Plan for Lectures #4, 5, & 6

Theme Of Lectures: Nano-Fabrication

- Quantum Wells, SLs, Epitaxial Quantum Dots
- Carbon Nanotubes, Semiconductor Nanowires
- Self-assembly and Self-organization

Two Approaches To Nano-Fabrication

Top-down ↔ Bottom-up

- lithography does the work
- let the atoms do the work

Emphasis Of These Lectures: Atomic Control in the Growth of Nanostructures

Classification of Nanostructures by Dimensionality

2D  Quantum wells, superlattices, L-B, membranes, ...
1D  Nanotubes, nanowires, nanorods, nanobelts, ...
0D  Nano dots from the gas phase (plasma)
    Strained epitaxial nano dots
    Colloids and nanoparticles by other methods
3D  Nanocomposites, filamentary composites, cellular materials, porous materials, hybrids, nanocrystal arrays, block co-polymers,
ZnO Nanowires on Al₂O₃

Park et al, APL 02  MOVPE DEZn, O₂, Ar
Initial LT Growth (coarsening) before 400-500°C growth.

catalyst-free

Quantum Wells & Superlattices

Si/Ge layers grown by MBE on relaxed SiGe(100)

High Resolution Transmission Electron Microscopy (TEM)

Diehl et al, Physica E 2003
Semiconductor Quantum Dots

Fabrication of Semiconductor Nanostructures

2D Quantum wells, superlattices, L-B, membranes, ...

1D Nanotubes, nanowires, nanorods, nanobelts, ...

0D Nano dots from the gas phase (plasma)

Strained epitaxial nano dots

Colloids and nanoparticles by other methods

3D Nanocomposites, filamentary composites, cellular materials, porous materials, hybrids, nanocrystal arrays, block co-polymers,

today’s lecture  next 2 weeks
**Pre-Growth Considerations**

- **What substrate to use?** (doping, surface orientation, wafer size, pre-pattern, surface cleaning, pre-treatment, etc.)
- **How to prepare the surface?** (in situ cleaning, buffer, surface composition, reconstruction, step management, characterization, etc.)
- **What structure to grow?** (composition, # layers, thickness, doping, morphology, defect level, etc.)
- **How to grow?** (equipment, growth technique, source material, growth rate, temperature, growth monitor, pressure, flow rates, etc.)
- **Additional processing?** (post-annealing, passivation, metallization, cap, etc.)
- Ex-situ processing, characterization of device and material quality.

**Special Considerations For Nanostructures**

**Surface Morphology**

- Strain
- Steps, kinks, islands, adatoms.
- Surface Energy
- Impurity stabilization
- Surface Structure & Diffusion Anisotropy
- Defects and Inhomogeneity
Molecular Beam Epitaxy (MBE)

Al Cho and John Arthur are given the credit for inventing the molecular beam epitaxy (MBE) technique.

An MBE system is essentially a very clean (UHV) deposition chamber with atomic level control, using (mostly) physical processes. Differentiations: Solid-source MBE, gas-source MBE, MOMBE, CBE, ...

Metal-organic Chemical Vapor Deposition (MOCVD)
Structure, Lattice Parameter, and Bandgap

Alloying often allows wide ranges of lattice constants and band gaps.

Common Substrates For Epitaxial Growth

Si(100): Substrate of choice for Si ULSI device.

GaAs(100): Convenient substrate for compound semiconductor devices (heterojunctions, optoelectronic devices, etc.)

Si(111): Popular substrate for epitaxial growth of assorted material. Has 7x7 reconstruction, rich in surface science studies. Cleavage surface.

Sapphire(0001): Insulating substrate for epi-growth.
Surface Preparation

Ex situ cleaning and etching
Thermal evaporation of oxide
Sputtering and annealing
Cleaving
H-termination
Buffer growth (MBE,...)

Surface Cleanliness

Auger Electron Spectroscopy (AES)

Fig. III.3a,b. Differential Auger electron spectra (dE/E) measured with a primary electron energy of 2000 eV on a GaAs(100) surface prepared by Metal-Organic Molecular Beam Epitaxy (MOMBE). (a) After the sample was transferred through an analysis chamber for AES analysis. This spectrum corresponds to the As-terminated surface. (b) After annealing to about 500°C the arsenic film is desorbed and the characteristic spectrum of the GaAs surface reappears, with very slight contamination due to N [III.4]

Fig. III.3. Schematic plot of a standard experimental set-up for Auger Electron Spectroscopy (AES). The primary electron beam is generated by an electron gun which is integrated on the central axis of a Cylindrical Mirror Analyzer (CMA). An additional sputter ion gun provides the possibility of depth analysis.
Surface Cleanliness

Low Energy Electron Diffraction (LEED) ~55eV
A- & B- NiSi$_2$ on Si(111)

Beam energy: ~20-200eV

Reconstruction of Si(100) Surface

Stacking sequence: -abcdabcd-
Alternating dangling bond direction.

from regions differing by odd number of planes

"2x1"
"1x2" plus "2x1"
Scanning Tunneling Microscopy (STM)

Fig. 6. Schematic diagram of a tunnelling microscope. A tungsten tip is scanned on a piezoelectric stage which moves the tip in the x-y plane of the sample surface, and in the z direction normal to the surface, with atomic resolution. The x and y positions that move the tip in the plane of the sample surface are driven by an x-y raster scan generator. The diameter of the sample is scanned along the z axis, normal to the sample surface, driven by a feedback position controller that attempts to maintain the tunnel current at a reference level by adjusting the tunnel gap width. By plotting the feedback voltage \( V_z \) as a function of the tip's x-y position on the surface, a scanning image of the surface is obtained.

Si(100) Dimer Rows

Swartzentruber et al, PRB 1993
Vicinal Si(100) Surface

Swartzentruber PRB 1993

Terraces and Steps on Si(100)

Type of Steps:
$S_A$, $S_B$, $D_A$, $D_B$

Calculations (Chadi):
$S_A$ more stable than $S_B$.
$D_A$ more stable than $D_B$.
$D_B$ more stable than $S_A + S_B$.

Note: dimer direction is perpendicular to dimer row direction!

Step A: upper terrace dimer rows are parallel to step
Step B: upper terrace dimer rows are perpendicular to step
Effect of Strain on the Stability of Si(100) Domains

![Graph showing the ratio of the intensity of the (1/2,0) and 60, 1 LEED beams to their values at zero strain plotted as function of the calculated surface strain. The data were measured at fixed position along the bar for various definitions of the sec. The domain compressed along the dimer bond is favored.](image1)

Men et al, PRL 1988

7x7 Reconstruction on Si(111)

![Graph showing the intensity of the (1/2,0) superlattice reflection as a function of time after applying and removing the external compressive stress. These data were taken at 350°C. The time constant is 114 ± 7 sec.](image2)

9 dimers
12 adatoms
19 dangling bonds
102 atoms first 3 layers

DAS model of Takayanagi
Reconstruction and Strain

Si(111) above ~850°C 1x1
Si(111) crystal surface 7x7
Si grown on SiGe (tensile) 5x5

Ge(111) crystal surface C(2x8)
Ge thin layer on Si (compression) 7x7
SiGe grown on Si (mild compression) 5x5

(2m+1)x(2m+1) reconstruction:
3m dimers, m(m+1) adatoms

Reconstructions on (111)
relieve compressive stress.
Most favorable reconstruction
depends on strain condition of semiconductor (layer).

Polar and Non-polar Surfaces (Comp. Semicond.)

GeAs (110) - (1x1)

Fig. 3.3a-d. Atomic positions of the GeAs(110) surface: ideal, non-reconstructed and relaxed as a space after cleavage in UHV. (a) Top view; the (1x1) unit mesh is printed as a broken line. (b) Side view. (c) Spheres model. Dark circles designate Ge atoms and shaded circles As. Smaller circles indicate deeper atomic layers.
Stoichiometry and Reconstruction on GaAs(100)

Farrell & Palmstrom JVST 1990

“2-by” due to As dimers
“by-2” due to Ga-dimers

Misorientation, Steps, Step Bunching, etc.

Si(111) 4° toward [112]

Phaneuf, et al PRL 1991

$T_o = 857°C$
Low Energy Electron Microscopy

Fig. 1. Schematic of the UHV surface microscope: (1) magnetic deflection field, (2) field emission electron gun, (3) quadrupoles, (4) beam forming lens, (5) cathode lens, (6) stigmator, (7) specimen, (8) screen, (9) intermediate lens, (10) projector lens, (11) filter lens (12) multi-channel plates, (13) TV camera, (16) beam alignment cells. For operation as an emission microscope a Hg lamp (14) and a conventional electron gun (15) are attached.

Ernst Bauer

LEEM Images of Si(100)

Tilt sample slightly toward [110] or [-1 10]
Proof of Wulff Construction

Let (one half of) the surface of a crystal with equilibrium shape be represented by $h(x,y)$, then the surface normal $\hat{n}$ is given by (up indicates unit vector)

$$\hat{n} = \frac{\nabla h}{|\nabla h|}$$

(1)

where $\partial x, \partial y, \partial z = -h\hat{x}, \hat{y}$. Therefore,

$$\hat{n} = \left( -\frac{\partial h}{\partial x} \hat{x} - \frac{\partial h}{\partial y} \hat{y} \right) + \sqrt{\left( \frac{\partial h}{\partial x} \hat{x} + \frac{\partial h}{\partial y} \hat{y} \right)^2 + 1}$$

(2)

An element of the surface area, $dA$, is given by

$$dA = \sqrt{\left( \frac{\partial h}{\partial x} \right)^2 + \left( \frac{\partial h}{\partial y} \right)^2 + 1} \, dx \, dy$$

(3)

The total surface energy, which must be minimized, is

$$\int h \, dA$$

(4)

and the constant volume constraint is

$$\int \hat{n} \, dA = \text{constant}$$

(5)

This is a typical problem which can be solved by Lagrange's undetermined multiplier method. The solution is

$$h = \lambda \left( x^2 + y^2 + z^2 + \sigma \left( \frac{\partial h}{\partial x} \hat{x} + \frac{\partial h}{\partial y} \hat{y} \right)^2 + 1 \right)^{-\frac{1}{2}}$$

(6)

where $\lambda$ is a constant (multiplier). Since a radius vector to any point on the equilibrium surface is

$$\hat{r} = x \hat{x} + y \hat{y} + z \hat{z}$$

(7)

one can combine Eqs. (2), (6), and (7) to arrive at

$$\hat{r} \cdot \hat{n} = \lambda \sigma$$

(8)

which simply describes the condition that $\hat{r}$ lies on the inner envelope of the Wulff construction.
Si Equilibrium Crystal Shape

FIG. 1. The equilibrium shape of Si. Typical annealed void shape imaged in high resolution down [110] axis. Void is small enough to be completely enclosed in transmission electron microscopy cross section. Note flat [111] facets and rounded [100] facets, and curved facet intersections at [100] and near [311].

Eaglesham et al PRL 1993

Steps and Adatoms: Key to Surface Dynamics

FIG. 2. The surface energy per unit length for Si. Surface energy ratio extracted by reverse Wulff construction from voids such as that in Fig. 1. Averaged over three particles and symmetrized on the assumption that [110] and [001] are both mirror planes.
Adatoms and Step Fluctuation

STM image of the Si(001)-(2 × 1) showing the fluctuations of step edges at 693K. Size= 300 × 300 Å Frame Rate= 1/31 sec.

E. Ganz, Univ. Minn.

Island Coarsening

Assume spatial variation of chemical potential for adatoms.

FIG. 1. LEEM images of rippling of single atomic layer height islands on Si(001) at various times after the temperature was increased to 650°C (a) 91 s, (b) 293 s, (c) 684 s, and (d) 1040 s. Alternate dark and bright regions denote islands in the same atomic plane (bitter site). The field of view is 23 μm.

Bartelt et al, PRB 1996
Fluctuation In Island Shape

STM images showing the fluctuations of islands at 620K. The edge rows of islands fluctuate the fastest, and when fluctuations at one's two ends cross, the row disappears. Due to the sticking anisotropy, it is then difficult to nucleate a new row, and the island shrinks. Note that the small lower right hand island disappears all together. Size= 350 × 350 Å
Frame Rate= 1/32min.

E. Ganz, Univ. Minn.

Equilibrium Island Shape

FIG. 1. Evolution of 2D Si island size and shape on an extremely large (10×15 μm²) single-domain Si(001) terrace during very slow, near-equilibrium, chemical beam epitaxy of Si at 855°C. The time after observing island nucleation is given in seconds. The island shape evolves with increasing island size, from initially elliptical to "American-football"-like and eventually with 2D faceting (swallow tail at t=72 s) for island diameters larger than 6 μm. The field of view is 9 μm. The frame at t=19 s shows part of one long mesa edge (gray area at lower left); the base terrace extends beyond the field of view in all other frames. Inhomogeneities in the image (bright area at the corner of the terrace) are due to imperfect focus and inhomogeneities in the channel plate.

field of view: 9μm

There is a finite density of “adatoms” on the terraces of a surface. The higher the temperature, the higher the adatom concentration. Some adatoms are not visible in STM.

Adatoms are continuously captured and released by the steps. Adatoms have a finite desorption rate, which increases with temperature.

Adatoms can be captured by “defects”, and they can group together to form islands.
Si(100): Dimer Diffusion Along Row

STM images showing the diffusion of a single dimer along a dimer row at 410K. This is composed of empty state images, so the surface rows appear dark and the troughs appear bright. The dimer's orientation flips between parallel and perpendicular to the rows (types A and B respectively) while it progresses along the row; however, at this temperature the two orientations are indistinguishable. Size= 166 × 166 Å Frame Rate= 1/18sec.

E. Ganz Univ. Minn.

Ehrlich-Schwoebel Barrier

Fig. 16. Simple models of atomic diffusion are based on the idea of discrete hops between preferred binding sites as shown here. (However, diffusion by an exchange mechanism in which one atom displaces a neighbor is also known to be a lower-energy path in many cases.) On the terraces, the binding sites might be on-top, bridge or hollow sites. In this illustration, the binding sites are assumed to have the same spatial periodicity as the substrate atoms (which would not be the case for instance for bridge bonding), and a simple activation barrier $E_{\text{act}}$ for hopping between sites. In moving onto a step bonding site (which may have many possible binding configurations), from the upper step-edge, it is physically reasonable to assume that the activation energy involves a lower-coordination than for hopping on the terrace, and thus will have a higher activation energy, $E_{\text{act}}$. It might also be assumed that hopping onto the step from the lower terrace would involve a somewhat more accessible activated state, and thus a slightly lower activation energy $E_{\text{act}}$. Calculated values of activation energies near steps are listed in Table 6.

Ehrlich and Schwoebel (independently) proposed that it was more difficult for adatoms to hop down a step.
Deposition (\(=\)Adding Adatoms)

\[
\text{Supersaturation} = \frac{\text{deposition rate}}{\text{desorption rate}}
\]

At a Si deposition rate of 0.4nm/s, the supersaturation varies from \(4.4 \times 10^3\) at 950°C to \(3 \times 10^{16}\) at 450°C.

Understanding Growth At The Atomic Level

We need control on the atomic level, in order to grow nanostructures.

Pre-existing Steps And Adatoms

\[ x^2 \frac{\partial^2 \varphi}{\partial y^2} - \varphi + \tau_y v \frac{\partial \varphi}{\partial y} = 0 \]

BCF Theory (Burton, Cabrera, and Frank)

low supersaturation - step flow

Fig. 1. (a) Scheme of a monocrystalline surface with low-index planes separated by misorientation steps. (b) Moving coordinate system used in Sect. 1

Fig. 4a and b. Supersaturation difference \( \varphi \) as a function of \( \delta / \delta_y \) for \( \delta_y = 4 \) (a) and \( \delta_y = 20 \) (b) and for various \( \delta \) values

Homoeptaxial Growth On Si(111)

Tung PRL 1989

Fig. 3. Plan-view TEM micrographs illustrating the initial stages of Si homoeptaxial growth at 650°C. (a) A substrate with a small misorientation toward [112]. (b), (c) Surfaces after the deposition of 1- and 2-ML Si, respectively, on this substrate. (d) A substrate with a small [111] misorientation; (e), (f) the topographies after the deposition of 1- and 2-ML Si, respectively.

2 -1 -1 steps preferred over 1 1 -2 steps
Step Flow vs. Nucleation on Terraces

Tung PRL 1989

FIG. 2. Dark-field TEM images of CoSi$_2$ layers grown on Si surfaces after Si MBE growth. (a) Substrate surface, and (b)-(f) surfaces after the growth of 50-Å Si at a rate of 0.5 Å/s. Deposition temperature was (b) 750°C, (c) 650°C, and (d) 550°C. (a)-(d) were imaged with $g = [220]$

Reflection High Energy Electron Diffraction (RHEED)

Fig. VIII-4. (a) Schematic of the experimental set-up for RHEED. The inset shows two different scattering situations on a highly enlarged surface area: surface scattering on a flat surface (below) and bulk scattering by a three-dimensional crystalline island on top of the surface (above). (b) The Ewald sphere construction for RHEED. $k$ and $k'$ are primary and scattered wavevectors, respectively. The sphere radius $k - k'$ is much larger than the distance between the reciprocal lattice rods $(hk)$. For more details, see Sect.4.2 and Figs.4.2,3
RHEED From GaAs(100)

Fig. 3. RHEED patterns recorded during growth in the [130] (a, c) and [110] azimuth (b, d) at growth conditions leading to a (2 x 4) (a, b) and a (4 x 2) reconstruction (c, d), respectively. Growth parameters: (a, b) \( T_g = 625°C, \text{BEP}_{As} = 40, \text{BEP}_{Ga} = 3 \); (c, d) \( T_g = 704°C, \text{BEP}_{As} = 40, \text{BEP}_{Ga} = 3 \).

Nucleation of Steps (high supersaturation) RHEED Oscillation

Fig. 1. Intensity oscillations of the specular beam in the RHEED pattern from a GaAs (100)–2 x 4 reconstructed surface, [110] azimuth. The period exactly corresponds to the growth rate of a single Ga + As layer and the amplitude gradually decreases. Note that the marked reflections at the beginning and end of growth result from ambient light changes as the shutters are opened and closed.
RHEED Oscillations During Si MBE

FIG. 1. RHEED intensity oscillation on Si(111) taken from (111) azimuth, $T_s = R.T., 300 \degree C$, and $800 \degree C$.

FIG. 2. RHEED intensity oscillation on Si(100) taken from various azimuths, $T_s = 400 \degree C$.

Preferential Nucleation Of Islands

“Anti-Phase Domain Boundary”
**Si Growth On Si(100) Terraces**

STM images showing the growth of islands at 533K. Coverage increases from 0 to 0.1 ML at a rate of approximately 0.01 monolayers deposited per frame. The movie begins with the clean substrate before deposition. At this temperature 1-D islands form and coalesce. Size= 800 × 800 Å Frame Rate= 1/33min.


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**Roughening Of Surface Morphology**

Island nucleation growth mode of Si on Si(001) (T = 575 K, F = 0.6 Ml/h, 250 Å × 250 Å) The straight $S_1$ and the rough $S_3$ steps run horizontally. The terraces, divided by the monatomic steps, descend from the top to the bottom of the image. In (b), nucleation of elongated islands is observed. During further growth three open layers are observed on each terrace; one layer being closed, one main growing layer, and one layer with islands nucleating on the growing layer. The coverages in images (b)-(f) are 0.34, 0.67, 1.02, 1.34, and 1.67 ML, respectively.
Heteroepitaxial Growth Issues

Lattice mismatch, misfit dislocations, strain inhomogeneity, other strain-related issues

Dissimilar structure, symmetry-related defects, interface energy, nucleation issues, ...

Inter-diffusion, segregation, phase separation, ...

Interface dipole, valence mismatch, ...

Common Lattice Matched Systems

<table>
<thead>
<tr>
<th>Al</th>
<th>Ga</th>
<th>In</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>5.45</td>
<td>5.45</td>
</tr>
<tr>
<td>As</td>
<td>5.62</td>
<td>5.65</td>
</tr>
<tr>
<td>Sb</td>
<td>6.13</td>
<td>6.12</td>
</tr>
</tbody>
</table>

*All have the zincblende structure. The side of the conventional cubic cell (in angstroms) is given.

GaAs ⇔ AlAs
InP ⇔ InGaAs
GaSb ⇔ InAs
GaN ⇔ AlN (wurtzite)