# Summer school on Epitaxy MATEPI2025





CONVERSITÉ CONSUMERSITÉ Clermont Auver

## Porquerolles June 22-27 2025

## .// matepi

## Alberto Pimpinell **Clermont-Ferrand, France**





## Introduction to the **Physics of Epitaxial Growth: nucleation**



October 2017<u>MRS Communications</u> 7(04):1-6



Crystal Technology Consulting rudolph@ctc-berlin.de

### Kinetics

- nucleation kinetics
- atomistic interface models
  - Kossel-Stranski and PBC models
  - surface diffusion
  - surface roughening
- growth modes
  - atomically rough interface
  - atomically smooth interface
  - stepped face
  - step bunching

### Transport

heat transport

conduction

radiation

#### mass transport

diffusion

convection

boundary layers

distribution effects

segregation

external forces



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### Kinetics

- nucleation kinetics
- atomistic interface models
  - Kossel-Stranski and PBC models
  - surface diffusion
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## **Interface processes** during crystal growth



A Compressed Approach to the Theory of Crystal Growth. **Thermodynamics, Kinetics and Transport** 

P. Rudolph

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## Driving force of crystal growth: supersaturation

$$\mu G = G(T, P, N), \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$$
$$\mu(T, P) = \left(\frac{\partial G}{\partial N}\right)_{T,N}$$

 $\Delta \mu = k_B T \ln(1 + \Delta P/P_e)$ 

A Compressed Approach to the Theory of Crystal Growth. Thermodynamics, Kinetics and Transport

> P. Rudolph Crystal Technology Consulting rudolph@ctc-berlin.de



## Driving force of crystal growth: supersaturation

$$G = G(T, P, N), \quad V = \left(\frac{\partial G}{\partial P}\right) \begin{bmatrix} \text{Epitaxy me} \\ \text{Relative su saturation} \end{bmatrix}$$

$$\mu(T, P) = \left(\frac{\partial G}{\partial N}\right)_{T,N} \begin{bmatrix} \text{Driving for } \\ \text{J/mol} (T = 1) \end{bmatrix}$$

 $\Delta \mu = k_B T \ln(1 + \Delta P/P_e)$ 

#### A Compressed Approach to the Theory of Crystal Growth. Thermodynamics, Kinetics and Transport

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thod	LPE	VPE	MOCVD	MBE
per- S	~ 0.02 - 0.1	~ 0.5 - 2	~ 50	~ 10 - 1
се Δµ .000 К)	~ 165 - 800	~ ( <b>3-9)</b> ×10 <sup>3</sup>	~ 3.3 x 10 <sup>4</sup>	~ (2-4) >



## Classical nucleation theory

- Close to equilibrium (free energy, chemical potential)
- nucleation barrier

• Computes the size (radius) of the critical cluster,

# Classical nucleation theory $\Delta G = 2\pi\gamma bR - \pi\Delta\mu bR^2$ b $\Delta G_c = \pi b \frac{\gamma^2}{\Lambda \mu} = \pi b \frac{\gamma}{R_c}$



## **Numerical models** and crystal growth

### Ideal lattice with abrupt interface

#### A Compressed Approach to the Theory of Crystal Growth. **Thermodynamics, Kinetics and Transport**

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## Interface models Lattice models Numeric calculation ab-initio, MD, MC, PF **Real lattice** dislocations, impurities, interface effects melt $\Delta IF$ Diffuse interface crystal 8 8 9 0 0 0 0 0 0

## An example of numerical methods Kinetic Monte Carlo (kMC)



## Diffusion is a random walk!

## (case $p_{\leftarrow}$ $P(i, N) = \frac{1}{2}P(i + 1, N)$ Defining: $t = N\tau$ , x = $P(x,t) = \frac{1}{2}P(x+l,t)$ We rewrite this by subtracting $P(x, t - \tau)$

$$\frac{P(x,t) - P(x,t-\tau)}{\tau} = \frac{P(x+l,t-\tau) + P(x-l,t-\tau) - 2P(x,t-\tau)}{2\tau}$$

we get

$$\frac{\partial P(x,t)}{\partial t} \approx \frac{l^2}{2\tau} \frac{\partial^2 P(x,t)}{\partial x^2}$$

In the limit au o 0, l o 0 but where the ratio  $l^2/ au$  is finite, this becomes an exact relation.

Diffusion is a random walk!

$$p_{-}=p_{
ightarrow}$$
)  
 $-1)+rac{1}{2}P(i-1,N-1)$   
 $i\ell$  we have:  
 $(t- au)+rac{1}{2}P(x-l,t- au)$   
) and dividing by  $au$ 

## An example of numerical methods Kinetic Monte Carlo (kMC)

 $p_i = \nu_0 e^{\frac{-iE}{k_bT}}$ 

 $E = 0.1 \, \text{eV}$ 



(a)



## My own The Big Bang Theory moment

MECHANICAL IGINEERING LAP

2



-



#### ACS APPLIED MATERIALS & INTERFACES

### High-Resolution Mapping of Thermal History in Polymer Nanocomposites: Gold Nanorods as Microscale Temperature Sensors

W. Joshua Kennedy,<sup>†,‡</sup> Keith A. Slinker,<sup>†,‡</sup> Brent L. Volk,<sup>‡</sup> Hilmar Koerner,<sup>‡</sup> Trenton J. Godar,<sup>§,‡</sup> Gregory J. Ehlert,<sup>‡</sup> and Jeffery W. Baur<sup>\*,‡</sup>



Research Article

www.acsami.org



## N = 1728, T = 300K time evolution



## N = 675, T = 700K time evolution







## Equilibration time: time needed to attain an aspect ratio of 1.2



# The Roughening Transition Step Free Energy: work needed to create a step, per bond



 $\Delta G^* = \pi h \gamma^2 / \Delta \mu$ 

[110] step on a (100) surface

# The Roughening Transition

## Step Free Energy: work needed to create a step, per bond

• Step: random walk from left to right (fixed ends) • Number of steps = number of bonds = 2L• Bond energy =  $W_1$ • Total energy =  $2LW_1$ • Number of configurations =  $2^{2L}$ • **Entropy** =  $2L k_B \ln 2$ 



# The Roughening Transition

## Step Free Energy: work needed to create a step, per bond



 $\gamma = e - Ts$ 

 $\gamma = W_1 - k_B T \ln 2$  $\gamma = 0 \rightarrow T_R = \frac{W_1}{k_B \ln 2}$ 



## **Surfaces:** smooth and rough $\gamma = 0 \rightarrow T_R = \frac{W_1}{k_B \ln 2}$ $T < T_R$ $\langle [z(\vec{r} + \vec{R}) - z(\vec{r})]^2 \rangle \sim \text{const.}$ $T > T_R$

 $\langle [z(\vec{r} + \vec{R}) - z(\vec{r})]^2 \rangle \sim (4\pi k_B T/\tilde{\sigma}) \ln R$ 





## Classical nucleation theory







 $\Delta G = 2\pi \gamma bR - \pi \Delta \mu bR^2$  $\Delta \mu = \gamma/R_c$ 

## **Nucleation and critical nucleus**



## $\Delta \mu = k_B T \ln(1 + \Delta P/P_e)$

#### A Compressed Approach to the Theory of Crystal Growth. **Thermodynamics, Kinetics and Transport**

## Deposition, diffusion, nucleation and aggregation on substrates



## Deposition, diffusion, and aggregation on substrates



Graphene on Cu















## $R_c = 1 \, !!$ "critical nucleus" is a monomer!



# Task: building a kinetic theory of nucleation

## Nucleation Kinetics Critical Nucleus Size



# nucleation

## **Nucleation Kinetics Critical Nucleus Size**


# Kinetic theory of nucleation

- Rate equations
- Clusters with s monomers have density  $N_s$
- Diffusing monomers have density *n*
- Assume critical nucleus is cluster with size s = i



### Parameters: deposition rate *F*; diffusion constant *D*; Critical Nucleus Size *i*

$$\dot{n} = F - 2Dn^2 - DnN$$

$$\begin{split} \dot{N}_s &= \sigma_{s-1}nN_{s-1} - \sigma_s nN_s + \frac{1}{\tau_{s+1}}N_{s+1} - \frac{1}{\tau_s}N_s \quad s < i \\ \dot{N}_i &= \sigma_{i-1}nN_{i-1} - \sigma_i nN_i - \frac{1}{\tau_i}N_i \\ \dot{N} &= \sigma_i nN_i \end{split}$$

$$\dot{n} = 0, \qquad n \ll N$$
  
 $n = \frac{F}{DN}$ 

## Simplest cases: i = 1 and i = 2

$$i = 1$$
  

$$\dot{n} = F - 2Dn^2 - DnN$$
  

$$\dot{N} = Dn^2$$

$$\begin{split} i &= 2\\ \dot{n} &= F - 2Dn^2 - DnN_2 + \frac{1}{\tau_2}\\ \dot{N}_2 &= Dn^2 - DnN_2 - \frac{1}{\tau_2}N_2\\ \dot{N} &= DnN_2 \end{split}$$

## $-N_2 - DnN$

## Simplest cases: i = 1 and i = 2

i = 1 $\dot{n} = F - 2Dn^2 - DnN \approx 0 ; n \ll N \to n \approx \frac{F}{DN}$  $\dot{N} = Dn^2 \approx F \frac{F}{DN^2}$  $\dot{n} = F - 2Dn^2 - DnN_2 + \frac{1}{\tau_2}N_2 - DnN \; ; \; n, N_2 \ll N \to n \approx \frac{F}{DN}$  $\dot{N}_2 = Dn^2 - DnN_2 - \frac{1}{\tau_2}N_2 \approx Dn^2 - \frac{1}{\tau_2}N_2 \approx 0 \to N_2 \approx (D\tau_2)n^2$  $\dot{N} = DnN_2 \approx D(D\tau_2)n^3$ 

## Simplest cases: i = 1 and i = 2

i = 1 $n \approx ---$ DN $\frac{dN}{d\theta} \approx \frac{F}{DN^2}; \ \theta = Ft$ i = 2 $n \approx \frac{D}{FN}$  $N_2 \approx (D\tau_2)n^2$  $\frac{dN}{d\theta} \approx \frac{D}{F} (D\tau_2) \left(\frac{F}{DN}\right)^3 = (D\tau_2) \left(\frac{F}{D}\right)^2 N^{-3}$ 



Simplest cases: i = 1 and i = 2

i = 1 $n \approx \frac{F}{DN}$  $N^2 \frac{dN}{d\theta} \approx \frac{F}{D} \to N^3 \approx \frac{F}{D} \to N \approx \left(\frac{F}{D}\right)^{1/3}$ i = 2 $n \approx \frac{D}{FN}$  $N_2 \approx (D\tau_2)n^2$  $\frac{dN}{d\theta} \approx (D\tau_2) \left(\frac{F}{D}\right)^2 N^{-3} \to \Lambda$ 

$$N \approx (D\tau_2)^{1/4} \left(\frac{F}{D}\right)^{1/2}$$

## General i



Integrating, we obtain

$$N \sim \left(\frac{F}{D}\right)^{i/(i+2)} e^{E_i/[k_B T(i+2)]} = \left(\frac{F}{D_0}\right)^{i/(i+2)} \exp\left[\frac{iE_D + E_i}{(i+2)k_B T}\right],$$

where  $E_D$  is the hopping energy barrier and  $E_i$  is the cohesion energy of a cluster of size *i* (the critical nucleus in this approach.)

$$\dot{N}_s = 0$$
) one finds the solution  
 $\dot{N}_s = \left(\prod_{k=2}^s \sigma_{k-1} \tau_k\right) n^s.$ 

Scaling!

 $N \sim \left(\frac{F}{D}\right)^{i/(i+2)}$ 





b)

**Growth Time** 

Rehan Kapadia<sup>1,2\*</sup>, Zhibin Yu<sup>1,2\*</sup>, Hsin-Hua H. Wang<sup>1,2</sup>, Maxwell Zheng<sup>1,2</sup>, Corsin Battaglia<sup>1,2</sup>, Mark Hettick<sup>1,2</sup>, Daisuke Kiriya<sup>1,2</sup>, Kuniharu Takei<sup>1,2</sup>, Peter Lobaccaro<sup>2,3</sup>, Jeffrey W. Beeman<sup>2</sup>, Joel W. Ager<sup>2</sup>, Roya Maboudian<sup>3</sup>, Daryl C. Chrzan<sup>2,4</sup> & Ali Javey<sup>1,2</sup>

Scaling!

 $N \sim \left(\frac{F}{D}\right)^{i/(i+2)}$ 

**"Byproduct":** measuring diffusion coefficient by counting islands

#### A direct thin-film path towards low-cost large-area III-V photovoltaics



SCIENTIFIC **REPORTS** | 3 : 2275 | DOI: 10.1038/srep02275





# Organic molecules!

#### Journal of Crystal Growth 405 (2014) 73–80

Molecular orientation transformation of pentacene on amorphous SiO<sub>2</sub>: A computational study on the initial growth stage of physical vapor deposition

Yuanqi Zeng, Bo Tao\*, Zhouping Yin

#### Growth dynamics of pentacene thin films

Frank-J. Meyer zu Heringdorf, M. C. Reuter & R. M. Tromp



Pentacene  $\bullet$  SiO<sub>2</sub>



Pentacene • Si(001)





F = 90 min/ML



F = 8 min/ML



F = 10 min/ML



F = 4.5 min/ML



Appl. Phys. A 78, 787–791 (2004) DOI: 10.1007/s00339-003-2432-x Applied Physics A Materials Science & Processing

M.C. REUTER R.M. TROMP

#### F.-J. MEYER ZU HERINGDORF<sup>M</sup>,\* The nucleation of pentacene thin films

IBM T.J. Watson Research Center, Yorktown Heights, P.O. Box 218, NY 10598, USA



FIGURE 4 Influence of the deposition rate on the nucleation density for pentacene on cyclohexene on Si(001). a typical PEEM image after island nucleation, b PEEM image after additional nuclei were formed by an increased rate





Fig. 1 AFM surface topography (10 µm × 10 µm) of 0.5 nm-thick pentacene films grown on a 200 nm-thick SiO 2 substrate (a) at various deposition rate for a fixed substrate temperature of 65 °C and (b) at different substrate temperatures for a fixed deposit...

Sirapat Pratontep , Martin Brinkmann , Frank Nüesch , Libero Zuppiroli **Nucleation and growth of ultrathin pentacene films on silicon dioxide: effect of deposition rate and substrate temperature** Synthetic Metals, Volume 146, Issue 3, 2004, 387 - 391 http://dx.doi.org/10.1016/j.synthmet.2004.08.017

# Deposition, diffusion, nucleation and aggregation



Sur At He L. 7



Surface Science Letters

Attachment limited versus diffusion limited nucleation of organic molecules: Hexaphenyl on sputter-modified mica



L. Tumbek, A. Winkler \*

Scaling? 3  $N \sim \left(\frac{F}{D}\right)^{i/(i+2)} \text{ (Injection of the second se$ 2 -0 --1 --2 --3 -

Surface Science Letters Attachment limited versus diffusion limited nucleation of organic molecules: Hexaphenyl on sputter-modified mica L. Tumbek, A. Winkler \*





Different exponents mayimply different aggregation processes Diffusion Limited (DLA) Attachment Límíted (ALA) 3D Clusters (3D) ...  $\alpha_{\rm DLA} = i/(i+2)$ 

 $\alpha_{\rm ALA} = 2i/(i+3)$ 

 $\alpha_{3D} = 2i/(2i+5)$ 

Ga droplets on GaAs(111)A 2° vicinal



Can one extract from the islands pattern more information about the nucleation process?

# Average island density $N = \frac{}{\langle A \rangle}$ Average area per island

# Beyond island densities



## Simulations of *i*=0,1 *Circular* Islands

Mulheran & Blackman, PRB 53 (96) 10261



0.20 ML

0.15 ML





0.20 ML

0.15 ML

## Simulations of *i*=0,1 *Circular* Islands

Mulheran & Blackman, PRB 53 (96) 10261



0.20 ML

0.15 ML









PRL 99, 226102 (2007)

PHYSICAL REVIEW LETTERS

# Aphenomenologícal model for the CZD

## Nucleation rate between islands $\dot{N}(A)$

## $\dot{N}_{i+1} \approx DnN_i \approx Dnn^i = Dn^{i+1}$

week ending 30 NOVEMBER 2007

#### **Capture-Zone Scaling in Island Nucleation: Universal Fluctuation Behavior**

Alberto Pimpinelli<sup>1,2,\*</sup> and T.L. Einstein<sup>2,†</sup>

# A phenomenologícal model for the CZD



$$\dot{N}(A) \sim D \int_A drr[n(r)]^{i+1} \sim A^{i+2}$$

 $\dot{N}(A) \sim D\bar{n}^{i+1}P$ 

$$\begin{split} D\bar{n}^{i+1}P(s), & s = A/\langle A \rangle \\ & & \downarrow \text{ probability of a capture zone} \\ & & \text{having area } s = A/$$

# A phenomenologícal model for the CZD



$$\dot{N}(A) \sim D \int_A drr[n(r)]^{i+1} \sim A^{i+2}$$

 $\dot{N}(A) \sim D\bar{n}^{i+1}P(s), \qquad s = A/\langle A \rangle$  $\bar{n} = (F/D)^{i+1} \langle A \rangle^{i+1}$ 

# A phenomenologícal model for the CZD

$$\beta = i + 2$$

 $P(s) = a_{\beta}s^{\beta}\exp(-b_{\beta}s^2)$ 

## Wigner distribution

$$\beta_{\rm ALA} = (i+3)/2$$



## Experiments: III-V droplet epitaxy



### R. Jouanneaud, G. Monier, L. Bideux, AP, C. Robert-Goumet Équipe Surfaces Interfaces, Institut Pascal, CI-Fd





Sample	β	$i=\beta-2$
T1 (300 °C)	$4.3 \pm 0.4$	$2.3\pm0.4$
T2 (350 °C)	$3.0 \pm 0.4$	$1.0 \pm 0.4$
T3 (400 °C)	$4.0 \pm 0.2$	$2.0 \pm 0.2$
T4 (450 °C)	$6.0 \pm 0.3$	$4.0 \pm 0.3$

$$\beta_{ALA} = (i+3)/2$$
  
 $\beta_{DLA} = i+2$ 

## **Ga droplets** on GaAs(111)A 2° vicinal



#### **Temperature Activated Dimensionality Crossover in the** Nucleation of Quantum Dots by Droplet Epitaxy on GaAs(111)A **Vicinal Substrates**

Published online: 10 October 2019

Artur Tuktamyshev <sup>1</sup>, Alexey Fedorov<sup>2</sup>, Sergio Bietti<sup>1</sup>, Shiro Tsukamoto<sup>1</sup> & Stefano Sanguinetti



#### (112)

#### Ga droplets on GaAs(111)A 2° vicinal

 $\begin{array}{c}
1,50\\
1,25\\
1,00\\
0,00\\
0,50\\
0,50\\
0,00\\
0,0
\end{array},5$ 

 $\beta_{300^0C} \approx 5$ 

(112)  $i_{DLA} \approx 3$  $i_{ALA} \approx 4$ 



#### Ga droplets on GaAs(111)A 2° vicinal

 $\begin{array}{c}
1,50\\
1,25\\
1,00\\
0,00\\
0,50\\
0,50\\
0,25\\
0,00\\
0,0 \\
0,5 \\
1,0 \\
0,5 \\
1,0 \\
0,5 \\
1,5 \\
2,0 \\
0
\end{array}$ 

 $\beta_{300^0C} \approx 5$ 

(112)  $i_{DLA} \approx 3$  $i_{ALA} \approx 4$ 



# Tuning nucleation: alloys









R. Jouanneaud, G. Monier, L. Bideux, AP, C. Robert-Goumet Équipe Surfaces Interfaces, Institut Pascal, CI-Fd

# Tuning nucleation: alloys





R. Jouanneaud, G. Monier, L. Bideux, AP, C. Robert-Goumet Équipe Surfaces Interfaces, Institut Pascal, CI-Fd

# **Tuning nucleation: impurities**



PHYSICAL REVIEW B 77, 205328 (2008)

#### Effect of impurities on pentacene island nucleation

B. R. Conrad, Elba Gomar-Nadal, W. G. Cullen, A. Pimpinelli,\* T. L. Einstein, and E. D. Williams<sup>†</sup> Physics Department and Materials Research Science and Engineering Center, University of Maryland, College Park, Maryland 20742-4111, USA (Received 11 February 2008; published 27 May 2008)

### experiments: pentacene islands with quinone impurities







# **Tuning nucleation: impurities**

Sim.



Exp.





0.5 % Pentacene/PentaceneQuinone B Conrad, et al. PRB 77, 205328 (2008)

## Modeling nucleation: elasticity

In theory there is no

difference between

practice there is.

theory and practice. In



#### Yogi Berra




#### **Hydrice Nzomo Simulation flow chart** Équipe Surfaces Interfaces, Institut Pascal, CI-Fd



## Modeling nucleation: elasticity





#### Effet élastique

La direction de diffusion est choisir par un nombre aléatoire ( $\Delta E_{el} = E0 + E_{EL}(i, j) - E_{EL}(ni(d), nj(d))$ )

 $p(d) = D_0 * \exp(-(Ed + \Delta E_{el})/K_BT)$ 















#### TAILLE DE LA GRILLE 250\*250

#### Simulations







Delaunay triangulation



#### Experiments

Delaunay triangulation

Island density vs. 1/T



#### Simulations







Delaunay triangulation



#### Experiments

Delaunay triangulation

Island density vs. 1/T









# $c(R) = c(\infty) \exp\left(\Omega \frac{2\sigma}{R} k_B T\right)$







 $\vec{J} = -D\nabla C$ 









t=100

t=500









t=20000



t=1000



t=4000







#### YOUR LIFE AMBITION - What Happened??



## Ouestions?

WWW. PHDCOMICS. COM

## Exponent relations (2D islands)

 $P(s) = a_{\beta} s^{\beta} \exp(-b_{\beta} s^2)$ 

 $\beta_{\text{DLA}} = i + 2$ 

 $\beta_{\rm ALA} = (i+3)/2$ 

 $N \sim (F/D)^{\alpha}$ 

 $\alpha_{\rm DLA} = i/(i+2)$ 

 $\alpha_{\rm ALA} = 2i/(i+3)$ 



### $P(s) = a_{\beta} s^{\beta} \exp(-b_{\beta} s^2) \qquad N \sim (F/D)^{\alpha}$



#### **Exponent relation**



## **Exponent relation**

#### $P(s) = a_{\beta} s^{\beta} \exp(-b_{\beta} s^2) \qquad N \sim (F/D)^{\alpha}$

#### $\alpha(2\beta + d - 2) = 2i$

#### for d-dimensional islands!

## **Exponent relation**

#### $P(s) = a_{\beta} s^{\beta} \exp(-b_{\beta} s^2) \qquad N \sim (F/D)^{\alpha}$

## $\alpha(2\beta + 1) = 2i$

## for 3D islands