Becquerel (1839)
- Demonstrated the photovoltaic effect
- Best results with UV or blue light
- Electrodes covered with light sensitive materials AgCl and AgBr

Adams & Day (1877)
- Photoconduction in Selenium
- First demonstration of photovoltaic effect in an all solid state device
- Several decades before the effect could be explained

Fritts (1883)
- First thin film Selenium photovoltaic device
- Fabricated by compressing molten Selenium between plates
- Gold leaf contact for large area 30 cm²

Grondahl (1927)
- Copper-Cuprous junctions
- First used wire then sputtered metal

Bergmann (1931)
- Reawaken interest in Selenium
- Selenium proved to be superior to Cu-based devices
- Became commercial dominant product of the 30’s
Ohl (1941)

- Recrystallized melts of pure silicon
- Barriers noted
- Light or heat created a negative potential on one end (n-type)
- Performance was similar to thin film devices of the era but required excessive processing

Chapman, Fuller & Pearson (1954)

- First modern silicon cell
- Dual rear contact structure
- Efficiency of 6% a factor of 15 times better than previous devices

Current Solar Cell Technologies

- A) Crystalline Silicon
- B) Thin Film
- C) Group III-IV Cells

Types of Crystalline Silicon

- Carefully made Silicon forms crystals. Different levels of crystal structure may exist ranging from single crystal to totally non-crystalline
  - Single crystal silicon
  - Multi-crystal silicon
  - Polycrystalline
  - Ribbon silicon
  - Amorphous silicon
- The main difference between each is the crystal grain size and their growth technique

Different Forms of Silicon

<table>
<thead>
<tr>
<th>Crystal Type</th>
<th>Symbol</th>
<th>Crystal Grain Size</th>
<th>Common Growth Techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-crystal</td>
<td>mc-Si</td>
<td>&gt; 10 cm</td>
<td>Czochralski (Cz), Float-Zone (FZ)</td>
</tr>
<tr>
<td>Multicrystalline</td>
<td>mc-Si</td>
<td>100µm</td>
<td>Cast, Spheroid Sheet, ribbon</td>
</tr>
<tr>
<td>Polycrystalline</td>
<td>pc-Si</td>
<td>1µm – 1mm</td>
<td>Evaporation, CVD, sputtering</td>
</tr>
<tr>
<td>Microcrystalline</td>
<td>mc-Si</td>
<td>&lt; 1µm</td>
<td>Plasma Deposition</td>
</tr>
</tbody>
</table>

A) Crystalline Silicon

- Most common for commercial applications
- Advantages
  - Well known standard processing
  - Silicon is very abundant
- Disadvantages
  - Requires expensive highly pure silicon
  - Competes with silicon with electronics industry
Single Crystal Solar Cells

All atoms arranged in pattern, one single crystal of silicon

Single Crystal Silicon

Czochralski Growth Techniques

• Czochralski Growth (Cz)
  – Most single crystal silicon made this way
  – Lower quality silicon than FZ with Carbon and Oxygen present
  – Cheaper production than FZ
  – Produces cylinders and circular wafers

• Float Zone (FZ)
  – Better Quality than Cz
  – More Expensive than Cz
  – Produces cylinders and circular wafers

Czochralski Method

• Pure Silicon is melted in a quartz crucible under vacuum or inert gas and a seed crystal is dipped into the melt
• The seed crystal is slowly withdrawn and slowly rotated so that the molten silicon crystallizes to the seed (Rock Candy)
• The melt temperature, rotation rate and pull rate are controlled to create a ingot of a certain diameter

Czochralski Technique

The melt temperature, rotation rate and pull rate are controlled to create a ingot of a certain diameter

Czochralski Growth

• Entire ingots of silicon produced as one big crystal
• Very high quality material with few defects
• No boundaries between crystals because it is one crystal in one orientation
• Si crystal inevitably contains oxygen impurities dissolved from the quartz crucible holding the molten silicon
**Float Zone Method**
- Produced by cylindrical polysilicon rod that already has a seed crystal in its lower end
- An encircling inductive heating coil melts the silicon material
- The coil heater starts from the bottom and is raised pulling up the molten zone
- A solidified single crystal ingot forms below
- Impurities prefer to remain in the molten silicon so very few defects and impurities remain in the forming crystal

**Slicing into Wafers**
- Ingots are cut into thin wafers for solar cells (300 μm)
- Two Techniques
  - Wire sawing
  - Diamond blade sawing
- Both results in loss of silicon from “kerf losses” → silicon saw dust
- Time consuming
- Water Cooled, Dirty

**Single Crystal Silicon**
- What we are using
- Currently supplies a significant but declining solar cell market share
- Advantages
  - Produced for electronics industry
  - Allows for higher efficiency solar cells
- Disadvantages
  - Requires higher quality of feed stock
  - More expensive and slower to produce
  - Circular shape leads to lower packing density in panels or larger waste of silicon

**Ribbon Silicon**
- Ribbon silicon is a technique used to grow multi-crystalline silicon
- Two graphite filaments are placed in a crucible of molten silicon
- The molten silicon is grown horizontally through capillary action along the filaments
- Produces a ribbon-like sheet of multi-crystalline silicon which is already a long wafer → no kerf losses

**Ribbon Silicon (+/-)**
- Advantages
  - Thickness can be varied by the filament width & the pull speed
  - Cheaper - less wasted silicon due to sawing wafers
- Disadvantages
  - Lower Solar Cell Efficiencies due to more defects
  - Irregular surface characteristics leading to poorer cell performance

**Ribbon Silicon Method**
- Growing Ribbons
- Solid-Melt Interface
- Molten Silicon
- Graphite
Poly-crystal Silicon

Grains
Grain Boundary
Regions of single crystalline silicon separated by grain boundaries with irregular bonds

Poly& Multi-Silicon Method

- Produced by melting silicon source material in a large rectangular crucible
- The material is slowly directionally cooled
- Impurities drift to the edges which cool last
- These edges are sawn or acid etched off
- These blocks are sawn into smaller blocks and then sawn into thin wafers

Directional Solidification Furnace

Silicon Melt
RF Heating Elements
Hot Chamber
Cold Chamber
Graphite Crucible
Quartz Liner
Water Cooled Support Pedestal and shaft
Pull Direction

Multicrystalline Silicon

Wafer Fabrication

Ingot
Ingot Slicing
Water Slicing
Multicrystalline Silicon Wafer

Multi-crystalline

- Significant differences in the size of crystal grains
- Advantages
  - Cheaper
  - Faster Processing
- Disadvantages
  - Less efficient than single crystal due to grain boundaries where electrical losses occur

Amorphous Silicon

Hydrogen Passivation
Dangling Bond

Less regular arrangement of atoms leading to dangling bonds and passivation by hydrogen
Property Changes

• Band gap increases from 1.1 eV to 1.7 eV
• Absorption coefficient is much higher
• Presence of large number of dangling bonds cause a high density of defects and low diffusion lengths

Schematic of a-Si:H Solar Cell

B) Thin Film

• Thin film of semiconductor 1-10 microns compared to 200-300 microns
• Created by depositing a thin expensive semiconductor on a cheaper glass substrate
• Advantages
  – Requires little semiconductor material
  – Cheaper to produce:
    • glass is cheap
    • semiconductor expensive
• Disadvantages
  – Difficult to manufacture good films
  – Lower efficiencies

Three Main Thin Films

• Amorphous Silicon (a-Si)
• Cadmium Telluride (CdTe)
• Copper Indium Gallium Diselenide (CIGS)

Amorphous Silicon (a-Si)

• Made by evaporating silicon onto a glass base
• More random orientation than crystalline
• More electrons not bound to SI atoms
• Unbounded electrons attract impurities and degrade the electrical performance of the cell
• Hydrogen is often added to the material to deactivate the dangling bonds
**Amorphous Silicon (+/-)**

- **Advantages**
  - Absorbs low and high intensity light
  - Less Semiconductor needed → Lower Cost
  - High temperatures do not significantly reduce performance

- **Disadvantages**
  - Lower Efficiency (lower grade Si)
  - Long term degradation of material under sunlight
  - Production requires hazardous gases

**Cadmium Telluride (CdTe)**

- **Advantages**
  - p-type made from Cadmium and Telluride
  - n-type from Cadmium Sulfide
  - High Efficiencies compared to a-Si (over 16%)

- **Disadvantages**
  - Requires high processing temperatures
  - CdTe is unstable and will degrade
  - Cadmium is toxic and costly to dispose of
  - Sensitive to water ingress and cell degradation

**Copper Indium Gallium Diselenide (CIGS)**

- Extremely good light absorption (99% of light absorbed in the first micron)
  - → an optimal and effective PV material
- The addition of gallium boosts its light absorption band gap for the solar spectrum
- No performance degradation over time
- Much higher efficiencies than other thin films (19%)

**CIGS (+/-)**

- **Advantages**
  - Highest efficiency for thin film cells
  - Clear pathways to improve performance and efficiencies
- **Disadvantages**
  - Gallium and Indium are scarce materials
  - Requires expensive vacuum processing
**C) Group III-V**

- Compounds of Group III and V on periodic table
- Compound is a material that combines multiple elements in a single structure (not just a mixture)
- Used extensively in the electronics and optoelectronics industries as well as space satellites
- Makes excellent but very expensive solar cells
- Can create multi-junction cells for higher efficiency

**Single Junction III-V Cells**

- Made from combination of two materials
  - Gallium Arsenide (GaAs)
  - Indium Phosphide (InP)
- Best efficiency is at 27.6%
  - 1000 W/m² of sunlight produces 276 Watts of usable power

**Single Junction III-V Cells (+/-)**

- **Advantages**
  - Very high efficiencies
  - Low weight
  - Resistant to damage from cosmic radiation
- **Disadvantages**
  - Expensive
  - Required materials are not abundant

**Multi-Junction III-V Cells**

- Stacked p-n junctions on top of each other
- Each junction has a different band gap energy so each will respond to a different part of the solar spectrum
- Very high efficiencies, but more expensive
- Each junction absorbs what it can and lets the remaining light pass onto the next junction
- Widely used for space applications because they are very expensive
- Overall record for electrical efficiency is 35.2%

**Engineering Band Gaps**

**Intermediate Band**
Criteria of Heterojunction for PV

- Band gap of smaller band-gap material
  - Band gap near 1.4 eV to maximize absorption of solar radiation, while minimizing diode current that limits open circuit voltage (silicon is 1.1 eV)
- Band gap of larger band-gap material
  - As large as possible while maintaining low series resistance
- Conductivity type
  - Smaller band-gap material should be p-type because of longer electron diffusion lengths

Criteria of Heterojunction for PV (2)

- Electron Affinities
  - Materials should be chosen such that no potential spike occurs at the junction for the minority photoexcited carriers
- Diffusion Voltage
  - As large as possible, since the maximum open circuit voltage is proportional to the diffusion voltage
Criteria of Heterojunction for PV

3

- Lattice Mismatch
  - As little mismatch in lattice constant between two materials as possible, this appears to minimize interface density of states and recombination losses through such states
- Electrical Contacts
  - It should be possible to form low-resistance electrical contacts to both n- and p-type materials

Criteria of Heterojunction for PV

4

- Material Availability
  - Supplies of the material should be sufficient to allow large area cell production
- Material Cost
  - Cost of the material should be competitive with alternative systems
- Material toxicity
  - Materials should be nontoxic, or control of toxicity should be possible
- Cell Stability and Lifetime
  - Cell must have an operating lifetime sufficient to pay back economic and energy costs required to produce it.

Energy Research Center of the Netherlands (ECN)

ECN Design Pin Up Module (PUM)

Integration of Cell and Module

Module Substrate
Module technology

ECN’s PUM result:
- Full size module (71x147 cm²)
- 128 Wp (16.8% encapsulated cell efficiency)
- 0.6-0.8% absolute efficiency gain

Best PUM cell result up to now:
- 16.7% (235 cm²)

At this moment PUM is the only integrated concept for cell and module

SunPower Technology

SunPower

- ~20%
- High quality
- Expensive
- Rear Contacts

BP Solar

- Laser Grooved Buried Contacts
- Single Crystal Silicon