# International School of Oxide Electronics



# Oxide thin films growth

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# Thin films epitaxy

- Brief definitions
- Epitaxial strain as a control parameter
- Materials, substrates

# **Growth process**

- Growth modes and growth mechanisms
- In situ monitoring of 2D growth
- Growth techniques
- Structural characterization

# The case of ferroelectrics

- In-situ diagnostic tools
- Monitoring of ferroelectricity during the epitaxial growth interface contributions









#### Thin films research and applications



- Tune the physical properties of bulk (strain, confinement effects, etc...)
  Create new materials (stabilizing new states of matter), multilayers and
- **Create** new materials (stabilizing new states of matter), multilayers and new interfaces

#### Reproduce bulk properties in

reduced dimensions, technologically relevant design, etc...

D MATL.





Phys. Rev. Lett. 61 (1988) 2472. Phys. Rev. B 39, (1989) 4828. Fe

Cr

Fe

Thin films research and applications



Adv. Funct. Mater. 2018, 1804782



A wide variety of textures, mophologies, applications...



Spray pyrolysis, sol-gel deposition, Langmuir-Blodgett, evaporation, molecular beam epitaxy, pulsed laser depostion, sputtering, chemical vapor deposition, etc...



J. Mater. Chem., 2011,21, 16018-16027





épi-táxis « on top» «order»

Ordered growth of single crystalline material using an oriented single crystal as a substrate

Control:

- crystallinity of the film
- orientation of the film
- strain state of the deposited lattice
- (unit cell symmetry breaking, bond angle)



Phys. Rev. B 85, 035211 (2012)

D MATL.



Oxide electronics: Ferroelectrics (B-driven) Boost of polarization



Phys. Rev. Lett. 95, 257601 (2005)

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Phys. Rev. B 85, 035211 (2012)

# Oxide electronics: Ferroelectrics (Bdriven) Boost of Transition temperature



J. Phys.: Condens. Matter 33 293001 (2021)

**ETH** zürich

# **Oxide electronics: Ferroelectrics**

Domain engineering, polarization orientation



Nano Lett, 8, 2, 405–410 (2008) Nat. Commun. 5 4289 (2014)





Adv. Mater. 19 2662 (2007)

#### D MATL.

# **Oxide electronics: Inducing a polarization**

Designing new multiferroics



# Finding the right substrate



J. Phys.: Condens. Matter 28 263001 (2016)

Pseudo cubic unit cells



# Finding the right substrate





# D MATL.

Pr +

Pr -

# Finding the right substrate and buffers...





Scientific Reports 6, 31870 (2016)

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Voltage (V)

pristine sample

after 5x10<sup>10</sup> cycles

10

**Oxide electronics: Ferroelectrics** Domain engineering with anisotropic in-plane strain

The scandates

The case of  $DyScO_3$  (DSO) Orthorhombic

 $a_o = 0,544 \text{ nm}$  $b_o = 0,571 \text{ nm}$  $c_o = 0,789 \text{ nm}$ 





Adv. Mater. 2006, 18, 2307-2311

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#### **Oxide electronics: Ferroelectrics**

Domain engineering with anisotropic in-plane strain



#### **Oxide electronics: Ferroelectrics**

Domain engineering with anisotropic in-plane strain



Nature Communications 5, 4677 (2014) Nature 530, 198–201 (2016)



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#### The case of ferroelectrics

- In-situ diagnostic tools
- Monitoring of ferroelectricity during the epitaxial growth
  - interface contributions

#### 105 Topics in Applied Physics

#### K. Rabe Ch, H. Ahn (Eds) Physics of Ferroelectrics A Modern Perspective







What do we need to get controlled two dimensional epitaxial growth

**During deposition** 



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What do we need to get controlled two dimensional epitaxial growth

**During deposition** 



What do we need to get controlled two dimensional epitaxial growth

Screening charges at the surfaces set the final direction of the polarization



Control from the **bottom** interface

PNAS 109 9710 (2012) Nat. Commun 8, 1419 (2017) Nat. Commun. 11, 5815 (2020) PNAS. 117, 28589 (2020)

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D MATL.

Chem. Soc. Rev., 2014, 43, 2272

SrO terminated  $SrTiO_3$ : 1300C in air TiO<sub>2</sub> terminated  $SrTiO_3$ : water + etching solution + 950 C

What do we need to get controlled two dimensional epitaxial growth

**During deposition** 



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Thermodynamic approach: surface free energies of the films, substrates and interfaces determine the morphology of the film



What do we need to get controlled two dimensional epitaxial growth

# $\gamma_{\rm F}$ $\gamma_{\rm S}$ Intensity (a.u.) (i) (ii) (iii) (iv)

40

80

FIG. 3.  $\varphi$ -scans of the Pt {311} planes for the following three types of Pt films: (i) deposited directly on YSZ (111), (ii) with a further annealing at 800 °C for 48 h, and (iii) deposited using Ti adhesion layer.  $\varphi$ -scans of the substrate peak YSZ {422} are given in (iv).

φ (°)

120 160 200 240 280 320 360

Volmer Weber  $\Delta \gamma > 0$ 



# Pt on Y doped Zirconia



J. Appl. Phys. 105, 106101 (2009)

What do we need to get controlled two dimensional epitaxial growth

# 2D growth modes

 $\Delta \gamma < 0$  (during growth homoepitaxy)

The 2D growth behavior is determined by kinetic parameters

- the surface diffusion coefficient Ds of the ad-atoms

- the sticking coefficient of an atom at the edge of a terrace

- the energy barrier to descend the edge to a lower terrace (Ehrlich–Schwoebel barrier Journal of Applied Physics 37, 3682–3686 (1966))

+0+ 0+00 (800)

Ds determines the average distance an atom travels before being trapped

 $l_D = \sqrt{\tau} . D_s$ and  $D_s = \upsilon . a^2 e^{-Ea/K_BT}$ ETH zürich

τ residence time before evaporation,
 u attempt frequency,
 a characteristic jump distance,
 E<sub>n</sub> activation energy for diffusion

Temperature controls the diffusivity

What do we need to get controlled two dimensional epitaxial growth

#### 2D growth modes

 $\Delta \gamma < 0$  (during growth homoepitaxy)

Step flow growth



If the diffusion of the ad-atoms is too high,  $l_p >>$  average terrace width L

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What do we need to get controlled two dimensional epitaxial growth

#### 2D growth modes

 $\Delta \gamma < 0$  (during growth homoepitaxy)

Step flow growth



Lower diffusion of ad-atoms, the probability for atoms to bond to an existing island exceeds the probability to form a new one (high impact of the diffusion to a lower terrace).

Ideal case, layer by layer : Atoms first have to reach the island edge and diffuse to a lower terrace



What do we need to get controlled two dimensional epitaxial growth

#### 2D growth modes

 $\Delta \gamma < 0$  (during growth homoepitaxy)

# Step flow growth



What do we need to get controlled two dimensional epitaxial growth



#### 2D and 3D growth modes

Why do we need layer by layer?

ETH

What do we need to get controlled two dimensional epitaxial growth



#### 2D and 3D growth modes

#### **Reflection High Energy Electron Diffraction (RHEED)**

In-situ monitoring of surface structure and roughness



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What do we need to get controlled two dimensional epitaxial growth



#### 2D and 3D growth modes

300

С

RHEED intensity (a.u.)

0 1-

NGO

Unit cell and sub-unit cell thickness accuracy using RHEED

Dis N.C. RHEED intensity Phys. Rev Mater. 4, 124403 (2020) 800 1200 1400 200 400 600 1000 Time (s) 100 200 300 500 400 5 nm Time (s) NGO [1 1 0] 0.8 nm Intensity (arb. units) 2D growth Ga1 Adv. Mater Inter. 2000202 (2020) ACS Appl. Electron. Mater. 1, 1019 (2019) 100 200 300 400 500 600 700 0 Time (s)

(a)

PLD start

a 001 ~ Q cos(q-u-p)

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►[120]

#### Phys. Rev. Mater. 3, 124416 (2020)

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3D growth

We need an incident flux, high temperature

# Oxide molecular beam epitaxy (OMBE)



K. Rabe, C. H. Ahn, J.-M. Triscone (Eds.): Physics of Ferroelectrics: A Modern Perspective, Topics Appl. Physics **105**, 219–304 (2007) © Springer-Verlag Berlin Heidelberg 2007

# Atomically precise interfaces from non-stoichiometric deposition

Y.F. Nie<sup>1,2,\*</sup>, Y. Zhu<sup>3,\*</sup>, C.-H. Lee<sup>1</sup>, L.F. Kourkoutis<sup>3,4</sup>, J.A. Mundy<sup>3</sup>, J. Junquera<sup>5</sup>, Ph. Ghosez<sup>6</sup>, D.J. Baek<sup>7</sup>, S. Sung<sup>3</sup>, X.X. Xi<sup>8</sup>, K.M. Shen<sup>2,4</sup>, D.A. Muller<sup>3,4</sup> & D.G. Schlom<sup>1,4</sup>



superlattice period is shown.

We need an incident flux, high temperature

# Oxide molecular beam epitaxy (OMBE)





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FIG. 6. Shuttered RHEED intensity oscillation observed from the beginning of the growth of a [(BaTiO<sub>3</sub>)<sub>6</sub>/(SrTiO<sub>3</sub>)<sub>13</sub>]<sub>15</sub> superlattice (sample no. 12) on a TiO<sub>2</sub>-terminated (001) SrTiO<sub>3</sub> substrate. The intensity of the 01 RHEED streak along the [110] azimuth of the first superlattice period is shown.

Sr shutter open

Time (sec.)

400

500

300

700

600

Ba shutter open

200

100

0

https://www.mbe-komponenten.de

We need an incident flux, high temperature

# Oxide molecular beam epitaxy (OMBE)



K. Rabe, C. H. Ahn, J.-M. Triscone (Eds.): Physics of Ferroelectrics: A Modern Perspective, Topics Appl. Physics **105**, 219–304 (2007) © Springer-Verlag Berlin Heidelberg 2007

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# + Fine control on the atomic plane level

- + Large surface
- Calibration (precise timing of shutters)
- High temperatures get high flux, slow deposition

We need an incident flux, high temperature







We need an incident flux, high temperature

APL Mater 4, 086111 (2016)

D MATL.



We need an incident flux, high temperature



- + in situ monitoring
- Small area only

K. Rabe, C. H. Ahn, J.-M. Triscone (Eds.): Physics of Ferroelectrics: A Modern Perspective, Topics Appl. Physics **105**, 219–304 (2007) © Springer-Verlag Berlin Heidelberg 2007



We need an incident flux, high temperature

### Pulsed laser deposition (PLD)

Differential pumping, beam enclosing, screen geometry Now compatible with high pressure oxide thin films processes



Surface reconstruction and absolute temperature measurement



In plane lattice parameter determination



Streak-Position



Journal of Vacuum Science & Technology B: Microelectronics Processing and Phenomena 4, 890 (1986)

Appl. Phys. Lett. 65, 630 (1994)

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We need an incident flux, high temperature

### Pulsed laser deposition (PLD)

Differential pumping, beam enclosing, screen geometry Now compatible with high pressure oxide thin films processes





Growth modes.

Thesis Rijinders (2001)

We need an incident flux, high temperature

# Pulsed laser deposition (PLD)

Electron beam irradiation, Auger electron emission, characteristic of the atomic element.



Sr/Ti P2P (au)



We need an incident flux, high temperature, not just PVD



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the case of atomic layer deposition

For Ferroelectric  $HfO_2$  based compounds, precursors:  $Hf(diethylamino)_4$  and  $H_2O$ 



**Growth techniques** We need an incident flux, high temperature

Substrate lattice and surface morphology is important

OMBE, RF sputtering and PLD bring the control parameter to achieve layer by layer growth

> How do we characterize an epitaxial deposition?



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Structural characterization

# X-ray diffraction experiments

- Identification of the material, phase
- Strain state
- Epitaxial relationship

Investigation of the reciprocal space







Thesis Nordlander doi.org/10.3929/ethz-b-000446702

Structural characterization

# X-ray diffraction experiments

- Identification of the material, phase
- Strain state
- Epitaxial relationship



Structural characterization

# X-ray diffraction experiments

- Identification of the material, phase
- Strain state
- Epitaxial relationship



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Structural characterization

# X-ray diffraction experiments

- Identification of the material, phase
- Strain state
- Epitaxial relationship



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Appl. Phys. Lett. 91, 202504 2007



# Advice to young scientists;)

Never start a conversation like this:

"We are finishing a paper on [...] and would like to include a thickness dependence that supports our amazing interpretation. How can you help?"

When talking to a thin film grower

\* (Good growth akes time

\* The results from growth ay or may not agree with your theory
 \* That's OK because (good' experiment and its comparison with experiment is theory to will allow you to learn about your problem

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100011-01



Growth of ferroelectric in the polar phase

600

600



J. Phys.: Condens. Matter 33 293001 (2021)

Nat. Commun. 11, 2630 (2020)

#### In-situ monitoring techniques for ferroelectricity X-ray diffraction

Probing the functionality noninvasively, the ferroelectricity

Phys. Rev. Lett. 94, 047603





D MATL.

Film Thickness (unit cells)

**In-situ monitoring techniques for ferroelectricity** Probing the functionality noninvasively, the ferroelectricity



PRL. 107, 187602 (2011) Nat Commun. 9, 3809 (2018) Adv. Electron. Mater. 6, 2000852 (2020) Adv. Funct. Mater. In press



1.4					l
Heat treatment time 10 min	1 h	4 h 40 min	7 h	8 h 30 min	9 h 20 min
0.1%	10%	50%	75%	90%	100% of deposition time

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**In-situ monitoring techniques for ferroelectricity** Probing the functionality noninvasively, the ferroelectricity



Final state

During growth

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# SHG checklist (courtesy of referee #2)

-data fitted considering point group symmetry -temperature dependence (cooldown, heating up) -sample orientation dependent -substrate/ buffer / surface contribution?

> Adv. Mater. 27, 4871. (2015) Nat. Commun 8, 1419 (2017) Appl. Sci., 8, 570 (2018) Materials, 12, 3108 (2019)

D MATL.







Real time monitoring of polarization during the growth









#### Direct access to

- the critical thickness
- the Tc (strain dependent)
- the polarization dynamics and domain formation

Adv. Mater. 27, 4871. (2015) Nat. Commun 8, 1419 (2017) Appl. Sci., 8, 570 (2018)

Real time monitoring of polarization during the growth

# **Critical thickness for ferroelectricity** in perovskite ultrathin films

#### **Javier Junquera & Philippe Ghosez**



**ETH** zürich



Nat. Commun. 11, 5815 (2020)

(a) 3.2

Average stoichiometry

3.1

3.0

2.9

2.8 2.7

1.2 1.1

1.0

0.9 0.8

The growth of PbTiO<sub>3</sub>

Defect gradient formation affect the net polarization state





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The growth of PbTiO<sub>3</sub>

Polarization orientation dependent



Nature 530, 198-201 (2016)



Nat. Commun. 11, 5815 (2020) PNAS. 117, 28589 (2020) STO

SMO

D MATL.



D MATL.

TbSc0

Defect

Defect

#### Spontaneous surface reconstruction







Ark. Kemi. 1, 463 (1949)

Nature 1995, 374, 627. Appl. Phys. Lett. 2001, 78, 4175. J. Mater. Res. 2007, 22, 1439.



### D MATL.



Aurivillius thin films





# Layered ferroelectrics Aurivillius thin films

Combination of structural and functional properties monitoring in real time







Strain and electrostatics in complex heterostructures







#### at ferroelectric-dielectric interfaces

Nature 2016, 530, 198-201. Nature 2019, 568, 368–372

at ferroelectric-metal interfaces

### What's next?

Epitaxy with simultaneous, structural, chemical and symmetry monitoring

- identification of optimal growth processes
- reproducibility of the depositions
- identification of phase transition in situ
- design of antiferroic properties

Epitaxy on non-crystalline substrates, VdW epitaxy and freestanding membranes for beyond «classical epitaxial design» capacity





Sci. Adv. 8, eabg5860 (2022)