Epitaxy vs Crystal Growth
Crystals In and Out of Equilibrium

(Héraud, Métois, 1987)
1. Introduction

Thermodynamics, kinetics and transport are the mainstays of the science of crystal growth belonging to the basic knowledge of each specialist or student dealing with practice of bulk crystallization or epitaxy [1] (see Fig. 1.1).

Fig. 1.1: The three mainstays of fundamentals of crystal growth

The classic thermodynamics [1,2] is concerned with macroscopic equilibrium state between starting (fluid) phase, crystalline phase and separating interface of quasi-closed systems. It helps to find out the most effective phase transition, i.e. growth method and the value of the driving force of crystallization. Using thermodynamic principles one can estimate the nucleation and existence conditions of a given crystalline phase and measures of in-situ control of the crystal composition during growth. Considering the quasi-open state of each crystallization system, i.e. continuous flows of heat and matter, one uses the linear non-equilibrium thermodynamics [1].

The elementary processes of attachment of individual building units (atoms, molecules) to and from the crystal surface (interface, crystallization front) is the target of kinetics [3]. The central question to be solved using kinetic approach is the entering mechanism of the fluid atoms at the crystal interface, i.e. growth mode, and growth velocity from atomistic point of view. This requires, at first, the determination of the atomistic morphology of the growing faces.

Transport
- heat transport
  - conduction
  - radiation
- mass transport
  - diffusion
  - convection
  - boundary layers
  - distribution effects
  - segregation
- external forces

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

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Before the atoms (molecules) pass over from a position in the fluid medium to their place in the crystal face they must be transported in the fluid towards the interface by diffusion or convection. Further, the heat, translated by the species on their way to the crystal by conductive and convective transport, needs dissipate in the solid phase by thermal conductivity and radiation in order to maintain a stable propagating interface. Additionally, the heat of fusion, realizing at the propagating interface, must be transported away through the growing crystal. These transport processes can be either fast or slow compared to the attachment kinetics. Then the rate with which a crystal grows is limited by interfacial kinetics or by the macroscopic transport, respectively.

Fig. 1.2 demonstrates the diversity of acting processes at crystallization front propagating with normal growth velocity $v$. Thermodynamically, $v$ depends on the driving force of crystallization $\Delta \mu$ which is the potential difference between the phases, at melt growth proportional to the difference between the equilibrium temperature $T_{eq}$ and undercooled value $T$ at the interface.

The microscopic processes are described by kinetics. It shows the various interface nature from atomistic view and its growth mode as function of it atomically smoothness and roughness as well as of the presence of defects and foreign atoms. Finally, each crystallization requires temperature, concentration or pressure gradients. This is due to the necessarily control of the transport of heat and mass towards and away from the interface. At the same time, undesired foreign atoms (impurities) should be repulsed at the growing interface as effectively as possible.

As can be seen crystal growth processes prove to be very varied and versatile that requires a comprehensive study. Here, however, we will show the compressed basic principles of thermodynamics, kinetics and transport phenomena only. Possible reviews on transport processes and thermodynamics for crystal growth are given by the author in [4] and [8], respectively.
Driving force of crystal growth: supersaturation

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

\[ \mu(T, P) = \left( \frac{\partial G}{\partial N} \right)_{T,N} \]

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

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<table>
<thead>
<tr>
<th>Epitaxy method</th>
<th>LPE</th>
<th>VPE</th>
<th>MOCVD</th>
<th>MBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative supersaturation ( S )</td>
<td>( \sim 0.02 - 0.1 )</td>
<td>( \sim 0.5 - 2 )</td>
<td>( \sim 50 )</td>
<td>( \sim 10 - 100 )</td>
</tr>
<tr>
<td>Driving force ( \Delta \mu ) J/mol (( T = 1000 \text{ K} ))</td>
<td>( \sim 165 - 800 )</td>
<td>( \sim (3-9) \times 10^3 )</td>
<td>( \sim 3.3 \times 10^4 )</td>
<td>( \sim (2-4) \times 10^4 )</td>
</tr>
</tbody>
</table>
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

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After the structure and the incorporation processes are clarified, the kinetic-driven velocity of propagation of a given crystal plane can be determined. Generally speaking, the rate (or velocity) of crystallization can be expressed as the product of the four terms characteristic of distance, frequency, atomical interface structure, and thermodynamic driving force as

\[ R = v = a Q^+ f (1 - \exp' \mu/kT) \] (3.1)

with:
- \(a\) - atomic or molecular diameter of the "growth units",
- \(Q^+\) - attachment frequency of an atom/molecule to a favourable incorporation site (kink),
- \(f\) - the roughness factor of the growing interface (fraction of interface sites which are favourable incorporation sites), and
- \(\mu/kT\) - relative driving force of crystallization (chemical potential difference between the fluid and solid phases, introduced in ch. 2.8.1 for melt, solution and vapor growth, respectively).

### 3.2 Atomistic models of crystal faces

#### 3.2.1 Overview on the concepts used

Fig. 3.2 gives an overview on classical lattice models which have been mostly used to describe the interface kinetics [44]. Newer numeric simulations, such as ab-initio, molecular dynamic (MD), Monte Carlo (MC) or phase field (PF) methods are added [45]. At the present, considerable progress has been done by using of numeric modeling due to the availability of powerful computers and softwares. Many impressive results are given in the current literature. Note, in detail the lattice models are more versatile than simplified sketched in Fig. 3.2. Diverse theoretical approaches more and more specifying the given growth situation are shown in the literature (see e.g. ref. [46]). One of the most important questions is how to describe the energetical interaction between the growth units and atoms/molecules within the growing crystal surface as precisely as possible. Further, are there adsorbates (e.g. surfactants) and structural reconstruction as shown in Fig. 3.10? Which activation energy must be overcome at transition from fluid to solid phase? Are there associated states within the mother phase and how they dissociate in the ad-layer? Should be the interfaces treated as a diffuse instead of abrupt one?

In our compressed approach, especially designated for beginners and further study, the basic situations of kinetics of crystal growth can be summarized only.
Crystals In and Out of Equilibrium
Crystal facets: high symmetry
Crystal facets: high symmetry

Pb particle on a Cu(1 1 1) substrate equilibrated at 440 K.

Substrate for epitaxy? Rough? Flat (smooth)?
Crystal facets: vicinals

Si (111) vicinal, 400 x 400 nm²

Surfaces: smooth and rough
The Roughening Transition

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

[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 = $2Lk_B \ln 2$
The Roughening Transition

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

$$\gamma = e - T_s$$

$$\gamma = W_1 - k_B T \ln 2$$

$$\gamma = 0 \rightarrow T_R = \frac{W_1}{k_B \ln 2}$$
Surfaces: smooth and rough

\[ \gamma = 0 \rightarrow T_R = \frac{W_1}{k_B \ln 2} \]

\[ T < T_R \]
\[ \langle [z(\vec{r} + \vec{R}) - z(\vec{r})]^2 \rangle \sim \text{const.} \]

\[ T > T_R \]
\[ \langle [z(\vec{r} + \vec{R}) - z(\vec{r})]^2 \rangle \sim (4\pi k_B T/\tilde{\sigma}) \ln R \]
Average distance between kinks $\ell$

Interaction energy $\epsilon$

Kink density

$$n_k = \frac{1}{\ell} \approx \exp(-W_1/k_BT)$$

$$k_BT_R \ n_k(T_R) \approx \epsilon \rightarrow T_R \approx \frac{\epsilon}{k_B} \exp(W_1/k_BT_R)$$
Facets:
smooth and rough
Facets: smooth and rough
Titania single crystals with a curved surface

Owing to its scientific and technological importance, crystallization as a ubiquitous phenomenon has been widely studied over centuries. Well-developed single crystals are generally enclosed by regular flat facets spontaneously to form polyhedral morphologies because of the well-known self-confinement principle for crystal growth. However, in nature, complex single crystalline calcitic skeleton of biological organisms generally has a curved external surface formed by specific interactions between organic moieties and biocompatible minerals. Here we show a new class of crystal surface of TiO$_2$, which is enclosed by quasi-continuous high-index microfacets and thus has a unique truncated biconic morphology. Such single crystals may open a new direction for crystal growth study since, in principle, crystal growth rates of all facets between two normal {101} and {011} crystal surfaces are almost identical. In other words, the facet with continuous Miller index can exist because of the continuous curvature on the crystal surface.

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Equilibrium crystal shape: the surface free energy

(Héraud, Métois, 1987)
Equilibrium crystal shape: the surface free energy...

• The total energy of a crystalline object can be written as

\[ E = AV + BV^{2/3} + CV^{1/3} + D + \ldots \]

Bulk \hspace{1cm} Surface \hspace{1cm} Edge \hspace{1cm} Corner
Equilibrium crystal shape: the surface free energy...

- The total energy of a crystalline object can be written as

\[ E = AV + BV^{2/3} + CV^{1/3} + D + \ldots \]

Bulk        Surface        Edge        Corner
... and the Wulff construction

• The equilibrium shape for reasonable sizes minimizes $E$ at a fixed volume
• Find the shape that optimizes the surface energy

$E = AV + BV^{2/3} + CV^{1/3} + D + \ldots$

Bulk  Surface  Edge  Corner
Surface free energy density
\[ \sigma = \sigma(n_f) \]

Faceted crystal
\[ h_f = R \cdot n_f \]
\[ A_f \quad \text{area of facet } f \]

G. Z. Wulff, Kristallogr. Mineral 34, 4490 (1901); M. Z. Von Laue, Kristallogr. 105, 124 (1943); A. Z. Dinghas, A. Z. Kristallogr. 105, 304 (1944)
Wulff Construction

Surface free energy density
\[ \sigma = \sigma(n_f) \]

Surface free energy
\[ \mathcal{F}_{\text{surf}} = \int_A \sigma(n) dS \]
\[ \mathcal{F}_{\text{surf}} = \sum_f \sigma(n_f)A_f \]

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Wulff Construction

Crystal volume

\[ V = \frac{1}{3} \sum_{f} h_f A_f \]

Minimize the surface free energy at constant volume

\[ \delta[\mathcal{F}_{\text{surf}} - \lambda V] = \sum_{f} [\sigma(n) - \lambda h_f/3] \delta A_f = 0 \]

\[ h_f = \frac{3}{\lambda} \sigma_f \]

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Wulff Construction

Rewriting the minimization as

\[ \delta [ \mathcal{F}_{\text{surf}} - \lambda v N ] = 0 \]
\[ \lambda v \delta N = \mu \delta N \]

yields

\[ \lambda = \mu / v \]
\[ \mu = 3v \frac{\sigma_f}{h_f} \]
Wulff Construction

Wulff’s construction: the equilibrium shape of a crystal is found by taking, for each direction \( \mathbf{n} \), the point \( H \) defined by \( OH = \sigma(\mathbf{n}) \), lying on the polar plot \( \Sigma \) of the surface free energy, and the plane \( \Pi \) orthogonal to \( OH \) and cutting \( \Sigma \) in \( H \). The crystal surface \( S \) is then the inner envelope of the planes such as \( \Pi \). The envelope of \( \Pi \) is called the pedal of the surface \( \Sigma \) spanned by \( H \).

French: podaire
Polar plot of the surface free energy

Wulff Construction
Copper vs Gold

Curtesy Paul Wynblatt
Chemisorption Dependent

Curtesy Paul Wynblatt
Chemisorption Dependent

\[
\Delta E = 2J_1 + J_2 + 2W_{(10)} - W_{(11)}
\]
Chemisorption Dependent

If \(2J_1 + J_2 > 0\) then the (11) facet does not belong to the equilibrium shape.
Chemisorption Dependent

But if $2W_{(10)} < W_{(11)}$ and $2J_1 + J_2 < |2W_{(10)} - W_{(11)}|$ then the (11) facet appears in the “equilibrium” shape
Owing to its scientific and technological importance, crystallization as a ubiquitous phenomenon has been widely studied over centuries. Well-developed single crystals are generally enclosed by regular flat facets spontaneously to form polyhedral morphologies because of the well-known self-confinement principle for crystal growth. However, in nature, complex single crystalline calcitic skeleton of biological organisms generally has a curved external surface formed by specific interactions between organic moieties and biocompatible minerals. Here we show a new class of crystal surface of TiO$_2$, which is enclosed by quasi-continuous high-index microfacets and thus has a unique truncated biconic morphology. Such single crystals may open a new direction for crystal growth study since, in principle, crystal growth rates of all facets between two normal {101} and {011} crystal surfaces are almost identical. In other words, the facet with continuous Miller index can exist because of the continuous curvature on the crystal surface.

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Growing crystals
Kinematic Wulff Construction

Facet growth rate
\[ \nu = \nu(n_f) \]

Faceted crystal
\[ h_f = R \cdot n_f \]

G. Z. Wulff, Kristallogr. Mineral 34, 4490 (1901); M. Z. Von Laue, Kristallogr. 105, 124 (1943); A. Z. Dinghas, A. Z. Kristallogr. 105, 304 (1944)
Growing crystals
Kinematic Wulff Construction

**Kinematic Wulff’s construction** – A self-similar crystal growth shape is obtained by considering for each vector \( \mathbf{n} \) the point \( H \) defined by \( \mathbf{OH} = \mathbf{n}v(\mathbf{n}) \) and the plane (\( \Pi \)) perpendicular to \( \mathbf{OH} \). The crystal surface is the interior envelope of (\( \Pi \)).

\[
N = M + \mathbf{v}(\mathbf{n})dt
\]

\[
MN' = \lambda\mathbf{OM}dt
\]

\[
\frac{\mathbf{OH}}{\mathbf{MN}} = \frac{\mathbf{OM}}{\mathbf{MN}'}
\]

\[
\mathbf{OH} = \mathbf{OM} \frac{\mathbf{MN}}{\mathbf{MN}'} = \mathbf{OM} \frac{\mathbf{v}(\mathbf{n})dt}{\lambda\mathbf{OM}dt} = \frac{\mathbf{v}(\mathbf{n})}{\lambda}
\]
Growing crystals

(a) $T > T_R$

(b) $T \approx T_R$

(c) $T < T_R$

Growth rate of rough orientations > than flat ones
Rough regions “grow out of existence” leaving only flat facets
Growth rate of rough orientations > than that of flat ones

Rough regions “grow out of existence” leaving only flat facets
Surface kinetics at long length scales

- At scales $\ell \gg a$, where $a$ is the lattice spacing, a crystal surface can be treated as a continuous object $z = z(x, y)$.

- Assuming as reference state a flat surface, $z(x, y) = z_0$, an undulating surface is characterized by an excess chemical potential, proportional to the local curvature $\nabla^2 z$: $\delta \mu = -\tilde{\sigma} \left( \frac{\partial^2 z}{\partial x^2} + \frac{\partial^2 z}{\partial y^2} \right)$, where $\delta \mu > 0$ for $\delta \mu < 0$.
Surface kinetics at long length scales

- Linear thermodynamics yields two types of dynamics, corresponding to two different transport modes:
  - Non conserved: \( \dot{z} = -K\delta\mu = K\tilde{\sigma}\nabla^2 z \)
  - Conserved: \( \dot{z} = -\text{div} \vec{J}; \quad \vec{J} = -D_s \vec{\nabla}\delta\mu \), so that \( \dot{z} = -\tilde{\sigma}D_s \nabla^4 z \)

- These equations can describe the growth, dissolution or equilibration kinetics of a rough surface at long length scales
Surface kinetics at long length scales

- In particular, if $\tau(L)$ is the characteristic time scale of the surface evolution at length scale $L$:
  
  - Non conserved: $\dot{z} = K\tilde{\sigma}\nabla^2 z$ implies $\tau(L) \sim L^2$
  
  - Conserved: $\dot{z} = -\tilde{\sigma}D_s\nabla^4 z$ implies $\tau(L) \sim L^4$

- Ex. Equilibrium fluctuations of a surface step
Changing Shapes in the Nanoworld

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

W. Joshua Kennedy,†,# Keith A. Slinker,†,# Brent L. Volk,‡ Hilmar Koerner,‡ Trenton J. Godar,‡,# Gregory J. Ehlert,‡,# and Jeffery W. Baur*‡,#
Changing Shapes in the Nanoworld

AKA Thermal reshaping of plasmonic nanorods
nanorods
$N = 675, \ T = 700\text{K}$ time evolution
$N = 1728, \ T = 300K$ time evolution
Equilibration time: time needed to attain an aspect ratio of 1.2
creases for larger crystallites [15], which implies [Eq. (1)]

to the size dependence of nucleating germ is given by [13]

energy is defined as the number of atomic bonds times the bond transitions from one faceted configuration to the next. The total motion of the time logarithm for a 1728-atom cluster at two tem-

FIG. 3. Evolution of the total energy of crystallites as a func-

We use a classical umbrella sampling technique [14]

Total Energy

Log (time)

-790
-840
-890
-940
-7
-6
-5

700 K

D

UMBER

-85, N

112

DE

RICE|SCI

SMALLEY-CURL INSTITUTE
High T

Roughening transition

Low T
Mullins (surface diffusion) 3D

\[ t_{eq} \sim L^4 \sim N^{4/3} \]
Classical nucleation theory

\[ \Delta G = 2\pi \gamma bR - \pi \Delta \mu bR^2 \]

\[ \Delta \mu = \gamma / R_c \]
2D platelets
\[ p_i = \nu_0 \exp \left( \frac{-iE}{k_B T} \right) \]

\[ E = 0.1 \text{ eV} \]

\[ E_{\text{act}} = 0.2 \text{ eV} \]

\[ E_{\text{act}} = 0.3 \text{ eV} \]

(a)  
(b)
Kinetic Monte Carlo

\[ N = 6250, \quad T = 500\text{K} \]
Kinetic Monte Carlo

\[ N = 6250, \ T = 500K \]

\[ N = 6250, \ T = 83K \]
Equilibrium shapes
High temperatures

\[ t_{eq} \approx \frac{1}{\Gamma \nu_0} N^2 \exp \left[ \frac{3E}{(k_B T)} \right] \]

Low temperatures

\[ t_{eq} \approx \frac{D_0}{\nu_0^2} N \exp \left[ \frac{4E}{(k_B T)} \right] \]
\[ \log_{10}(t_{\text{relax}}) \]

\[ \log_{10}(N) \]

- 83 K (1.32)
- 100 K (1.38)
- 125 K (1.52)
- 250 K (1.94)
- 500 K (2.00)
Tunable Colloidal Clusters in Time-Varying Field

Clusters growth $N \sim t^{0.6}$

Magnitude of time-varying field controls the phase behavior

- **Liquid-Like**
  - $B = 8.5$ Gauss
  - $U_{\text{min}} = -5.8 \, k_B T$

- **Disordered Boundary**
  - $B = 9.0$ Gauss
  - $U_{\text{min}} = -6.6 \, k_B T$

- **Crystallite**
  - $B = 11$ Gauss
  - $U_{\text{min}} = -9.8 \, k_B T$
Coalescence of clusters at different states - liquid (5.2 \k_B T)

Speed x10

\sim 11 \text{ minutes}
Coalescence of clusters at different states - intermediate state (6.6 k_BT)
Coalescence of clusters at different states - crystallites (9.8 k_BT)

Formation of grain boundary migrating towards the interface and out of the cluster
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Du & SLB, Soft Matter, 13 (8), 2017, pp 1548
Hilou & SLB, Phys. Review Materials, 2(2), 2018
Du & SLB, Soft Matter, 14(18), 2018, pp 3463
When crystals grow unstable

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

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Cu (0,2,24)  Cu (1,1,17)

Cu (1,1,17)
$J = -D \nabla c$

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

Net current “up”: leads to curved steps and/or 3D islands (mounds)
Inverse Schwoebel effect

$J_{\text{down}} > J_{\text{up}}$

Net current “down”

Leads to step bunching

Fig. 3. Surface morphologies after growth of 1000 ML at two deposition rates, on substrates with different slopes, for an ES barrier $E/p_49 = 1$ eV. One can see mounding on a #sat substrate ($m_J = 0$, $p_32 = 10$ ML/s) (a), initial step bunching followed by mounding for $m_J = 0.2$ and $p_32 = 1$ ML/s (b), fully developed step bunching with the beginning of a meandering (BZ) instability for $m_J = 0.4$ and $p_32 = 1$ ML/s (c), and BZ instability without bunching for $m_J = 0.8$ and $p_32 = 10$ ML/s (d).

The analytical results estimations are assembled in Fig. 2 together with the results of our kMC simulations. Indeed, triangles mark parameter values where simulations show mound formation, circles denote the formation of step bunches, and diamonds indicate the step meandering (BZ) instability.

Figs. 3a–d show four examples of surface morphologies after deposition of 1000 layers when the ES barrier for precursors is $E/p_49 = 1$ eV, at the points shown as closed symbols in Fig. 2. When the surface slope ranges from $m_J = 0$ (Fig. 3a) to $m_J = 0.8$ (Fig. 3d) (i.e. from #at to #l = 5), the surface morphology changes from a mound pattern on the #at surface (Fig. 3a, $p_32 = 10$ ML/s) to the step meandering (BZ) instability without bunching for $m_J = 0.8$ and $p_32 = 10$ ML/s (d).
Real surfaces out of equilibrium

Cu vicinals — unstable growth: curved step + 3D pyramids
ing energy is $E_{ai} = 0.2$ eV. With these values, the simulations produce morphologies indistinguishable from the experimental picture. On looking carefully, one notes that in the experiments the pyramids tend to align along the step direction, a feature missing in the simulations. Elastic interactions, or a slightly varying average step density, both obviously absent in the simulations, may explain the discrepancy.

Figure 4 exhibits the different computed morphologies for various impurity concentrations, ranging between 0 and 0.05, for both close-packed and open steps.

In order to quantify the simulated morphologies, we computed the surface roughness as a function of the concentration of deposited impurities. This is presented on Fig. 5. The roughness increases linearly for small concentrations, twice as fast for close-packed steps as for open ones, then it saturates exponentially for larger impurity densities.

As we have seen, impurities seem to hold the answer to the riddle of the pyramids. Figure 6 shows that they may also provide the solution to the riddle of the wavelength. Indeed, in the top panel the morphology of the unstable surface at different deposition rates, without impurities, may be seen. In the leftmost bottom panel, the wavelength of the mean-downing structure is plotted as a function of $F$. A power law of the form $m = F^{-1/2}$ is apparent, with consistent with the BZ value 1/2.
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The rightmost panel shows the $m$ vs $F$ plot for varying concentrations of impurities. For strongly interacting impurities, $E_{ai} = 0.2 \text{ eV}$, the power decreases steadily with the concentration.

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FIG. 2. Top panel Experimental STM pictures of the $0 2 24$ and of the $1 1 17$ Cu surfaces, undergoing unstable step flow. The rightmost picture shows the $1 1 17$ surface at a larger scale. Small, square-based pyramids appear to cover the unstable pattern.

Bottom panel Simulated $0 0 24$ and $1 1 17$ surfaces. Parameters are chosen in such a way that the period of the instability coincides with the experimental one in units of the average terrace width. The rightmost panel is a larger-scale view, showing that pyramids are absent in the simulations of the pure system.

FIG. 3. Experimental left and simulated right micrograph of the $1 1 17$ surface. Impurities are added during the simulated deposit. Small, square-based pyramids now appear both in the experiment and the model see text for simulation parameters.

FIG. 4. Simulated unstable vicinal surfaces in the presence of varying impurity concentrations. Top panel is for compact steps; bottom panel for open steps.

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Impurities!
Epitaxy on a crystal

Figure 1. Top panel: The initial shape of the core nanoparticle that spans 125 FCC lattice spacings along the shown coordinate axes (see text for details). The white segments were added...
Low T, low and high growth rates

Figure 2. Top panel: Particle shape obtained for growth with parameter values $\alpha = 2$, $n = 4 \pm 10$, $L = 5 \pm 10$. The core was initially the same as in Fig. 1. Bottom panel: Shape obtained for the same value of $\alpha = 2$, but with $n = 2 \pm 10$, $L = 10$. In both cases approximately $4.4 \times 10^3$ atoms were deposited.

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Low T, high T and intermixing

Figure 2. Top panel: Particle shape obtained for growth with parameter values $\alpha = 2$, $\mu = 4\times10^{-1}$, $\tau = 5\times10^2$. The core was initially the same as in Fig. 1. Bottom panel: Shape obtained for the same value of $\alpha = 2$, but with $\mu = 2\times10^1$, $\tau = 10^0$. In both cases approximately $4.4\times10^1$ atoms were deposited.

Figure 3. Top panel: Onset of clustering in growth at low temperatures, for $\alpha = 2.5$, $\mu = 2\times10^1$, $\tau = 10^0$. Here the core remains practically intact. The atoms originally in the core are color coded in green, whereas the added atoms are color coded in burgundy. The shell is primarily formed by the added atoms and its growth morphology is initially governed by the emergence of ziggurat-type clusters. For the selected process time the shell contains approximately 6% of atoms when compared to the number of atoms in the core. Bottom panel: Absence of any significant clustering at high temperatures. Here $\alpha = 1$, with the same $\mu = 2\times10^1$, but the simulation time was taken as $\tau = 5\times10^1$. The growing surface remains rather smooth even for the large time selected, and it includes a significant admixture of atoms from the original core. For this process time the shell here contains about 25% atoms when compared to the initial count of atoms in the core.
Very low T, high and low growth rate: Instability nucleated by pyramid growth growth

Figure 4. Top panel: Development of clustering for the same particle as shown in the top panel of Fig. 3, but for large time. Here $\alpha = 2.5$, $\varepsilon = 2 \pm 10$, and $\tau = 8 \pm 10$. Bottom panel: Smaller-scale clustering for the case of $\alpha = 2.5$, $\varepsilon = 6 \pm 10$, and $\tau = 3 \pm 10$.

Figure 5. Illustration of the morphology of pyramid-shaped instabilities initiating the irregular cluster-mode growth in situations such as those presented in Fig. 4, and also in the top panel in Fig. 3 (for larger times than shown there). Top panel: Pyramidal clusters developing on growing (100) type FCC faces, with all the side faces of the type (111). Bottom panel: Pyramidal clusters developing on growing (111) type FCC faces, compared to a schematic depicting a pyramidal shape made of fragments of various (111) and (100) FCC faces.

Figure 3. Top panel: Onset of clustering in growth at low temperatures, for $\alpha = 2.5$, $\varepsilon = 2 \pm 10$, and $\tau = 10$. Here the core remains practically intact. The atoms originally in the core are color coded in green, whereas the added atoms are color coded in burgundy. The shell is primarily formed by the added atoms and its growth morphology is initially governed by the emergence of ziggurat-type clusters. For the selected process time the shell contains approximately 6% of atoms when compared to the number of atoms in the core. Bottom panel: Absence of any significant clustering at high temperatures. Here $\alpha = 1$, with the same $\varepsilon = 2 \pm 10$, but the simulation time was taken as $\tau = 5 \pm 10$. The growing surface remains rather smooth even for the large time selected, and it includes a significant admixture of atoms from the original core. For this process time the shell here contains about 25% atoms when compared to the initial count of atoms in the core.
Modeling of Growth Morphology of Core-Shell Nanoparticles
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Abstract
We model shell formation of core-shell noble metal nanoparticles. A recently developed kinetic Monte Carlo approach is utilized to reproduce growth morphologies realized in recent experiments on core-shell nanoparticle synthesis, which reported smooth epitaxially grown shells. Specifically, we identify growth regimes that yield such smooth shells, but also those that lead to the formation of shells made of small clusters. The developed modeling approach allows us to qualitatively study the effects of temperature and supply of shell-metal atoms on the resulting shell morphology, when grown on a pre-synthesized nanocrystal core.

Keywords: core-shell; crystal; diffusion; epitaxy; growth; morphology; nanoparticle

Shell Growth and Morphology in Synthesis of Core-Shell Nanocrystals

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Chemistry: the role of precursors

Synthesis of Al nanocrystals

Figure 7. (A) TEM images of reactions after three hours with different ratios of AlH$_3$ to Tebbe's reagent. 10:1 Inset: possibly an Al nanocube seed. (B) SEM of Al nanorods from an Al nanocube reaction with a 200:1 ratio of AlH$_3$ to Tebbe's reagent. Inset: 45° tilted SEM image of an individual Al nanorod with a pentagonal cross-section. (C) 45° tilted SEM of trigonal right bipyramidal Al nanocrystals produced alongside Al nanocubes. (D) Statistics of Al nanocrystal shapes from three separate Al nanocube reactions (472 particles measured).

The ratio of AlH$_3$ to Tebbe's reagent is critical to controlling the Al nanocube morphology as depicted in Figure 7. When there is too much Tebbe's reagent in the reaction, irregular cubic Al nanocrystals with lumpy surfaces are produced (Fig 7A, 10:1 ratio of AlH$_3$:Tebbe). As the ratio of AlH$_3$ to Tebbe's reagent increases, Al nanocubes with concave high index facets are produced alongside the cubic Al nanoclusters with bumpy surfaces (Fig 7A, 50:1 ratio). Between a 100:1 and 200:1 ratio of AlH$_3$ to Tebbe's reagent, regular Al nanocubes terminated by {100} facets are the major product of the reaction (Figure 7A and Figure 7B). Further increasing the ratio of AlH$_3$ to Tebbe's reagent results in the truncation of the Al nanocubes, exposing {111} facets at the corners of the cubes (Fig 7A, 500:1 ratio). The formation of truncated Al nanocubes with low amounts of Tebbe's reagent is attributed to the reduced concentration of the molecular species responsible for producing {100} faceted Al nanocubes.
Chemistry: the effect of precursors
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The effect of the ratio of TIBA to Tebbe's reagent on the final Al nanocrystal morphology is illustrated in Figure 5. Top row: Representative TEM images of reactions with 100:1, 140:1, 200:1, and 300:1 ratios of TIBA to Tebbe's reagent produce isotropic Al nanocrystals, branched Al nanowires, and Al nanowire bundles, respectively. Bottom row: High magnification TEM images display the diversity of the morphology of these Al nanocrystals. Using fresh Tebbe's reagent, the molar ratio of TIBA to Tebbe's reagent was found to dramatically influence the morphology of the Al nanocrystals produced by this reaction (Figure 5). With a 100:1 molar ratio of TIBA to Tebbe, isotropic Al nanocrystals with an average size of 20-30 nm were produced (Figure 5). As the molar ratio of TIBA to Tebbe increased to 140:1, long multiply branched Al nanowires with a typical diameter of 35 ± 3 nm were observed.
Chemistry: the effect of precursors
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Since the supply of Al atoms is effectively controlled by the amount of Tebbe's reagent and the reaction temperature, these parameters can be optimized for the growth of highly anisotropic Al nanocrystals. It is worth noting that precursor concentration would also influence this rate but was not explored owing to the sensitivity of reactions more dilute than ~25 mM of AlH₃ on the Schlenk line.

Recent kinetic Monte Carlo simulations of the diffusive growth of nanoparticles based on the relative flux of incoming atoms (which was controlled by concentration and temperature) and surface migration of adatoms have shown that increasing the incoming flux leads to the growth of highly anisotropic nanoparticles such as concave cubes. By increasing the incoming atom flux beyond a certain threshold, the growth of nanoparticles with bumpy surfaces was observed using kinetic Monte Carlo simulations of the diffusive nanoparticles growth. This family of nanoparticle morphologies are considered kinetic products because during crystal growth, an atom is deposited at the reactive sites (undercoordinated atoms at corners, edges and steps) before the previous adatom has time to diffuse on the surface to a thermodynamically favored position in the crystal lattice. As the nanocrystal grows, these atoms become kinetically trapped in thermodynamically unfavorable positions that manifest in Al nanocrystals with high-index surfaces and anisotropic shapes such as concave cubes.
Based on these observations, thermal decomposition of TIBA in an suitable solvent may be reliable method to produce Al nanocrystals. To investigate this hypothesis TIBA was pyrolyzed in hexadecane, dioctylether, trioctylamine, and trioctylphosphine. Scanning electron microscopy (SEM) images of the resulting particles are shown in Figure 2.

Without a coordinating atom in the solvent as in the case with hexadecane, coral-like Al microstructures were produced. Introducing Lewis bases with O, N, or P coordinating atoms resulted in the production of large Al nanocrystals. In the cases with trioctylamine and dioctylether a small fraction of the nanocrystal geometries included single crystalline Al nanorods. To the best of our knowledge, this work demonstrates the first heat-up synthesis of colloidal Al nanocrystals and Al nanorods.

Figure 4. Colorized SEM images of the diversity of Al nanocrystals synthesized by high-temperature pyrolysis of TIBA or DIBAH in trioctylamine. For scale, the edge of each image is ~3 microns. Interestingly, {111} facets appear smoother than {100} facets.