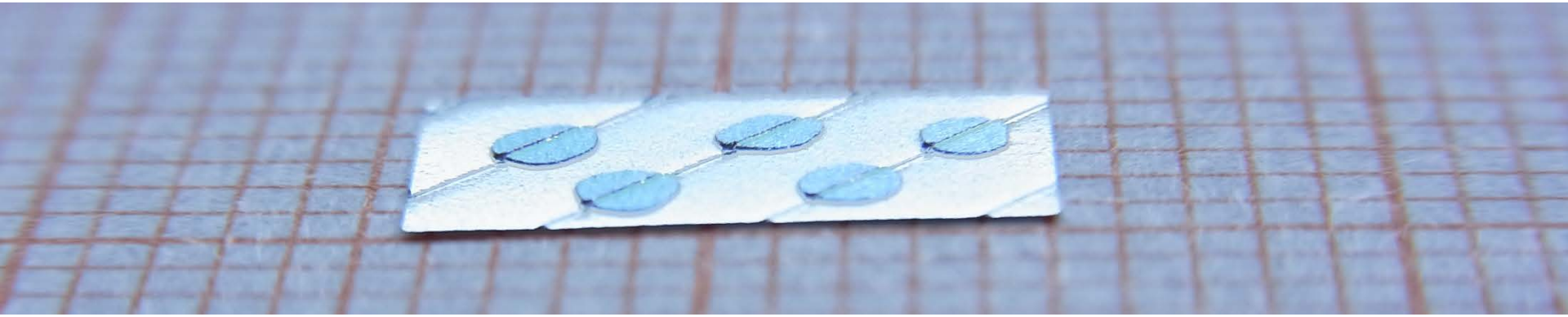
ღრმა დონეების გადასვლების სპექტროსკოპია

Deep level transient spectroscopy (DLTS)

თეიმურაზ მჭედლიძე



1. DLTS მეთოდის საფუძვლები
2. ნიმუშების მომზადება, გაზომვები, მონაცემების დამუშავება…
3. DLTS მეთოდის გამოყენება ფოტოვოლტაიკური მასალების დასახასიათებლად

Part 1. DLTS fundamentals

- Introduction
- Principe and physical basis
- Samples and measurements
- Data processing and results
- Advanced technique and other possibilities
- Summary

D.V. Lang, Journal Applied Physics **45**, p.3023 (1974)

D.K. Schroder "Semiconductor Material and Device Characterization" 2nd Edition Wiley-Interscience 1998 ISBN 0-471-24139-3 (a section on DLTS)

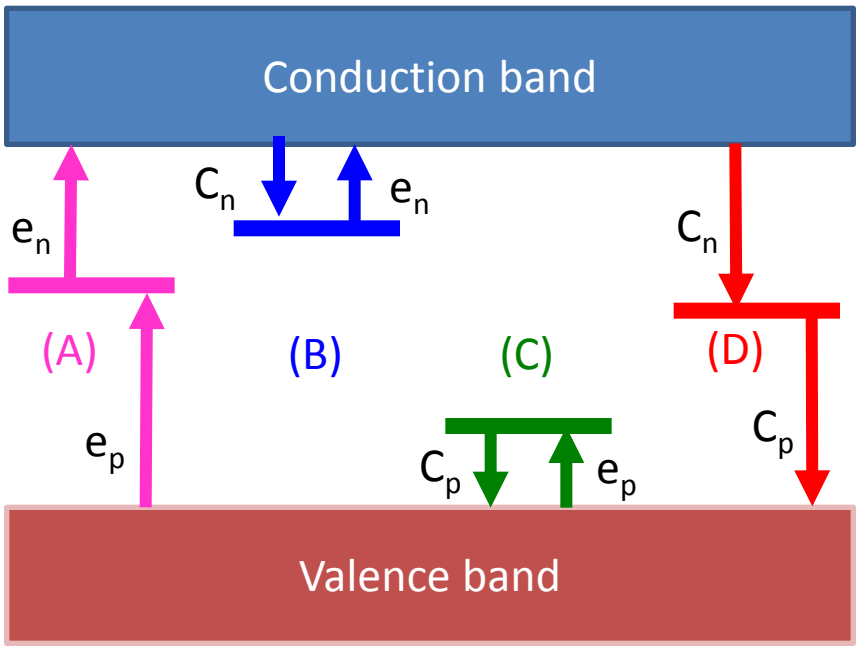
P. Blood and J.W. Orton "The Electrical Characterization of Semiconductors: Majority Carriers and Electron States", Academic Press 1992 ISBN 0-12-528627-9 (detailed section on DLTS)

Introduction

- Semiconductor material properties
  - Electrical (carrier-related) properties
    - Carrier recombination-generation, trapping
      - Trap characterization:
        - position of the trap level in the energy bandgap
        - Carrier capture cross-section
        - Trap density
        - Charge state
        - …

DLTS

Trapping, recombination and generation



(A) - Generation

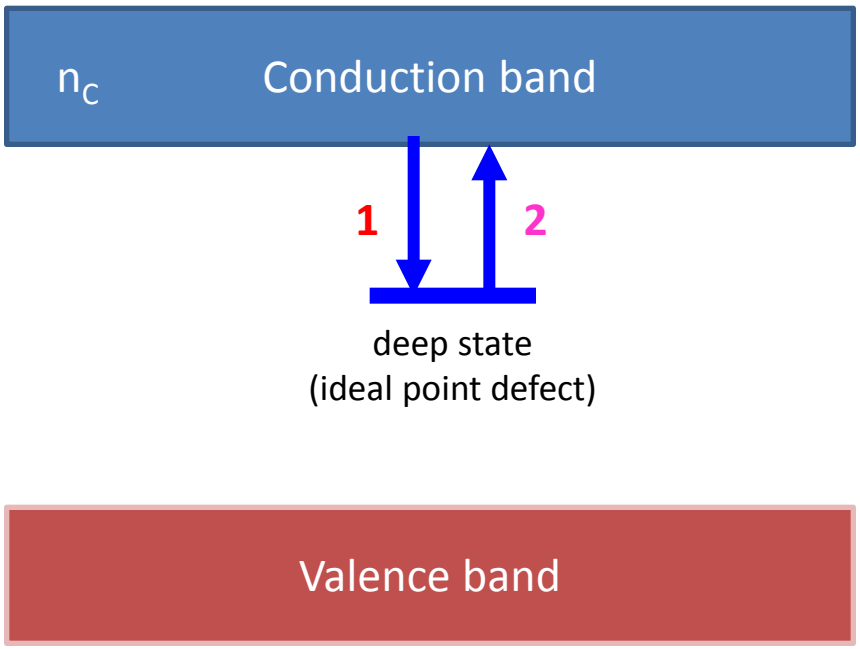
(B) - Electron trapping

(C) - Hole trapping

(D) - Recombination

- *(A) is responsible for leakage currents and, hence, GENERATION lifetime*
- *(D) determines carrier RECOMBINATION lifetime*
- *Processes (B) & (C) can be a source of noise. They can be used to determine the trap parameters*

Capture and thermal emission of carriers

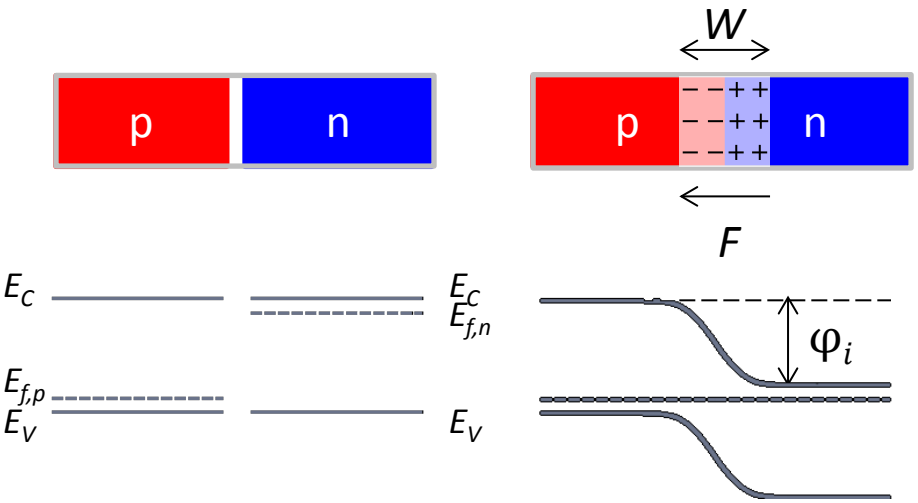


Stage **1** when $n_C >> 0$
capture of electrons
$C_n = n\ \sigma_n V_{th}$

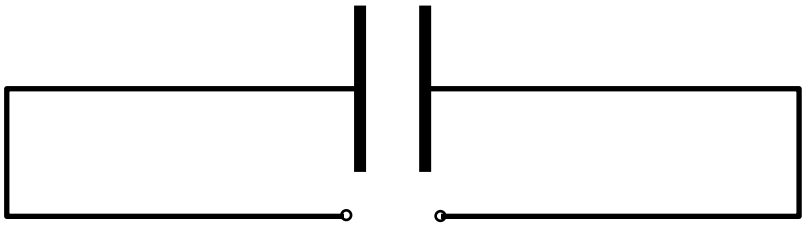
Stage **2** when $n_C \approx 0$
emission of electrons
$e_n = A \exp(-E_a / kT)$

- DLTS measurements use a two stage carrier capture **(1)** and emission **(2)** process (trapping) to characterize defects and impurities
- Charge exchange in a depletion region of a pn-junction or in Schottky barrier can be estimated by measurements of depletion capacitance value.

Physical aspects of pn-junction



$$C = \varepsilon_r \varepsilon_0 \frac{A}{W}$$



1. Doped atoms near the metallurgical junction lose their free carriers by diffusion.

2. As these fixed atoms lose their free carriers, they build up an electric field which opposes the diffusion mechanism.

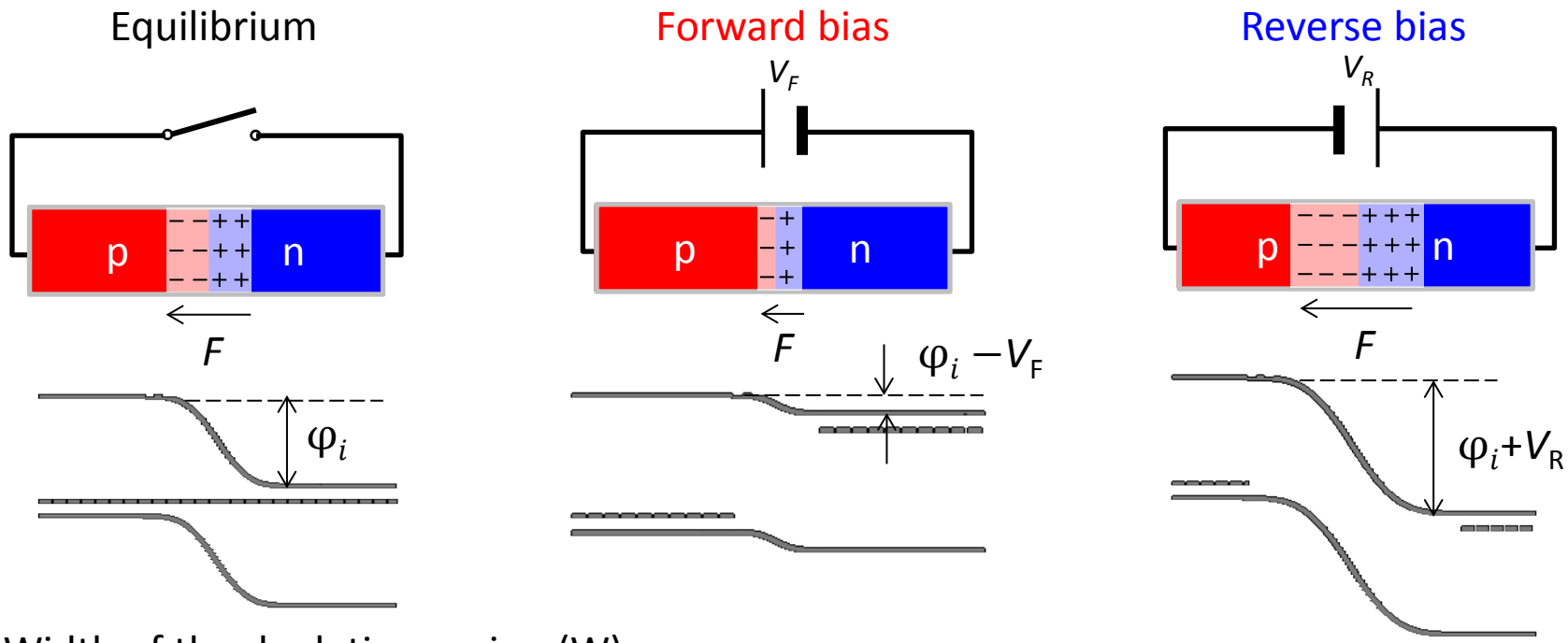
3. Equilibrium conditions are reached when:

Current due to diffusion =

Current due to electric field

Thus, pn-junction under depletion conditions is similar to a capacitor.

Physical aspects of pn-junction



Width of the depletion region (W):

– Changes with applied voltage and doping concentration

– High doping / forward bias → small W

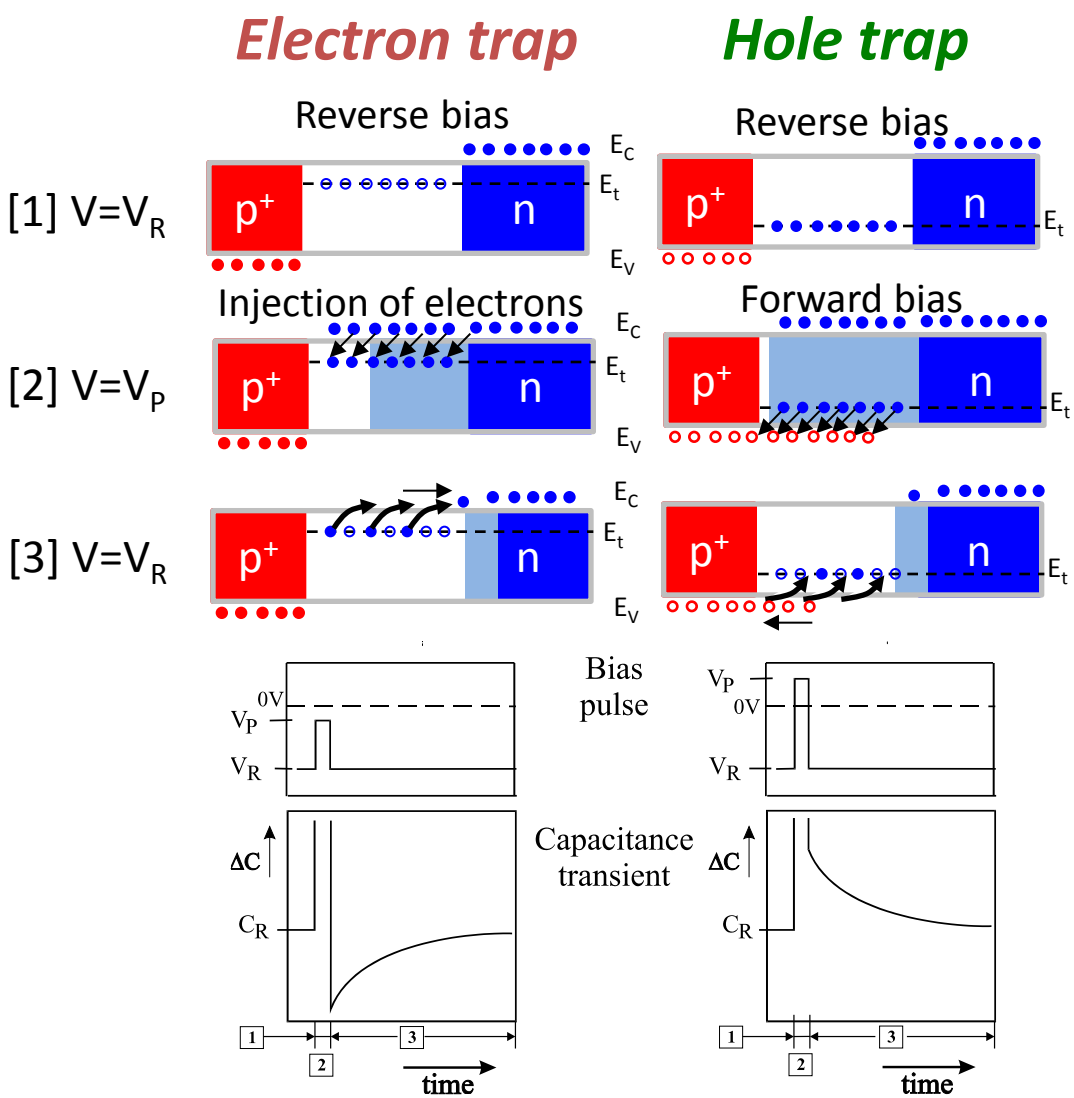
– Low doping / reverse bias → large W

Since $W = f(V_D)$ we finally have:

$$C_J = \frac{A\varepsilon_{Si}}{W(VD)} = A\sqrt{\frac{q\varepsilon_{Si}N_A N_D}{2(N_A+ND)(\varphi_i - V_D)}}$$

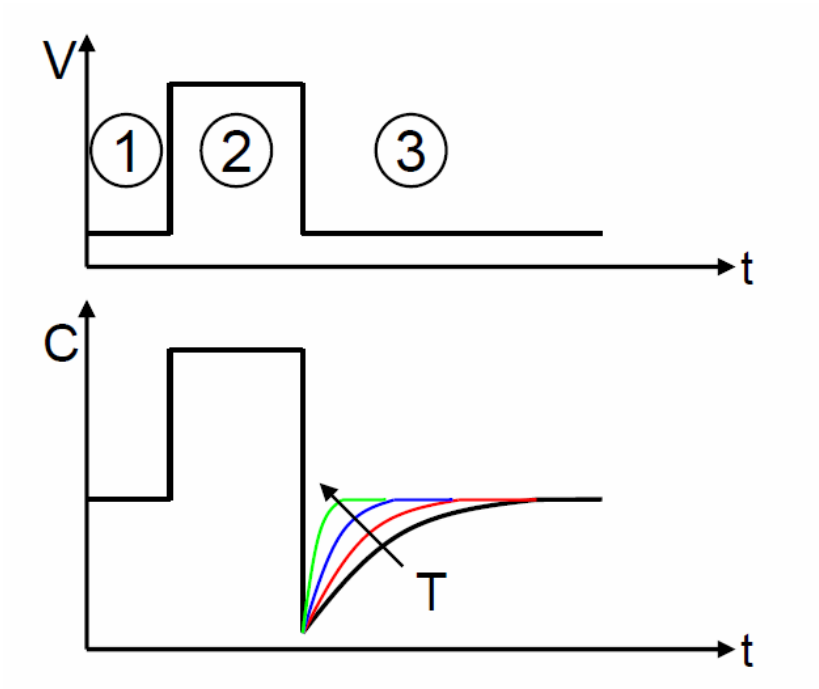
- Asymmetric doping (p^+n) will cause W to extend mostly into low-doped material in order to keep charge balance

Traps in the space charge region of a p^+n diode

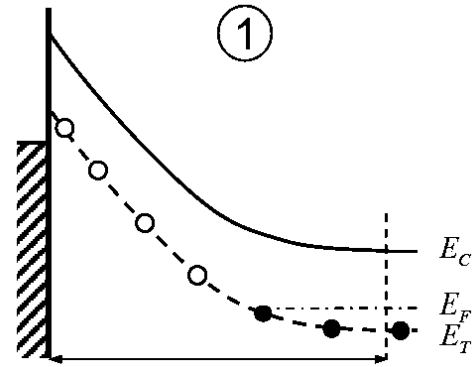


	electron trap	hole trap
[1]	Constant reverse bias (V_R)	
	traps empty	traps filled
[2]	Carrier injection (V_p)	
	electron capture ($V_p < 0$)	hole capture ($V_p > 0$)
[3]	Thermal emission of trapped carriers (V_R)	
	electron emission	hole emission
	Capacitance transients $\Delta C(t) = C(t) - C_R$ for $t > t_p$	
	negative	positive

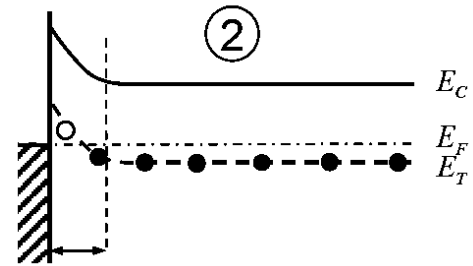
Measurement sequence



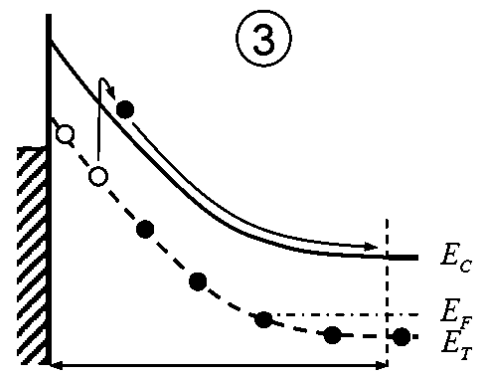
Steady state



Charging



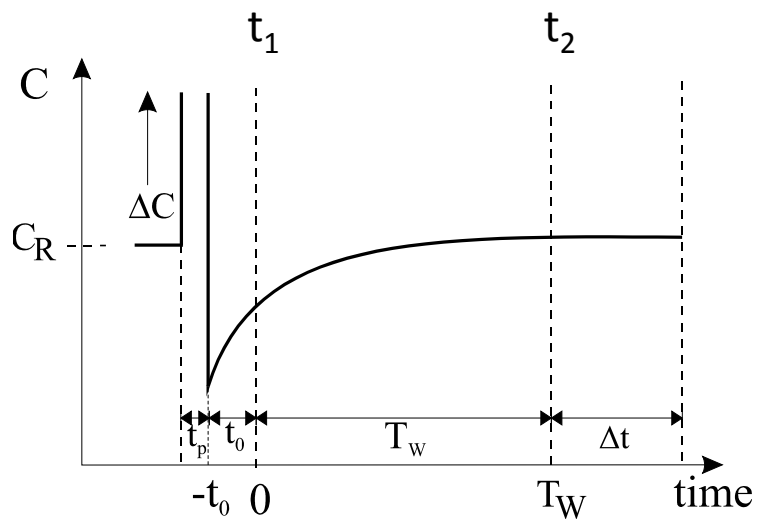
Emission



1) At steady state traps in depletion region are empty
2) Part of them are filled by pulse
3) Returning to steady state initiates emission from the traps.

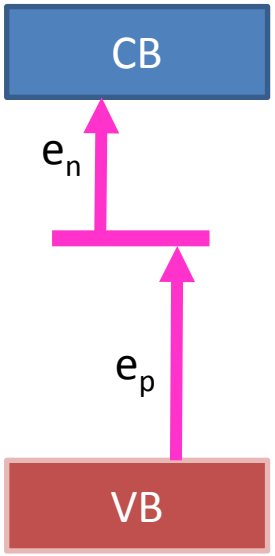
Emission depends on temperature (T)!

Capacitance transient



$$\Delta C(t) = C(t) - C_R$$
$$= \Delta C_0 \cdot \exp(-(t+t_0)/\tau_e)$$

Here τ_e is emission time constant

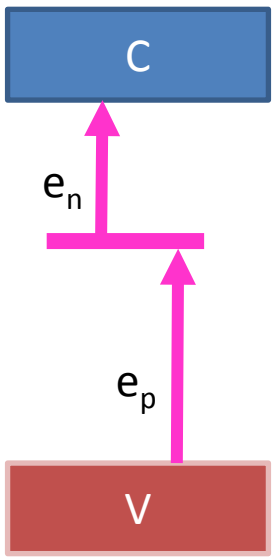


$$1/\tau_e = e_n + e_p$$

e_n and e_p are emission rates for electrons and holes.

for $e_n \gg e_p$ → $1/\tau_e = e_n$

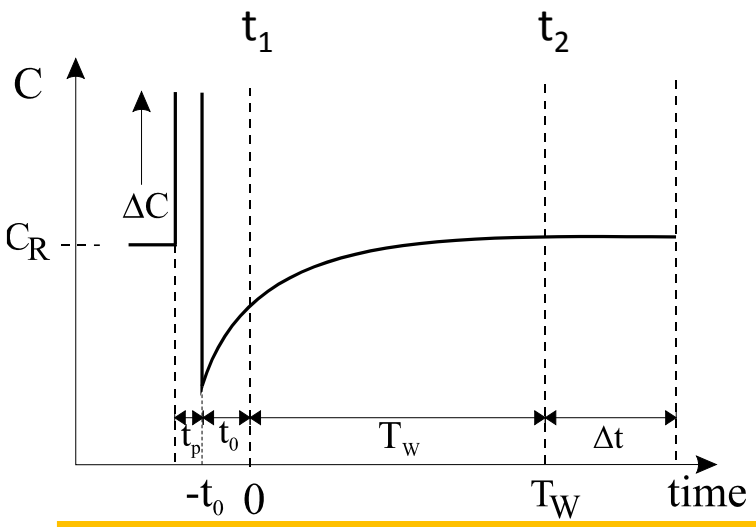
Capacitance transient



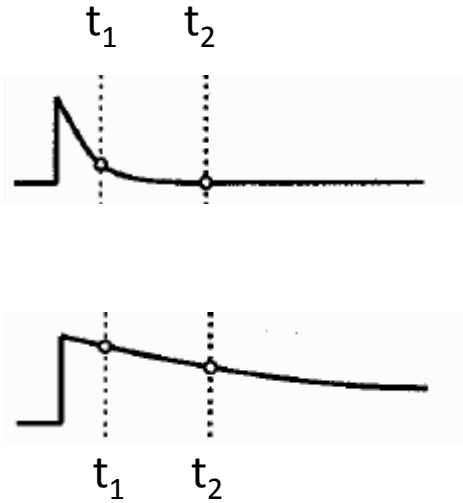
On the other hand emission rate depends on temperature, T and on activation energy, E_a:

$$e_n = A \exp(-E_{an}/kT) \text{ and } e_p = A \exp(-E_{ap}/kT)$$

Since $E_{an} < E_{ap}$ we have $e_n >> e_p$



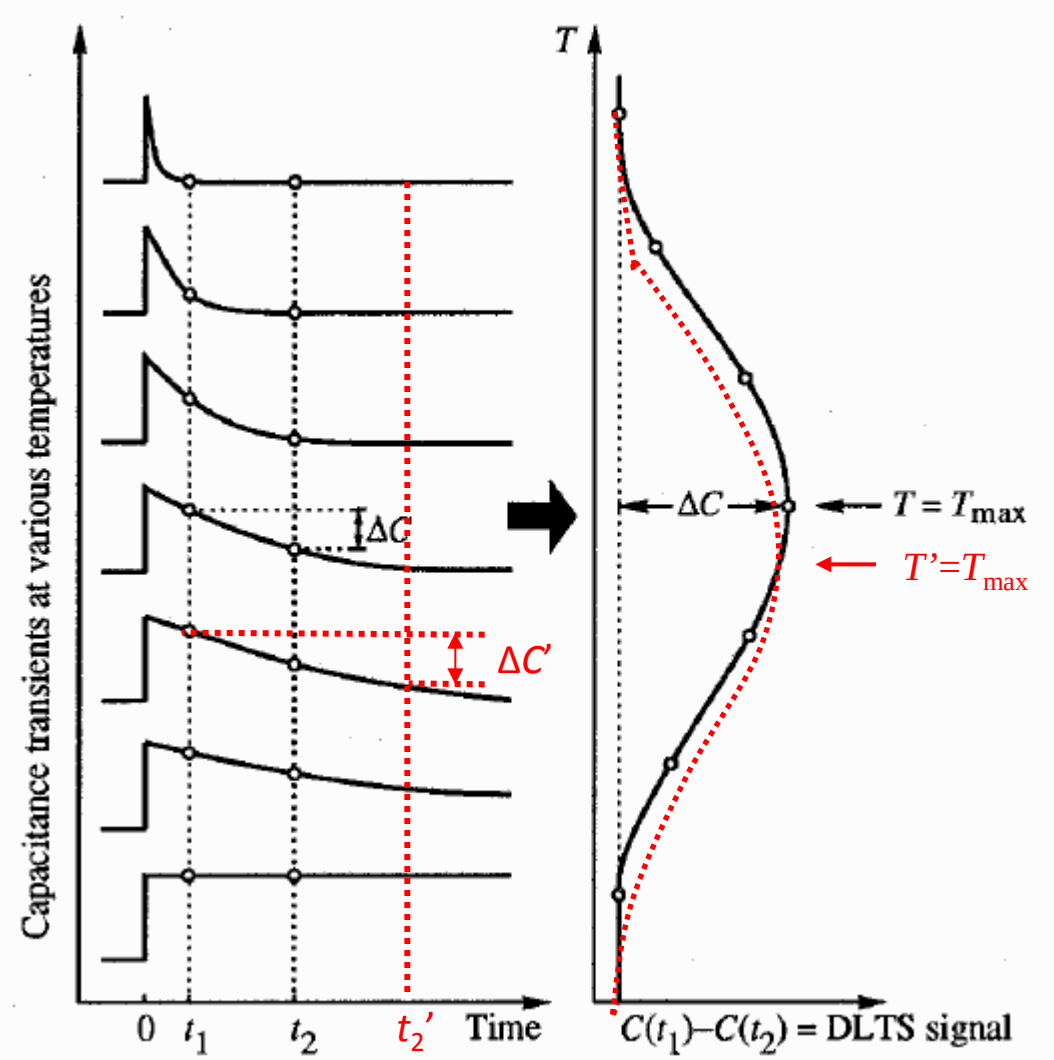
$T_w = t_2 - t_1$



T large
E_a /kT small

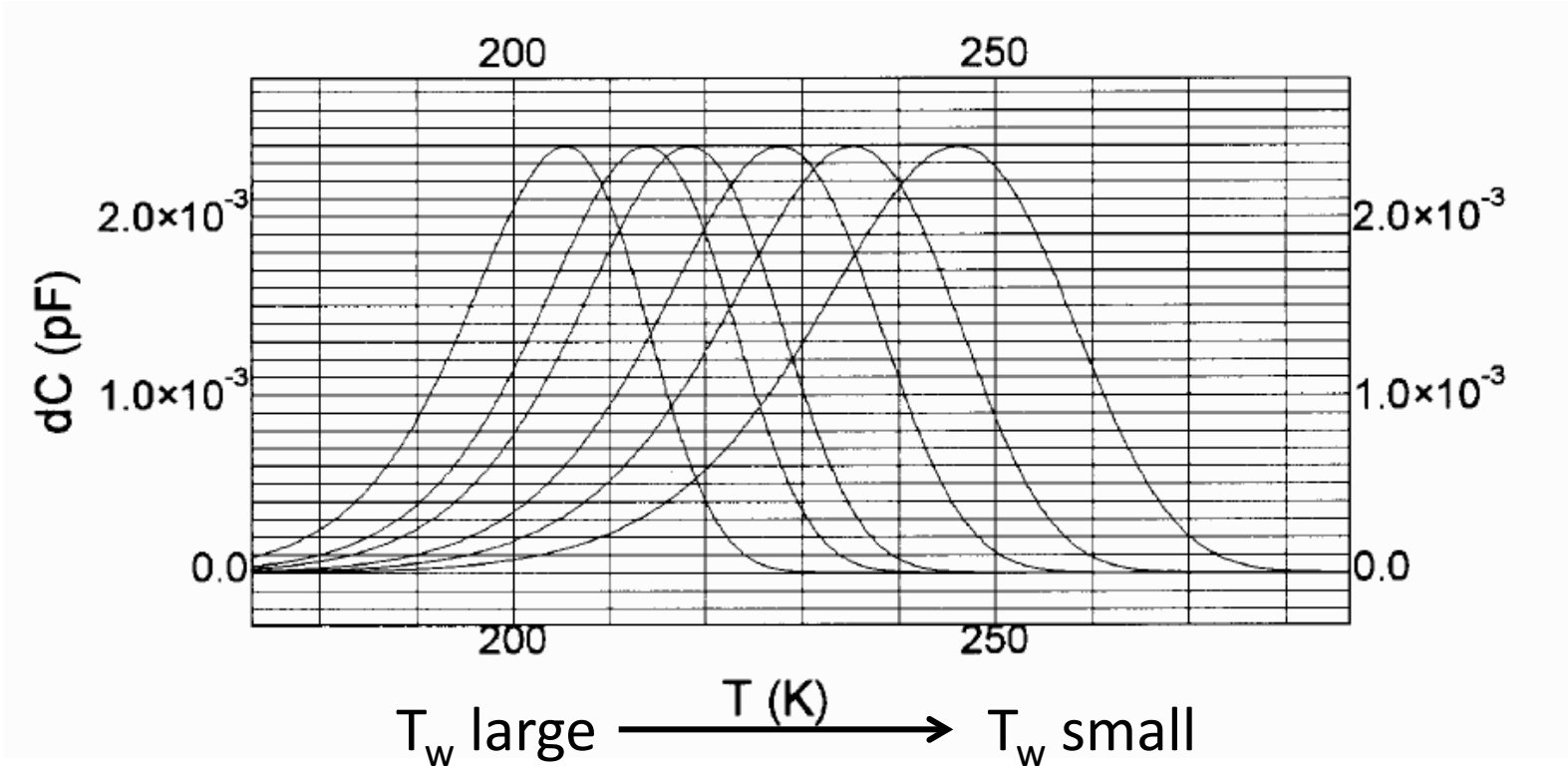
T small
E_a /kT large

DLTS peak



- In conventional DLTS the T varies and $\Delta C = C(t_1) - C(t_2)$ is detected.
- This produces a peak when the emission rate matches a 'standard' rate (the rate window).
- The rate window is determined by the positions of t_1 and t_2.

Changing rate window



By repeating the temperature scan with different settings of t_1 and t_2 the system "filters out" different rate windows so that each T_{max} corresponds to the temperature at which the trap emits carriers at that specific rate window.

Correlation of e_n and T

For two point correlation (t_1 and t_2) one obtains the following condition for the DLTS peak to appear:

$$e_{n,p}=\ln(t_2/t_1)/(t_2 - t_1)$$

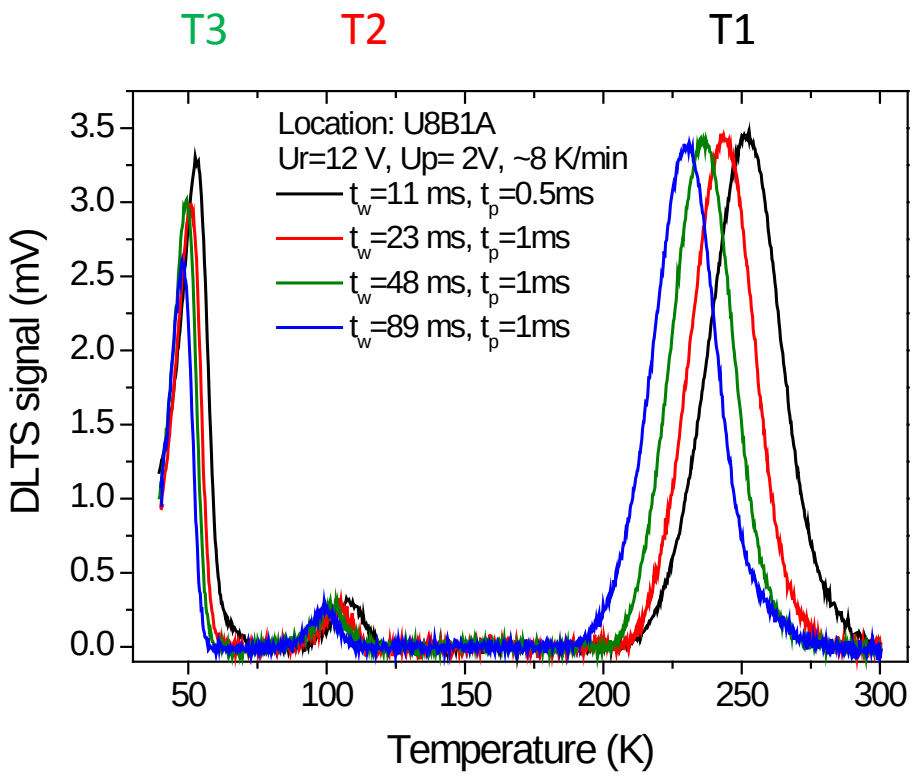
On the other hand $e_{n,p}(T)= A(T)\exp(-E_{a,n,p}/k_BT)$, namely

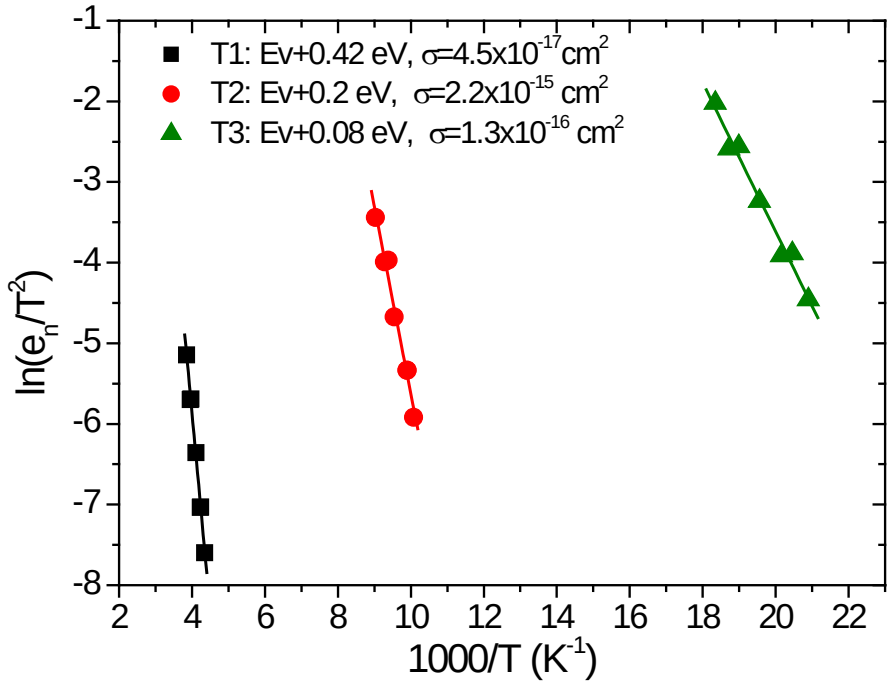
$$e_{n,p} = \sigma_{n,p}\upsilon_{th,n,p}N_{C,V}\exp\left(-\frac{E_{a,n,p}}{k_BT}\right)$$

Where $\sigma_{n,p}$ is carrier capture cross-section of a trap, $\upsilon_{n,p}$ and $N_{C,V}$ are functions of T ($\upsilon_{th}N_{C,V} \sim T^2$). Assuming $\sigma_{n,p}$ is independent of temperature (not always!!), one can get:

$$\ln\left(e_{n,p}/T^2\right) = \ln\left(\sigma_{n,p}\right) - \frac{E_{a,n,p}}{k_BT} \quad \Longleftrightarrow \quad y = a + bx,\ x=1/T$$

Arrhenius plot





Such analyses provide activation energy (E_a) and carrier cross-section (σ) for the detected traps:

$$\ln\left(e_{n,p}/T^2\right) = \ln\left(\sigma_{n,p}\right) - \frac{E_{a,n,p}}{k_B T}$$

Determination of trap density

- In total depletion approximation, the rf (~1MHz) capacitance of a p^+n junction ($N_A >> N_D$) having a homogeneous doping concentration is:

$$C_J = A\sqrt{\frac{q\varepsilon_{Si}N_D}{2(\varphi_i - V_D)}}$$

- A donor-like trap level of concentration N_t in an n-type sample biased under a reverse bias V_D, the capacitance change by recharging these levels will be:

$$\Delta C_J = C_J(N_D) - C_J{}'(N_D + N_t) \approx \frac{C_j N_t}{2N_D}$$

- The last identity holds approximately if $N_t << N_D$ holds. Then the trap concentration calculates from the capacitance change ΔC as:

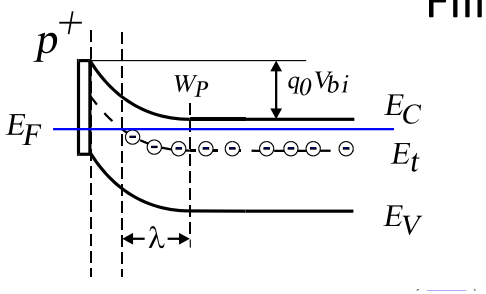
$$N_t \approx \frac{2N_D \Delta C_J}{C_J}$$

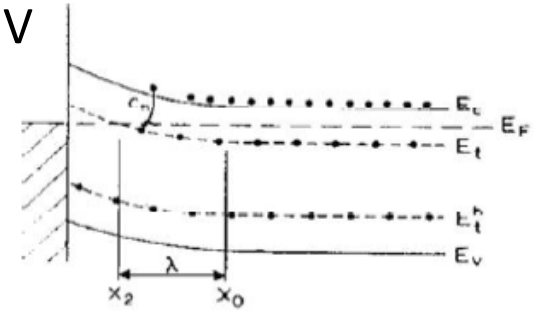
Various samples

p^+-n junction

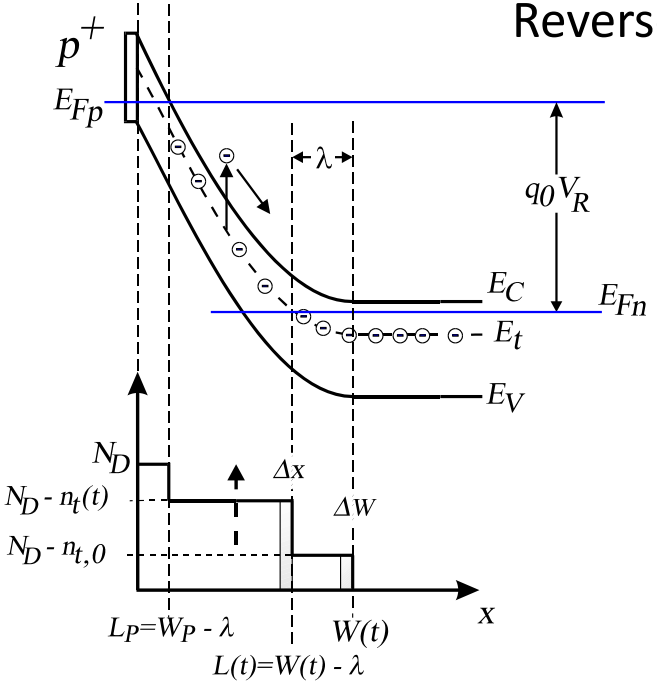
Schottky diode

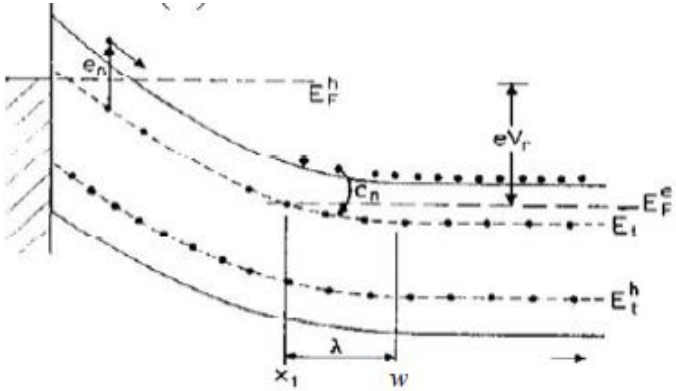
Filing pulse: $V=V_p=0$ V





Reverse bias: $V=V_R$



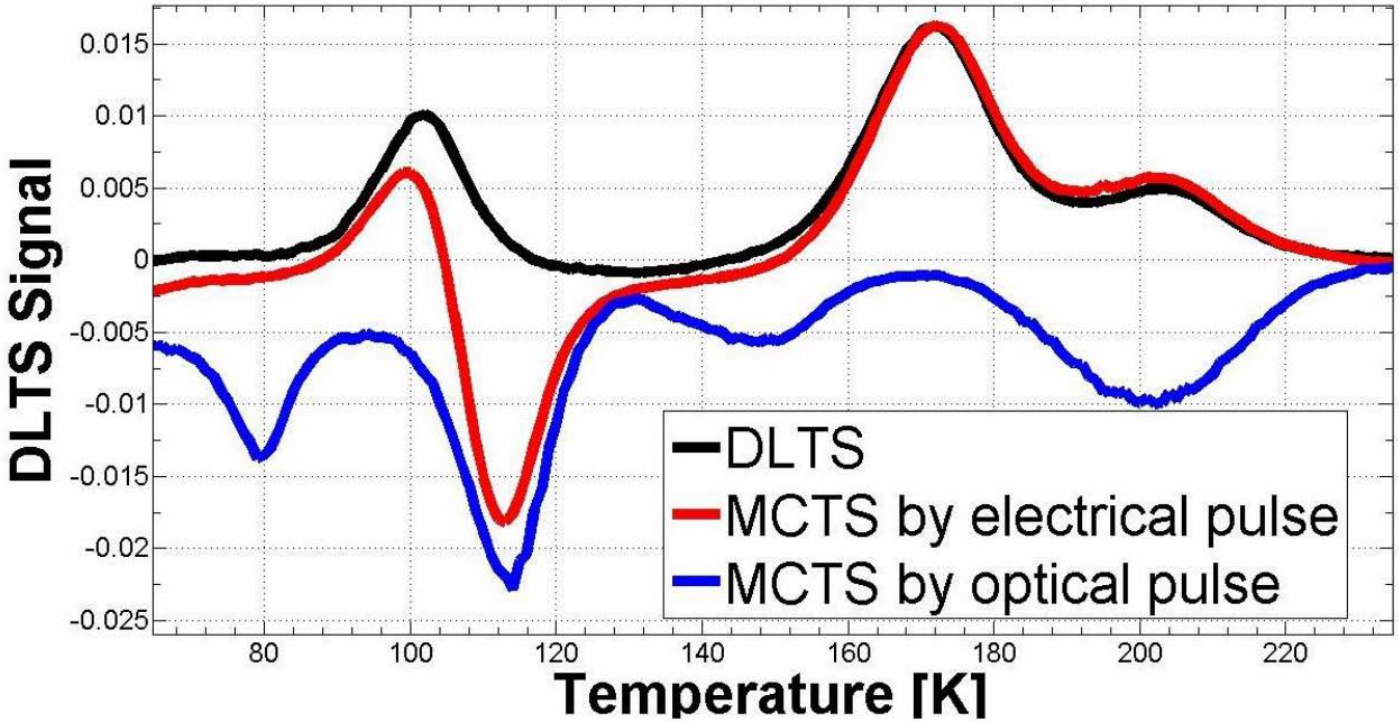


DLTS: standard modes of operation

- DLTS temperature scan
  - Average concentration of traps in investigated volume
  - Only majority carrier traps are seen
  - Forward bias pulses on a Schottky-junction probes interface defects
- Depth Profiling
  - By varying the charging pulse
  - Good for implantation damage profiles
- Capture Cross Section measurements
  - Varies the pulse length to see when signal is saturated

Advanced DLTS methods

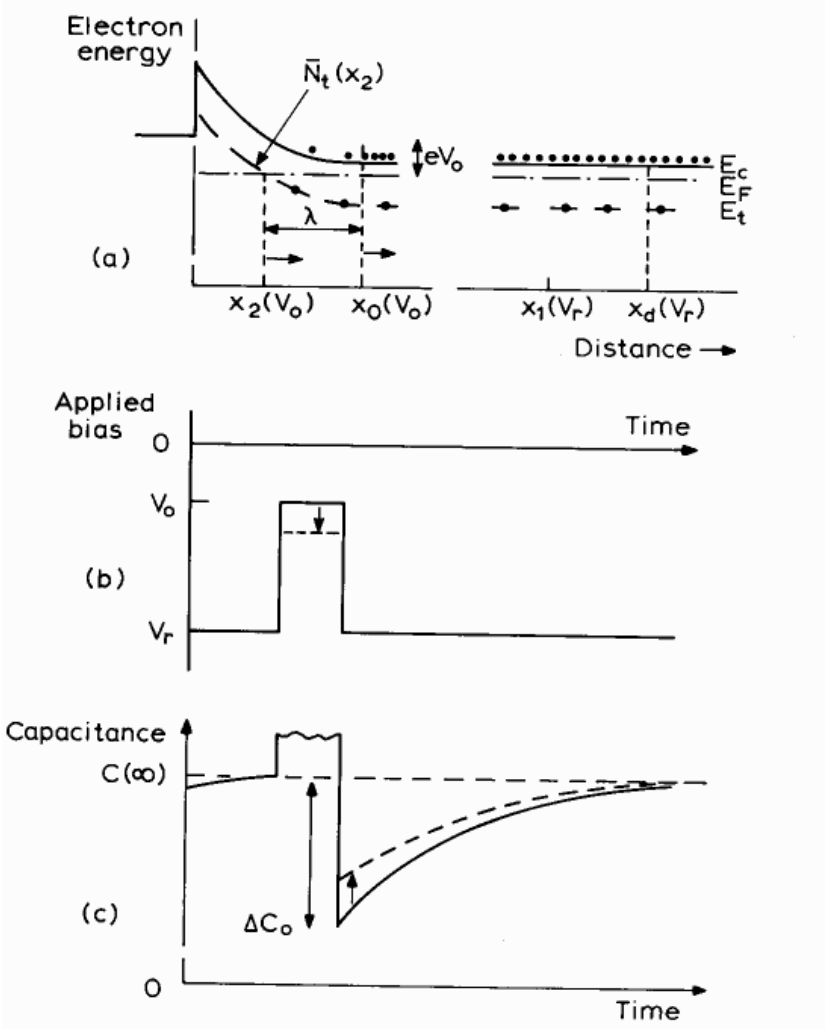
- Minority Carrier Transient Spectroscopy
  - Forward biasing a pn-junction inject minority carriers into depletion region
  - Minority carrier traps will result in peaks with negative amplitude
  - Can also be obtained by optical excitation with $E>E_g$



R. Brunwin, Electronics Letters **15**, 349 (1979)

Advanced DLTS methods

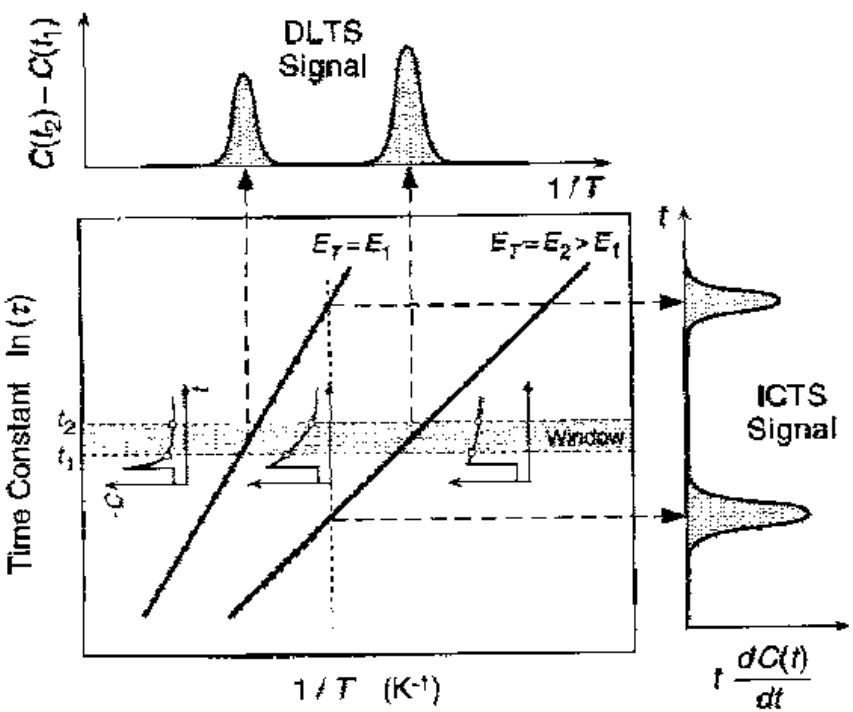
- There are many deep level **depth profiling** techniques. Here the reverse bias is held constant and the magnitude of the filling pulse changed so different regions of the depletion region are sampled.
- Correct calculation of the true profile is far from simple because of the Debye tail (λ region) and changes in the carrier concentration.



V. C. Venezia, et al., Appl. Phys. Lett. 73, 2980 (1998)

Advanced DLTS methods

- Conventional DLTS varies the temperature and produces a peak when the emission rate matches a 'standard' rate (the rate window).
- **ICTS** (isothermal capacitance transient spectroscopy) holds a fixed temperature and sweeps the rate window. This allows much more accurate determination of the sample temperature to be made and is the way high resolution (**Laplace DLTS**) is done.



H. Okushi , et al., Jpn. J. Appl. Phys. **19**, L335 (1980).

L. Dobaczewski, et al., J. Appl. Phys. 7**6**, 194 (1994)

L. Dobaczewski, et al., J. Appl. Phys. **96**, 4689 (2004)

Summary

- DLTS gives possibility to obtain main parameters of a trap:
  - ✓Trap density
  - ✓Carrier capture cross-section
  - ✓Energy level position in bandgap
- Sensitivity is about 10^{-4} N_D;
- Defect profiling possible:
- Higher resolution possible with Laplace DLTS;
- Additional technique used together with DLTS allows studying various properties of traps.

Part II. Samples, measurements, results….

- Sample preparation
- Measurement parameters
- IV & CV measurements
- Measurement setup
- Measurement process
- Data processing and results

Samples

Material: semiconductor slab, moderately doped (10^{13}-10^{16} cm^{-3}), p^+n / (n^+p) diode, MIS capacitor.

Schottky contacts: metal films, ~10 nm thick, deposited on chemically polished semiconductor surface:

Al or Ti for p-type Si

Au for n-type Si

Back ohmic contacts: InGa scratched into mechanically polished back surface or sintered Al film.

Requirements:

- Low series resistance for direct current
- Low leakage current

Measurement parameters

1. Contacts:
   - n-area: Al bus,
   - p-area: back Al contact
2. Isothermal measurements:
   - Measurement of IV curves: -1 V→5 V
   - Measurement of CV curves for pn-diode: -0.3 V→ 5 V
3. Measurements of DLTS spectra:
   1. Majority carrier traps: U_R=2 V U_P=0.01 V
   2. Minority carrier traps: U_R=2 V U_P=-2 V

   Other Parameters:

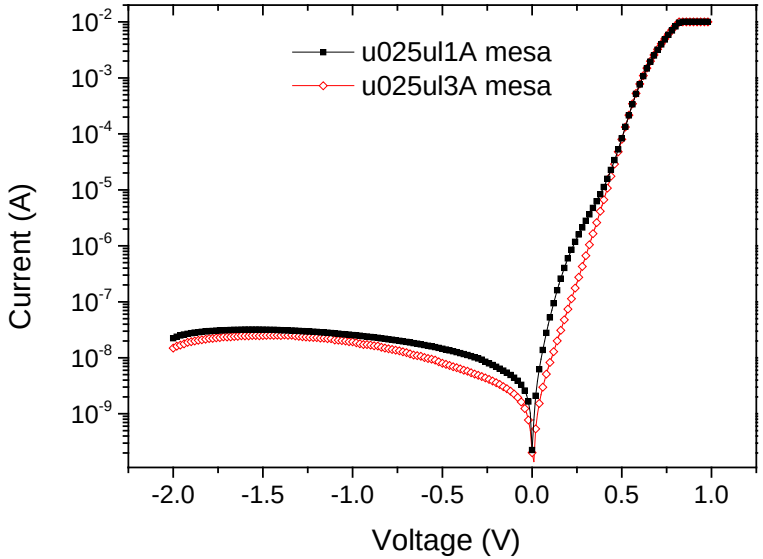
   Temperature scan speed: 8 K/min

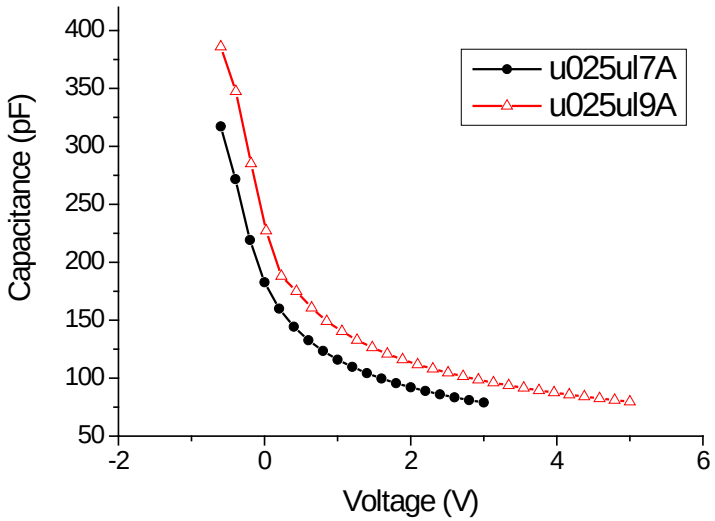
   Temperature scan range: 40-300 K

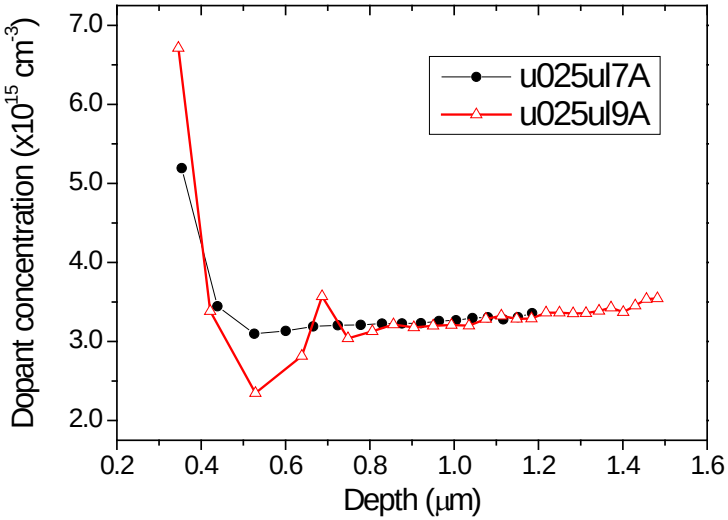
   Sampling times (t_w): 5 ms → 357 ms.

   Pulse durations (t_p): 0.1 ms → 1 ms.

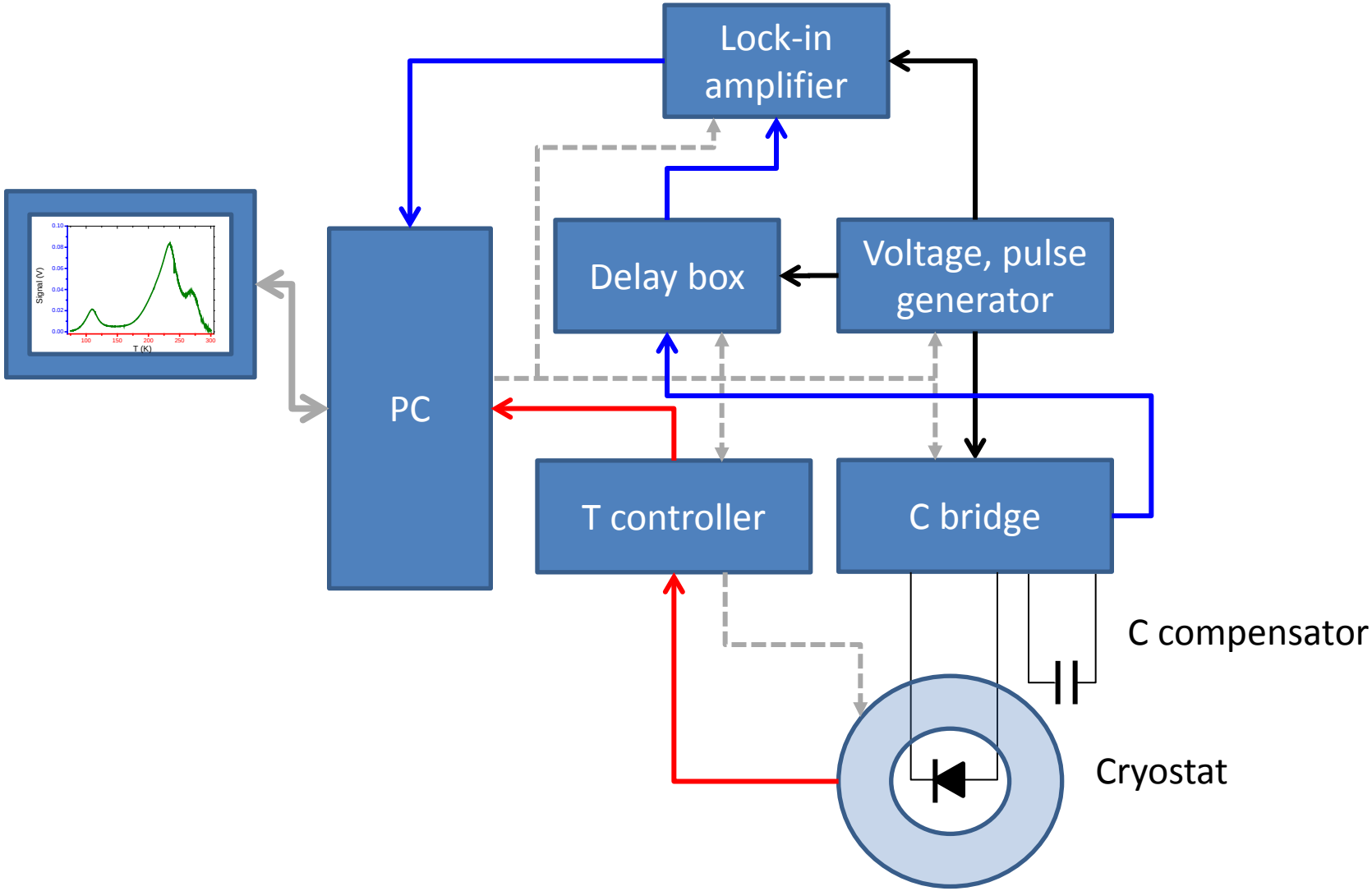
Examples of IV, CV and $N_D(x)$







DLTS setup


Lock-in amplifier
Delay box
Voltage, pulse generator
PC
T controller
C bridge
C compensator
Cryostat
Signal (V)
T (K)

“Lock-in” detection method

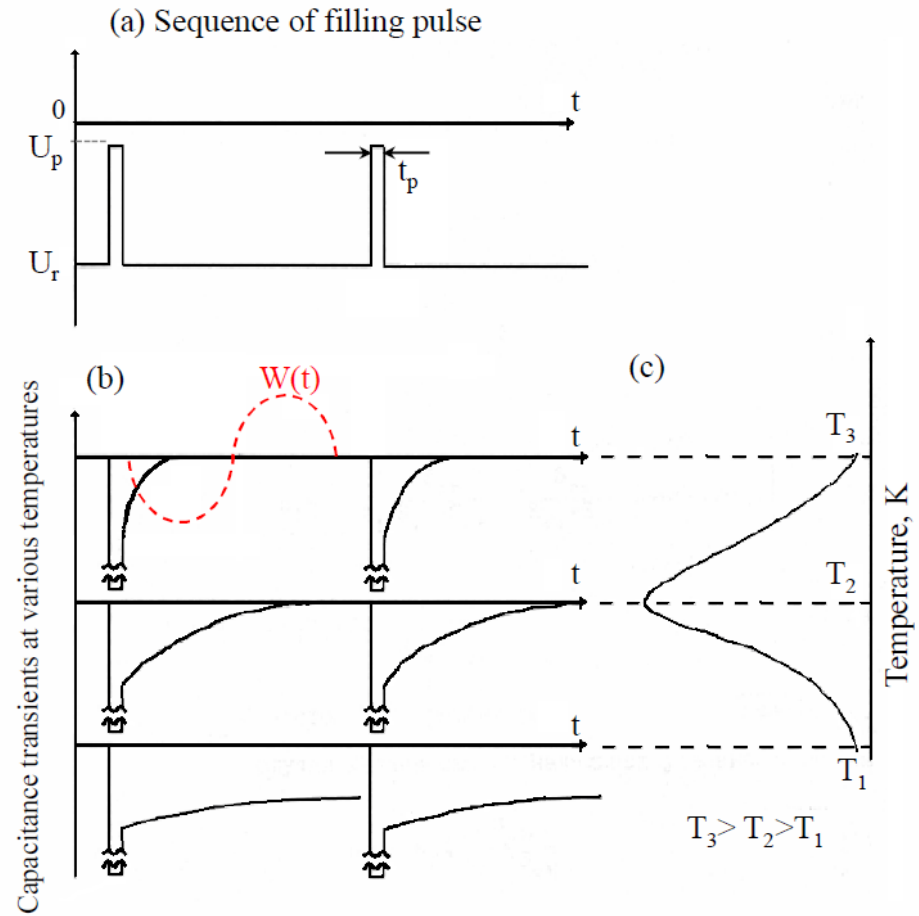
At every particular temperature, lock-in detector multiplies the capacitance transients

$$\Delta C \cdot exp(-e_n t),$$

where ΔC is the relaxation amplitude, with the correlation function $W(t)$ and integrates it over a specified time. In our example the correlation function is *sin*-like function

$$W(t)=sin(2\pi t/T_C)$$

of the period width T_C, which is also called “rate window”;



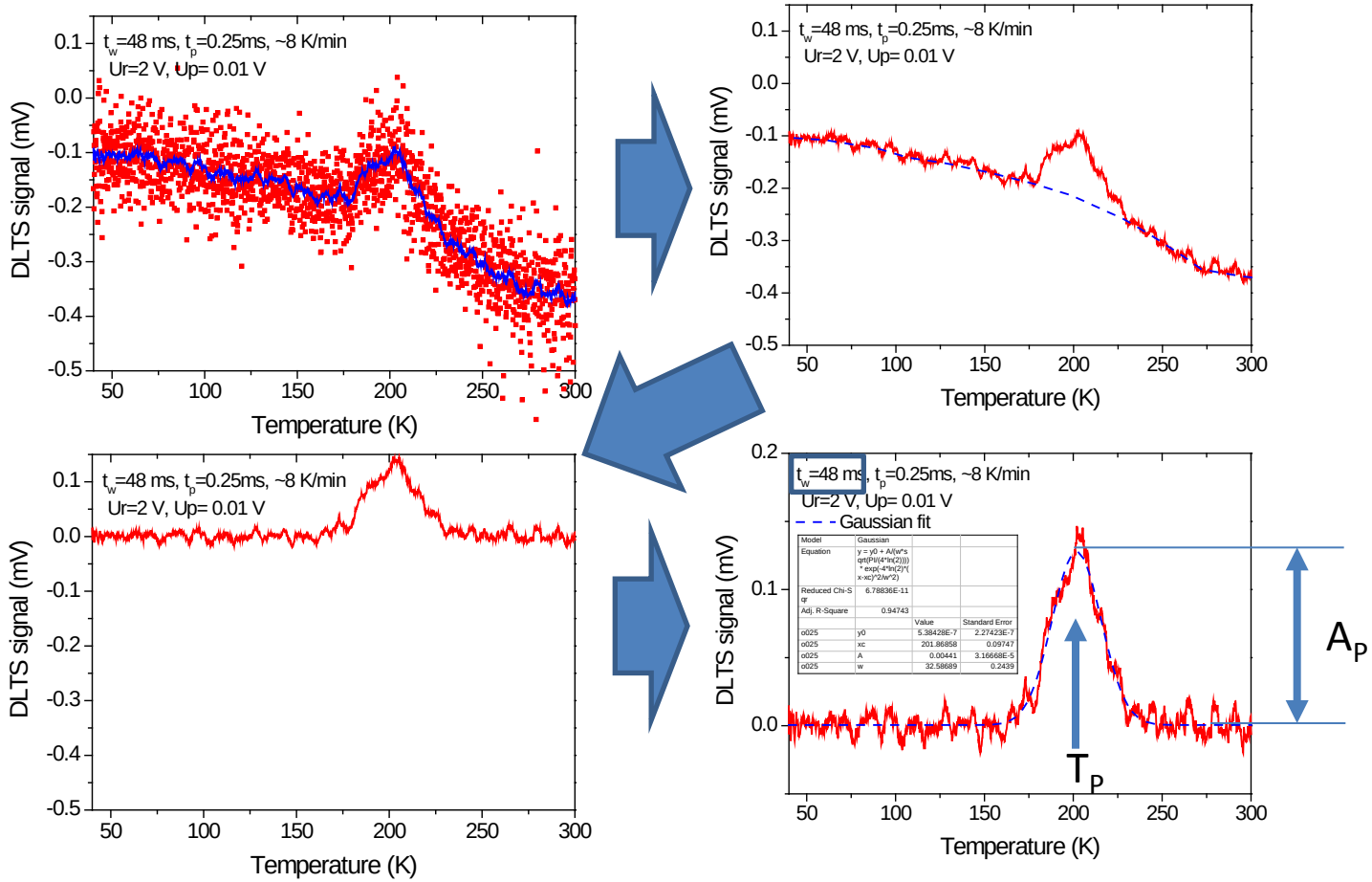
Measurement process

1. Sample preparation
2. Check IV, mount sample in cryostat
3. Measure CV
4. Measurements of DLTS spectra
   a. Measure temperature dependence –spectra
   b. Change measurement parameters
   c. Repeat temperature scan
   d. …
5. Take sample out

Data processing and results

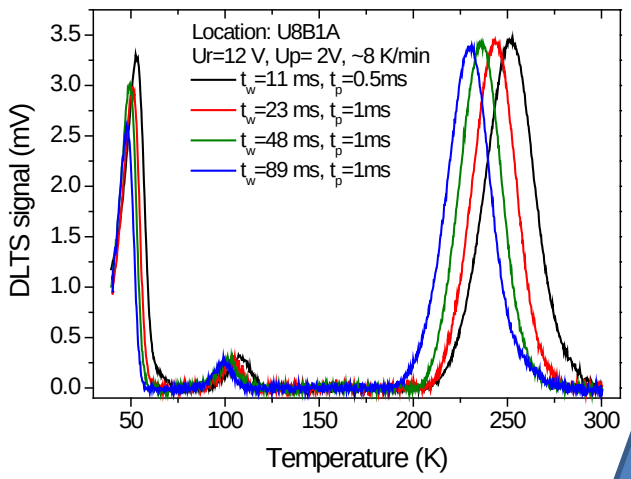
1. Data “filtering”, background subtraction
2. Determination of peak parameters
3. Obtaining Arrhenius plot
4. Fit of Arrhenius plot, calculating trap parameters
5. Calculation of trap concentration
6. Preparation of report

Data processing and results

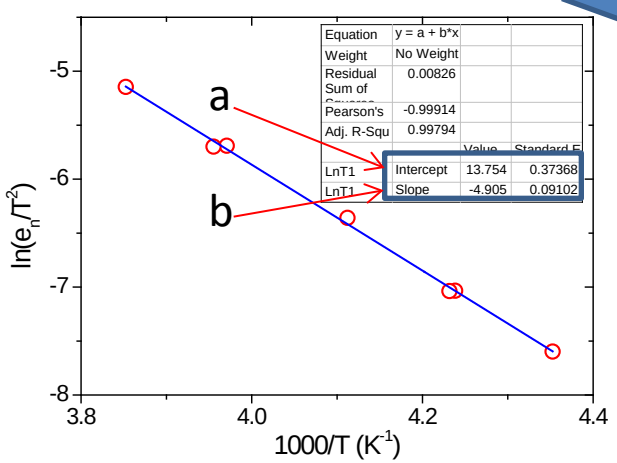


Model	Gaussian		
Equation	y = y0 + A/(w*sqrt(PI/(4*ln(2)))) * exp(-4*ln(2)*(x-xc)^2/w^2)		
Reduced Chi-Sqr	6.78836E-11		
Adj. R-Square	0.94743		
		Value	Standard Error
o025	y0	5.38428E-7	2.27423E-7
o025	xc	201.86858	0.09747
o025	A	0.00441	3.16668E-5
o025	w	32.58689	0.2439

Data processing and results



Tw (ms)	T_P (K)	$1000/T_P$ X	$\ln(e_n/(T_P)^2)$ Y
6	259.5	3.85246	-5.14512
11	251.8	3.97067	-5.69081
11	252.8	3.95518	-5.69863
23	243.1	4.11215	-6.35839
48	235.9	4.23829	-7.03367
48	236.3	4.23169	-7.03679
89	229.7	4.35259	-7.59788



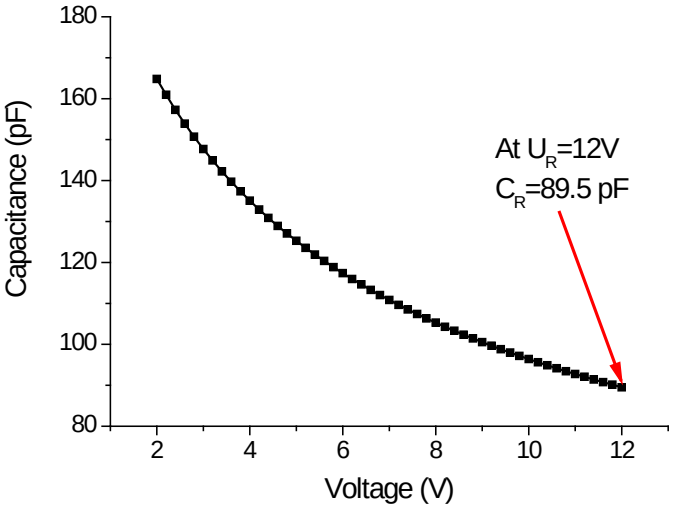
$$\ln\left(e_{n,p}/T^2\right) = \ln\left(\sigma_{n,p}\right) - \frac{E_{a,n,p}}{k_B T}$$

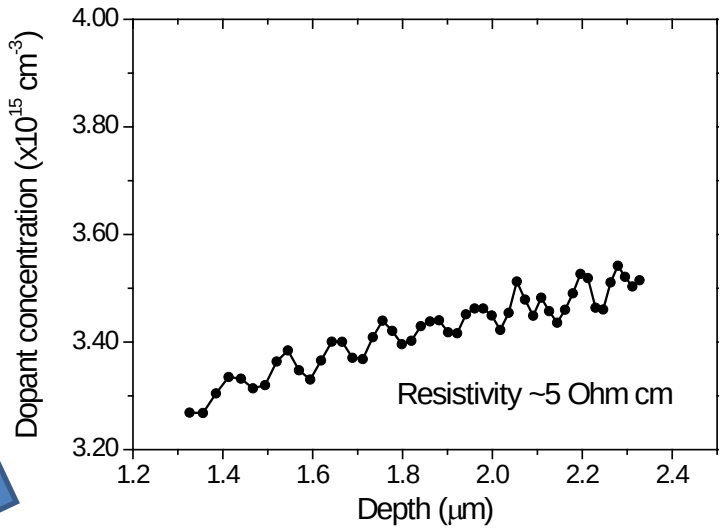
$$y = a + bx,\ x = 1/T$$

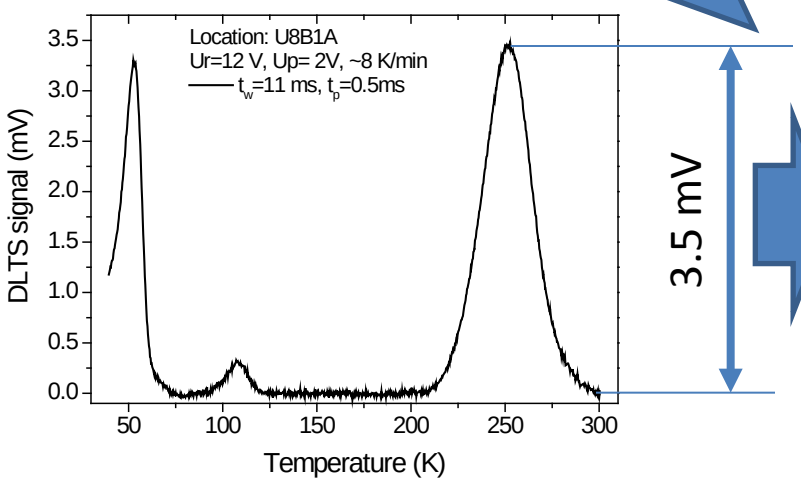
$\sigma_p = \exp(a)/2.1\times10^{22}\ cm^{-2} = 4.5\times10^{22}\ cm^{-17}$

$E_t = b*0.0862\ eV = 0.42\ eV$

Data processing and results







1 mV→0.05 pF; ΔC=0.175 pF

$$N_t = \frac{2\,\Delta C}{C_0} N_D = 1.3\times10^{13}\,cm^{-3}$$

Report: $E_t = E_V + 0.42\ eV$

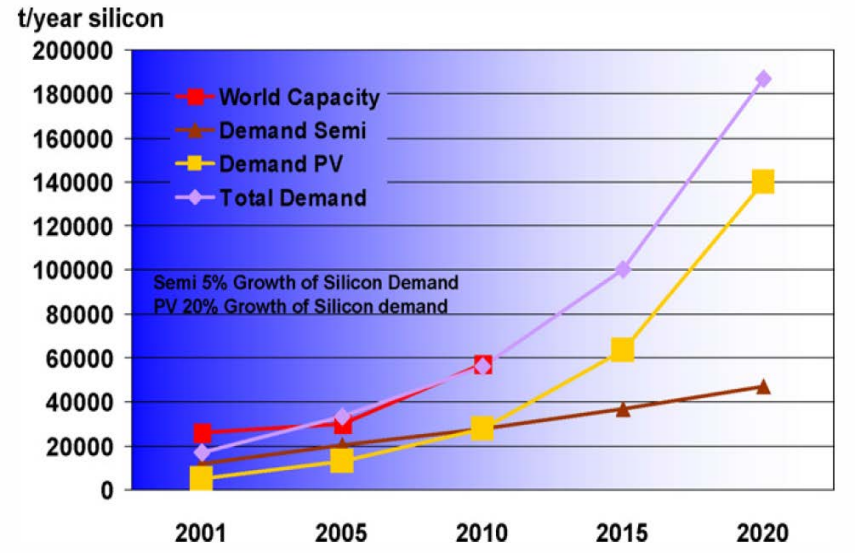
$\sigma_p = 4.5\times10^{17}\ cm^{-2}$

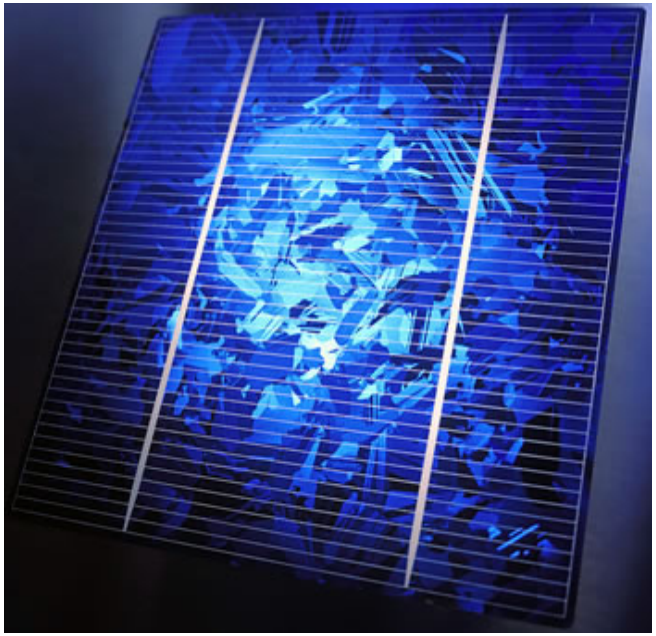
$N_t = 1.3\times10^{13}\,cm^{-3}$

Part III. Practical topics: DLTS for PV-Si.

- Introduction
  - Multi-crystalline silicon (mc-Si) for photovoltaic applications
- Samples & experimental
  - Samples from bulk material
  - Samples from processed material
  - Samples from finished solar cells
- Results of DLTS analyses
  - Crystalline material: near-to-junction defects in solar cells
  - mc-Si: Capability and specific for measurement of GBs
  - mc-Si: distribution of iron near walls of mc-Si ingot
- Summary

Si for photovoltaic applications



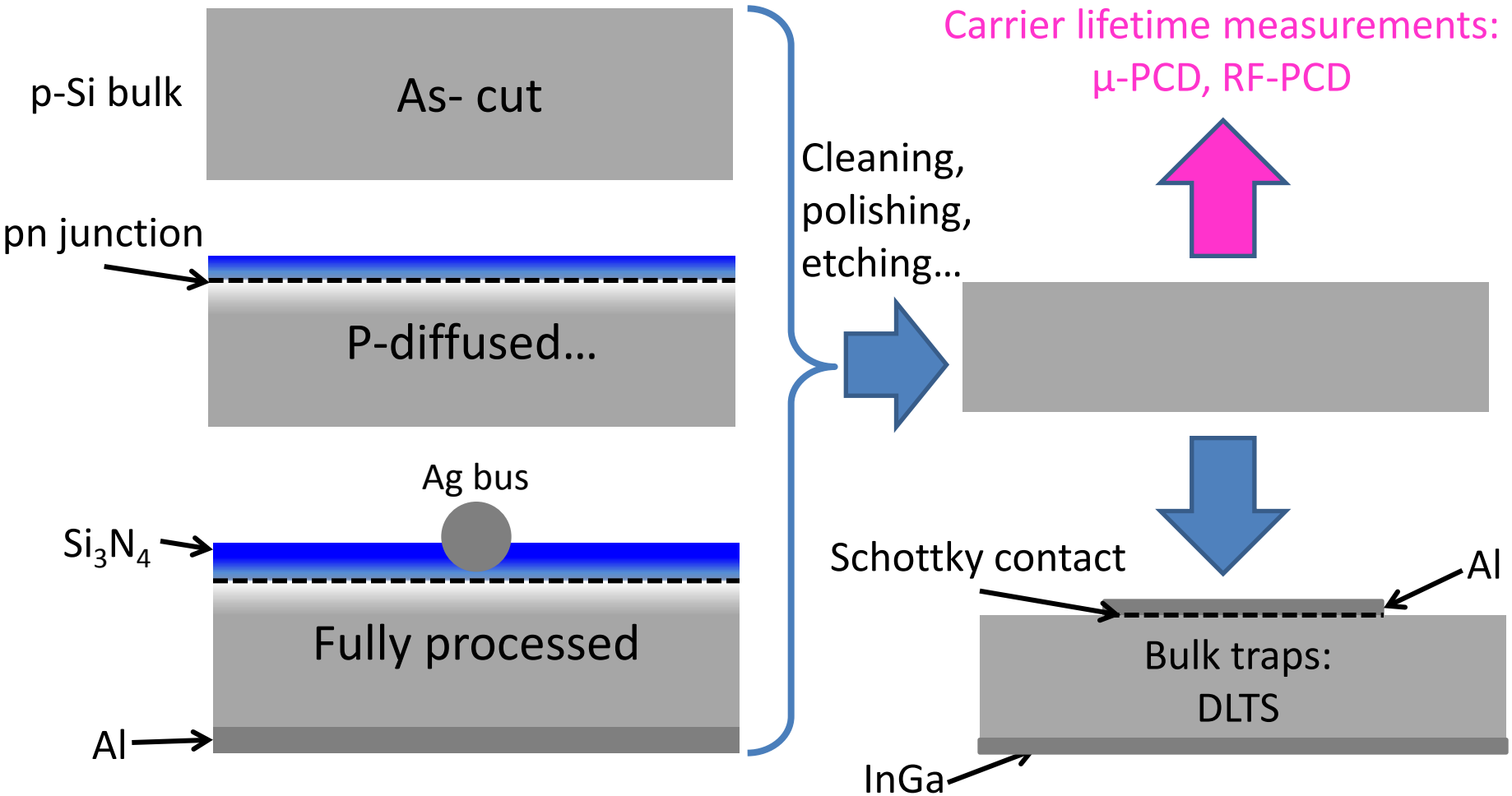


Future global solar silicon demand (in tonnes).

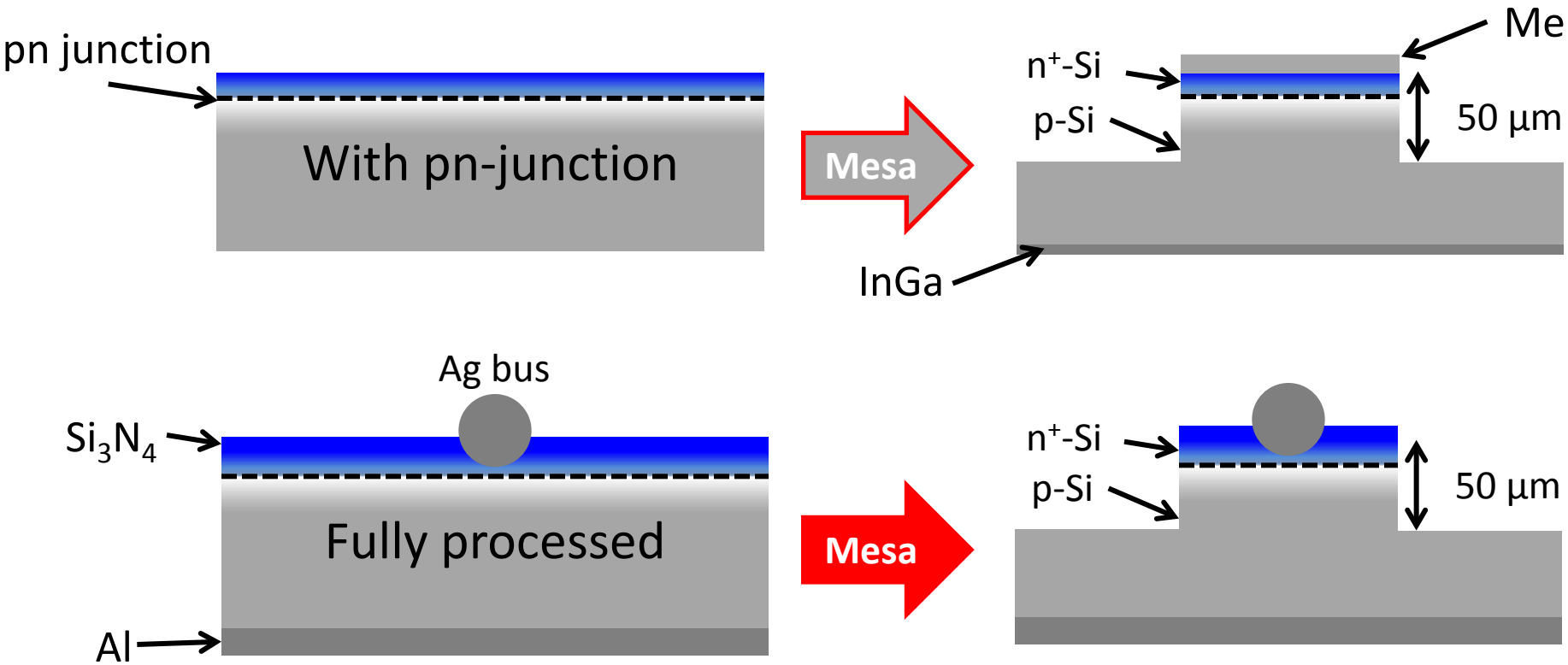
Müller et al., Mat. Sci. Eng B **134**, 257 (2006)

Lifetime and DLTS for PV-materials

- "Traditional" approach:



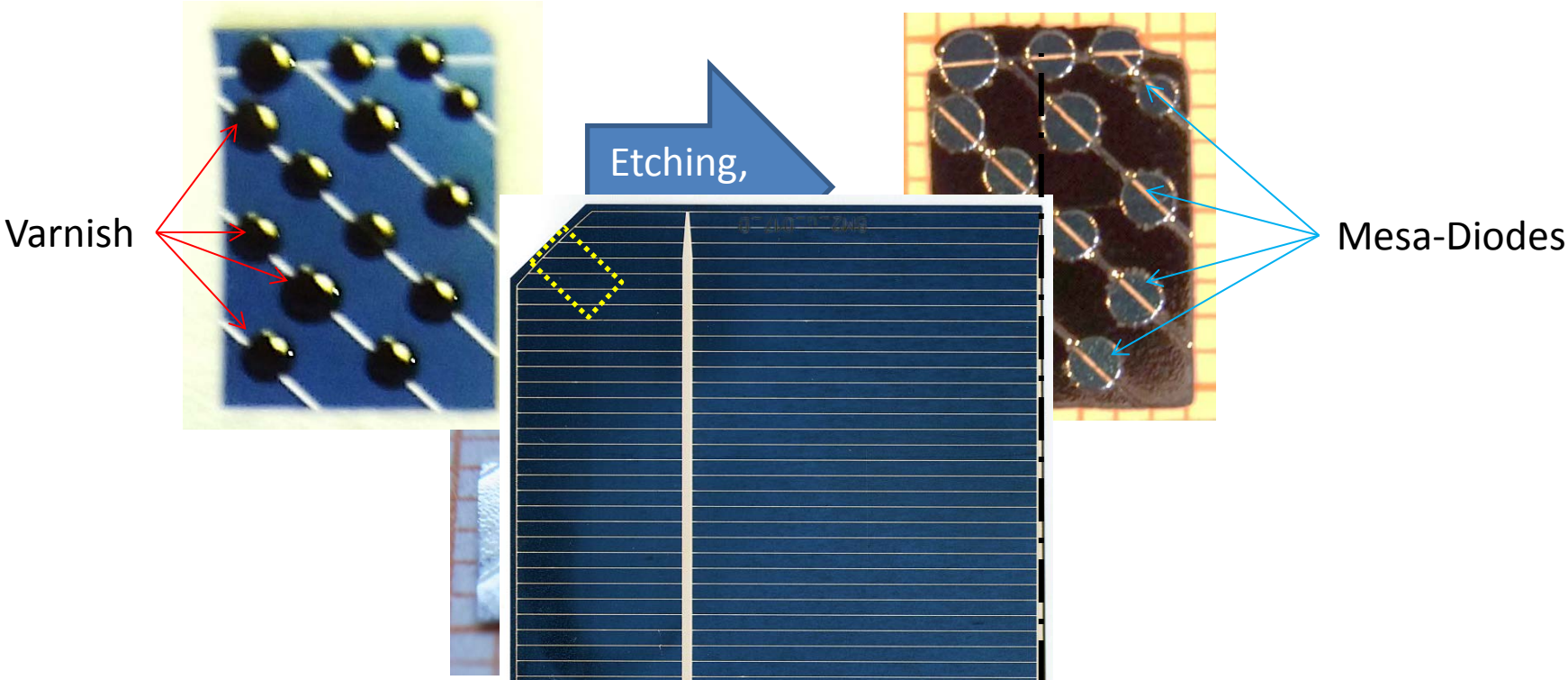
DLTS for PV-materials: smart approach



DLTS: Detection of traps in near-to-junction volume (NJV)

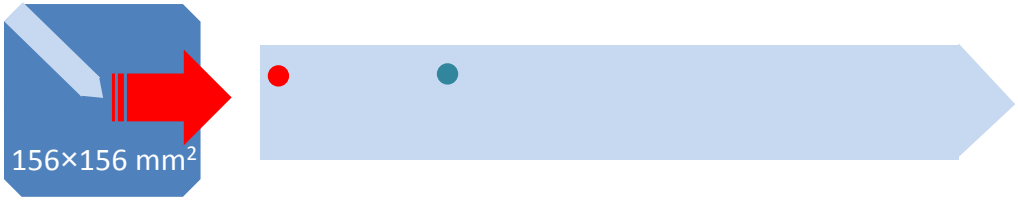
T. Mchedlidze, et al., Appl. Phys. Lett. **103**, 013901 (2013)

Mesa diodes on solar cells

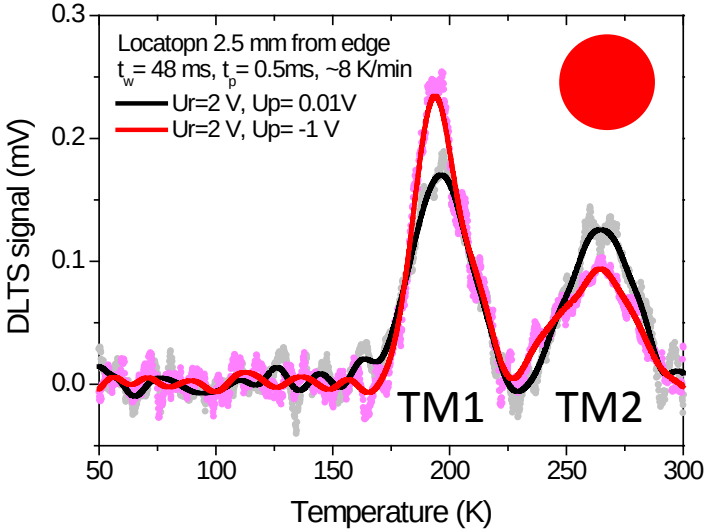


- Possibility to choose [illegible] ven shape of a diode;
- All operations are performed at RT, even no hydrogen introduced;
- Volume of/near the pn-junction of a cell is investigated;
- Majority and minority carrier traps could be detected;
- High quality diodes – nice DLTS signals.

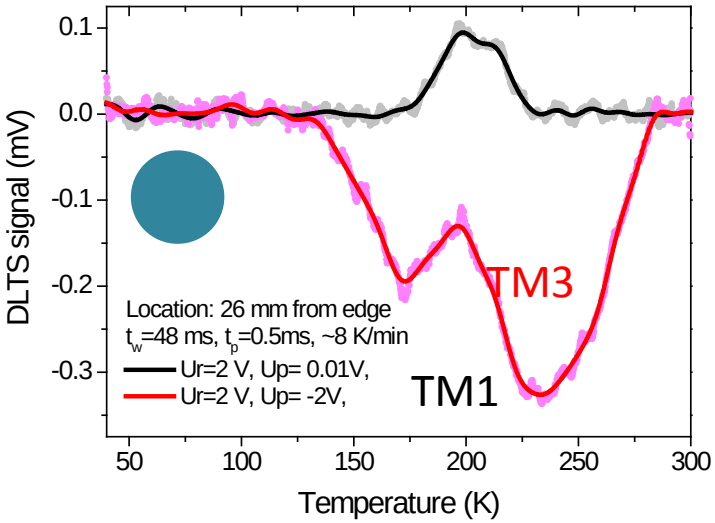
Traps in the mesa-diodes



Majority carrier traps

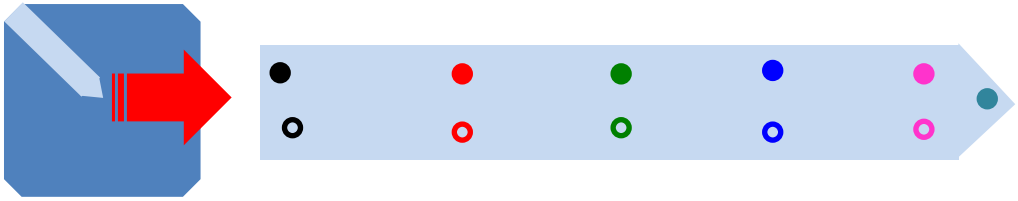


Minority carrier traps

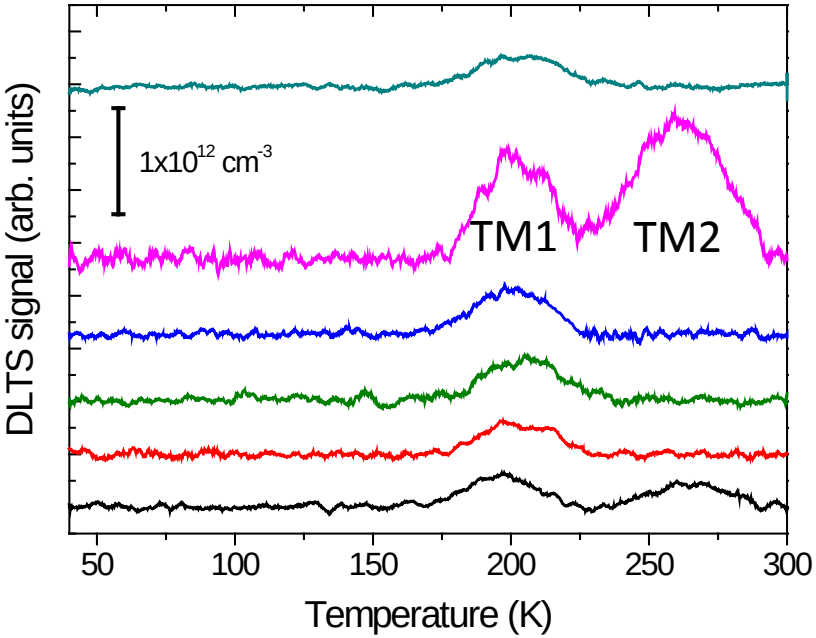


- Deep majority carrier traps, labeled TM1 and TM2 and a minority trap, labeled TM3 were detected in the volume of pn-junction.

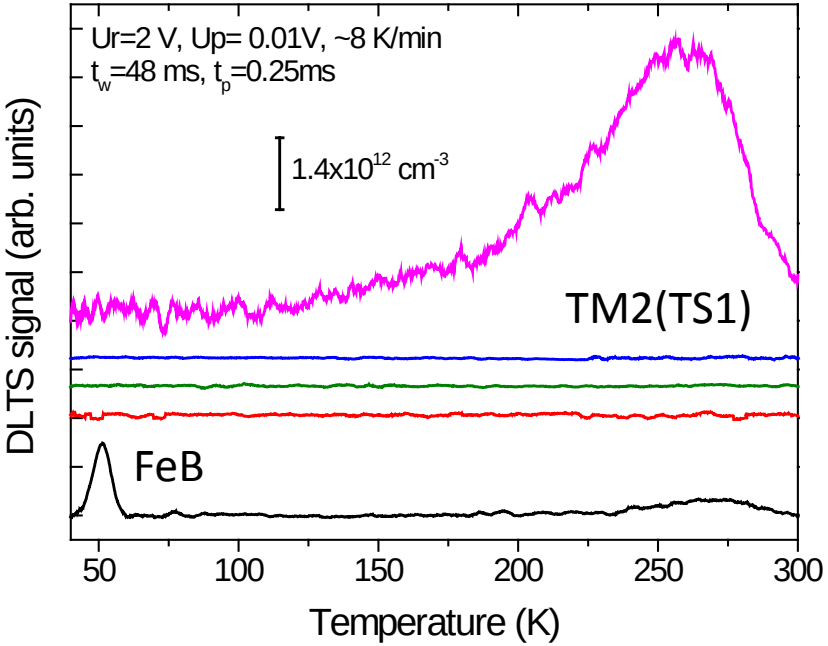
Distribution of the traps



Mesa-pn-junctions

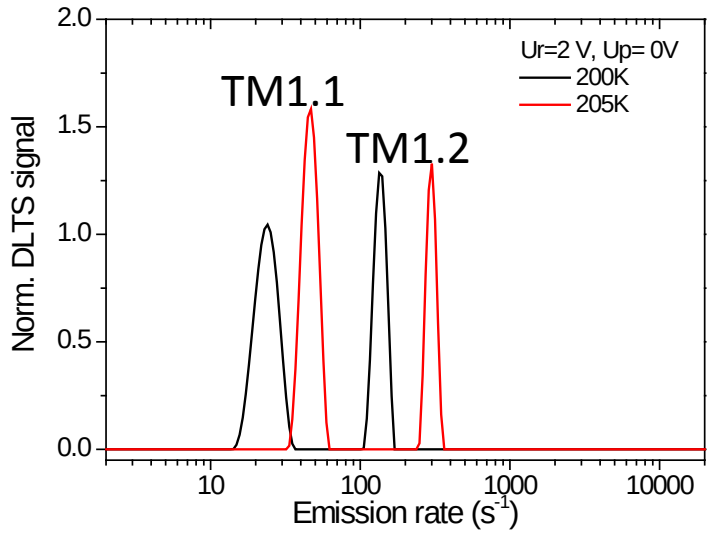


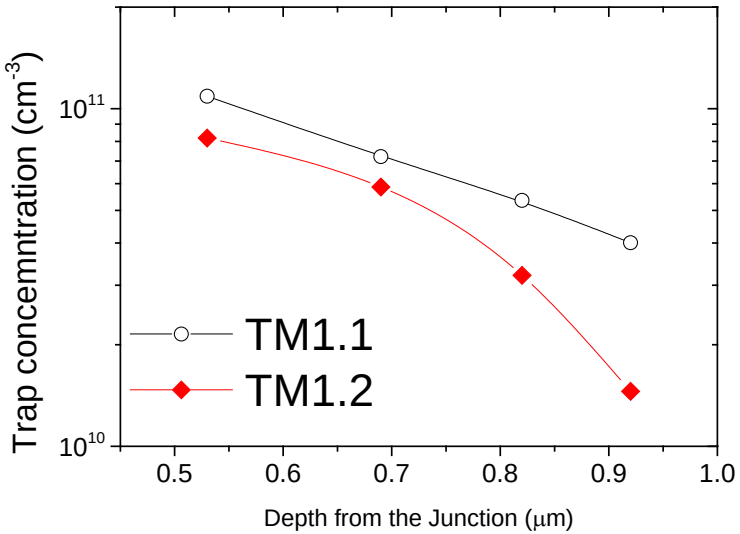
Schottky diodes

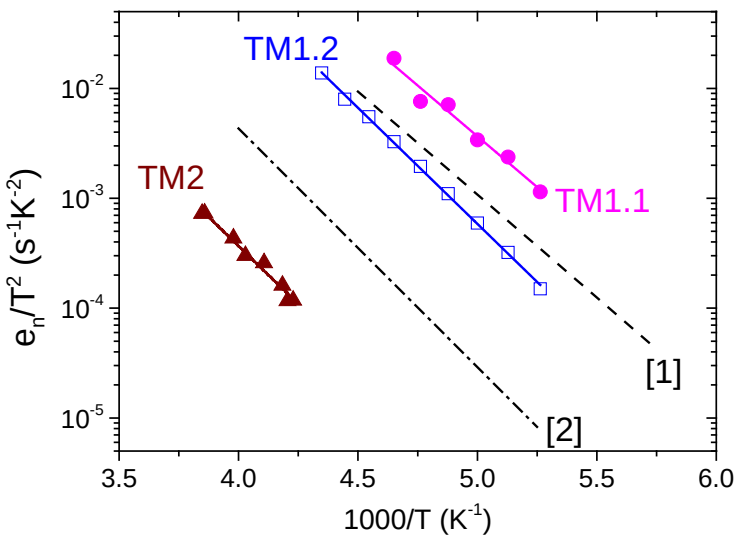


- TM1 signal: only in the mesa-diodes, for all measured locations;
- Other signals: in the both type of diodes, only for several locations.

Trap analyses (LDLTS)





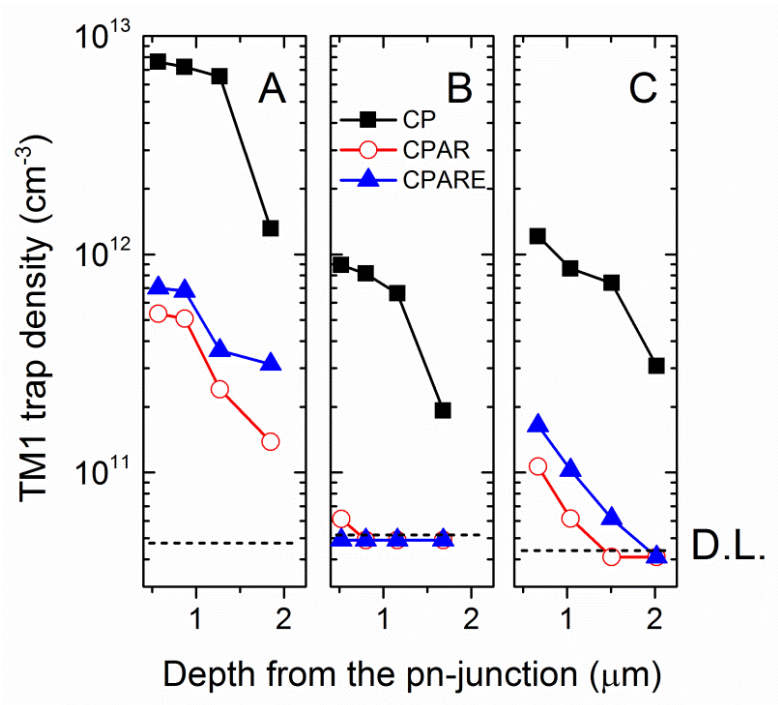


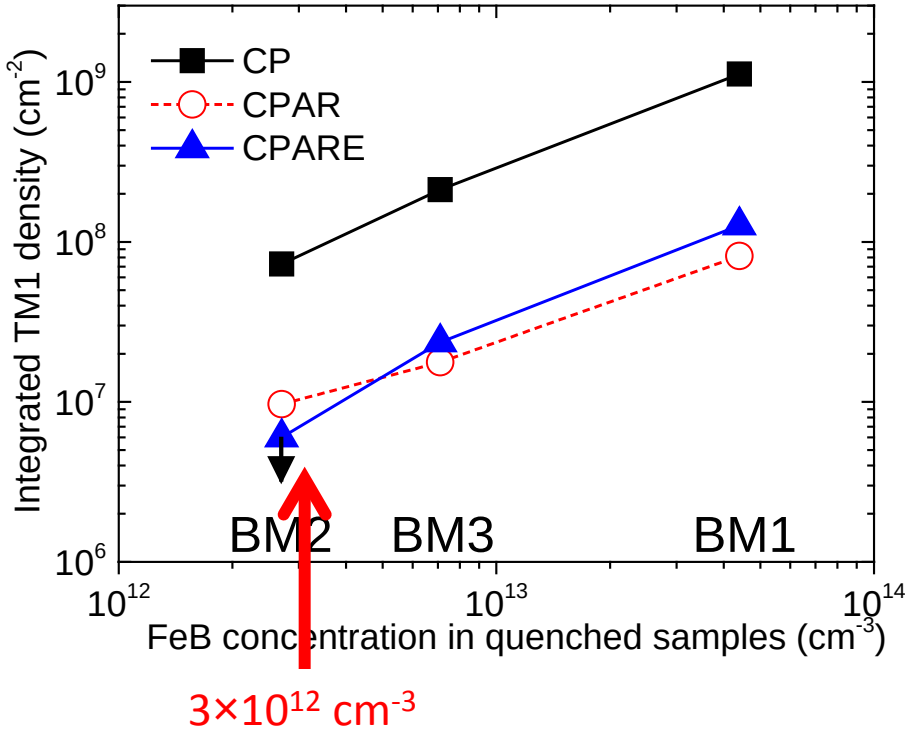
- TM1.1 & TM1.2 signals originate from point-like defects, no el.-field dependence detected;
- TM1.2 well match properties of Fe_i [1,2];
- TM1.1 may originate from FeV or FeVP [3, 4].

[1] P. Kaminski, et al.,Jpn. J. Appl. Phys. **42**, 5415 (2003).
[2] T. Sadoh, et al., J. Appl. Phys. **82**, 3828 (1997).
[3] D. Abdelbarey, et al., J. Appl. Phys. **108**, 043519 (2010).
[4] T. Mchedlidze, et al., J. Phys.: Cond. Mat. **16**, L79 (2004).

T. Mchedlidze, et al., Appl. Phys. Lett. **103**, 013901 (2013)

Profile integration for NJV traps





- Profiles fitted with distribution function and integrated → trap density per area (I_{TM1});

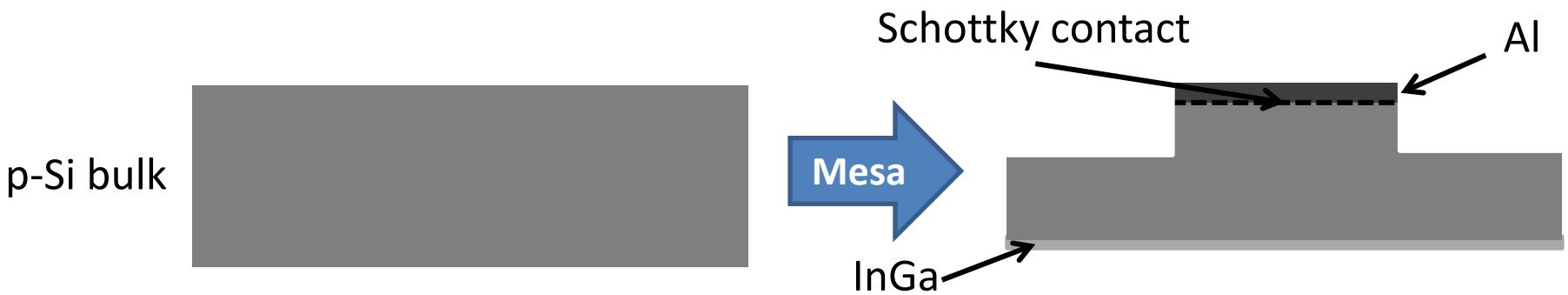
- $I_{TM1} \sim C_{Fe}(Tot)$
- Fe concentration which is tolerable for the applied PV-process in Cz-Si crystal is $C_{Fe} \leq 3\times10^{12}$ cm^{-3}.

Mchedlidze et al., Phys. Stat. Sol (b) 25, 1608 (2014)

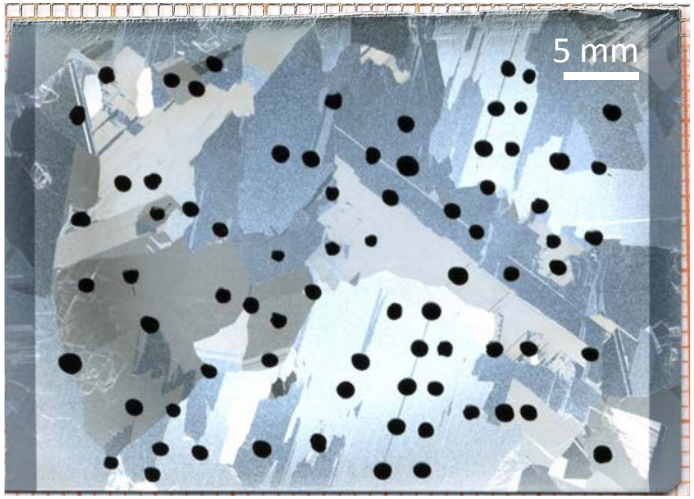
DLTS for mc-Si PV-materials: local analyses

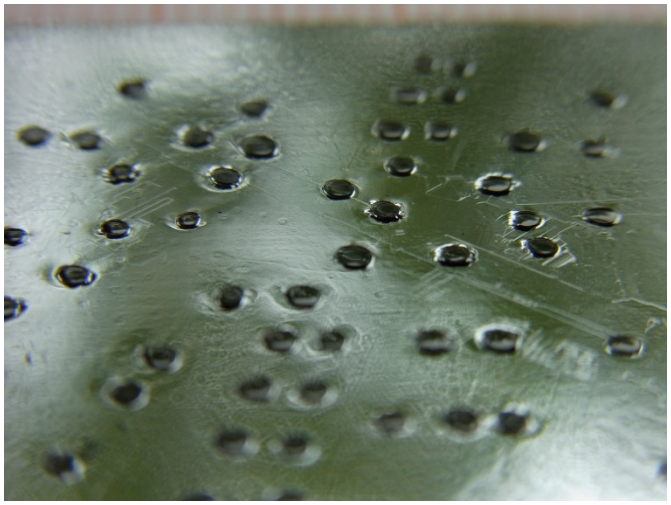
On the capability of deep level transient spectroscopy for characterizing multicrystalline silicon

T. Mchedlidze et al., J. Appl. Phys. **115**, 012006 (2014)



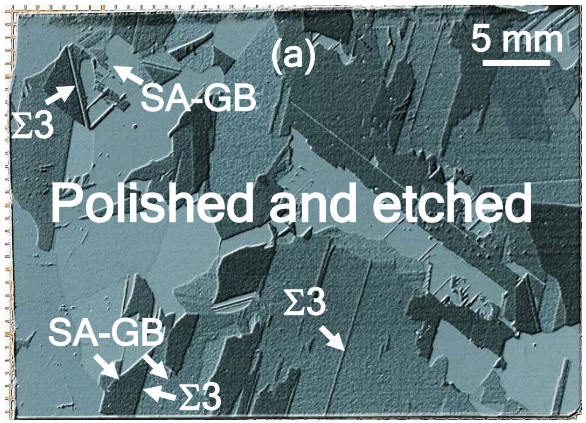
Mesa diodes on bulk mc-Si

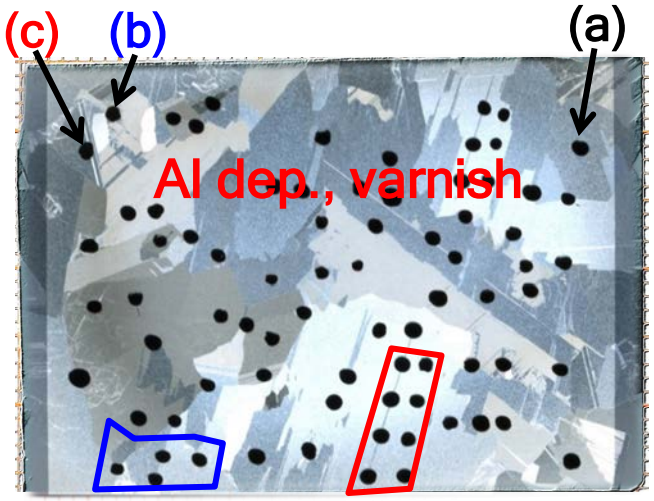




- Possibility to choose a location of interest and even shape of a diode;
- Smaller leakage currents due to mesa-structure…

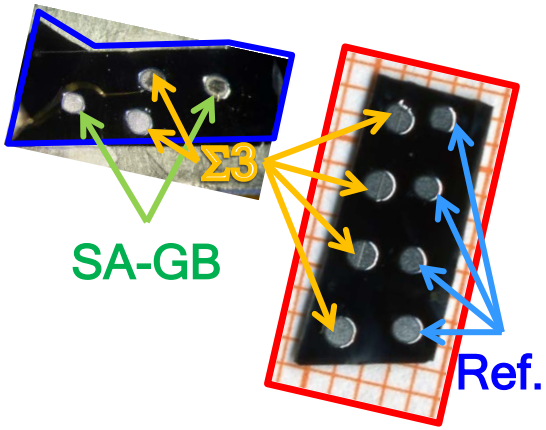
Locations for measurements



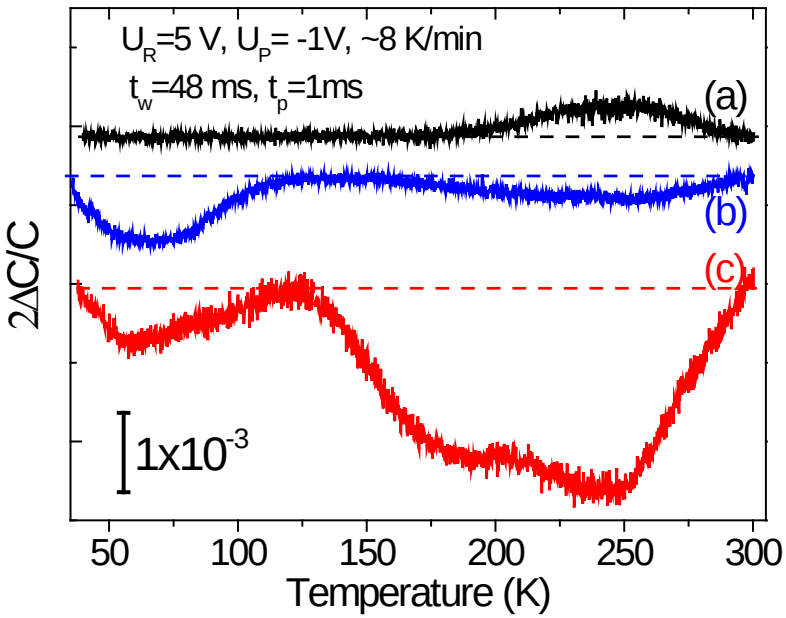


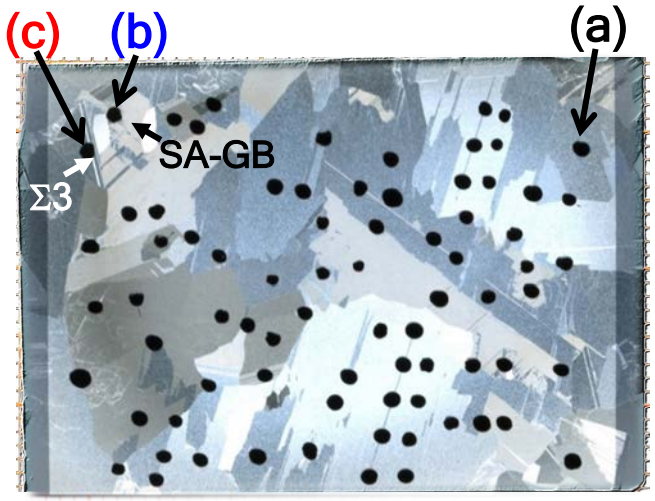
Investigated locations:

- reference locations (no GB);
- with various GB type;
- with various lifetime.



Spectra from “clean” locations

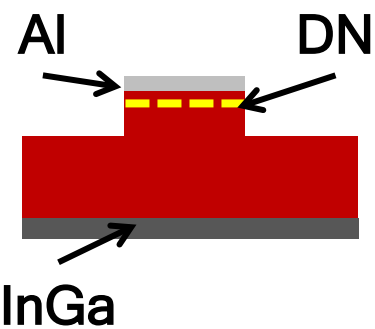




- The signals in (b) and (c) have negative sign and are similar to reported in [1].
- Except sign, (b) and (c) look similar to signals from dislocations or from oxide precipitates;
- The signal in (a) corresponds to those from oxide precipitates;
- *Supposition:* extended defects close to GBs exchange carriers with neighbor GB after finish of filling pulse.

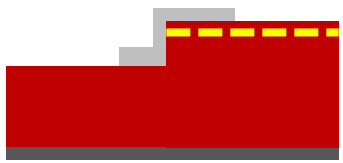
[1] J. Chen et al., ECS Trans. 33, 71 (2011).

Experiments with dislocation networks



(d)

DN parallel to Schottky inside SCR

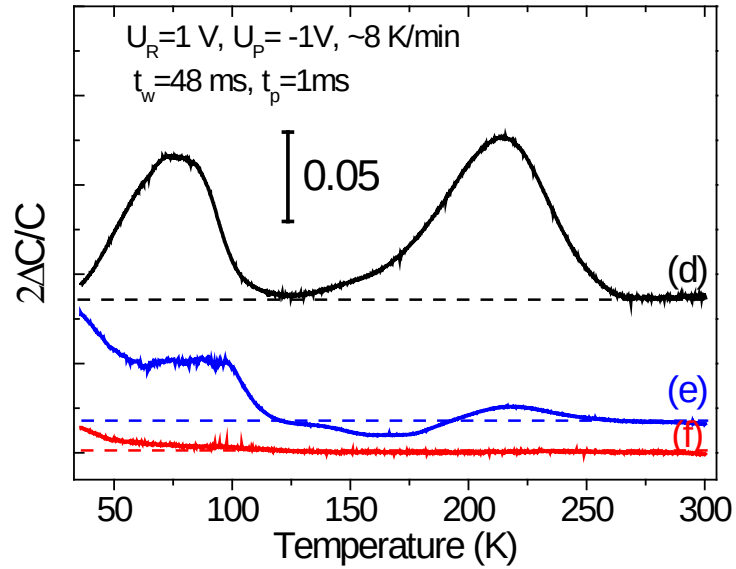


(e)

DN inclined into Schottky

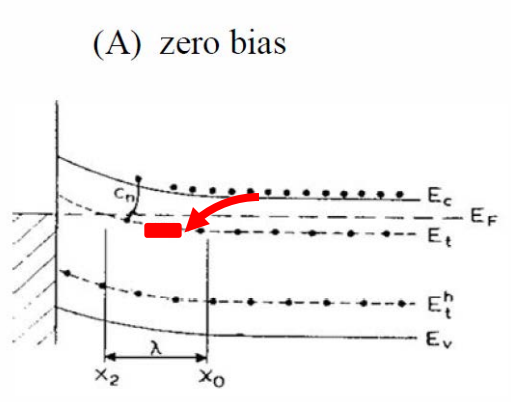
(f)

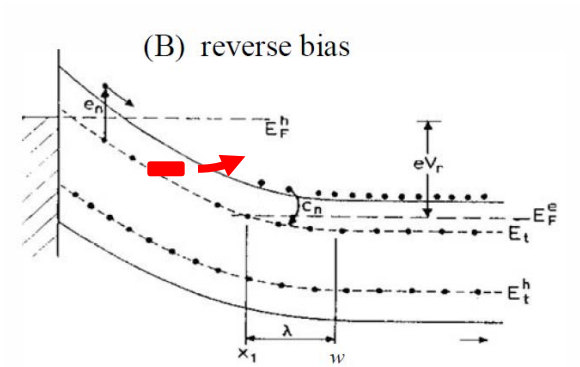
DN "perpendicular" to Schottky

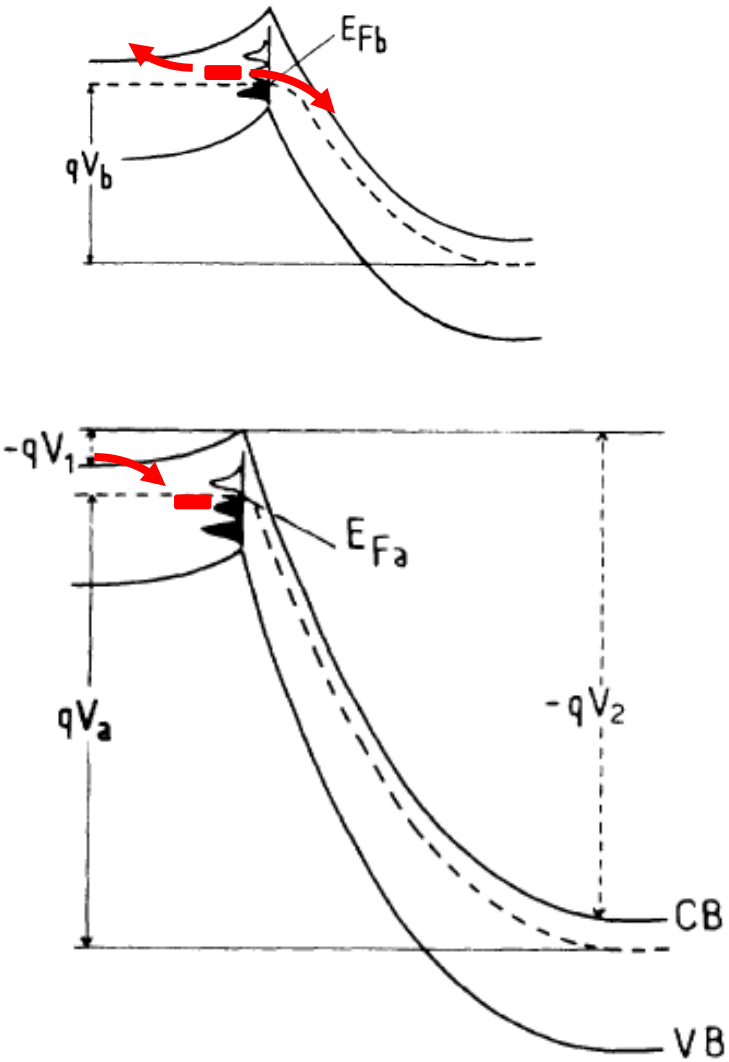


- The spectra obtained in the mesa-configuration (d) coincides to those reported previously for DN with similar structure;
- For the configuration (e) the signal associated with DN is much weaker and distorted.
- For (f) nothing was left from the DN spectrum from (d).

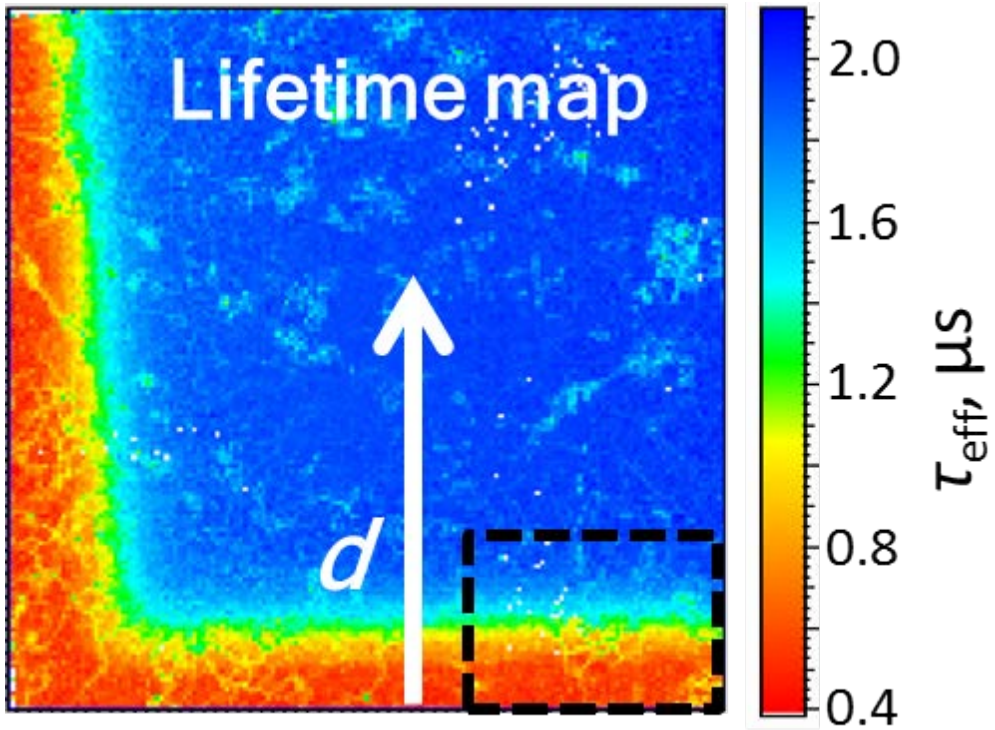
Why negative signals?

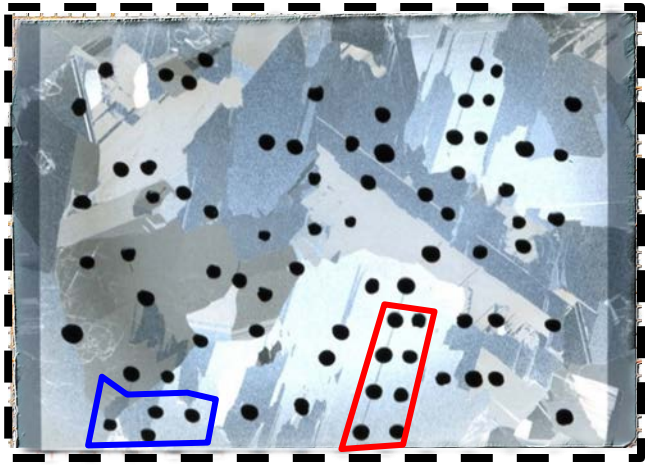


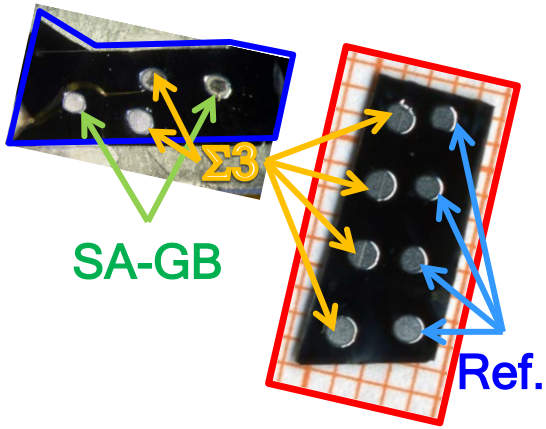




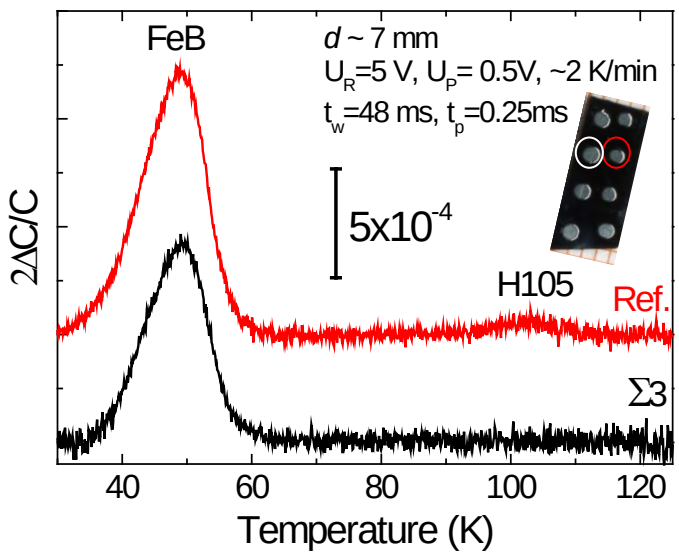
Lifetime vs. DLTS

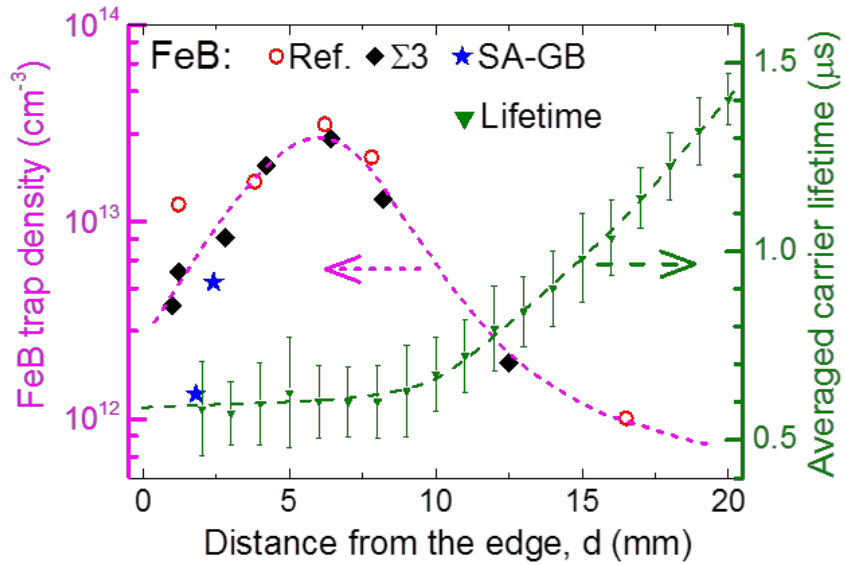






Lifetime vs. DLTS





- A peak related to FeB traps and a weak peak at ~105 K (H105) were detected;
- Strong, nonmonotonic dependence of the FeB trap density from the distance, *d* from the edge of the wafer;
- From *d* > 20mm, FeB under the detection limits;
- FeB trap density: $I(FeB)_{Ref.} > I(FeB)_{\Sigma 3} > > I(FeB)_{SA\text{-}GB}$.
- The H105 - only at Ref. locations. The peak intensity was ~ 0.1-0.15 of $I(FeB)_{Ref.}$ and showed the same dependence from *d*.

Summary

- DLTS is sensitive and qualitative measurement method for electrical characterization of “one-dimensional” carrier traps in semiconductors.
- DLTS can be used for systems where capacitance could be built by application of proper voltage (pn-junctions, Schottly-diodes, MIS capacitors, etc.).
- A sensitivity limit of DLTS could be roughly estimated as a value, four orders of magnitude below the doping level of the bulk material.
- For investigation of extended defects (GB, dislocations, precipitates, etc.) DLTS could be applied only after proper configuration of the electric field in the sample. And even after that, the method is not capable of giving precise qualitative results for such defects.
- Proper preparation of samples, i.e. application of mesa-diodes, opens possibilities for analyses of near to pn-junction volume of solar cells and spatially resolved analyses of mc-Si samples.