In situ X-ray studies of the early stage of ZnO Atomic Layer Deposition on InGaAs and the synthesis of lamellar dichalcogenides thin films prepared by Molecular Layer Deposition and thermal annealing

H. Renevier

LMGP, Grenoble INP & CNRS, Grenoble, France

EPIDOX November 17 2021

Talk outline

Part 1

In situ growth studies of Atomic or Molecular Layer Deposition (ALD or MLD) at LMGP

Part 2

In situ X-ray studies of the early stage of ZnO Atomic Layer Deposition on InGaAs

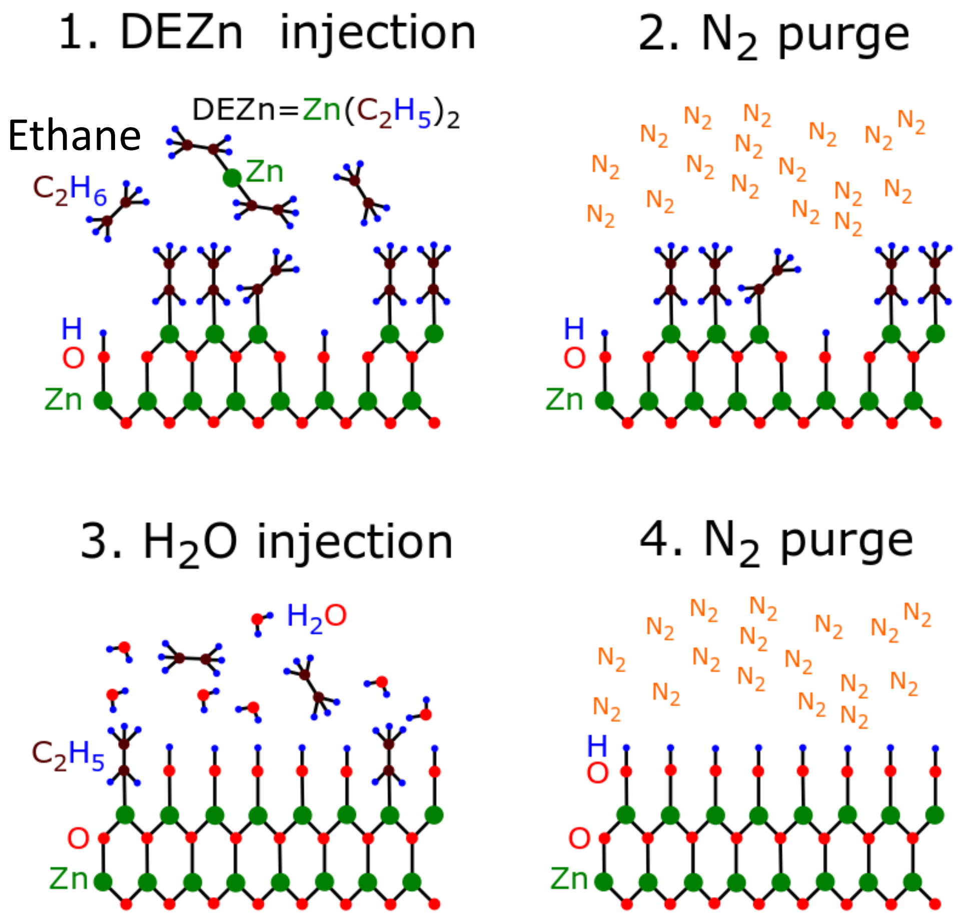
Part 3

In situ X-ray studies of dichalcogenides thin films prepared by Molecular Layer Deposition and thermal annealing

In situ growth study of ALD or MLD

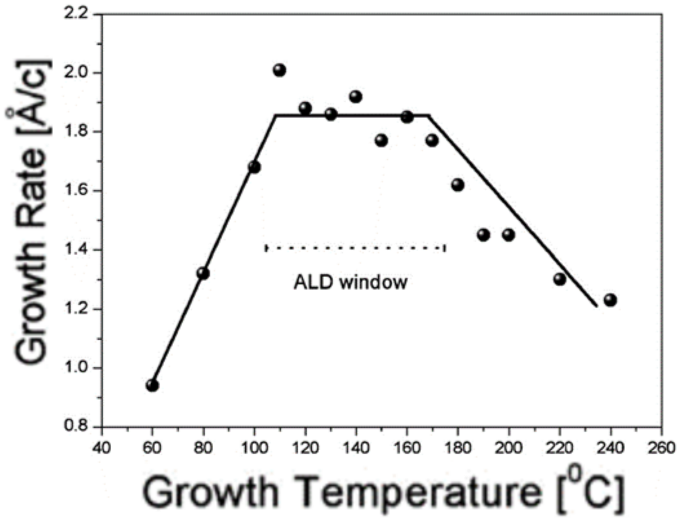
ZnO ALD (DEZn and H_2O)

(Self-limiting saturated surface reaction)



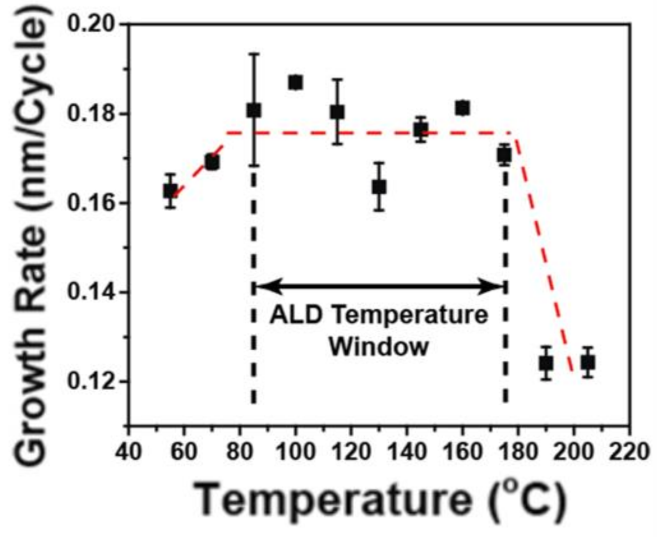
$Zn(C_2H_5)_2$ is Diethylzinc or DEZn

ALD window (DEZn and H_2O)
(steady growth)



ALD ZnO on Si

500 and 1000 cycles *



ALD ZnO on Si

20 ALD cycles **

T_{sub} between 100°C and 200°C GPC 0.16-0.22 nm.cy^{-1}

**Guziewicz et al. JAP 103 3 (2008)*

***Gao et al. JVST A 34 1 (2016)*

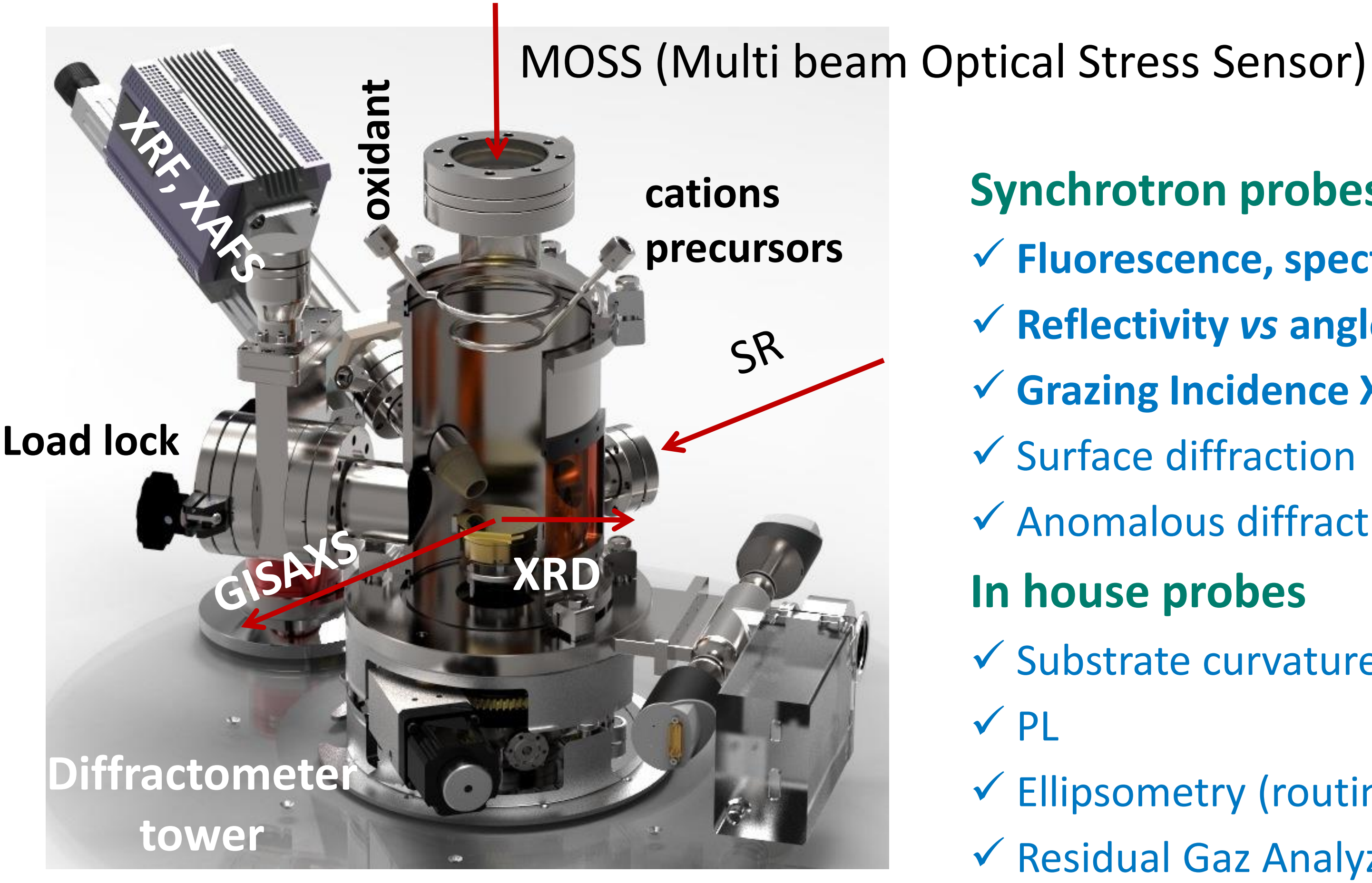
In situ growth study of ALD or MLD

Thermal ALD

Allows:

- ✓pressures from atmosphere to vacuum
- ✓ Thermal ALD: temperatures from room to 800°C

- ✓ Counter-rotating flange



Designed and built under the guidance of D. de Barros

Synchrotron probes

- ✓ **Fluorescence, spectroscopy (XAFS)**
- ✓ **Reflectivity *vs* angle, energy, thickness**
- ✓ **Grazing Incidence XRD**
- ✓ Surface diffraction
- ✓ Anomalous diffraction, DAFS spectroscopy

In house probes

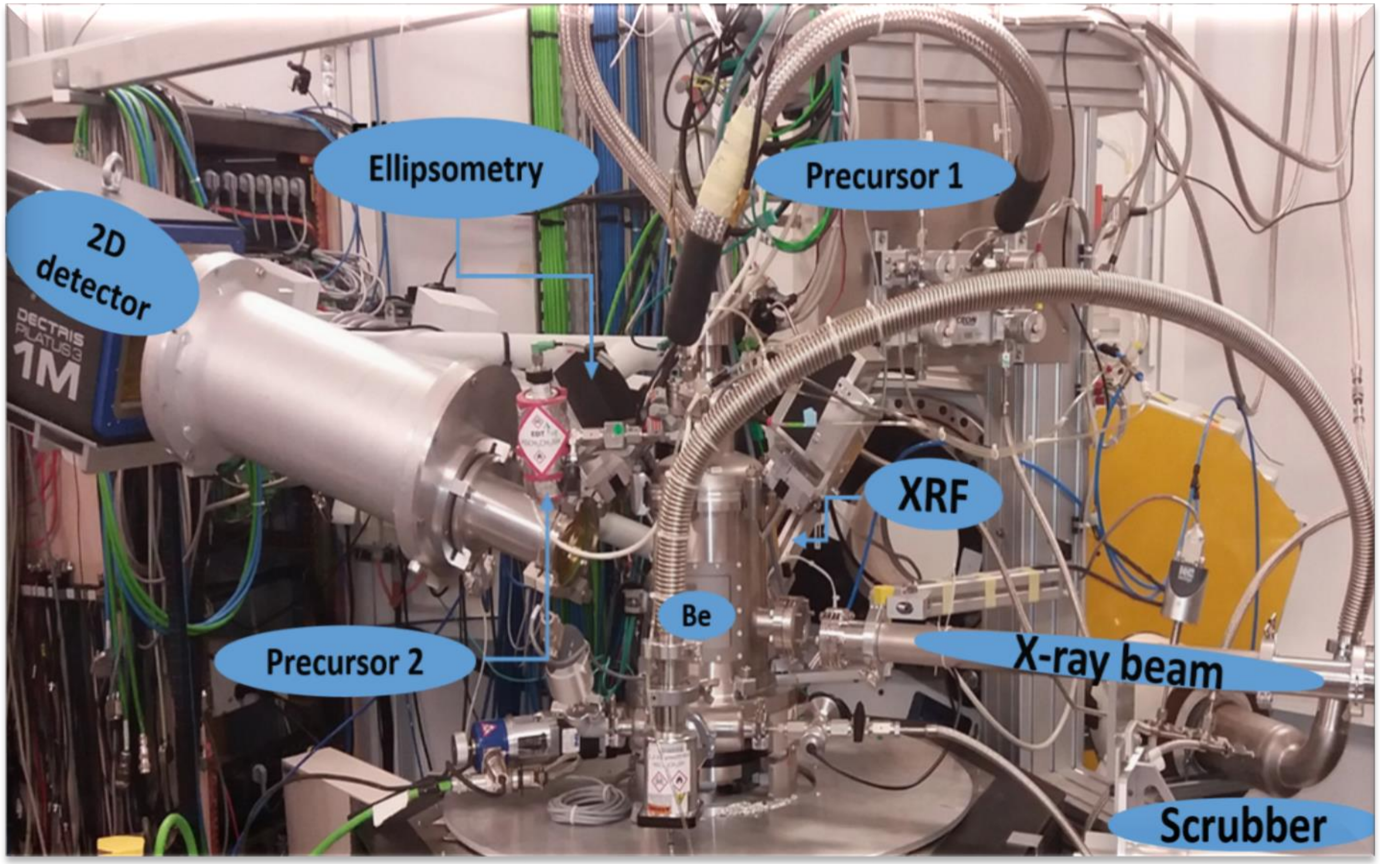
- ✓ Substrate curvature (MOSS)
- ✓ PL
- ✓ Ellipsometry (routinely used)
- ✓ Residual Gaz Analyzer (near future)

Chem. Mat. 28 592 (2016)
Cryst. Growth Des.16 5339 (2016)

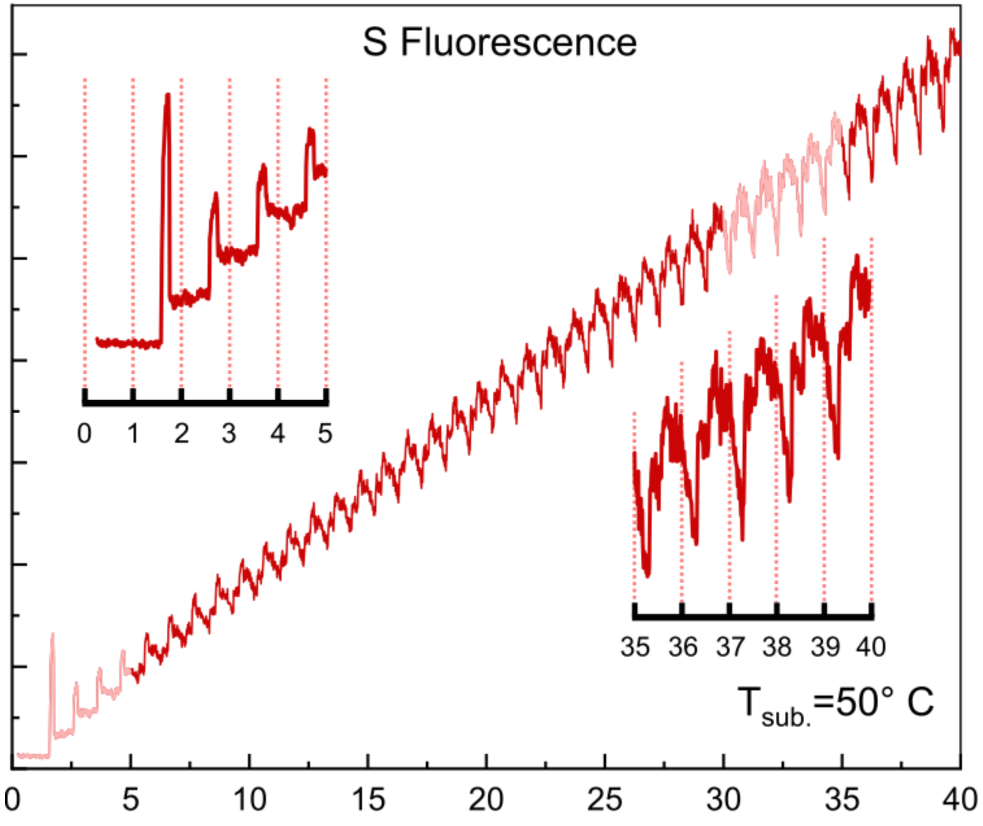
AGENCE NATIONALE DE LA RECHERCHE ANR
nano SCIENCES FONDATION

In situ growth study of ALD or MLD

ALD setup @ SOLEIL
SIRIUS beamline (tender X-ray range)
September 2021



S K_α fluorescence (2.41 keV)



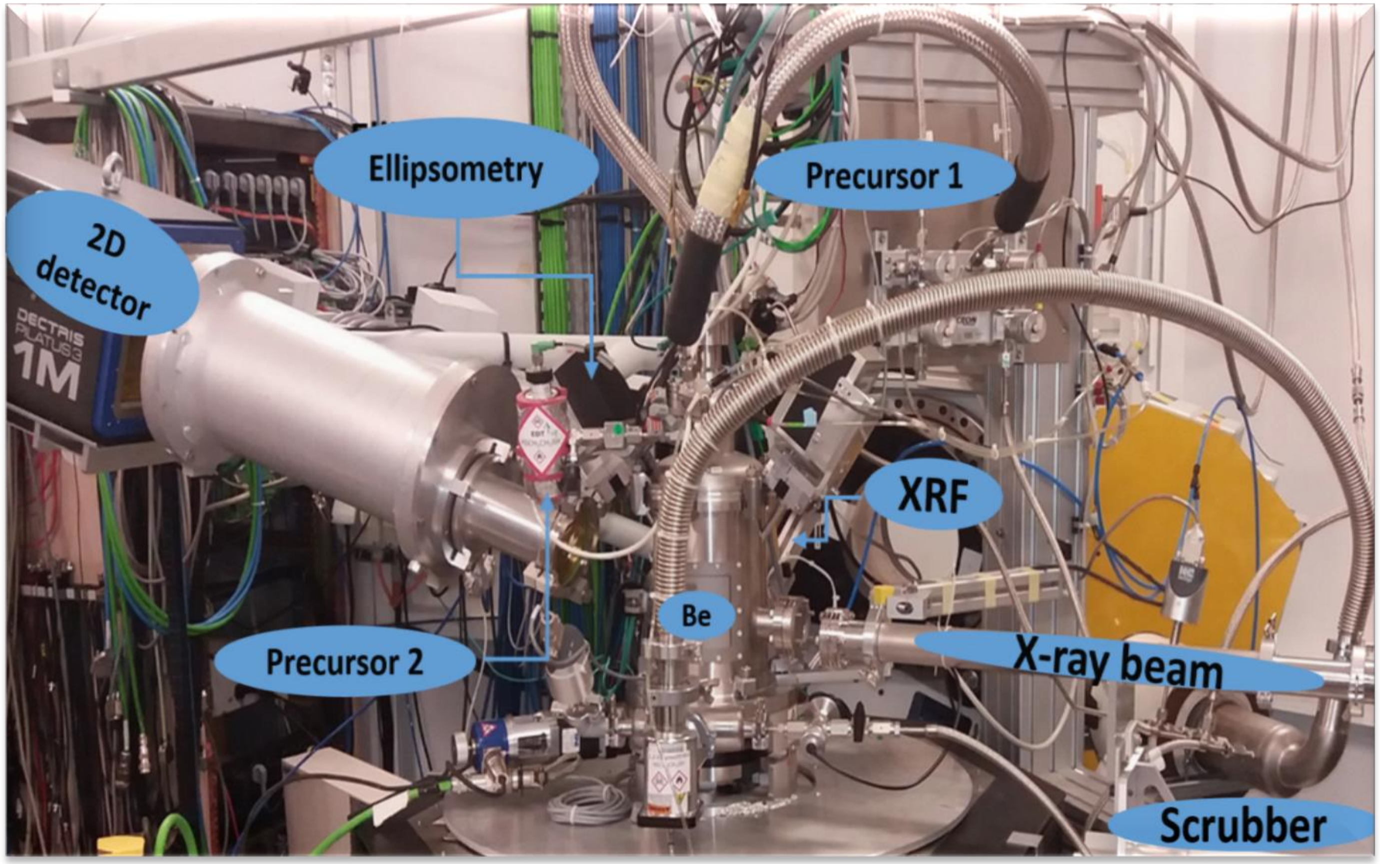
Number of cycles

In situ growth study of ALD or MLD

ALD setup @ SOLEIL

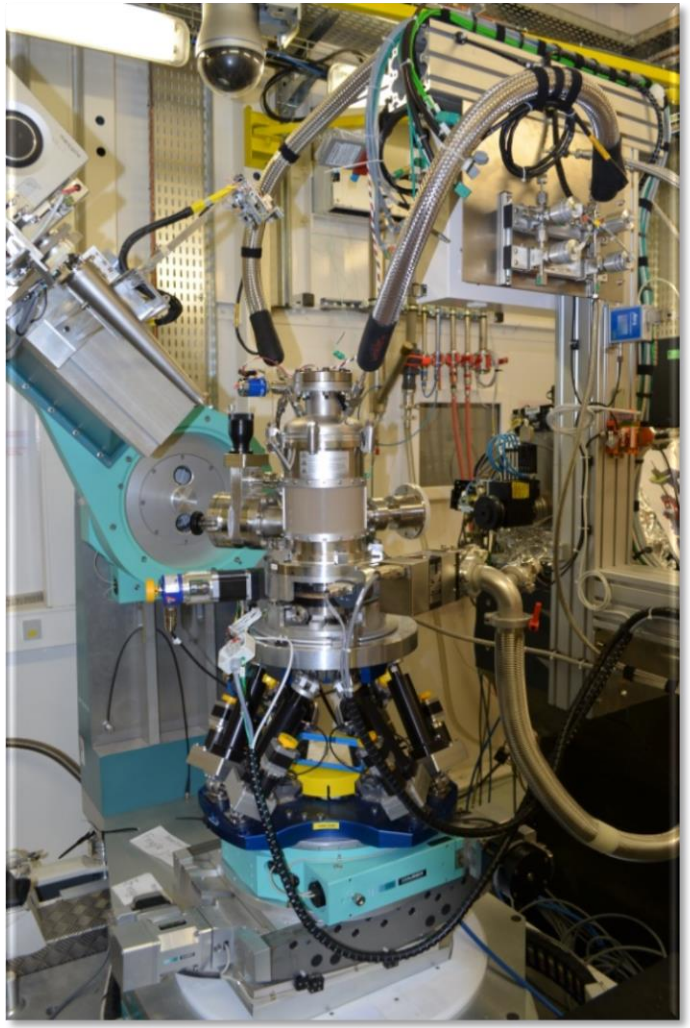
SIRIUS beamline (tender X-ray range)

September 2021



ALD setup @ ESRF

ID3 beamline



Fast in-plane x-ray diffraction

In situ ALD reactors

B. Stephenson, P. H. Fuoss (CVD)
J. W. Elam, A. S. Hock, T. Proslier (ALD)

CoCOON group (C. Detavernier,
J. Dendooven)

S. Bent's group

G.B. Stephenson et al., MRS Bull. 24, 21 (1999)
D. Fong et al., Annu. Rev. Mater. Res 36, 431 (2006)
Devloo-Casier et al. Appl. Phys. Lett. 98, 231905 (2011)
Devloo-Casier et al. J. Vacc. Tech. A, 32, 01801 (2014)
S.M. Geyer et al., Rev. Sci. Ins. 85, 055116 (2014)
J. Klug et al., Rev. Sci. Ins. 86, 113901 (2015)
B. Boichot et al., Chem. Mat. 28, 592 (2016)
J. Dendooven et al., Rev. of Sci. Ins. 87, 113905 (2017)
Ju et al., Rev. of Sci. Ins. 88.3, 035113 (2017)

J. Dendooven et al., Rev. of Sci. Ins. 87, 113905 (2017)

XRF, GISAXS

Ju et al., Rev. of Sci. Ins. 88.3, 035113 (2017)

Coherent X-ray Diffraction

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Part 2

In situ X-ray studies of the early stage of ZnO Atomic Layer Deposition on InGaAs

Part 3

In situ X-ray studies of Dichalcogenides thin films prepared by Molecular Layer Deposition and thermal annealing

Collaborators

E. V. Skopin*, L. Rapenne, S. Quessada, I. Gelard, H. Roussel, J.-L. Deschanvres & A. Claudel (NÉEL Institute, Grenoble)

* Minos Phd

LMGP, UGA & CNRS, Grenoble, France

M.-I. Richard

Aix-Marseille Univ., IM2NP-CNRS, Marseille, France

D. D. Fong

Argonne National Laboratory, Argonne, USA

G. Ciatto, N. Aubert

Synchrotron SOLEIL, Saint Aubin, France

ID3 (ESRF) staff : **F. Carla, H. Isern, T. Dufresne, L. Pithan**

E. Blanquet

SIMAP, UGA & CNRS, Grenoble, France

V. Bolcato

CIME, UGA & CNRS, Grenoble, France

C. Gomez

PTA, Grenoble, France

X. Mescot

IMEP-LAHC, Grenoble, France

P. Rodriguez, M. Bertrand

Leti, technology research institute, Grenoble (France)

Labex MINOS

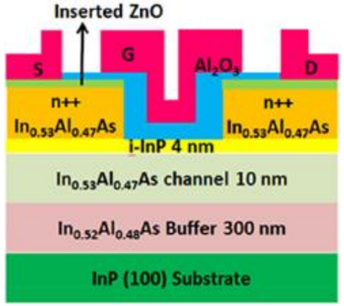
ANR

nanoSCIENCES FONDATION

Communauté Université Grenoble Alpes

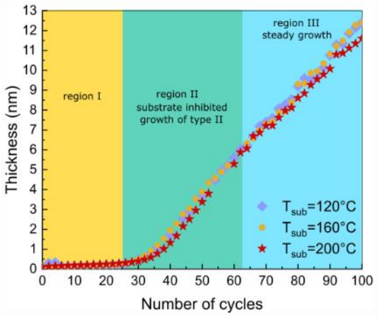
Talk outline

Motivation: ZnO for MIS junctions, IPL

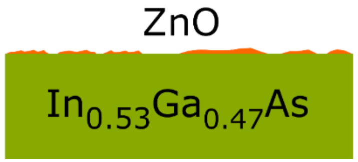


The early stage of ZnO ALD on $In_{0.53}Ga_{0.47}As$

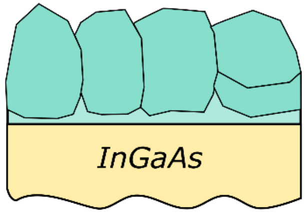
Substrate temperature effect



Transient regime of growth



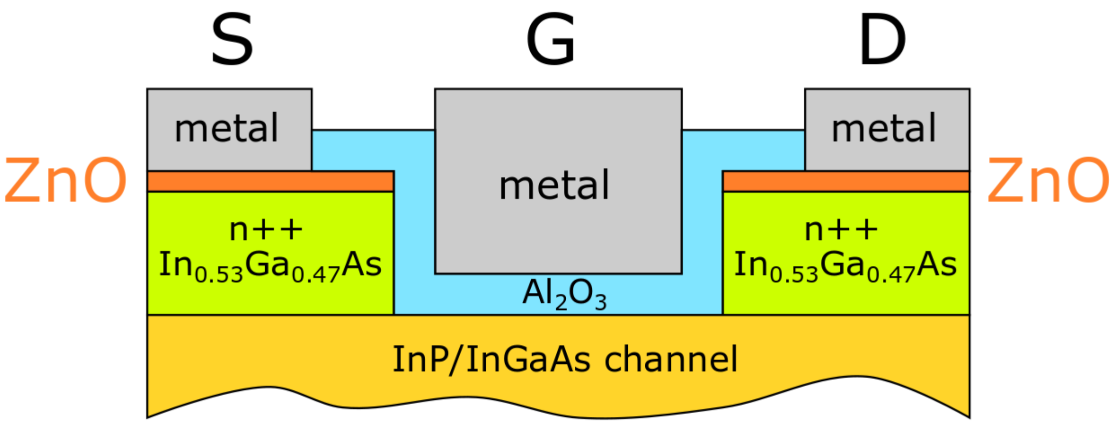
ZnO cristallisation



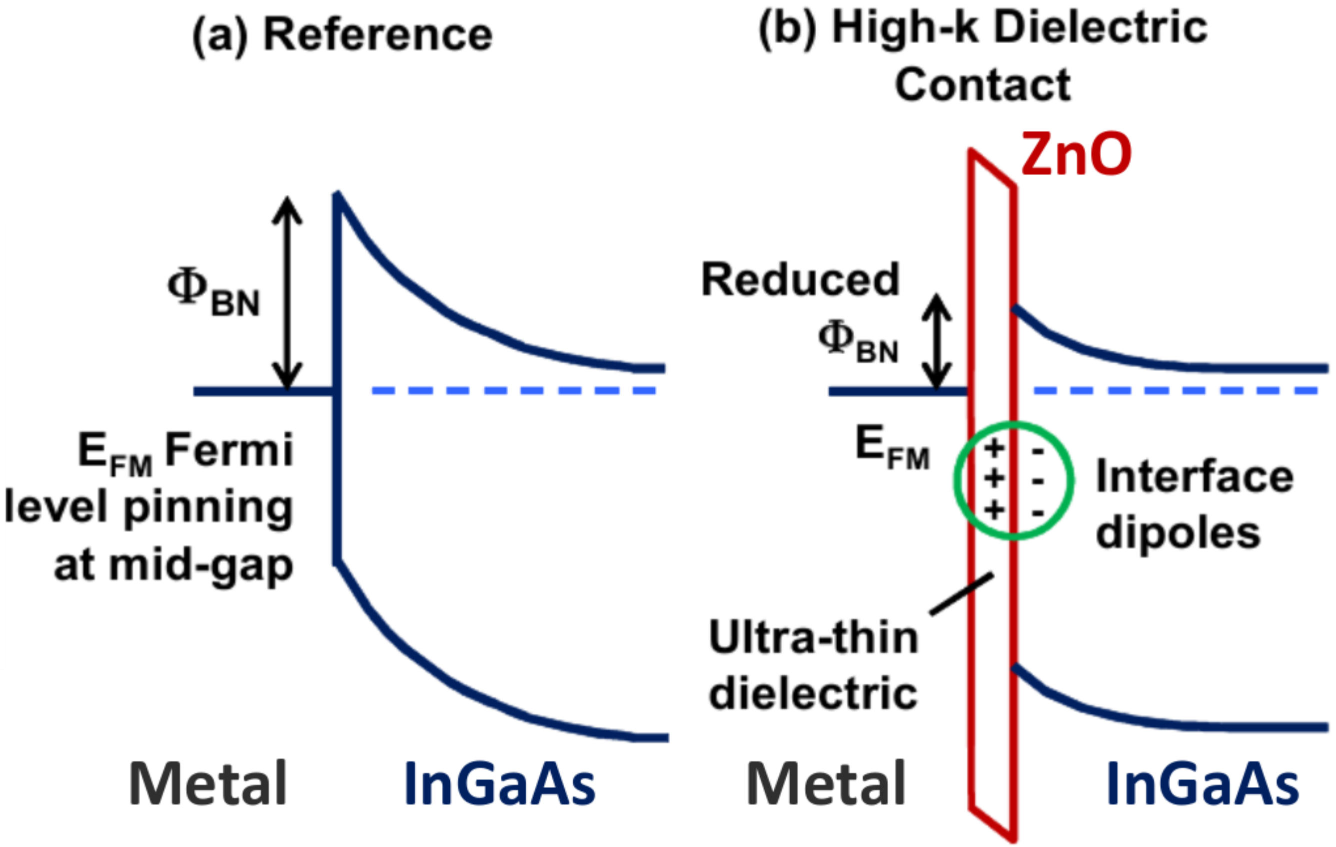
Conclusion

Source/Drain specific contact resistivity

MOSFET



ZnO to reduce source/drain specific contact resistivity

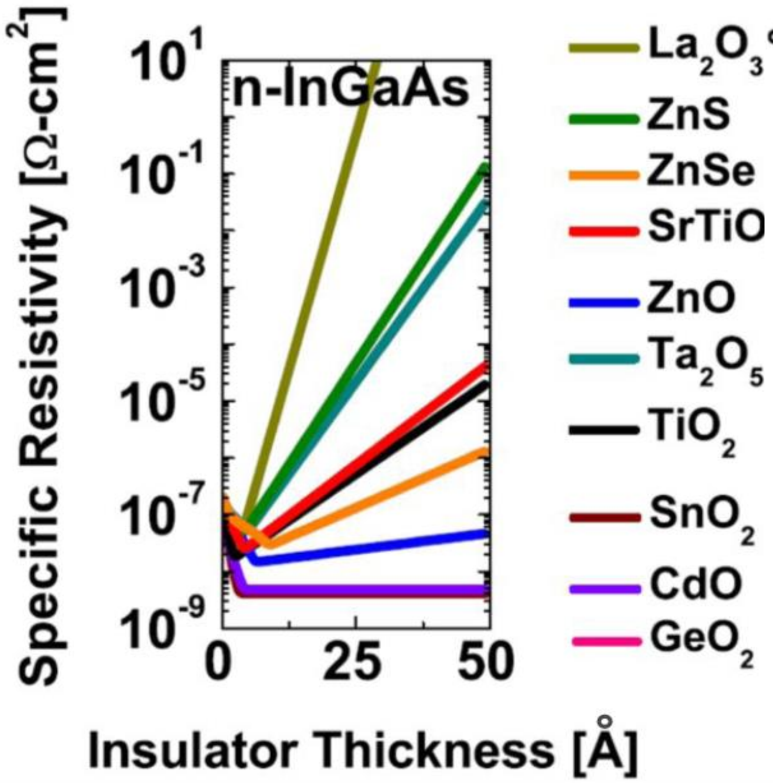

(a) Reference

(b) High-k Dielectric Contact

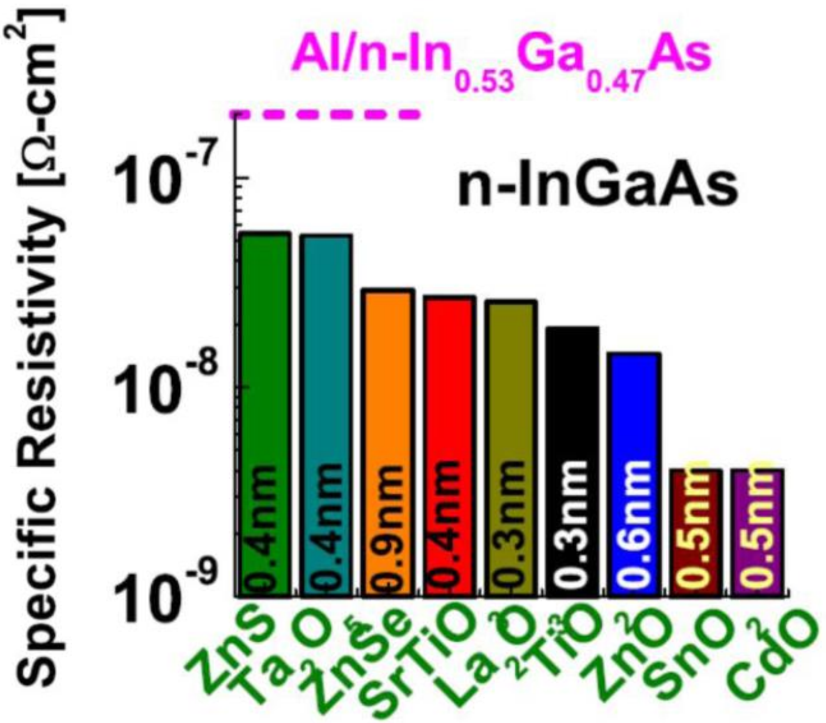
Liao et al., Appl. Phys. Lett. 103, 072102 (2013)
Ang et al., IEDM (2012) 18.6.1

Optimal ZnO thickness

Al/Insulator/n-InGaAs



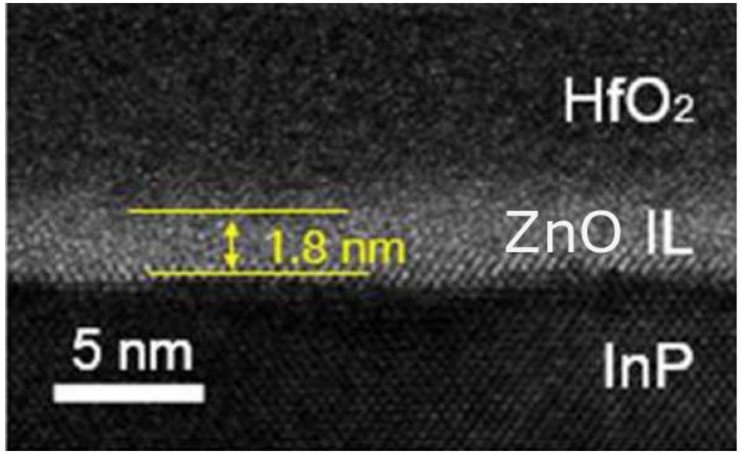
Optimal thickness



calculations

A. Agrawal et al. APL 101 042108 (2012)

ZnO interfacial passivation layer (IPL)



- ✓ suppresses film crystallization
- ✓ reduces interface state density

S.H. Kim et al. ACS App. Mat. & Int. 8.32 (2016)

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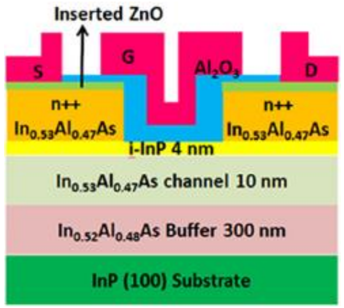
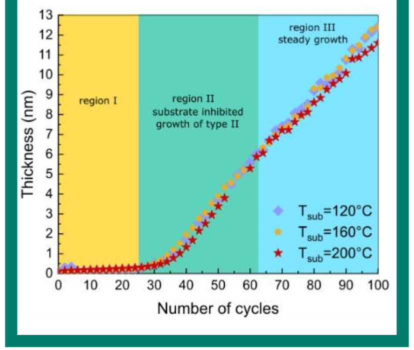
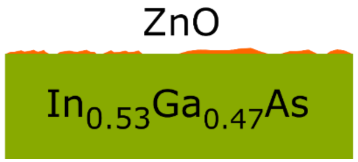


The early stage of ZnO ALD on $In_{0.53}Ga_{0.47}As$

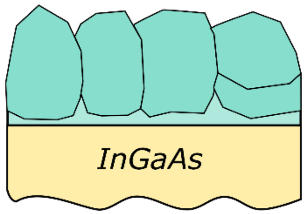
Substrate temperature effect



Transient regime of growth

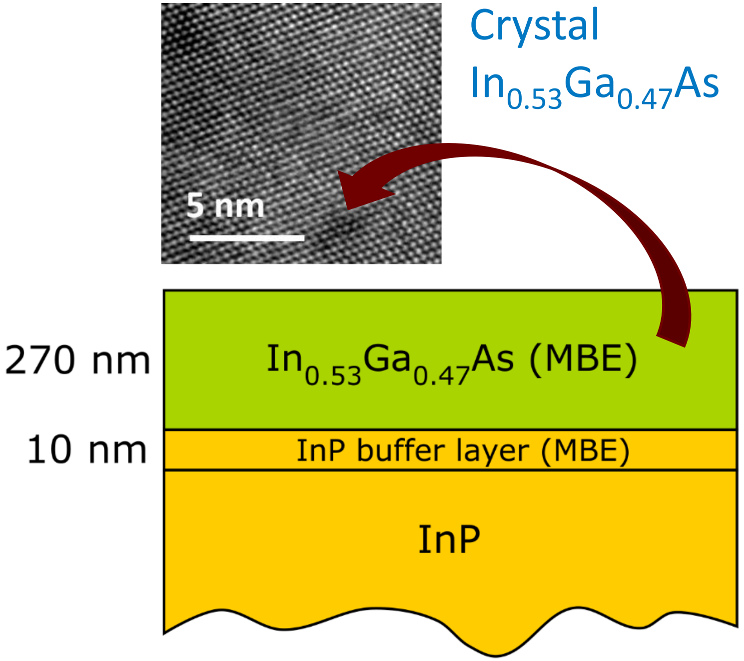


ZnO cristallisation



Conclusion

ZnO ALD on $In_{0.53}Ga_{0.47}As$ substrate

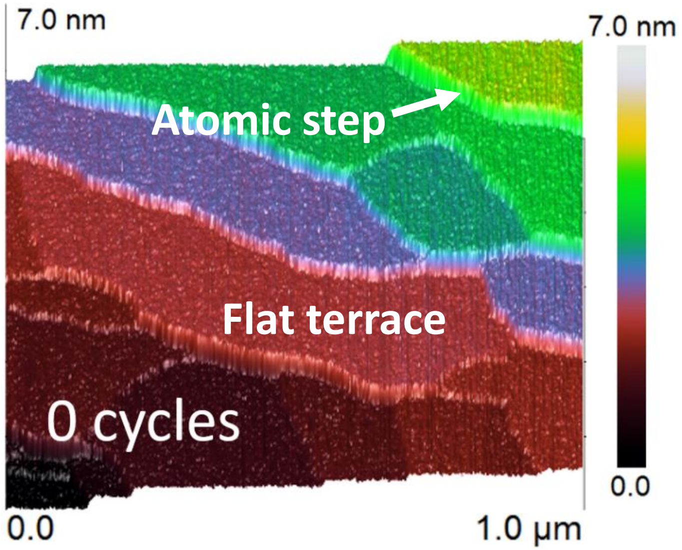


n-InGaAs & p-InGaAs provider : III-V Lab^{TM}

Etched 5 min in a 4M HCl solution

APL 93, 194103 (2008)

$In_{0.53}Ga_{0.47}As$ terraces



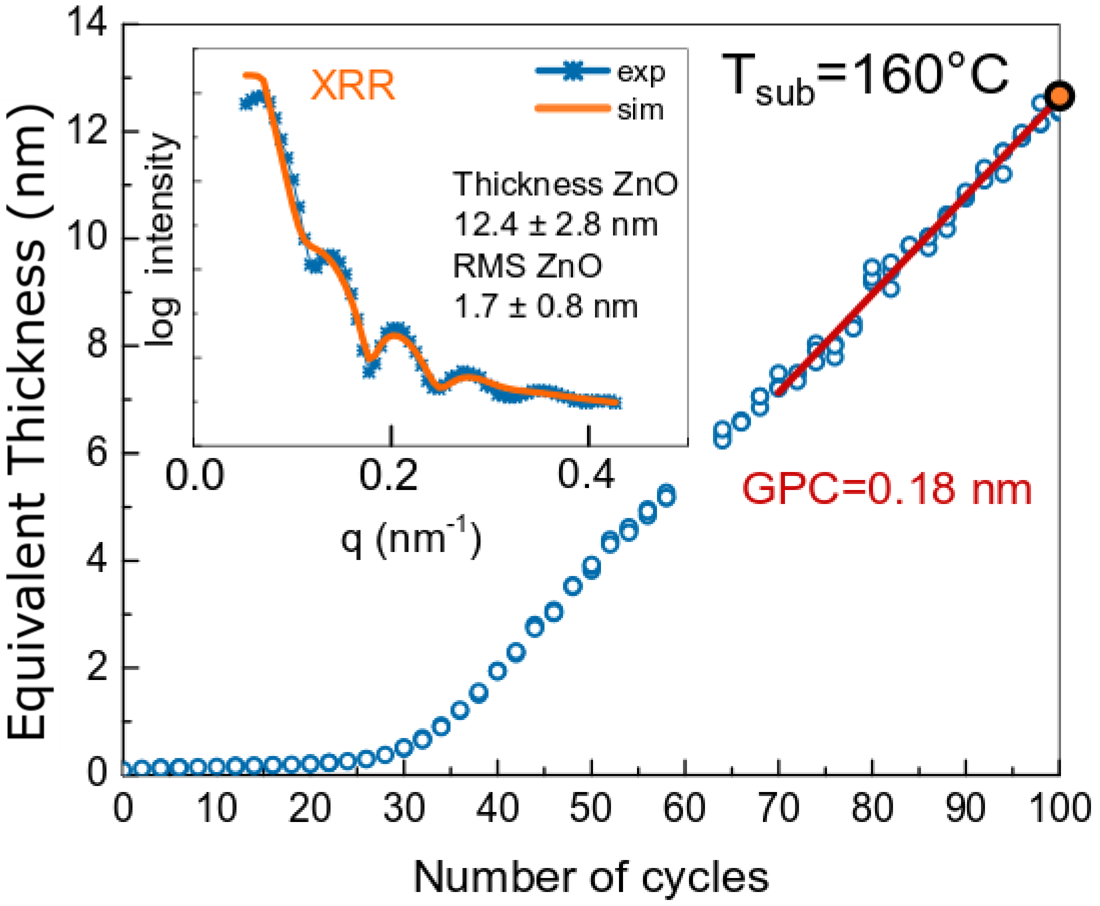
3D AFM image

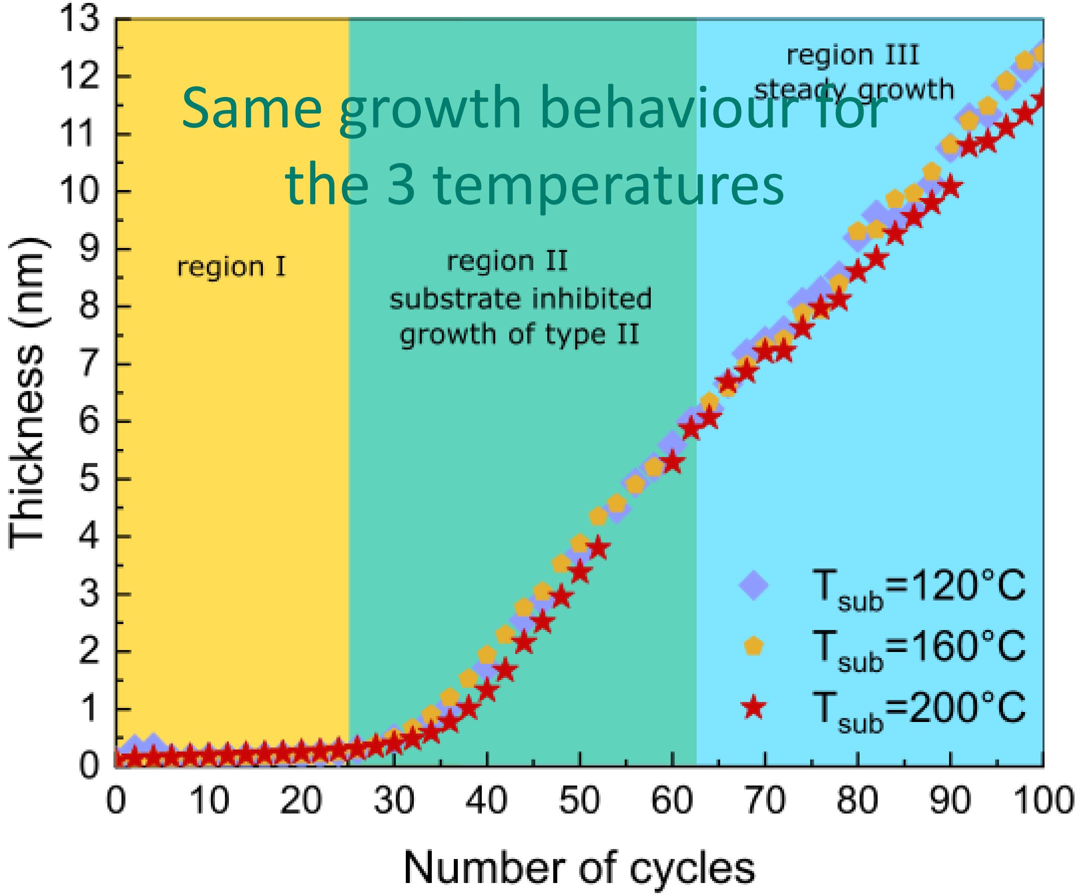
Substrate temperature effect

- Substrate temperature = 120°C, 160°C, 200°C
- Number of cycles = 100

- DEZn/ H_2O/ N_2 flow = 5sccm/2.6sccm/1000sccm
- DEZn/ H_2O/ N_2 inj. or purge time = 5s/40s/45s

ESRF
ID03





Same growth behaviour for the 3 temperatures

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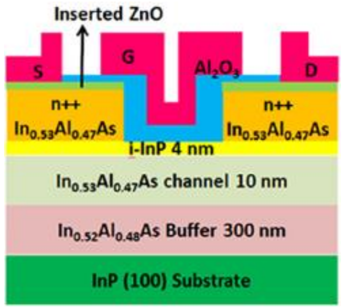

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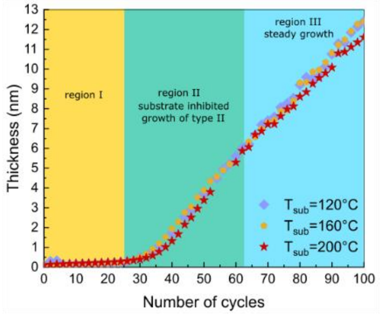
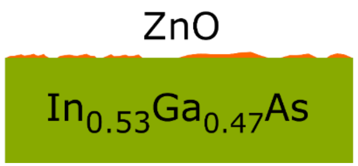
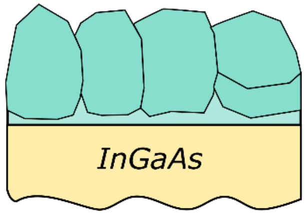


Transient regime of growth



ZnO cristallisation

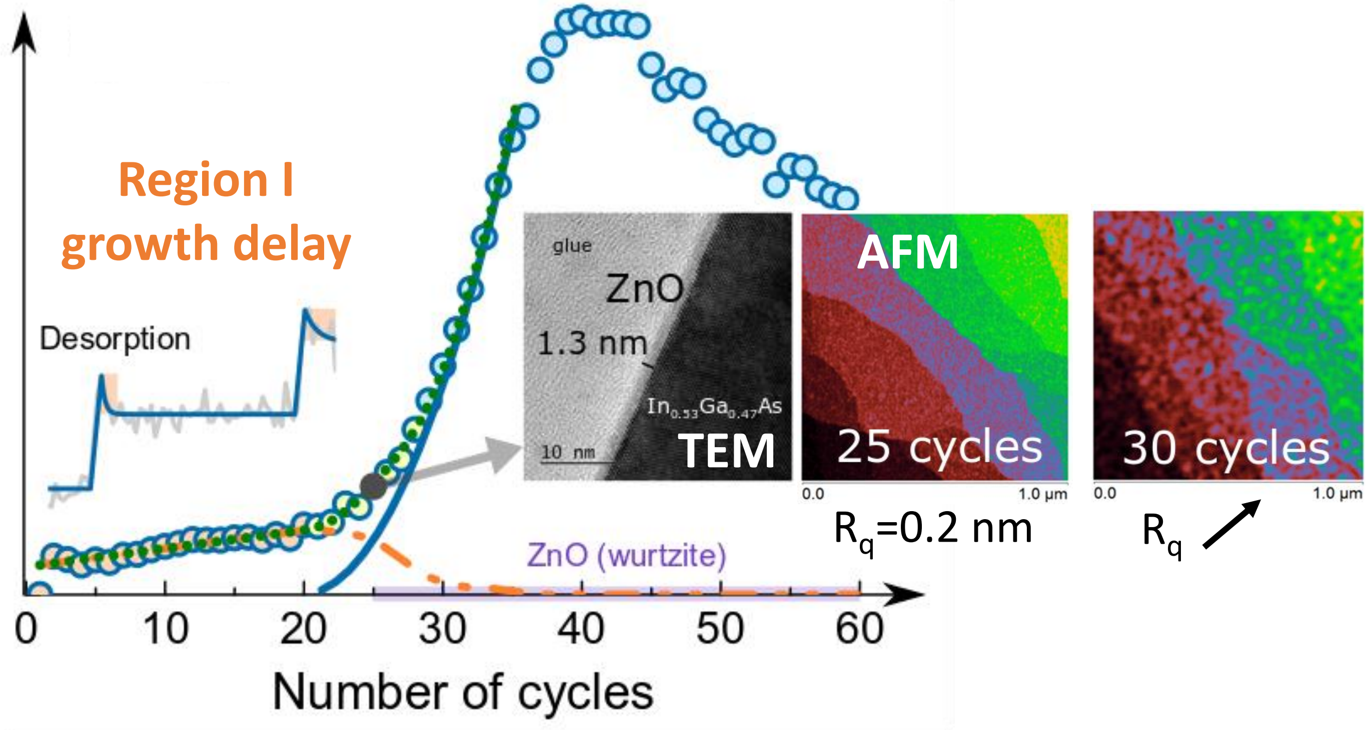


Conclusion

ZnO transient growth on InGaAs

Growth Per Cycle (GPC)

Region II
S-shape growth



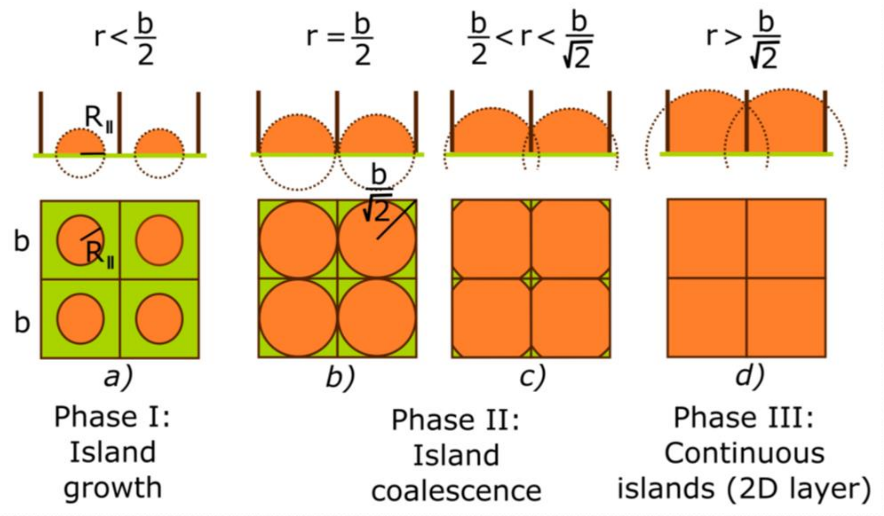
R_q=0.2 nm

R_q ↗

SIRIUS beamline

Nanoscale, 10, 11585 (2018)

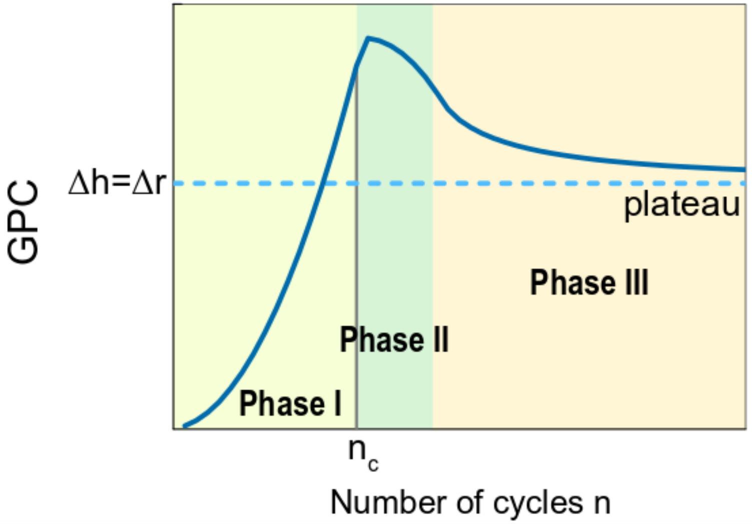
Region II: island growth model



Phase I:
Island
growth

Phase II:
Island
coalescence

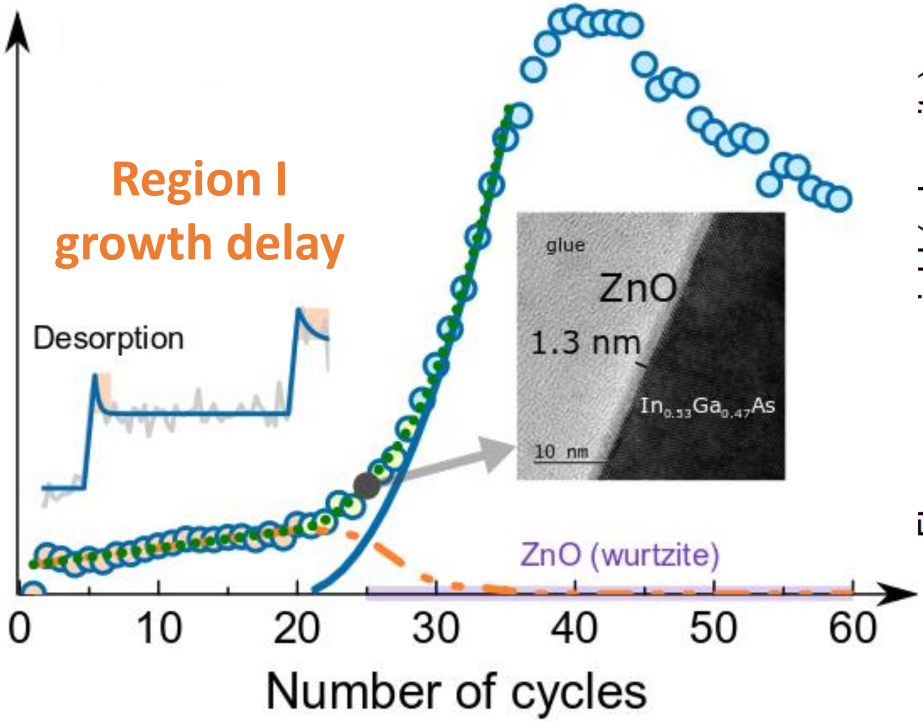
Phase III:
Continuous
islands (2D layer)



ZnO transient growth on InGaAs

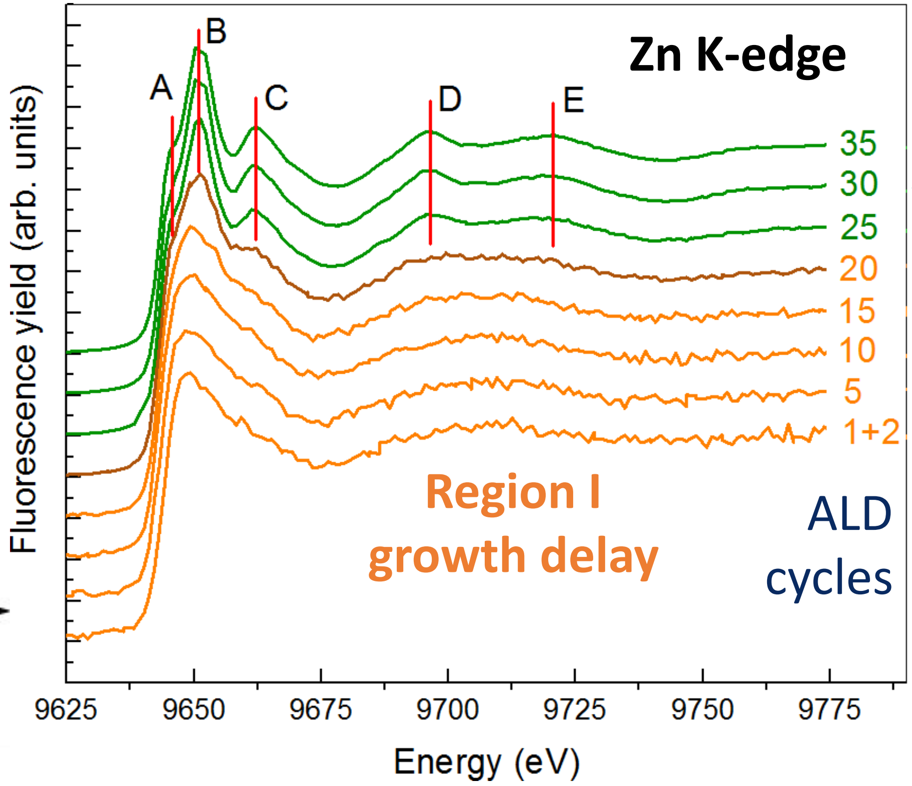
Growth Per Cycle (GPC)

Region II
S-shape growth



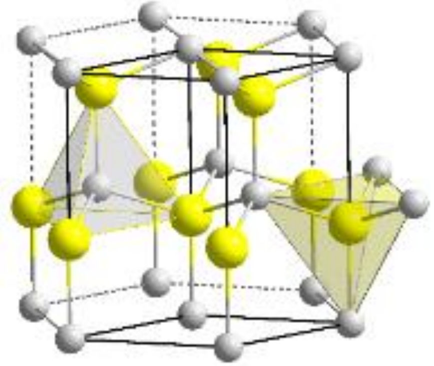
Region I
growth delay

X-ray Absorption Near Edge Structure

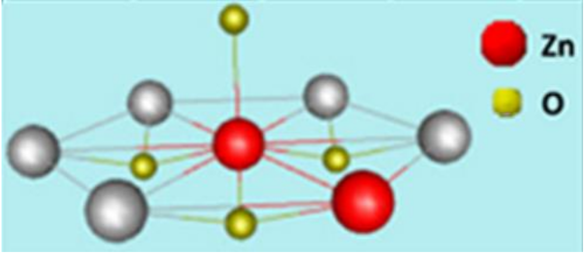


Region I
growth delay

ALD cycles



Wurtzite structure



Disordered Zn local environment/ small islands

Cryst. Growth Des. 16, 5339 (2016)

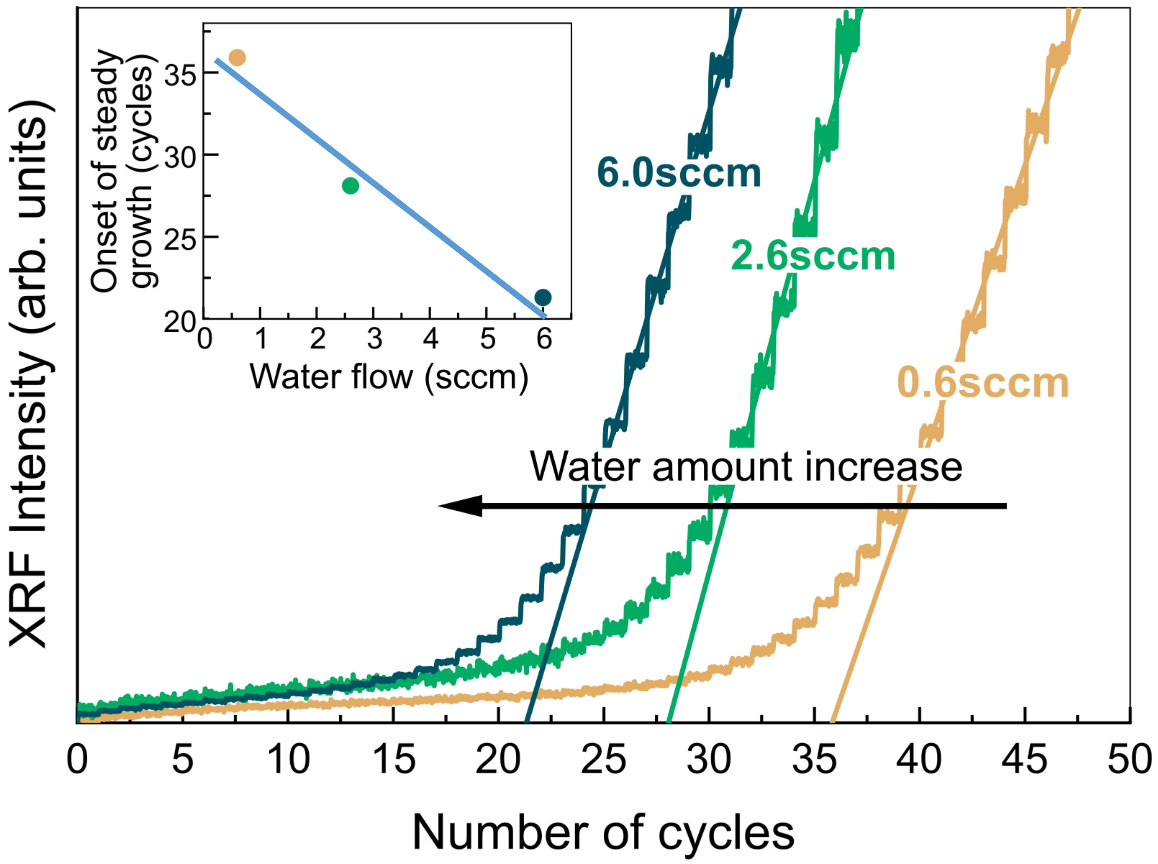
SOLEIL SYNCHROTRON
SIRIUS beamline

Nanoscale, 10, 11585 (2018)

Precursor flow/inj. time effect on growth delay (region I)

in situ X-ray Fluorescence

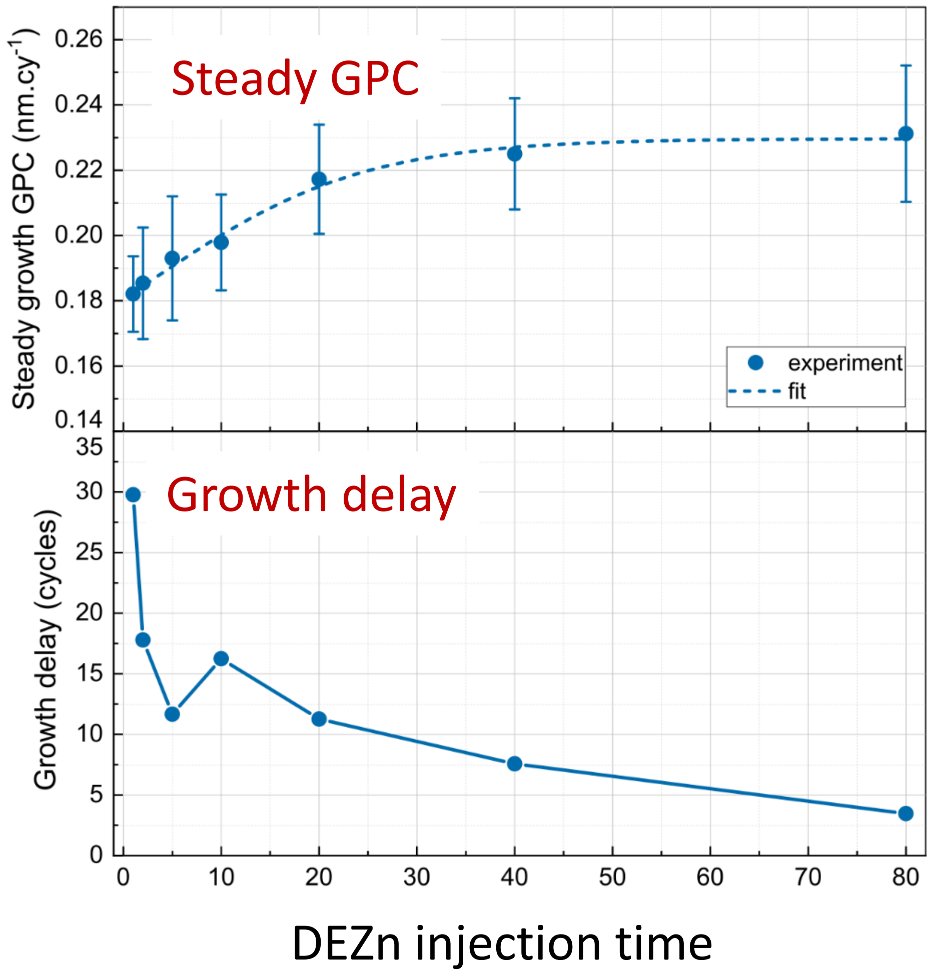
ESRF
ID03



PHYSICAL REVIEW MATERIALS **4**, 043403 (2020)

in situ ellipsometry

LMGP

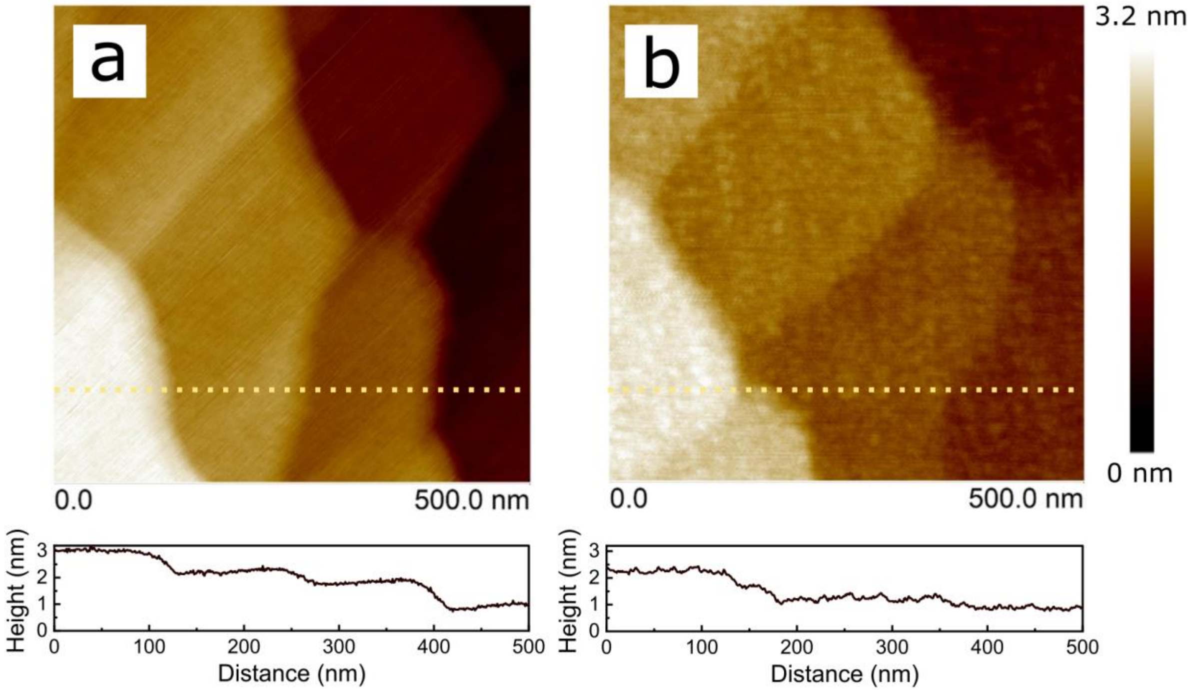


Phys. Status Solidi A 1900831 (2020)

Precursor flow/inj. time effect on growth delay (region I)

AFM

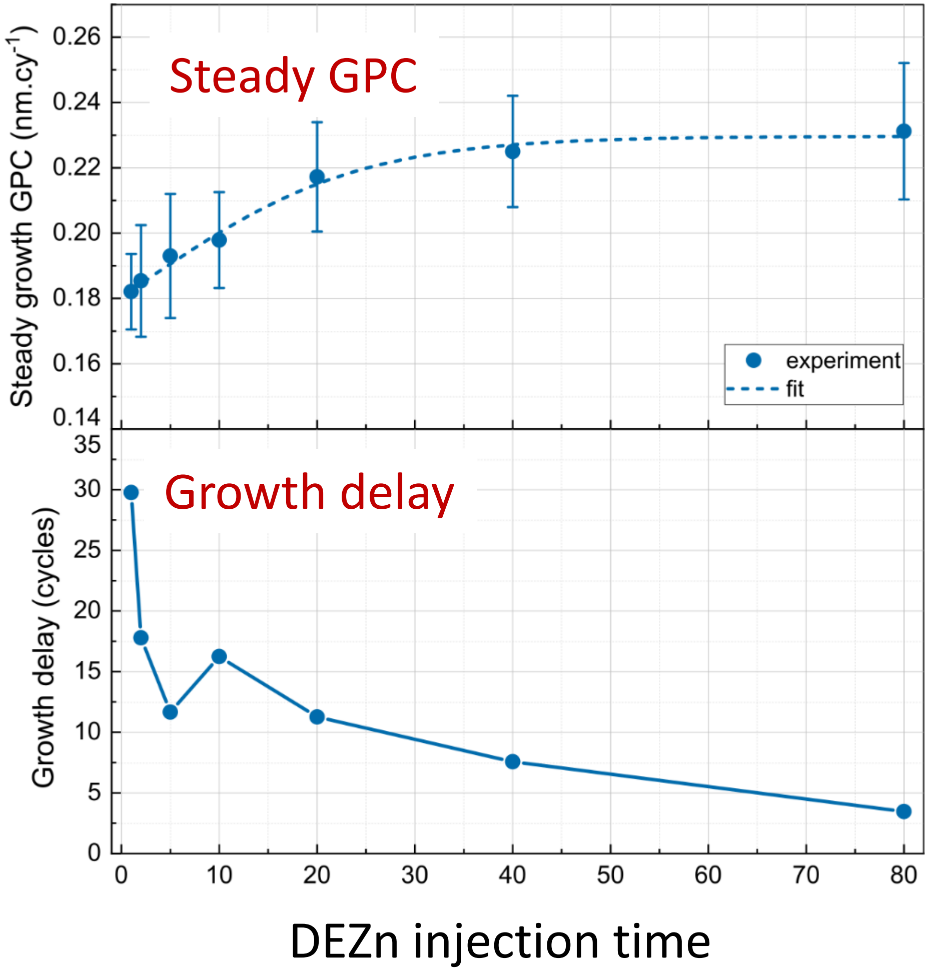
InGaAs surface



after cleaning, before deposition

after one ALD cycle including a long DEZn injection time

in situ ellipsometry



Phys. Status Solidi A 1900831 (2020)

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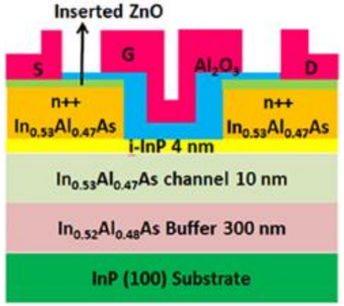
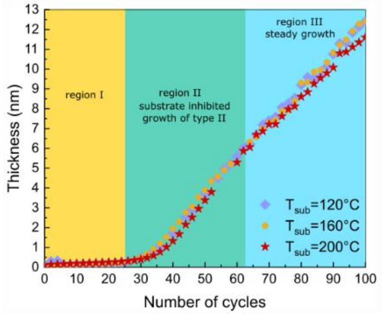
Motivation: ZnO for MIS junctions, IPL

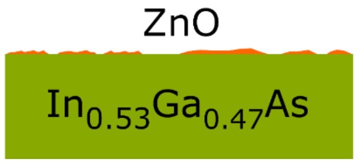


The early stage of ZnO ALD on $In_{0.53}Ga_{0.47}As$

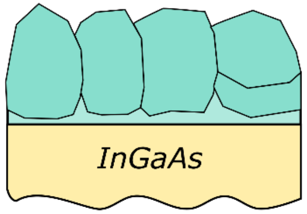
Substrate temperature effect



Transient region of growth



ZnO cristallisation

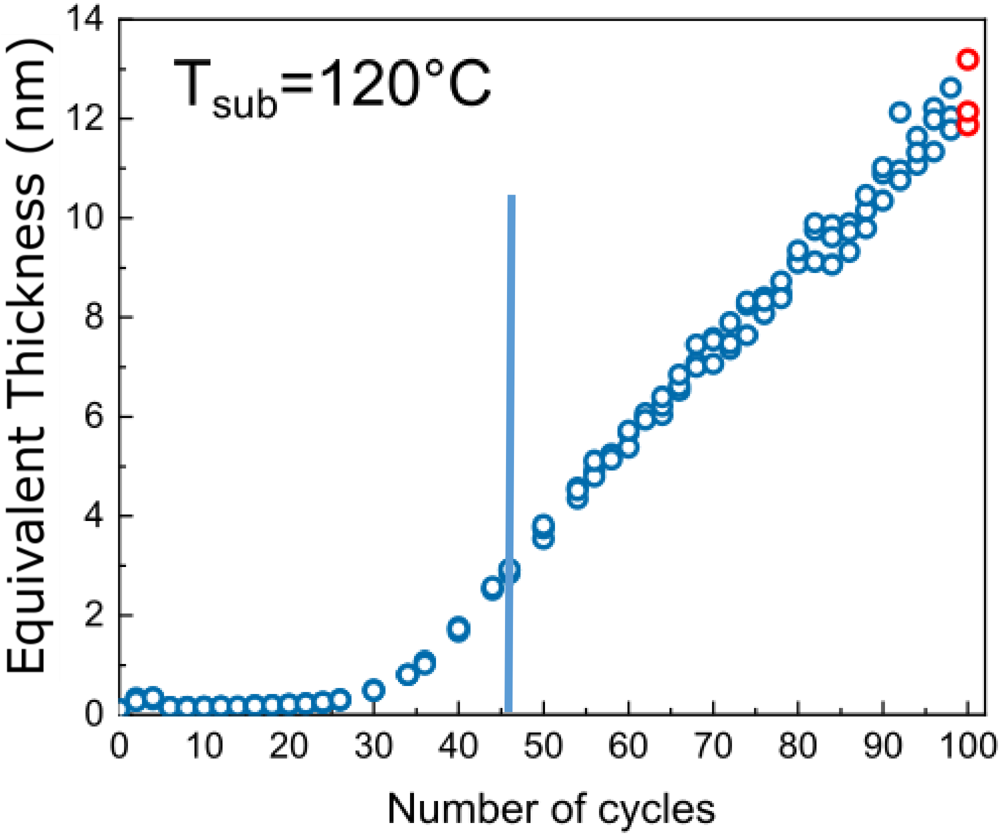


Conclusion

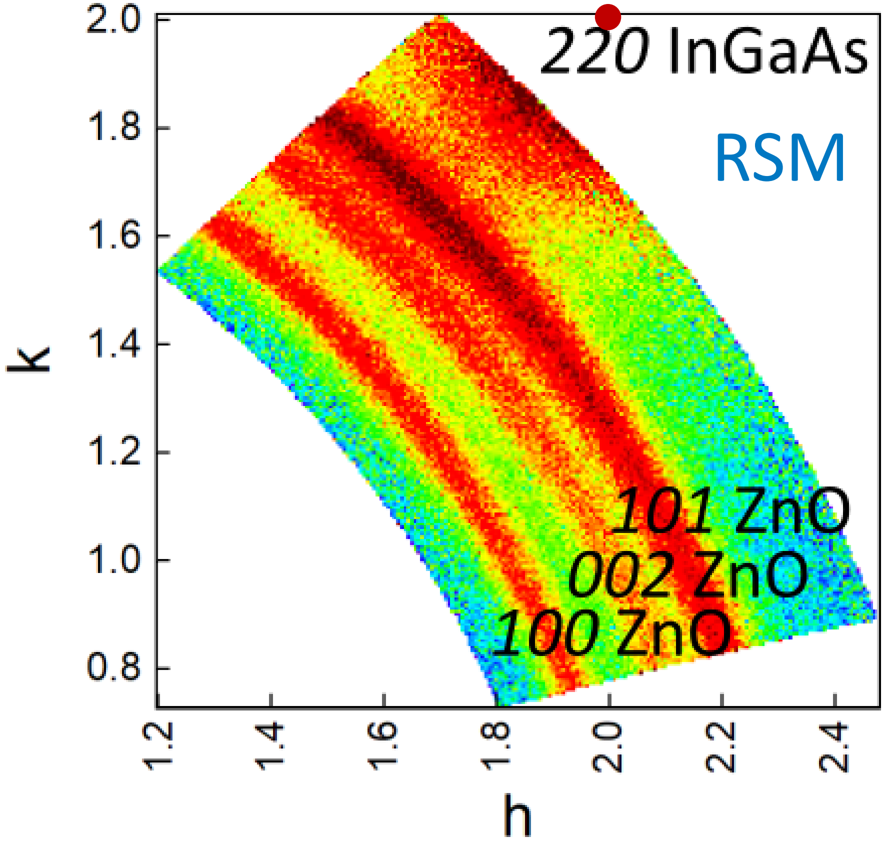
In-plane RSM vs ZnO film thickness

ESRF
ID03

Fast in-plane diffraction



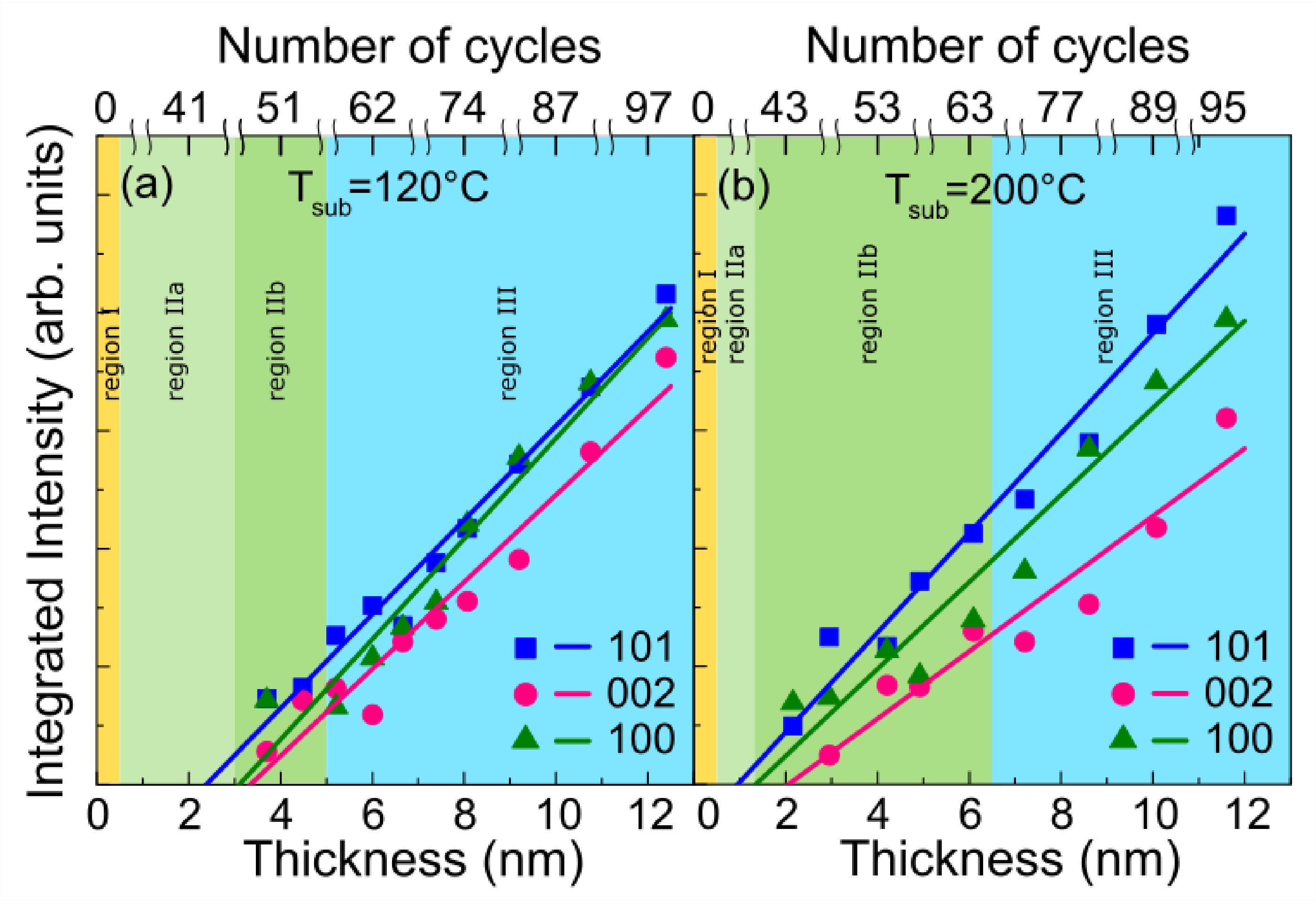
100 cycles

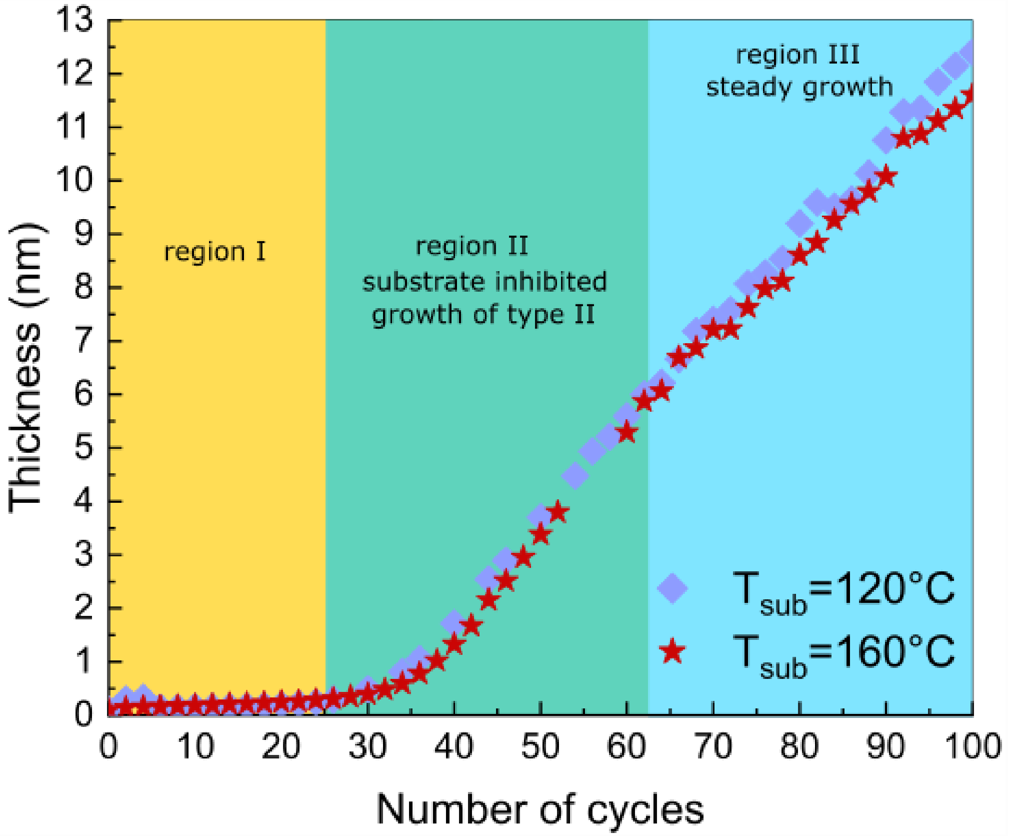


RSM : reciprocal space map

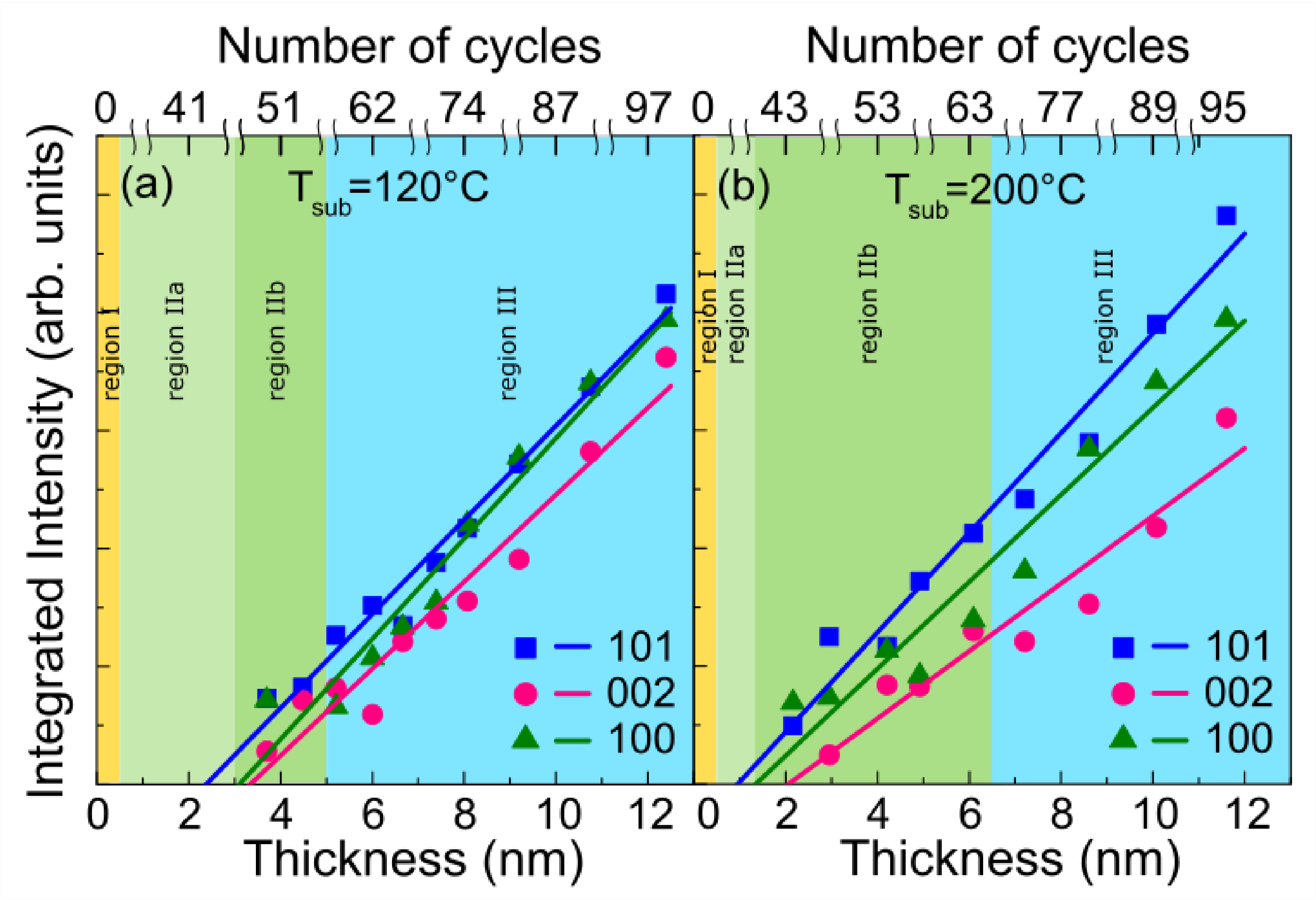
No in-plane texture

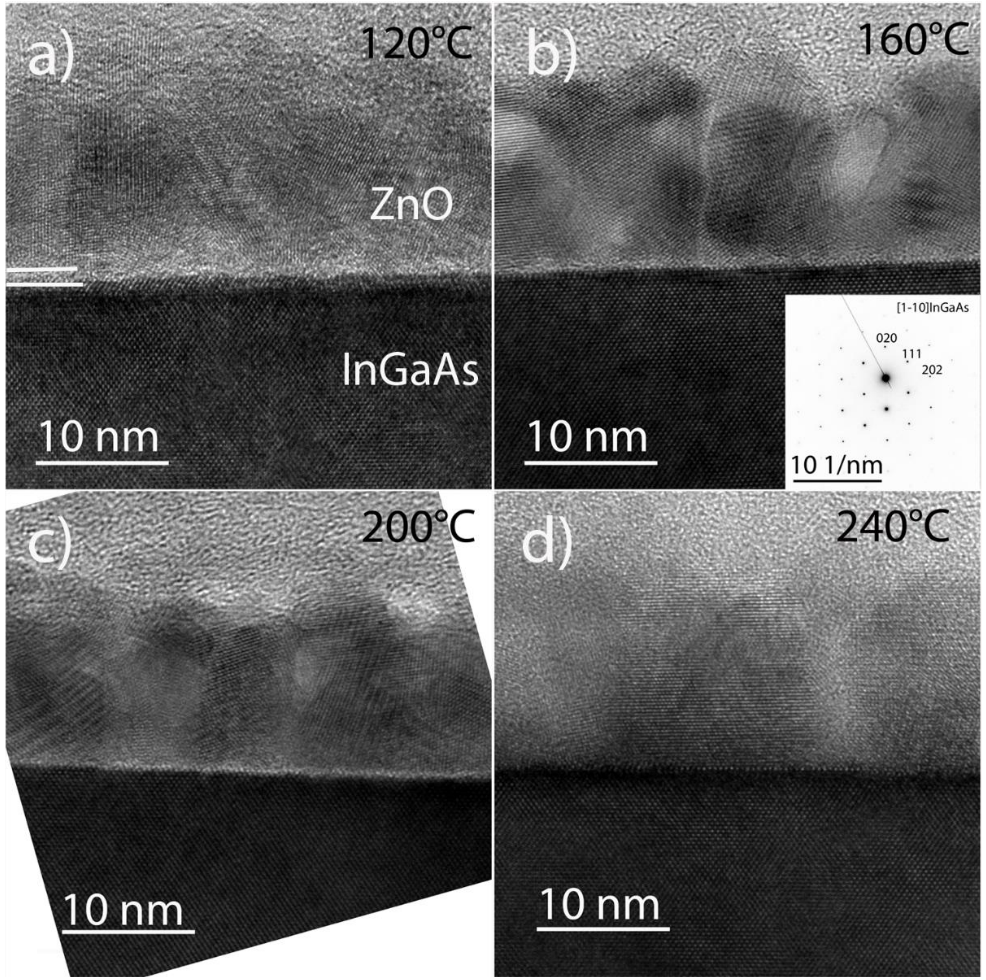
ZnO crystallization during growth



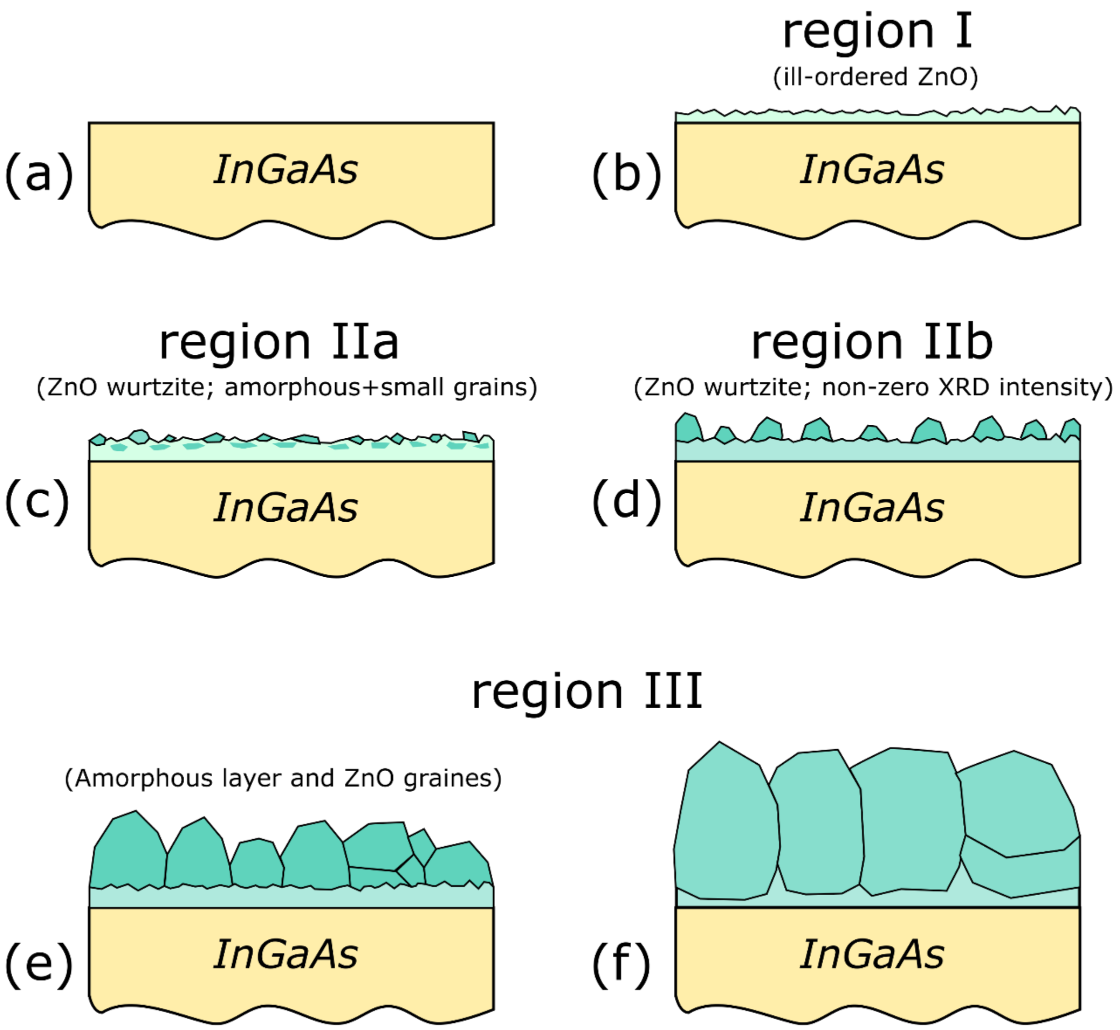


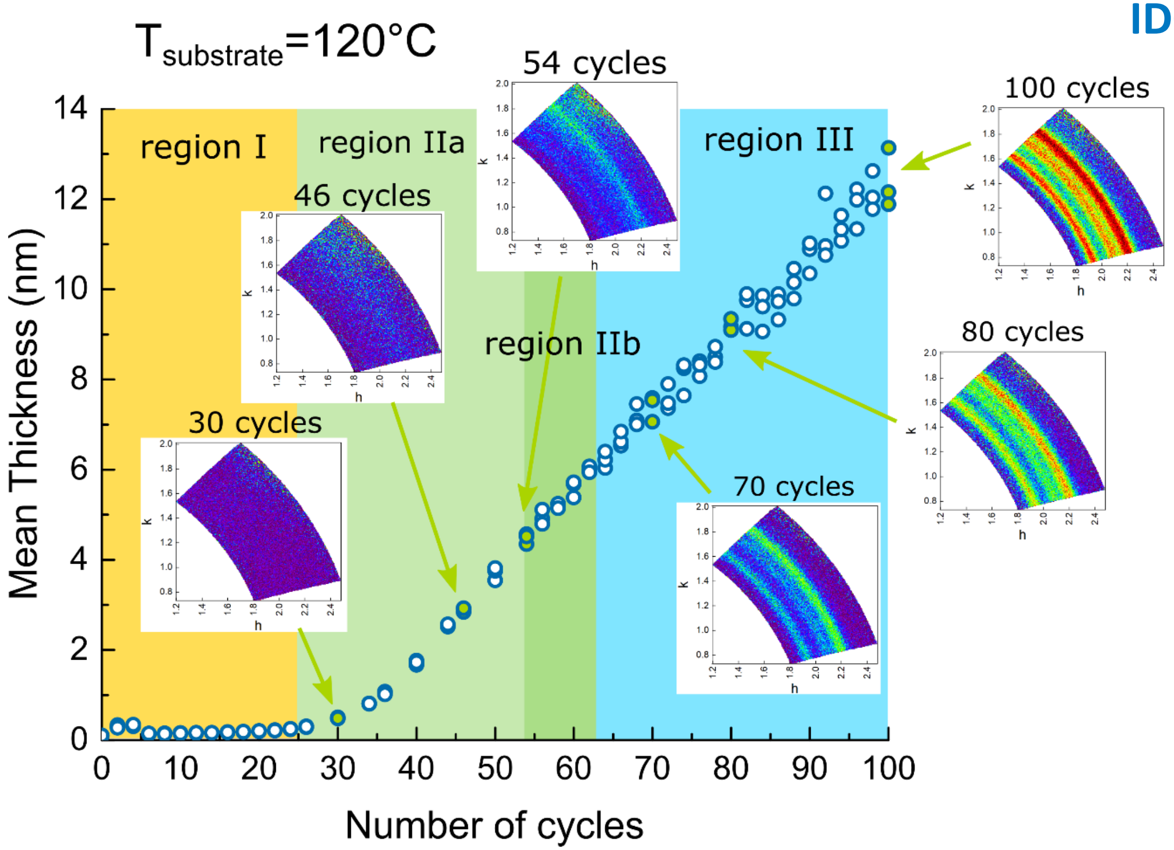
ZnO crystallization during growth





ZnO cristallisation on InGaAs

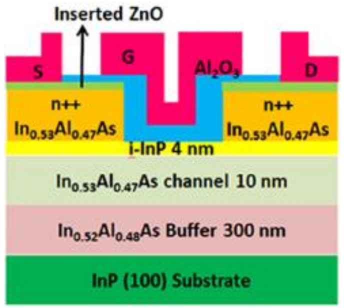




PHYSICAL REVIEW MATERIALS **4**, 043403 (2020)

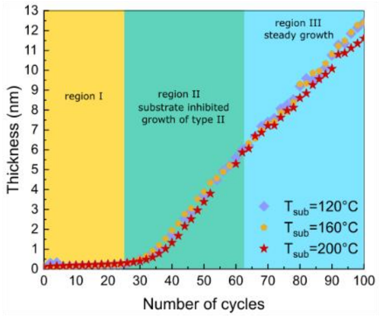
Talk outline

Motivation: ZnO for MIS junctions, IPL

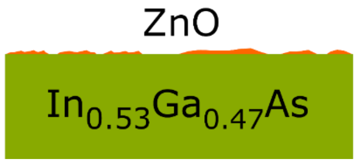


The early stage of ZnO ALD on $In_{0.53}Ga_{0.47}As$

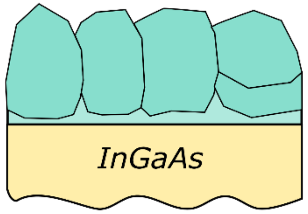
Substrate temperature effect



Transient region of growth



ZnO cristallisation

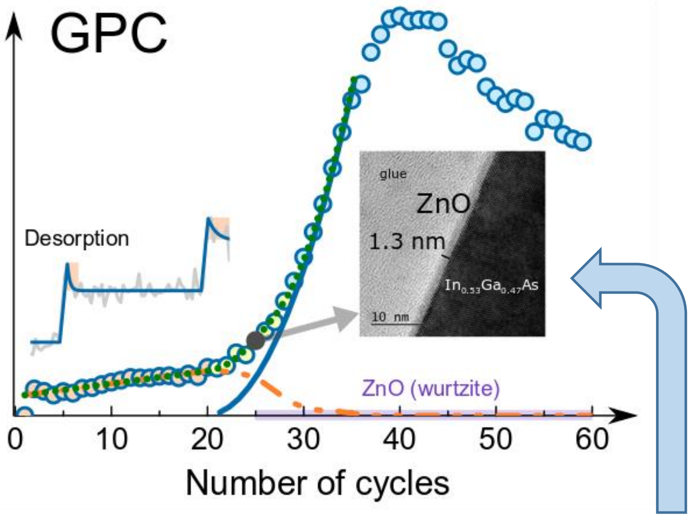


Conclusion

Conclusion (part 2)

- ✓ **GPC of ZnO ALD on InGaAs ~0.2nm.cy^{-1} in steady growth regime & ALD temperature window**

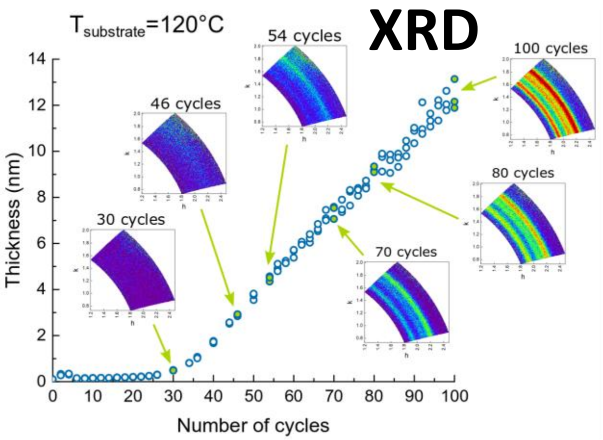
- ✓ **Evidenced a transient growth regime (prior to steady growth)**

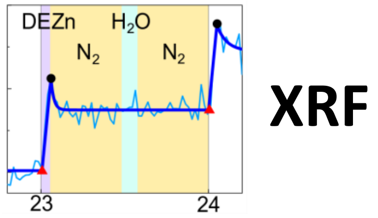


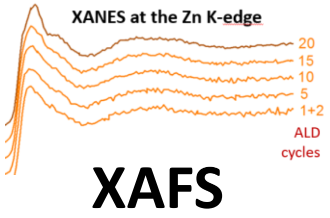
- ✓ **1-2 nm thick, continuous, ill-ordered ZnO film**

Nanoscale 10 11585 (2018)

- ✓ **Further demonstrated the interest of *in situ* synchrotron experiments for studying the incipient growth during ALD**







PHYSICAL REVIEW MATERIALS **4**, 043403 (2020)

- ✓ **Still to be performed : systematic electrical measurements**

Talk outline

Part 1

In situ growth studies of Atomic or Molecular Layer Deposition (ALD or MLD)

Part 2

In situ X-ray studies of the early stage of ZnO Atomic Layer Deposition on InGaAs

Part 3

In situ X-ray studies of Dichalcogenides thin films prepared by Molecular Layer Deposition and thermal annealing

Collaborators - Framework

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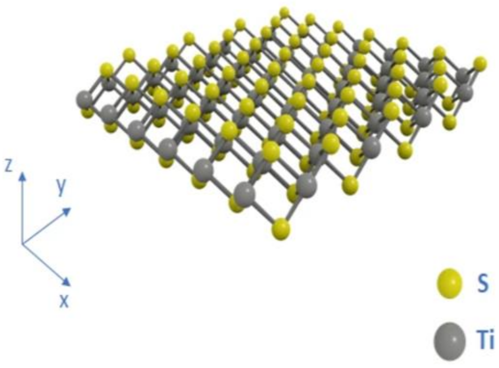
Project funding: ANR project ANR-18-CE09-0031-03 (ULTIMED project)
Partners: C2P2 & IRCELYON, IPVF, SOLEIL, LMGP
ULTIMED: Atomic-level control over ultrathin 2D layers of Transition Metal Dichalcogenides by a Molecular Layer Deposition route

Talk Outline

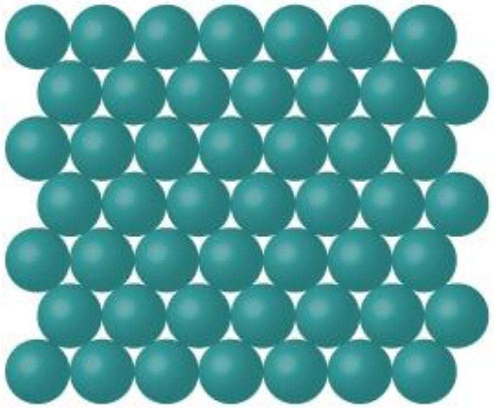
To be published

Motivation:
TiS_2 prepared by MLD route



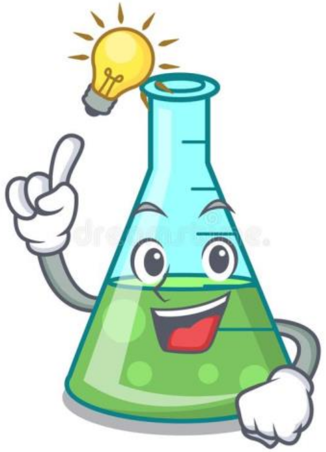
Ti-thiolate MLD:
in situ x-ray studies

Annealing *en route* to TiS_2



Crystalline

Conclusion



Thank you for your attention!