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Studies on Relative Effects of Charged and Neutral Defects in Hydrogenated Amorphous Silicon

Final Report
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NREL

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PREFACE

This report covers the third year of a continuing research study to understand the relative importance of charged and neutral defects in Amorphous Silicon. It is well known that neutral defects exist (E.S.R.) and act as recombination centers limiting $\mu\tau$ products. On the other hand, charged defects can exist and they would be traps and not limit $\mu\tau$ but might even enhance $\mu\tau$. A continuing research program to understand the relative importance of charged and neutral defects could help us better understand efficiency and stability. This work at the University of North Carolina in collaboration with other institutions is both experimental and theoretical.

The earliest proposals for charged defects came from Professor David Adler (deceased) of MIT who suggested that negative correlation energies would yield charged defects as in the Chalcogenides. This model could explain a wide variety of experimental results such as optical absorption, luminescence and temperature dependence of photoconductivity. However, Adler's model had difficulty explaining the spin signal. More recently, thermodynamic models including a positive correlation energy have been more successful.

It is therefore now time to reconsider these problems in more detail both experimentally and theoretically. In this connection we will continue our studies on electroluminescence, recombination, electronic transport and photocarrier generation in intrinsic material. This information will certainly be relevant to solar cell efficiencies and evaluation of various models for photo-degradation.

The work performed at UNC-Chapel Hill is a collaborative effort of visiting scientists and graduate students. A list of the group members are:

Professor Marvin Silver

Daxing Han - Research Associate

Keda Wang - Research Associate

Mattieu Kemp - graduate student (no cost to research budget)

We have also benefited from numerous discussions with our Condensed Matter Theorists: J. P. Hernandez and K. S. Dy. At other institutions we have collaborated with H. Bassler, University of Marburg; F. Shapiro, Drexel; A. Delahoy, Chronar and most particularly with H. Branz, S.E.R.I.

SUMMARY

Objectives

Our objectives continue to be to explore the electronic structure, including neutral and charged defects, and optoelectronic effects including the formation of Staebler-Wronski defects. To attempt to achieve these goals we have concentrated on exploring electroluminescence (E.L.) experimentally and interpreting the results employing a simple guiding model.

The simple guiding model assumes an exponential density of states and recombination rate constants (radiative and non-radiative) which are governed by hopping transitions. While the interpretation of the data may not be quantiatively exact, it does provide a qualitative picture of these optoelectronic processes. We find that we can independently estimate the temperature dependence of non-radiative and radiative recombination processes. We observed that only the non-radiative process seems to depend upon temperature, but not the radiative process.

We also made measurements as a function of photodegradation of the material. It was clear from our results that recombination centers such as neutral dangling bonds do not affect the radiative lifetime.

These results implicate that the radiative recombination processes are not distant pair tunneling but rather results from electrons hopping down due to the coulomb interaction.

Preliminary experiments have been made on the effect of photodegradation on transient space charge limited currents in n/i/n structures. These experiments can directly yield information on the occupied defect centers induced by the photodegradation and are not a result of recombination processes. To date our results seem to be consistent with a picture which places the doubly occupied defects at quite a high energy ($\simeq 0.4$ e.v. below the conductionband).

Our research last year has resulted in 10 papers being published (seven submitted last year) and 3 submitted for publication.

Table of Contents

I. *Introduction*

During the past year we concentrated on experiments on electroluminescence (E.L.) and on transient space charge limited currents as a function of the various experimental parameters and photodegradation. This emphasis came from our desire to better understand radiative and non-radiative processes and the density of states generated by photodegradation.

In section II we first present a simple model in order to help guide an understanding of the experimental results on E.L. We then present our results on forward bias current, (j_F), and E.L. vs voltage temperature and photodegradation. Finally, we show some results on transient space charge limited currents .

Perhaps our most interesting results are the temperature dependence of the radiative and non-radiative lifetimes vs temperature. We found that only is the non-radiative lifetime temperature dependent but the radiative lifetime is temperature independent. We propose a simple model to explain these results as well.

II. *Results*

A) Model for E.L

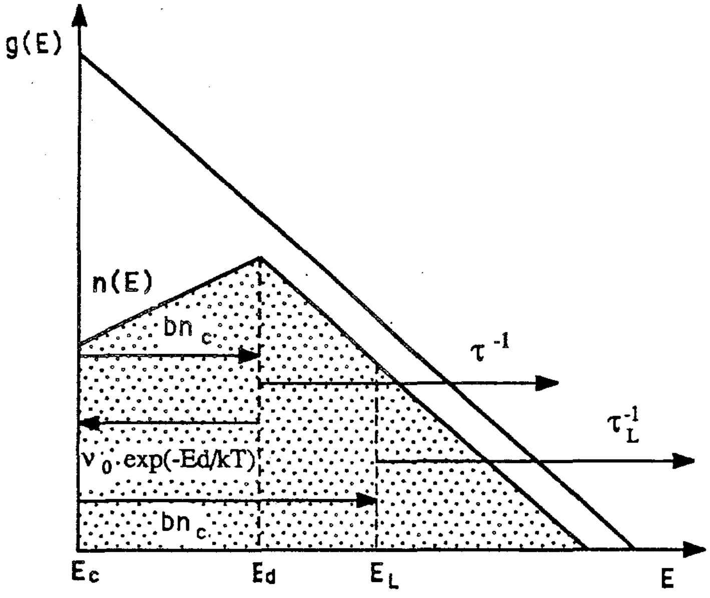

Fig. 1 Schematic diagram of the density of electronic states and their population under double injection conditions. Shaded areas are filled states. The demarcation levels E_d and E_L are indicated. The transitions into and out of states at E_d and E_L are indicated by the arrows.

A simple way to qualitatively understand forward bias currents and E.L. can be seen with the use of figure 1 and the assumptions of Lampert and Mark[1]. According to Lampert and Mark, the total excess charge of each sign $Q^{\pm}$ that can form an injected plasma in an insulator is

$$(1) \qquad Q^{\pm} \approx CV \frac{\bar{\tau}}{t_0}$$

where $\bar{\tau}$ is the common average lifetime and t_o is the common average free carrier transit time. It is assumed that both holes and electrons are freely injected from their n^+ and p^+ contacts such that $E(n^+) = E(p^+) = 0$. Since $t_o \propto V^{-1}$ equation (1) leads to the result that

$$(2) \qquad Q^{\pm} \propto V^2 .$$

Most of the injected electrons are trapped in tail states at ε_d and only the free carriers contribute to the current. Therefore, the forward bias current

$$(3) \qquad j_F \propto \frac{CV}{L} \frac{\tau}{t_o^2} \frac{g_c}{g_d} \exp(-\varepsilon_d/kT)$$

where g_c and g_d are the density of states at the mobility edge and at ε_d, respectively. Using the exponential density of states and the definition of ε_d, one obtains

$$(4) \qquad j_F \propto \frac{CV}{Lt_o^2 v} \exp[(T/T_o) \ln v\tau] = \frac{CV}{Lt_o^2 v} (v\tau)^{T/T_o}$$

Any temperature-independent non-radiative recombination mechanism would yield $j \propto e^T$.

We now consider the EL signal. To maintain steady state for the level ε_L it is clear from Figure 1 that

$$(5) \qquad EL \approx n_c g(\varepsilon_L) kT_o b .$$

Most of the luminescing carriers are located at ε_L. Since $n_c \propto j_F$, algebra similar to that yielding eqn. (4) gives

$$(6)\qquad EL \propto \frac{CV}{t_o} \exp\left[-(T/T_o)\ln\frac{\tau_L}{\tau}\right] = \frac{CV}{t_o}\left(\frac{\tau}{\tau_L}\right)^{T/T_o}$$

where we have used the relation $\varepsilon_L = kT \ln \nu\tau_L$ where τ_L is the radiative lifetime. Notice that the magnitude of E.L. is proportional to V^2.

From Eqns (4) and (6) we find

$$(7)\qquad \frac{EL}{j_F} \propto (\nu t_o)(\nu\tau_L)^{-T/T_o}\ .$$

Thus

$$(8)\qquad \ln\left(\frac{EL}{j_F}\right) = \text{const.} - \frac{T}{T_o}\ln(\nu\tau_L)$$

Guided with the relationships given by equations 4, 6, and 7 we can gain insight into the recombination mechanisms from a study of j_F and E.L. vs T and V. j_F depends principally upon τ , E.L. depends upon the ratio τ/τ_L and E.L./j then depends only upon τ_L . Independent studies of these effects can give insight into the recombination mechanisms.

B) *Experimental Results*

i) Electroluminescence

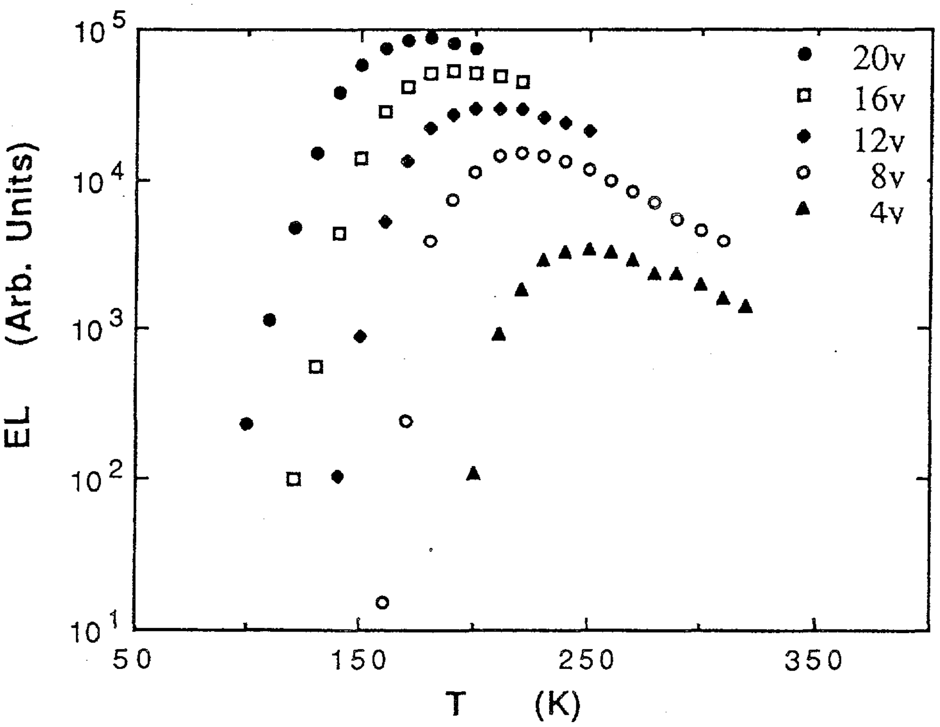

Fig. 2 Temperature dependence of steady-state EL at constant voltage condition for several applied voltages.

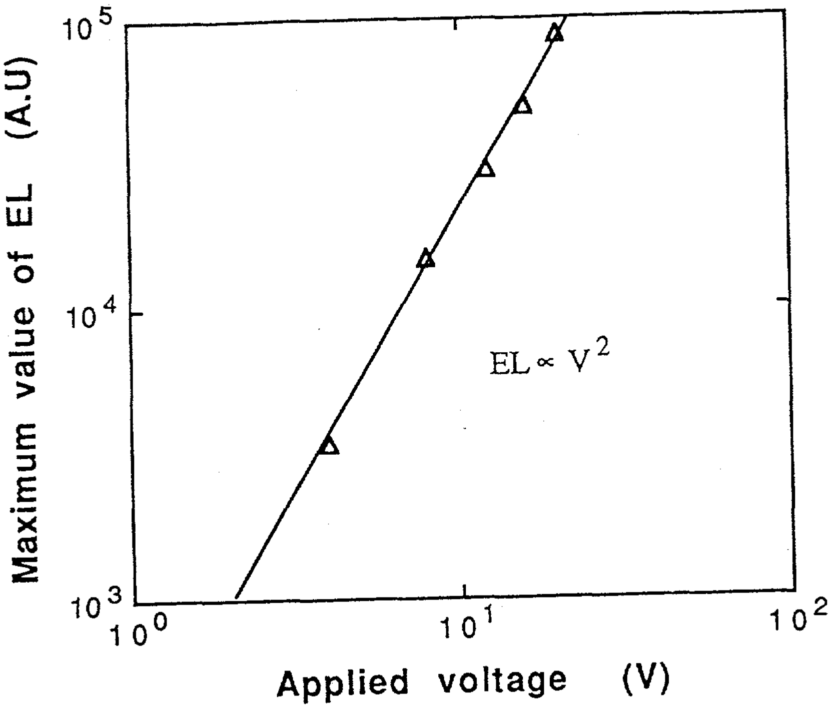

Fig. 3 EL (Tmax) versus applied voltage. Data from Fig. 2.

The temperature dependence of steady-state EL at constant applied voltage is shown in Figure 2. As can be seen, EL versus T shows a maximum at temperatures which depend upon the applied voltage V. The shapes of the curves resemble the photoluminescence results. However, the temperature of the EL maximum (T_{max}) is much higher in these EL experiments. We plot EL (T_{max}) versus V in Figure 3. As can be seen, EL (T_{max}) $\propto V^2$. No such simple correlation could be made between EL (T) and j_F, although in some cases EL is proportional to j_F at high current levels.

Shapiro and Silver have shown that the non-radiative lifetime in a transient double injection experiment can be obtained from the shape of the transient current. According to their simulations, τ/t_o, where t_o is the free carrier transit time, is obtained from the ratio of the minimum current during a transient to the final (maximum) current. Figure 4 shows a typical transient forward bias current displaying both the minimum and maximum current. We have computed τ/t_o as a function of temperature and voltage. A comparison between EL versus T and τ/t_o versus T at 12 volts is shown in Figure 5. The temperature dependences are similar. In Figure 6 we show T_{max} for the EL (from Fig. 2) and the temperature of the maximum in $\tau(T)$ As can be seen, the voltage dependence of these two independent measurements are remarkably similar. This suggests that the T dependence of EL is governed primarily by the non-radiative lifetime, τ .

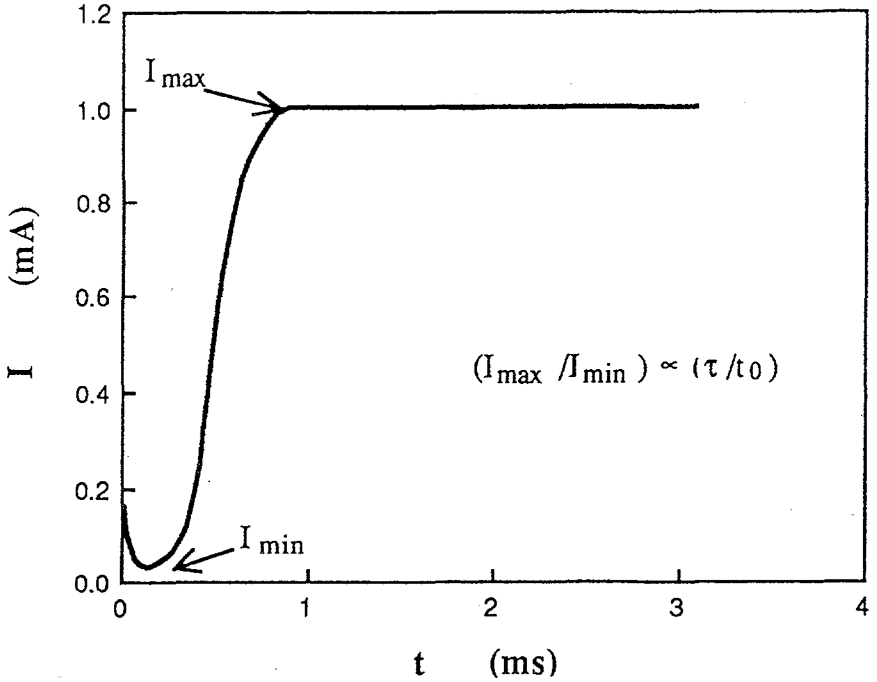

Fig. 4 A typical transient forward bias current curve. Note that the current displays a minimum and a final maximum.

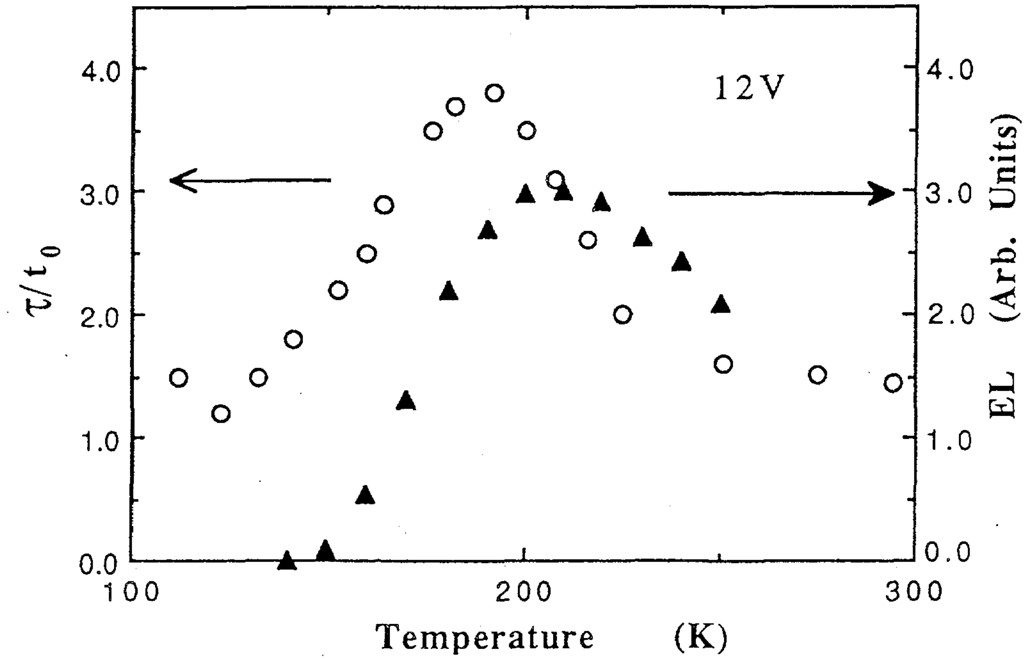

Fig. 5 EL and τ/t_0 versus T at 12V. Both show a maximum at approximately the same temperature.

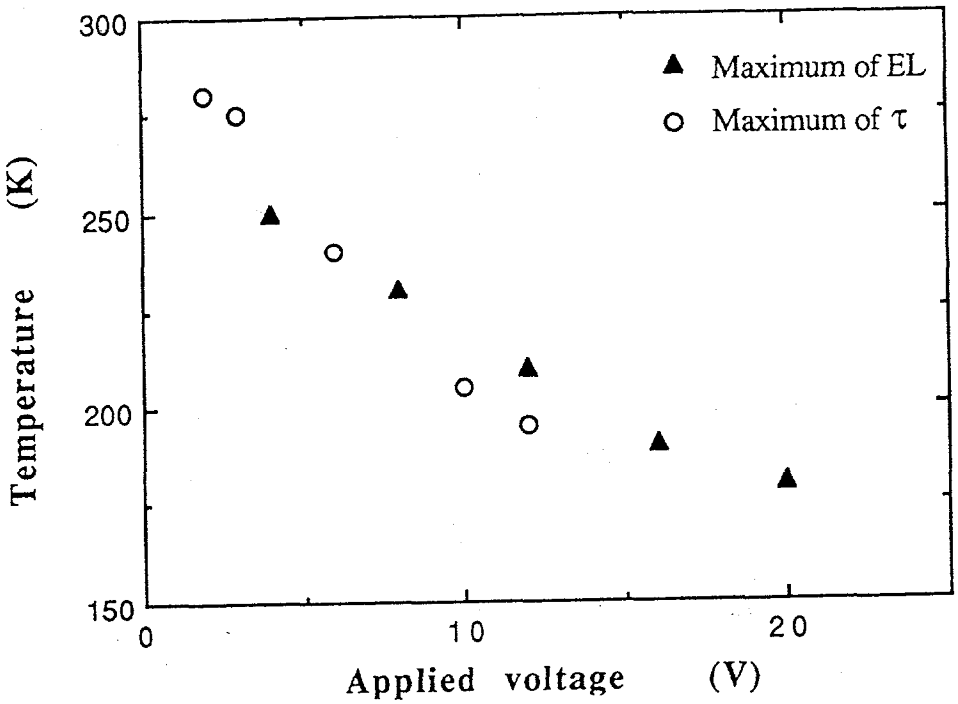

Fig. 6 Temperature for maximum EL and maximum τ versus voltage. Note the similar voltage dependences of these two independent results.

We have preliminary data on the effect of photodegradation on the forward bias current and E.L. These results are shown in figures 7, 8, and 9. What to be noted is that the major effect of degradation is found at low temperatures (T < 200°K). The really interesting result is shown in figure 9 (E.L./j_F) which depends upon the radiative lifetime. τ_L (see Eq. 7). Degradation seems to have no effect upon τ_L . We believe that this insensitivity is due to carriers hopping down in energy due to the Coulomb interaction.

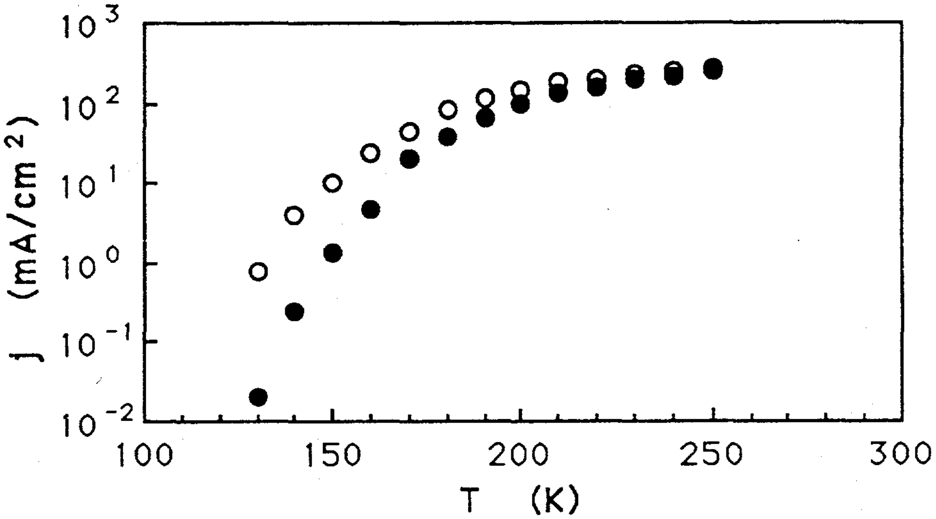

Fig. 7 Forward-bias current vs temperature for pin device before and after light-soaking. Open squares before, dark squares after degradation.

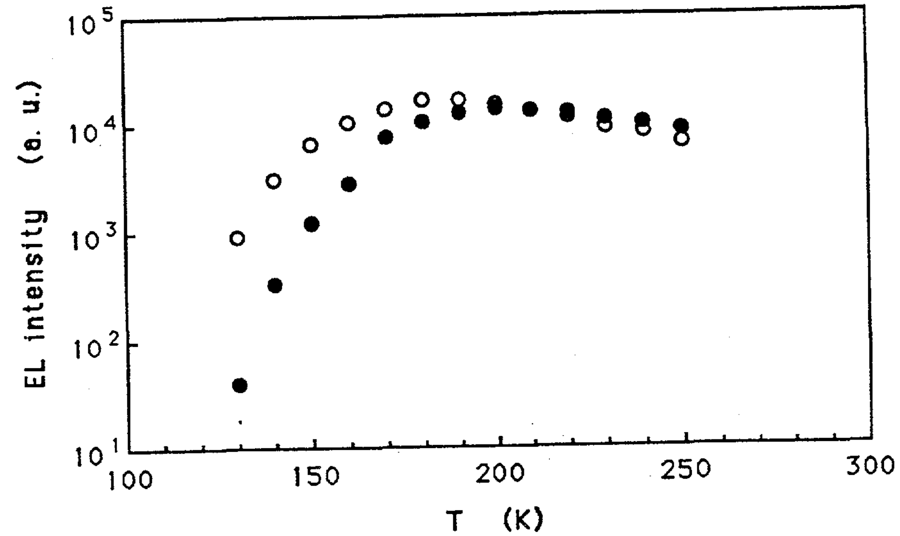

Fig. 8 EL vs temperature before and after light-soaking for the same sample under the same conditions as in Fig. 7.

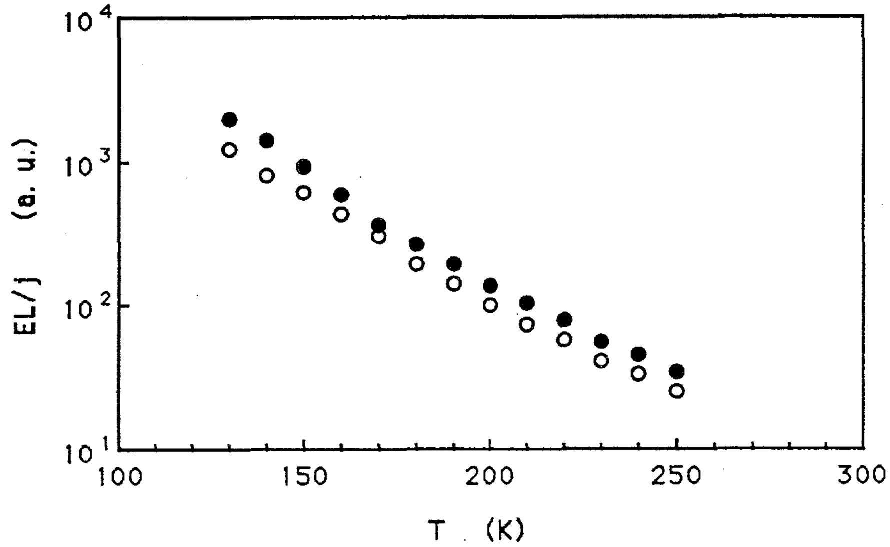

Fig. 9 EL/j_F vs temperature before and after light-soaking. EL and j_F data are from Figs. 7 and 8. Open circles before, dark circles after degradation.

Figure 10 shows a schematic diagram showing a possible microscopic model for radiative and non-radiative transitions. The lifetime for a radiative transition τ_L is composed of two parts: (1) a transport time τ_T and (2) a local radiative lifetime τ_r. It is assumed that $\tau_T << \tau_r$ so that τ_L the net lifetime is temperature independent.

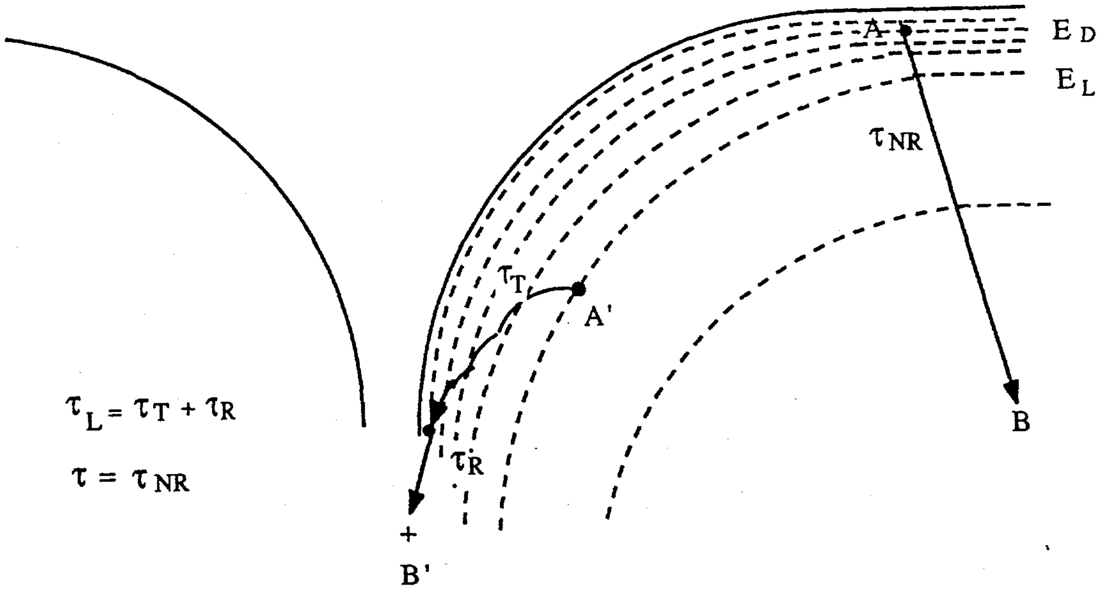

Fig. 10 Schematic diagram of a possible microscopic process for radiative and non-radiative transitions. A is a localized state at E_d (see Fig. 1). B is a neutral recombination center. A′ is a localized state at E_L and B′ is a charged recombination center.

ii) Space Charge Limited Currents

The time dependence of space charge limited currents (TSCLC) reflect the density, capture rate constant and energy of deep states. We have obtained preliminary data on the TSCLC in nin samples before and after photodegradation. A typical set of results is shown in figure 11. (State A refers to the annealed sample and B to the degraded sample). The sharp decay at about 10^{-6} sec in state B compared with state A probably reflects the increased density of deep defects (likely D_3^0) which capture the carriers thereby lowering the Gusse current. What is interesting is that the current in state A shows only a small decay compared with state B and from the shape of the curve, we estimate that the occupied deep level has an energy of only about 0.4 - 0.5 e.v. below the conduction band. While these results are only preliminary, it is reasonable to expect that TSCLC will be a probe of the effect of photodegradation.

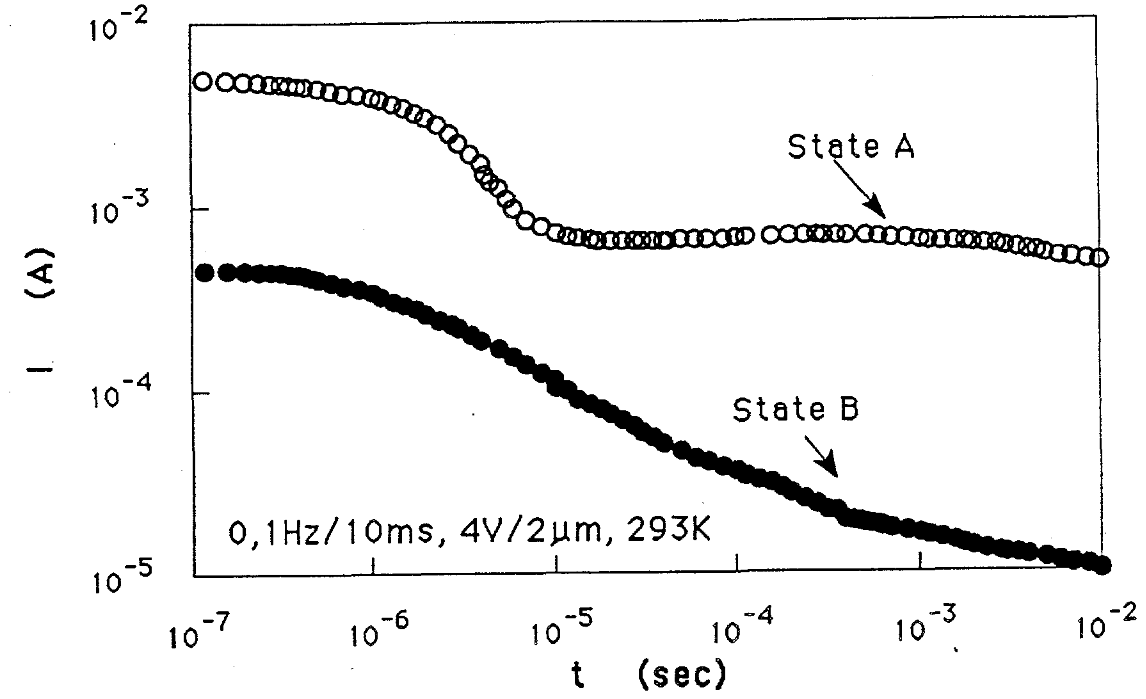

Fig. 11 A typical set of transient space charge limited current curves before and after light-soaking for a nin sample. State A is annealed state, state B is light-soaked state.

C. *Publications*

Published

1. "Current-Voltage Characteristics - What do Experiments Really Tell Us?" (with Finley Shapiro), Mat. Res. Soc. 149, 351 (1989).

2. "Electronic Transport at Low Temperatures in Amorphous Silicon" (with W. E. Spear), Mat. Res. Soc. 149, 351 (1989).

3. "A Unified Model for Exponential Band Tails, Optoelectronic Properties and Metastabililty in A-Si:H Based on Charged Dangling Bonds" (with G. Winborne - UNC/Chapel Hill; H. Branz - S.E.R.I.; L. Pautmeier and H. Bassler - Philipps University), Journal of Non-Crystalline Solids 114, 244-246 (1989).

4. "Charged Dangling Bonds," (with H. Branz), J. Non. Cryst. Sol. 114, 639 (1989).

5. "Experimental Determination for the Transition Temperature Between Ballistic and Hopping Controlled Recombination in a-Si:H (with M. E. Avanut, K. Wang and D. Han) MRS 192, 305 (1990).

6. "Defect Thermodynamics, Inhomogeneity and the Density of Gap States in Hydrogenated Amorphous Silicon." (with H. M. Branz) MRS 192, 261-272 (1990).

7. "Potential Fluctuation Due to Inhomogeneity in Hydrogenated Amorphous Silicon and the Resulting Charged Dangling-Bond Defects," with H. Branz. Phys. Rev. B42 , 7420 (1990)

Submitted for Publication

8. "Temperature and Current Dependence of Electroluminescence (with K. Wang, D. Han and M. E. Zvanut) Phil. Mag. 61 (to be published 1990).

9. "Electroluminescence Studies of Recombination in Hydrogenated Amorphous Silicon p-i-n devices. To be published Solar Cell. 1990.

10. "Low T. Transport in a-Si:H" (with M. Kemp) 3rd. International Hopping Conference .

Figure Captions

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16. Abstract (Limit: 200 words)

This report covers the third year of a continuing research study to understand the relative importance of charged and neutral defects in amorphous silicon. The objective of the study is to explore the electronic structure, including neutral and charged defects, and optoelectronic effects including the formation of Staebler-Wronski defects. The study concentrated on exploring electroluminescence experimentally and interpreting the results employing a simple guiding model. The simple guiding model assumes an exponential density of states and recombination rate constants (radiative and non-radiative) which are governed by hopping transitions. Measurements were also made as a function of photodegradation of the material. The results implicate that the radiative recombination processes are not distant pair tunneling but rather results from electrons hopping down due to the coulomb interactions. Preliminary experiments have been made on the effect of photodegradation on transient space charge limited currents in n/i/n structures. These experiments can directly yield information on the occupied defect centers induced by the photodegradation and are not a result of recombination processes. To date the results seems to be consistent with a picture which places the doubly occupied defects at quite a high energy (≈ 0.4 e.v. below the conduction band).

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