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# Self-Assembled $\text{TiSi}_x$ Nanostructures formed by Chemical Vapor Deposition

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**[www.hpl.hp.com/research/qsr](http://www.hpl.hp.com/research/qsr)**

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# Outline

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- Motivation
- Ti deposition
- Island formation during deposition
- Island modification during annealing
- Nanowire growth
- Nanowire alignment

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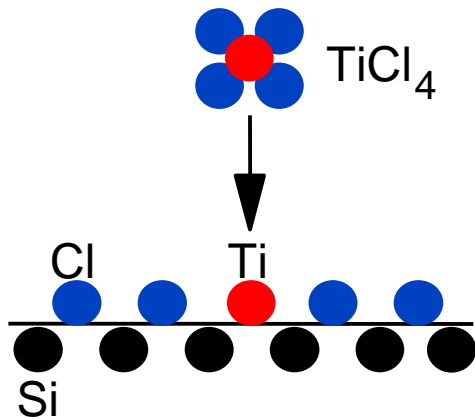
## Moore's (Second) Law and Self Assembly

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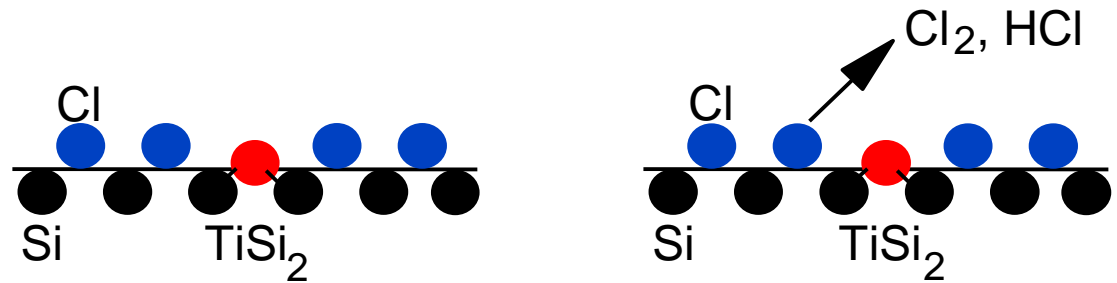
- The **cost** of IC fabrication facilities continues to increase
- Much of cost relates to **lithography** of very small features
- Using **self-assembly** to form the smallest features can potentially reduce the escalating cost
- **Coarser lithography** can be used to position the fine features formed by self-assembly
- Features formed **thermodynamically** will have large numbers of defects
- Coupling self-assembly with a **defect tolerant computer architecture** is attractive



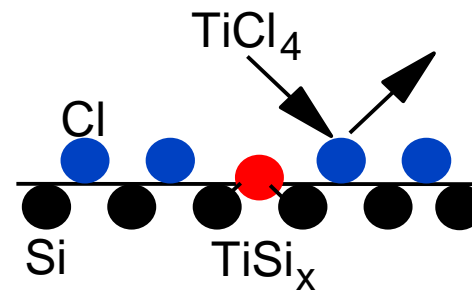
# Deposition from $\text{TiCl}_4$



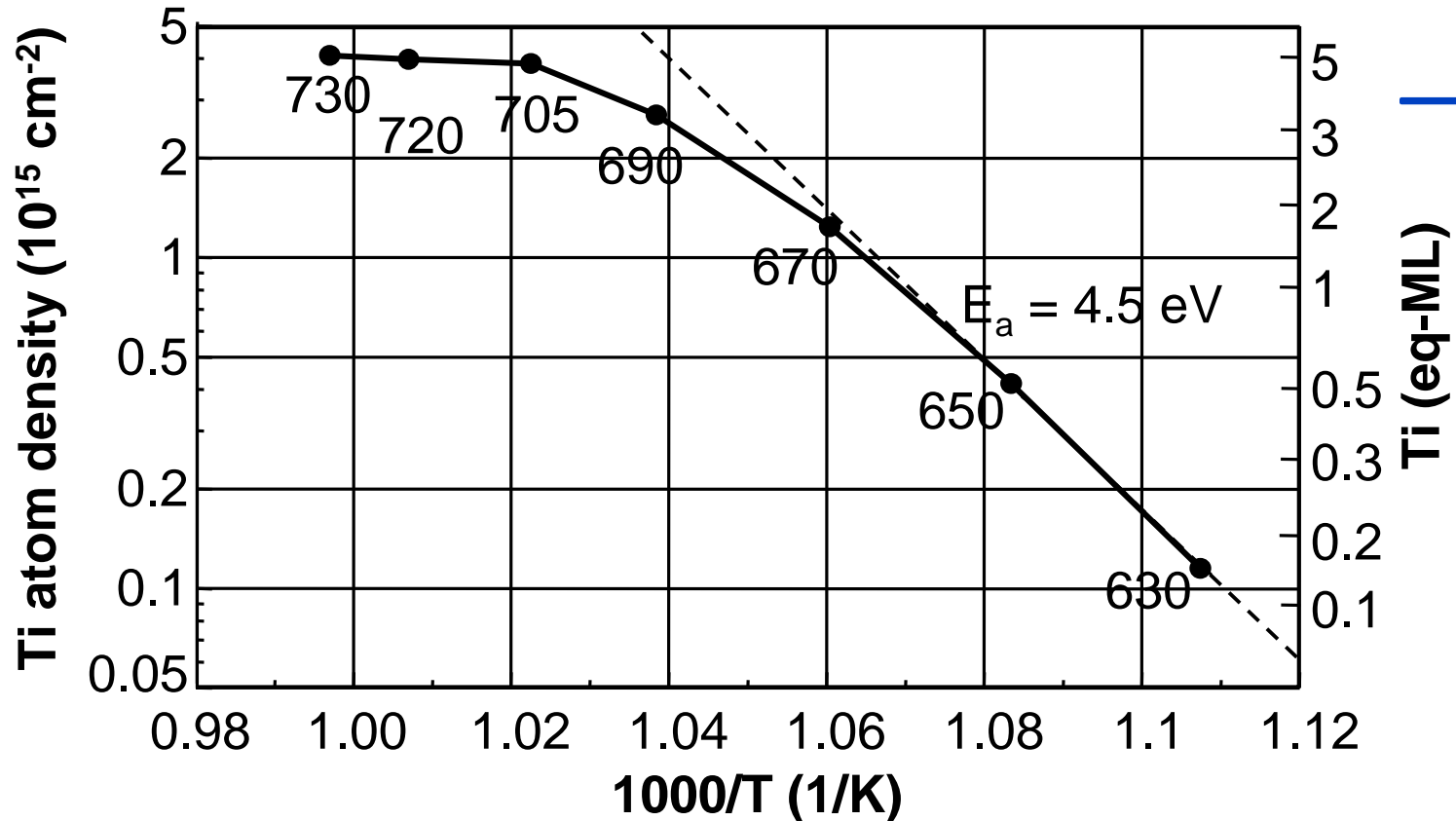
Higher Temperatures ( $T > 700^\circ\text{C}$ )



Lower Temperatures ( $T < 700^\circ\text{C}$ )



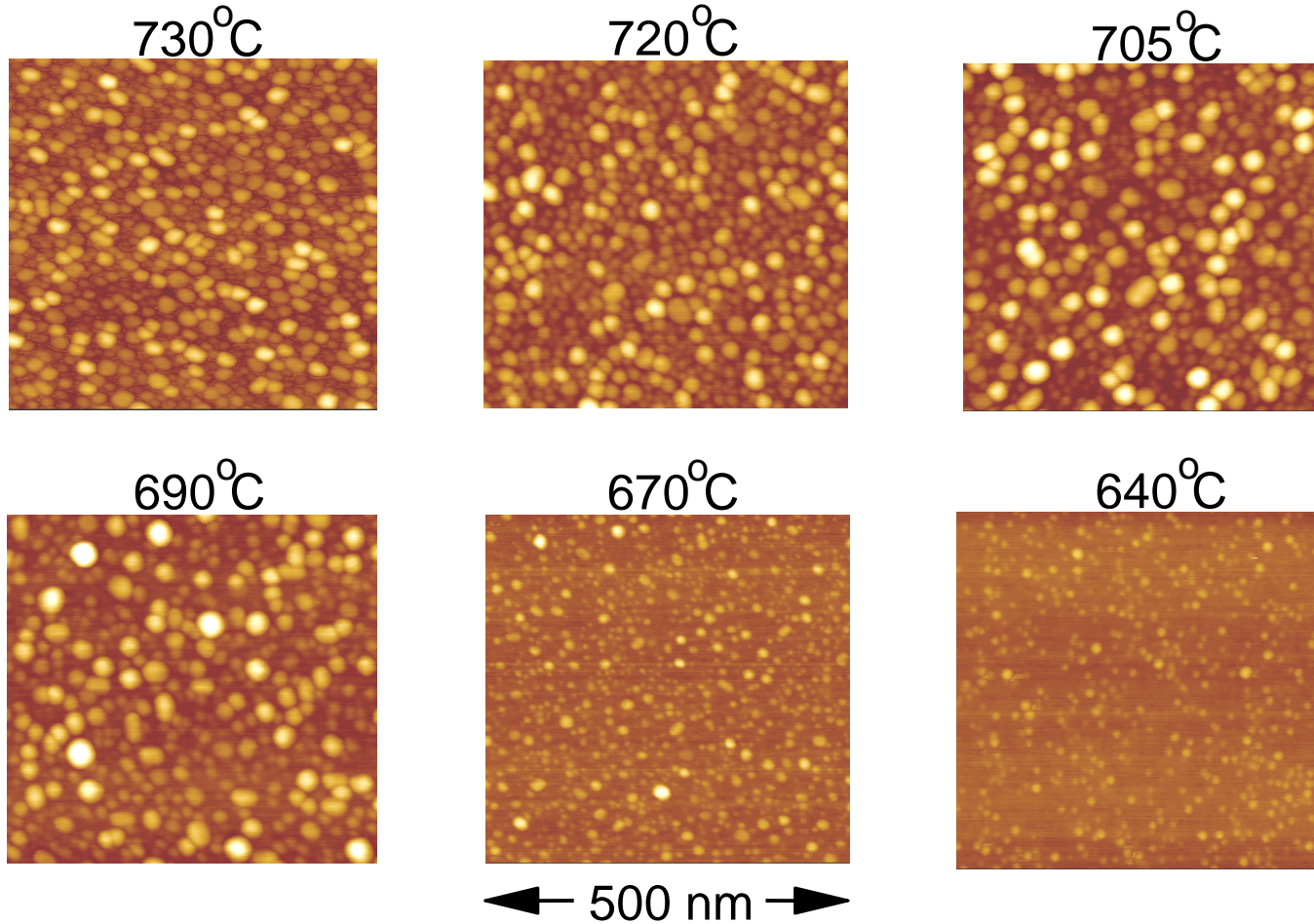
# Ti Deposition Rate



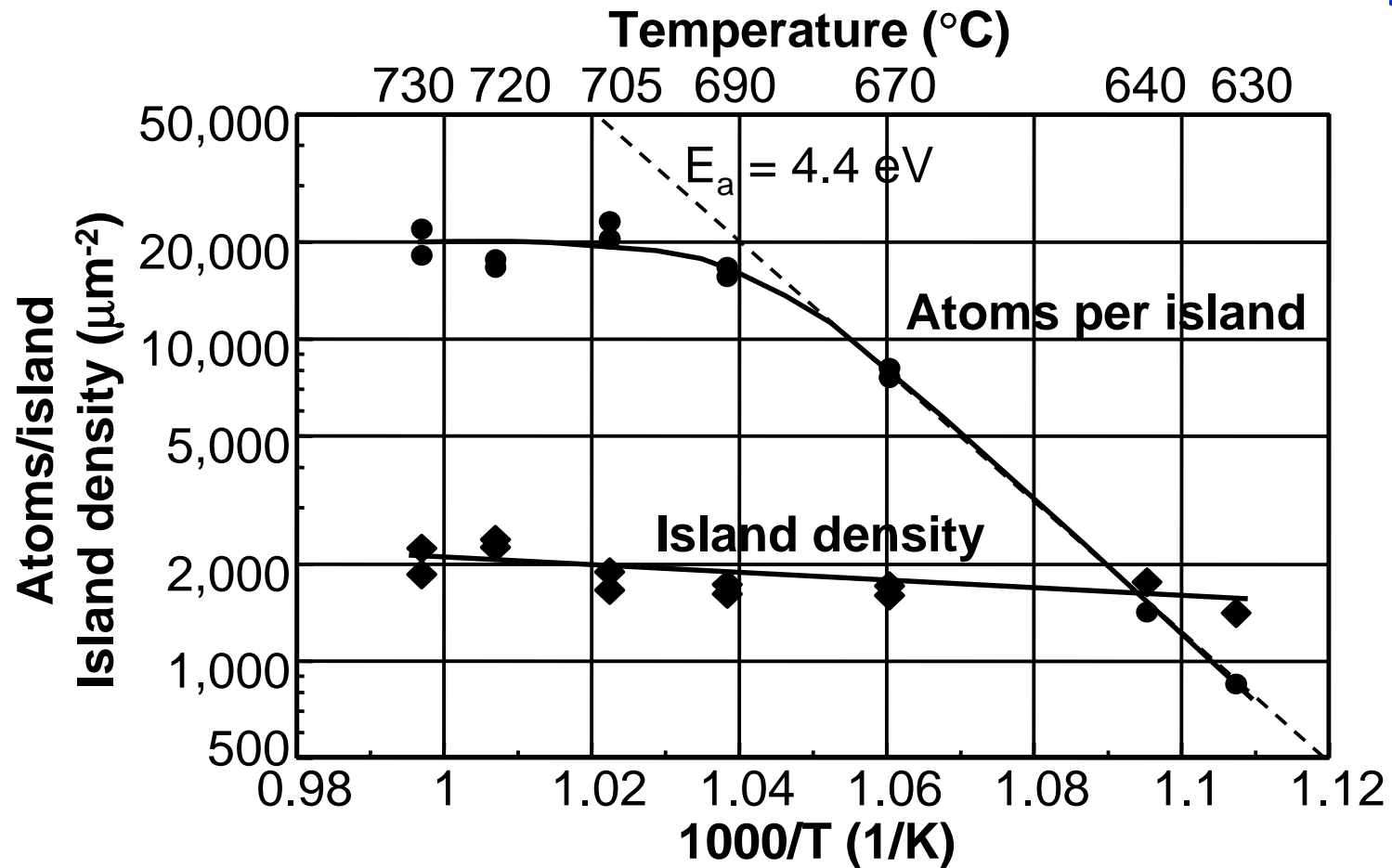
Controlled submonolayer deposition  
by varying deposition temperature  
(10 s depositions)

# Islands after Deposition

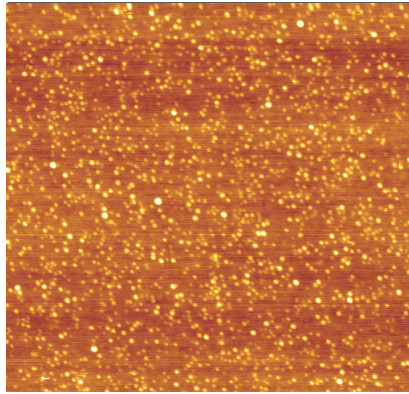
Large (7%) lattice mismatch → island formation



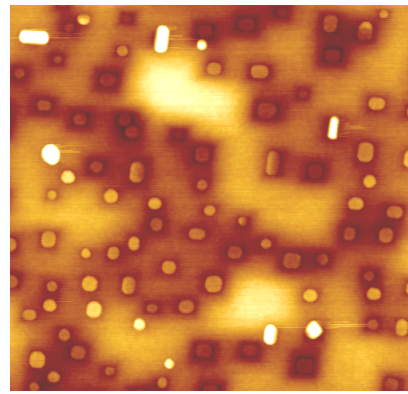
# Island Density and Size after Deposition



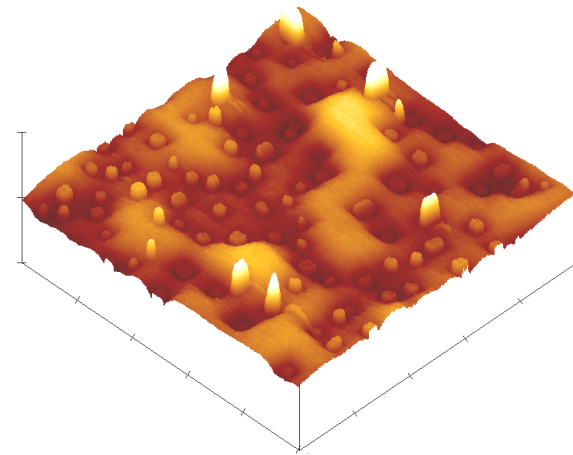
# Annealing of CVD $\text{TiSi}_x$ Islands



Deposition at 640°C



← 1.0 μm →



Annealing at 920°C

## During annealing

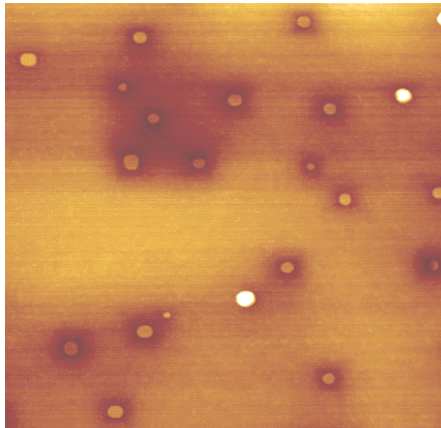
Amount of Ti on surface remains the same

Island density decreases

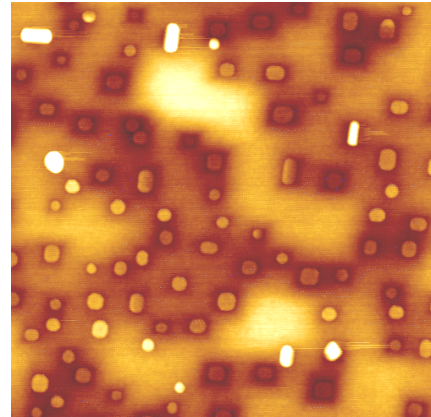
Islands take characteristic shapes



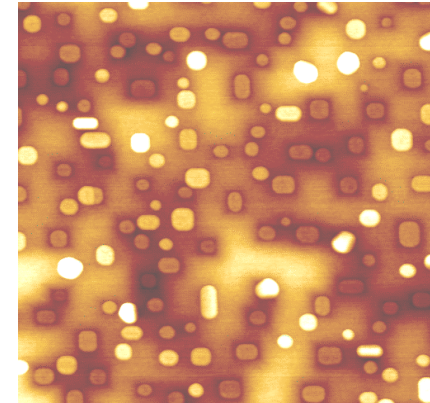
## Islands after Annealing TiSi<sub>2</sub> on Si(001)



$3 \times 10^{14}$  Ti/cm<sup>2</sup>



$1.5 \times 10^{14}$  Ti/cm<sup>2</sup>  
(1 μm × 1 μm images)

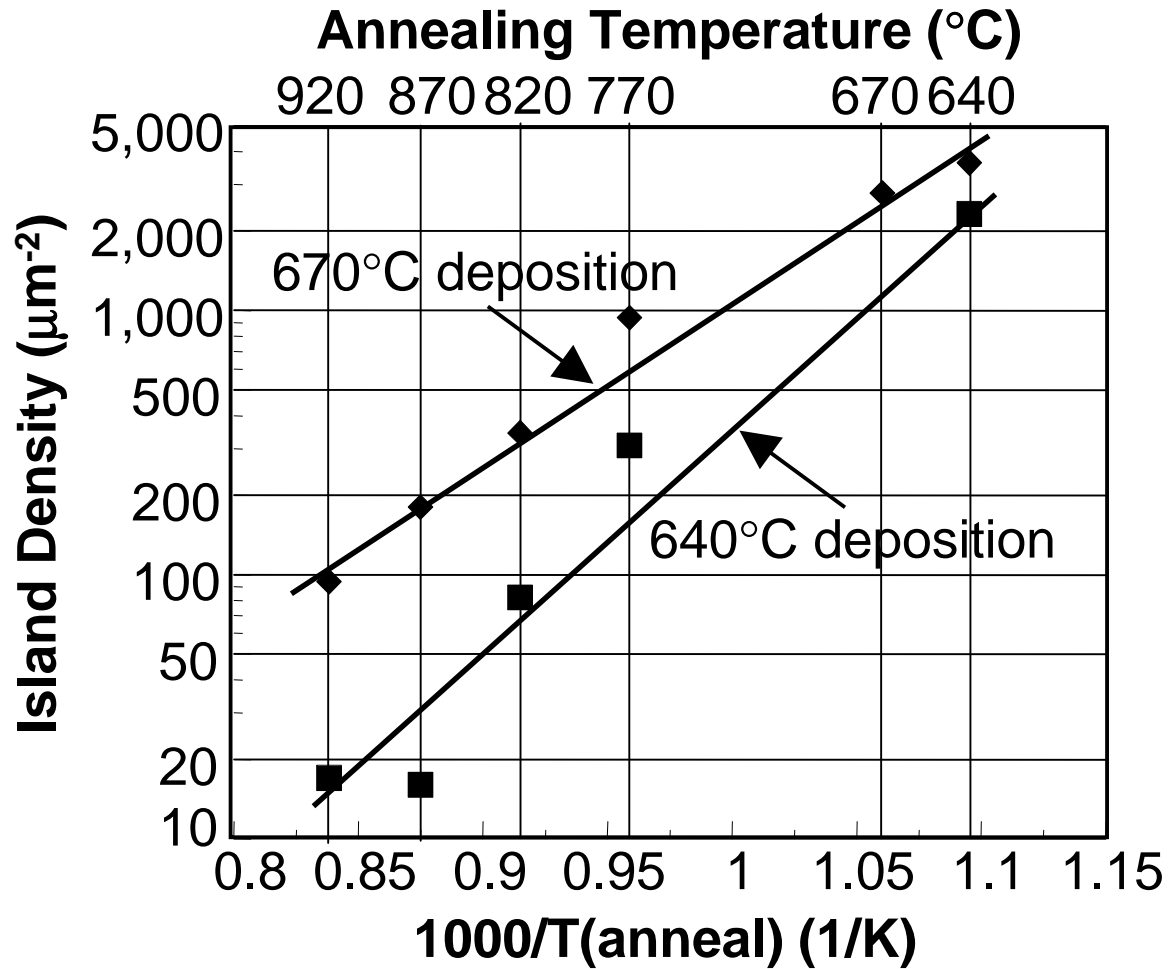


$3 \times 10^{15}$  Ti/cm<sup>2</sup>

### **After annealing**

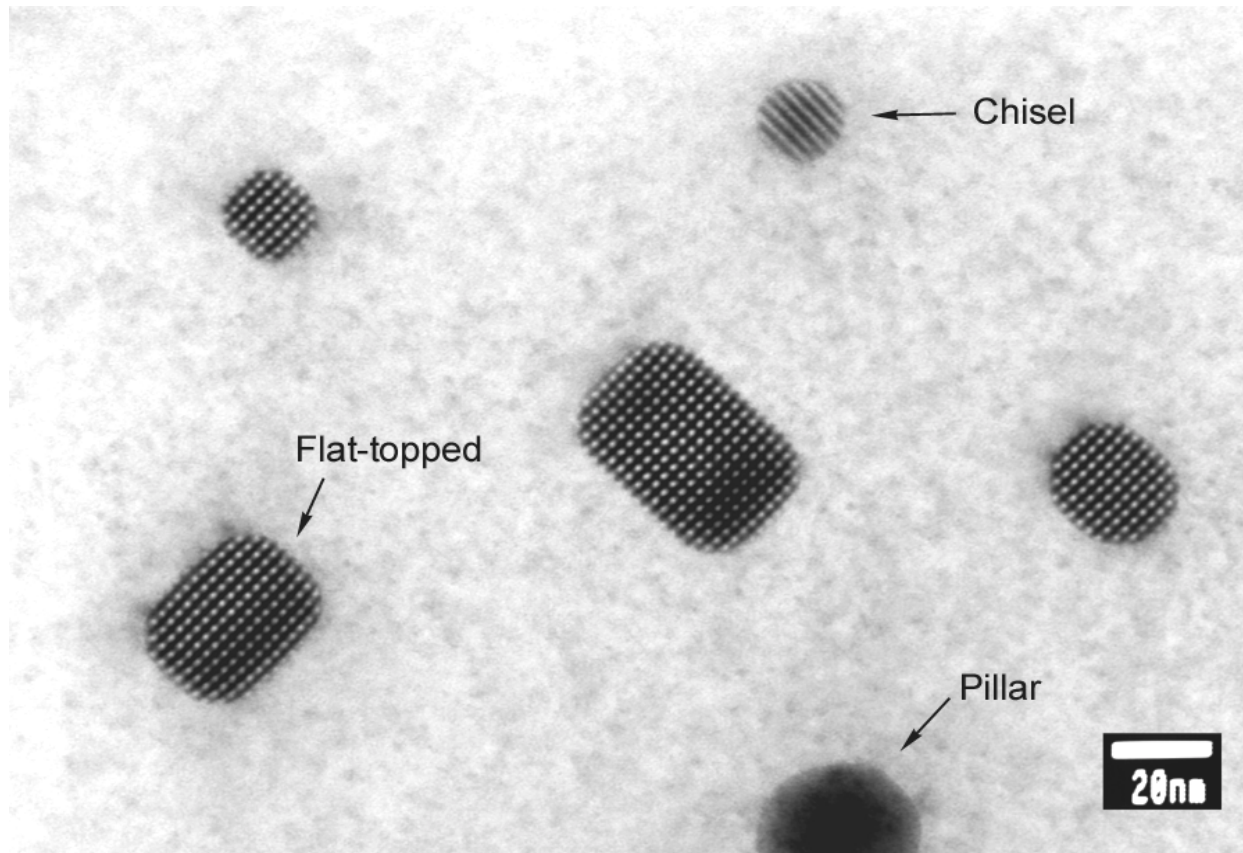
Island size depends only weakly on the amount of Ti  
Island density increases with increasing amount of Ti

# Island Density after Annealing



# Plan-View TEM: $\text{TiSi}_2/\text{Si}(001)$

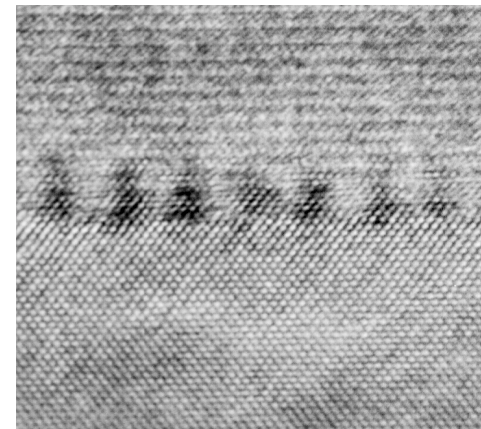
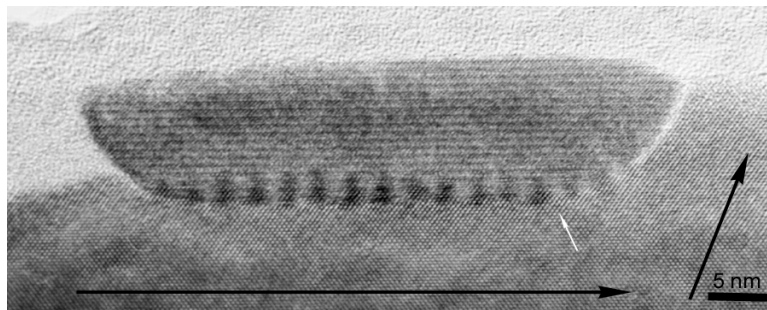
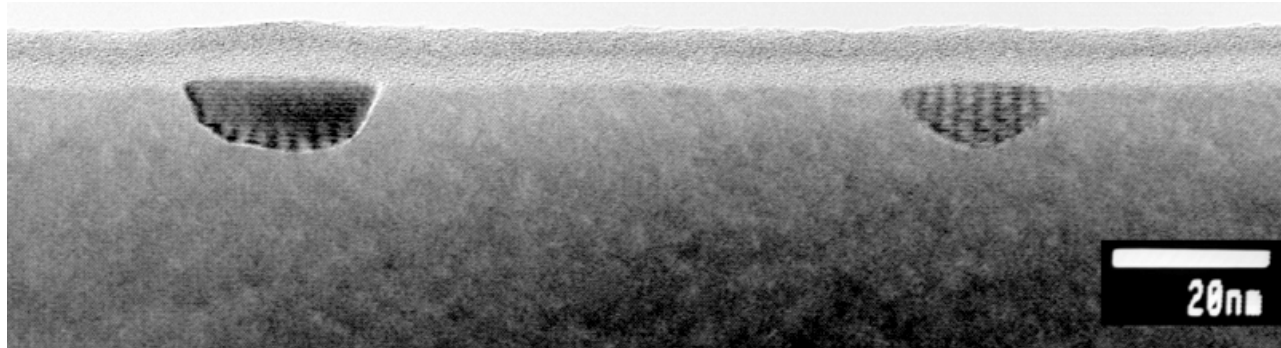
## Three Island Types



**Most numerous islands**  
Flat-top  
Square or rectangular  
Mostly recessed into  
surrounding surface  
(C49  $\text{TiSi}_2$ )

Transmission electron micrograph courtesy of  
D. P. Basile and M. Wong of Agilent Technologies

# Cross-Section TEMs: TiSi<sub>2</sub>/Si(001) Embedded Islands



Islands mainly recessed into the surrounding Si surface  
The period of the structure at the TiSi<sub>2</sub>/Si interface  
corresponds to the difference in lattice constant.

# Ti-Catalyzed Si Nanowires

Possible interconnections  
for molecular electronics

## Forming wires

### 1) Form nuclei

Expose to vapor  $\text{TiCl}_4$  at 600-700°C

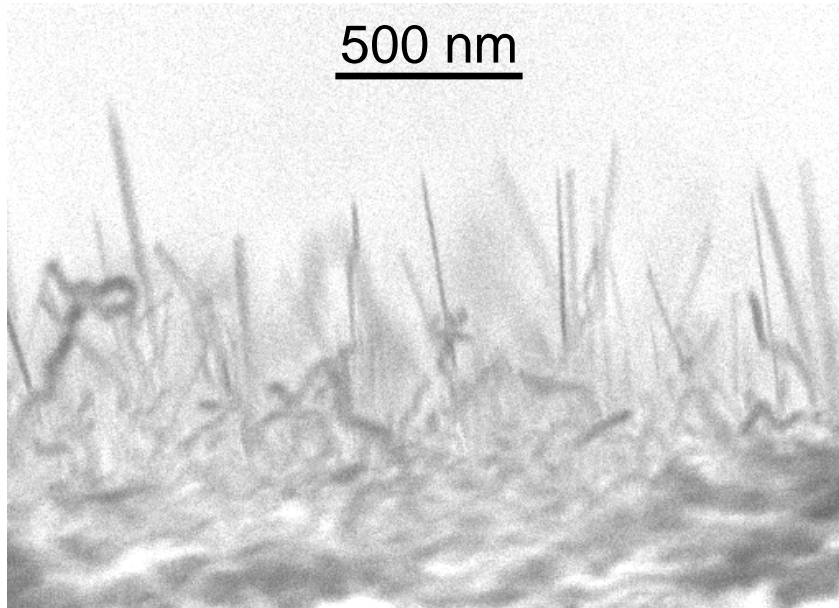
$\text{TiSi}_x$  islands form on Si(001)

by strain energy from lattice mismatch

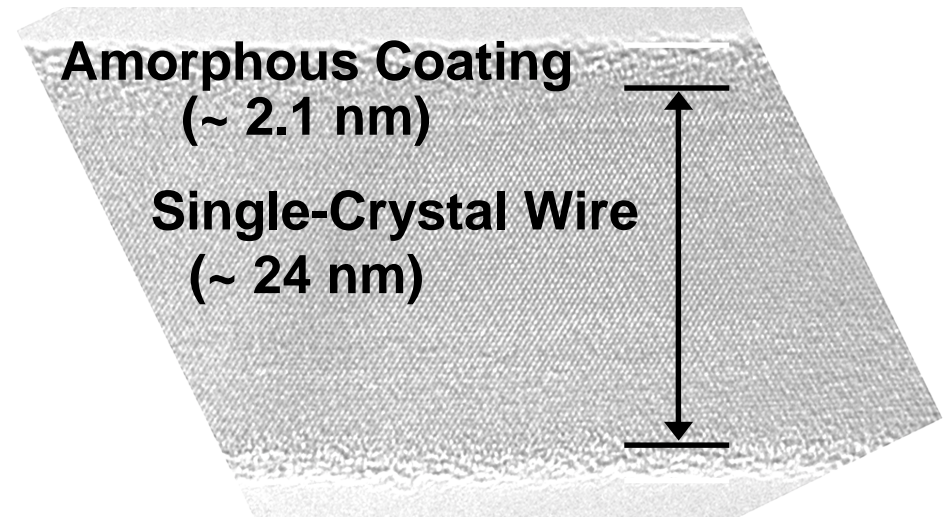
### 2) Form nanowires

Expose to vapor  $\text{SiH}_4$  or  $\text{SiH}_2\text{Cl}_2$  at 600-700°C

# Ti-Catalyzed Si Nanowires



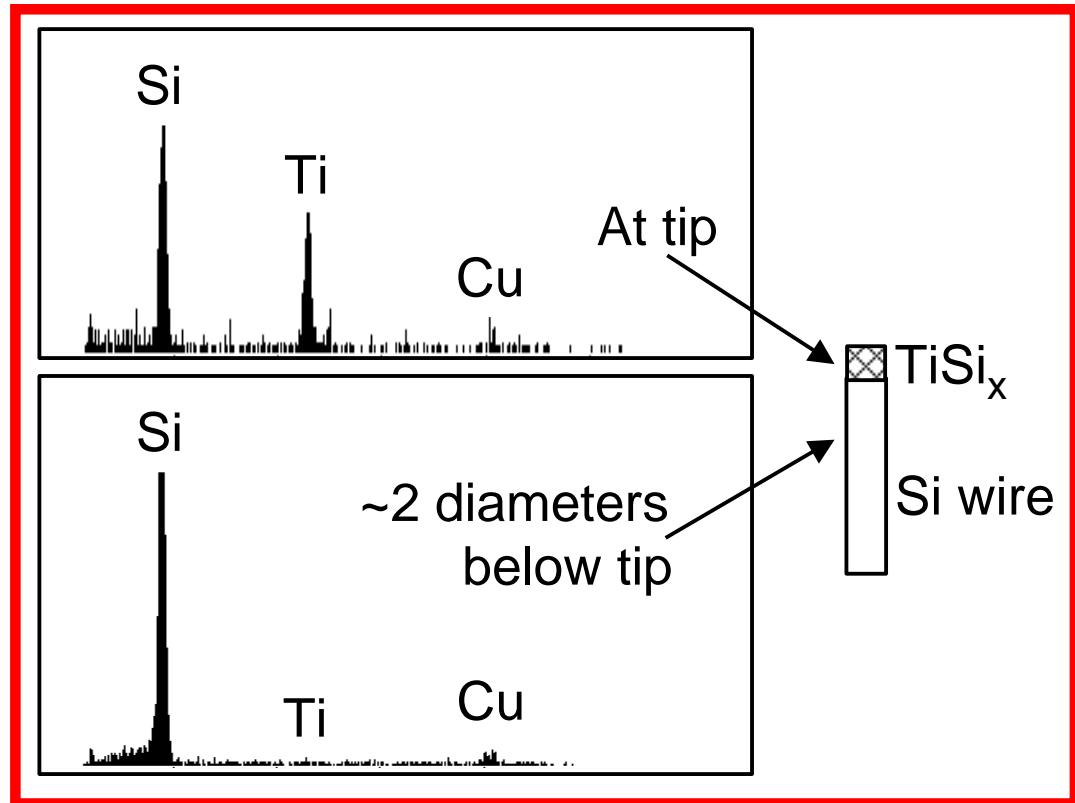
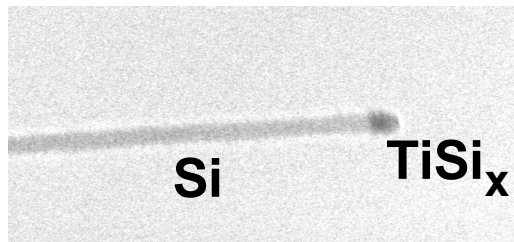
Shallow-angle scanning  
electron micrograph



High-resolution transmission  
electron micrograph

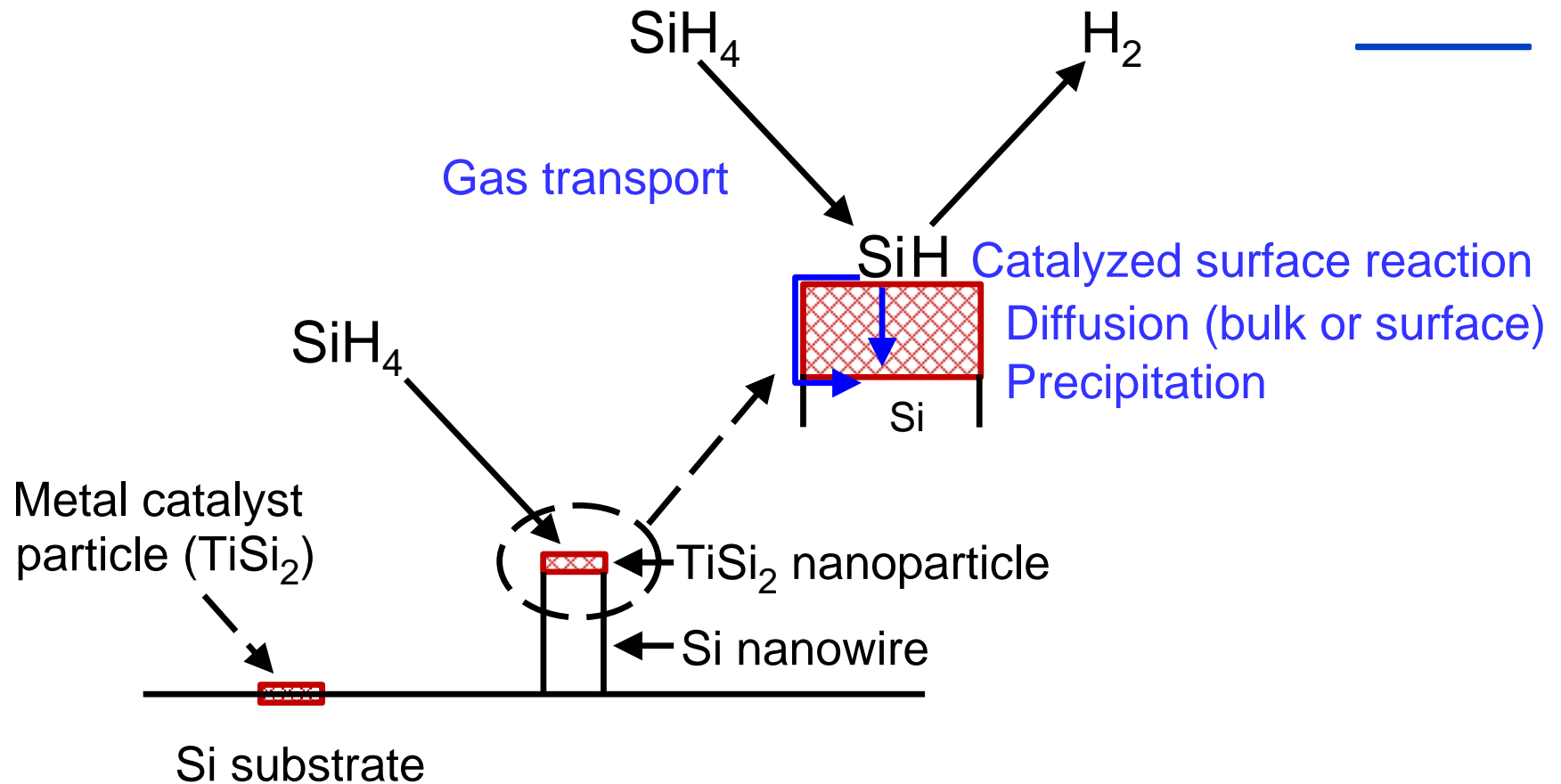
Micrographs courtesy of Tor Hesjedal  
Stanford University

# Single-Crystal Si Wire with $\text{TiSi}_x$ at Tip



EDS analysis courtesy of  
Tor Hesjedal, Stanford University, and  
David Basile, Agilent Technologies

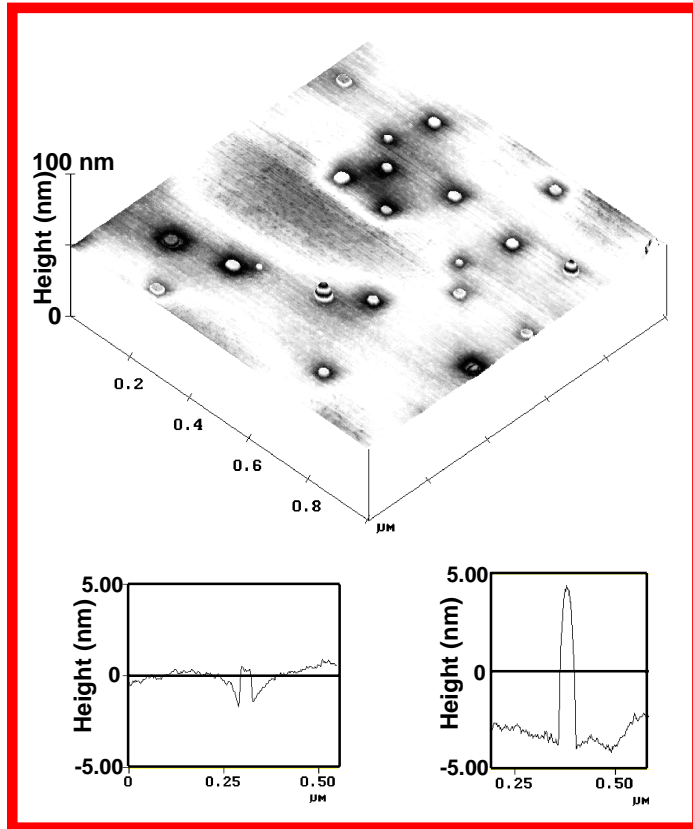
# Mechanism of Nanowire Growth



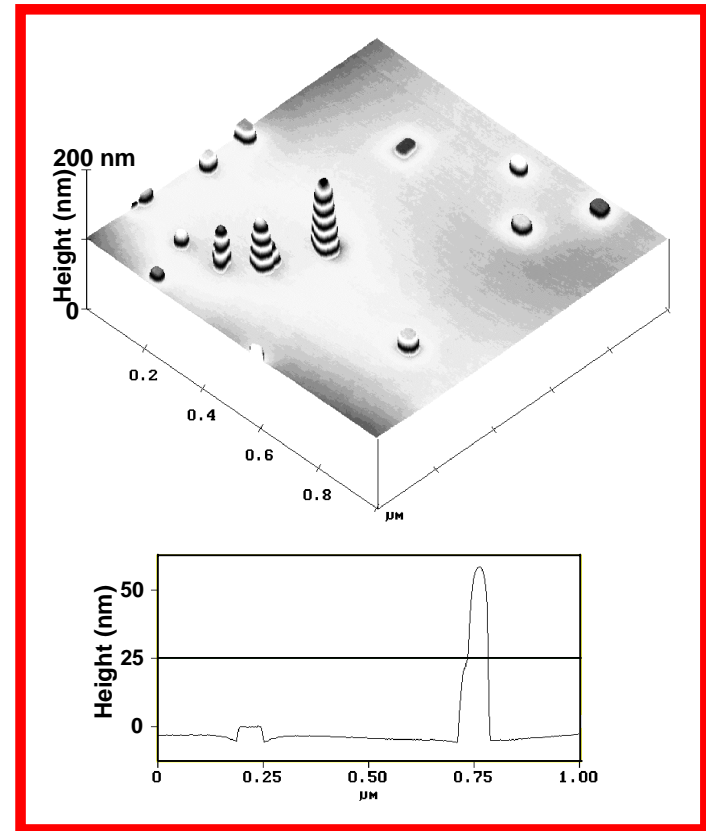


# Surface-Reaction-Rate-Limited Growth

## Initial Stage of Wire Growth



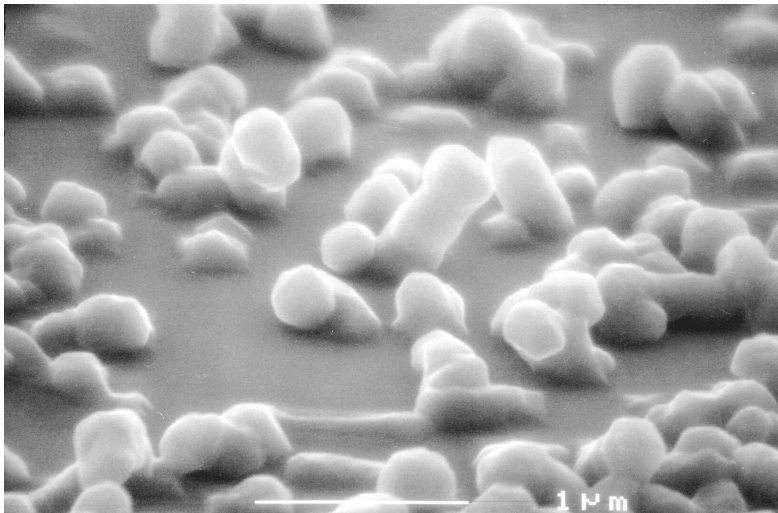
## Subsequent Stage of Wire Growth



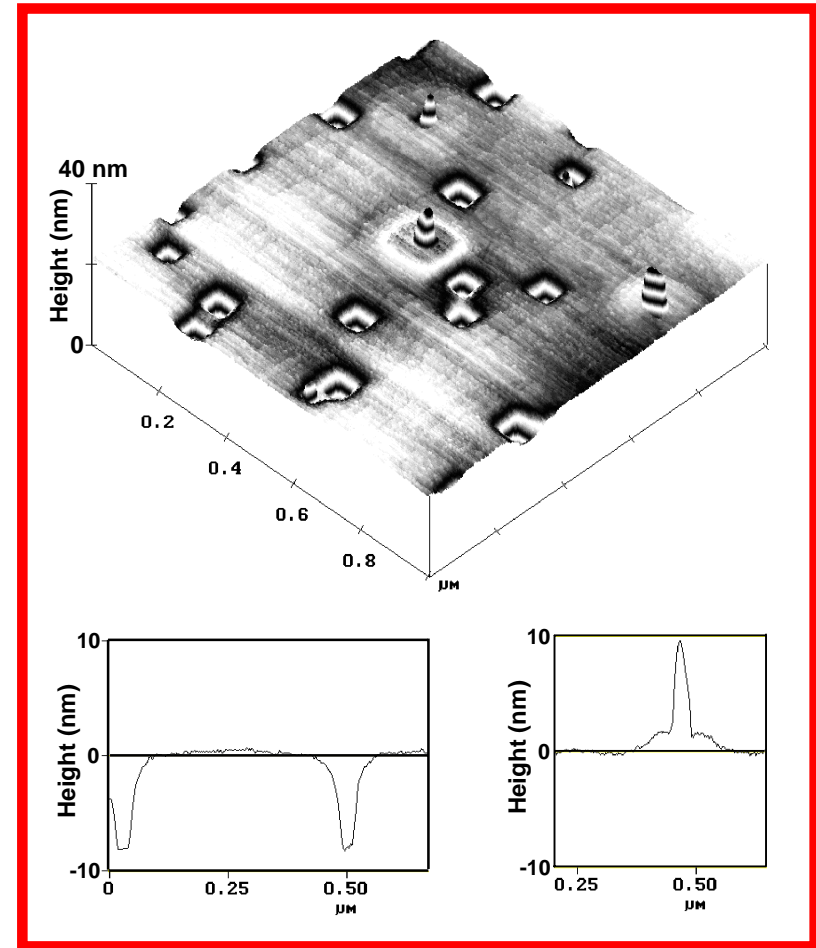
# Higher Temperature

Uncatalyzed growth rate significant

Surface-Reaction-Rate Limited  
 $\text{SiH}_2\text{Cl}_2$  at  $920^\circ\text{C}$

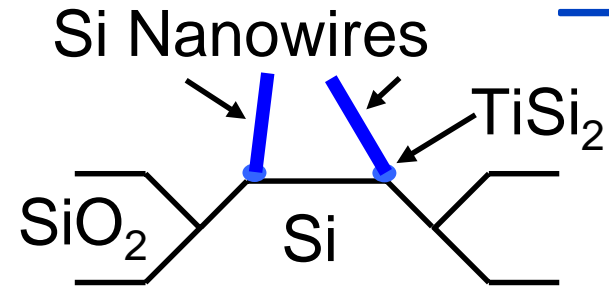
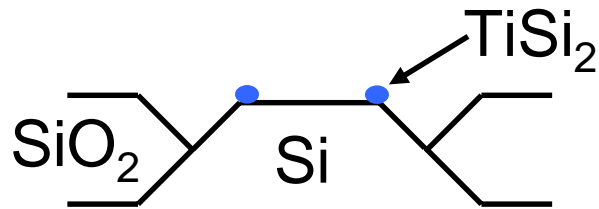


Mass-Transport Limited  
 $\text{SiH}_4$  at  $920^\circ\text{C}$

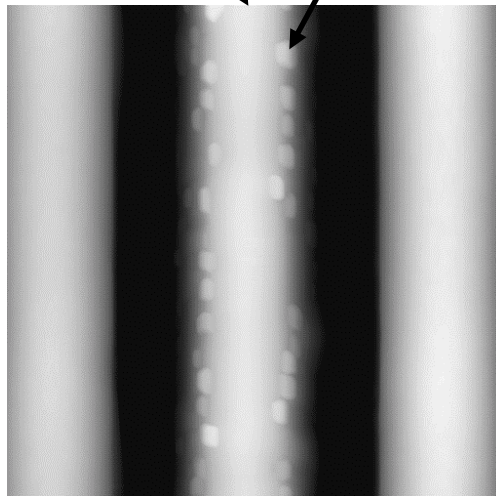


# Positioning Islands and Nanowires

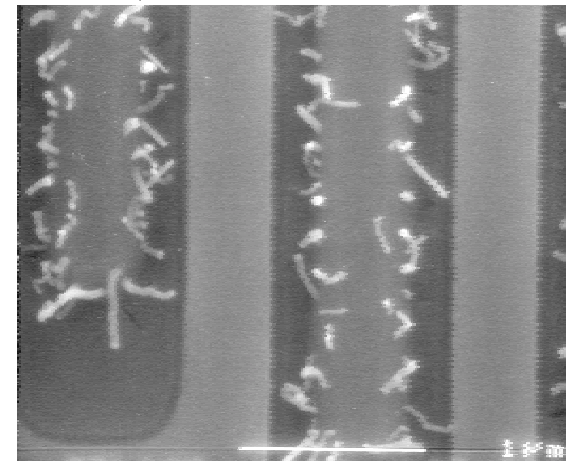
## Oxide-Patterned Si Substrate



Si TiSi<sub>2</sub> islands

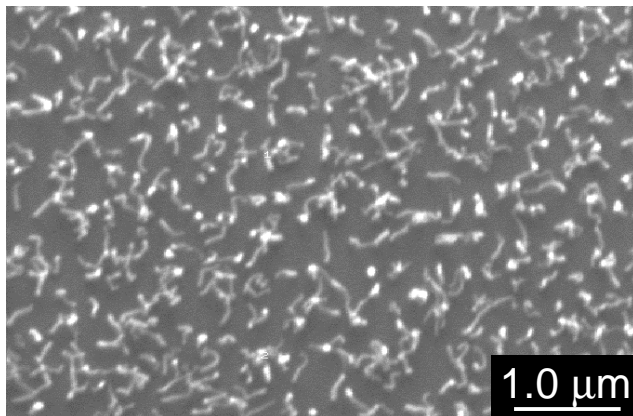
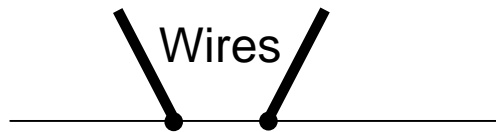


Si wires

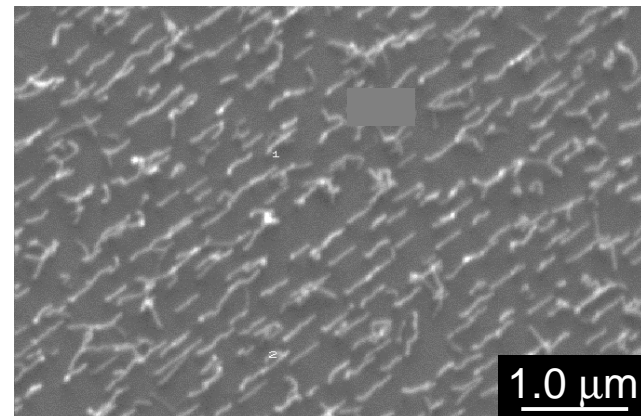
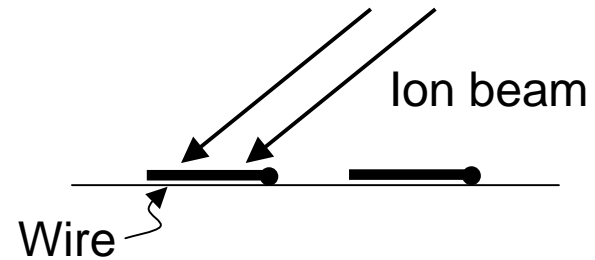


# Aligning Nanowires Using an Ion Beam

Sparse array:  
after deposition

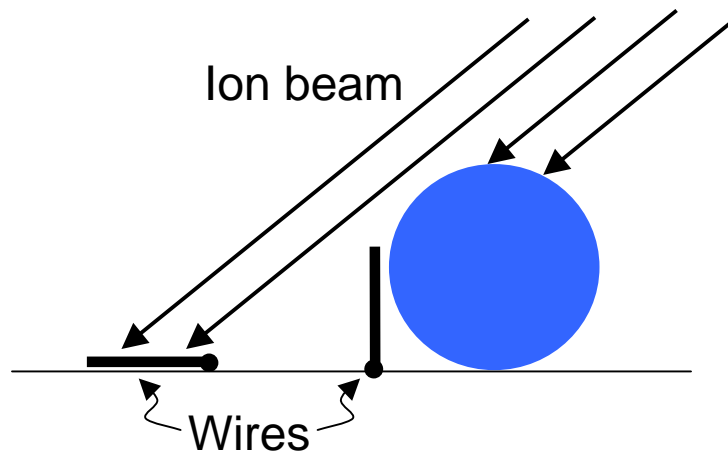


Sparse array:  
after alignment

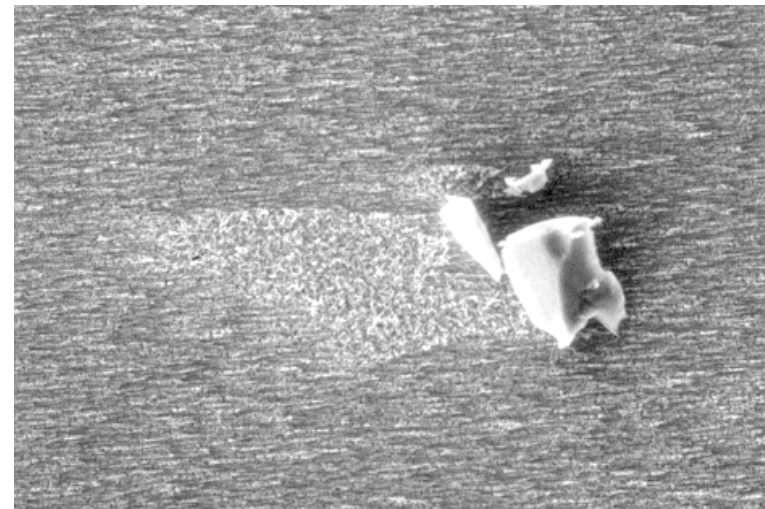


# Aligning Nanowires Using an Ion Beam

Shadowed wires



Dense array after shadowed alignment



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## Summary

- **Ti deposition**
  - Rate decreases as temperature decreases
- **Island formation** during deposition
  - Size decreases as temperature decreases
  - Density varies only weakly with temperature
- **Island modification** during annealing
  - Islands coarsen
- **Nanowire growth**
  - Ti catalyzes  $\text{SiH}_4$  and  $\text{SiH}_2\text{Cl}_2$  decomposition
  - Ti remains at tip of growing wire
- **Nanowire alignment** using an ion beam