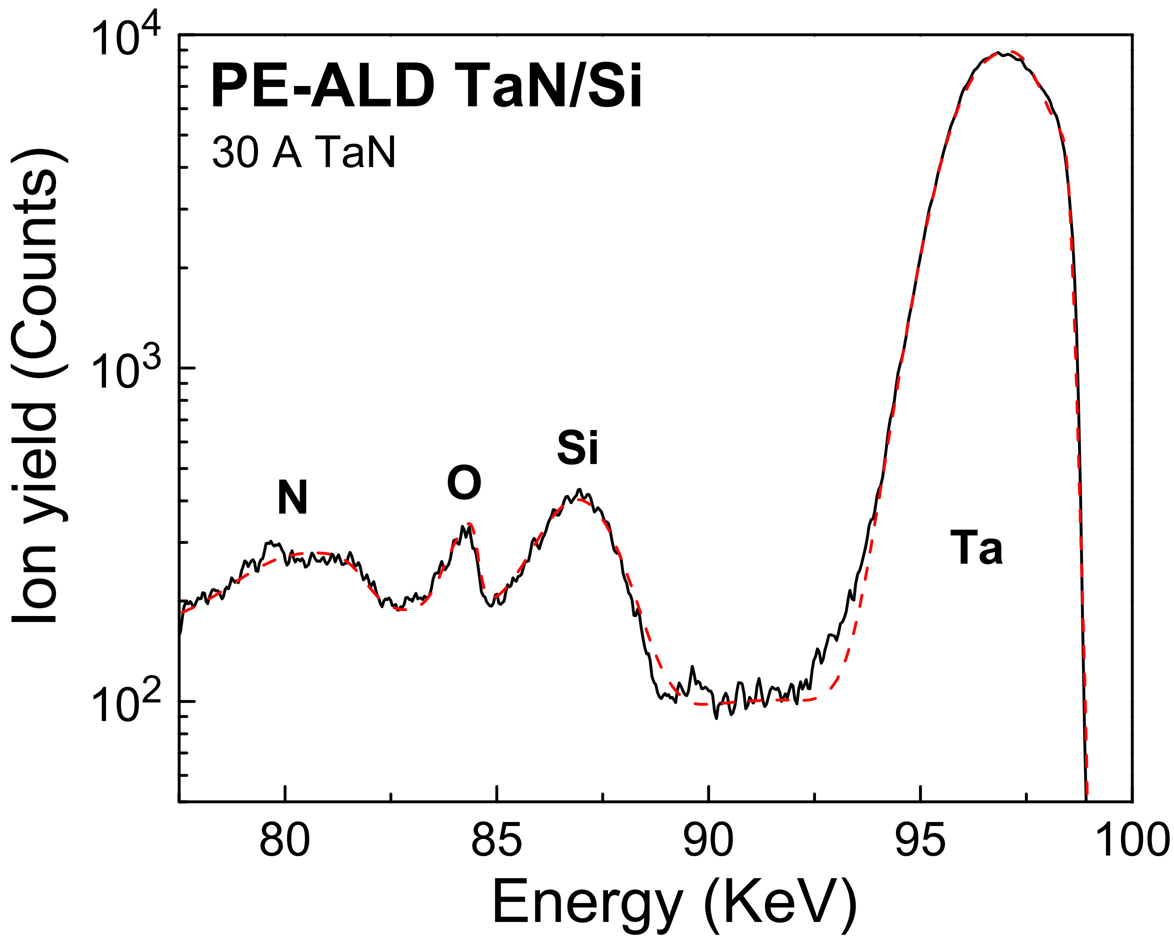


PE-ALD TaN: Resistivity



- ρ ~ 300 – 400 μΩ cm for N/Ta = 1

PE-ALD TaN: MEIS (Medium Energy Ion Spectroscopy)



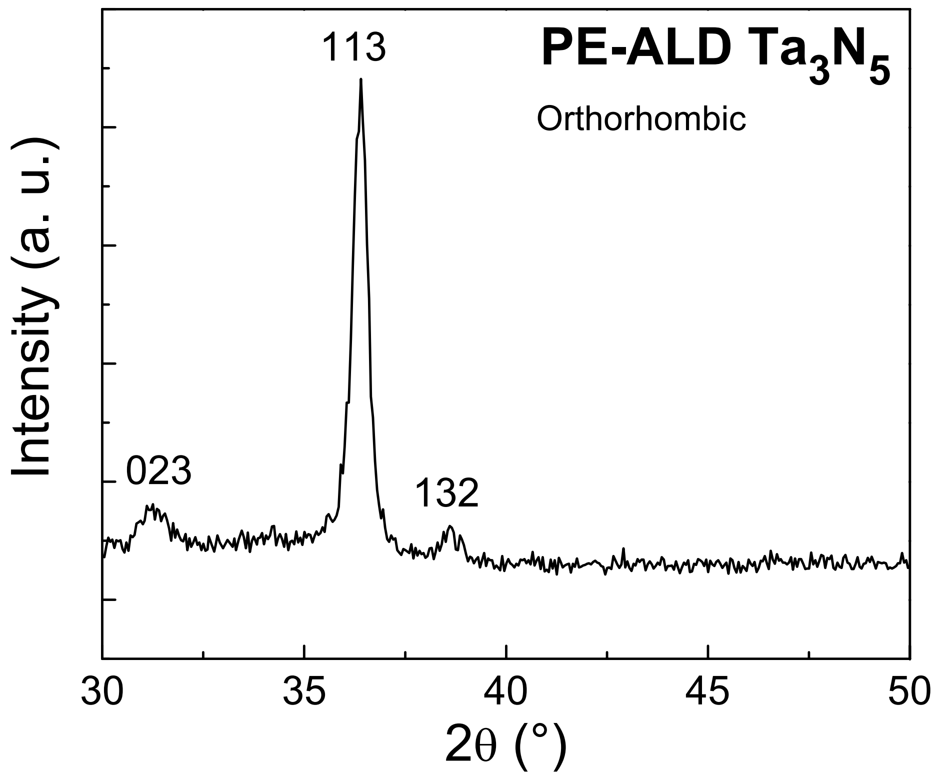
Comparison with Previously Reported ALD TaN

	Precursors	Phase	Resistivity (μΩcm)	Impurity[b] (at %)	Density (g/cm³)	Growth rate (A/cycle)	Ref.
Thermal	$TaCl_5$[a) + NH_3	Ta_3N_5	$> 10^5$	Cl < 1	-	0.24	1)
	$TaCl_5$[a) + NH_3+Zn	TaN	> 900	Cl < 4	-	0.15 – 0.2	1)
	$TaCl_5$+DMHy	Amorphous	Too high	Cl < 0.5	-	0.13 – 0.31	2)
	$TaCl_5$[a)+^{t}BuNH$_2$ (allylNH$_2$)+(NH$_3$)	TaN	> 1300	Cl > 2 C: 1 - 20	-	0.1 – 0.35	3)
	$TaCl_5$ +NH_3+TMA	Ta(Al)N(C)	> 6600	Al: 30-32 Br: 4	-	0.66 – 0.94	4)
	TBTDET+ NH_3	Amorphous	$> 10^5$	C: 15	3.6	1.1	5)
Plasma	TBTDET+H	TaN	400 - 2000	C: 15-35	7.9	0.8	5)
	$TaCl_5$ +H+N	TaN	350	Cl < 0.5	9.8	0.24	**This study**

a) Similar results for $TaBr_5$
b) Cl content at 400 °C

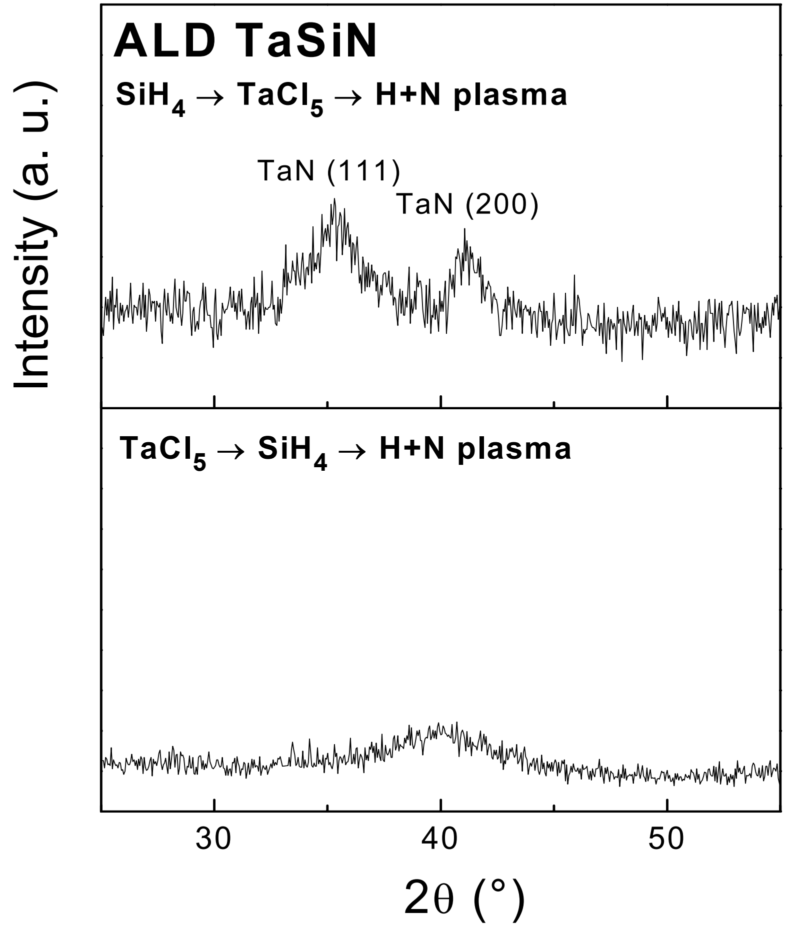
1) M. Ritala, P. Kalsi, D. Riihelä, K. Kukli, M. Leskelä, and J. Jokinen, Chem. Mater. **11**, 1712 (1999).
2) M. Juppo, M. Ritala, and M. Leskela, J. Electrochem. Soc. **147**, 337 (2000).
3) P, Alén, M. Juppo, M. Ritala, M. Leskelä, T. Sajavaara, and J. Keinonen, J. Mater. Res. 17, 107 (2002).
4) P, Alén, M. Juppo, M. Ritala, T. Sajavaara, J. Keinonen, and M. Leskelä, J. Electrochem. Soc. **148**, G566 (2001).
5) J.-S. Park, H.-S. Park, and S.-W. Kang, J. Electrochem. Soc. **149**, C28 (2002).

PE-ALD TaN_x : With nitrogen plasma



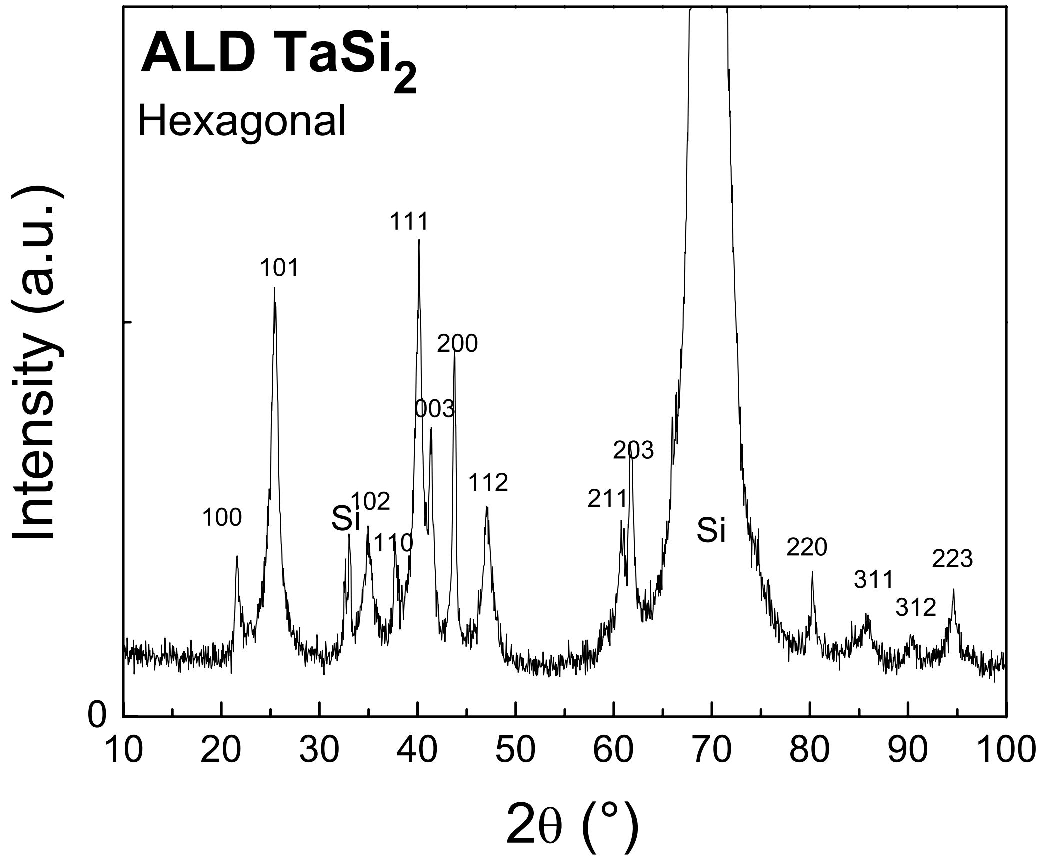
- N/Ta = 1.3, $\rho = 10^5$ $\mu\Omega$ cm: high resistivity Ta_3N_5 phase
- Low Cl (< 1%)

PE-ALD TaSiN



- Use SiH_4 as Si source
- a: SiH_4 → $TaCl_5$ → H+N plasma
  - High resistivity, polycrystalline
  - Ta (15%) N(45%) Si(40 %)
- b: $TaCl_5$ → SiH_4 → H+N plasma
  - Low resistivity, amorphous film
  - Ta (20%) N(25%) Si(55 %)

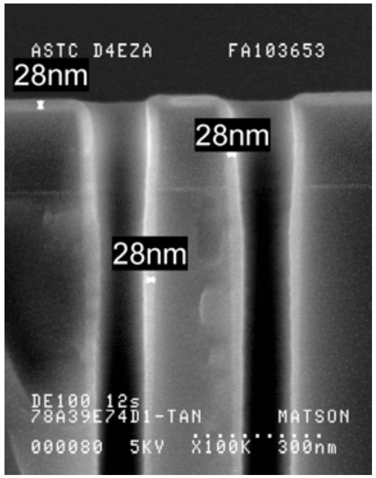
Thermal ALD $TaSi_2$

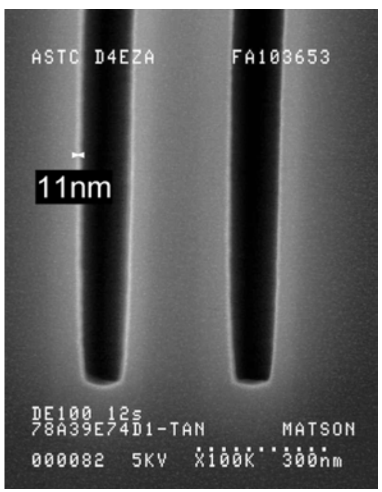


- Growth without plasma :$TaCl_5 + SiH_4$
- RBS: Ta/Si = 0.5, Cl < 1%, no H

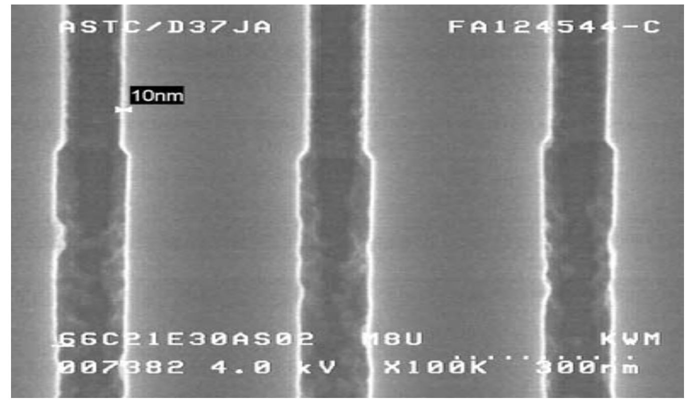
Conformality

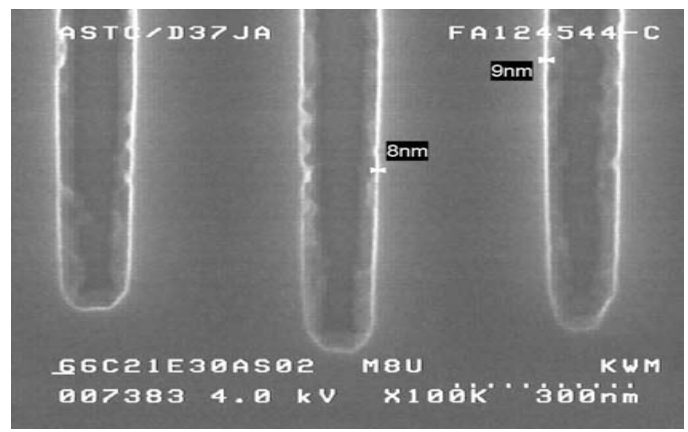
Ta



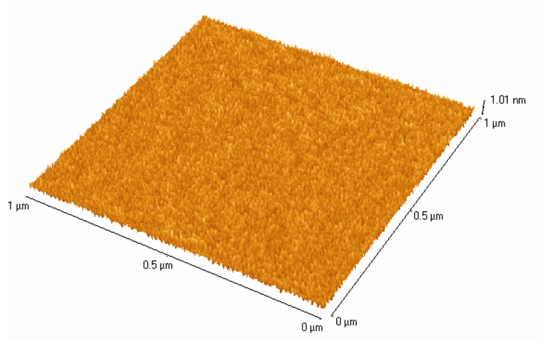
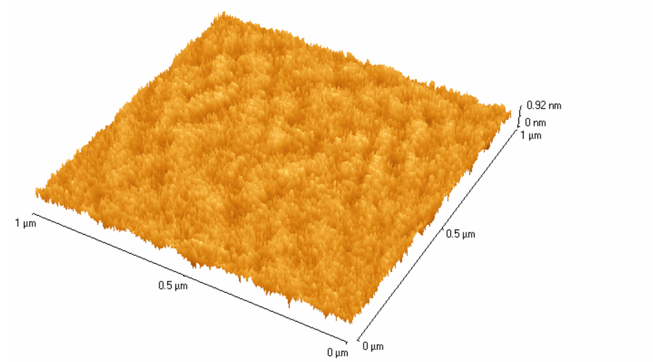
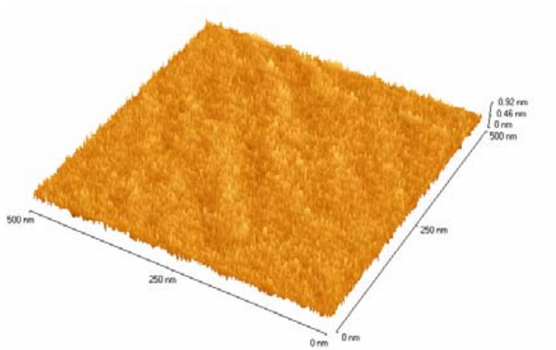
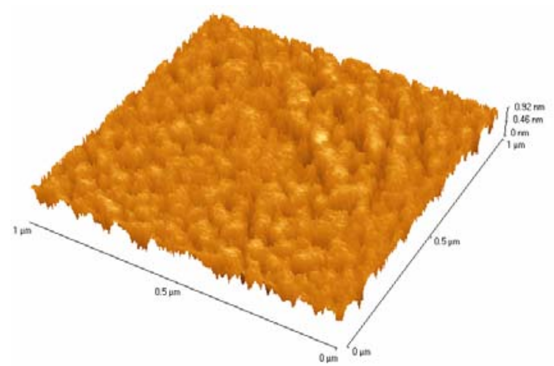


TaN

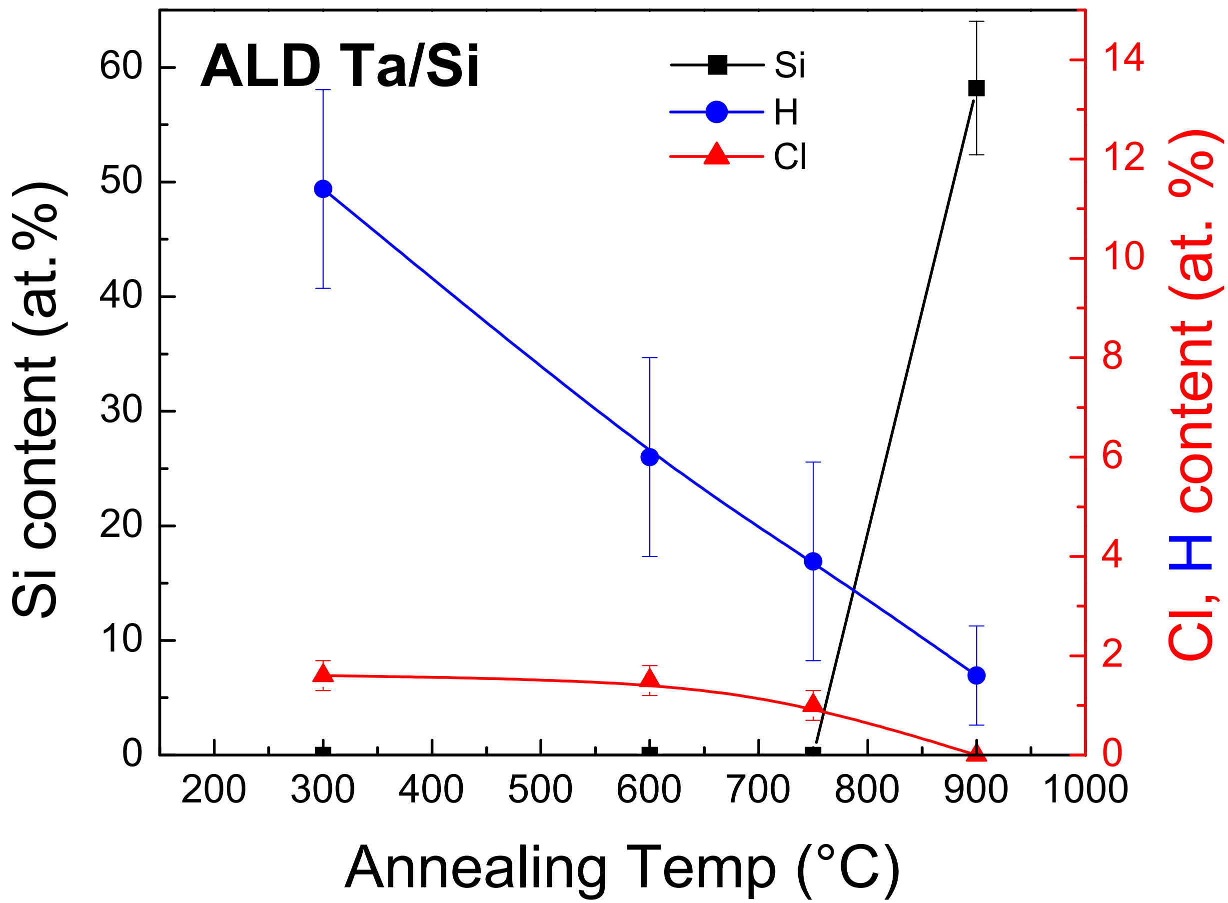




Morphology

	Ta	TaN
200 cycles	 RMS: 0.123 nm	 RMS: 0.153 nm
1600 cycles	 RMS: 0.106 nm	 RMS: 0.206 nm

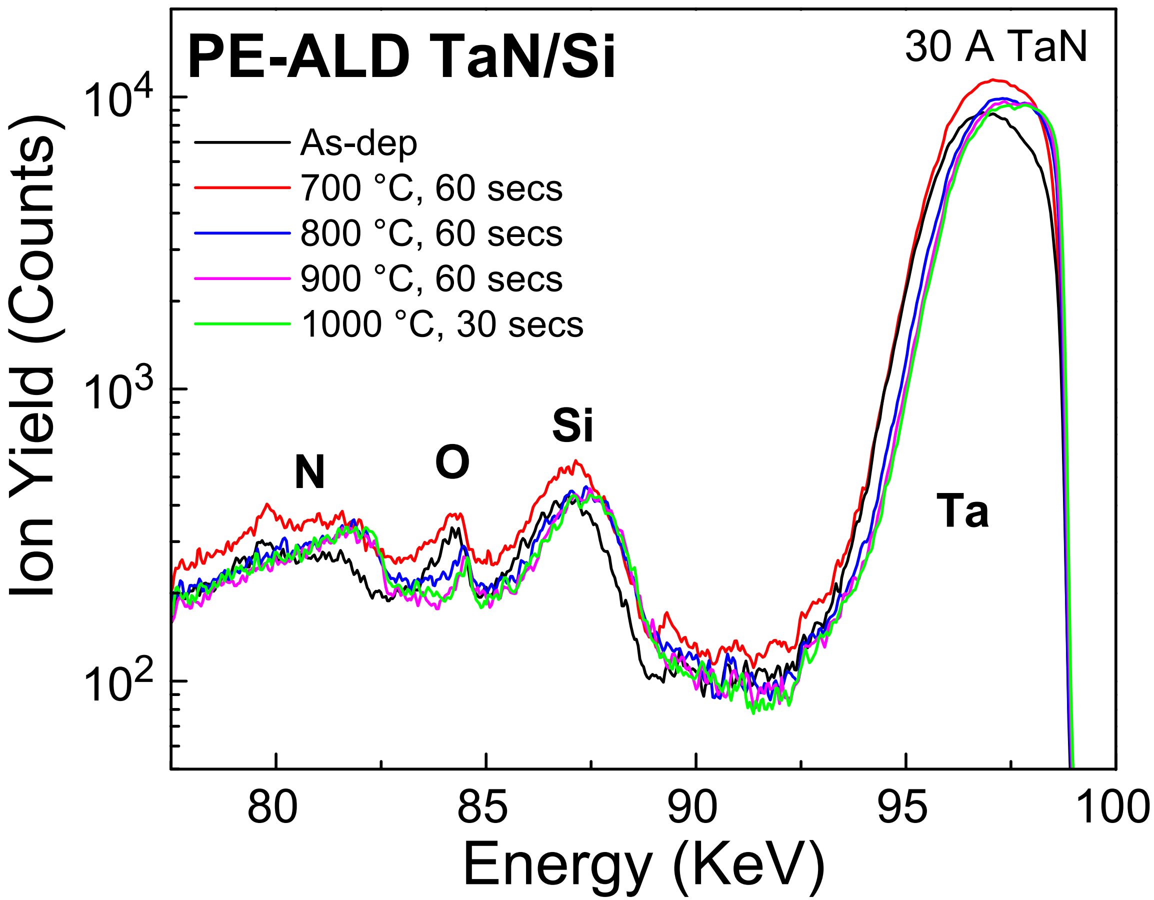
Thermal Stability: PE-ALD Ta



- 30 minutes annealing in He.
- PVD Ta reacts with Si at 700 °C.[Ref]

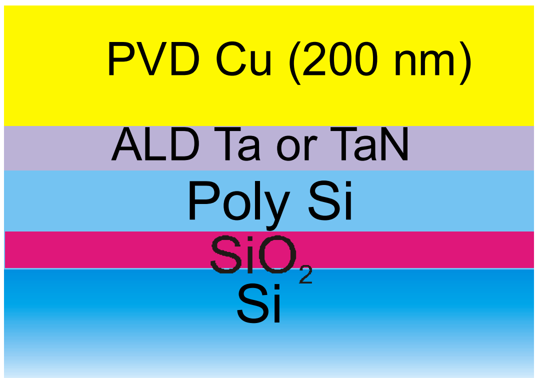
Ref) K. Holloway, P.M. Fryer, C. Cabral, Jr. J.M.E. Harper, P.J. Bailey, KH. Kellerher, JAP **71**, 5433 (1992)

Thermal Stability: PE-ALD TaN



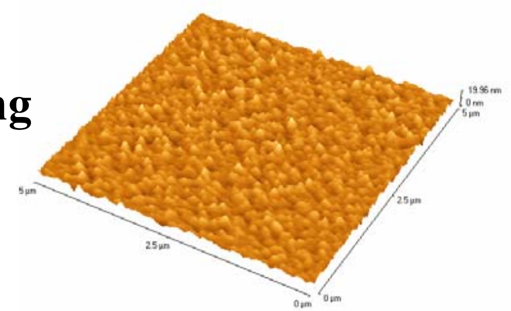
- Surface O reduced by annealing. (3Å thick after 900 °C)

Cu Diffusion Barrier Property Test Structures



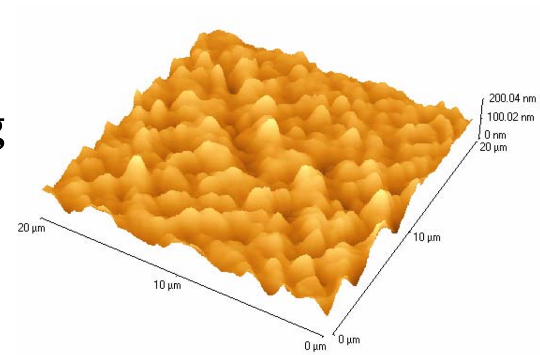
Cu/Ta/Poly Si

Before annealing



RMS: 2.126 nm

After annealing

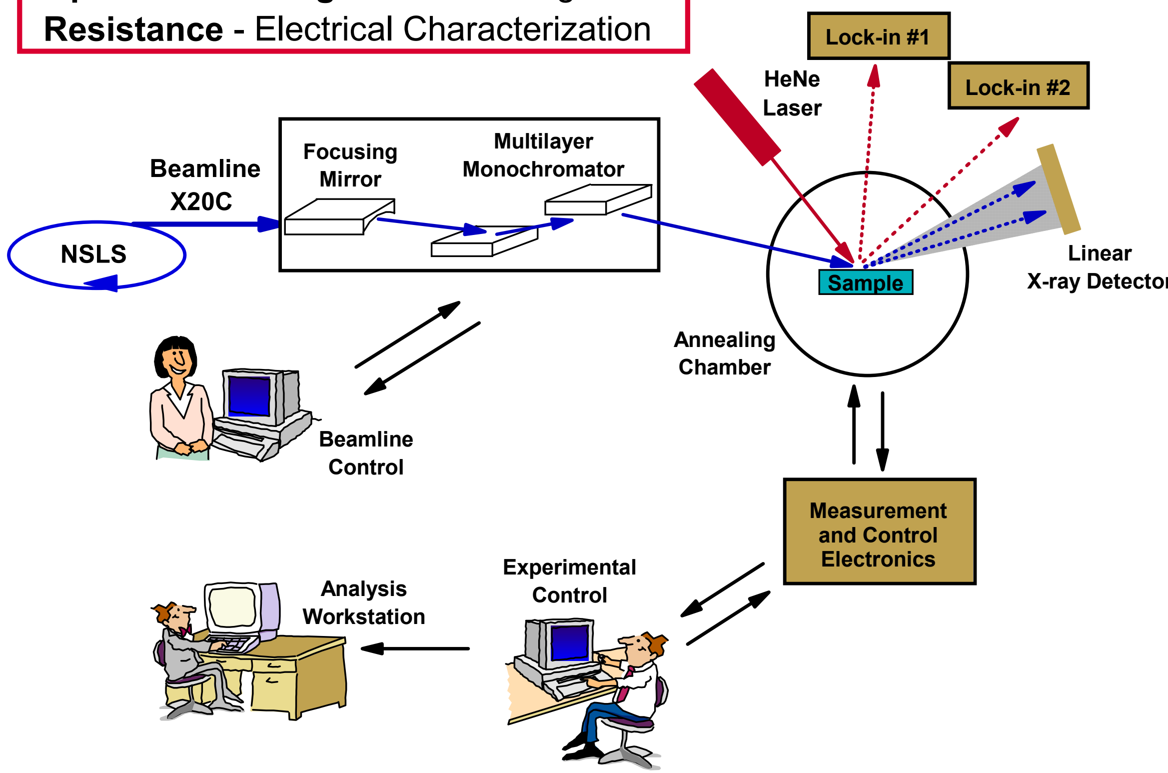


RMS: 23.51 nm

- Roughness, resistivity, phase change

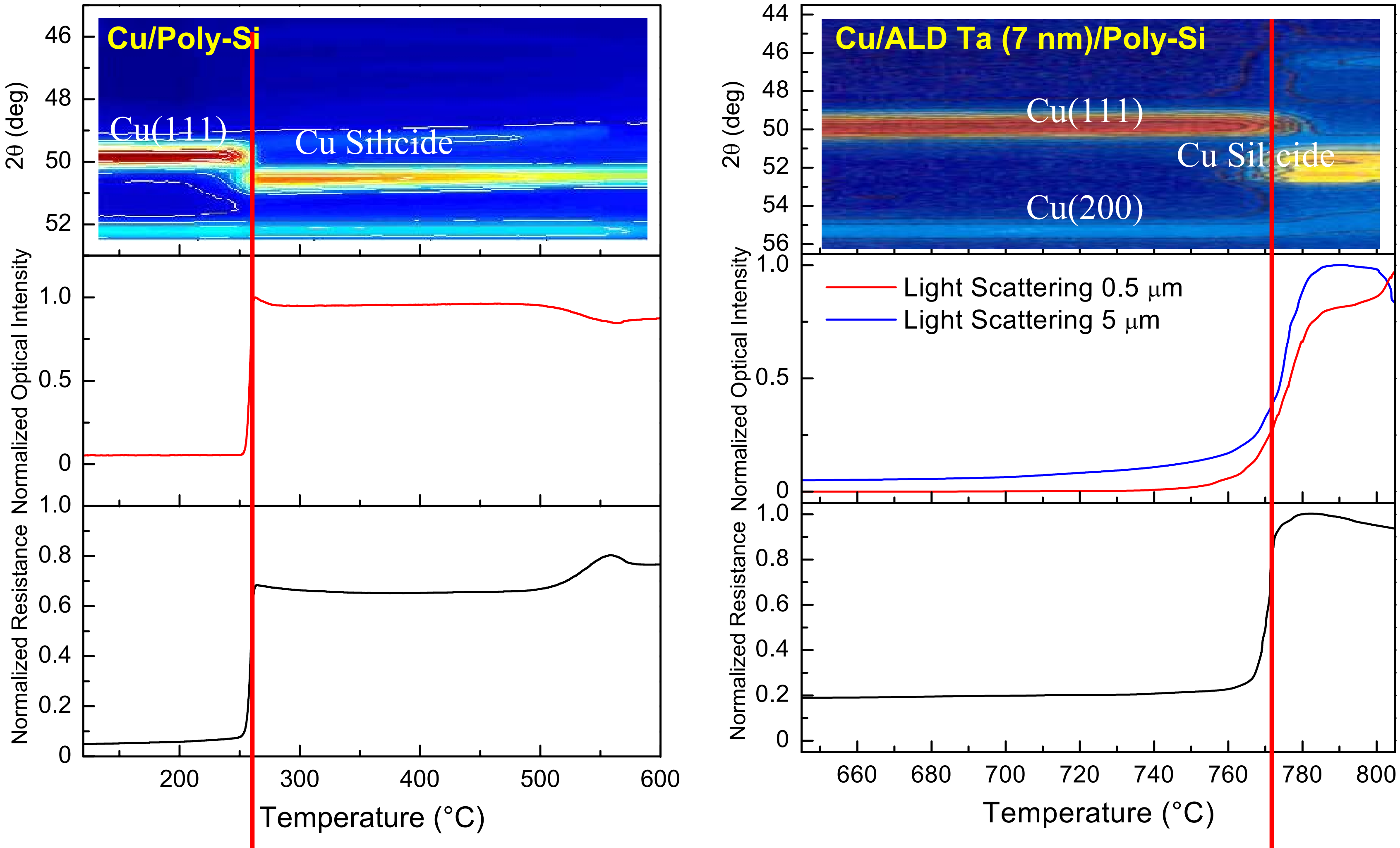
In Situ Characterization During Rapid Thermal Annealing

X-Ray Diffraction - Phase Formation
Optical Scattering - Surface Roughness
Resistance - Electrical Characterization



- At National Synchrotron Light Source, Brookhaven National Laboratory.
- 3 °C/s in He, from 100 to 1000 °C.
- Similar system without XRD for routine measurements

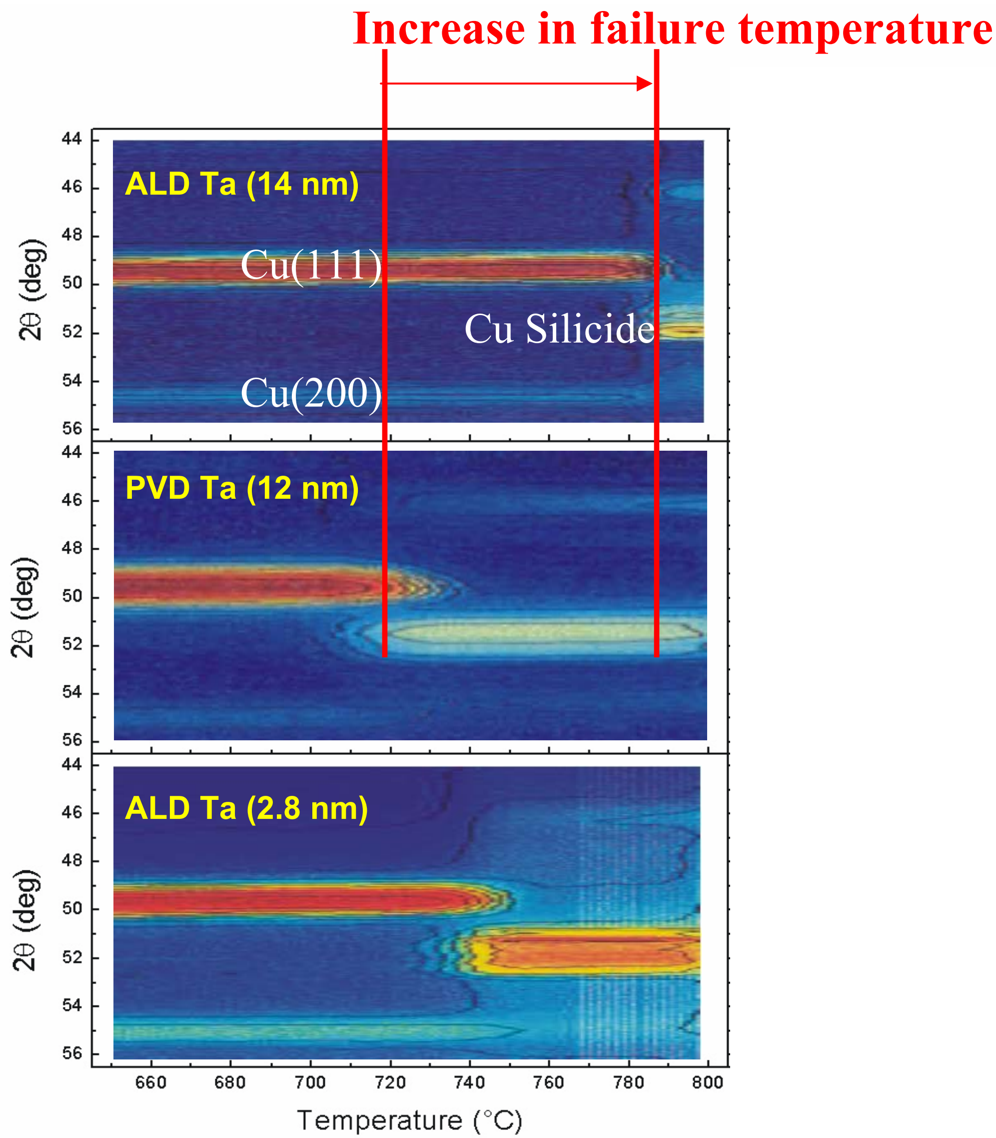
PE-ALD Ta: Diffusion Barrier Failure Temperature



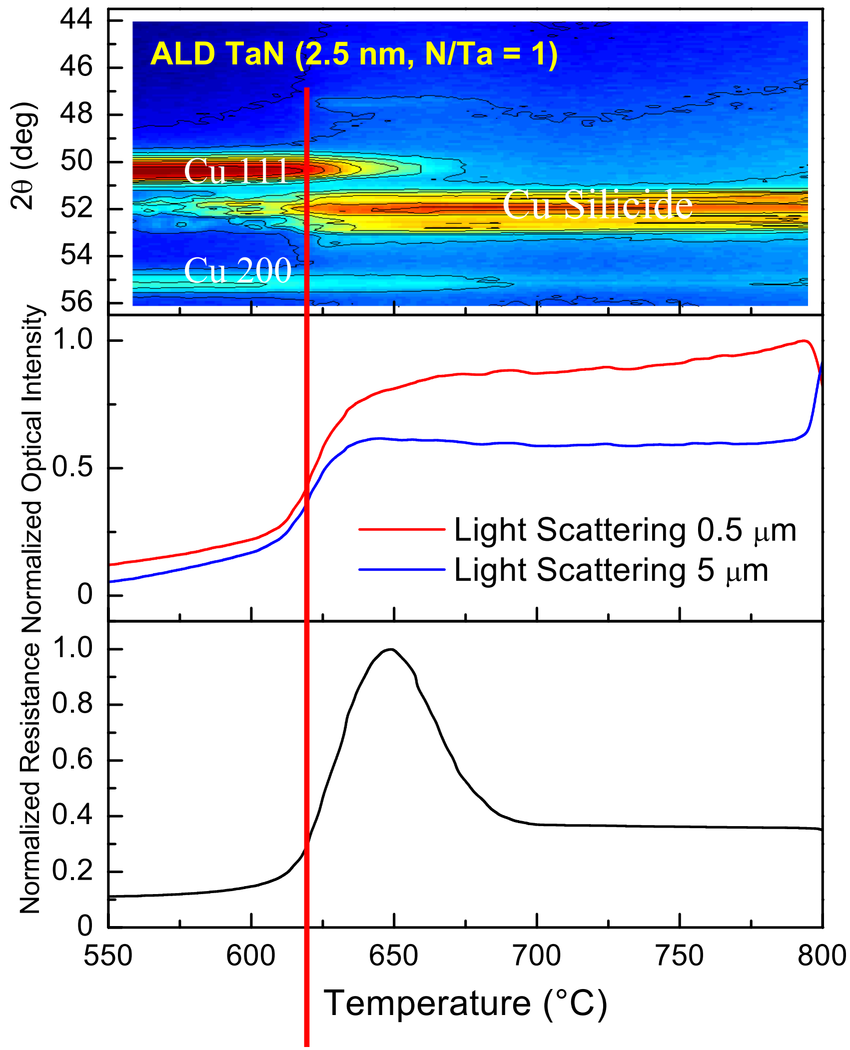
Cu silicide formation: 260 °C

Cu silicide formation: 773 °C

PE-ALD Ta: Comparison with PVD Ta

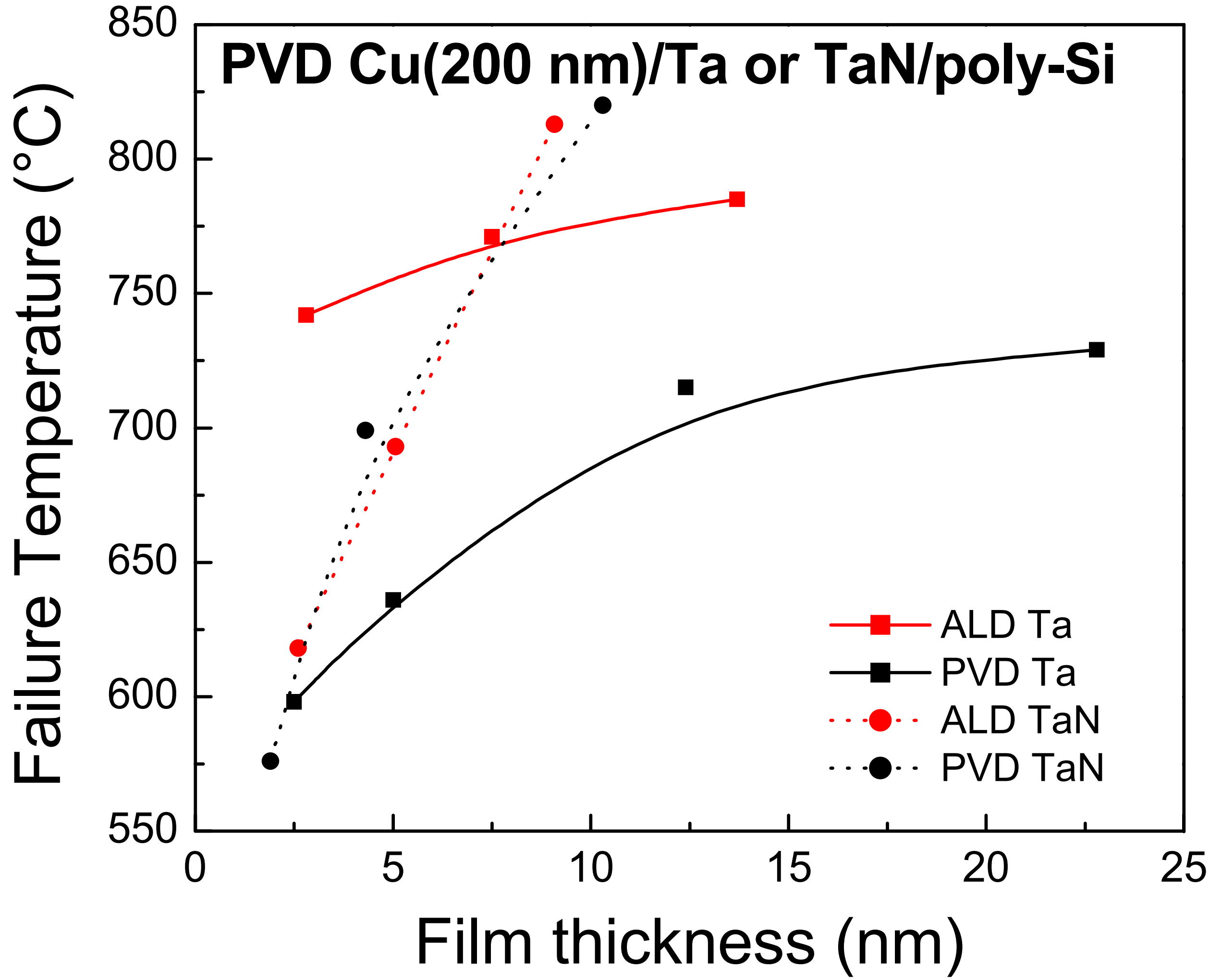


PE-ALD TaN: Diffusion Barrier Failure Temperature

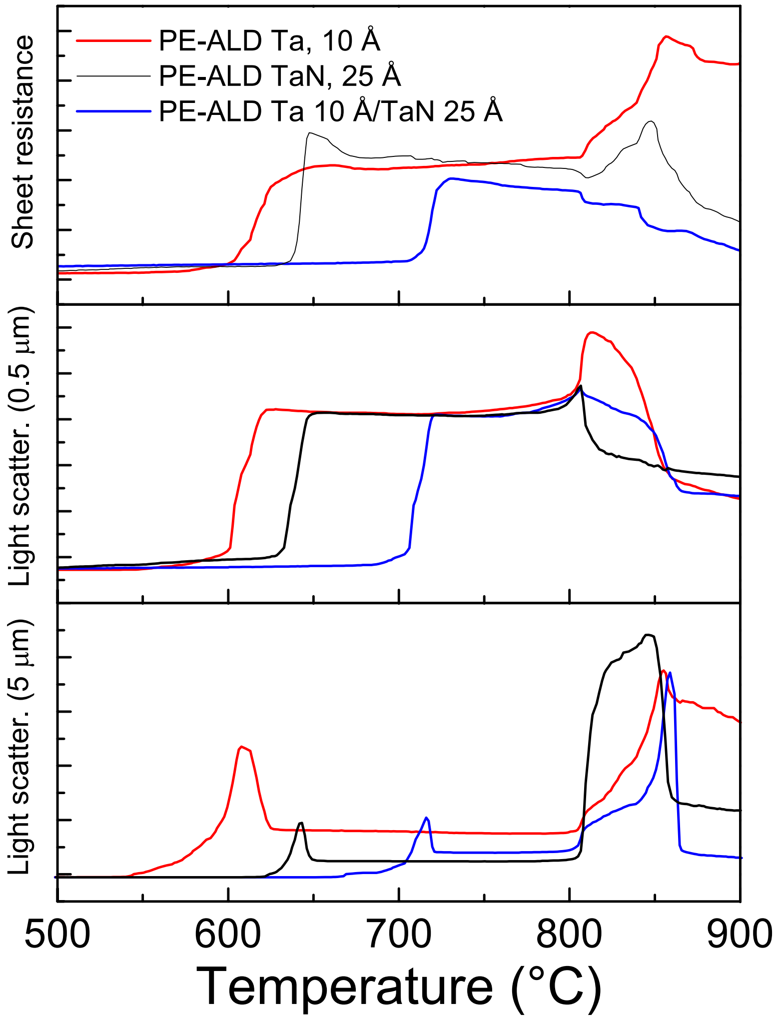


Cu silicide formation: 620 °C

PE-ALD Ta and TaN: Diffusion Barrier Failure Temperature



PE-ALD Ta/TaN Bilayer Cu Diffusion Barrier



- Bilayer deposition by switching off nitrogen flow

Metal Gate for CMOS

- **Problems with poly-Si gate**
  - Gate depletion at inversion: increase in t_{eq}
  - High gate resistance
  - Reaction with high k
  - Boron Penetration

→ **Metal gate**

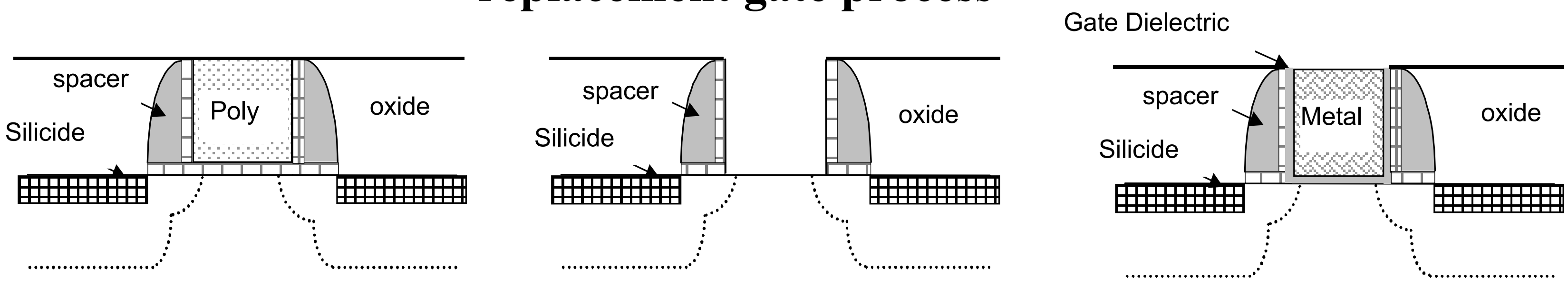
- **Requirements**
  - Workfunction : ❾ 0.2eV from E_c(n-FET) or E_v(p-FET)
    - nFET : Ta, Ti, TaN, TaSiN…
    - pFET: Ru, Pt…
  - Thermal & chemical stability with gate oxide
  - Low resistivity

Deposition Technique of Metal Gate

- Little damage to gate oxide
- Low temperature deposition with low impurity to avoid reaction with gate oxide
- Conformality at nanoscale structure

→ **ALD of metal gate**

replacement gate process[Ref)]



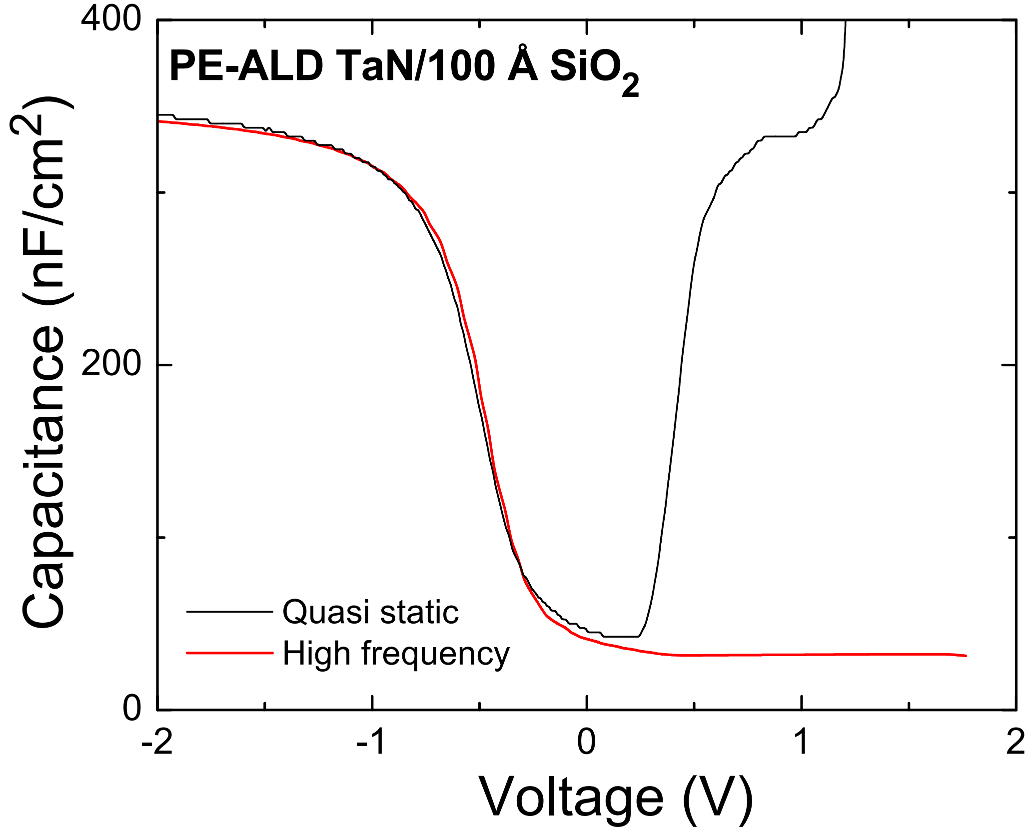
a. Conventional Device Fabrication and oxide CMP

b. Remove Sacrificial Gate Stack

c. Deposit New Gate Stack and CMP patter gate

Ref) A. Chaterjee et al, IEDM Tech. Digest, 821 (1997)

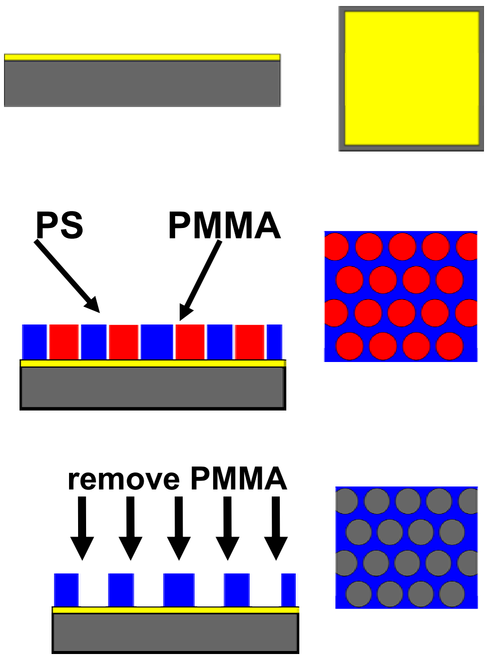
PE-ALD TaN as Metal Gate



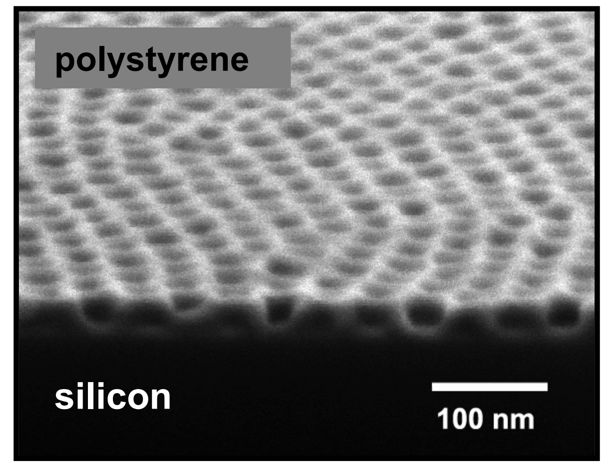
- **Capacitor structure:** PE-ALD TaN/100 Å SiO_2
- Work function: 4.4 ± 0.1 eV
- Little change in t_{ox} up to 1000 °C RTA

Nanoscale Device Fabrication

- **Self-assembling diblock copolymer process**
  - Alternative to photoresists for nanoscale dimensions



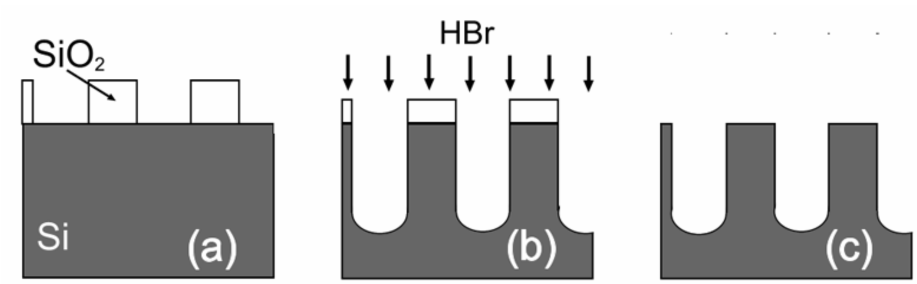
1. surface pretreatment
2. spin diblock copolymer and bake
3. liquid develop

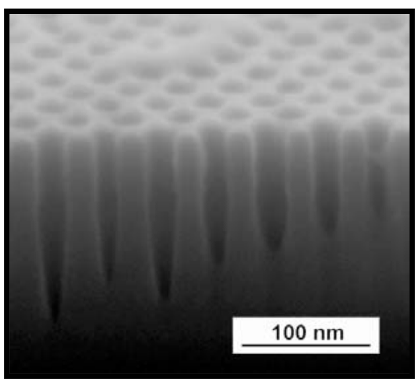


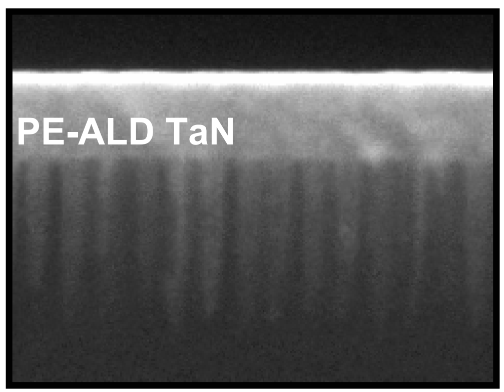
K.W. Guarini, C. T. Black, Y. Zhang, H. Kim, and I. V. Babich, 2002 3-Beams Conference, Anaheim, CA

PE-ALD TaN Electrode

- **Pattern transfer to Si substrate:** enhanced surface area
- **Fabrication of capacitor with high storage capacity**







aspect ratio	capacitance increase
0.5:1	9%
1:1	98%
5:1	570%
10:1	1159%

20 nm pores, 42 nm spacing
4 nm oxide thickness

Conclusions

- Successful growth of Ta based metals/nitrides at low T_s by ALD using chloride precursor and plasma.
- Ta and TaN PE-ALD processes as a function of key growth parameters
- Analysis of PE-ALD Ta and TaN thin film properties
- Applications of PE-ALD Ta based metals/nitrides in modern semiconductor devices processing

Collaborators

- Andrew Kellock
- Cyril Cabral, Jr.
- Christian Lavoie
- Christophe Detavernier
- Dae-Gyu Park
- James Harper
- Kathryn Guarini
- Matt Copel
- Michael Lane
- Mike Gribelyuk
- Roy Carruthers
- Vijay Narayanan

Evaluation for Cu liners(ref)

Table I. Evaluation factors for Cu liners.

attribute↓	Cr	TiN	TiN/Ti	Ti/TiN	TiN/Ta	TaN	β-Ta	TaN/Ta	TaSiN	WNx
Cu barrier	X	✓	✓	✓	✓	✓	✓	✓	✓	✓
Adhesion to ILD	✓	✓	✓	✓	✓	✓	X	✓	✓	✓
Cu on liner adh.	✓	X	✓	X	✓	X	✓	✓	X	?/X
Liner on Cu adh.	✓	?	?	✓	?	✓	✓	✓	✓	?
Low in-plane R	✓	X	✓	✓	?	X	X	✓	X	X
Cu poisoning	✓	✓	X	✓	✓	✓	✓	✓	?	✓
CMP	?	X	X	X	X/✓	✓	✓	✓	✓	?
Single chamber	✓	✓	✓	✓	X	✓	✓	✓	✓	✓
Via, contact R	✓	✓	X	?	✓	✓	✓	✓	✓	?/✓
Contact-R	✓	✓	✓	✓	✓	✓	✓	✓	✓	?
Cu corrosion	?	X	X	X	X/✓	✓	✓	✓	✓	?
Thermal stability	?	✓	X	X	✓	✓	✓	✓	?	✓
Stress, cracking	X	✓	✓	✓	✓	✓	✓	✓	✓	✓
Step coverage	?	✓•▲	✓•▲	✓•▲	✓▲	✓▲	✓▲	✓▲	✓	✓•
final	X	X	X	X	X	X	X	✓	X	X

• = CVD available, ▲ = Ionized-PVD available, ? = not investigated

Ref) D. Edelstein et al, Proc. 2001 IITC, 9 (2001).