Recombination and Metastability in Amorphous Silicon and Silicon Germanium Alloys

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PREFACE

This report covers the second year of a continuing research study to understand how recombination, trapping and band-mobility modification affecting the electronic properties of amorphous semiconductors can be measured, characterized and described by an appropriate spectrum of defect states and how light-induced defects in a-Si:H and native defects in a-SiGe:H affect transport properties in these materials.

It is well known that light-induced effects (SWE) increase the density of states near the dark Fermi-level. There is a concomitant increase in the spin density probably due to an increase in the dangling bond density. The question that arises is can one relate the decrease in carrier lifetime directly to the measured increase in the density of deep states? To answer this we study experimentally and theoretically electroluminescence, recombination, electronic transport and photocarrier generation in a-Si:H and a-SiGe:H alloys. The information gleaned will certainly be relevant to the Staebler-Wronski effect.

The work at Chapel Hill is performed by:

Professor Marvin Silver

Dr. Daxing Han - Research Associate Professor

Dr. Keda Wang - Research Associate

Dr. Mathieu Kemp - Research Associate

SUMMARY

During the contract year, February 1, 1992 - January 30, 1993, we continued our experiments on electroluminescence (EL) and transient forward bias current as well as photocurrent before and after light soaking. We started a program to study thin ($0.4\text{ }\mu\text{m}$) p-i-n solar cells which were obtained from Solarex. In collaboration with Professor E. Schiff at Syracuse, we studied the effect of optical bias on charge transport in a-Si:H films.

On the theoretical side, we have performed analytical calculations on a model which predicts an exponential energy region for band tails due to dilute random charges. We have developed a model for the carrier-recombination-lifetime distribution. In collaboration with H. Branz of NREL, we have solved the equations for H-diffusion including deep trap levels. Finally, in collaboration with Professor S. Fonash at Penn State, we have been analyzing simulation data under forward bias in p-i-n devices.

Perhaps the most interesting and important results were obtained on the EL spectra in thin solar cell devices. We found that at elevated temperatures thin p-i-n devices displayed primarily defect luminescence ($0.8\text{--}0.9\text{ eV}$) while thick ($> 2\text{ }\mu\text{m}$) the luminescence observed was the main band ($1.1\text{--}1.2\text{ eV}$). Further, we found that in thin cells with buffered layers, p-b-i-n's, the main band luminescence was more pronounced than in simple p-i-n's. For the first time, we have distinguished between bulk and junction controlled recombination.

The optical bias effect on charge transport and slow decay of transient forward bias current show that there is a very slow relaxation when changing the charge state of deep defect states. This slow relaxation may have a profound effect upon the interpretation of recombination results.

The analysis of hydrogen diffusion in the presence of deep traps goes a long way in clarifying the early time experimental data.

Our research last year has resulted in seven papers being submitted for publication.

Publications:

(also as references)

1. "Electroluminescence and Forward Bias Current in p-i-n and p-b-i-n a-Si:H Solar Cells," Keda Wang, M. Silver, and Daxing Han, to be published in J. Appl. Phys. May, 1993.
2. "Time-resolved Transient Electroluminescence in a-Si:H," Keda Wang, Daxing Han, M. Kemp and M. Silver, Appl. Phys. Lett. **62** (1993) 157.
3. "The puzzle surrounding luminescence models", M. Kemp and M. Silver, J. Non-Cryst. Sol. **141** (1992) 88.
4. "Reverse Recovery and Decay of Stored Excess Carriers in a-Si:H p-i-n Diode", Daxing Han, Keda Wang and M. Silver, MRS spring meeting, April 27- May 1, 1992, San Francisco, p.837.
5. "Optical Bias Effects in Electron Drift Measurements and Defect Relaxation in a-Si:H," Daxing Han, E. A. Schiff, and M. Silver, submitted to Phys. Rev. B.
6. "Effect of Photo Degradation on Transient and Steady State Forward Bias Characteristics of a-Si:H p-i-n Diode", R. Amokrane, R. Vanderhaghen and M. Silver, MRS spring meeting, April 27- May 1, 1992, San Francisco, p.467.
7. "A Monte Carlo investigation of low-temperature geminate pair recombination dynamics in amorphous semiconductors," M. Kemp and M. Silver, Phil. Mag. Lett. **66** (1992) 169.
8. "Analytic solution of trap-controlled tracer diffusion in amorphous solids", Phys. Rev. B **47** (1993) 7061.

I. Introduction

Prolonged illumination of silicon-hydrogen based solar cells clearly lowers the efficiency. It is well known that the prolonged illumination increases the density of dangling bonds and possible other defects which decreases the recombination lifetime of photogenerated carriers. There are two major problems: 1) what is the mechanism and kinetics of the formation of these photogenerated recombination centers and 2) what are the factors governing the recombination itself.

In our research, we have chosen to attempt to understand the recombination. Through this understanding, remedial procedures may be suggested. The radiative- and non-radiative- recombination can determine the electroluminescence and the forward bias current in p-i-n devices. The results reported below came from our second year activity under this sub-contract.

II. Results

A) Experimental Results

Fig. 1 EL spectra for a $0.4 \mu\text{m}$ p-i-n at 300 K, 200 K, 140 K and 80 K, respectively.

—○—, —□—, —△—, —×— are correspond to the EL spectra at 300 K 200 K, 140 K and 80 K respectively.

Fig. 2 EL spectra for a $0.4 \mu\text{m}$ p-b-i-n solar cell at 300, 200, 140, and 80 K, respectively.

—○—, —□—, —△—, —×— are correspond to the EL spectra at 300 K 200 K, 140 K and 80 K respectively.

The steady-state and transient electroluminescence (EL) measurements have been done to study the carriers recombination in p-i-n devices.^{1,2} The EL spectra for thin p-i-n and p-b-i-n cells as a function of temperature are given in figures 1 and 2. As one can see, while both show main band of 1.2 eV luminescence at 80 K, at higher temperature, $T > 140$ K, the 0.85 eV band (defect band) is more pronounced in both p-i-n and p-b-i-n cells. However, the main band is more pronounced in the p-b-i-n samples compare with that in the p-i-n samples even at higher temperatures, it will be seen more clearly in Fig.3.

In figure 3 where we show the 200K results of the comparison of the EL spectra between p-i-n and p-b-i-n cells. One can see that the 1.2 eV luminescence is more pronounced in p-b-i-n cells but the 0.85 eV defect luminescence more pronounced in p-i-n cells.

Fig. 3 Comparison of EL spectra between $0.4 \mu\text{m}$ p-i-n and p-b-i-n cells at 4V, 200 K.

—○—, —●— are correspond to the EL spectra for p-i-n and p-b-i-n, respectively.

In order to see other differences of recombination processes between p-i-n and p-b-i-n cells, we studied the lifetime distribution.^{1,2} These results are shown in figure 4.

Fig. 4 Lifetime distribution in $0.4 \mu\text{m}$ p-i-n and p-b-i-n cells at 4 V, 120 K.

Fig. 5 Temperature dependence of lifetime distribution for a $2 \mu\text{m}$ p-i-n diode.

As one can see in Fig. 4 at 120K, we find only one peak in the lifetime at 10^{-6} sec for both 0.4 μm p-i-n and p-b-i-n cells. While in 2.0 μm thick samples one sees two peaks,² one at 10^{-6} sec and one at $10^{-3} - 10^{-6}$ sec. These results are shown in figure 5.

Fig. 6 The peak position of slow and fast lifetimes vs. $1/T$.
Data from the same sample as in Fig. 5.

In figure 6 we plot the peak position τ_s and τ_f of slow and fast lifetimes in Fig. 5 as a function of temperature. One can see that the lifetime τ_s becomes shorter as T is raised. This results from a transport-controlled recombination rather than the nearest neighbor. We are sure that the 10^{-6} sec peak τ_f is due to nearest neighbor recombination because it does not vary with temperature.³

Fig. 7 Negative bias dependence of forward current on a 10 μm p-i-n at State A.

Fig. 8 The same sample as in Fig. 7 at State B.

Forward bias transients as well as reverse recovery were studied. One of the interesting results relates to the shape of the forward bias transient when a reverse bias was applied between pulses. These results are shown in figures 7 and 8 for 10 μm annealed and degraded samples. The curves were taken at 1.0Hz of 8V pulse frequency with varied negative bias between the pulses at room temperature. Two common features are to be noted : (1) the higher the reverse bias between pulses the higher is the initial space charge limited current and (2) the longer is the time for the current to rise. Furthermore, two different features between state A and state B are also to be noted: (1)

a slightly steeper slope of the transient space charge limited current at state B, and (2) a longer rise time delay at state B. The explanations remain unclear. However, we suggest that the common features are due to long-lived traps in the i-layer adjacent to the p-junction, and the light-induced effects contribute to the deep-trapping processes. The long time relaxation may also be seen in the repetition rate response of the forward bias transient.⁴

Fig. 9 Forward current decay for a 2 μm p-i-n under 3V and 5V pulses. Data were taken by interrupted forward bias from 10^{-7} to 10^{-2} sec, by varying repetition rate from 10^{-4} to 10^3 sec.

This result is shown in figure 9. At earlier time ($t < 10^{-2}$ sec) the data were taken by interrupted forward pulses technique, at longer time ($t > 3 \times 10^{-4}$ sec) the data were taken by frequency dependence of the forward bias current. Detail are given in reference 4. Apparent effects due to previous pulses can be seen even after 10^4 sec. We do not believe that this is due to one electron emptying of deep states near the Fermi level. 10^4 sec means emptying electrons from 0.9 eV below the conduction band which is much too big an energy difference.

Slow relaxation may also be inferred from a comparison of the transient charge collection with and without optical bias.⁵ These results are shown in Figure 10.

Fig. 10 The transient photocharge $Q(t)/(d^2/Q_0 V)$ recorded at four optical bias levels and in the dark in an a-Si:H specimen in a light-soaked state. The DC currents through the specimen were: 2.7×10^{-7} A, 1.8×10^{-8} A, 1.0×10^{-9} A, 4.8×10^{-10} A, and 5.0×10^{-11} A, from the top to the bottom curves.

The collected transient photocharge $Q(t)$ has been normalized by $(d^2/Q_0 V)$ where d is the separation between two electrodes, Q_0 is the photogenerated charge, and V is the applied voltage across the electrodes. Since $Q(t)/(d^2/Q_0 V)$ equals to $\mu\tau$, one can obtain several parameters, such as deep-trapping-lifetime, re-emission-time, and recombination-lifetime, from these curves.⁵

The signature of deep trapping in a charge collection experiments is a "S" shape. Such a shape is observed only for bias light currents less than 10^{-8} A which means that the quasi Fermi level is at most 0.1 eV higher than the dark Fermi level which yields a current of 5×10^{-11} A. Notice that the deep trapping processes between 10^{-6} - 10^{-3} sec is apparent from the "S" shape of the charge collection response as shown the bottom curve in Fig. 10. On the other hand, the deep trapping is suppressed with optical bias. We believe that this results from a shift in energy between the relaxed and unrelaxed defect states which is due to the optical bias excitation.

Finally, we have some data obtained in collaboration with R. Vanderhaghen of LPICM at Palaiseau, France, on forward bias dark and photocurrent.⁶ The forward photocurrent is much larger than the reverse indicating a large gain of order 30 for these samples. This implies that the lifetime is longer than the transit time in a $2.0\text{ }\mu\text{m}$ p-i-n sample. These results are shown in Fig. 11 where one sees the reverse- and the forward-photocurrent on the same graph. Notice that $I_{\text{phR}} \ll I_{\text{phF}}$.

Notice that the photocurrent tends to saturate above about 2 V. The reason for this is that above this voltage, the recombination is bi-molecular as the lifetime τ is inversely proportional to the density of dark injected carriers.

B. Theoretical Results

Fig. 12 Distribution of potential fluctuation v due to a dilute density of charges.

Figure 12 shows typical results of our analytic calculations on the density of states due to random charges.⁷ The distribution is gaussian for small potential fluctuation v (low energies) and exponential for large values. The logarithmic slope in the exponential region depends primarily on the dielectric constant and the size of the localized site. With increased system size α , the width of the gaussian increases, but the characteristic energy of the exponential remains unchanged.

We have also studied recombination kinetics in order to distinguish between geminate and non-geminate recombination. Figures 13a and 13b show the results of our simulations on the lifetime distribution and the geminate fraction vs. excitation density. Notice that both the lifetime and the geminate fraction start to decrease above an excitation density of 10^{17} cm^{-3} . These results show non-geminate recombination is faster

than geminate contrary to prior misconceptions because the recombination pathway to a non-geminate partner is shorter at high excitation density than to its geminate pair.

(a)

(b)

Fig. 13 Effect of the excitation density: (a) the lifetime peak remains constant at 10^{-4} sec until $\rho_x \approx 10^{17} \text{ cm}^{-3}$, above which it decreases; (b) the geminate recombination fraction remains unity until $\rho_x \approx 10^{17} \text{ cm}^{-3}$, above which it decreases.

Furthermore, since hydrogen diffusion plays an important role in the metastable effect of a-Si:H, we have considered the problem of deuterium diffusion at early times including traps.⁸ One can see in Fig. 14 an exponential tail as a function of D position. From the slope of the tail one can estimate the mean distance an atom moves normal to the surface, and the number of the jumps it makes before deep trapping. We estimate the distance to be of order 200Å and the number of jumps to be 10^4 .

Fig. 14 D diffusion profile for four different times after the onset of diffusion. Position, x , is scaled by the mean atomic displacement between trapping events λ . Time, t , is scaled by the detrapping time τ . Tracer concentration, θ , is scaled by the initial tracer density θ_0 .

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16. Abstract (Limit: 200 words) <p>This report describes work during the second year of a continuing research study. The work is designed to help us understand how recombination, trapping, and band-mobility modification affecting the electronic properties of amorphous semiconductors can be measured, characterized, and described by an appropriate spectrum of defect states. We also worked to determine how light-induced defects in a-Si:H and native defects in a-SiGe:H affect transport properties in these materials. During this second year, we continued our experiments on electroluminescence (EL) and transient forward bias current, as well as photocurrent before and after light soaking. We started a program to study thin (0.4 μm) p-i-n solar cells, and we studied the effect of optical bias on charge transport in a-Si:H films. We performed analytical calculations on a model that predicts an exponential energy region for band tails from dilute random charges. We developed a model for the carrier-recombination-lifetime distribution. We solved the equations for H-diffusion including deep trap levels. Lastly, we analyzed simulation data under forward bias in p-i-n devices. The most interesting and important results were obtained on the EL spectra in thin solar cell devices. We found that, at elevated temperatures, thin p-i-n devices displayed primarily defect luminescence (0.8–0.9 eV), while in thick ($> 2 \mu\text{m}$) devices the luminescence observed was the main band (1.1–1.2 eV). We also found that, in thin cells with buffered layers, p-b-i-n's, the main band luminescence was more pronounced than that in simple p-i-n's. For the first time, we have distinguished between bulk and junction-controlled recombination.</p>			
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