In theory, there is no difference between theory and practice. In practice, there is.





Crystals in and out of equilibrium **Part 2: Growth modes**

Physics of Crystal Growth

Alberto Pimpinelli and Jacques Villain





2D platelets



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

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

(a)

Kinetic Monte Carlo







Kinetic Monte Carlo



Kinetic Monte Carlo



N = 6250, T = 83K

Equilibrium shapes



High temperatures

Low temperatures





When crystals grow unstable

Spontaneous structural pattern formation at the nanometre scale in kinetically restricted homoepitaxy on vicinal surfaces

CEA Saclay, DSM/Drecam/Spcsi, 91191 Gif Sur Yvette, France



Cu (0,2,24)



N Néel, T Maroutian, L Douillard and H-J Ernst



Cu (1,1,17)





Net current "up": leads to curved steps and/or 3D islands (mounds)

Ehrlich-Schwoebel effect

 $\mathbf{J} = -D\nabla c$

 $J_{\rm down} < J_{\rm up}$



2D to 3D: interlayer transport barriers ("Schwoebel")





Curved steps "Meanders"

Real out of equilibrium surfaces



Culied

2

Cu vicinals — unstable growth: curved step + 3D pyramids



BEN-HAMOUDA et al.

Cu (0 2 24)



800x800, L=15, T=250K, F=5e-3ML/s $E_b = 0.1 eV, E_d = 0.4 eV, E_a = 0.15 eV,$ 20 ML

PHYSICAL REVIEW B 77, 245430 (2008)

Cu (1 1 17) Cu (1 1 17)

360x360, L=5, T=280K, F=5e-3ML/s $E_b=0..07eV, E_d=0.4eV, E_a=0.12eV,$ 20 ML

800x800, L=5, T=285K, F=5e-2ML/s, $E_b = 0..07 eV, E_d = 0.4 eV, E_a = 0.12 eV,$ 40 ML



BEN-HAMOUDA et al.

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R.L. Schwoebel, J. Appl. Phys. 40 (1968) 614.

Inverse Schwoebel effect

$J_{\rm down} > J_{\rm up}$ Net current "down"

Leads to step bunching

Common wisdom is:

Surface current "up": step meandering;

Surface current "down": step bunching

Common wisdom is:

Surface current "up": step meandering;

Surface current "down": step bunching

 $\nu_{\parallel} = \ell J(\ell)$

(step meandering if < 0)

Common wisdom is wrong

$$\nu_{\perp} = -\ell^2 \frac{dJ(\ell)}{d\ell}$$

(step bunching if < 0)

Complex growth: multiple components



Journal of Crystal Growth 220 (2000) 631-636

www.elsevier.nl/locate/jcrysgro

A new model of morphological instabilities during epitaxial growth: from step bunching to mounds formation

Masha Vladimirova^{a,*}, Alberto Pimpinelli^b, Arnaud Videcoq^b

^aIRRMA, EPFL, CH-1015 Lausanne, Switzerland ^bLASMEA, UMR 6602 CNRS/Université Blaise Pascal, Clermont 2, F-63177 Aubière Cedex, France

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Available online at www.sciencedirect.com

SCIENCE DIRECT.

Journal of Crystal Growth 258 (2003) 14-25

Direct condensation modelling for a two-particle growth system: application to GaAs grown by hydride vapour phase epitaxy

> E. Gil-Lafon*, J. Napierala, A. Pimpinelli, R. Cadoret, A. Trassoudaine, D. Castelluci

LASMEA, UMR CNRS 6602, Université Blaise Pascal, Clermont-Ferrand II, Complexe Scientifique des Cézeaux, Les Cézeaux, F-63177 Aubière Cedex, France



ELSEVIER

Available online at www.sciencedirect.com



Journal of Crystal Growth 258 (2003) 1-13

CRYSTAL GROWTH

www.elsevier.com/locate/jcrysgro

Two-particle surface diffusion-reaction models of vapour-phase epitaxial growth on vicinal surfaces

Alberto Pimpinelli*, Robert Cadoret, Evelyne Gil-Lafon, Jérôme Napierala, Agnès Trassoudaine

LASMEA, Université Blaise Pascal Clermont-2, Les Cézeaux, 63177 Aubière Cédex, France





 $D_{\mathbf{B}}\nabla^2 c^{\mathbf{B}} - v_{\mathbf{B}}c^{\mathbf{B}} + \boldsymbol{\Phi}_{\mathbf{B}} = 0,$





Epitaxy on a crystal



Low T, low and high growth rates













Low T, high T and intermixing





Very low T, high and low growth rate: Instability nucleated by pyramid growth















Shell Growth and Morphology in **Synthesis of Core-Shell Nanocrystals**

Vyacheslav Gorshkov,^a Vasily Kuzmenko,^a and Vladimir Privman^{b,*}

J. Phys. Chem. C 118 (43), 24959-24966 (2014)



DOI 10.1021/jp506331u

Chemistry: the role of precursors Synthesis of Al nanocrystals

A 10:1

50:1



49

100:1

500:1

Chemistry: the role of precursors Synthesis of Al nanocrystals

100:1

140:1





200:1

300:1



Chemistry: the role of precursors Synthesis of Al nanocrystals

RICE UNIVERSITY

Shape-Controlled Synthesis of Aluminum Nanocrystals

by

Benjamin Daniel Clark

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy in Chemistry

APPROVED, THESIS COMMITTEE

Naomi J. Halas, Chair Stanley C. Moore Professor of Electrical and Computer Engineering, Professor of Biomedical Engineering, Chemistry, and Physics and Astronomy, Director, Laboratory for Nanophotonics

Mail D. T.



10 nm

50 nm





Stacking 1 over 2: wetting & elasticity

Contact angles on flat and patterned surfaces in an ESEM Increasing condensation flat



Static contact angle (98°)



Static contact angle (129°)

Wetting



Increasing evaporation



Advancing contact angle (101°) Receding contanct angle (95°)









Receding contanct angle (127°)







Solid wetting

$\sigma_{\rm substrate}$





Solid wetting

$\sigma_{\rm substrate}$

$\Delta \mathcal{F} = \mathscr{A}(2\sigma_{\text{film}} - \sigma_{\text{substrate}} - \sigma_{\text{film}} + \sigma_{\text{interface}})$







Solid wetting

*σ*_{substrate}

$\Delta \mathcal{F} = \mathscr{A}(2\sigma_{\text{film}} - \sigma_{\text{substrate}} - \sigma_{\text{film}} + \sigma_{\text{interface}})$ $= \mathscr{A}(\sigma_{\text{film}} + \sigma_{\text{interface}} - \sigma_{\text{substrate}})$ *o*_{interface}

- $\sigma_{\rm substrate}$



$\sigma_{\rm film} + \sigma_{\rm interface} - \sigma_{\rm substrate} \leq 0$

2D growth

$\sigma_{\text{substrate}} \geq \sigma_{\text{film}} + \sigma_{\text{interface}}$

$\sigma_{\text{film}} + \sigma_{\text{interface}} - \sigma_{\text{substrate}} \leq 0$

$\sigma_{\rm film} + \sigma_{\rm interface} - \sigma_{\rm substrate} > 0$



2D growth

$\sigma_{\text{substrate}} \geq \sigma_{\text{film}} + \sigma_{\text{interface}}$



3D growth

$\sigma_{\text{substrate}} < \sigma_{\text{film}} + \sigma_{\text{interface}}$

$\sigma_{\text{film}} + \sigma_{\text{interface}} - \sigma'_{\text{first layer}} = ?$

$\sigma_{\rm film} + \sigma_{\rm interface} - \sigma_{\rm first \, layer} > 0$ 2D+3D growth

Reconsider 2D growth

$\sigma'_{\text{first layer}} \geq \sigma_{\text{film}} + \sigma_{\text{interface}}$

$\sigma'_{\rm first \, layer} < \sigma_{\rm film} + \sigma_{\rm interface}$

Crystal-crystal interface misfit create strain: larger in the (thin) film than in the substrate



Epitaxial growth modes





Frank-van der Merwe mode (2 dimensional growth mode)

Volmer-Weber mode (Island growth mode)

Thin Film Growth Process



Stranski-Krastanov mode

Epitaxial growth and elasticity Growing deformable layers over a deformable substrate

The harmonic crystal





 $E(\{x_i\}) = \frac{k}{2} \sum_{i} (x_{i+1} - x_i - a)^2 \sim \frac{1}{2} \left[\left(\frac{\partial u}{\partial x}\right)^2 \right]$ $\epsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$ $x_{i+1} - x_i \to u \ ai \to x_i$



The elastic crystal

 $\mathscr{F}_V = \int_V \varphi\left(\{\epsilon(\mathbf{r})\}\right) \mathrm{d}^3 r$



 $P = -\frac{1}{3}\sum \sigma_{ii}$

 $\varphi\left(\{\epsilon\}\right) = \frac{\lambda}{2} \left(\sum_{\alpha} \epsilon_{\alpha\alpha}\right)^2 + \mu \sum_{\alpha\gamma} \epsilon_{\alpha\gamma}^2$

Stress $\sigma_{ij} = \sum_{i} C_{ijkl} \epsilon_{kl}, \qquad \epsilon_{ij} = \sum_{i} S_{ijkl} \sigma_{kl}$

Strain

 $\epsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_i} + \frac{\partial u_j}{\partial x_i} \right)$

The elastic crystal



 $\epsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_i} + \frac{\partial u_j}{\partial x_i} \right)$





 x_1

Solids are not Liquids

- Solids are not Liquids
- What is surface tension?

- Solids are not Liquids
- What is surface tension?
- Why we should never speak of surface tension for solids

Applying a tensile stress on a liquid A





 $\mathcal{F}_s = \gamma_0 A$

$\delta \mathcal{F}_s = \delta(\gamma_0 A) = \gamma_0 \delta A$

Applying a tensile stress on a solid



 $\mathcal{F}_{S} = \gamma A$ $\delta \mathcal{F}_{s} = \delta(\gamma A)$ $= \frac{\partial \gamma}{\partial \epsilon_{xx}} \delta \epsilon_{xx} A_0 + \gamma \delta A$ $= \left| \frac{\partial \gamma}{\partial \epsilon_{xx}} + \gamma \right| A_0 \delta \epsilon_{xx}$

where $\delta A = A_0 \delta \epsilon_{xx}$

The Shuttleworth Equation: surface stress



$\delta \mathcal{F}_{s} = s_{xx} \, \delta A$ Work of the surface stress



Atomistic picture of the surface stress

$$\frac{3}{2}f_1 - \frac{\sqrt{3}}{2}f_2 = f_1$$



In a liquid, the surface energy does not depend on the strain

 $S_{xx} = \gamma_0$ $\delta \mathcal{F}_{s} = s_{xx} \,\delta A = \gamma_{0} \delta A$

In a liquid, the surface free energy can be called "surface tension"

Elastic instabilities: Grinfeld



Misfit-induced strain: $\epsilon_{xx} = \epsilon_{yy}$

= $-\frac{E}{1}$

 p_0



$$y = \epsilon_0 = \delta a/a$$

$$\frac{E}{-\zeta}\epsilon_0 = \frac{E}{1-\zeta}\frac{\delta a}{a}$$

Contributions to the free energy of the undulating film $\delta Z(x) = h \cos(qx)$

1) $d\mathcal{F}_{cap}/d\mathcal{A} = \sigma h^2 q^2/2$

2) $d\mathcal{F}_{relax}/d\mathscr{A} \approx -hp_0\epsilon$

3) $d\mathcal{F}_{\rm el}/d\mathcal{A} \approx C\epsilon^2/(2q)$

$\delta Z(x, y) = Z(x, y) - \bar{Z}$

Capillarity (surface free energy) curvature ~ $\partial^2 z / \partial x^2 \rightarrow z_a q^2 \sim h q^2$ $dV = hd\mathcal{A}$

Relaxation, proportional to elastic energy and to volume change

 $dV = hd\mathcal{A}$

Elastic energy cost proportional to penetration length of the strain $\lambda \approx 1/q$



Minimizing 2 and 3 with respect to ϵ yields:

$$\epsilon \approx hqp_0/C$$

The total free energy in the undulating film is the sum of 1), 2) and 3):

$$d\mathcal{F}/d\mathcal{A} = \sigma h^2 q^2 / 2 - h^2 p_0^2 q / (2 - h^2 p_0^2) q /$$





Kinetics 2D to 3D: misfit-induced, layer-dependent interlayer transport barriers ("effective Schwoebel")



 $E_n = 0, n < 3$ $E_n > 0, n \ge 3$



EUROPHYSICS LETTERS

Europhys. Lett., 65 (3), pp. 372–378 (2004) DOI: 10.1209/epl/i2003-10090-6

Temperature dependence of the 2D-3D transition in the growth of PTCDA on Ag(111): A real-time X-ray and kinetic Monte Carlo study

B. KRAUSE¹(*), F. SCHREIBER^{1,2}(**), H. DOSCH^{1,2},

