High Temperature Chemical Vapor Deposition of Aluminium Nitride, Growth and Evaluation

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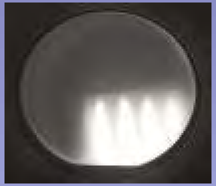
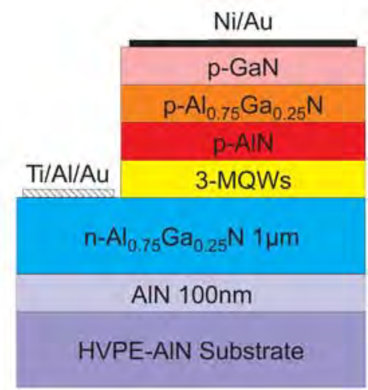
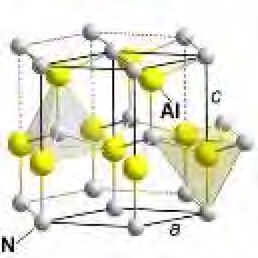
Outline





1. Introduction : AlN



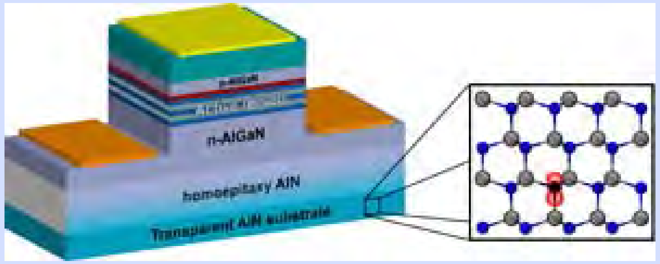
2. Experimental set-up

- ✓ High temperature Hydride Vapor Phase Epitaxy (800-1600 °C)

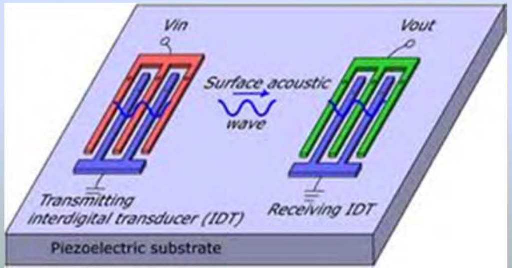
3. AlN coatings in nuclear industry

- ✓ Thick and polycrystalline coatings for fuel claddings of IV generation

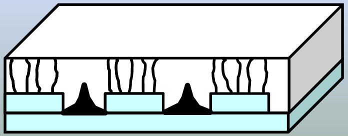
4. AlN epitaxy for D-UV and SAW devices



- ✓ High quality epitaxial growth , defect reduction ..
- ✓ Highly oriented films of high quality



5. Conclusions



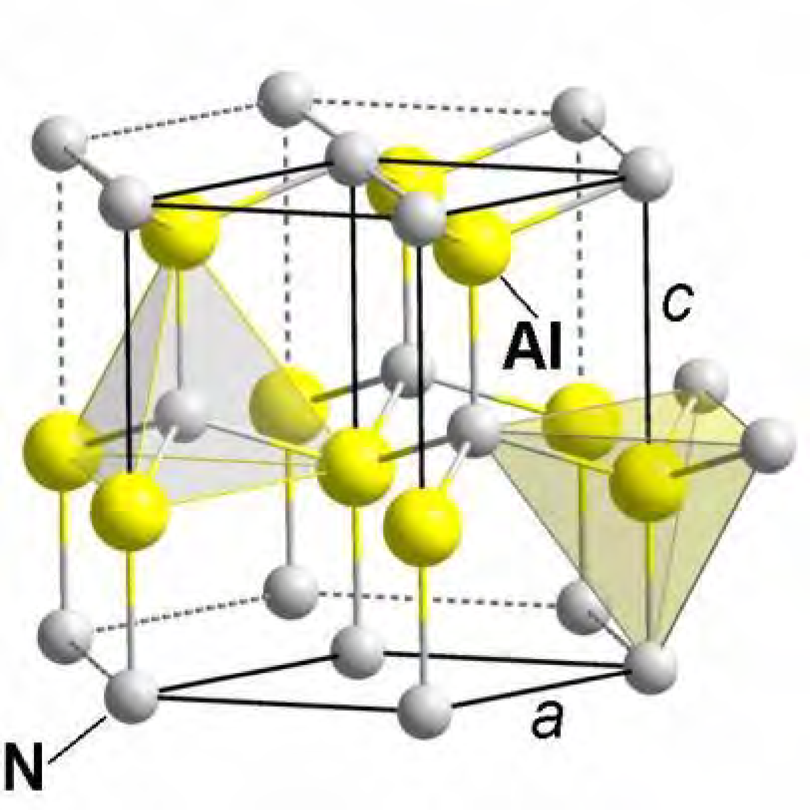
- ✓ Defect reduction improvements

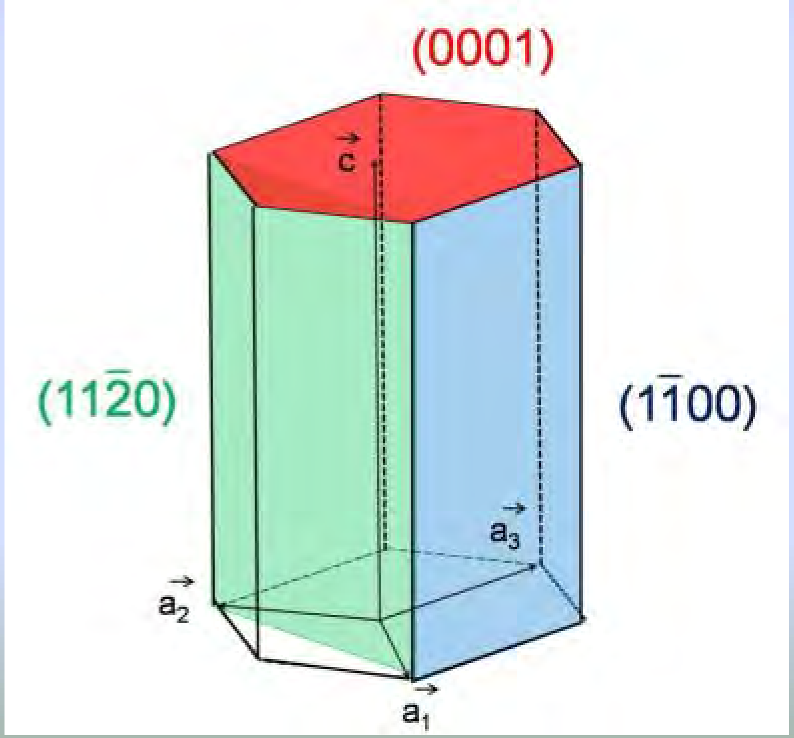
Aluminum nitride

❑ Hexagonal Würtzite structure

a = 3,11 Å and *c* = 4,98 Å

=> AlN 2H polytype





❑ Polar plane: ***c*** (0001)

❑ Non polar planes: ***m*** $(\bar{1}100)$ et ***a*** $(11\bar{2}0)$

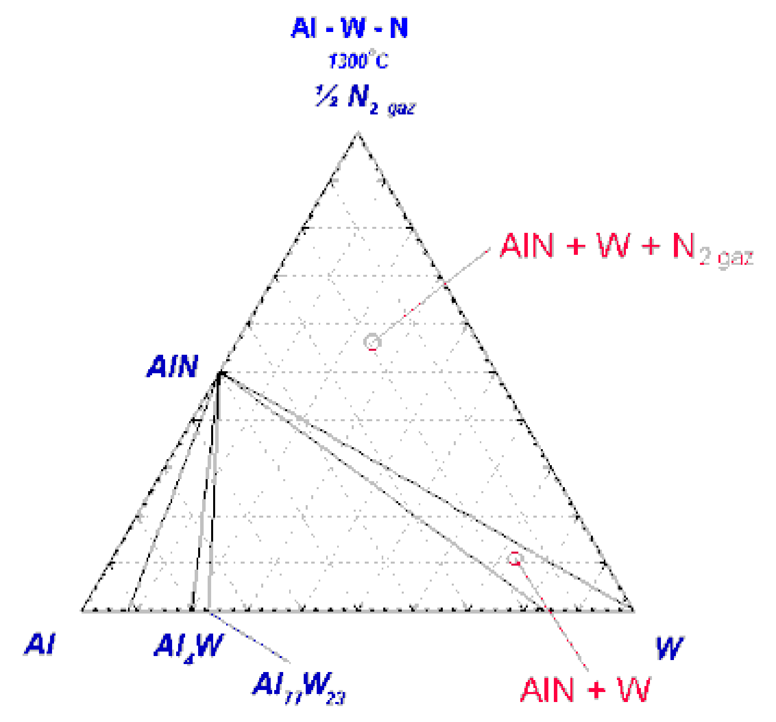
❑ Semi polar planes: (hkjl) avec l ≠ 0

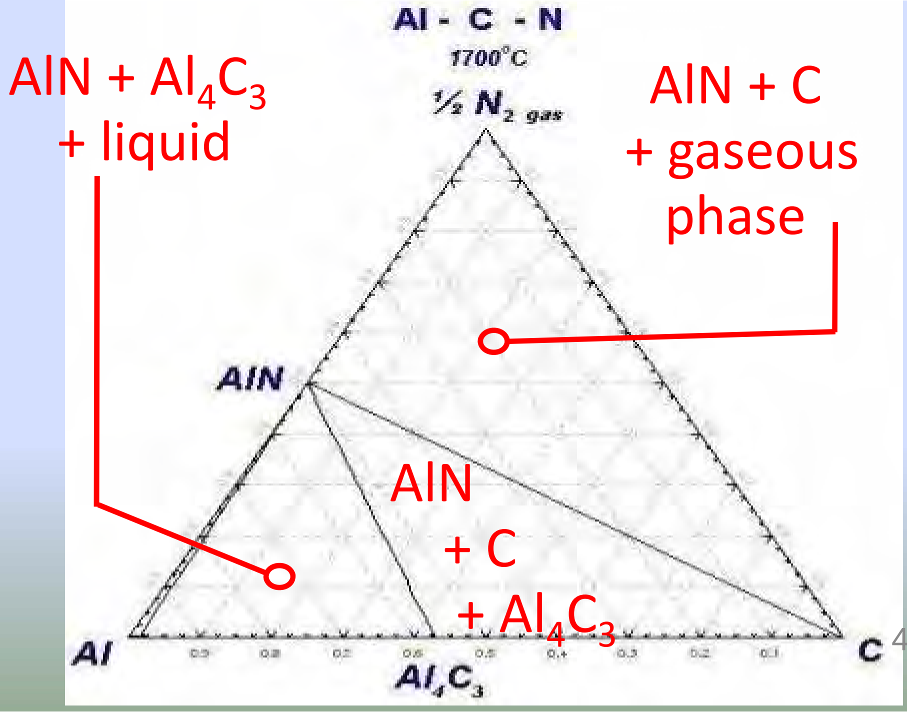
Aluminum nitride : Properties

- Intrinsic properties :
  - Refractory:

    high decomposition temperature around 2400°C
  - Good chemical stability

    for instance stability versus carbon and metals
  - High resistance to wear
  - High resistance to oxidation
  - High resistance to etching
- Wide bandgap III-V semiconductor
  - Eg th. = 6.2 eV
  - Optically transparent throughout UV, visible and near infra-red regions

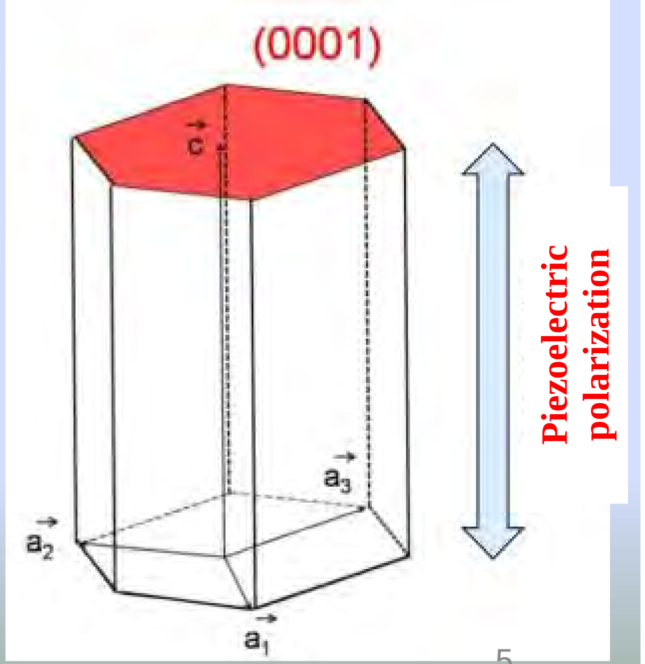




Aluminum nitride : Properties

- ☐ Intrinsic properties :
  - ☐ Thermal expansion coefficient (ca. 4 10^{-6} K^{-1}) close to that of other semiconductors
  - ☐ High thermal conductivity ca. 200 $W.m^{-1}.K^{-1}$: 80% compared to Cu
  - ☐ High electrical resistivity (insulating : 10^8 to 10^{13} Ω.cm)
  - ☐ Piezoelectric (along the c-axis)

AlN is one of the few materials with electrical insulating properties together with high thermal conductivity.



Aluminum nitride : Applications

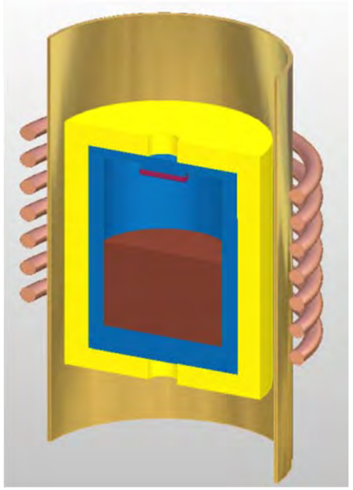
- ☐ Metallurgical coatings: Protective coatings, diffusion barriers
- ☐ Microelectronics: Diffusion barriers, Packaging
- ☐ Optoelectronic devices (medical use, dissociation of pollutant material i.e. water purification, semiconductor illumination, laser for High Density Optical Recording); UV Light Emitting Diode LED, UV LD, white LED
- ☐ High temperature, voltage, frequency Transistors (HEMT)
- ☐ Piezoelectric devices : Sensors- Surface Acoustic Wave (SAW)

- **Objectives: designing the function by controlling structure, purity, defects, thickness, growth mode on different foreign substrates**
- **Originality: temperatures higher than 1200 °C**

Aluminum nitride : Processing techniques

PVT : Physical Vapor Transport

☺ Growth rate up to 1 mm/h
☺ Crystalline quality
☹ Oxygen pollution: Crucible materials/ powder purification
☹ Process control

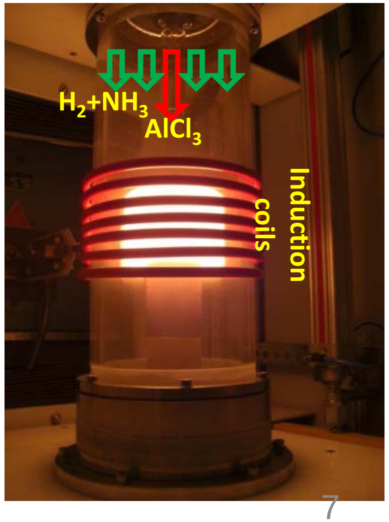


MOCVD : Metal-Organic Chemical Vapor Deposition

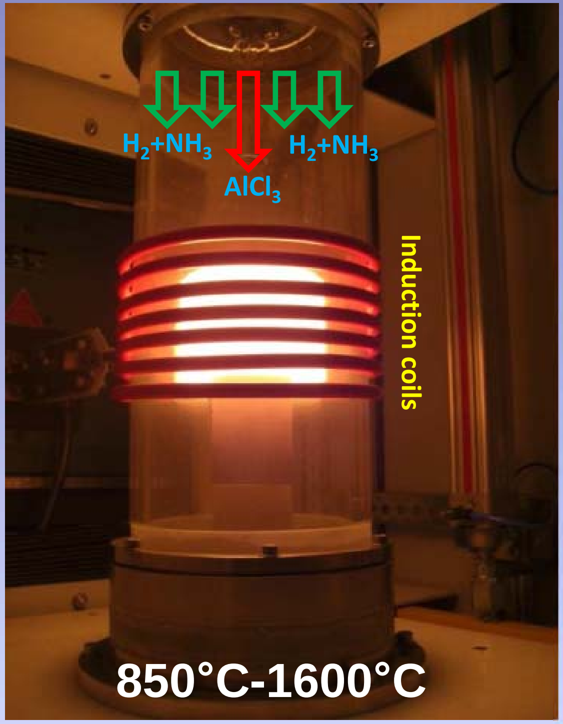
☺ High purity crystals
☺ Epitaxial or polycrystalline (depending on supersaturation)
☹ Use of gas (toxic , …)
☹ Low growth rates (0.1 to 10 µm/h)
☹ Aluminum condensation for low N/Al ratio

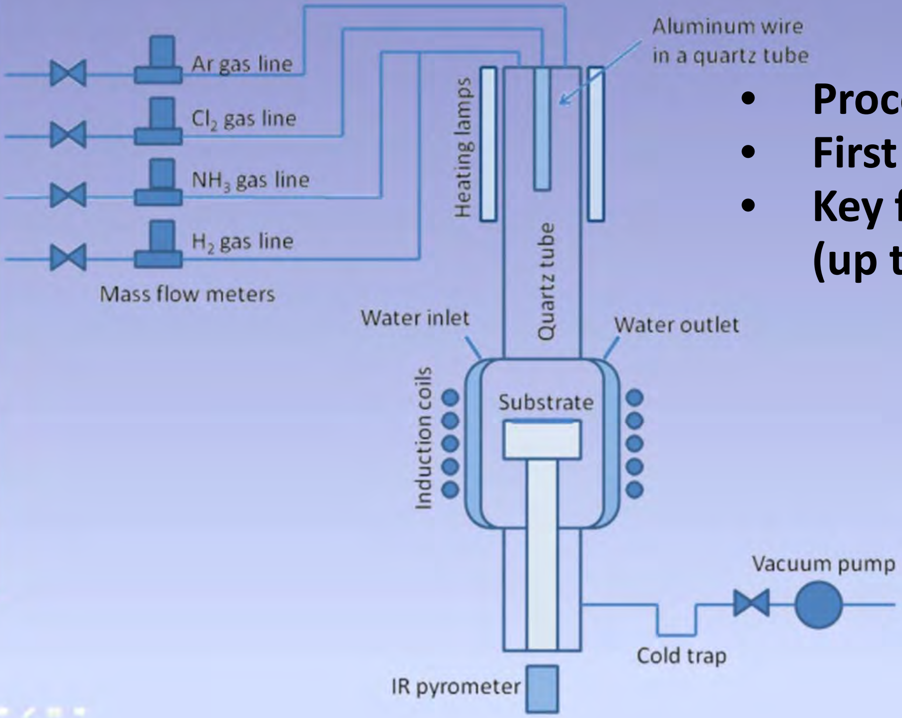
HTCVD, HVPE : High Temperature CVD, Hydride Vapor Phase Epitaxy

☺ Epitaxial or polycrystalline (depending on supersaturation)
☺ Control of N/Al ratio
☹ Use of gas (corrosive , …)
☹ Higher growth rates (50 µm/h epitaxial, 300 µm/h polycrystalline)



Our choice: HVPE process (T>1200 °C)





- **Process developed in the 1960s**
- **First epitaxial method for GaN**
- **Key features : high growth rate (up to 100 µm/h)**

- **Cold wall CVD reactor**
- **In-situ $AlCl_x$ (Cl_2, Al metal)**
- **NH_3**
- **Primary vacuum**

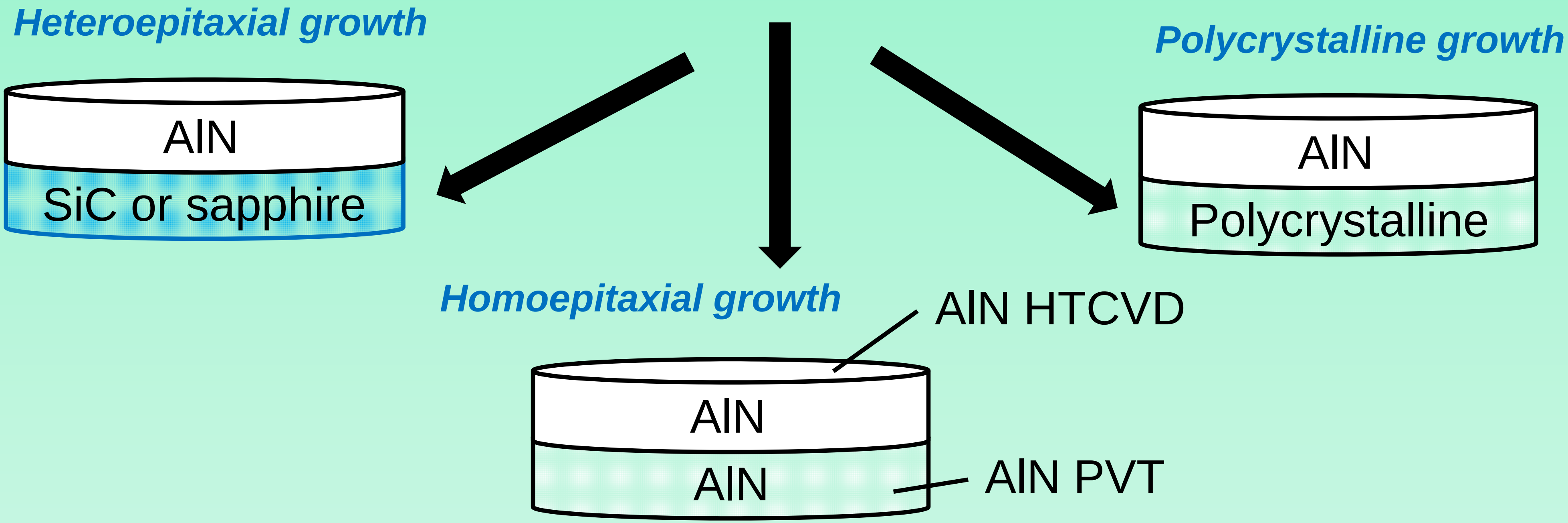
Typical working conditions :

- **Pressure : 133 to 1330 Pa**
- **Temperature : 900-1600°C**
- **H_2 flow rate : 1000 sscm**
- **NH_3 flow rate : 10-100 sccm**
- **Cl_2 flow rate : 5-50 sccm**

- **Ability to grow thick, high quality AlGaN and AlN**
- **Demonstrated by TDI company (now Oxford Instruments) at 1200 °C**
- **Carbon free environment for epitaxial growth**
- **Self-cleaning effects by HCl : low background doping**

Fabrication : thin or thick films at 1300-1700 °C

3 possible approaches



Heteroepitaxial growth

AlN

SiC or sapphire

Homoepitaxial growth

AlN HTCVD

AlN

AlN

AlN PVT

Polycrystalline growth

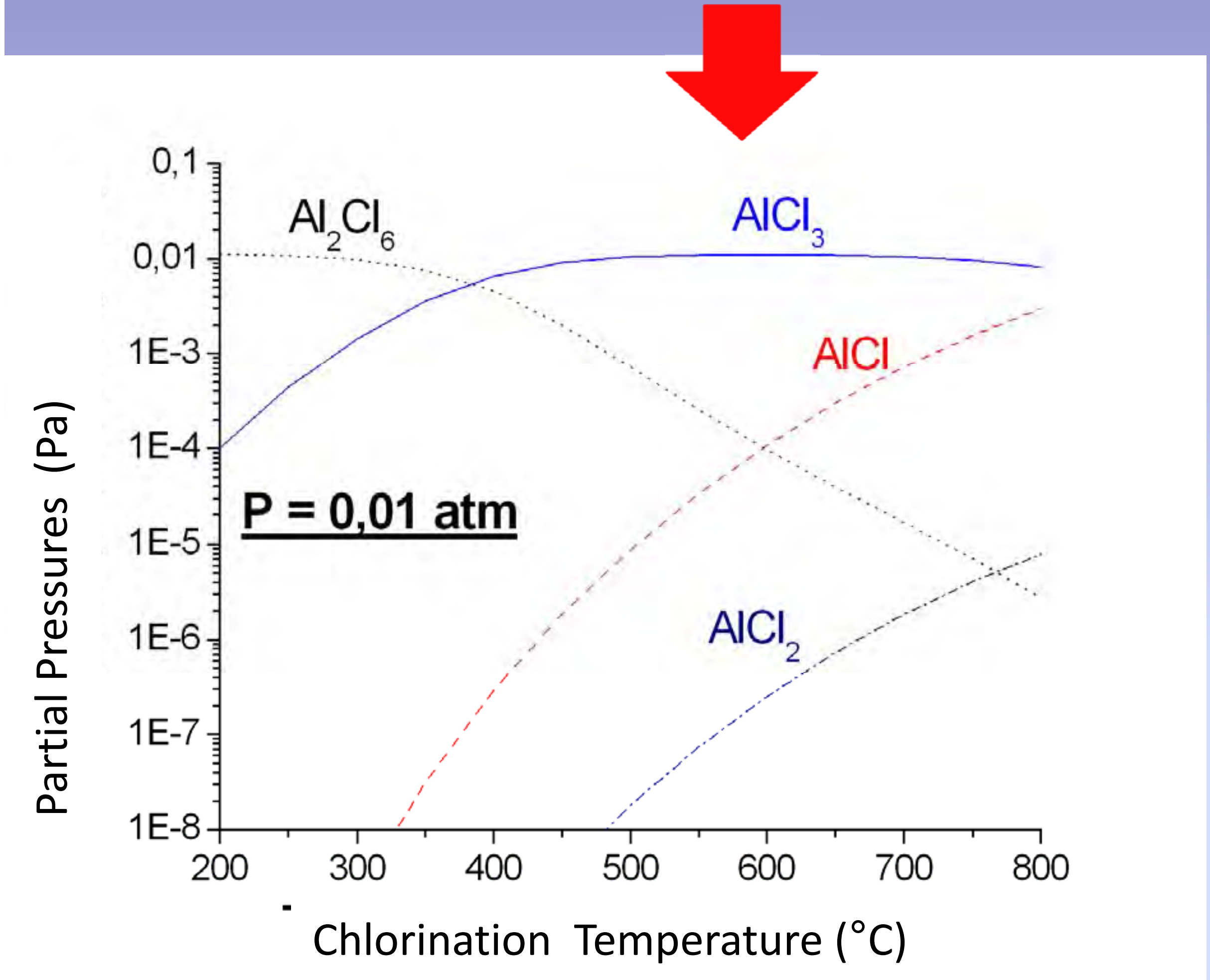
AlN

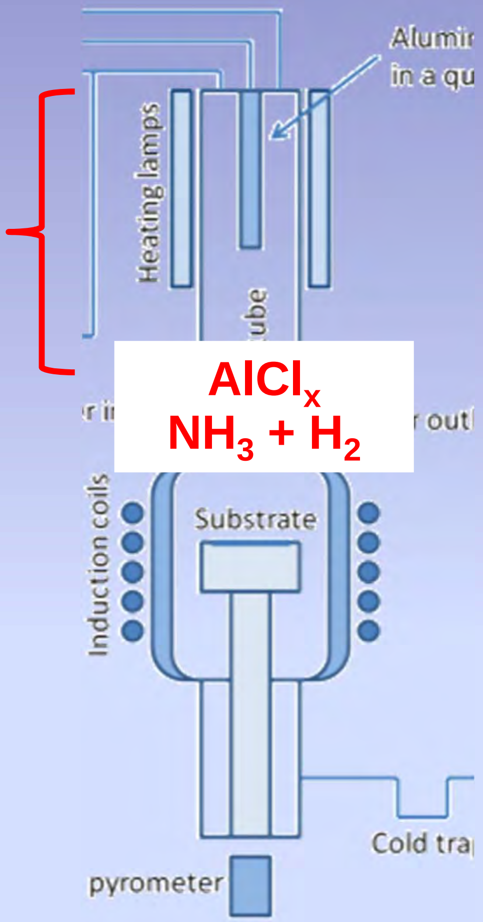
Polycrystalline

- ☺ High crystalline quality substrate
- ☺ price /availability (→ 4 " - 100 mm)
- ☹ High dislocation density (10^8-10^9 cm^{-2})
- ☹ Cracks (see the paper for a quantitative description of stress origin)

- ☺ Low dislocation density(10^4 cm^{-2})
- ☺ No or few cracks
- ☹ price/availability (0.5 " - 12 mm)

Al chlorination by Cl_2 at 600 °C





$AlCl_x$
$NH_3 + H_2$

- Evolution of chloride amounts vs T
- $AlCl_3$ major species (AlCl < 5 %) at 600°C

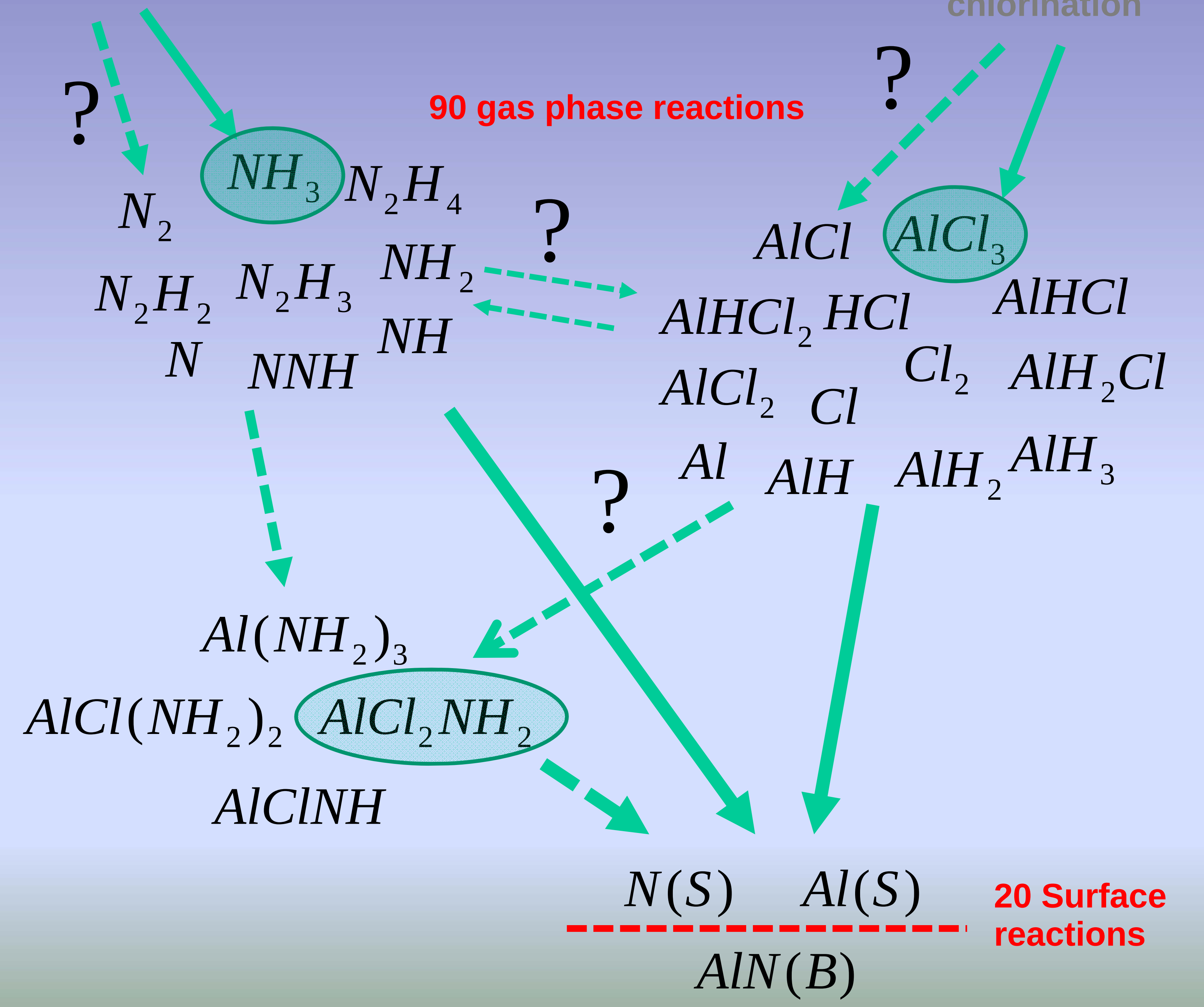
($T_{melting}$ Al = 660 °C)

- Cold-wall reactor
- Low quantity of AlCl

To avoid etching of quartz and silicon and oxygen doping

Al-Cl-N-H system kinetic mechanisms

Al-Cl-N-H system



AlN deposition: Process Modeling

A simplified scheme was proposed (R. Boichot et al. Surf. Coat. Technol. 2010).

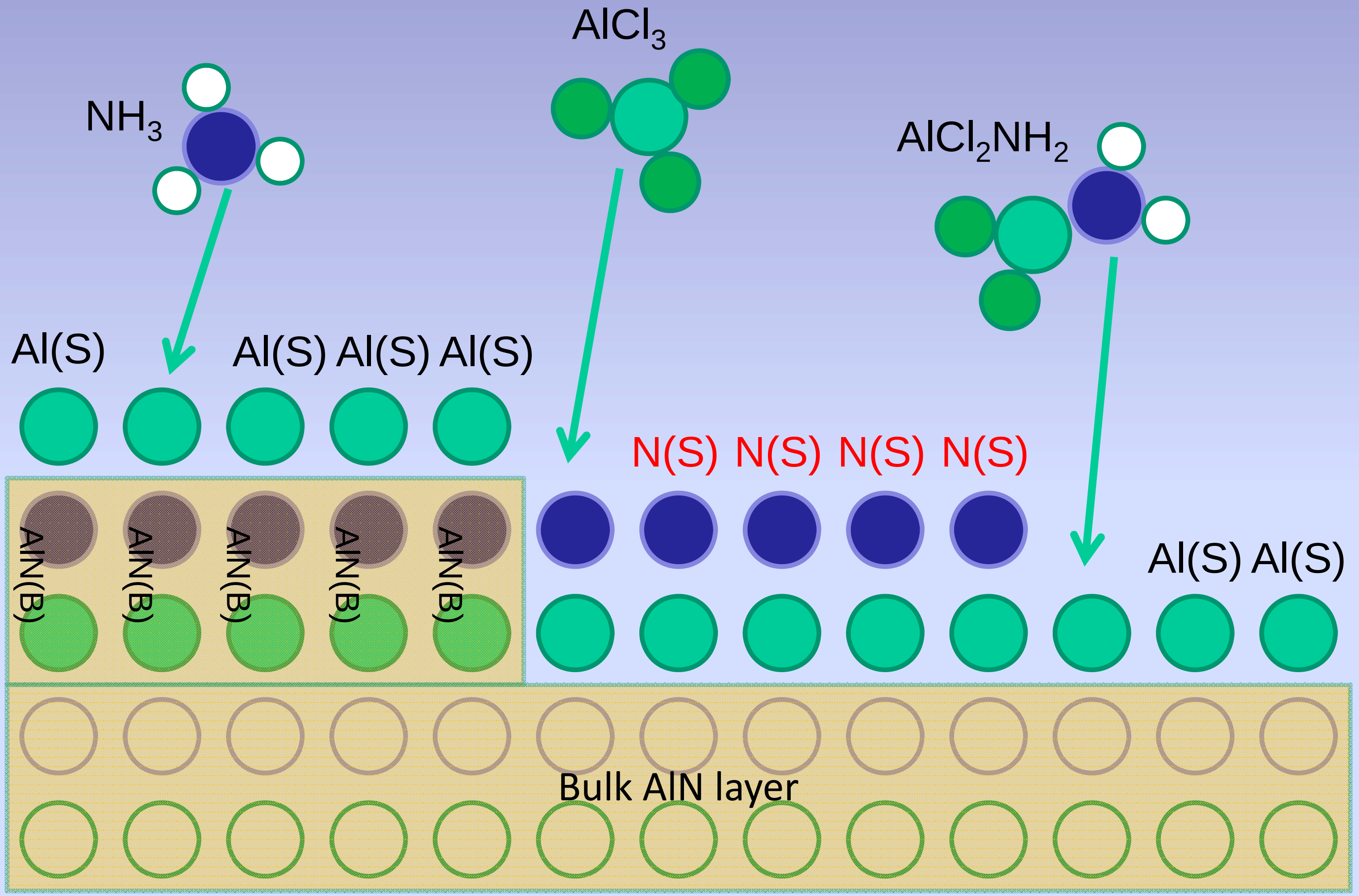
☐ Gas phase:

$AlCl_3 + NH_3 <-> AlCl_2NH_2 + HCl$
$H + Cl + M <-> HCl + M$
$2Cl + M <-> Cl_2 + M$
$H + HCl <-> Cl + H_2$
$Cl_2 + H <-> Cl + HCl$
$2H + H_2 <-> 2H_2$
$H_2 + M <-> 2H + M$

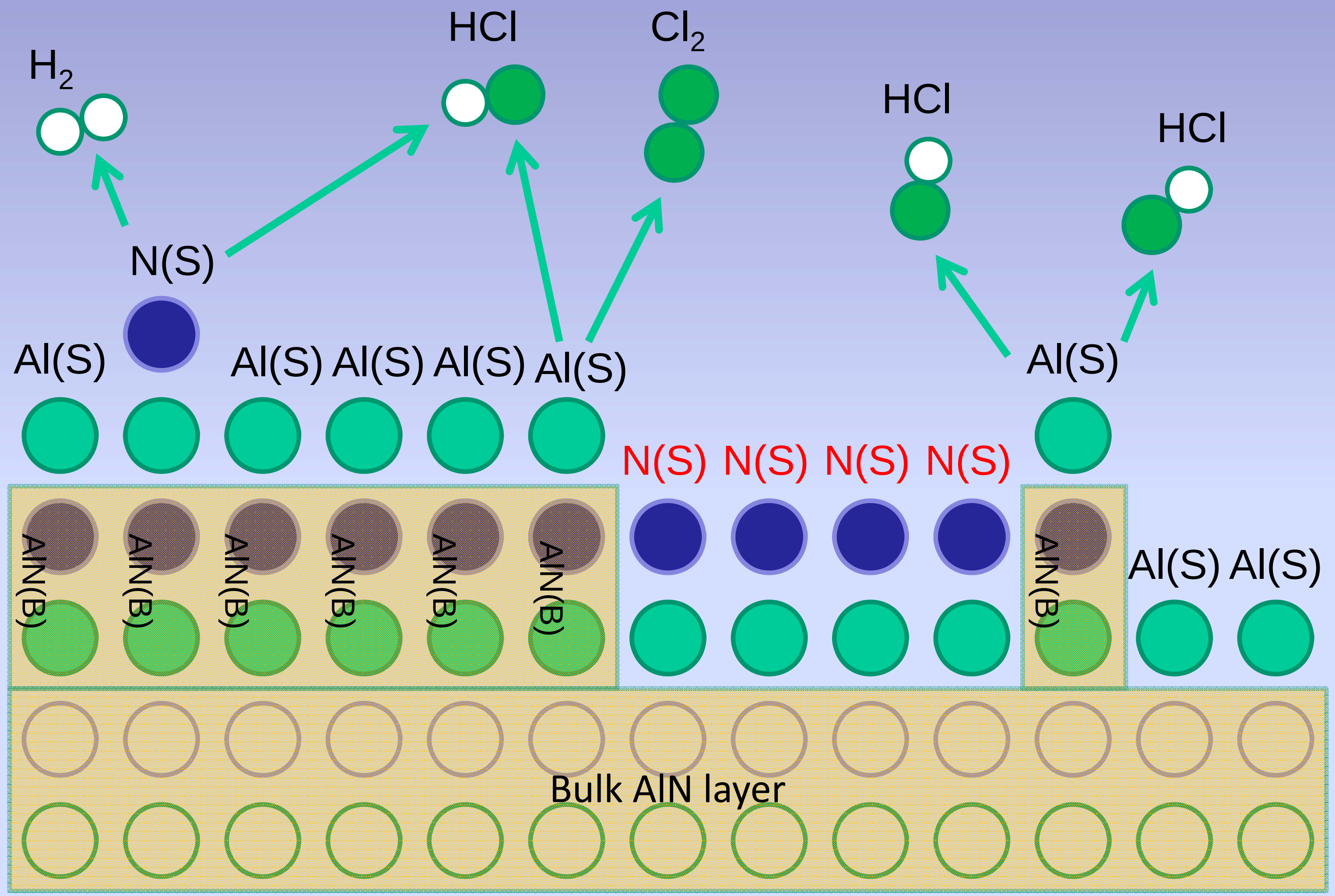
☐ Surface (Atomic site formalism):

$NH_3 + Al(S) \leftrightarrow N(S) + H_2 + H$ Ea = 71.9 kJ/mol
$AlCl_3 + N(S) \leftrightarrow AlN(B) + Al(S) + CL + Cl_2$ Ea = 64.0 kJ/mol
$AlCl_2NH_2 + Al(S) \leftrightarrow AlN(B) + Al(S) + 2HCl$ Ea = 42.0 kJ/mol
$AlCl_2NH_2 + N(S) \leftrightarrow AlN(B) + N(S) + 2HCl$ Ea = 42.0 kJ/mol

AlN deposition: Surface reaction kinetic

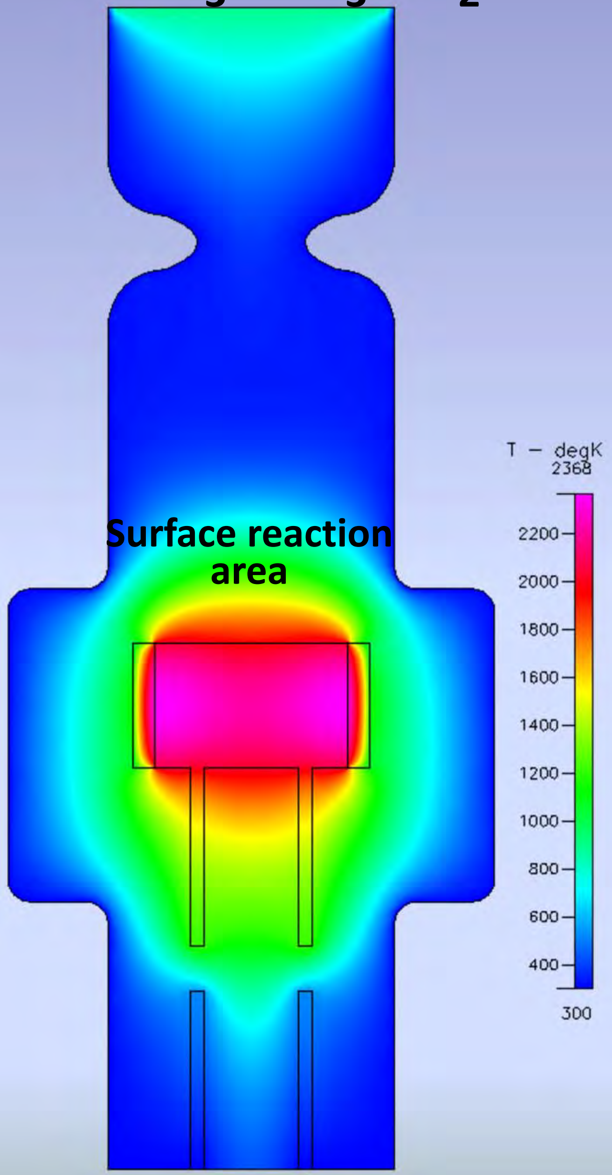


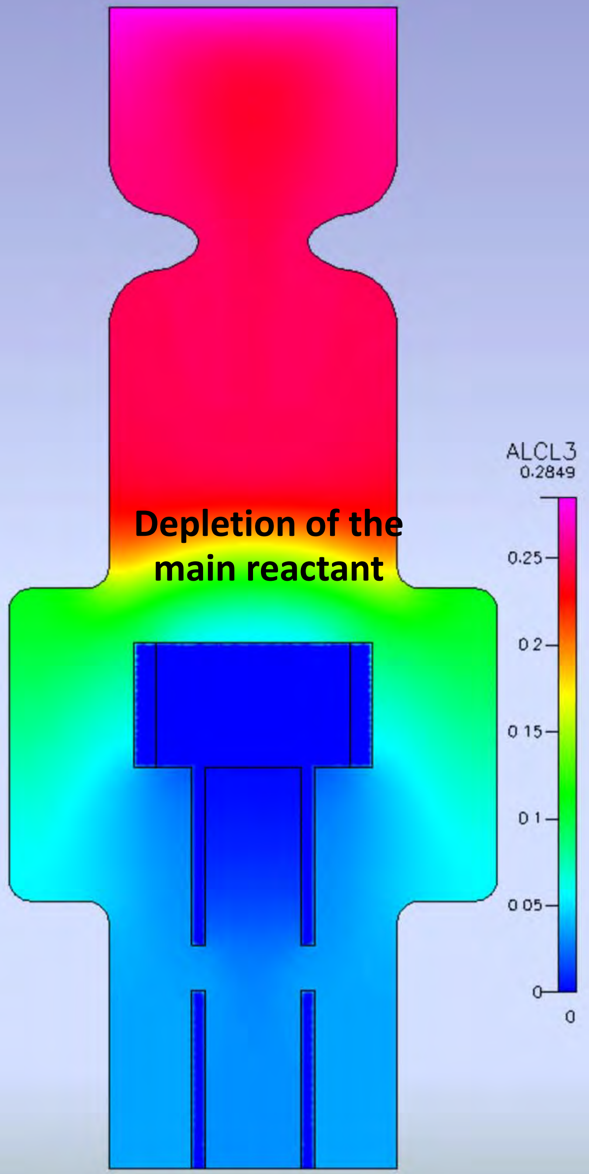
AlN deposition: Surface reaction kinetic

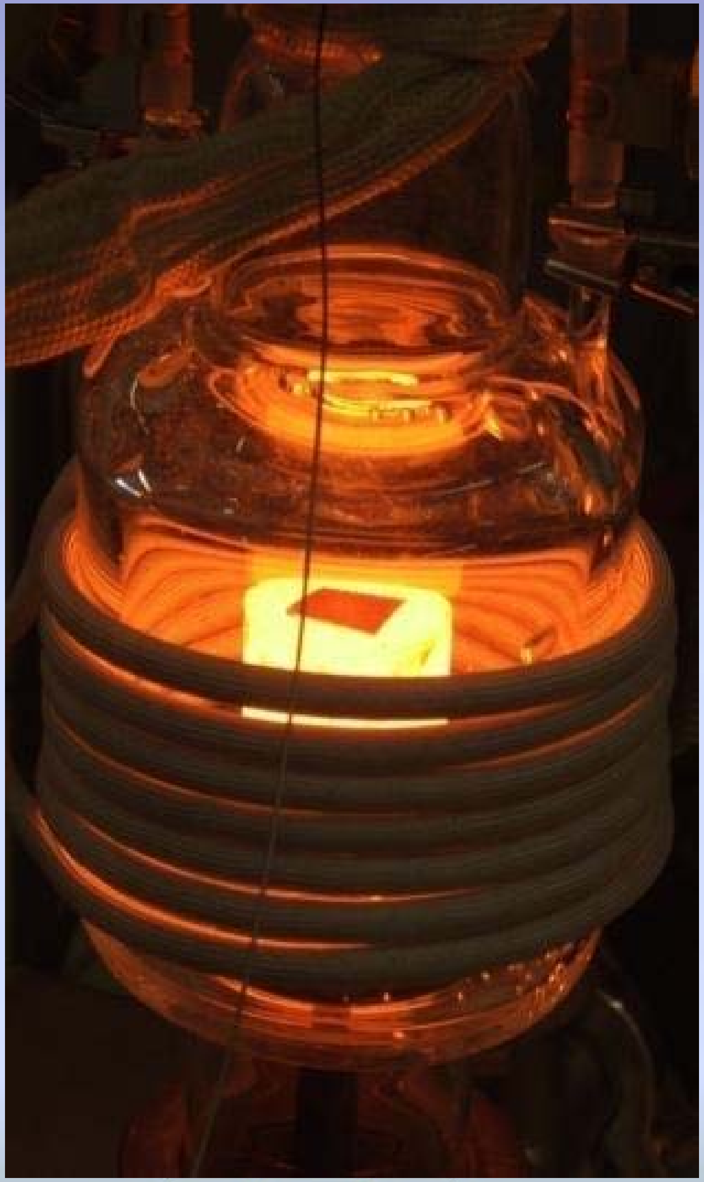


CFD simulation : AlN CVD process

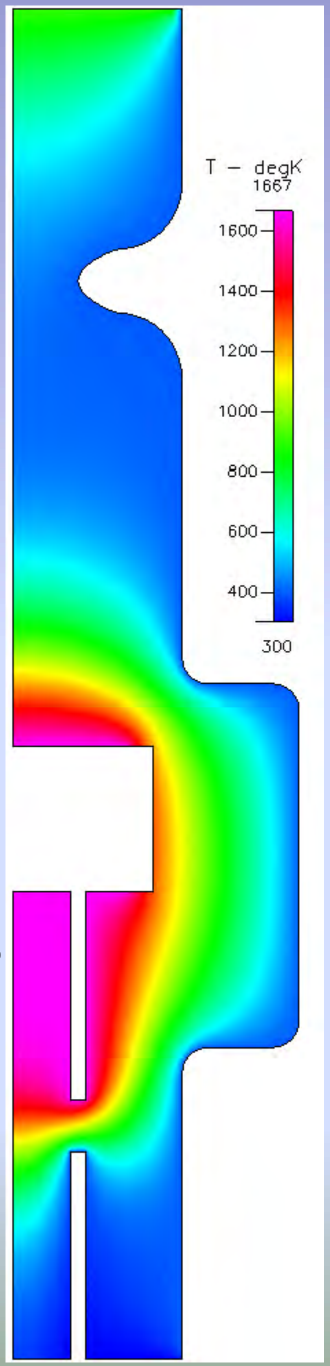
$AlCl_3, NH_3 : H_2$


Surface reaction area

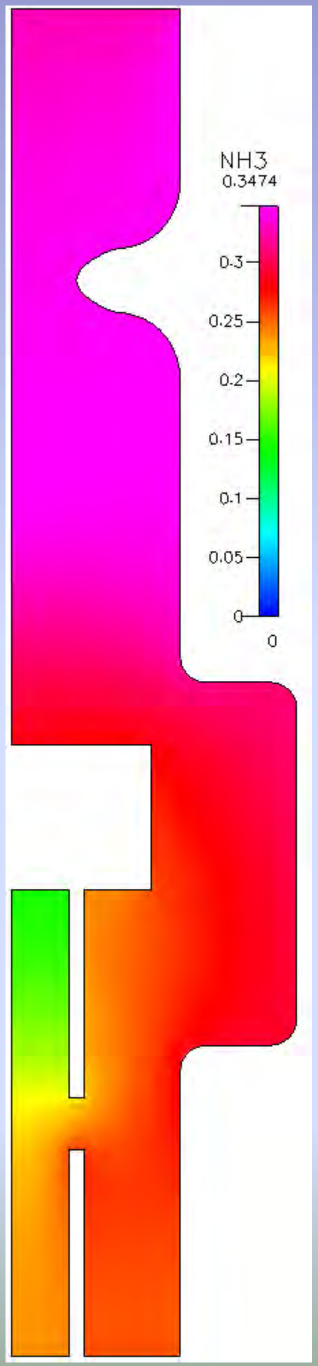

Depletion of the main reactant



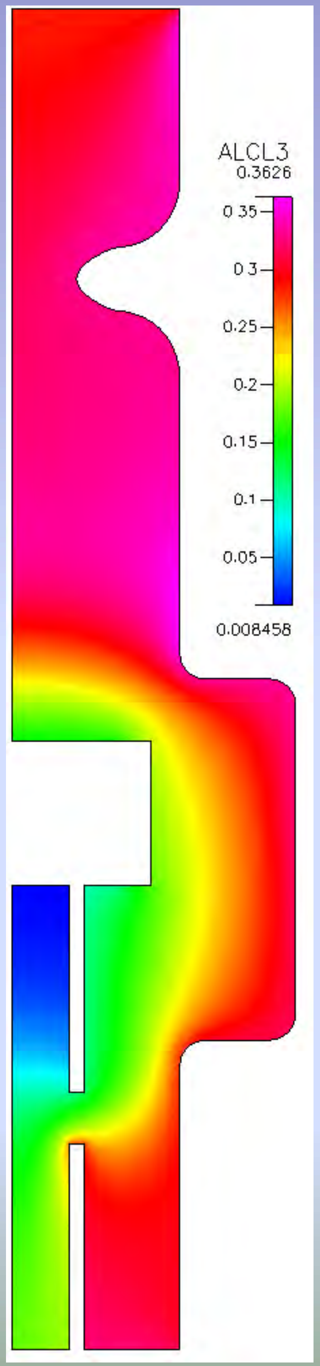
Growth at 1660 K



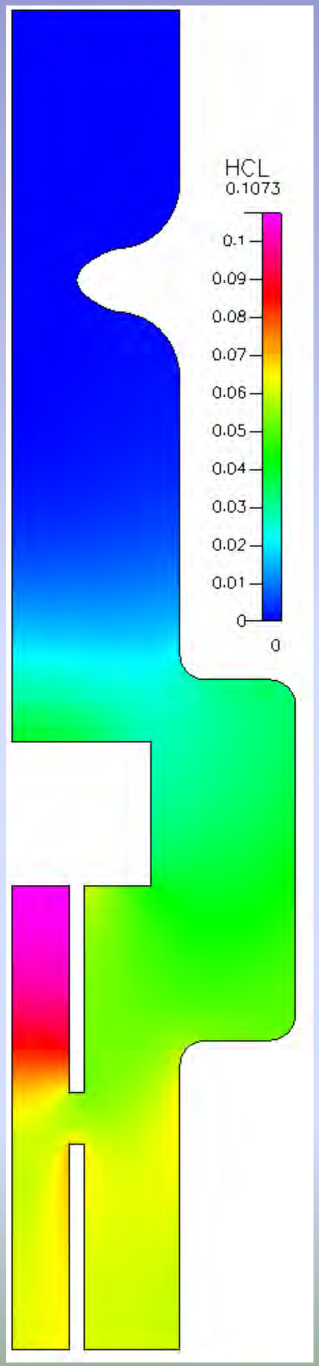
Temperature distribution



NH_3 mass fraction



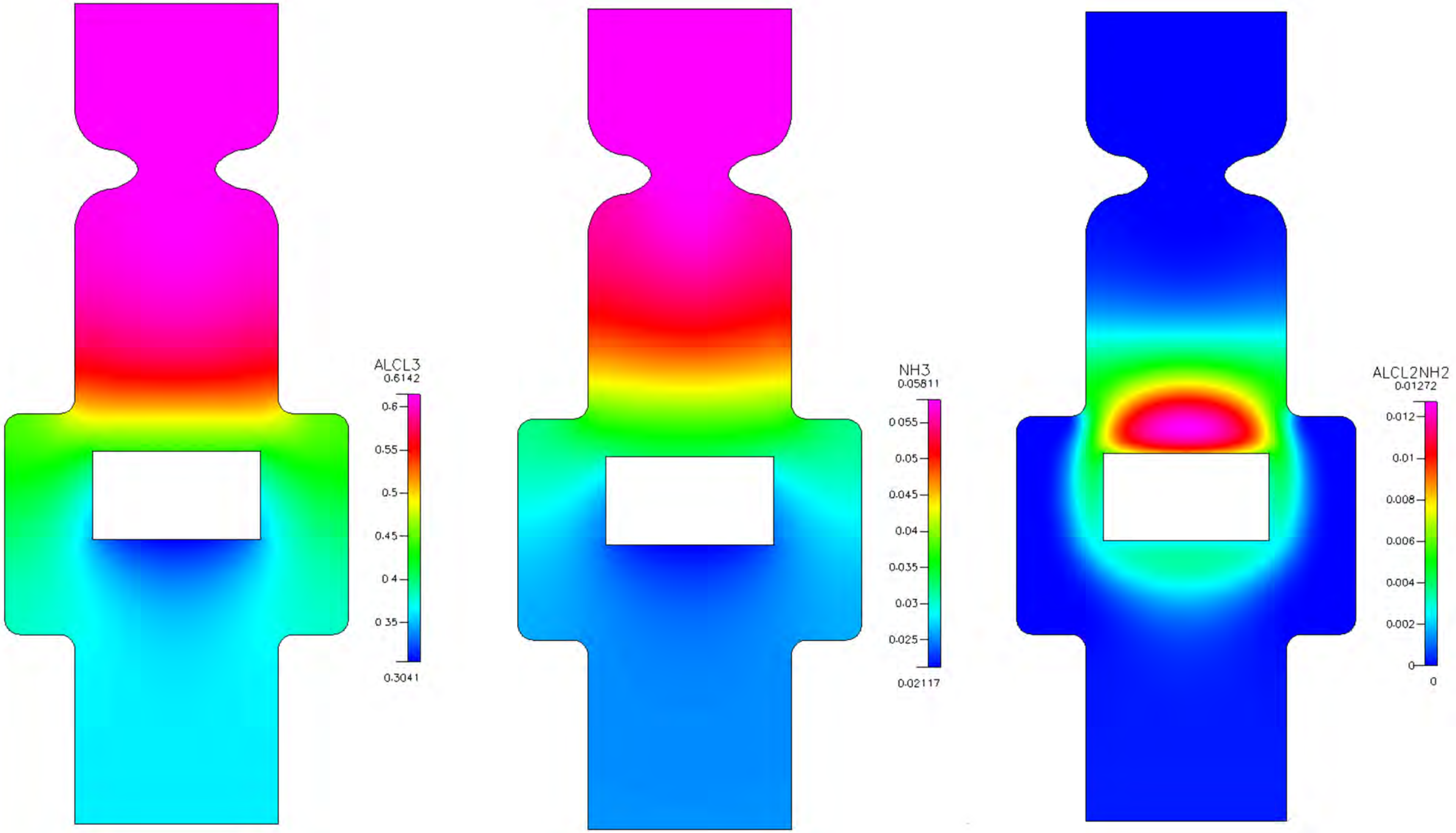
$AlCl_3$ mass fraction



HCl mass fraction

Simulation results

$AlCl_3$ mass fractions : N/Al = 0.75 at 1400°C

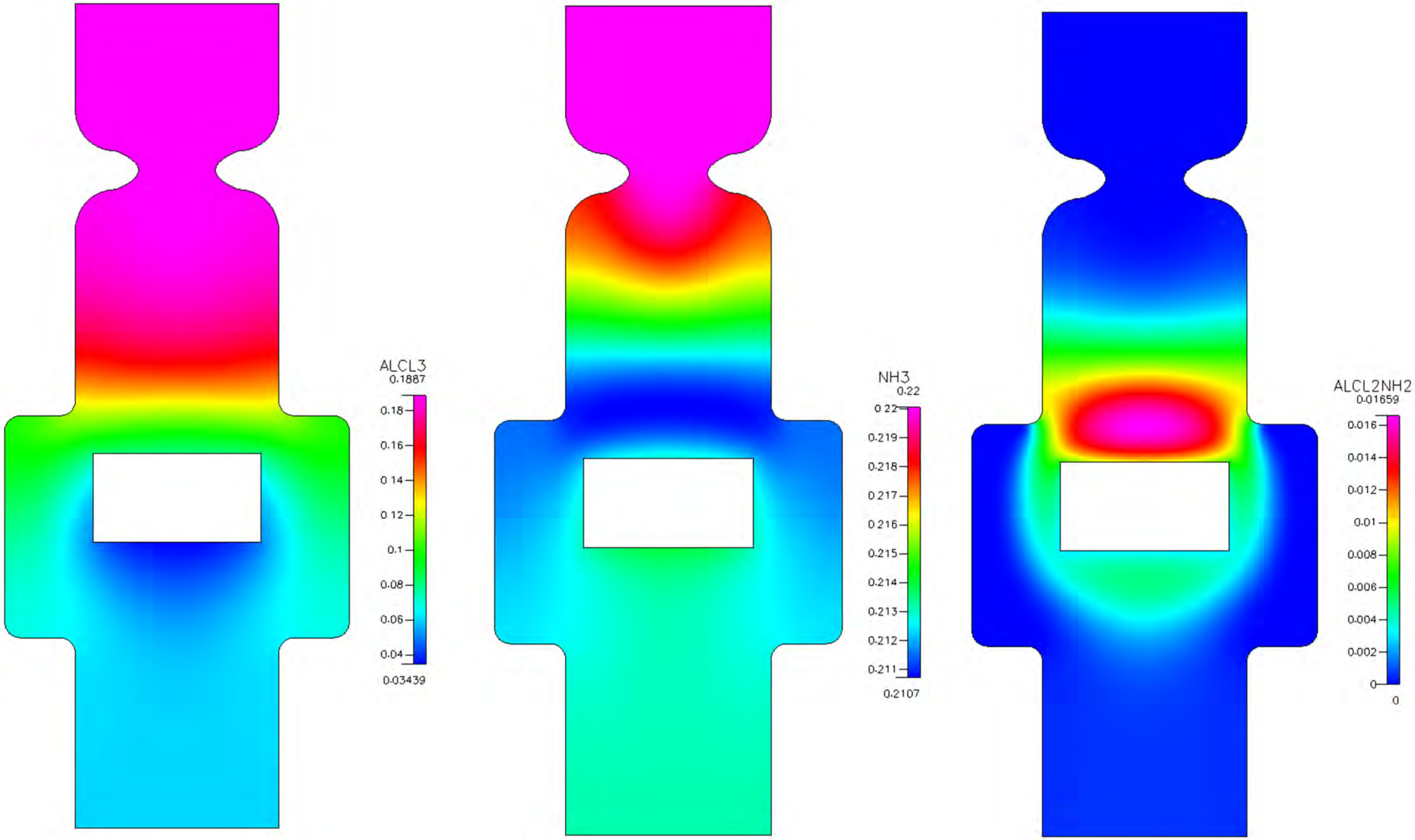


At 1400°C and N/Al = 0.75, both NH_3 and $AlCl_3$ are limiting the AlN growth rate. The intermediary compound $AlCl_2NH_2$ is present just above the susceptor.

Simulation results

Simulation results

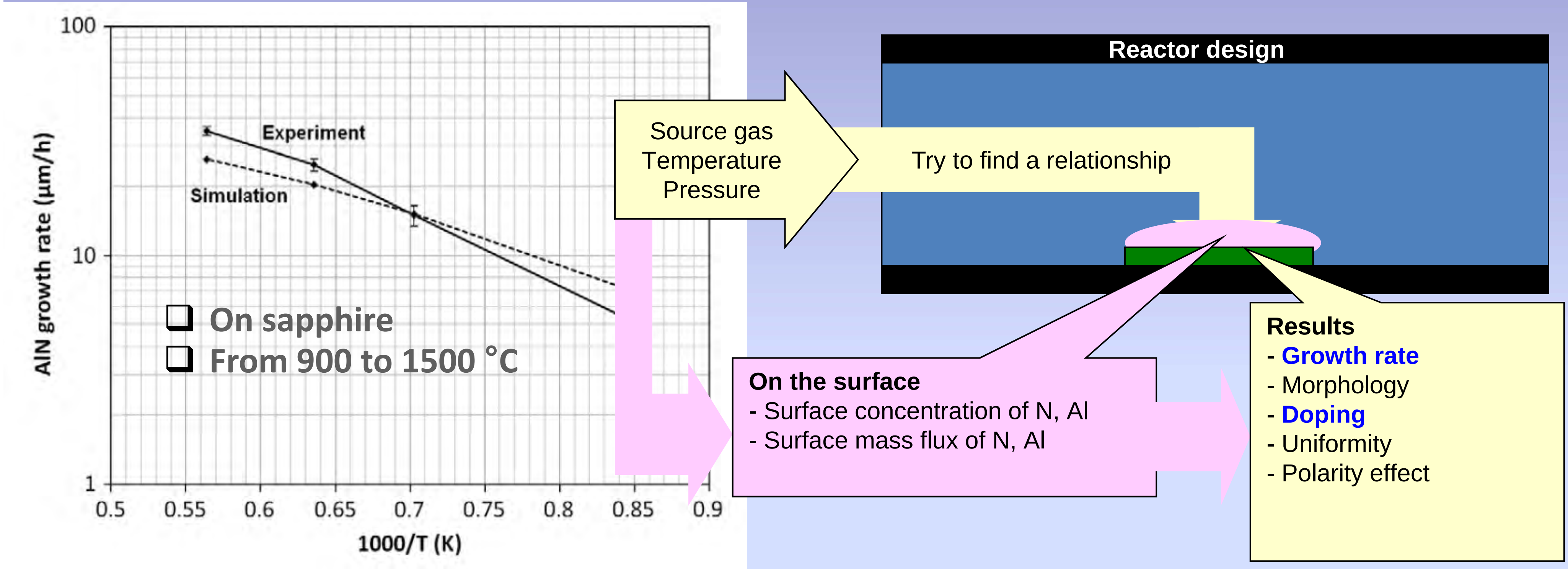
$AlCl_3$ mass fractions : N/Al 9 at 1400°C



At 1400°C and N/Al = 9, $AlCl_3$ only is limiting the AlN growth rate. NH_3 depletion is mainly due to $AlCl_2NH_2$ formation. Is there any influence of gas species on surface quality ?

AlN simulation results : Modeling local Surface Flux and Supersaturation

- Comparison with experiments **(R. Boichot et al. Surf. Coat. Technol. 2010)**



☐ **On sapphire**
☐ **From 900 to 1500 °C**

Source gas
Temperature
Pressure

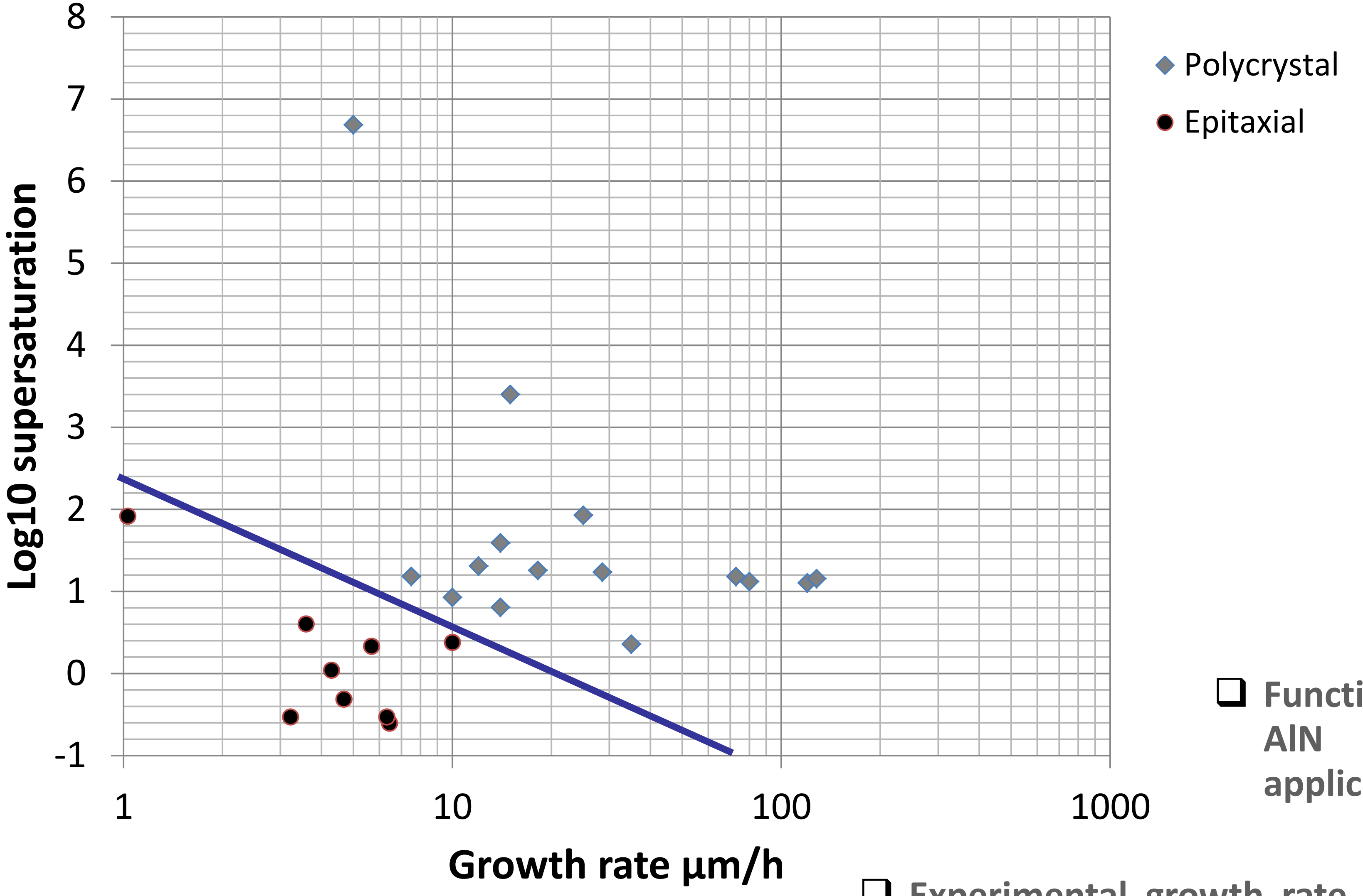
Try to find a relationship

On the surface
- Surface concentration of N, Al
- Surface mass flux of N, Al

Results
- **Growth rate**
- Morphology
- **Doping**
- Uniformity
- Polarity effect

☐ **Find local values of N/Al and supersaturation**
☐ **Reactor independent**
☐ **Universal model for designing experiments and new reactor configuration**

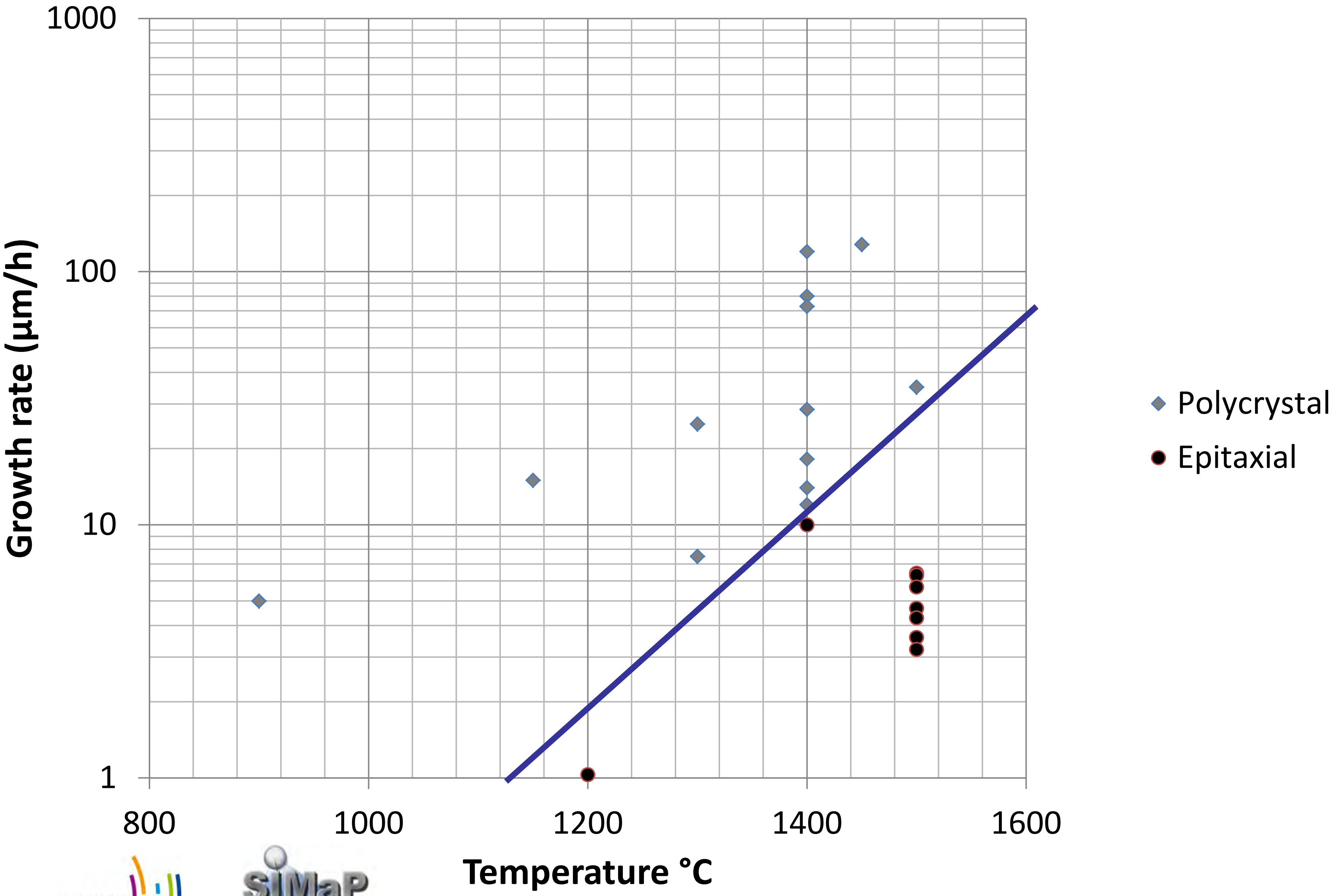
Modeling local Surface Flux and Supersaturation



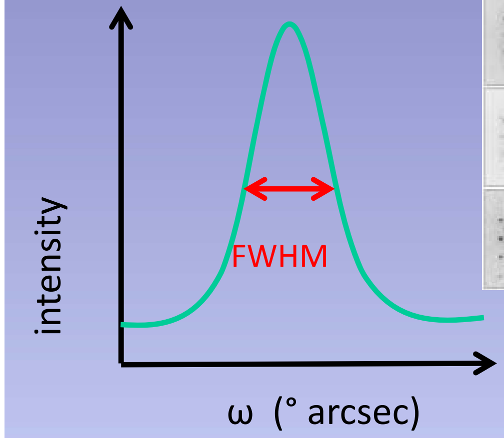
- ❑ **Functionalization of AlN for different applications**

- ❑ **Experimental growth rate as a function of local values of supersaturation at 1500 °C**
- ❑ **Growth rate optimization**
- ❑ **Universal model for designing experiments**

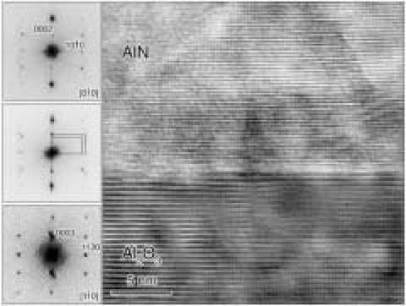
Modeling local Surface Flux and Supersaturation



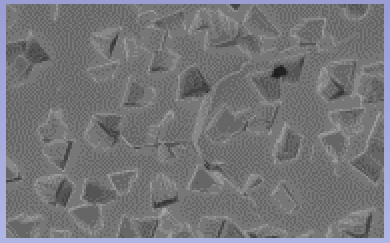
Characterization techniques

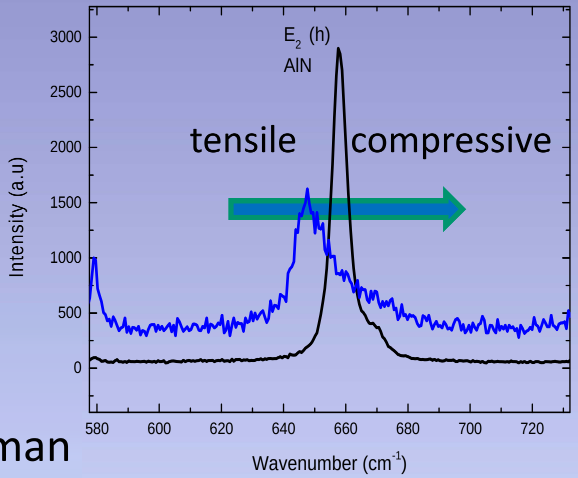


DRX, Raman, TEM, EBSD

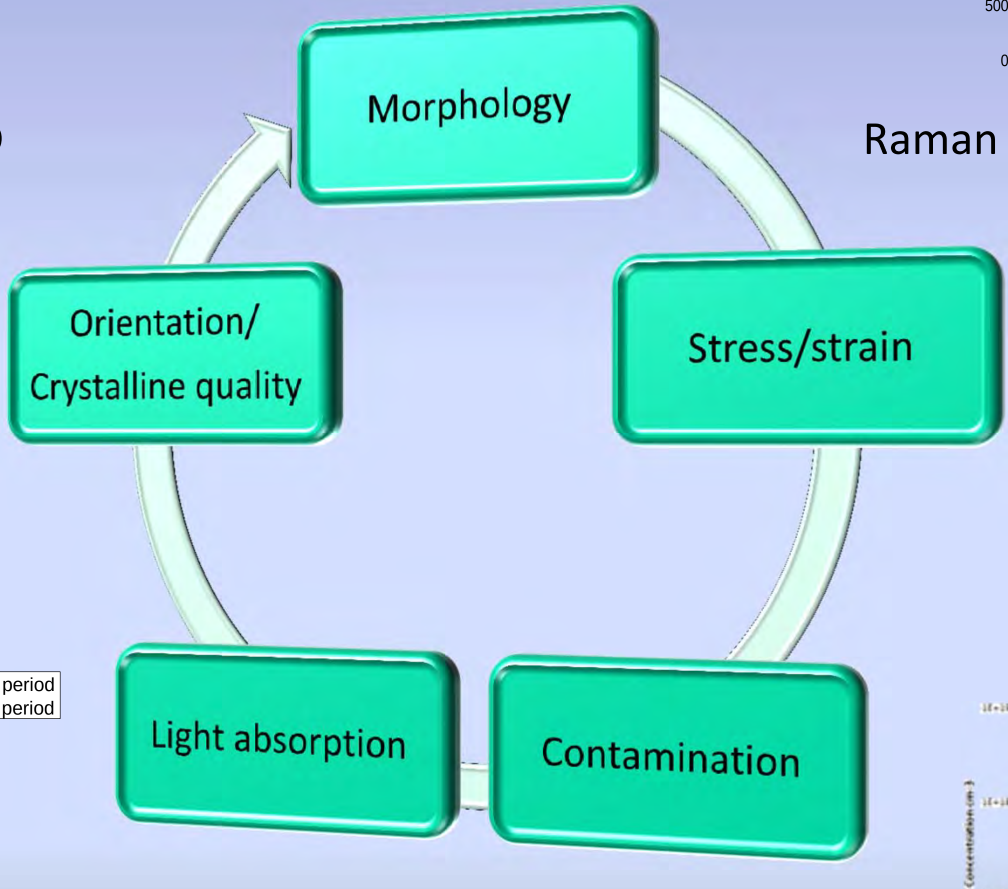


SEM, AFM





Raman



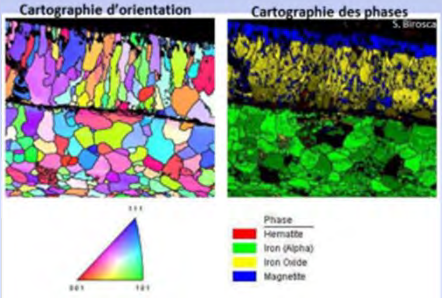
Morphology

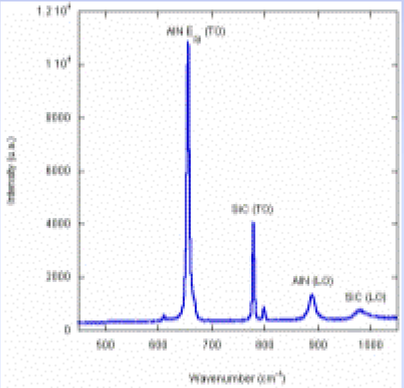
Stress/strain

Contamination

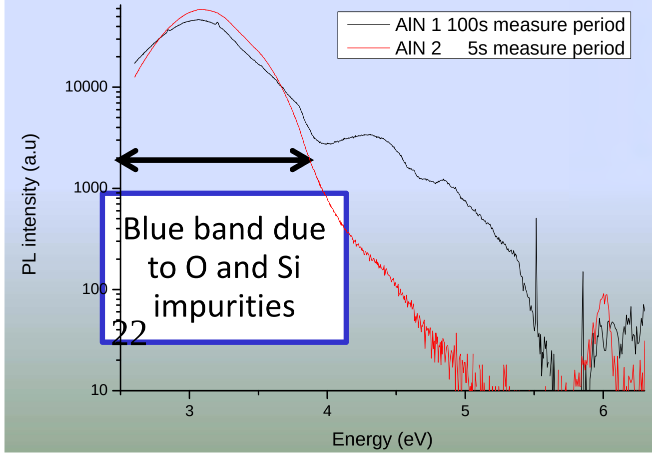
Light absorption

Orientation/
Crystalline quality



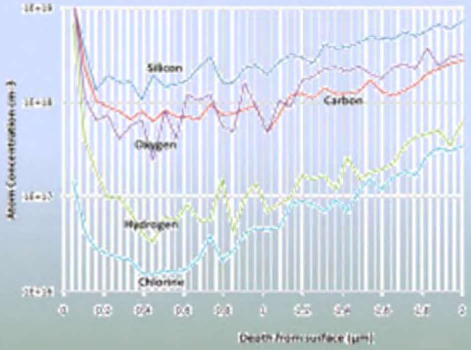


PL @ 193 nm, optic
transmission



Blue band due
to O and Si
impurities

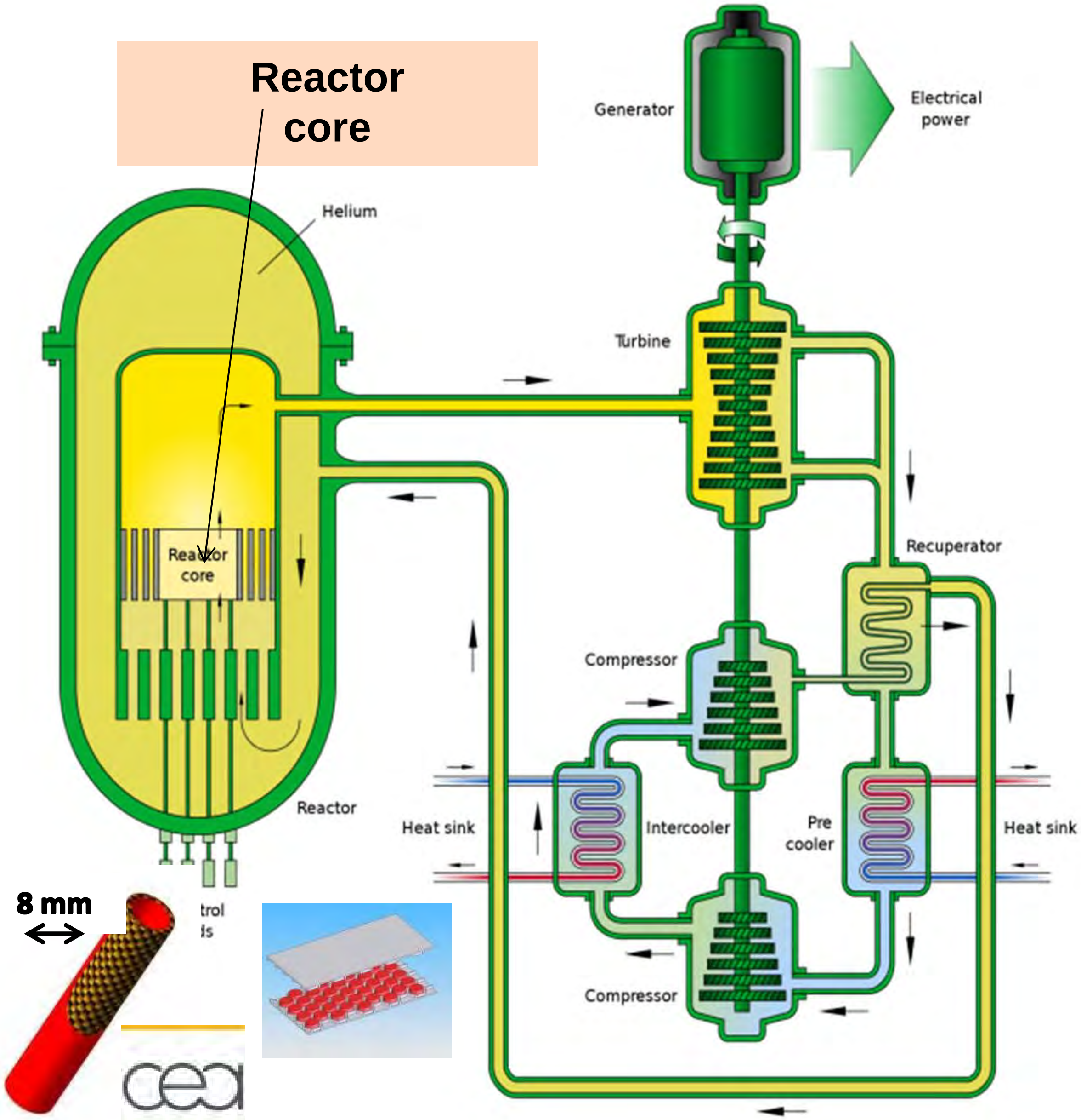
SIMS



Composite materials for Gas Fast Reactor (GFR) FUEL CLADDING...a material challenge

- **6 reactor types were considered initially. Three systems are nominally thermal reactors and three fast reactors. These systems offer significant advances in sustainability, safety and reliability, economics, proliferation resistance and physical protection.**

- **The gas-cooled fast reactor (GFR) system features a fast-neutron spectrum and closed fuel cycle for efficient conversion of uranium compounds and management of actinides.**
  - The reactor is helium-cooled, with an outlet temperature of 850 °C and a high thermal efficiency.
  - Several fuel forms are being considered for their potential to operate at very high temperatures and to ensure an excellent retention of fission products.
  - Core configurations are being considered based on pin- or plate-based fuel assemblies.



Reactor core

Specifications sheet for fuel cladding

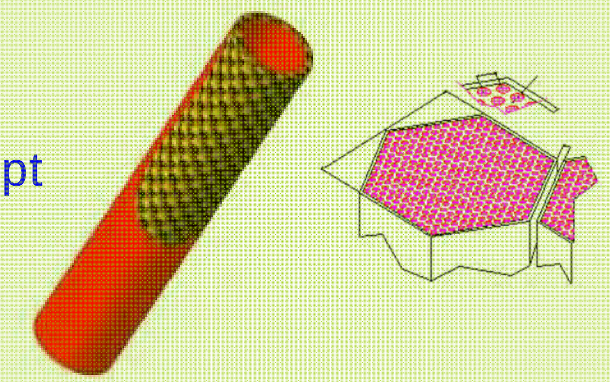
❑ ***Neutronic requirements and operating conditions:***

- *Neutrons transparency and low activity ; Operating temperatures T ~ 900-1200°C*
- *Accidental temperature: T = 1400°C-2000°C*
- *Irradiation Conditions : E > 0.1MeV, 2.10^{27} n/m^2 ……(3 years)*

❑ ***Main issues for cladding***

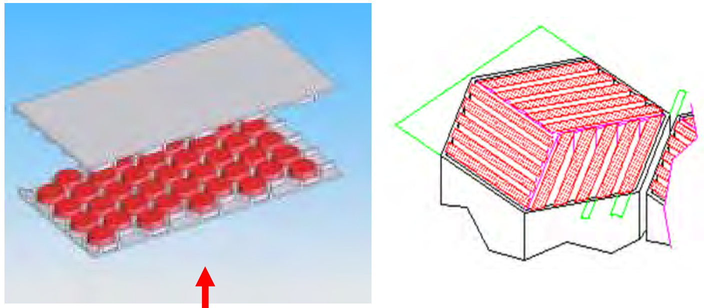
- *Hermetic sealing He, F P up to 1600°C*
- *Mechanical integrity up to 2000°C*
- *Damage tolerance: $\varepsilon\sim0.5\%$*
- *Chemical compatibility with fuel (carbide)*
- *Thermal conductivity (> 10 W/m.K)*

Pin concept



Choice of the pin concept

Plate concept

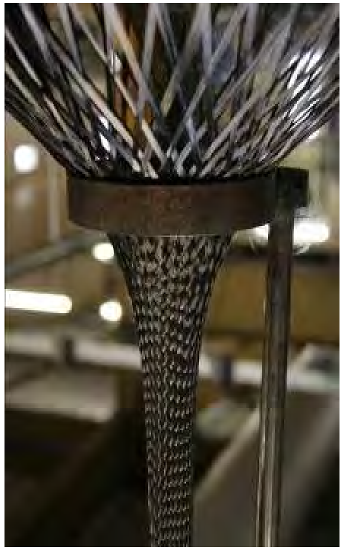


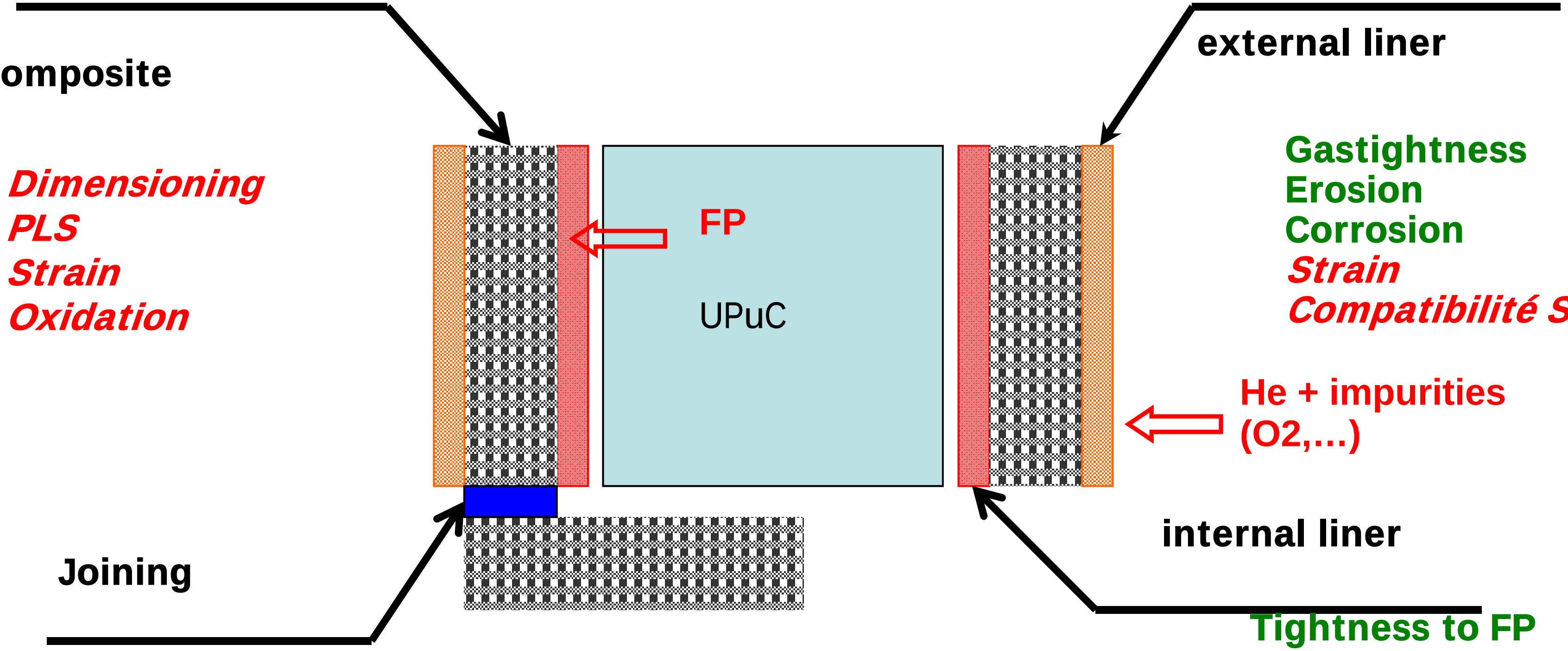
Fabricability not possible as designed

❑ *SiC composite*
❑ *W alloys*
❑ *Multilayered structure*

Specificity of *SiC/SiC composites*

- **CMC: Damage tolerant behavior ←→**
- **Release of the stress by the production of cracks**
- ***→ doesn't match the tightness barrier function!***
- ***Challenge: add a liner ensuring perfect hermetic sealing even in case of damage***





Composite

Dimensioning
PLS
Strain
Oxidation

FP

UPuC

external liner

Gastightness
Erosion
Corrosion
Strain
Compatibilité SiC

He + impurities
(O2,…)

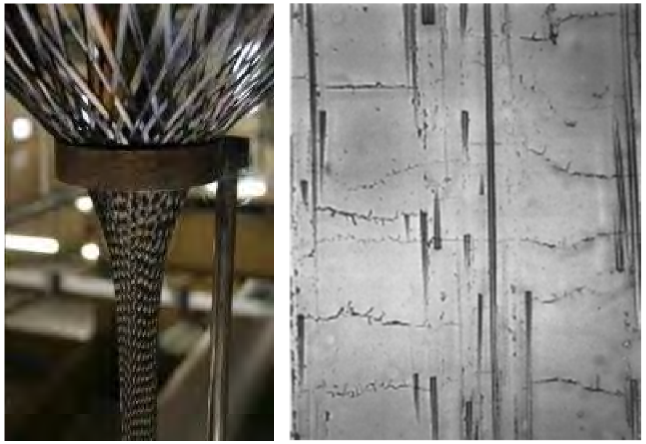
Joining

Nuclear process
Fracture stress

internal liner

Tightness to FP
compatibility SiC, UPuC
Strain

Multilayered structure



How to make the cladding gastight?

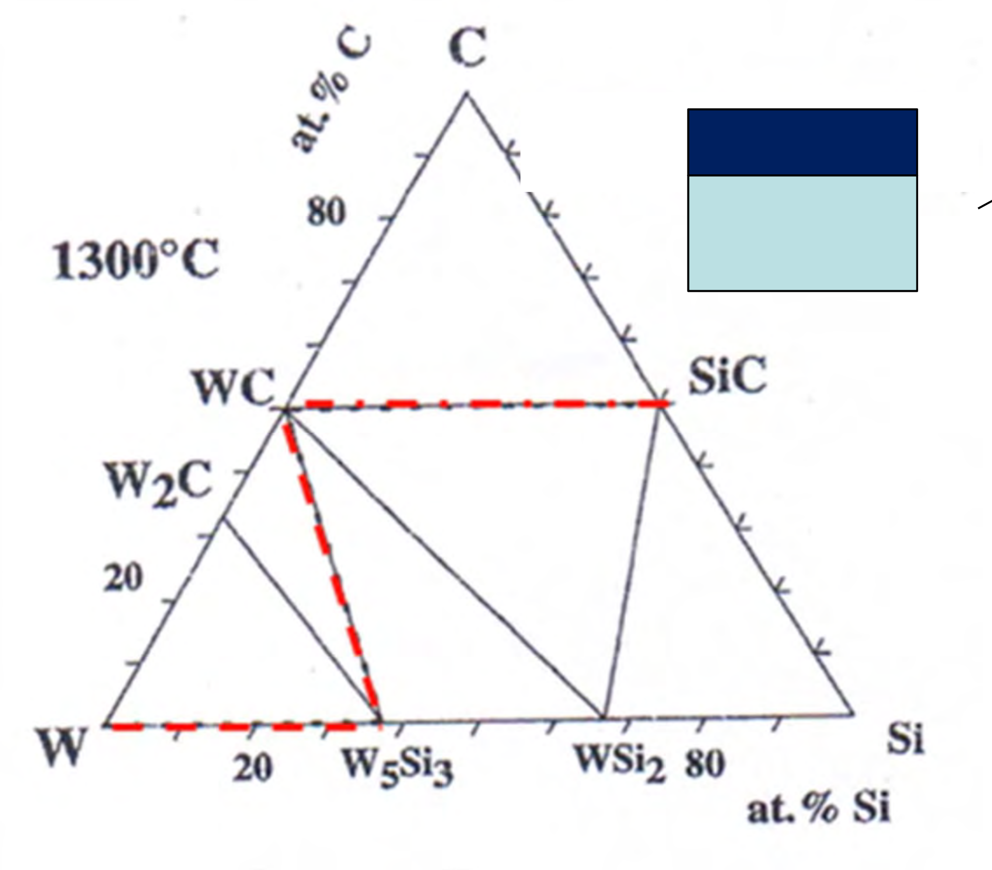
- Need for a gastight system able to sustain strain in operating conditions (F, high q, strain) and compatible with fuel
- Thermochemistry criterion: towards W (W-Re 5% alloy) *(back up Ta)*
  - Effect of irradiation: to be evaluated: concerns with pure W and W-10Re (Seidman, 85)

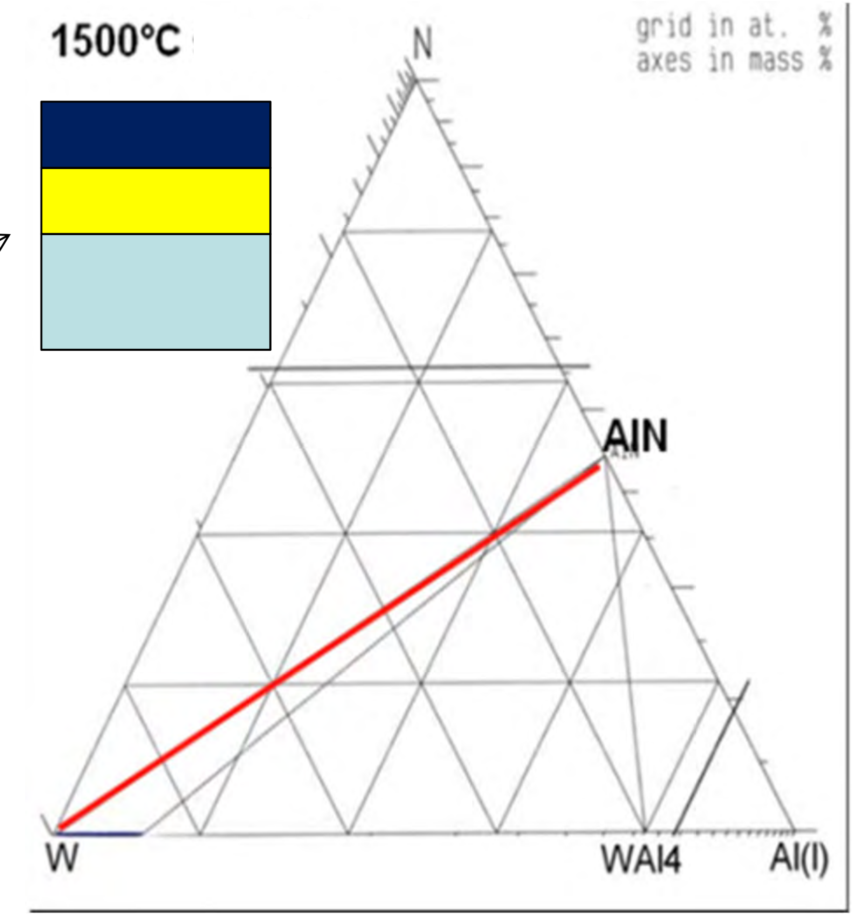
    →Program of irradiation with Jannus facility
- Study of multilayers system allowing the management of differential thermal expansion and chemical reactivity at high temperatures
  - ANR program COMPOSIC in association with SNECMA PS, Acerde, SIMaP and CEA (3 years from 2009)

Thermodynamics computations : liner SiC/AlN/W

- ❑ W-C-Si ternary phase diagram between 1533 and 1780K
- ❑ Diffusion path at 1573K between W and SiC from F. Goesmann and R. Schmid-Fetzer - - -

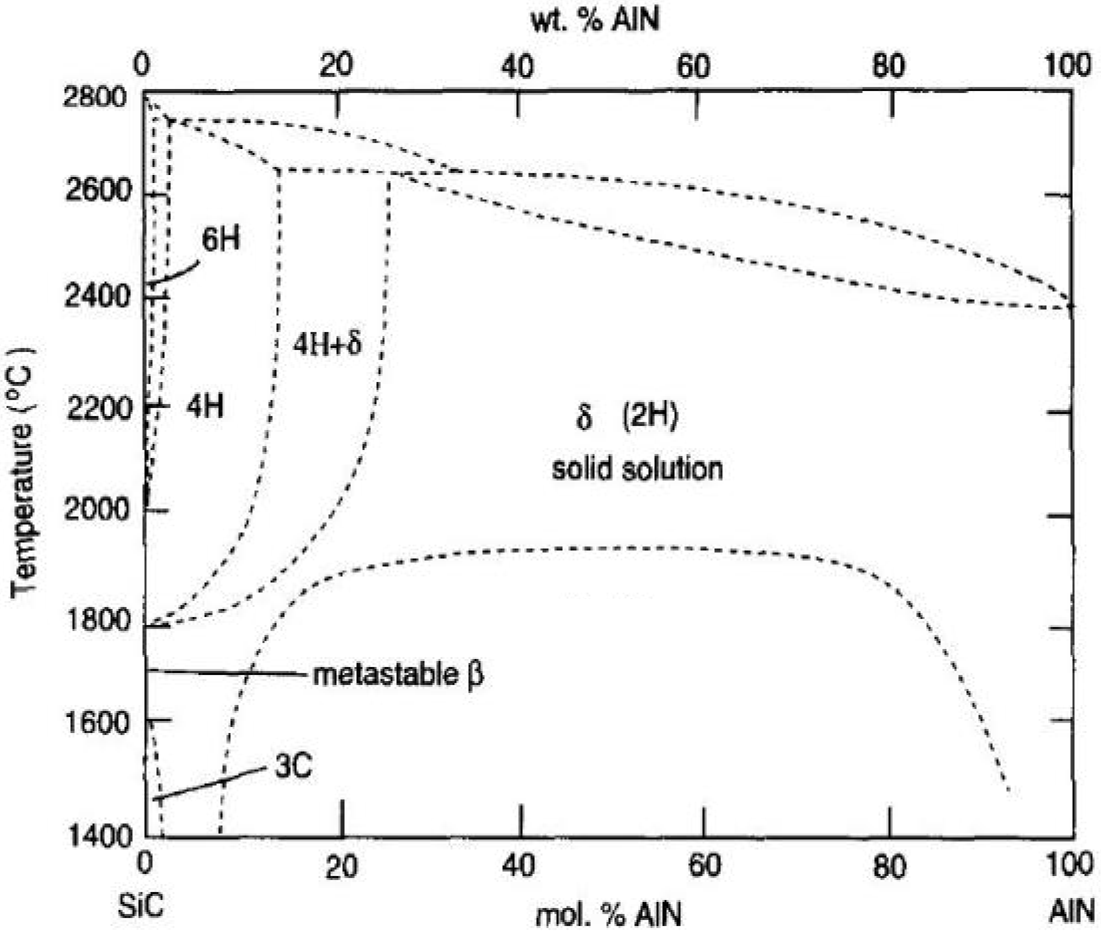
- ❑ Experimental Isothermal section 1773K from Schuster and Nowotny



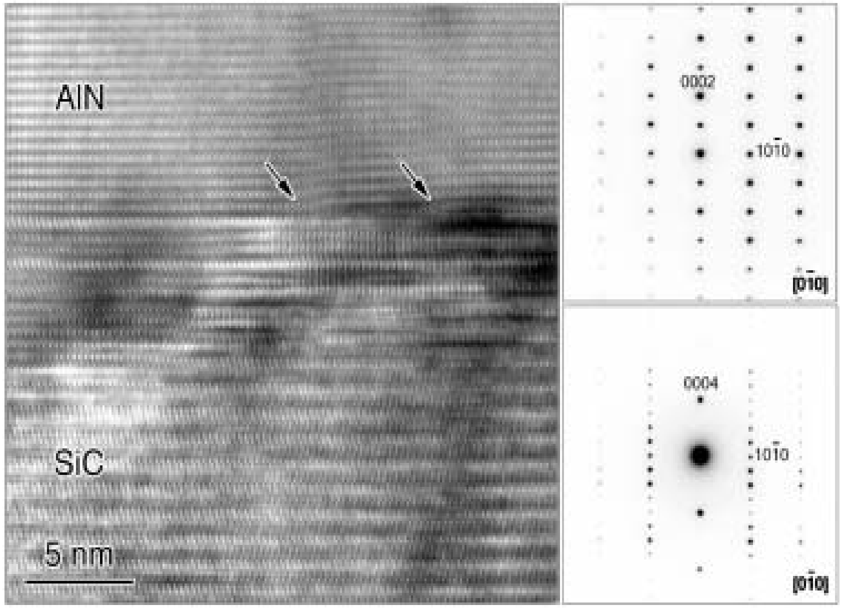


SiC and AlN

- **SiC and AlN : solid solution**

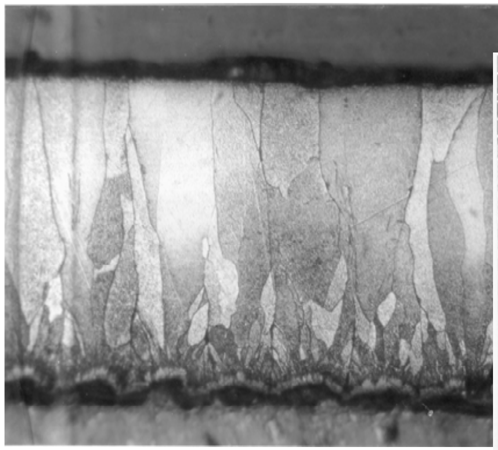


- **SiC and AlN : stable interface at temperature above 1600° C (J. Crystal Growth 2009)**

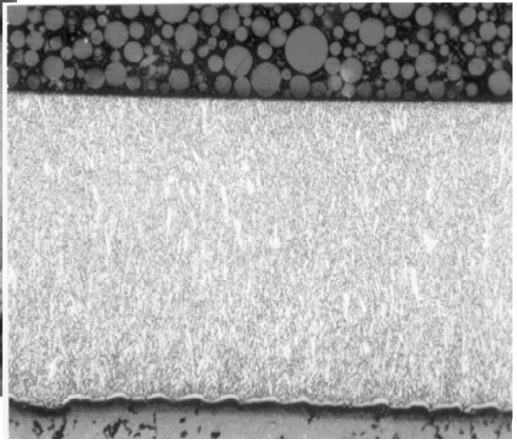


Thermodynamics computations : liner SiC/AlN/W(Re)

- **From W to W_xRe_y**
- **Improvement of mechanical properties**

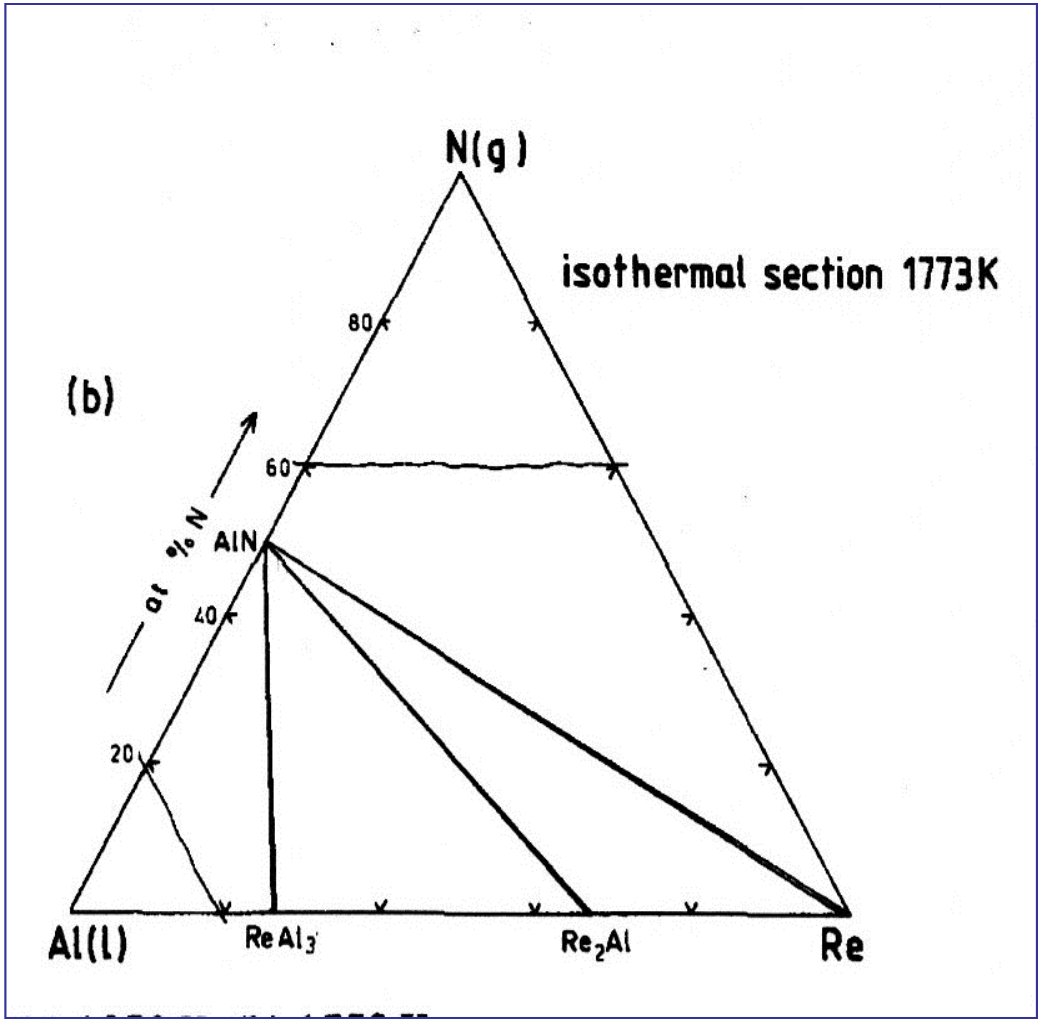


(a) 100 µm



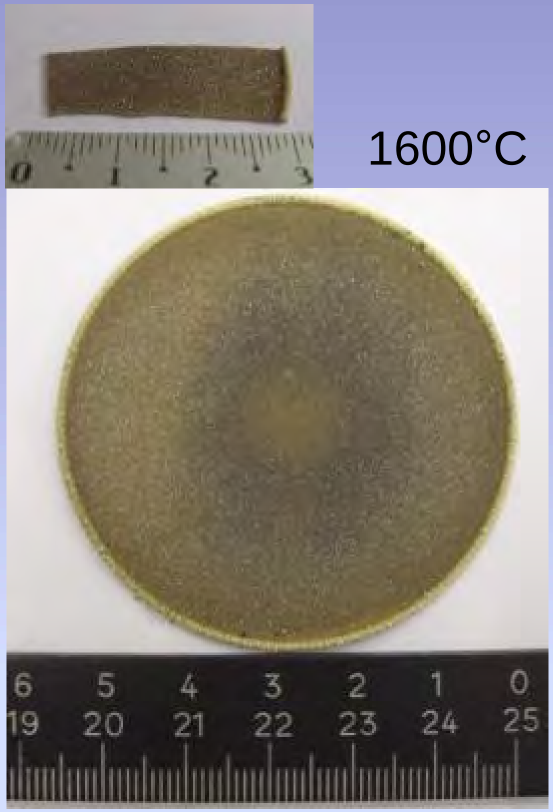
(b) 100 µm

- **Experimental Isothermal section 1773K from Schuster and Nowotny**



AlN polycrystal

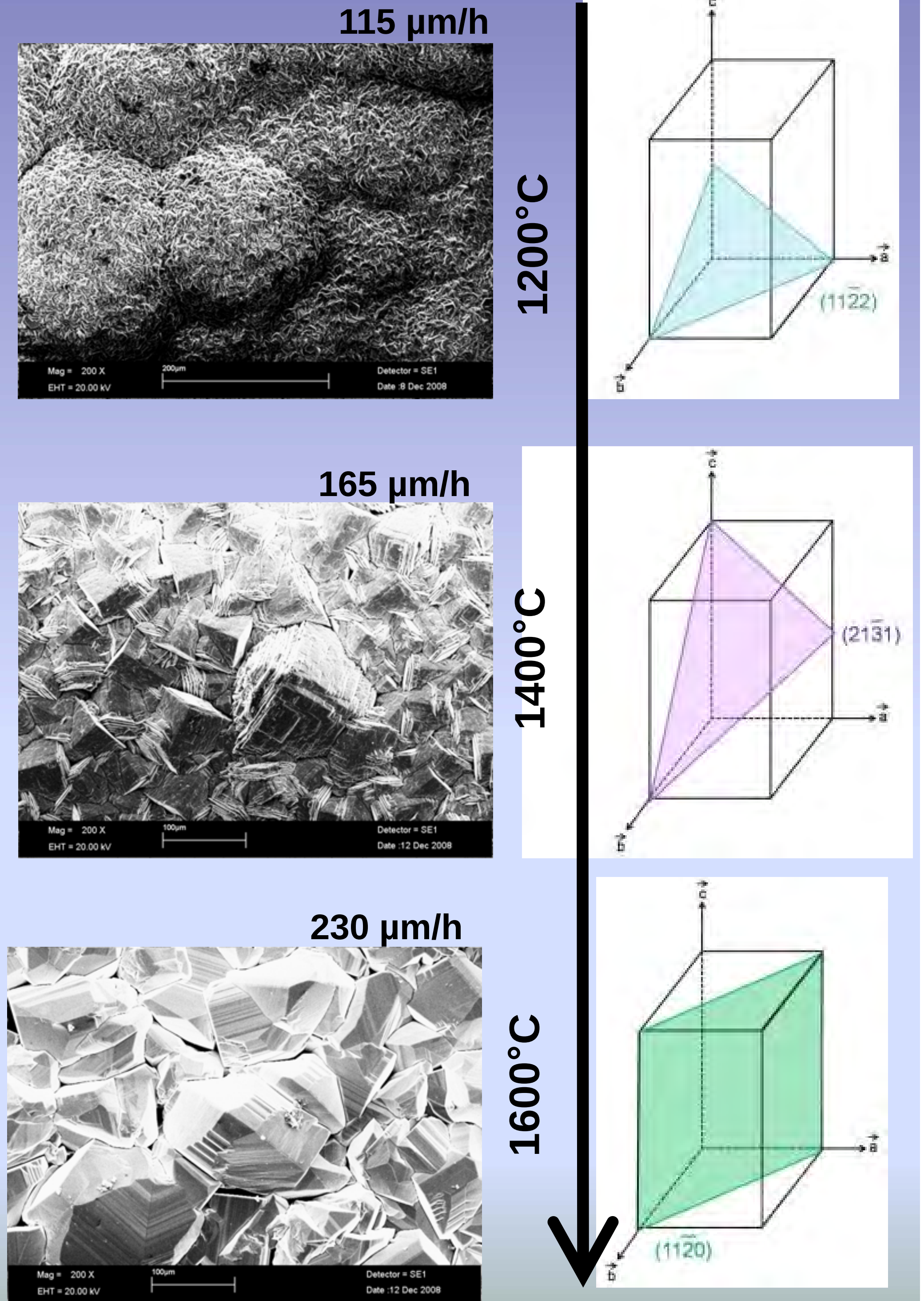
AlN polycrystal



1600°C

Key points

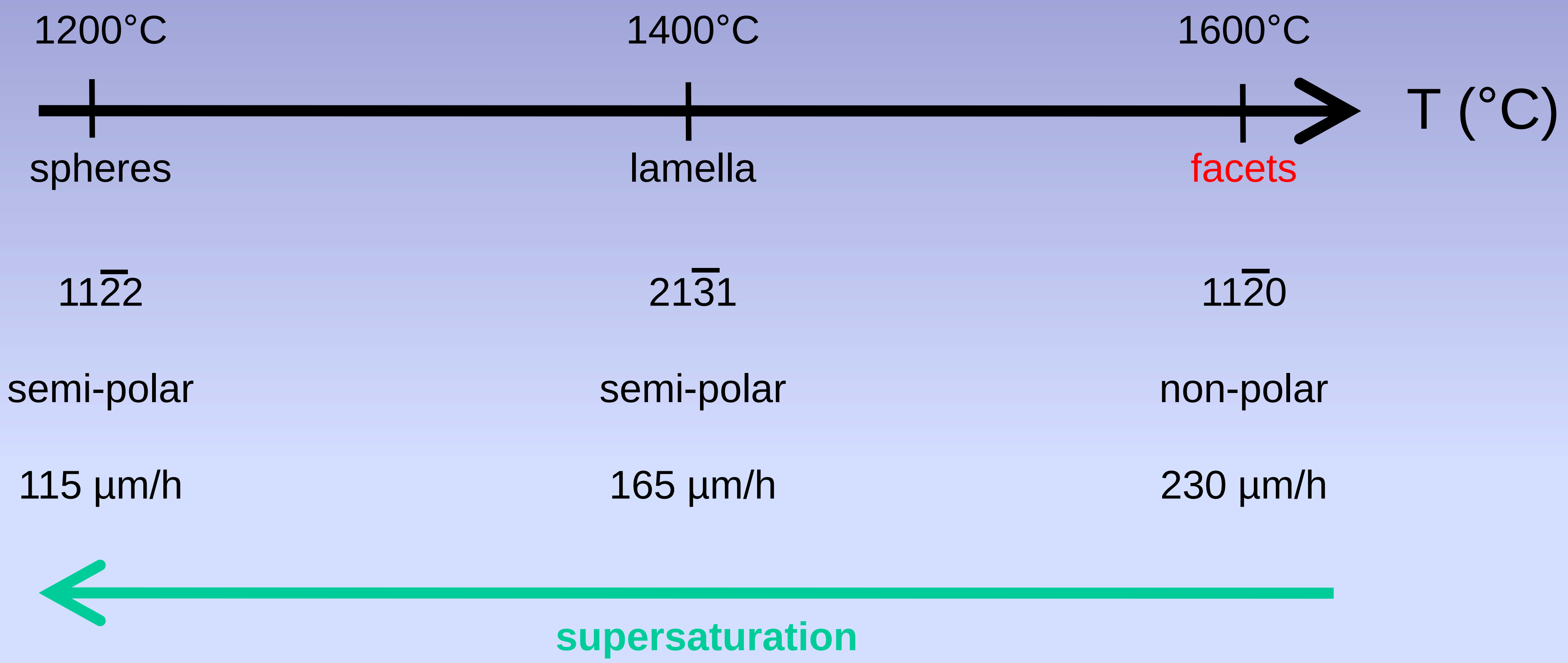
At 1600°C :
- High growth rate (> 100 µm/h)
- 200 µm grain
- Non polar growth



Surfaces (SEM)

(A. Claudel et al. J. Electroch. Soc.2011)

Microstructure evolution : polycrystalline AlN on SiC

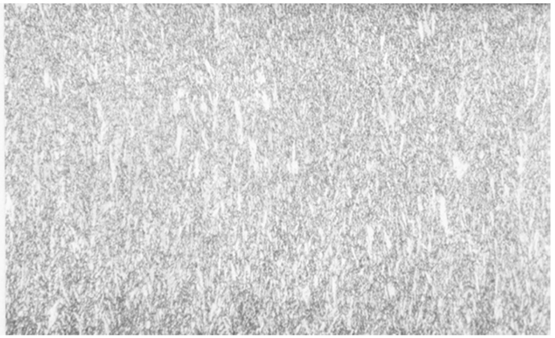


1200°C	1400°C	1600°C
spheres	lamella	facets
$11\bar{2}2$	$21\bar{3}1$	$11\bar{2}0$
semi-polar	semi-polar	non-polar
115 µm/h	165 µm/h	230 µm/h

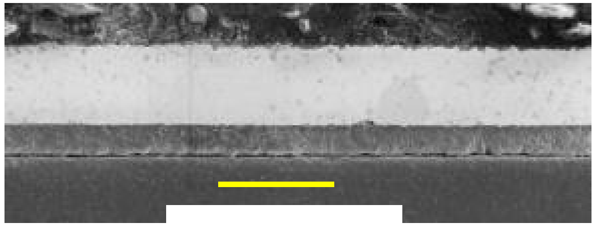
- ✓ Polycrystalline AlN at high growth rate
- ✓ Morphology: sphere → facets
- ✓ Orientation from semi-polar → non-polar

W-5%Re on SiC/AlN

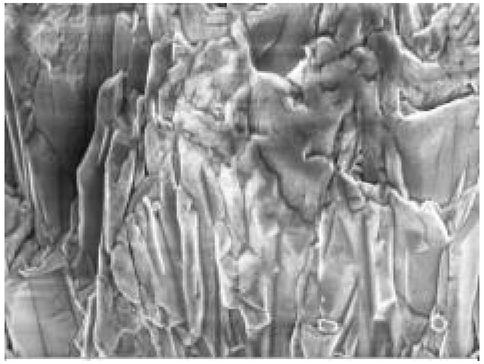
- ❑ **Columnar and fine microstructure for AlN**
- ❑ **Fine microstructure for W-5%Re**
- ❑ **A new multilayered structure never reported in the literature**



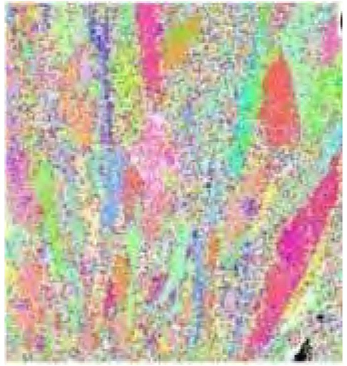
(b) 50 µm



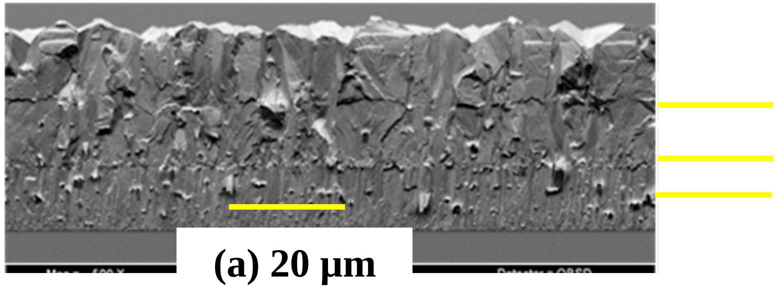
(a) 50 µm



(b) 2 µm

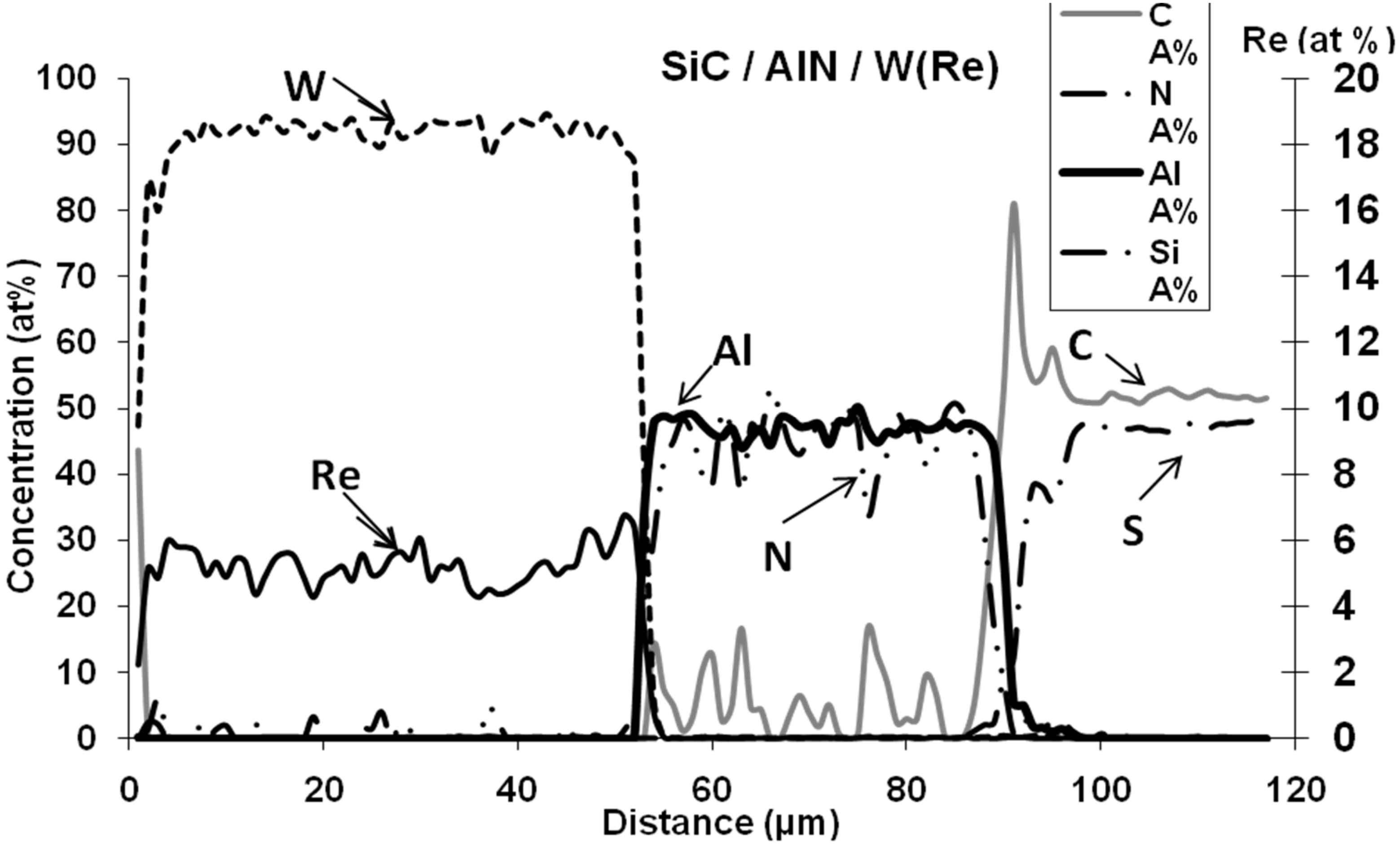


(c) 2 µm



(a) 20 µm

❑ Profile after 100h at 1600 K



Conclusions

- The thermodynamic analysis, carried out to select the interlayer material, AlN, between SiC and $W_{1-x}Re_x$, showed that this multilayered stack could be chemically stable at high temperature.

- AlN/ $W_{1-x}Re_x$ thick films were deposited on SiC by chemical vapor deposition to study their chemical stability.

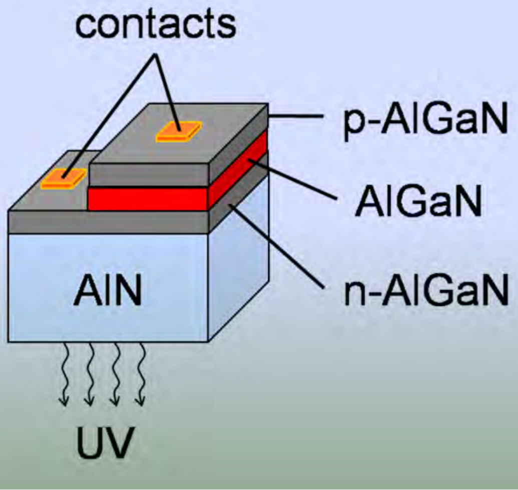
- If the long term chemical and mechanical stability is confirmed, this knowledge will be transferred for the sealing of composites by AlN and their compatibility at high temperature with refractory metals.

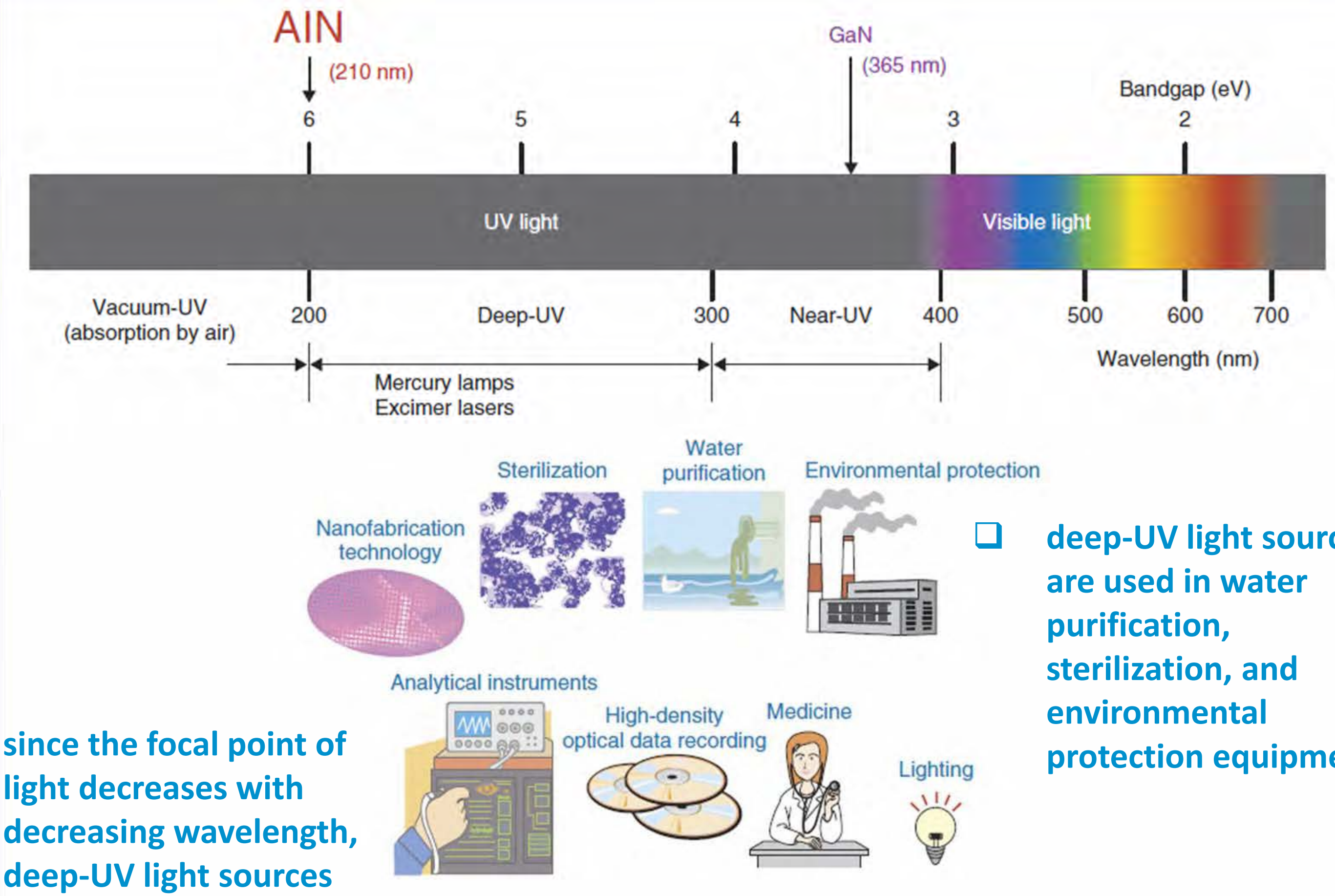
Application of AlN to UV light sources

Yoshitaka Taniyasu and Makoto Kasu NTT Technical Review, 8, 2010

- **Widest direct band gap, 6.2 eV, -> Deep-UV light emitters with a wavelength of 210 nm**
- **the photon energy of deep-UV light sources is high enough to kill bacteria and viruses and decompose harmful stable substances, such as dioxin and polychlorinated biphenyls (PCBs).**

- **Crystalline quality of AlN is still the challenge to have the best efficiency of the emitters**





- **since the focal point of light decreases with decreasing wavelength, deep-UV light sources have potential for use in high-density optical data recording and nanofabrication technology**

- **deep-UV light sources are used in water purification, sterilization, and environmental protection equipment**

Aluminum nitride : Applications

- Optoelectronic devices : UV Light Emitting Diode LED, UV LD, white LED

Requirements: High crystalline quality, epitaxial layers

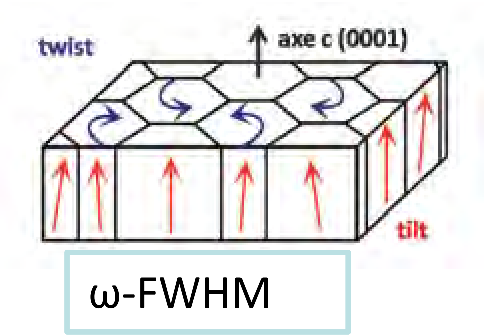
FWHM < 100 arcsec (0002) reflection

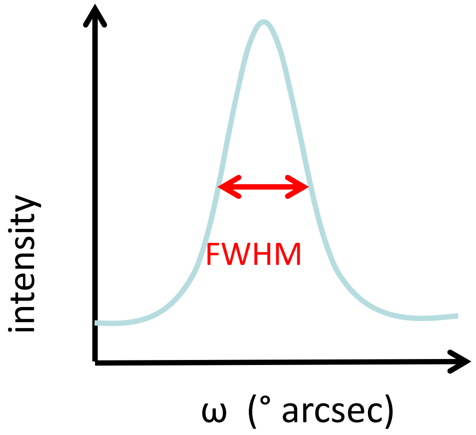
Low defect density

No cracks

Doping control

Purity



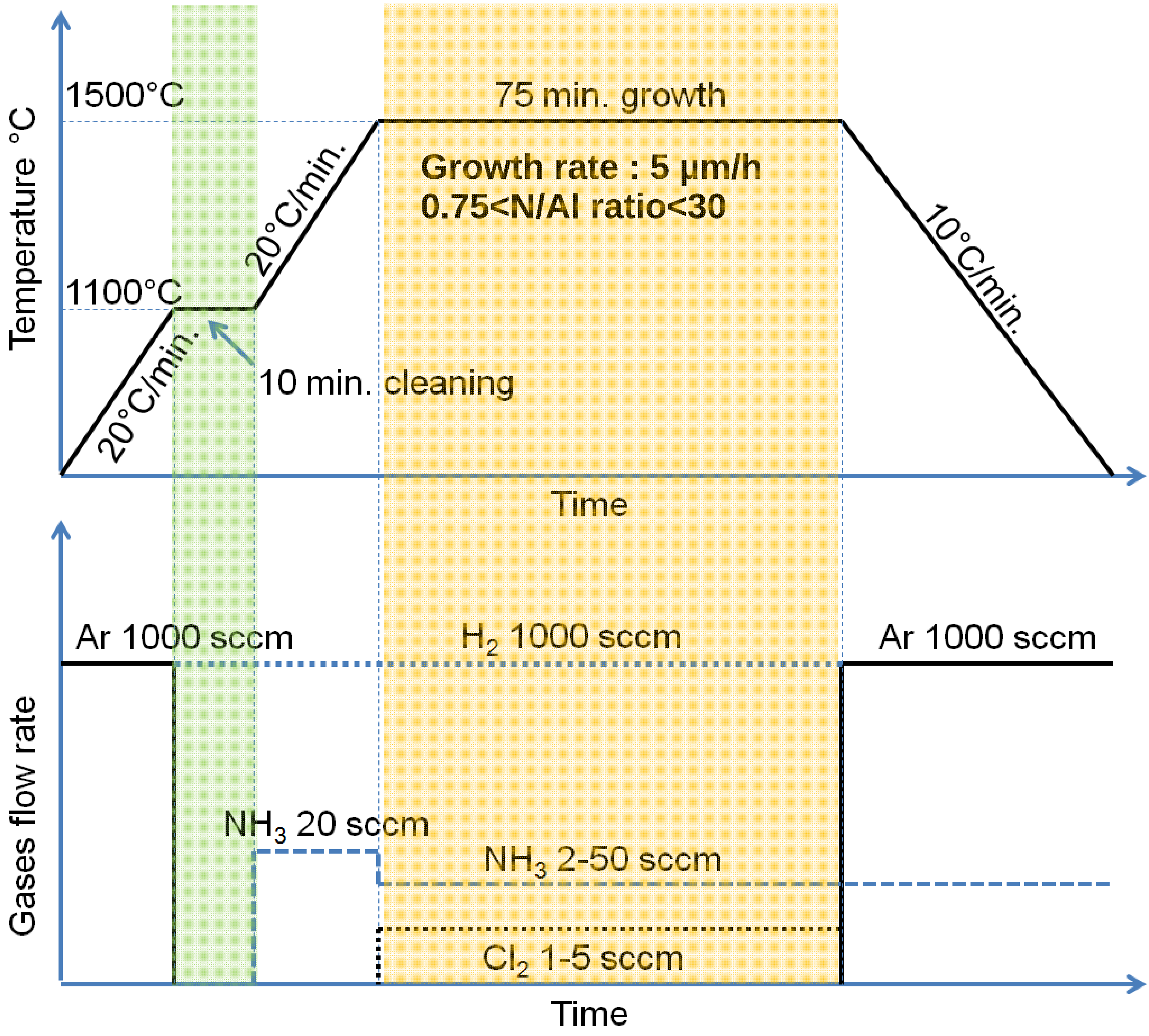


1-10 μm thick layer on foreign substrates

or bulk material used as substrates

2. One step deposition

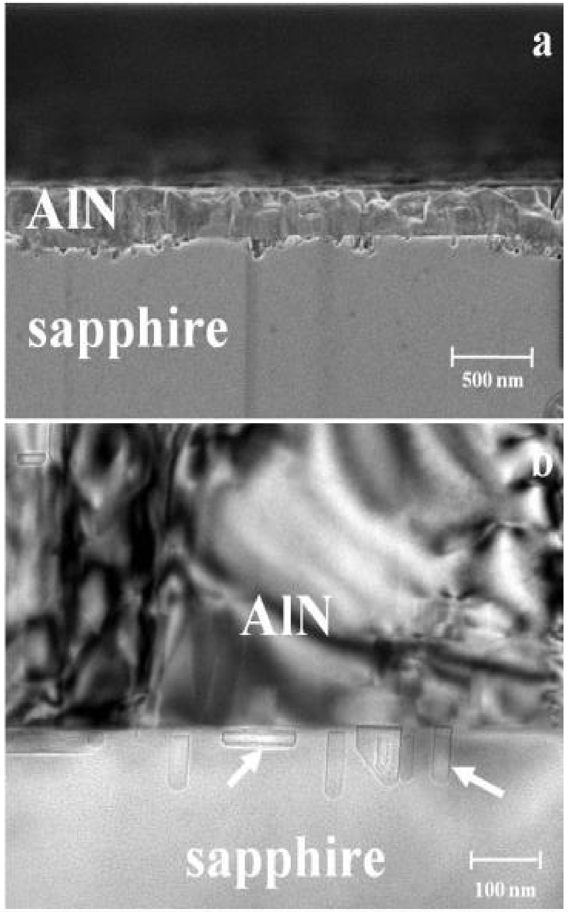
One step growth sequence on sapphire substrate

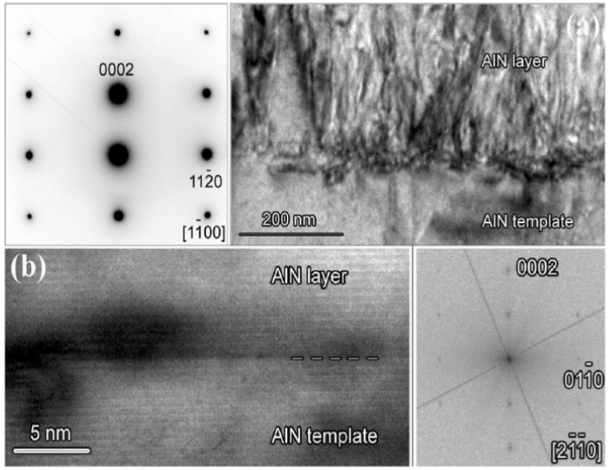


Growth rate : 5 µm/h
0.75<N/Al ratio<30

2. One step deposition

One step growth sequence

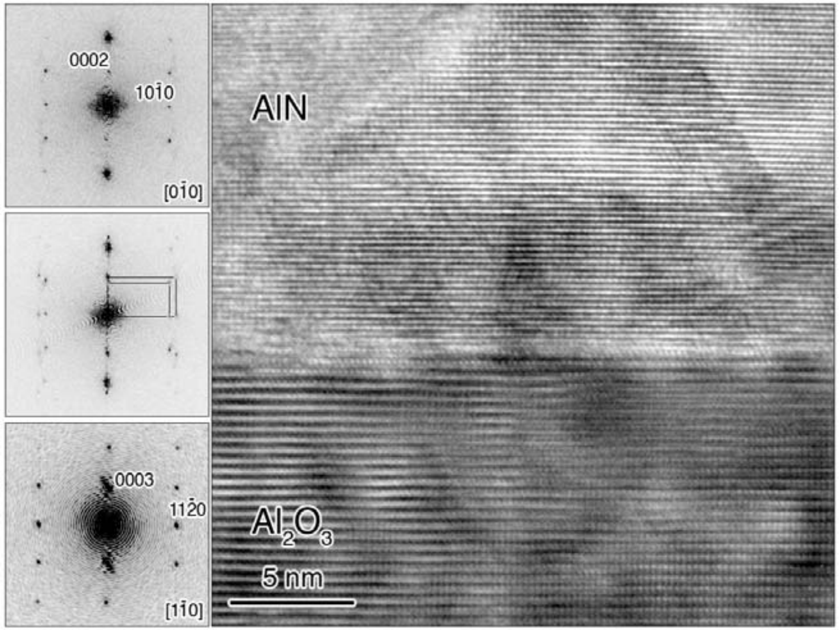


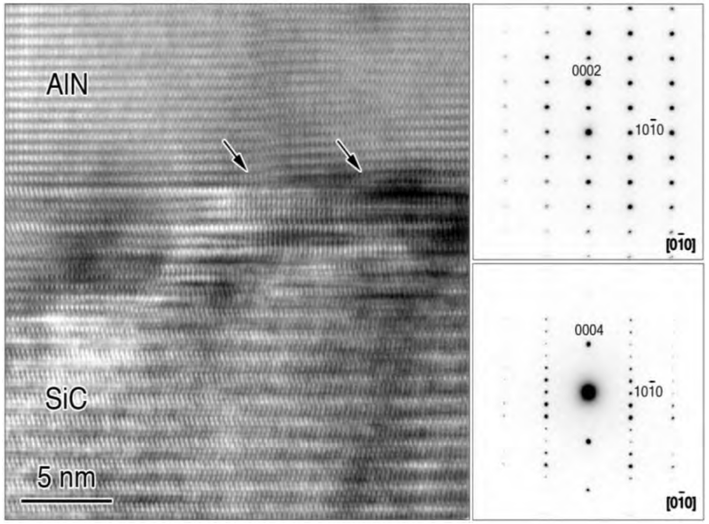


☺ Crystallographic relationship : (0001) AlN // (0001) Al_2O_3 (perpendicular to the interface) and (10-10) AlN // (11-20) Al_2O_3.

☹ A high level of stress is due to the high lattice mismatch >12 % and TEC difference (see paper for more details)

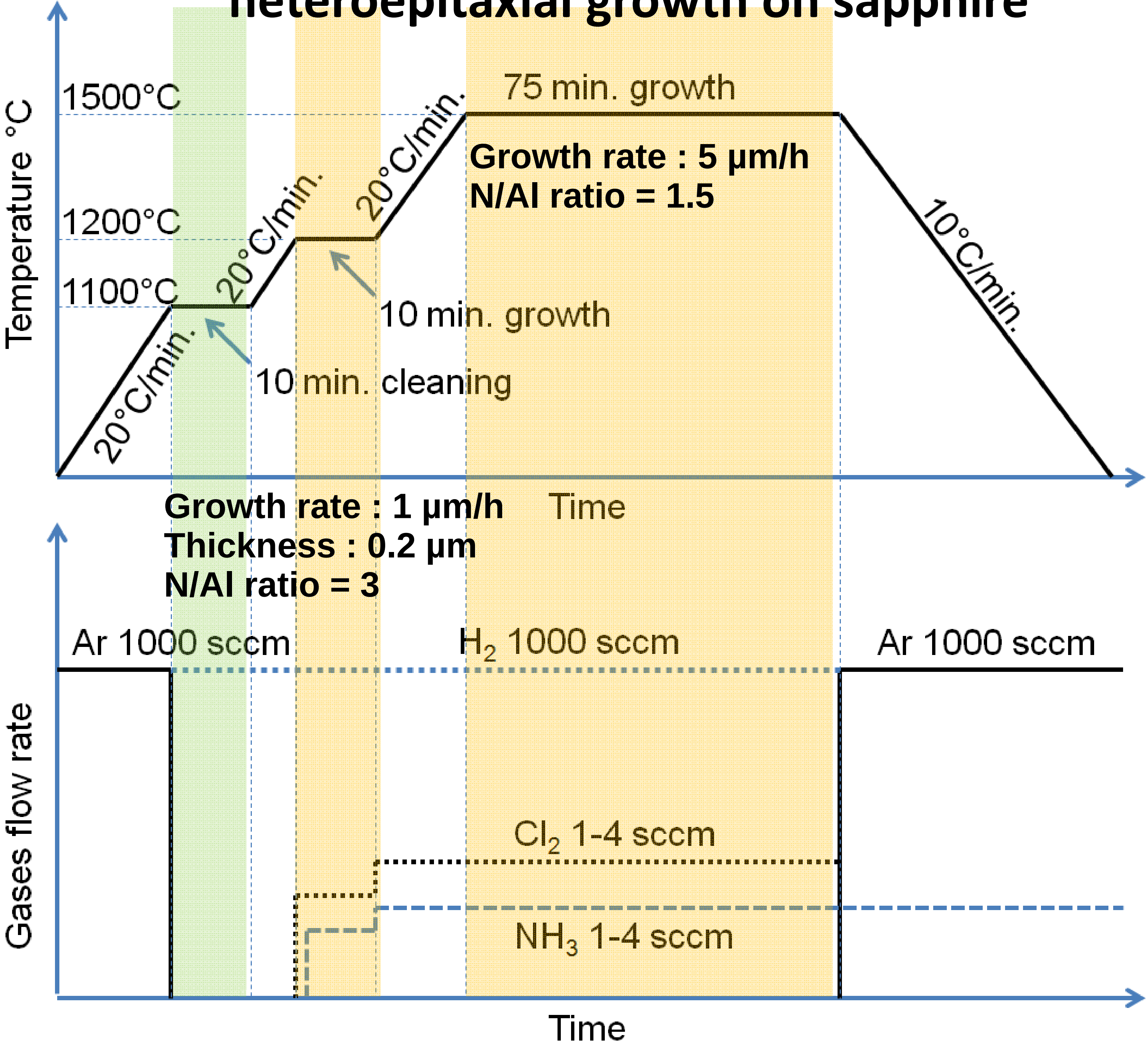
☹ Voids at the interface revealing etching during the initial stages of the growth





☺ We had better results on SiC and AlN single crystals.

Two steps growth sequence : heteroepitaxial growth on sapphire



Growth rate : 5 µm/h
N/Al ratio = 1.5

Growth rate : 1 µm/h
Thickness : 0.2 µm
N/Al ratio = 3

AlN/Sapphire

AlN on c-plane sapphire
a bird eye view

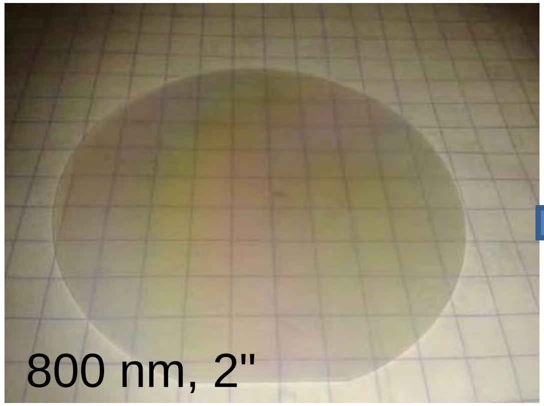
How to manage cracks?
➔control of the stress in AlN layers

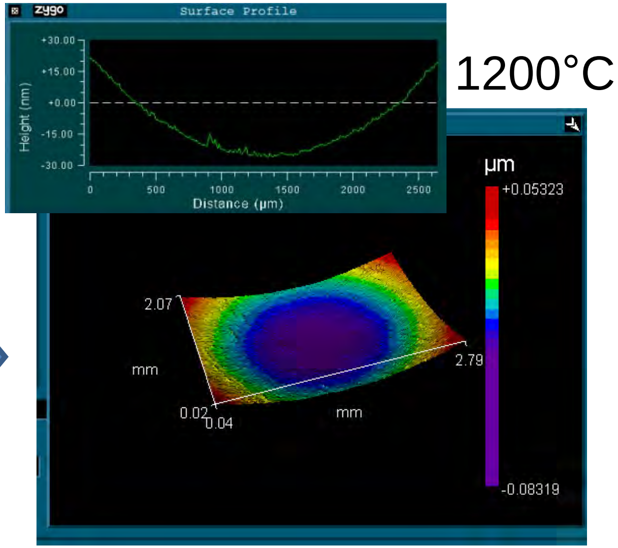
Measured stress at RT = growth stress+cooling stress

Tensile @1200°C
Compressive @1500°C

Competition between tensile stress during nucleation and compressive stress during cooling

AlN protective layer on
2" sapphire grown at 1200℃

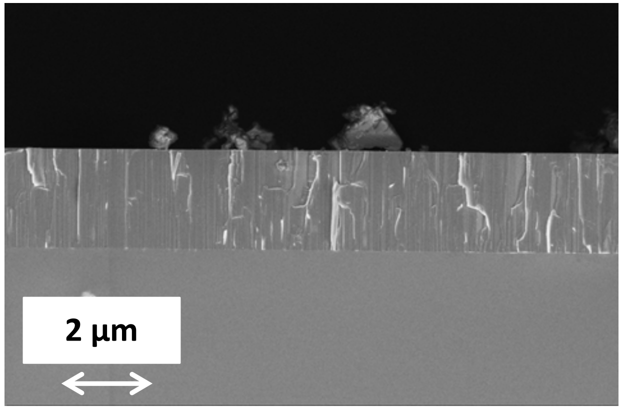




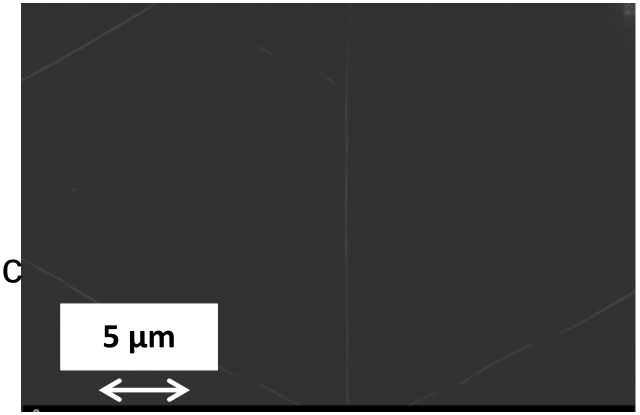
1200°C

Optical profilometer

Protective layer (1200°C) + thick layer (1500°C)



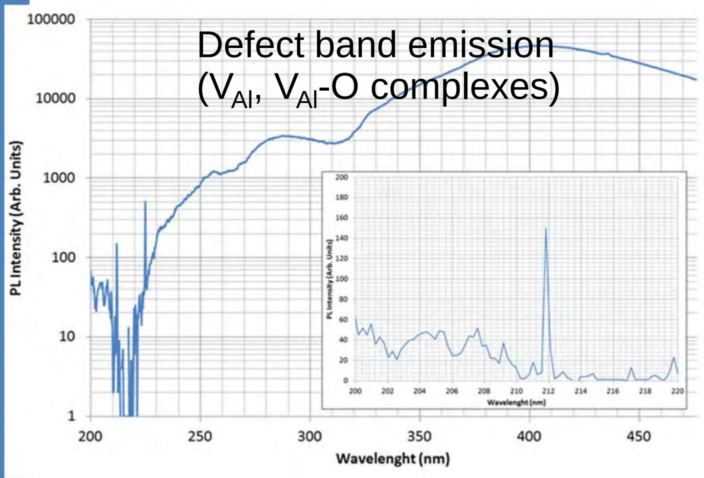
FWHM:
0.12° - 327 arcsec



Balance of tensile/compressive stress➔ reduction of cracks

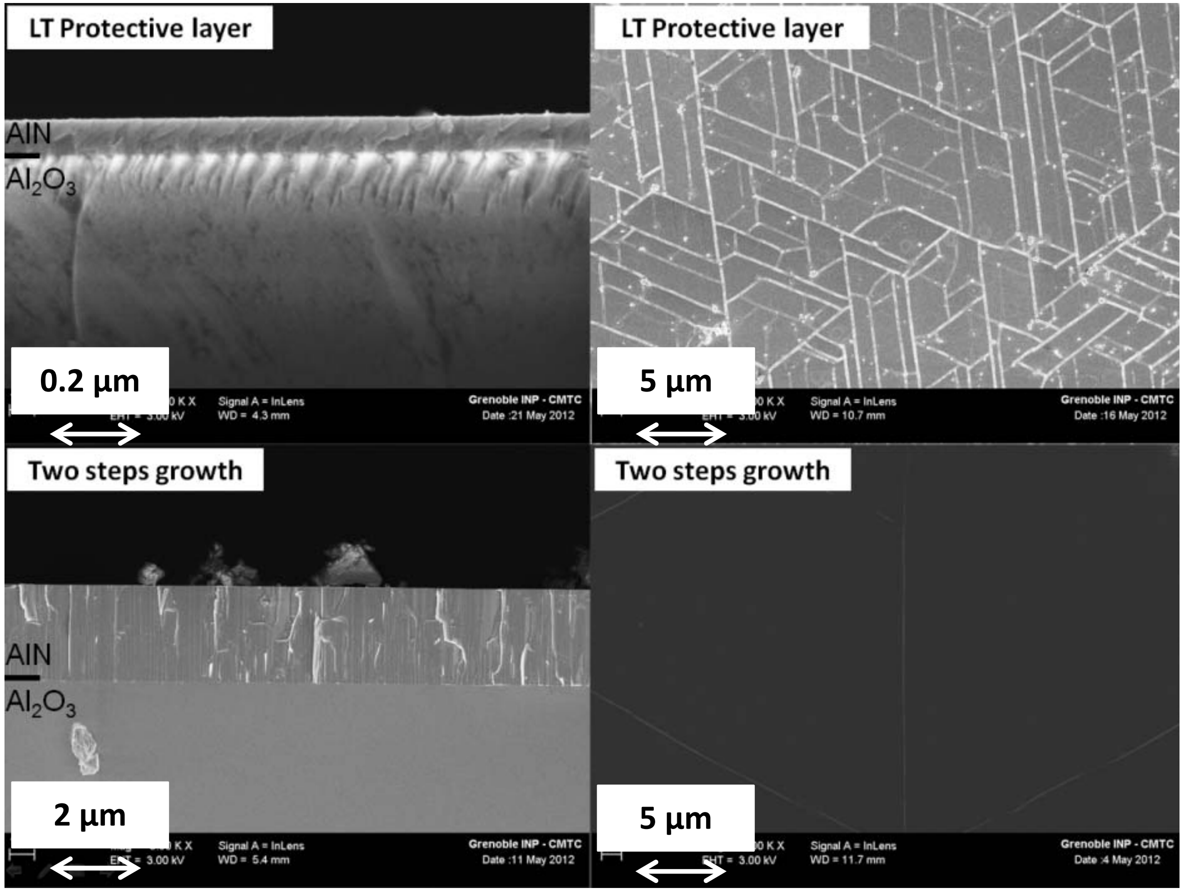
Surface and cross section morphology

FWHM (0002) : 327 arcsec
E_2(h) 643.94 cm^{-1}(657.4)
AFM RMS roughness : 9.492 nm
TD : 1.1x10^8 cm^{-2}



Defect band emission (V_{Al}, V_{Al}-O complexes)

Near Band Edge emission at 5.85 eV



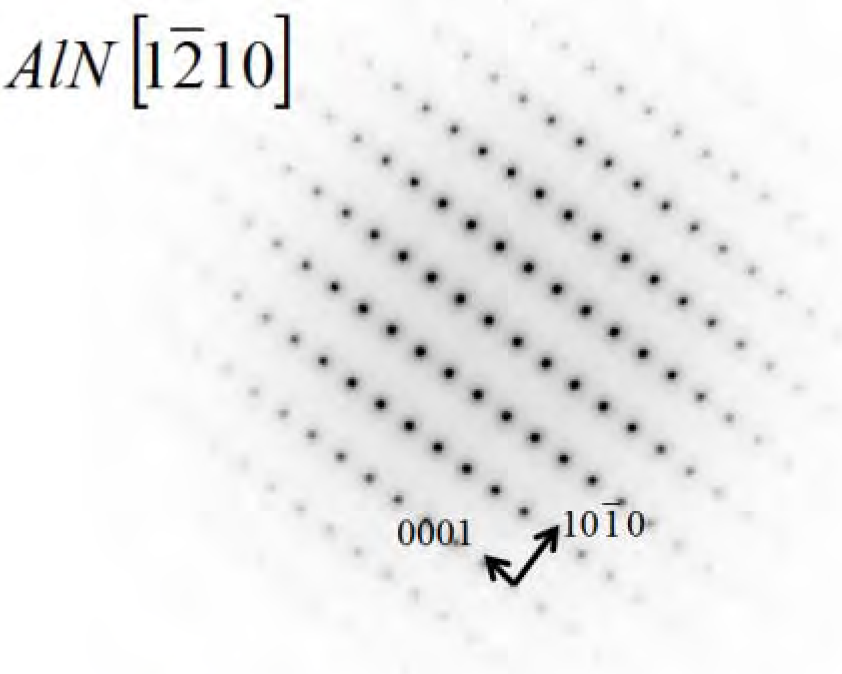
FWHM (0002) : 3800 → 376 arcsec
E_2(h) : 660.54 cm^{-1} → 658.18 cm^{-1} (657.4)
AFM RMS roughness : 15 nm
TD : 1.7x10^8 cm^{-2}

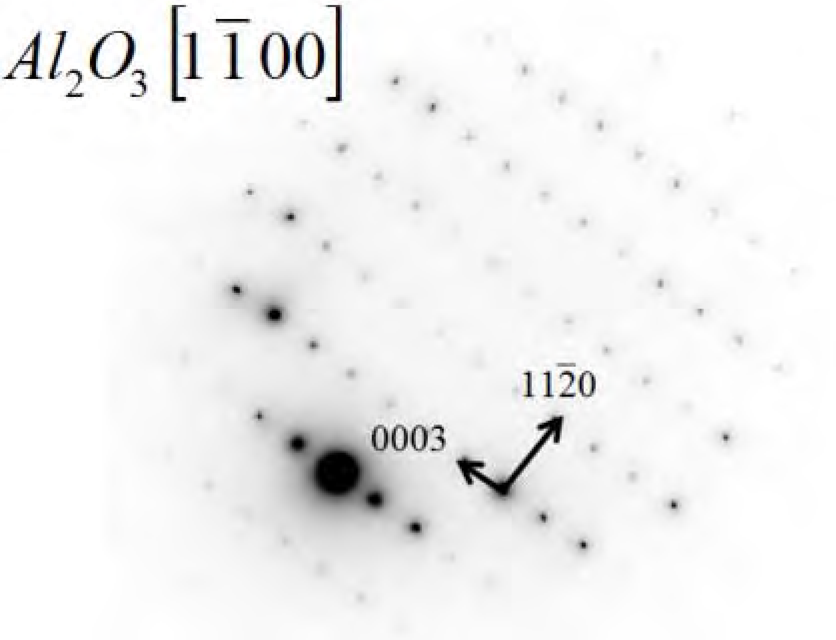
For Deep UV LED

Al, Si and O vacancies must be lowered
TD : 1.7x10^8 cm^{-2} -> 1.0x10^6 cm^{-2}

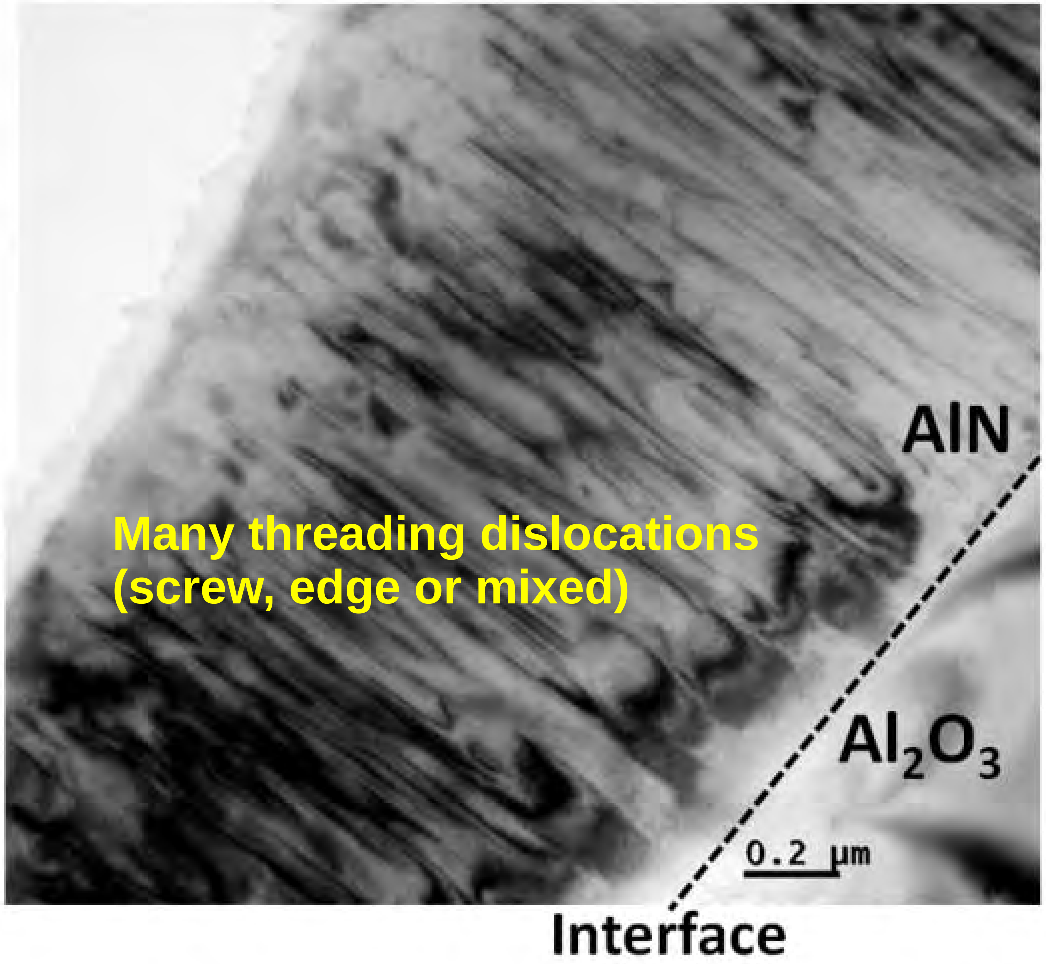
4. Char. of the two steps layer

TEM cross section morphology



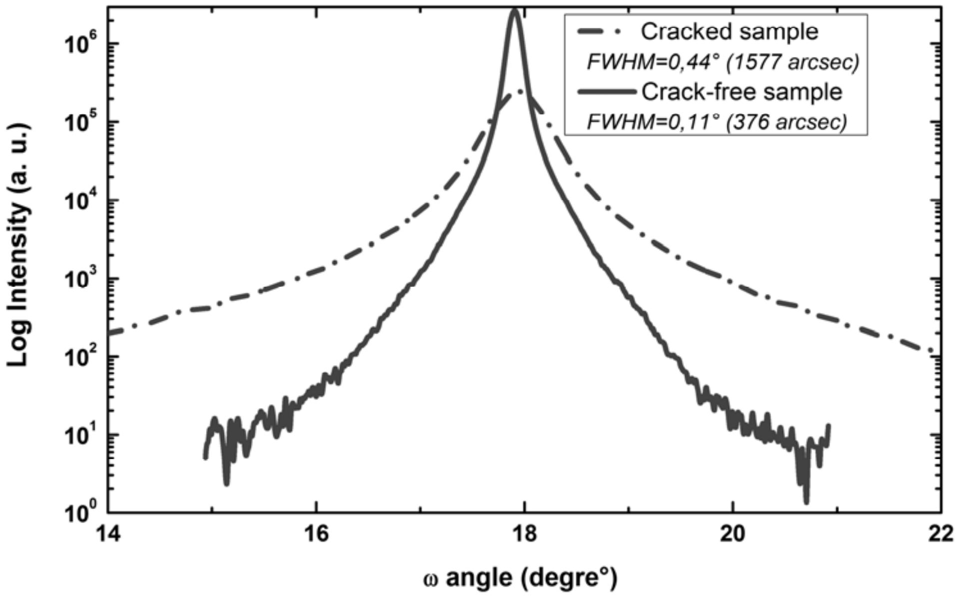


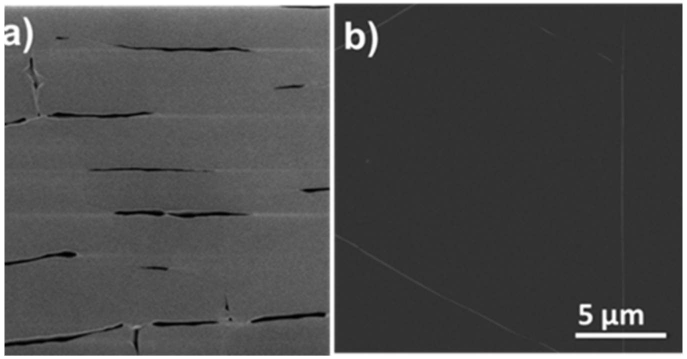
$(0001)AlN//(0001)Al_2O_3$,
with <10-10>AlN // <11-20> Al_2O_3



5. Conclusions

Substrate requirements for UV LEDs applications: Dislocation density < 10^6





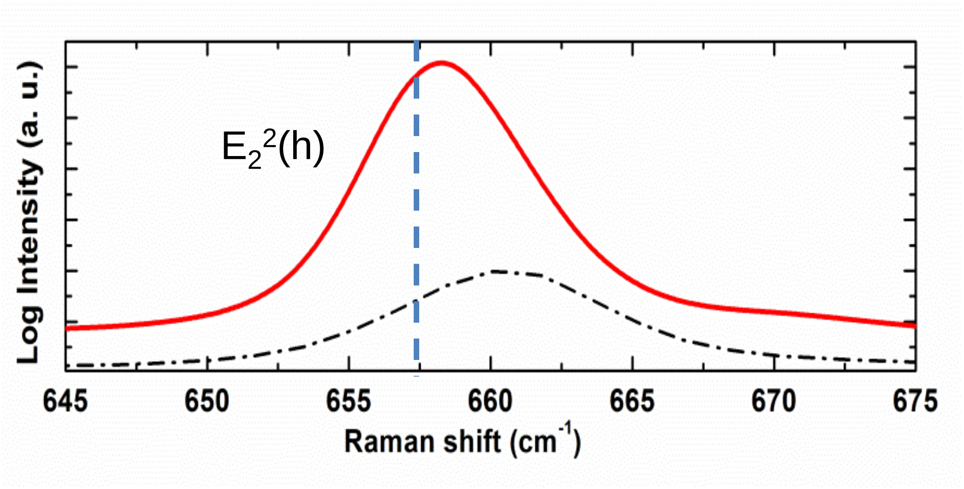
☺ X-Ray rocking curves (Full-Width at Half-Maximun) shows a strong improvement

- Disorientation : 376 arcsec (0.12 °)
- Dislocation density : 1,7 x 10^8 cm^{-2}
- A high residual stress but lower

☹ A high level of stress is due to the high lattice mismatch >12 % and thermal stress : 1.6 GPa

- Tensile stress of protective layers due to grain calescence
- Compressive stress of the final layer due to TEC difference

Tension - 657,4 cm^{-1} - compression



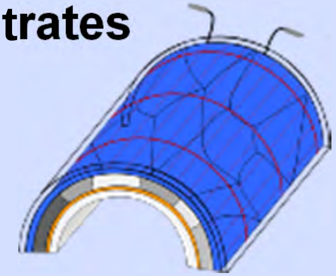
SIMS measurements: Si : $2x10^{18}$ $at.cm^{-3}$, C : $8x10^{17}$ $at.cm^{-3}$, O : $3x10^{17}$ $at.cm^{-3}$, H : $4x10^{17}$ $at.cm^{-3}$, Cl : $2x10^{16}$ $at.cm^{-3}$; **Photoluminescence** : 5.85 eV (6.2 theory)

Conclusions

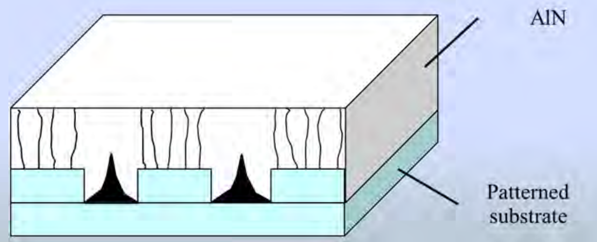
✓ Growth of a wide variety of AlN thin and thick films or coatings
✓ Control of the process windows by mass transport modeling
✓ Epitaxial growth (from 0.1 to 15 µm.h^{-1})
✓ Polycrystalline growth (up to 300 µm.h^{-1})

- Too high density of dislocations for deep UV LEDs
- Emission at 210 nm but too much impurities
- Insulating properties $\rho = 10^{8}$ à 10^{11} Ω.cm

- Excellent coating for high temperature applications (C/C, SiC/SiC composites, metals and alloys ..)
- Potential properties for SAW devices for high frequency applications
- Good buffer layer for the fabrication of silicon quasi-substrates on formable steels



Perspectives



☐ Improvement of the crystalline quality
☐ A growth in two steps was the first improvement
☐ The second improvement is LTO : lateral overgrowth (looks like LTO GaN thick films)