The University of Manchester

identifying point defects in technologically important semiconductors

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Outline

- ➢Defects in Semiconductors
- ➢Techniques
    - ➢Junction Spectroscopy
    - ➢Photoluminescence
- ➢Case Study Boron-Oxygen degradation in solar cells
- ➢Gallium and Indium alternative dopants
- ➢How could ISOLDE help?

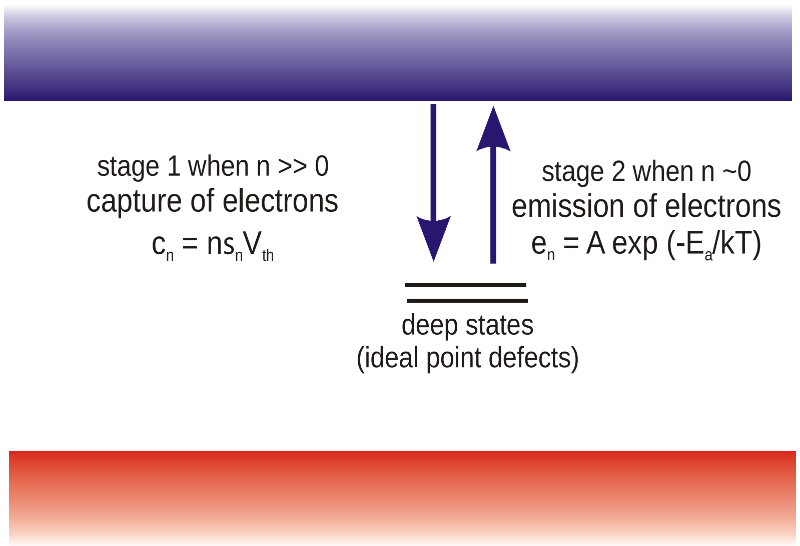
Semiconductor Defects

- Unintentional impurities and intrinsic defects can have a dramatic effect on the performance of semiconductor devices
- These can be present in starting materials, introduced during epitaxial growth or in device processing or develop during device operation due to diffusion, field stressing or in hostile environments due to radiation.
- Can be significant in VERY small concentrations $<10^{12}$ cm^{-3} in the semiconductor bulk or just a few atoms in the active volume of extremely scaled CMOS. They act as recombination-generation centres affecting lifetime, junction leakage and as carrier traps.
- Well established spectroscopic techniques are well developed for Si and Ge to quantify electrical effects and in some cases identify the defects. Deep Level Transient Spectroscopy (DLTS) is the best known of these techniques.
- DLTS and related techniques do not work as well in wide band gap materials. Here we review DLTS techniques explain their limitations and describe what we are doing to develop defect spectroscopy in wide gap materials.

Junction Spectroscopy & Defects

- Has been used for 40+ years to characterize deep levels in semiconductors *CT Sah et al Solid State Electronics 13, 759 (1970)*
- Can detect defects at densities around 10^{-5} of the carrier concentration (typically in Si devices 10^{11} defects cm^{-3})
- Needs a depletion region to work well and quantify concentrations and defect parameters ie uses a Schottky or p-n junction or an MOS device.

- Exchange of charge is measured by monitoring either capacitance or current in the depletion region after the carrier occupancy is changed by an applied bias
- Time dependent exponential transients of carriers from defect states at different temperatures are then analysed to derive electrical properties and fingerprint the defects.

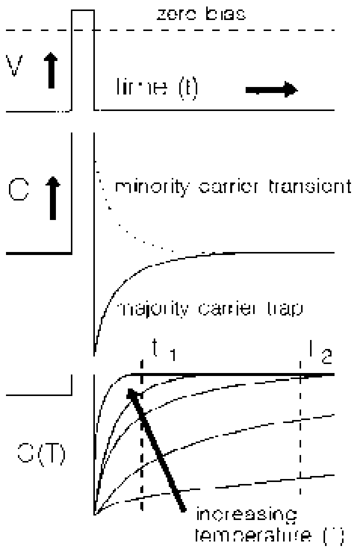


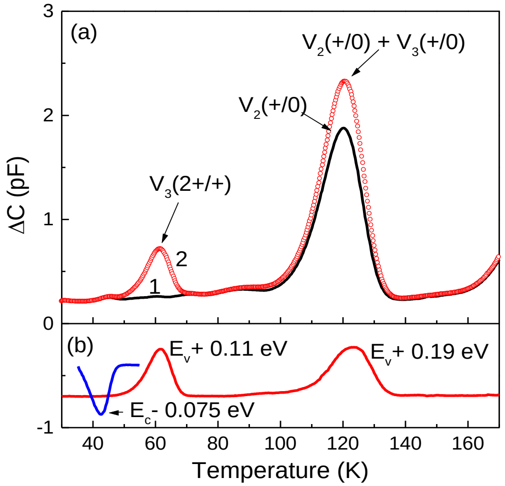
Making the transient meaningful … DLTS

The first task is to convert the transient from the time domain to the frequency domain separating the exponentials to quantify emission rates.

In 1976 Lang *(J Appl Phys 45, 3023)* developed a simple analogue technique (DLTS) to do this. DLTS samples the transient at two points and plots the difference as the temperature is swept. The output is a sequence of peaks each representing the emission from a defect. The magnitude relates to the concentration of the defect.

These f(T) and measurements of e_n or e_p at multiple T give an activation energy. Together these are a fingerprint of the defect.

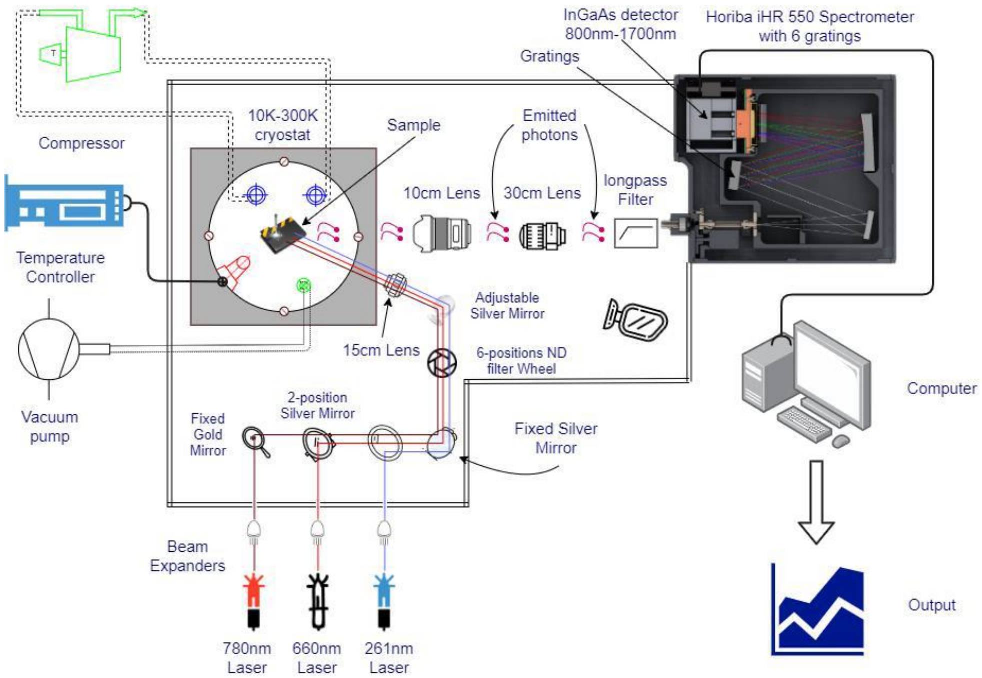




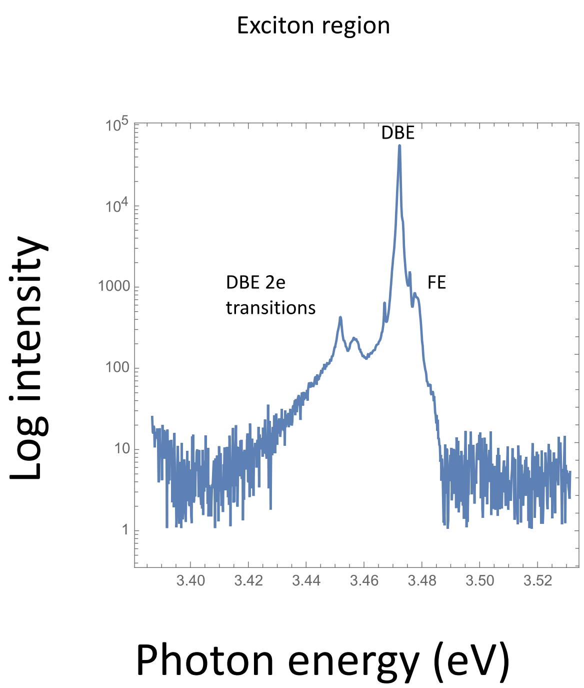
Si 6 MeV electrons (red) + anneal (black)

Photoluminescence

- A semiconductor illuminated by light with energy above its bandgap will emit light as the carriers relax
- The spectrum of this light can carry a vast amount of detailed information about impurity states
- Can detect defect concentration in the part per trillion level.

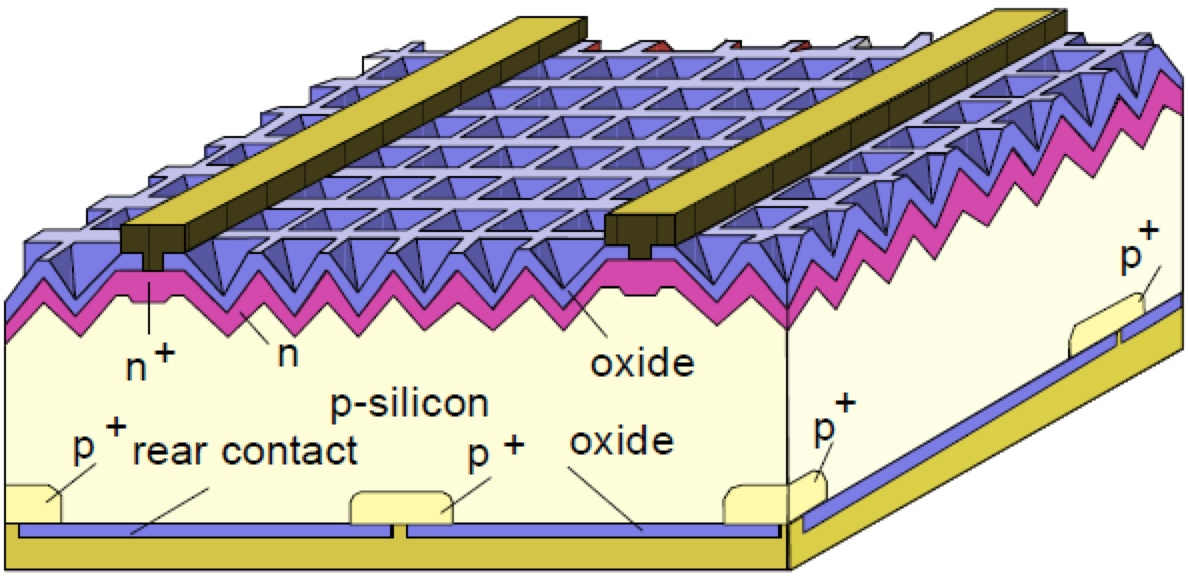


PL GaN unipress Warsaw



PERL solar cells

- 90% of solar cells manufactured last year we p-type silicon cells
- Totally installed capacity is now 773 GW, vast majority is silicon based
- In these cells Boron dopes silicon absorbs the sunlight The minority carriers (electrons) have to diffuse to the n-type emitter Minority carrier lifetime is the essential figure of merit for solar silicon
- The main loss mechanism in the bulk is Shockley-Reed-Hall recombination at Defects

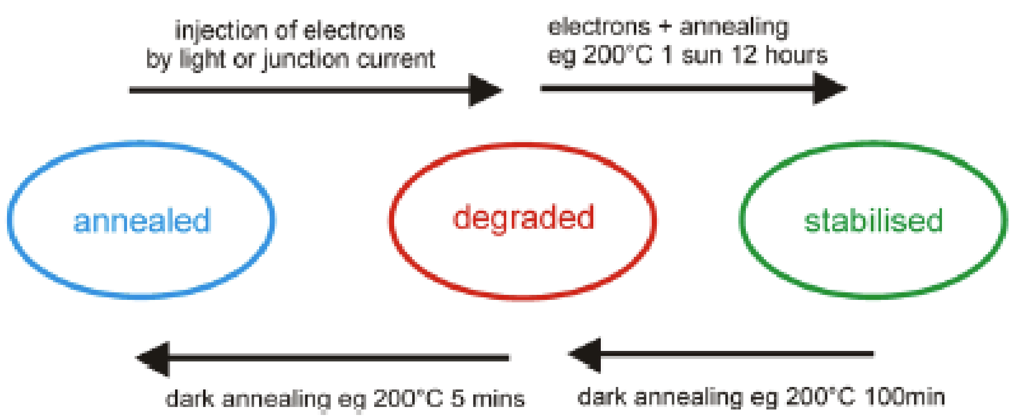


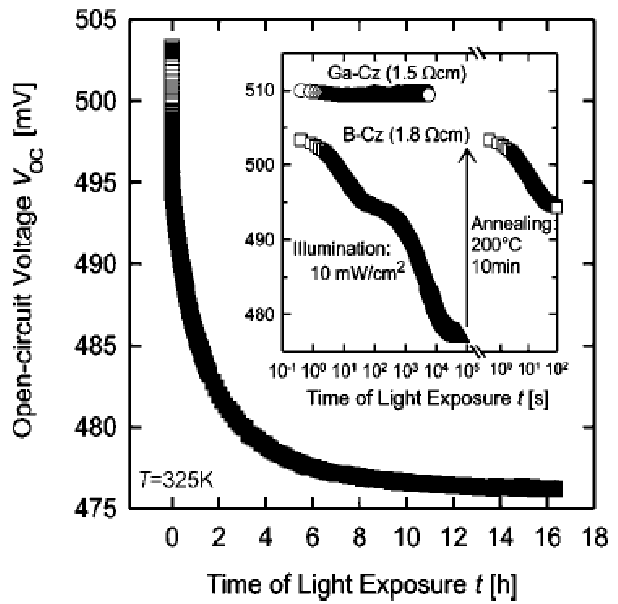
Overview BOLID

- Boron is p-type dopant and Oxygen strengthens Si so it can be sawed into thin wafers
  - These cells show light induced degradation (LID) in their first few hours of use. Despite 100's of articles studying the problem over 40 years this defect has never been identified although it reduces efficiency by 4-6% relative
  - Effect scales as [B] and $[O]^2$ so a B-O_2 defect likely involved
- Si dominates solar PV power >460TWh per year in 2017, this is not likely to change soon
  - By a very conservative estimate the B-O point defect loses >25TWh per year of electricity or >25M tonnes of CO_2 (from coal) across the planet annually
  - Origin is an enduring mysteries of semiconductor physics

Behavioral data

- Defect appears to have at least 3 states
- Annealing in the dark at 200⁰C produces the annealed state- no degradation this is the state as-made cells start in
- Injection of electrons by light or in a forward bias PN junction degrades the cell
- Annealing at 200⁰C with illumination stabilizes the defect
  - (only metastable and not industrially viable)
- Some evidence there may be two degraded states





Karsten Bothe and Jan Schmidt
Journal of Applied Physics 99, 013701 (2006)

Electrical signals from defect

Despite 40 years of study there has been no definite evidence for an electrical signal from this defect in eg Junction Spectroscopy
Given the impact on minority carrier lifetime of the defect this is surprising

I) <u>Samples</u>

Czochralski-grown Si crystals doped with B (ρ from 0.7 to 10 Ohm.cm).

II) <u>Processing for electrical measurements</u>

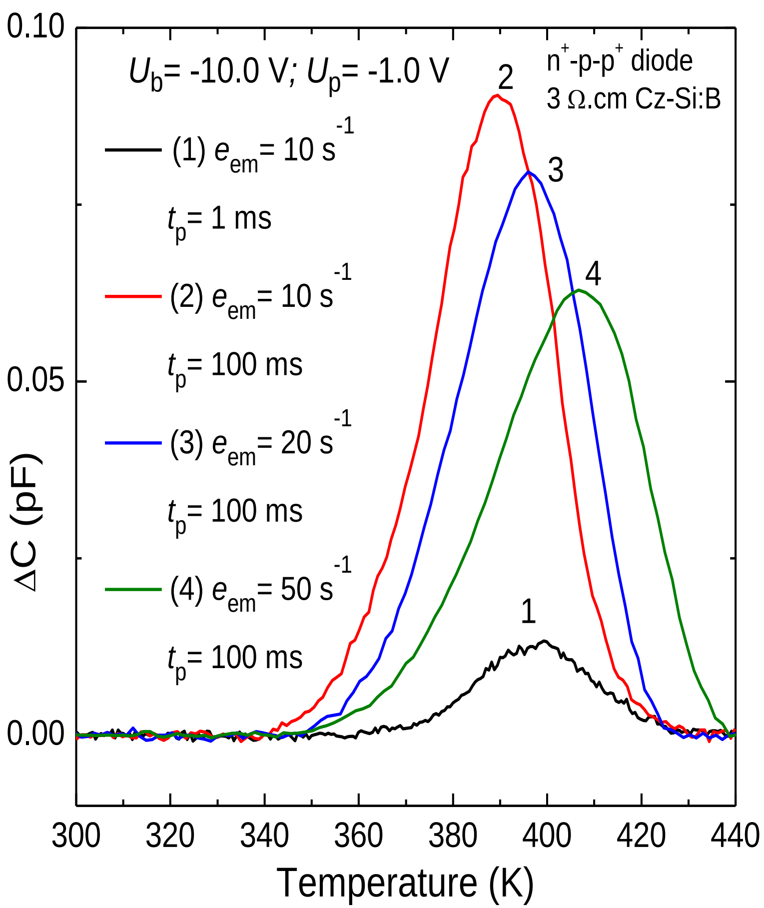
a) n^+-p-p^+ diodes on Si wafers with resistivity of 3 and 10 $\Omega\cdot$cm

b) Ti/Al Schottky diodes on Si:B+O samples

III) <u>Measurements</u>

a) IV-CV, DLTS and Laplace DLTS in the range 30 to 450 K
b) Minority carrier lifetime measurements on diodes with the use of reverse-recovery method, and on bare wafers using μ-PCD technique (WT-2000 PVN) with iodine surface passivation
c) Photoluminescence measurements of different types

DLTS signal from deep donor



Michelle Vaqueiro-Contreras et al
Journal of Applied Physics 125, 185704 (2019)

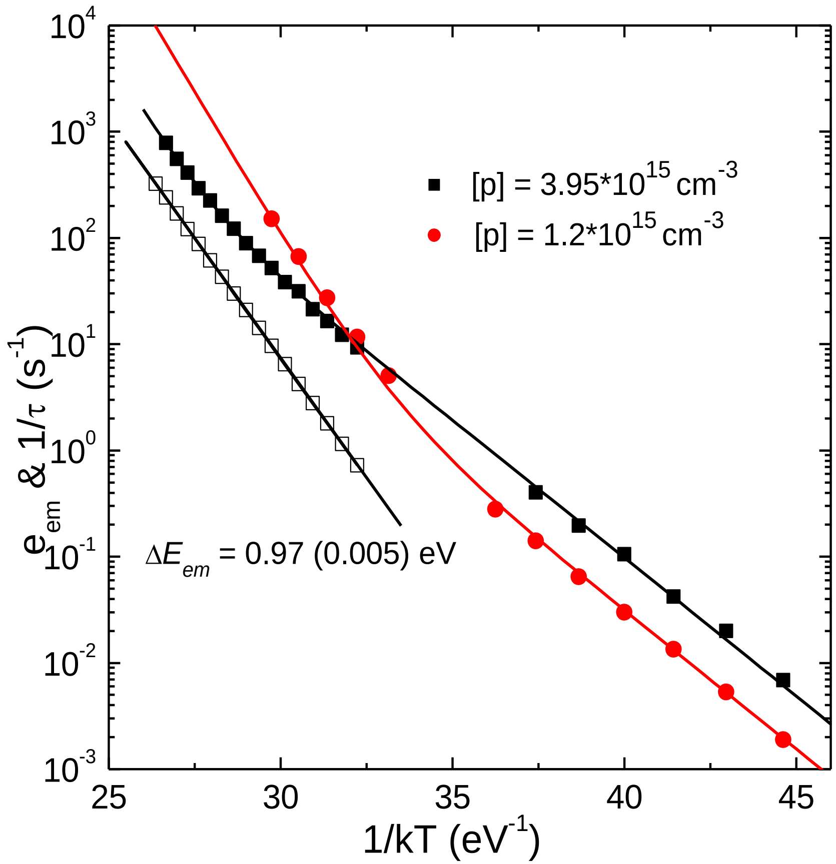
- The high-temperature DLTS emission signal have not been detected previously because of its unusual (for defects in Si crystals) emission and capture properties. The emission and capture rates are rather slow compared to those for majority of defects in Si, so high temperatures and long filling pulses are required for its detection.

- The DLTS emission signal has been observed in all as-processed n^+-p junction and Schottky barier diodes on Cz-Si samples.

- The DLTS signal has not been observed in the diodes on boron-doped Fz-Si crystals.

- A decrease of the trap magnitude with R_W (temperature) $\Rightarrow$ smaller population with holes

Nature of defect

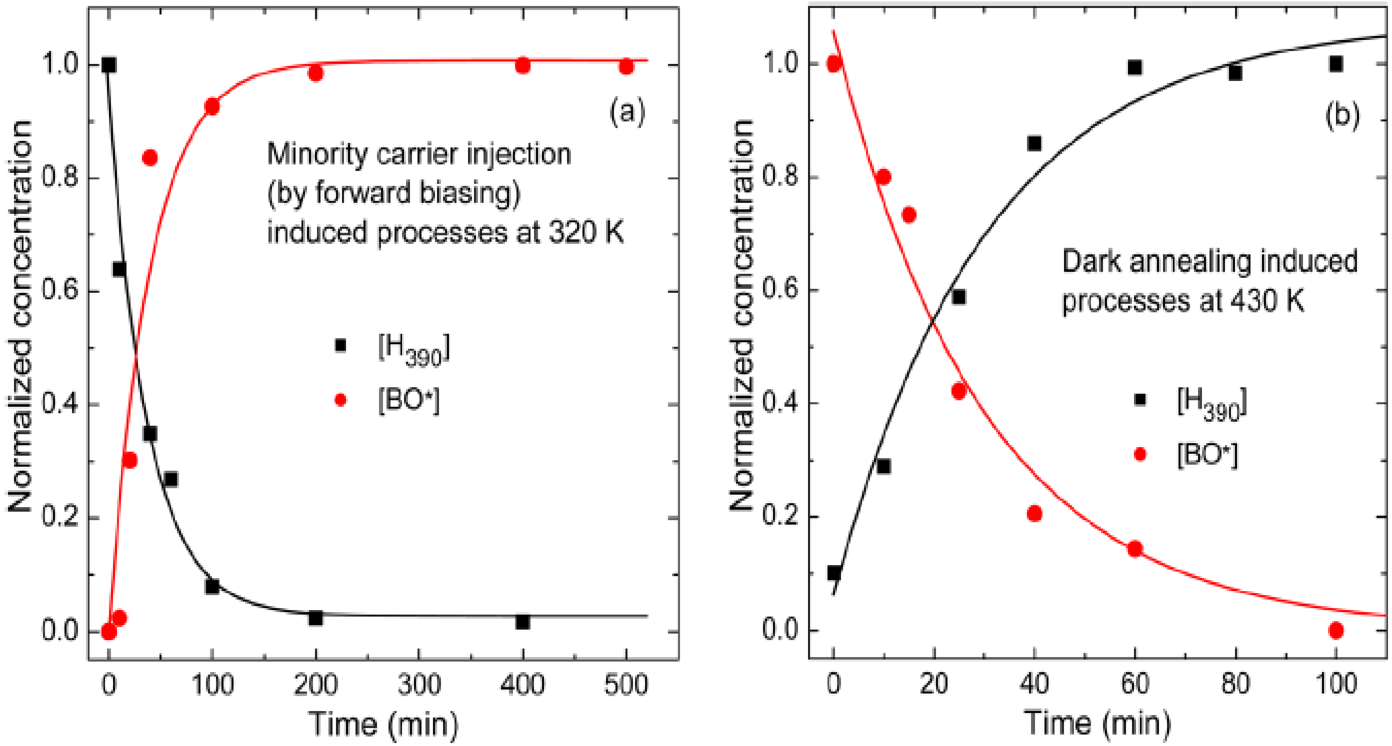


- An analysis of temperature dependencies of emission (e_p) and capture (C_p) rates in materials with different [p] allows to elucidate electronic structure of the defect and determine energy differences and barriers.

- Non-equilibrium occupancy statistics developed for defects with negative-U properties and a metastable state between two stable states has been used ***(V.P. Markevich et al, Mat. Sci Forum 258-263, 217 (1997)).***

- There some unusual features in $C_p(T)$ dependences $\Rightarrow$ capture rate of holes is inversely proportional to [p] in high-T range.

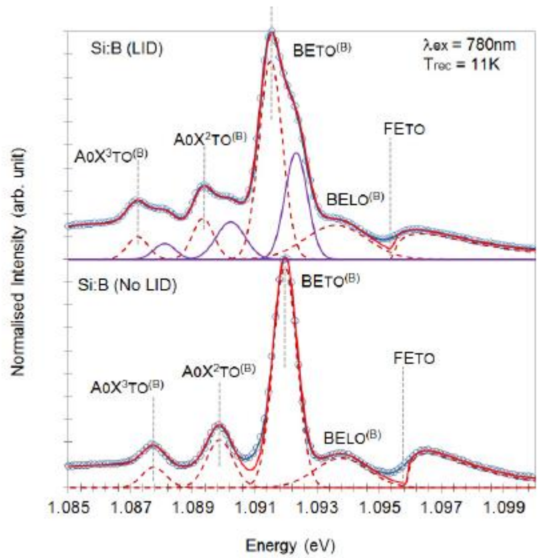
Does this defect cause BOLID?

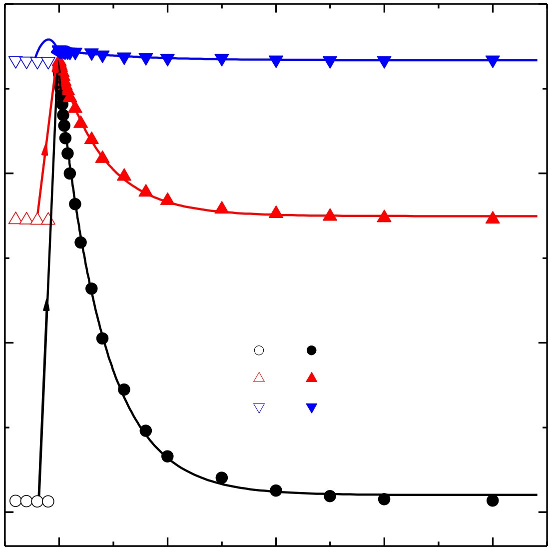


- τ has been measured in the diode by reverse-recovery method.
- τ changed from 26.3 μs in the annealed state to 21.9 μs in the degraded state.
- [BO*] has been calculated as

$$\left[\left(1/\tau_{eff(t)} - 1/\tau_{eff(ann)}\right) / \left(1/\tau_{eff(degr)} - 1/\tau_{eff(ann)}\right)\right]$$

PL and capacitance changes indicated new shallow acceptor formed

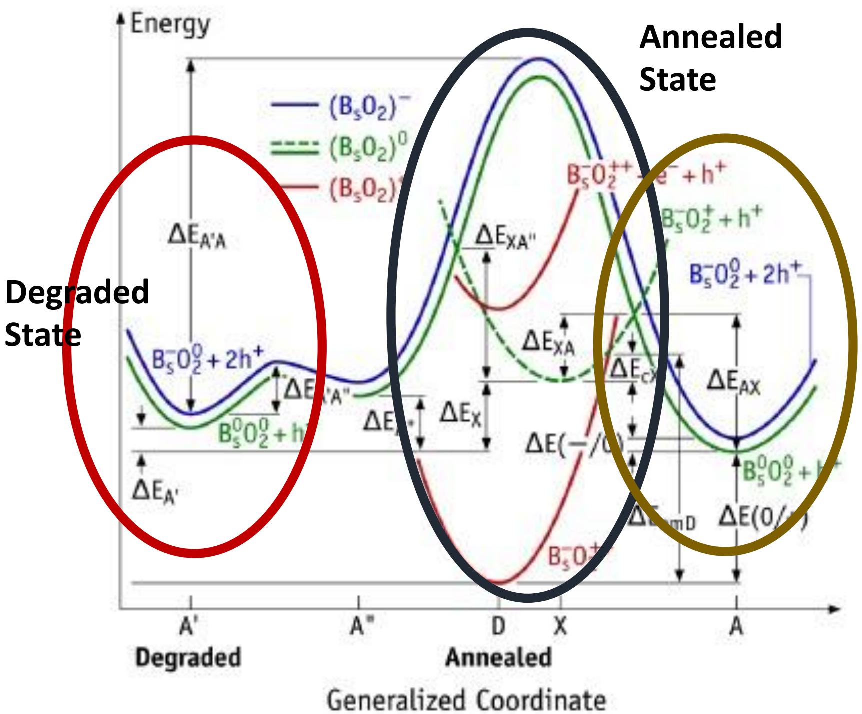


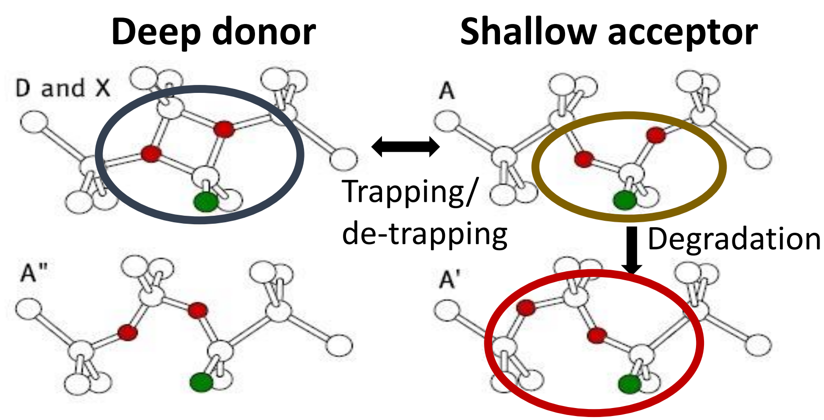


Photoluminescence of Excitons bound to acceptors in Silicon. After LID (top) second shallow acceptor is observed. Also a small increase in carrier concentration is observed in admittance spectroscopy

diode capacitance changes associated with the disappearance of the deep donor trap upon LID indicates that a shallow acceptor defect (similar to the A state) is created.

Proposed structure of centre





The B_sO_2 defect is a negative-U center with an E(+/-) occupancy level at ~0.32 eV above the valence band edge.
E(0/+) @E_v + 0.58 eV; E(-/0) @E_v + 0.04 eV
DE_{emD} = 0.97 eV; DE_{AX} = 0.67 eV

Study of other group III dopants

- To determine electronic characteristics of the traps in Cz-grown silicon doped with either indium, aluminum, and gallium atoms.

- To investigate the occupancy function of the traps and examine if the traps exhibit properties of a negative-U defect similar to the boron-di-oxygen complex (B_sO_2).

- To determine if these too can degrade cell performance

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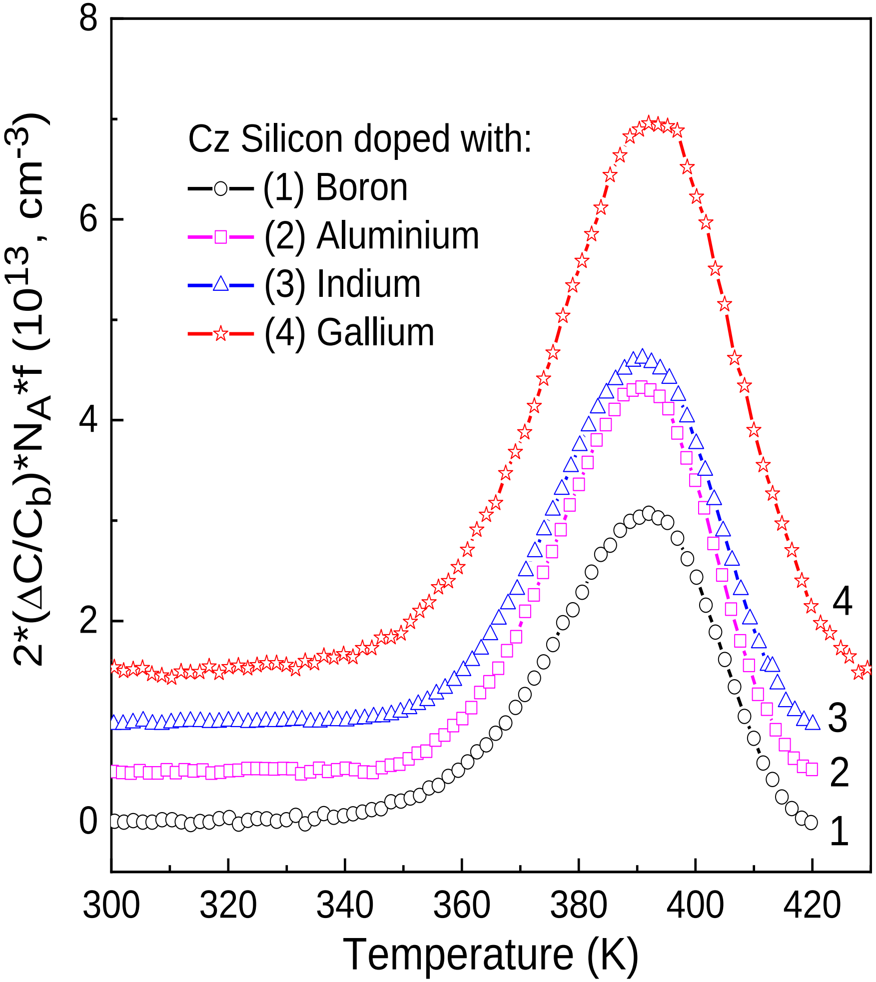
Sample Details

Cz-Si Sample	Dopant	Diode	Acceptor Concentration (N_A) from CV at 300 K (cm^{-3})	Interstitial Oxygen [O_i] (cm^{-3})
B-1	Boron	n^+-p-p^+ /Schottky	1.2×10^{15}	$9.5 \pm 1 \times 10^{17}$
B-2	Boron	n^+-p-p^+ /Schottky	4.0×10^{15}	$(6\text{-}9) \times 10^{17}$
Ga-1	Gallium	Schottky	9.2×10^{15}	$\sim 8 \times 10^{17}$
Al-1	Aluminium	Schottky	5.2×10^{15}	$\sim 8 \times 10^{17}$
In-1	Indium	Schottky	6.5×10^{14}	$\sim 6 \times 10^{17}$
In-2	Indium	Schottky	1.7×10^{15}	$\sim 6 \times 10^{17}$
In-3	Indium	Schottky	4.5×10^{15}	$\sim 5 \times 10^{17}$

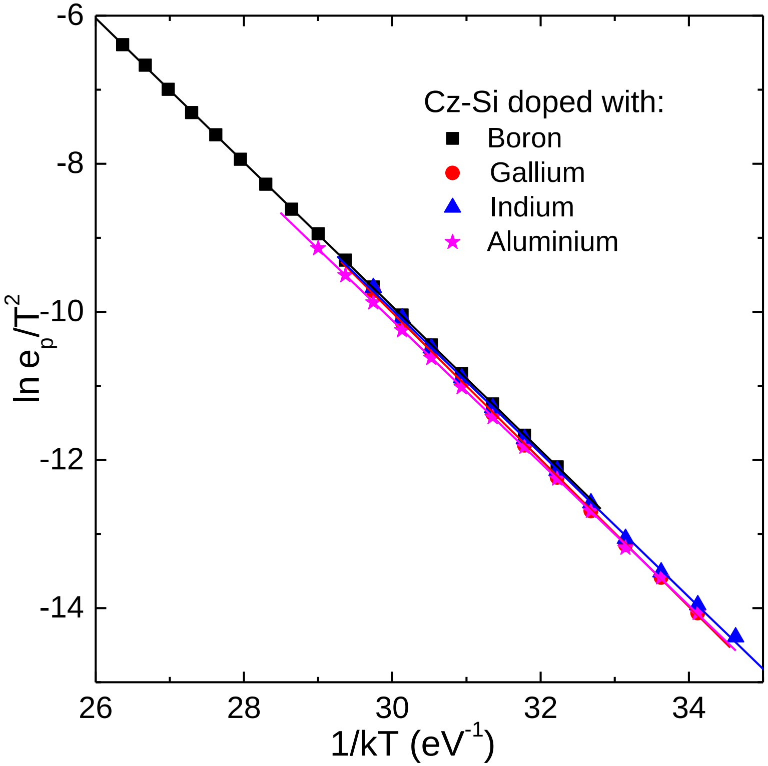
Junction spectroscopy techniques (DLTS, L-DLTS, MCTS, C-T) have been used to detect and characterize defects in the diodes.

DLTS Spectra for Cz-Si samples (Schottky diodes) doped with either B, Al, Ga, or In atoms



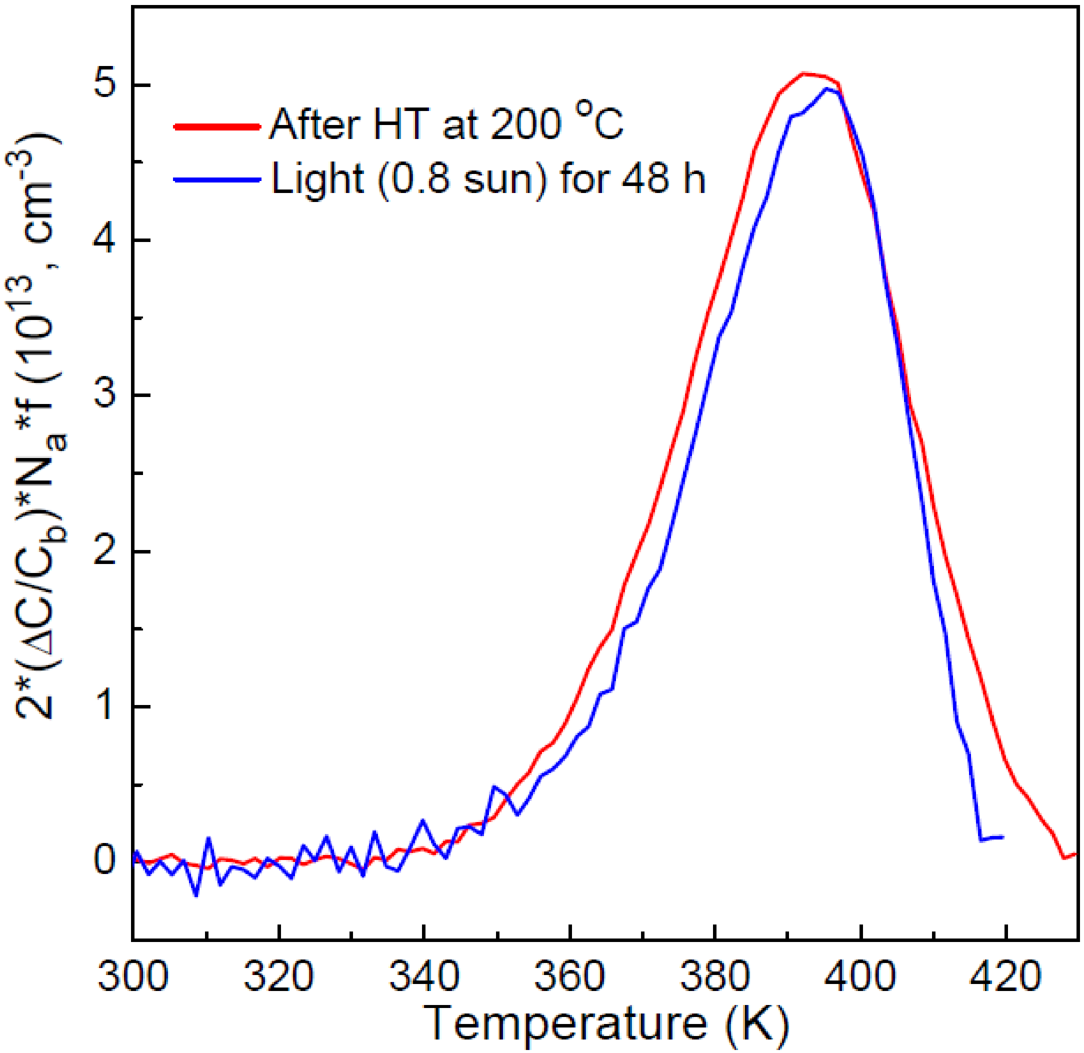
Hole emission signal with its maximum at 390 K (H_{390} trap) in B-doped Cz- Si was also observed in Cz silicon doped with either Ga, In, or Al.

Activation energies and pre-exponential factors for hole emission from the H_{390} trap



Dopant	N_A (cm^{-3})	Activation Energy (eV)	Pre-exponential factor ($s^{-1}K^{-2}$)
Boron	4.0×10^{15}	0.97 (0.01)	2.3×10^{8}
Gallium	9.2×10^{15}	0.99 (0.01)	3.85×10^{8}
Indium	4.5×10^{15}	0.97 (0.01)	2.05×10^{8}
Aluminium	5.2×10^{15}	0.96 (0.01)	1.4×10^{8}

Do these defects cause degradation?



Contrary to the case of CZ-Si:B, light soaking does not result in the disappearance of the detected deep donor signal in Cz-Si materials doped with either Al, Ga, or In.

Why is Boron different?

- At this time we do not know!
- Important technologically as industry is moving to Ga doping in the belief that Cells will last 30 years or more
- Also the exact mechanism of the degradation process is unclear, its actually not certain the defect is Ga related!
- Radioisotope studies could be very helpful
- Candidates:-
  - ^{72}Ga -> ^{72}Ge 14hr ½ life Ge is isoelectonic with Si
  - ^{71}Ge -> ^{71}Ga 11d ½ life
- Also other systems
  - Carbon in GaN important for power transistors
  - Iron in GaN for RF devices…

Conclusions

- Understanding Defects in Semiconductors remain vital for many device operations
- Junction spectroscopy and PL can detect defect levels at very low concentrations
- A good example of why this matters is BOLID in solar PV
  - A DLTS signal related to hole emission from the deep donor trap with ΔE_{em} = 0.97 eV has been found in all as-grown Cz-Si samples doped with B, Ga, Al, or In atoms.
  - The B_sO_2 complex is argued to be responsible for LID of minority carrier lifetime and efficiency of solar cells from B-doped Si.
  - Other A_sO_2 defects do not appear to undergo light induced changes under normal conditions
  - Radioisotopes could be essentially in solving this mystery.

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*Currently University of New South Wales, Sydney, Australia

Theory University of Aveiro, Portugal
J.Couthino

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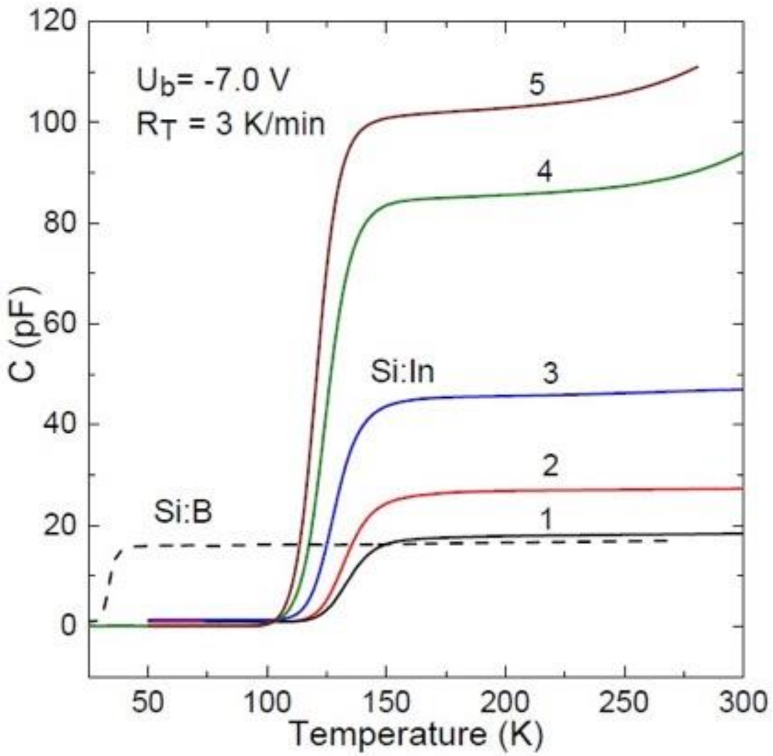
Boron Contamination?



Boron often present residually or deliberately (to improve uniformity in the boule)- is this the cause of the signal?

The absence of capacitance in the region 50 to 100 K is indicative that the silicon is intrinsic in this temperature range - no significant concentration of boron in the indium doped slices.

The H_{390} trap in Al, Ga, and In-doped Cz-Si samples is not related to B_sO_2.