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SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

14 April - 18 June 1982

ELECTRONIC TRANSPORT IN NON-CRYSTALLINE SEMICONDUCTORS
(Part I)

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Predictions

- optical absorption
- luminescence
- recombination
- drift of carriers + trapping
- dc, ac conductivity
- thermopower
- Hall effect
- ---

Model Concepts

- Electronic States
- Localization
- Mobility Edge
- Random Phase
- Hopping
- Percolation
- ---

Measurements

- ✓ Density of states $N(E)$ — field effect / C–V / DLTS / transient decay / xerographic / ---
- ✓ Drift mobility
- ✓ μ_0
- Luminescence
- ✓ photoconductivity, rise + decay
- paramagnetic resonance

Discoveries

- ✓ photostructural changes
- ✓ Photo-creation of defects
- ✓ field-enhanced doping
- anomalous C_v, κ, R
- characteristic differences — material classes

③

Reality

compositional } heterogeneities ✓
structural }

Surfaces and interfaces ✓

Dependence of properties on preparation conditions

④

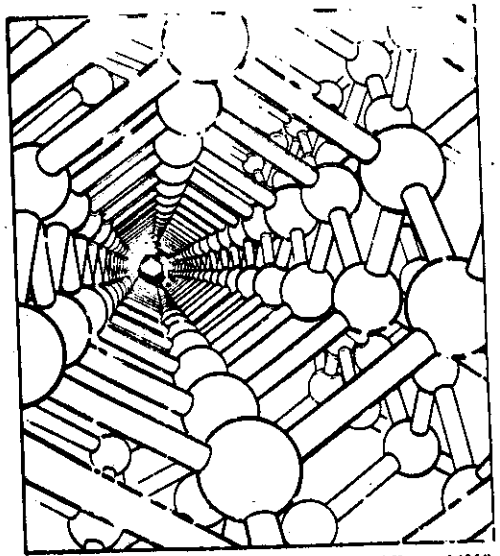


Fig. 9. Model of the diamond lattice (after Pauling and Hayward 1964).

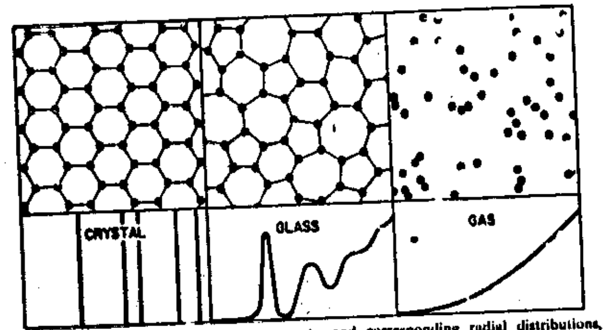
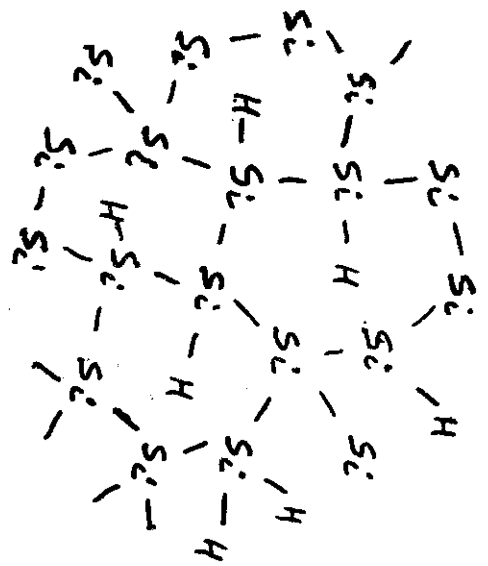
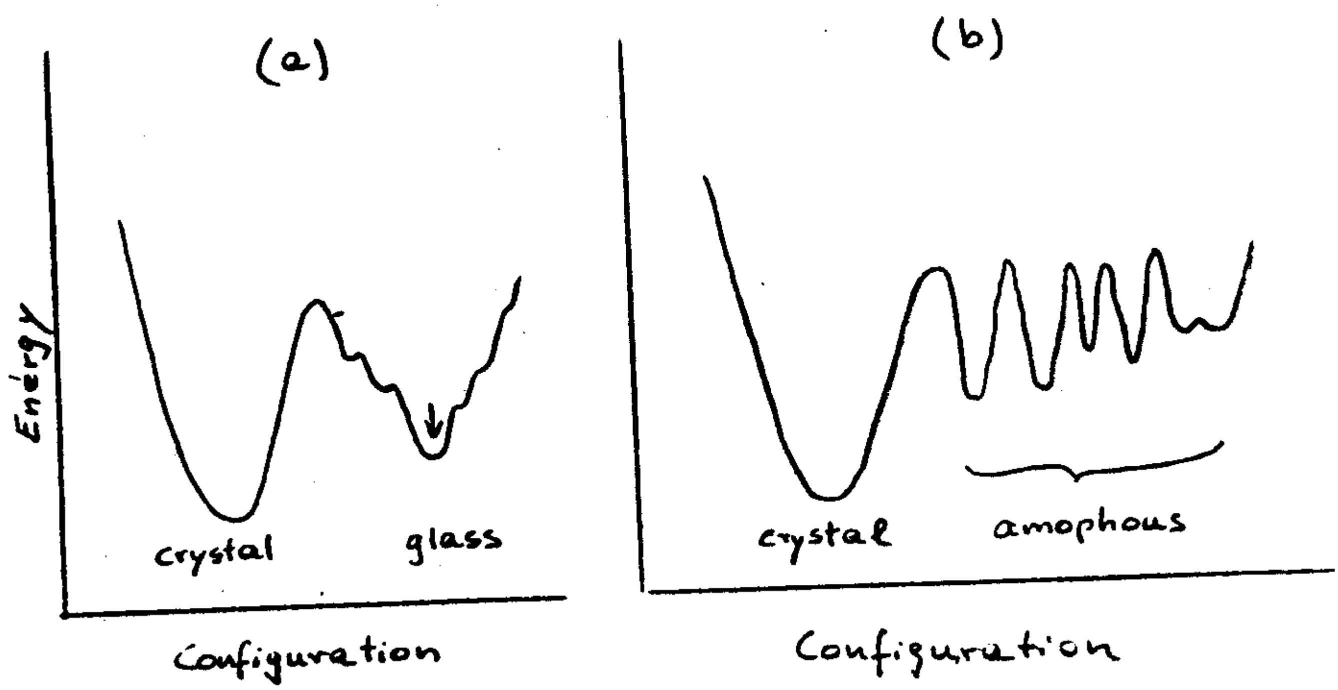
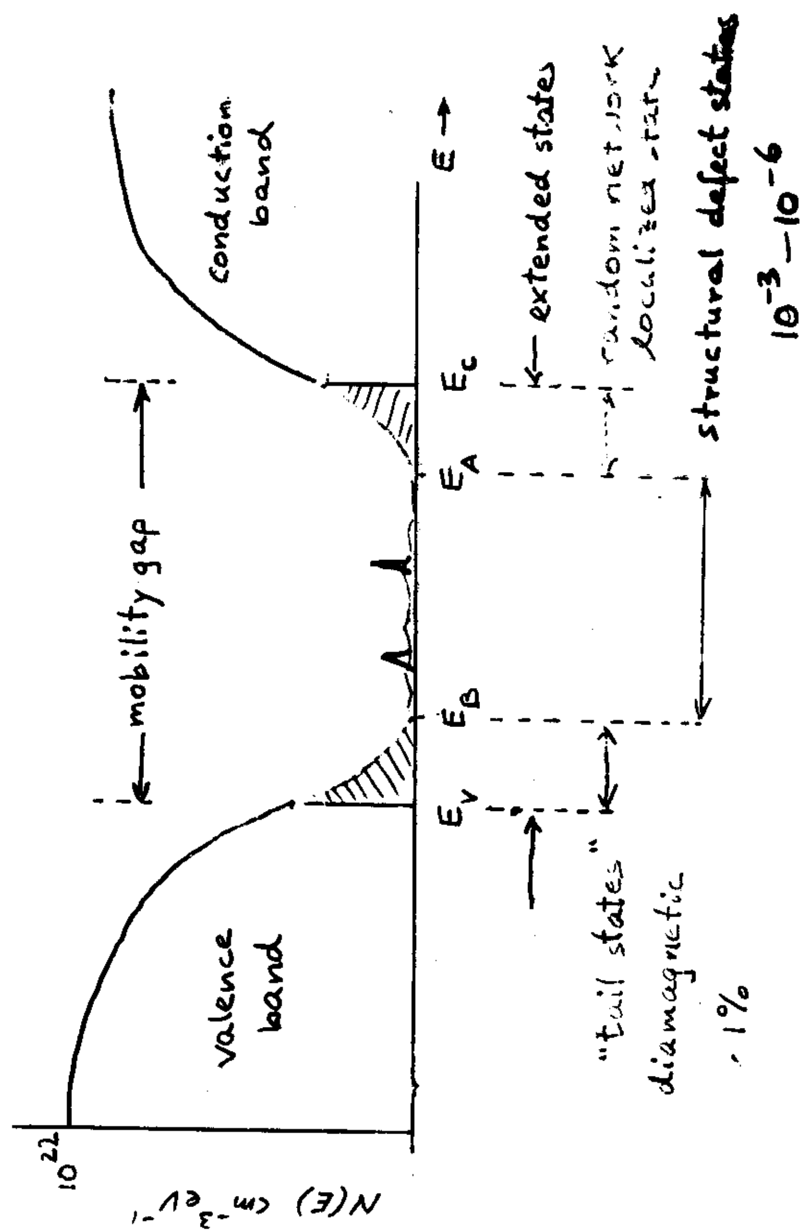


Fig. 1. Sketches of the atomic arrangements, and corresponding radial distributions, representative of crystalline solids, amorphous solids, and gases.



(5)

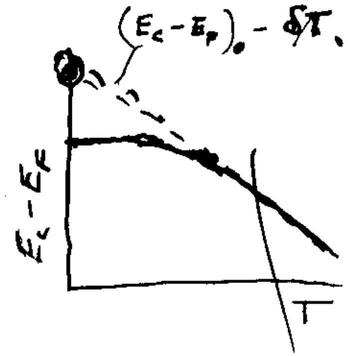

(a)
Energy
crystal
glass
Configuration
(b)
crystal
amophous
Configuration



$$\sigma = \sigma_{min}\, e^{-(E_c - E_F)/kT}$$

$$= \sigma_{min}\, e^{\delta/k}\, e^{-(E_c - E_F)_0/kT}$$

$$= \sigma_0\, e^{-\Delta E/kT}$$



$$\sigma_{min} = 0.06 \left(\frac{6}{2}\right)^2 \frac{\hbar}{d_c}$$

$$N(E_c) \sim 10^{21}\ eV^{-1} cm^{-3}$$

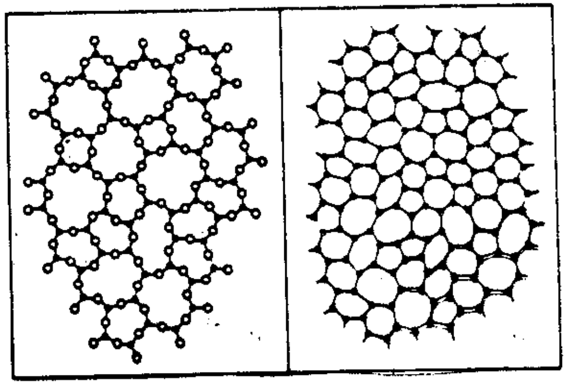
$$N_c = N(E_c)\, kT \sim 2.5 \times 10^{19}\ cm^{-3}$$

$$d_c = \left(\frac{3}{4\pi}\right)^{1/3} \frac{1}{N_c^{1/3}} \sim 20\ Å$$

$$\therefore \quad \left.\begin{array}{l} \sigma_{min} \approx 200\ ohm^{-1} cm^{-1} \\ \sigma_{min} = e N_c \mu_c \end{array}\right\} \mu_c \sim 40\ cm^2/Vs$$

$$\mu_c = \frac{e}{kT} D = \frac{1}{6} \frac{e}{kT} d_c^2 \nu_{el} \sim 5\ cm^2/Vs$$

9



Conduction

$$\sigma = e\, N_c\, \mu_c\, e^{-\frac{E_c - E_F}{kT}}$$

- $\mu_c = \frac{1}{6} \frac{e}{kT} d^2 \nu_{el} \approx 4\ cm^2/Vs$
- $N_c = N(E_c)\, kT \approx 2.5 \times 10^{19}\ cm^{-3}$
- $e = 1.6 \times 10^{-19}\ C$

$$\sigma = 16\, e^{-\frac{(E_c - E_F)}{kT}}$$

$$= 16\, e^{\delta/k}\, e^{-\frac{(E_{c0} - E_F)}{kT}}$$

$e^{\delta/k} = 30$ with $\delta = \frac{1}{2}\gamma = 2.3 \times 10^{-4}\ eV/K$

$$\sigma = 500\, e^{-E_a/kT}$$

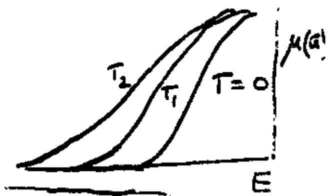
($500 = \sigma_0$)

$$S = \frac{k}{e}\left(\frac{E_a}{kT} - \frac{\delta}{k} + A\right)$$

1. $E_c(T) = E_{c0} - \delta_c T$

   $\delta_c = 5 \times 10^{-4}\ eV/K$

2. $E_F(T)$ moves away from E_c or E_v and decreases σ_c



3. Heterogeneities, potential barriers

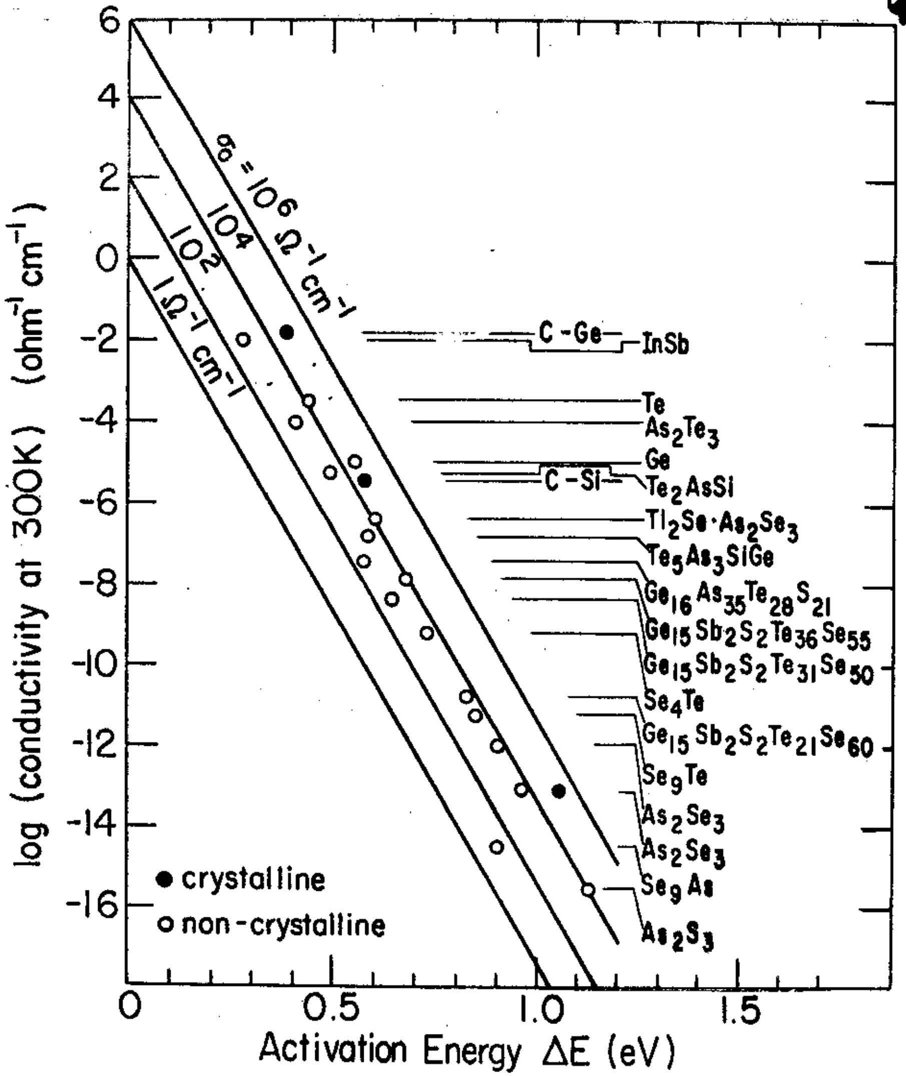
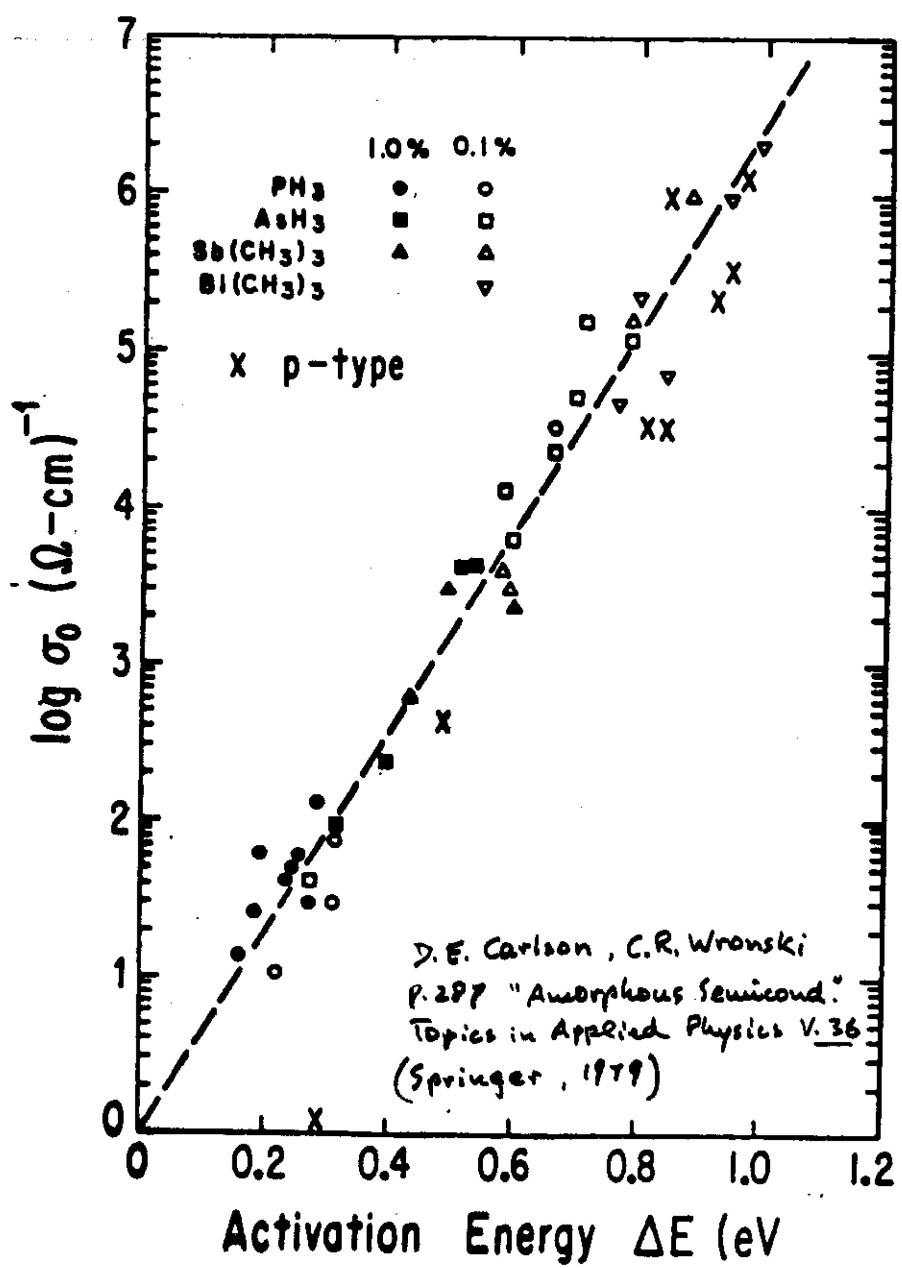
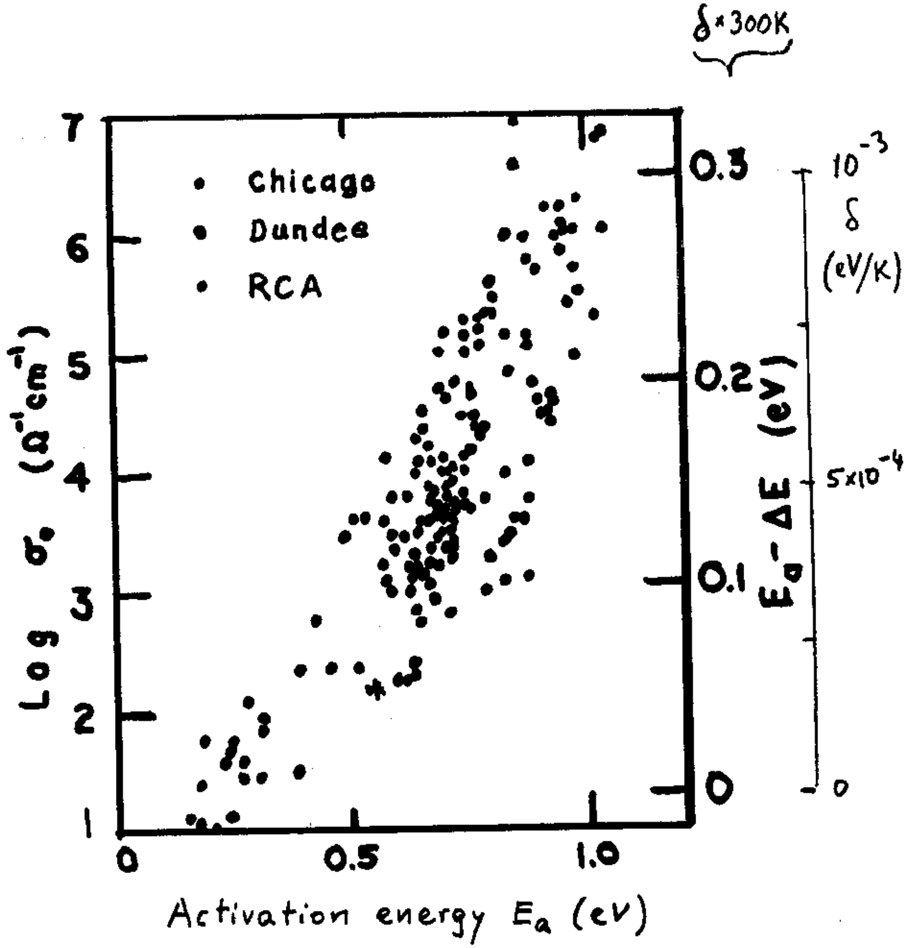


Fig.5.6

From: H. Fritzsche "Amorphous & Liquid Semicond." edited by J. Tauc, Academic Press

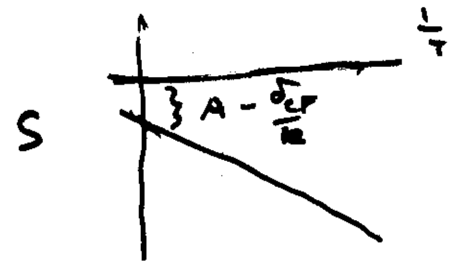




$$S = -\frac{k}{e}\left[\frac{(E_c - E_F)_0}{kT} + A_c - \frac{\delta_{cF}}{k}\right] \quad \text{for } E > E_c$$

$$S = \frac{k}{e}\left[\frac{(E_F - E_V)_0}{kT} + A_v - \frac{\delta_{vF}}{k}\right] \quad \text{for } E < E_v$$

$$A_c = \int_0^\infty \frac{\varepsilon}{kT}\,\sigma(\varepsilon)\,d\varepsilon \Big/ \int_0^\infty \sigma(\varepsilon)\,d\varepsilon \qquad \varepsilon = E - E_c$$



$$E_c - E_F = (E_c - E_F)_0 - \delta_{cF} T$$

H. Fritzsche, Sol. State Commun. 9 (1971) 1813

Metallic conduction

$f(1-f) = -kT\,df/dE$

expanding $g(E)\mu(E)$ in a Taylor series

$$S = -\frac{\pi^2}{3}\frac{k}{e}kT\left[d\ln\sigma(E)/dE\right]_{E_F} \quad \text{(Mott)}$$

Thermopower S

$\Delta V = S \, \Delta T$

$S = \Pi / T$

Peltier coefficient Π = energy transported by the current carriers per unit charge

Energy measured relative to E_F

$$\Pi = -\frac{1}{e}\int_{-\infty}^{+\infty} (E - E_F) \, \frac{\sigma(E)\, dE}{\sigma}$$

$$S = -\frac{k}{e}\int_{-\infty}^{+\infty} \frac{E - E_F}{kT} \, \frac{\sigma(E)\, dE}{\sigma}$$

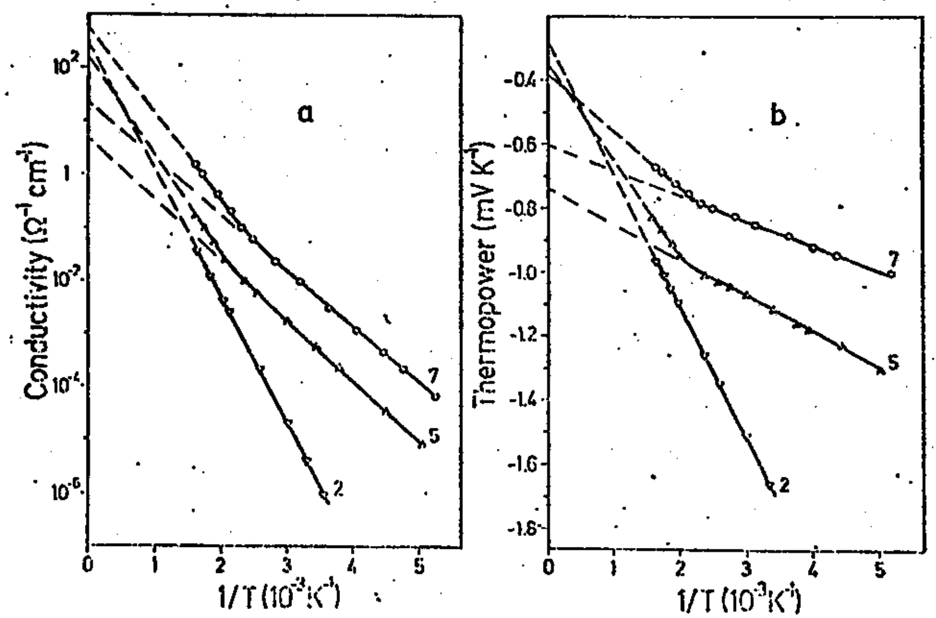
$$\sigma(E) = e\, g(E)\, \mu(E)\, f(E)\left[1 - f(E)\right]$$

$$\sigma = \int_{-\infty}^{+\infty} \sigma(E)\, dE$$

$$\mu = \mu_0 \, e^{-W/k_BT}$$

Table 1

Sample	σ_0^M ($\Omega^{-1}cm^{-1}$)	E_σ (eV)	E_S (eV)	γ_σ (meV/K)	γ_F (meV/K)
2	600	0.47	0.40	0.05	0.06
5 (a)	590	0.23	0.11	0.15	0.41
5 (b)	280	0.38	0.30	0.15	0.03
7 (a)	290	0.21	0.08	0.20	0.23
7 (b)	600	0.31	0.18	0.20	0.01



W. Beyer and R. Fischer Appl. Phys. Lett. 31 (1977) 12

Fig. 1

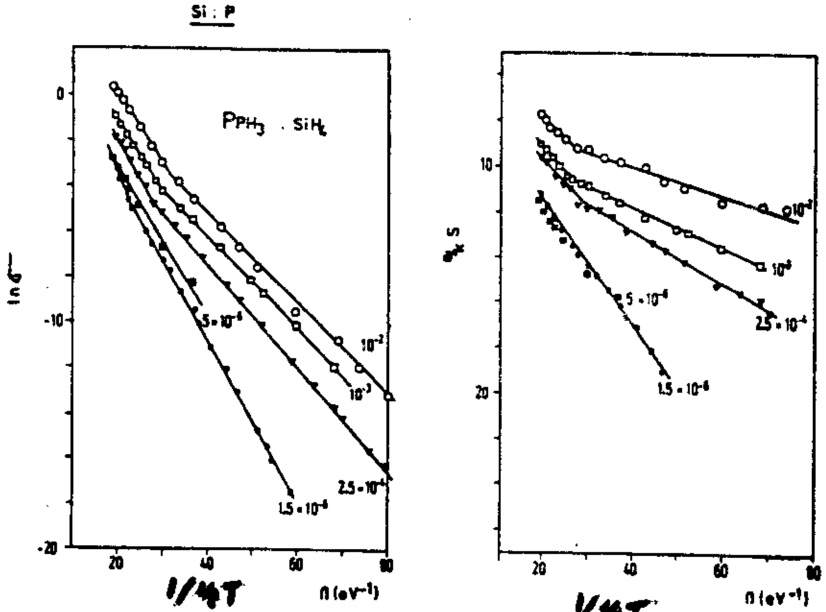


Fig. 1 Conductivity (a) and thermopower (b) of gd Si films doped with phosphorus vs β . The doping level is given in terms of the phosphine/silane pressure ratio.

W. Beyer and H. Overhof
Solid State Commun. 31 (1979) 1.

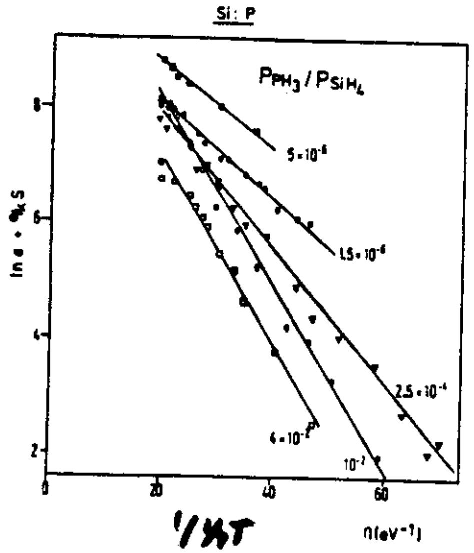


Fig. 2 lnσ + $\frac{e}{k}$S from the data of fig 1 vs β.

W. Beyer and H. Overhof
Solid State Commun. 31 (1979) 1.

$$\sigma = \sigma_{min}\, e^{-\left(\frac{E_c - E_F}{kT}\right)}$$

$$\frac{e}{k} S = -\frac{k}{q}\left(\frac{E_c - E_F}{kT} + A\right)$$

$$\ln \sigma = \ln \sigma_{min} - \left(\frac{E_c - E_F}{kT}\right)$$

$$\ln \sigma - \frac{e}{k} S = \ln \sigma_{min} + A$$

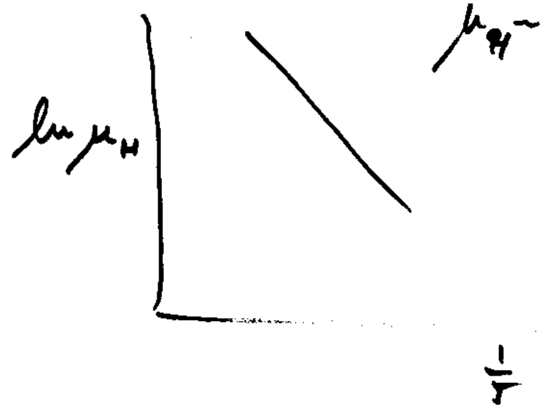
However, general observation:

$\ln \sigma - \frac{e}{k} S = \frac{E_\mu}{kT} + C$ with $E_\mu \approx 0.15$ eV

Hall effect

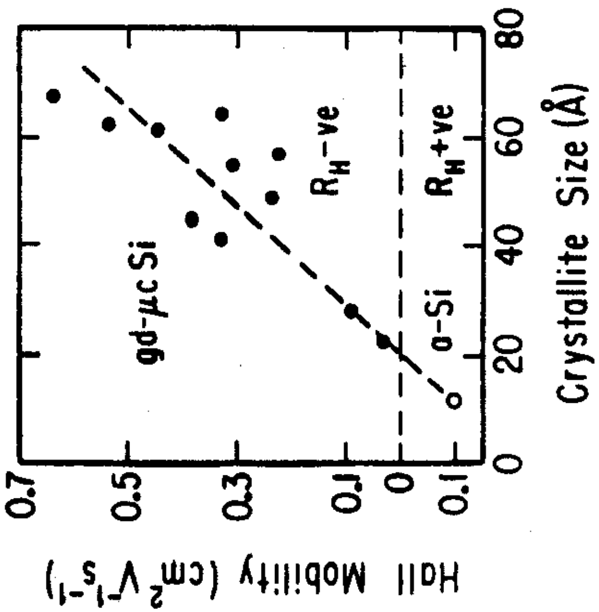
J. Dresner, Appl. Phys. Lett 37 (1980) 742 — $\frac{0.15}{kT}$

$\mu_H \sim 8$ e ≡ ?



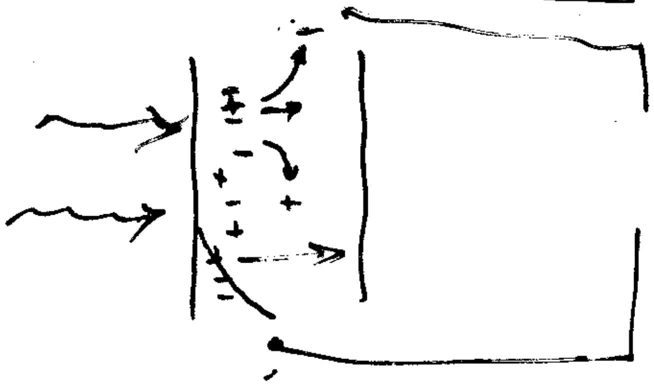
sign anomaly !!

W.E. Spear, G. Willeke, P.G. Le Comber, A.G. Fitzgerald
Grenoble '81, J. de Physique C4-10 (1981)



Photoelectromagnetic Effect

A. R. Moore



I_{sc}

A.R. Moore, Appl. Phys. Lett. 37 (1980) 327.

$$I_{sc} = 10^{-8} B w q (\mu_e + \mu_h) I_0 L_p \frac{\alpha L_p}{1 + \alpha L_p}$$

$$L_p^2 = D_p \tau_p = \frac{kT}{q} \mu_p \tau_p$$

holes $\mu\tau = 3.2 \times 10^{-9}\ cm^2/V$ $\qquad L_p = 0.09\,\mu m$

$\tau = 3.4 \times 10^{-7}\ sec$

electrons $\mu\tau = 7.8 \times 10^{-8}\ cm^2/V$

$\tau = 1.7 \times 10^{-6}\ s$

$\mu_? = 0.05\ cm^2/Vs$ ←

Sign of effect normal

Summary of 1st Lecture

1. $\sigma = \sigma_0 \exp -(E_c - E_F)_0/kT = \sigma_0 \exp(-E_\sigma/kT)$

   $\sigma_0 = \sigma_{min} \exp(\delta_{cF}/k)$

   $5 \le \mu_0 \le 20\ cm^2/Vs$

   $10^3 \le \sigma_0 \le 10^4\ ohm^{-1}cm^{-1}$ for nearly all glasses

   - However: in a-Si:H

   $\sigma_0 \propto \exp(A E_\sigma)$ Meyer-Neldel Rule

   with $A \simeq 0.070$ eV and $\sigma_0 > 10^6\ ohm^{-1}cm^{-1}$ for large E_σ

2. $S = -\frac{k}{e}\left(\frac{E_S}{kT} + A - \frac{\delta_{cF}}{k}\right)$

   $Q \equiv \ln\sigma - \frac{e}{k} S = \ln\sigma_{min} + A - \frac{E_\sigma - E_S}{kT}$

   - However: $E_\sigma - E_S \neq 0$

   $0.1 \le E_\sigma - E_S \le 0.2$ eV quite generally

3. Hall mobility $\mu_H = R\sigma = \mu_0 \exp(-E_\mu/kT)$

   in a-Si:H with $\mu_0 \sim 8\ cm^2/Vs$ and $E_\mu \sim 0.15$ eV

   - However: Hall effect has sign opposite to carrier

4. Photoelectromagnetic effect has correct sign and yields reasonable values for diffusion length.

Determination of Density of Gap States.

1. Field Effect

a-Si:H W.E. Spear + P. LeComber, J. Non-Cryst. Sol. 8-10 (1972) 727
A. Madan, P. LeComber, W.E. Spear, ibid 20 (1976) 239
N.B. Goodman, H. Fritzsche + H. Ozaki, ibid 35-36 (1980) 599
N.B. Goodman, H. Fritzsche, Phil. Mag. B42 (1980) 149

2. C–V

a-Si:H M. Hirose, T. Suzuki, G.H. Döhler, Appl. Phys. Lett. 34 (1979) 234
T. Tiedje, C.R. Wronski, B. Abeles, J. Cebula, Solar Cells 2 (1980)

3. Deep Level Transient Spectroscopy (DLTS)

a-Si:H D.V. Lang, J.D. Cohen, J.P. Harbison, Phys. Rev. B25 (1982) 5285
J.D. Cohen + D.V. Lang, ibid. B25 (1982) 5321

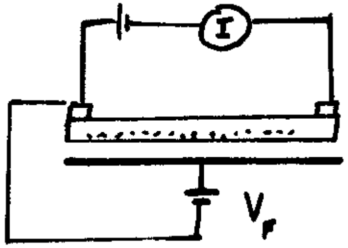
4. Xerographic Spectroscopy

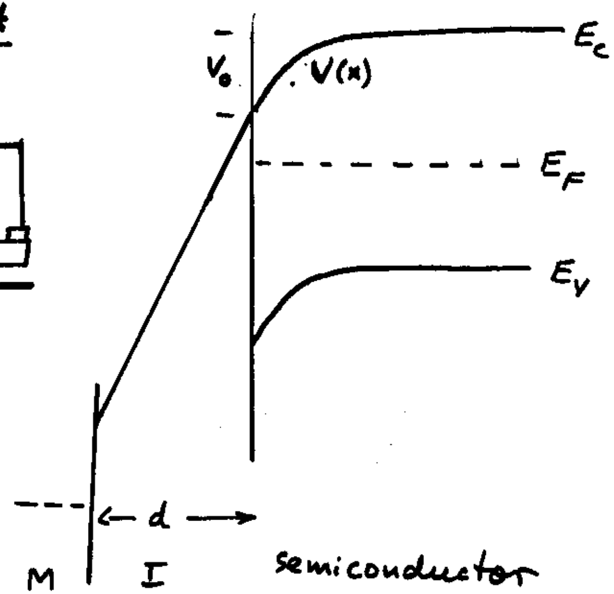
Si glasses M. Abkowitz and R.C. Enck, Phys. Rev. B25 (1982) 2867

5. Space-Charge-Limited Current Method

W. den Boer, J. de Physique 42 (1981) C4-451

1. Field Effect





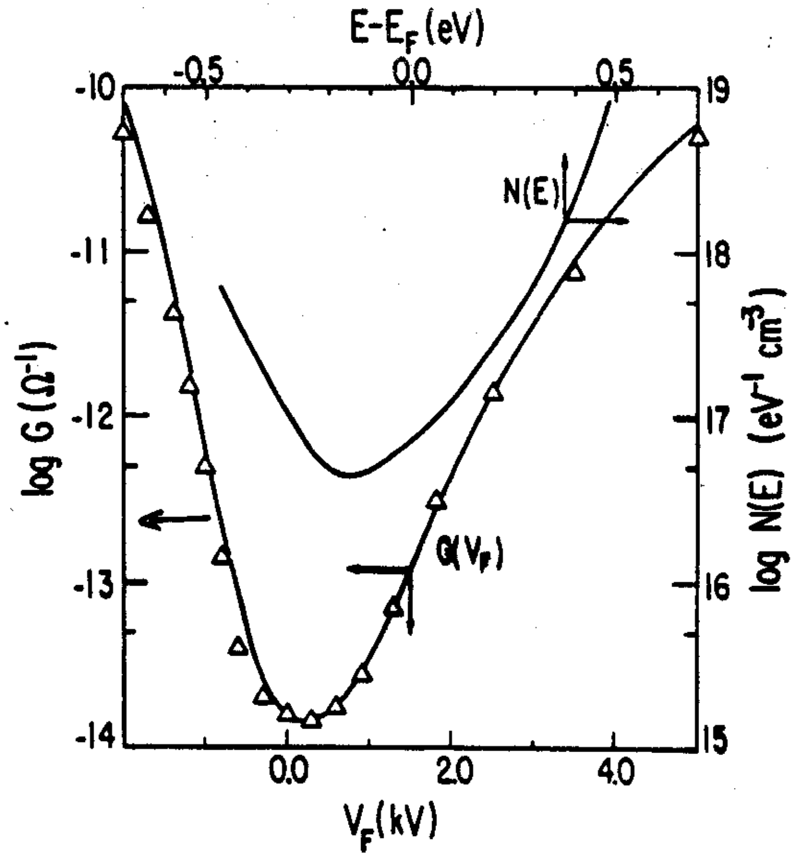
Poisson:
$$\frac{d^2V(x)}{dx^2} = \frac{4\pi e}{\varepsilon_s}\rho(x)$$

$$\rho(x) = \int_{-\infty}^{+\infty} dE\, g(E)\left[f(E - eV(x)) - f(E)\right]$$

$$\frac{G}{G_0} = \frac{\alpha}{\alpha+1}\frac{1}{t}\int_0^t dx\, \exp(eV(x)/kT) + \frac{1}{\alpha+1}\frac{1}{t}\int_0^t dx\, \exp(-eV(x)/kT)$$

$$\left.\begin{aligned} G_0 &= G_0(\text{electrons}) + G_0(\text{holes}) \\ \alpha &= G_0(\text{el}) / G_0(\text{holes}) \end{aligned}\right\} \text{ at } V_F = 0$$

25


E-E$_F$ (eV)
-0.5
0.0
0.5
-10
-11
-12
-13
-14
19
18
17
16
15
log G (Ω^{-1})
log N(E) (eV^{-1} cm^{-3})
N(E)
G(V$_F$)
0.0
2.0
4.0
V$_F$(kV)

26

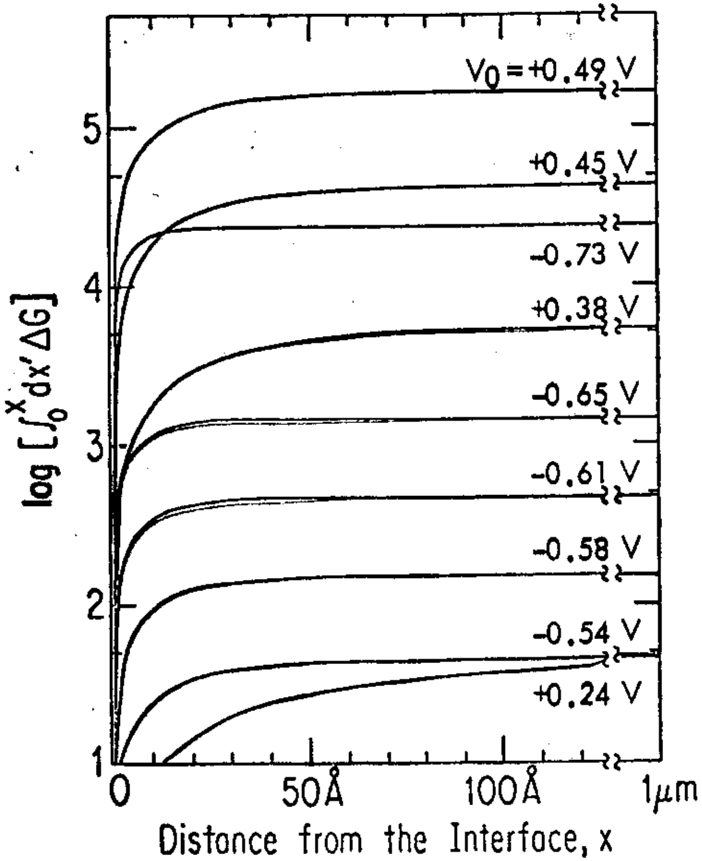
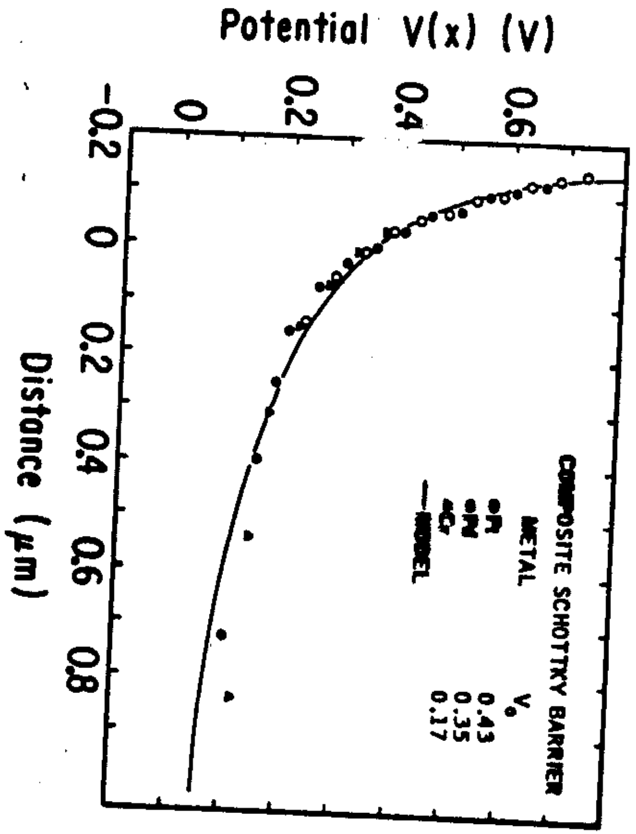

V$_0$ = +0.49 V
+0.45 V
-0.73 V
+0.38 V
-0.65 V
-0.61 V
-0.58 V
-0.54 V
+0.24 V
5
4
3
2
1
log [$\int_0^x dx' \Delta G$]
0
50Å
100Å
1μm
Distance from the Interface, x

Fig. 15



Tiedje, Wronski et al., Solar Cells 2 (1980)

Difficulties:

1. at large V_F current flows in 50 Å thick layer
2. $g(E)$ in first 50 Å layer ??
3. Localization condition in 2-dim. potential well, rigid shift ~ $V(x)$ of mobility edge ?
4. Is σ_0 = const in $\sigma = \sigma_0 \exp[-(E_c(x)-E_F)/kT]$?

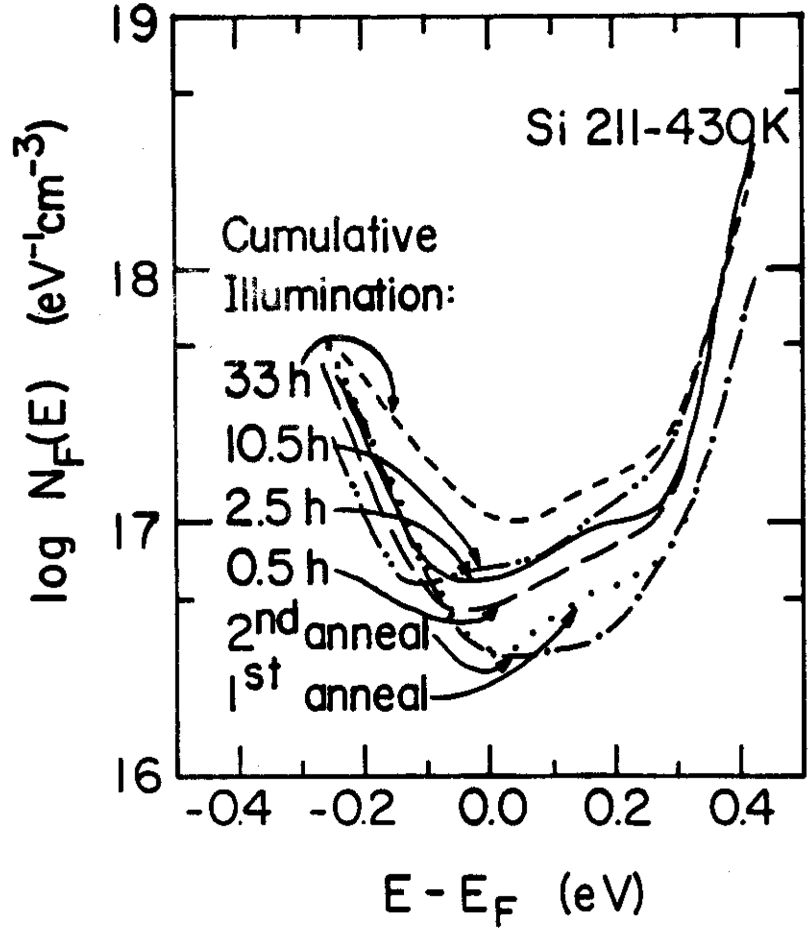
   if $\sigma_0 = \sigma_{00} \exp A[E_c(x) - E_F]$ Meyer-Neldel Rule

   then $g(E)$ will be lower by factor 5–10
5. No interface states !

Success: Observation of photocreation of defects
of thermal annealing of defects
of thermal creation of defects.

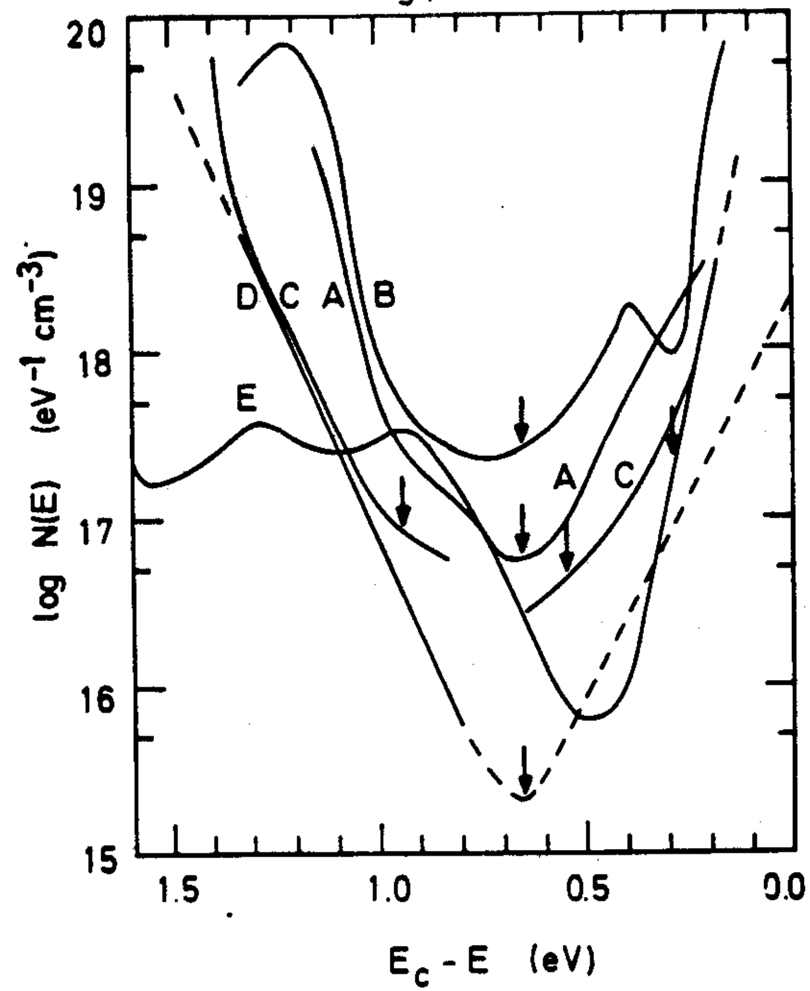
(29)

N. B. Goodman

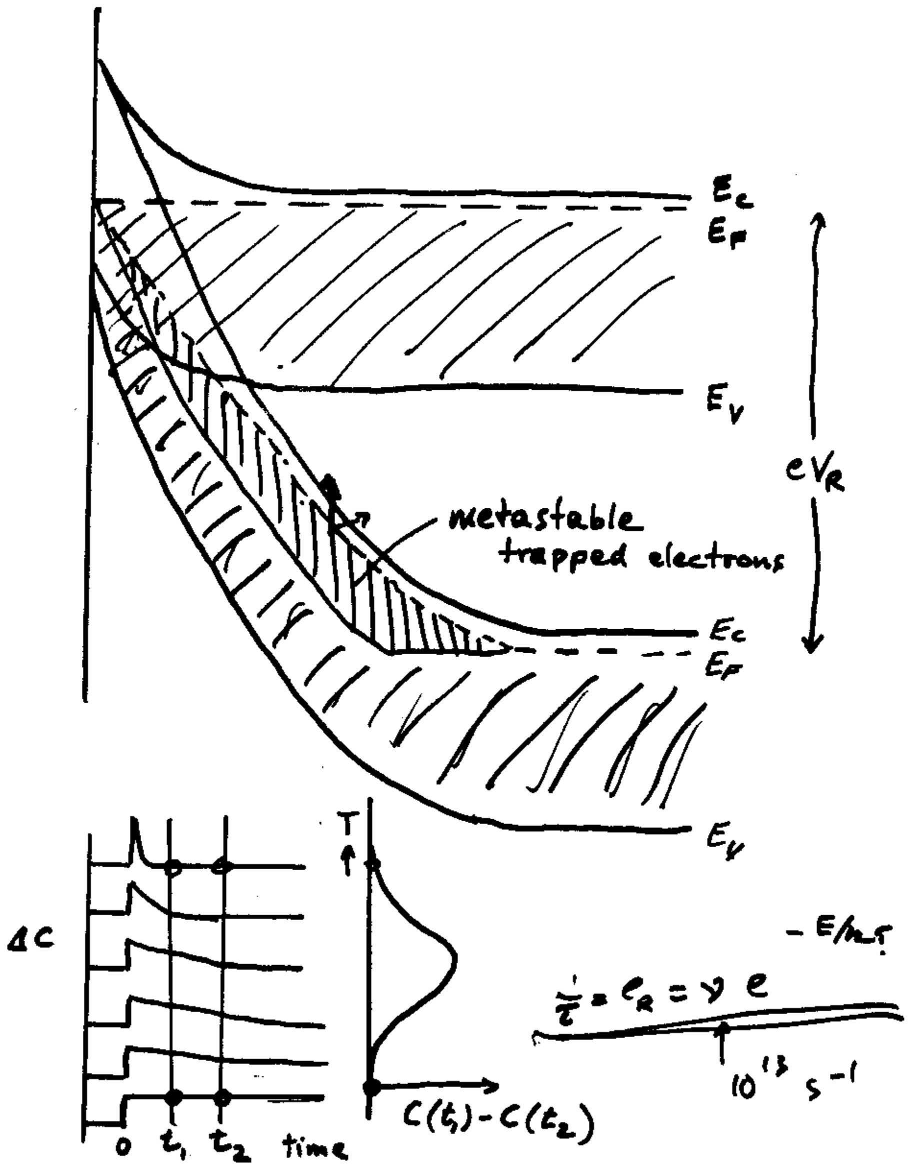


(30)

A. Field Effect : Goodman + Fritzsche
B. " " : Spear + LeComber
C. C-V : Hirose, Suzuki + Döhler
D. C-V : Tiedje, Wronski, Abeles, Cebula
E. DLTS : Lang, Cohen, Harbison



DLTS ΔC transient



thermal emission rate $\frac{1}{\tau_e} = \nu_0 \exp(-E/kT)$

$$\tau_{max} = \frac{t_2 - t_1}{\ln(t_2/t_1)} = \frac{1}{\text{DLTS rate window}}$$

$$\frac{\Delta C}{C} \simeq 2\,\frac{N_t}{N_s}$$

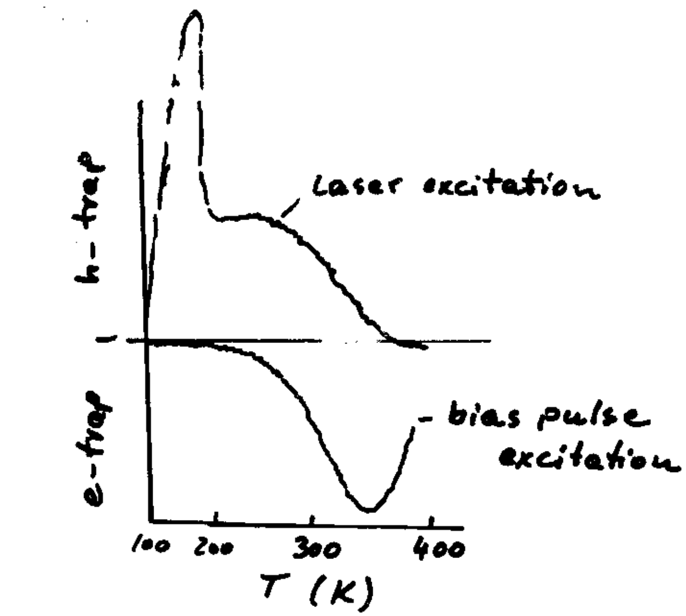
N_s = density of shallow levels which determine shape and size of depletion layer

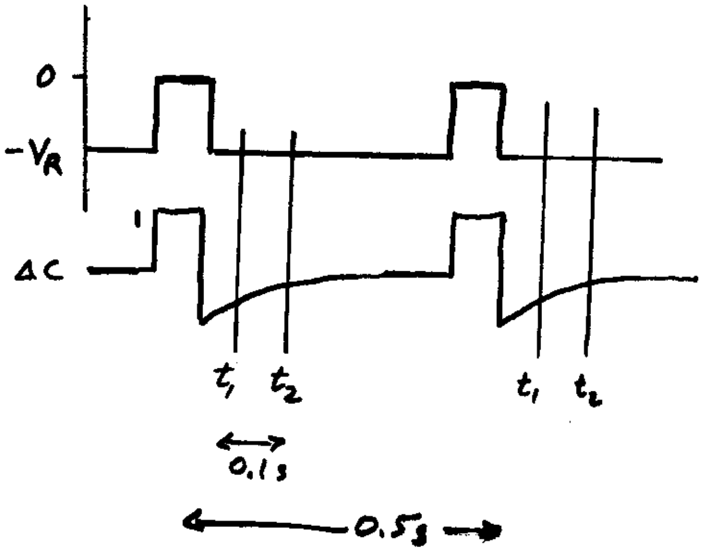
Difficulties

1. Assumption: attempt to escape frequency ν_0

   $\nu_0 = \sigma_t\, v_{th}\, N_c$ = same for all gap states

2. thermal release independent of internal field ~ 10^5 V/cm





thermal emission density of states for constant capture coefficient.