From electronic to solar grade silicon: a challenging promise

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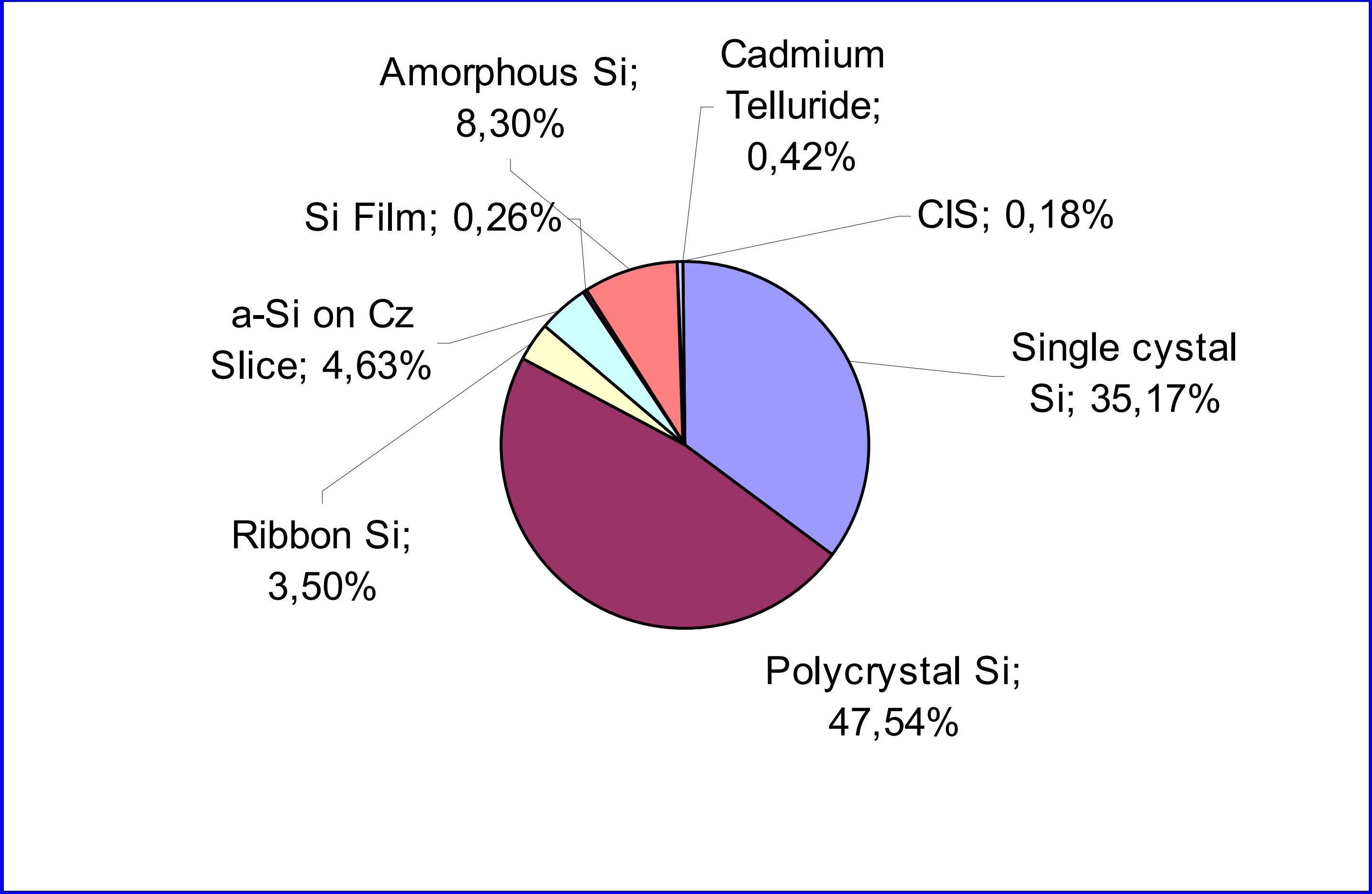
Festkolloquium zum 65 Geburtstag von Herr Prof. Dr.Horst P.Strunk

Outline

- ***Introduction: past and present of silicon and silicon feedstocks for solar cell fabrication***
- ***Impurity segregation and monitoring in multicrystalline silicon for PV applications***
- ***Defect monitoring in EFG-grown silicon ribbons by room temperature PL spectroscopy***
- ***Defect engineering and defect monitoring in n-type materials***
- ***Towards solar grade silicon***

the PV market today



What future for PV?

- Silicon (in various forms) will remain the key PV material?
- Organic solar cells have a chance?
- Could be the photovoltaic sun harvesting not a dream but a true market-attractive business?

Open problems

- **High cost impact / high energy content of silicon from the classical Siemens route (ca 90€/ 300 KWhr/Kg)**
- **Limited future availability of low cost EG-Si scraps as feedstocks**
- **Relaxed gas phase processes (Wacker, Tukoiama, REC/ASiMi are low cost (ca. 20-30 €/Kg) but not sufficiently low for PV**
- **How far one could play with a relaxed purity of silicon?**
- **(Inorganic) materials different from Si are either rare or toxic**
- **Organic cells are poorly efficient**

Future solutions?

- only purified MG-silicon feedstocks could satisfy at an acceptable cost (4-5 €/Kg) the material demand for PV power plants alternative to coal or natural gas (the today production of MG Si amounts to several Mtons) $\rightarrow$ but what are the acceptable purity limits ?
- thin silicon films are a possible alternative
- $In_{1-x}Ga_xN$ films and organic/polymeric cells are promising

general constraints

- Any new process addressed at the production of a PV feedstock must be cost effective, should use available technologies, should be environmentally friend. In addition, the feedstock must be produced in large quantities and offered by many commercial sources.
- The conversion efficiency achievable should be at least higher than 14-16%. This condition could limit the applicability of organics, where the charge separation and the charge collection still demand impressive innovation.
- Vacuum (CVD) processes are demanding as well innovation

Today and tomorrow within the silicon route

- Use of n-type scraps: less problems with impurities (absence of B-O defects, lower cross section of metallic impurities) but need of removing the excess P, As and Sb dopants in the case of n^+ materials. Due to their limited availability, they are not the true solution but they open new potentialities to MG silicon in terms of achieved knowledge
- Moving towards solar silicon (SG-Si)
- $\rightarrow$ learn how to work with defective & impure materials (new gettering/passivation procedures)
- $\rightarrow$ use syntetic feedstocks to forecast SG-Si properties
- *Develope procedures for fast growth of silicon wafers, consider consciously the advanced Si thin films*

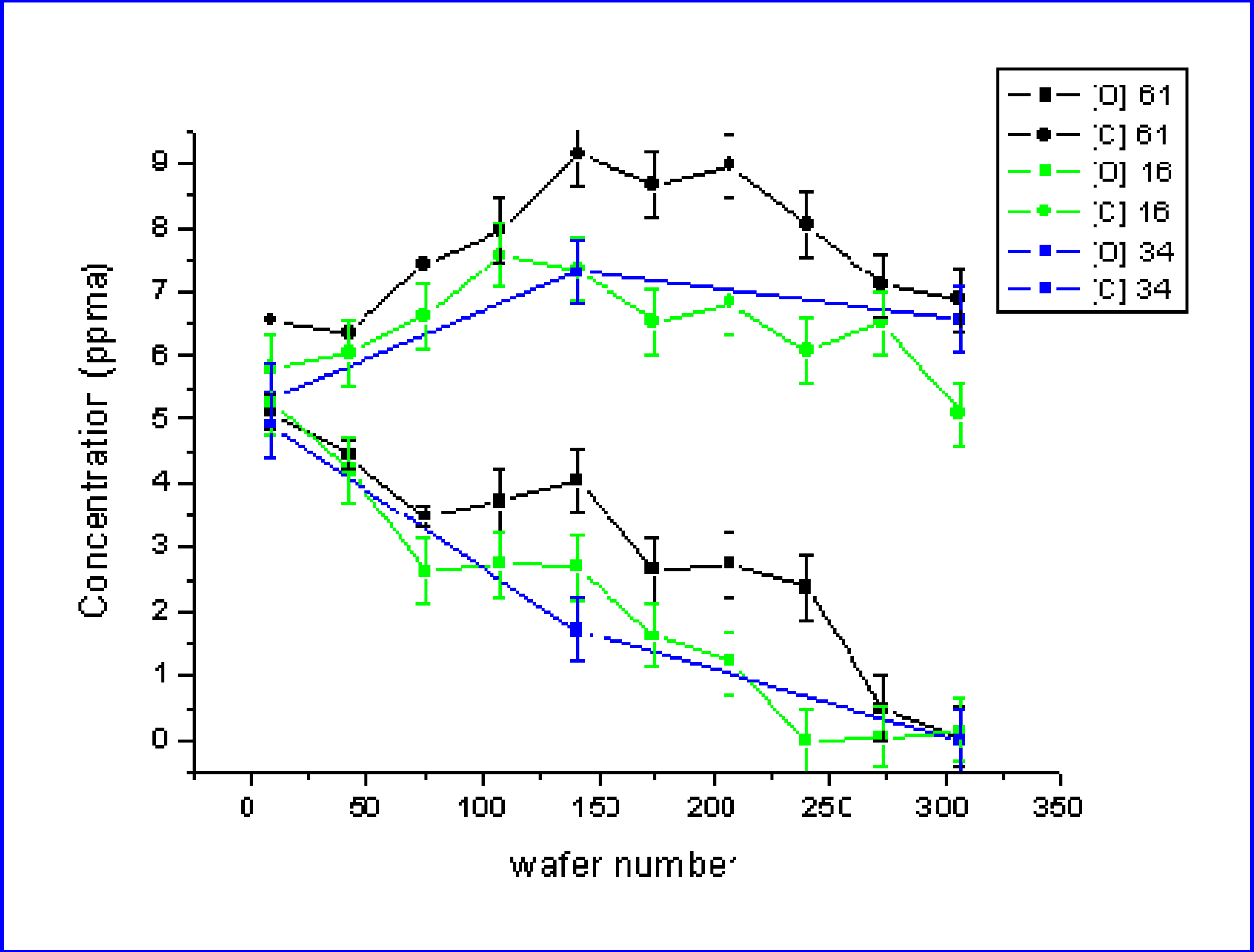
Present knowledge : generalities

- Extended defects (Dislocations and GBs) in “clean” Si are normally harmful for PV applications unless dangling bonds are reconstructed or passivated
- Grain size in excess of mm allows effective sun harvesting in “clean” Si provided the orientation of GBs is parallel to the carrier drift and diffusion
- Thermodynamics shows that GBs and dislocations are powerful (chemical) traps for impurities: the effect is to increase the minority carrier recombination activity of GBs and dislocations
- Thermodynamics shows also that GBs and dislocations compete with external gettering and passivation sites

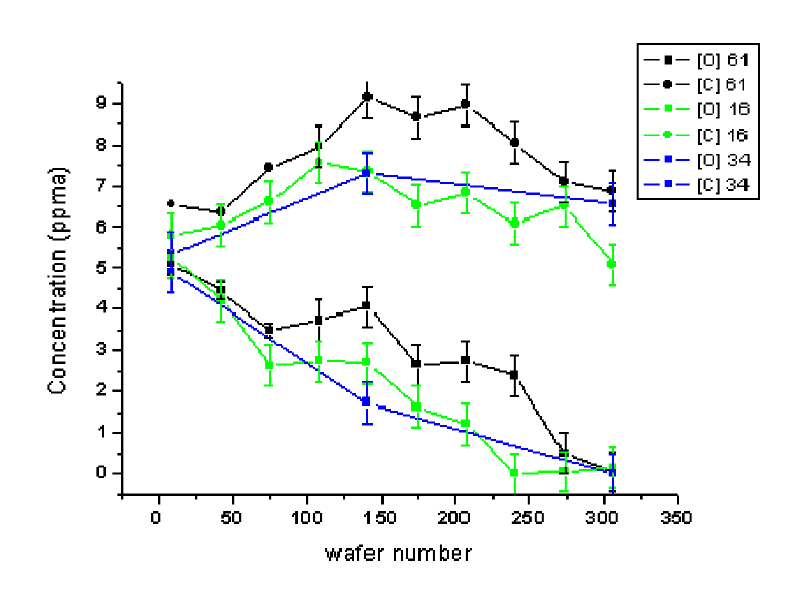
Playing with impurities, some key examples:

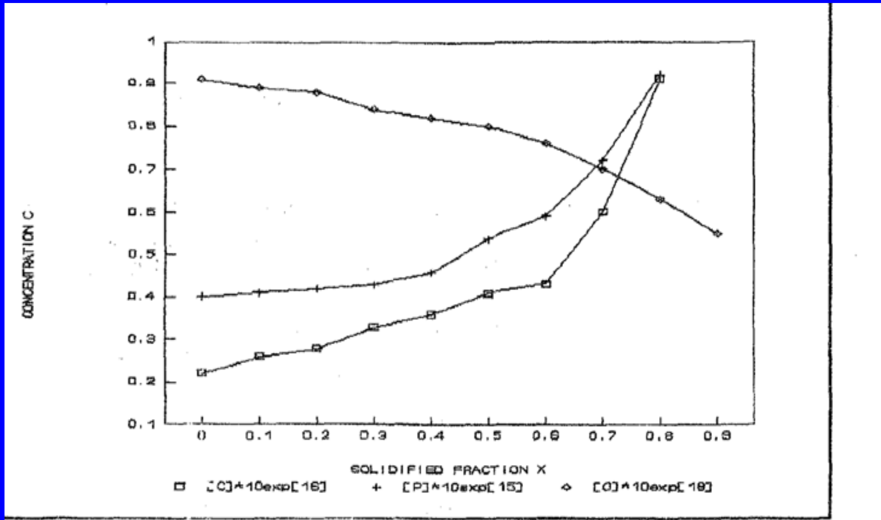
I. C,O and metal segregation during growth and after thermal treatments

Segregation of O and C in a n-type DS as-grown ingot



Comparison between mc-Si and n-type Cz-grown ingot





'igure 1.Typical axial distribution of P,O and C
content for a 12.5 Kg Cz Si single crystal ingot

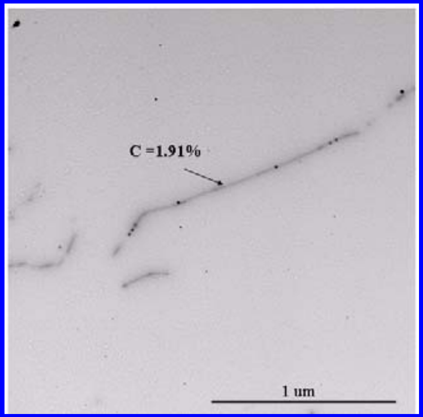
additional existing knowledge

- Above 10 ppma [C] saturates *(pizzini JES1988)*
- Doping *(X.Huang et al JCG 1995)* and microstructure influences the segregation of oxygen and carbon. In p-type silicon B-O complexes might play a role
- Heat treatments below 650°C are uneffective on the C vs O segregation: both segregate at GB and dislocations at higher T (up to 1150°C)
- Carbon enhances the oxygen segregation (*pizzini 1989, rozgonyi 2003*)
- C and O segregate separately at GBs (mechanical equilibrium rules the segregation) after heating at 1150 *(pizzini apl1987*)
- In as grown Si GB are slightly active when C and O are in equimolar (or close to) equimolar ($N_O \approx N_C$) concentration

Effect of non-equilibrium growth & defectivity on the segregation coefficients of metallic impurities

Element	K_s (CZ-EG Si)	K_s (DS-MG Si)
Cu	6.9 10^{-4}	2 10^{-3}
Cr	1.1 10^{-6}	3.7 10^{-3}
Fe	6.4 10^{-6}	1.6 10^{-4}
Ni	3.2 10^{-5}	9 10^{-4}
Ti	3.6 10^{-6}	2,5 10^{-3}
Zr	1.5 10^{-8}	7.7 10^{-4}

Effect of impurity segregation in n-type mc-Si on recombination activity of GBs



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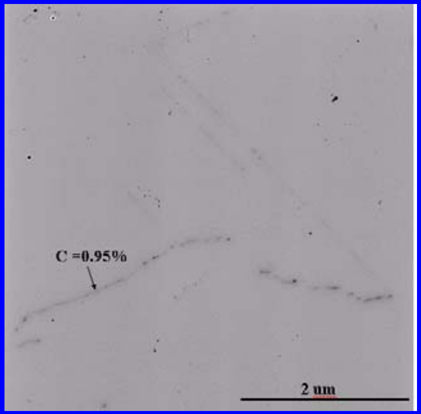

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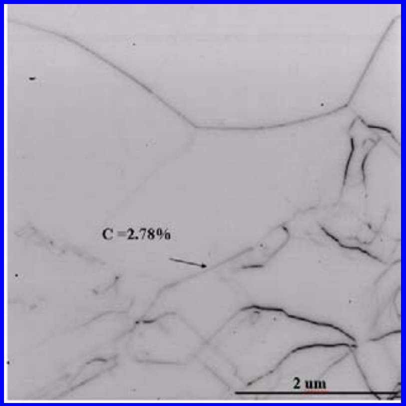

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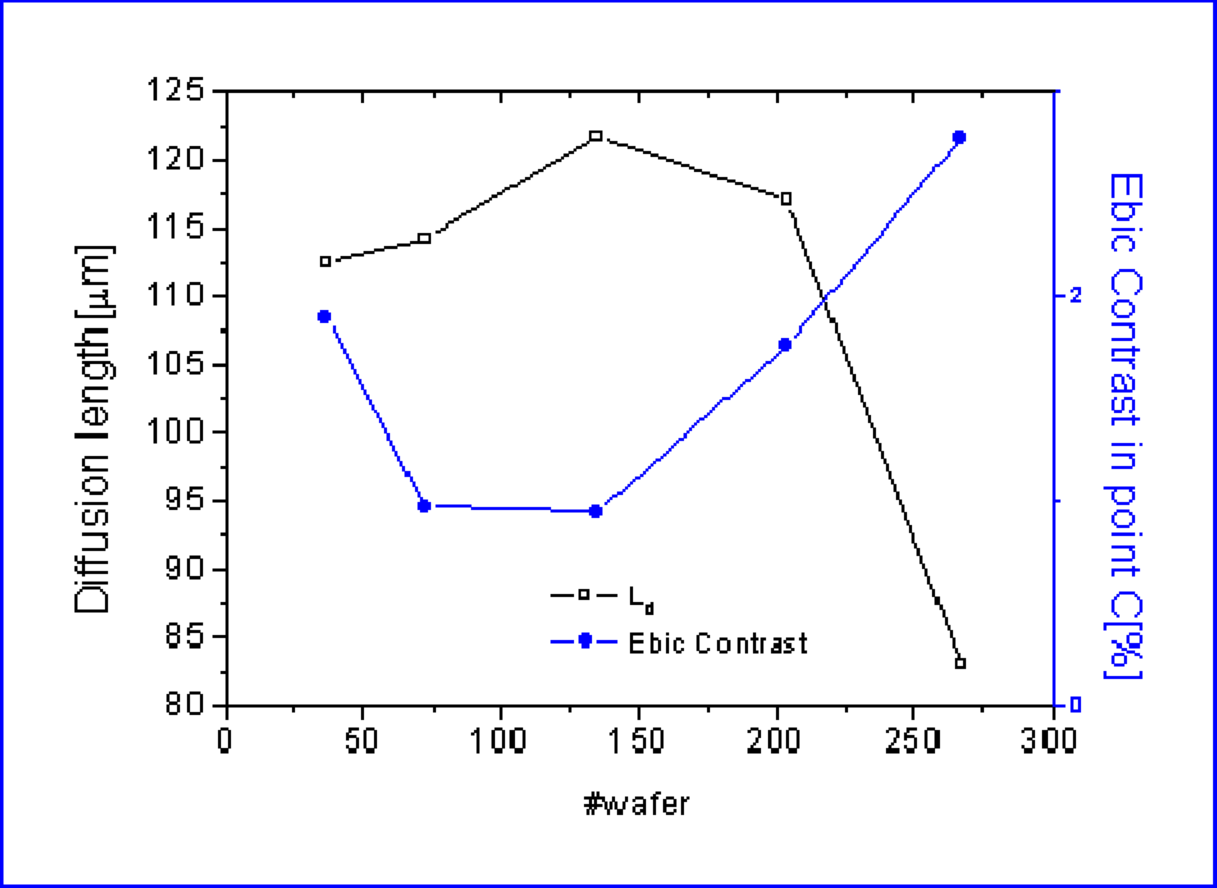
EBIC Contrast vs diffusion length:dependence on impurity segregation in n-type mc-Si



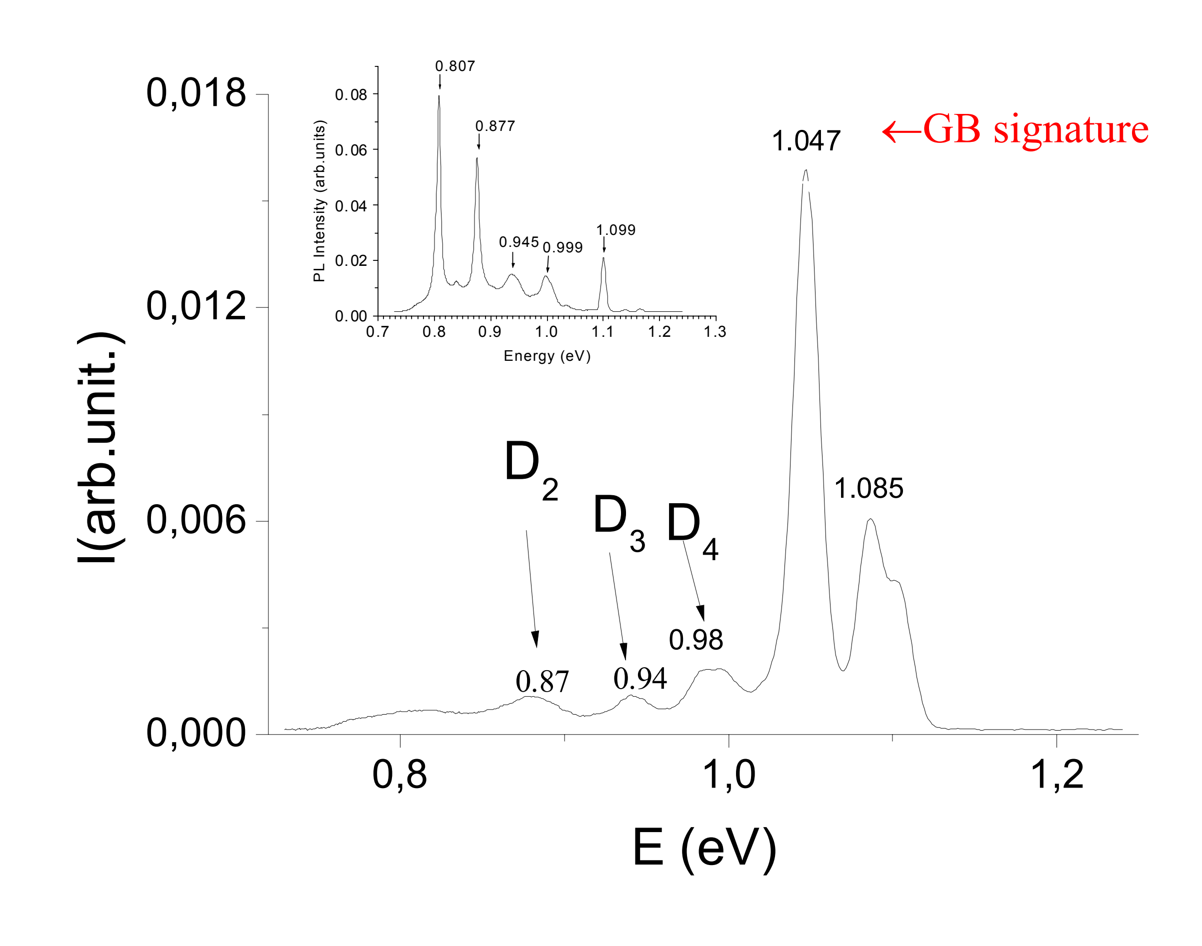
Remarks

- In refined-MG feedstocks impurity segregate massively at GBs and other extended defects
- In mc-Si DS-grown from EG-Si feedstocks minute amounts of impurities coming from the crucible, from the feedstock and from furnace misoperation might deteriorate a significant part of the ingot

II. Defect engineering in n-type DS-grown mc-Si

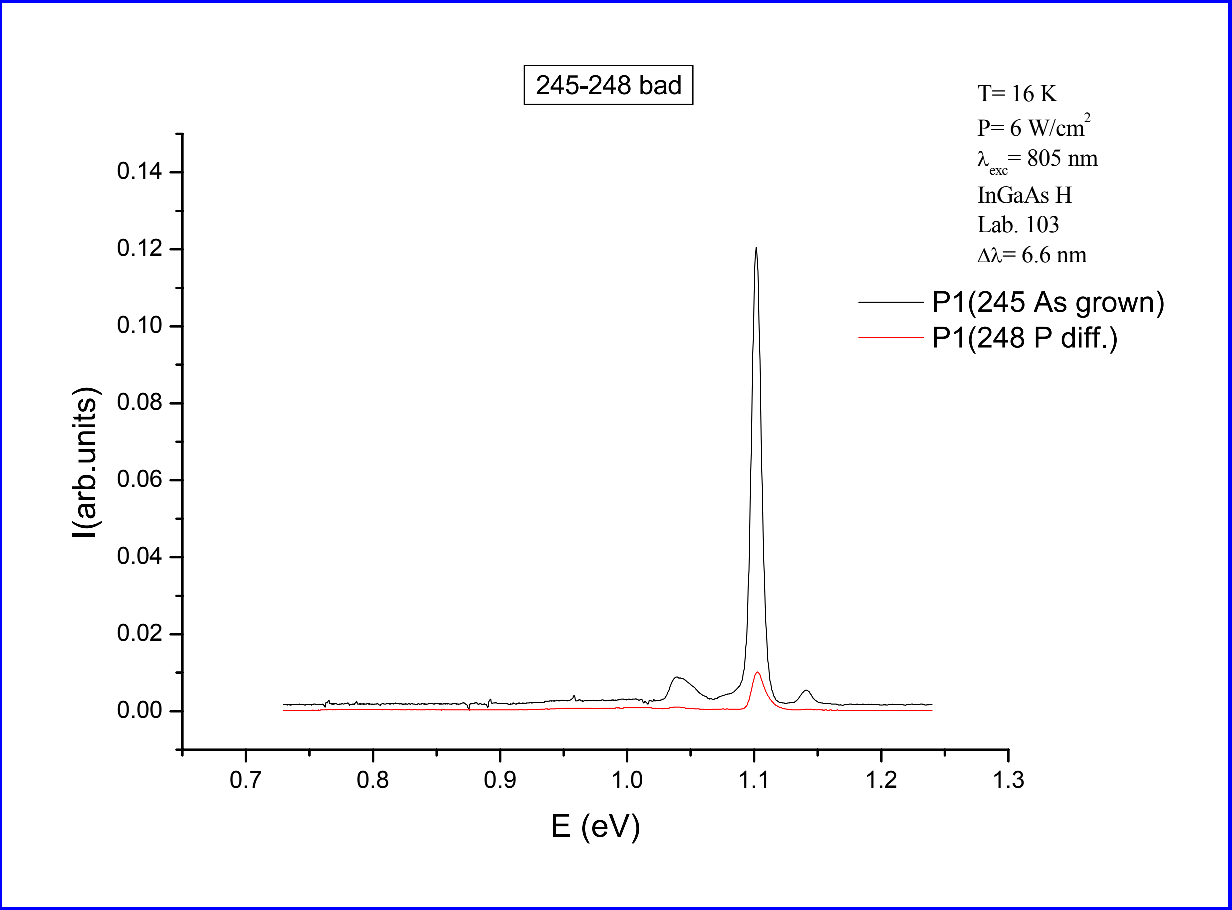
- $POCl_3$ gettering after B-diffusion for junction formation (800-900°C)
- Hydrogen passivation during the AR deposition step (Nitridation)
- Defect monitoring via PL at 12 K *(the intensity of the excitonic PL is a qualitative measure of the quality of the material)* and EBIC contrast measurements at room temperature

PL spectrum (12 K) in a GB-rich region

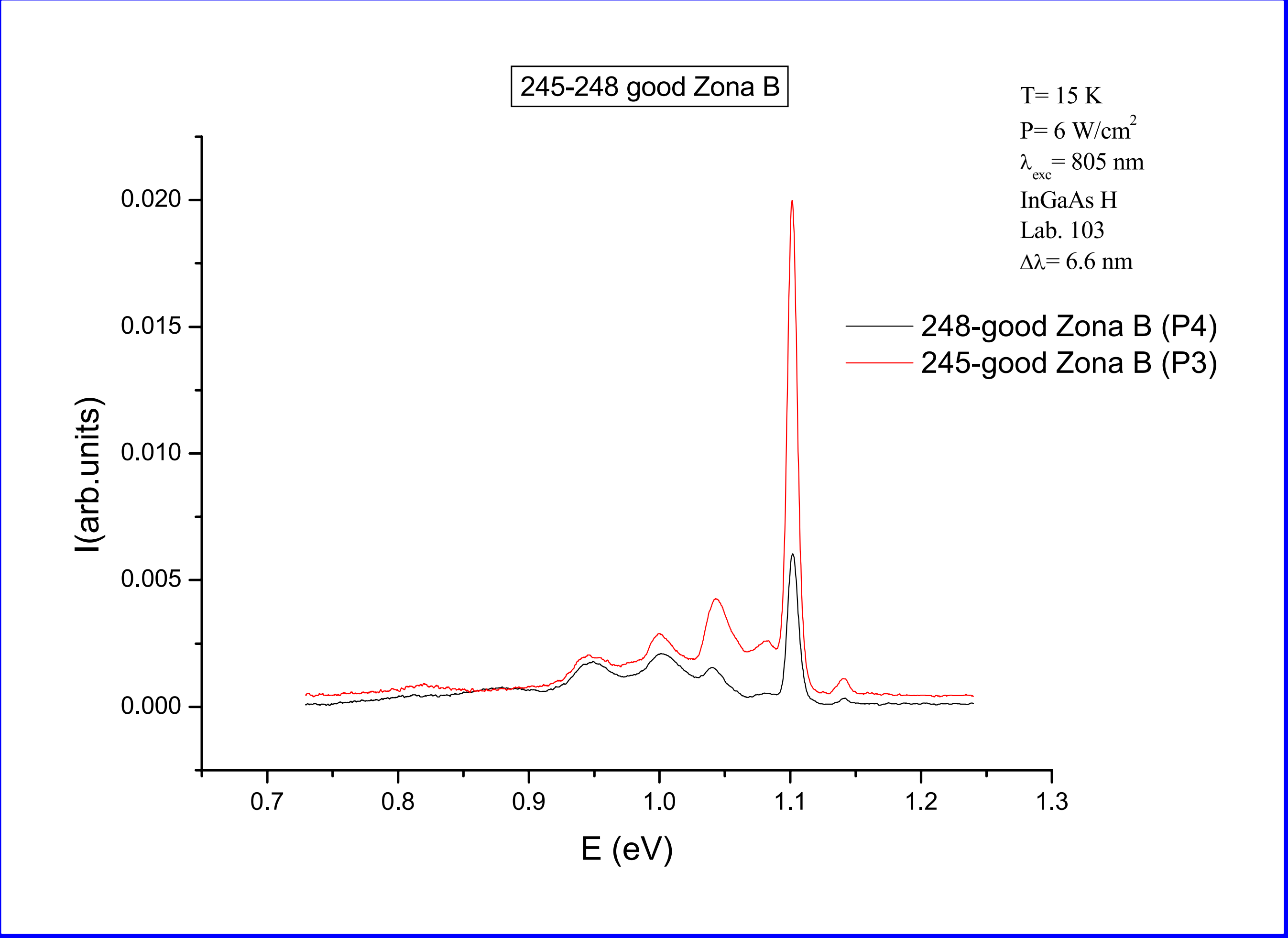


A ≈1.05 eV peak appeares systematically in the presence of GBs, generally associated to dislocation luminescence

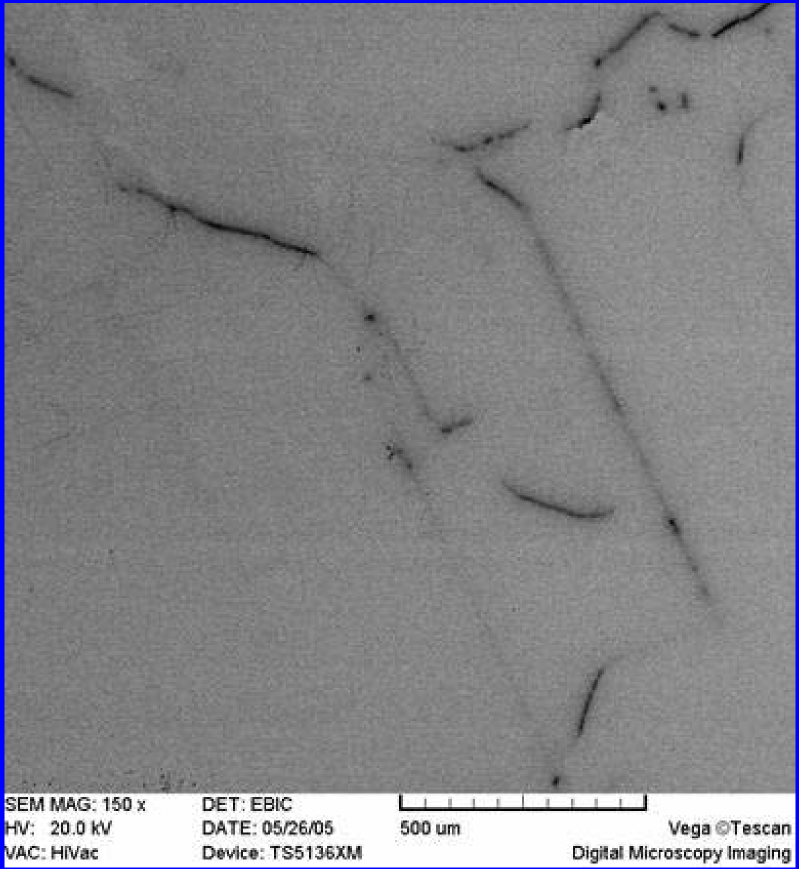
PL spectrum before and after gettering (low lifetime, high defectivity region)



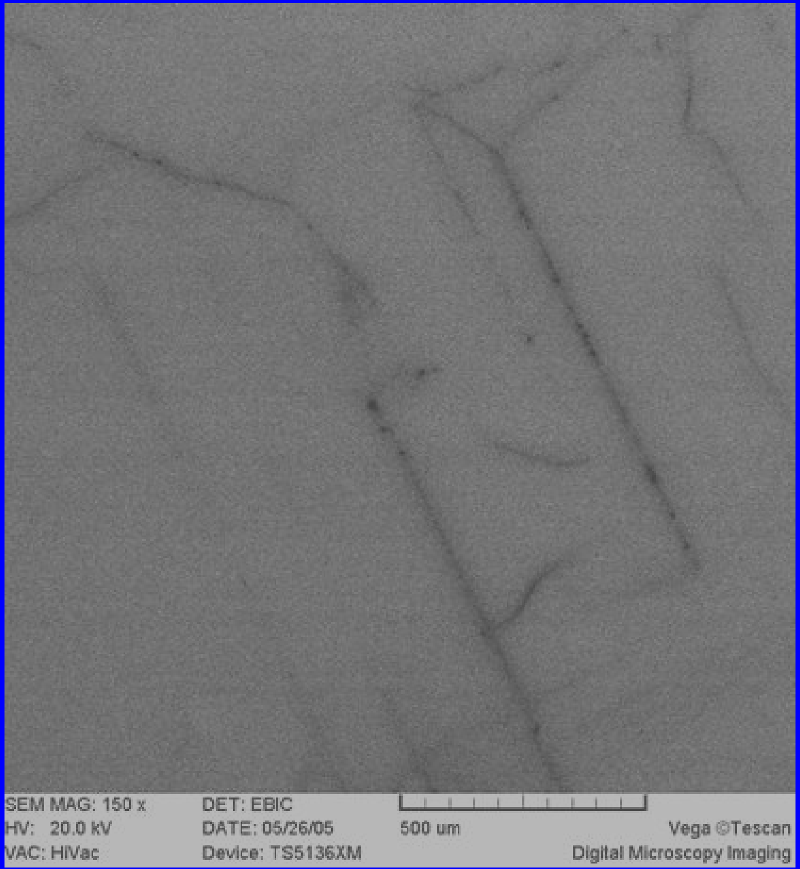
PL spectrum before and after gettering (high lifetime, low defectivity region)



EBIC maps before and after gettering



As grown sample



After POCl3 gettering

Effect of $POCl_3$ gettering

The average lifetime increases from

τ_{eff} = 89 μs to τ_{eff} = 140 μs

but the (beneficial) effect of gettering is inhomogeneous

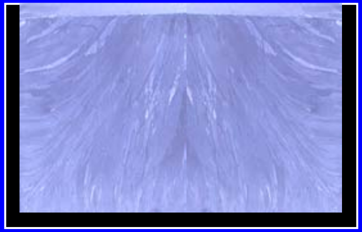
Remarks

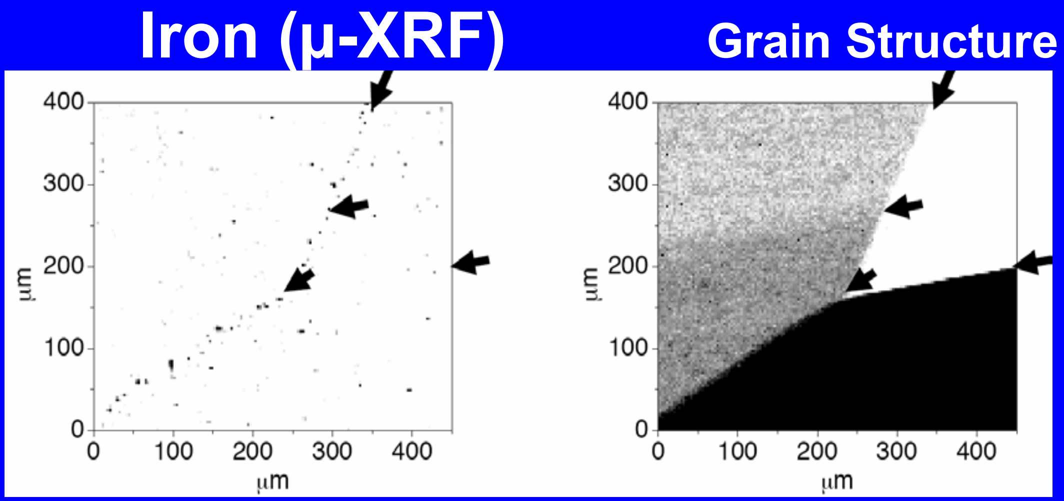
GBs compete with external gettering in agreement with thermodynamic predictions

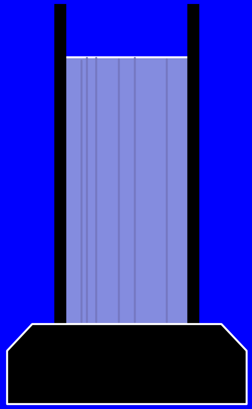
$$\mu_{i,GB,dislo} \approx \mu_{i,\, surf}$$

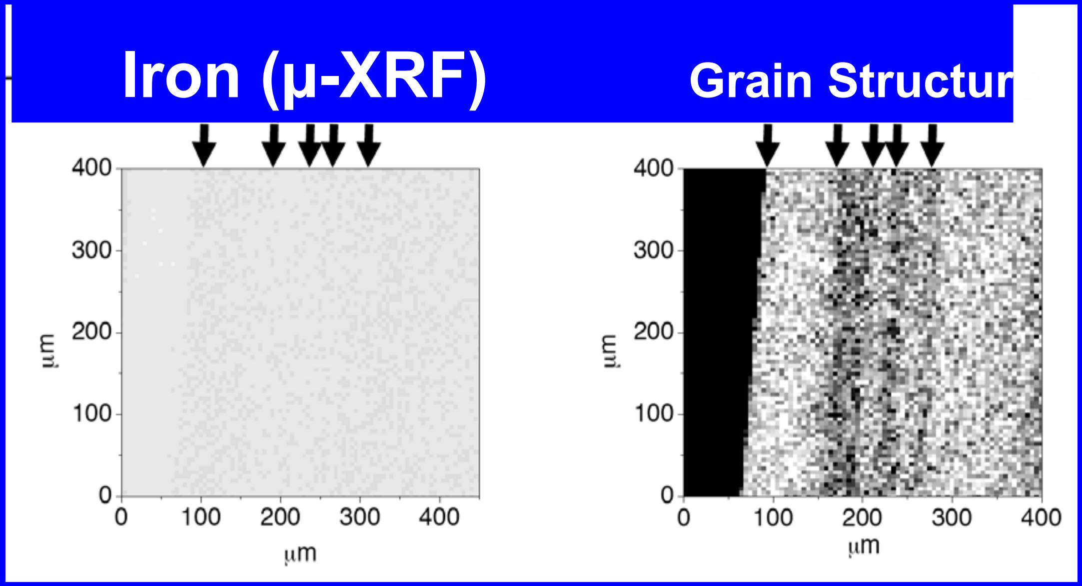
and with recent literature *[T.Buonassisi, M.A Marcus, A.Istratov, M.Heuer, T.F.Ciszek, B.Lai, Z.Cai, E.R.Weber, J.Appl.Phys. 97, 063503 (2005)]* who demonstrated, using XR fluorescence, that gettering of iron occurs at GBs.

mc-Si Growth Method Affects Metal Distribution

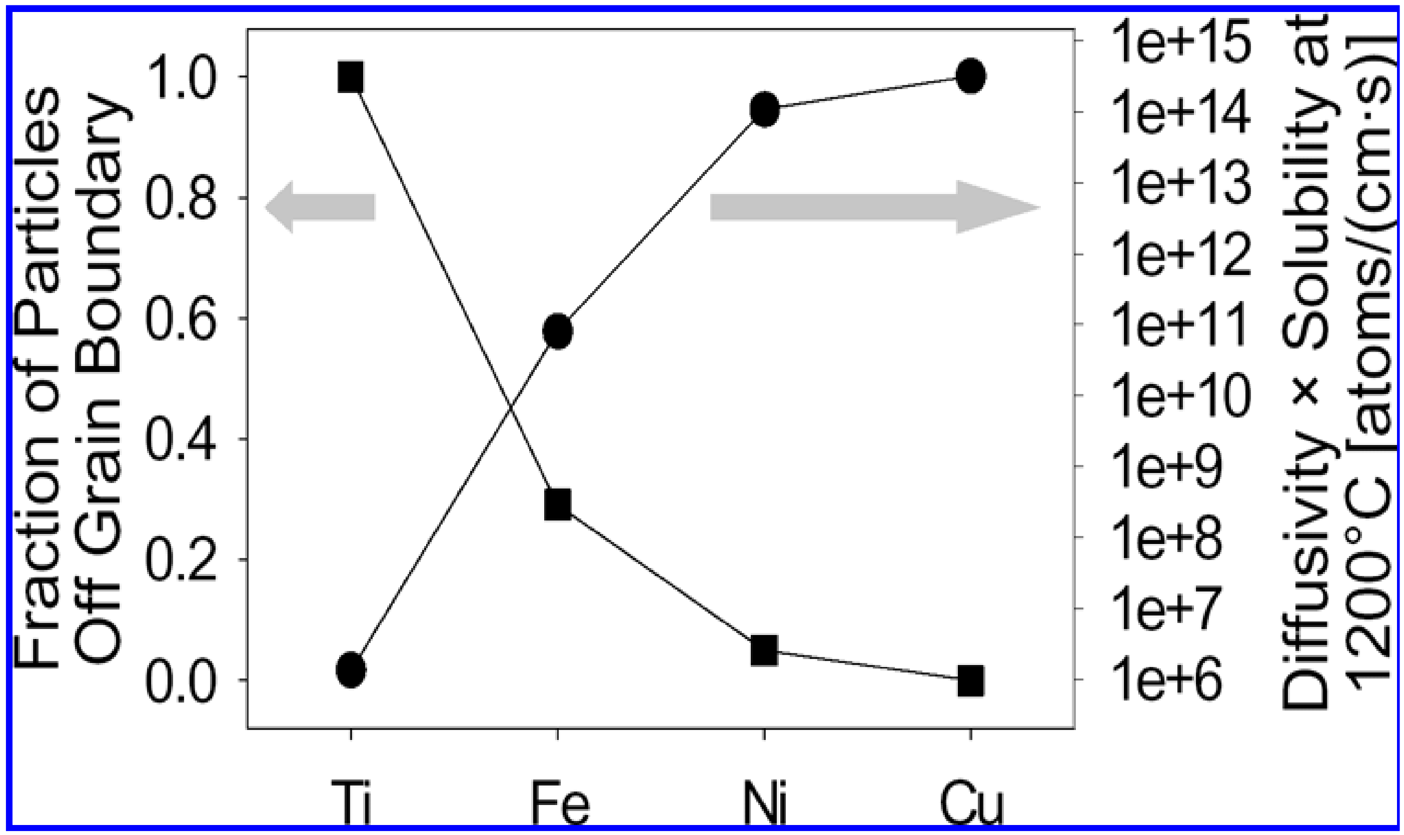








T. Buonassisi, A.A. Istratov *et al.*, submitte



Cu and Ni tend to accumulate at a few energetically-favourable regions within the device (e.g., high sigma twins, non-twinning GBs); **Ti and Fe** elements tend to be more dispersed throughout the device. Their low diffusivity also means they are less easily gettered. These facts, combined with their point defect-related deep levels within the bandgap, combine to make these more dangerous for device performance.

T. Buonassisi, A.A. Istratov *et al.*, submitted (2005).

Past experience in our Lab with syntetic feedstocks

- The effect of Ti,V, Cr and Fe doping on the diffusion lenght of mc-Si by was studied (*), by taking into consideration the interaction with both GB and dislocation. It was found that above 10^{13} cm^{-3} interaction occurs, which strongly increases the minority carriers recombination

(*)S.Pizzini et al JES 133, 2363 (1988)

III: Defect monitoring in EFG-grown silicon ribbons and p-type mc-Si by RT-PL spectroscopy

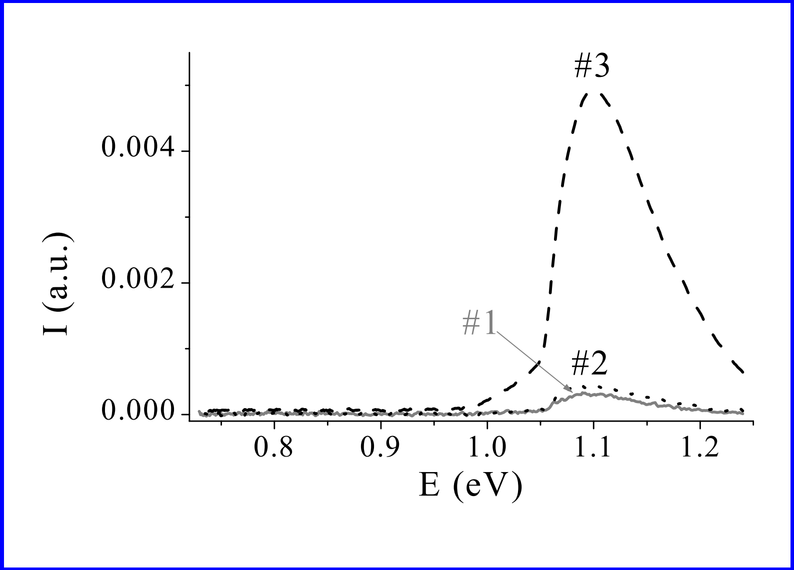
PL measurements at room temperature might monitor material improvements or failures during solar cell processing. Only the excitonic luminescence might be used.

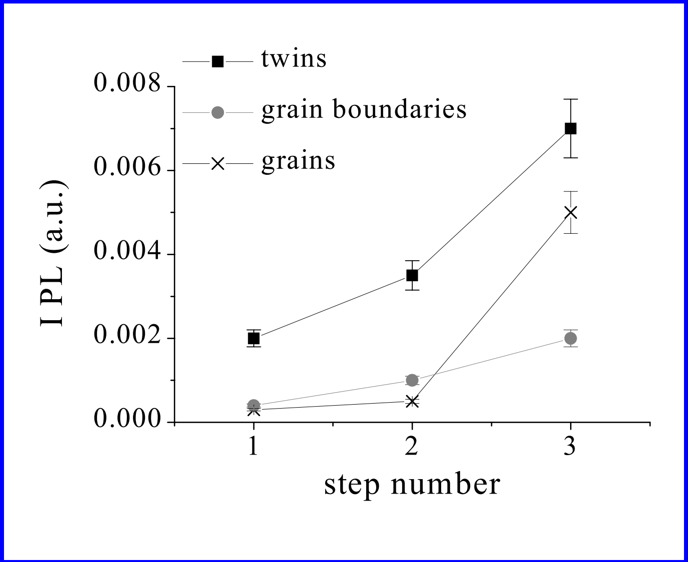
To avoid surface recombination effects, carrier injection is carried out 10 μm deep in the sample

The sample inhomogeneity is accounted for by testing regions with similar morphology

Evolution of the EFG ribbon properties with processing

grain region

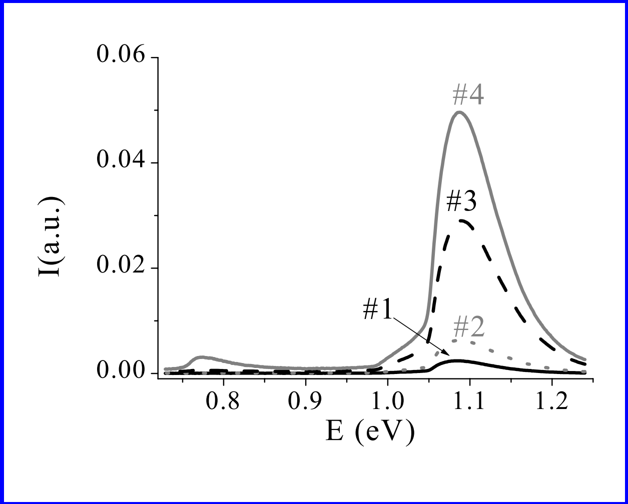


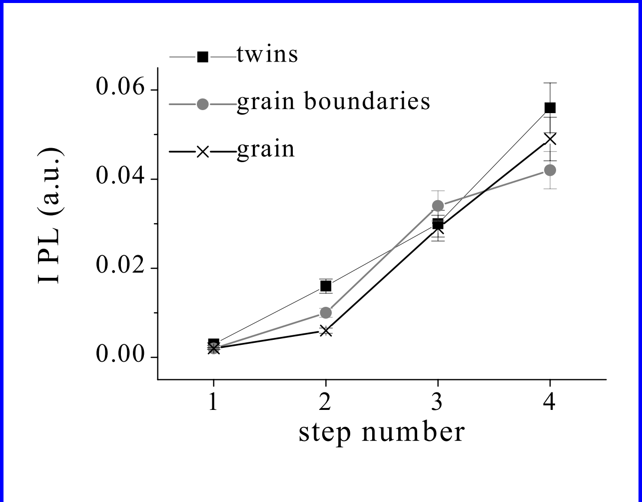


#1 as grown # after junction # after AR coating

Comparison with multicrystalline silicon

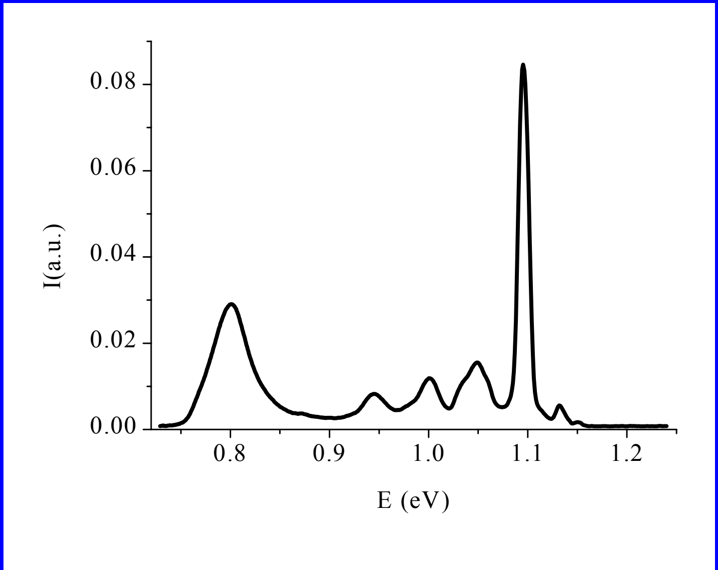
grain region

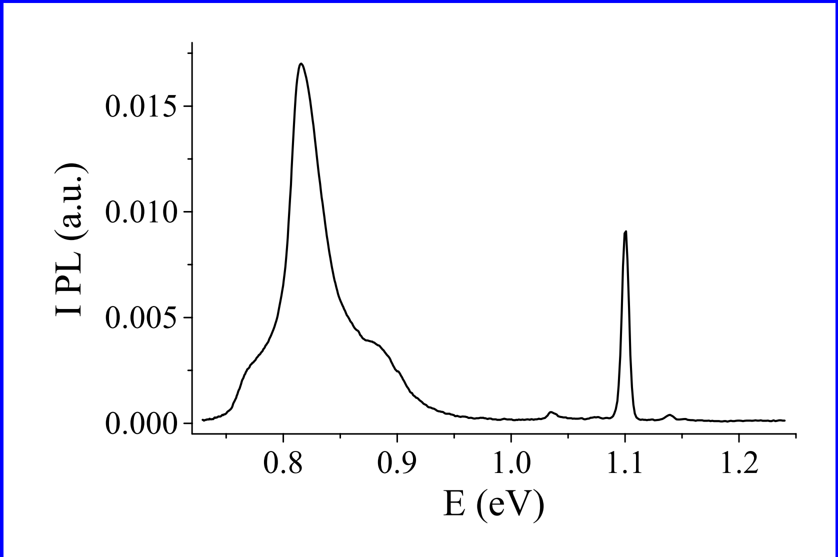




#1 as grown # after junction # after AR coating

Effect of P-diffusion/gettering





a)PL spectrum of mc-Si at 12 K after junction formation
b) of dislocated EG silicon after heat treatment at 800°C used to segregate oxygen

Remarks

- RT-PL might be used to follow the effect of process steps on the material performance
- In EFG-Si GBs are only slightly affected by P-gettering and hydrogen passivation, different from mc-Si
- In p-type mc-Si the P-diffusion/gettering induces the segregation of oxygen, the enhancement of the dislocation luminescence

  and the decrease of the excitonic luminescence
- A complex interplay of impurities and extended defects dominates the local lifetime of mc-Si. The interplay of impurities and ED is affected by many factors (ED structure, ED reconstruction, chemical reactivity of single and multiple impurities, thermal history).

Final remarks

- Impurities segregated at dislocations and GBs might be tolerated only to a certain extent, which depends on the microstructural features of the specific material used
- Impurities segregated at dislocations and GBs might be (at least partially) removed by P-and Al-gettering
- Defect engineering must be addressed towards the improvement of both intragrain and ED properties.
- Defect monitoring essential for designing specific defect engineering processes needed for solar grade silicon

Towards the use of "solar grade" silicon: our past achievements

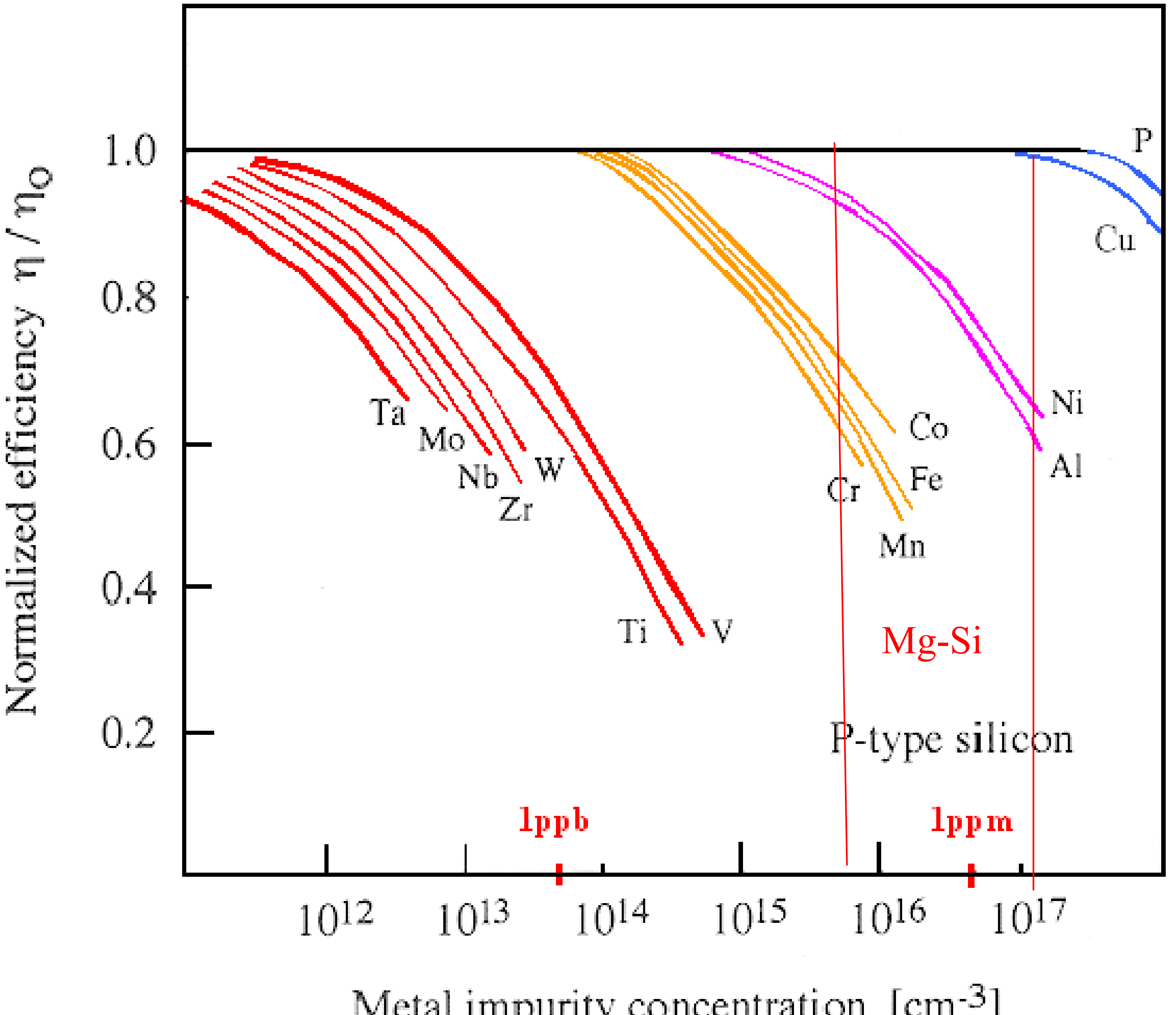
- We followed the route

  ultra pure natural quartz and ultra pure syntetic carbon -> arc furnace ->twice DS growth

The experiments were carried out in a MG silicon and silicon alloys factory

Compositional analysis of two MG si ingots

Element (ppma)	MG-Si (SiC+ quartz)	After one DS sol	After two sol	MG-Si HP10	After one	After two sol
Al	376	2.6	<1	107	5.1	2.08
B	13.9	12.4	10.4	15.3	6.7	8
P	14.7	1.8	3.3	10.6	4.8	5.9
Fe	615	<1	1.9	33	9	1.3
Mg	14	<1	78	32	14	16
Ca	49.7	39	>175	50	128	19
Ti	83	<1	<1	37	<1	<1



Normalized efficiency η / η0
1.0
0.8
0.6
0.4
0.2
P
Cu
Ta
Mo
Nb
Zr
W
Ti
V
Co
Cr
Fe
Mn
Ni
Al
Mg-Si
P-type silicon
1ppb
1ppm
10^12
10^13
10^14
10^15
10^16
10^17
Metal impurity concentration [cm^-3]

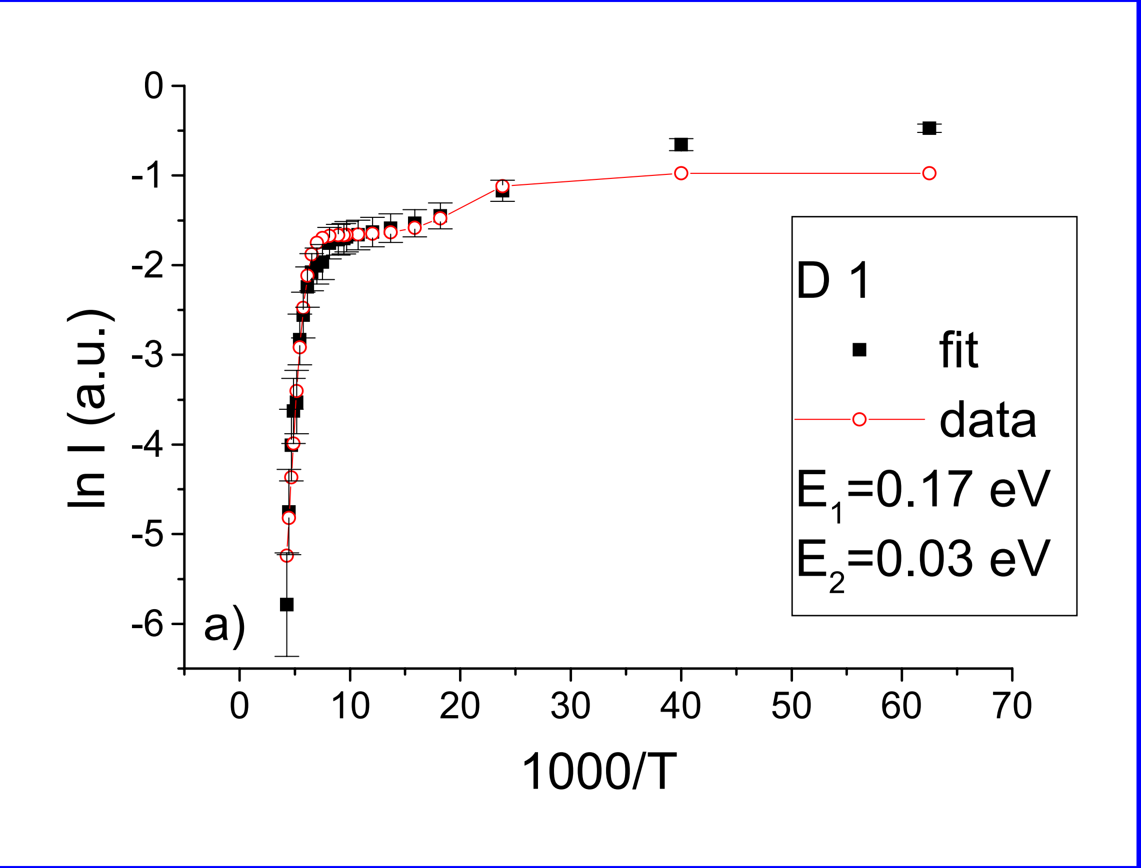
Conclusions

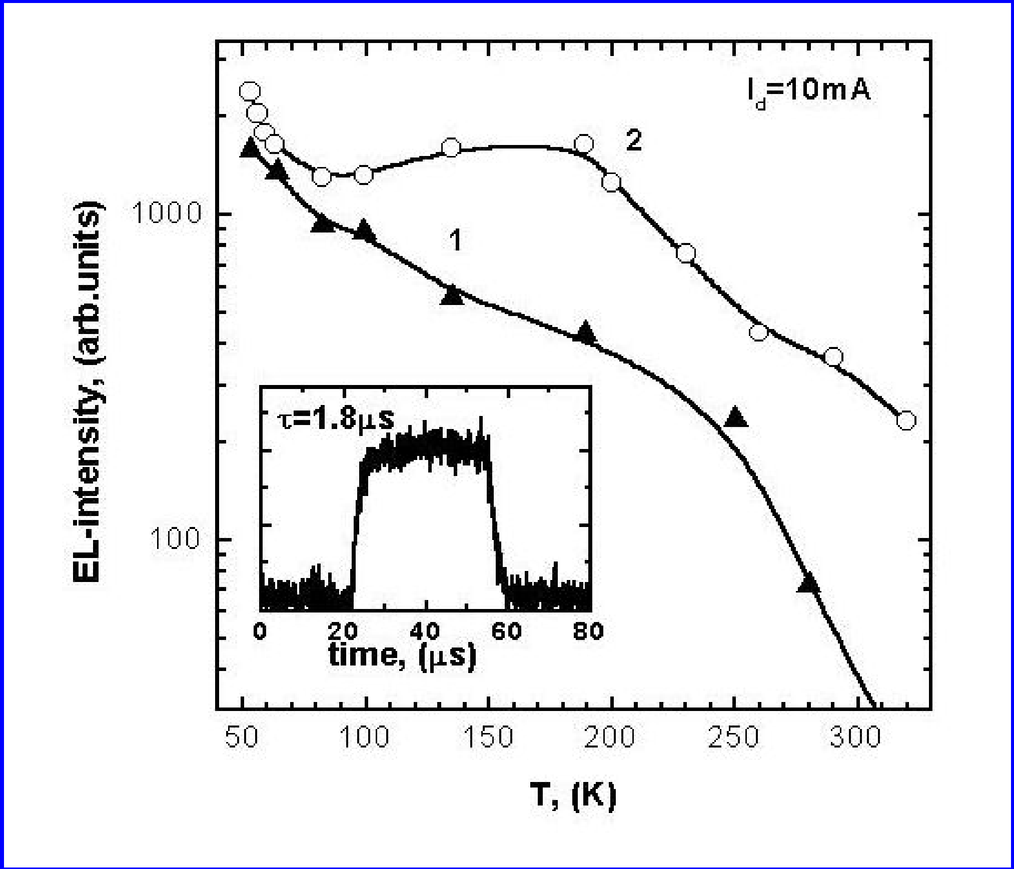
- In both materials the impurities are well above the EG-Si limits
- Cells realized with this material (without gettering procedures) had normalized efficiencies in excess of 6% (one would expect a quite lower efficiency)
- Impurities segregated at GB and dislocations have a only a limited (but not negligible) effect on carrier recombination
- Environmental control and proper gettering should be the needed practice
- It is possible that within five years solar silicon will be available

Acknowledgments

The author is warmly endebted to Simona Binetti and Maurizio Acciarri for years of common work in this field

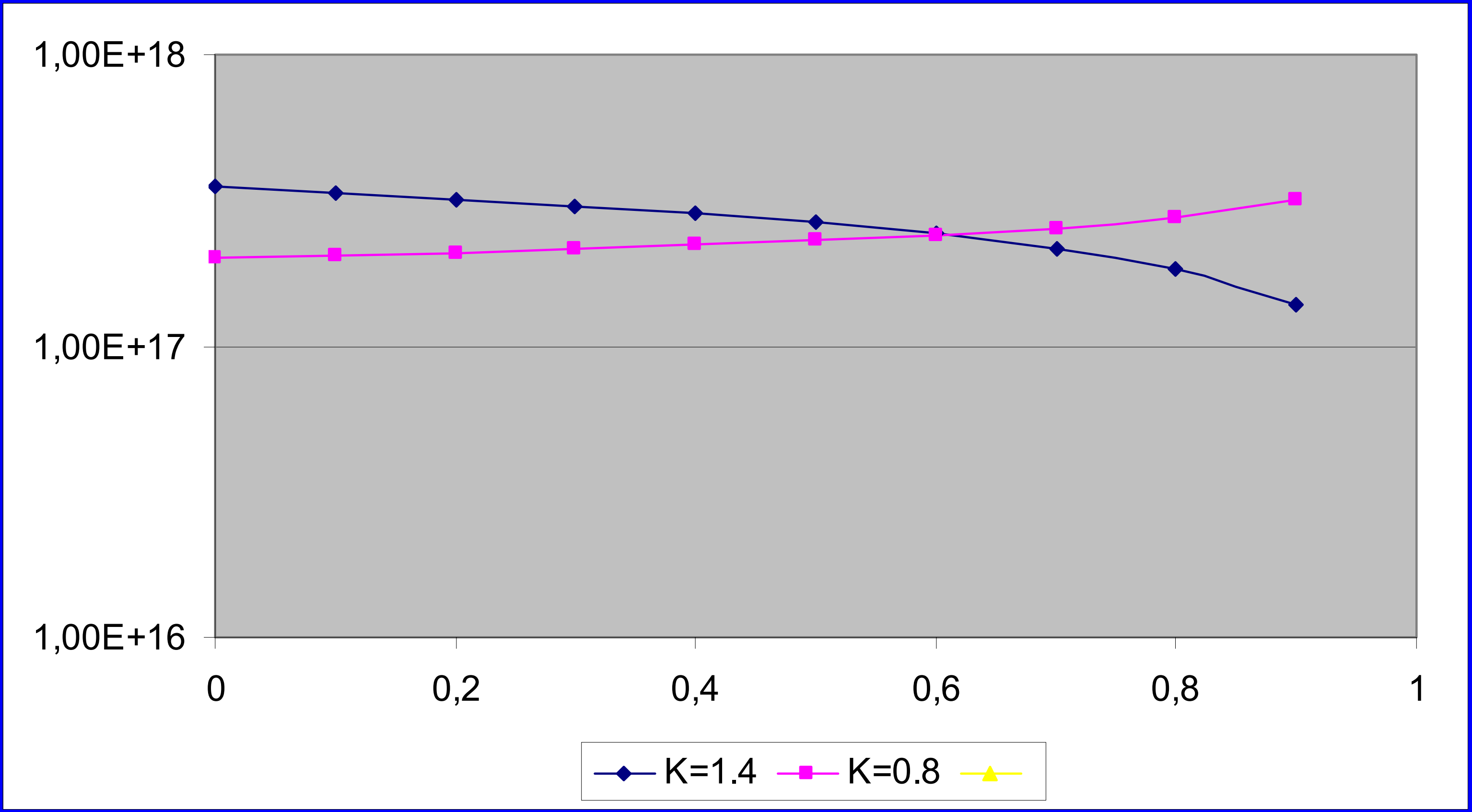
IV. gettering & passivation of impurities at dislocations





1. After P- gettering 2. after hydrogen passivation

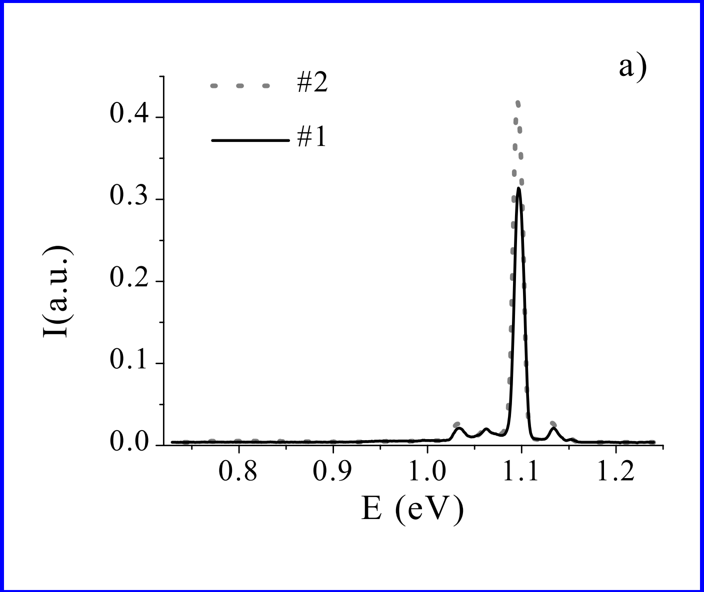
Theoretical distribution of O in a CZ ingot

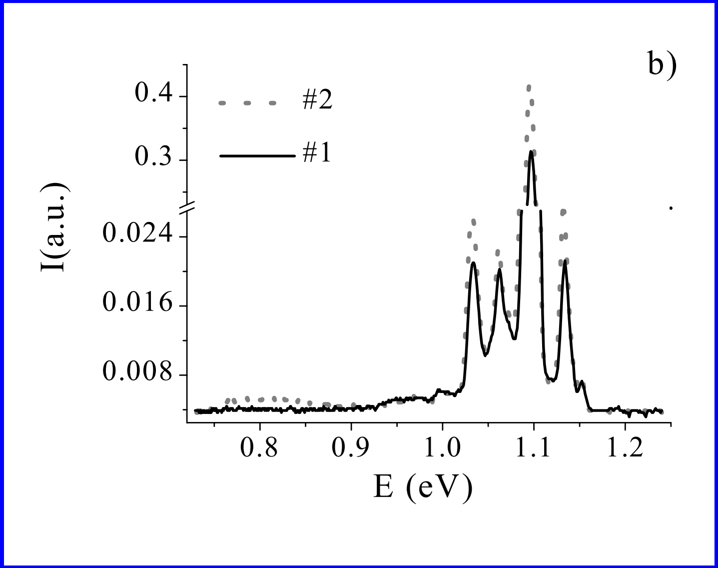


About carrier recombination

- Carrier recombination might occur via radiative and non-radiative channels. Dislocations are active radiative and non-radiative recombination defects. GBs, so far, were considered only non-radiative recombination defects.

Low temperature PL spectra of mc-Si





a) PL spectra at 12K of the as grown and texturized mc-Si

b) higher magnification of the same spectrum : the D3+D4 dislocation lines, the phonon replicas and the emission at 1.05 eV are visible)

Remarks

- **A complex interplay of impurities and extended defects dominates the local lifetime of mc-Si. The interplay of impurities and ED is affected by many factors (ED structure, ED reconstruction, chemical reactivity of single and multiple impurities, thermal history).**

$\sqrt{Dt}$

- **ED compete with the external surface as impurity gettering sites. An impurity denuded zone is formed, whose thickness depends on the diffusion length of every single impurity, while the driving force is the bonding energy. Their recombination (radiative and non radiative) activity depends on contamination**