UNIVERSITY OF TWENTE.

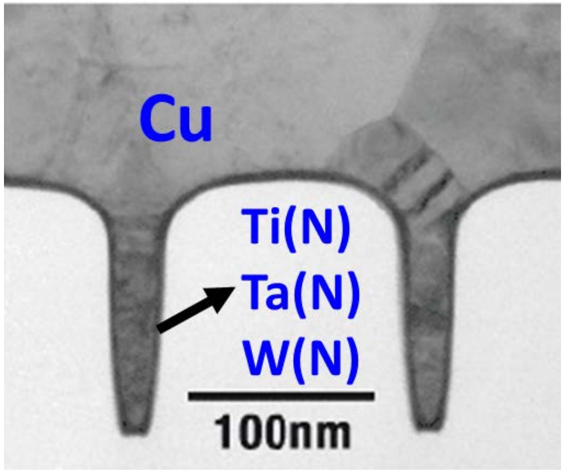
Hotwire-assisted Atomic Layer Deposition of Pure Metals and Metal Nitrides

Alexey Kovalgin

MESA+ Institute for Nanotechnology
Semiconductor Components group
a.y.kovalgin@utwente.nl

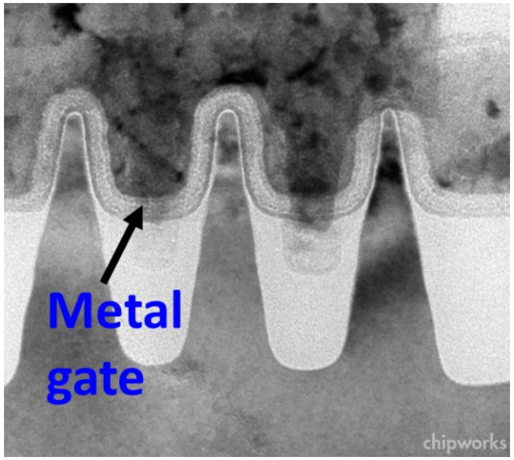
Motivation

1. Materials



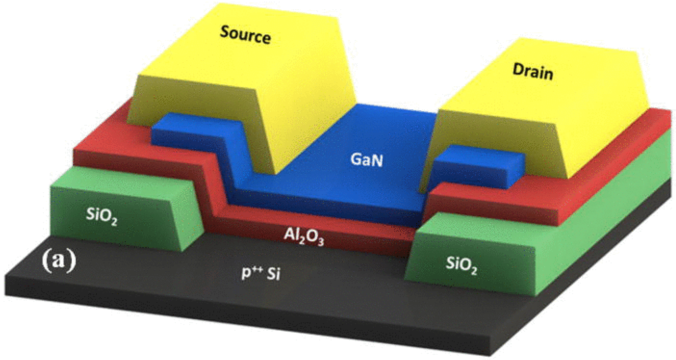
CMOS backend:
seed layers & barriers

(chipworks.com)



Multi-gate transistor

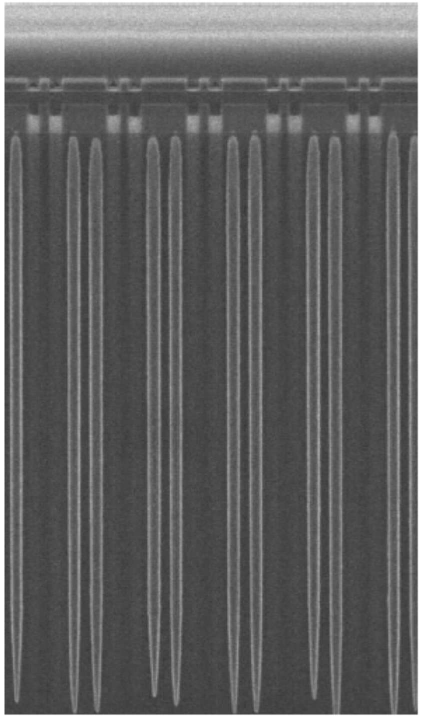
(chipworks.com)



Group III – Nitride TFTs

(S. Bolat et al. *Appl. Phys. Lett.* 2014)

2. Deposition method

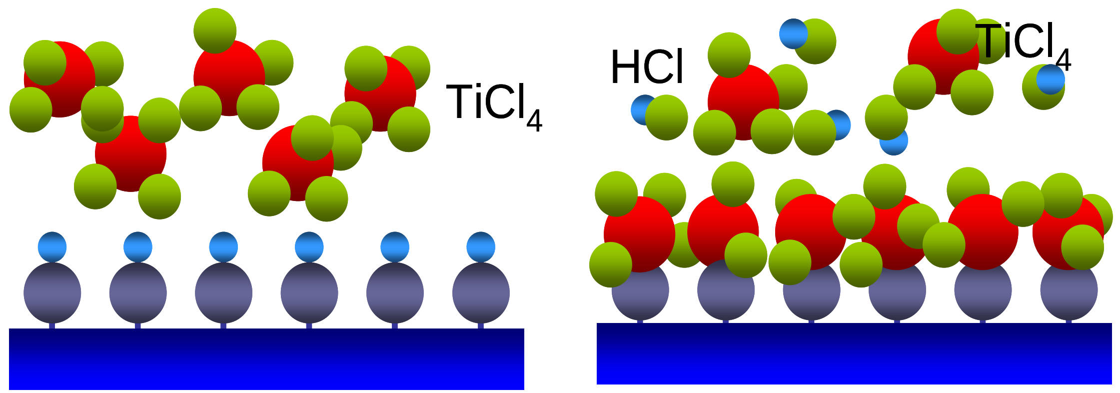


High aspect ratio
structures
(e.g. memories)

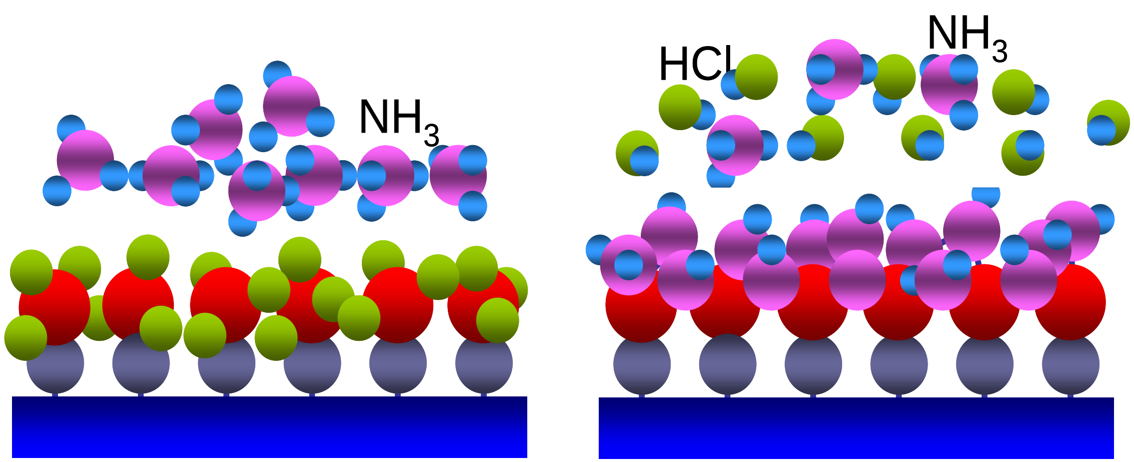
(chipworks.com)

Classic example of *thermal* ALD

Courtesy of
Hao Van Bui



$$-OH + TiCl_4 \rightarrow -OTiCl_3 + HCl$$

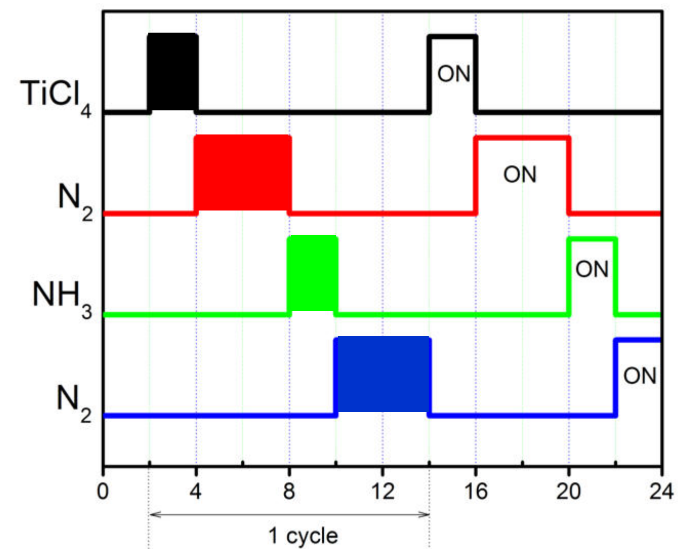


$$-TiCl + NH_3 \rightarrow -TiNH_2 + HCl$$

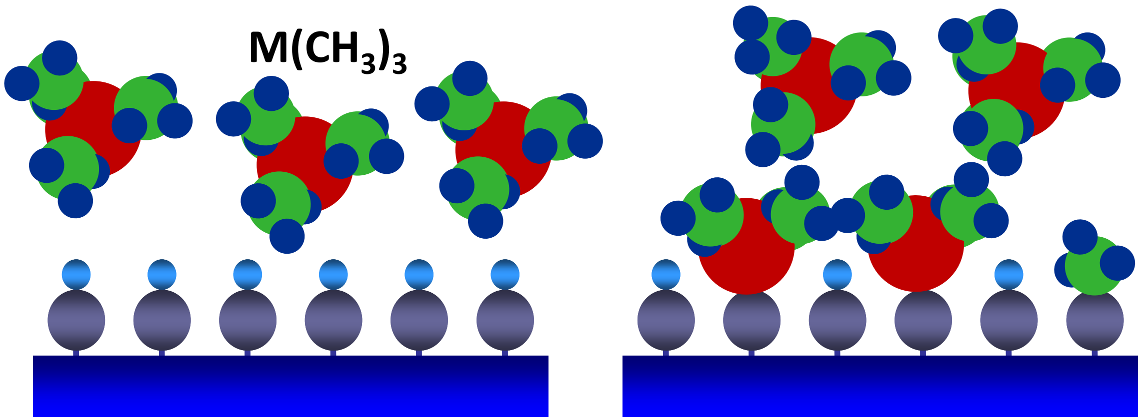
Metallic TiN films

ALD:

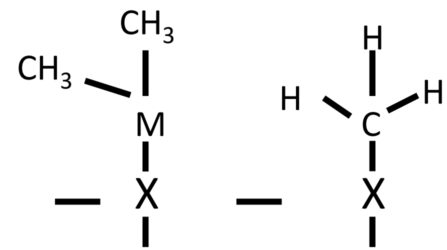
- ✓ Self-limiting reactions
- ✓ Thickness control
- ✓ High aspect ratio structures

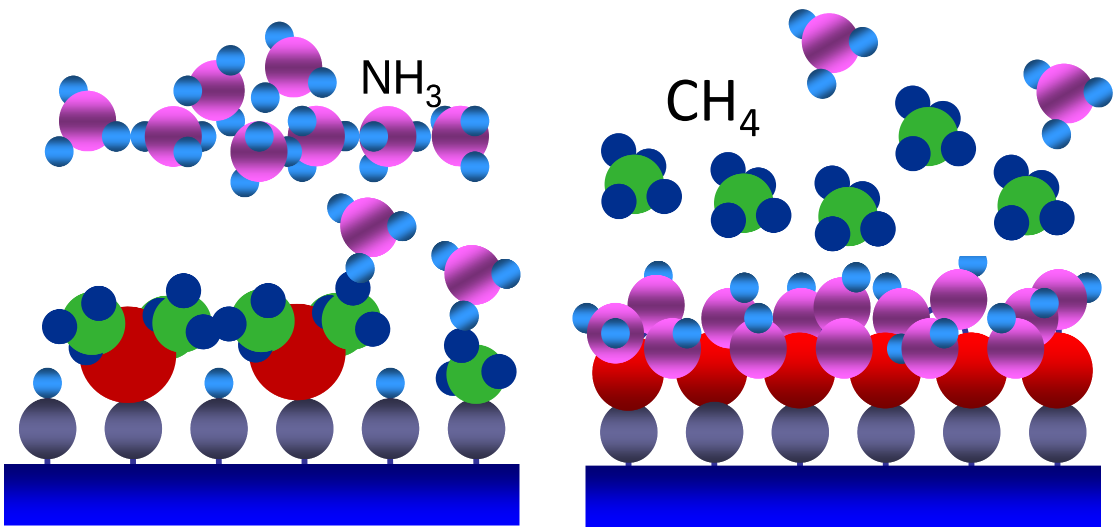


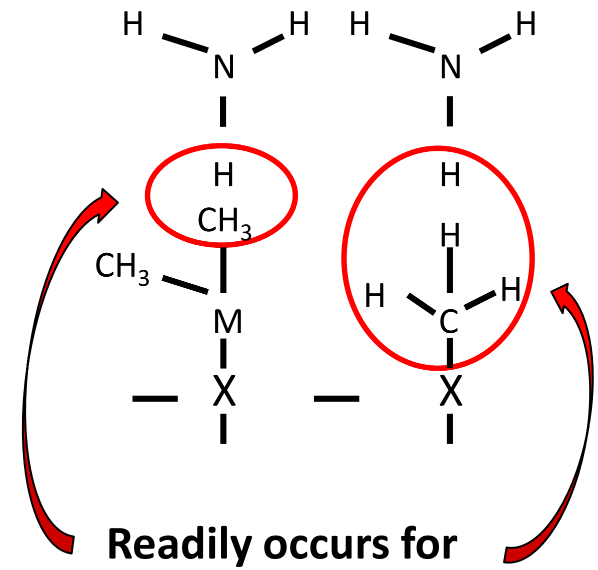
Need for extra activation



M = Al, Ga





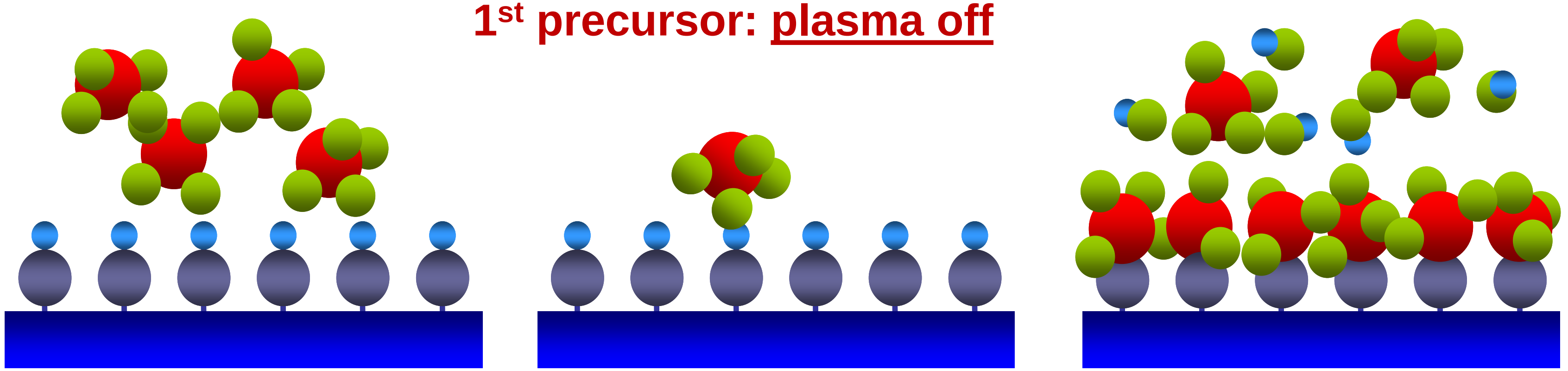


Readily occurs for Al, difficult for Ga

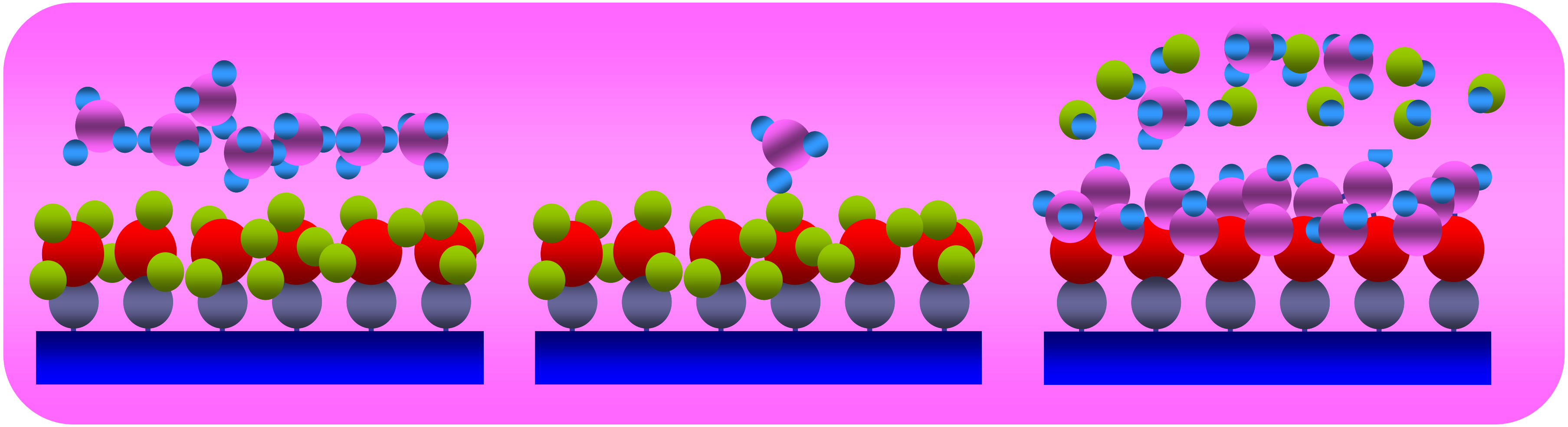
Need for additional activation of NH$_3$

Plasma-Enhanced ALD (PEALD)

1st precursor: plasma off



2nd precursor: plasma on



ALD classification

- **Atomic Layer Deposition**
  - **Thermal**
  - **Radical-Enhanced**
    - **PEALD**
    - **Making radicals w/o plasma?**

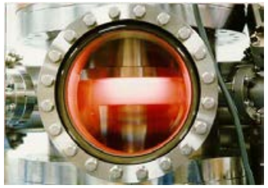
⇧

Cat. dissociation of H_2 on
hot tungsten filament

Joe N. Smith and Wade L. Fite,
J. Chem. Phys. 32, 898, (1962)

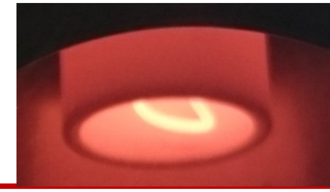
<u>Purpose</u>: Hot-wire generated radicals (H, NH_x, …) for ALD w/o plasma

Plasma versus Hot Wire



Plasma

1. Breaking molecules by electrons or excited species
2. Number of chemical reactions can be significant
3. Ions are present => more reactions & charging
4. UV light emission



Hot Wire

1. Catalytic dissociation by a hot (1600-2000 ^{o}C) tungsten wire
2. Lower pressures possible
3. Number of reactions is limited
4. No ions
5. No UV

Our study: Hot-wire assisted ALD (HWALD)

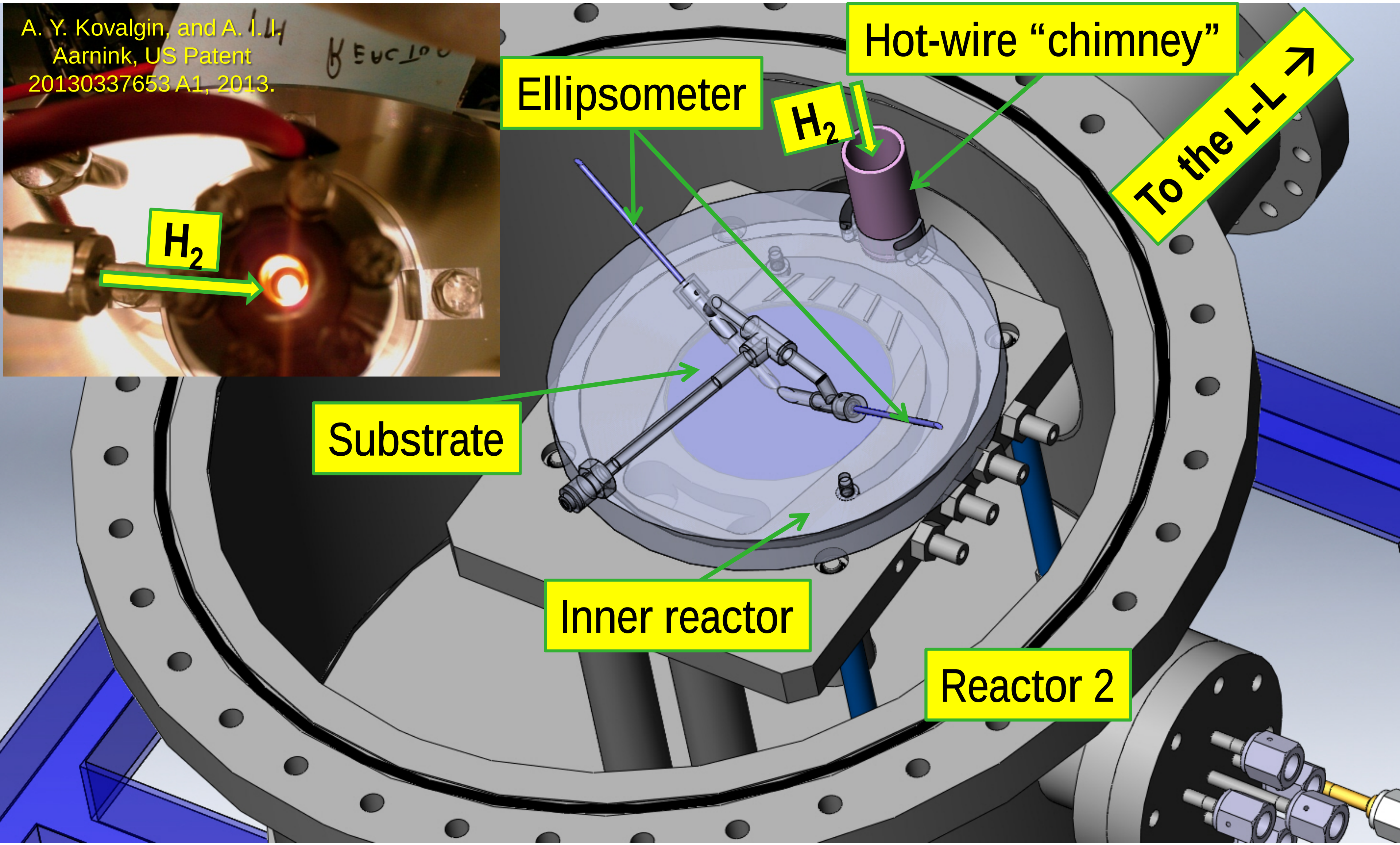
Outline

- Motivation
- Hotwire-Assisted Deposition:
  - Confirmation of the Presence of Atomic Hydrogen
  - HWALD of Tungsten (W) Films
  - On the Growth of Titanium (Ti) Films
  - Confirmation of the Presence of Nitrogen radicals
  - On the Growth of Aluminum Nitride (AlN) Films
- Conclusions

HWALD: Which radicals can be formed?

Confirmation of the Presence of Atomic Hydrogen

Reactor details



Is at-H delivered to the wafer surface?

- *Atomic* hydrogen reacts with Te surface producing TeH_2:

  $$2H + Te(s) \rightarrow TeH_2(g) \rightarrow \text{etching Te film}$$

- There is no reaction between *molecular* hydrogen and Te.

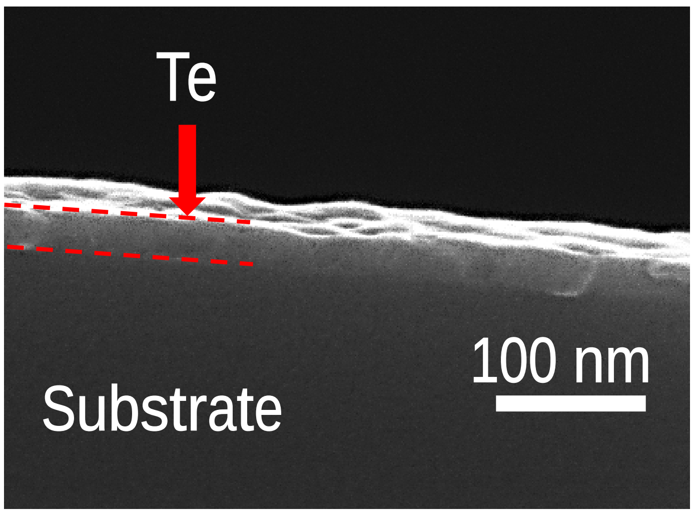
Real-time monitoring of Te etching

The etching of Te was real-time monitored by in-situ SE

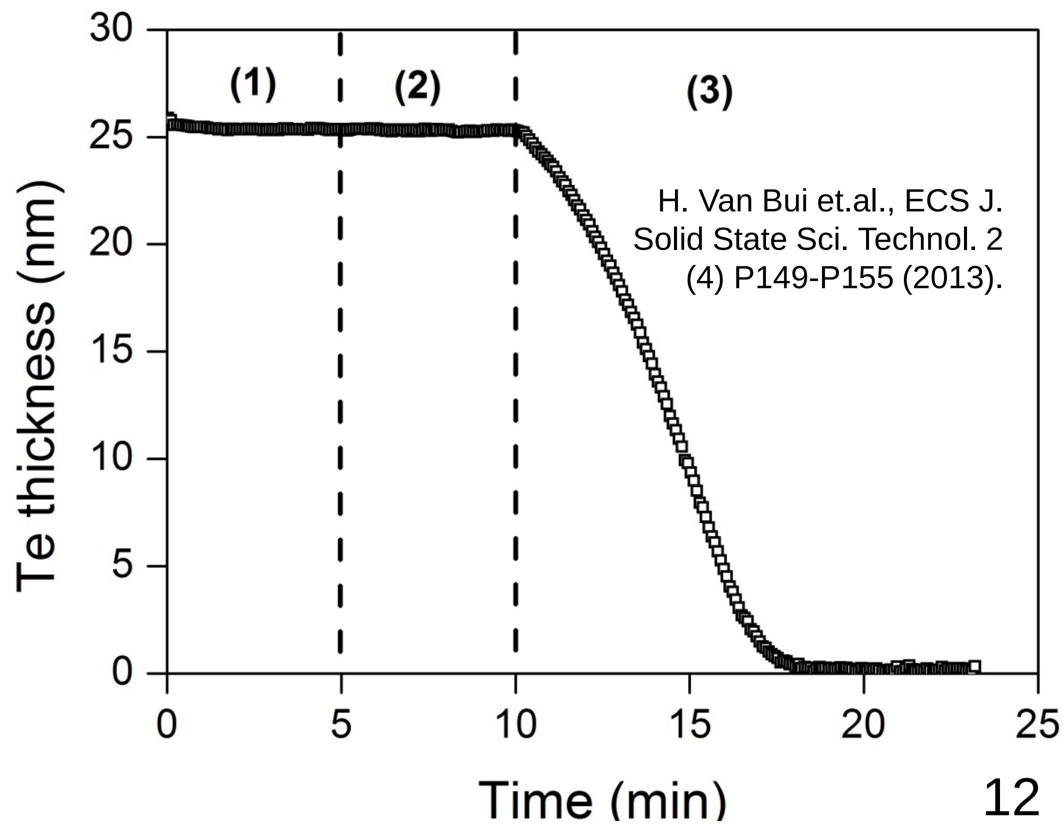
(1) Introducing H_2, **FILAMENT OFF**

(2) Stop introducing H_2, **heat up the filament**

(3) Introducing H_2 with **FILAMENT ON**



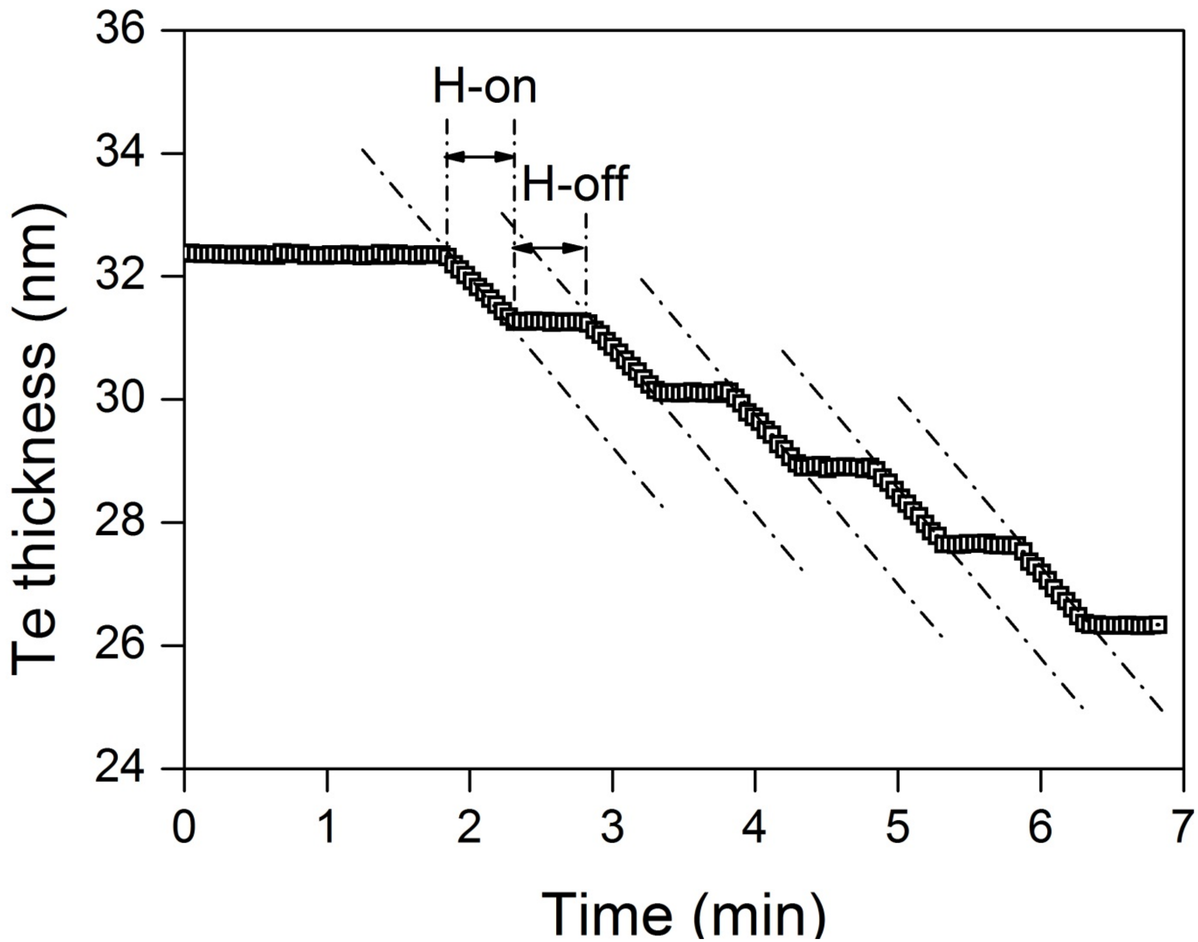
Thickness verification by SEM



Etching of Te by H-pulses

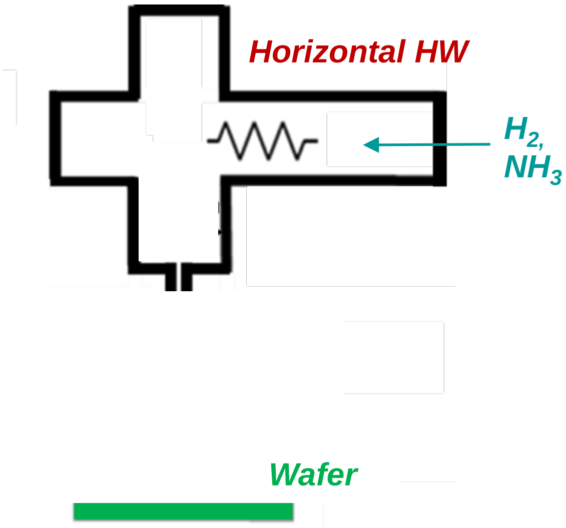
H. Van Bui et al.: ECS journal of solid state science and technology 2 (4) P149-P155 (2013).

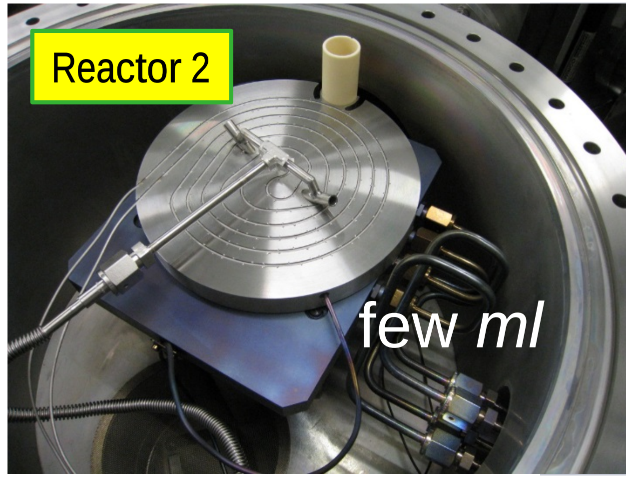
Bridge to Hot Wire ALD (HWALD)

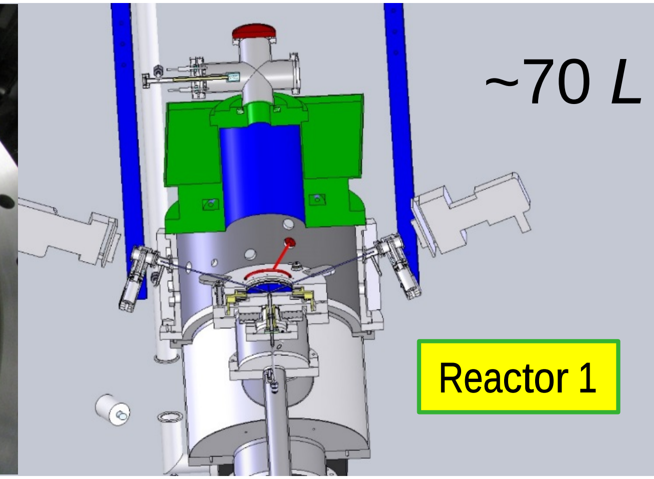


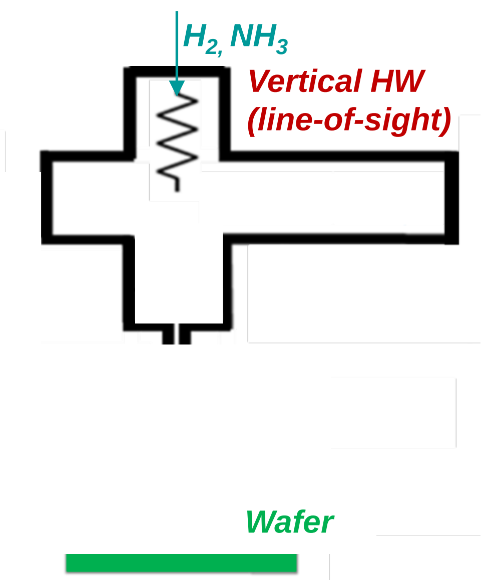
Delivering atomic-H goes easily

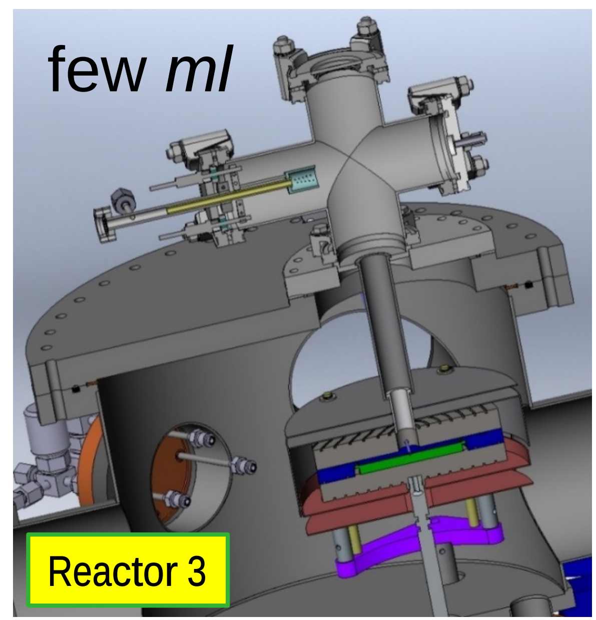
Adv. Mater. Interfaces ***2017***, *1700058*







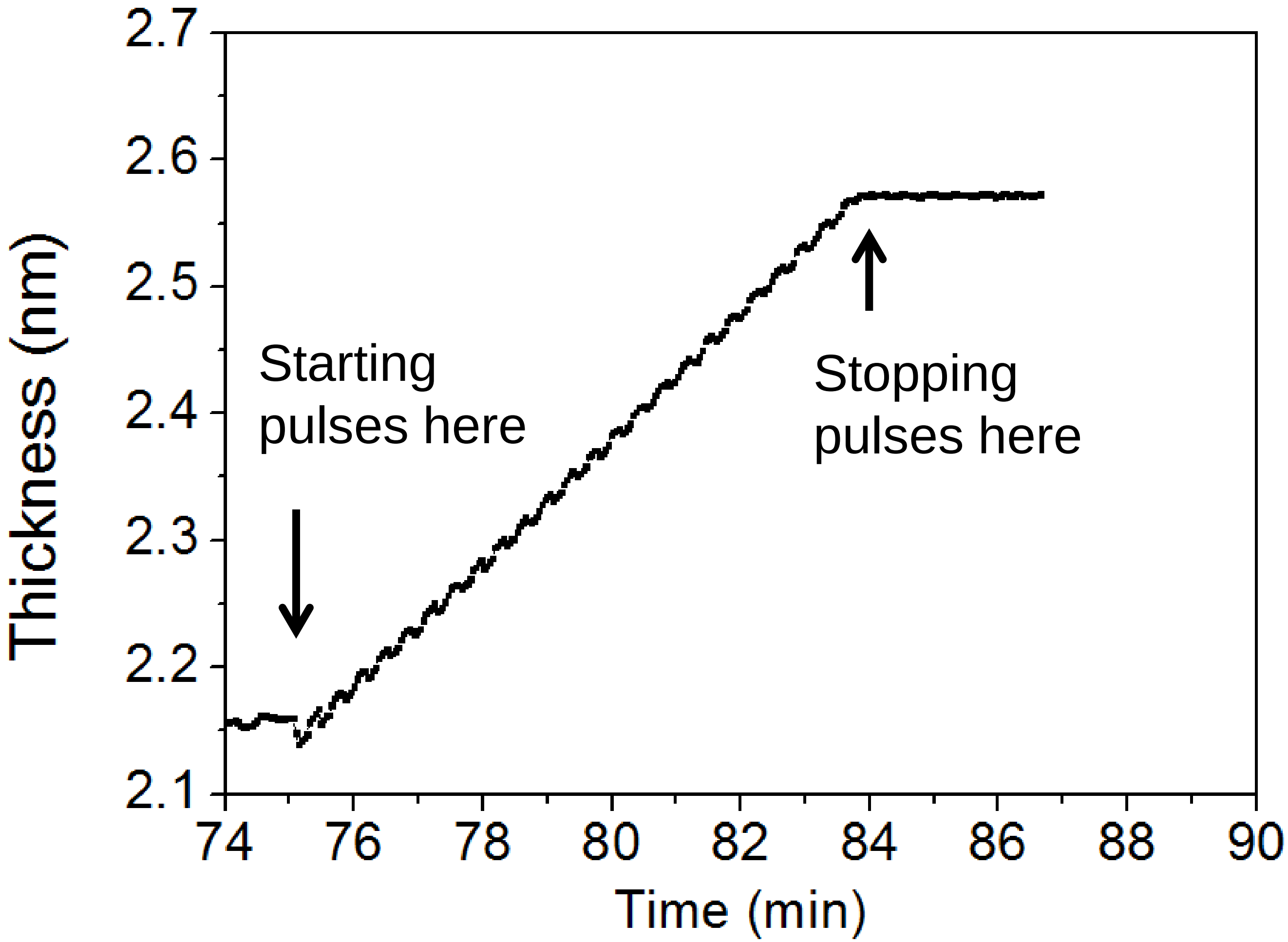




HWALD of Tungsten (W) Films

In-situ SE monitoring

- Sequential pulses of WF_6 and at-H
- Well-defined ALD window can be found

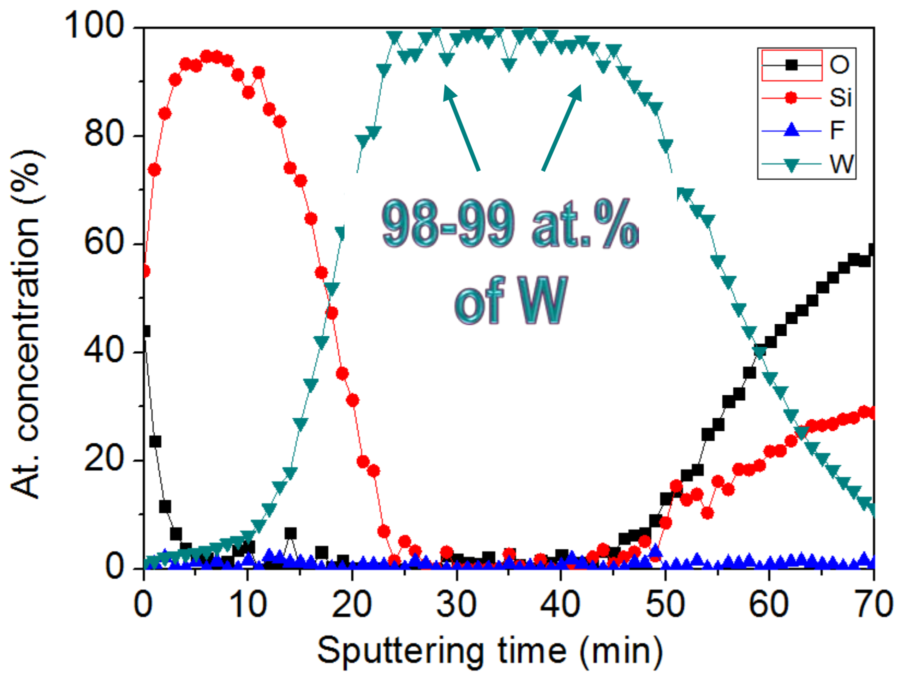


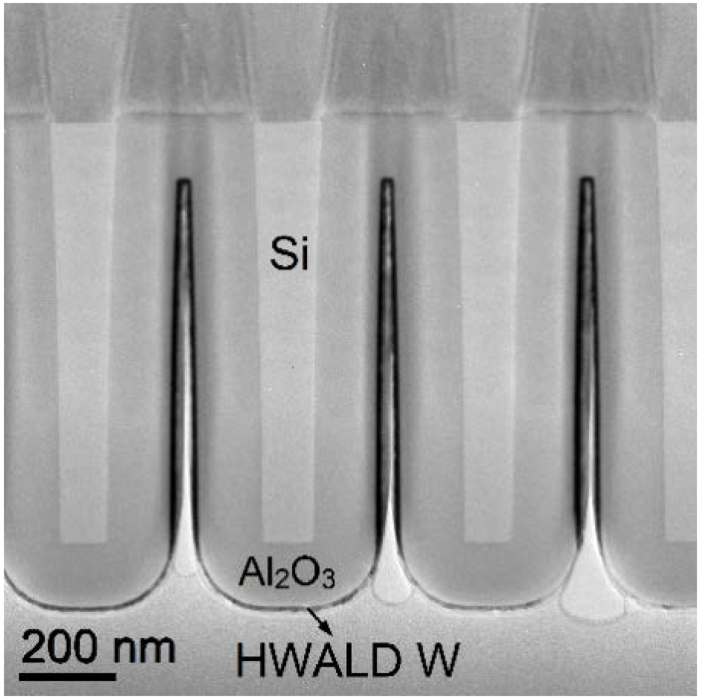
One ALD cycle:

1. at-H
2. Purge
3. WF_6
4. Purge

Properties of W

✓ High purity





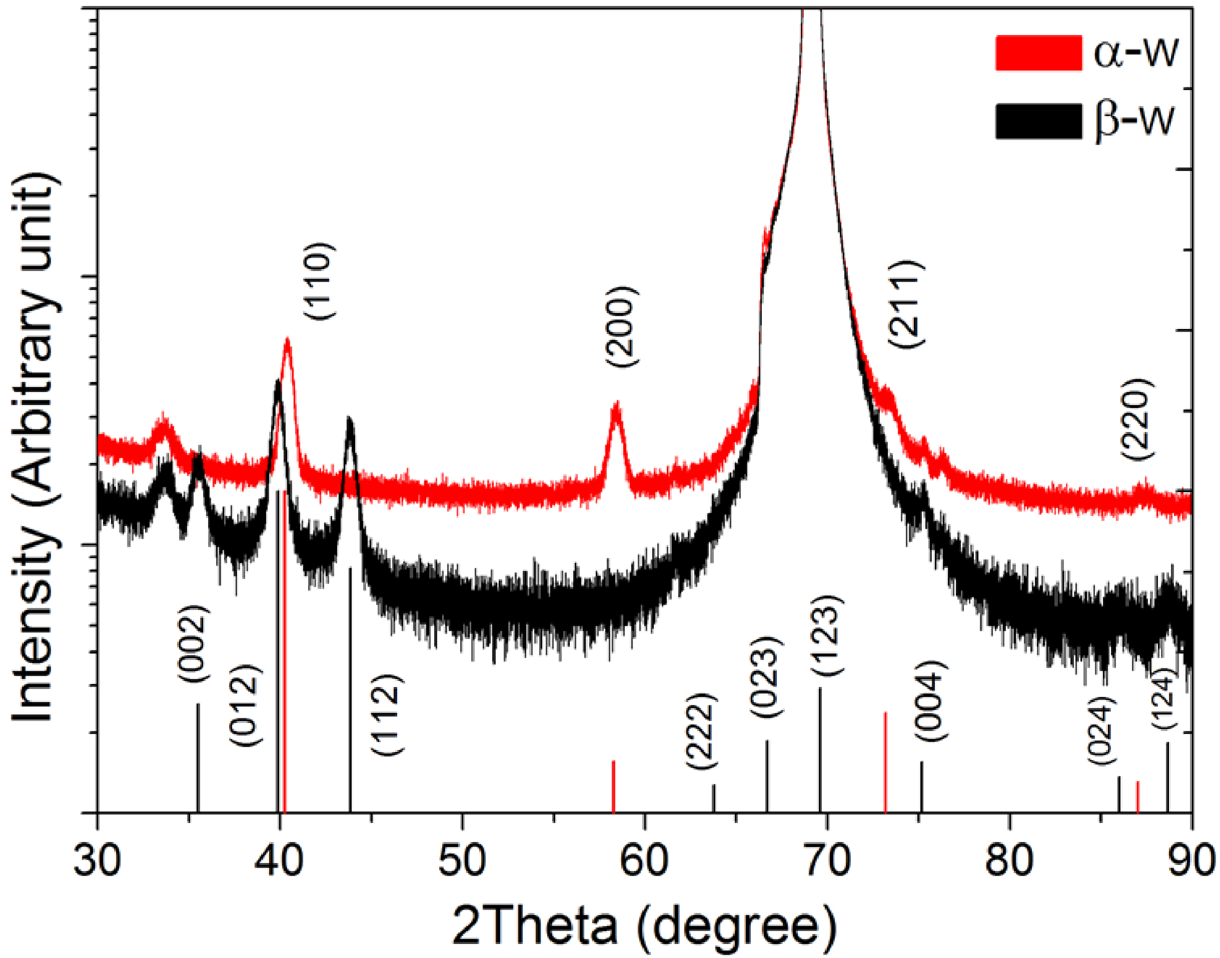
✓ Excellent step coverage

Yang et al., *Thin Solid Films,*
https://doi.org/10.1016/j.tsf.2017.12.011

Crystallinity

Yang et al., *Thin Solid Films*,
https://doi.org/10.1016/j.tsf.2017.12.011

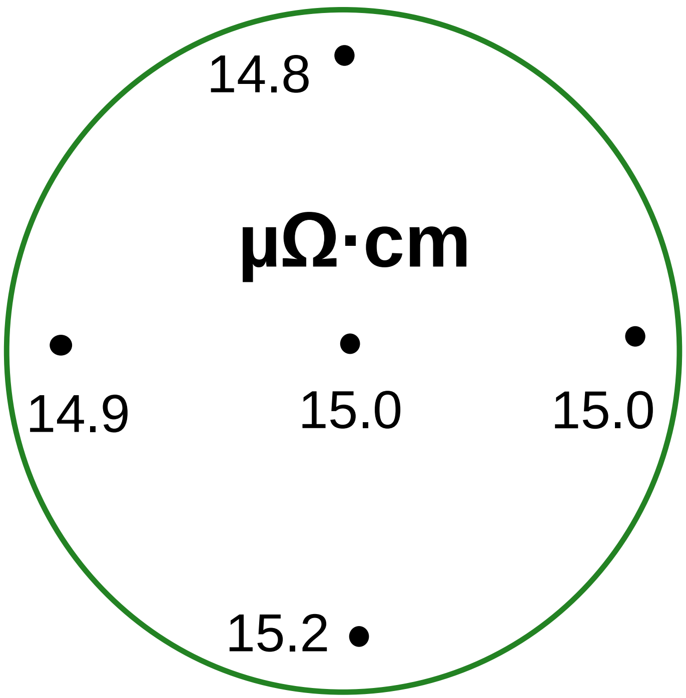
Growing either α- or β-phase W possible



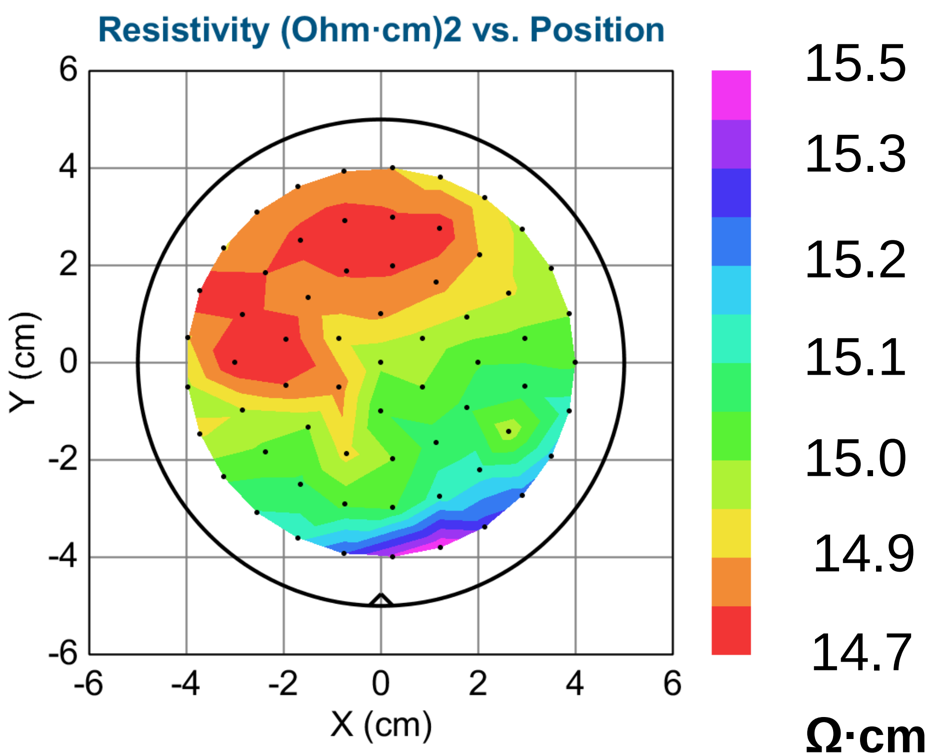
Resistivity

Yang et al., *Thin Solid Films*,
https://doi.org/10.1016/j.tsf.2017.12.011

Film thickness: 10-12 nm
RMS: 1.4 nm



Resistivity mapping



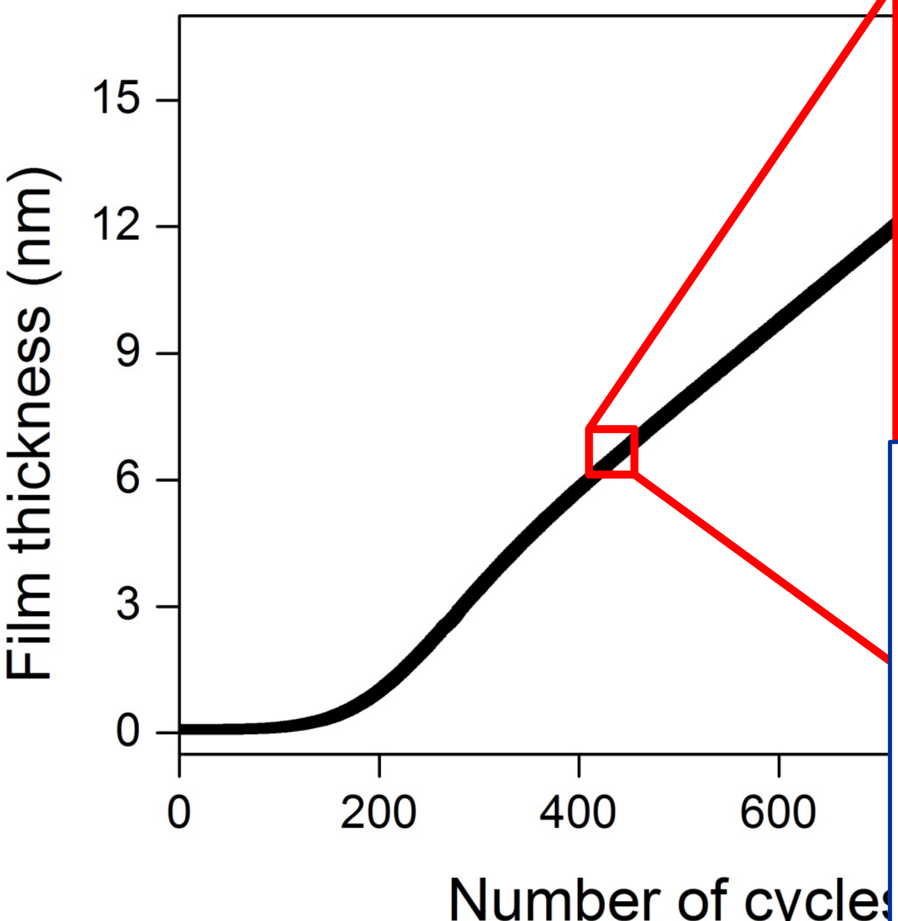
✓Resistivity:

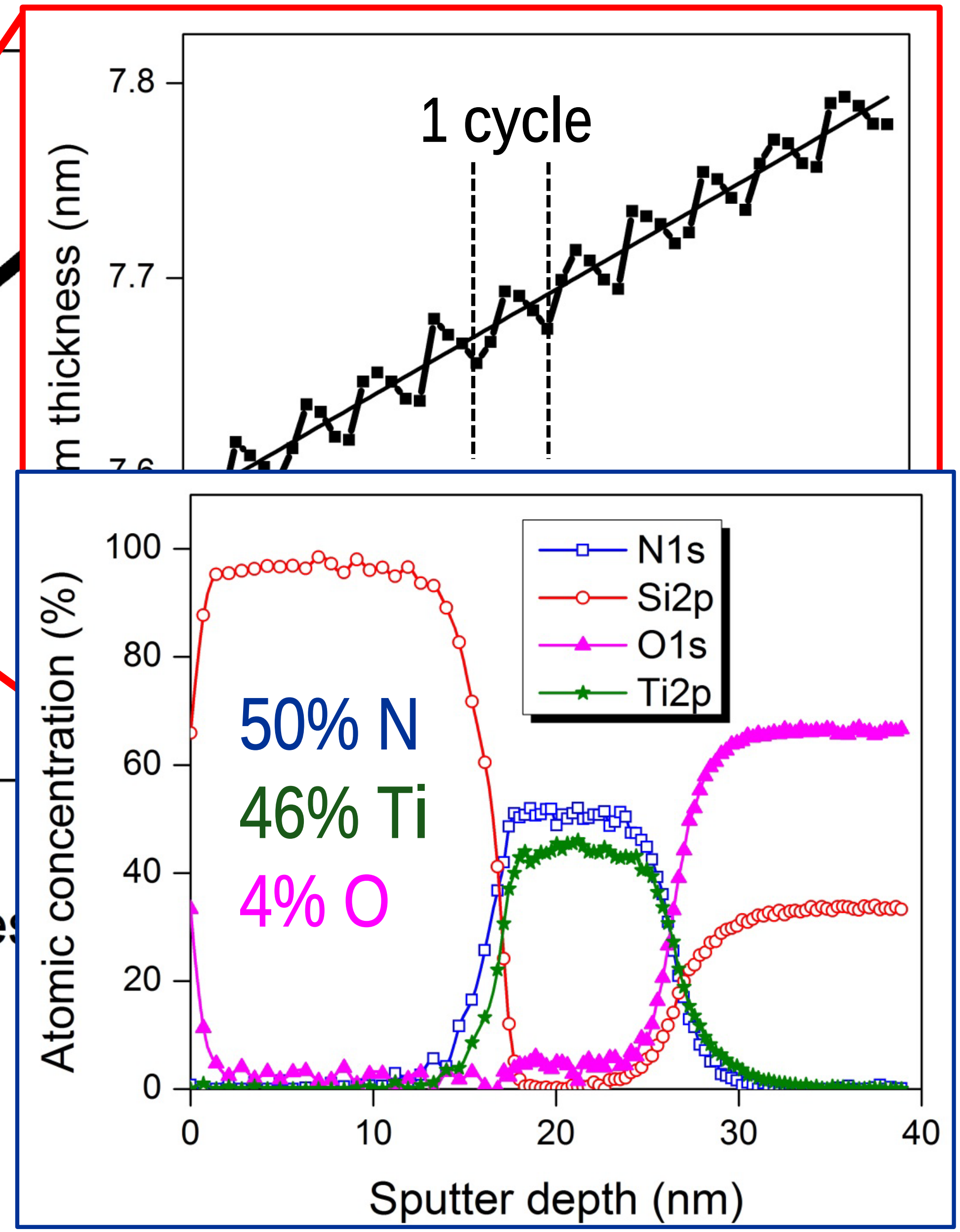
- 100 **μΩ**·cm, β-phase
- 15 **μΩ**·cm, α-phase

HWALD: On the Growth of Titanium (Ti) Films

(Let's replace WF_6 by $TiCl_4$ while keeping at-H)

Reference: ALD of TiN by $TiCl_4$/NH_3 pulses





H. Van Bui, A. Y. Kovalgin, and R. A. M. Wolters. ECS journal of solid state science and technology 1 (6) P285-P290 (2012).

$TiCl_4/H/NH_3$ pulses

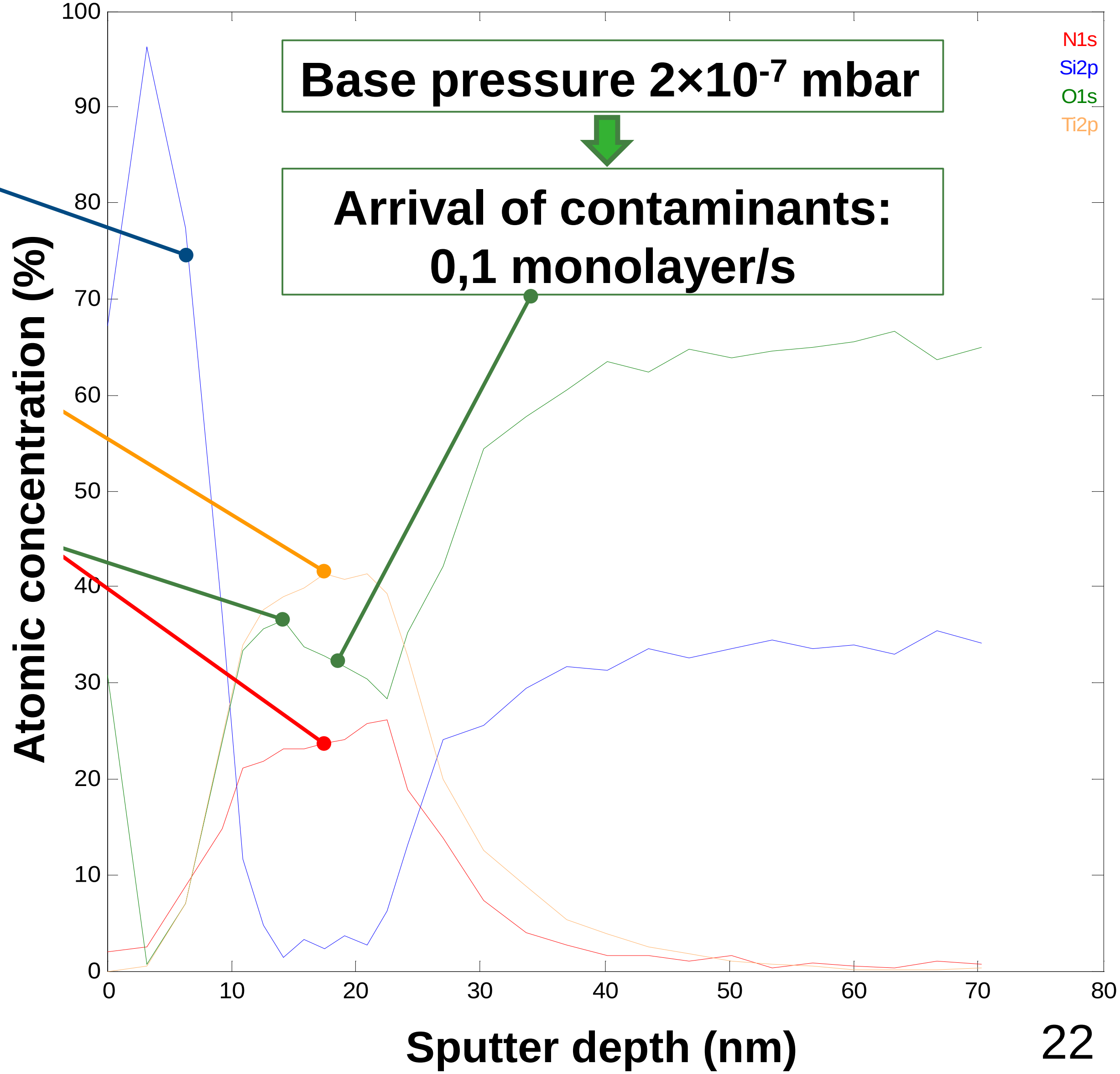
H. Van Bui et al.: ECS journal of solid state science and technology 2 (4) P149-P155 (2013).

Surface passivation by a-Si

43 at.% Ti

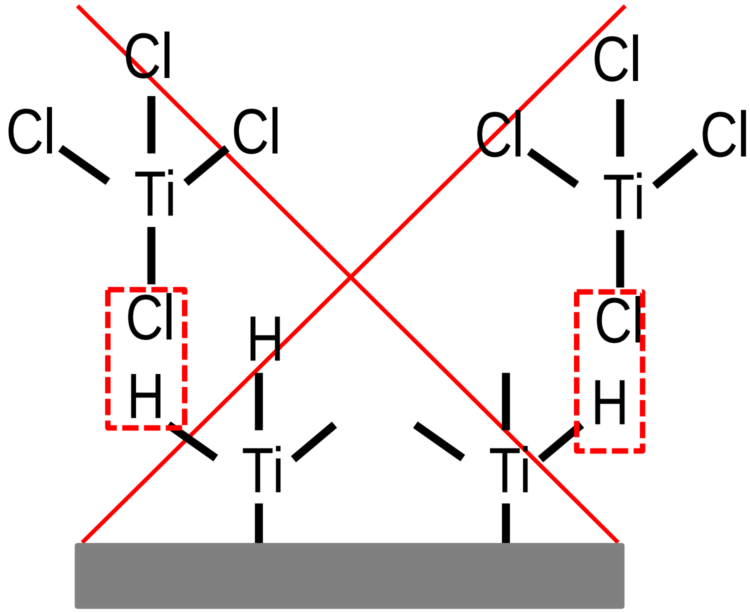
25 at.% N

35 at.% O (was 3-5 %)



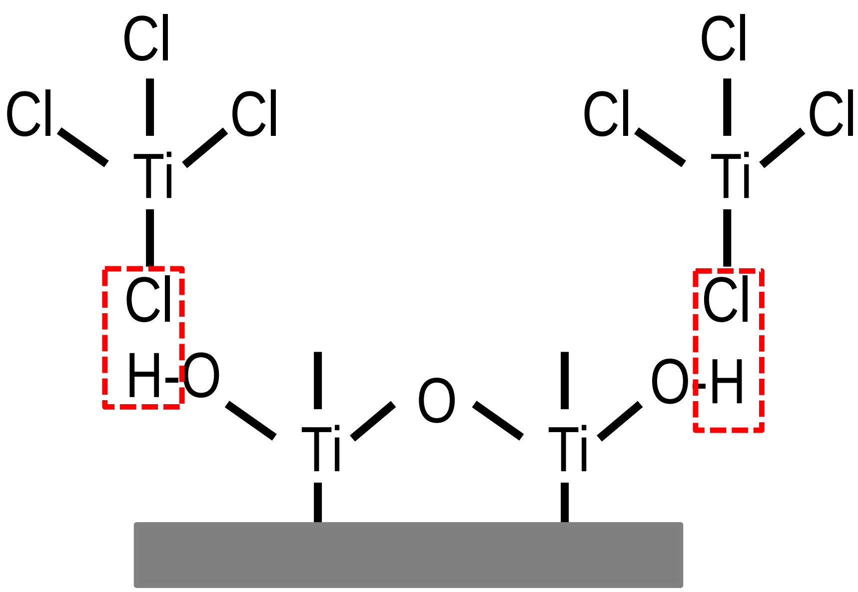
$TiCl_4$/H pulse sequence

- H reduces –Cl groups, releasing HCl and leaving dangling bonds…



Case #1: H atoms occupy dangling bonds

→ Would be great…
but: 10^{-7} mbar of residual H_2O



Case #2: O atoms occupy dangling bonds

→ TiO_2 will continue growing but very slowly as it is limited by the supply of H_2O

It does work for W…
Why not for Ti, Al, ...?

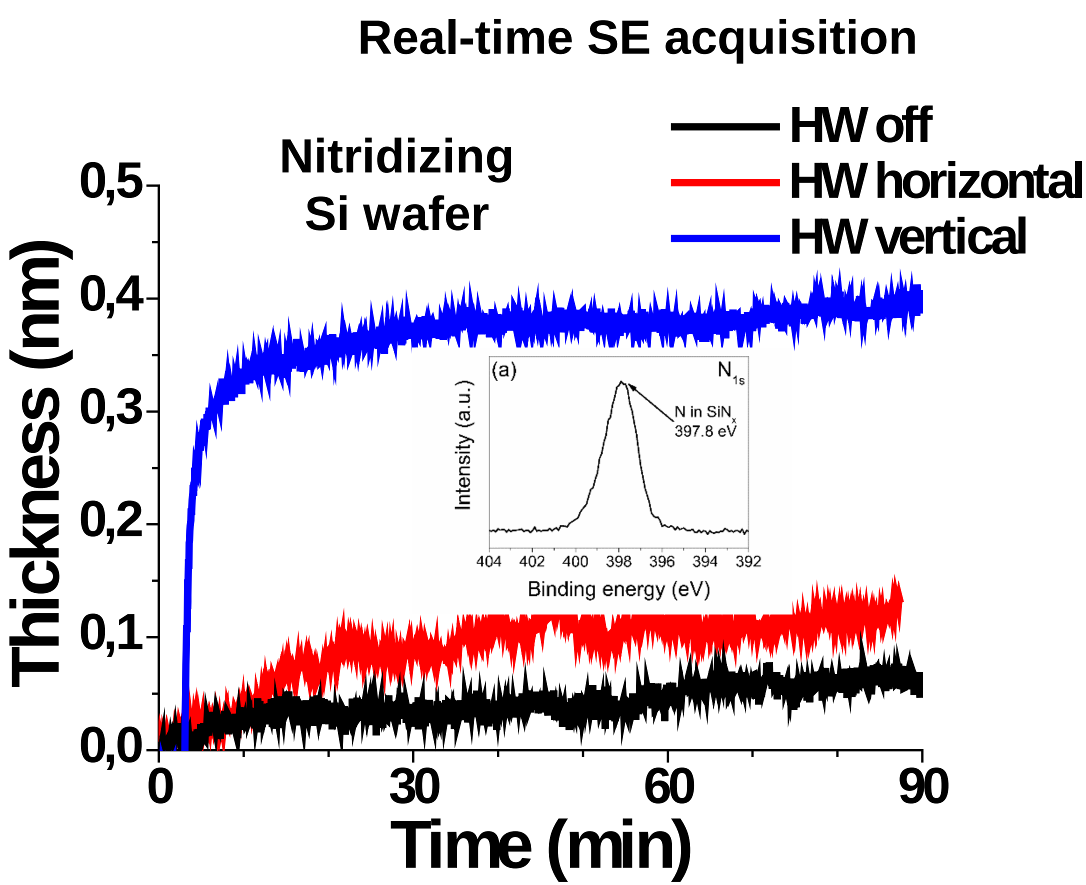
WO_x can be reduced by at-H to metallic W whereas TiO_2 and Al_2O_3 cannot

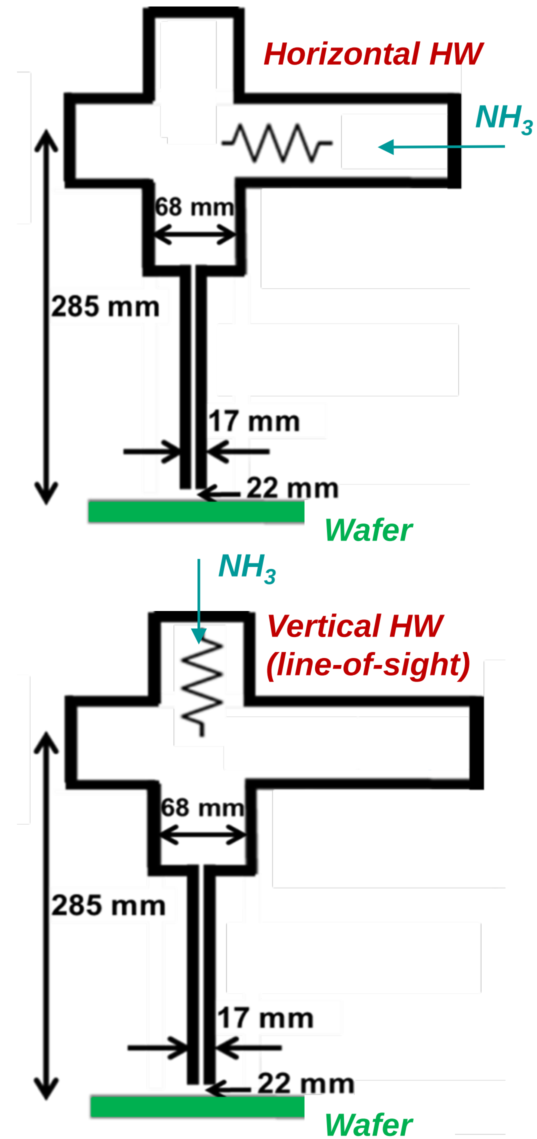
HWALD: Which radicals can be formed?

On the Presence of Nitrogen Radicals

N-radicals delivered in line of sight

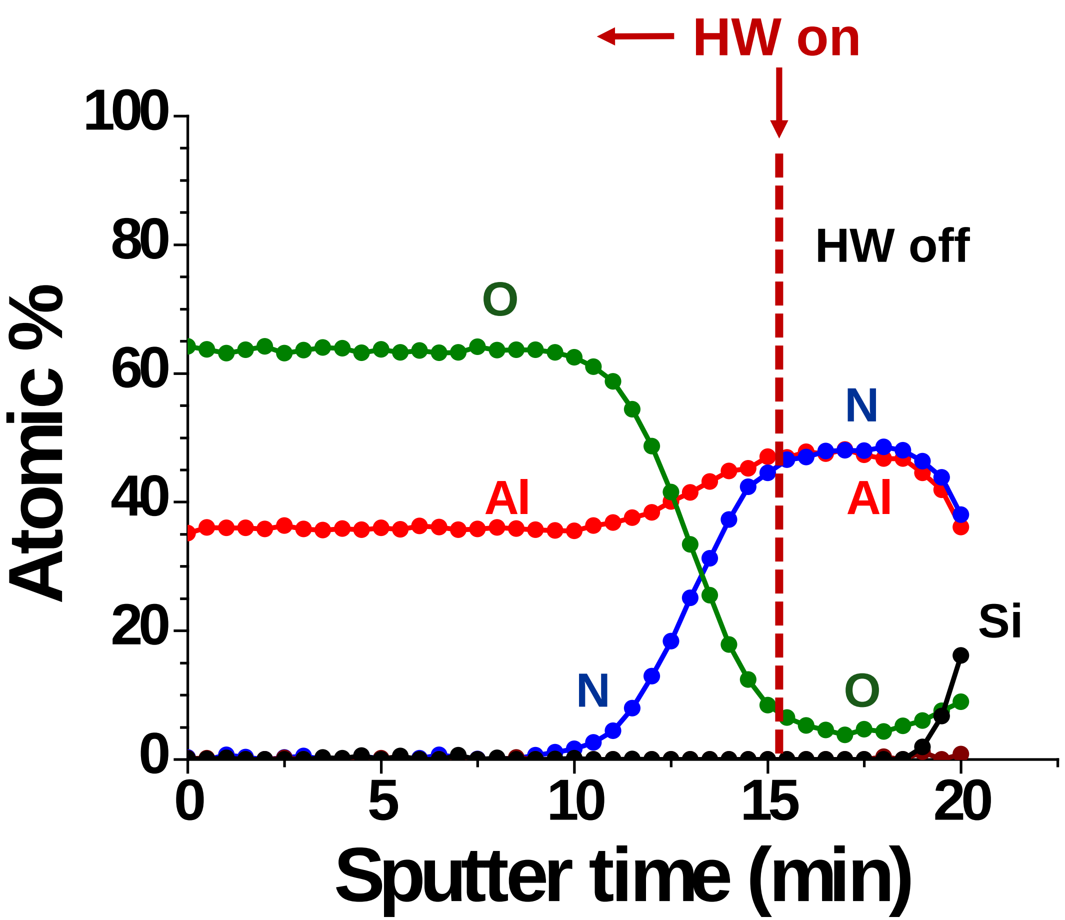
Adv. Mater. Interfaces ***2017***, *1700058*

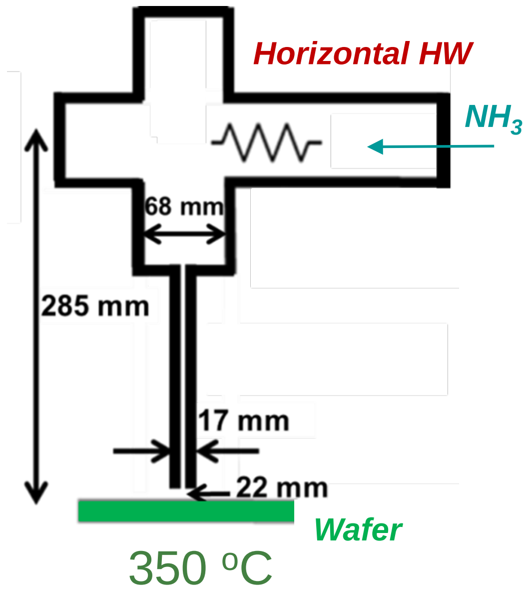




Towards AlN: HW *out of line-of-sight*

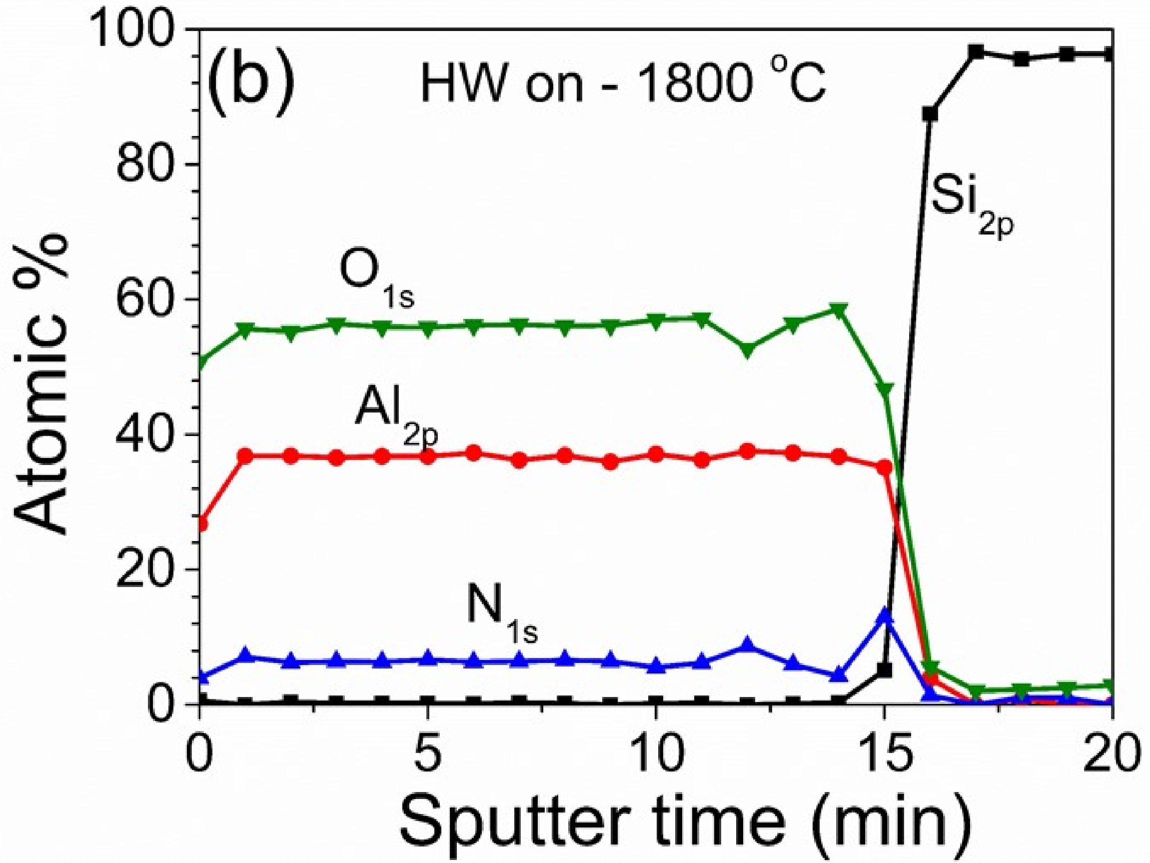
Adv. Mater. Interfaces ***2017***, *1700058*

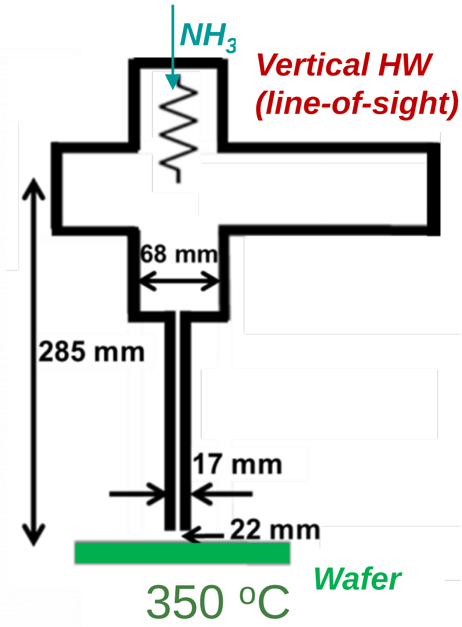




Towards AlN: HW *in line-of-sight*

Adv. Mater. Interfaces ***2017**, 1700058*





Conclusions

- ALD = self-limiting surface reactions => advantages
- Additional means to supply energy sometimes required
- HW can (to some extent) replace plasma:
  - Generation of at-H confirmed by etching of Te films
  - at-H: delivery in both *in* and *out* of *line-of-sight* possible
  - Generation of Nitrogen radicals confirmed by nitridation of Si
  - Nitrogen radicals: delivery *in line-of-sight* only
  - Obviously (residual) oxidants can also be activated by HW
  - Metal oxidation and reduction of the oxides should be taken into account
- HWALD enables (so far):
  - Area-selective growth of high-qiality W using WF_6/at-H
  - Deposition of TiO_x using $TiCl_4$/at-H
  - Deposition of AlN_yO_z using TMA and NH_3 via HW

Many thanks to:


- Mengdi Yang (PhD student – HWALD W)
- Sourish Banerjee (PhD student – AlN/GaN ALD)
- Hao Van Bui (graduated PhD student – Te etching, TiN ALD)
- Ramazan Oguzhan Apaydin (PhD student – BN)
- Tom Aarnink (technical support of deposition tools)
- Rob Wolters (discussions)
- Jurriaan Schmitz (discussions)
- Dirk Gravesteijn (discussions)
- Mark Smithers, Gerard Kip (MESA+) for SEM and XPS analyses.
- This work is financially supported by the Netherlands Organization for Scientific Research (NWO) and ASM International.






SC SEMICONDUCTOR COMPONENTS The Chip Builders

NWO Netherlands Organisation for Scientific Research

ASM

MESA+ INSTITUTE FOR NANOTECHNOLOGY

Thank you for your attention!

NWO Netherlands Organisation for Scientific Research

SC SEMICONDUCTOR COMPONENTS The Chip Builders

MESA+ INSTITUTE FOR NANOTECHNOLOGY

ASM