Effect of Phosphorus on Ge/Si(001) Island Formation

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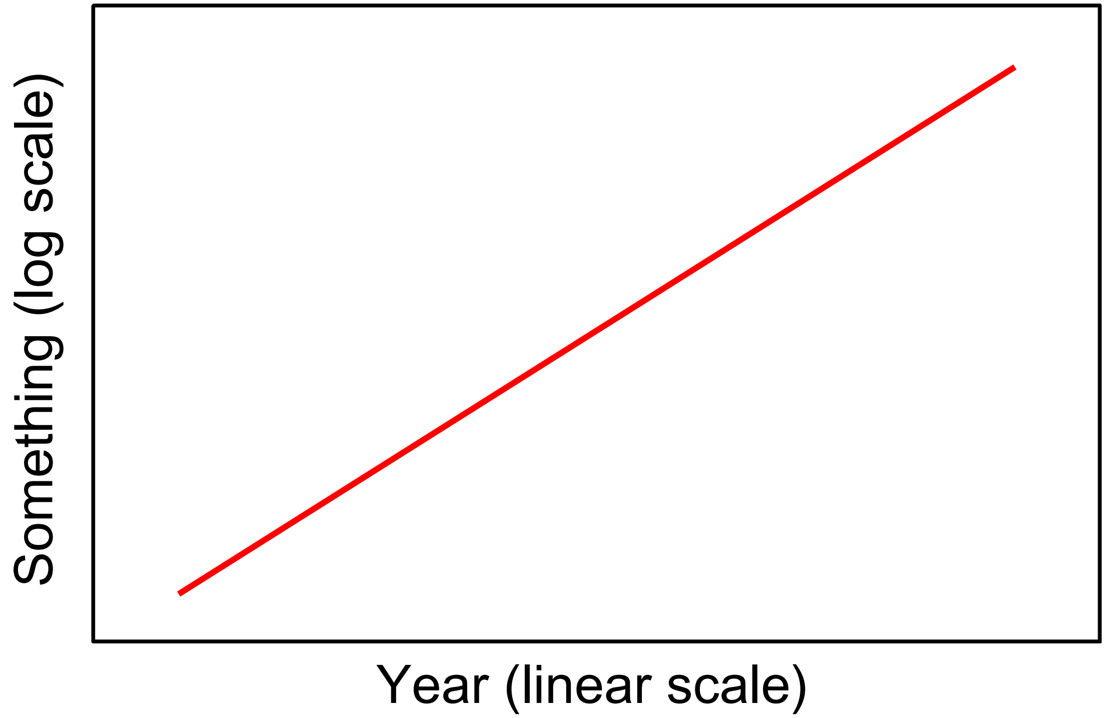
Outline

- Limits of Moore's law
- Forming a feature
  using "self assembly"
- Strain from lattice mismatch
  between two materials
- Ge islands on Si substrate
  - Undoped
  - **Phosphorus doped**
- Thermodynamics *vs.* kinetics

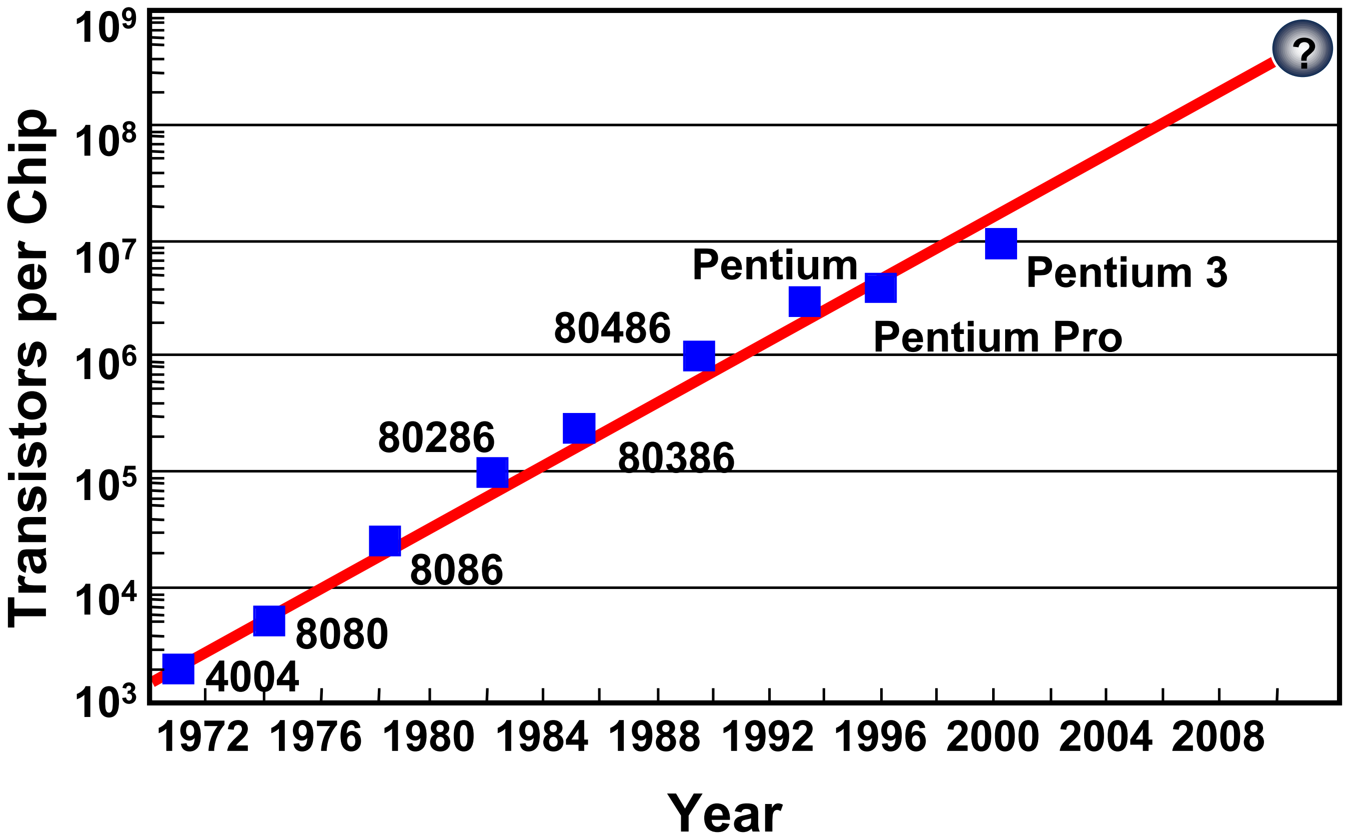
Moore's Law (General Case)



Even Dilbert uses Moore's Law

(Reference: Scott Adams “Dilbert,” July 15, 1997)

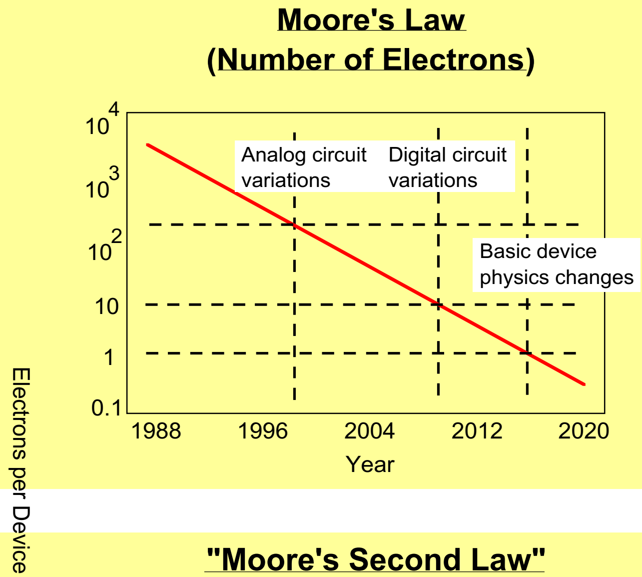
Moore's Law
Number of Transistors



Critical Issues

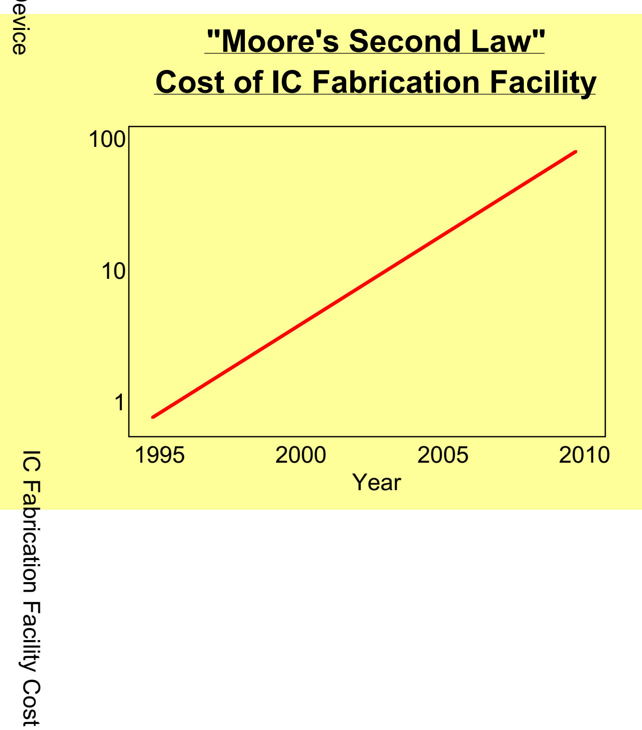
Device size and density

- Physically small features
- Operation with small features
- Limited number of electrons
- Interconnections



Cost ("Moore's second law")

- Simpler architecture
- Defect-tolerant architecture
- Minimize expensive lithography
- Self (or directed) assembly



Self-Assembled Nanostructures

0D Islands and 1D Nanowires on Si

Conventional scaling will reach its limits

- Use self and directed-assembly to extend Moore's law
- Determine critical dimensions by choice of materials and deposition kinetics ("self assembly"), not lithography
- Use lithography to position devices or arrays of devices ("directed assembly")

Use small-size effects for logic, storage, and computation

- Coulomb blockade
- Quantum confinement

Methods of self- or directed- assembly

- Strain from lattice mismatch
- Catalytic wire growth on nanoparticle

Thermodynamically assembled structures

- Several percent defects
- Need defect-tolerant architecture

hp invent

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Forming Self-Assembled Islands (Quantum Dots)

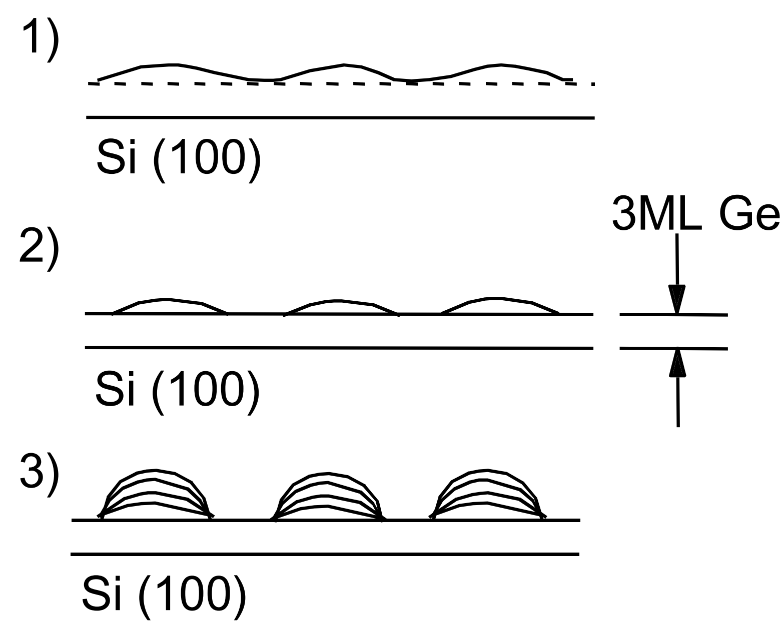
Deposit one material on another

- Different lattice constants → strain
- Large strain → islands
  - ($\varepsilon_x = \varepsilon_y$)
- Small islands → quantum or Coulomb-blockade effects
- Island shape determined by volume, facet, interface, and edge energies

Focus on Ge on Si

- Why Ge on Si?
  - Compatible with Si IC technology
  - Model system

Energy and Kinetics Influence Island Formation



Undoped Ge Islands

Deposition by

CVD: $GeH_4 + H_2$

PVD: e-beam evaporation

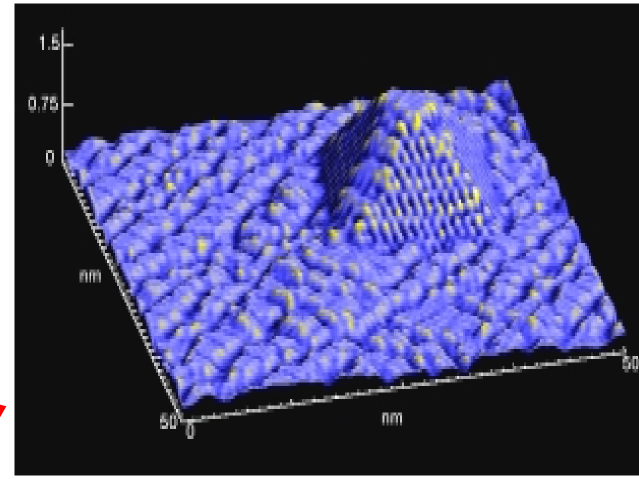
<u><4 ML Ge</u>: Uniform Ge layer

No islands

Three types of islands:

<u>6 eq-ML</u>: Pyramids

Bounded by {105} facets

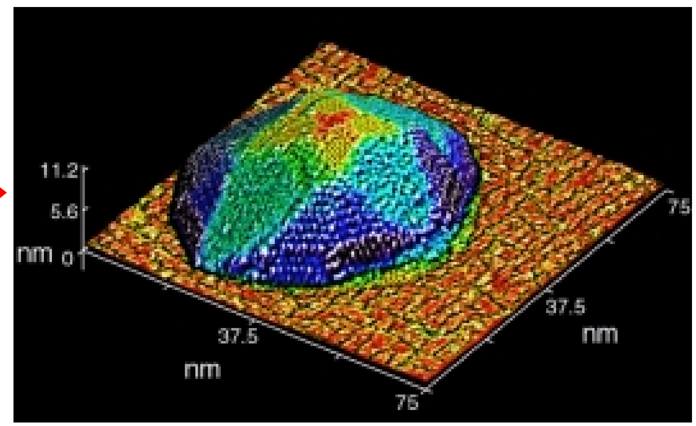


<u>11 eq-ML</u>: Domes

Taller to reduce interface area

Bounded by steeper facets

Strain relaxation near top of island

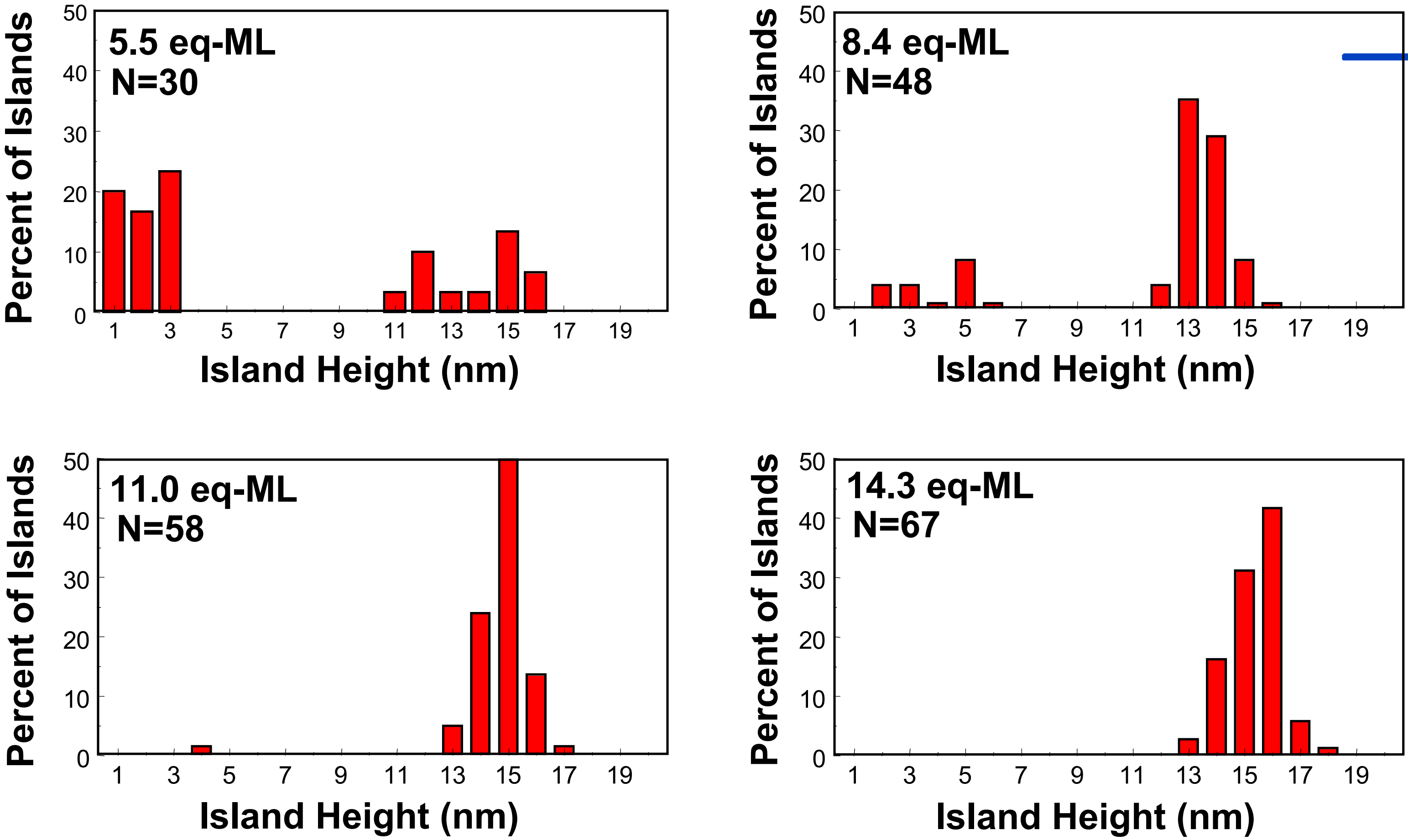


<u>>14 eq-ML</u>: “Super-domes”

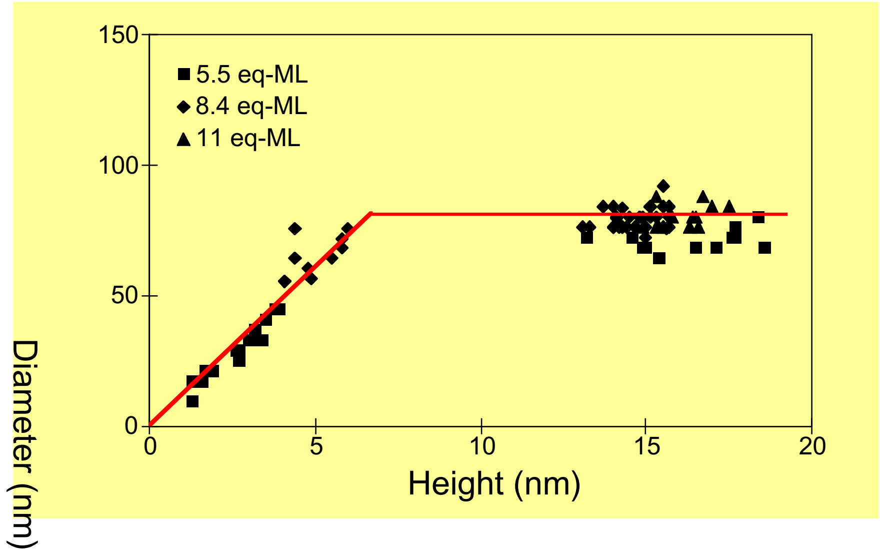
Steep facets; defects

Scanning Tunneling Micrographs
by G. Medeiros-Ribeiro, HPL&LNLS

Distribution of Island Heights

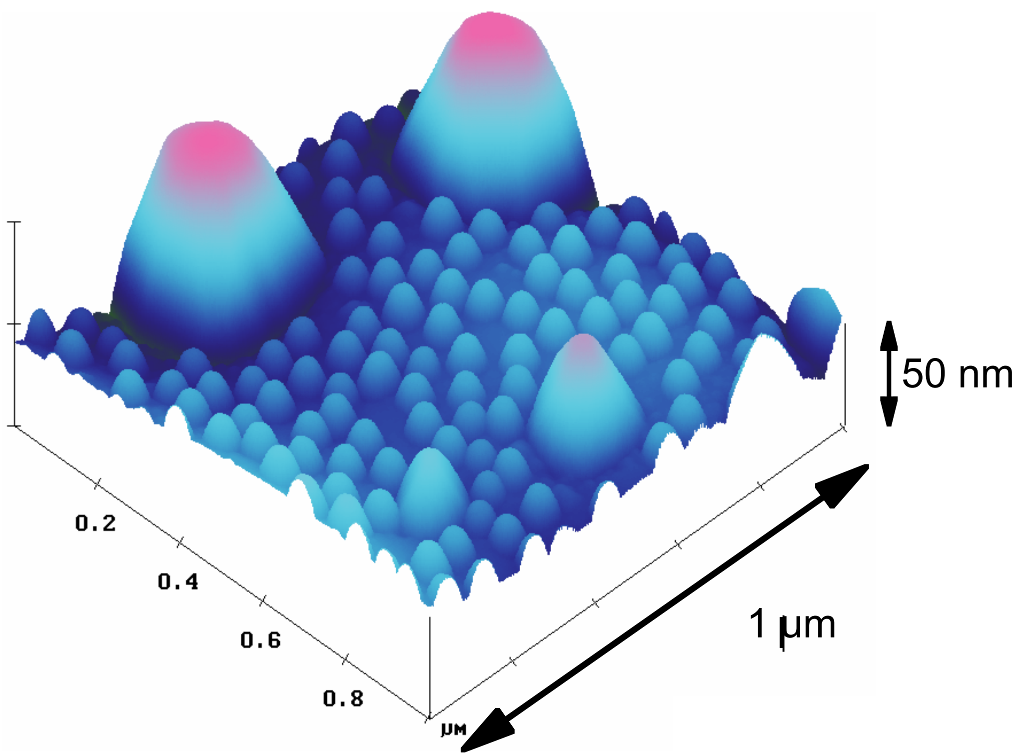


Island Distribution



Domes have favored size
Pyramids do not

Ge/Si(001): ~44 eq-ML at 600°C (Barrier to Dome Growth)



Manipulating Islands

Domes have narrower distribution
Potentially more useful

How to get smaller domes?

Add something that binds well to surface, changes surface energy (and perhaps ratio of energies of different surfaces)

- Add HCl during deposition:
  Primarily changes kinetics

- Etch with HCl after deposition
  Reduces island height, not base

- Use Ti ($TiSi_x$)
  Larger lattice mismatch
  (But Ge/Si system beneficial)

- Add other impurities to Ge/Si

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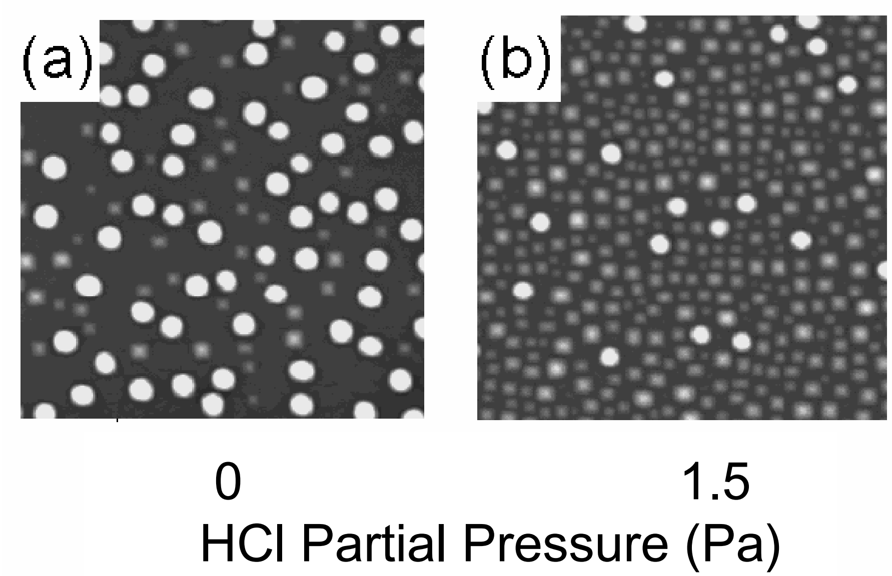
Using HCl to Control Islands

Adding HCl during Deposition



Adsorbed Cl impedes Ge surface diffusion

Changes kinetics, rather than thermodynamics

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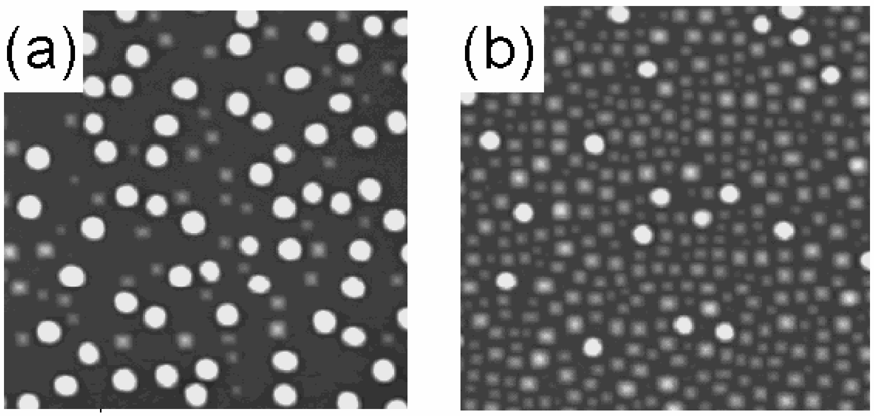
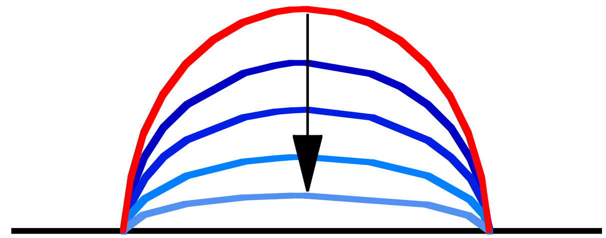


0 1.5

HCl Partial Pressure (Pa)

Etching with Gaseous HCl after Deposition



Shorter, but not narrower

Adsorbed Cl impedes Ge surface diffusion

Changes kinetics, rather than thermodynamics

Manipulating Islands

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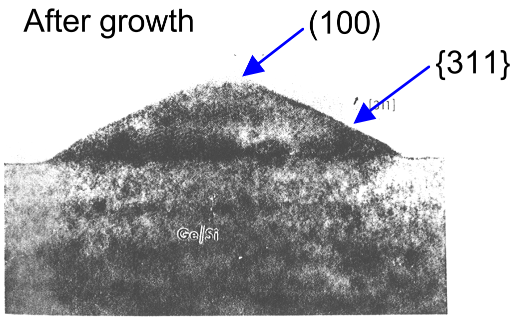
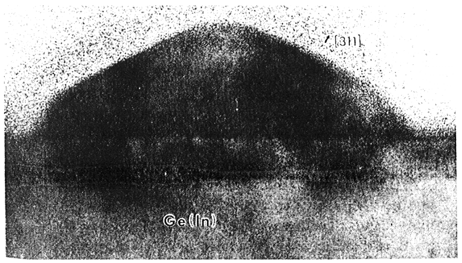
Effect of Impurities on Equilibrium Island Shape

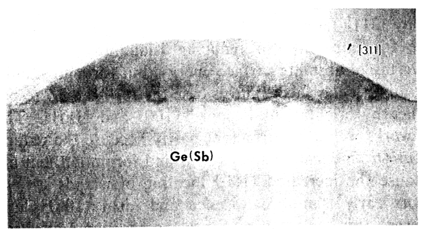
After growth



Indium: enhances {311}



Antimony: enhances (100)

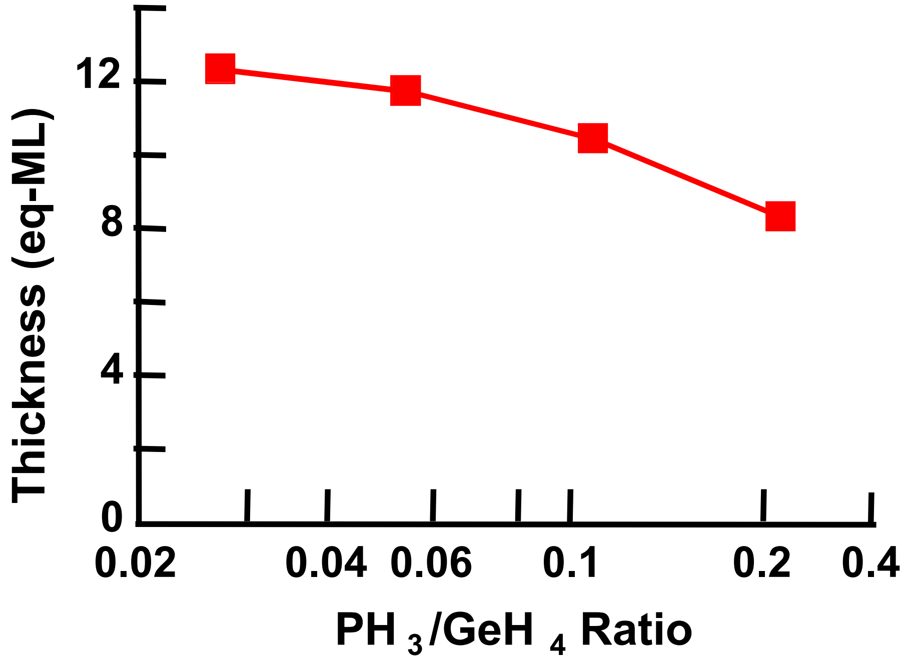


D. J. Eaglesham, F. C. Unterwald, and D. C. Jacobson, Phys. Rev. Lett. 70, 966 (1993)

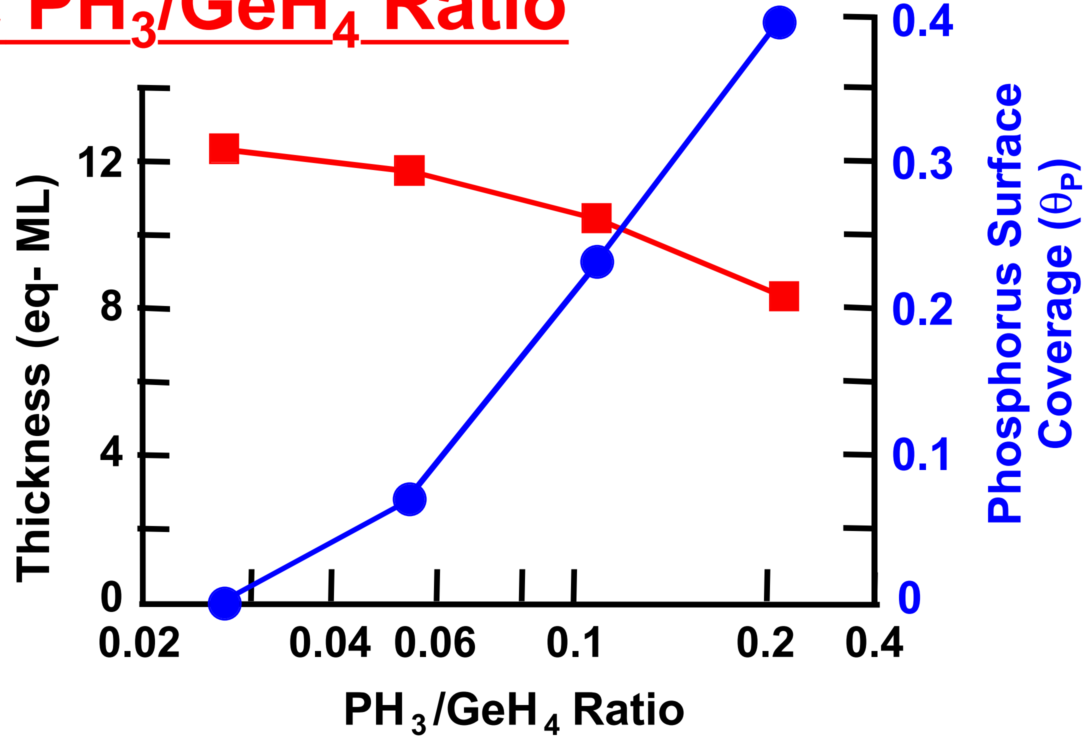
Surface impurities change
  surface energy *anisotropy*

Phosphorus or arsenic
  n-type dopants
Initiation of arsenic
    incorporation slow
  Little in thin layer
Phosphorus more useful as
    dopant
Theromodyamics *vs.* kinetics

Ge Thickness *vs.* PH_3/GeH_4 Ratio Competitive Adsorption



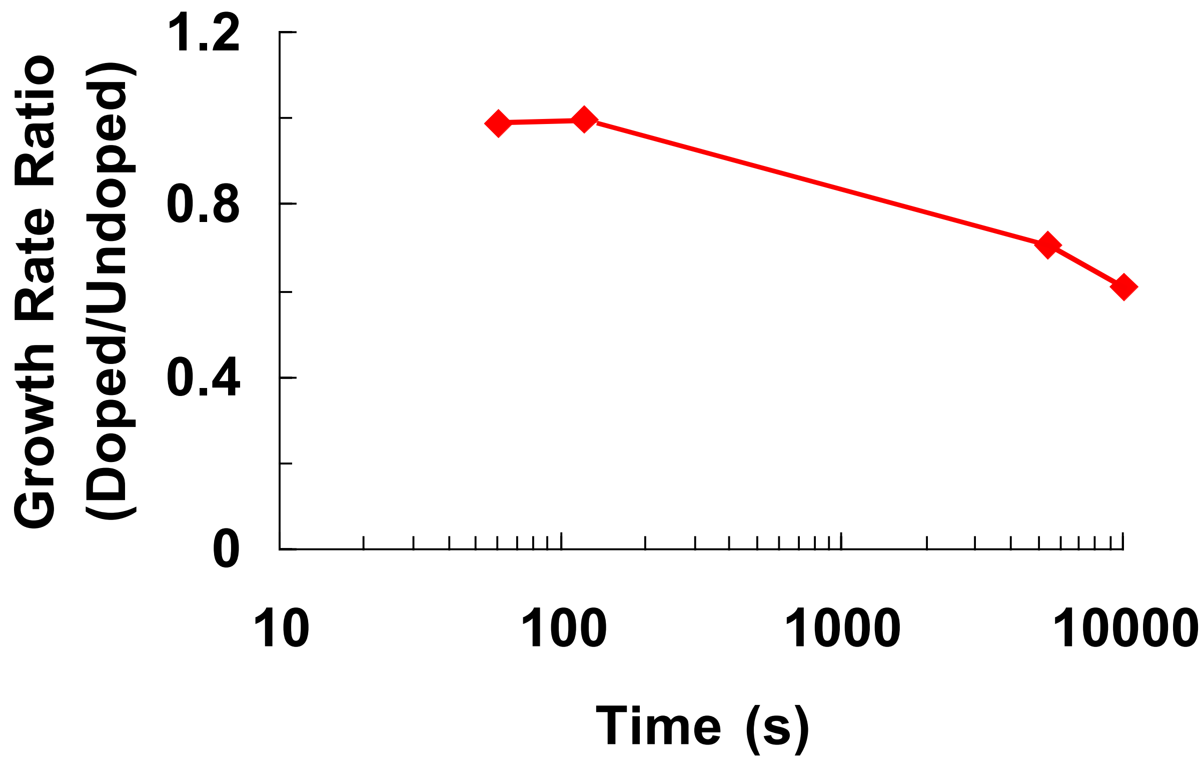
Phosphorus Surface Coverage *vs.* PH_3/GeH_4 Ratio



$$\theta_P = \frac{C_P \exp(-\Delta H/kT)}{n_{Ge} - C_P\,[1 - \exp(-\Delta H/kT)]}$$

$\Delta H \sim -0.4$ eV

Growth Rate Ratio *vs.* Time



Slow increase of surface phosphorus concentration

Doped Ge islands

$GeH_4 + PH_3 + H_2$

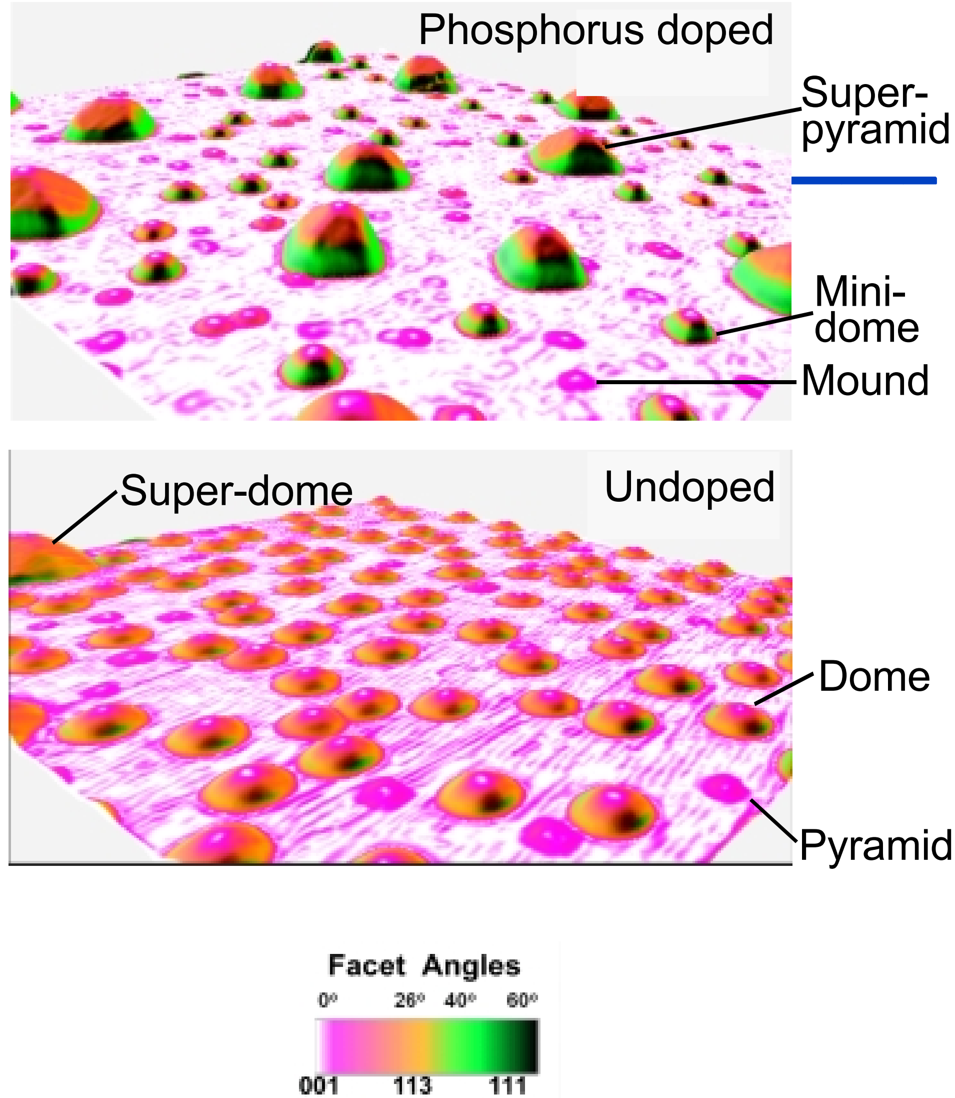
Temperature: 600°C

Partial pressures:

H_2: 1.3 kPa (10 Torr)

GeH_4: 3-6×10^{-2} Pa (2.5-5×10^{-4} Torr)

PH_3: 1.7×10^{-3} Pa (1.4×10^{-5} Torr)

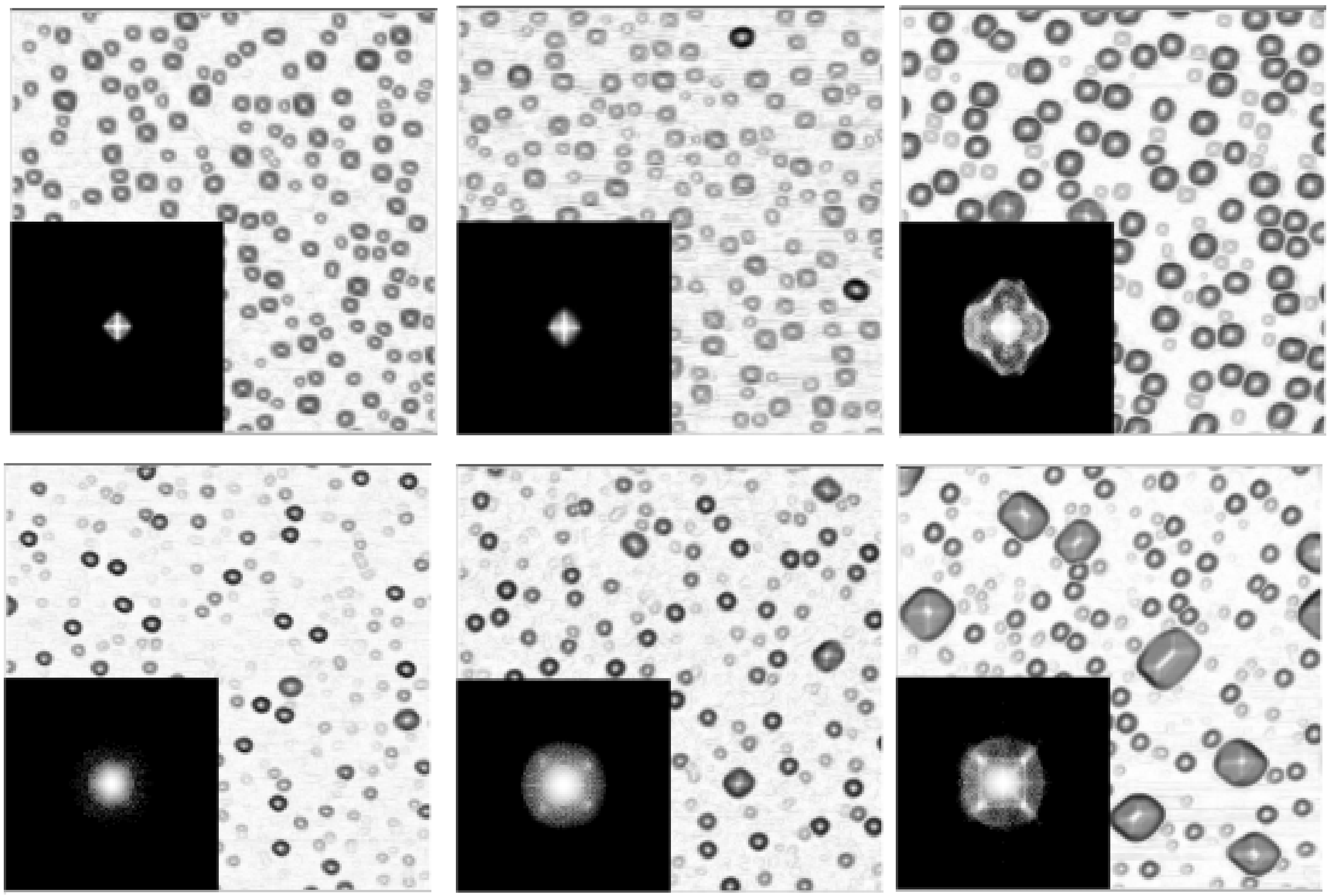


Shape evolution: Doped *vs.* undoped

56 s | 60 s | 120 s

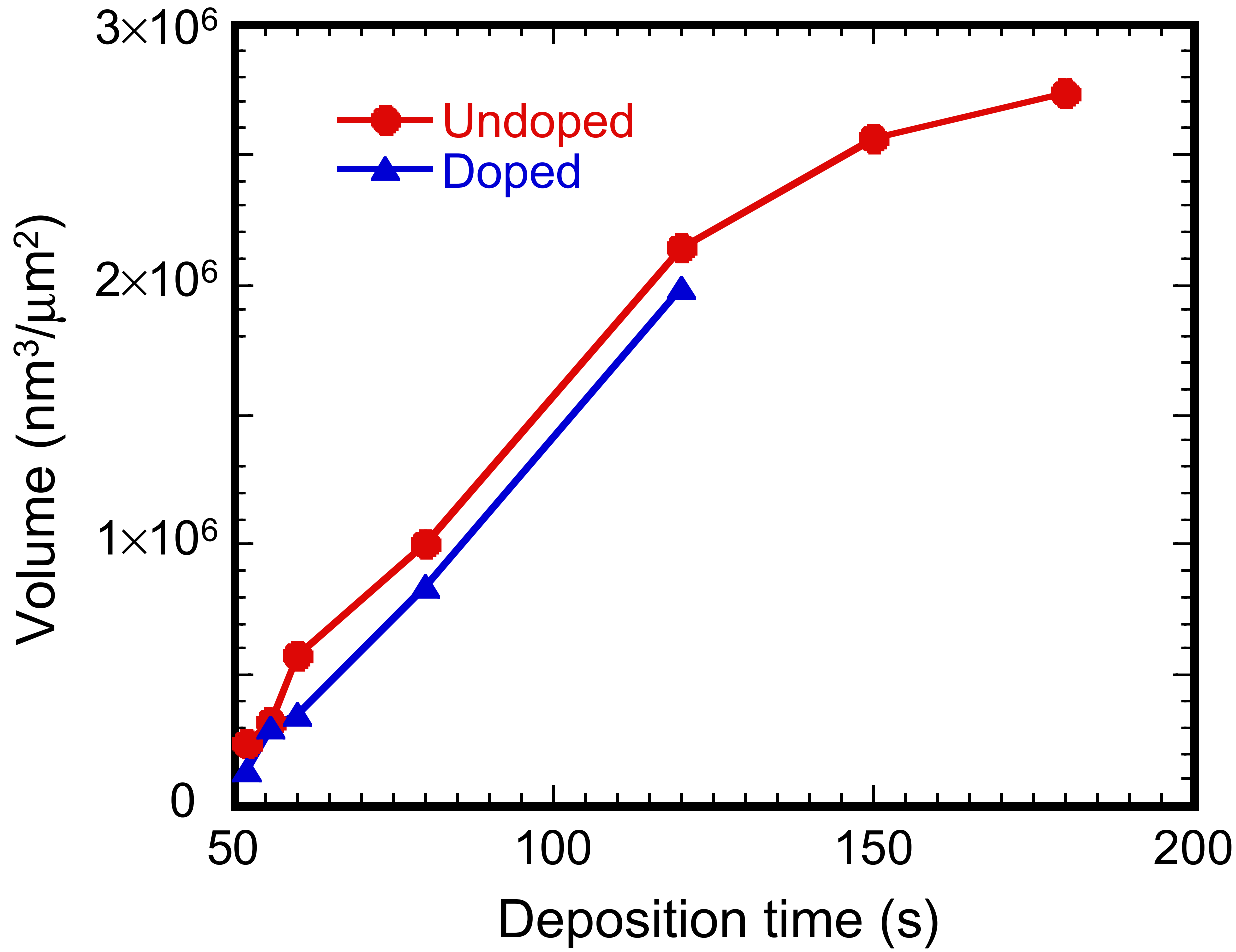
Undoped

Doped



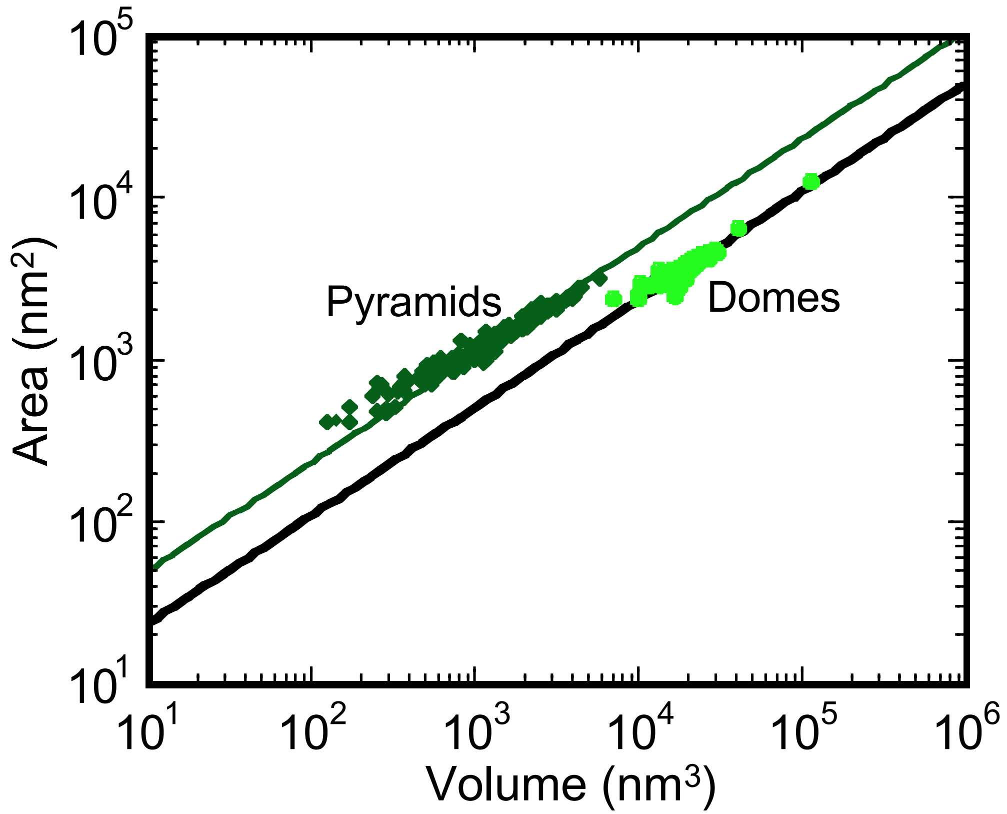
Island Volume: Doped *vs.* undoped

Integrated AFM volumes *vs.* deposition time



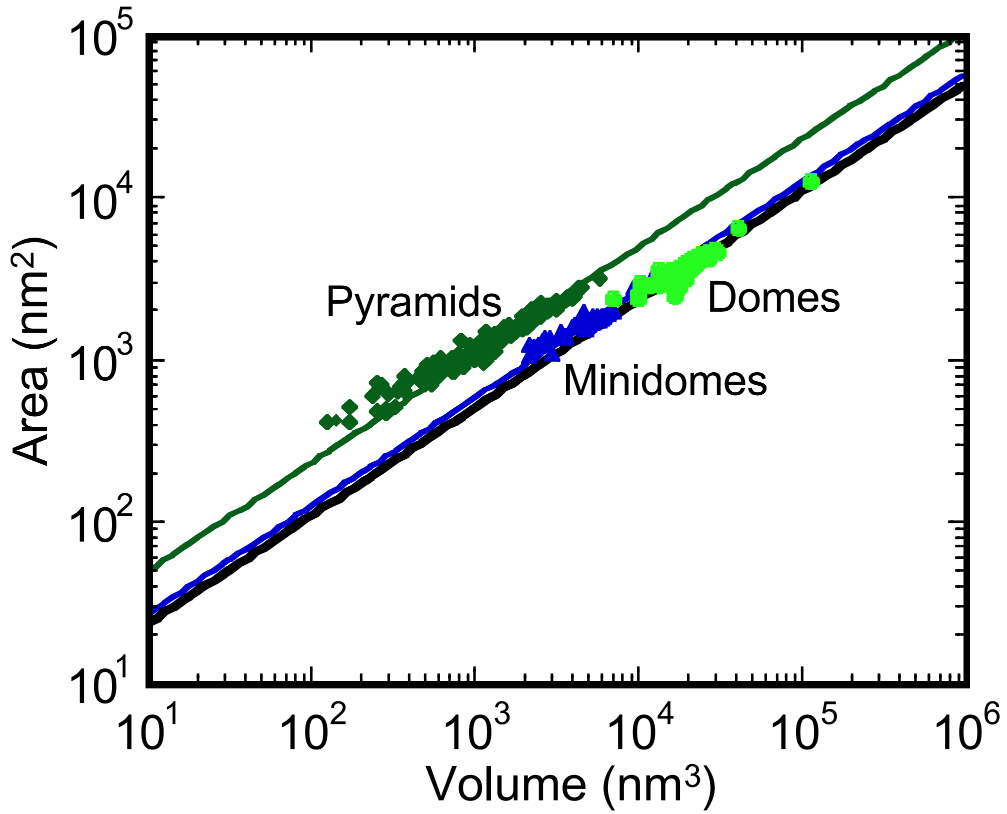
Island Shape Analysis

Points of one shape lie on line with slope = 2/3
Different intercept for different shapes
Undoped: Pyramids and Domes

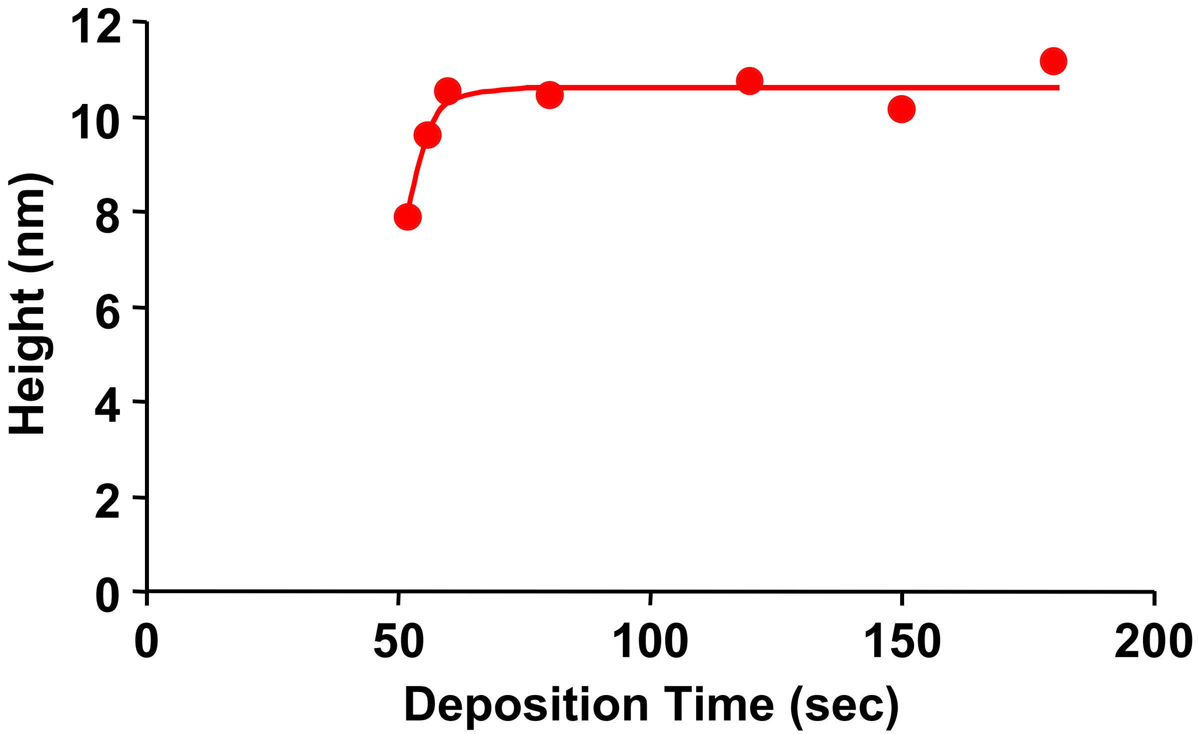


Island Shape Analysis

Points of one shape lie on line with slope = 2/3
Different intercept for different shapes
Undoped: Pyramids and Domes
Doped: Mini-domes

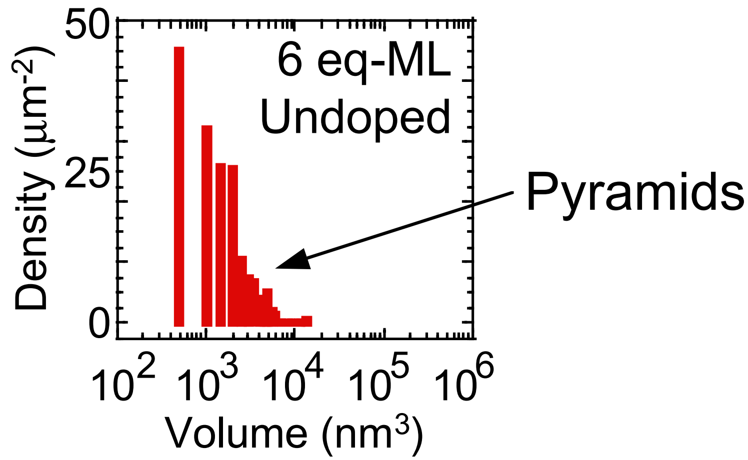


Mini-Dome Height

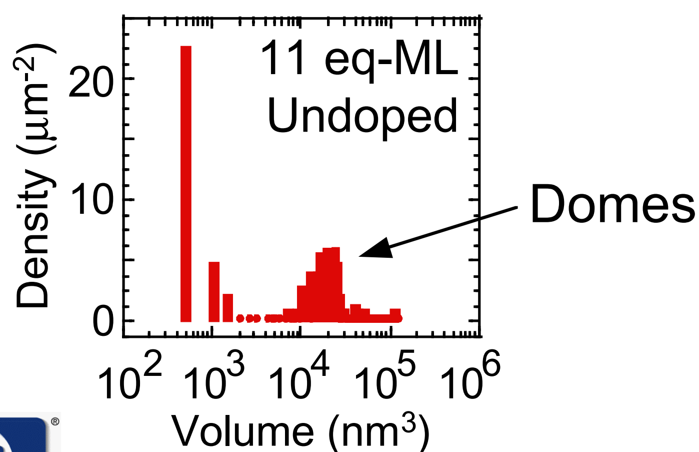


Undoped Ge islands

6 eq-ML

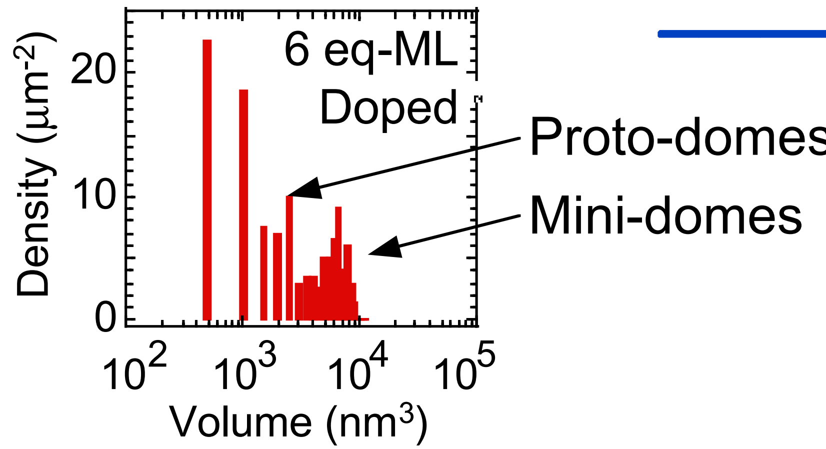


11 eq-ML



Doped Ge islands

6 eq-ML



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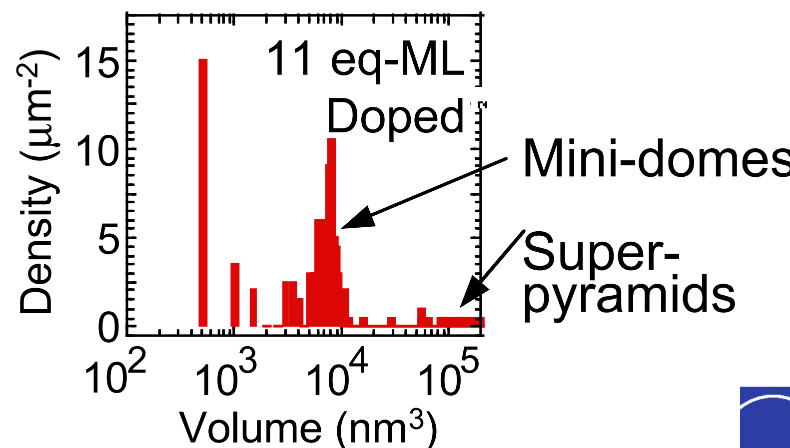
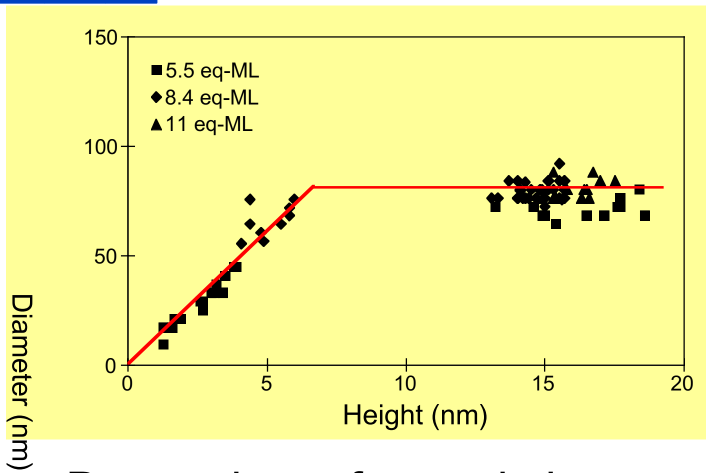
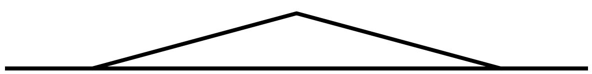


Island Distribution



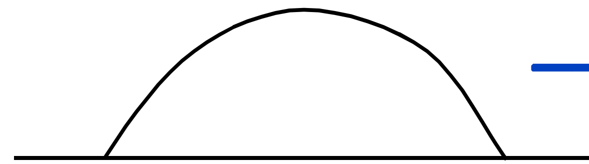
Domes have favored size
Pyramids do not

Pyramids



Bounded by {105} facets only
Proportional:
- Surface area
- Interface area
- Edge length

Domes



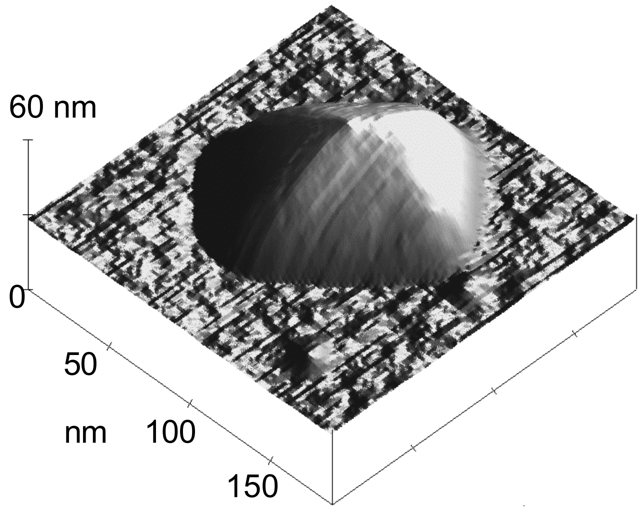
Bounded by several facets
- Area ratio can vary

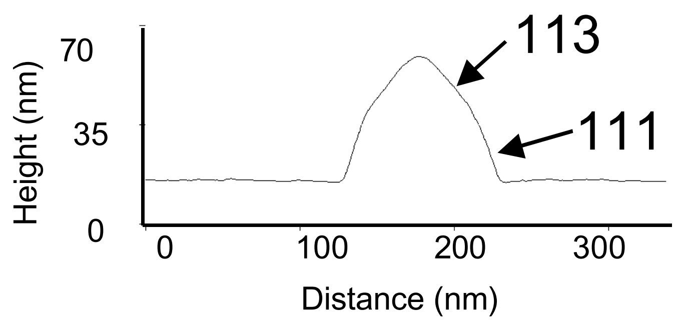
Need not be proportional:
- Surface area
- Interface area
- Edge length

Can vary to minimize energy
Harder to add atoms beyond
this energy minimum

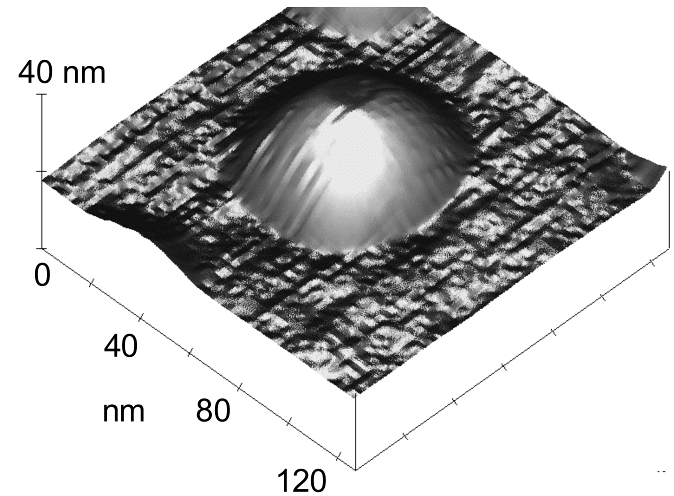
Strain relaxation near top of island

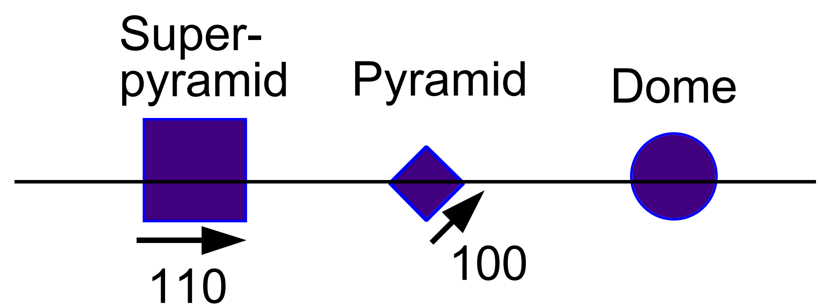
“Superpyramid”





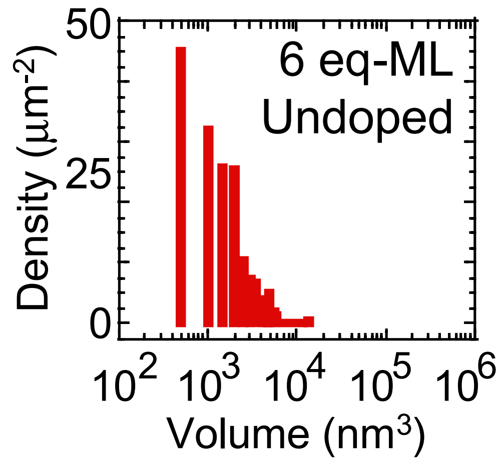
For comparison: Dome

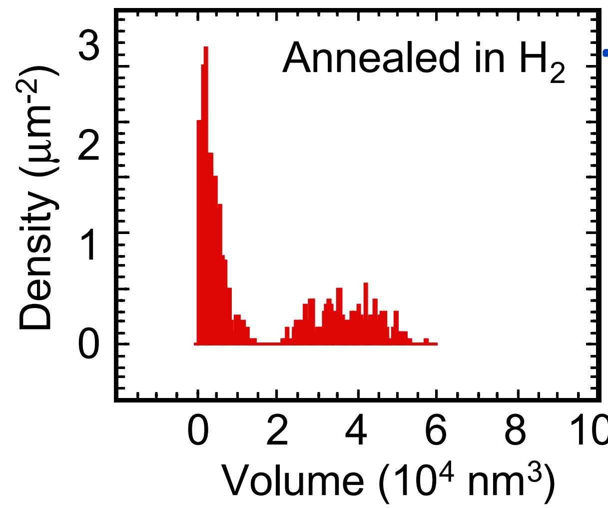




Phosphorus Also Changes Annealing Kinetics

6 eq-ML undoped Ge
Mainly pyramids

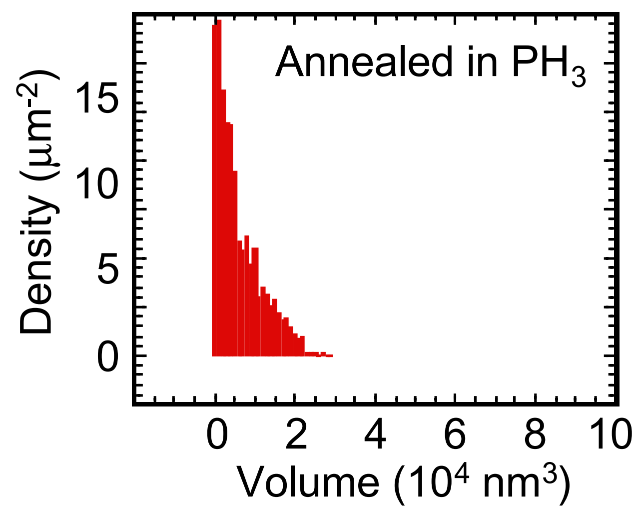




Effect of annealing

H_2: Islands coarsen
Many pyramids
convert to domes

PH_3: Coarsening retarded



Summary
Phosphous-Doped Ge/Si Islands

- Phosphorus…
  - Modifies energies and relative energies of different surface planes
  - Changes favored island shapes
  - Island shape influenced by surface energy (Thermodynamics)
  - Retards coarsening (Kinetics)
- Additional method for controlling island size, shape, and uniformity
- Deposition rate decreases with increasing PH_3/GeH_4 ratio and increasing time
  - Slow increase of surface phosphorus
  - PH_3 changes island shape in thin layers $\rightarrow$ Significant phosphorus on surface in thin layers
- Phosphorus concentration near solid solubility limit ($\sim 5\times10^{19}$ cm^{-3}) (SIMS)

invent