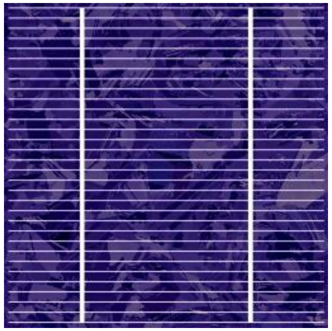
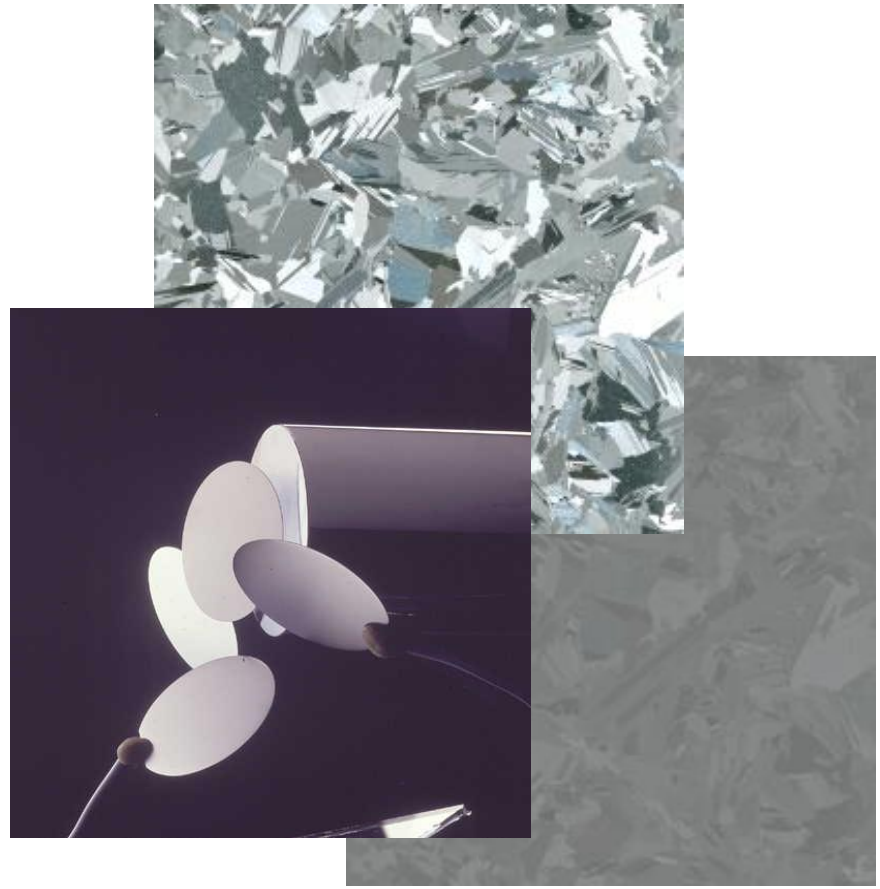
Silicon as a photovoltaic material



Overview

- A brief introduction to silicon (Si)
- Si for solar cells
- Defects in Si
    - Classification
    - Point defects
        - The effect of impurities
        - Impurity complexes
    - Extended defects
- Handling impurities
    - Impurity management
    - Segregation
    - Gettering and passivation



Topsil, IFE

Silicon (Si)

- Group IV A element
- Abundant
  - Second most abundant element in crust (~ 26 $\%_{wt}$ Si)
- Industrially important
  - Semiconductor industry
  - Photovoltaic industry (~ 98%)
- Non-toxic
  - However, fine Si-containing powders can be hazardous
    - Explosive
    - Silicosis
- Si never occurs pure in nature
  - Forms oxides and silicates
  - Challenge: making **pure** Si

Physical properties of ^{14}Si

Atomic weight	28.085
Atomic density	$5.0 \cdot 10^{22}$ cm^{-3}
Melting point	1410 ^{o}C
Boiling point	2355 ^{o}C
Density	2.33 g cm^{-3}
Volume of contraction (on melting)	9.5 %
Energy gap	1.12 eV
Crystal structure	diamond

A brief history of silicon production

- The use of Si-based materials is as old as civilization itself
  - Neolithic era flint tools and silicate glass (12 000 BC)

- Main dates of Si-related discoveries and inventions
  - 1824: First preparation of elemental Si *[Berzelius]*
  - 1854: First preparation of Si crystals (electrolysis) *[Sainte-Claire Deville]*
  - 1895: Production of Si in arc furnace *[Moisan]*
  - 1897-8: Industrial production of Si *[Bozel and Rathenau]*
  - WWII: Preparation of pure Si metal (Purity > 96 %)

- Si becomes industrially important towards the end of the 19th century for use in steel production

Main applications of silicon

- Metallurgical industry
  - Si is used to modify the properties of different melts and alloys
- Chemical industry
  - Silicones
    - $Si(s) + 2CH_3Cl(g) \rightarrow (CH_3)_2Si(OH)_2$
  - Silica
    - Optical fibre feedstock, silicone rubber additive, food…
  - Functional silanes
    - $SiH_{4-x}Cl_x\,(g)$
- Semiconductor industry
  - Based on "poly Si" (ultra-pure Si)
  - Important from 1950's

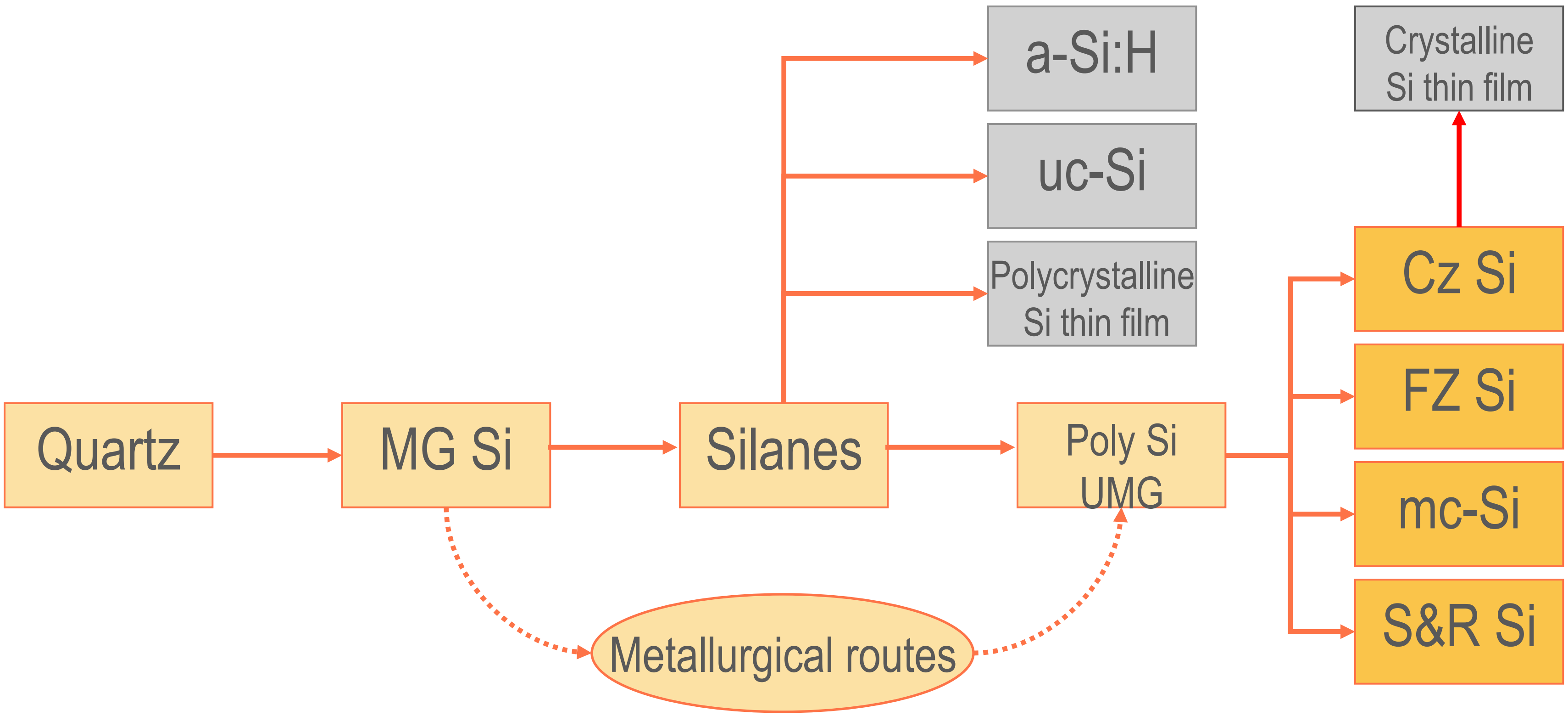
Silicon for solar cells

- Solar cells are made up of different types of Si precursors
  - Thin-film Si (amorphous, micro/nanocrystalline, crystalline)
    - Deposition from silanes ($SiH_{4-x}Cl_x$)
    - Quantity and cost not very critical, low material consumption
  - Crystalline Si substrates
    - sc and mc-Si grown by different processes from melts of poly-Si
      - Until recently mostly from semiconductor-grade Si
    - Quantity and cost critical, high material consumption

- Q: *"How pure must Si be if it is to be used in a solar cell?"*

  - Different solar cell designs have different material requirements!

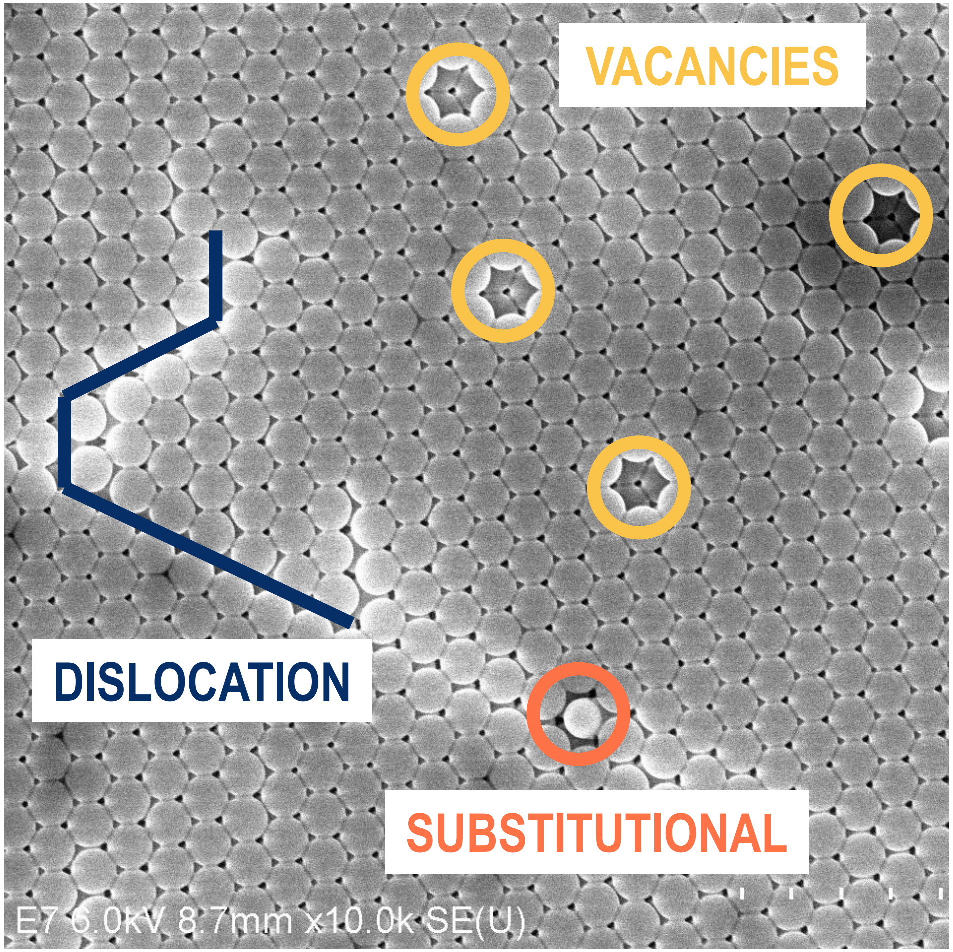
Silicon for solar cells



What do we know so far?

- Semiconductor theory describes the behaviour of a **perfect** Si crystal and an **ideal** solar cell very accurately
- **Real** Si crystals and solar cells always contain imperfections
  - Imperfections will affect or in some cases even determine the overall properties of Si materials and Si-based solar cells
- The effect of a number of isolated defects is well known
- Main challenges:
  - To fully understand the role of and interplay between different defects and impurities occuring **simultaneously** in a Si material
  - To develop suitable processes for Si material and solar cell production

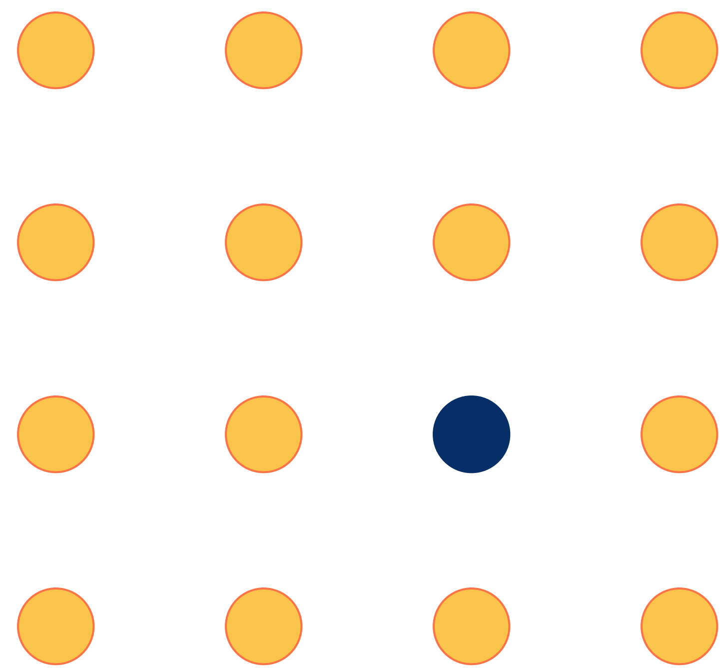
Crystal defects



H. Granlund (IFE)

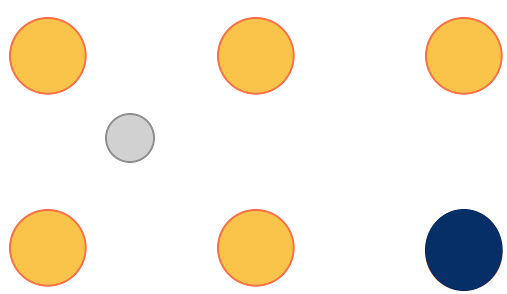
Defects in Si

- Overview of things to come
  - Classification
  - Impurities
    - Donors and acceptors
    - Metallic impurities
    - O, C and N
  - Dislocations
  - Interfaces
  - Precipitates



Classification

- Point defects
  - Vacancies
  - Impurities
    - Substitutional and interstitial
  - Si self-interstitials

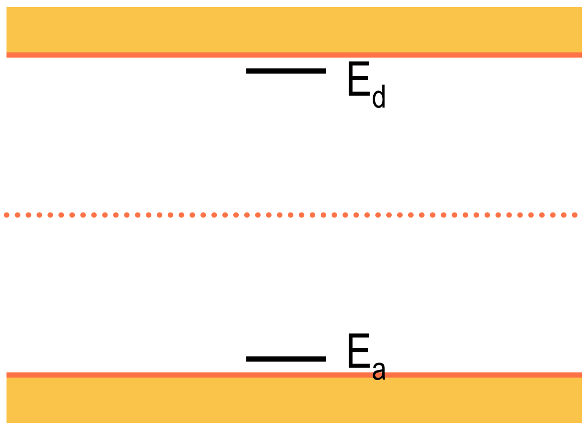


- Extended defects
  - Line defects
    - Dislocations
  - Area defects
    - Grain boundaries
    - Sub-grain boundaries (Misorientation $< 5^{0}$)
    - Twin boundaries
    - Stacking faults
  - Volume defects
    - Precipitates

Donors and acceptors

- Point defects
- Substitutional impurities
- Donors: elements from group IIIA
  - B, Al, Ga…
- Acceptors: elements from group VA
  - P, As, Sb…
- Form defect levels close to the band edges
- All donors and acceptors ionized at room temperature

- Source: feedstock, intentional doping



Metallic impurities

- Transition metals
  - Interstitial metals
    - Cu, Fe, Co, Cr, Ag …
  - Substitutional metals
    - Zn, As, Sb, Sn …
- The main effect of metals is to reduce the lifetime of the material
- Can easily supersaturate during cooling of melt and form precipitates
  - Metal particles, silicides …

- Source: feedstock, furnace, crucible …

Metallic impurities

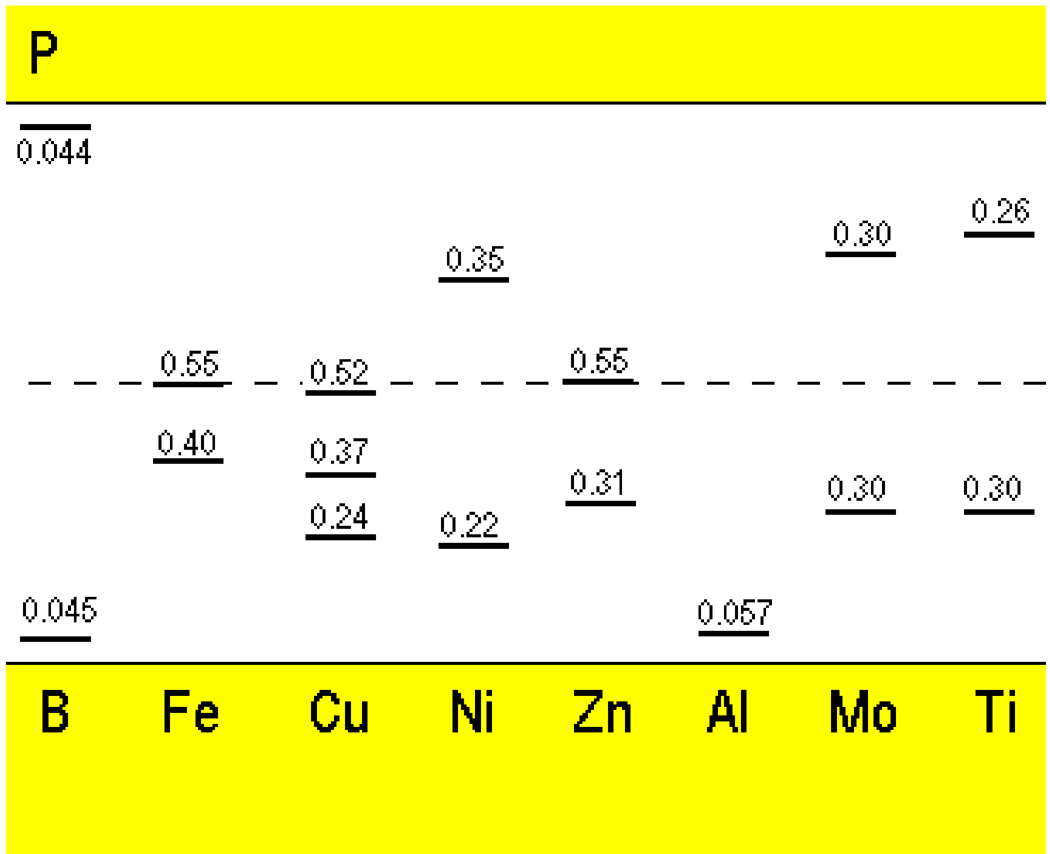
- Recombination centres for minority carriers

$$\tau = (\sigma v N)^{-1}$$

  - σ = capture cross section
  - v = thermal electron velocity
  - N = impurity concentration

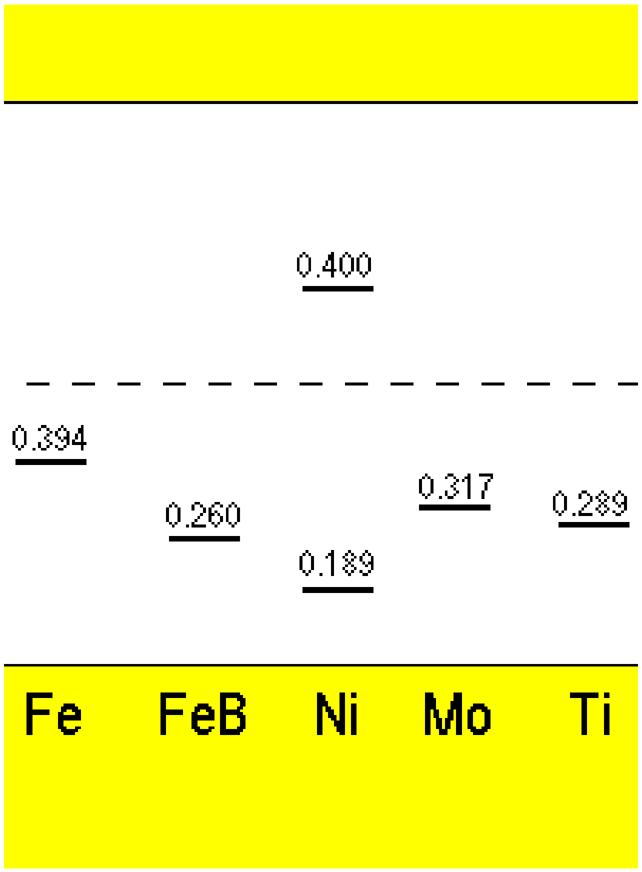
- Elements with high σ are often called lifetime killers

Impurity levels in Si



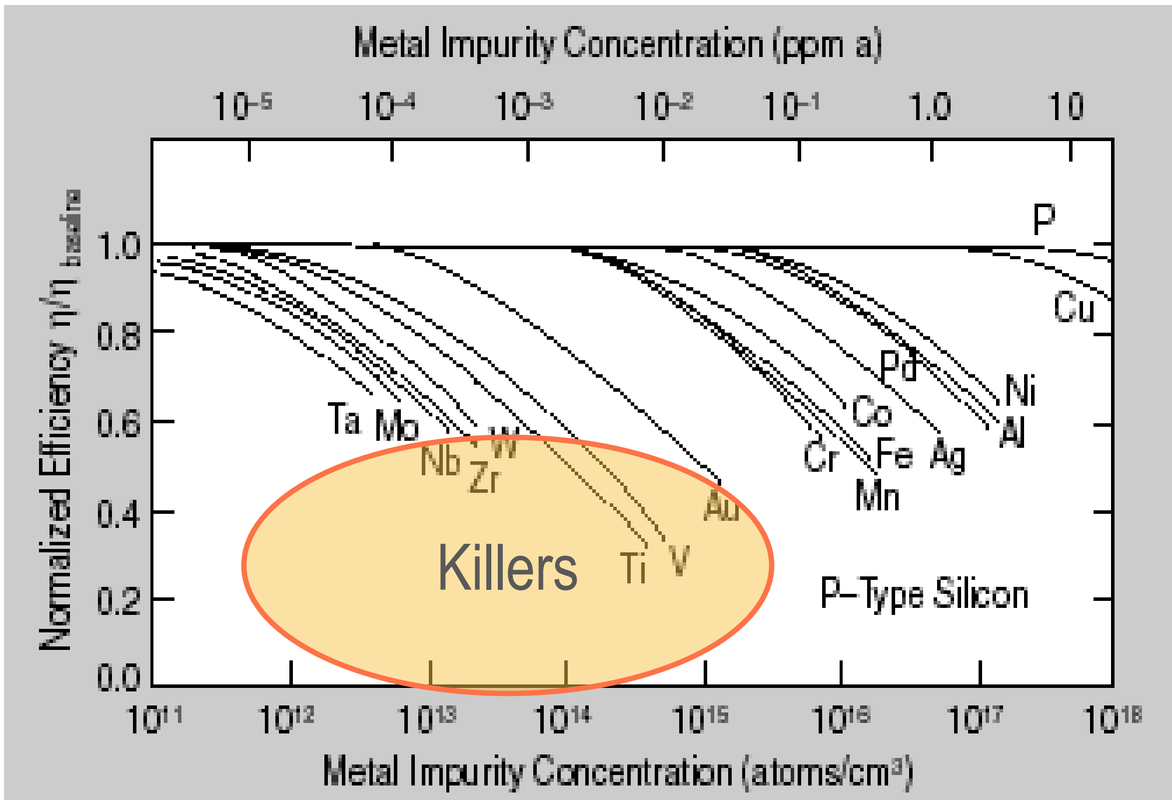
Data from O'Mara (1990) and Goetzberger

Impurity levels in Si from lifetime



S. Rein: "Lifetime Spectroscopy", Springer 2005

The effect of metal impurities



Davis Jr., IEEE Trans. El. Dev., 1980

Carbon, oxygen and nitrogen

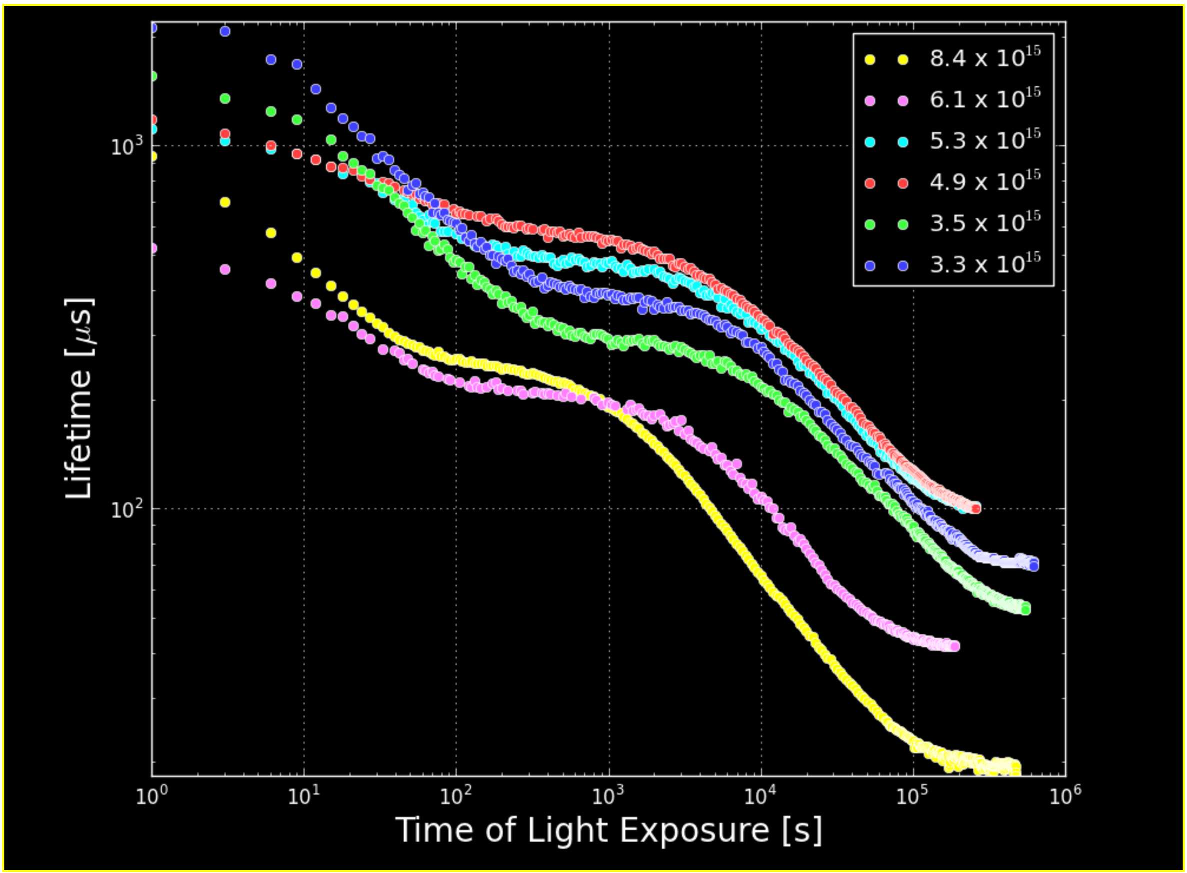
- C
  - Substitutional element
  - Can form various precipitates
    - SiC
  - Source: feedstock, graphite furnace parts, atmosphere …
- O
  - Interstitial element
  - Fast diffuser
  - Participates in the formation of a range of defects and precipitates
  - Source: crucible …
- N
  - SiN precipitates
  - Source: crucible coating …

B-O complexes
Light induced degradation

- B_s and O_i can form complexes in Si under illumination
  - More generally: under any minority carrier injection
  - Causes formation of states in the band gap
  - Proposed candidate: B_sO_{i2}
- Solar cells made from B-doped Cz Si show an appreciable degradation of the efficiency under illumination
  - Important to state stable efficiencies
- Example
  - Solar cell made from Cz(B) immediately upon illumination: ~21.0 %
  - Same cell, stable efficiency: ~19.5 %

B-O complexes

Light induced degradation



Nærland/IFE

Fe-B complexes

- B_s and Fe_i can form complexes in Si
  - Important for B-doped Si
  - These pairs dissociate under illumination
  - Pairs reform if samples are left in darkness for some time
- J_{SC} and η will always degrade as a result of this dissociation
  - Degradation depends on Fe concentration, can be several $\%_{rel}$
- Constructive use:
  - The lifetimes of the whole and dissociated pairs are different
  - Estimates of the Fe concentration in a material can be made

Line defects – dislocations

- Sites for heterogeneous or strain assisted nucleation of precipitates
- In n-Si: Bonds at a dislocation can be filled with e^- from donor atoms, making the dislocation negatively charged
  - A negative dislocation surrounded by positive donor ions result in the formation of cylindrical space charge regions
- In p-Si: Bonds at dislocation can be filled with h^+ from acceptor atoms, making the dislocation positively charged
  - A positive dislocation surrounded by negative acceptor ions also result in the formation of cylindrical space charge region
- Dislocations decorated with impurity atoms can cause shunting
- Dislocation density affects lifetime

Plane defects

- Grain boundaries
- Sub-grain boundaries
  - Misorientation < 5^{0}
- Twin boundaries
  - Highly symmetrical grain boundaries

- Boundaries can introduce recombinative interface states in the band gap
  - Affects lifetime
- Boundaries can accumulate charge and/or impurity atoms

Volume defects

- Precipitates
  - Precipitates can affect lifetime and diffusion lengths
  - Certain precipitates can cause trouble during subsequent processing (e.g. sawing or cell fabrication processes)
  - Certain precipitates can cause shunting

- Origin of precipitates
  - Silicide particles, as well as SiC and SiN particles can form during the casting of the material
  - Large oxidized precipitates with several metal constituents (often slow diffusers) can come from particles falling into the Si melt …

Metallic impurities – dilemma

- Many recent studies indicate that the concentration of metals in solar grade Si is orders of magnitude higher than the lifetime indicates
  - Explanation 1: metals mostly present in passive states
  - Explanation 2: metals extremely inhomogeneously distributed

Precipitates

- Much of the metal atoms present are present within various precipitates
  - Cause a reduction of diffusion lengths

$$L = 0.7 \cdot (N_p)^{-1/3}$$

  - Generally more benign than fully dissolved and homogenously distributed metal impurities
  - Few large and isolated precipitates: L larger
  - Many smaller precipitates: L shorter

Handling impurities

- A certain amount of metallic impurities must probably be allowed in the Si material
- The effect of these impurities can be reduced
  - Reduction of recombination strength (passivation)
  - Redistribution of remaining metal atoms
    - Precipitate formation (impurity management)
    - Transport of impurities to non-critical sites within the solar cell (gettering)
- Thermal processing both during Si crystal growth and Si manufacture critical

Case study 1 – Cooling rates

- High-purity mc-Si with controlled additions of Cu, Fe and Ni
- Samples subjected to different cooling treatments after impurity addition at 1200 ^{o}C
  - Slow cool (3 – 8 ^{o}C/s)
    - Low density of large particles forms
    - L ~ 30 μm
  - Rapid quenching (200 ^{o}C/s)
    - Predominantly dissolved impurities
    - Homogeneous distribution
    - L < 10 μm

Buonassisi et al., Nature Materials 2005

Case study 2 – RTP

- Rapid thermal processing (RTP) of mc-Si wafers in solar cell processing
  - As-grown material
    - $FeSi_2$, Cu_3Si and Ni-rich ($NiSi_2$(?)) precipitates built up during casting
  - Low-T RTP
    - $FeSi_2$ remains, fewer Ni-rich precipitates, no more Cu_3Si
  - High-T RTP
    - Fewer $FeSi_2$ remain (50% of Fe atoms) , no Ni-rich or Cu_3Si remain
  - Lessons
    1. Metal silicides and particles an important source for metals during processing
    2. Metal impact can be reduced by forming precipitates during casting and disturbing these as little as possible during subsequent processes
       - Use low T
       - … as Schultz did when he made his famous 20.3 % mc-Si solar cell

Buonassisi et al., Appl. Phys. Lett. 2005