

Electrical characterization of defects using junction spectroscopy

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Electrical characteristics of point defects?

The lattice model of defects



Electrical characteristics of point defects?



- Energy level position, (E_T)
- Trap/dopant concentration, N_T
- Acceptor/donor
- Capture cross section, σ
- Spatial variation
- ..
- Identity, configuration

Outline

- Basics capture and emission from defects
 Thermodynamics of defects and dopants
- Steady-state electrical spectroscopy
 - \circ Capacitance of a junction
 - Thermal Admittance Spectroscopy
- Transient electrical spectroscopy
 - Deep Level Transient Spectroscopy

Capture and emission







Capture rates [1/s]
$$\begin{array}{c} c_n n \\ c_p p \end{array}$$
 Emission rates [1/s] $\begin{array}{c} e_{n,p} \end{array}$

Capture coefficients [cm³/s]

$$c_{n,p} = \sigma_{n,p} v_{n,p}^{thermal}$$

$$\sigma_{n,p}$$
 Capture cross sections [cm²]

$$v_{n,p}^{thermal} = \sqrt{\frac{3kT}{m_{n,p}^*}}$$

Capture and emission



If total concentration of trap T is N_T and N(t) is the concentration of filled traps (cm⁻³), the change in filling is given by:

$$\frac{dN(t)}{dt} = c_n n(N_T - N(t)) - e_n N(t) - c_p pN(t) + e_p(N_T - N(t))$$

electrons holes

Emission and capture in depletion regions

$$\frac{dN(t)}{dt} = c_n n(N_T - N(t)) - e_n N(t) - c_p p N(t) + e_p (N_T - N(t))$$

Gives the solution

Assume:

- A depletion layer $e_p >> c_n n$ and $e_n >> c_p p$
- A level in the upper part of the band gap e_n>>e_p

$$N(t) \approx N_T e^{e_n(t)}$$

 i.e. the number of trapped electrons at level T decreases exponentially with time. Thermodynamically, the energy of deep bandgap states is better described by a Gibbs Free energy (G) than the "normal" energy E.



$$E_c - E_T = \Delta G_{C,T} = \Delta H_{C,T} - T \Delta S_{C,T}$$

From "detailed balance equation" we can write the emission as

$$e_n = N_C c_n \exp\left(-\frac{G_C - G_T}{kT}\right) = \sigma_n N_C v_n^{thermal} \frac{g_0}{g_1} \exp\left(\frac{\Delta S_n}{k}\right) exp\left(-\frac{\Delta H_{C,T}}{kT}\right)$$

Temperature dependence

 Thermodynamically, the energy of deep bandgap states is better described by a Gibbs Free energy (G) than the "normal" energy E.



$$E_c - E_T = \Delta G_{C,T} = \Delta H_{C,T} - T \Delta S_{C,T}$$

From "detailed balance equation" we can write the emission as (AH = 0)

$$e_n = N_C c_n \exp\left(-\frac{G_C - G_T}{kT}\right) = \sigma_n X_n T^2 exp\left(-\frac{\Delta H_{C,T}}{kT}\right)$$
$$e_p = \sigma_p X_p T^2 exp\left(-\frac{\Delta H_{V,T}}{kT}\right)$$

In electrical characterization we normally neglect the entropy, i.e. measure the enthalpy: E_T≈ΔH

Key messages

- The rate equation of filled traps can be simplified in the <u>depletion region</u> of a junction
- The number of trapped electrons at level T decreases <u>exponentially</u> with time
- In electrical characterization we measure the <u>enthalpy</u>

Junction Spectroscopy Techniques

Steady-state junction spectroscopy

- TSCAP Thermally stimulated capitance
- TAS Thermal Admittance Spectroscopy
- TSC Thermally stimulated current
- TDRC Thermal Dielectric relaxation current

Transient junction spectroscopy

- DLTS Deep-level Transient Spectroscopy
- I-DLTS Current DLTS
- CC DLTS Constant capacitance DLTS
- L DLTS Laplace DLTS
- MCTS Minority carrier transient spectroscopy
- ODLTS Optical DLTS
- F DLTS Frequency scan

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The pn-junction/Schottky barrier

- The emission and capture process can be manipulated using a pn-junction
- Parallell plate capacitor

$$C = \frac{\epsilon A}{W}$$

Depletion width(p+n):

$$W = \sqrt{\frac{2\epsilon(V_0 - V_r)}{qN_d}}$$



 In an asymmetric junction the depletion region mainly extends into the low doped region

Measuring charge variations: Capacitance

- Charge variations can be monitored in the space charge region of a junction by measuring capacitance
- A small AC voltage superimposed on the DC voltage across the junction
- Typical frequency range 1kHz-1MHz

$$I = \frac{dQ}{dt} = \frac{dQ}{dV}\frac{dV}{dt} = C\frac{dV}{dt}$$





Admittance is composed of a conductance and a suceptance Y(f) = G(f) + iS(f)

Susceptance is related to the capacitance:

 $S(f) = 2\pi f C(f)$







Extracting activation energy

Measure conductance/capacitance for different frequencies Find peak conductance or ΔC_{step}



Conc. and probing region



 Change in capacitance is proportional to concentration

$$C = \frac{\epsilon A}{W}$$
 $W = \sqrt{\frac{2\epsilon(V_0 - V_r)}{qN_d}}$

 Probing region determined by applied DC bias

The TAS system



On the n-type conductivity in ZnO



Hydrothermally grown ZnO samples typically show several shallow donor levels.

• D1

- D2
 - ~55 meV

$$- ~1 \times 10^{17} \text{ cm}^{-3}$$

 -10^{16} - 10^{17} cm⁻³

R. Schifano, E. V. Monakhov, L. Vines, B. G. Svensson, W. Mtangi, and F. D. Auret, *J. Appl. Phys.*, **106**, 043706 (2009)

On the n-type conductivity in ZnO

Possible identifications:

- Zinc interstitial (Zn_I)
- Oxygen vacancy (V_O)
- Impurities (AI,H,Ga,In,Si,...)

However,

- Theory predicts VO to be too deep, and Zn₁ too mobile
- Zn_I not normally observed by other techniques (PL, EPR etc.)
- Several impurities present in most materials, irrespective of growth technique



Example: Shallow donors in ZnO



TABLE II. Al, Ga, In, Ll, Na, and K concentrations in 10¹⁷ cm⁻³ for samples A, B, and C, as determined by SIMS.

	Al	In	Li	Na	Ga, K
A B	$\begin{array}{c} 1.3 \pm 0.1 \\ 1.5 \pm 0.1 \end{array}$	≲0.001 ≲0.001	1.6 ± 0.3 1.9 ± 0.5	≲0.01 ≲0.01	≲0.005 ≲0.005
С	1.3±0.1	≲0.001	0.9±0.1	≲0.01	≲0.005

Hydrothermally grown ZnO samples typically show several shallow donor levels.

- D1~25 meV
- D2~55 meV
- E3~300meV
- Combining TAS, Hall and chemical characterization, and identification can be proposed

R. Schifano, E. V. Monakhov, L. Vines, B. G. Svensson, W. Mtangi, and F. D. Auret, *J. Appl. Phys.*, **106**, 043706 (2009)

Summary TAS

- Steady state technique
 - Measure conductance/capacitance as a function of probing frequency and temperature
- Dominant traps/dopants
- Energy level position
- Quantitative if V_0 , E_f , and N_{eff} is known
- Depth variations can be monitored by changing the reverse bias voltage

Other steady state techniques: Thermally dielectric relaxation current

Suitable to study traps at oxide-semiconductor interface (and in the bulk)

- Apply voltage to fill traps
- Cool down
- Change to discharging voltage to bring capacitor into depletion
- Measure <u>current</u> as the sample is heated up again



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Deep level transient spectroscopy (DLTS)



Deep level transient spectroscopy





Trap concentration



$$C(t) \approx C_{rb} - \Delta C(t)$$
$$\Delta C(t) = \frac{C_{rb}N_T}{2N_d}e^{e_n t}$$

Uniform trap concentration $N_{\rm T}$

$$\frac{\Delta C_{max}}{C_{rb}} = \frac{N_T}{2N_d}$$

Langs DLTS



- Emission rate depend on energy position in band gap
- The fermi level is scanned by varying the temperature

D.V. Lang J. Appl. Phys., vol. 45, p. 3014, 1974.

Langs DLTS



UiO: Universitetet i Oslo Data processing

Today the lock in technique is used instead of box car to use more of the transient. Also other type of weighting functions are used to enhance resolution or supress noice.



The DLTS signal S is formed by multiplying the capacitance transient with a weight function and integrating over the sampling time t_{i} .

$$S = \frac{1}{t_i} \int_0^{t_i} \Delta C(t) w(t) dt$$

Data Processing

- Several time windows are used to form a set of DLTS spectra with different T_{max}



$$\frac{\Delta C}{C} = F \times S = \frac{N_T}{2N_d}$$

S= DLTS signal

Extracting activation energy

$$e_{n} = \sigma_{n} v_{n}^{thermal} N_{C} X_{n} exp\left(-\frac{H_{C} - H_{T}}{kT}\right) = \sigma_{n} \beta T^{2} exp\left(-\frac{H_{C} - H_{T}}{kT}\right)$$



Sensitivity and limitation

Assume:

 $N(t) \approx N_T e^{e_n(t)}$

- Only valid for: ΔC <10-20% C
- Limits the quantification of trap concentrations.

$$\frac{\Delta C}{C} = -\frac{1}{N_d W^2} \int_{W(0)}^{W(V)} x \Delta x$$

- Sensitivity increase with depth
- Motion within space charge region can be detected
- Since sensitivity is related to N_d, DLTS is very sensitive and trap concentrations down to 10⁸ cm⁻³ can be measured

Field enhanced emission:



Poole-Frenkel

- $ln(e_n)$ vs. \sqrt{E} should be linear
- occurs for <u>charged</u> defect states only (e.g. donors in n-type material)

Phonon-assisted tunnelling

In(e_n) vs. E² should be linear

Direct tunnelling

- For electric fields > 8 × 10⁷ V/m
- Relevant in highly doped
 material

Capture cross section



Filling of a trapped charge is $N_T f \cong N_T [1 - e^{-c_n t}]$

 By varying the pulse width duration the capture coeff. is obtained

$$c_{n,p} = \sigma_{n,p} v_{n,p}^{thermal}$$

Trap concentration profiles

By changing the filling pulse height it is possible to assess different depths in the sample.



 λ -effect



 The actual probing volume is shifted a distance, λ, compared to the depletion region

$$\lambda = \sqrt{\frac{2\epsilon(E_f - E_T)}{q^2 N_d}}$$

The DLTS system



Minority carrier traps (ODLTS/MCTS)

- Conventional DLTS only probe majority carrier traps
- Minority carrier traps can be probed by
 - Optical injection of minority charge; illumination during filling pulse
 - Electrical injection; forward bias during filling pulse



Example: Electrically active defects in n-type ZnO



- 1) EV Monakhov, AY Kuznetsov, BG Svensson, J. Phys. D, 42, 153001 (2009)
- 2) V. Quemener, L Vines, EV Monakhov, BG Svensson, Appl. Phys. Lett. (2011)

The E2 (Ec-0.2eV) and E4 defects (Ec-0.58eV)



V. Quemener L. Vines and B.G. Svensson, Appl. Phys. Lett., 100, 112108 (2012)

Assignment of E2 (E_c-0.2 eV)

- Increases in O-rich/removes in Zn-rich
- Poole-Frenkel effect
 - Donor like defect



Quemener et al., Appl. Phys. Lett., 102, 232102 (2013)

Assignment of E2 (E_c-0.19 eV)



- Clear correlation between the E2 and the iron concentration
- E2 corresponds of about 30% of the Fe concentration in each sample
- Iron remain constant with the annealing conditions

 Fe_{Zn}^{2+} limits change in the defect configuration

- Expected as a donor in ZnO with ionization energy of $\sim 0.24 \pm 0.05 \text{eV}^{-2}$

1)Quemener et al., *Appl. Phys. Lett.*,**102**, 232102 (2013) 2)Y.Jiang et al., J. Appl. Phys., 101, 093706 (2007)

Assignment of E4

- Increases in Zn-rich/decreases in O-rich
 - V_O, Zn_i, Zn_O
- Concentration remains constant

- Thermal equilibrium is reached

$$c/N_{sites} = \exp\left(-E_{form}/kT\right)$$



Quemener et al., Appl. Phys. Lett., 102, 232102 (2013)

- Often the dominant deep level defect
- Observed in all materials irrespective of growth technique
- Not influenced by electron/proton irradiation or heavy ion implantation
- Large variations in E3 between samples
- Post growth annealing do not alter [E3] significantly



- Observed in all samples irrespective of growth technique
- Not influenced by electron or heavy ion irradiation

But,

- Increase after hydrogen implantation
- \rightarrow H related



A. Hupfer, C. Bhoodoo, L. Vines and B.G. Svensson, Appl. Phys. Lett. 104, 092111 (2014)

 The increase in E3 is not stable, reach equilibrium concentration after a few days at RT



A. Hupfer, C. Bhoodoo, L. Vines and B.G. Svensson, Appl. Phys. Lett. 104, 092111 (2014)

- The increase in E3 is not stable, reach equilibrium concentration after a few days at RT
- \rightarrow Low dissociation barrier
- → Dissociation will release H, which later can passivate acceptor
 - → May explain the lack of stability of p-type dopants



A. Hupfer, C. Bhoodoo, L. Vines and B.G. Svensson, Appl. Phys. Lett. 104, 092111 (2014)

Deep defects - E5 and E6



Defect levels around 1.0 and 1.2 eV below Ec:

- Introduced through polishing
 - Removed by etching/H passivation
- Form after ion implantation irradiation
 - Dose dependant
 - Redistribution after 410K anneal (during DLTS scan)
- PAS indicate vacancy related clusters prevail after polishing ³⁾

1)Quemener et al., *Appl. Phys. Lett.*, **99**, 112112 (2011) 2)Vines et al., *Appl. Phys Lett.*, **100**, 212106 (2012) Intrinsic (vacancy related?)

3)Selim et al., *Phys. Rev. Lett.*, **99**, 085502 (2007)

Electrically active defects in n-type ZnO



Formation and annealing kinetics of V_2 and V_2O in Si

At elevated temperatures V_2 in Si can migrate and form V_2O .

 $V_2 + O_i \rightarrow V_2O$

The diffusivity of V_2 and formation of V_2O can be studied by DLTS



N. Ganagona, L. Vines, E.V. Monakhov, B.G. Svensson, *J.App. Phys.*, **115**, 034514 (2014)

Formation and annealing kinetics of V_2 and V_2O in Si

At elevated temperatures V_2 in Si can migrate and form V_2O .

 $V_2 + O_i \rightarrow V_2O$

The diffusivity of V_2 and formation of V_2O can be studied by DLTS

Diffusivity of V₂ is given by: (1.5 ± 0.7) × $10^{-3}e^{-(1.31\pm0.03)eV/kT}$

N. Ganagona, L. Vines, E.V. Monakhov, B.G. Svensson, J.App. Phys., 115, 034514 (2014)



Summary DLTS

- DLTS can be used to extract
 - Energy level position, apparent capture cross section, trap concentration and depth distribution
- Sensitive technique, down to 10⁸cm⁻³ traps can be detected, depending on doping conc.
- Require a good Schottky/pn-junction