Solar Cells

App.1: Market
App.2: Absorption of Light
App.3: Other Materials

EECS 598 Week 10

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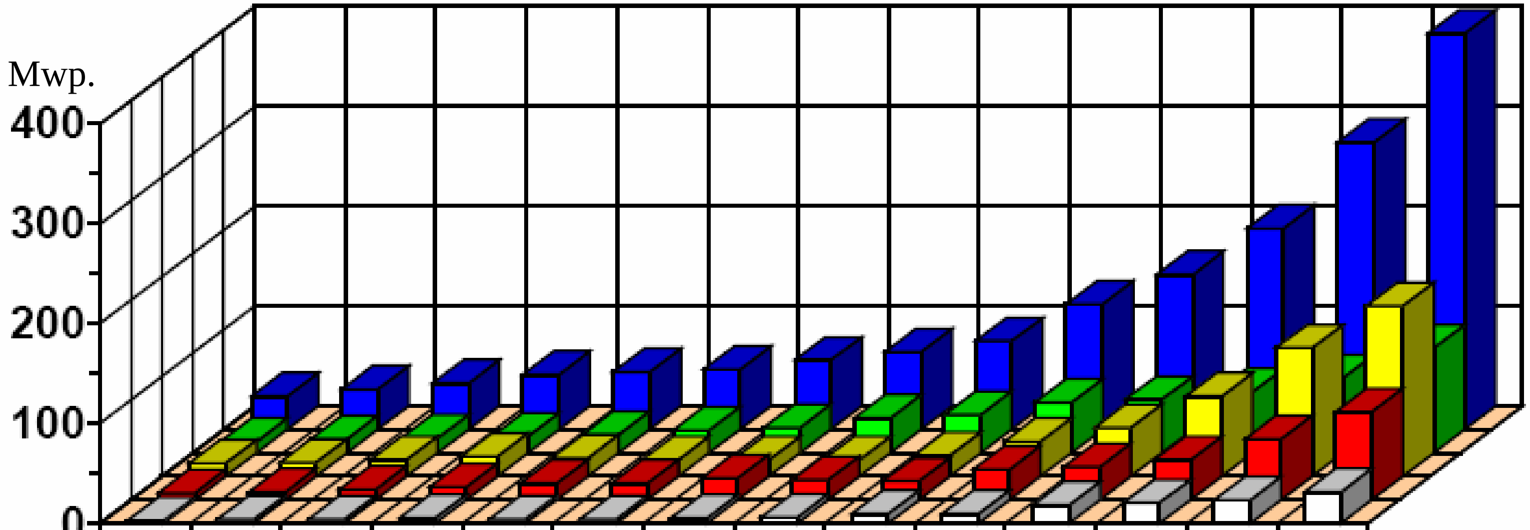
App. A

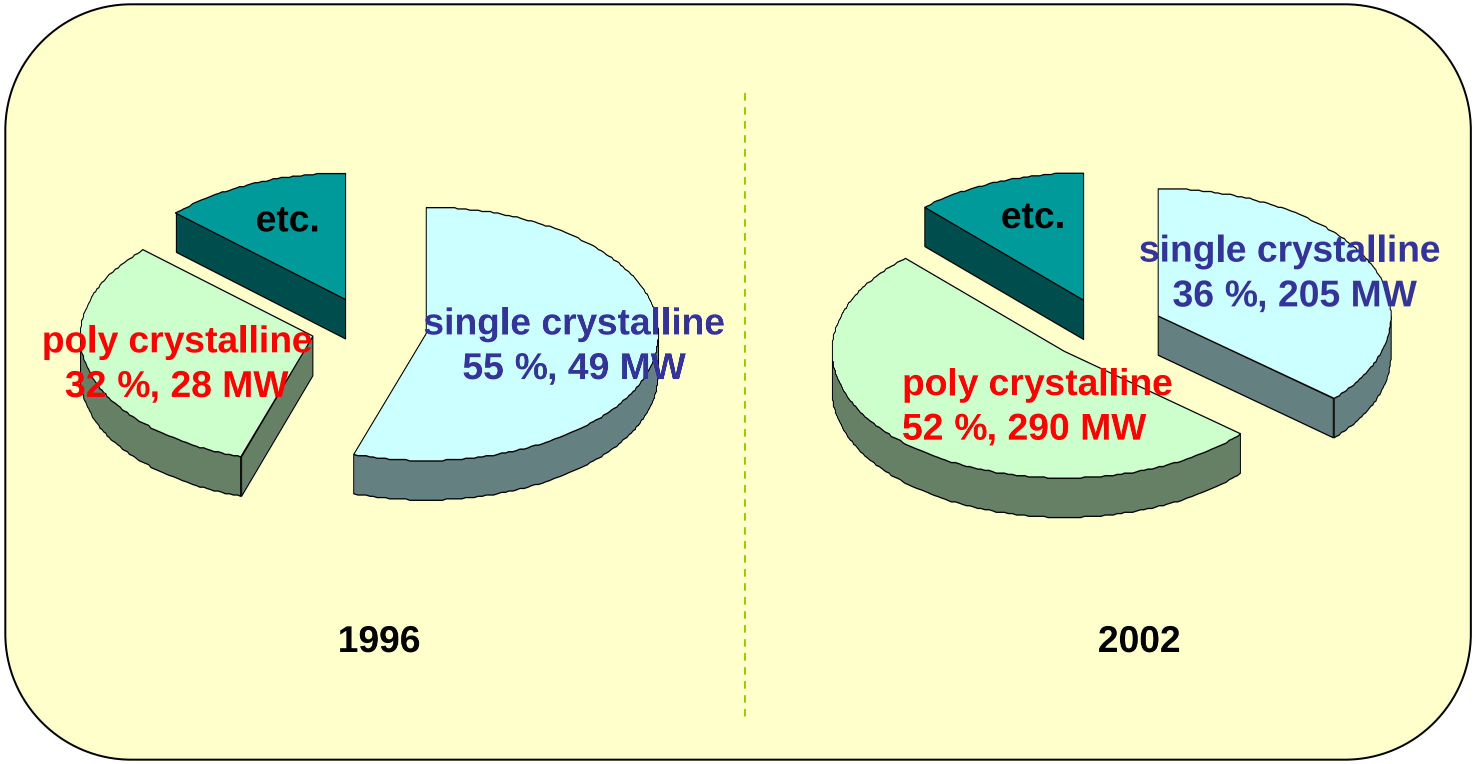
- **World Cell/Module production**



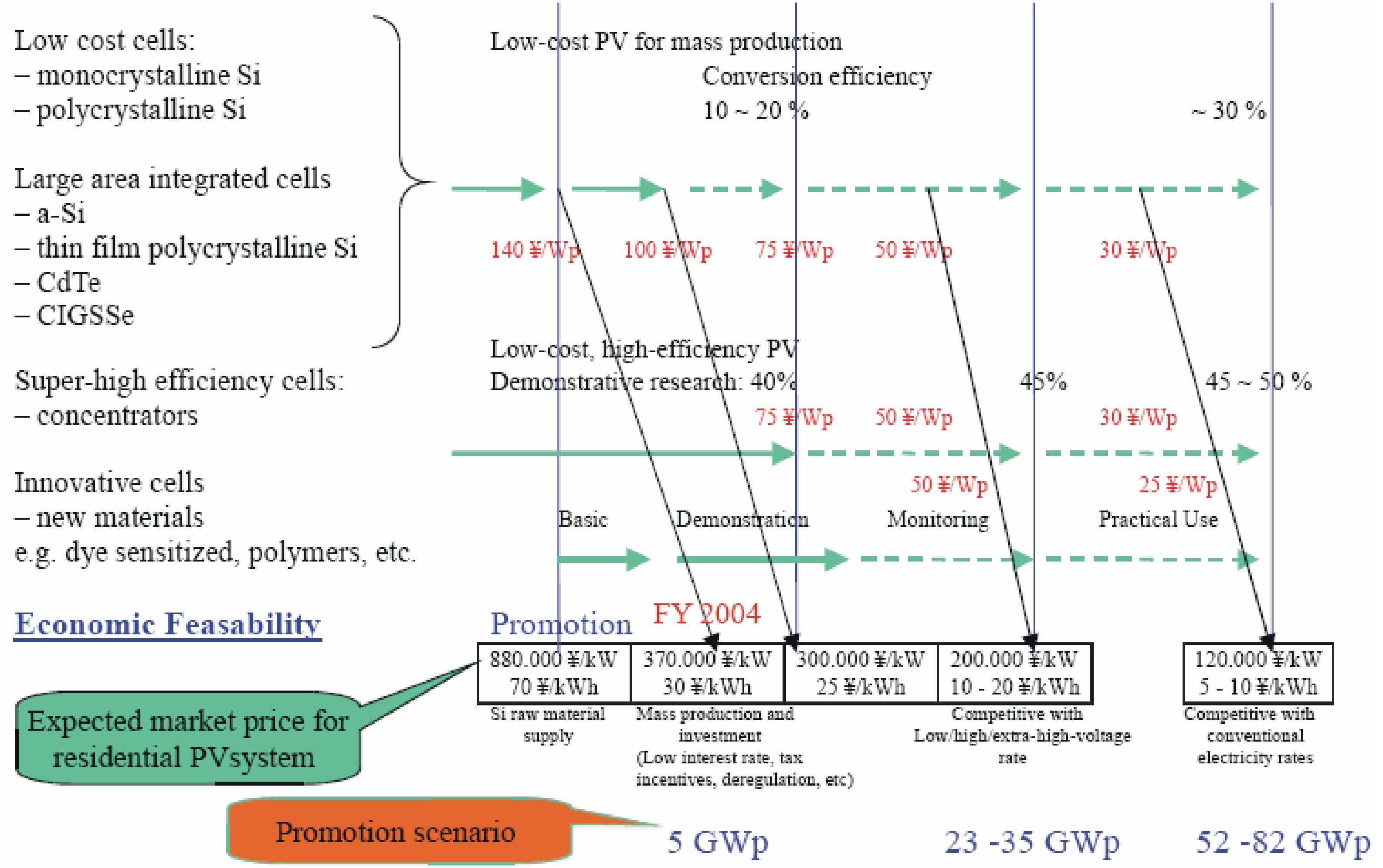
	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001
Rest of World	3	4	4,7	5	4,6	4,4	5,6	6,35	9,75	9,4	18,7	20,5	23,42	31,6
Europe	6,7	7,9	10,2	13,4	16,4	16,55	21,7	20,1	18,8	30,4	33,5	40	60,66	88,22
Japan	12,8	14,2	16,8	19,9	18,8	16,7	16,5	16,4	21,2	35	49	80	128,6	171,22
United States	11,1	14,1	14,8	17,1	18,1	22,44	25,64	34,75	38,85	51	53,7	60,8	74,97	105,1
Total	33,6	40,2	46,5	55,4	57,9	60,09	69,44	77,6	88,6	125,8	154,9	201,3	287,65	396,14

Paul Maycock, PV News, February 2002

Market Share of Solar Cells



Roadmap (Japan)

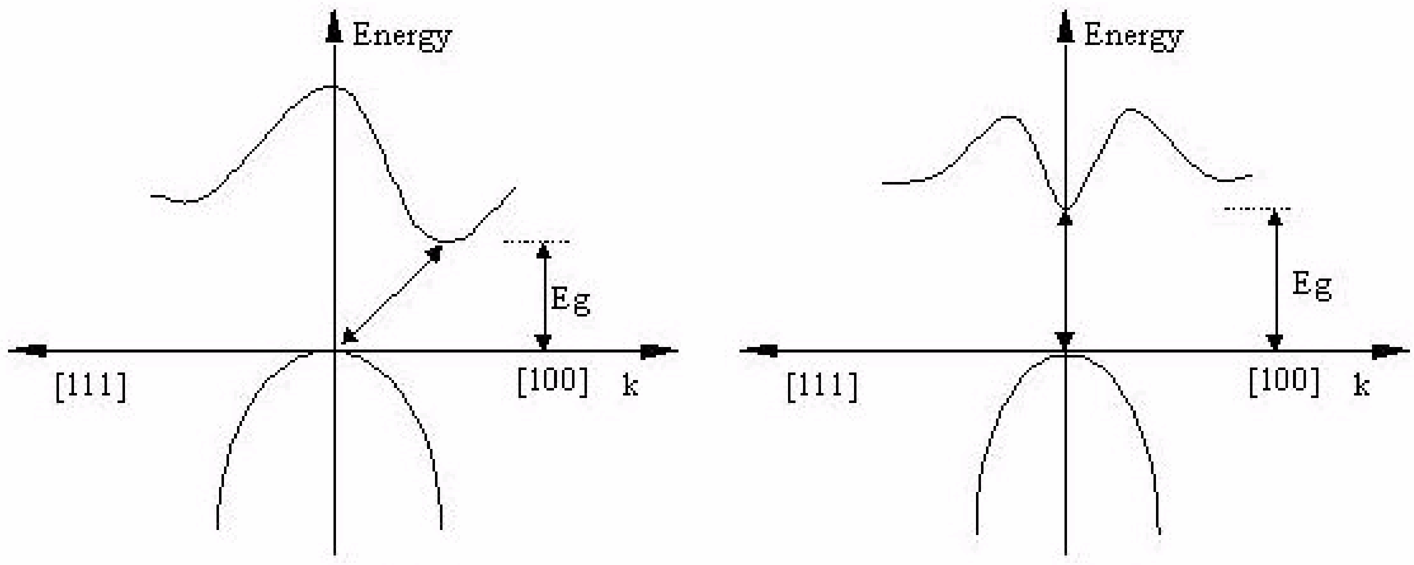


MichiganEngineering 1 8 5 4 - 2 0 0 4

App.2 - Absorption of light

Direct & Indirect Semiconductor

- **The light absorption coefficient of the direct gap semiconductor is much larger than that of indirect gap semiconductor**

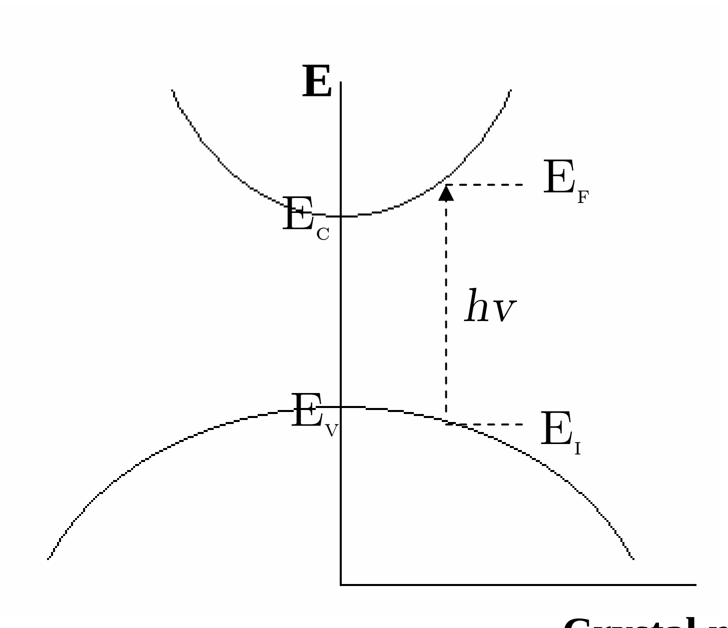


(a) Indirect semiconductor (b) Direct semiconductor

Absorption of Light

- **Direct-band-gap Semiconductor**
  - Absorption of photons :

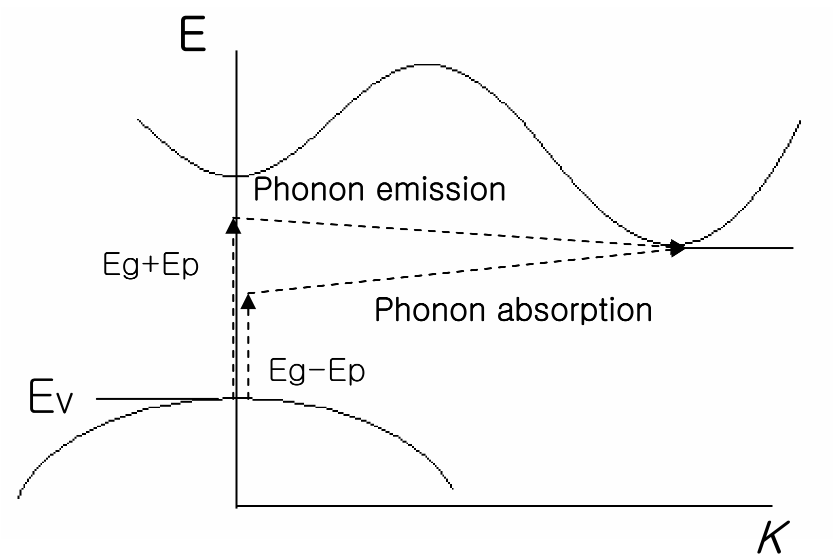
    Excitation of electrons from the valence band into the conduction band



$$E_f - E_i = h\nu$$

Absorption of Light

- **Indirect-band-gap Semiconductor**
  - The minimum energy in the conduction band and the maximum energy in the valence band occur at difference values of momentum

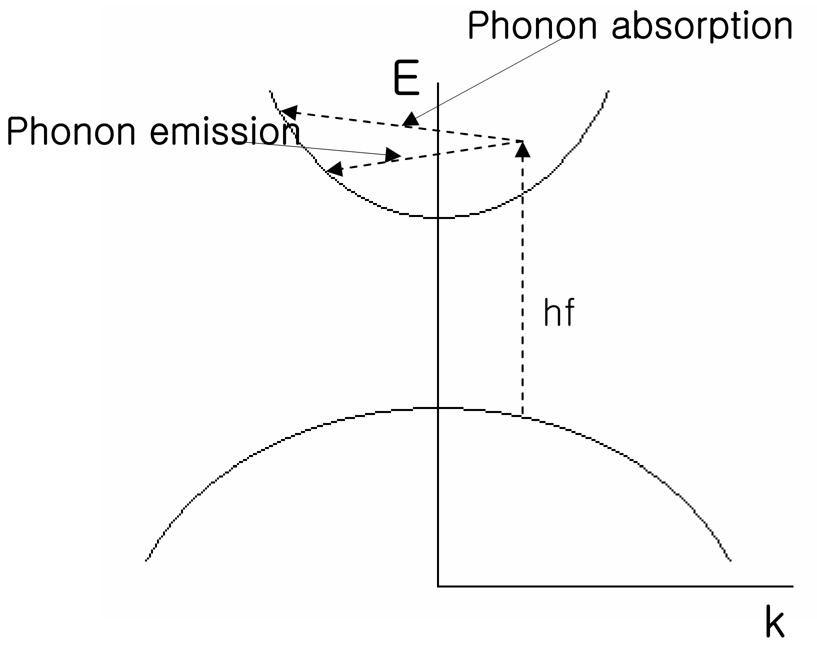


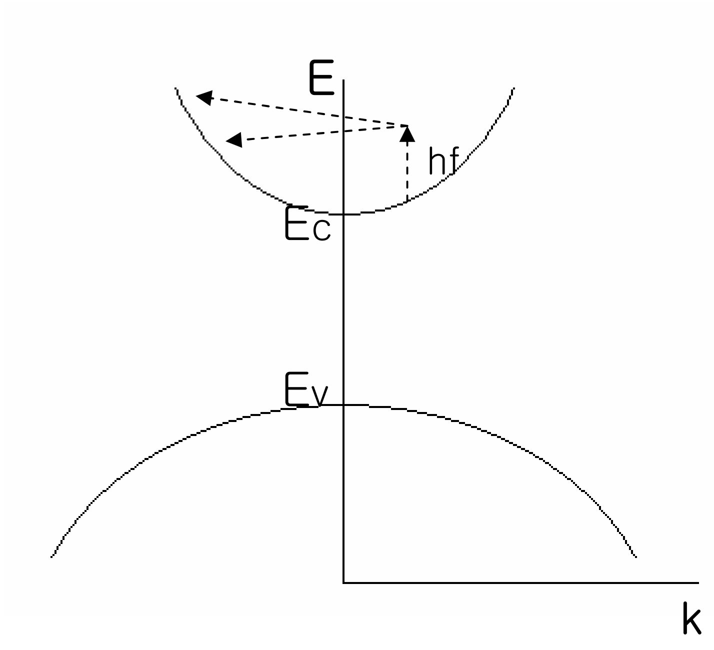
$$\alpha_a(hf) = \frac{A(hf - E_g + E_p)^2}{\exp(E_p/kT) - 1}$$

$$\alpha_e(hf) = \frac{A(hf - E_g - E_p)^2}{1 - \exp(-E_p/kT)}$$

Other Absorption Process

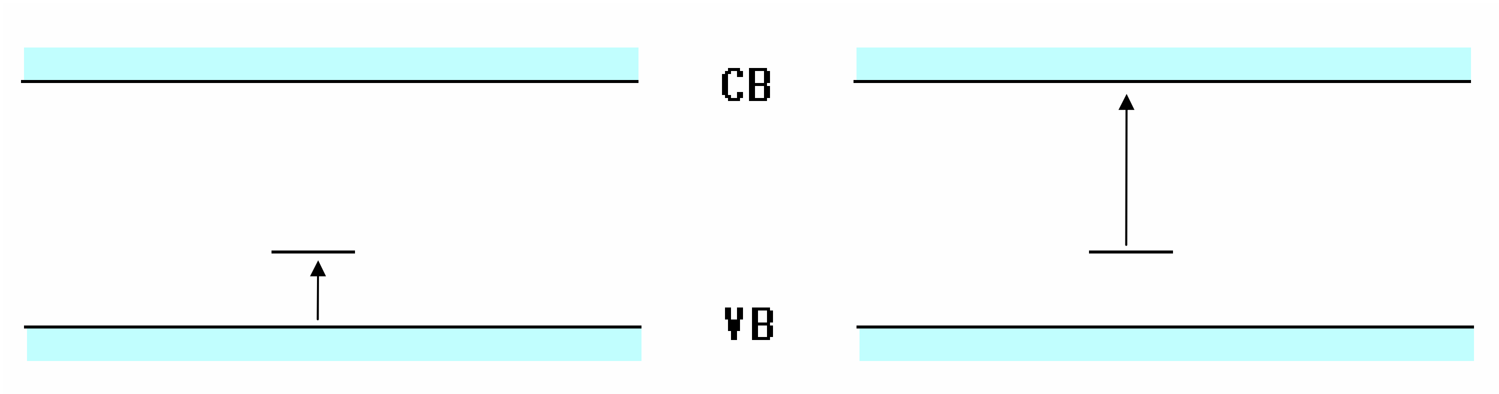
- **Two step absorption involving emission or absorption of phonons can also occur in direct-band-gap semiconductor**





Other Absorption Process

- Impurities and defects in semiconductor can give allows to allowed energy levels within the forbidden gap.



App.3 – Tech. for Low Cost Cells

Silicon Sheet

Ingot Technology

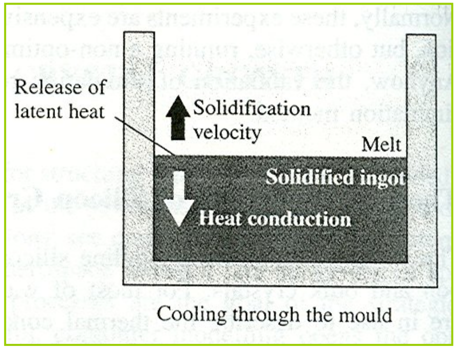
- CZ process

  cylindrical ingots *(not so good for solar cell applications)*

- square cross section (silmilar to casting) → polycrystalline ingot

  not ideal for solar cell applications

  but with careful control → large grained polycrystalline silicon



- **the Heat Exchange Method (HEM)**

  control the rate of solidification

  essentially single crystal ingots of quite massive proportions with a "casting" approach

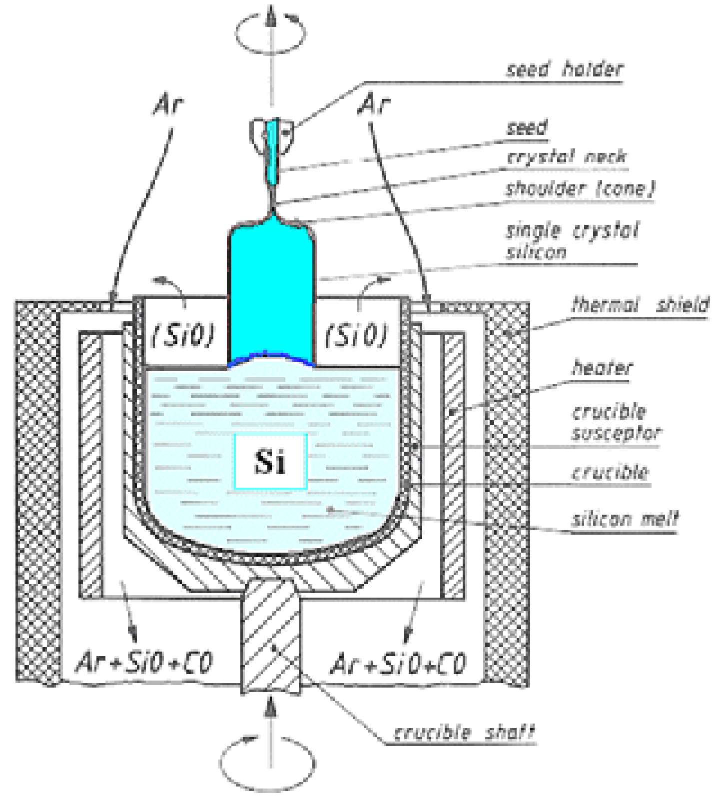
  cell performance is comparable to that of CZ materials

Single-Crystal Growth

- **Czochralski process**

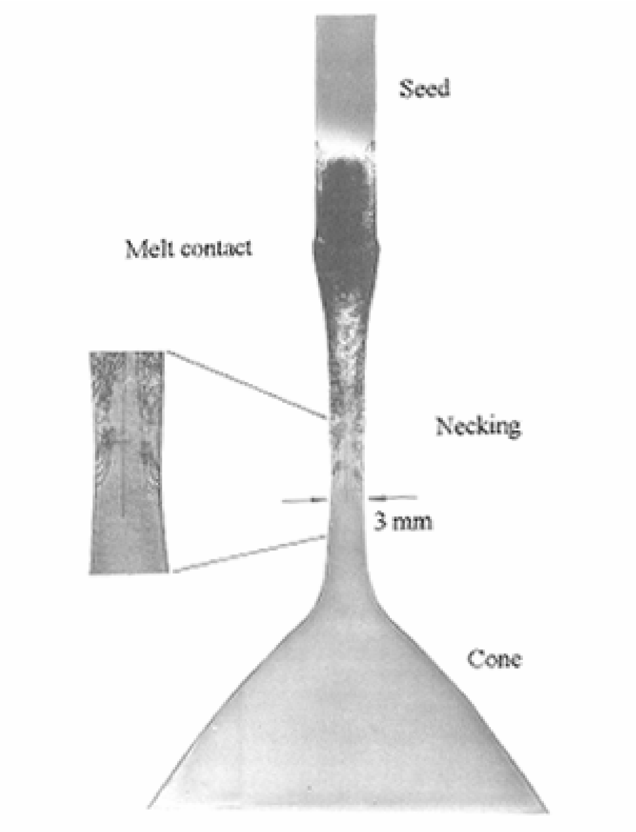
  - J. Czochralski in 1916
  - A crystal is “pulled” out of a vessel containing liquid Si by dipping a seed crystal.
  - The pulling rate(usually ~ mm/min) and the temperature profile determines the crystal diameter.
  - As crystal grows, the impurity concentration increases in melt.
  - Control of the rotation speeds, growth speed, temperature, and Magnetic field.

Beginning of crystal growth



<Czochralski process for single crystals>

Dash process(Necking) and finished product



<X-ray topograph of the first part of crystal growth>

<Picture of 200mm Si crystal>

Ribbon Silicon Technology

To overcome the limitation of the ingot approach

→ forming the silicon directly into sheets or ribbons

vertical growth

the edge-defined film-fed growth (EFG) method

the dendritic web (WEB) method

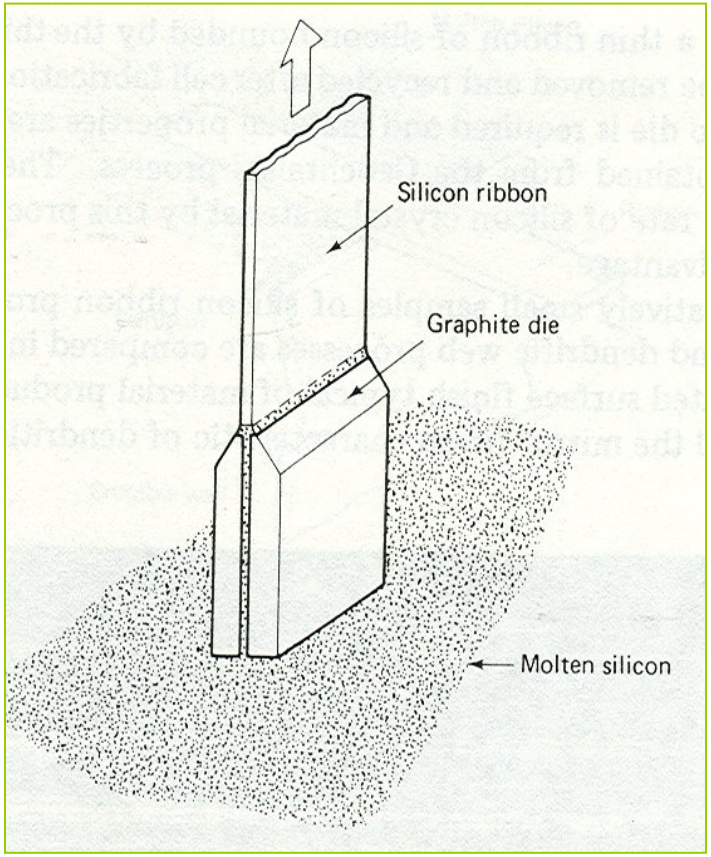
string ribbon (STR) method

horizontal growth

ribbon growth on a substrate (RGS) method

silicon film (SF) method

“ Edge-defined Film-fed Growth (EGF) “ Method



- capillary action
- shape and thickness are defined by a graphite “ die “
- very high production rates (several ribbon or polygon)

- poor crystallographic quality
- impurities from die, crucible, etc. (carbon is dominant)
- reaction between molten silicon and the graphite die

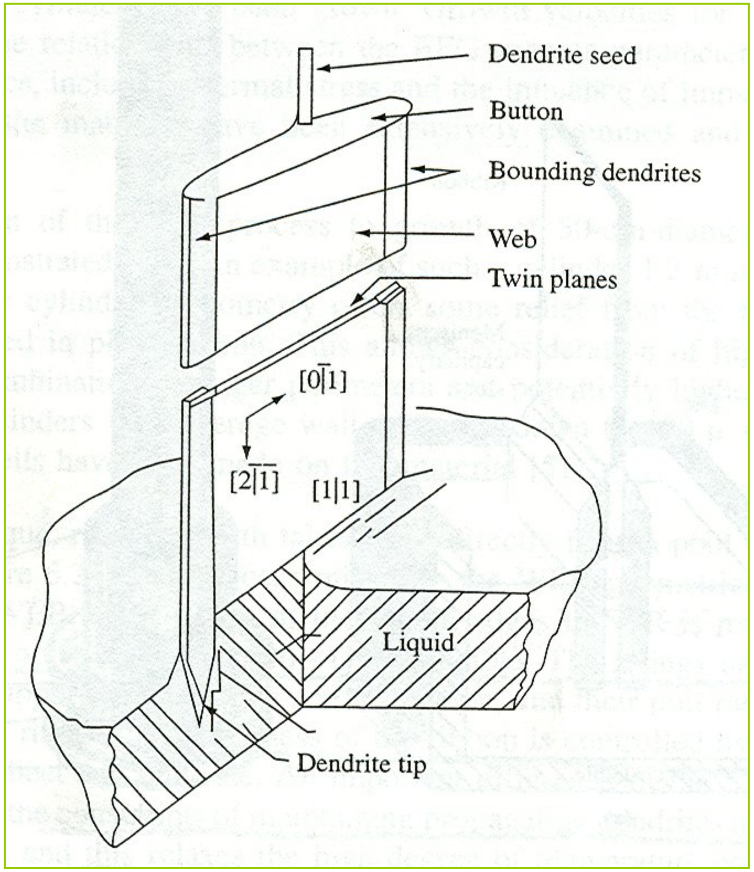
  silicon carbide

  → disrupt its growth

  degrade the properties of solar cells

- corrugated surface

“ Dendritic Web (WEB) “ Method

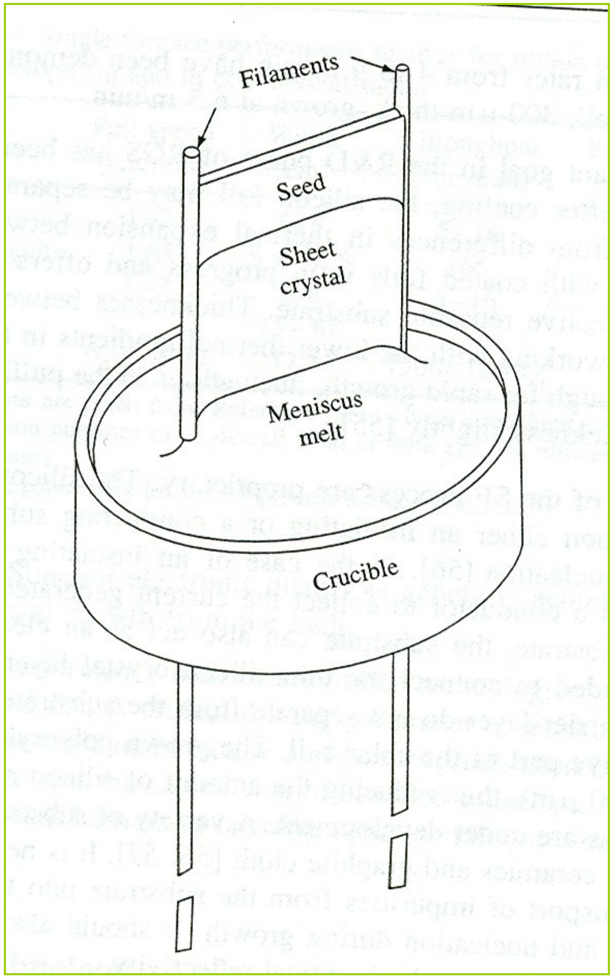


- parallel dendrites
- no die is required
- material properties are nearly as good as those from CZ

- relatively low production rate
- dominant impurity is oxygen from quartz crucible

- mirror surface

" String Ribbon (STR) " Method



- parallel strings
- strings are drawn upward
- thickness is controlled by

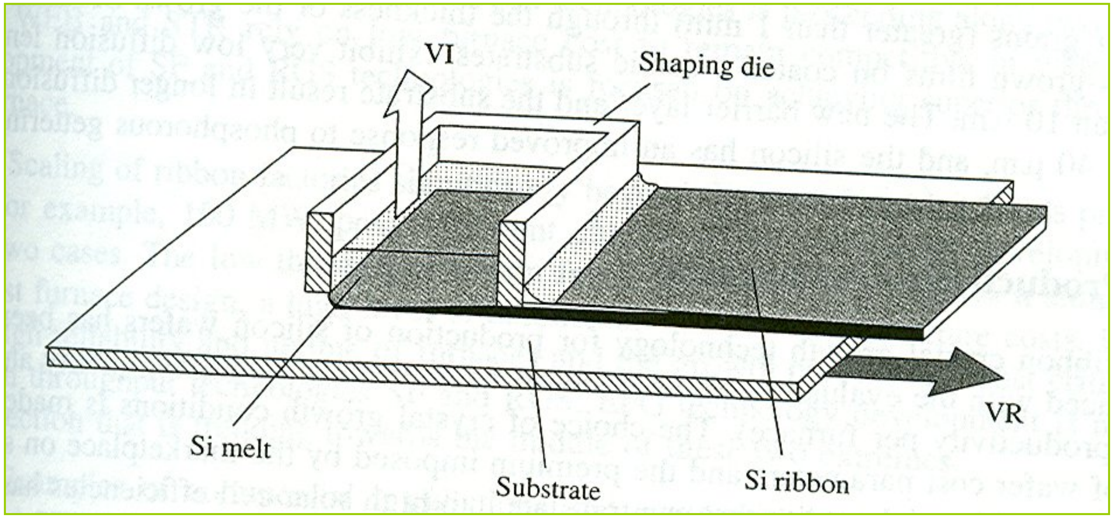
  surface tension, heat loss from the sheet and pull rate

- difference from WEB growth is

  the constraints of maintaining propagating dendrites and a supercooled melt are eliminated

- sufficiently flat surface to be made into solar cells

" Ribbon Growth on a Substrate (RGS) " Method



- silicon melt reservoir and die on the substrate (graphite or ceramic)
- large wedge-shaped crystallization front
- die contains the melt and acts to fix the width of the ribbon
- direction of crystallization and growth are nearly perpendicular
- area >> thickness → latent heat is extracted into the substrate, thermal gradients are small, reduce stress
- reusing the substrate → cost effective

" Silicon Film (SF) " Method

- the details of the SF process are proprietary

- silicon crystal is grown directly on either an insulating or a conducting substrate with a barrier layer
- in the case of an insulating substrate,
  the barrier layer act as a conductor to collect the current generated in the cell
- in the case of a conducting substrate,
  the substrate act as an electrical conductor
- the barrier layer promotes nucleation

- the SF thin film and barrier layer do not separate from the substrate as in RGS
  but become the active part of the solar cells
- very thin (<< 100 um) film is possible → reducing the amount of silicon required
- variety of substrate materials (steel, ceramics, graphite, …)

Historic Record & Solar Cell Efficiency Levels for Ribbon Technologies

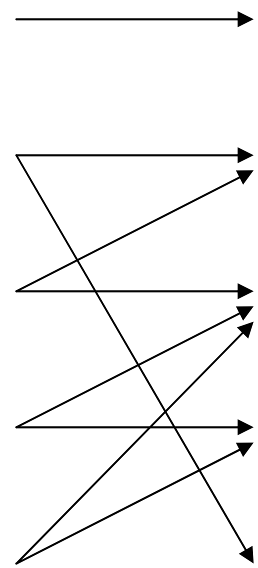
Method / year started	1990	2000	2001
WEB / 1967	R&D, < 0.1 MW	R&D, < 0.2 MW	Pilot, 0~1 MW
EFG / 1971	Pilot, 1.5 MW	Production, ~12 MW	Production, ~20 MW
STR / 1980	R&D	Pilot, < 0.5 MW	Production, < 5 MW
SF / 1983		Pilot, 1~2 MW	Production, > 5 MW
RGS / 1983	R&D	R&D	Pilot, < 1 MW

Method	Resistivity (ohm cm)	Carbon (cm^{-3})	Oxygen (cm^{-3})	Efficiency (%)
EFG	2~4, p-type	10^{18}	$< 5 \times 10^{16}$	15~16
WEB	5~30, n-type	not detected	10^{18}	17.3
STR	1~3, p-type	4×10^{17}	$< 5 \times 10^{16}$	15~16
SF	1~3, p-type	5×10^{17}	$< 5 \times 10^{17}$	16.6
RGS	2, p-type	10^{18}	$< 2 \times 10^{18}$	12.0

Process Technology

Fabrication Techniques for Low Cost & Higher Efficiency Cells

- substrate texturing
- anti-reflection coating, passivation
- p-n junction (doping)
- back surface field (BSF)
- metallization



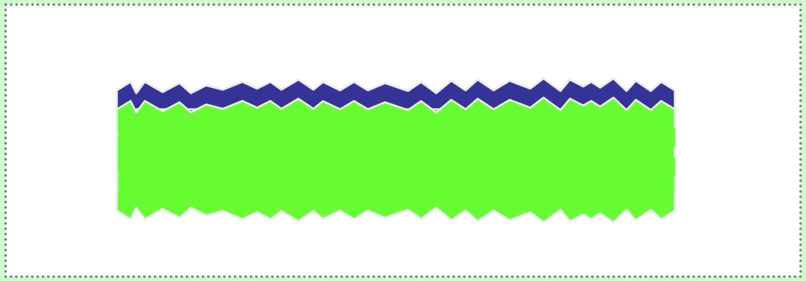
- wet chemical etching process
- spray (spin on dopant) process
- rapid thermal annealing process
- screen printing
- hydrogen plasma treatment

Cell Fabrication and Interconnection

● Texturing : light trapping, reduce reflection

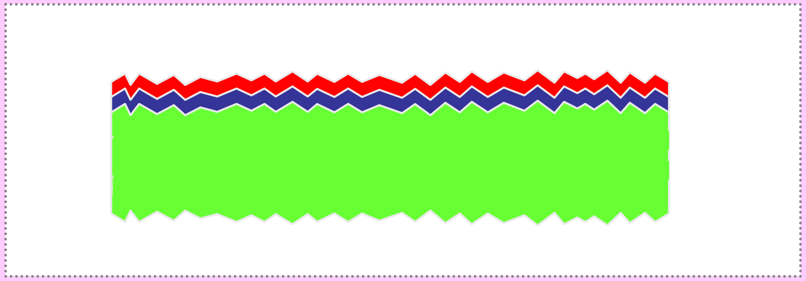
- wet chemical (acid or alkaline solution) etching
- dry etching (RIE)

● Doping (p-n junction formation)



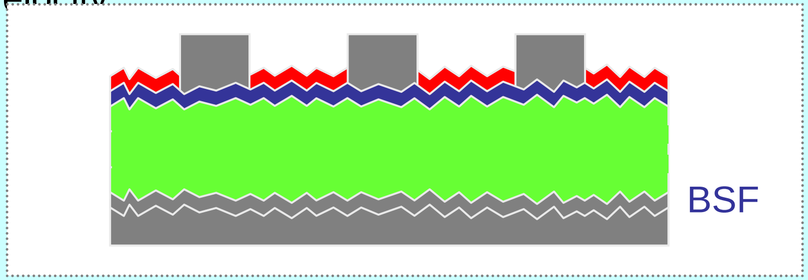
- spin on dopant + RTP annealing
- cf. $POCl_3$ or I/I doping + furnace annealing

● ARC/Passivation : reduce reflection



- CVD or spray SiO_2 / SiN deposition
- in-situ H_2 plasma treatment

● Metallization : low Rs / Rc, low recombination velocity



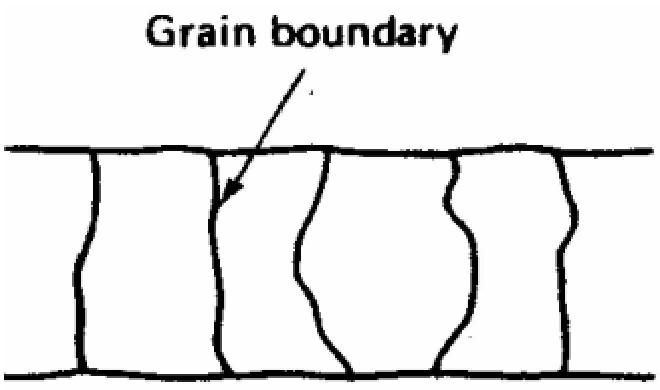
- Ag, Al screen printing + RTP annealing
- front / backside co-firing

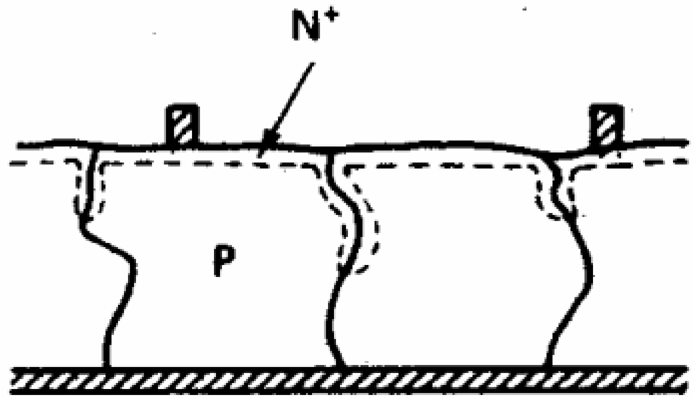
App.4 – Other Materials

- **Polycrystalline Silicon**
- **Amorphous Silicon**
- **Gallium Arsenide (GaAs)**
- **Copper Sulfide / Cadmium Sulfide (Cu_2S / CdS)**
- **Summary**

Polycrystalline Silicon

- **Less critical than single crystal silicon to produce**
- **Grain and grain boundary**
  - Block majority carrier flows as a large series resistance
  - Effective recombination centers: allowed level into the forbidden gap
  - 'Sink' for minority carrier : Attract to the boundary and recombine
  - ⇨ Need large lateral dimension of grains compared to minority carrier diffusion lengths to avoid significant loss in current output
  - Preferential diffusion of dopants during the junction formation step : provide shunting path for current flow across the p-n junction





Polycrystalline Silicon

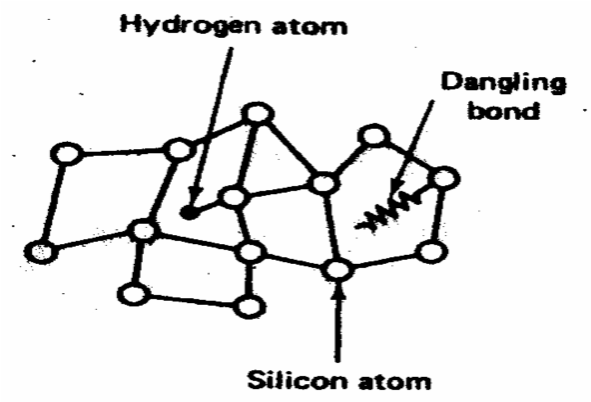
- **Require large grains size for performance**
  - Good photovoltaic performance: ~ 0.1mm diffusion length
  - Larger lateral dimensions of grains (the order of a few millimeters)

  ⇨ Columnar grain structure
  - Decrease the total length of grain boundaries per unit area of cell : decrease the shunting effects
- **Efficiency**
  - Over 10% efficiency of solar cell in 1976 and over 14% Larger-grained material solar cell

Amorphous Silicon

- **No long-range order in the structural arrangement of the atoms**
  - Small deviations of bonding angle, bonding lengths and etc.
- **No photovoltaic properties itself**
  - dangling bond: the microvoids within the structure of the material with associated unsatisfied bond
  - Large allowed states across the forbidden band gap
- **Hydrogenated amorphous silicon (a-Si:H)**
  - Glow discharge decomposition of silane(SiH_4)
  - Reasonable proportion of the total atoms (5-10%)
  - Saturate the dangling bond on microvoids of the films

⇨ Reduce the density of states of the forbidden gap and allow the material to be doped



Amorphous Silicon

- **Properties of a-Si:H**
  - larger band gaps than crystalline silicon (1.7 ~ 2.0 eV)
  - 1㎛ film thickness
  - Able to deposit onto a various of substrates
  - Control the doping level during deposition
  - Minority carrier diffusion length: less than 1 ㎛

  ⇨ Need a narrow depletion layer as collecting layer
  - Easy to fabricate : small interconnected individual cell
  - Commercial products: watches, calculators in 1980
- **a-Si:F:H films**
  - Decomposition of SiF_4 in hydrogen gas
  - More desirable properties for photovoltaic action

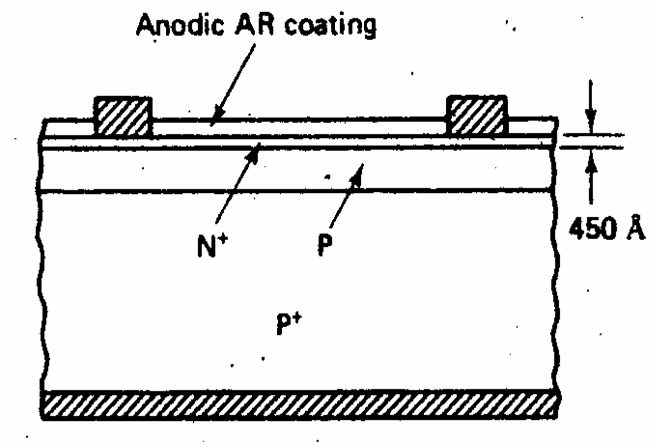
GaAs (gallium arsenide)

- **Compound semiconductor material with direct-band gap**
  - Short minority carrier lifetime & diffusion lengths
  - ⇨ Different cell design concepts
- **GaAs / AlAs alloy: $Ga_{1-x}Al_xAs$**
  - Good match of lattice spacing (only 0.14% mismatch)
  - Intermediate lattice spacing and band gap
  - Low densities of interfacial states and ideal properties
  - Terrestrial efficiency: over 22% under AM1
  - Expensive material : ideal for use in systems that concentrate sunlight
  - Toxic nature of arsenic

GaAs (gallium arsenide)

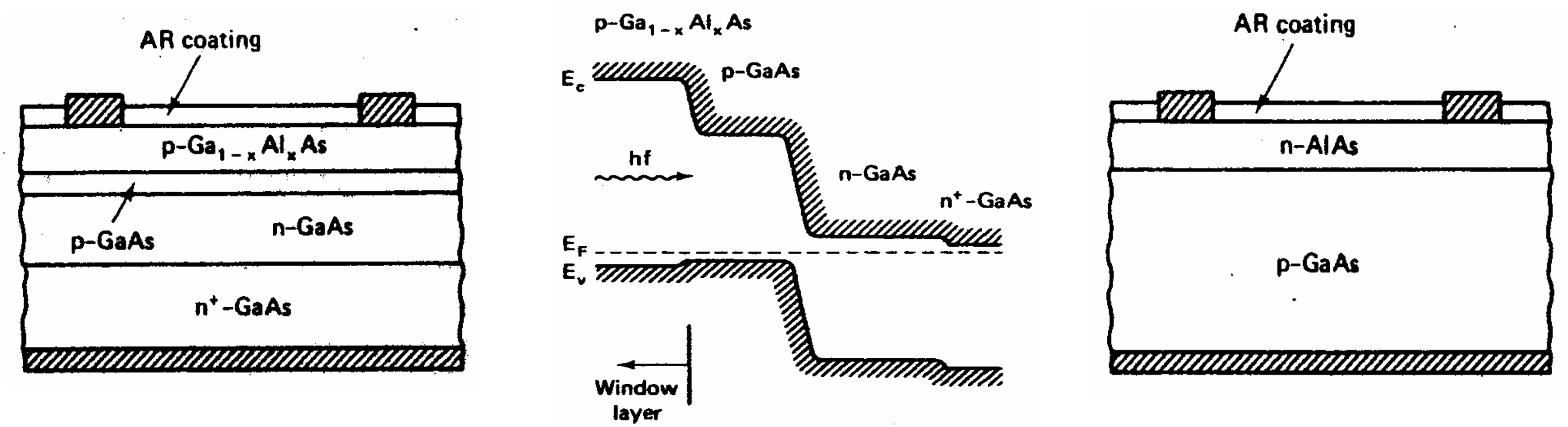
- **Problem for GaAs solar cells: high surface recombination velocity**

  ⇨ **homojuntion, heteroface and heterojunction solar cells**
- **Homojunction**
  - Thin top layer of the homojunction
  - 20% efficiency of N^+PP^+ solar cells
  - Epitaxial layer
    - ✓ Chemically build up layers incorporating the required dopant density
    - ✓ LPE, VPE and MBE



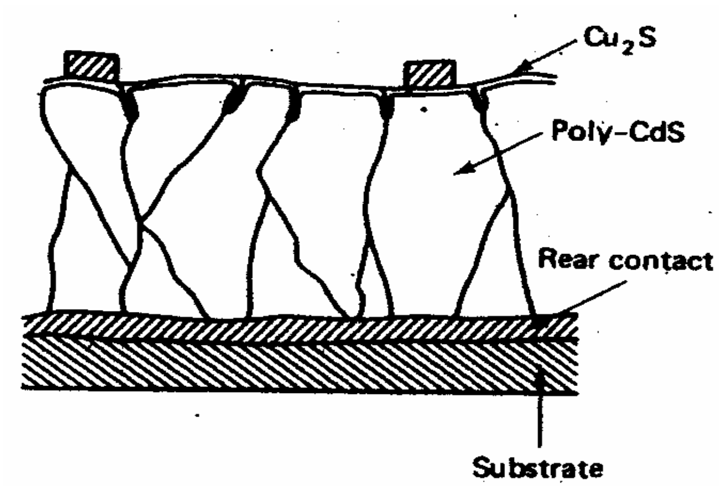
GaAs (gallium arsenide)

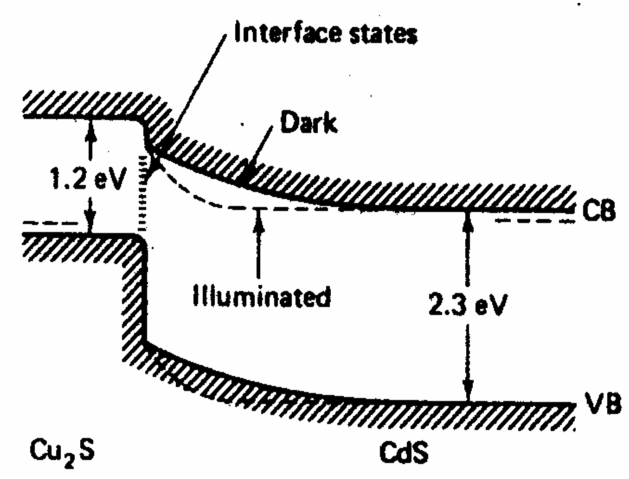
- **Heteroface junction**
  - Heteroface structure with $Ga_{1-x}Al_xAs$ on the surface of a homojunction cell
  - Large indirect band gap if x=0.8 : window layer
  - Passivate the surface of the underlying GaAs
- **Heterojunction**
  - n-type AlAs + p-type GaAs
  - Large band gap: window layer of AlAs
  - Spike in the conduction band energy of the heterojunction due to mismatch in the electron affinity ⇨ heavily doped AlAs



Cu_2S/CdS (copper sulfide/cadmium sulfide)

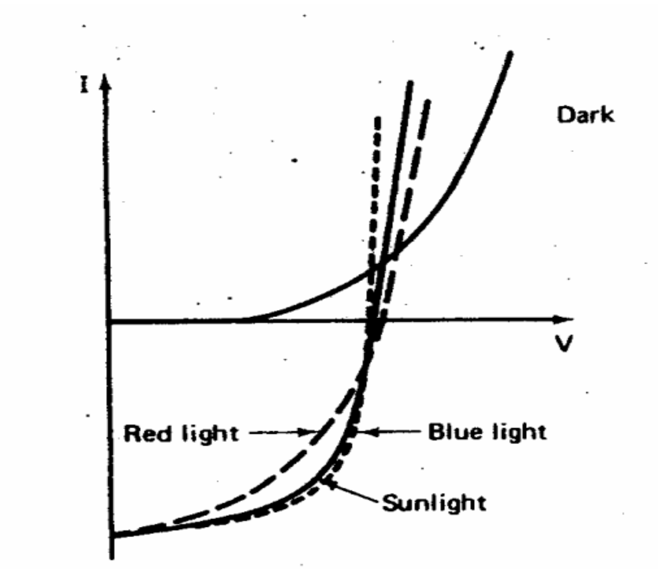
- **CdS cells**
  - Developed in 1954
  - Easy to fabricate: Clevite process
    - Deposited CdS onto metal sheet or a metal-covered plastic or glass sheet (20㎛)
    - Dipped in a cuprous chloride solution (80~100℃) for 10 to 30s
    - Substituted Cu for Cd in a thin surface region (1000~3000Å)
  - Over 9% efficiency

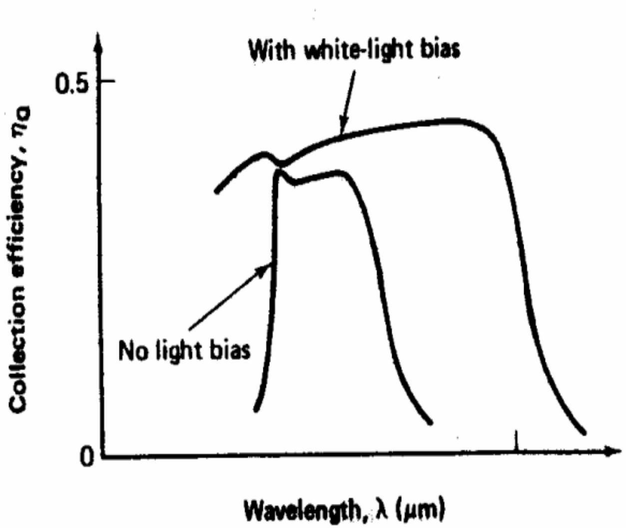




Cu_2S/CdS (copper sulfide/cadmium sulfide)

- **Nonlinearities characteristics of Cu_2S/CdS solar cells**
  - Crossover of dark and illuminated curves of current & voltage characteristics
  - Change the capacitance when illuminated
    - Depletion width change due to the trapping level
  - Dependence on the spectral contents of the illumination
    - With no bias light, fields become small and recombination rate increase : Poor spectral response





Cu_2S/CdS (copper sulfide/cadmium sulfide)

- **Advantage of Cu_2S/CdS solar cells**
  - Easy to fabricate on a variety of supporting substrate, making the cells well suited for large-scale automated production
  - Produced very inexpensively
- **Disadvantage of Cu_2S/CdS solar cells**
  - Low efficiency and lack of stability
  - Rule of thumb : 10% module efficiency is the lowest that can probably be tolerated for cost-effective large-scale generation of photovoltaic power
  - Encapsulation costs of the cells

Cu_2S/CdS (copper sulfide/cadmium sulfide)

- **Degradation modes : high humidity, high temp. in air, illumination at high temp., load voltage exceeds 0.33V**
  - High humidity
    - Creates additional traps : decrease the short-circuit current
    - Reversible process : appropriate heat treatment
  - High temperature (> 60℃) in air
    - Irreversible change : Cu_2S → CuO or Cu_2O
  - Illumination at high temperature
    - Decrease the efficiency when illuminated at high temperature even if air is not present
    - The light-activated phase change in stoichiometry : Cu_2S → Cu_xS ($x<2$)
  - High voltage exceeds 0.33V
    - Cause a light-activated change of Cu_2S to CuS or Cu
    - Cu : form the fine filaments, shunting the junction
- **Eliminated by minor changes in the cell fabrication method and by encapsulation of the cells**

Summary (App.4)

- **A wide range of solar cell materials**
  - Polycrystalline silicon
    - Required the large grain sizes
  - Amorphous silicon
    - The most promising solar cells materials
  - Gallium arsenide
    - Most efficient solar cells materials
    - Homojuntion, heteroface, heterojunction
    - High cost
  - Copper sulfide/cadmium sulfide
    - Low cost technology
    - Need encapsulation to prevent degradation