Photovoltaics: Solar Electricity and Solar Cells Efficiency

Outline

Introduction.

Raw materials for solar electricity.

Typical solar cell design.

Efficiency (cost per Watt) and possible losses.

Recombination losses in mc-Si and possible ways of their reduction.

URGENCY

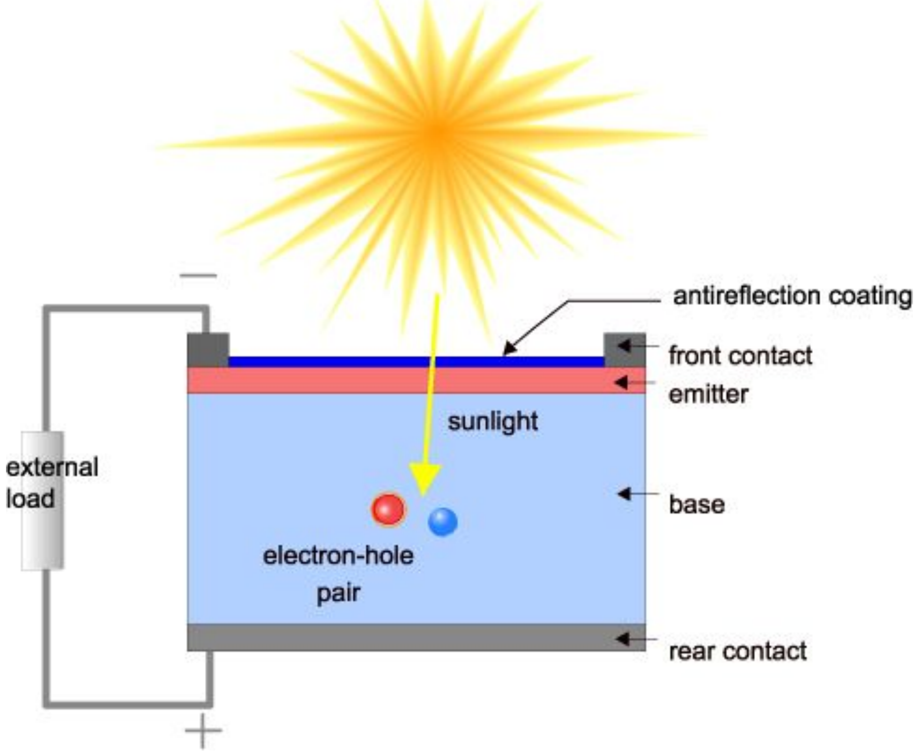
Semiconductor(electronic)-grade silicon industrial production is 10 000-12 000 tons/year worldwide

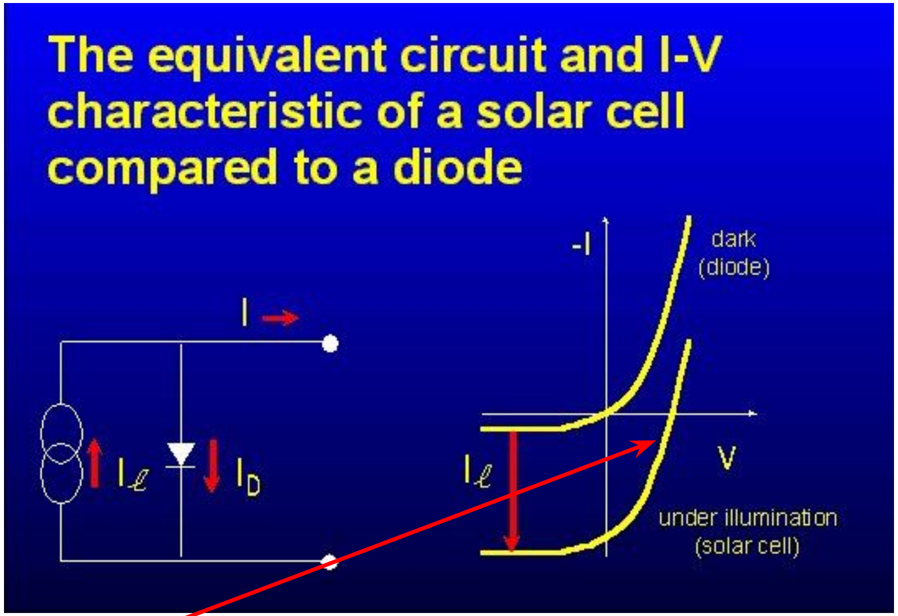
Requirement forecast for 2010-2011 is 10 000-12 000 tons/year worldwide

Solar-grade (SoG-Si) silicon industrial production is 8 000-10 000 tons/year worldwide

Requirement forecast for 2010-2011 is 16 000-25 000 tons/year worldwide

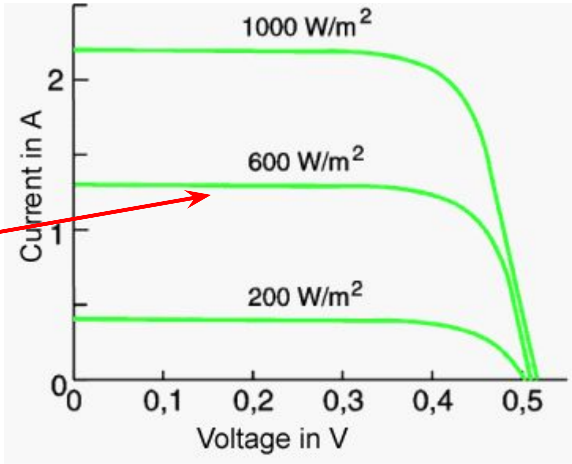
Photovoltaic effect





The equivalent circuit and I-V characteristic of a solar cell compared to a diode

$$I = I_0\left[\exp\left(\frac{qV}{nkT}\right)-1\right]-I_L$$



$$I = I_L - I_0\left[\exp\left(\frac{qV}{nkT}\right)-1\right]$$

Materials for solar cells

Si(all types), Ge, *SiC*, GaAs, CdTe, GaN, $CuInSe_2$, CdS, ZnS

Over 95% of all the solar cells produced worldwide are composed of Silicon !!!

Si material	Common Growth Techniques	Level of efficiency in % Lab	Level of efficiency in % Production
Monocrystalline(single crystal) Silicon	Czochralski (CZ) float zone (FZ)	approx. 24	14 to17
Polycrystalline Silicon	Cast, sheet, ribbon	approx. 18	13 to15
Amorphous Silicon		approx. 13	5 to7

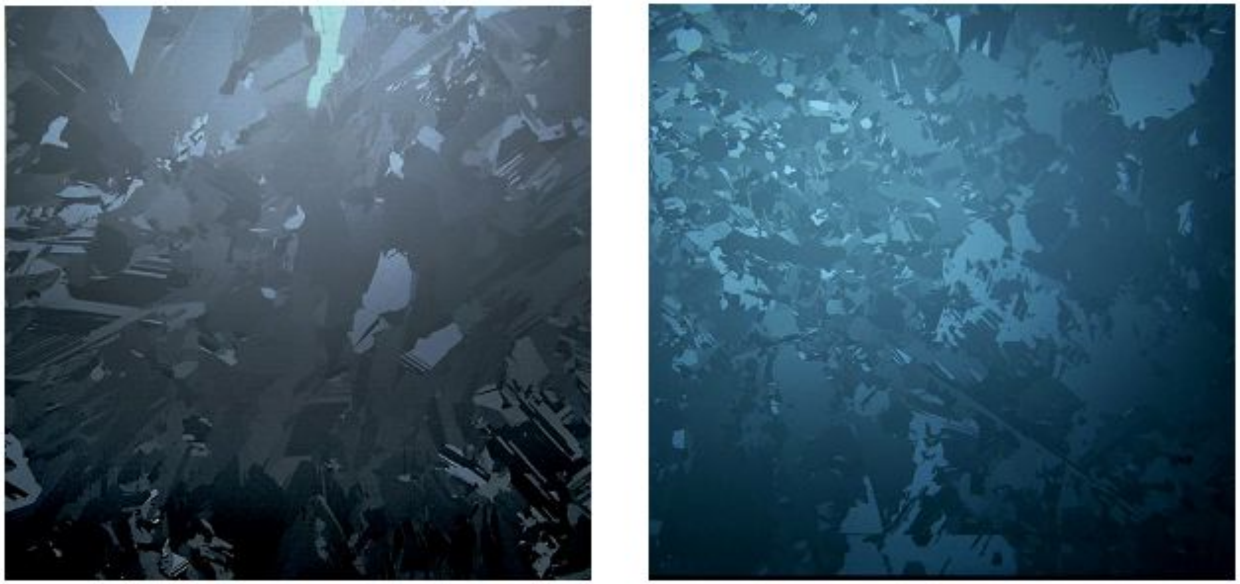
Question: what is more important

high efficiency → for mobile module

or

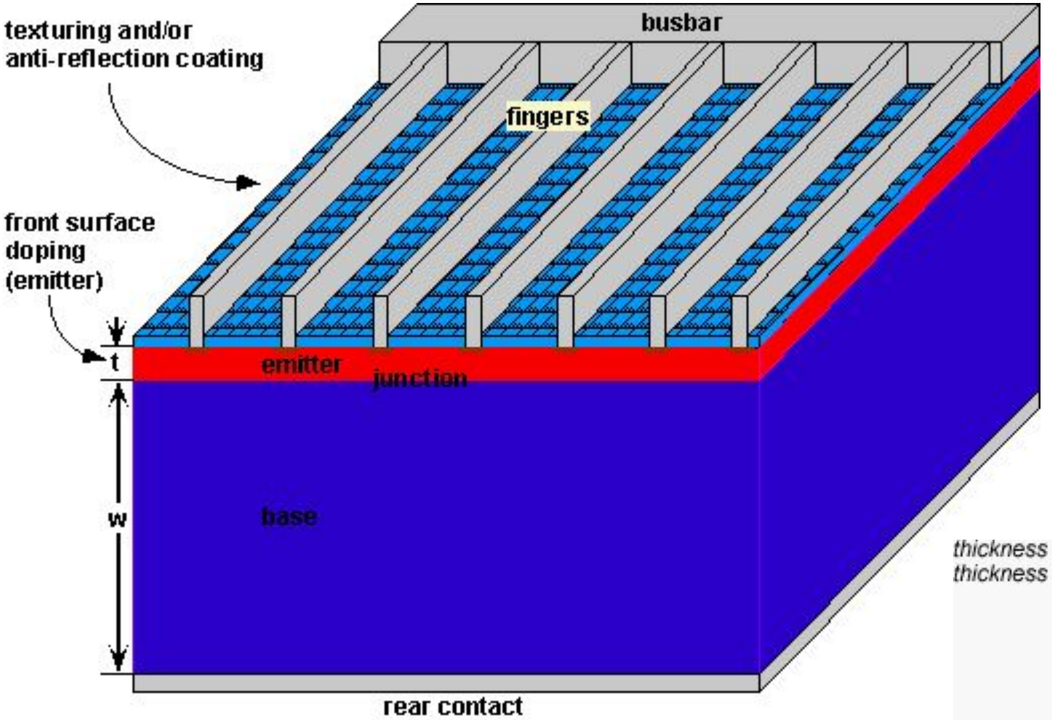
low cost per Watt → for terrestrial module

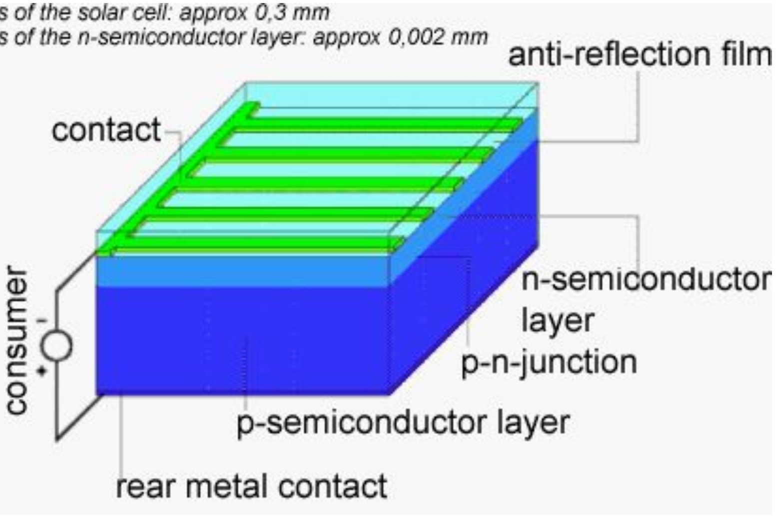
Descriptor	Symbol	Grain Size	Growth Techniques
Multicrystalline	mc-Si	1mm-10cm	Cast, sheet, ribbon
Polycrystalline	pc-Si	1μm-1mm	Chemical-vapour deposition
Microcrystalline	μc-Si	<1μm	Plasma deposition



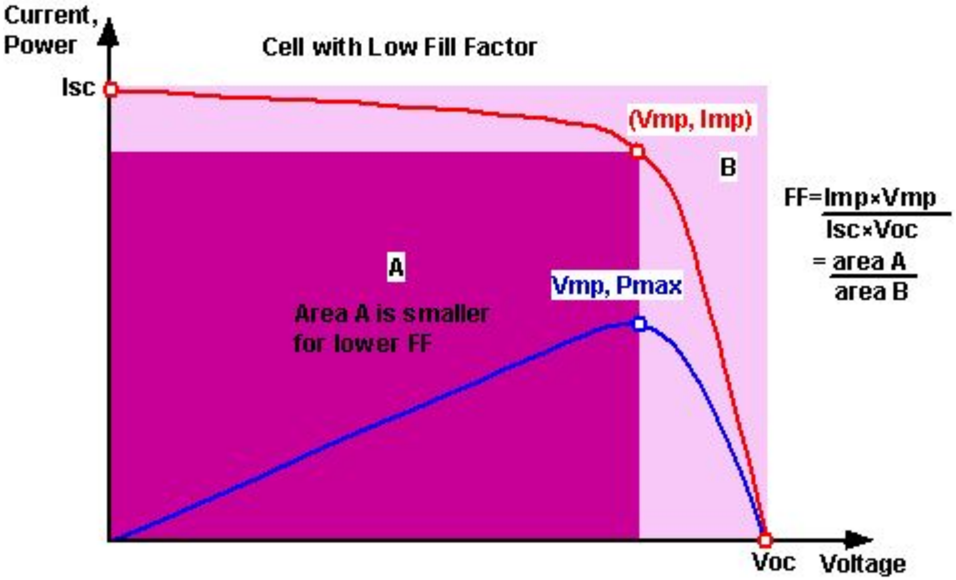
Multicrystalline Si with SiNx ARC and different grain size.
Wafer 156X156 mm, 200 μm thickness.
Produced by Millinet Solar Co. Ltd., Republic of Korea, Daego.

Typical design of Si solar cell





Fill factor and efficiency



$$FF = \frac{Imp \times Vmp}{Isc \times Voc} = \frac{\text{area A}}{\text{area B}}$$

$$\eta = \frac{V_{OC} I_{SC} FF}{P_{in}}$$

Energy losses in single-junction mc-silicon solar cell

Unavoidable, unremovable losses

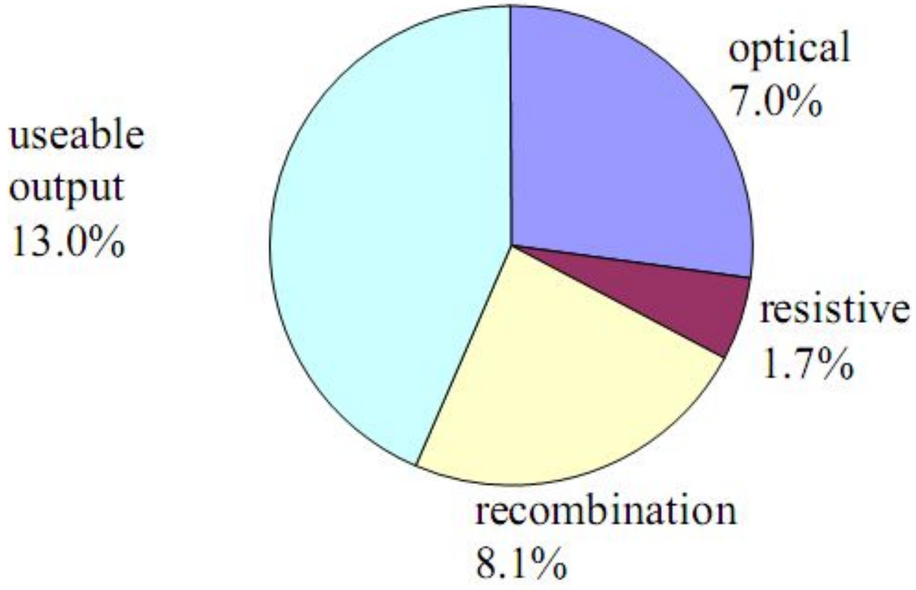
Losses related to the energy of the photons not exactly matching the band gap of silicon

Losses caused by radiative and Auger recombination

In concert, these intrinsic processes reduce the maximum attainable efficiency for a non-concentrating silicon solar cell to around 29.8%

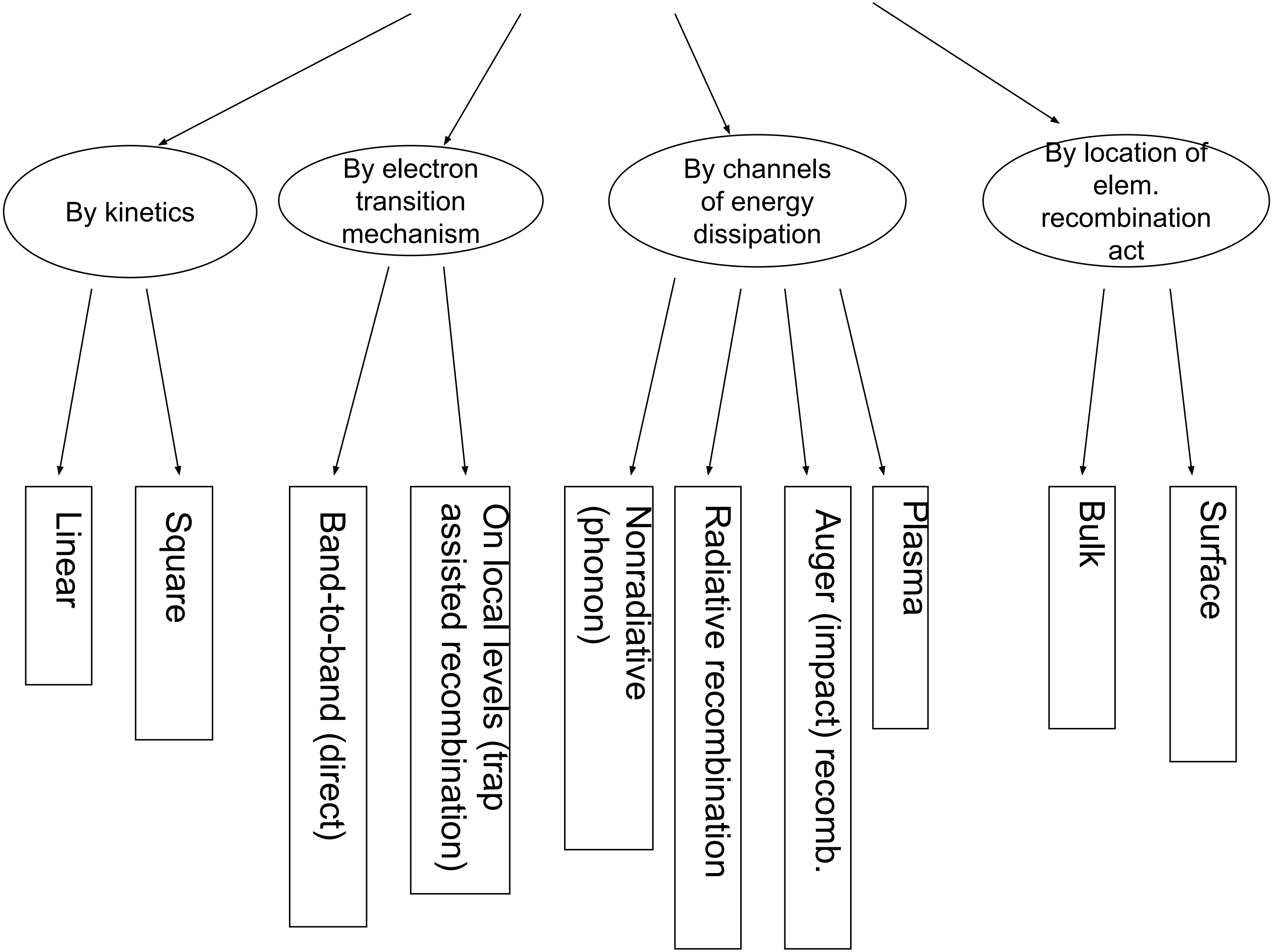
Commercially produced mc-Si cells do not come close to this upper limit. They typically have efficiencies around 13-14%.

Breakdown of avoidable losses in a typical commercial cast mc-Si solar cell



The pie chart indicates the source of avoidable losses as categorized into three broad groups - optical, resistive and recombination losses. Percentage is approximate values of this losses typical for a standard cast mc-Si cell produced commercially using screen-printed contacts on a heavily doped, homogeneous emitter with (ARC) and aluminium back-surface-field (BSF).

Classification of types of recombination



By kinetics

- Linear
- Square

By electron transition mechanism

- Band-to-band (direct)
- On local levels (trap assisted recombination)

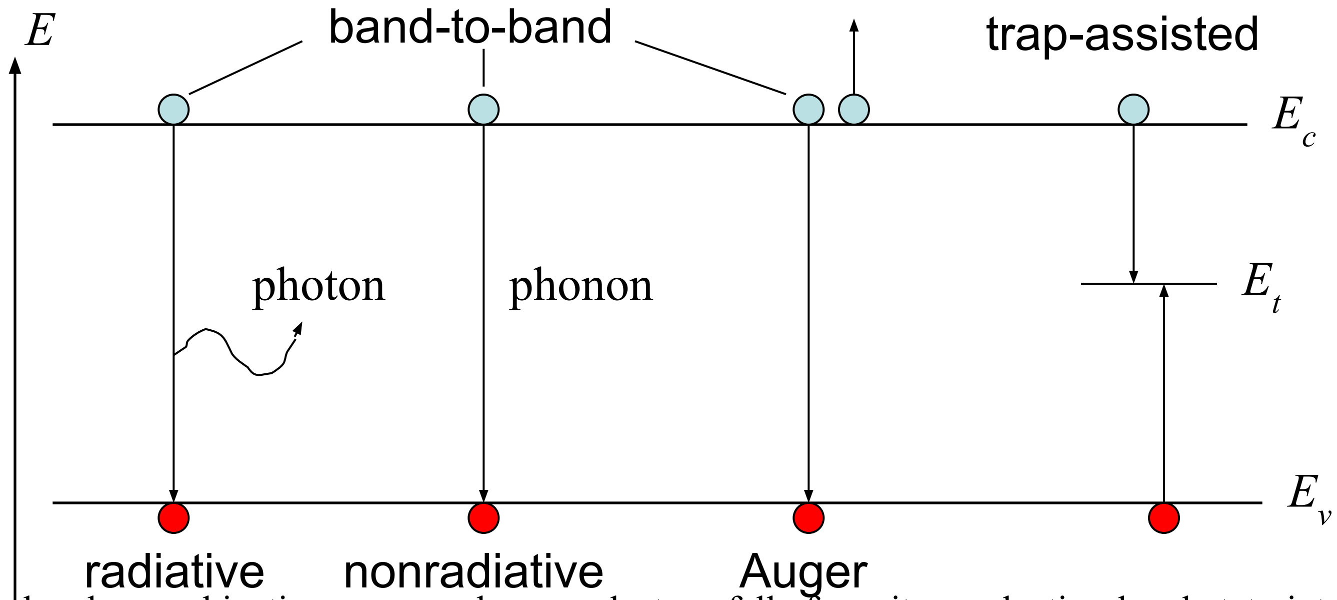
By channels of energy dissipation

- Nonradiative (phonon)
- Radiative recombination
- Auger (impact) recomb.
- Plasma

By location of elem. recombination act

- Bulk
- Surface

Band-to-band and trap-assisted recombination

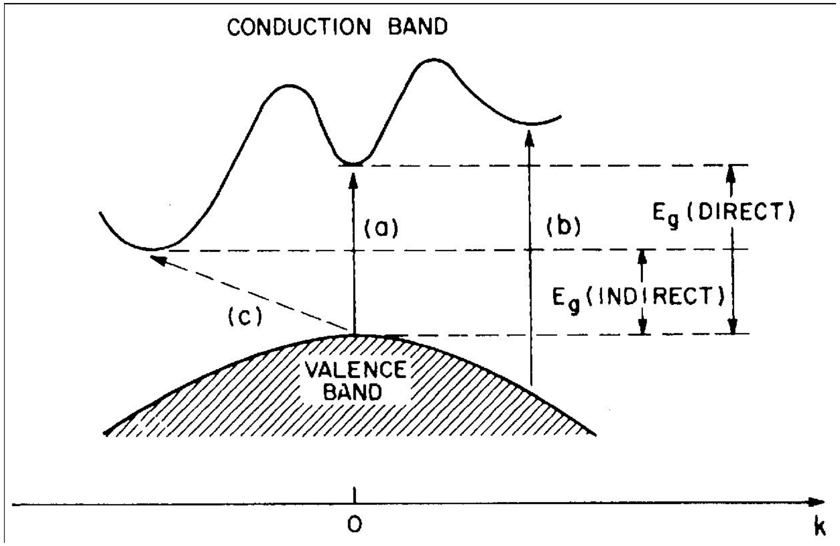


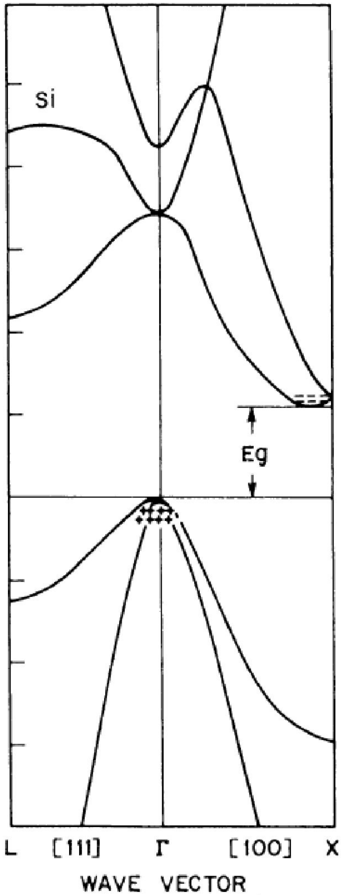
- Band-to-band recombination occurs when an electron falls from its conduction band state into the empty valence band state associated with the hole. It may be radiative (photon) or nonradiative (phonon).
- Auger recombination is a process in which an electron and a hole recombine in a band-to-band transition, but now the resulting energy is given off to another electron or hole. The involvement of a third particle affects the recombination rate so that we need to treat Auger recombination differently from band-to-band recombination.
- Trap-assisted recombination occurs when an electron falls into a "trap", an energy level within the bandgap caused by the presence of a impurity atom (often metal atom) or a structural defect. Once the trap is filled it cannot accept another electron. The electron occupying the trap, in a second step, falls into an empty valence band state, thereby completing the recombination process. One can envision this process as a two-step transition of an electron from the conduction band to the valence band or as the annihilation of the electron and hole, which meet each other in the trap. It is well described by Shockley-Read-Hall (SRH) model.

Probability

- The analysis of extensive experimental data and theoretical estimations shows that band-to-band radiative, nonradiative and Auger recombination are not among the most probable recombination processes in silicon. These recombination mechanisms are more typical for direct bandgap semiconductors with narrow bandgap (< 0,5 eV).

For silicon, wide-bandgap (1,1 eV) semiconductor with indirect bandgap, more probable is recombination through local levels or trap-assisted recombination.





Shockley–Read–Hall model

$$\tau = \tau_{p_0} \frac{n_0 + n_1 + \Delta n}{n_0 + p_0 + \Delta n} + \tau_{n_0} \frac{p_0 + p_1 + \Delta p}{p_0 + n_0 + \Delta p}$$

$$\left.\begin{aligned} \tau_{p_0} &= \frac{1}{S_p \upsilon_p^T N_t} \\ \tau_{n_0} &= \frac{1}{S_n \upsilon_n^T N_t} \end{aligned}\right\}$$

$$n_1 = N_c e^{-\frac{E_c - E_t}{kT}}$$

$$p_1 = N_v e^{\frac{E_v - E_t}{kT}}$$

If $\Delta n << n_0 + p_0$ - low injection (low excitation level)

$$\tau = \tau_{p_0} \frac{n_0 + n_1}{n_0 + p_0} + \tau_{n_0} \frac{p_0 + p_1}{p_0 + n_0}$$

If $\Delta n >> n_0$; $\Delta p >> p_0$; $\Delta n >> n_1$, $\Delta p >> p_1$ $\quad \tau_\infty = \tau_{po} + \tau_{no}$

Which of metallic impurities affect solar cell efficiency(recombination rate) in order?

Question formulation is incorrect, naive.

1. Fe, Cr, Ti, V, Mo, Zn, Au…….
2. Au, Mg, Zn, Cu, Fe, Cr,……..
3. Cu, Mn, Co, Ca, Ti, V, Ni…….

- The recombination “strength” of a given impurity is determined by three parameters: the energy level and the capture cross sections for both electrons and holes.

Impurity	RT lattice site	Type	Energy (eV)	s_n (cm^2)	s_p (cm^2)	$k=s_n/s_p$
Ti	Interstitial	Donor	$E_C-0.27$	3.1×10^{-14}	1.4×10^{-15}	22
	Interstitial	D.donor	$E_V+0.26$	1.3×10^{-14}	2.8×10^{-17}	460
V	Interstitial	D. donor	$E_V+0.36$	5×10^{-14}	3.0×10^{-18}	17000
Cr	Interstitial	Donor	$E_C-0.22$	2.3×10^{-13}	1.1×10^{-13}	2
Mo	Interstitial	Donor	$E_V+0.28$	1.6×10^{-14}	6.0×10^{-16}	30
Fe	Interstitial	Donor	$E_V+0.38$	5×10^{-14}	7×10^{-17}	700
Au	Substitutional	Acceptor	$E_C-0.55$	1.4×10^{-16}	7.6×10^{-15}	0.02
Zn	Substitutional	Acceptor	$E_V+0.33$	1.5×10^{-15}	4.4×10^{-15}	0.34
	Substitutional	D. acceptor	$E_C-0.47$	1.3×10^{-19}	6.6×10^{-15}	0.00002

- Of course, lifetime depends not only on the recombination strength but also on concentration of recombination impurity.

Specific recombination strength

- Let's introduce a new parameter, so called *specific recombination strength* of a given recombination center, which is equal to product of N_t and lifetime for defined temperature and doping level. For example, in highly doped p-type semiconductor it will be equal to

$$\tau_{no} N_t = \frac{1}{s_n v_{thn}}$$

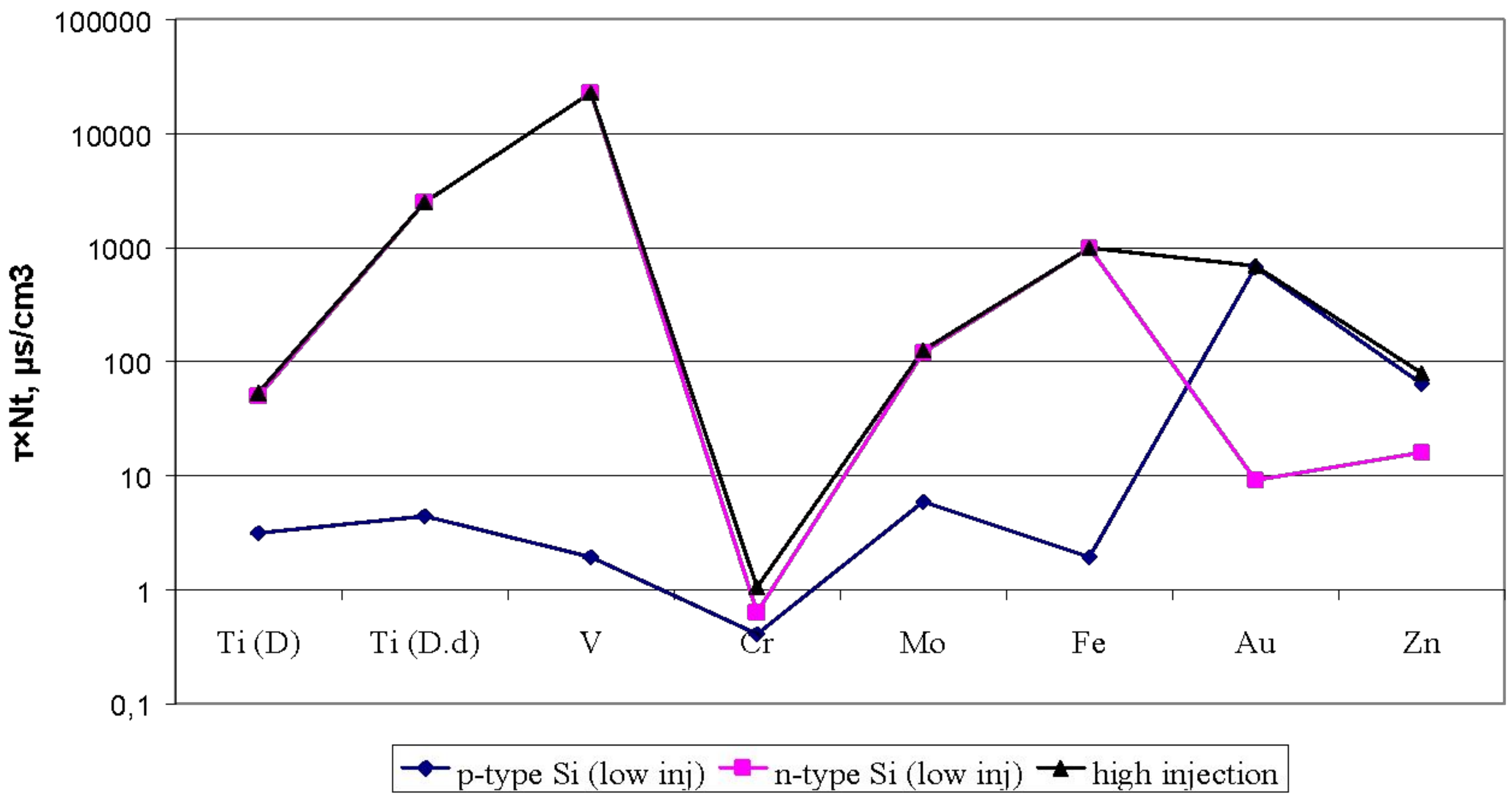
- in highly doped n-type

$$\tau_{po} N_t = \frac{1}{s_p v_{thp}}$$

Calculated values of this parameter for doping level 1,3·10^{16} cm^{-3} (typical for base resistivity of solar mc-Si), T=300 K for low injection (in p-type and n-type) and high injection

Impurity	Type	$\tau \times N_t$ (p-type), s/cm^3	$\tau \times N_t$ (n-type), s/cm^3	High injection, s/cm^3
Ti	Donor	$3{,}1 \cdot 10^6$	$5{,}0 \cdot 10^7$	$5{,}3 \cdot 10^7$
	D. donor	$4{,}4 \cdot 10^6$	$2{,}5 \cdot 10^9$	$2{,}5 \cdot 10^9$
V	D. donor	$1{,}9 \cdot 10^6$	$2{,}3 \cdot 10^{10}$	$2{,}3 \cdot 10^{10}$
Cr	Donor	$4{,}1 \cdot 10^5$	$6{,}3 \cdot 10^5$	$1{,}0 \cdot 10^6$
Mo	Donor	$5{,}9 \cdot 10^6$	$1{,}2 \cdot 10^8$	$1{,}3 \cdot 10^8$
Fe	Donor	$1{,}9 \cdot 10^6$	$9{,}9 \cdot 10^8$	$9{,}9 \cdot 10^8$
Au	Acceptor	$6{,}8 \cdot 10^8$	$9{,}1 \cdot 10^6$	$6{,}9 \cdot 10^8$
Zn	Acceptor	$6{,}4 \cdot 10^7$	$1{,}6 \cdot 10^7$	$8{,}0 \cdot 10^7$
	D. accep.	$7{,}4 \cdot 10^{11}$	$1{,}1 \cdot 10^7$	$7{,}4 \cdot 10^{11}$

"Specific recombination strength" of some metallic impurities in Si



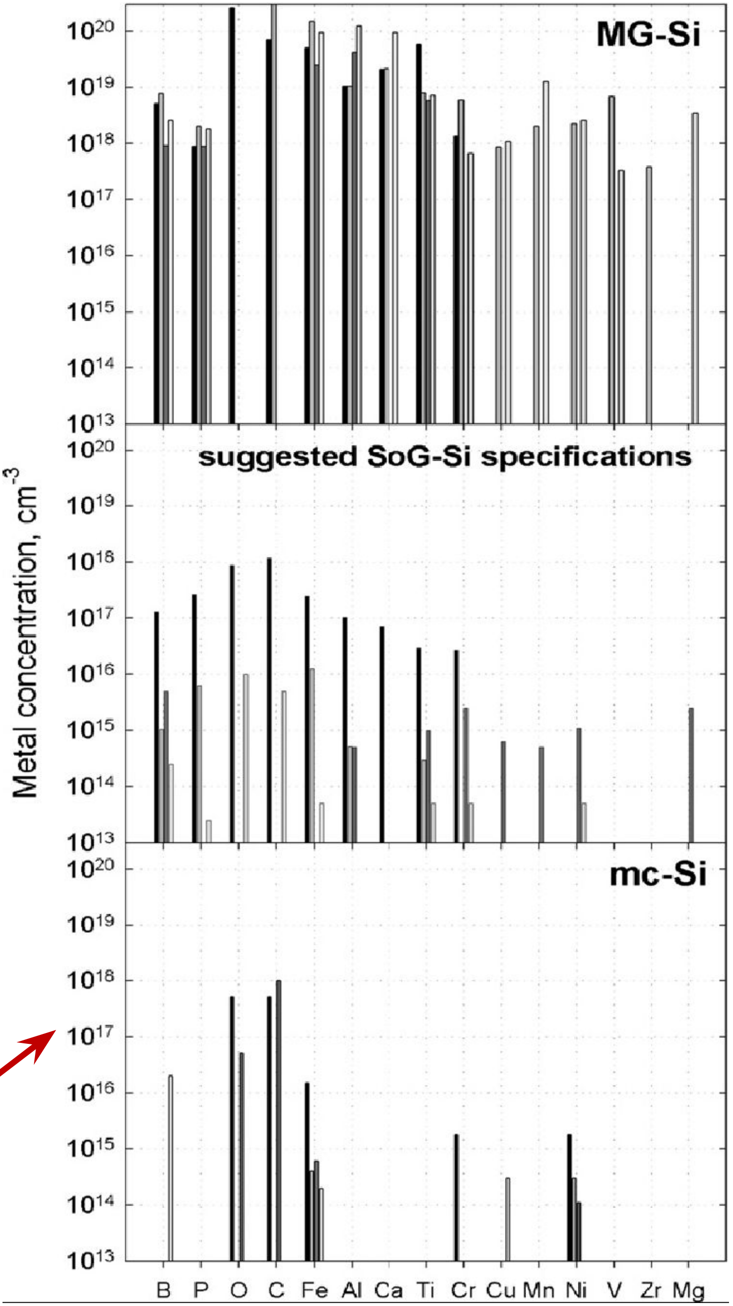
- Recombination activity most of metals is *higher in p-type silicon* because of higher electron capture cross sections. ***Cr, Fe, V, Ti are the most undesirable point-like metal impurities***. It is obvious that if lifetime value is near 1μsec the concentration of majority of impurities is around ***10^{12} cm^{-3}.***

But measured values of these contaminations is much higher in mc-Si !!!

It can means only one thing - *these impurities are not in a state of homogeneously distributed point-like defects.*

Extensive studies revealed that, in fact, the *majority of transition metals are found in metal precipitates or inclusions at grain boundaries or intragranular defects. In this state, the recombination activity per metal atom is reduced as compared to interstitially dissolved metals, and the tolerance of solar cells to metal contamination increases.*

It is even possible to manipulate the distribution of metals in mc-Si to change lifetime (so called *defect engineering)*



Typical concentrations of impurities in metallurgical grade (the top graph), solar-grade (the middle graph), and multicrystalline silicon solar cells (the bottom graph).

Summarizing discussed details it is possible to state:

- the impurity content and structural features (grain size) of mc-Si can vary significantly from one purification technology to another and from one manufacturer to another (by one to two orders of magnitude);

- concentration of many background impurities such as Ti, Mo, V, Zr, Mn, Zn, Cr may be below the detection limit of NAA and other techniques, though at the same time they essentially influence carrier lifetime;

- recombination activity of metallic impurities depends strongly on their chemical state and spatial distribution in mc-Si;

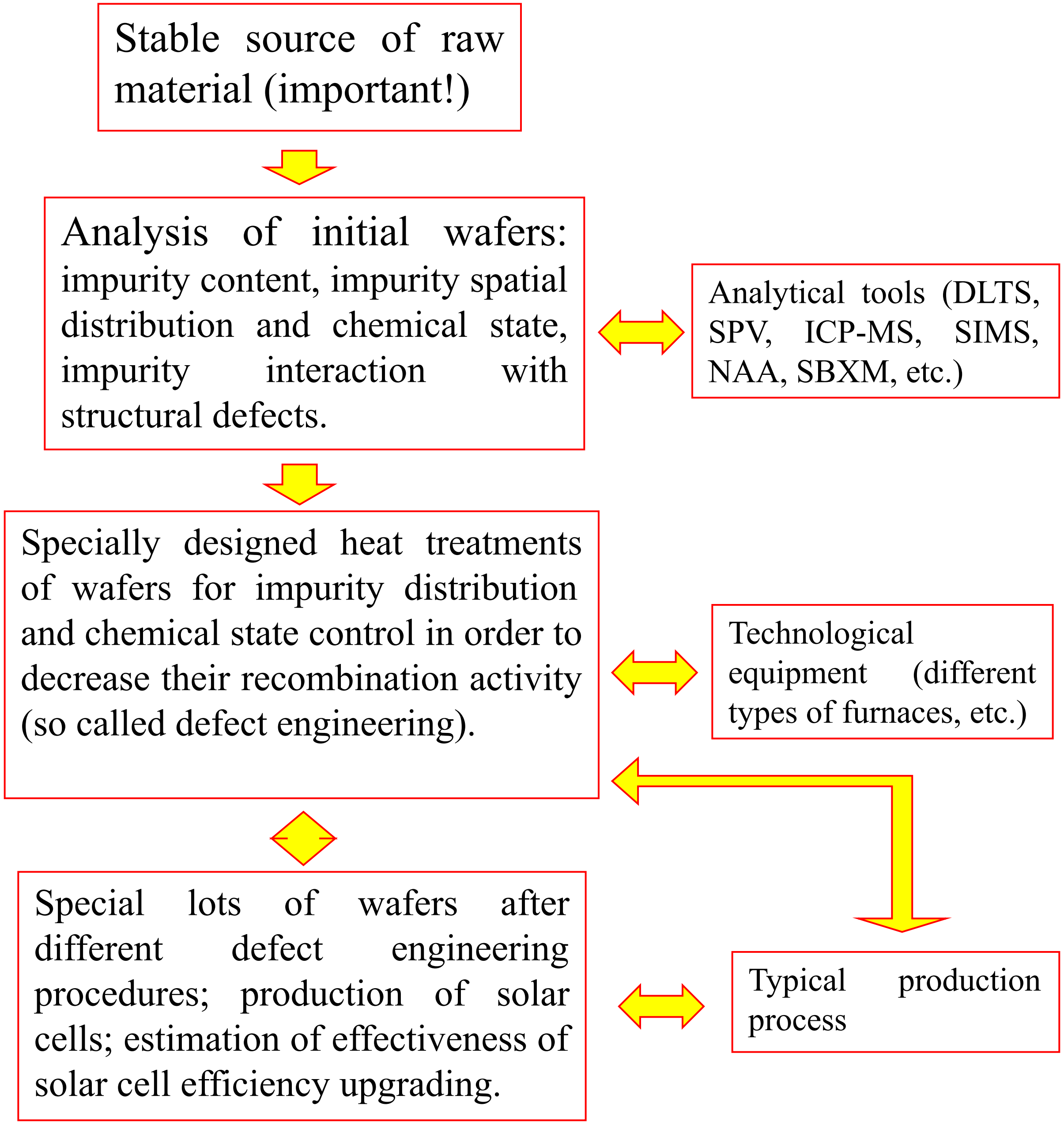
- recombination strength of one and the same impurity in various Si samples can be rather different depending on type of Si conductivity (n-type or p-type), impurity chemical state, resistivity, injection level, temperature, etc. (for example, recombination strength of Ti, Mo, Fe, V is considerably higher in p-type silicon, than in n-type silicon).

Two possible approaches

To add an additional purification steps to reduce the metal content by two to three orders of magnitude.

To gain a deeper understanding of the interaction between metals and with structural defects in mc-Si in order to defect-engineer metals into their least recombination active state (specially designed heat treatments, optimization of growth conditions to favor the formation of preferred types and densities of grain boundaries or dislocations, etc.

Simplified algorithm of proposed procedures



Stable source of raw material (important!)

Analysis of initial wafers: impurity content, impurity spatial distribution and chemical state, impurity interaction with structural defects.

Analytical tools (DLTS, SPV, ICP-MS, SIMS, NAA, SBXM, etc.)

Specially designed heat treatments of wafers for impurity distribution and chemical state control in order to decrease their recombination activity (so called defect engineering).

Technological equipment (different types of furnaces, etc.)

Special lots of wafers after different defect engineering procedures; production of solar cells; estimation of effectiveness of solar cell efficiency upgrading.

Typical production process

Recombination kinetics

For thermodynamic equilibrium: $G_0 = R_0$, [cm^{-3}s^{-1}] $R_0 = \gamma_r n_0 p_0$

For steady nonequilibrium state : $G = R = \gamma_r np$

If the source of nonequilibrium generation is switched off :
$$-\left(\frac{dn}{dt}\right)_r = -\left(\frac{dp}{dt}\right)_r = \gamma_r np - G_0$$

or
$$-\left(\frac{dn}{dt}\right)_r = \gamma_r \left(np - n_0 p_0\right) = \gamma_r \left(n_0 + p_0 + \Delta n\right)\Delta n$$

$\Delta n << n_0 + p_0$ (low injection)

linear

$$\frac{dn}{dt} = -\gamma_r \left(n_0 + p_0\right)\Delta n$$

$$\tau = \frac{1}{\gamma_r \left(n_0 + p_0\right)}$$

$$\frac{dn}{dt} = -\frac{n - n_0}{\tau} = -\frac{\Delta n}{\tau}$$

$$\Delta n(t) = \Delta n(0) e^{-\frac{t}{\tau}}$$

$\Delta n >> n_0 + p_0$ (high injection)

square

$$\frac{dn}{dt} = -\gamma_r \left(\Delta n\right)^2$$

$$\tau_{\text{мгн}} = -\frac{\Delta n}{\left(\frac{dn}{dt}\right)_r}$$

$$\Delta n(t) = \frac{\Delta n(0)}{1 + \gamma_r \Delta n(0) \cdot t}$$