Lecture 2: Crystal Growth

The topics covered the following:
Review of Crystal Structures and Properties
Basic Techniques to grow single-crystal ingots
Wafer Shaping
Wafer Characterization – electrical, physical
Modeling Wafer Growth
Periodic Structures

- A crystalline solid is distinguished by the fact that the atoms making up the crystal are arranged in a periodic fashion. There is some basic arrangement of atoms that is repeated throughout the entire solid.

- Not all solids are crystal; some have no periodic structure at all – *amorphous solids*, others are composed of many small regions of single-crystal material – *polycrystalline solids*.
Structure of Solids (3D View)

- **Crystalline**
  - All atoms are arranged on a common lattice.

- **Amorphous**
  - All atoms are disordered (no lattice).

- **Polycrystalline**
  - Different lattice orientation for each grain.
Crystal Lattice

- The periodic arrangement of atoms in a crystal is called **lattice**.
- The lattice contains a volume called a **unit cell**, which is representative of the entire lattice and is regularly repeated throughout the crystal.
- The smallest unit cell that can be repeated to form the lattice is called a **primitive cell**.
- From the unit cell the distance between nearest atoms and next nearest atoms can be found for calculating the forces holding the lattice together. The density of the solid and the atomic arrangement can also be known by looking at the fraction of the unit cell volume filled by atoms.
Simple Cubic Lattice

- Atoms per cell: $8 \times \frac{1}{8} = 1$
- No. of nearest neighbors: 6
- Nearest neighbor distance: 1
- No. of 2nd nearest neighbors: 12
- 2nd nearest neighbor distance: $\sqrt{2a}$

e.g., Polonium
Body Centered Cubic (BCC) Lattice

- Elements with BCC lattice: Cr, Fe, K, Li, Mo, Na, Ta, and W.
Face Centered Cubic (FCC) Lattice

- Elements with FCC lattice: Al, Ag, Ca, Cu, Ni, Pb, and Pt.
Diamond Lattice

- Two interleaving FCC cells offset by 1/4 of the cube diagonal form the lattice.

- Atoms in diamond lattice have four nearest neighbors (covalent bonds).
Zincblende Lattice

- Similar to diamond lattice, except that the lattice contains two different types of atoms.
- Each atom has four covalent bonds, but bonds with atoms of the other type.
Miller Indices

- Miller Indices are a symbolic vector representation for the orientation of an atomic plane in a crystal lattice and are defined as the reciprocals of the fractional intercepts which the plane makes with the crystallographic axes.
Miller Indices of a plane

- Establish the coordinate axes along the edges of the unit cell.
- Note where the plane intercepts the axes.
- Divide each intercept by the unit cell length along the respective coordinate axis.
- Record the normalized intercepts in x,y,z order.
- Compute the reciprocal of each intercept.
- Multiply the intercepts by the smallest overall constant that yields whole numbers.
Miller Indices: Example

- Normalized intercepts: 1, 2, 3
- Reciprocals: 1, 1/2, 1
- Multiplier is 6
- Miller indices for this plane: (6, 3, 2)
Miller Indices: Special Cases

- When plane does not intersect an axis, the intercept is infinity and the Miller index is zero.

- Place a bar over negative intercept.
- Miller indices: \((2,2,1)\)

- When plane does not intersect an axis, the intercept is infinity and the Miller index is zero.
- Miller indices: \((1\ 0\ 1)\)
Crystal Planes

(1,0,0) planes
- Different chemical and electrical properties.
  e.g.: oxidation rate, interface density >
  capacitances and currents.

(1,1,1) planes
Crystal Growth

- Starting with pure form of sand (SiO₂) called quartzite. It is placed in a furnace with various forms of carbon to produce MGS with purity of 98%.
  \[ \text{SiC(solid)} + \text{SiO}_2\text{(solid)} \rightarrow \text{Si(solid)} + \text{SiO(gas)} + \text{CO(gas)} \]

- Next, the silicon is pulverized and treated with HCl at 300°C to form trichlorosilane (SiHCl₃).
  \[ \text{Si(solid)} + 3\text{HCl(gas)} \rightarrow \text{SiHCl}_3\text{(gas)} + \text{H}_2\text{(gas)} \]

- The trichlorosilane (SiHCl₃) is a liquid form at room temperature (it has a boiling point of 32°C). It goes thru a fractional distillation to remove impurity. The purified SiHCl₃ is then used in a hydrogen reduction reaction to prepare the EGS.
  \[ \text{SiHCl}_3\text{(gas)} + \text{H}_2\text{(gas)} \rightarrow \text{Si (solid)} + 3\text{HCl(gas)} \]
Growth Techniques

- Methods to turn polycrystalline silicon into single crystalline silicon ingot.
  - Czochralski (CZ)
  - Float zone (FZ)

- Methods to turn polycrystalline GaAs into single crystalline ingot.
  - Czochralski (CZ)
  - Bridgman Technique
Process flow from starting material to polished wafer.
Czochralski crystal puller. BW, clockwise; CCW, counterclockwise.
CZ Growth (1)

- CZ is the dominant growth process as it can create large diameter crystals
- The silicon is contained as a liquid in a crucible during growth; as a result oxygen and carbon contaminants the growing crystal.
CZ Growth (2)

- EGS is placed in a silica crucible along with doped silicon and melted.
- The material is held just above the melting point of silicon (1417°C).
CZ Growth (3)

- A single crystal seed is lowered into the melt
- The orientation of the seed will determine the orientation of the pulled crystal
- The seed is slowly pulled out of the melt; silicon atoms from the melt bond to atoms in the seed, once lattice plane at a time.
CZ Growth (4)

- The diameter of the crystal is controlled by the rate at which the crystal is pulled (slower=bigger)
- The seed and crucible are rotated in opposite directions to promote mixing; this increases corrosion of the crucible by the melt.
- As a result oxygen is absorbed from the crucible and carbon from the graphite susceptor supporting it.
Distribution of Dopant

- Equilibrium Segregation Coefficient, $k_o$

\[ k_o = \frac{C_s}{C_l} \]
Curves for growth from the melt showing the doping concentration in a solid as a function of the fraction solidified.
Doping distribution near the solid-melt interface.

\[ C_s = k_e C_e \]

\( \delta \)

\( C_1(0) \)

\( C(x) \)

\( C_1 \)

\( k_0 < 1 \)
CZ Crystal Growing Equipment
300-mm (12 in.) and 400 mm (16 in.) Czochralski-grown silicon ingots. (Photo courtesy of Sin-Etsu Handotai Co., Tokyo.)
Float Zone Process (1)

- Principle difference from CZ: no crucible is used
- Not using a crucible reduces the impurity level in the crystal
- Used to create materials with high resistivities and/or low oxygen content (e.g. detectors or power devices)
- Is a small fraction of the silicon market
- Difficult to scale up crystal diameter due to stability of the liquid zone in a gravity environment; FZ wafers have greater microscopic resistivity variations than CZ
Float Zone Process (2)

- An EGS rod is clamped with the bottom in contact with a single crystal seed.
- Power is supplied by an RF coil. The coil melts the silicon locally through resistive heating.
- The molten zone is 2cm in length.
- Surface tension and levitation by the RF field creates system stability.
- When melting is initiated in a zone at the seed end and slowly moved up the rod, a single crystal results.
- Liquid atoms from the melt bond to the solid one lattice plane at a time.
Float-zone process. (a) Schematic setup. (b) Simple model for doping evaluation.
Curves for the float-zone process showing doping concentration in the solid as a function of solidified zone lengths.

\[ \frac{C}{C_0} = 1 - (1 - k_c)e^{-k_c \frac{x}{L}} \]

\( C_0 = 1 \) for all curves
Relative impurity concentration versus zone length for a number of passes. $L$ denotes the zone length.
(a) Typical lateral resistivity distribution in a conventionally doped silicon.

(b) Silicon doped by neutron irradiation.
Phase diagram for the gallium-arsenic system.
Partial pressure of gallium and arsenic over gallium arsenide as a function of temperature. Also shown is the partial pressure of silicon.
Bridgman Technique

Technique for growing single-crystal gallium arsenide, and a temperature profile of the furnace.
(a) Silicon wafer cut at the (100) plane with a (011) flat to help orient the wafer during IC fabrication.

(b) The standard notation for crystal planes is illustrated.
Wafer Orientation

Orientation
Slice the single crystalline unit
<100> - in vertical plane;
<111> - corner-to-corner;

Application
<100> - MOS devices;
<111> - Bipolar devices;
Identifying flats on a semiconductor wafer.
Why $<100>$, $<111>$ for different applications?

- $<111>$ plane – easier and cheaper to grow
  - For all possible devices, incl. Bipolar

- $<111>$ plane - Threshold Voltage ($V_t$) is adversely affected by $<111>$ orientation;

- $<111>$ Oxide film – lower reliability, quality, and higher noise.
200-mm (8 in.) and 400-mm (16 in.) polished silicon wafers in cassettes. (Photo courtesy of Sin-Etsu Handotai Co., Tokyo.)
Point defects.
(a) Substitutional impurity.
(b) Interstitial impurity.
(c) Lattice vacancy.
(d) Frenkel-type defect.
(a) Edge and (b) screw dislocation formation in cubic crystals.
Stacking faults in semiconductor. (a) Intrinsic stacking fault. (b) Extrinsic stacking fault.
Wafer Measurement Methods (1)

Electrical measurements

- **Dopant determination: hot point probe**
  - Two probes make ohmic contact with the wafer surface
  - One probe is heated 25 - 100°C hotter than the other
  - The potential difference is measured; the polarity indicates if the material is P or N type (thermal emf or Seebeck voltage).

- **Sheet resistance: four point probe**
  - Measure the sample resistance by measuring the current that flows for a given applied voltage
  - Use four probes (rather than two) to minimize the effect of contact resistance and current spreading.

- **Resistance and mobility: Hall effect**
  - Can determine material type, carrier concentration, and carrier mobility
  - Uses the fact that a transverse voltage exists across a conductor subjected to a magnetic field
  - Generally not used to measure implants or diffusions due to depth variations requiring multiple measurements and material removal
Physical measurements

- Defect detection in silicon: Etches
  - Preferentially attack strained regions in the silicon associated with defects
  - Produces pits whose shapes can be correlated with specific kinds of defects and observed using optical microscopy

- Fourier Transform Infrared Spectroscopy
  - Used to detect interstitial oxygen and carbon, SiO$_2$ clusters

- Electron microscopy
  - High resolution imaging
  - Scanning electron microscopy (SEM) (5nm resolution)
  - Transmission electron microscopy (TEM) (2 Å resolution)
Modeling Crystal Growth: Relationship between pull rate and diameter

- Freezing occurs between isotherms $X_1$ and $X_2$
- Heat of fusion must be removed from the freezing interface by heat conduction
- The latent heat of crystallization + heat conducted from melt to crystal = heat conducted away
Modeling Crystal Growth (2)

\[ L \frac{dm}{dt} + k_L \frac{dT}{dx_1} A_1 = k_S \frac{dT}{dx_2} A_2 \quad (1) \]

- \(L\) = latent heat of fusion
- \(\frac{dm}{dt}\) = amount of freezing per unit time
- \(k_L\) = thermal conductivity of liquid

where:
- \(\frac{dT}{dx_1}\) = thermal gradient at isotherm \(x_1\)
- \(k_S\) = thermal conductivity of solid
- \(\frac{dT}{dx_2}\) = thermal gradient at \(x_2\)
Modeling Crystal Growth (3)

- The rate of growth of the crystal is

\[
\frac{dm}{dt} = v_p AN
\]  \hspace{1cm} (2)

where \(v_p\) is the pull rate and \(N\) is the density.

- Neglecting the middle term in Eqn. (1) we have:

\[
v_{p\text{MAX}} = \frac{k_s}{LN} \frac{dT}{dx_2}
\]  \hspace{1cm} (3)

- In order to replace \(dT/dx_2\), we need to consider the heat transfer processes.

* Neglect heat flow due to thermal gradients
Modeling Crystal Growth (4)

- Heat radiation from the crystal (C) is given by the Stefan-Boltzmann law

\[ dQ = (2\pi r dx) \left( \sigma \varepsilon T^4 \right) \]  \hspace{1cm} (4)

Heat conduction up the crystal is given by

\[ Q = k_S \left( \pi r^2 \right) \frac{dT}{dx} \]  \hspace{1cm} (5)

Differentiating (5), we have

\[ \frac{dQ}{dx} = k_S \left( \pi r^2 \right) \frac{d^2T}{dx^2} + \left( \pi r^2 \right) \frac{dT}{dx} \frac{dk_S}{dx} \equiv k_S \left( \pi r^2 \right) \frac{d^2T}{dx^2} \]  \hspace{1cm} (6)
Modeling Crystal Growth (5)

- Substituting (6) into (4), we have

\[
\frac{d^2T}{dx^2} - \frac{2\sigma\varepsilon}{k_S r} T^4 = 0
\]  \hspace{1cm} (7)

- \(k_S\) varies roughly as \(1/T\), so if \(k_M\) is the thermal conductivity at the melting point,

\[
k_S = k_M \frac{T_M}{T}
\]  \hspace{1cm} (8)

\[
\therefore \frac{d^2T}{dx^2} - \frac{2\sigma\varepsilon}{k_M r T_M} T^5 = 0
\]  \hspace{1cm} (9)
Modeling Crystal Growth (6)

• Solving this differential equation, evaluating it at $x = 0$ and substituting the result into (3), we obtain

$$v_{PMAx} = \frac{1}{LN} \sqrt{\frac{2\sigma k_M T_M^5}{3r}}$$  \hfill (10)