Semiconductor Processing and Characterization Techniques: Crystal Structure and Crystal Growth

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Planar Processing with Semiconductors (Silicon): Course Map

- Crystal growth (semiconductors)
- Wafer doping (*in situ*)
- Wafer characteristics
- SiO₂ growth*
- Defects and impurities

- SiO₂ growth*
- Lithography
- Masked diffusion doping
- Vacuum Systems
- Thin Films: CVD, MBE, PVD, ALD
- Implantation
- Wet and Dry Etching
- Integration
Why are semiconductors useful?
Why is Silicon an important semiconductor and why is it so popular in planar processing?

• 26% by mass of Earth’s crust

• Over 90% of Earth’s crust is silicate materials.
Silicon is abundant

*from P.H. Stauffer et al, Rare Earth Elements - Critical Resources for High Technology, USGS (2002)
A brief introduction to crystal structure

Crystal Structure = Lattice + Basis
Crystals—Periodic Structures
Different carbon crystals can have markedly different properties.
A crystal—lattice of a repeating motif (basis)
A brief introduction to crystal structure

Crystal Structure = Lattice + Basis

A lattice is defined by a set of fundamental translation vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, such that the atomic arrangement looks the same from the perspective of both $\mathbf{r}$ and $\mathbf{r}'$, where

$$\mathbf{r}' = \mathbf{r} + u_1 \mathbf{a}_1 + u_2 \mathbf{a}_2 + u_3 \mathbf{a}_3$$

and $u_1, u_2, u_3$ are arbitrary integers.
The basis

Lattice?

Basis
Cubic lattices

(a) Simple cubic
(b) Body-centered cubic
(c) Face-centered cubic
A few examples of cubic lattices

Salt is FCC with basis containing one Na and one Cl.

Diamond is FCC with two identical basis atoms:

All group IV elements can crystallize into diamond, including C and Si.
Index system for crystal planes

Crystal planes are identified using Miller indices in the following way:

1. Find the intersection of the axes in terms the basis of the fundamental translation vectors $a_1, a_2, a_3$.
2. Take the reciprocal and reduce to three integers having the same ratio, usually the smallest three integers. The result is enclosed in parentheses $(hkl)$ and called the index of the plane. Negative integers are denoted with bars $(\overline{hkl})$.

Also, planes equivalent by symmetry are denoted with braces $\{hkl\}$.

- The set of cube faces is $\{100\}$.

The indices $[uvw]$ of a direction in a crystal are the set of the smallest integers that have the ratio of the components of a vector in the desired direction.

- The $a_1$ axis is the [100] direction, the $-a_2$ axis is the [010] direction.
- **NB:** In cubic crystals, the direction $[hkl]$ is perpendicular to the plane $(hkl)$ having the same indices.
Index system for crystal planes

Plane intercepts the vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ axes at $3\mathbf{a}_1, 2\mathbf{a}_2, 2\mathbf{a}_3$. Reciprocals of these numbers are $\frac{1}{3}, \frac{1}{2}, \frac{1}{2}$. Small integers having the same ratio are 2, 3, 3, thus indices of the plane are (233).
Examples of indexed crystal planes

Si (100)

Si (111)
Crystal Growth: Silicon and Gallium Arsenide

Advantages of Si

- Cheaper
- More stable and less defects, better for Very Large Scale Integration (VLSI)
- Bigger wafers (12”)
- SiO₂
- Higher hole mobility (for CMOS)
- Pure element, easier to make

Advantages of GaAs

- Higher electron mobility
- Higher saturation velocity
- Good for μwave electronics (250GHz)
- Direct Band Gap: emits and absorbs efficiently; for LEDs, Lasers, and PVs
- Can make AlₓGa₁₋ₓAs which allow HEMTs.
- Harder to grow large crystals (2” wafers)

• How we make single-crystal Si and GaAs?
• How we shape into wafers?
• Characteristics of wafers
• Epitaxial Growth and Defects
Growth of Single-crystal Silicon
Manufacture of high purity polycrystalline Silicon using the Siemens Process

$\text{SiC (solid)} + \text{SiO}_2 (\text{solid}) \rightarrow \text{Si (solid)} + \text{SiO (gas)} + \text{CO (gas)}$

98% pure MGS, which is then pulverized

$\text{Si (solid)} + 3\text{HCl (gas)} \xrightarrow{300^\circ C} \text{SiHCl}_3 (\text{gas}) + \text{H}_2 (\text{gas})$

Forms trichlorsilane (boils at 32 C), which is then distilled for hydrogen reduction

$\text{SiHCl}_3 (\text{gas}) + \text{H}_2 (\text{gas}) \rightarrow \text{Si (solid)} + 3\text{HCl (gas)}$

Produces very pure polycrystalline EGS on a heated Si rod in chamber (Siemens Process.) Impurity range is in ppb
Manufacture of single-crystal Silicon using the Czochralski (CZ) technique
The CZ crystal puller

[Diagram showing the CZ crystal puller with labeled parts: Front opening door, Seal, Argon, Front opening chamber, Seed holder, Seed, Valve, Viewing port, Seed shaft, Vacuum pump, Optical system, Argon, Silica crucible, Graphite susceptor, Graphite heater, Thermal shield, Crucible shaft, CW, Ar + SiO + CO, CCW.]
Wafer size projections

The bigger, the cheaper?
In situ doping of Silicon
Doping profiles of Silicon ingots

The concentration of dopant in liquid and solid phases of Si is not the same and changes during growth.

The equilibrium segregation coefficient:

\[ k_0 = \frac{C_s}{C_l} \]

Equilibrium concentrations

<table>
<thead>
<tr>
<th>Dopant</th>
<th>(k_0)</th>
<th>Type</th>
<th>Dopant</th>
<th>(k_0)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>(8 \times 10^{-1})</td>
<td>(p)</td>
<td>As</td>
<td>(3.0 \times 10^{-1})</td>
<td>(n)</td>
</tr>
<tr>
<td>Al</td>
<td>(2 \times 10^{-3})</td>
<td>(p)</td>
<td>Sb</td>
<td>(2.3 \times 10^{-2})</td>
<td>(n)</td>
</tr>
<tr>
<td>Ga</td>
<td>(8 \times 10^{-3})</td>
<td>(p)</td>
<td>Te</td>
<td>(2.0 \times 10^{-4})</td>
<td>(n)</td>
</tr>
<tr>
<td>In</td>
<td>(4 \times 10^{-4})</td>
<td>(p)</td>
<td>Li</td>
<td>(1.0 \times 10^{-2})</td>
<td>(n)</td>
</tr>
<tr>
<td>O</td>
<td>1.25</td>
<td>(n)</td>
<td>Cu</td>
<td>(4.0 \times 10^{-4})</td>
<td>(-^a)</td>
</tr>
<tr>
<td>C</td>
<td>(7 \times 10^{-2})</td>
<td>(n)</td>
<td>Au</td>
<td>(2.5 \times 10^{-5})</td>
<td>(-^a)</td>
</tr>
<tr>
<td>P</td>
<td>0.35</td>
<td>(n)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a^{Deep-lying impurity level.}\)

\(k_0 < 1\) means dopants are rejected by solid Si into the melt, so concentration in melt increases during growth. Also, if \(C_l\) increase, then \(C_s\) will too.
How does an increasing/decreasing dopant concentration in the liquid ($C_l$) affect the dopant concentration ($C_s$) in a growing Si crystal?
Doping distribution of Silicon ingots during growth

\[ C_s = k_0 C_0 \left(1 - \frac{M}{M_0}\right)^{k_0 - 1}. \]
Effective Segregation Coefficient

During crystal growth, the dopant can accumulate near the liquid-solid interface and cause a dopant concentration gradient ($k_0 < 1$):
How can we model the system to account for the stagnant layer?

Mass transport by diffusion and drift
Single-crystal Silicon via the Float-zone process
Equilibrium dopant concentration in the Float-zone process
Doping profiles in Float-zone Si ingots

\[ \frac{C_x}{C_0} = 1 - (1 - k_e)e^{-k_x x/L} \]
\[ C_0 = 1 \text{ for all curves} \]
Doping profiles in Float-zone Si ingots
Doping uniformity of fractional transmutated Si

(a) Conventionally doped silicon

(b) Neutron irradiated silicon
Single crystal Growth of GaAs

Zinc blend: like diamond but two different atoms in basis; **FCC**

Challenges with growing GaAs:

- Complicated phase diagram of binary compound.
- **As** has high vapor pressure (evaporates easily, doesn’t like staying in liquid phase); can begin evaporating before GaAs melts.
Phase diagram for GaAs
Vapor Pressure of As and Ga

Water at 100 °C
GaAs Crystal Growth

- Czochralski Method with $\text{B}_2\text{O}_3$ liquid encapsulation.
- Bridgman:
  - Sealed Quartz ampule in two-zone furnace
  - As at 620 °C to keep As overpressure.
  - GaAs melt held just above melting point of 1240 °C.
  - Zones move to allow crystallization
  - Forms 2-3 “ wafers.
Wafer shaping and characteristics

Steps
1. Grind surface to some diameter.
2. Grind flats along length of ingot for identification.
3. Wafer is sliced with diamond saw
4. Lapping and polishing.
Identification flats

{111} \textit{n-type}

{111} \textit{p-type}

{100} \textit{n-type}

{100} \textit{p-type}
Typical wafer specifications

<table>
<thead>
<tr>
<th>Parameter</th>
<th>125 mm</th>
<th>150 mm</th>
<th>200 mm</th>
<th>300 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (mm)</td>
<td>125±1</td>
<td>150±1</td>
<td>200±1</td>
<td>300±1</td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>0.6–0.65</td>
<td>0.65–0.7</td>
<td>0.715–0.735</td>
<td>0.755–0.775</td>
</tr>
<tr>
<td>Primary flat length (mm)</td>
<td>40–45</td>
<td>55–60</td>
<td>NA(^a)</td>
<td>NA</td>
</tr>
<tr>
<td>Secondary flat length (mm)</td>
<td>25–30</td>
<td>35–40</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Bow (μm)</td>
<td>70</td>
<td>60</td>
<td>30</td>
<td>&lt; 30</td>
</tr>
<tr>
<td>Total thickness variation (μm)</td>
<td>65</td>
<td>50</td>
<td>10</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Surface orientation</td>
<td>(100) ± 1°</td>
<td>Same</td>
<td>Same</td>
<td>Same</td>
</tr>
<tr>
<td></td>
<td>(111) ± 1°</td>
<td>Same</td>
<td>Same</td>
<td>Same</td>
</tr>
</tbody>
</table>

\(^a\)NA: not available.

RMS roughness < 1 μm
CVD Basics
Basic Processes in CVD
Basic Processes in CVD

Important Processes:
- Kinetics
- Gas phase (homogeneous) reactions
- Surface (heterogeneous) reactions
- Mass transport phenomena
Reaction Kinetics

First order reaction (thermal): \[ \mathcal{R} = kC_B \]

where \[ k = k_0 \exp\left(-\frac{E_{a,f}}{RT}\right) \]

Energy

Reaction coordinate
Mass Transport vs. Surface Reaction

Arrhenius Plot

- Mass transport control: \( \propto h_g C_g \)
- Transition: \( \propto k_s C_g \)
- Reaction control: \( \propto \frac{k_s C_g}{T} \)

Growth rate (um/min)

Temperature (°C)

1300 1200 1100 1000 900 800 700 600

Eversteyn

- \( \text{SiH}_4 \)
- \( \text{SiH}_2\text{Cl}_2 \)
- \( \text{SiHCl}_3 \)
- \( \text{SiCl}_4 \)
Thickness Measurement Ellipsometer
Polarized Light

Light – electromagnetic radiation; transverse electric and magnetic fields

\[ E_y \]
\[ E_x \]

Linearly Polarized
Circularly Polarized
Thickness Measurement Ellipsometer

- The ellipsometer is used to measure the thickness and refractive index of transparent films.
- It is made of a light source and polarizer on one side and a analyzer and detector on the other side.

- Light from the source is polarized and reflected off the film.
- The analyzer is rotated till no light passes through it.
- The angle of rotation depends on the thickness and optical constants of the film.