

Revisited Thermal and Plasma Enhanced Atomic Layer Deposition combined with Chemical Vapor Deposition processes of metal nitrides: challenges and opportunities

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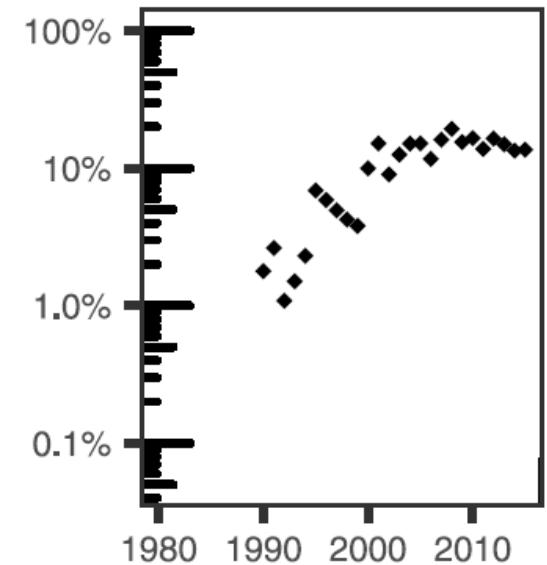


Fabrication of metal nitride films

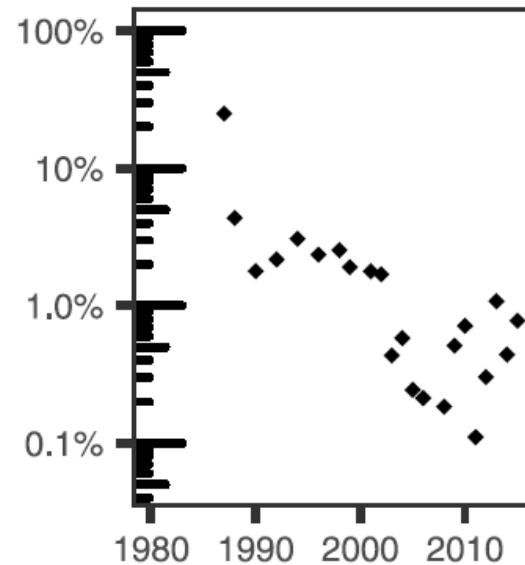
- ❑ Applications
- ❑ Challenges
- ❑ Fabrication Strategies

ALD and Nitrides

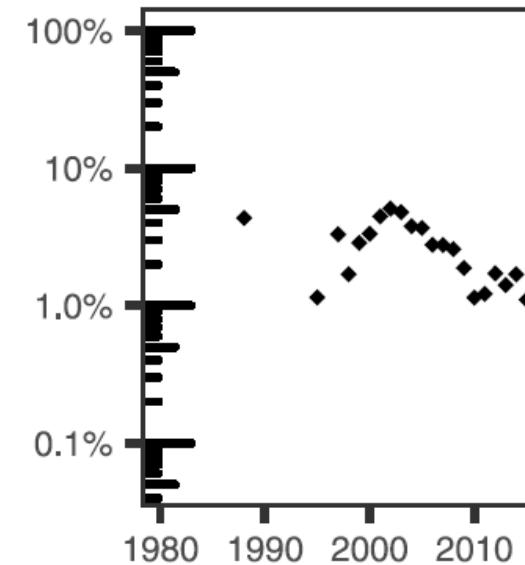
Oxide



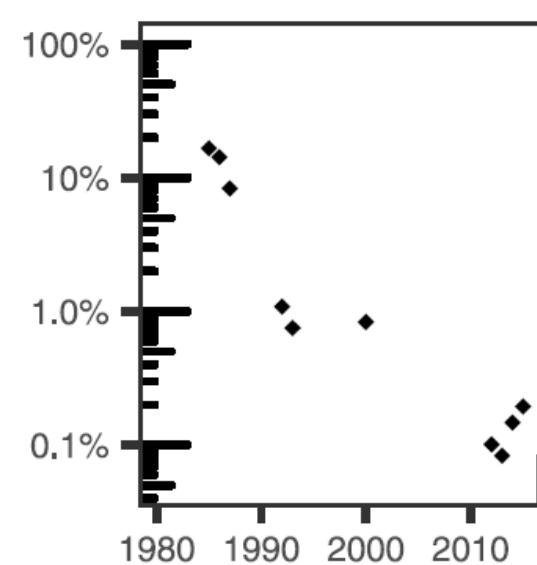
Sulfide



Nitride



Chalcogenide



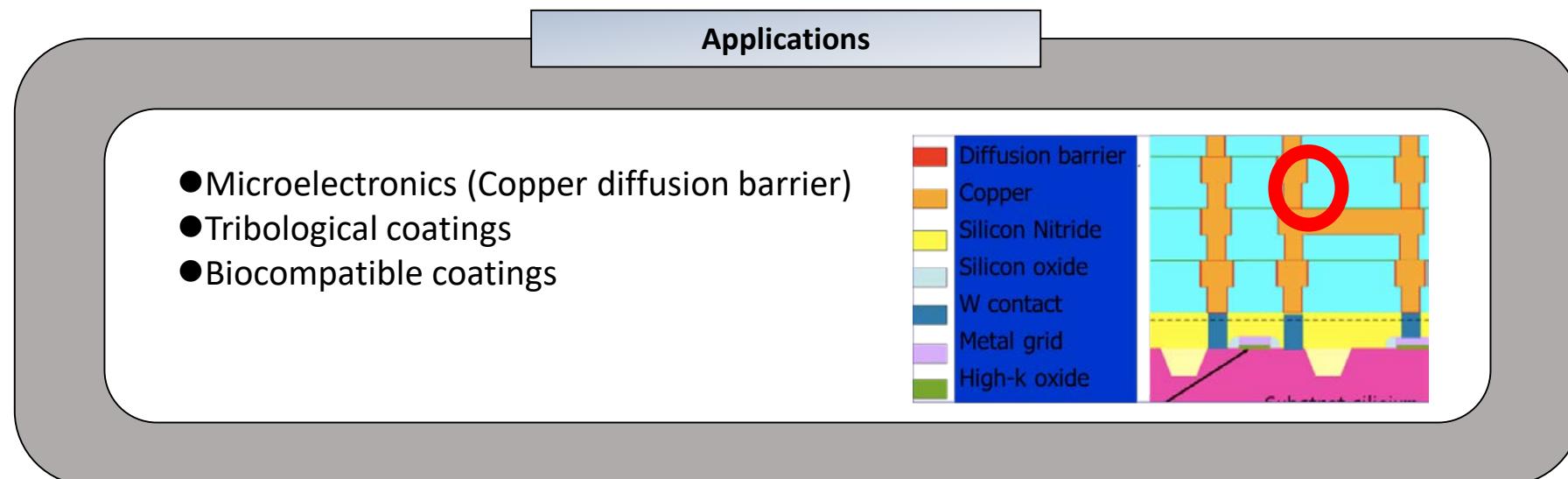
E. Alvaro, A. Yanguas-Gil (2018)

Characterizing the field of Atomic Layer Deposition: Authors, topics, and collaborations. PLoS ONE 13 (1): e0189137.

<https://doi.org/10.1371/journal.pone.0189137>

Applications: TaN

Properties	
● High electrical conductivity	Structure @ RT
● High oxidation resistance	Melting point
● High wear resistance	Electrical resistivity@RT
● High stability	Vickers hardness
● Biocompatibility	cubic 3090 °C <300 $\mu\Omega\cdot\text{cm}$ (CVD) 20-30 (Gpa)



Applications: NbN

Properties

- Superconductivity
- High hardness

Structure @ RT	cubic
Melting point	3090 °C
T _c (K)	17.8 (9 Nb)

Applications

- Superconductive layer
 - RF cavities
 - Single photon detection devices

CEA Saclay



Satellite communications (Lunar Laser Communications Demonstration)



Applications: AlN

Properties	
●High oxidation resistance	Structure @ RT
●High thermal conductivity	Melting point
●High electrical isolation (SC)	Resistivity
●High stability	Thermal conductivity @RT
●Large Band gap	Vickers hardness (25N)
●Piezoelectric	Hexagonal, hcp
	3000 °C
	10^8 to 10^{13} Ω.cm
	3,3 Wcm ⁻¹ K ⁻¹ (80% Cu)
	1225

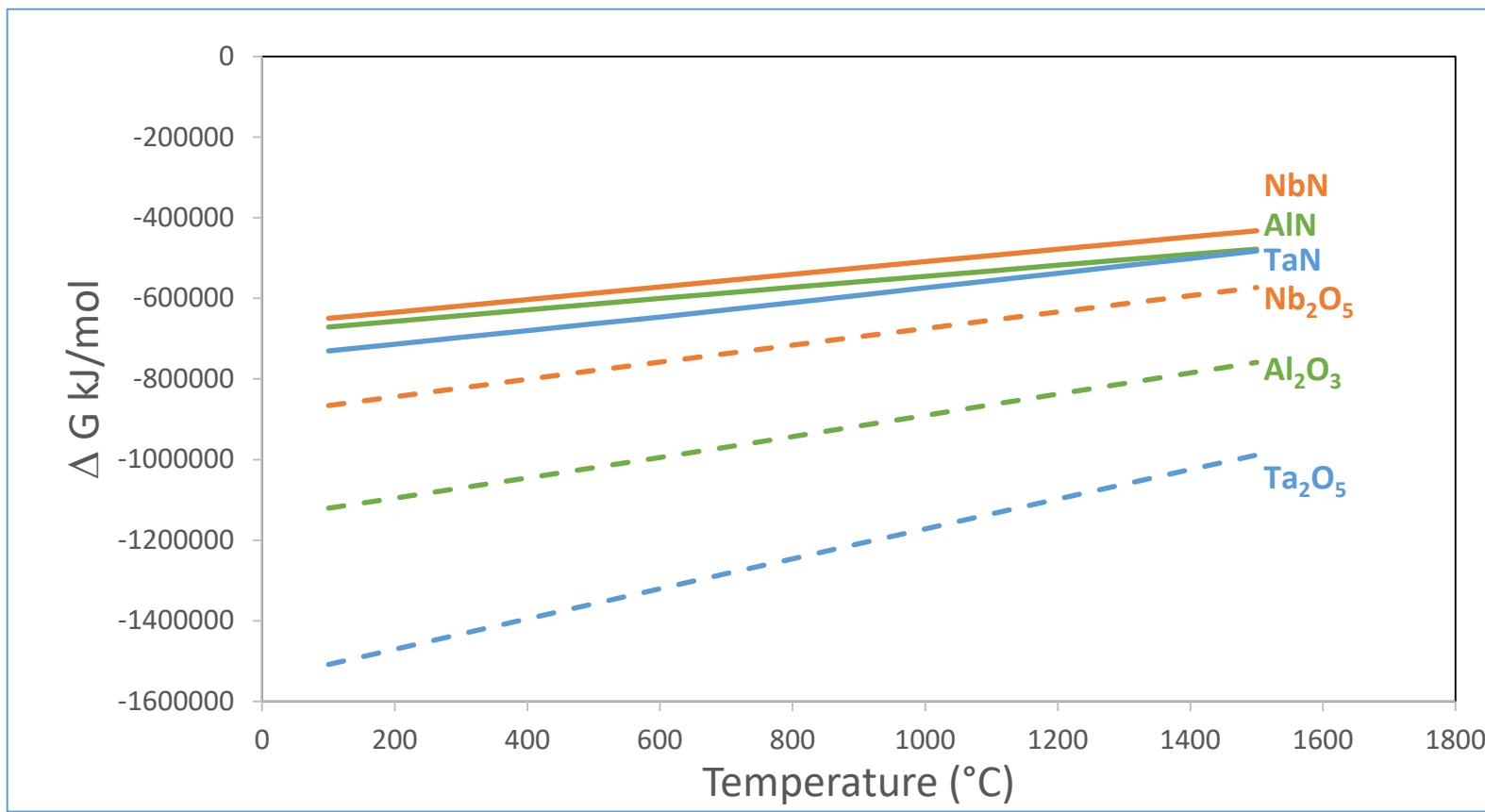
Applications	
●Power devices	
●Optoelectronics devices	
●SAW	
●Thermal barrier	

Few important challenges

Objective :deposition of a metal nitride type MN

- Stability nitrides vs oxides

Few important challenges

 Stability nitrides vs oxides

Looking for O presence!

Oxides much more stable than nitrides

Few important challenges

Objective: deposition of a metal nitride type MN

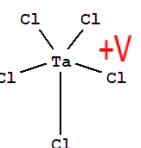
- Stability nitrides vs oxides
- Deposition of a metal nitride type MN where M oxidation state (o.s.)= +III
- Metallic Precursors: halides, non halide molecular precursors with C-M or N-M bonds (where M o.s. \geq +III)
- Reactive gases (Reducing gases): H₂, NH₃, hydrazine N₂H₄, Zn +++
 - use of additional plasma assistance

Ta_N: litterature

1. TaCl₅ and NH₃ T> 400°C

TaCl₅ + NH₃ + Zn

TaCl₅ + H₂ / N₂ plasma T=300°C



Formation of Ta₃N₅ (Ta^{+V})

M. Ritala et al, Chem. Mat., 1999

P. Alen et al, J. Electrochem. Soc., 2001

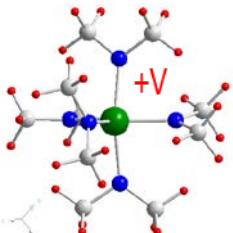
H. Kim et al, J. Appl. Phys., 2004

2. PDMAT and NH₃

PDMAT + NH₃

PDMAT + NH₃ plasma

PDMAT + H₂ / N₂ plasma



Oxygen contamination in the films

A. Furuya et al, J. Vac. Sci. Technol. B, 2005

H. Kim et al, J. Appl. Phys., 2005

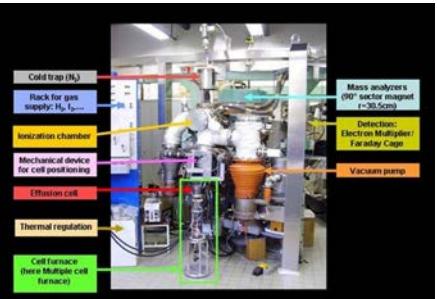
Z. Fang et al, J. Cryst. Growth, 2011

V. Brize et al, Chem. Vap. Depos., 2011

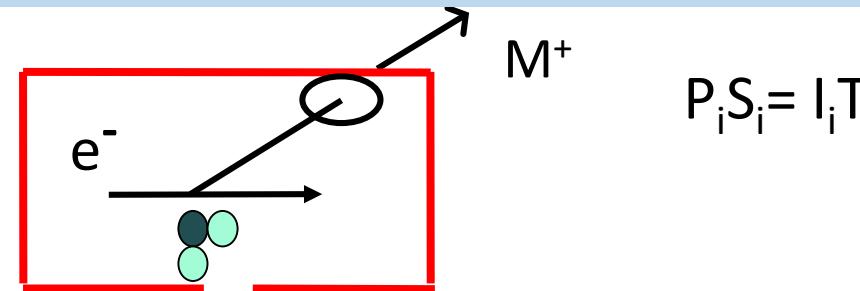
F. Volpi et al, Thin Solid Films, 2018

Knowledge of nature and thermodynamics of the gaseous compounds from Knudsen Cell - type mass spectrometry

Looking for Oxygen origin: developed device



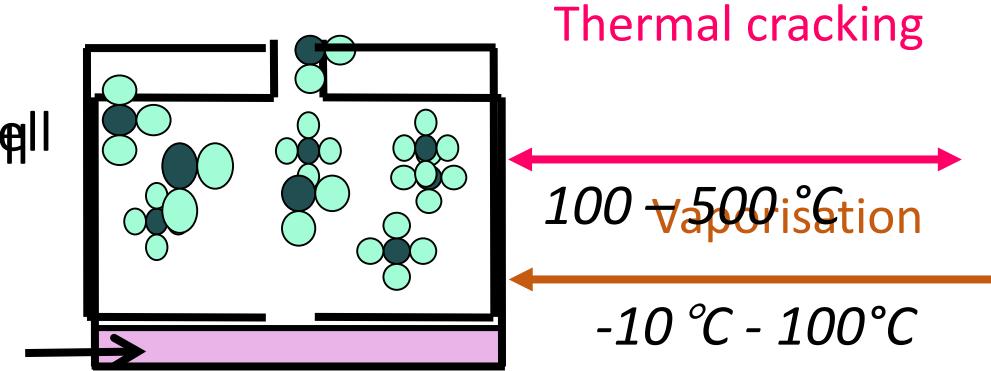
Mass Spectrometer



$$P_i S_i = I_i T$$

Evaporation cell

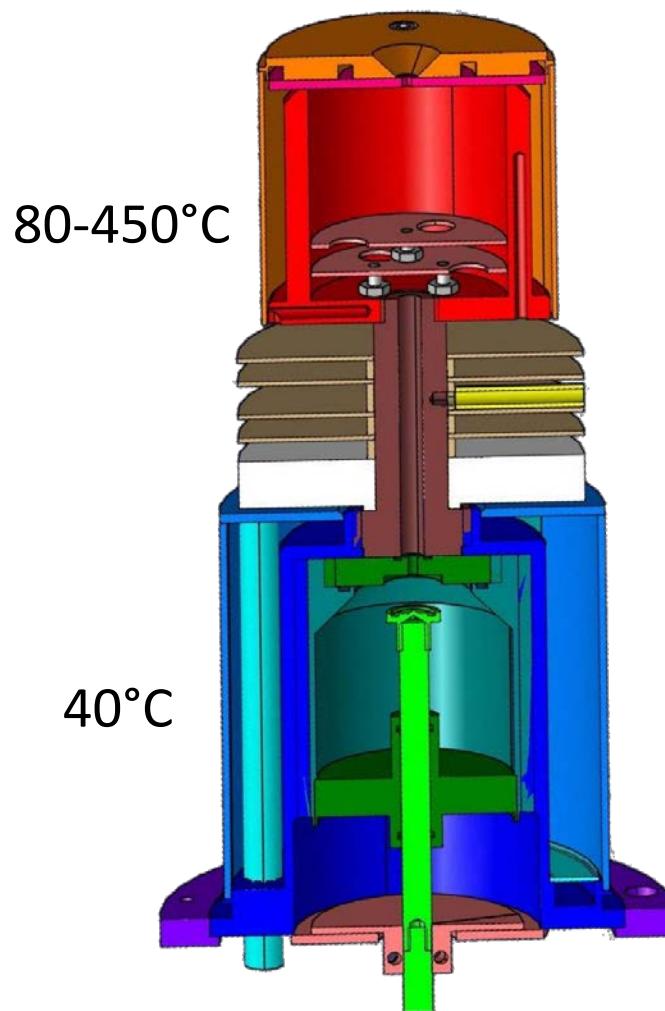
Molecular Sample



ALD deposition zone

Knudsen Cell Mass Spectrometry adapted to Molecular precursor

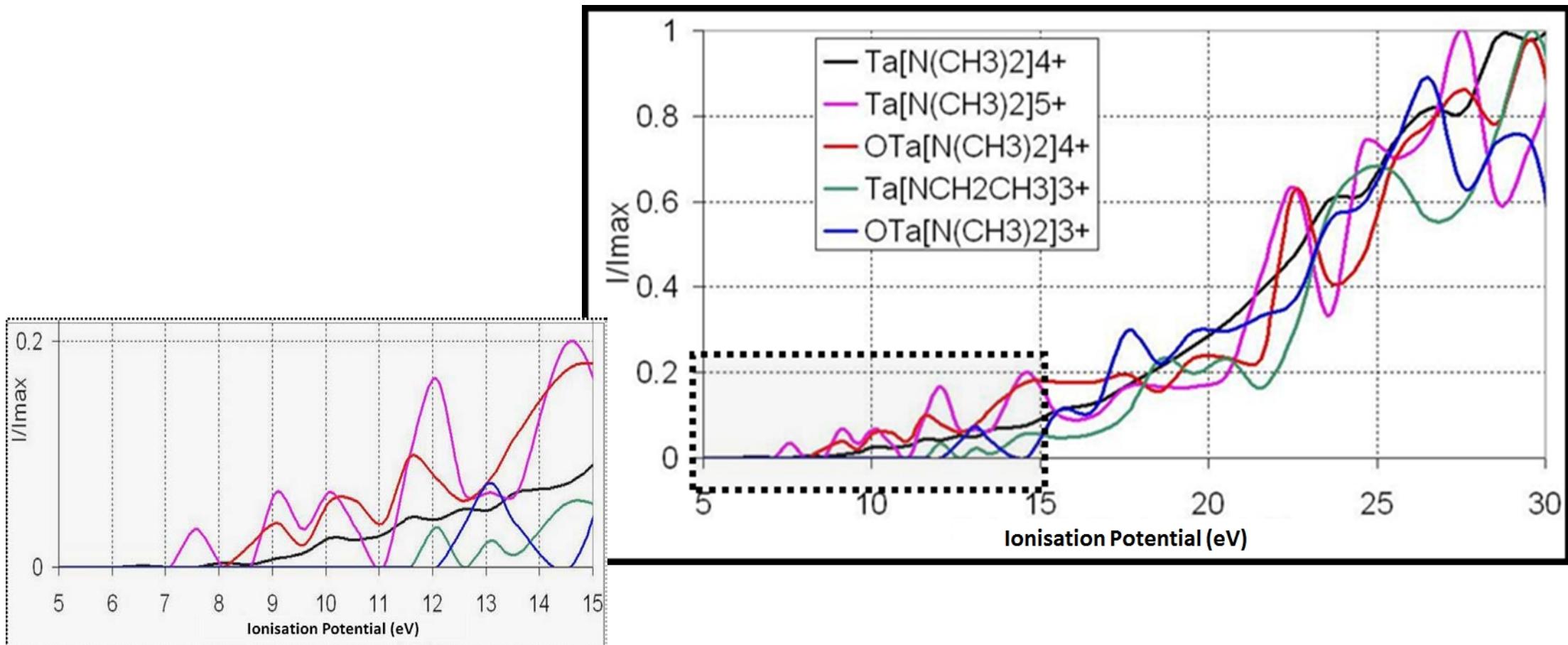
Looking for Oxygen origin: developed device



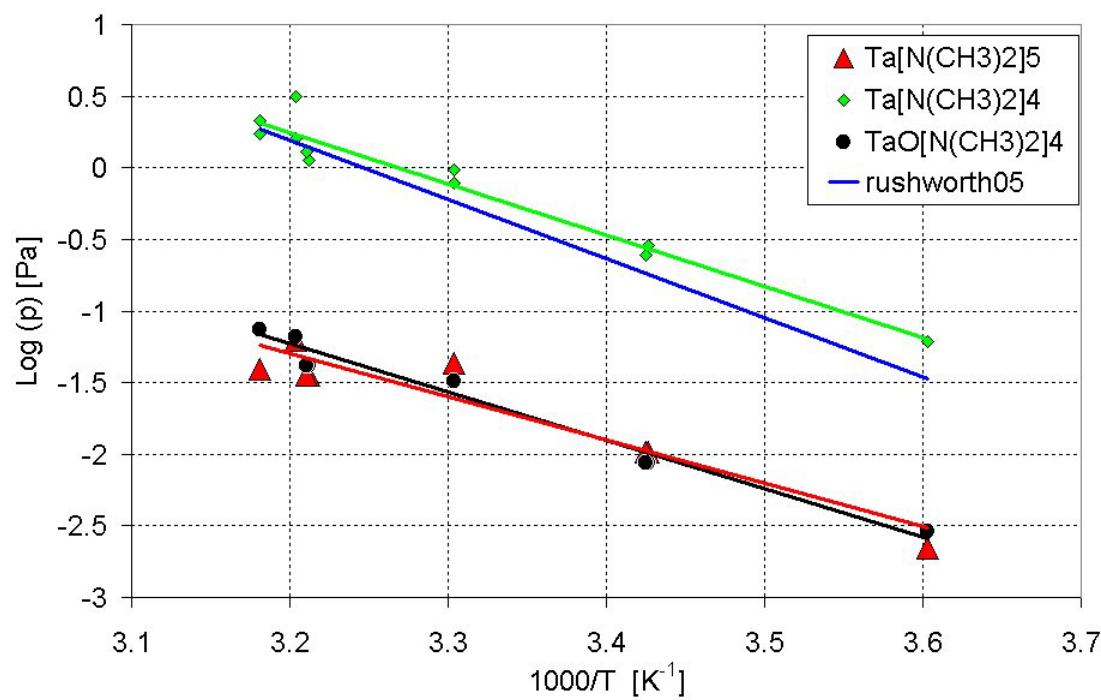
Looking for Oxygen origin

Target ions: O- containing ions; metallic impurities (Al, Li, Na...)

21 observed but only 5 with concentration > 1%



PDMAT vaporisation



Gaseous phase = $\text{Ta}[\text{NMe}_2]_4$; $\text{Ta}[\text{NMe}_2]_5$; $\text{OTa}[\text{NMe}_2]_4$

Me= CH₃

PDMAT Thermal behaviour

Vaporisation

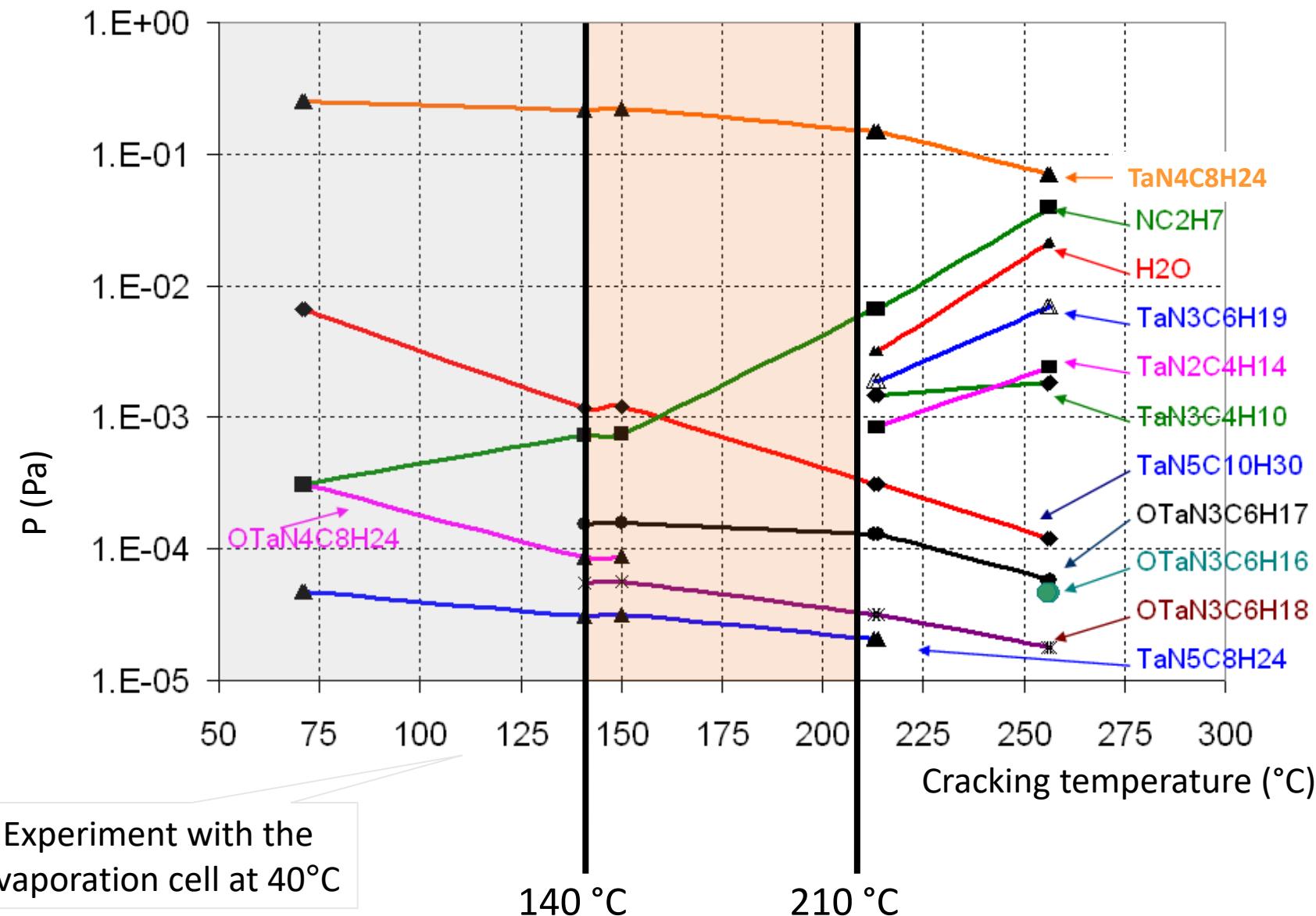
 $\text{Ta}[\text{NMe}_2]_4$ $\text{Ta}[\text{NMe}_2]_5$ $\text{OTa}[\text{NMe}_2]_4$

Cracking

Target Molecules:

 $\text{Ta}[\text{NMe}_2]_4, \text{ Ta}[\text{NMe}_2]_5, \text{ OTa}[\text{NMe}_2]_4$ $\text{Ta}[\text{NMe}_2]_3, \cdot\text{NTa}[\text{NMe}_2]_4, \text{ MeN}\cdot\text{Ta}[\text{NMe}_2]_3,$ $\text{Ta}[\text{NMe}_2]_2, \text{ Ta}[\text{NMe}_2].....$ $\text{HNMe}_2, \text{ Me}, \text{ H}_2\text{O}, \text{ C}_2\text{H}_4.....$

PDMAT Thermal behaviour



Looking for Oxygen origin: PDMAT for TaN deposition

❑ PDMAT Vaporisation:

- ❑ Gaseous phase: $\text{Ta}[\text{N}(\text{CH}_3)_2]_4$, $\text{Ta}[\text{N}(\text{CH}_3)_2]_5$ and $\text{OTa}[\text{N}(\text{CH}_3)_2]_4$
- ❑ Not congruent vaporization: $\text{Ta}[\text{N}(\text{CH}_3)_2]_5$ is not the major molecule originated from the vaporization

❑ PDMAT Thermal behavior:

- ❑ $\text{Ta}[\text{N}(\text{CH}_3)_2]_4$ (g) (=Ta^{+IV}) is present till 250°C but decomposes at low temperature, 150°C
- ❑ Many gaseous decomposition products from 150 °C
- ❑ Presence of oxygen in the gas phase

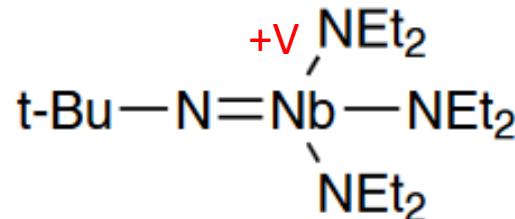
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- Stability nitrides vs oxides
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- Metallic Precursors: halides, non halide molecular precursors with C-M or N-M bonds (where M o.s. \geq +III)
- Reactive gases (Reducing gases): H₂, NH₃, hydrazine N₂H₄, Zn +++
 - use of additional plasma assistance

Fabrication strategies: example of NbN

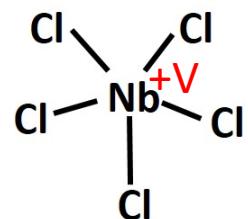
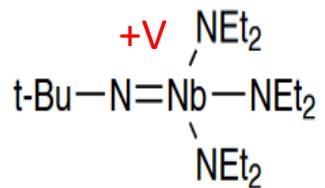
Metallic precursors: non halides molecular precursors with C-M ou N-M bonds
(Oxidation state M ≥ +III)



Metallic precursor Nb^{+V} : TBTDEN

NIOBIUM (Compounds)			
41-0450 NEW HAZ	(t-Butylimido)tris(diethylamino)niobium(V), min. 98% (210363-27-2) C ₁₆ H ₃₉ N ₄ Nb; FW: 380.41; yellow to brown orange, low melting solid air sensitive, moisture sensitive	t-Bu— $\overset{\text{NEt}_2}{\text{N}}$ =Nb— $\underset{\text{NEt}_2}{\text{N}}$	1g 5g
93-4104 amp HAZ	Niobium(V) ethoxide (99.9+-Nb) (3236-82-6) Nb(OC ₂ H ₅) ₅ ; FW: 318.22; yellow to orange liq.; m.p. 6°; b.p. 142°/0.1mm; d. 1.32 moisture sensitive		5g 25g
41-5300 HAZ	Pentakis(dimethylamino)niobium(V), 99% (19824-58-9) Nb[N(CH ₃) ₂] ₅ ; FW: 313.29; purple-black xtl. moisture sensitive		1g 5g
41-7000 HAZ	Tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)niobium(IV), 99% [Nb(TMHD) ₄] (41706-15-4) Nb(C ₁₁ H ₁₉ O ₂) ₄ ; FW: 826.00; black xtl.; m.p. 219-220°; b.p. dec. 325°		1g 5g 25g
41-0510 HAZ	Trihydridobis(pentamethylcyclopentadienyl)niobium(V) (93558-77-1) [(CH ₃) ₅ C ₅ H ₅] ₂ NbH ₃ ; FW: 366.38; light-brown pwdr. air sensitive		100mg 500mg

NbN: litterature

1. NbCl₅ and NH₃NbCl₅ + NH₃T_c = 10 KGoal T_c > 9 K*L. Hiltunen et al, Thin Solid Films, 1988*NbCl₅ + Zn + NH₃ improved T_c from 3 to 5 K*T. Proslier et al, ECS Trans., 2011*2. TBTDEN and H₂ plasmaTBTDEN + H₂ plasma

10 K O: 11 at. %

*M. Ziegler et al, Supercond. Sci. Technol., 2013*TBTDEN + H₂ plasma

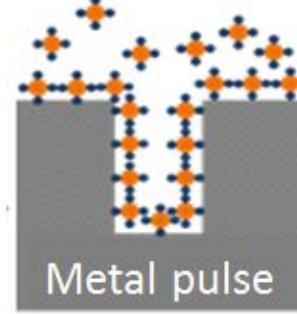
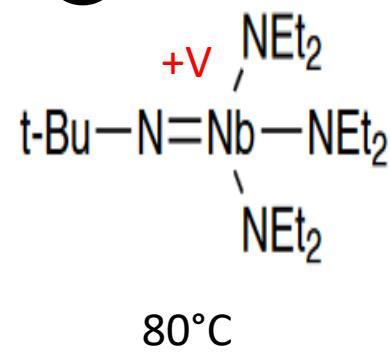
13.8 K O: 11 at. %

*M. Ziegler et al, IEEE Trans. Applied Superconductivity, 2017*TBTDEN + H₂ / N₂ plasma

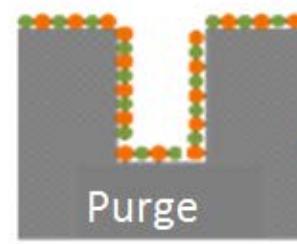
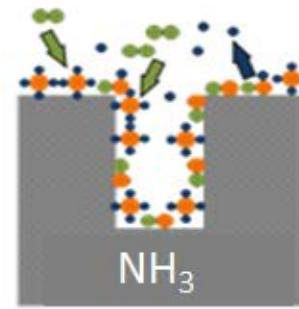
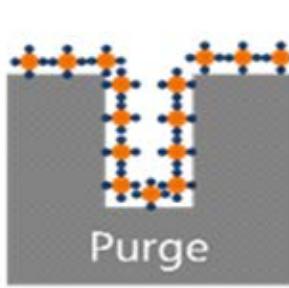
13.7 K O: 15 at. %

*M. J. Sowa et al, J. Vac. Soc., 2017*Best value of T_c for TBTDEN PEALD deposited films

Fabrication strategie #1: Thermal ALD

1

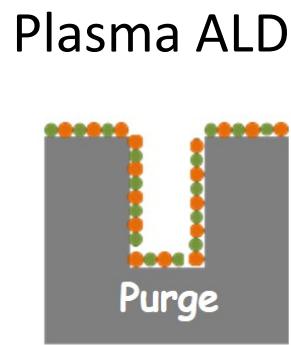
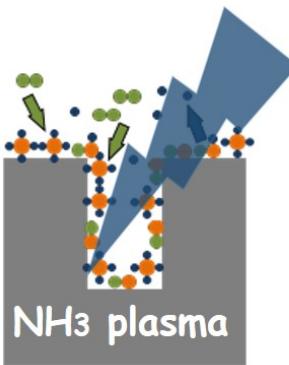
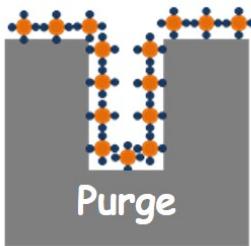
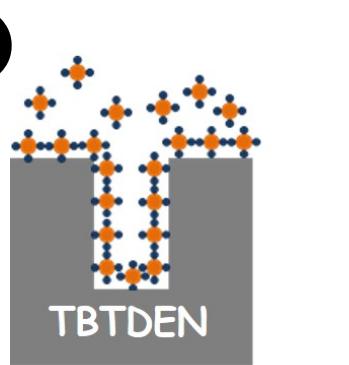
Thermal-ALD

 Nb^{III}

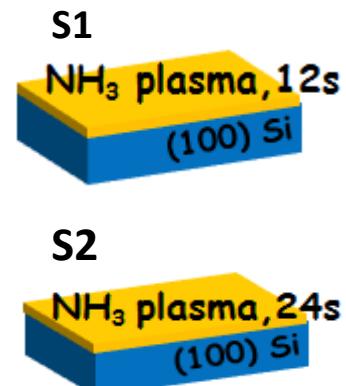
No deposition

Fabrication strategies #2 and 3: plasma ALD w/o & w supercycle

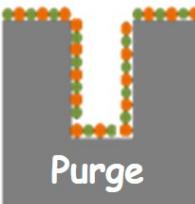
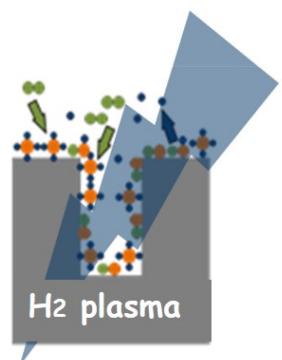
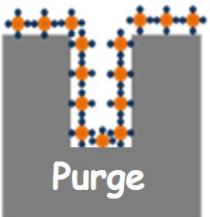
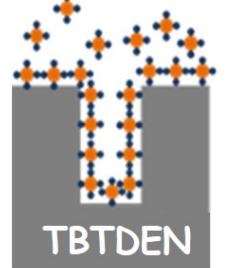
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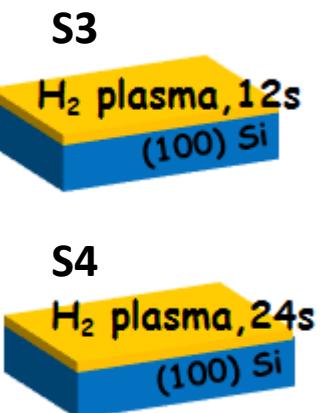
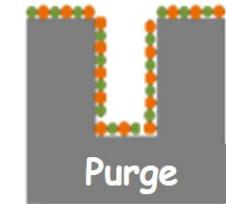
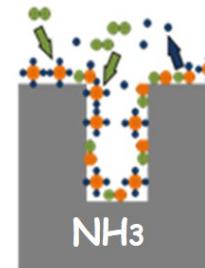
Plasma ALD



3



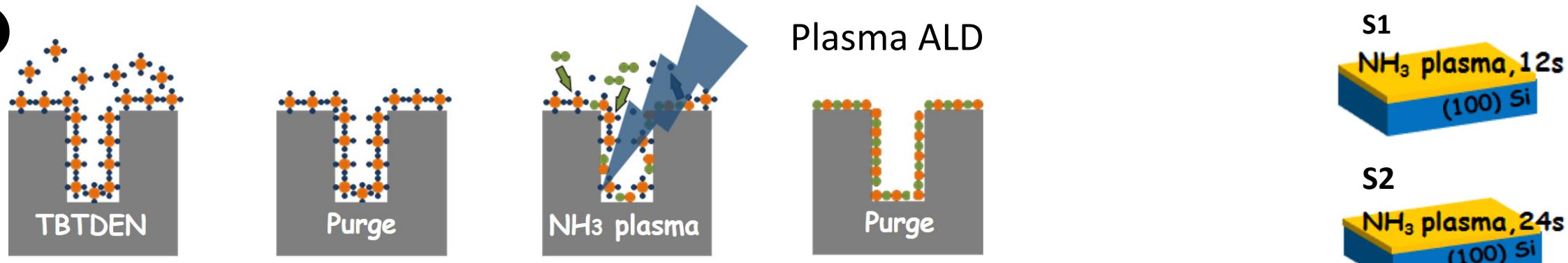
Plasma ALD with supercycle



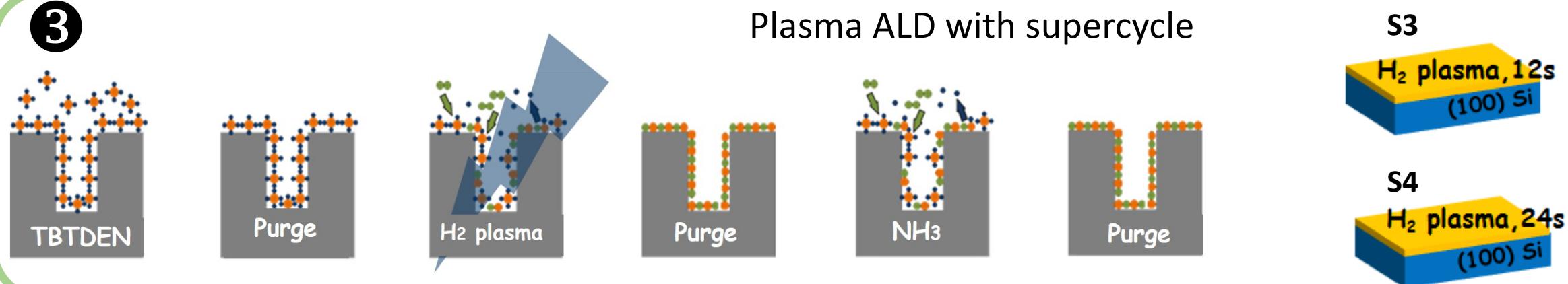
New deposition strategy with supercycle uses hydrogen to break TBTDEN ligands and facilitates surface chemical reactions with NH₃

Fabrication strategies #2 and 3: plasma ALD w/o & w supercycle

2



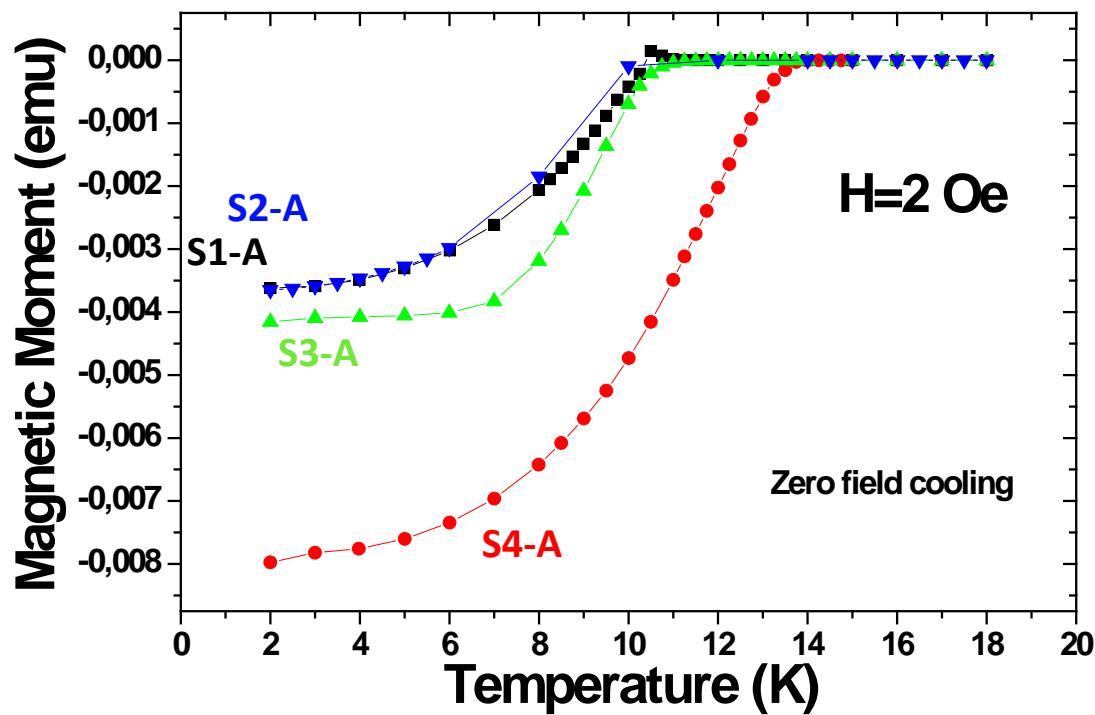
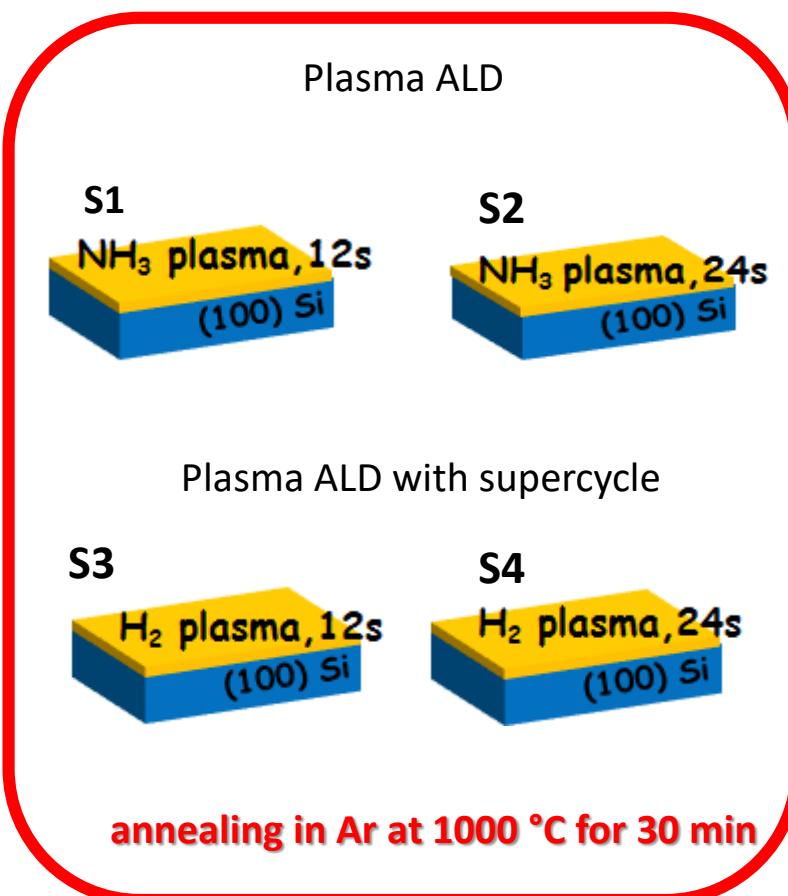
3



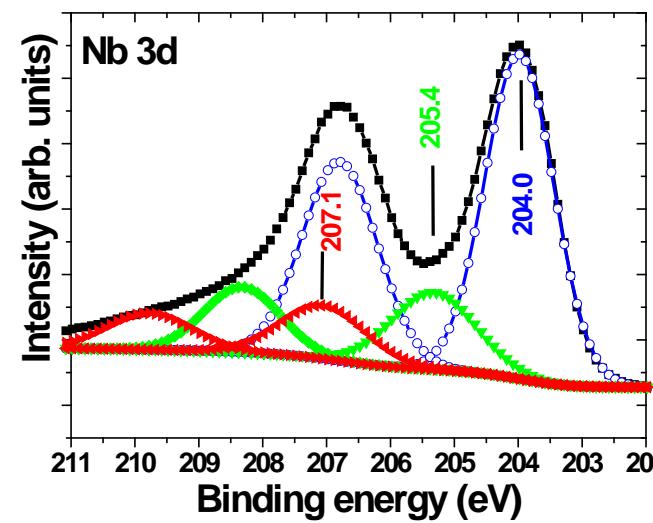
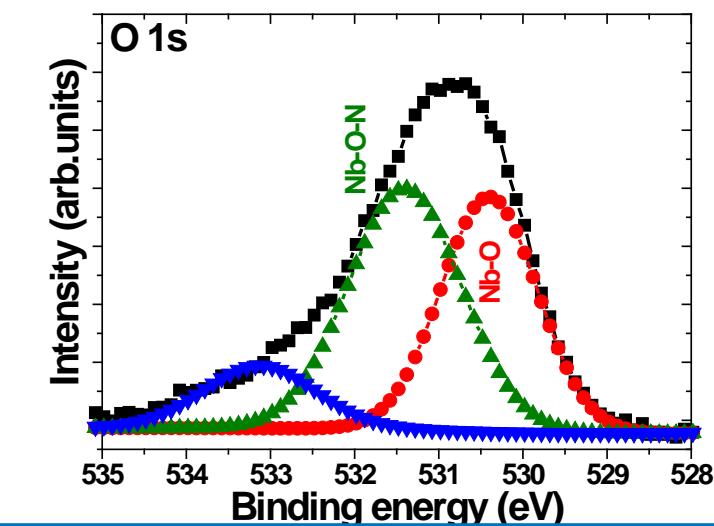
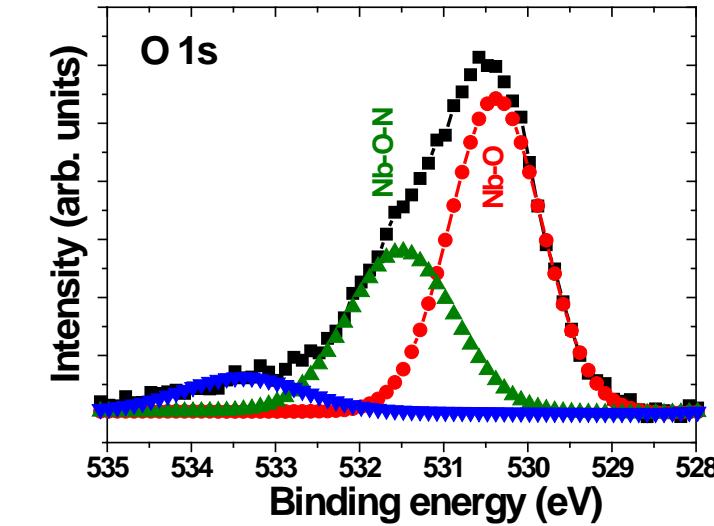
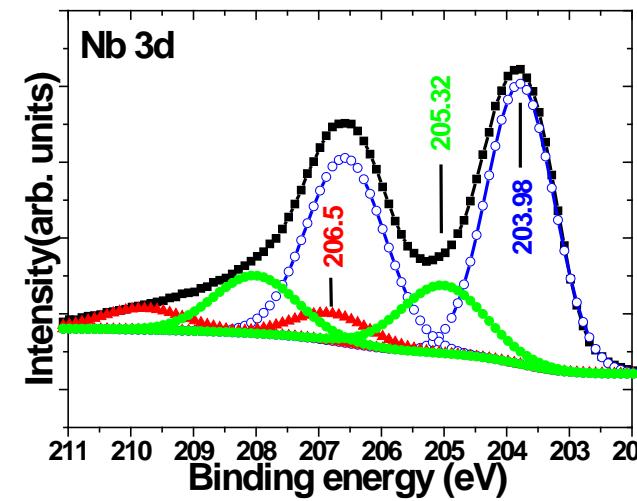
Add best annealing step: annealing in Ar at 1000 °C for 30 min

Films superconducting properties

50 nm thick layers

All the samples have a $T_c > 9.2$ KT_c up to 13.8 K for S4 conditions after annealing

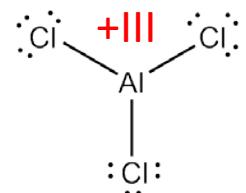
Films chemical properties

As grown**Annealed at 1000°C,
30 min.**

Reduction of Nb-O, increase of Nb-O-N contribution after annealing

AlN: litterature

1. AlCl_3 and NH_3

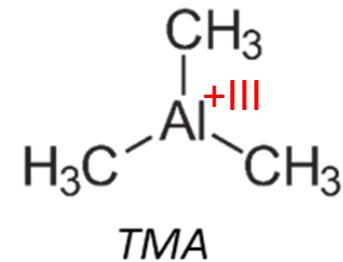


M. Alevli et al, J. Cryst. Growth, 2011

D. Riihelä et al, Chem. Vap. Deposit., 1996
References in

$T > 400\text{-}500^\circ\text{C}$

2. TMA and H_2 plasma



TMA + NH_3 plasma

TMA+ H_2 / N_2 plasma

N. Nepal et al, Appl. Phys. Lett., 2013

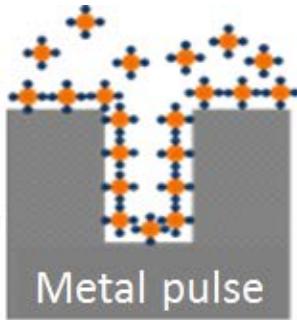
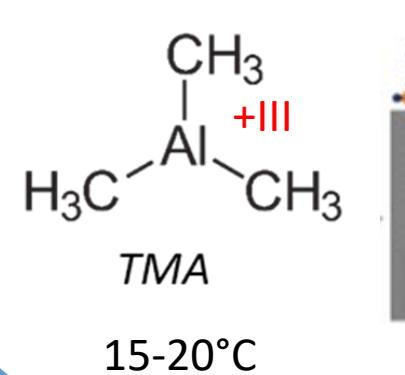
S. Banerjee et al, Phys. Status Solidi, 2015

P. Motamed et al, J. Cryst. Growth, 2015

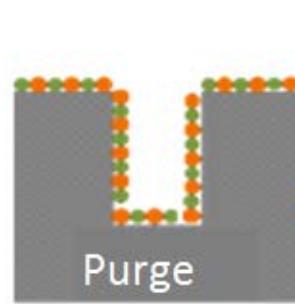
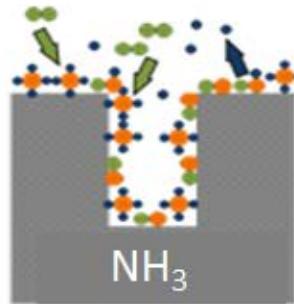
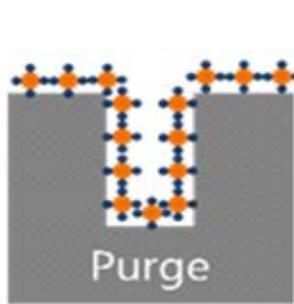
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N containing species plasma?

Fabrication strategies: AlN

1

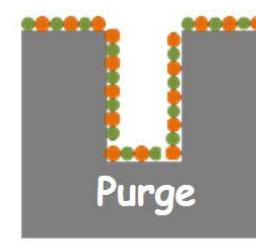
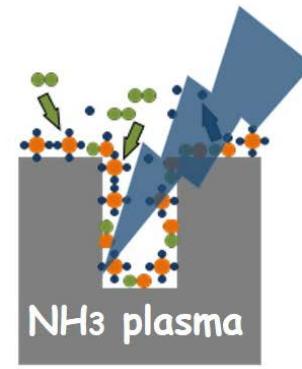
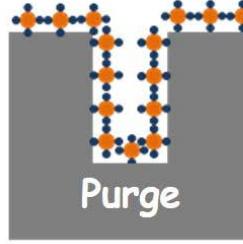
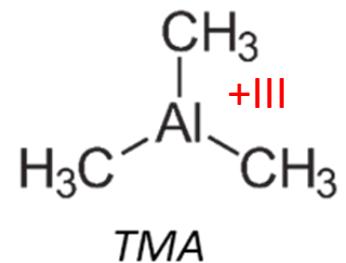
Thermal-ALD



NH₃ reacts with TMA at T> 350°C
TMA decomposes at T>375°C
Deposition around 375 °C

Fabrication strategies: AlN

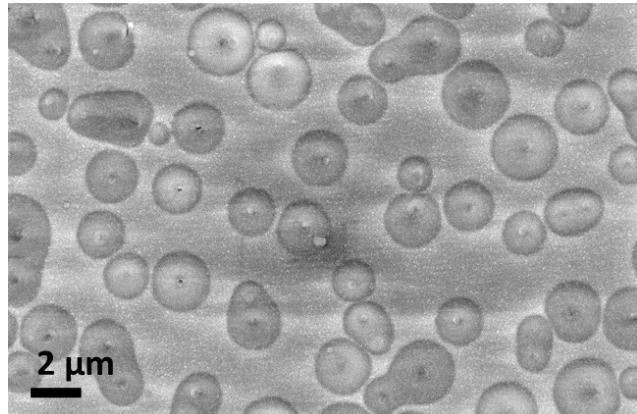
2



+III
AlN

15-20°C

P = 2800 W

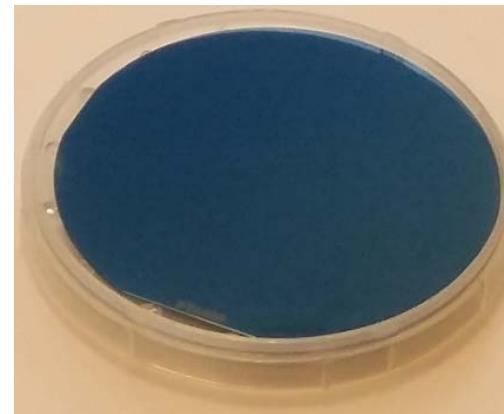
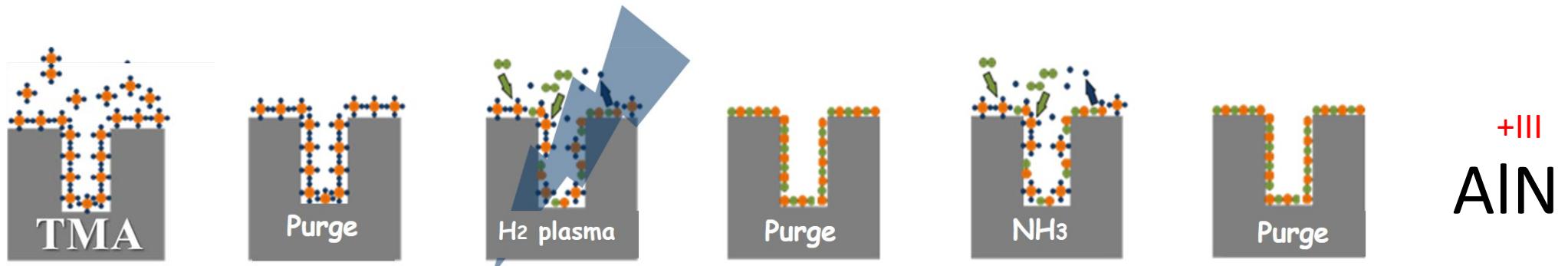


NH₃ is too much reactive and
AlN surface is etched

Temperature : 350°C

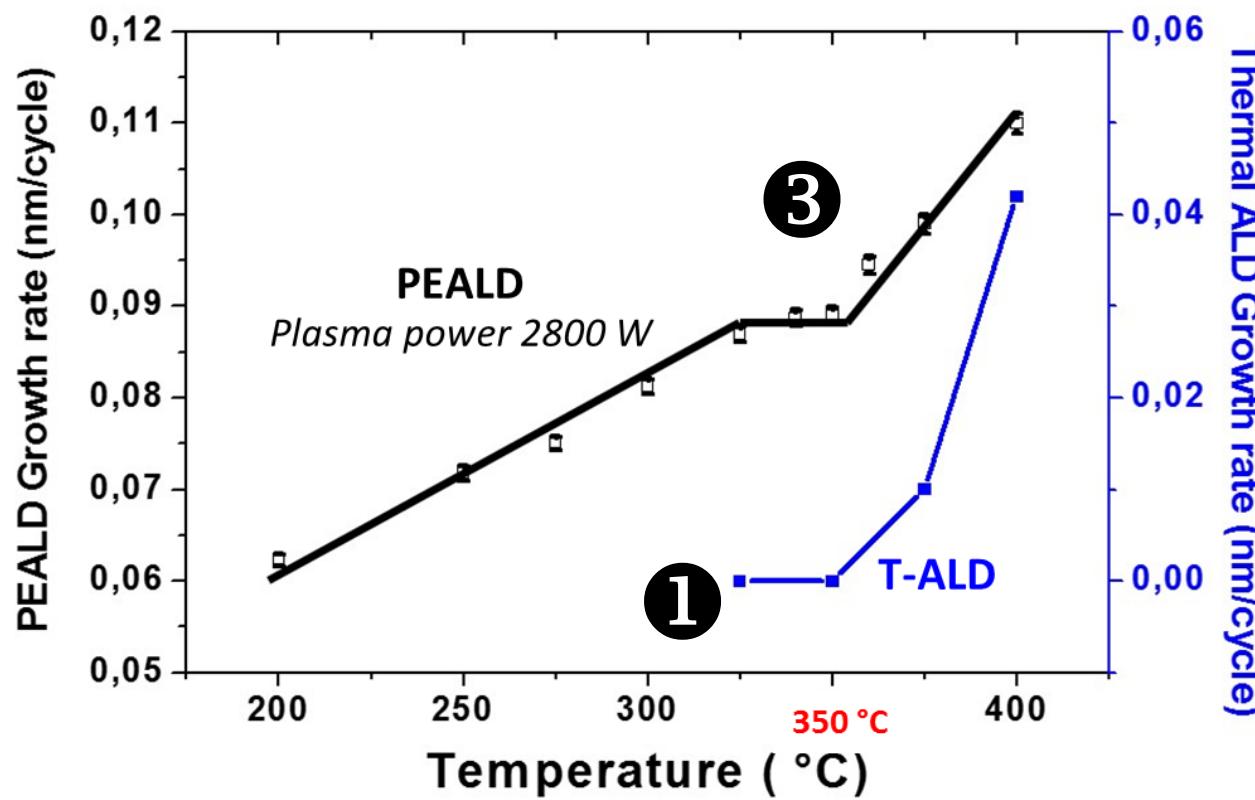
Fabrication strategies: AlN

3



Plasma H₂ : breaks the metal ligand bond in TMA and favors surface reactions
NH₃ : nitriding agent at temperatures below 400°C

Process optimisation : T



③ TMA / purge / plasma H₂ / purge / NH₃ / purge

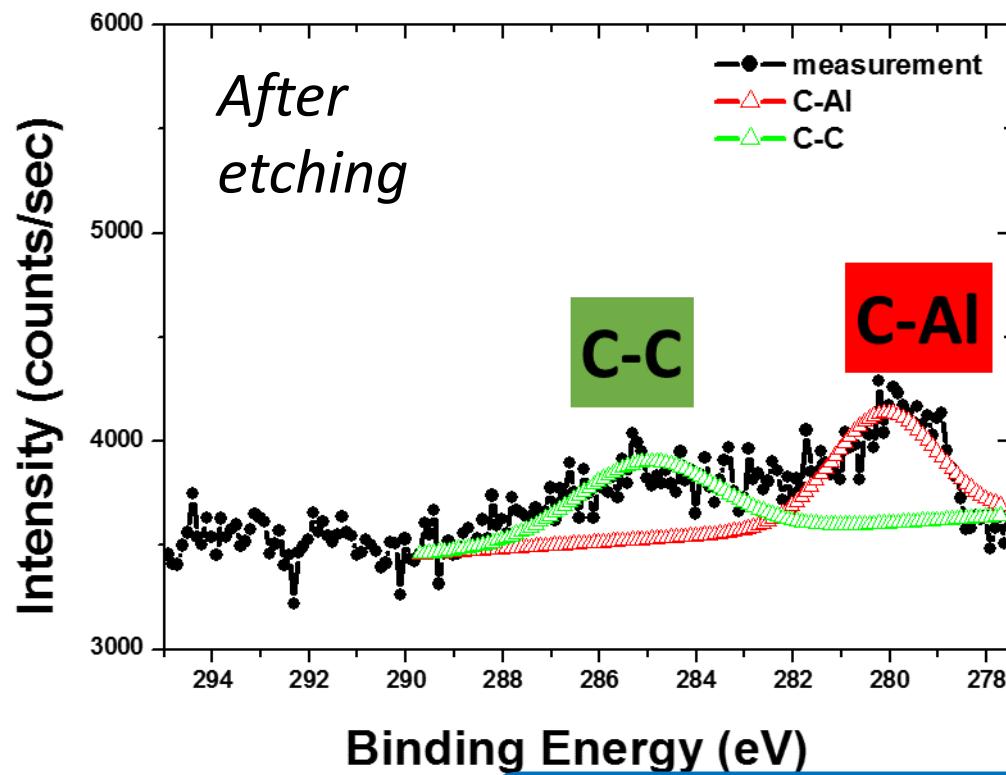
① TMA / purge / NH₃ / purge / Thermal ALD

PEALD: ALD window between 325 °C – 350 °C
Thermal ALD : No ALD window

Films chemical properties

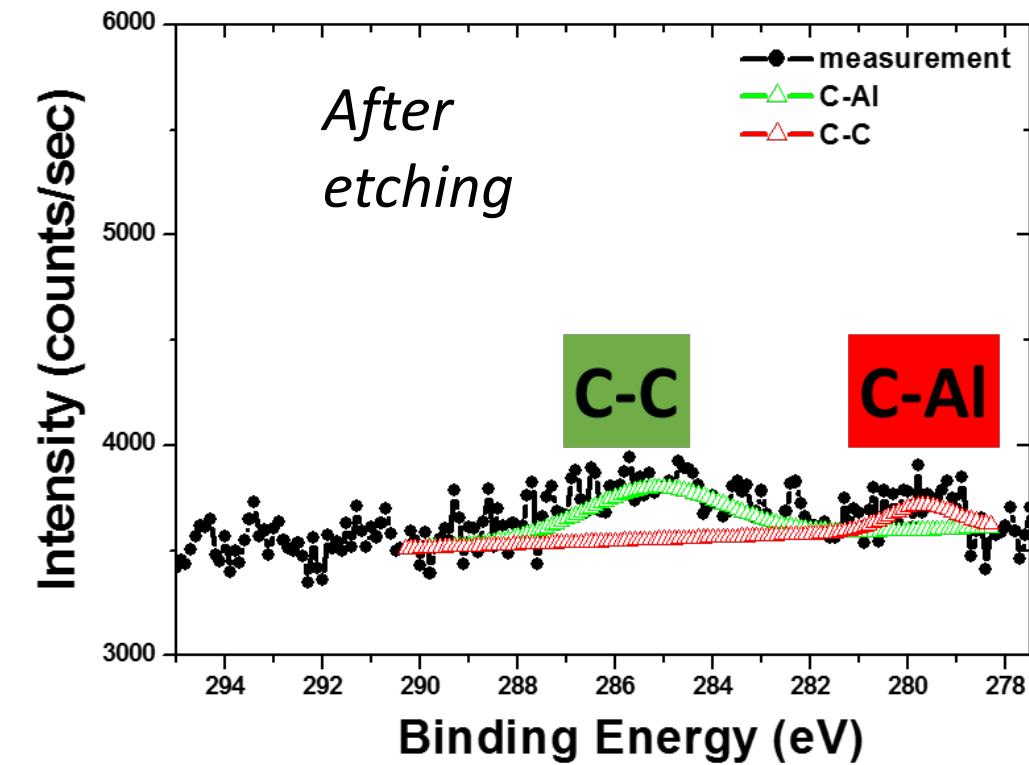
① TMA / purge / NH₃ / purge
Thermal ALD

T_{substrate} : 400°C



③ TMA / purge / plasma H₂ / purge / NH₃ / purge

T_{substrate} : 350°C

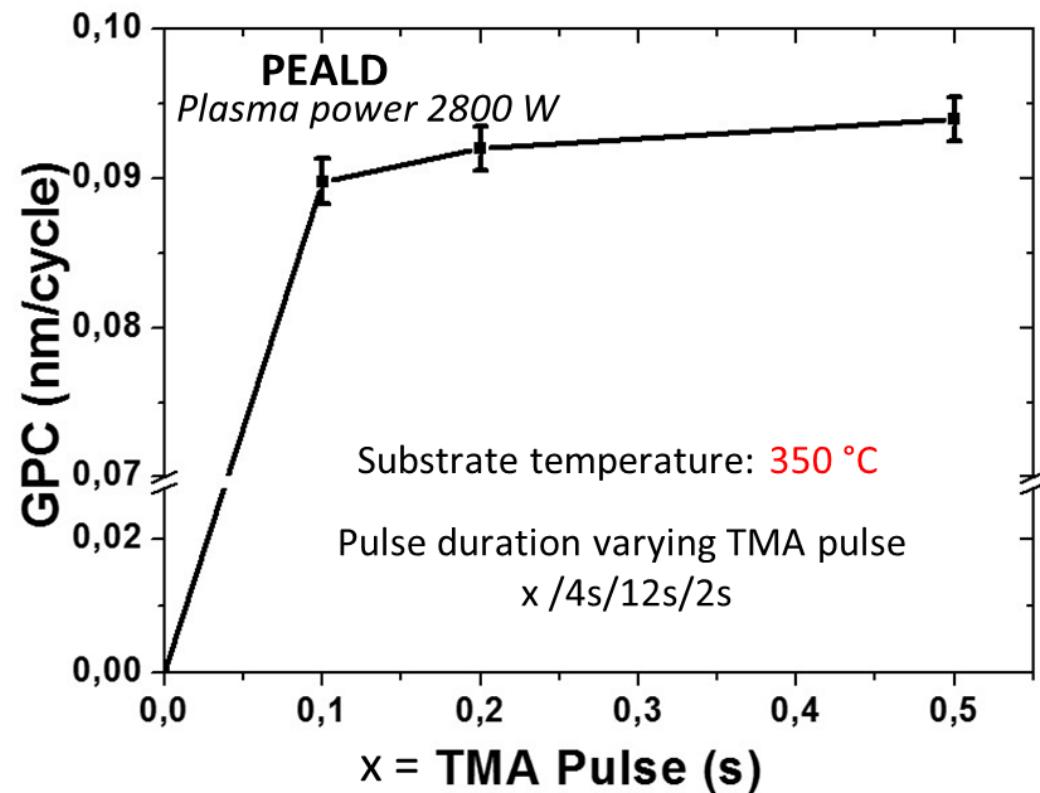


Plasma H₂ is efficient to break Al-CH₃ bonds in TMA

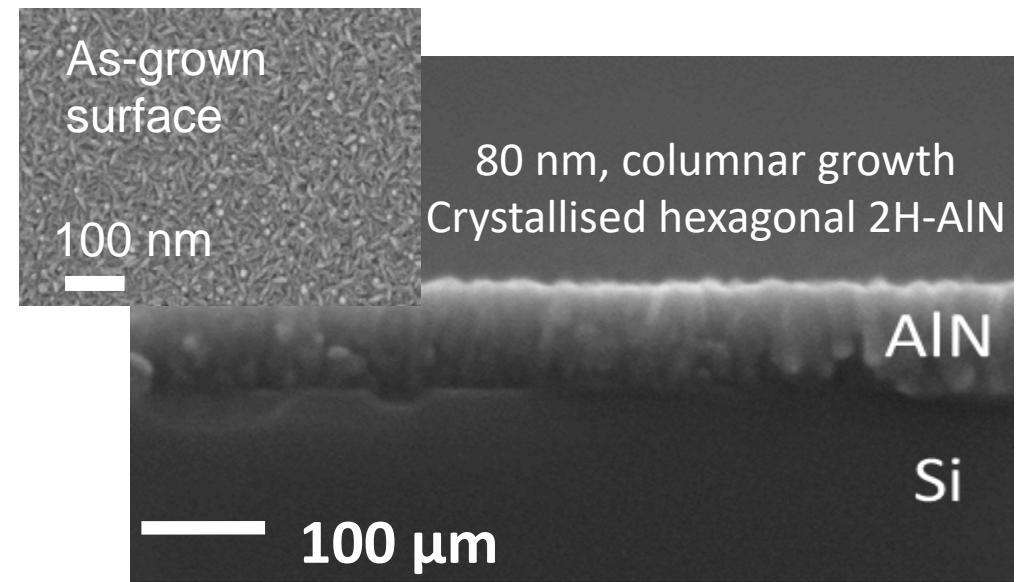
5% C contamination level with thermal ALD

1% C contamination level with PEALD

Process optimisation : TMA pulse duration



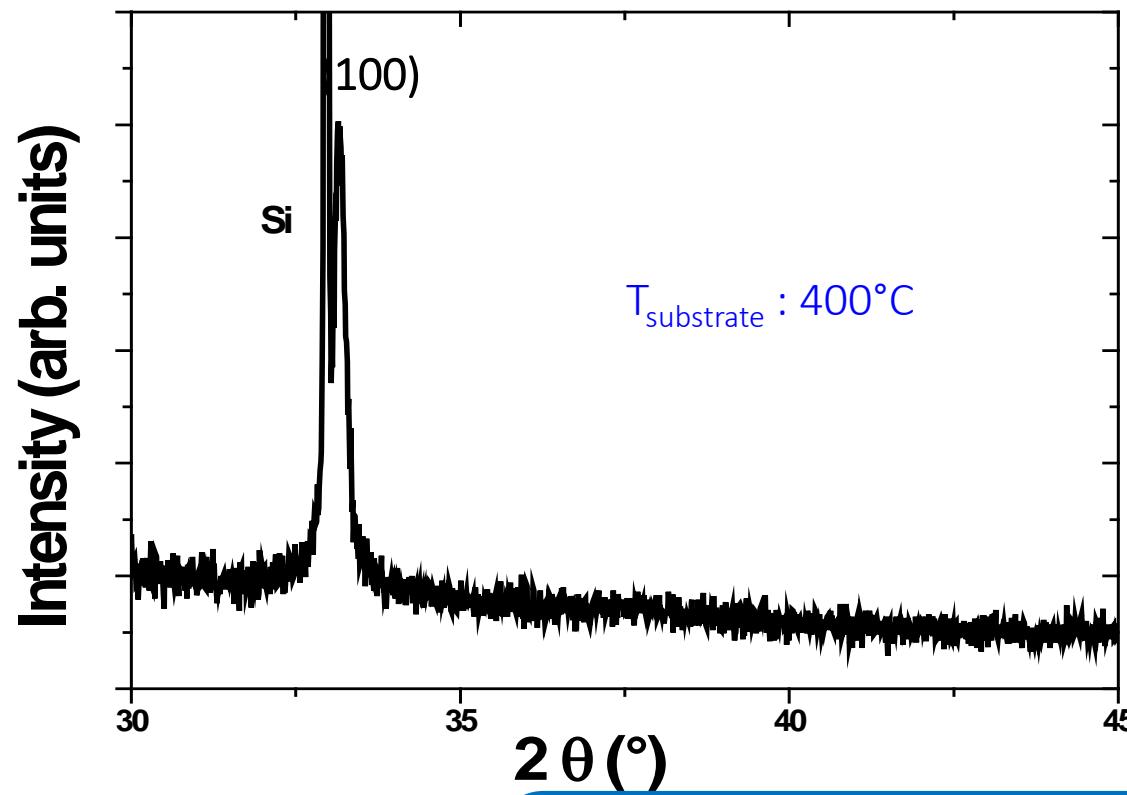
③ TMA / purge / plasma H₂ / purge / NH₃ / purge



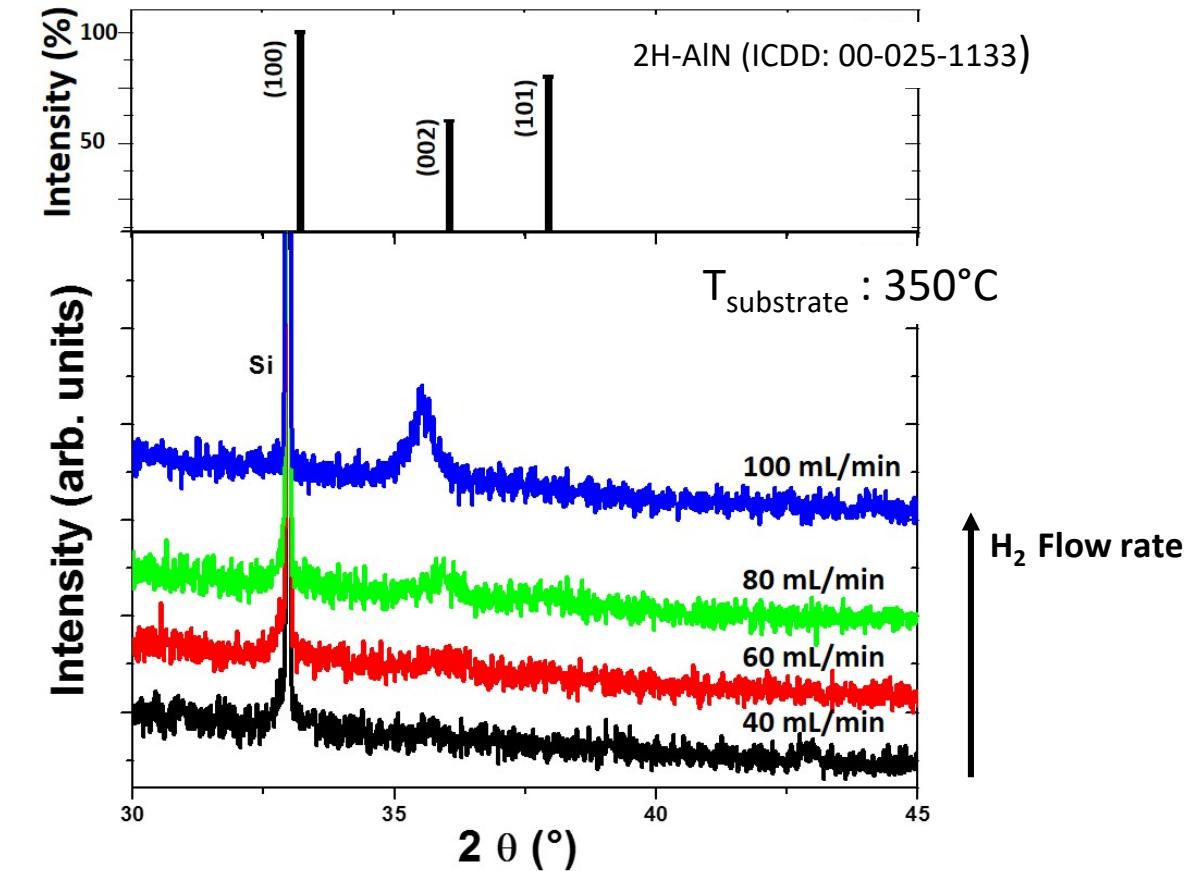
Saturation above 100 ms

Films structural properties

① TMA / purge / NH₃ / purge / Thermal ALD



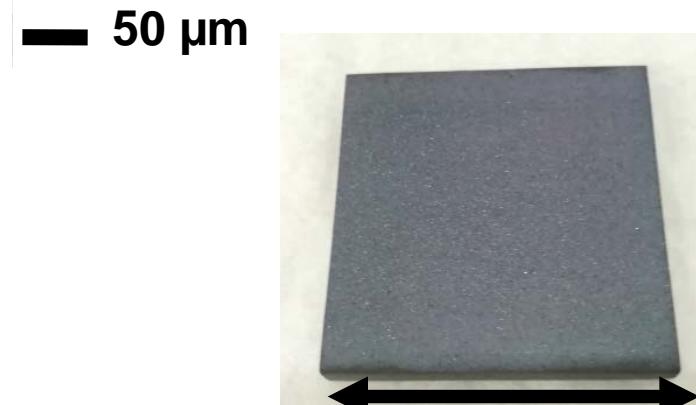
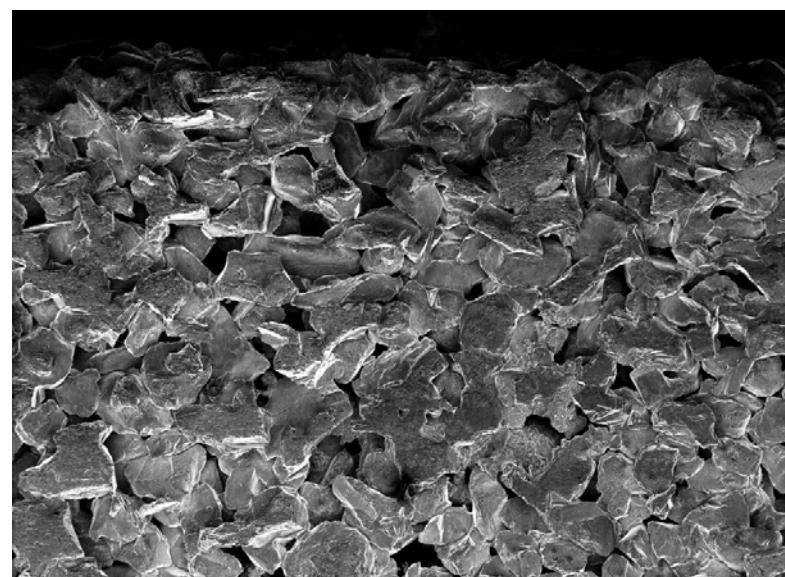
③ TMA / purge / plasma H₂ / purge / NH₃ / purge



Cristallisation –Würtzite phase AlN
 Thermal ALD : preferential orientation (100)
 PEALD: preferential orientation (002)

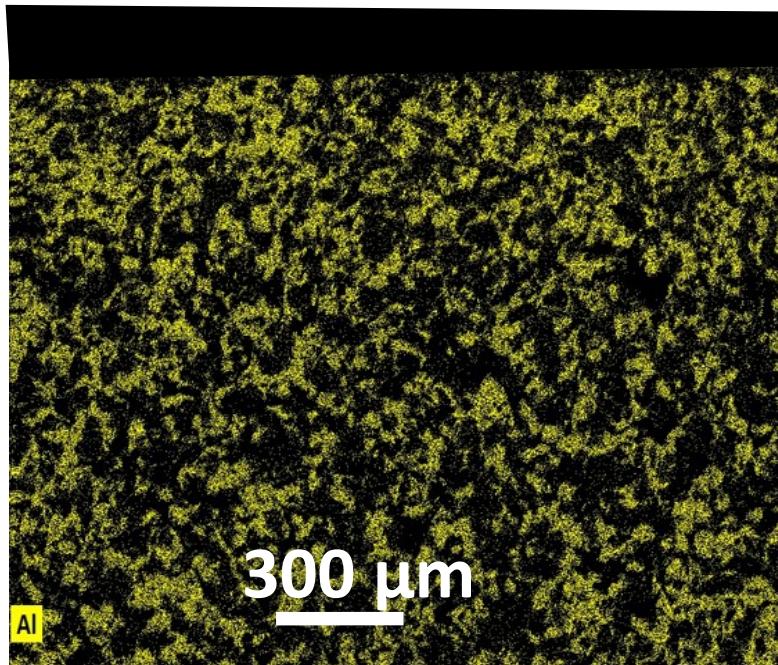
Application- Infiltration porous SiC : pores size 14 μm , 5 mm thickness, 43 % porosity

SiC Substrate

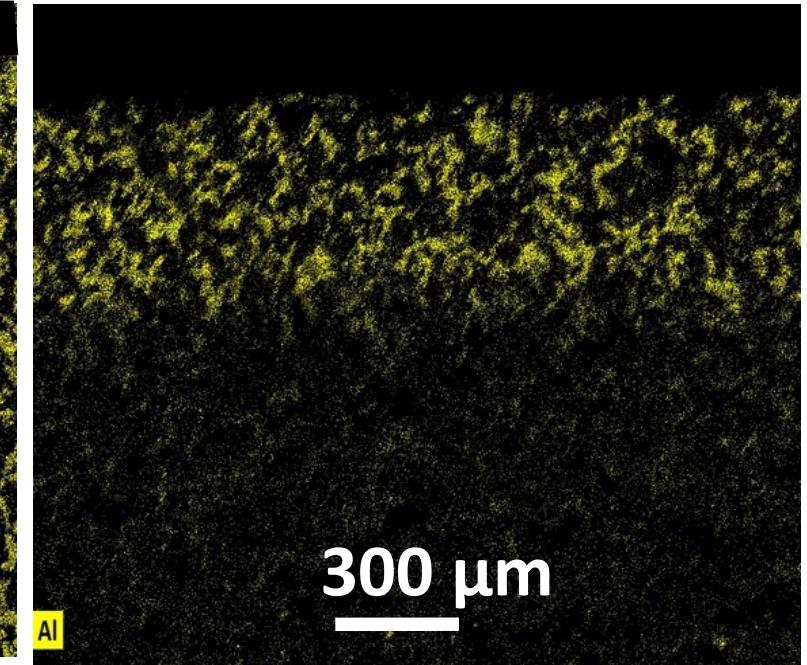


5 cm

Thermal ALD



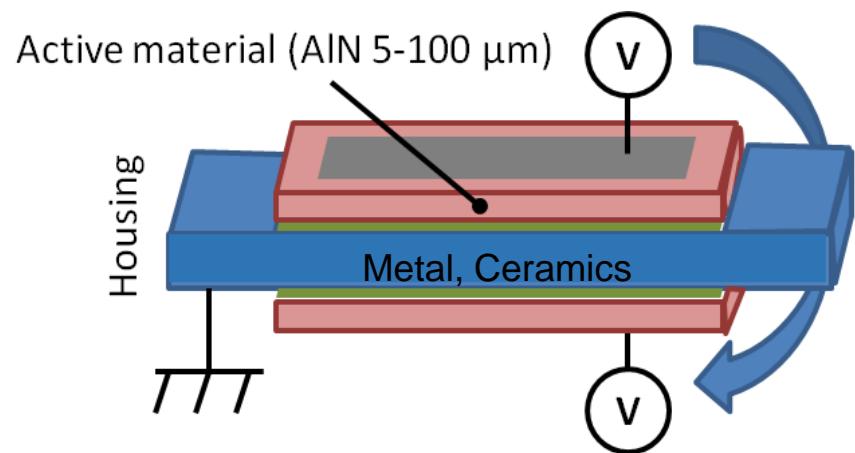
PEALD



3 mm
↑
↓

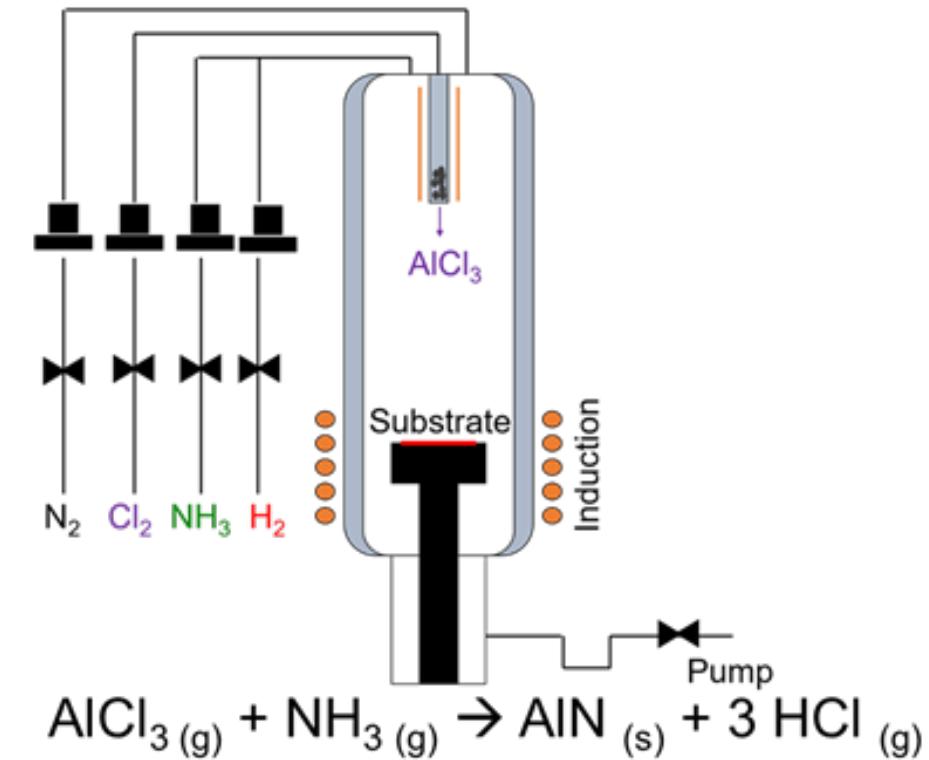
Thermal ALD : infiltration length= 3000 μm – 60%
PEALD infiltration length = 500 μm – 10 %

Application-piezoelectric « smart coatings »



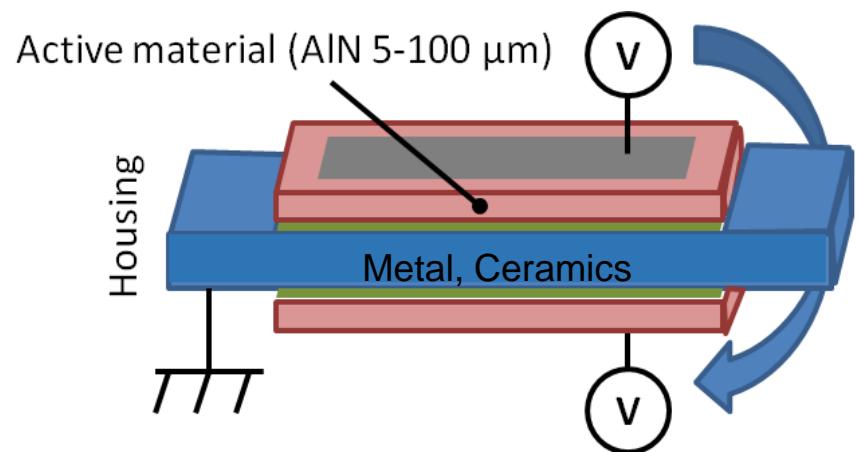
Classic hard coating
Piezoelectric Sensor
Metal, Ceramics

Polycrystalline TiN CVD
(002) AlN CVD
Oriented (002) AlN ALD
TiN by CVD
WC-Co

Chemical Vapor Deposition (CVD)

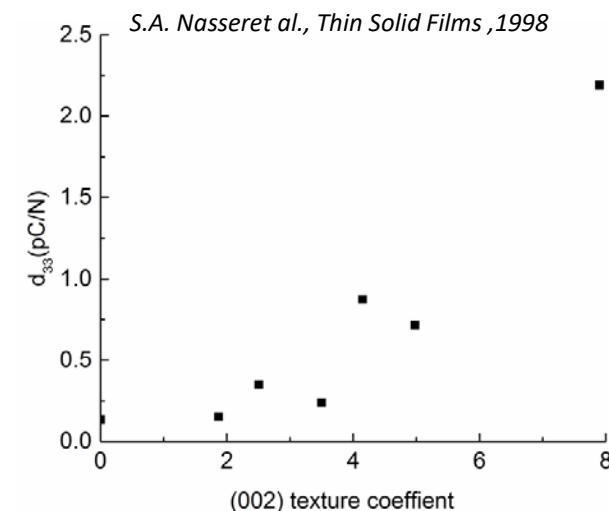
Reaction with substrate

Application-piezoelectric « smart coatings »: coupling ALD/CVD



Classic hard coating
Piezoelectric Sensor
Metal, Ceramics

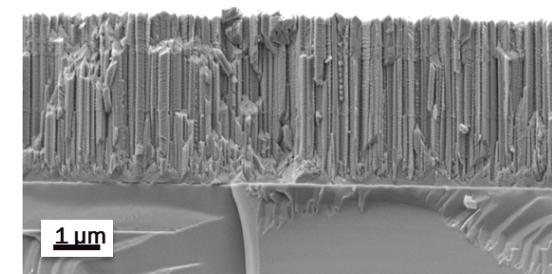
Polycrystalline TiN CVD
(002) AlN CVD
Oriented (002) AlN ALD
TiN by CVD
WC-Co



The higher the (002) texture coefficient is, the higher piezoelectric coefficient is obtained

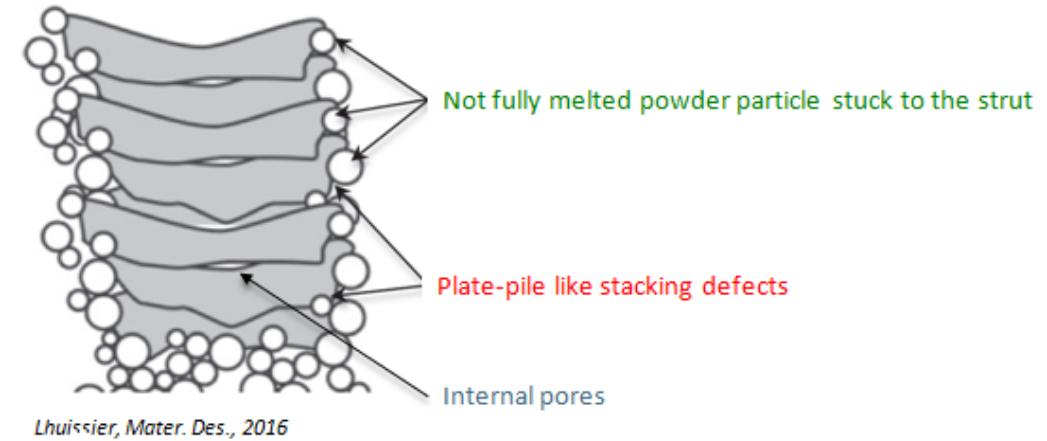
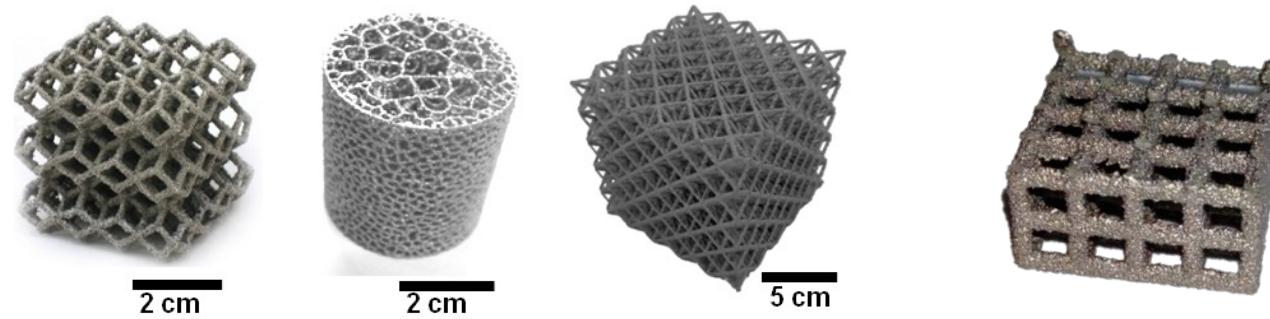
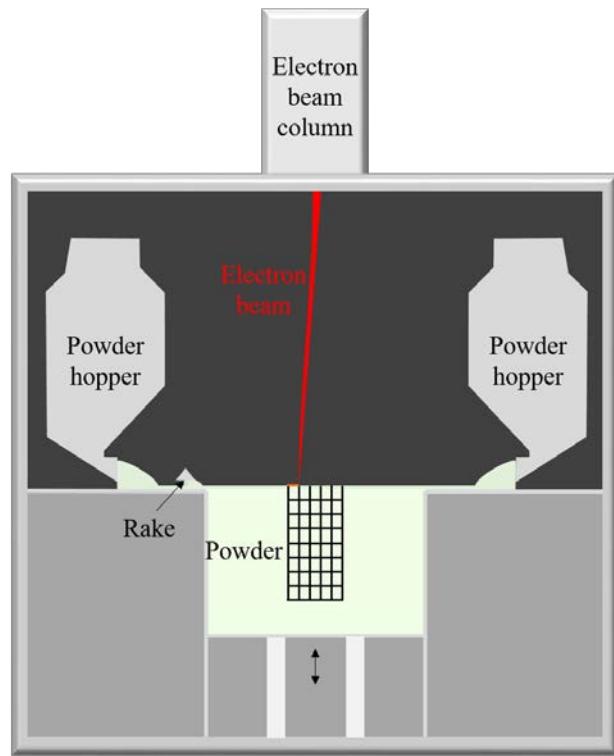
$$d_{33\text{ bulk}} = 6 \text{ pC/N}$$

$$d_{33} = 2.2 \text{ pC/N}$$



Alternative Piezoelectric material with promising properties

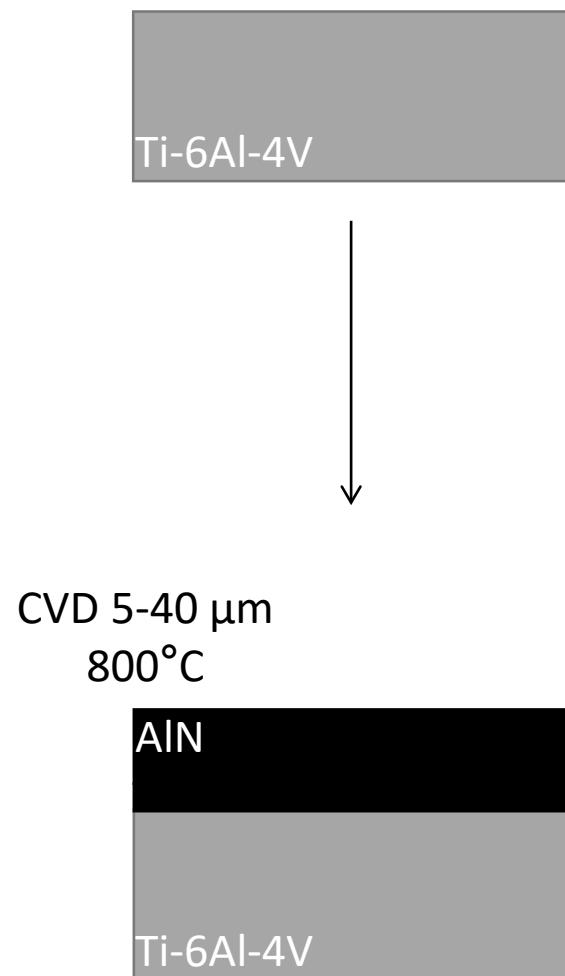
Application: Surface modification of EBM-made 3D Ti-6Al-4V architectures



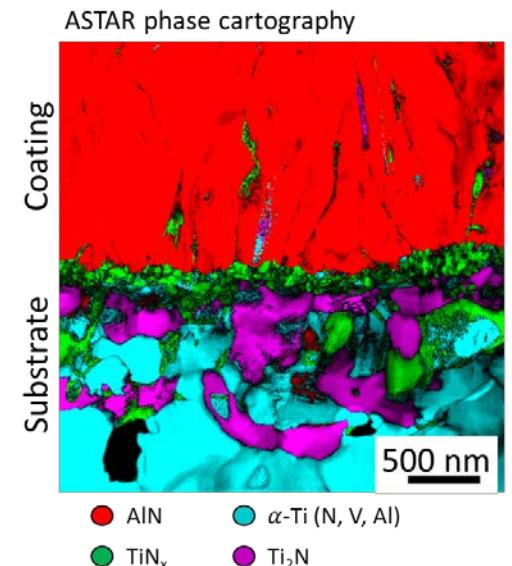
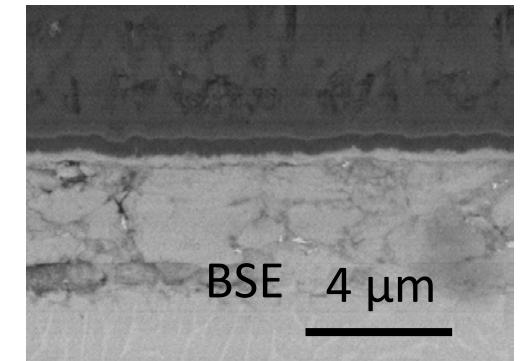
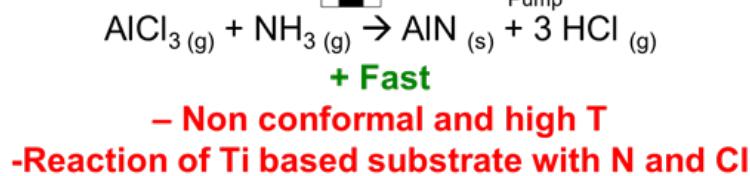
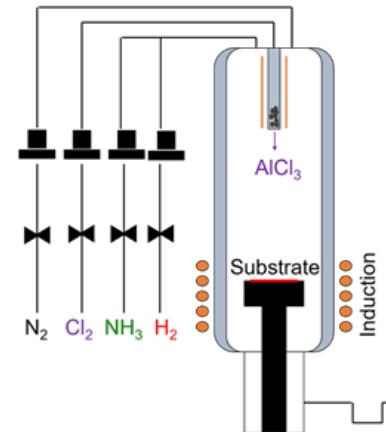
- Possibility to cover surface defects acting as crack initiators
- Decrease of roughness with thick films

Application: Surface modification of EBM-made 3D Ti-6Al-4V architectures

Strategy

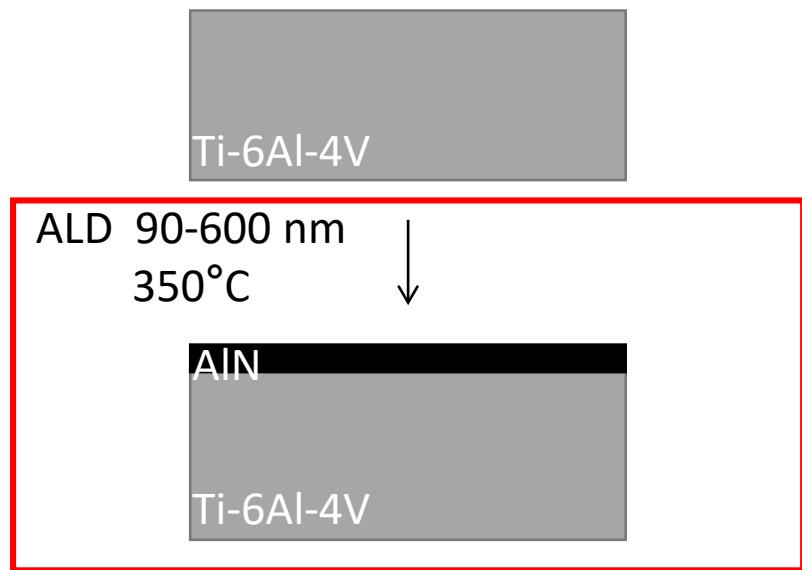


Chemical Vapor Deposition (CVD)



Applications : deposition on of EBM-made 3D Ti-6Al-4V architectures

Strategy



ALD 90-600 nm
350°C

AlN

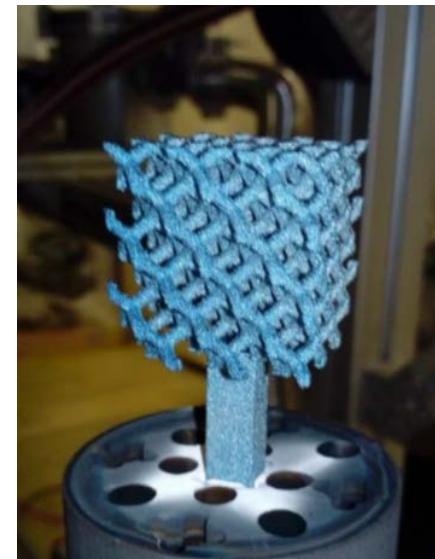
Ti-6Al-4V

CVD 5-40 μm
800°C

AlN

Ti-6Al-4V

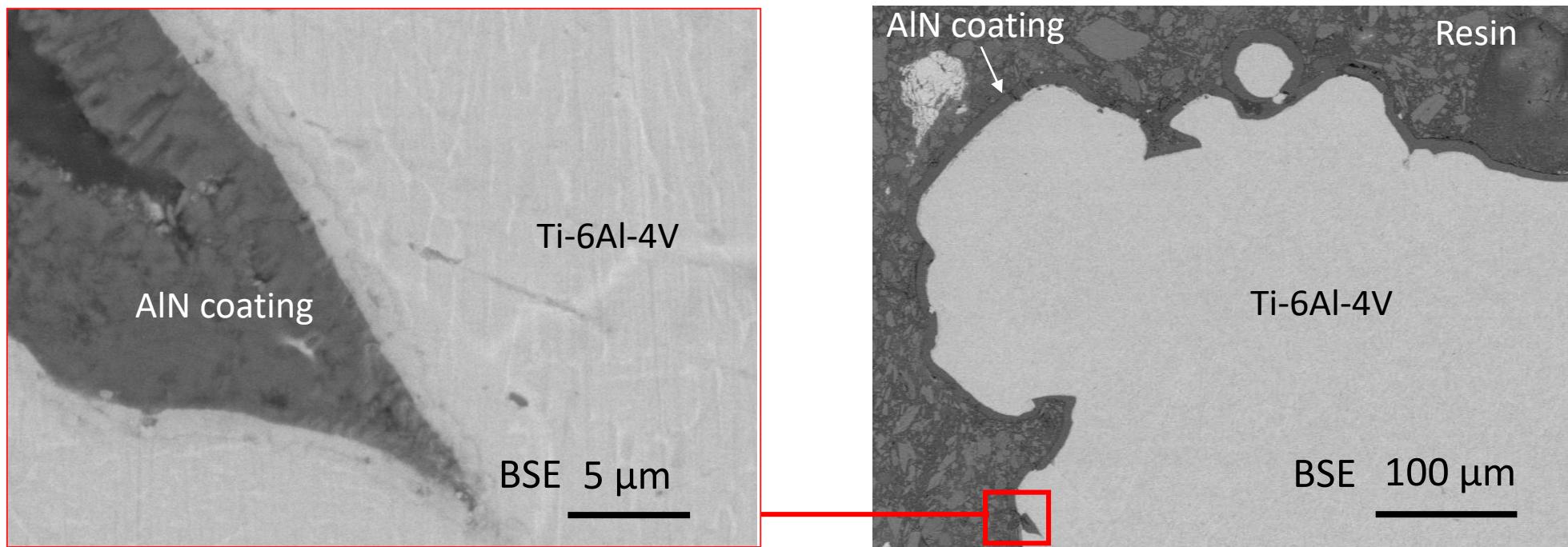
with a 300 nm ALD film



and few microns CVD film

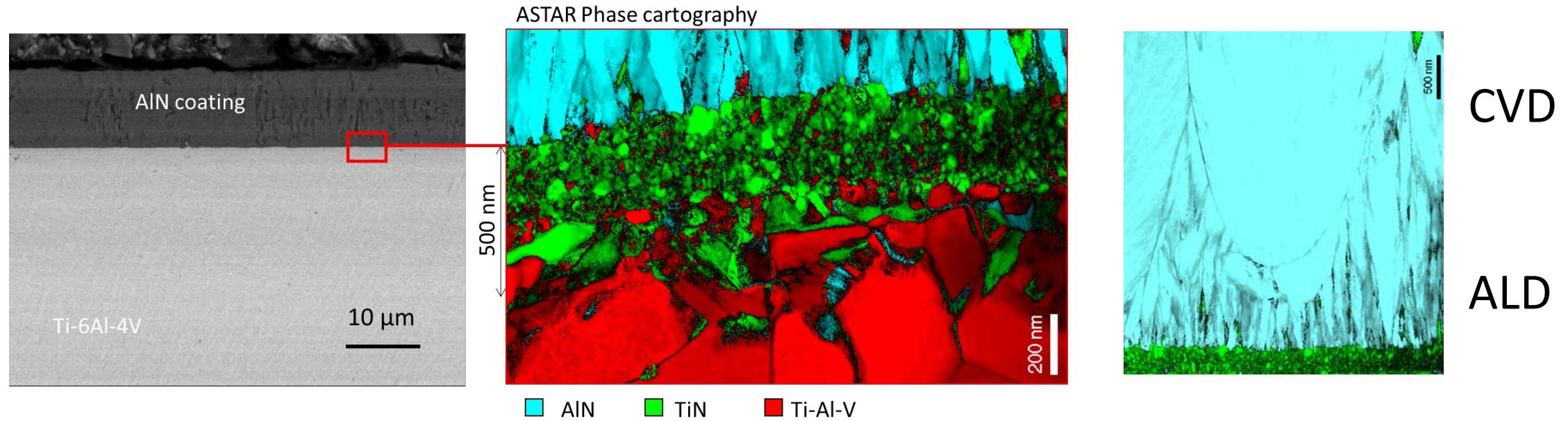


Applications : deposition on of EBM-made 3D Ti-6Al-4V architectures



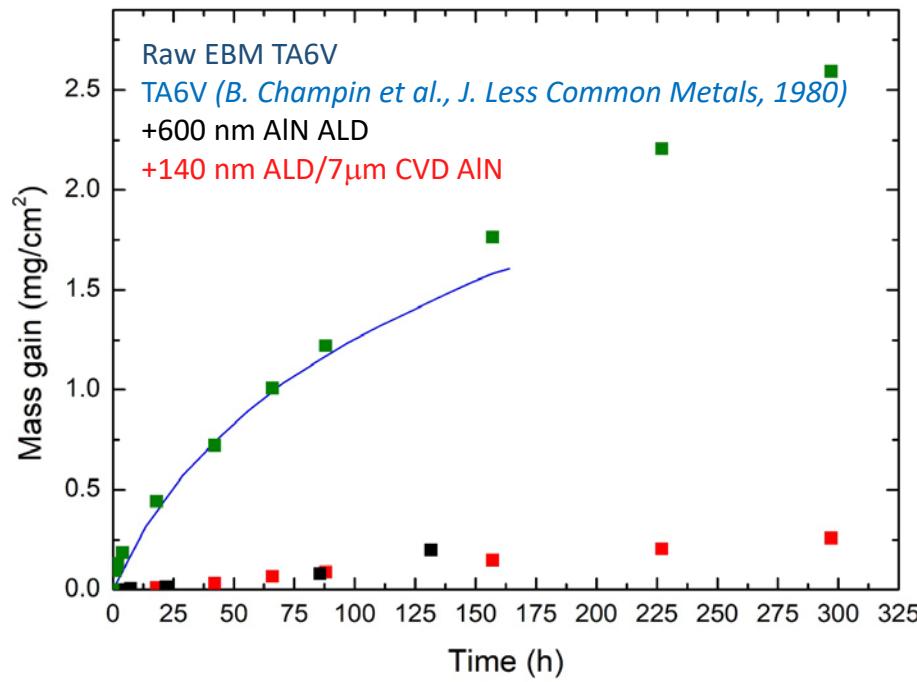
Deposition of dense and nearly conformal coating by ALD/CVD despite high roughness of Ti-6Al-4V

Applications : deposition on of EBM-made 3D Ti-6Al-4V architectures



Protective ALD AlN
Piezoelectric response?

Applications : deposition on of EBM-made 3D Ti-6Al-4V architectures – protection against oxidation



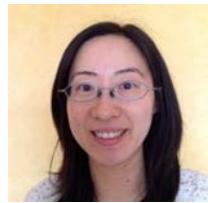
Corrosion protection effect of a 140 nm thin film deposited by ALD and 7 μm AlN deposited by CVD on a EBM made Ti-6Al-4V (TA6V) sample under cyclic oxidation, Air, 650°C

AIN coating by CVD and ALD on complex architectures made by EBM:
Extension of the temperature range of use
Expected modification of mechanical and thermal behavior

Conclusions

Growth of a variety of metal nitrides

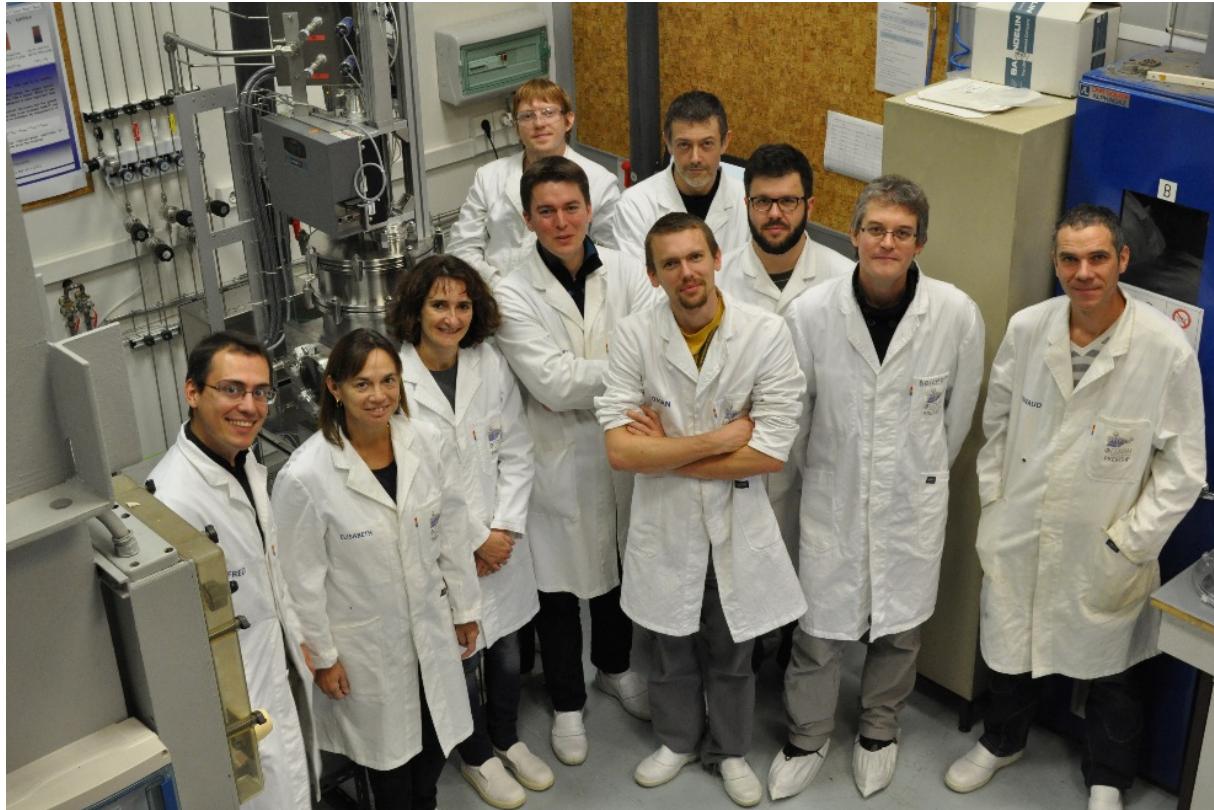
- Special attention to the precursor selection, handling, ...
- Evaluation of its thermal behavior –thermodynamics
- Control of the film properties with ALD/PEALD sequences
- Combine ALD/CVD to explore wider range of properties



L. Tian



A. Moll





Thank you for your attention



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