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

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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$_2$O)  
(Self-limiting saturated surface reaction)

1. DEZn injection
2. N$_2$ purge
3. H$_2$O injection
4. N$_2$ purge

DEZn = Zn(C$_2$H$_5$)$_2$

ALD ZnO on Si
- 500 and 1000 cycles *
- $T_{sub}$ between 100°C and 200°C GPC 0.16-0.22 nm.cy$^{-1}$

ALD window (DEZn and H$_2$O)  
(steady growth)

Zn(C$_2$H$_5$)$_2$ is Diethylzinc or DEZn

*Guziewicz et al. JAP 103 3 (2008)
**Gao et al. JVST A 34 1 (2016)

20 ALD cycles **
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

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)
In situ growth study of ALD or MLD

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

S Kα fluorescence (2.41 keV)

Number of cycles

Temperature: T_{sub.} = 50° C
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)
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)

XRF, GISAXS

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


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Motivation:
ZnO for MIS junctions, IPL

The early stage of ZnO ALD on In0.53Ga0.47As

Substrate temperature effect
Transient regime of growth
ZnO cristallisation

Conclusion
ZnO to reduce source/drain specific contact resistivity

Ang et al., IEDM (2012) 18.6.1
Optimal ZnO thickness

Al/Insulator/n-InGaAs

Optimal thickness

ZnO interfacial passivation layer (IPL)

- suppresses film crystallization
- reduces interface state density

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

A. Agrawal et al. APL 101 042108 (2012)
Motivation:
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ZnO ALD on In$_{0.53}$Ga$_{0.47}$As substrate

Crystal In$_{0.53}$Ga$_{0.47}$As

270 nm In$_{0.53}$Ga$_{0.47}$As (MBE)
10 nm InP buffer layer (MBE)
InP

n-InGaAs & p-InGaAs provider: III-V Lab™

Etched 5 min in a 4M HCl solution

*APL 93, 194103 (2008)*
Substrate temperature effect

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

- DEZn/ H₂O/ N₂ flow = 5sccm/2.6sccm/1000sccm
- DEZn/ H₂O/ N₂ inj. or purge time = 5s/40s/45s

Same growth behaviour for the 3 temperatures
Motivation:
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The early stage of ZnO ALD on In$_{0.53}$Ga$_{0.47}$As

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Transient regime of growth

ZnO crystallisation

Conclusion
ZnO transient growth on InGaAs

Growth Per Cycle (GPC)

Region I
growth delay

Desorption

ZnO (wurtzite)

ZnO

1.3 nm

InGaAs

Region II
S-shape growth

R_q=0.2 nm

AFM

25 cycles

30 cycles

R_q

Number of cycles

Phase I: Island growth
Phase II: Island coalescence
Phase III: Continuous islands (2D layer)

Δh=Δr

Phase I

Phase II

Phase III

R_q

Growth Per Cycle (GPC)

R = b/2

r < b/2

r > b/2

R

Phase I

Plateau

n_c

Number of cycles n

Nanoscale, 10, 11585 (2018)
ZnO transient growth on InGaAs

Growth Per Cycle (GPC)

Region I
- growth delay

Region II
- S-shape growth

Desorption

ZnO (wurtzite)

Number of cycles

Fluorescence yield (arb. units)

Zn K-edge

X-ray Absorption Near Edge Structure

9625 9650 9675 9700 9725 9750 9775

Energy (eV)

Wurtzite structure

Disordered Zn local environment/ small islands


Nanoscale, 10, 11585 (2018)
Precursor flow/inj. time effect on growth delay (region I)

**in situ X-ray Fluorescence**

![Graph showing XRF intensity vs. number of cycles](image)

- **XRF Intensity (arb. units)**
- **Water flow (sccm)**: 0, 1, 2, 3, 4, 5, 6
- **Onset of steady growth (cycles)**: 20, 25, 30, 35, 40, 45, 50

**ESRF ID03**

- Water amount increase

**Steady GPC**

**Growth delay**

**DEZn injection time**

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

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

**AFM**

InGaAs surface

- **a** after cleaning, before deposition
- **b** after one ALD cycle including a long DEZn injection time

**in situ ellipsometry**

- **Steady GPC**
- **Growth delay**

**DEZn injection time**

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Substrate temperature effect

Transient region of growth

ZnO crystallisation

Conclusion
In-plane RSM vs ZnO film thickness

Fast in-plane diffraction

RSM : reciprocal space map

No in-plane texture
ZnO crystallization during growth

(a) $T_{\text{sub}} = 120^\circ C$

(b) $T_{\text{sub}} = 200^\circ C$

Integrated Intensity (arb. units)

Thickness (nm)

Number of cycles

Thickness (nm)

Number of cycles

Region I

Region II

Region III

Region I substrate inhibited growth of type II

Region II steady growth

Region III
ZnO crystallization during growth
ZnO crystallisation on InGaAs

(a) \textit{InGaAs}  
(b) \textit{InGaAs}  
(c) \textit{InGaAs}  
(d) \textit{InGaAs}  
(e) \textit{InGaAs}  
(f) \textit{InGaAs}

region I  
(iii-ordered ZnO)

region IIa  
(ZnO wurtzite; amorphous+small grains)

region IIb  
(ZnO wurtzite; non-zero XRD intensity)

region III  
(Amorphous layer and ZnO grains)

\begin{center}
\begin{figure}
\centering
\includegraphics[width=\textwidth]{chart.png}
\caption{Graph showing the mean thickness (nm) vs. number of cycles for different regions under a substrate temperature of 120°C.}
\label{fig:chart}
\end{figure}
\end{center}

PHYSICAL REVIEW MATERIALS 4, 043403 (2020)
Motivation: ZnO for MIS junctions, IPL

The early stage of ZnO ALD on In$_{0.53}$Ga$_{0.47}$As

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Transient region of growth

ZnO crystallisation

Conclusion
Conclusion (part 2)

- GPC of ZnO ALD on InGaAs ~0.2 nm/cycle 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

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

Still to be performed: systematic electrical measurements

Nanoscale 10 11585 (2018)
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*In situ* X-ray studies of Dichalcogenides thin films prepared by Molecular Layer Deposition and thermal annealing
Collaborators - Framework

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Partners: C2P2 & IRCELYON, IPVF, SOLEIL, LMGP
ULTIMED: Atomic-level control over ultrathin 2D layers of Transition Metal Dichalcogenides by a Molecular Layer Deposition route
Motivation:
TiS$_2$ prepared by MLD route

Ti-thiolate MLD: *in situ* x-ray studies

Annealing *en route* to TiS$_2$

Conclusion

To be published
Thank you for your attention!