Research on Defects and Transport in Amorphous-Silicon-Based Semiconductors

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PREFACE

This final report covers the work performed at Syracuse University for the period February 20, 1991 to April 19, 1994 under National Renewable Energy Laboratory Sub-contract XG-1-10063-7. Dr. Bolko von Roedern was the technical monitor of this project. The principal contributors to this report and their present institutions are:

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We have benefitted from collaborations with

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Dr. Jan Tauc (Brown University),
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SUMMARY OF PRINCIPAL RESULTS

1. Electron and Hole Drift Measurements in $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ and $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ pin Solar Cells.

Multijunction solar cells incorporating modified bandgap $a\text{-Si:H}$ in a triple junction structure are generally viewed as the most promising avenue for achieving an amorphous silicon based solar cell with 15% stabilized conversion efficiency. $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ and $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ alloys have been intensely developed as materials with bandgaps narrower and wider than $a\text{-Si:H}$, respectively. When designing the individual, component cells of these triple-junction structures the thickness of the individual cells is largely dictated by a combination of hole diffusion lengths and hole mobilities.

The specific objective of this task of the research project has been to document the mobilities and deep-trapping mobility-lifetime products for electrons and holes in $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ and $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ alloy materials. One result which is of clear significance to solar cells is that hole mobilities are *not* degraded by increasing the bandgap using carbon alloying; previous work had shown that holes are little affected by narrowing the bandgap using germanium alloying. Extensive work both at Syracuse (in this project) and elsewhere has shown that bandgap modification does degrade electron mobilities, but probably not enough to seriously degrade solar cell performance. The result on holes is crucial; degradation of the hole mobility by bandgap modification would almost certainly have precluded the application of these materials in solar cells.

Work on the $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ system has been in collaboration with Dr. Subhendu Guha (United Solar Systems Corp.); specimens were deposited at Energy Conversion Devices, Inc.. Time-of-flight measurements, optical characterization, as well as photovoltaic studies were performed. We found a very good correspondence between the bandgap of $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ alloys and the conduction bandtail width, suggesting that present deposition technology has achieved the minimum conduction bandtail width required by alloying itself. For p-i-n cells with a 0.35 micron i-layer we found a satisfactory correlation of time-of-flight parameters with "blue" fill factors, but the causal relationship is not established. Open-circuit voltages were very well accounted for by the alloy bandgap, and thus for these cells were probably *not* significantly affected by the conduction bandtail width or the defect density.

Work on the $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ system has been in collaboration with Dr. Yuan-Min Li of Solarex Corp. and with Charles T. Malone of the Pennsylvania State group. Essentially nothing was known directly about drift mobilities in these materials prior to our research, although of course there had been several proposals based on inference from other measurements. For electrons the increase in the bandgap clearly reduces the drift mobility, presumably due to a broadened conduction bandtail. For holes we find no change in the drift mobility which can be attributed to the increased bandgap. Our results on electrons have recently been confirmed in measurements conducted at Swansea University on Utrecht University $a\text{-Si}_{1-x}\text{C}_x\text{:H}$.

2. Electroabsorption Measurements and V_{bi} in Solar Cells

The built-in potential V_{BI} in a pin solar cell may be limiting V_{OC} in wide bandgap cells ($E_G > 1.8$ eV such as are currently proposed as the top cell for 15% triple junction

devices. Electroabsorption measurements were applied to estimating V_{BI} ten years ago by the Osaka University group. In our view this technique, in the state of development reported by Osaka University, has significant quantitative errors (about 0.2 V or larger) which preclude using the earlier measurements to conclusively resolve the role of V_{BI} in determining V_{OC} .

We built an electroabsorption apparatus and used it to study pin solar cells from several laboratories; our principal collaborator has been Steven Hegedus at the Institute of Energy Conversion. In our research we addressed four issues which need to be resolved before the method can yield an error less than 0.1 V. The details are presented in the body of this report. Three of the issues are now conclusively resolved. We have made substantial progress on the fourth issue - a wavelength dependence to the electroabsorption estimate - but the results are not conclusive at present. Our best estimate of V_{BI} for a photo-CVD pin diode incorporating an a-Si_{1-x}C_x:H p^+ layer is 0.97 ± 0.06 V, and agrees with an earlier estimate of about 1.03 V based on transport measurements. Both these estimates tend to support the recent proposal that V_{OC} in wide bandgap a-Si_{1-x}C_x:H cells is limited by V_{BI} .

3. Defect Relaxation and Shockley-Read Kinetics in a-Si:H.

Quantitative modeling of solar cells is usually based on "Shockley-Read kinetics." An important and seemingly self-evident assumption of this approach is that the rate of emission of a photocarrier trapped on a defect is independent of quasi-Fermi level location.

We have made measurements of electron drift in the presence of optical bias which appear inconsistent with this assumption. This research was a collaboration with Dr. Daxing Han and Dr. Marvin Silver at University of North Carolina, Chapel Hill. We have proposed that relaxation of a deep level between differing atomic configurations may explain the effect. As a consequence the "trap depth" describing emission depends upon the defect's history of charge state transitions. This view is consistent with those developed at University of Oregon to account for capacitance transient observations, and more recently for modulated photocurrent measurements. The latter are essentially equivalent to transient photocurrent measurements under optical bias.

A breakdown in Shockley-Read kinetics has a profound effect on the structure of models for photocarrier transport. For example, the classic Rose explanation for the sublinear photocurrent/optical flux relationship observed in many semiconductors invokes an exponential distribution of trap states. We showed that this same behavior can be explained by invoking slow defect relaxation.

Finally, in a collaboration with Howard Branz at NREL, we showed that the energy scales involved in these proposed defect relaxation models are consistent with well-known theoretical studies of the dangling bond defect in amorphous silicon. The slowness of relaxation, which is actually the primary reason that relaxation yields surprising optical bias and transient capacitance effects, is currently under study by Branz and Fedders and by others.

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1. INTRODUCTION

The principal results of this research project as well as their significance for solar cells have been summarized above. Here we describe how we shall present the results further in this report. We have made significant recent progress in two tasks: drift-mobility measurements in $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ and $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$, and estimates of V_{BI} based on electroabsorption. These results are described in some detail in sections 2 and 3 of this report, respectively.

Several of the research tasks supported by this project are completed and have been published. Some of this work is secondary to our main photovoltaic research objectives; some of it is very preliminary. We do not reproduce this earlier material here. Instead we have compiled an annotated bibliography of the published work supported by the research project as the following section 1.1. The bibliography is complete as of April, 1994.

Some of the work which is not described in detail in this report is:

- Measurements of electron transient photocurrents in $a\text{-Si:H}$ over a very large dynamic range and including optical bias effects, as well as the interpretations and models invoking slow defect relaxation. See [5-7].
- Measurements of the temperature-dependence of the spin density in $a\text{-Si:H}$. These measurements addressed two issues. They were used to confirm that the D-center has a positive electronic correlation energy near the Fermi energy in undoped $a\text{-Si:H}$ [11,23]. They also tend to confirm a model invoking the two phases of bound hydrogen in $a\text{-Si:H}$ as the origin of thermal metastability effects on the spin density [16-18].
- Measurement of the effect of light soaking on the electron drift mobility in $a\text{-Si:H}$ [10,22]. We established a maximum magnitude of 20% for this effect in the three specimens studied.
- Studies of electron drift for very high electric fields [8,9,19]. We believe that these measurements allow us to reject hopping in exponential bandtails as the fundamental transport mechanism in $a\text{-Si:H}$.

1.1 Annotated Bibliography of Publications

1. "Built-in Potentials Via Electroabsorption Measurements in $a\text{-Si:H}$ pin Solar Cells: A Critical Assessment," Qi Wang, E. A. Schiff, and S. Hegedus, in *Amorphous Silicon Technology - 1994*, edited by E. A. Schiff, M. Hack, A. Madan, A. Matsuda, and M. Powell (Materials Research Society, Pittsburgh, 1994), *in press*. See section 3 of this report.
2. "Hole Drift Mobility in $a\text{-Si}_{1-x}\text{C}_x\text{:H}$," Qing Gu, Qi Wang, E. A. Schiff, Y.-M. Li, and C. T. Malone, in *Amorphous Silicon Technology - 1994*, edited by E. A. Schiff, M. Hack, A. Madan, A. Matsuda, and M. Powell (Materials Research Society, Pittsburgh, 1994), *in press*. See section 2 of this report.
3. "Electron Drift Mobility Measurements and Conduction Bandtails in Hydrogenated Amorphous Silicon-Germanium Alloys," Qi Wang, Homer Antoniadis, E. A. Schiff, and S. Guha, *Phys. Rev. B* **47**, 9435 (1993). See section 2 of this report.
4. "Electron Time-of-Flight Measurements in $a\text{-Si}_{1-x}\text{C}_x\text{:H}$," Qi Wang, E. A. Schiff, and Y.-M. Li, in *Amorphous Silicon Technology - 1993*, edited by E. A. Schiff, *et al* (Materials Research Society, Pittsburgh, 1993), p. 419. See section 2 of this report.
5. "Optical Bias Effects on Transient Photocharge Measurements and Defect Relaxation

- in Amorphous Silicon," D. Han, D. C. Melcher, E. A. Schiff, and M. Silver, *Phys. Rev. B* 48, 8658 (1993). We showed that optical bias makes electron photocarrier deep-trapping unimportant in a-Si:H near room temperature. We believe that this result is due to defect relaxation; this is the same view put forward by the University of Oregon group for interpreting modulated photocurrent measurements, which are also optically biased.
6. "Dangling Bond Relaxation and Deep Level Measurements in Hydrogenated Amorphous Silicon," H. M. Branz and E. A. Schiff, *Phys. Rev. B* 48, 8667 (1993). This paper shows that the energy scale of defect relaxation required to explain transient capacitance measurements and optically biased transient photocurrent measurements are consistent with theoretical models of the dangling bond. The time scale uncovered by the University of Oregon group is not explained.
 7. "Photocarrier Drift and Recombination in a-Si:H : The Vital Importance of Defect Relaxation," E. A. Schiff, H. Branz, D. Han, D. Melcher, and M. Silver, *J. Non-Cryst. Solids* 164-166, pp. 331-334(1993). This paper points out that standard modeling of photoconductivity and devices will need to be reconsidered if slow defect relaxation occurs.
 8. "High-field Electron Drift in Amorphous Silicon," Qing Gu, E. A. Schiff, J.-B. Chevrier, and B. Equer, in *Amorphous Silicon Technology - 1993*, edited by E. A. Schiff, *et al* (Materials Research Society, Pittsburgh, 1993), p. 425. This paper extends earlier experimental work by our laboratory on electron transport at very high fields. We find an enormous enhancement of the electron drift mobility, but no apparent change in the effective temperature.
 9. "Hopping in Exponential Bandtails in High electric Fields and Transport Models in Amorphous Silicon," R. I. Devlen, H. Antoniadis, E. A. Schiff, and J. Tauc, *Phil. Mag. B* 68, 341 (1993). This paper presents a theoretical model which confirms that high fields should increase the effective temperature for photocarrier transport if the fundamental transport mechanism is hopping in exponential bandtails.
 10. "Electron drift mobility measurements on annealed and light-soaked hydrogenated amorphous silicon," Qi Wang, Homer Antoniadis, and E. A. Schiff, *Appl. Phys. Lett.* 60, 2791-2793 (1992). We found little effect of light soaking on electron mobility in a-Si:H.
 11. "Modulated Electron-Spin-Resonance Measurements and Defect Correlation Energies in Amorphous Silicon," J.-K. Lee and E. A. Schiff, *Phys. Rev. Lett.* 68, 2972-2975 (1992). We believe that a correlation energy of 0.3 eV is satisfactory for the D-center in a-Si:H.
 12. "Transient photocharge measurements and electron emission from deep levels in undoped a-Si:H," Homer Antoniadis and E. A. Schiff, *Phys. Rev. B* 46, 9482-9492 (1992). We found a new technique for measuring deep trap emission times in a-Si:H, and reported an apparent "Meyer-Neldel" rule connecting the trap depth and escape frequency.
 13. "Effects of hydrogen plasma treatment on hydrogenated amorphous silicon," J.-K. Lee and E. A. Schiff, in *Amorphous Silicon Technology - 1992*, edited by M. J. Thompson, *et al* (Materials Research Society, Pittsburgh, 1992), pp. 185-190. We conducted a

rough experiment attempting high temperature plasma hydrogenation of as-deposited a-Si:H. No improvements in electronic properties were noted, and in fact we speculated that the plasma may have dehydrogenated specimens more rapidly than thermal treatment alone would indicate.

14. "Delayed field transient photocurrent measurements in a-Si:H," Homer Antoniadis and E. A. Schiff, in *Amorphous Silicon Technology - 1992*, loc. cit., pp. 783 - 788. We believe this technique may be promising for probing deep level effects in a-Si:H, but no remarkable effects were found in this preliminary study.
15. "Optically detected photocarrier transport in amorphous silicon: A Review," R. I. Devlen and E. A. Schiff, *J. Non-Cryst. Solids* 141, 106 - 116. This paper primarily reviews optical techniques for measuring photocarrier transport on very short time scales. The paper also speculates that the band mobility for holes can be extracted from the experiments.
16. "Role of Hydrogen Microstructure in Amorphous Silicon," Sufi Zafar and E. A. Schiff, in *Amorphous Silicon Technology - 1992*, loc. cit., pp. 199-209. A review of previous work connecting the clustered and dilute phases of bonded hydrogen in a-Si:H to its electronic defects.
17. "Hydrogen and Defects in Amorphous Silicon," Sufi Zafar and E. A. Schiff, *Phys. Rev. Lett.* 66, pp. 1493-1496 (1991). This paper reports on experimental evidence which supported a hydrogen-mediated model for defect formation in a-Si:H. The novel feature of the model was its emphasis on pairing of hydrogen on certain defects, which then become essentially the "defect pool" hypothesized in other models.
18. "Spin Equilibration in Hydrogen Depleted Amorphous Silicon," Sufi Zafar and E. A. Schiff, *J. Non-Cryst. Solids* 137& 138, pp. 323-326 (1991). A study of the timescale for thermal defect equilibration in amorphous silicon compared to the defect density. The equilibration time scales inversely with defect density over many orders of magnitude. The activation energy for equilibration is similar to that for hydrogen diffusion.
19. "High-Field Electron Drift in a-Si:H," Homer Antoniadis, R. I. Devlen, Sergei Esipov, S. Guha, E. A. Schiff, and J. Tauc, *J. Non-Cryst. Solids* 137& 138, pp. 407-410 (1991). A brief review of the principal experiments showing high electric field effects for electron transport in a-Si:H, and a brief summary of the three principal models.
20. "Unraveling the $\mu\tau$ -Mystery in a-Si:H," Homer Antoniadis and E. A. Schiff, *J. Non-Cryst. Solids* 137& 138, pp. 435-438 (1991). A preliminary report; see ref. 12 above.
21. "Femtosecond Studies of Photoinduced Bleaching and Hot Carrier Dynamics in a-Si:H and a-Ge:H," M. Wraback, J. Tauc, D. Pang, W. Paul, J.-K. Lee, and E. A. Schiff, *J. Non-Cryst. Solids* 137& 138, pp. 531-534 (1991). Syracuse furnished specimens for this project.
22. "The Effect of Light Soaking on Electron Mobilities in Hydrogenated Amorphous Silicon," Homer Antoniadis, Qi Wang, E. A. Schiff, and S. Guha, in *Amorphous Silicon Technology - 1991*, edited by A. Madan, et al (Materials Research Society, Pittsburgh, 1991), pp. 33-38. A preliminary report on this topic superseded by a later *Appl. Phys. Lett.*.
23. "Effects of Temperature and Charge Depletion on the Spin Density in Hydrogenated Amorphous Silicon," J.-K. Lee and E. A. Schiff, in *Amorphous Silicon Technology -*

1991, edited by A. Madan, *et al* (Materials Research Society, Pittsburgh, 1991), pp. 605-610. A preliminary report on these effects superseded by a later *Phys. Rev. Lett.*

2. ELECTRON AND HOLE DRIFT MOBILITIES IN AMORPHOUS SILICON ALLOYS

2.1 Introduction

In this research project we have essentially completed a comprehensive study of electron and hole drift mobilities in a-Si materials with modified bandgaps. The principal result of importance to solar cells is that there appears to be no intrinsic degradation of hole mobilities by bandgap modification, although such an effect was very clearly observed for electrons. This result on holes is fairly encouraging for photovoltaic applications of these materials. Any significant further degradation of the hole mobilities found in current a-Si based solar cells would lead to an illumination-induced collapse the internal electric field.

Reduced bandgap materials created by germanium alloying have been studied for some years and are now incorporated in state-of-the-art solar cells. It is established that the reduction in optical bandgap is generally accompanied by significant changes in electronic properties [1-5]: the defect density typically rises, and the electron drift mobility declines. The hole drift mobility is apparently little affected.

In particular, extensive studies of the electron drift mobilities in $\text{a-Si}_{1-x}\text{Ge}_x\text{:H}$ were made as part of the present research project in collaboration with Dr. Subhendu Guha (Energy Conversion Devices, Inc. and United Solar Systems Corp.). This work confirmed earlier work suggesting that bandgap reduction leads directly to a reduction of the electron drift mobility, arguably simply by a broadening of the conduction bandtail $E_{0,c}$. Remarkably, this correlation is quite strong even without controlling for the separate roles of hydrogen and germanium content in determining the bandgap, which strongly suggests that the same structural aspects which determine E_G also dominate $E_{0,c}$. Work from other laboratories has indicated that hole drift mobilities are little affected by the bandgap; we did not perform hole measurements on $\text{a-Si}_{1-x}\text{Ge}_x\text{:H}$.

Quite recently there have been great strides in the electronic properties and photovoltaic performance of amorphous silicon alloys with widened bandgaps, including both hydrogenated amorphous silicon-carbon alloys ($\text{a-Si}_{1-x}\text{C}_x\text{:H}$) and amorphous silicon (a-Si:H) with high hydrogen content [6-8]. We made the first electron and hole drift mobility measurements in $\text{a-Si}_{1-x}\text{C}_x\text{:H}$ as part of this project. The electron measurements have been published [9], but will be summarized here, along with recent work by an Utrecht/Swansea collaboration which largely confirms them [10]. The results reveal a decline in electron mobility with increasing bandgap which complements the work on amorphous silicon-germanium alloys ($\text{a-Si}_{1-x}\text{Ge}_x\text{:H}$). We present the recent hole drift mobility measurements for $\text{a-Si}_{1-x}\text{C}_x\text{:H}$ materials at some length here. As for $\text{a-Si}_{1-x}\text{Ge}_x\text{:H}$, there is relatively little degradation as the bandgap is modified. At the end of this section we shall summarize our current knowledge of drift mobilities for both narrow bandgap and wide bandgap materials, and we show the simple pattern which has emerged.

2.2 TIME-OF-FLIGHT EXPERIMENTS

TABLE I

Table I: Summary of properties of samples used in TOF measurement. d - thickness of the intrinsic layer; E_G - optical bandgap; E_U - Urbach energy; μ_h - Average hole drift mobilities at 298 K. Note that Urbach energies, E_U , in the table were measured by different groups (SLX - PDS; ECD - PDS; PSU - CPM). E_U might be equipment dependent.

<i>Specimen I.D.</i>	<i>structure</i>	d (μm)	E_G (eV)	E_U (meV)	μ_h (cm^2/Vs)
SLX A3006-1	glass/CrNi/i/Al	1.6	1.91	57	3.1×10^{-3}
SLX A3047-1	glass/CTO/ <i>pin</i> /Al	1.1	1.87	55	2.2×10^{-3}
SLX S20521TD	glass/CTO/ <i>pin</i> /Al	1.57	1.90	—	1.0×10^{-3}
PSU 267SS300	glass/CTO/ <i>pi</i> /Ni	0.7	1.94	48	1.4×10^{-4}
ECD 1689	glass/Cr/ <i>nip</i> /Pd	2.65	1.72	47	2.3×10^{-3}

2.2.1 Specimens and Instruments

The $\text{a-Si}_{1-x}\text{C}_x\text{:H}$ structures used in this research were prepared at Solarex Corp. (SLX) and at Pennsylvania State University (PSU) using plasma deposition of hydrogen-diluted methane/silane mixtures. One specimen from Solarex Corp. (S20521TD) was deposited using disilymethane (DSM). Additional information on photovoltaic properties and deposition procedures for similar materials are given in references 7, 8 (SLX) and 11 (PSU). We also studied an unalloyed a-Si:H specimen deposited at Energy Conversion Devices, Inc. (ECD). The bandgaps E_G and Urbach parameters E_U for comparable materials were estimated from optical measurements. We have given the structures and the optical parameters for the specimens studied in Table I, as well as average hole drift mobilities estimated at 298 K.

Time-of-flight measurements were done using a transient photocurrent apparatus and procedures which have been described in detail elsewhere [3]. Except as noted below, we used a laser wavelength of 500 nm to obtain carrier generation within about 1000 Å of the illuminated interface. A pulsed bias voltage is used to ensure a uniform electric field across the specimen; by selecting the bias voltage polarity correctly the resulting transient photocurrent is dominated by hole motion.

2.2.2 Transient photocurrent measurements

In this section we present some of the transient photocurrent measurements from

Fig. 2.1: Normalized transient photocurrents $i(t)d^2/Q_0V$ for holes at 298 K; d is the specimen thickness, V the applied bias voltage, and Q_0 the total photocharge in the specimen. Transients for several bias electric fields (in kV/cm) are shown. The specimen had an optical bandgap $E_G = 1.94$ eV (PSU 267SS300); the laser wavelength was $\lambda = 500$ nm. The “hump” in $i(t)$ for earlier times is probably due to electron motion close to the n^+ interface; see the text for further discussion. The inset shows the field-dependence of the charge $Q(E)$ obtained by integrating $i(t)$ to 10^{-4} s. The field-independent plateau at 240 pC is consistent with complete collection of holes following the transit time, and was used to estimate the total photocharge Q_0 . The transit time t_T indicated for the 29 kV/cm transient was obtained from Fig. 2.4; it agrees fairly well with the rougher criterion of t_T as the time at which a “break” occurs in the transient.

which we estimated transit times and drift mobilities. In Fig. 2.1 we present the family of normalized transient photocurrents $i(t)d^2/Q_0V$ taken at 298 K in the Penn State specimen for several bias voltages. d is the i-layer thickness, V is the applied voltage, and Q_0 is the total photocharge generated in the structure. For longer times $t > 3 \times 10^{-7}$ s the transients illustrate the characteristic pattern of time-of-flight measurements in amorphous silicon based materials. An extensive discussion of this subject has been given in a recent paper [3], and we restrict ourselves to the following remarks:

- (i) The ratio $i(t)/V$ shows a field-independent "envelope" curve. The envelope curve is illustrated as the relatively slowly decreasing straight line in the figure, which represents a decay $t^{-(1-\alpha)}$. α is the "dispersion parameter".
- (ii) The individual transients break away from this envelope at times which decrease as the voltage is increased. These breaks can be used to obtain rough estimates of transit times. In practice we used a different procedure to determine transit times which will be briefly reviewed shortly. The value of t_T which results is shown for the 29 kV/cm transient.
- (iii) The inset to Fig. 2.1 shows the photocharge obtained by integrating the photocurrent beyond these transit times. The essentially constant value of $Q \sim 240$ pC for high voltages is consistent with the transit time picture and was used to determine total photocharge Q_0 generated in the structure. For lower voltages the photocharge falls; this effect is due to deep-trapping of holes, and can be used to estimate a deep-trapping mobility-lifetime product $\mu\tau_{H,T} = 5 \times 10^{-9}$ cm²/V for this specimen at 298 K [12].

The short-time behavior of the transient cannot be accounted for in terms of hole motion in the external field. This portion of the transit is due to a combination of two effects: collection of electrons from the photogeneration zone, and internal fields near this zone. Note that even when carriers are generated with strongly absorbed light they are spread out over about 1000 Å from the top interface. Most of the ultimate photocharge Q_0 is associated with the transit of holes across the remaining 6000 Å to the p^+ layer, but about 15% of the photocharge is due to electron motion up to the top. We estimate that this displacement would occur too rapidly to be temporally resolved; the risetime for current measurements in the present work varies in the range 20 - 200 ns, depending on the sample capacitance. This displacement is largely due to internal fields near the top metal contact; the internal fields also sweep the holes some distance into the specimen before the uniform external field dominates their motions.

We illustrate the temperature-dependence of the transient photocurrents for a Solarex specimen in Fig. 2.2. Note that the magnitude of the photocurrent declined with temperature, and correspondingly the characteristic transit times increased greatly. The initial feature which we have associated with internal fields and electron motion is relatively temperature-independent.

Specimen SLX 3047-1 has a *pin* structure. In this specimen we had difficulty in obtaining good electrical estimates of the total photocharge Q_0 . Results with a laser wavelength $\lambda = 500$ nm were completely unsatisfactory. We attributed the problem to the photocharge generated in the n^+ layer, which has a smaller bandgap than the intrinsic layer. We believe that the charge photogenerated in the n^+ layer bleeds more and more as applied fields become high. We checked this idea by measuring the photocharge using λ

Fig. 2.2: Normalized transient photocurrents $i(t)d^2/Q_0V$ for holes for an electric field of 62.5 kV/cm. Transients at several temperatures are indicated in Kelvins. The optical bandgap was 1.91 eV (SLX A3006-1); measurements were done with $\lambda = 500$ nm. Hole sweepout is observed in all cases, with the characteristic transit time occurring at longer times as the temperature declined. The inset shows the field-dependence of the photocharge collected at 40 μ s and 298 K. The open symbols ($E > 0$) correspond to the hole measurements; solid symbols refer to electron transients (obtained with $E < 0$), which are not illustrated. The saturated charge measured for larger fields (about 50 pc) was used to estimate Q_0 . The feature at earlier times noted for Fig. 2.1 is again observed.

= 337 nm, which is absorbed still more strongly in the n^+ layer. As anticipated, the field dependence of Q for high fields was even stronger.

For this specimen we therefore used uniformly absorbed illumination ($\lambda = 700$ nm), for which the measured photocharge was reasonably field-independent. The transients are presented as Fig. 2.3. With this wavelength electrons and holes each contribute half of the ultimate photocharge. Based on our prior measurements of electron drift mobility in this specimen, we know that electron transit occurs within 100 ns for these data. Holes are much slower, and we therefore used the photocharge at 150 ns as an estimate of $Q_0/2$ in normalizing these transients.

Finally we measured transients on SLX 20532TD using essentially the same procedures as for SLX 3047-1. The results were very similar, and will not be presented separately here.

2.2.3 Displacement Graphs

In Fig. 2.4 we have presented normalized photocharge measurements $Q(t)d/Q_0E$ obtained using the pre-transit regions in low voltage transients. This procedure has a simple physical meaning. Consider the time t required for a photocarrier distribution to be displaced a distance L in some electric field E . These times could in principle be determined using transit time estimates; in any case the time t is determined only by the ratio L/E even for "dispersive" transport. Finally, it turns out that a plot of $Q(t)d/Q_0E$ is equivalent to an L/E vs. t plot, and often experimentally preferable. To emphasize this fact we have labeled the vertical axis of Fig. 2.4 as L/E .

Each of the four panels in Fig. 2.4 represents results for a different specimen. For Fig. 2.4(d), where uniformly absorbed illumination was used, one needs to subtract the electron contribution to the photocharge. The data in Fig. 2.4(d) are the values for $[(Q(t)/Q_0) - (1/2)]d/E$, which estimates L/E for the holes. The different curves in each panel are the results for various temperatures. The decline in the magnitude of the curves with temperature, and also the change in slope, is usually interpreted as evidence for hole multiple-trapping in the valence bandtail; we shall return to this issue later.

These displacement plots can be used to estimate transit times as follows. For example, in Fig. 2.1 we show transients obtained at four electric fields. To estimate the transit time t_T for the 29 kV/cm transient we first determine the L/E ratio. Since transit is detected when carriers have traversed about half the specimen's thickness d , $L/E = d/2E = 0.6 \times 10^{-4}/2(29 \times 10^3) = 1.03 \times 10^{-9}$ cm²/V. From Fig. 2.4(c) we determined a transit time estimate of 3 μ s. We have indicated this estimate on Fig. 2.1; it agrees adequately with the time at which the 29 kV/cm transients breaks away from the envelope curve.

To compare drift mobilities measurements for different materials, or for different temperatures in a given material, it is essential to specify a particular value for L/E for which the transit times are estimated. We have found it convenient in amorphous-silicon based materials to use $L/E = 2 \times 10^{-9}$ cm²/V; this value was also used in previous work on electron transport in a-Si_{1-x}C_x:H and a-Si_{1-x}Ge_x:H by Wang, *et al* [3,9].

2.3 DISCUSSION

2.3.1 Effects of Bandgap Modification on Drift Mobilities

Transit times are usually used to estimate a drift-mobility μ_D according to the ex-

Fig. 2.3: Normalized transient photocurrents $i(t)d^2/Q_0V$ in SLX A3047-1 for an electric field of 18.2 kV/cm. Results at three temperatures are indicated (in Kelvins). Measurements were done using $\lambda = 700 \text{ nm}$, for which both electron and hole photocarriers are generated uniformly through the specimen. The early time behavior is again attributed to sweepout of electrons from the structure; the later time behavior is attributed to holes.

Fig. 2.4: Logarithmic plots of displacement-field ratio L/E for holes as a function of time since photogeneration; each panel (a) - (d) shows results a different temperatures for a particular specimen. The procedures used to obtain L/E are described in the text. The open circle in panel (c) is based on a direct estimate of the transit time from Fig. 2.1. The decrease with temperature of the magnitude and slope of the curves for a given specimen is usually explained invoking hole multiple-trapping in the valence bandtail. These plots were used to obtain transit times corresponding to a specific value $L/E = 2 \times 10^{-9} \text{ cm}^2/\text{V}$ used for comparing different materials.

pression:

$$\mu_D = \frac{L}{Et_T} \quad (1)$$

In Fig. 2.5 we present the temperature-dependence of μ_D both for holes and for electrons in several specimens ranging in bandgap from 1.55 eV (for an a-Si_{1-x}Ge_x:H specimen) to 1.94 eV (for an a-Si_{1-x}C_x:H specimen). All values correspond to $L/E = 2 \times 10^{-9}$ cm²/V. The data for holes (open or shaded symbols) include the present work on a-Si_{1-x}C_x:H and a-Si:H as well as a previously published result on a-Si_{1-x}Ge_x:H. The electron measurements on these same specimens were reported previously as noted in the figure caption.

In all cases μ_D is apparently simply activated (ie. a straight line can be fitted through the temperature dependence for each specimen). In all cases the electrons are clearly more mobile than holes. However, the electron drift mobility is much more strongly affected by alloying than is the hole drift mobility. Only one specimen (PSU 267SS300) has a clearly distinguishable hole mobility; these results are indicated by the shaded points in Fig. 2.5.

Because of the relatively simple activated behavior of these drift mobilities, a clearer representation of the effects of bandgap changes can be obtained by simply plotting μ_D at a fixed temperature as a function of bandgap. This has been done in Fig. 2.6. We have included in this figure all usable measurements in a-Si_{1-x}C_x:H and a-Si_{1-x}Ge_x:H of which we are aware. The open symbols are hole drift mobilities at 298 K; most measurements are from the present work. The solid symbols are the electron drift mobilities at 200 K; most of these measurements are previously reported, but we have also included an electron measurement on specimen PSU 267SS300. We have included the L/E vs. t_T data for this specimen in Appendix 1.

The result is a "house plot" suggested by the dashed lines. The roof corresponds to electrons, for which the drift mobility is largest near 1.72 eV, and declines as the bandgap shrinks or grows. The broad agreement between results from different laboratories suggests that electron mobilities are near some "limiting curve" representing an intrinsic upper limit to the electron mobility (or a lower limit to the exponential bandtail width) at a given bandgap.

There is no clear corresponding effect for holes, and our own view is that there is little evidence for change in hole mobility which is intrinsic to change in the bandgap. It is of course always possible to lower hole mobilities by changes in deposition conditions; the interesting aspect of Fig. 2.6 is that it suggests that hole mobilities in amorphous silicon have some intrinsic, upper limit.

In interpreting this plot, we caution the reader that bandgap estimates vary substantially depending on the details of the fitting. The a-Si_{1-x}C_x:H gaps reported here correspond to absorption coefficient $\alpha = 2 \times 10^3$ cm⁻¹, which yields estimates similar to the Tauc procedure used for other specimens. Transit time estimates from different laboratories also vary somewhat because fitting procedures are not standardized.

2.3.2 Bandtails

It is customary to fit drift-mobility measurements in a-Si:H to the well known multiple-trapping model for exponential bandtails [13]. This model involves three parameters in each specimen: a band mobility μ_0 , and bandtail attempt-frequency ν , and a bandtail width $\mathcal{E}_0$. Fitting to these parameters is a commonplace of the amorphous silicon drift

Fig. 2.5: Semilogarithmic plot of hole and electron drift mobility μ_D as a function of reciprocal temperature $1000/T$ at a displacement/field ratio of $L/E = 2 \times 10^{-9} \text{ cm}^2/\text{V}$. Each symbol shape corresponds to a particular material; open symbols indicate holes, and solid symbols indicate electrons. References are: *Circles*: $\text{a-Si}_{1-x}\text{C}_x\text{:H}$, 1.87 eV (SLX A3047-1); electrons [7]. *Hexagons*: $\text{a-Si}_{1-x}\text{C}_x\text{:H}$, 1.90 eV (SLX S20521TD). *Uptriangles*: $\text{a-Si}_{1-x}\text{C}_x\text{:H}$, 1.91 eV (SLX A3006-1). *Downtriangles*: $\text{a-Si}_{1-x}\text{C}_x\text{:H}$, 1.94 eV (PSU 267SS300). *Squares*: a-Si:H , 1.72 eV (ECD 1689); electrons [7]). *Diamonds*: $\text{a-Si}_{1-x}\text{Ge}_x\text{:H}$, 1.55 eV (Stuttgart; electrons and holes [2]).

Fig. 2.6: Correlation of electron and hole drift mobilities ($L/E = 2 \times 10^{-9} \text{ cm}^2/\text{V}$) with optical bandgap E_G . Electron mobilities (solid symbols) are reported at 200 K; hole mobilities (open symbols) are reported at 298 K. The symbol shapes indicate the laboratory which prepared the specimens: *Circles*: (Solarex; this work and [9]). *Squares*: (ECD; this work and [3]). *Downtriangles*: (Pennsylvania State University; this work). *Diamonds*: (Stuttgart [2]). *Uptriangles*: (Utrecht [10]). The dashed lines outlining a "house" indicate that the dependence of the drift mobility on bandgap is much stronger for electrons than for holes.

mobility literature. We chose to do fits to the displacement graphs of Fig. 2.4 using a generalized least squares fitting procedure described in Appendix 2.

The resulting fitting parameters are summarized in Table II; we only give the fittings done on three specimens with the widest range of data. The parameters collected in Table II give a very good account for the displacement data in Fig. 2.4. The parameters indicate a trend of bandtail broadening with bandgap. μ_0 and ν also increased significantly.

Despite the success of the fitting, these results seem problematic. First, bandtail broadening appears to contradict the bandgap independent behavior of the drift mobility for $L/E = 2 \times 10^{-9} \text{ cm}^2/\text{V}$ in Fig. 2.5 and 6. Second, μ_0 is unphysically large in specimens with wider bandgaps. We believe that these puzzling results probably reflect some invalidity to the model of multiple-trapping in exponential bandtails. The bandtail

Table II: Summary of multiple-trapping fitting parameters for specimens SLX A3006-1, PSU 267SS300 and ECD 1689.

<i>Specimen I.D.</i>	E_G (eV)	$\mathcal{E}_0$ (meV)	μ_0 (cm ² /Vs)	ν (Hz)
ECD 1689	1.72	48	0.27	7.7×10^{10}
SLX A3006-1	1.91	66	115	3.5×10^{13}
PSU 267SS300	1.94	72	68	3.8×10^{13}

may not be purely exponential, or the transport mechanism may be more complex than simple multiple-trapping. We chose not to explore further refinements to fitting these data. It may be worth noting that the difficulties with exponential bandtail multiple-trapping did not arise in earlier work on electrons in a-Si_{1-x}Ge_x:H [3].

If we accept the broad validity of bandtail multiple-trapping, then we would anticipate a good correlation between optical measurements of the Urbach parameter E_U , which are usually identified with the valence bandtail width, and the magnitude of the hole drift-mobility. There was in fact no detailed correlation between the hole mobilities we measured and the Urbach parameters (cf. Table I), and we conclude that - at present - Urbach parameters should be used with some caution in predicting hole drift mobilities. The absence of such correlations on a grosser scale was interpreted recently as evidence for the role of potential fluctuations in limiting hole transport in compensated a-Si:H [14], but the absence could just as well be attributed in the present case to uncertainties in extracting Urbach parameter from the optical measurements.

2.3 Appendix: Fitting to Bandtail Multiple Trapping

We fit the bandtail multiple trapping parameters using a procedure which has not, to our knowledge, been used before. We start by considering the form predicted for the displacement plots (cf. Fig. 2.2.4) within bandtail multiple trapping:

$$L/E = (\mu_0/\nu)(\nu t)^{kT/\mathcal{E}_0} \quad (2)$$

This equation can be rewritten in a form suitable for fitting using a generalized least squares procedure:

$$\{\ln(L/E)\} = [\ln(\mu_0/\nu)] + [(1/\mathcal{E}_0)]\{kT \ln(t)\} + [(\ln(\nu)/\mathcal{E}_0)]\{(kT)\} \quad (3)$$

In this equation the unknown fitting parameters are collected in the square brackets []. The experimental data correspond to vectors ($L/E, t, T$); the components of the data vectors are collected in the curly brackets { and }.

Standard textbook procedures [15] exist for determining the three unknown constants using a least-squares or maximum likelihood procedure. We wrote a simple computer program to implement this procedure; we used about 30 points ($L/E, t, T$) as input, and obtained least squares estimates for μ_0, ν , and $\mathcal{E}_0$.

Earlier fitting procedures were sequential: first one parameter of the model was fitted using part of the data, and then the additional parameters were obtained using a linear regression approach. The present fitting procedure has the virtue that it fits all three parameters simultaneously.

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3. ELECTROABSORPTION MEASUREMENTS AND BUILT-IN POTENTIALS IN SOLAR CELLS

The built-in potential V_{BI} across a single-junction solar cell is usually accepted as an upper limit to the open-circuit voltage V_{OC} of the cell under illumination. For amorphous silicon based p-i-n solar cells incorporating wide bandgap intrinsic layers it has recently been proposed that this limitation has in fact been reached [1] for some device designs. In Fig. 3.1 we present some data suggesting this view. In the first figure we show the dependence of V_{OC} upon the optical gap E_G for a series of a-Si_{1-x}Ge_x:H cells deposited at Energy Conversion Devices, Inc. [2]. The straight line through the data fits a very simple model: each 0.1 eV increase in the gap yields essentially the same increase in V_{OC} . Under these conditions it is clear that V_{OC} is *not* limited by V_{BI} . V_{BI} is largely determined by the p^+ and n^+ layers of the solar cell, and these layers were kept the same for this series of devices. The shaded area indicates the range of V_{OC} and E_G achieved in a-Si_{1-x}C_x:H devices by Solarex Corp. [1]. It is clear that the simple, one-to-one increase of V_{OC} with E_G has ceased. This apparent saturation of V_{OC} suggests that V_{BI} may have been reached, at least for these particular a-Si_{1-x}C_x:H devices.

To confirm this hypothesis, independent estimates of V_{BI} are very important. Unfortunately, there is currently no consensus among amorphous silicon researchers regarding either the values for V_{BI} or procedures for measuring this parameter. One attractive approach to estimating V_{BI} is the electroabsorption (EA) technique developed by the Osaka University group [3] some years ago.

The essence of this technique is the following. The absorption coefficient in amorphous semiconductors has a weak, quadratic dependence on electric field. In the electroabsorption measurements one applies two external voltages: (i) an essentially static, DC voltage V_{DC} , and (ii) a rapid sinusoidal voltage (a modulation voltage). The modulated transmittance of the specimen $\Delta T/T$ is measured as a function of V_{DC} .

An example of such measurements is presented as Fig. 3.2. We shall show subsequently that the simple, linear dependence of $\Delta T/T$ is a result of the quadratic dependence of electroabsorption on field. The key point is that the voltage-axis intercept V_0 of this linear dependence is displaced substantially from $V_{DC} = 0$. This is due to the additional, built-in voltage V_{BI} across the cell, and even without further analysis it seems clear that V_0 is a good estimate of V_{BI} .

Here we report our work using this approach. We have applied improved signal averaging techniques to the EA measurement, leading to very good reproducibility of the measurements and revealing several effects not included in the original treatment. Most of the new effects can be readily accounted for by extension of the original model. These include the effects of the illumination intensity, the frequency with which the external bias voltage V_{DC} is modulated, and the variation of the sample's capacitance with the external DC reverse bias across the sample. We shall present these extensions in the section describing the "single-layer model." We also found a slight but significant wavelength dependence to the measurements which could not be accommodated using this model. We believe that this effect is due to the portion of V_{bi} which is dropped in the p^+ layer. From a preliminary discussion of this effect we concluded that $V_{bi} = 0.97 \pm 0.06$ V for the solar cell discussed in this report. This cell had V_{OC} of 0.82 V and efficiency of 9% . this result

Fig. 3.1: Correlation of the open circuit voltage V_{OC} with the optical bandgap for amorphous silicon based alloy solar cells. The open circles represent measurements in the $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$ system [2]. The shaded band indicates a series of measurements on $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ cells [1]. The straight line has the slope 1 V/eV, indicating limitation of V_{OC} by the intrinsic bandgap. As is evident, $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ cells lie below this line, suggesting limitation by V_{BI} or some other cell property.

agrees adequately with the range 1.00 - 1.05 V obtained by current-voltage-temperature (JVT) measurements [4,5] in similar devices. Both of these results support the proposal that V_{OC} in wide bandgap solar cells incorporating a-SiC p+ layers is limited by V_{bi} .

We have conducted preliminary measurements also on a series of a-Si:H cells from Solarex Corp. and on one cell from United Solar Systems Corp.. Work on these cells is not sufficiently advanced to warrant a quantitative estimate of V_{BI} , and will not be described here.

3.1 Experimental Details

The p-i-n solar cells were prepared at the Institute of Energy Conversion (IEC) using photo chemical vapor deposition [6]. Devices had the structure glass/ SnO_x /p(a-SiC)/i/n/ITO/Ni. The SnO_x was textured; the i layer was about 5000 Å a-Si:H. The Ni tab on the back was used for a robust ohmic contact to the thin ITO. Here we mostly report on a specific substrate (ID 237-212); individual cells had an area of 0.105 cm². The photovoltaic performance of similar cells has been reported elsewhere [6].

The electroabsorption (EA) experimental arrangement is shown in Fig. 3.3. We used

Fig. 3.2. Plot of the electric field modulated transmittance $\delta T/T$ vs. the reverse bias across an a-Si:H pin solar cell. Measurements at three different RMS modulation voltages are shown (from top to bottom $V_{ac}=0.70$, 0.50 , and 0.30 V, respectively). The straight lines through data points are the linear regressions; note that they focus at a common voltage axis intercept V_0 . Estimation of V_{BI} is based on measurements of this intercept.

three different lasers: a 5 mW He-Ne laser (633 nm wavelength), and two 5 mW laser diodes (670 and 690 nm wavelengths); these lasers were attenuated using neutral density filters. The light transmitted through the sample was detected using a Si photodiode and an EG& G model 181 current sensitive preamplifier. The bias voltage V_{DC} was a slow ramp originating from a signal generator. A variable-frequency sinusoidal voltage was added to V_{DC} using an operational amplifier adder circuit; we generally use frequencies in the range $10^2 - 10^5$ Hz. The amplitude and phase of the corresponding modulation of the laser beam's intensity were measured using an EG& G model 5208 two-phase lock-in amplifier.

We considerably improved the signal/noise ratio of our electroabsorption measurements by introducing a signal averaging scheme. We swept the unmodulated part of the voltage bias across the sample using a slow ramp at 0.5 Hz. These sweeps were averaged and recorded using a personal computer equipped with a multipurpose analog input/output

Fig. 3.3: Block diagram of the electroabsorption measurement apparatus. An essential feature is the use of signal averaging of the lockin amplifier outputs by repeating sweeps of the reverse bias voltage about every 2 s.

card (National Instruments model AT-MIO-16). The software was developed using the National Instruments LabVIEW interfacing package. We have averaged as many as 10,000 sweeps in certain of our measurements, but for most purposes a few hundred are sufficient.

In Fig. 3.2 we presented some of our measurements using the improved technique. The vertical axis indicates the RMS modulation of the transmittance $\Delta T/T$ obtained by dividing the RMS detector photocurrent (in-phase with the voltage modulation) by the

DC photocurrent. There were some small quadrature signals measured at 10 kHz which were we attribute to small amplifier phase shifts.

Measurements at three different modulation amplitudes are indicated. Each set of data was obtained by averaging 1000 or more sweeps of the DC voltage. The solid lines through the data are linear regression fits. We denote the intercept of one of these lines with the voltage axis as V_0 . In the simplest models this intercept is identified with V_{BI} , although we shall not make this identification here. It is evident that V_0 is essentially independent of the modulation amplitude.

3.2 Single Layer Model

Although a model relating electroabsorption measurements to V_{BI} was presented together with the early Osaka University measurements, we have adopted a somewhat different approach which we present here. Both the original and the present model assume that the electroabsorption comes from a single, optically homogeneous layer. In actual solar cells we believe that we have observed effects due to the p+ layer as well, as shall be discussed subsequently.

It is generally accepted that the absorption coefficient $\alpha(\lambda, E)$ depends quadratically upon electric field E [6,7]:

$$\alpha(\lambda, E) = \alpha^0(\lambda) + \alpha''(\lambda)E^2 \quad (3.1)$$

where $\alpha^0(\lambda)$ is the field-independent absorption and $\alpha''(\lambda)$ is the electroabsorption parameter. We measure the transmittance T of the sample; neglecting the sample's reflectivity for the moment, we have:

$$T(\lambda, E) = \exp \left\{ - \int_0^d dx \alpha(\lambda, E) dx \right\} \quad , \quad (3.2)$$

where d is the thickness of the material.

For interpreting our experiments, we assume that the following 3 terms in the electric field E :

$$E(x, t) = E_i(x) + E(x) + \delta E \sin(\omega t) \quad (3.3)$$

These are (i) the internal field E_i , (ii) the externally applied DC field $E(x)$, and (iii) the modulation field $\delta E \sin(\omega t)$. It is important to note that we have assumed that the modulation field δE is *uniform*; in principle, this can be achieved by using a modulation frequency ω sufficiently large that dielectric relaxation within the layer can be neglected.

Substituting the above form for $E(x, t)$ into the equation for T we obtain:

$$T = \exp(-\alpha^0(\lambda)d) \left\{ 1 - \alpha''(\lambda) \int_0^d dx [E_i(x) + E(x) + \delta E \sin(\omega t)]^2 \right\} \quad . \quad (3.4)$$

We have assumed that $\alpha'' \ll \alpha^0$; note that $T \sim \exp(-\alpha_0 d)$. We normally detect the first harmonic modulated transmittance δT , which is the term multiplying $\sin(\omega t)$ in the expression resulting from squaring $E(x, t)$. We obtain:

$$\delta T = -T \left\{ \alpha'' 2\delta E d \int_0^d dx [E_i(x) + E(x)] \right\} \quad . \quad (3.5)$$

We relate these fields to the corresponding voltages as follows:

- (i) $\delta E = C\delta V/\kappa\epsilon_0 A$, where δV is the voltage modulation C is the cell's capacitance, A is the cell's area, and κ is the dielectric constant of the cell material. As discussed subsequently, we do not use the simpler result $\delta E = \delta V/d$.
- (ii) $V_{dc} = \int_0^d dx E(x)$.
- (iii) $V_{bi} = \int_0^d dx E_i(x)$. With these substitutions we obtain the main result:

$$\delta T/T = -2\alpha''(\lambda)\delta E(V + V_{bi}) \quad (3.6)$$

We comment briefly on the important features of this simple expression. First, we use the intercept of $\delta T/T$ to estimate V_{BI} . Despite the fact that α^0 and α'' depend strongly upon wavelength λ , the voltage intercept of $\delta T/T$ is predicted to be independent of wavelength. Second, the intercept is independent of the spatial distribution of either the internal field $E_i(x)$ or of the bias field $E(x)$. Third, the relationship between $\delta T/T$ is strictly linear in the product $V\delta E$. We have not assumed a small modulation amplitude δE , so this is quite strong.

In this treatment we have neglected the reflectance of the specimen and also its interference effects. A full optical treatment complicates the analysis enormously. A preliminary study of these effects has been reported by Hadjeris, de Rosny, and Equer [8]; the results appear rather inconclusive. At present we take the view that these additional effects may affect the slope of the $\delta T/T$ vs. V_{DC} plots such as Fig. 3.2. We doubt that they disturb the assignment of the voltage intercept of these plots with V_{BI} . There is an excellent linear dependence of $\delta T/T$ upon the external voltage; it seems reasonable even without an extended argument that the the voltage-axis intercept is due to V_{BI} .

3.3 Results and Discussion

Effects of Modulation Frequency and Illumination Intensity. Equation (3.6) actually makes several predictions which we checked. The measurements should be independent of both modulation frequency and illumination intensity. Experimentally, we needed to use fairly high modulation frequencies and weak illumination intensities to obtain this limit. In Fig. 3.4 we show the dependence of the voltage intercept V_0 upon the DC photocurrent i_{ph} in a cell. It is clear that the use of higher illumination intensities does affect V_0 . We attribute this effect to the violation of our assumption of uniform δE : the photocarriers inside the intrinsic layer can screen the applied modulation field. The effect is essentially *photocapacitance*. In Fig. 3.5 we show the dependence of V_0 upon modulation frequency $f = 2\pi\omega$. For low photocurrents ($< 100\mu A$) there is no significant dependence upon f . For higher photocurrents V_0 becomes markedly frequency dependent, consistent with an important role of the photocarriers in affecting the modulation field.

Capacitance Measurements. The capacitance C measured at the modulation frequency should also be independent of frequency and bias voltage. In fact, we measured about a 3Fig. 3.6. This is a clear indication that the modulation field δE was not simply constant $\delta V/d$ across the entire pin structure. We believe that the effect is due to an increase in the depletion width in the p+ layer as the reverse bias across the pin cell increased. Since formula 3.6 indicates that $\delta T/T$ is linear in V_{DC} when δE is constant, we actually studied plots of $\delta T/T\delta E$ when we extracted the voltage-intercept V_0 . We used $\delta E = C(V_{DC})\delta V/\kappa\epsilon_0 A$ to estimate δE .

Fig. 3.4: Plot of the intercept V_0 obtained by linear regression using data similar to those of Fig. 3.2 for different laser intensities (represented here by the short-circuit current in the solar cell) and for 2 lasers with different wavelengths. The low intensity limit is reached for $i_{ph} < 100 \mu\text{A}$. It is evident that V_0 depends upon wavelength.

One indication that this procedure is probably correct is that the plots of $\delta T/T\delta E$ vs. V_{DC} were substantially more linear than plots of $\delta T/T\delta V$ vs. V_{DC} . We calculated regressions incorporating quadratic and higher order terms. Incorporation of the $C(V)$ correction reduced the magnitude of the quadratic term by one order of magnitude; with this correction we had no statistically significant nonlinearity even after extensive signal averaging.

Wavelength Dependence. Equation (3.6) also indicates that the experimental parameter V_0 should be independent of the wavelength. This prediction is remarkable, since the actual absorption coefficients α_0 and α'' depend strongly on wavelength. In fact we observed a slight dependence of V_0 upon wavelength, as presented in Fig. 3.7.

Auxiliary $p+$ Measurements. We believe that the dependence of V_0 upon λ is another

Fig. 3.5: Plot of the intercept V_0 vs. modulation frequency f ; several different laser intensities are shown.

aspect of the small voltage drop in the p+ layer. In this case the effect involves the fact that the electroabsorption properties of a-Si_{1-x}C_x:H p+ are quite different than the a-Si:H in the intrinsic layer. This possibility is clearly indicated in the literature. We therefore measured the electroabsorption of the p+ material which was deposited in the cell. We used a 5000 Å p+ layer deposited on glass which had coplanar gap electrodes (0.01 cm gap). We measured $\Delta T = (T(E) - T(0))$, and verified that ΔT was proportional to V^2 as anticipated for quadratic electroabsorption. Assuming that the field E in the gap is uniform, a short calculation shows that

$$\alpha''(\lambda) = -\Delta T/T \left(\frac{w^2}{V^2 d} \right) \quad , \quad (3.7)$$

where w is the width of the electrode gap. α'' depends upon the angle between the electric field and the polarization vector of the light [7,9]; we polarized the laser so that its vector was perpendicular to the electric field, as it is for the cell measurements. The

Fig. 3.6: Plot of the capacitance at 10 kHz vs. the external bias voltage. Reverse biasing the solar cell diminishes the capacitance by several percent, which is attributed to depletion of the p^+ material.

measurements confirm that $\alpha''(\lambda)$ was quite different in the a-SiC p^+ and the a-Si:H i layers. This difference is due to two effects. For a given material, α'' depends upon λ , and this dependence is shifted for materials with different bandgaps. The second reason is more interesting: the maximum electroabsorption in a-Si_{1-x}C_x:H is larger than the maximum in a-Si:H[6]. The physics underlying these effects is, in our view, very poorly understood. Some discussion is given in refs. [7] and [9].

Effects of 2 Layers. A full treatment of the 2 layer model incorporating the p^+ depletion as well as the differing p^+ and i layer optical properties has not yet been completed. However, we propose the following simple procedure for obtaining V_{BI} from measurements of α_p'' , α_i'' , and V_0 at several wavelengths. If a wavelength exists such that $\alpha_p''/\kappa_p = \alpha_i''/\kappa_i$, then V_0 at this wavelength will correctly measure V_{BI} . The electroabsorption response to a given voltage drop is the same for either layer.

We therefore plot V_0 vs. the ratio α_p''/α_i'' obtained using the three laser wavelengths. This has been done in Fig. 3.8. If a well-defined curve existed, we would use the value V_0 for $\alpha_p/\alpha_i = 1$ to estimate V_{BI} . In the present case we used a linear regression to estimate V_{BI} . Taking into account the scatter in the plot, we assign $V_{bi} = 0.97 \pm 0.06$ V.

3.4 Section 3 References

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Fig. 3.7: Plot of the intercept V_0 (10 kHz, low intensity limit) vs. laser wavelength.

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Fig. 3.8: Plot of the intercept V_0 vs. the ratio α''_p/α''_i of the electroabsorption parameters for the p-layer and i-layer material. The value of V_0 when $\alpha''_p/\alpha''_i = 1$ is identified with V_{BI} for 2-layer models of electroabsorption modulation.

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13. ABSTRACT (Maximum 200 words) This report describes work on three individual tasks as follows. (1) Electron and hole drift measurements in a-Si _{1-x} Ge _x :H and a-Si _{1-x} C _x :H p-i-n solar cells. Multijunction solar cells incorporating modified band gap a-Si:H in a triple-junction structure are generally viewed as the most promising avenue for achieving an amorphous silicon-based solar cell with 15% stabilized conversion efficiency. The specific objective of this task was to document the mobilities and deep-trapping mobility-lifetime products for electrons and holes in a-Si _{1-x} Ge _x :H and a-Si _{1-x} C _x :H alloys materials. (2) Electroabsorption measurements and built-in potential (V_{bi}) in solar cells. V_{bi} in a p-i-n solar cell may be limiting the open-circuit voltage (V_{oc}) in wide-band-gap cells ($E_g > 1.8$ eV) currently under investigation as the top cell for 15% triple junction devices. The research addressed four issues that need to be resolved before the method can yield an error less than 0.1 V for V_{bi} . The details are presented in this report. (3) Defect relaxation and Shockley-Read kinetics in a-Si:H. Quantitative modeling of solar cells is usually based on "Shockley-Read kinetics." An important assumption of this approach is that the rate of emission of a photocarrier trapped on a defect is independent of quasi-Fermi level location.				
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