Elastic instabilities in silicon-germanium films

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Introduction

Pattern forming instabilities are ubiquitous in non-equilibrium dissipative system: three classical examples

Turing Structures

Chemical Turing patterns

Alan Turing
Hydrodynamics convection

Lord Rayleigh

Bénard

Assenheimer and Steinberg, PRL, 1993
Mullins-Sekerka instability

Dendritic growth, directional solidification, solid-liquid transition, Pocheau

W. Mullins
**Common denominator:**

- Finite wavelength instabilities, such that there exists a range of unstable wave numbers

\[ \exp(s t) \exp(i k x) \]
Motivation: Ge$_x$Si$_{1-x}$/Si (001) Coherent Islands: 
instability regime

Ge$_{0.2}$Si$_{0.8}$/Si (001) 
750$^\circ$C

Wetting Layer

{105} pyramids

domes

Floro et al, PRL 79, 3946 (1997)

Spencer, Voorhees, Davis and Mac Fadden, PRL, 1991

Spencer, Voorhees, Davis, PRB, 1993

Spencer, Voorhees, Tersoff, 2001

Ge/Si (001), 600$^\circ$C

Nucleation regime


Tromp

Lagally,
PRL 2000

Stangl et al,
RMP, 2004
Questions

• What is the coarsening dynamics?

• What is the influence of the anisotropy of surface energy?

• What is the influence of the film height?
Outline

• Asaro-Tiller-Grinfeld Instability
• The Mullins model for hetero-epitaxy
• Isotropic Case (Non interrupted Coarsening)
  • Anisotropic Case (Interrupted Coarsening)
• MBE experiments during annealing
• Conclusion and Perspectives
Grinfeld-instability of liquid-solid helium

Bodensohn 1986, Balibar 1991

Balibar 2005 RMP

Kassner, Misbah et al, 2001, Phys Rev E,

Phase field methods
The Asaro-Tiller-Grindfeld Instability: morphological instability of a stressed crystal

Germanium atoms are larger than silicon atoms

No cracks or dislocations for small misfit

\[ \text{Film} = \text{Si}_{1-x} \text{Ge}_x \]

\[ E_f, \nu_f \]

\[ E_s, \nu_s \]

Sillicium-germanium

Silicon

Stress due to the misfit

Stranski et Krastanov growth

MISFIT \( \delta a/a \) of the order of 4.2\%
Heteroepitaxy: paradigm Si/Ge systems

Stransky-Krastanov mode of growth. During annealing, islands, separated by a wetting layer, form and coarsen, dominated by surface diffusion.

\[ a = a_f, \delta a = a_{\text{film}} - a_{\text{substrate}} \]

Vegard Law: \[ a_{\text{film}} = x a_{\text{ge}} + (1-x) a_{\text{si}} \]

\[ l_0 = \frac{\gamma}{E(\delta a/a)^2} \]

\[ t_0 = \frac{l_0^4}{(D \gamma)} \]

Pimpinelli, Villain « Physics of crystal growth», 1998
Stangl et al, Review of Modern Physics 2004
Heteroepitaxy, Si/Ge (IV/IV) or group III/V InGaAs/GaAs

Elastic instability: island formation is ubiquitous

\[ l_0^{-1} = \frac{E}{\gamma} \left( \frac{\delta a}{a} \right)^2 \]

\[ t_0 = \frac{l_0^4}{(D\gamma)} \]

Nucleationless formation of islands in heteroepitaxy from surface ripples.

Floro et al., PRB 99

Sutter et al. PRL 2000

Berbezier, Ronda, PRB 2007, vicinal surface Si (001)
The « Mullins » surface diffusion model

No alloying, no volume diffusion

\[ \frac{\partial h}{\partial t} + \nabla \cdot \mathbf{J} = 0 \]

\[ \mathbf{J} = -D \nabla \mu \]

Elastic energy  Surface energy  Wetting potential

\[ \mu = \mathcal{E}[h] + \gamma(h) \kappa(h) + \gamma'(h) / \sqrt{1 + |\nabla h|^2}, \]

\( \kappa(h) \) is the curvature
Wetting potential model

\[ \gamma(h) = \gamma \left[ 1 + c_w \exp\left( -h/\delta \right) \right] \]

\( \delta \) is a few layers, \( \sim 2 \text{ nm} \)

Chiu, Gao, 1993,
Muller and Kern,
F. Liu
Spencer, Tekalign, Golovin,
Davis, Voorhess, PRB, 2003
Levine et al, Phys Rev B, 2007
Film and substrate elasticity

Elastic energy

\[ E^{(\alpha)} = \frac{1}{2} e_{ij}^{(\alpha)} \sigma_{ij}^{(\alpha)} \]

Strain tensor

\[ e_{ij}^{(\alpha)} = \frac{1}{2} (\partial_j u_{\alpha,i} + \partial_i u_{\alpha,j}) \]

\[ \sigma_{ij}^{(\alpha)} = \frac{E}{1 + \nu} e_{ij}^{(\alpha)} + \frac{\nu}{1 - 2\nu} e_{ll}^{(\alpha)} \delta_{ij} \]

\[ \alpha = \text{(Si soit Ge)} \]

Boundary conditions: Stress and strain are continuous at the Si/Ge interface, no dislocations.

\[ u_s = \tilde{u}_f \text{ and } \sigma_s \cdot \hat{z} = \sigma_f \cdot \hat{z} \text{ at } z = 0. \]

\[ \sigma_f \cdot \hat{n} = 0 \text{ at } z = h(x, y, t) \text{ No stress at the free boundary} \]

(Non-linear geometrical conditions)
Linear analysis:

\[ h(x, y, t) = h_0 + \delta h e^{i\mathbf{k}.\mathbf{r} + \sigma t} \]

\[ \nu = |\mathbf{v}| \]

\[ \sigma = -c_w k^2 + \left( \frac{\delta a}{a} \right)^2 k^3 - k^4 \]

\[ \gamma(h) = \gamma [1 + c_w \exp(-h/\delta)] \]

Flat film stable for \( h_0 < h_c \)
Small slope equation

\[
\frac{\partial h}{\partial t} = \frac{\partial^2}{\partial x^2} \left\{ - \left[ 1 + c_w f\left( \frac{h}{\delta} \right) \right] h_{xx} + \frac{c_w f'(h/\delta)}{\delta \sqrt{1 + h_x^2}} - \omega_1 \mathcal{H}(h_x) \right. \\
+ \omega_2 (2hh_{xx} + h_x^2) + \omega_2^* (2 \mathcal{H}\{[h\mathcal{H}(h_x)]_x\} + [\mathcal{H}(h_x)]^2) \left. \right\},
\]

**Singular term**  
**Nonlinear nonlocal terms which prevents the singularity.**

\[
\gamma(h) = \gamma_f \left[ 1 + c_w f(h/\delta) \right]
\]

\[
f(\xi) = \exp(-\xi)
\]

**f is the wetting potential**

\[
\mathcal{H}[h_x] = \mathcal{F}^{-1}\{k|\mathcal{F}[h]|\}
\]

**H is the Hilbert transform, multiplication by k in Fourier Space**
NO singularity when BOTH wetting (small, not diverging) & non-linear non-local effects are considered

\[ \gamma(h) = \gamma \left[ 1 + c_w \exp(-h/\delta) \right] \]

\[ c_w = 0.1 \]
Numerical Simulations using Spectral Methods

Non-interrupted coarsening

Large islands grow at the expense of the small ones
Coarsening dynamics: numerical simulations

1. roughness

\[ w(t) = \left[ \langle h^2 \rangle - \langle h \rangle^2 \right]^{1/2} \]

\[ w(t) \sim t^{\beta} \]

JNA, Frisch, Verga, PRB 07

2. Number of islands

\[ N(t) \sim 1/t^{\zeta} \]
Dynamics of the coarsening

Some discussion about the coarsening exponent:

\[ w(t) \sim t^\beta \]
\[ N(t) \sim 1/t^\zeta \]

<table>
<thead>
<tr>
<th>\beta</th>
<th>Levine, Golovin, Davis, Voorhees PRB 07</th>
<th>Pang, Huang PRB 06</th>
<th>Aqua, Frisch, Verga PRB PRB 07</th>
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<tbody>
<tr>
<td>\beta</td>
<td>2.88</td>
<td>0</td>
<td>0.7</td>
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<tr>
<td>\zeta</td>
<td>2.9</td>
<td>N/A</td>
<td>1.3</td>
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</table>

Annealing Hypothesis:

No facetting:
No alloying:
Silicon/germanium island are faceted.
Silicon Germanium island

AFM, RMP 04, Rastelli, the (105) is apparent
Surface energy anisotropy

\[ F^s = \int \gamma(h,n) \sqrt{1 + |\nabla h|^2} \, dr \]

\[ F^{el} = \int_{z<h(r)} E^{el}(r,z) \, dr \, dz. \]

\[ F = F^s + F^{el} \]

\[ \mu = \delta F / \delta h \]

The surface energy depends on the orientation and also on the elastic-strain.

We neglect the second effect but we take a minimum for the (105) orientation.
Effect of the anisotropy of surface energy (Gamma Plot)

\[ \gamma(h, n) = \gamma_f \left[ 1 + \gamma_n(n) + \gamma_h(h) \right] \]

In a crystalline solid, the surface energy depends on the orientation \( \gamma(n) \) and also on the elastic-strain.

We first grow a film of height $h_d$ and let it anneal.

The deposited height $h_d$ is the relevant parameter.
Evolution of the island density

FIG. 8. Numerical results of Eq. (32). Evolution of the island density versus time for, from bottom to top, the cases $(a, b, c, d, e, f)$. 
Time evolution
Top = 9 ML
L = 128 \( l_0 \)
\( l_0 = 27 \) nm

Bottom = 20.2 ML
Anneal time is 300 Minutes

Simulations
Evolution of the roughness

Coarsening is interrupted
Dots density and size can be controlled: coarsening is interrupted.

**Island Volume**

**Numerical simulation**

**density**

We can vary the dots density as a function of the deposited height.
Distribution of island sizes

(a) 9ML  
(b) 15 ML  
(c) 20 ML
Dispersion of island size distribution: r.m.s.

FIG. 14. Standard deviation $\Delta \nu$ of the island size distribution as function of the amount of matter and (inset) relative width $\Delta \nu/\langle \nu \rangle$. 
L \rightarrow L', the wetting energy increases, but the surface energy decreases and the elastic energy remains constant.

Aqua-Frisch, 2010, Phys Rev B 76

L > L', the wetting energy increases, but the surface energy decreases and the elastic energy remains constant.
Energetic model

\[ h = h_0 - nV. \]

\[ \Delta E = \gamma_f L^2 / \cos \alpha - L^2 \gamma(h_0) + (1/n - L^2) [\gamma(h) - \gamma(h_0)] - \lambda_e V. \]

Two-island model

Two free parameters are: the height of the wetting layer, and the surface density of pyramids.

V1 = V2 is a valley with a very small slope.

J.-N. Aqua, T. Frisch, PRB, 82, 085322, 2010
Effect of the flux

The flux does not really affect the density of island for $h_d = 11.7$
Experimental results

- $\text{Si}_{0.7}\text{Ge}_{0.3}$ annealed at 550 celcius for 54 hours for different deposited height.

MBE group of Isabelle Berbezier
Interrupted coarsening is also observed experimentally

Experiments, I.
Berbezier, 2002, J. Phys Cond Matters, SiGe/Si
AFM
Experiments

$Si_{0.70}Ge_{0.30}$ 550°C

as grown

15.8 Monolayers

18 Hours annealing

54 hours annealing

Time
$\text{Si}_{0.70}\text{Ge}_{0.30} (550^\circ C)$

$\rho_{\text{max}}$ as function of the amount of matter

Expriements density falls with the same order of magnitude as the theory but a more detailed comparison is needed:

In particular, we are doing Ab_Initio calculation to extract the value of the diffusion coefficient (V. Oison)

$1\text{ML SiGe30\%} = 3.169\text{A}$
Conclusion

- The elastic instability has a rich nonlinear regime

- We derived a fast methods for Stransky-Krastanov growth modeling in the instability regime

- Coarsening is interrupted due to the interplay between anisotropy of surface energy and the wetting effect.

- We may control the dots size on Si/Ge by varying the deposited height and the strain
How sensitive is the dynamics on the effect of surface energy anisotropy?

Question: For which values of $\gamma_2/\gamma_0$ the dynamics changes from non-interrupted coarsening to interrupted coarsening?

Is the sharpness at $\Theta_c$ is important?

Close the instability threshold, it can be possible to compute a bifurcated solution and to verify the existence of periodic solutions (Landau expansion with anisotropy). One ingredient is period-doubling or tripling.
Perspectives on alloying.

- **Alloying** phenomena during Si/Ge growth, effect of surface segregation effect,

- Application are on the III/V semiconductor.

- **Nonlinear** coupling between the compositional and the morphological instabilities. The alloys concentration is spatially inhomogenous and it has an impact on the opto-electronic properties.

- Electron Phase microscopy analysis of alloys composition (P. Donnadieu, SIMAP, Grenoble, and I. Berbezier IM2NP)

What is the island composition?

Medeiros-Ribeiro, PRL 2008, ESRF, Synchroton X

Floro et al, PRB 99
Collaborators: Adrien Gouye, Isabelle Berbezier, Antoine Ronda, Alberto Verga.

Relevant Publications:

J.-N Aqua, T. Frisch and A. Verga, Phys Rev E 2010 (Flux effect)

Graduate Student: Xian Bin Xue, and Philippe Gaillard

Si-Ge growth of FIB patterned substrate

Compositional and morphological coupling