Preparation of Clean, Well-Defined Surfaces

- There are several methods.
  - Not all methods are performed in ultra-high-vacuum, but many do use, or are performed in, UHV

**Methods**

1. crystal cleaving in UHV (or in solution)
   - useful but limited

2. sputtering and/or annealing
   - also limited to certain types of surfaces

3. epitaxial growth
   - most versatile with many technological applications
   - new material is deposited
   a. molecular beam epitaxy
   b. chemical beam epitaxy
   c. metal-organic chemical vapor deposition
   d. pulsed laser deposition
   e. sputtering
Surface Preparation

1. Cleaving
   - Works well for specific sample types
   - Requires brittle samples
   - Limited to only certain crystalline orientations

Since this can be done in UHV using mechanical manipulators ➔ clean, fresh surface(s) of interest (2)

Typically this method is used for semiconductors or insulators

One excellent application is to prepare large, atomically-flat semiconductor surfaces:

- (110) surfaces of III-V semiconductors such as GaAs(110), InP(110), etc.
  - in the zinc-blende structure

- (110) surface is non-polar so cleaves very easily
other semiconductor applications:

- Si(111) and Ge(111) prepared nicely by cleaving.
- Fresh-cleaved Si(111) has 2x1 superstructure (and Ge(111))
- Annealing leads to Si(111) 7x7 superstructure periodicity or Ge(111) 2x8 " " in diffraction.

- Also alkali halides
  - NaCl
  - KCl
  - ...

- Some oxides as well
  - ZnO (wurtzite)
  - TiO₂
  - SnO₂
An Excellent Application of Cleaning:

Cross-Sectional Scanning Tunneling Microscopy of Semiconductor heterostructures and homostructures

This is due to the fact that the (110) surface is perpendicular to the (001) epitaxial growth direction.

**Method**

1. Begin with epitaxial structure grown by, for example, molecular beam epitaxy (MBE).

   ![Diagram of semiconductor wafer and epilayer](image)

2. Cut the epilayer into approximately sized small pieces.

   - This can be done by hand or more efficiently using a dicing saw.

   ![Diagram of dicing saw](image)
3. Create a cleaning scratch or notch, but not all the way across the epilayer. The cleave will propagate from the point of nucleation (notch or scratch mark).

4. Mount the piece in a sample holder.

5. Load sample/sample holder into UHV chamber.

6. Cleave the sample by pushing on piece.

7. Place sample into microscope.
4 Unit Cell GaAs/2 Unit Cell AlAs
Short Period Superlattice

(a)

(b)

vertical average

missing unit cell

(c)

single

"Dilute" (Al)GaAs

Smith et al., APL 69, 1214 (1996).
2. Ion Bombardment and Annealing

- Ion bombardment: to remove surface contamination
- Annealing: to restore the surface structure

**Bombarding**
- Oxygen "kicked out"
- Oxide or contamination layer

**Annealing**
- Rough or disordered surface
- Restructured, smooth, mirror-like, atomically well-ordered
Bombardment / Annealing

- to get a good surface, sometimes many cycles are required
- annealing sometimes causes bulk impurities to diffuse to the surface

- advantage: the same sample surface can be refreshed over and over again, often just be annealing without further sputtering

- useful for elemental samples
  
  single element
  
  - noble metals (Au, Cu, Ag, ...)
  
  - other metals (Fe, Mo, ...)
  
  - elemental semiconductors (e.g., Si, Ge)

- disadvantage: not very effective for compound samples such as GaAs, or GaN
  
  - reason is that it is not possible to control or maintain the surfaces stoichiometry, which is the ratio between different elements e.g. Ga : N ratio
3. **Epitaxial Growth Methods**

- Very versatile, flexible
- Many technological applications
- Use to produce clean, smooth surfaces of elemental or compound materials with various crystalline orientations
- Can control the surface stoichiometry
- Applicable to metals, semiconductors, oxides, ...
- Can control impurity levels — doping
- Can grow multi-layer "heterostructures" and "homostructures"
- Can control growth with atomic-layer precision

The most famous and versatile of these epitaxial growth methods is:

**Molecular Beam Epitaxy (MBE)**
Sample is mounted on a sample holder using either metal clips or metal bonding, typically.

- Clip method: very useful but possible to contaminate sample surface by touching it with clip.
- Mo typical or Ta clip
- Typical Indium bonding
- Water held on by surface tension if it melts
- Too high Temp → it may not work

H. Lüth, Surfaces and Interfaces of Solid Materials, p. 48 (3rd Ed.)
MBE

- Surface growth occurs through arrival of atoms and/or simple molecules at the surface with a controlled flux rate $\Gamma$

  \[ \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \]

  Sample is often heated during growth $\Rightarrow$ heating $\Rightarrow$ surface diffusion

- The growth rate is dependent on the flux dosage

  unit of dosage is the Langmuir

  \[ 1 \text{ Langmuir} = \text{dosage corresponding to exposure of surface for 1 second to a gas pressure of } 10^{-6} \text{ Torr} \]

  or, e.g., for 100 s at $10^{-8}$ Torr
a layer-by-layer growth means that the next layer begins after the current layer is completed.
The flux at sample in molecular beam epitaxy begins with:

\[
\Gamma = \frac{P}{2m\langle v \rangle}
\]

\[
\langle v \rangle = \sqrt{\frac{3kT}{m}}
\]

\[
\rightarrow \Gamma = \frac{P}{2\sqrt{3mkT}} \quad \text{Flux at liquid-vapor interface}
\]

\[
\text{sample}
\]

\[
\text{divergence of flux leads to geometrical factor of}
\]

\[
\frac{a}{\pi L^2}
\]

\[
\rightarrow \Gamma = \frac{pa}{2\pi L^2 \sqrt{3mkT}}
\]

\[
\Gamma \approx \frac{pa}{\pi L^{3/2} \sqrt{2\pi mkT}}
\]
Note that the $p$ is $p(T)$ where $T$ is the temperature of the liquid melt.

Vapor pressure vs. liquid melt temperature

![Log-log plot]

$P \quad (\log \text{scale})$

$T \quad (\log \text{scale})$

Typical curve

Example:

From our experience, we get a flux at the sample of about

$$\Gamma = 2 \times 10^{-4} \text{ /cm}^2 \text{s}$$

Let's calculate the expected flux assuming Ga liquid surface is $T_{Ga} = 950^\circ \text{C}$.

From vapor pressure table:

$\text{Ga: } 950^\circ \text{C} \rightarrow p(950^\circ \text{C}) = 2 \times 10^{-4} \text{ atm}$
Question:
Can you determine the flux based on the measured film growth rate?

⇒ Yes! or at least the part of flux which was incorporated into the film - the total incident flux could be larger.

i.e. measuring the film thickness in Å (t)
and the growth time is T (T)

⇒\[ \text{growth rate } \Gamma = \frac{t}{T} = \frac{\text{Å}}{\text{s}} \]

Then we just need to know the number density of the flux atoms in the layer, \( n \)

\[ n = \frac{N}{V} \text{ = ideally units of } \frac{\text{Å}^{-1}}{\text{cm}^2 \text{Å}} \]

⇒ \( \Gamma \times n = \frac{t}{T} \times n = \frac{\text{Å}}{\text{s}} \times \frac{1}{\text{cm}^2 \text{Å}} = \frac{\text{Å}^{-1}}{\text{s}} = \Gamma \)

Example: Sc atoms in ScN

rocksalt structure

conventional cube is 4.50 Å on cube edge

and contains 4 Sc atoms \( 4.50\text{Å} = 4.50 \times 10^{-8} \text{cm} \)

⇒ \( n = \frac{4}{(4.50 \times 10^{-8}\text{cm})^3(4.50 \text{Å})} = 4.39 \times 10^{-4} \text{ Å}^{-2} \text{s}^{-1} \)