ECE 4813

Semiconductor Device and Material Characterization

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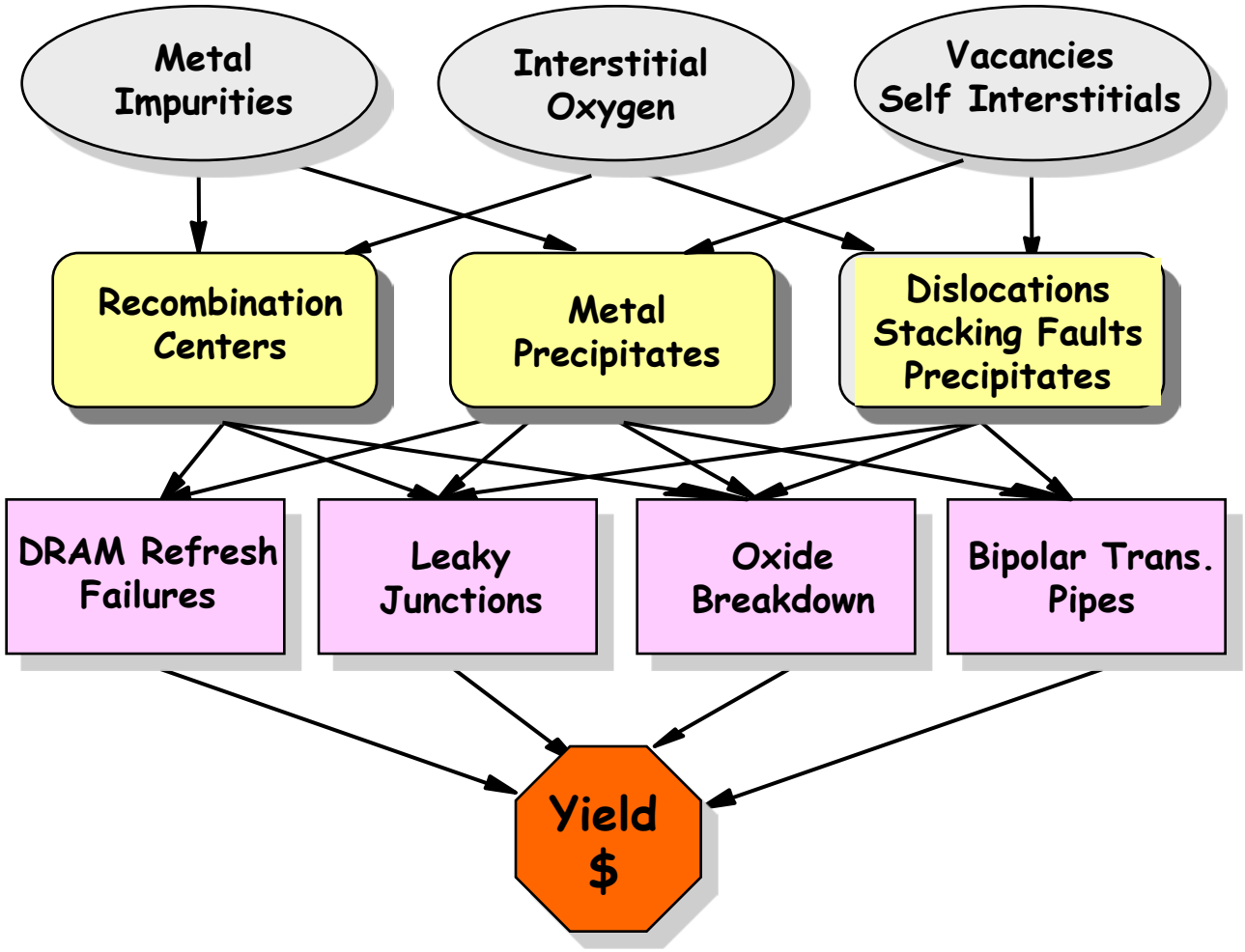
As with all of these lecture slides, I am indebted to Dr. Dieter Schroder from Arizona State University for his generous contributions and freely given resources. Most of (>80%) the figures/slides in this lecture came from Dieter. Some of these figures are copyrighted and can be found within the class text, *Semiconductor Device and Materials Characterization*. ***Every serious microelectronics student should have a copy of this book!***

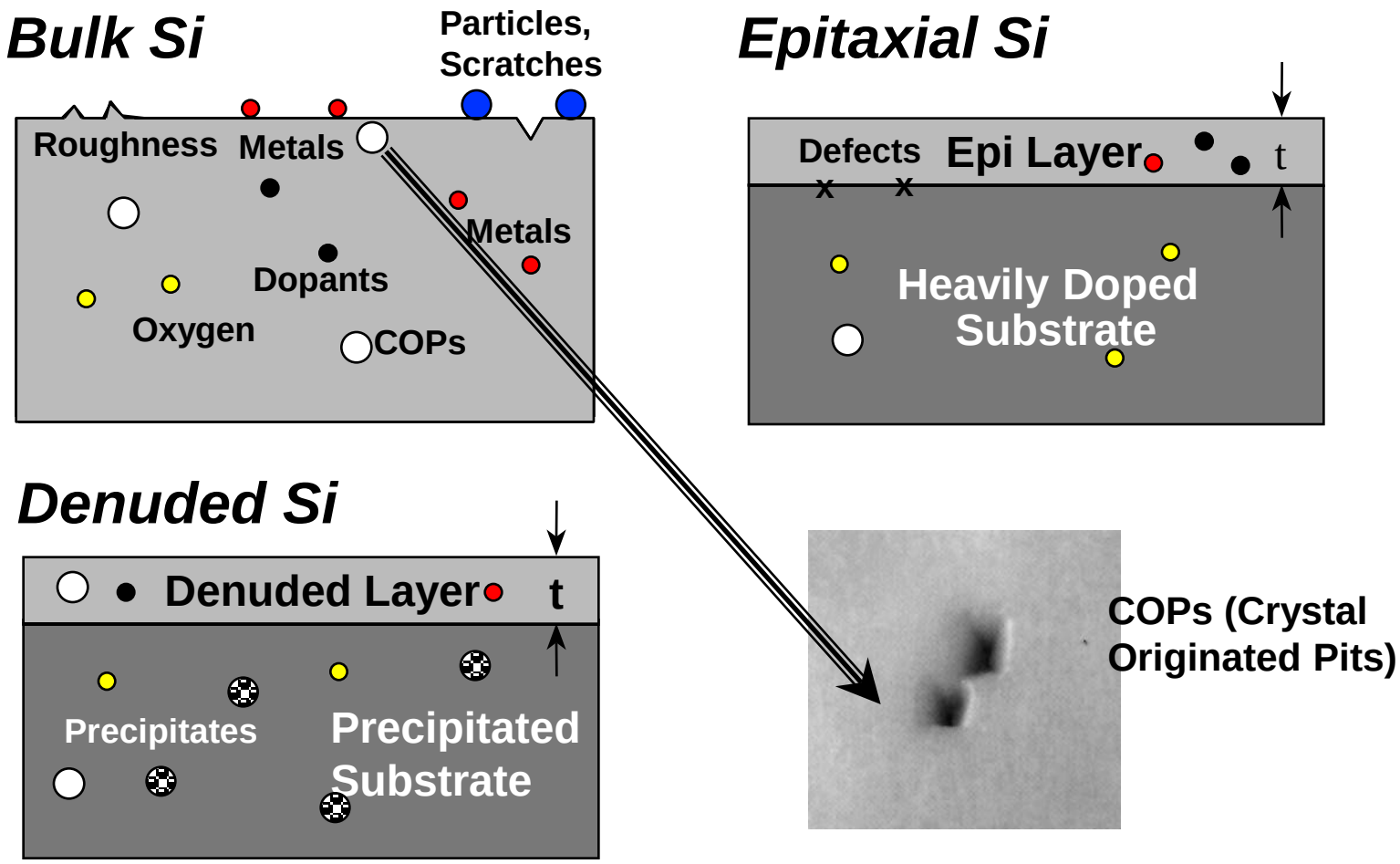
Defects

Types of Defects
Defect Etching
Generation – Recombination
Capacitance Transients
Deep Level Transient Spectroscopy

Defects and Yield



Wafer Defects



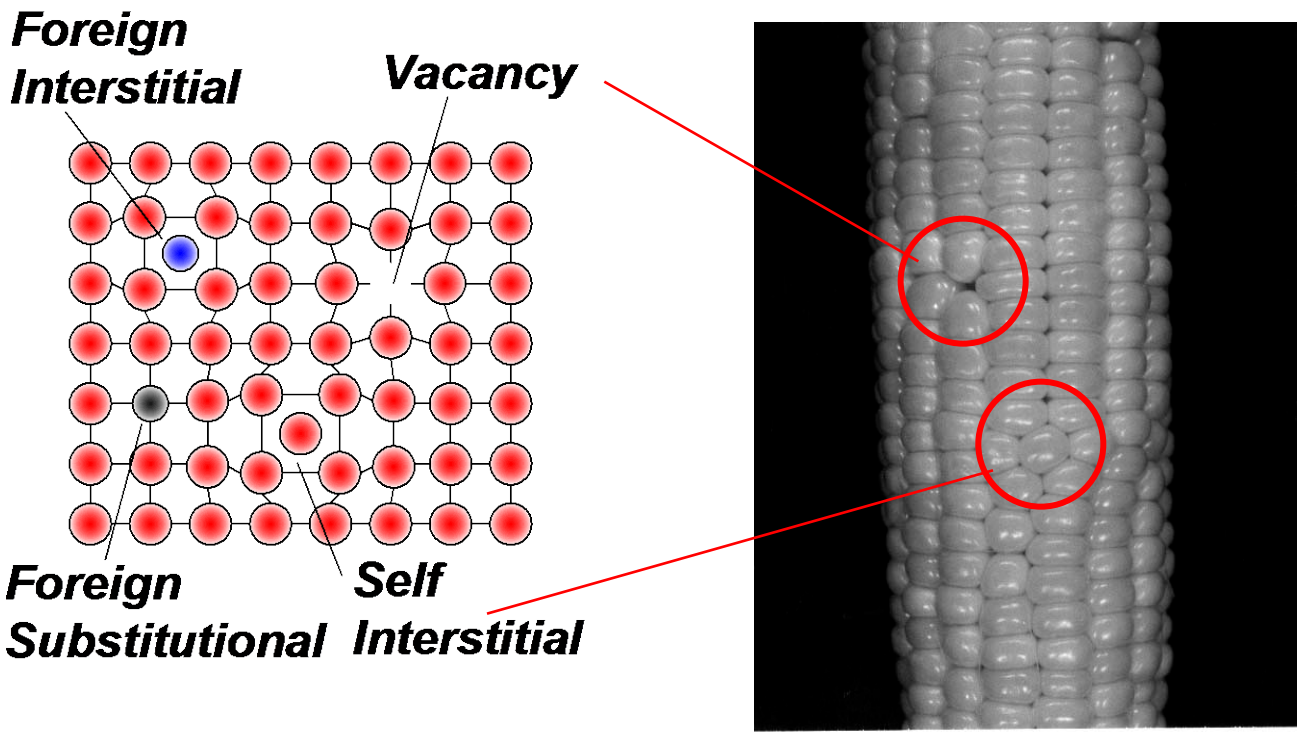
Defect Types

- Particles
- Residues
- Organics
- Light Metals
  - Alkali Metals, *e.g.*, Na
- Metals
  - Cu*, Fe*, Cr*, Ni*, Zn, Ca, Al (* Most important?)
- Crystal Originated Pits (COPs)
- Surface Roughness

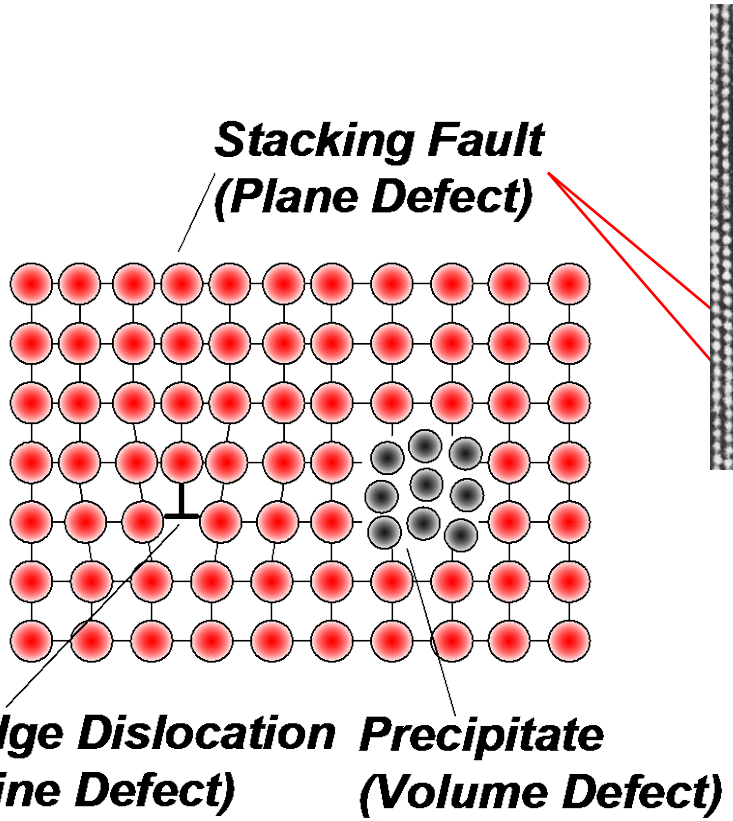
Defect Sources

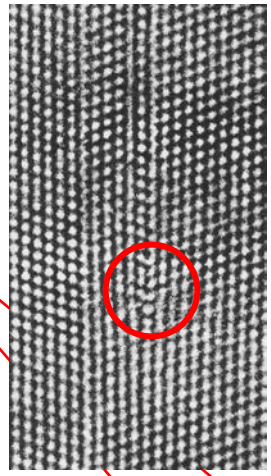
- Silicon Starting Material
- Silicon Growth
- Wafer Sawing, Polishing
- Wafer Packaging, Shipping
- Wafer Cleaning
- Liquids, Gases
- Oxidation, Diffusion
- Photoresist
- Ion Implantation
- Sputter Deposition
- Process Equipment
- Epitaxial Growth
- Reactive Ion Etching
- Polymer Containers/Pipes
- Door Hinges
- Light Switches
- Ball Bearings
- People

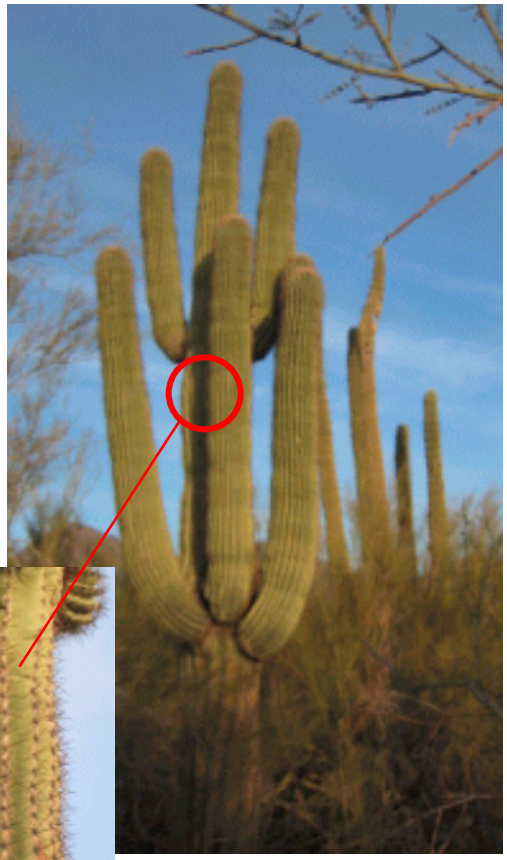
Point Defects

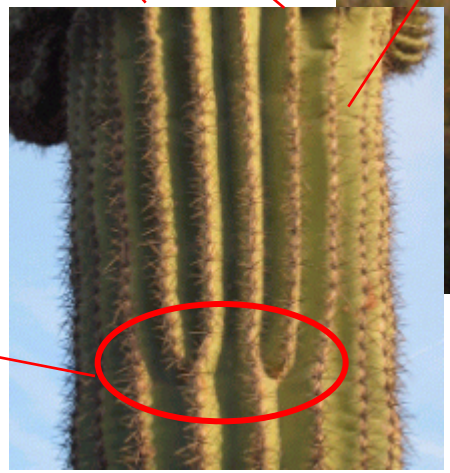


Line, Plane, Volume Defects



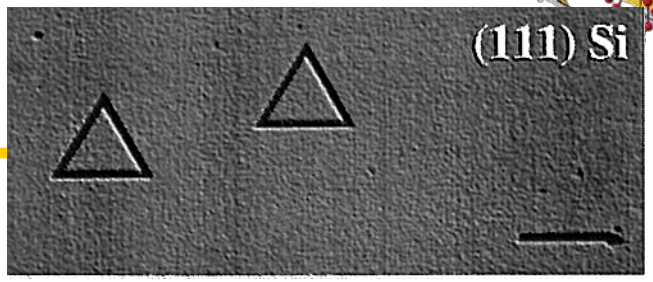


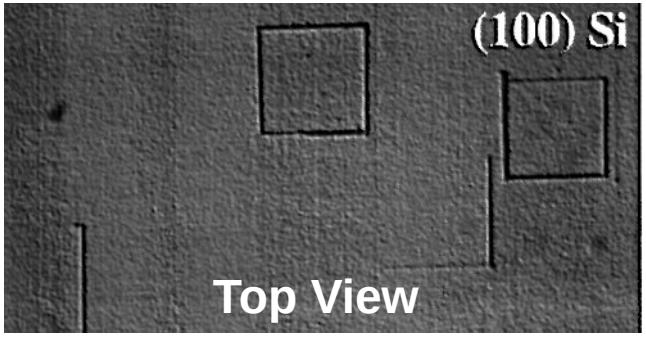


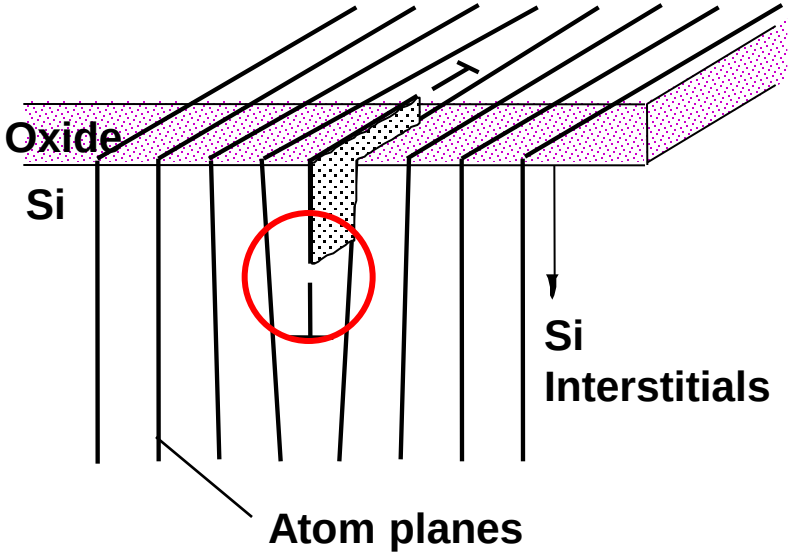


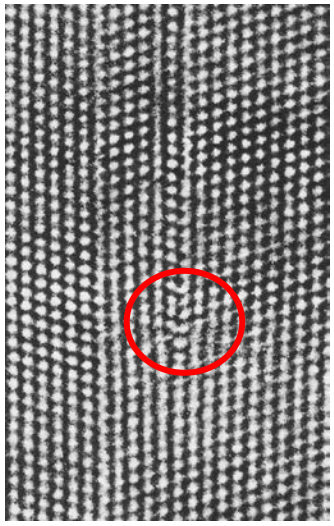
Stacking Faults

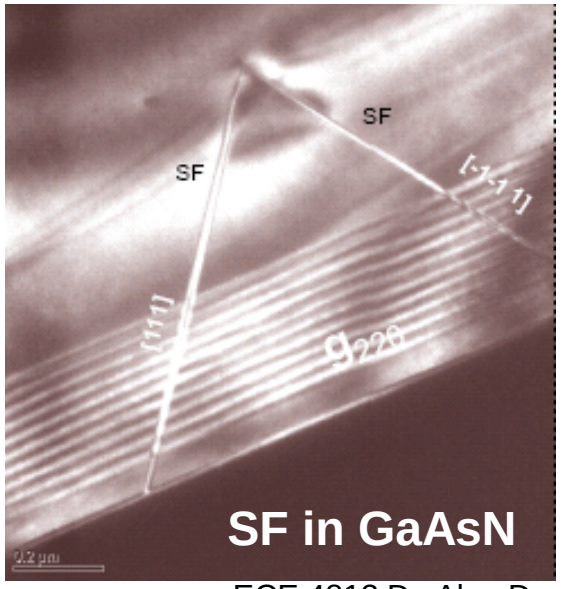
- Oxidation-induced SFs: Si interstitials are generated during oxidation and forced into the substrate
- SFs can also be generated at substrate/epi interfaces





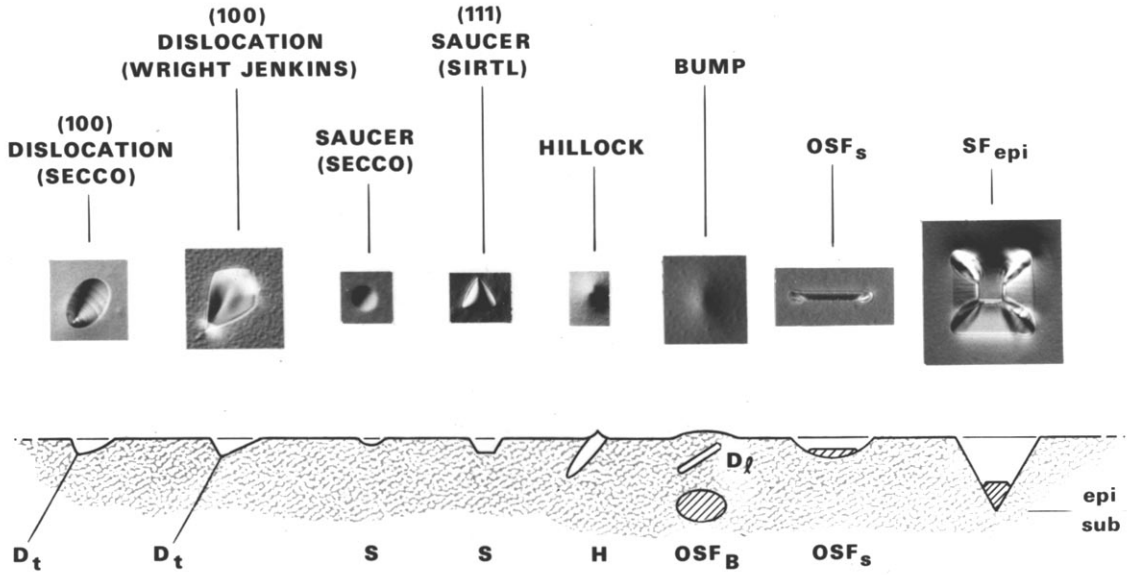






Defect Etching

- **Certain etches attack defective regions allowing defect identification (etch recipes given at end of notes)**

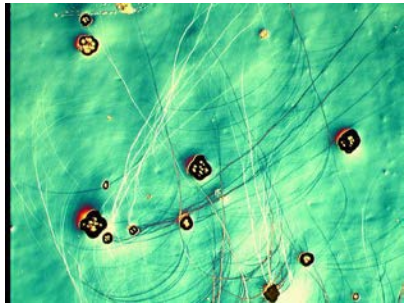


D.C. Miller and G.A. Rozgonyi, "Defect Characterization by Etching, Optical Microscopy, and X-Ray Topography," in *Handbook on Semiconductors* **3** (S.P. Keller, ed.) North-Holland, Amsterdam, 1980, 217-246. ASTM Standards F47 and F26, *1997 Annual Book of ASTM Standards*, Am. Soc. Test. Mat., West Conshohocken, PA, 1997.

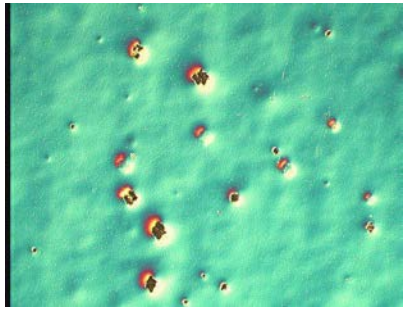
Defect Etching

- Different etches attack defective regions differently
- Can be accentuated through copper decoration

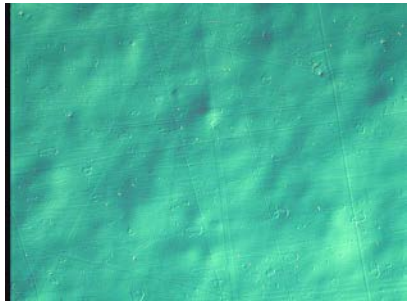
A Defects - Interstitials



Secco



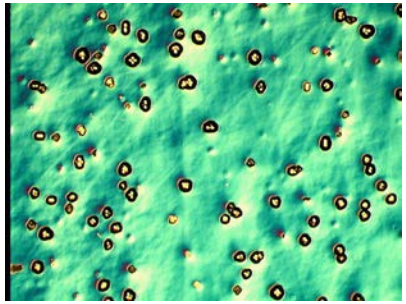
Wright



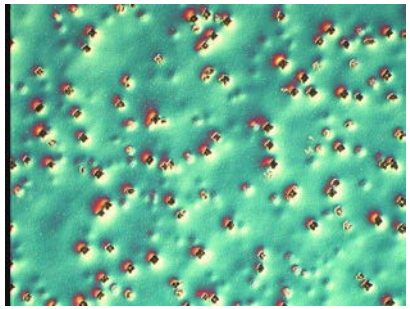
A Defects: $HF+HNO_3$

A Defects: $HF+HNO_3+H_3PO_4$

D Defects - Vacancies



Secco



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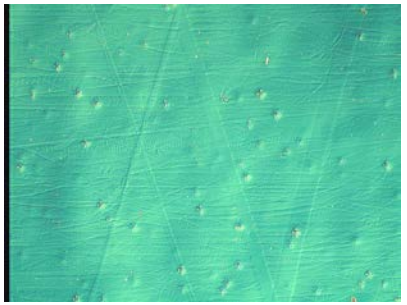
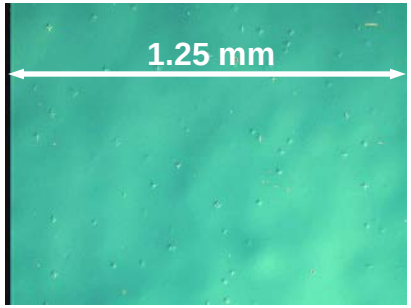


$HF+HNO_3$



$HF+HNO_3+H_3PO_4$

Micrographs courtesy of M.S. Kulkarni, MEMC (*J. Electrochem. Soc.* **149,** G153, Feb. 2002**)**

Defect Etch References

[1] E. Sirtl and A. Adler, "Chromic Acid-Hydrofluoric Acid as Specific Reagents for the Development of Etching Pits in Silicon," *Z. Metallkd.* 52, 529-534, Aug. 1961.

[2] W.C. Dash, "Copper Precipitation on Dislocations in Silicon," *J. Appl. Phys.* 27, 1193-1195, Oct. 1956; "Evidence of Dislocation Jogs in Deformed Silicon," *J. Appl. Phys.* 29, 705-709, April 1958.

[3] F. Secco d'Aragona, "Dislocation Etch for (100) Planes in Silicon," *J. Electrochem. Soc.* 119, 948-951, July 1972.

[4] D.G. Schimmel, "Defect Etch for <100> Silicon Ingot Evaluation," *J. Electrochem. Soc.* 126, 479-483, March 1979; D.G. Schimmel and M.J. Elkind, "An Examination of the Chemical Staining of Silicon," *J. Electrochem. Soc.* 125, 152-155, Jan. 1978.

[5] M.W. Jenkins, "A New Preferential Etch for Defects in Silicon Crystals," *J. Electrochem. Soc.* 124, 757-762, May 1977.

[6] K.H. Yang,"An Etch for Delineation of Defects in Silicon," *J. Electrochem. Soc.* 131, 1140-1145, May 1984.

[7] H. Seiter, "Integrational Etching Methods," in Semiconductor Silicon/1977 (H.R. Huff and E. Sirtl, eds.), Electrochem. Soc., Princeton, NJ, 1977, pp. 187-195.

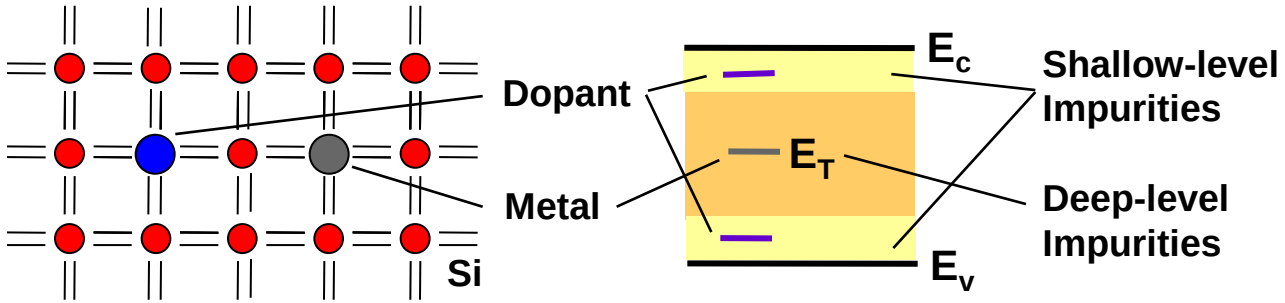
[8] K. Graff and P. Heim, "Chromium-Free Etch for Revealing and Distinguishing Metal Contamination Defects in Silicon," J. Electrochem. Soc. 141, 2821-2825, Oct. 1994.

[9] M. Ishii, R. Hirano, H. Kan and A Ito, "Etch Pit Observation of Very Thin {001}-GaAs Layer by Molten KOH," *Japan. J. Appl. Phys.* 15, 645-650, April 1976; for a more detailed discussion of GaAs Etching see D.J. Stirland and B.W. Straughan, "A Review of Etching and Defect Characterisation of Gallium Arsenide Substrate Material," *Thin Solid Films* 31, 139-170, Jan. 1976.

[10] D.T.C. Huo, J.D. Wynn, M.Y. Fan and D.P. Witt, "InP Etch Pit Morphologies Revealed by Novel HCl-Based Etchants," *J. Electrochem. Soc.* 136, 1804-1806, June 1989.

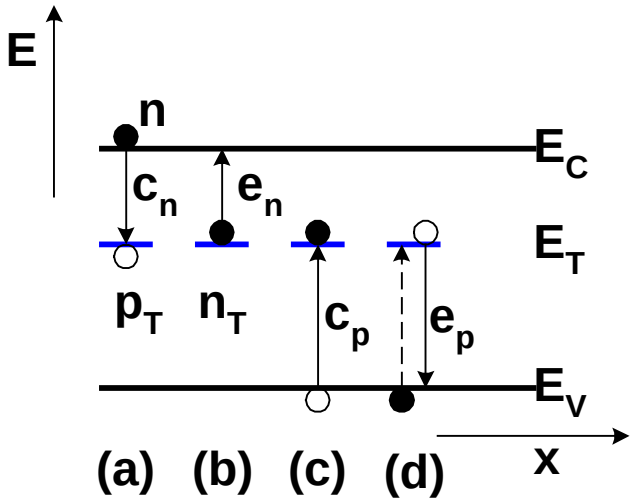
Impurities or Defects

- Shallow-level impurities (dopants) - measure *optically*
  - Photoluminescence
  - Photoelectron spectroscopy
- Deep-level impurities (metals) - measure *electrically*
  - Deep level transient spectroscopy (DLTS)
- Need to determine
  - Impurity density, N_T
  - Impurity energy level, E_T
  - Capture Cross section σ_T



Generation-Recombination

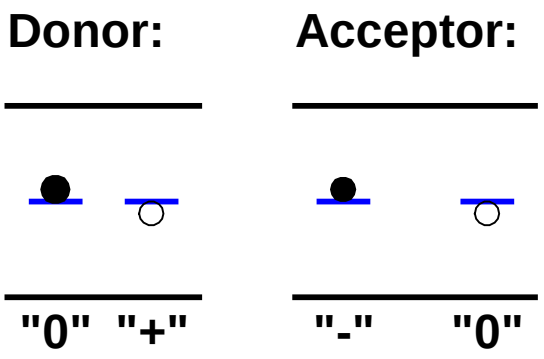
- Consider a semiconductor with a deep-level impurity at energy $E = E_T$
- Electrons and holes can be captured and emitted
- Capture is characterized by the capture coefficients c_n & c_p
  - $c_n = \sigma_n v_{th}$ where σ_n is the capture cross section [cm^2] and v_{th} is the thermal velocity of electrons. Similarly for holes.
- Emission is characterized by emission rates e_n and e_p
- The electron (n_T) and hole (p_T) occupation is also needed



$$n_T + p_T = N_T$$

Donors and Acceptors

- G-R centers can be *donors* or *acceptors*
- The charge state is :

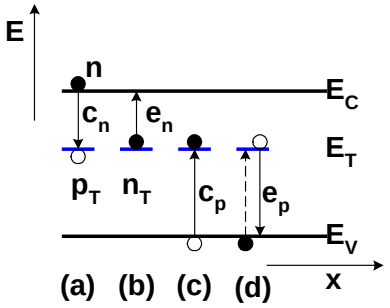


Carrier Statistics

- The change in electron and hole densities *n* and *p* is

$$\left.\frac{dn}{dt}\right|_{G-R} = (b)-(a) = e_n n_T - c_n n p_T$$

$$\left.\frac{dp}{dt}\right|_{G-R} = (d)-(c) = e_p p_T - c_p p n_T$$



- The change in trap density is

$$\left.\frac{dn_T}{dt}\right|_{G-R} = \frac{dp}{dt} - \frac{dn}{dt} = (c_n n + e_p)(N_T - n_T) - (c_p p + e_n)n_T$$

- This equation is difficult to solve because, in general, we do not know *n* and *p*

Carrier Statistics

- Solving the dn_T/dt equation gives

$$n_T(t) = n_T(0)\exp(-t/\tau) + \frac{(e_p + c_n n)N_T}{e_n + c_n n + e_p + c_p p}\left(1 - \exp(-t/\tau)\right)$$

$$\tau = \frac{1}{e_n + c_n n + e_p + c_p p}$$

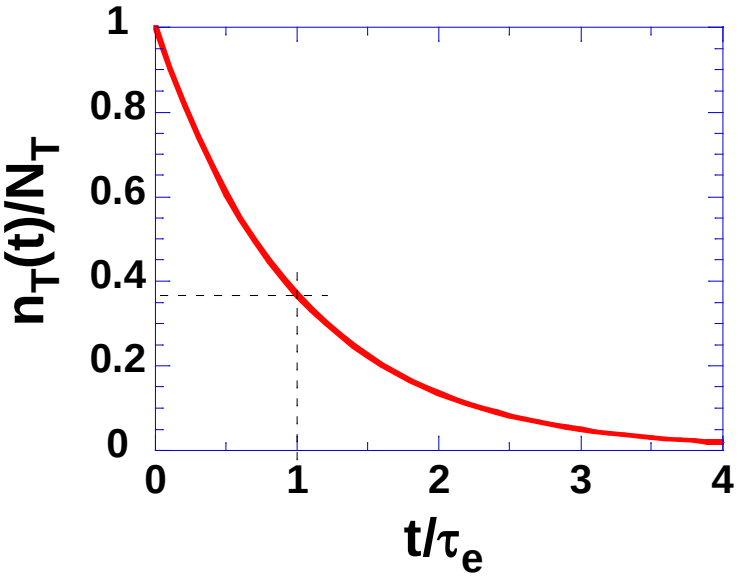
- Now consider an *n*-type semiconductor with electron capture and emission only

$$n_T(t) = \underbrace{n_T(0)\exp(-t/\tau_1)}_{\text{emission}} + \underbrace{\frac{c_n n}{e_n + c_n n} N_T\left(1 - \exp(-t/\tau_1)\right)}_{\text{capture}} \quad ; \quad \tau_1 = \frac{1}{e_n + c_n n}$$

Electron Emission

- **Simplifying Assumptions:**
  - **All G-R centers are *occupied* by electrons for $t < 0$**
  - **For $t \geq 0$, electrons are emitted**

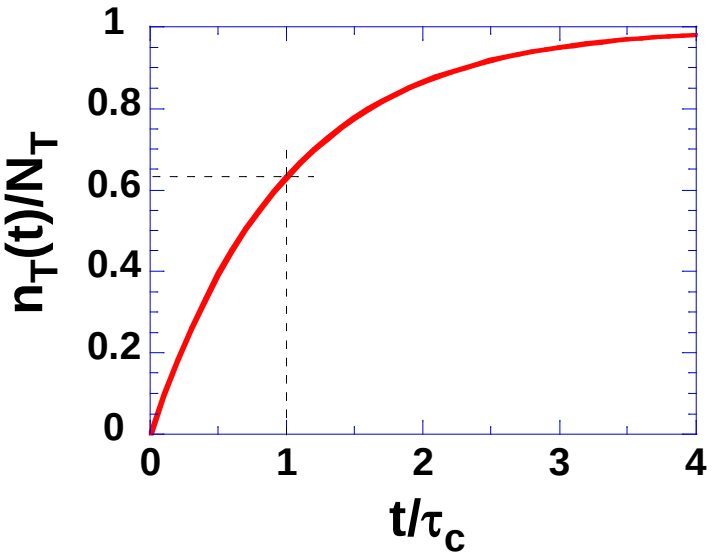
$$n_T(t) \approx n_T(0)\exp(\frac{-t}{\tau_e}) \approx N_T \exp(\frac{-t}{\tau_e});\ \tau_e = \frac{1}{e_n}$$



Electron Capture

- **Simplifying Assumptions:**
  - **All G-R centers are *empty* of electrons for $t < 0$**
  - **For $t \geq 0$, electrons are captured**

$$n_T(t) = n_T(0)\exp\left(\frac{-t}{\tau_c}\right) + N_T\left(1-\exp\left(\frac{-t}{\tau_c}\right)\right) \approx N_T\left(1-\exp\left(\frac{-t}{\tau_c}\right)\right);\ \tau_c = \frac{1}{c_n n}$$



Steady State

- We have assumed that all G-R centers are either completely occupied by electrons or completely empty
- From

$$n_T(t) = n_T(0)\exp(\frac{-t}{\tau}) + \frac{(e_p + c_n n)N_T}{e_n + c_n n + e_p + c_p p}\left(1 - \exp(\frac{-t}{\tau})\right)$$

- For Steady state, $t \to \infty$

$$n_T = \frac{e_p + c_n n}{e_n + c_n n + e_p + c_p p} N_T$$

… trap occupancy is a weighted average of the capture and emission rates.

- For $n \approx p \approx 0$ in the space-charge region

$$n_T = \frac{e_p}{e_n + e_p} N_T$$

… depletion region trap occupancy is a weighted average of only the emission rates.

- For G-R centers in the *lower* half of the band gap, $e_n << e_p$

$$n_T \approx N_T$$

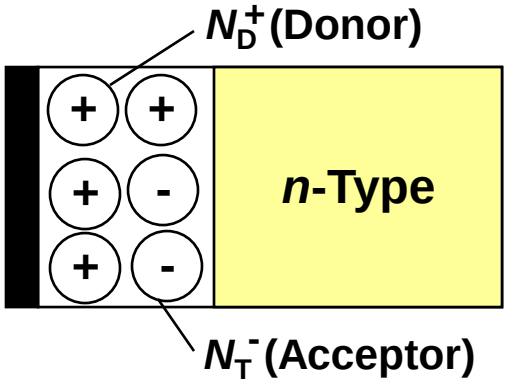
… traps in the lower ½ bandgap tend to fill up

Capacitance Transient

- When carriers are captured or emitted, the charge changes with time
- Can detect this by measuring current, capacitance, or charge
- *Capacitance* is most commonly measured

$$C = A\sqrt{\frac{qK_s\varepsilon_0 N_{scr}}{2(V_{bi}-V)}}$$

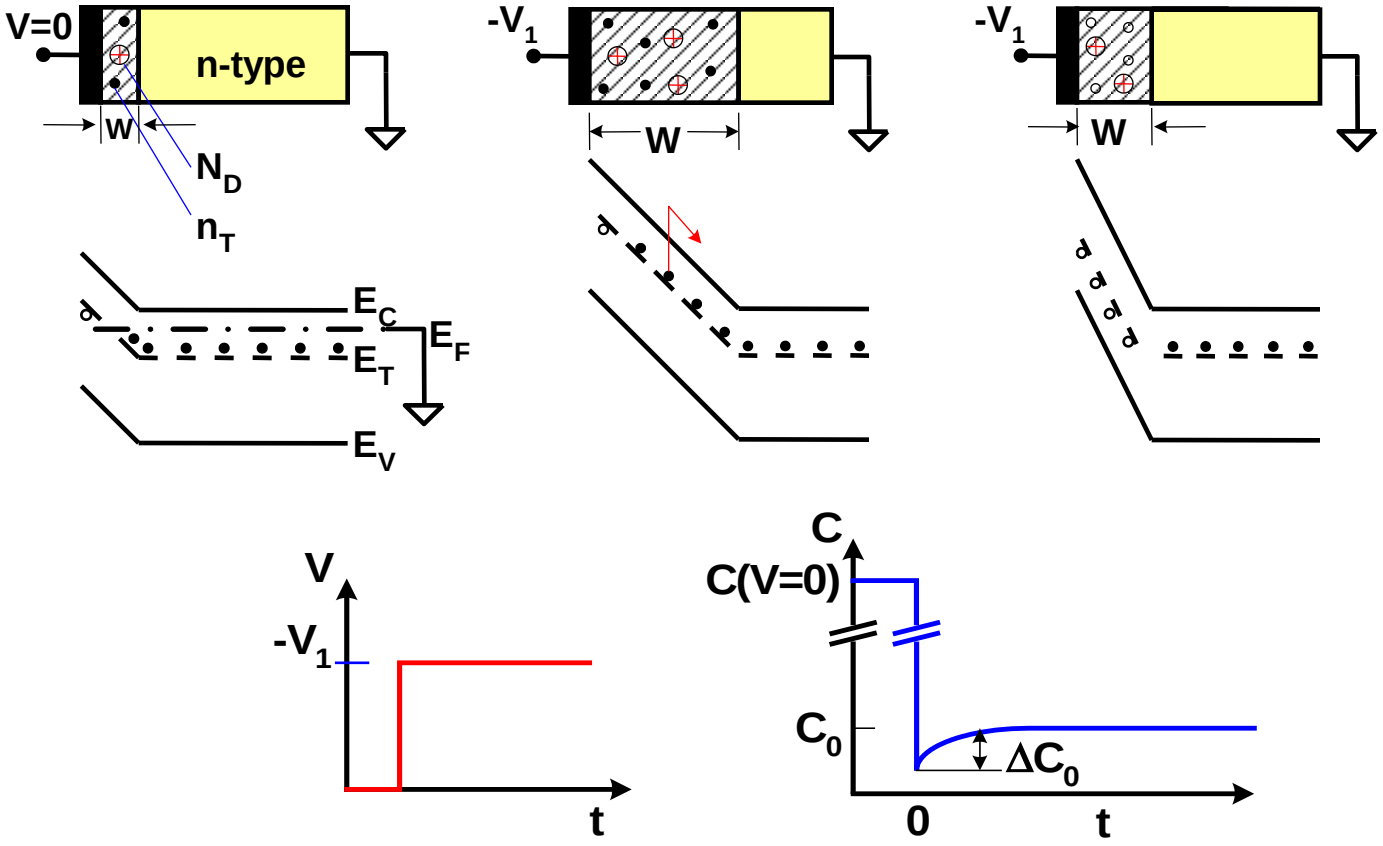
- N_{scr} is the *total* charge in the space-charge region ***<u>including both dopants and defects</u>***



$$N_{scr} = N_D^+ - N_T^-$$

Capacitance Emission Transient

- The Schottky diode is zero biased
- Assume all G-R centers are filled with electrons
- The diode is reverse biased
- Electrons are emitted from the G-R centers



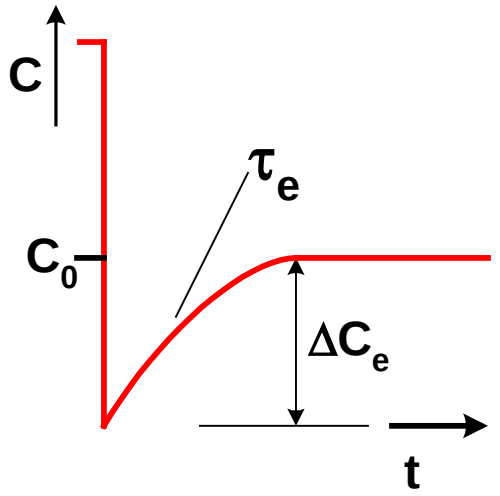
Capacitance Emission Transient

$$C(t) = A\sqrt{\frac{qK_s\varepsilon_0(N_D - n_T(t))}{2(V_{bi} - V)}} = C_0\sqrt{1 - \frac{n_T(t)}{N_D}};\ C_0 = A\sqrt{\frac{qK_s\varepsilon_0 N_D}{2(V_{bi} - V)}}$$

- Usually $N_T << N_D$

$$C(t) \approx C_0\left(1 - \frac{n_T(t)}{2N_D}\right) = C_0\left(1 - \frac{n_T(0)}{2N_D}\exp\left(\frac{-t}{\tau_e}\right)\right)$$

$$C(t=\infty) - C(t=0) = \frac{n_T(0)}{2N_D}C_0 = \Delta C_e$$



Capacitance Transient

- What information is contained in the capacitance transient?
- In thermal equilibrium *dn/dt* = *dp/dt* =0

$$e_{n0}n_{T0} = c_{n0}n_0p_{T0} = c_{n0}n_0(N_T - n_{T0})$$

$$n_0 = n_i \exp\left(\frac{(E_F - E_i)}{kT}\right); \quad n_{T0} = \frac{N_T}{1+\exp((E_T - E_F)/kT)} = N_T f(E_T)$$

- For $E_F = E_T$, $n_{T0} = N_T/2 = p_{T0}$, $n = n_1$

$$e_{n0} = c_{n0}n_1 = c_{n0}n_i \exp\left(\frac{E_T - E_i}{kT}\right) = c_{n0}N_C \exp\left(\frac{-(E_C - E_T)}{kT}\right)$$

Capacitance Transient

- **Then assume non-equilibrium emission and capture rates remain equal to their equilibrium values:**
  $e_{n0} = e_n$ and $e_{p0} = e_p$

$$e_n = c_n n_1; \quad e_p = c_p p_1$$

$$n_1 = N_C \exp\left(-\frac{E_C - E_T}{kT}\right); \quad p_1 = N_V \exp\left(-\frac{E_T - E_V}{kT}\right)$$

N1 and p1 describe the trap occupancy for electrons and holes

Capacitance Transient

- **Then assume non-equilibrium emission and capture rates remain equal to their equilibrium values:**

$$\tau_e = \frac{1}{e_n} = \frac{1}{c_n n_1}$$
$$= \frac{\exp\left(\left(E_c - E_T\right)/kT\right)}{\sigma_n \nu_{th} N_c}$$
$$= \frac{\exp\left(\left(E_c - E_T\right)/kT\right)}{\sigma_n K_1 T^{1/2} K_2 T^{3/2}}$$
$$= \frac{\exp\left(\left(E_c - E_T\right)/kT\right)}{\sigma_n \gamma_n T^2}$$

…where K_1 and K_2 are temporary constants used in the derivation

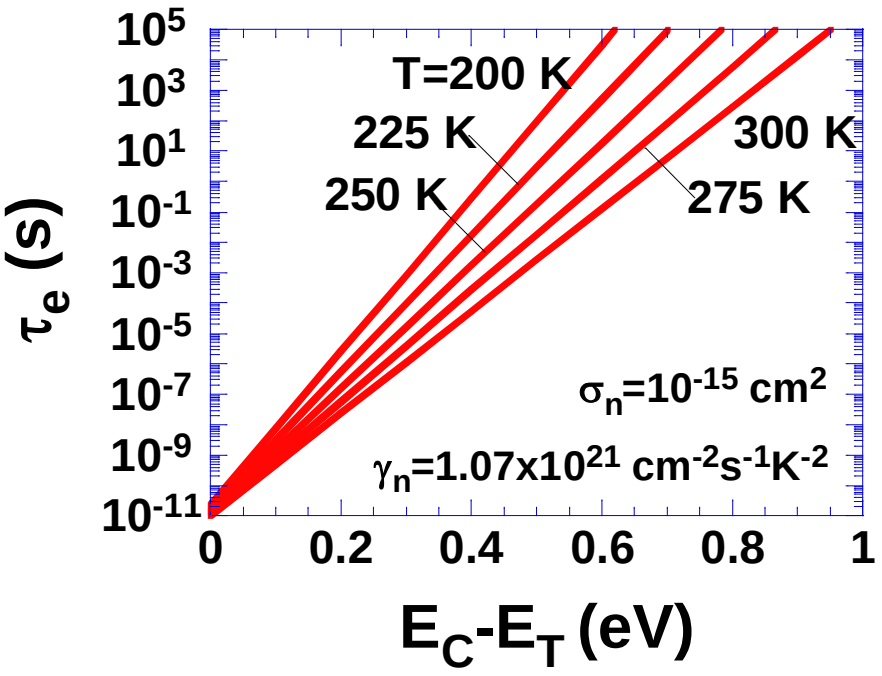
…where $\gamma_n = K_1 K_2 = 3.25 \times 10^{21} (m_n/m_o)$ $cm^{-2}s^{-1}K^{-2}$ is a constant derived from the temperature independent part of the thermal velocity and effective density of states.

where $N_c = 2\left(\frac{2\pi m_n kT}{h^2}\right)^{3/2}$, $\nu_{th} = \left(\frac{3kT}{m_n}\right)^{1/2}$

$$\tau_e = \frac{\exp\left(\left(E_c - E_T\right)/kT\right)}{\gamma_n \sigma_n T^2}$$

Emission Time Constant

$$\tau_e = \frac{\exp((E_c - E_T)/kT)}{\sigma_n \gamma_n T^2}$$



One can normalize this temperature variation by plotting $\ln(T^2\tau_e)$ instead of $\ln(\tau_e)$

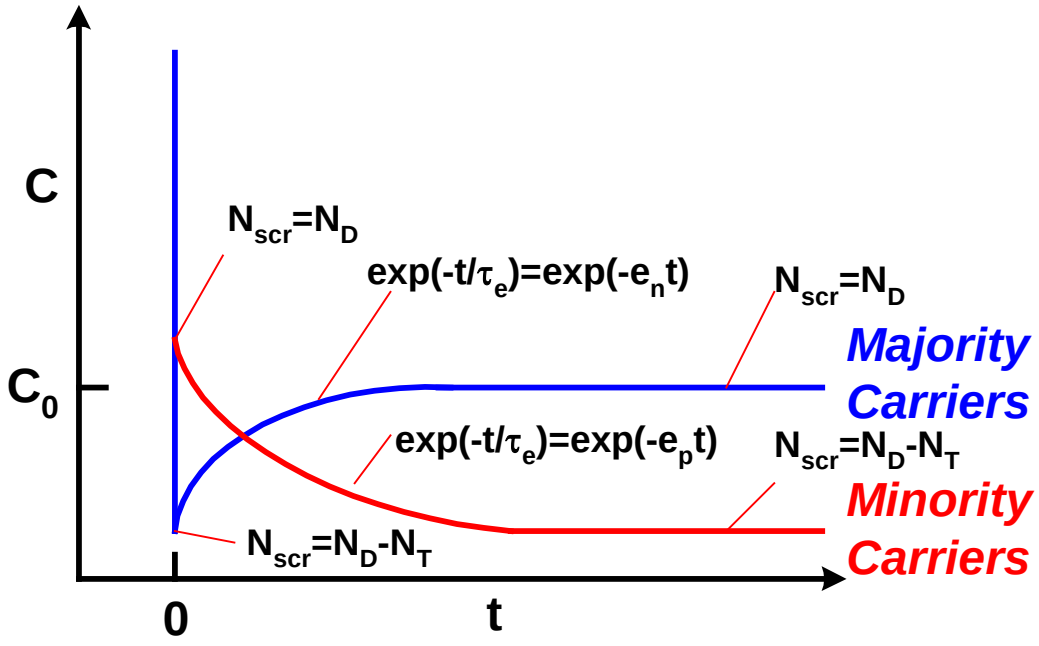
Minority Carrier Emission

- For majority carrier emission from acceptor impurities

$$N_{scr}(t=0)=N_D-N_T;\quad N_{scr}(t\to\infty)=N_D$$

- For minority carrier emission from acceptor impurities

$$N_{scr}(t=0)=N_D;\quad N_{scr}(t\to\infty)=N_D-N_T$$



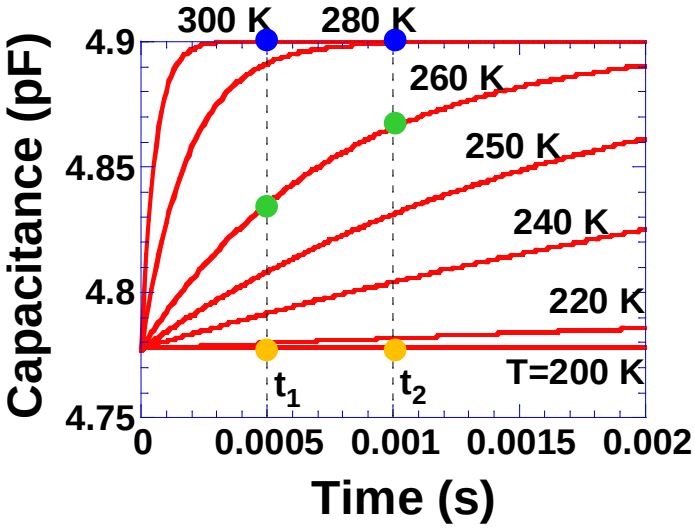
Deep-Level Transient Spectroscopy (DLTS)

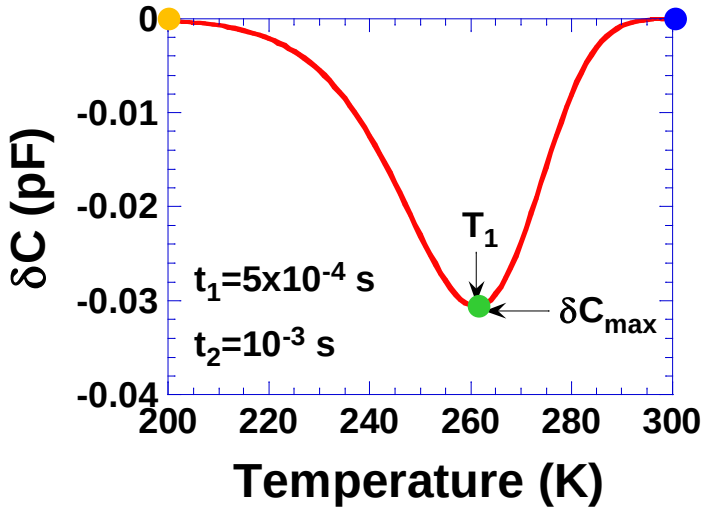
- DLTS is a method to automate the capacitance transient

$$C(t) = C_0\left[1 - \frac{n_T(0)}{2N_D}\exp\left(\frac{-t}{\tau_e}\right)\right]$$

- Measure C at $t = t_1$ and $t = t_2$, then subtract

$$\delta C = C(t_1) - C(t_2) = \frac{C_0 n_T(0)}{2N_D}\left(\exp\left(\frac{-t_2}{\tau_e}\right) - \exp\left(\frac{-t_1}{\tau_e}\right)\right)$$





DLTS

$$\delta C = C(t_1) - C(t_2) = \frac{C_0 n_T(0)}{2N_D}\left(\exp\left(\frac{-t_2}{\tau_e}\right) - \exp\left(\frac{-t_1}{\tau_e}\right)\right)$$

$$\tau_e = \frac{\exp\left((E_c - E_T)/kT\right)}{\sigma_n \gamma_n T^2}$$

- Differentiate δC with respect to T, set equal to zero and solve for τ_e

$$\tau_{e,\max} = \frac{t_2 - t_1}{\ln(t_2/t_1)}$$

- Now we have $\tau_{e,max}$ and T_1

- ***Each DLTS temperature scan (peaks in spectra) result in only one emission time constant-temperature pair. Several such scans are needed to be plotted in an Arrhenius plot***

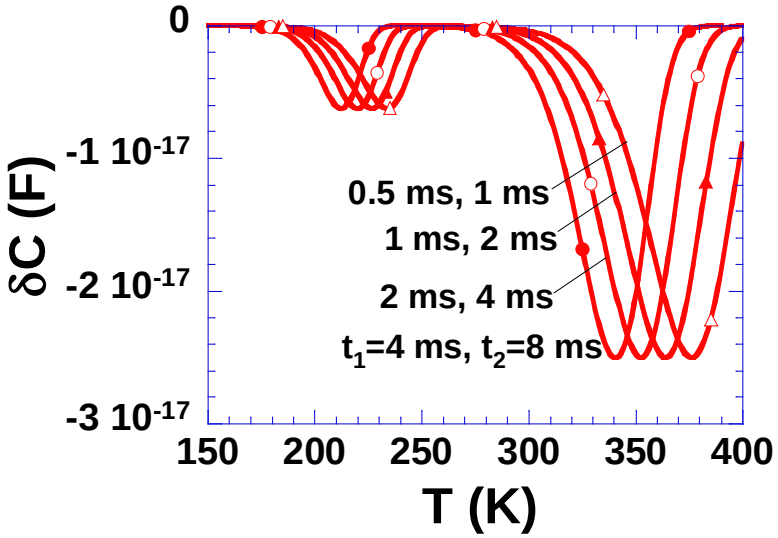
DLTS

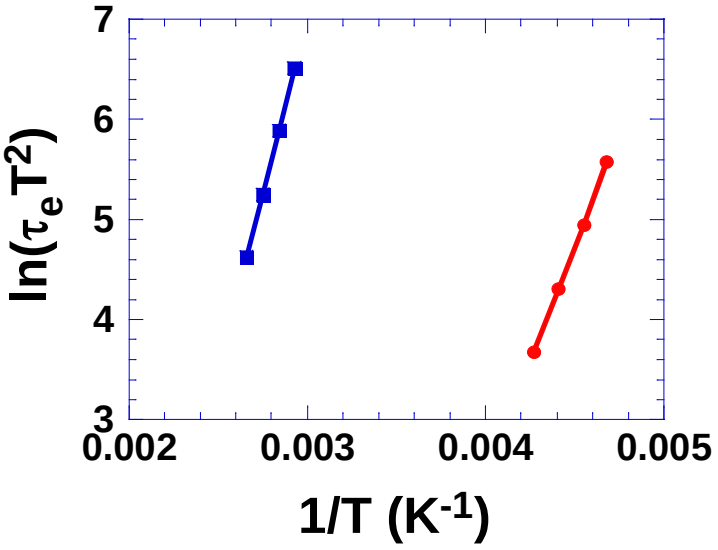
- DLTS plots are made for various t_1/t_2 ratios
- Determine $\tau_{e,max}$ and T_1 for each curve
- Plot $ln(\tau_{e,max} T^2)$ vs. $1/T$

$$\tau_e T^2 = \frac{\exp((E_c - E_T)/kT)}{\gamma_n \sigma_n}$$

- Slope gives $E_c - E_T$ and intercept gives σ_n

$$\ln(\tau_e T^2) = \frac{(E_c - E_T)}{kT} - \ln(\gamma_n \sigma_n)$$



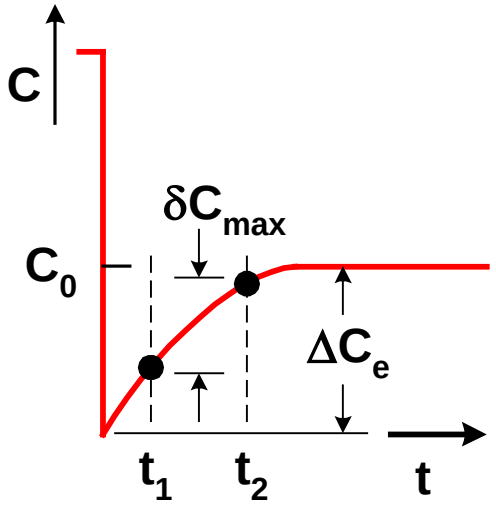


DLTS

- Since $\delta C_{max} \neq \Delta C_e$

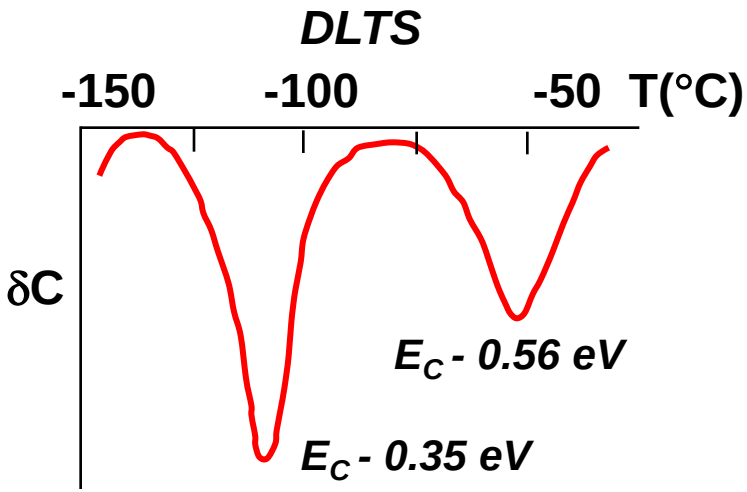
$$N_T = 2N_D \frac{\Delta C_e}{C_0} = \frac{\delta C_{max}}{C_0} \frac{2N_D r^{r/(r-1)}}{(1-r)} = -8N_D \frac{\delta C_{max}}{C_0} \quad for\ r = 2$$

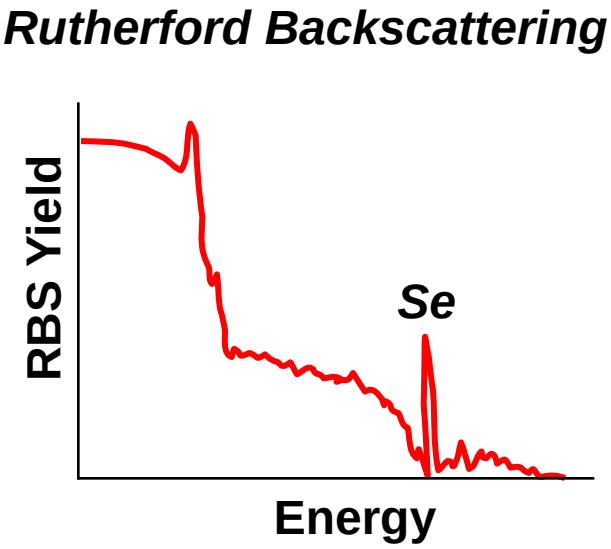
$$r = t_2/t_1$$



DLTS Example

- **Problem: BV_{CBO} of BJT degraded from 1000 V to 500 V**
  - **BV_{CBO} normal at T=77 K**
  - **Epi starting wafers were OK**
  - **Resistivity dropped after processing; 50 Ω-cm ⇒ 15 Ω-cm**
  - **Search for fast-diffusing deep donor impurity**





Selenium contamination from deteriorating rubber O-ring in sink

DLTS Variations

- **The primary task of a DLTS system is determine ΔC, τ_e vs T so as to extract N_T, E_T, and σ_n.**

- This goal can be performed by direct digitation and analysis of the capacitance transient without going to the extremes of using analog signal processing techniques →DSP or numerical fitting

- Trade offs in trap sensitivity versus trap energy resolution exist for all techniques and it can be shown that energy resolution improves as temperature decreases*

- Analog signal processing techniques (Boxcar, Lockin and correlation methods) can have extremely good trap sensitivity (detection of N_T<1e-6N_D) but tend to have poor energy resolution*

- DSP based processing (FFT, LaPlace, CMLPM, point differentials and non-linear fitting) tend to have very high energy resolution (E_1-E_2<10 meV) but poorer trap sensitivity (detection of N_T<1e-2N_D)*

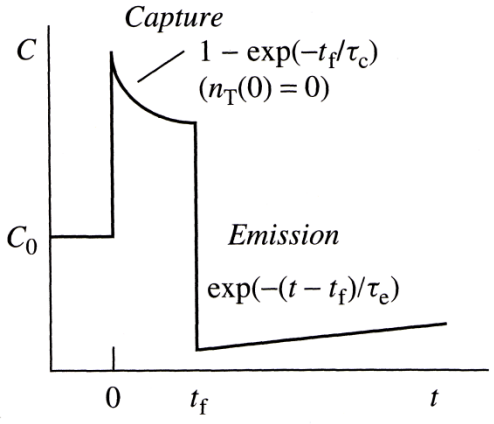
*W. A. Doolittle, and A. Rohatgi, "A new figure of merit and methodology for quantitatively determining defect resolution capabilities in deep level transient spectroscopy analysis," J. Appl. Phys., Vol. 75, No. 9, pp. 4570-4575, 1 May (1994)

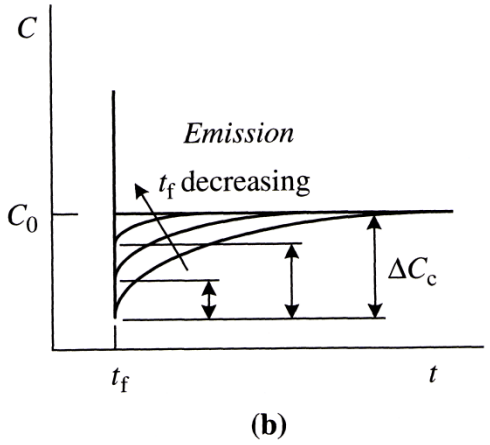
W. A. Doolittle and A. Rohatgi, "Comparison of Covariance Linear Predictive Modeling to the Modulation Function Method for Use in Deep Level Transient Spectroscopy," J. Appl. Phys., Vol. 75, No. 9, pp. 4560-4569, 1 May (1994).

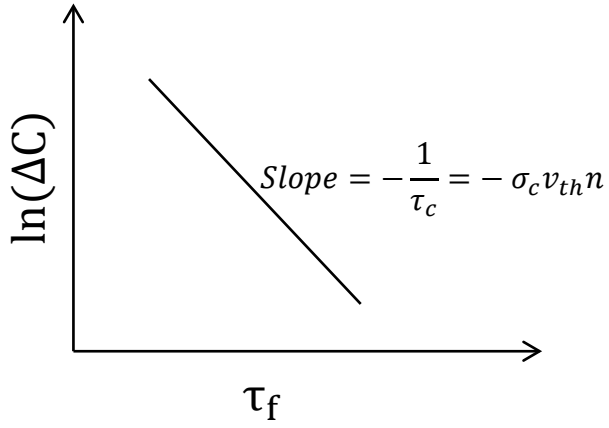
DLTS Variations

- σ_n can measured directly by making the filling pulse short enough in time (less than the capture time constant) to result in incomplete filling of the trap states (i.e. $t_f < \tau_C$)

$$ln(\Delta C) = ln\left(\frac{N_T - n_T(0)}{2N_D} C_0\right) - \frac{t_f}{\tau_{capture}}$$







DLTS Variations

- A seemingly small but important point:
- All thermal measurements (DLTS, Hall, etc…) measure the change in Gibbs free energy of a defect.

$$G=H-TS \quad \text{so} \quad \Delta G=\Delta H-T\Delta S$$

…where H is enthalpy and S is entropy

- All optical measurements (i.e. ones where an initial to final state transition occurs) are not effected by entropy (other than line broadening) making them measure ΔH not ΔG.
- Electrically determined activation energies are almost always lower than optically determined activation energies by a factor ΔS
- See Appendix 5.1 and references therein for details.

Review Questions

- Name some common defects in Si wafers.
- What do metallic impurities do in Si devices?
- Name some defect sources.
- What are point defects? Name three point defects.
- Name a line defect, an area defect, and a volume defect.
- How do oxidation-induced stacking faults originate?
- What determines the capacitance transient?
- Where does the energy for thermal emission come from?
- Why do *minority* and *majority* carrier emission have opposite behavior?
- What is *deep level transient spectroscopy* (DLTS)?
- What parameters can be determined with DLTS?