Creation and annealing of point defects in germanium crystal lattices by subthreshold energy events

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University of Sevilla 2013

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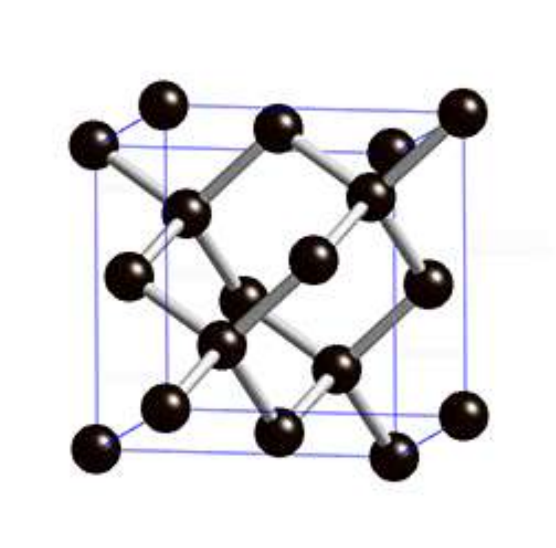
Outline

- Why study this? Low energy? Really?
- Germanium – ultrapure material
- Hydrogen in germanium
- DLTS – Deep Level Transient Spectroscopy
- An experiment: ICP annealing of E-center

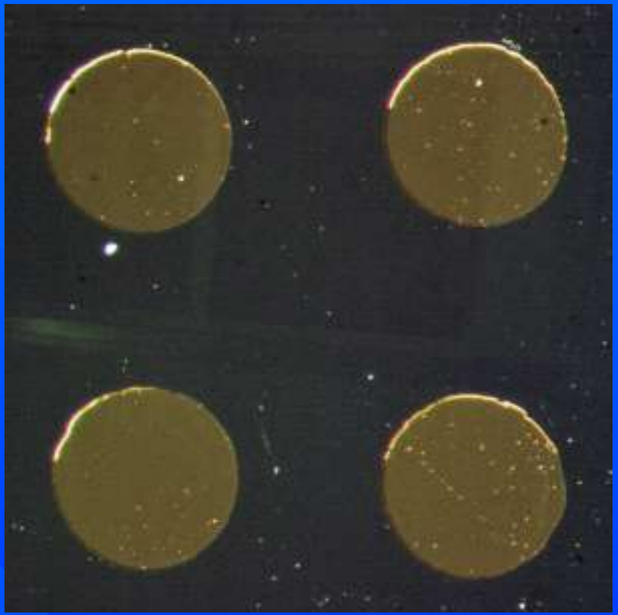
- Summary and conclusions

Why low energy?



- Why study this? Low energy? Really?
- Impacts generate Moving Intrinsic Localized Modes (ILMs) or Discrete Breathers (DBs) in Ge
- ILMs in Ge – Defect annealing 2600 nm deep
- Very efficient process – Technology applications
- Transferable to other systems

Germanium

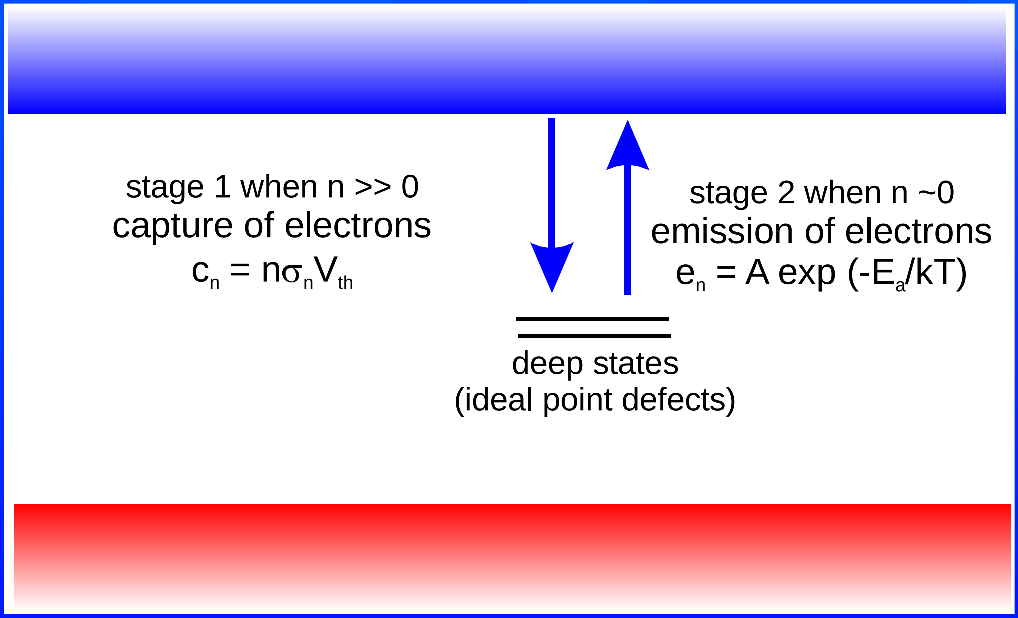


- Niche applications: Opto-electronics
- Purdue – Ultra pure Ge

  Low impurities
- Ohmic contact – easy (Au-Sb)
- Au SBD's
  - Resistive evaporation – No defects introduced
  - good current – voltage characteristics

Electrical Characterization of Defects

- Classic DLTS measurements use majority carrier capture and emission process to obtain a “fingerprint” of the defect.
- By monitoring the change of emission rate with temperature an activation energy is obtained.
- By observing the capture rate a cross section can be obtained.



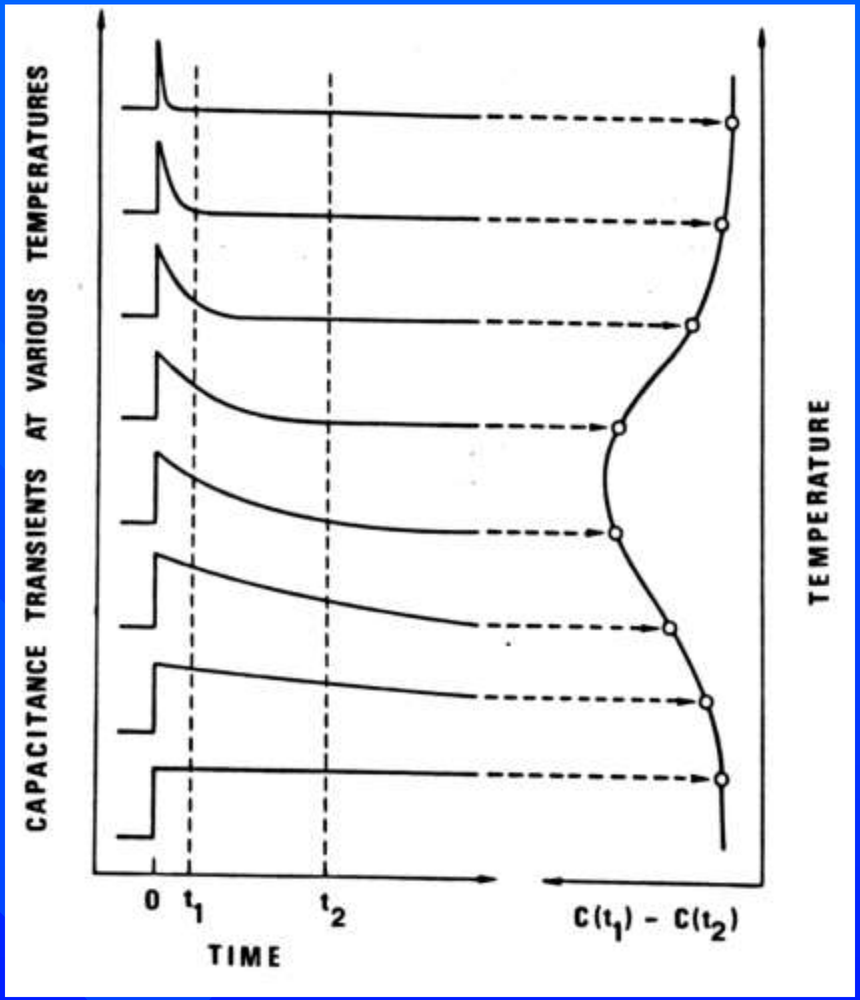
The DLTS Spectrum[1]

- Monitor transient as function of temperature, *T*
- Plot $S = C(t_1) - C(t_2)$ vs T

  ⇒ DLTS *peak*
- More than one level

  ⇒ DLTS *spectrum*
- At the maximum of a peak:

$$e_{max} = \frac{\ln(t_1 - t_2)}{t_1 - t_2}$$



- Typical rates: 0.1 - 1000 /s

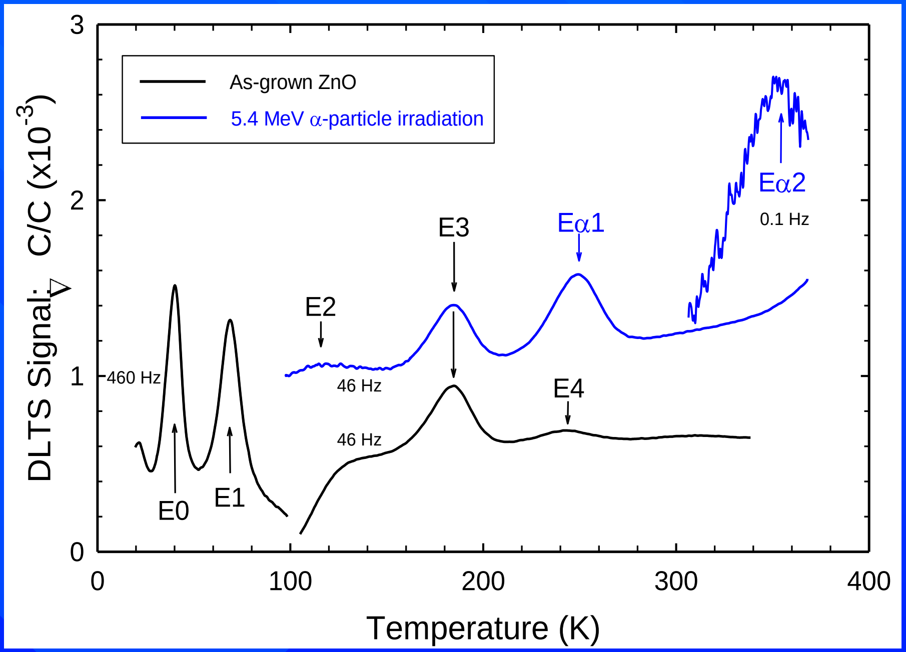
[1] D. V. Lang, JAP **45**, 2023 (1974) or Schroder, "Semiconductor Material and Device Characterization"

Deep Level Transient Spectroscopy

- DLTS requires a depletion (space charge) region
  - p-n, metal-semiconductor, MOS, …..
- Apply zero / forward bias – reverse bias pulse sequence
  - Monitor *C-t*, *I-t, …* as function of *T.*
  - Transient behaviour indicates the

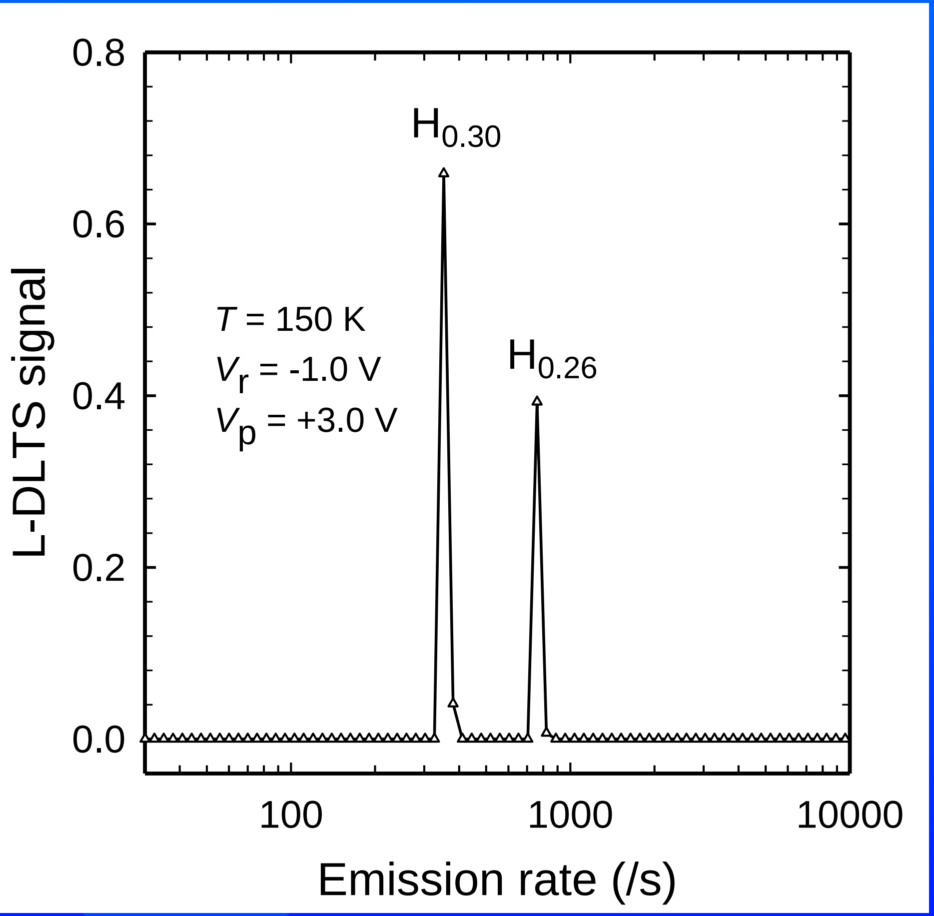
    Presence of defects with levels in the band gap

- Analysis of transient yields:
  - Distiction between majority and minority carrier defects
  - **Activation enthalpy (level position), E_T**
  - **Capture cross section, σ**
  - **Defect concentration, $N_T(x)$**
  - Electric field: defect *type* (donor, acceptor, …)
  - Uniaxial stress: defect *orientation and symmetry*



L-DLTS of ($H_{0.26}$+$H_{0.30}$) peak

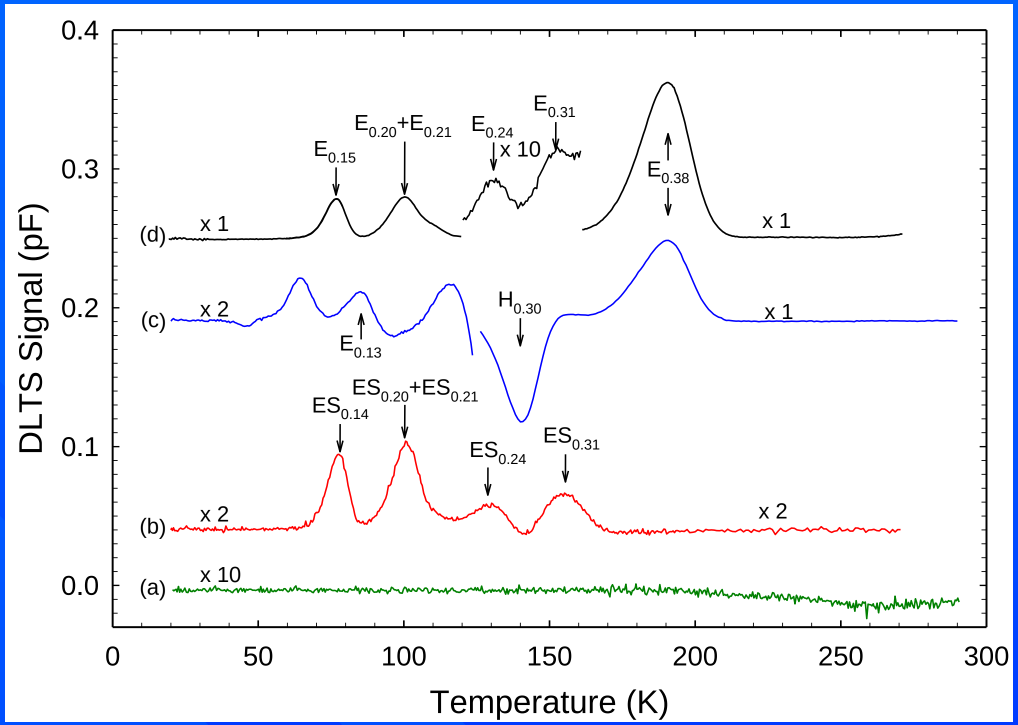
- The ($H_{0.26}$+$H_{0.30}$) DLTS peak is asymmetric
  - It consists of more than one superimposed peaks
- L-DLTS revealed that these peaks belong to
  - $H_{0.30}$ – (-/0) state of *V*-Sb
  - $H_{0.26}$ – unknown structure
- This is similar to what has been reported for electron & gamma irradiation of Ge[1].



[1] V. P. Markevich *et al*, J. Appl. Phys. **95**, 4078 (2004).

DLTS: different metallization methods

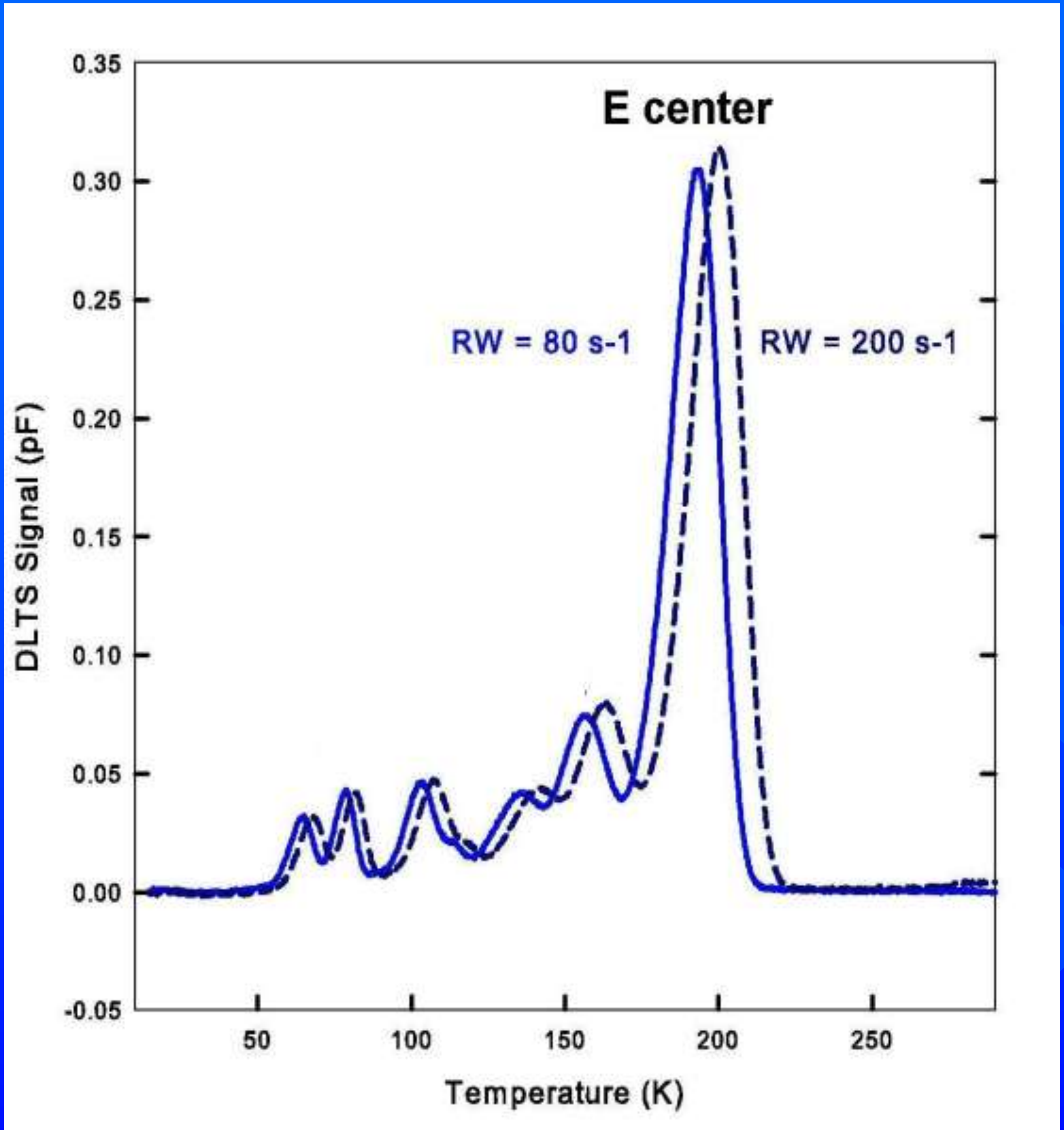
- Resistive deposition does not introduce defects
  - Curve (a)
- Sputter deposition introduced five electron traps[1]
  - Curve (b)
- EBD deposition introduced five electron traps
  - Curve (c)



- All the SD induced defects are also introduced by MeV electron irradiation
  - Curve (d)

[1] F. D. Auret *et al*, J. Electron. Mat. **36**, 1604 (2007).

DLTS: Example, two RW: Defect E center

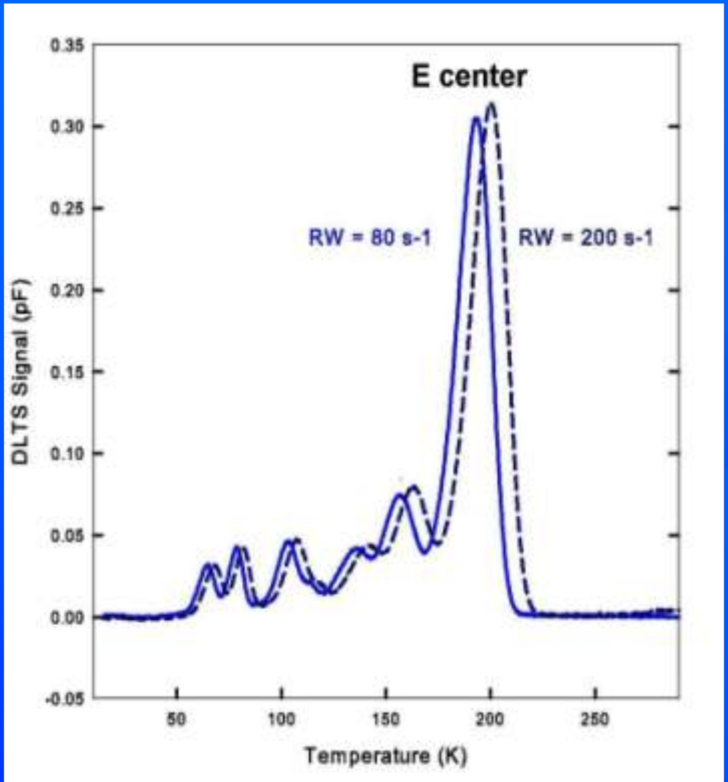


$$RW_1 = 80s^{-1} = e_n(T_1) = \sigma_n \gamma_n T_1^2 \exp(-\frac{E_T}{kT_1})$$

$$RW_2 = 200s^{-1} = e_n(T_2) = \sigma_n \gamma_n T_2^2 \exp(-\frac{E_T}{kT_2})$$

σ_n and E_T can be determined

Number of traps for n-type semiconductor:



N_D :concentration of donors

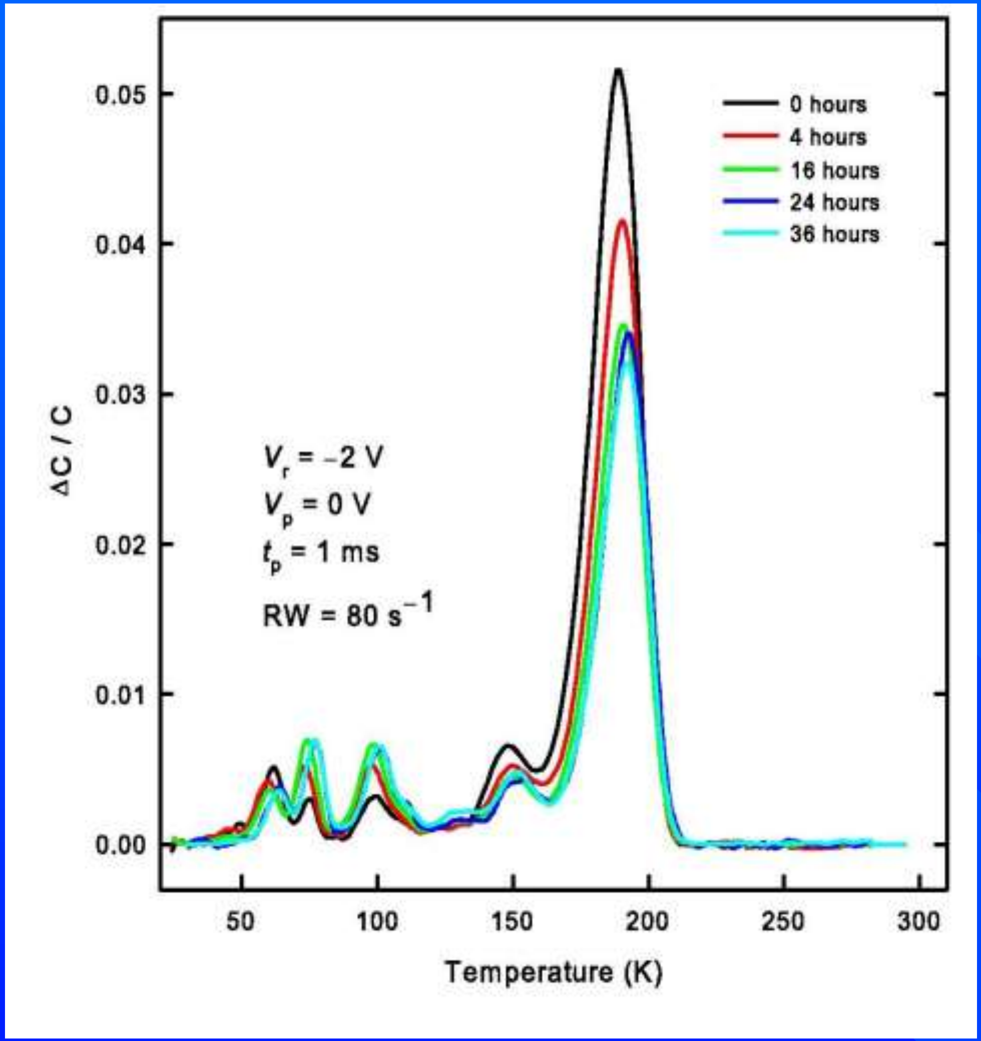
$$\frac{\Delta C}{C_0} = \frac{N_t}{2N_D}$$

The number of traps N_t can be determined

The depletion layer with W increases with the bias potential:

The profile $N_t(x)$ can be obtained

Annealing at room temperature



$$\frac{dN_t}{dt} = -k(T)N_t$$

$$k(T) \;\alpha\; \exp(-\frac{E_0}{k_B T})$$

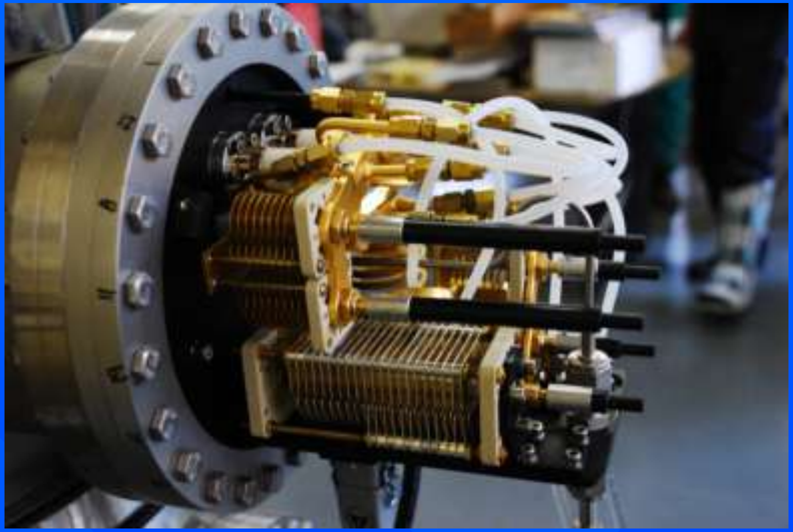
Annealing **rate constant** ***k(T)*** can be determined

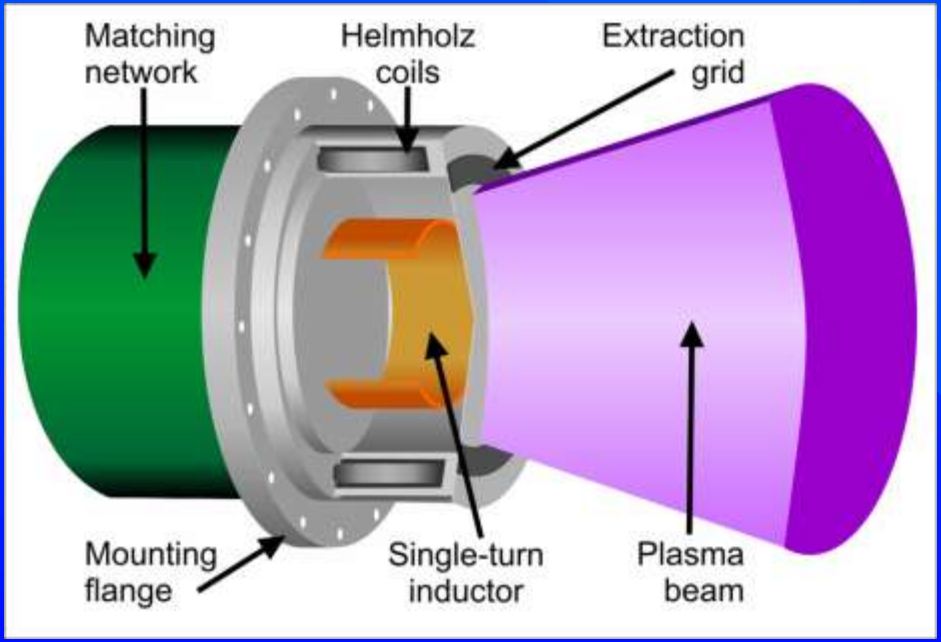
Isochronal annealing: same time, different temperatures

Annealing activation energy E_0 can be determined

Sample Preparation

- Chemical cleaning, ie degreasing
- Chemical etch – oxide removal
- RF Sputter etch – Ar ICP





- Use COPRA plasma source
  - Inductively coupled plasma (ICP)
  - Low energy Ar ions: 1 - 120 eV
  - Fluence rate: ± 10^{15} cm^{-2} s^{-1}
  - Etch rates: ± 0.1 nm s^{-1} for Ge
  - Area: several tens of square cm

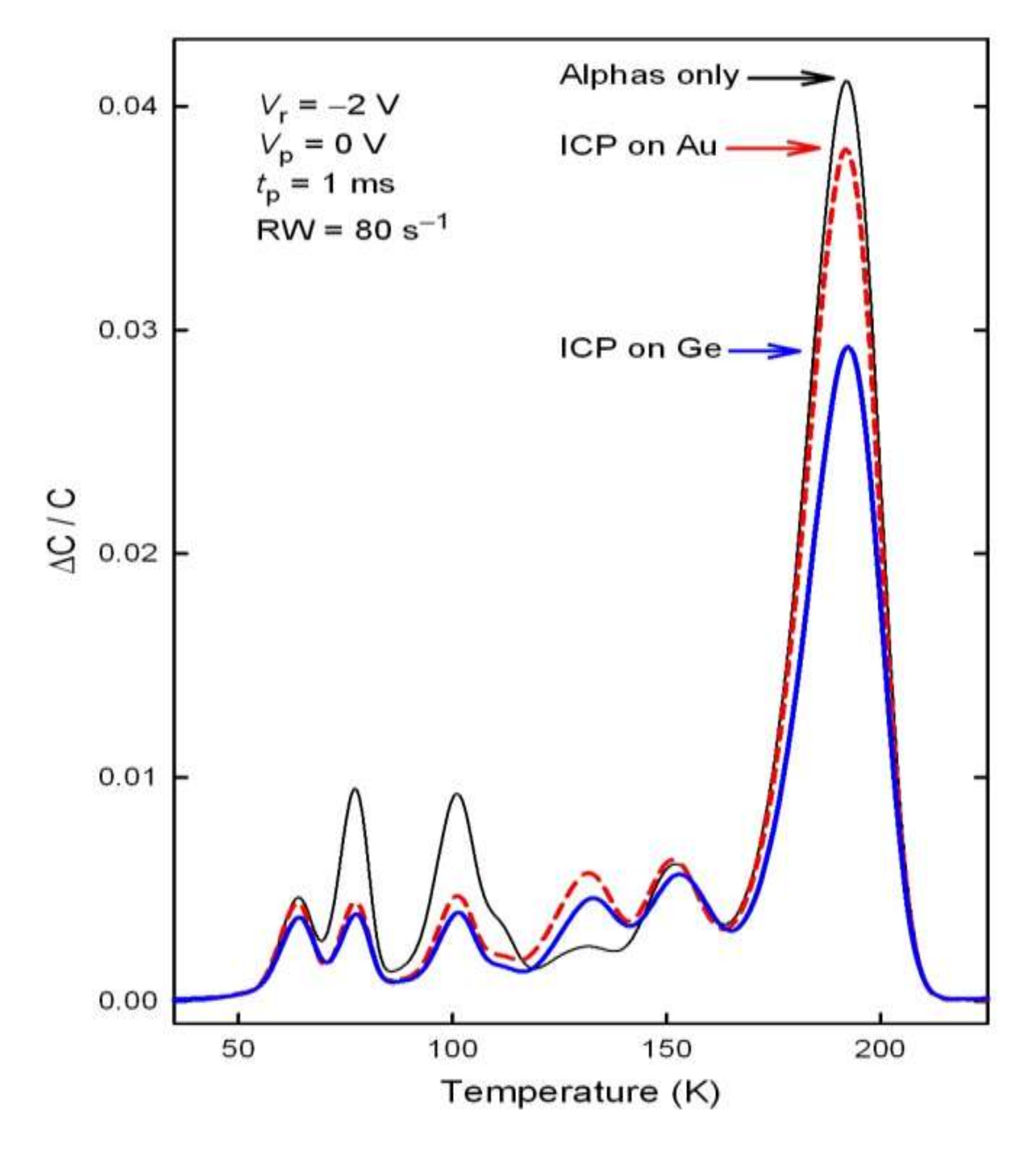
Caution

- 4 eV Ar ICP: Average at sample
- 3.7 eV transfer to Ge atom
- Sample temperature increases

  3 x 10 minute ICP (40°C)
- Annealing also in time and at increased temperature
- Sample temperature increases

  3 x 10 minute ICP (40°C)
- Hydrogen passivation of defects

Our basic experiment: 4 eV Ar-ICP plasma



1.-Sb doped Ge is damaged with 5 MeV alpha particles

Rest – 24 hours

2.-Au diode is evaporated in half the sample (half A)

3.- DLTS on A (black)

4.-ICP on A and B: 3 x 10 min

5.- Au RE - diode B

6.- DLTS on A (red-dashed)

7.- DLTS on B (blue)

Observations

- 4 eV ICP: E-center concentration -30%
- Effect depth in Ge: exceeds 2600 nm
- ICP through metal – less annealing
- Annealing diminished with higher sample temperature.

  1 x 30 minute ICP (70°C)

  8 eV Ar ICP (T ?)
- Compare to anneal with phonons:
  - Low T (40 °C) ~ 150 °C
  - High efficiency Lower efficiency

Our hypothesis: Ar ions impacting on Ge produce Intrinsic Localised Modes that travel through Ge and anneal defects. Why?

1.-ILMs with MD in metals by Hyzhnyakov group have 0.5-5 eV

2.-The maximum energy transfer from Ar to Ge is 3.6 eV

3.- The activation energy for annealing an E center is about 1.36 eV

4.- Energy remains localized exceeding 4000 lattice units

5.- Increasing the energy of the plasma does not enhance the effect, this is because ILMs typically have a definite range or energies.

6. Increasing sample temperature – effect diminished.

7.- At least stationary ILMs have been obtained for Si and Ge with MD.

Conclusions:

Plasma of 4eV produces annealing of defects very deep in Ge.

The energy delivered to E-center is ~1 eV.

Likely conclusions:

1. 4 eV Ar hit produces an ILM in Ge with very high efficiency .
2. ILM of energy ~3eV travel distances of the order of 10^4 lattice units or more.
3. The annealing efficiency of ILM with respect to phonons is extremely large.

Gracias

UNIVERSIDAD DE SEVILLA

Acknowledgements

- J. F. R. Archilla – many suggestions & hospitality
- South African NRF – Financial assistance
- Group members for listening & helpful comments.

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Our basic experiment: Facts

1.-Sb concentration: $1.3 \cdot 10^{15}$ cm^{-3} ($n_i = 2.4 \cdot 10^{13}$ cm^{-3}) ; 1 Sb per 10^8 Ge

2.- Metal (Au) thickness: 25nm

3.- After ICP on Ge the E center concentration drops 29% from $N_T = 1.07 \cdot 10^{14}$ cm^{-3}

4.- If ICP is done on Au, the E center reduction is smaller, but exists.

5.- ICP is done for 30' in intervals to prevent heating

6.- Defect annealing occurs up to 2600 nm or 4600 lattice units

7.- If the plasma energy is increased the effect is smaller

8.- Thermal annealing has to be done at 150°C to obtain a similar effect.

Some numbers

1.-Ion current can be measured, $\Phi_{Ar} = 1.25\cdot 10^{13}\,\mathrm{cm^{-2}s^{-1}} \approx 0.04 a^{-2} s^{-1}$

2.- DB creation efficiency: $\gamma : \quad \Phi_{DB} = \gamma \cdot \Phi_{Ar} \quad ; \quad \gamma < 1$

3.-Number of breathers: $n_{DB} = \dfrac{\Phi_{DB}}{c_s} \approx \gamma 2.3\cdot 10^{7}\,\mathrm{cm^{-3}}$

$$4.-\mathrm{Phonons:}\quad E_{ph} = 0.035\mathrm{eV} \quad \mathrm{n_{ph}} = \frac{3n_{Ge}}{\exp(E_{ph}/k_B T) - 1} \approx 4.6\cdot 10^{22}\,\mathrm{cm^{-3}}$$

$$\mathrm{For}\ \gamma = 1 \qquad -\frac{1}{N_T}\frac{dN_{T,DB}}{dt} \approx 2\cdot 10^{-4} s^{-1} \qquad -\frac{1}{N_T}\frac{dN_{T,RT}}{dt} \approx 2\cdot 10^{-11} s^{-1}$$

Relative annealing efficiency per DB or phonon: $\sim 10^{22}$

Relative annealing efficiency per eV of DB or phonons: $\sim 10^{20}$

Interaction cross-section and energy delivered by a breather

Interaction cross-section σ

$$-\frac{dN_T}{dt} = \sigma N_T \Phi_{DB} \exp\left(-\frac{E_0 - \Delta}{k_B T}\right)$$

Interaction cross-section $\sigma = \alpha\sigma_0 \quad ; \quad \alpha > 1$

Minimal interacion cross-section $\sigma_0 = n_{Ge}^{-2/3} \approx 10^{-15}\,\mathrm{cm}^2$

Apparent diminution of the activation energy because of DB interaction: Δ

$$-\frac{dN_T}{dt} = \alpha\gamma\sigma_0 N_T \Phi_{ions} \exp\left(-\frac{E_0 - \Delta}{k_B T}\right) \qquad \alpha, \gamma, \Delta \quad \text{unknown}$$

$$-\frac{dN_T}{dt} = \sigma_{ions} N_T \Phi_{ions} \qquad \sigma_{ions} \approx \frac{1}{50}\sigma_0 \approx 1.5 \cdot 10^{-17}\,\mathrm{cm}^2$$

$$\text{For } \alpha\gamma = 1, \quad \Delta \approx 1.2\,\mathrm{eV}$$

References

[1] J. F. R. Archilla, S. M. M. Coelho, F. D. Auret, V. I. Dubinko, and V. Hizhnyakov, Experimental observation of moving discrete breathers in Germanium. *To be published.*

[2] F. D. Auret, S. Coelho, G. Myburg, P. J. Janse van Rensburg and W. E. Meyer, Defect introduction in Ge during inductively coupled plasma etching and Schottky barrier diode fabrication processes *Thin. Solid. Films.* 518:2485, 2010.

[3] S. Flach and A. Gorbach, Discrete Breathers: Advances in Theory and Applications *Phys. Rep.* 467:1-116, 2008.

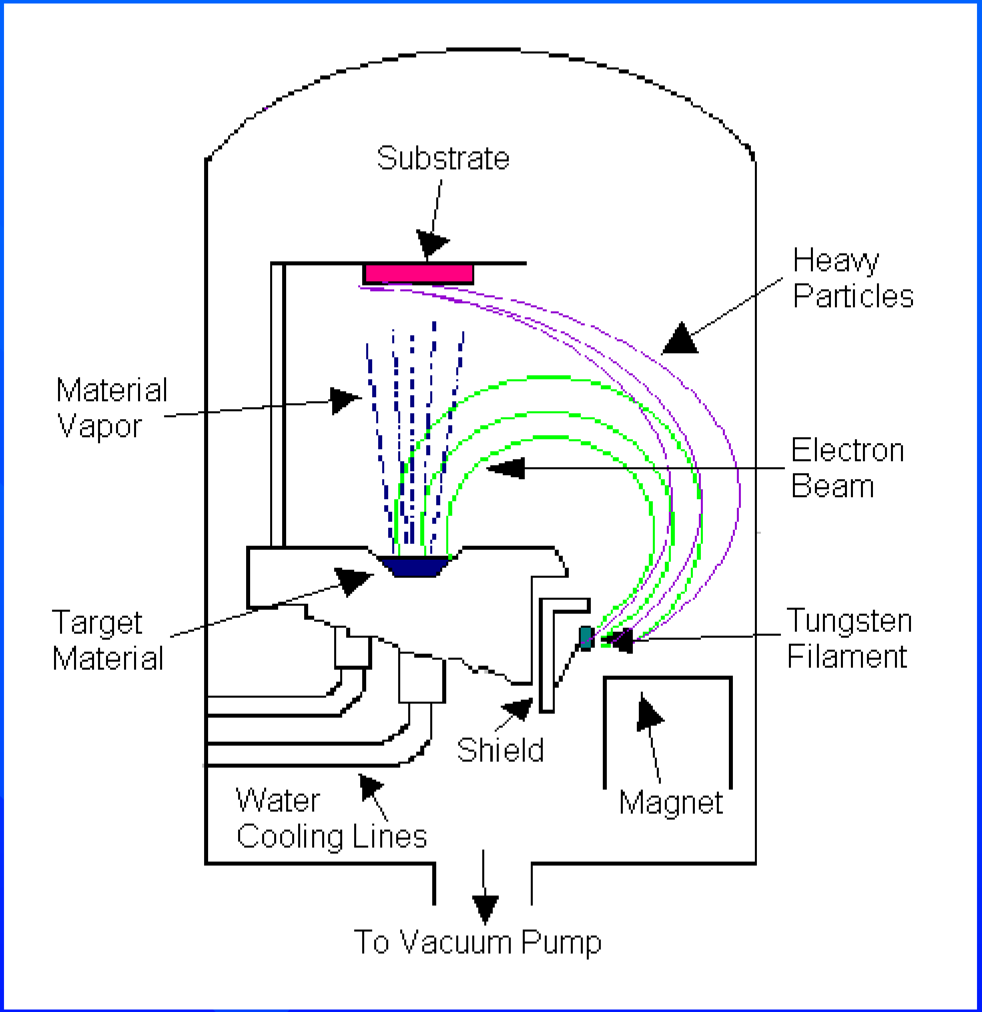
[4] M. Hass, V. Hizhnyakov, A. Shelkan, M. Klopov, and A. J. Sievers, Prediction of high-frequency intrinsic localised modes in Ni and Nb, *Phys. Rev. B* 84:144303, 2011.

[5] V. Hizhnyakov, M Haas, A Shelkan and M Klopov, 2013, Theory and MD simulations of intrinsic localized modes and defect formation in solids *Phys. Script.* To appear.

[6] V. I. Dubinko, P. A. Selyshchev, and J. F. R. Archilla, Reaction rate theory with account of the crystal anharmonicity, *Phys. Rev. E* 83:041124, 2011.

Electron beam deposition

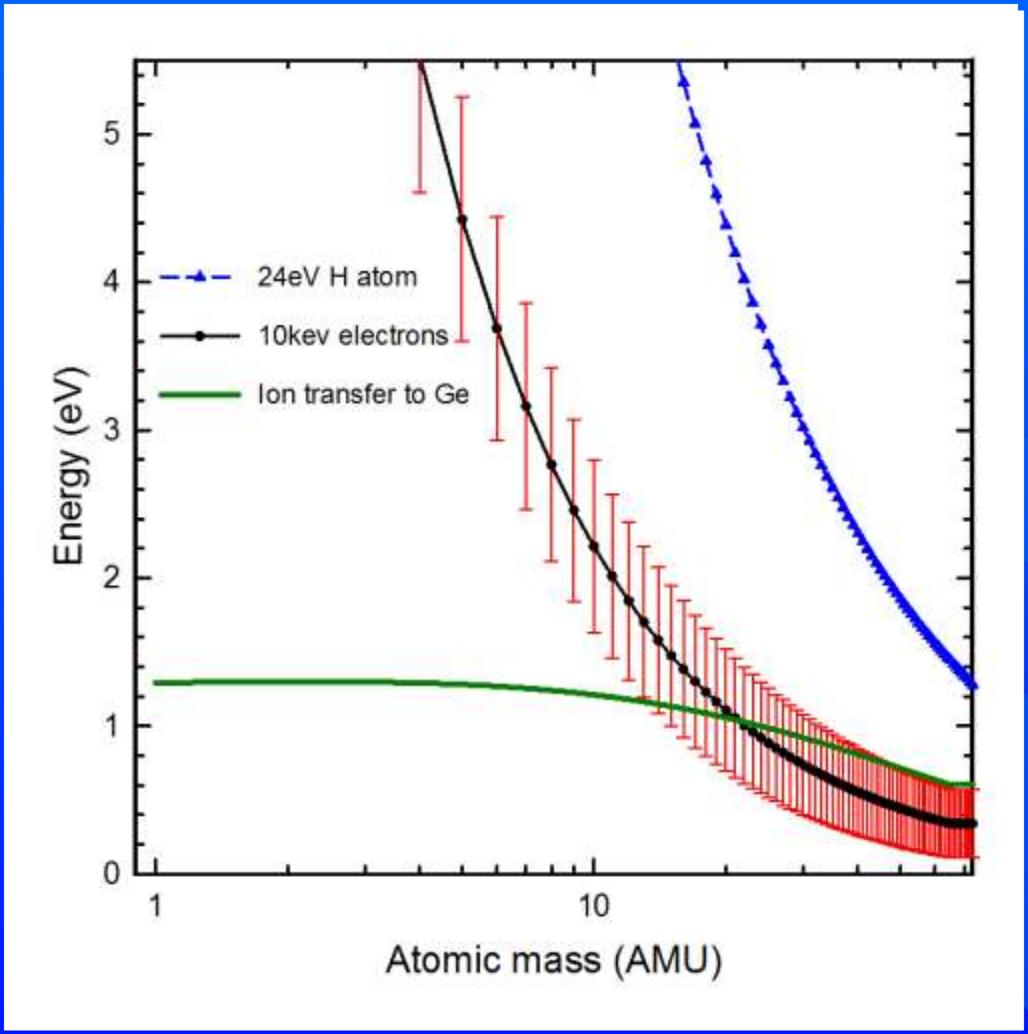
- Advantages:
  - Easily evaporates high melting point metals.
  - Highly controllable deposition rates.
  - Good adhesion.



- Disadvantage:
  - Introduces defects at and below the surface of semiconductors.

  - Chen et al
  - Mooney et al

E vs AMU for e or H



- 11.5 eV to create Frenkel pair
- 1st: electron-atom
- 2nd atom to crystal
- Example: e to H to Ge

The Defect Concentration

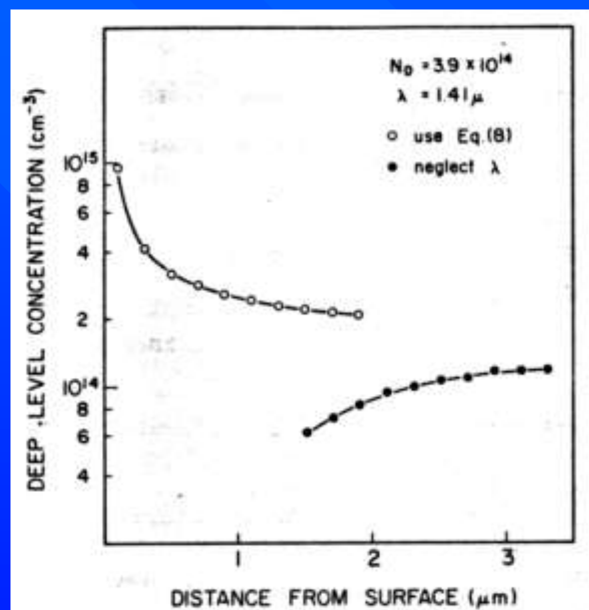
- Defect concentration from peak height, ΔC/C:[1]

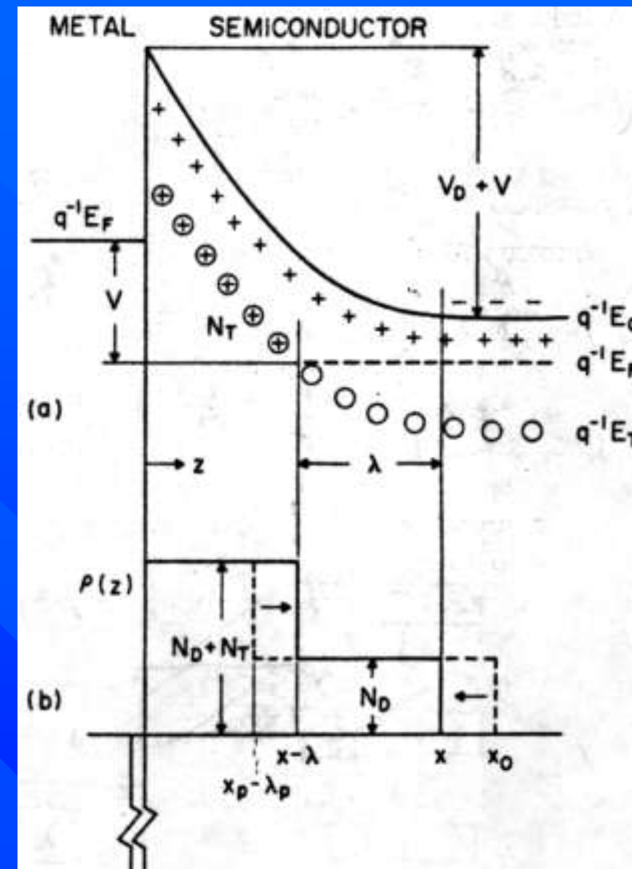
$$N_T(x_m-\lambda)=2N_D(x)\left(\frac{\Delta C}{C}\right)_{t=0}\left[\left(\frac{x-\lambda}{x}\right)^2-\left(\frac{x_p-\lambda}{x}\right)^2\right]^{-1}$$

$$x_m=(x+x_p)/2$$

$$x=\sqrt{\frac{2\varepsilon(V_{bi}+V)}{qN_D}}$$

$$\lambda=\sqrt{\frac{2\varepsilon(E_F-E_T)}{q^2N_D}}$$



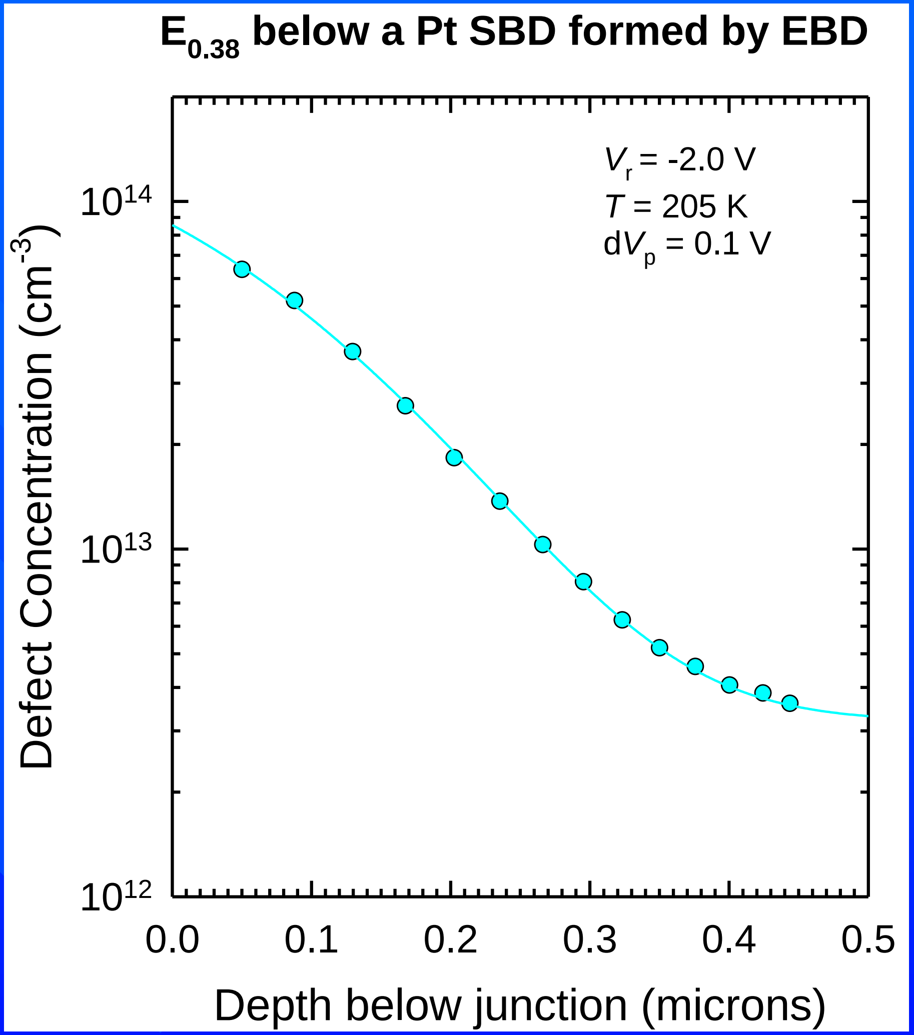


- N_T as low as 10^{10} defects /cm^3

[1] Y. Zohta et al, JAP. 53, 1809 (1982)

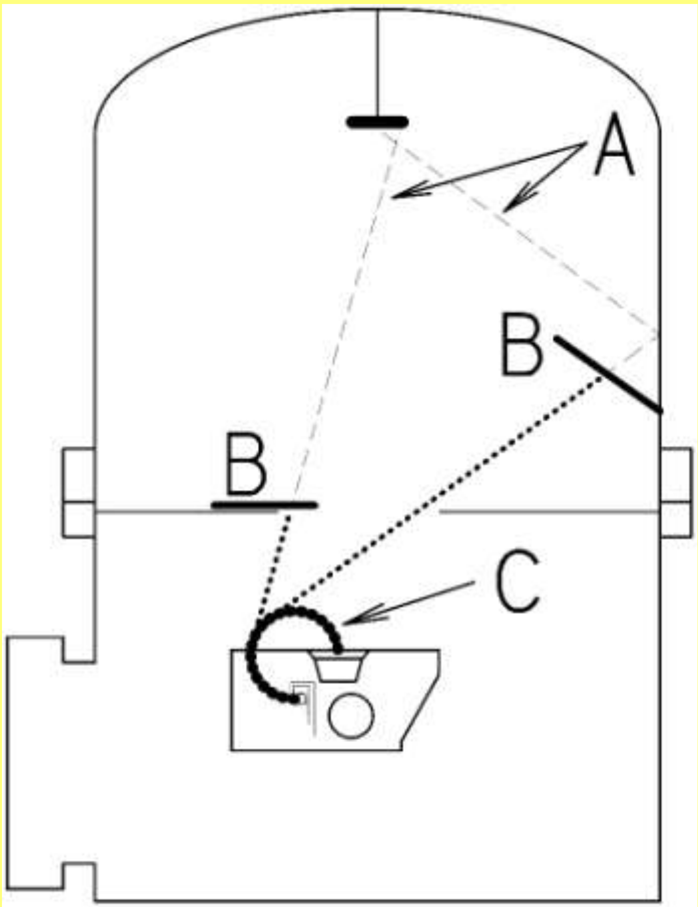
Depth Distribution of EBD defects

- Use fixed bias, variable pulse DLTS method
  - With "λ" correction[1].
- Not possible to profile the hole traps:
  - Hole concentration is not known.
- V-Sb ($E_{0.38}$):
  - Concentration decreases rapidly away from the surface.
  - Approaches 10^{14} cm^{-3} at surface.
  - Diffusion of vacancies from the surface?



[1] Y. Zohta *et al*. J. Appl. Phys. **53**, 1809 (1981)

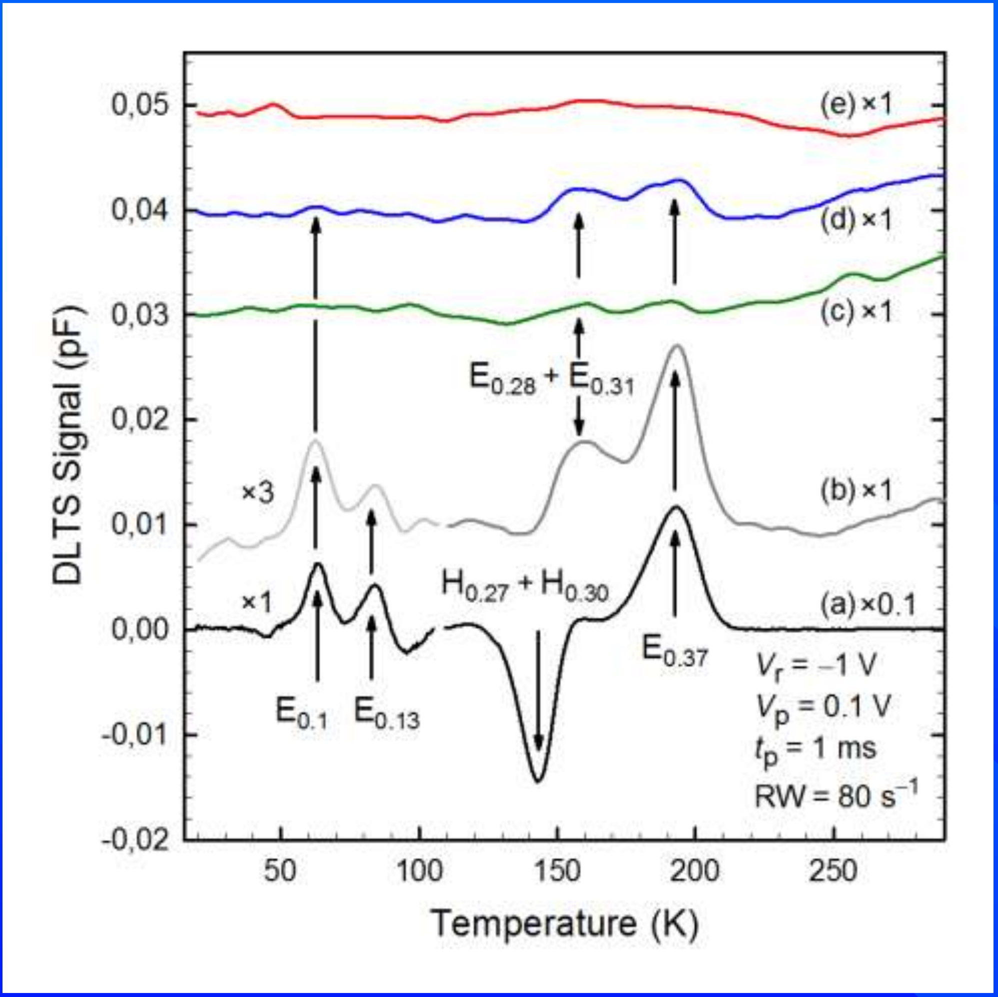
E-beam deposition - Pt



10 keV electrons
Beam path
Reflected electrons
Particles

Experiment 1

E-beam shielding e-traps



High vacuum-2 shields

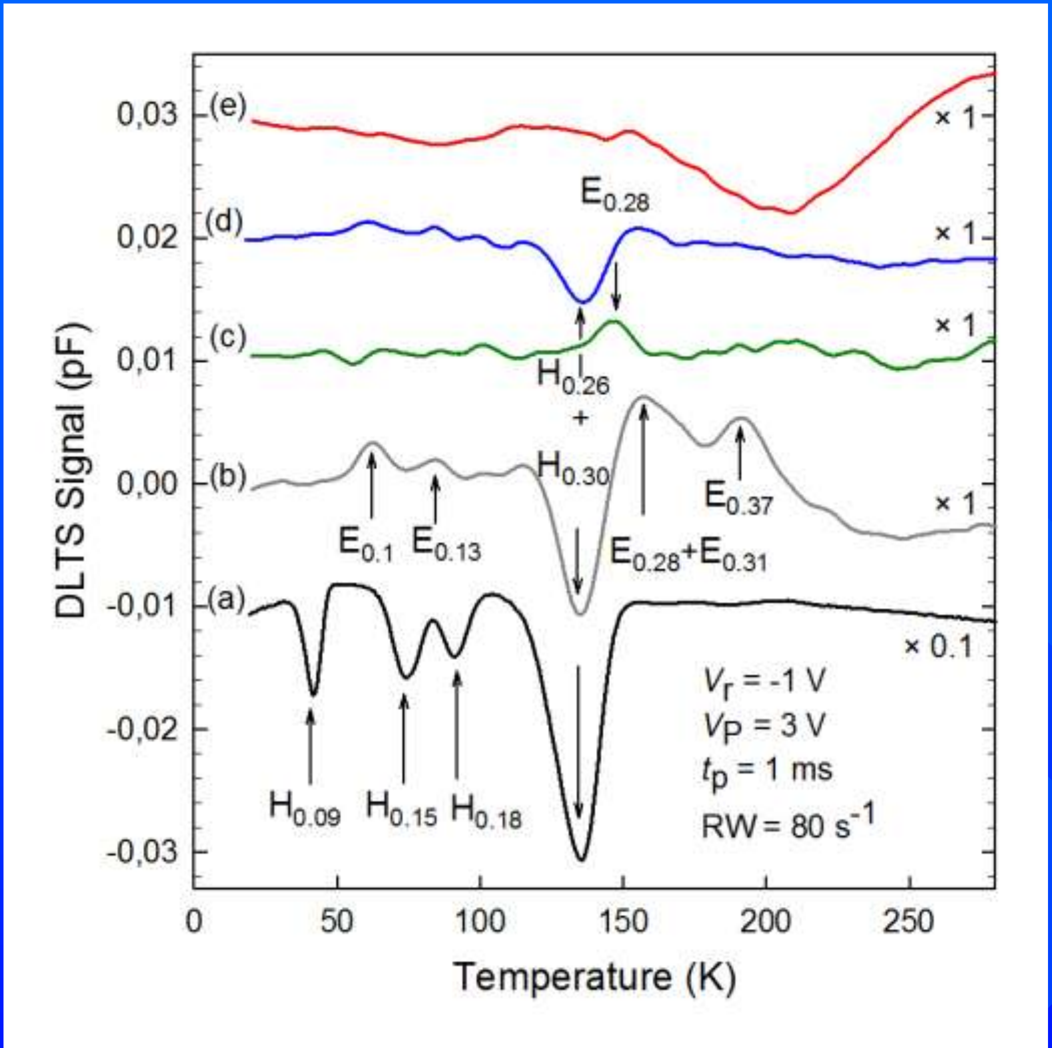
F/gas – 2 shields

F/gas – 1 shield

F/gas – no shields

“Standard EBD”

E-beam shielding h-traps



High vacuum-2 shields

F/gas – 2 shields

F/gas – 1 shield

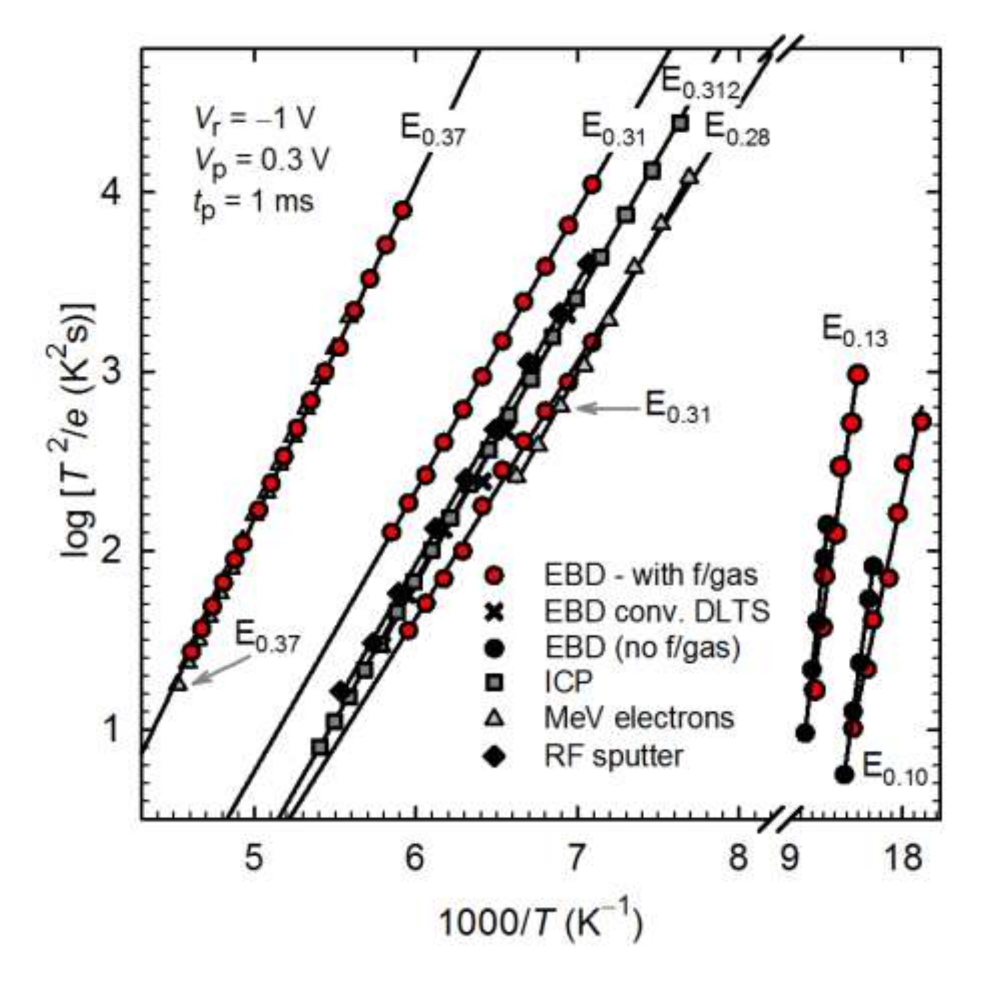
F/gas – no shields

“Standard EBD”

Energy levels

- $E_{0.37}$ – no surprise!
- $E_{.311}$ new
- $E_{0.28}$ new
- $E_{0.13}$
- $E_{0.10}$

- Use L-DLTS
- Conclusions 1



Experiment 2 - EBE
Deposition vs exposure

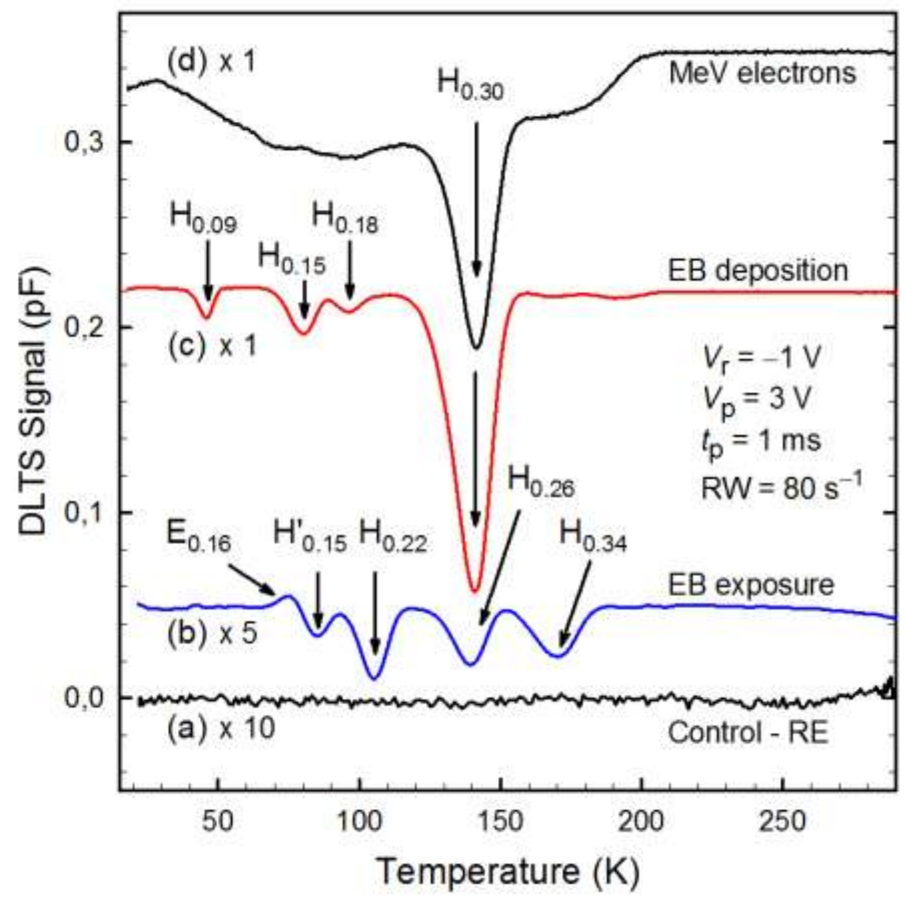
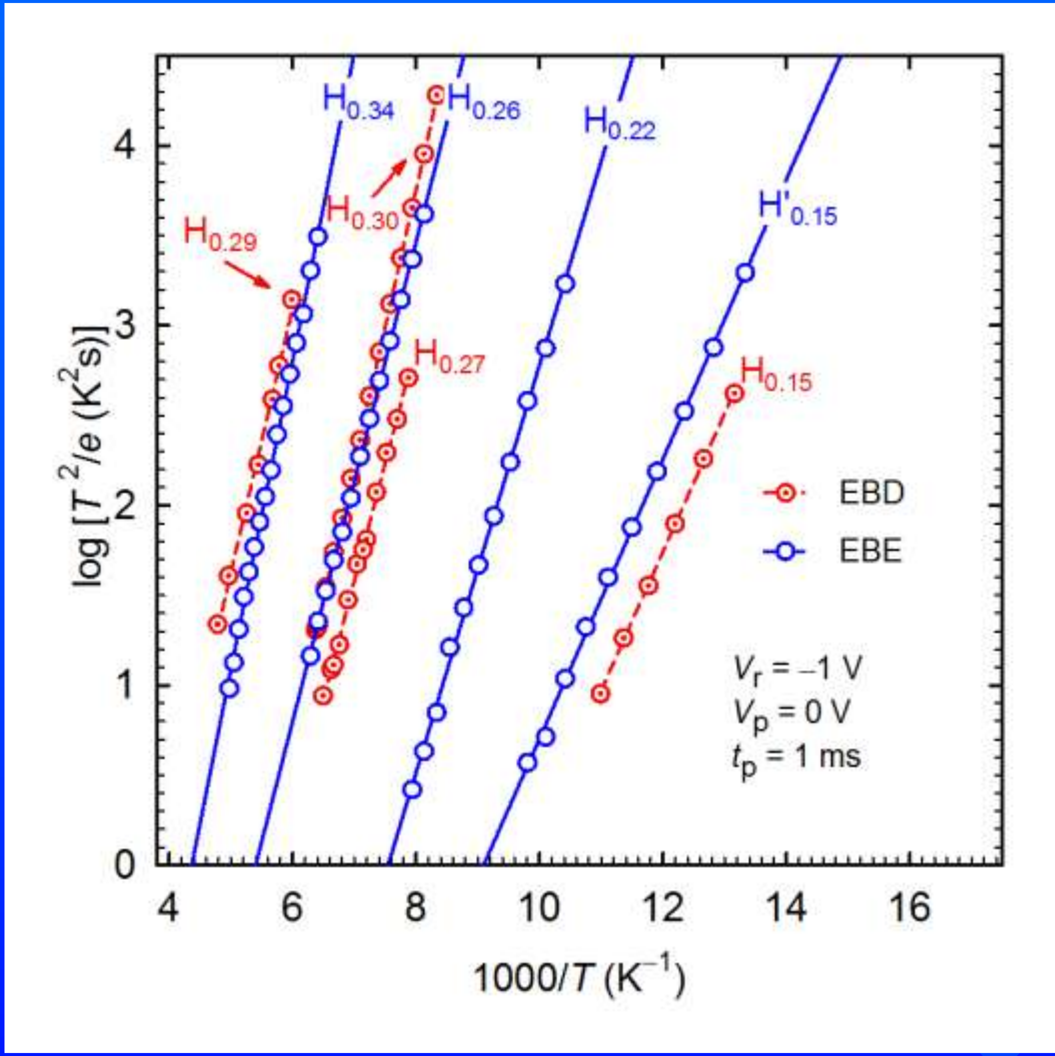


Fig. 5 (of 8), S. M. M. Coelho et al

No similarities

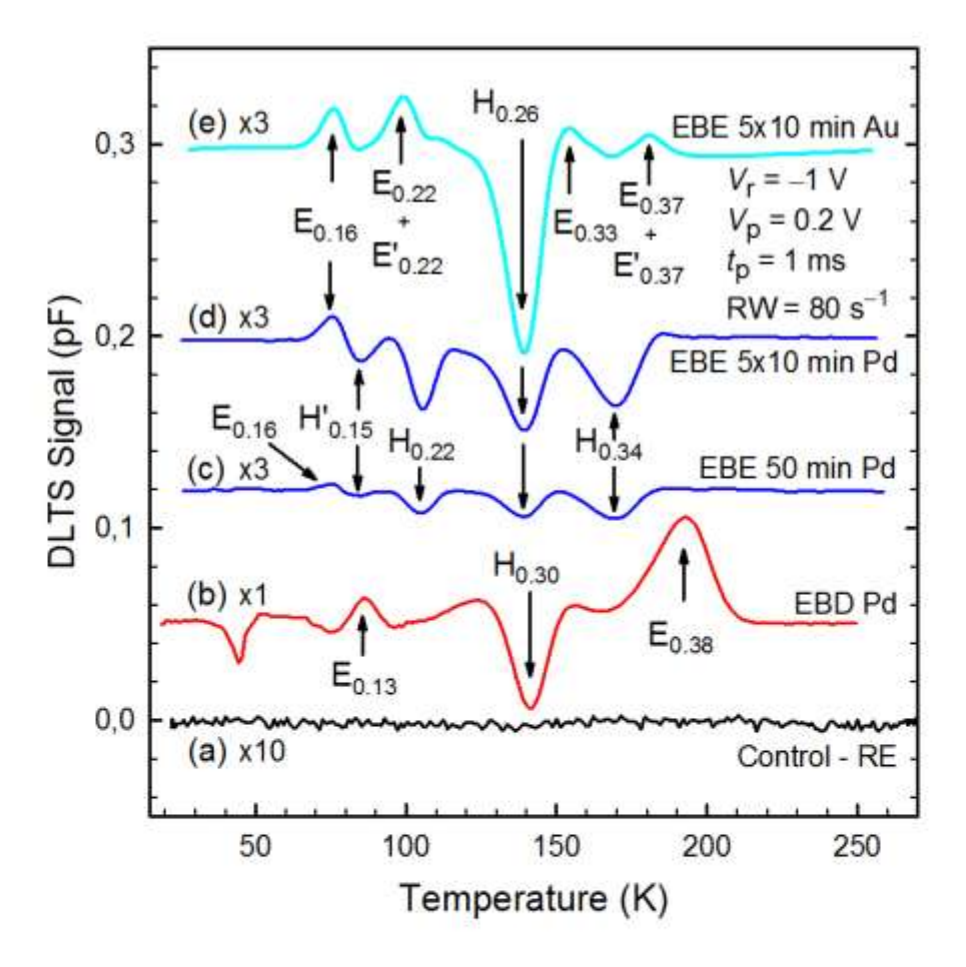
Arrhenius plots – L-DLTS



No hole traps in common

New defects – impurity related?

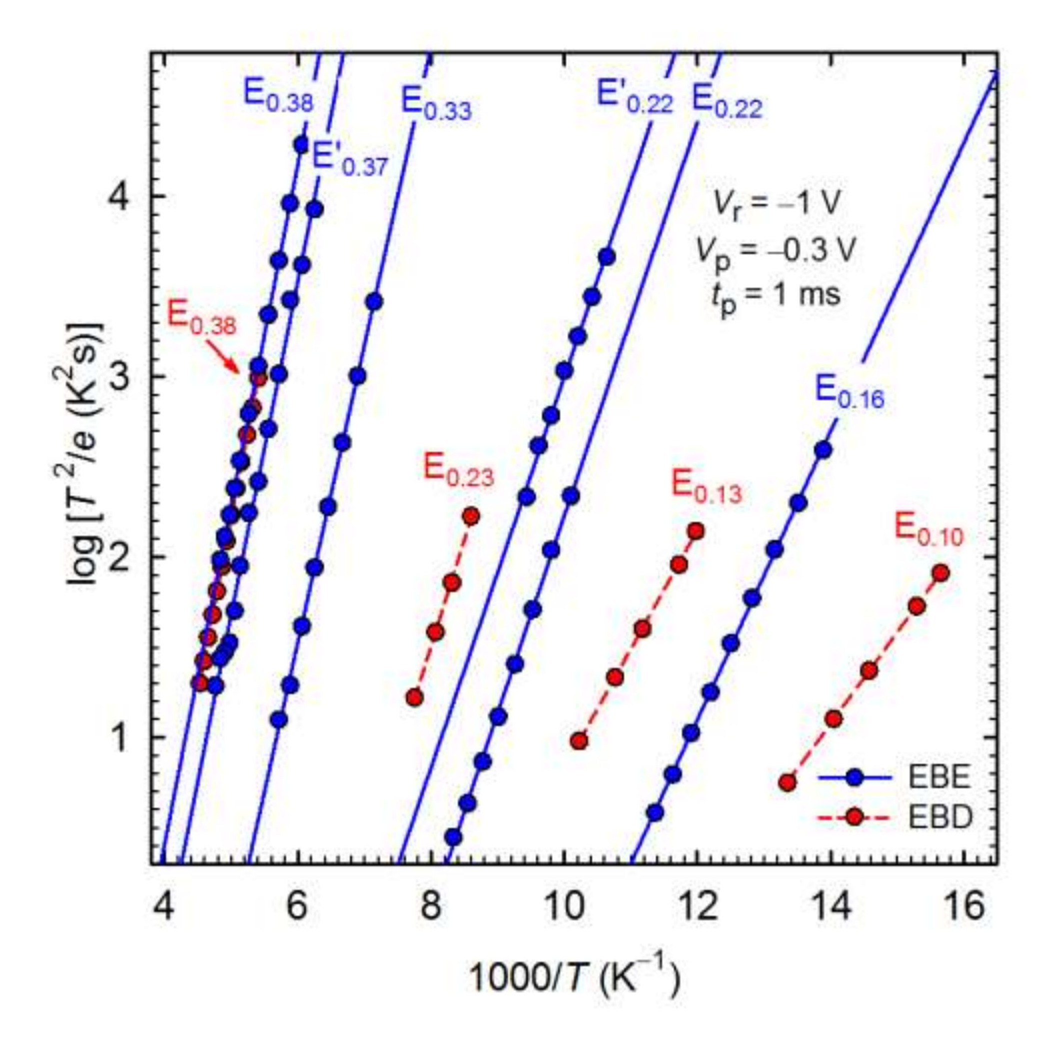
Experiment 2
Au & e-traps



E-traps dominant

Defect concentration

Arrhenius plots – L-DLTS



$E_{0.38}$
Common to both

New defects – perhaps not impurity related

Summary and Conclusions

- 1. Shielding lowers the defects introduced by EBD.

  Damage caused by impacts with ions / particles – not e.

- 2. Damage caused in 1^{st} 0.5 µm, at / near defect site.

  How was the energy transferred?

- 3. Damage caused by E < 1.3 eV transfer to Ge.

  Only enough to displace H or light atoms – single bond.

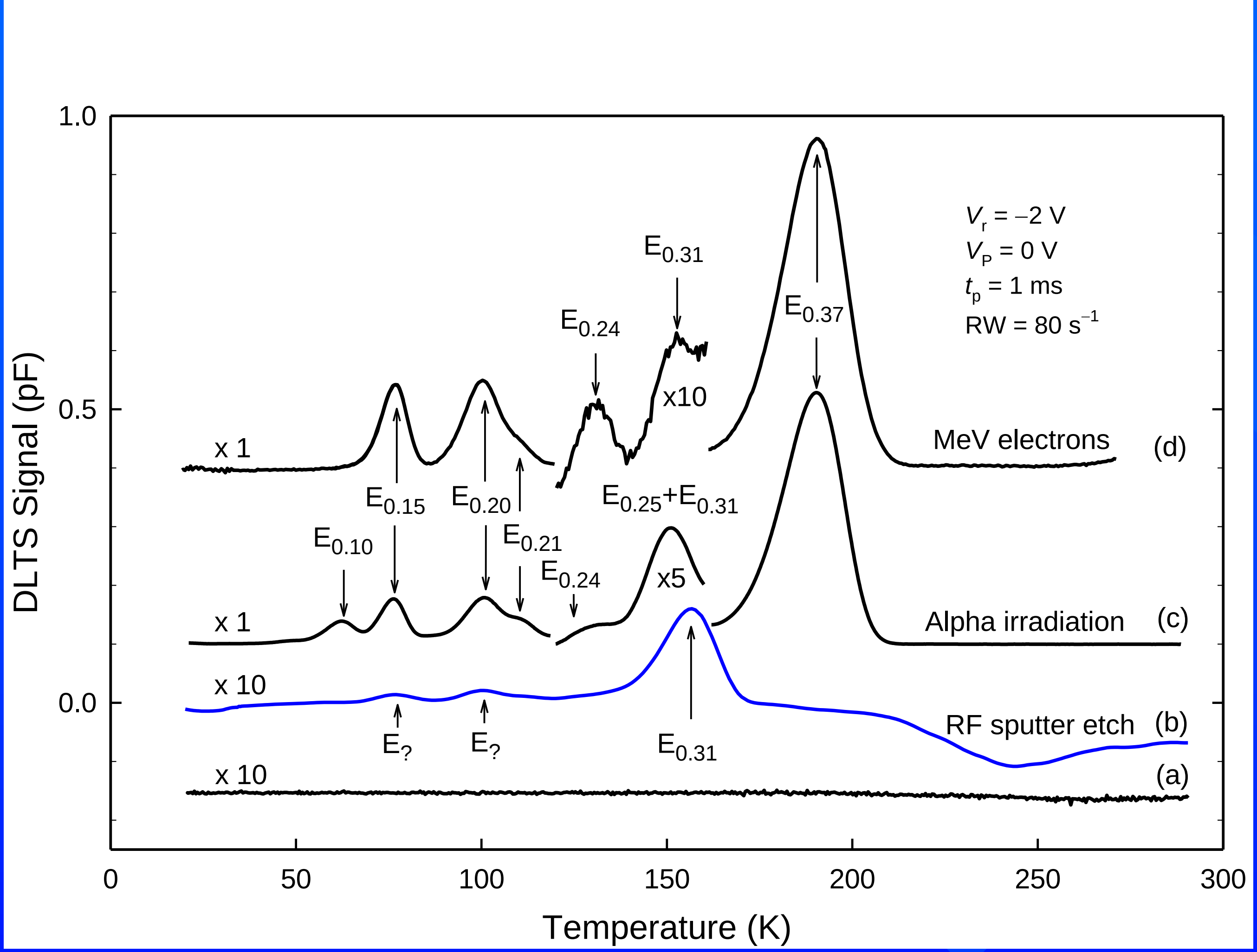
- Will DLTS be more useful in future?

Thank you

Acknowledgements

- J. F. R. Archilla – many suggestions & hospitality
- South African NRF – Financial assistance
- Group members for listening & helpful comments.

MeV electrons



Electron beam deposition

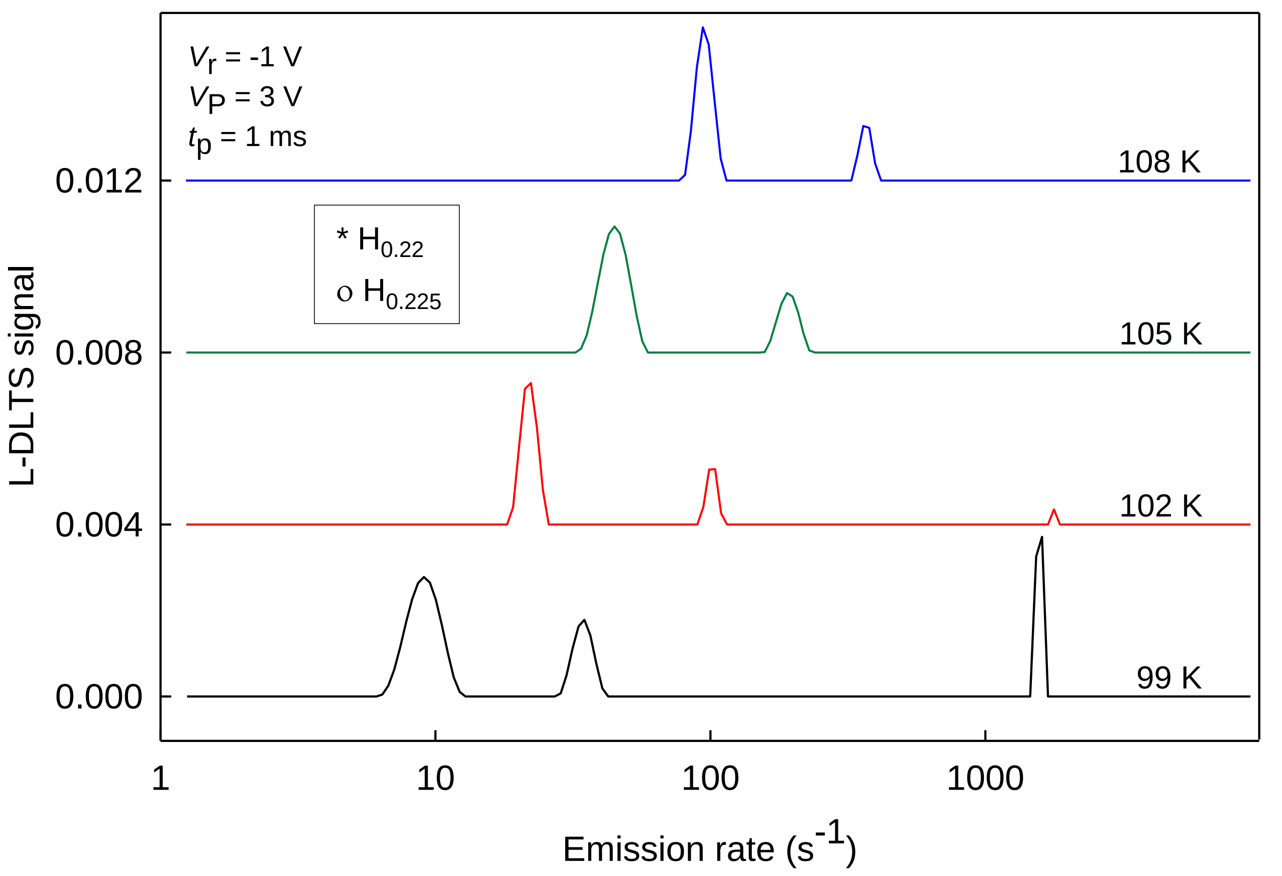
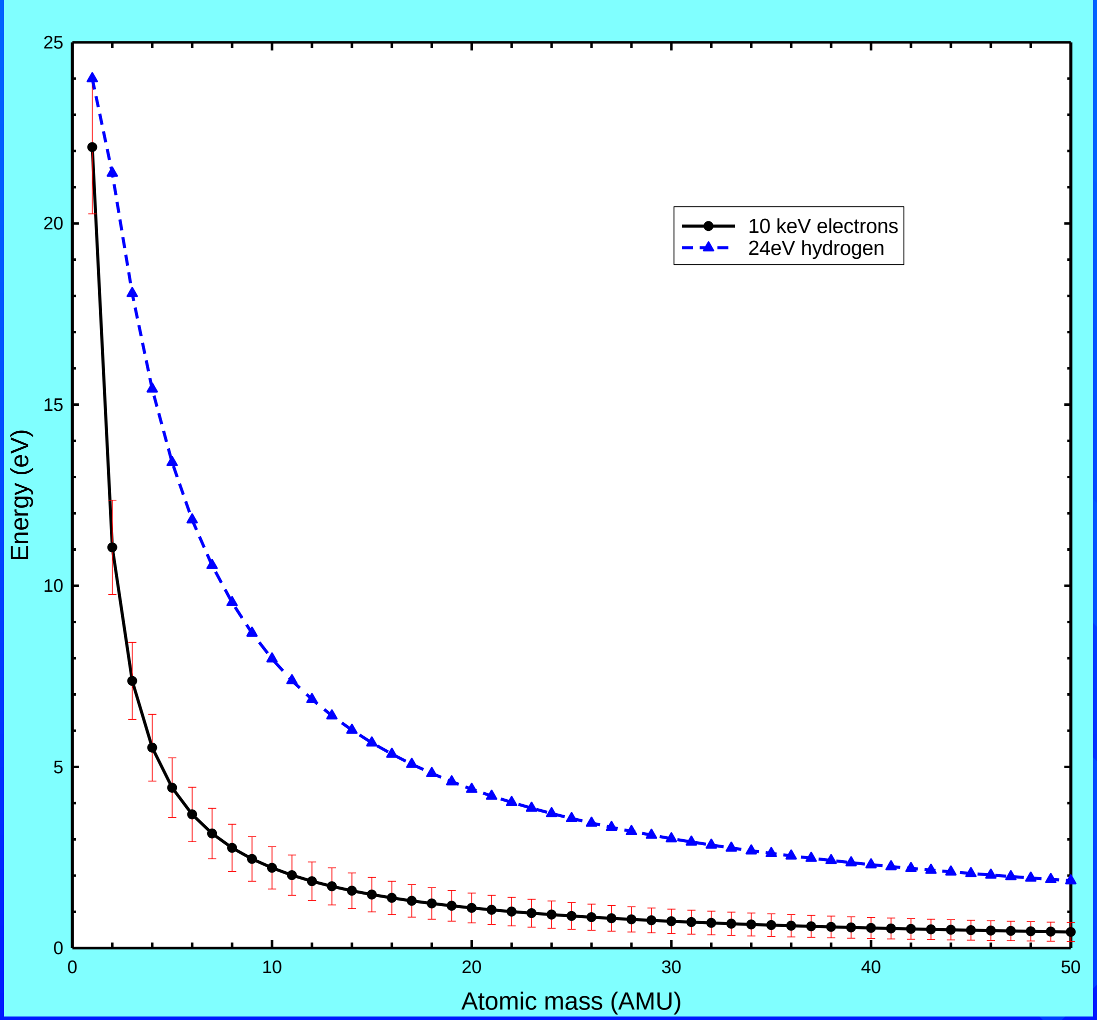


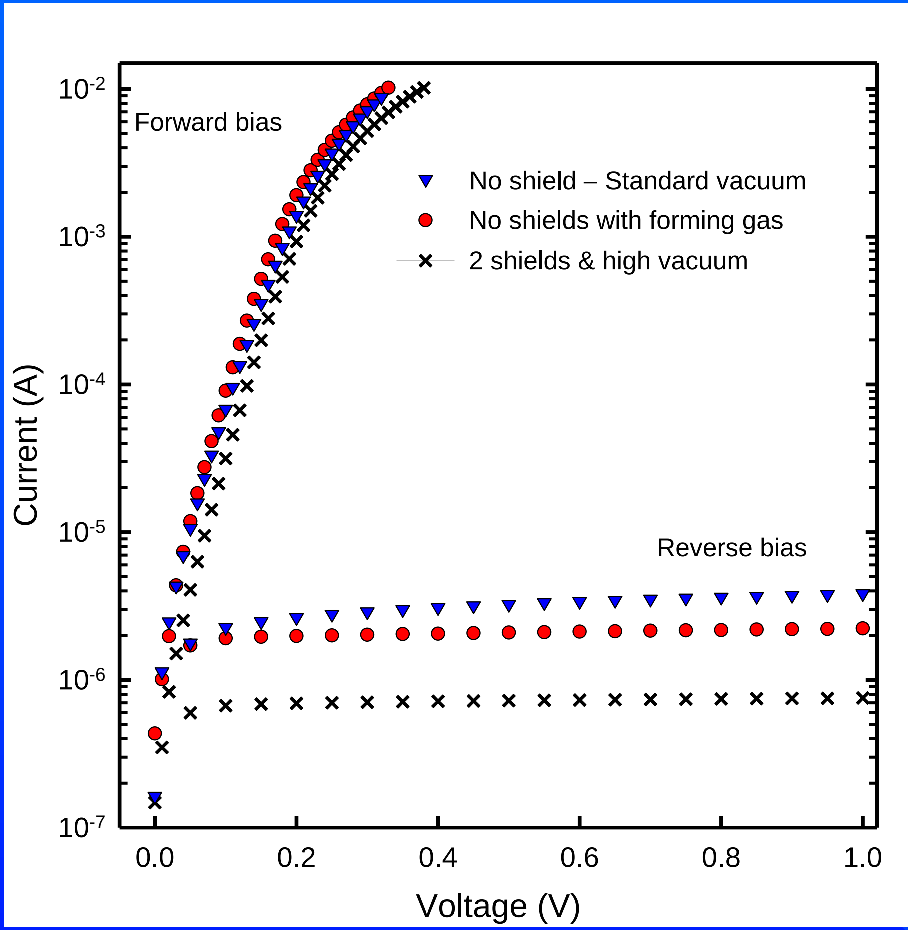
Fig. 7 (of 7), S. M. M. Coelho et al

E vs AMU for e or H



- 11.5 eV to create Frenkel pair

I-V: Pt diodes



Ideality = 1.02

Previous lowest: 1.05

Current – lowest measured

Defects linked to e-beam

Next experiment

Defects in Semiconductors

- Defects can be "good" or "bad"
  - Solar cells: "bad": eliminate them!!!
  - Fast switches: "good": deliberately introduce them!
- Defects are introduced during
  - Crystal growth, sawing / cutting and polishing
  - Critical processing steps
    - » Surface cleaning by particle processing (sputter etching)
    - » Metallization
  - Radiation
    - » Space, reactors
    - » Accelerators / implanters
- Important defect parameters
  - Energy level, E_T, in bandgap
  - Capture cross section, σ
  - Concentration, N_T