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UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

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SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

14 April - 18 June 1982

IMPURITIES, TRAPS AND RECOMBINATION CENTERS IN A SiHx

(Part I)

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AMORPHOUS SEMICONDUCTORS

Impurities Traps and Recombination Centers in a SiHx

Application to Solar Cells

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IMPURITIES, TRAPS AND RECOMBINATION CENTERS IN HYDROGENATED AMORPHOUS SILICON

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Abstract

The theme of the five lectures is the density of gap states (DGS) in hydrogenated amorphous silicon (a-SiH_x) and its significance to solar cells. The DGS in amorphous semiconductors is of fundamental importance because it provides information on the nature of the disorder and defects. The DGS is also of practical importance because it determines the ultimate performance of amorphous semiconductors in electronic devices. There are several reasons why a-SiH_x is enjoying prominence at this time over other amorphous semiconductors. First of all, of course, there is worldwide interest in this material because of its many novel technological applications (in particular for solar cells). From a scientific point of view a-SiH_x is so attractive because of its excellent photo-electric properties which allow one to probe the density of states with techniques known from crystalline semiconductors;

the ability to make reproducibly well characterized materials which can be doped n and p type and in which the density of states can be varied over many orders of magnitude. The central issue of amorphous semiconductor solar cells is the requirement of a low DGS combined with a low optical bandgap, (E_G ~1.5 eV). The low DGS is required to keep recombination at a low level so that most of the photogenerated carriers are extracted. A band gap of E_G ~1.5 eV is required so that a large portion of the solar spectrum is absorbed. In Lecture I we show that there exists a fundamental trade off between E_G and DGS--the lower the E_G is, the larger is the DGS. The optimum E_G a-SiH_x solar cells is near 1.7 eV. After discussing some of the basic concepts in photocarrier transport in Lecture I, we discuss in Lecture II transient photoconductivity techniques for studying the band tail DGS. The band tail states act as traps and determine the drift mobility of holes and electrons. In solar cells the band tails ultimately limit the open circuit voltage (Lecture V). In Lecture III we discuss the use of steady state photoconductivity techniques to determine the optical absorption and diffusion lengths of photocarriers. In Lecture IV we discuss deep level defect states and their capture cross section (e.g., dangling bonds), intrinsic to the material or induced by P or B doping, and observed in optical absorption ESR, photoluminescence and DLTS. An overview of the DGS of a-SiH_x is presented. In Lecture V we discuss the basic principles of operation of a thin film solar cell and the fundamental limits on the efficiency imposed by the DGS.

I. EFFECT OF DISORDER ON OPTICAL BAND GAP. BASIC CONCEPTS IN PHOTO-CARIER TRANSPORT

1. DENSITY OF STATES - FUNDAMENTAL CONCEPTS.

2. REQUIREMENTS ON DENSITY OF STATES FOR EFFICIENT SOLAR CELL.

3. RELATION BETWEEN EXPONENTIAL ABSORPTION EDGE AND BAND GAP.

4. FUNDAMENTAL CONCEPTS IN PHOTOCARRIER TRANSPORT - RECOMBINATION OF FREE CARRIERS - CAPTURE CROSS SECTION - QUASIFERMI LEVEL - DEMARCATION LEVEL - RESPONSE TIME, DRIFT MOBILITY AND FREE CARRIER MOBILITY.

II. BAND TAIL STATES

1. TIME RESOLVED TRANSPORT IN AMORPHOUS SEMICONDUCTORS - GENERAL PHYSICAL CONCEPTS

2. TIME OF FLIGHT EXPERIMENTS

3. MULTIPLE TRAPPING MODEL OF DISPERSIVE TRANSPORT - CURRENT DECAY AT SHORT TIMES ($t < t_T$) - TRANSIT TIME t_T - CURRENT DECAY AT LONG TIMES ($t > t_T$)

4. INTERPRETATION OF EXPERIMENTAL RESULTS OF TIME OF FLIGHT FOR a-SiH_x - BAND TAIL PARAMETERS OF a-SiH_x

5. PHOTOCURRENT DECAY IN a-SiH_x:P

6. INDUCED ABSORPTION

7. MOVIE: "MULTIPLE TRAPPING-DISPERSIVE AND NONDISPERSIVE TRANSPORT."

III. STEADY STATE PHOTOCONDUCTIVITY

1. PHOTOCONDUCTIVITY WITH OHMIC CONTACTS (P.C.) BASIC PRINCIPLES

2. NON-LINEAR LIGHT DEPENDENCE OF P.C.

3. BIAS LIGHT ILLUMINATION

4. COMPARISON OF P.C. WITH PHOTO-THERMAL DEFLECTION SPECTROSCOPY

5. INFRARED QUENCHING

6. PHOTOCONDUCTIVITY WITH BLOCKING CONTACTS (SOLAR CELL COLLECTION EFFICIENCY C.E.) BASIC PRINCIPLES

7. SAMPLE GEOMETRY AND TYPICAL EXPRIMENTAL RESULTS

8. INTERNAL PHOTOEMISSION

9. COMPARISON OF α DETERMINED FROM P.C. AND C.E.

10. C.E. WITH STRONGLY ABSORBED LIGHT

11. DIFFUSION LENGTH OF MINORITY CARRIERS FROM C.E.

IV. DEEP LEVEL DEFECT STATES IN a-SiH_x

1. HOW a-SiH_x FILMS ARE PREPARED.
2. DETERMINATION OF H, P AND B DOPING CONCENTRATIONS IN FILMS.
3. ELECRICAL AND OPTICAL PROPERTIES OF P AND B DOPED FILMS.
4. DENSITY OF STATE MODEL FOR THE OPTICAL ABSORPTION AND EVIDENCE FOR DANGLING BOND STATES.
5. CAPTURE CROSS SECTION FOR HOLES AND ELECTRONS
6. SPIN RESONANCE OF DEFECT STATES
7. QUENCHING OF PHOTOLUMINSCENCE BY DEFECTS.
8. DLTS OF a-SiH_x: P
9. DEFLECTION LAYER MODULATED ESR.
10. SUMMARY OF DENSITY OF STATES OF a-SiH_x.

V. AMORPHOUS SEMICONDUCTOR SOLAR CELLS

1. HOW THE SOLAR CELL WORKS.
2. SOLAR SPECTRUM AND THE IDEAL SOLAR CELL.
3. SOLAR CELL PARAMETERS - OPEN CIRCUIT VOLTAGE V_{OC}, SHORT CIRCUIT CURRENT I_{SC}, FILL FACTOR F, AND EFFICIENCY EF = $FI_{SC}V_{OC}$.
4. RECIPE FOR EFFICIENT THIN FILM SOLAR CELL.
5. COMPARISON BETWEEN c-Si, c-GaA_s and a-SiH_x solar cells.
6. FUNDAMENTAL LIMITATIONS ON V_{OC}, I_{SC} AND F IN AMORPHOUS SEMICONDUCTORS.
7. HOW TO FURTHER IMPROVE THE EFFICIENCY.

IMPURITIES, TRAPS AND RECOMBINATION CENTERS

IN HYDROGENATED AMORPHOUS SILICON

FIVE LECTURES

BASIC CONCEPTS OF DOS

I. EFFECT OF DISORDER ON OPTICAL BAND GAP.

BASIC CONCEPTS IN PHOTO-CARIER TRANSPORT

II. BAND TAIL STATES

TIME RESOLVED PHOTOCONDUCTIVITY

III. STEADY STATE PHOTOCONDUCTIVITY

MAINLY TECHNIQUES TO DETERMINE DEEP LEVEL STATES

IV. DEEP LEVEL DEFECT STATES IN a-SiH$_x$

DANGLING BONDS ECT

V. AMORPHOUS SEMICONDUCTOR SOLAR CELLS

RELEVANCE OF DOS

I. EFFECT OF DISORDER ON OPTICAL BAND GAP.

BASIC CONCEPTS IN PHOTO-CARIER TRANSPORT

1. DENSITY OF STATES - FUNDAMENTAL CONCEPTS.
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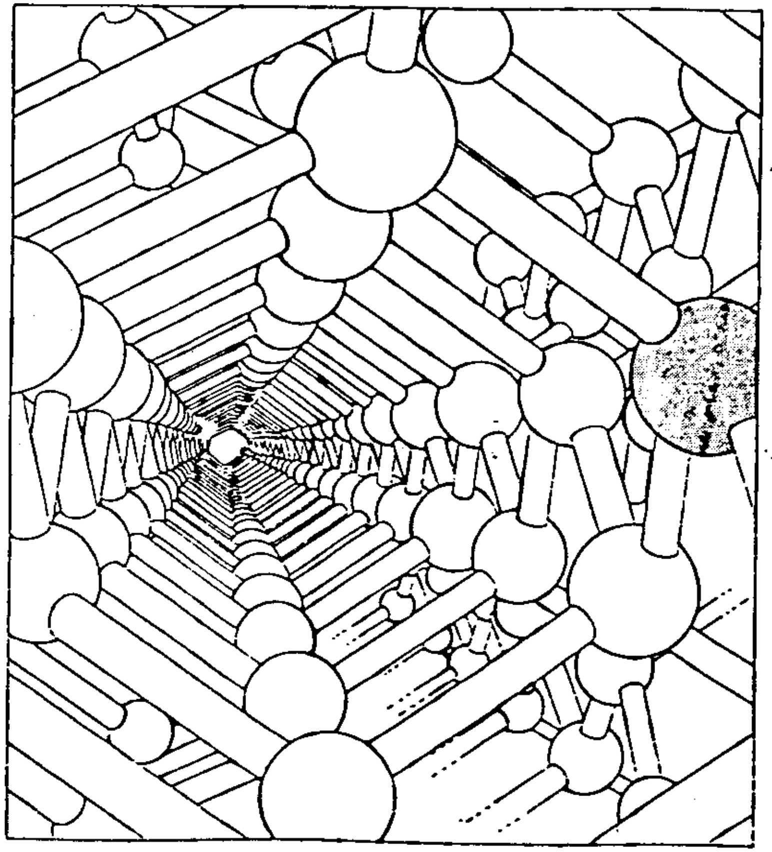
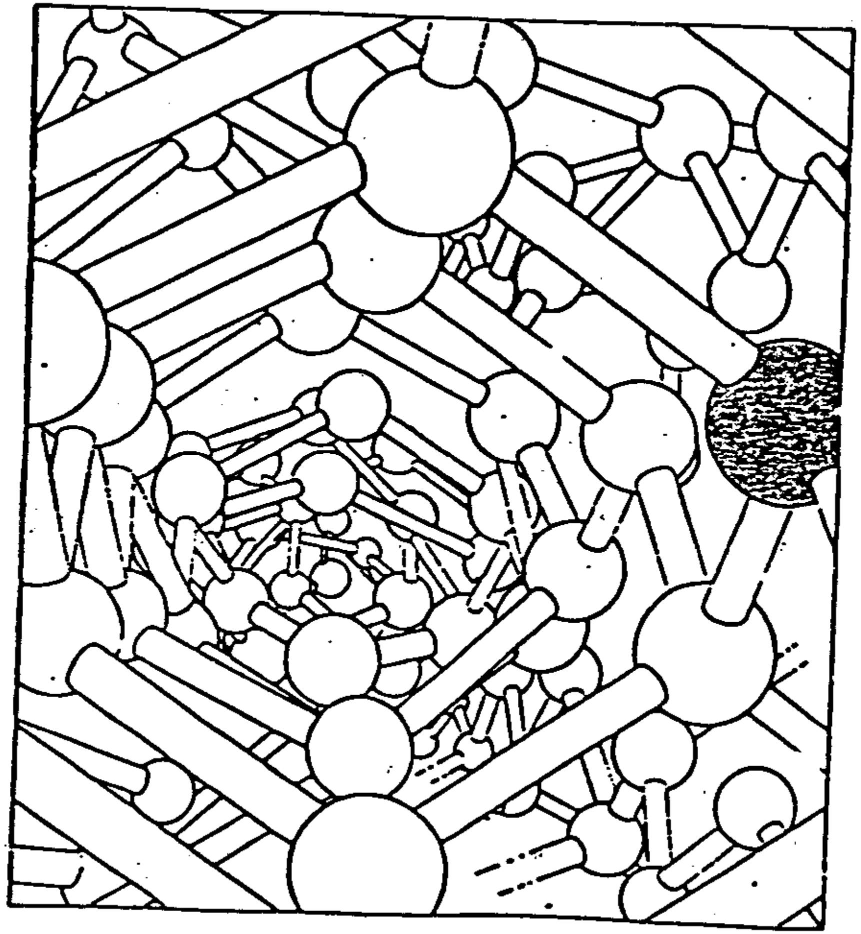
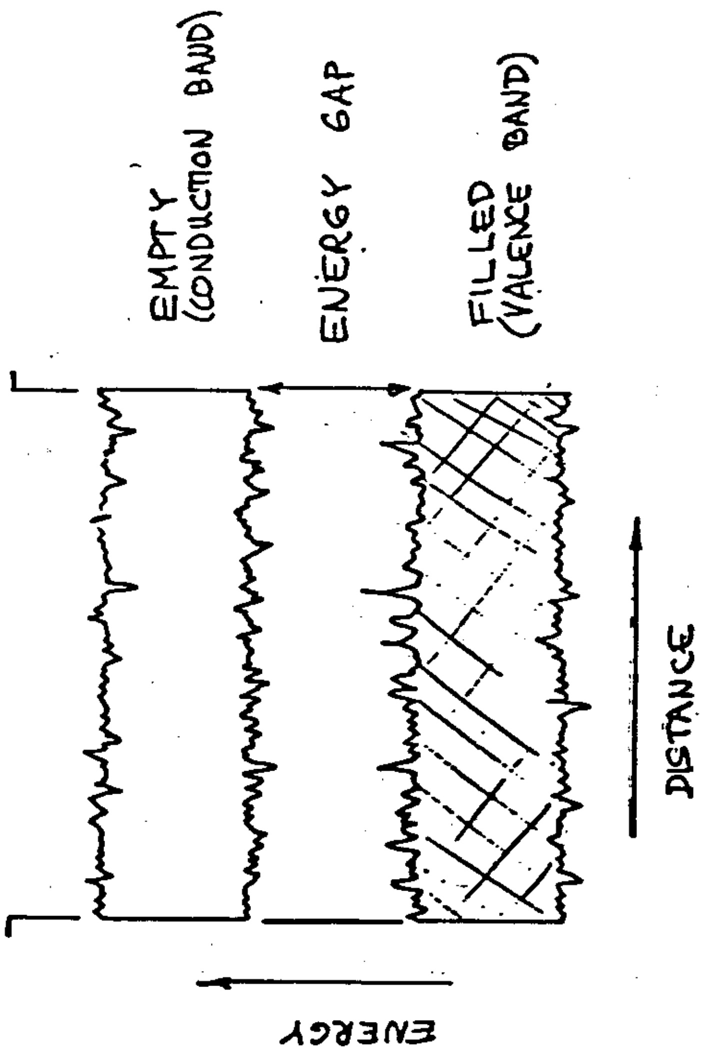
THE STRUCTURE OF CRYSTALLINE SILICON IS HIGHLY REGULAR AND SYMMETRIC



AMORPHOUS SILICON HAS NO LONG RANGE ORDER

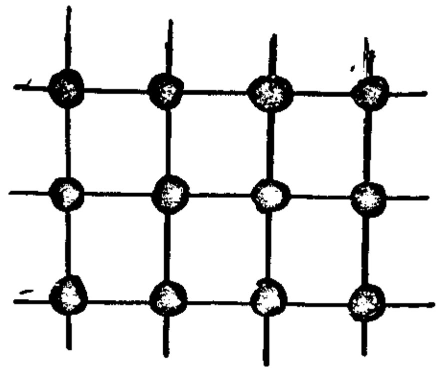


AN AMORPHOUS SEMICONDUCTOR



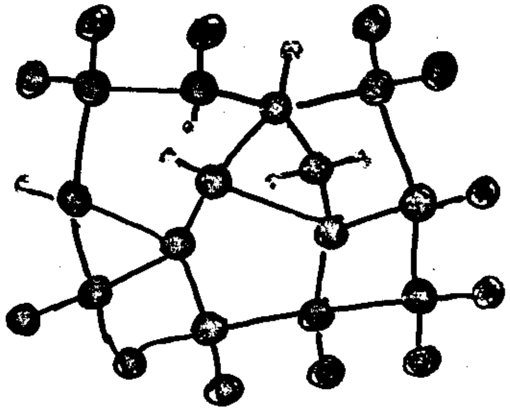
TETRAHEDRAL COORDINATION

c-Si

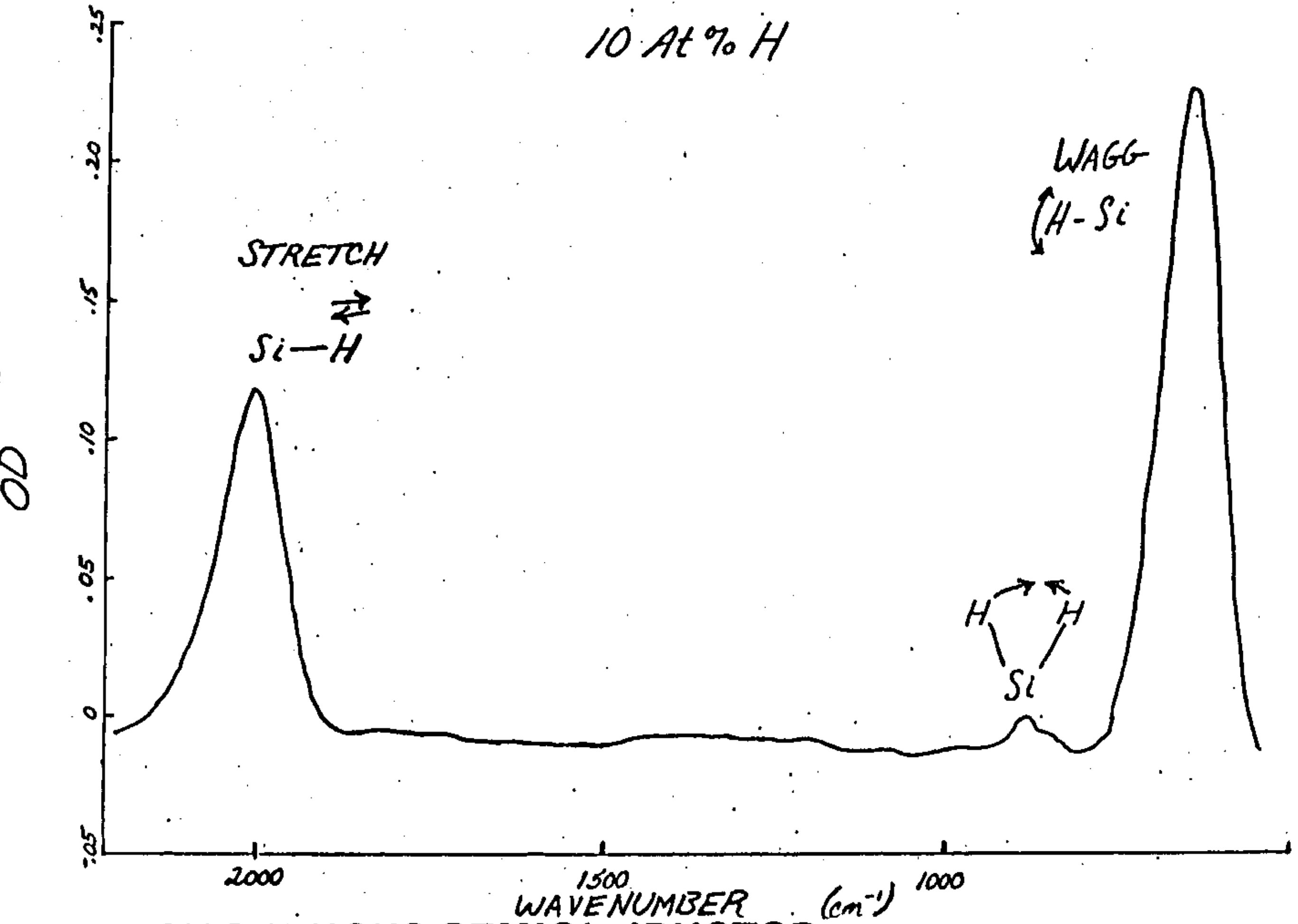


a-SiH$_x$

DANGLING BONDS ARE HEALED BY H

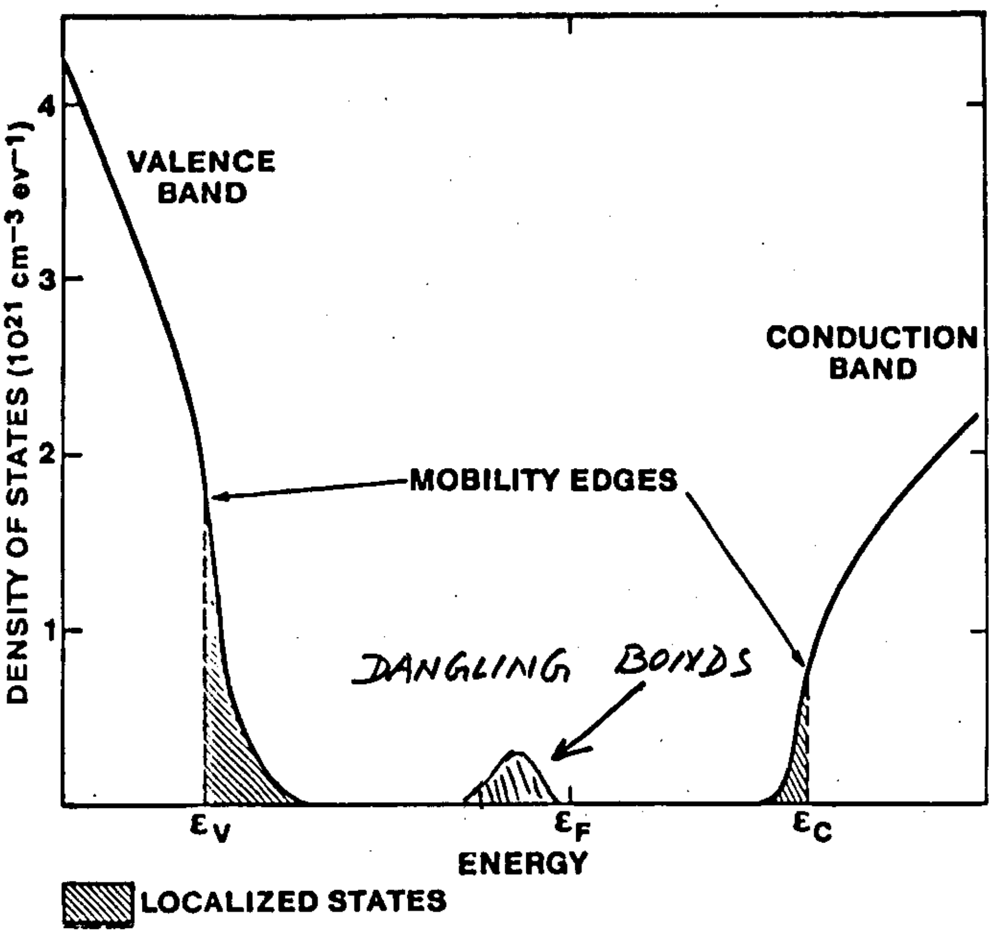


15



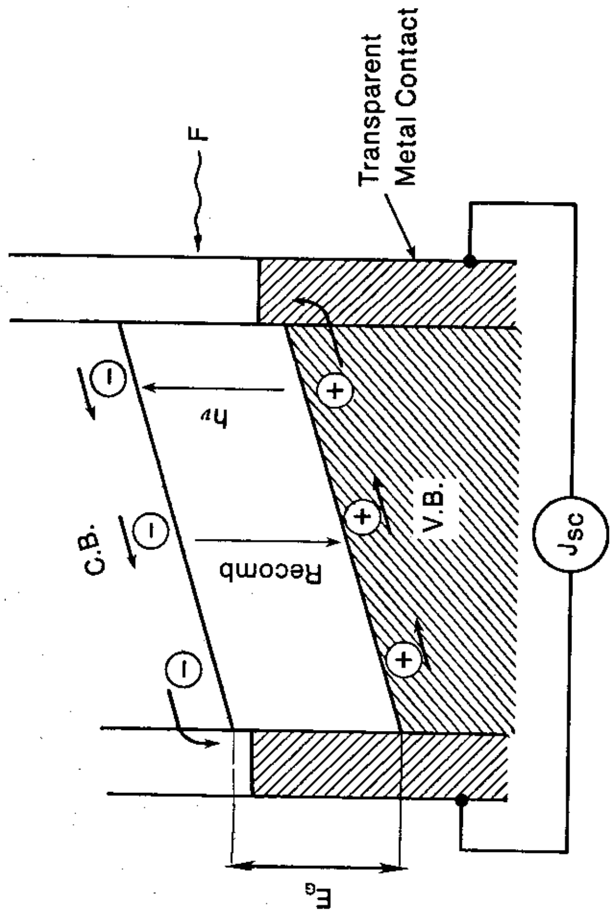
AMORPHOUS SEMICONDUCTOR

16

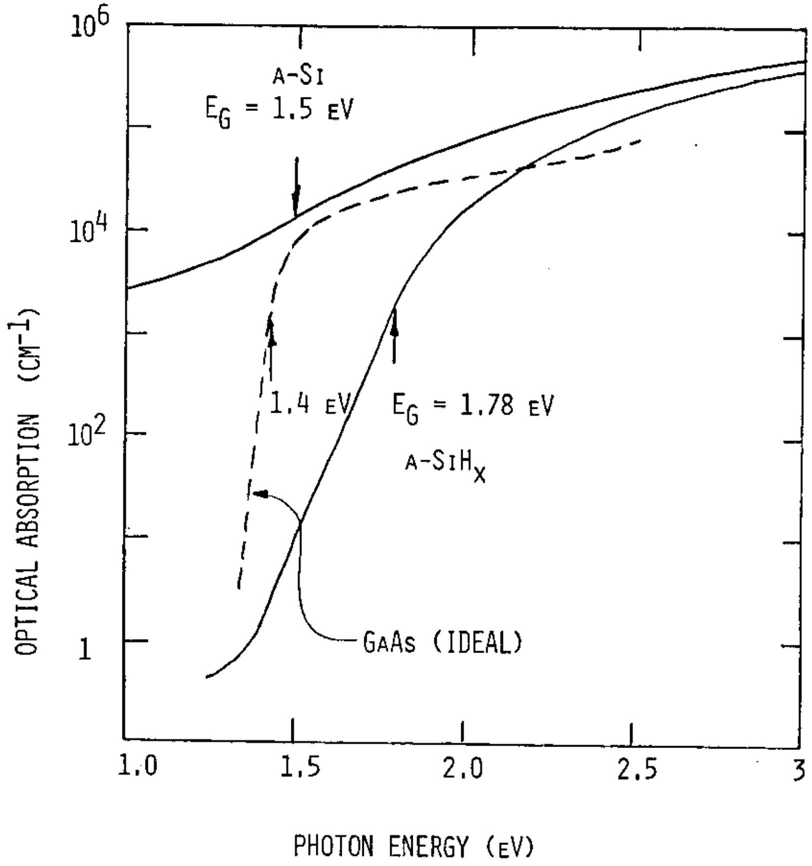


EFFICIENT THIN FILM SOLAR CELL

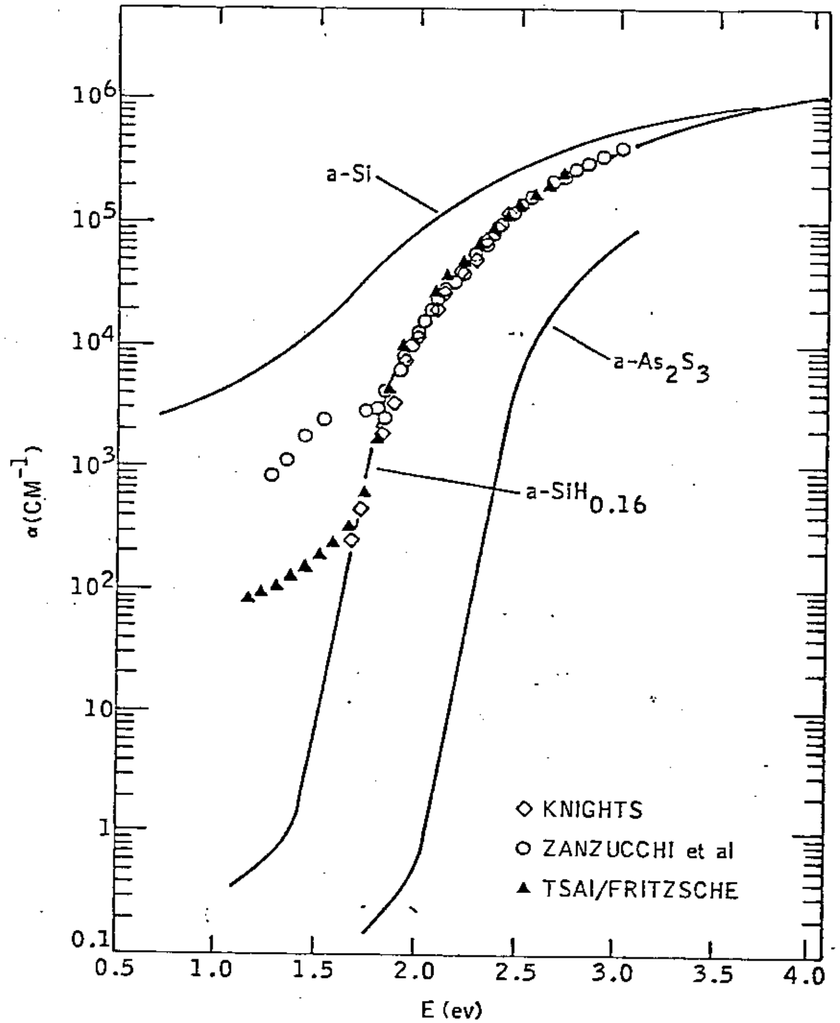
1. Band gap $E_G = 1.4$ eV
2. Strong optical absorption (d ~ 1 μm)
3. Photogenerated carrier extraction efficiency ~ 100%



THE BANDGAP OF AMORPHOUS SILICON DEPENDS ON HOW THE MATERIAL IS MADE

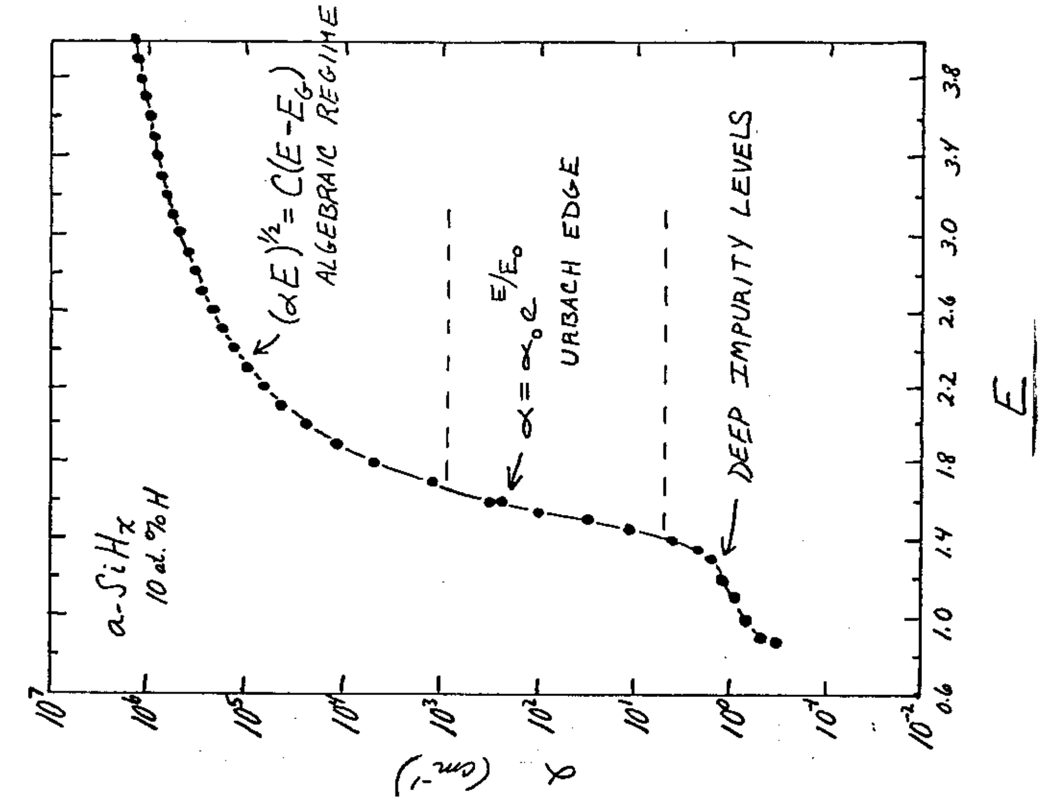


G. D. CODY
B. ABELES
C. R. WRONSKI



α(CM^{-1})
10^6
10^5
10^4
10^3
10^2
10
1
0.1
a-Si
a-As_2S_3
a-$SiH_{0.16}$
◇ KNIGHTS
○ ZANZUCCHI et al
▲ TSAI/FRITZSCHE
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0
E (ev)

19



a-SiHx
10 at. % H
$(\alpha E)^{1/2} = C(E - E_G)$
ALGEBRAIC REGIME
$\alpha = \alpha_0 e^{E/E_0}$
URBACH EDGE
DEEP IMPURITY LEVELS
α (cm^{-1})
E

20

OPTICAL ABSORPTION

$$\alpha(E) \propto \iint d\epsilon_1 \, d\epsilon_2 \, \delta(\epsilon_1 - \epsilon_2 - \epsilon)$$

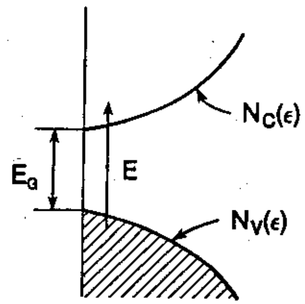
$$\times N_C(\epsilon_1) N_V(\epsilon_2) M(\epsilon_1, \epsilon_2)$$

$$\text{For } N_C(\epsilon) \propto (\epsilon - E_C)^{1/2}$$

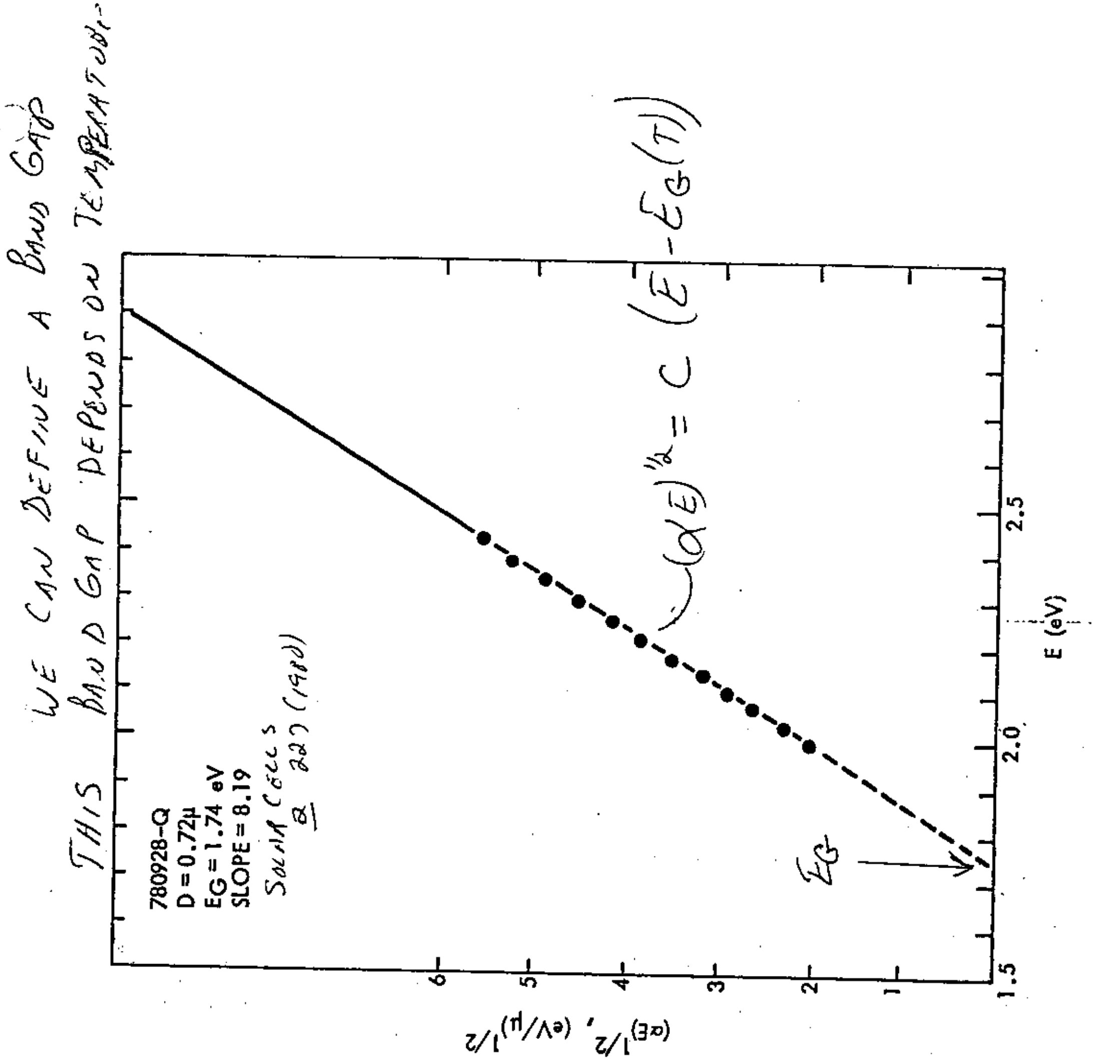
$$N_V(\epsilon) \propto (\epsilon - E_V)^{1/2}$$

$$M(\epsilon_1, \epsilon_2) = \text{const.}$$

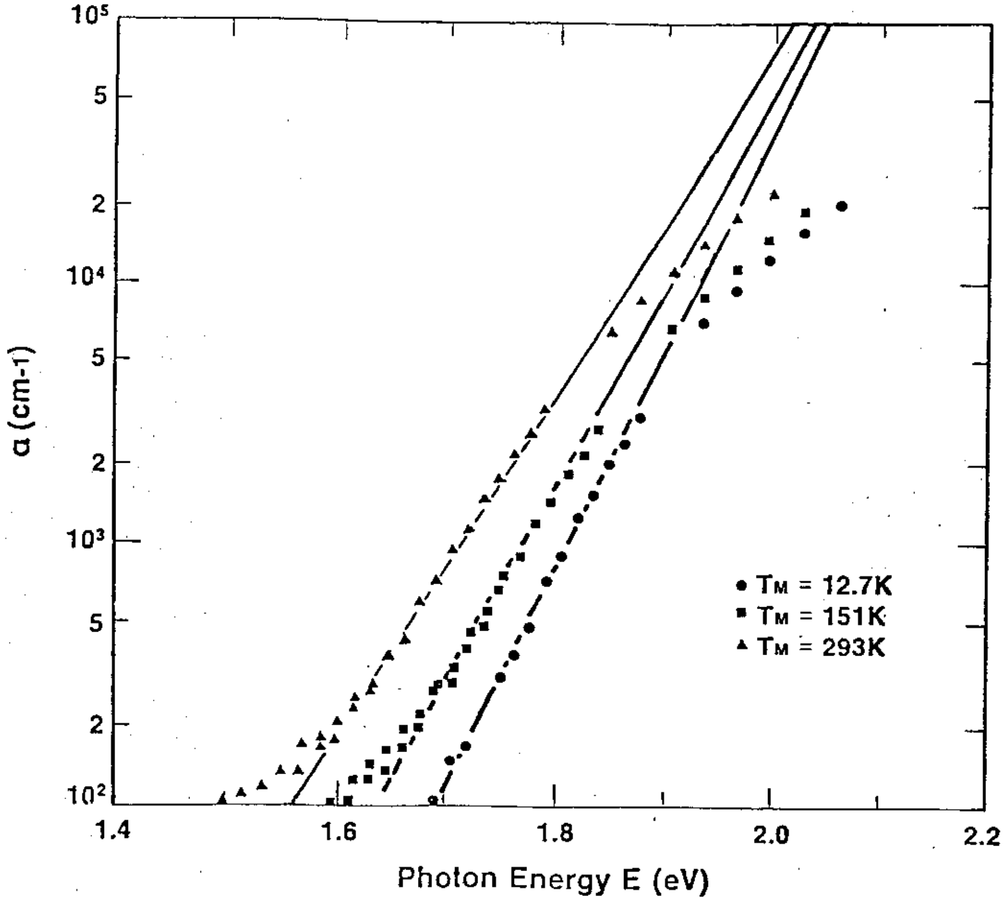
$$\alpha E \propto (E - E_G)^2$$



1. J. Tauc, in amorphous and liquid semiconductors, edited by J. Tauc(Plenum, London, 1976) Chapter 6.



THERMAL DISORDER BROADENS ABSORPTION EDGE AND LOWERS BANDGAP



G. D. CODY
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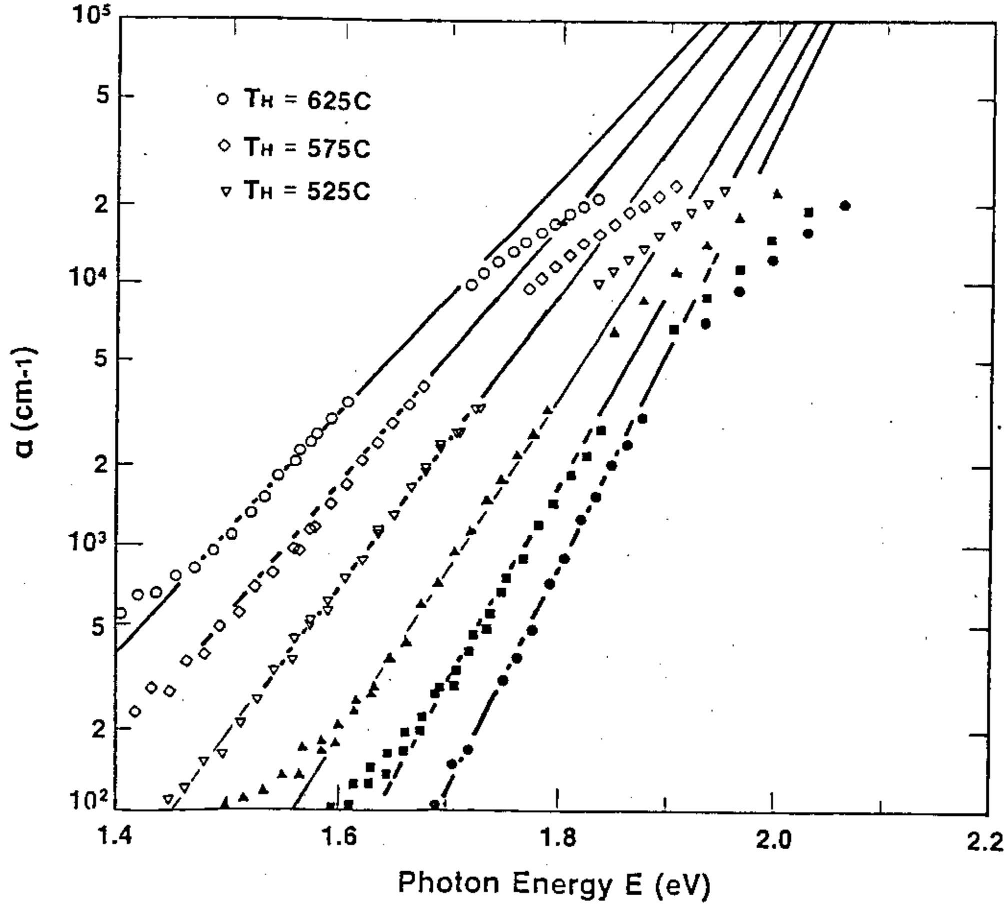
B. ABELES
B. BROOKS
Y. GOLDSTEIN

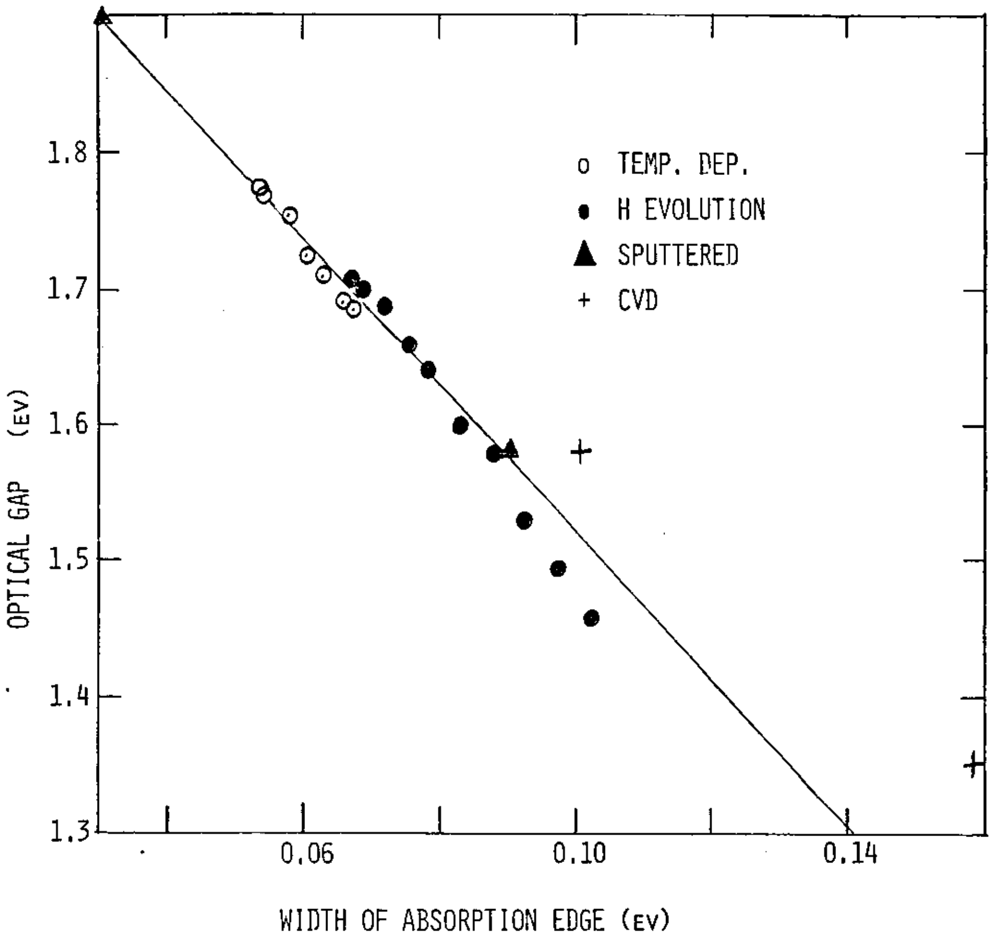
STRUCTURAL DISORDER ALSO BROADENS ABSORPTION EDGE AND LOWERS BAND GAP

- LATTICE DISORDERED BY HEAT TREATMENTS THAT EVOLVE HYDROGEN



G. D. CODY, T. TIEDJE, B. ABELES, B. BROOKS, Y. GOLDSTEIN

IN AMORPHOUS SILICON OPTICAL GAP AND WIDTH OF ABSORPTION EDGE ARE RELATED



G. D. CODY T. MOUSTAKAS
T. TIEDJE B. BROOKS
B. ABELES Y. GOLDSTEIN

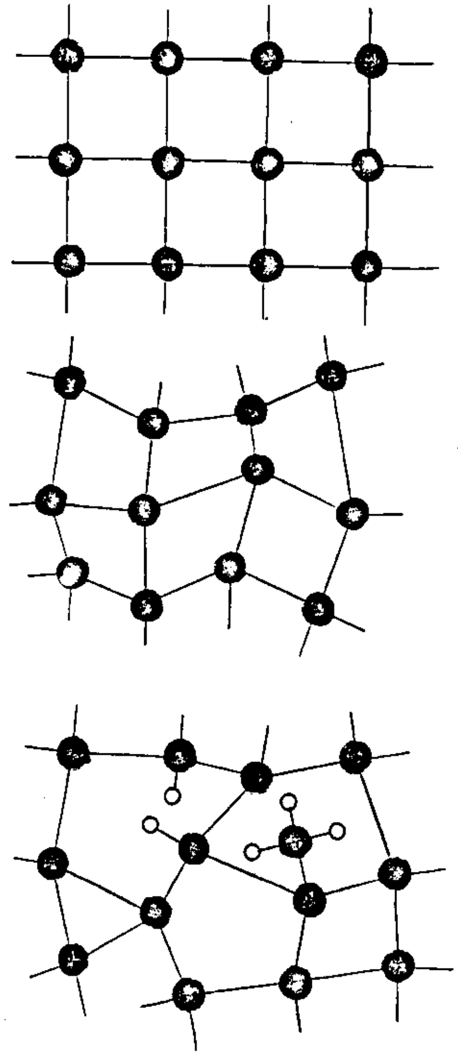
25

THERMAL AND STRUCTURAL DISORDER ARE SIMILAR

CRYSTAL AT 0^oK

CRYSTAL AT ROOM TEMPERATURE (SNAP SHOT)

AMORPHOUS MATERIAL



26

PHENOMENOLOGICAL MODEL[1]

EQUIVALENCE OF STRUCTURAL AND THERMAL DISORDER:

$E_0 (x, T) \propto \langle U^2 \rangle_T + \langle U^2 \rangle_X$

$E_G (T, x) = E_G (0, 0) - D \langle U_0{}^2 \rangle \left(\frac{E_0 (T,x)}{E_0 (0,0)} - 1 \right)$

$x = \frac{\langle U^2 \rangle_X}{\langle U^2 \rangle_0}$ DISORDER PARAMETER

$\langle U^2 \rangle_X$ = RMS STRUCTURAL DISORDER

$\langle U^2 \rangle_0$ = .08 Å RMS OF ZERO PT. MOTION

D = 30 eV/ $Å^2$ SECOND O DEF. POT.

$E_G (0,0)$ = 2.0 EV

1 CODY ET AL., PHYS. REV. LETT. 47, 1480 (1981).

COHERENT POTENTIAL APPROXIMATION

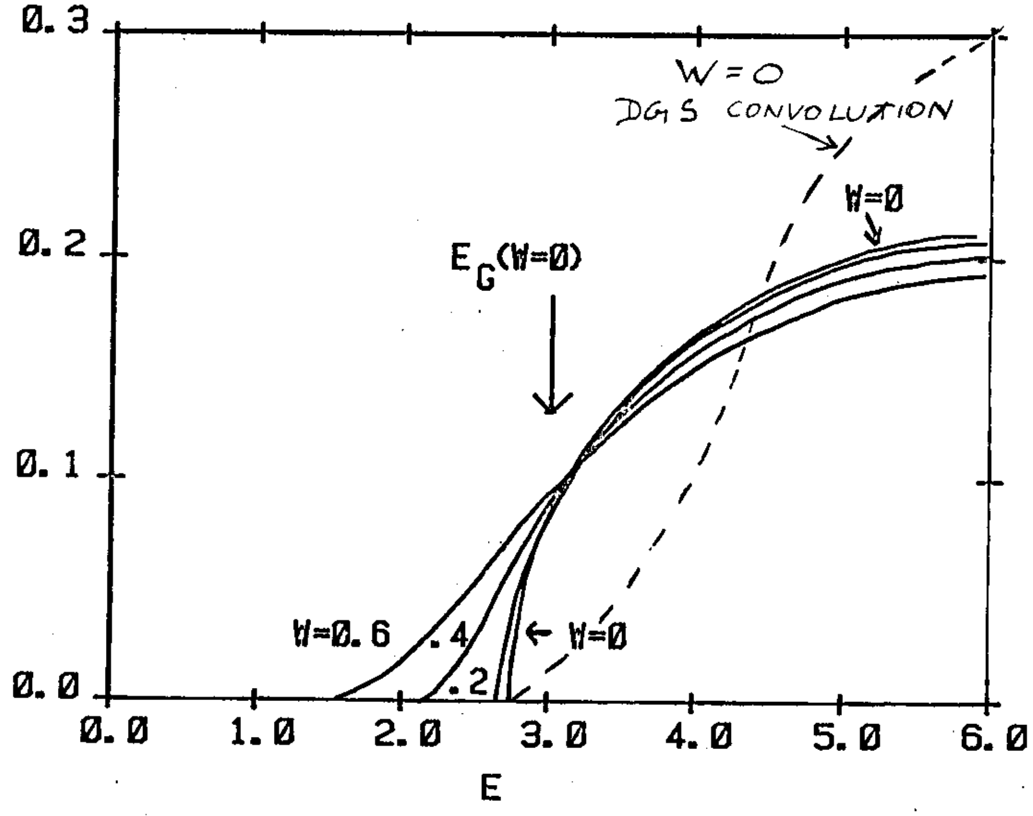
(ABE AND TOYOZAWA, J. PHYS. SOC. JAP 50, 2185 (1981)

- DISORDER CHARACTERIZED BY GAUSSIAN DISTRIBUTION WITH RMS OF RANDOM FLUCTUATIONS - W
- DENSITY OF STATES $\frac{1}{\pi B^2_\mu} \sqrt{(B_\mu{}^2 - \epsilon^2)}$
  ($B_{v,c}$ BAND WIDTH)

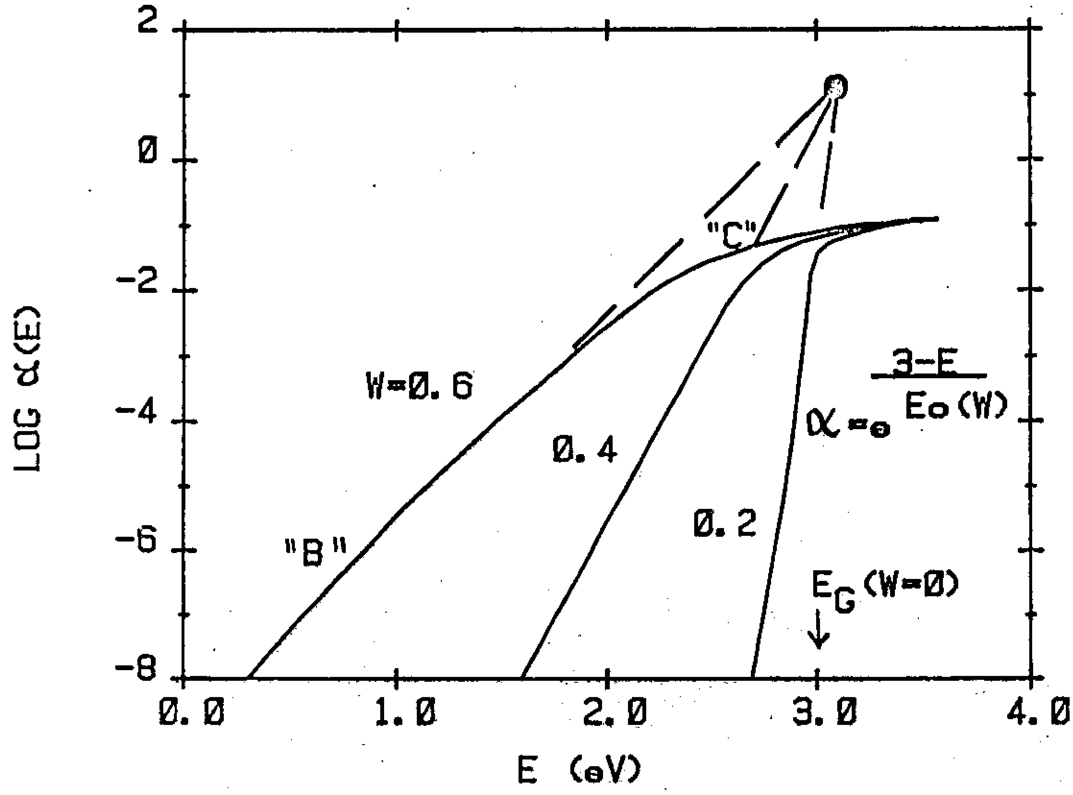
  MATRIX ELEMENT - κ RELAXATION AND DISORDER INDUCED SPATIAL CORRELATION
- THEORY: $E_0 \approx 0.5 \frac{W}{B}$
  $\alpha E \propto (E - E_G)^2$
  $E_G = 3 - 10\ E_0$
- EXPERIMENT:
  $E_G = 2.1 - 6.2\ E_0$

THE ONLY FEATURE IN THE THEORY IS
AT ZERO DISORDER (W=0)

ABE & TOYOZAWA
JPS JAPAN 50 2185 (1981)

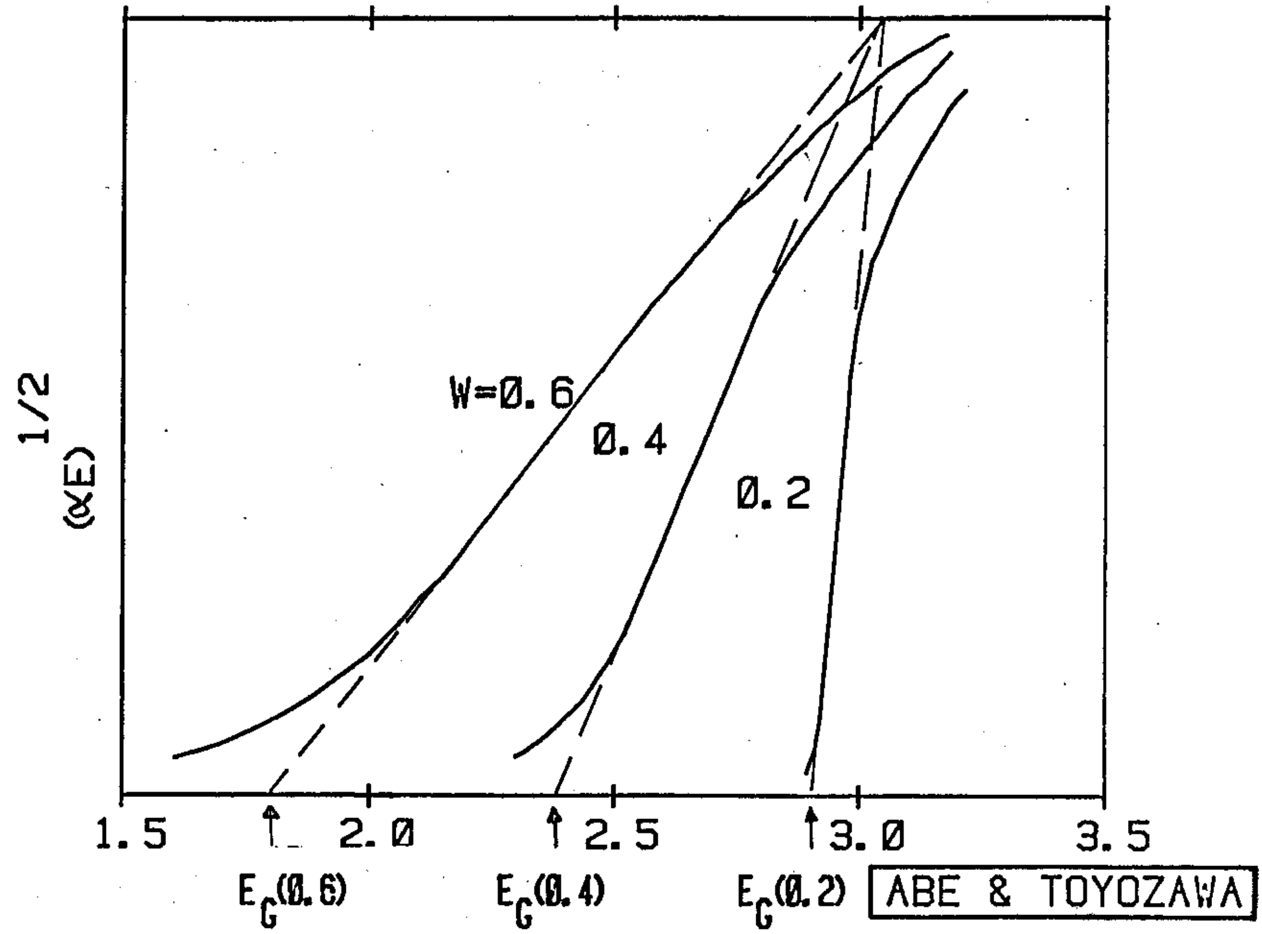


THERE IS AN URBACH REGION AND E_G(W=0) IS THE FOCUS



ABE & TOYOZAWA

THERE IS A PARABOLIC REGION, AND IN THAT REGION $E_G(w)$ CAN BE DEFINED AND $E_G(w) \doteq 3-10E_o(w)$



SUMMARY

- EDGE DEFINED BY E_G AND E_0, BUT THESE ARE LINEARLY RELATED AND BOTH DOMINATED BY STRUCTURAL AND THERMAL DISORDER
- RECENT THEORY SUGGESTS THAT EDGE IS THE BROADENING OF A DIRECT GAP OF 2.1-2.2 EV FOR A-Si:H_X (ABE/TOYOZAWA)
- SHARPENING THE EDGE IMPROVES A-Si:H_X "ELECTRICALLY." IT ALSO REDUCES THE COUPLING TO THE SOLAR SPECTRUM

CONCEPTS IN PHOTOCONDUCTIVITY AND ALLIED PROBLEMS

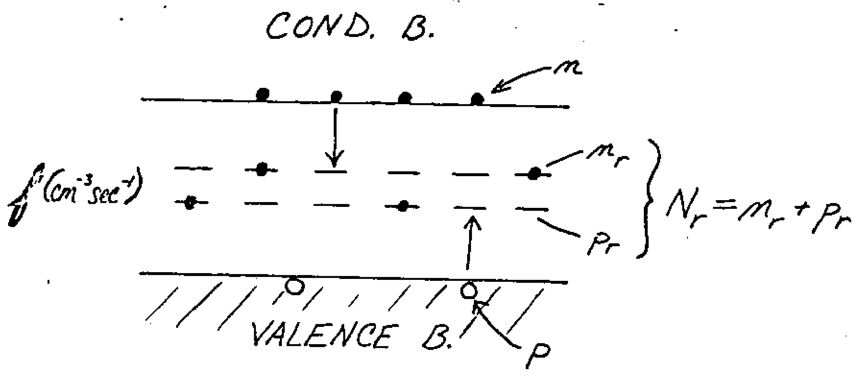
"ALL YOU EVER NEED TO KNOW ABOUT PHOTOCONDUCTIVITY

ALBERT ROSE

RCA Laboratories
Princeton, New Jersey

1978
ROBERT E. KRIEGER PUBLISHING CO.
Huntington, New York

SINGLE SET OF RECOMB. C., LOW LIGHT $n, p <$.



$$n = f\tau_n \qquad p = f\tau_p$$

n (p) = free electron (hole) density

n_r (p_r) = recombination c. occupied (unoccupied) by el.

τ_n (τ_p) = free electron (hole) lifetime

f = photogeneration rate

$$\tau_n^{-1} = K_n p_r \qquad \tau_p^{-1} = K_p n_r$$

K_n (K_p) capture probabilities

EXAMPLE: HIGH ILLUMINATION

1 SUN ~ 10^{17} photons/cm^2 sec

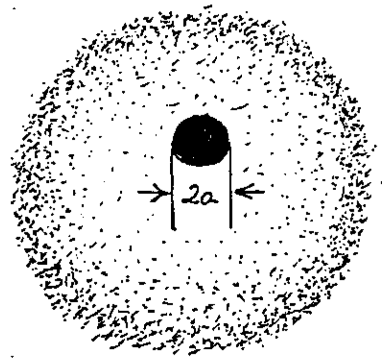
FILM 1 μm

$$f = \frac{10^{17}}{10^{-4}} = 10^{21} \text{ photons/cm}^{-3}\text{sec}^{-1}$$

$\tau_n = 10^{-6}$ sec
$n = 10^{15}$ cm^{-3}
$\tau_p = 10^{-8}$ sec
$p = 10^{11}$ sec

} TYPICAL a-SiH_x SOLAR CELL

A. DIFFUSIVE : $(\ell < a)$



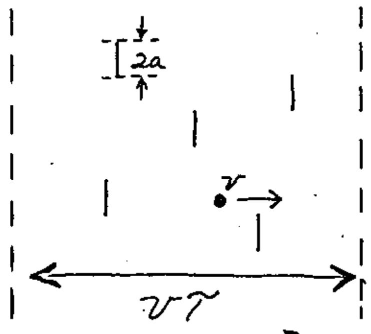
$$n(x) = \left(1 - \frac{a}{x}\right) n_o$$

$$\frac{dn_o}{dt} = -n_r 4\pi a^2 D \left.\frac{dn}{dx}\right|_{r=a}$$

$$\frac{dn_o}{dt} = -4\pi n_r a D n_o$$

$$\frac{1}{\tau} = 4\pi n_r a D \quad \text{or} \quad K = 4\pi a D$$

B. BALISTIC : $(\ell > a)$



$$n_r v \tau \pi a^2 = 1$$

$$\frac{1}{\tau} = n_r v \pi a^2$$

$$K = v \pi a^2$$

CAPTURE CROSS SECTION

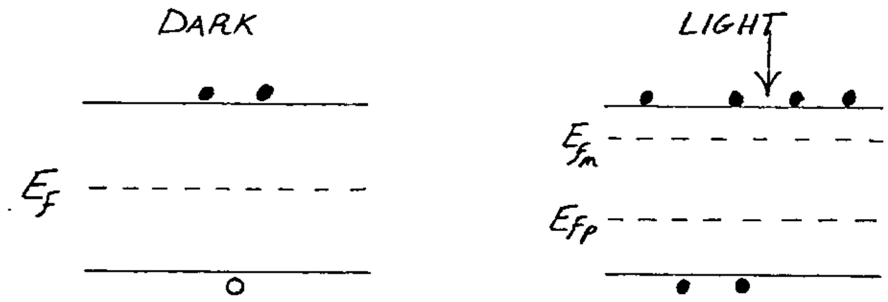
$$\frac{a_{bal}}{a_{diff}} = \sqrt{\left(\frac{4\,\mu kT}{e\,a_{diff} v}\right)}$$

$$a_{bal} = a_{diff}$$

$a_{diff} = 1$ (Å)
$\mu = 1\ cm^2/V\,s$
$v = 10^7$ cm/s
$T = 300$°K

Center	a_{diff} (Å)
Neutral (at dimens.)	1
Coulomb attractive ($kT = \frac{e^2}{\epsilon r}$)	50
Coulom repulsive	10^{-3}

QUASI-FERMI LEVELS



$$n = N_c e^{-\frac{(\epsilon - E_{Fn})}{kT}}$$

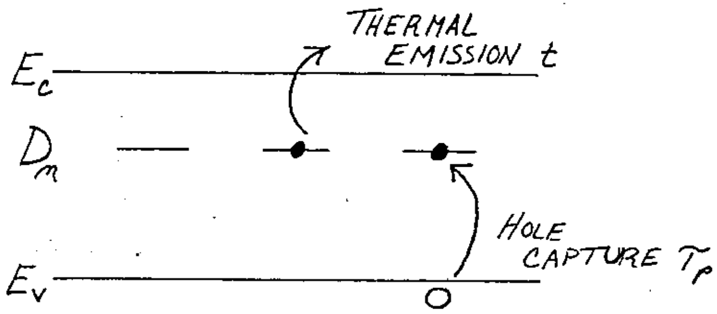
$$p = N_v e^{-\frac{(\epsilon - E_{Fp})}{kT}}$$

$$N_c = 2\left(\frac{2\pi m^* kT}{h^2}\right)^{3/2} = 2 \times 10^{19}\ cm^{-3}$$

$$(T = 300°K,\ m^* = m)$$

majority carrier n if $n > p$

DEMARCATION LEVELS



AT DEMARCATION LEVEL $t = \tau_p$

$$t = \omega^{-1} e^{\frac{E_c - D_n}{kT}}$$

$$\tau_p = \frac{1}{v S_p p}$$

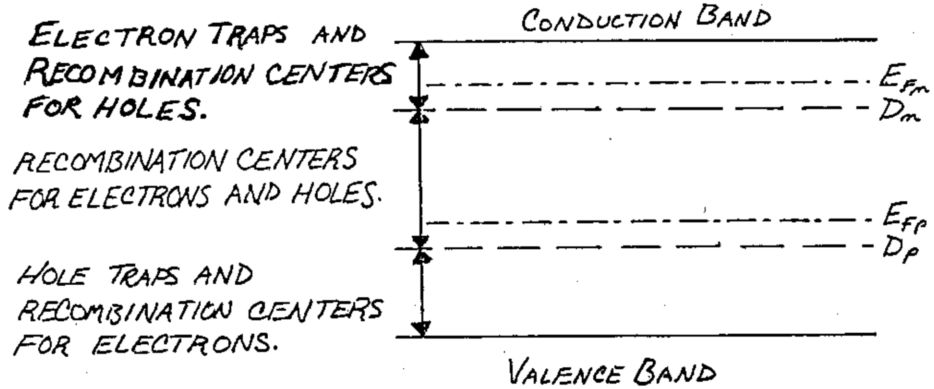
$\omega = N_c v S_p$ attempt frequency (by detailed balance)

$$\left.\begin{aligned} e^{-\frac{E_c - D_n}{kT}} &= \frac{\omega}{v S_p p} \\ e^{-\frac{E_c - E_{Fn}}{kT}} &= \frac{n}{N_c} \end{aligned}\right\}$$

$$E_c - D_n = E_c - E_{Fn} + kT \ln \frac{n S_n}{p S_p}$$

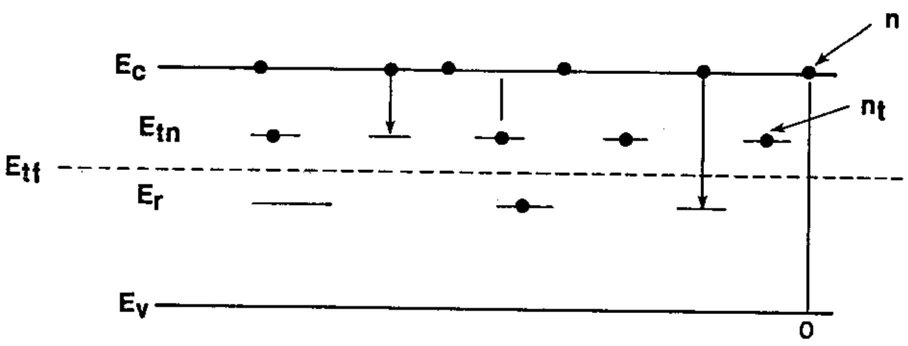
- BELOW D_n STATES ACT AS RECOMBINATION CENTERS FOR HOLES.

DEMARCATION LEVELS



$$E_{Fn} - D_n = E_{Fp} - D_p = kT \ln \frac{n S_n}{p S_n}$$

TRAPPING (Single Level)



$$\frac{n_t}{N_t} = \frac{n}{N_c} e^{\frac{-(E_c - E_{tn})}{kT}}$$

response time $\tau_{on} = (1 + \frac{n_t}{n})\tau_n$

drift mobility $\mu_{nD} = \mu_n \frac{n}{n_t + n}$

Free carrier mobility $= \mu_n$