Research on High-Band-Gap Materials and Amorphous-Silicon-Based Solar Cells

Annual Subcontract Report
15 May 1994 - 14 May 1995

E. A. Schiff, Q. Gu, L. Jiang, Q. Wang
Syracuse University
Syracuse, New York

NREL

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Preface

This research project has three broad objectives:

- We seek a deeper understanding of the open circuit voltage V_{OC} in amorphous silicon based solar cells, and in particular for cells employing wide bandgap modification of amorphous silicon as their absorber layer.

- We are working to improve V_{OC} in wide bandgap cells by searching for superior materials for the *p*-type "window layer" of the cell.

- We seek to improve our understanding of the fundamental electron and hole photocarrier transport processes in the materials used for amorphous silicon based solar cells.

In addition to the authors of this report, we have reported work which includes the contributions of several collaborators, in particular Reinhard Schwarz, Stefan Grebner, and Fuchao Wang of the Technical University of Munich, Bernard Equer and Jean-Baptiste Chevrier of Ecole Polytechnique, Palaiseau, and Richard Crandall, Eugene Iwanicszko, and Brent Nelson of the National Renewable Energy Laboratory.

We have also benefitted from the cooperation and interest of scientists and organizations which have made state-of-the-art a-Si:H based solar cells and materials available to us for this research. In particular we thank Subhendu Guha at United Solar Systems Corp., Xunming Deng at Energy Conversion Devices, Inc., Christopher Wronski at Pennsylvania State University, and Murray Bennett at Solarex Corp. Thin Films Division.

Summary

- We have conducted a survey of thin BP:H and BPC:H films prepared by plasma deposition using phosphine, diborane, tri-methylboron, and hydrogen as precursor gases. The objective of this research is to find out whether such films might offer a superior window layer film for application to wide bandgap a-Si solar cells. The research has shown good optical properties in a-BP:H films, but electrical properties acceptable for use in window layers have not been demonstrated yet.

- We have also found an interesting, conductive and transparent BPC:H film in a remote deposition region of the reactor, but have been unable to transfer deposition of this film to the standard interelectrode region.

- We have developed our capability to deposit *nip* sequence amorphous silicon based solar cells, and have demonstrated an open circuit voltage greater than 0.7 V.

- We have continued our studies of built-in potentials in a-Si based solar cells using the electroabsorption technique, extending our measurements to include cells with wider bandgap intrinsic layers and Schottky barrier test structures. We are working to explain the wavelength dependence of the electroabsorption dependence on external voltage; this dependence is the major limitation in the quantitative use of the technique.

- We have made the first time-of-flight drift mobility measurements on a-Si:H prepared by hot wire (HW) deposition. Initial work has shown that light-soaked HW material can have much better ambipolar diffusion lengths than the plasma-deposited material following extended light soaking. In a sample with about 2% H-concentration in the intrinsic layer, we find that the electron drift mobility is quite different from that of a-Si:H alloys prepared by normal glow-discharge CVD, even allowing for the reduced bandgap of the hot wire material. This result challenges the principle that the bandgap of optimized amorphous silicon based material is sufficient to predict the electron drift mobility.

- We have performed some theoretical work which addresses a difficulty in understanding photocarrier recombination in a-Si:H first identified by Marvin Silver. In particular, electron-hole recombination is much slower than expected from the well-known "diffusion-controlled" models for Onsager (geminate) recombination and Langevin recombination. This slowness is essential to the success of a-Si in solar cells, but is unexplained. We find that recent theoretical approaches emphasizing *fluctuations* have considerable value in a-Si, but many puzzles remain.

- We have done work on high field electron drift mobilities in a-Si:H and on the validity of the Einstein relation connecting the diffusion and drift of holes in a-Si:H. This work is indicated in the list of publications immediately following.

Phase I Publications Acknowledging This Subcontract

1. "Electron Drift Mobility in a-Si:H Prepared by hot wire deposition," Q. Gu, E. A. Schiff, R. S. Crandall, E. Iwaniczko, and B. Nelson, in *Amorphous Silicon Technology-1995*, edited by M. Hack, *et al* (Materials Research Society, Pittsburgh, 1995), *in press*.

2. "Diffusion, drift, and recombination of holes in amorphous silicon," R. Schwarz, F. Wang, S. Grebner, Q. Gu, and E. A. Schiff, in *Amorphous Silicon Technology-1995*, edited by M. Hack, *et al* (Materials Research Society, Pittsburgh, 1995), *in press*. In this work we show how steady-state photocarrier grating measurements (SSPG) of the hole diffusion length can be related to time-of-flight measurements of hole drift in a-Si:H. The key point is to evaluate the drift-mobility at the recombination response time for the SSPG measurement. This approach confirms the Einstein relation $D = (kT/e)\mu$ fairly well.

3. "Diffusion-controlled recombination of electrons and holes in a-Si:H," E. A. Schiff, *J. Non-Cryst. Solids* **190**, 1 (1995).

4. "High field electron drift and the mobility edge in hydrogenated amorphous silicon," Q. Gu, E. A. Schiff, J.-B. Chevrier, and B. Equer, *Phys. Rev. B* **52**, 5695 (1995). This paper discusses whether measurements of high field transient photocurrents show "field-dependent dispersion," and concludes that dispersion is field-independent. These observations tend to rule out pure hopping of electrons between bandtail states as the fundamental transport mechanism in a-Si:H. A field-dependent mobility-edge position is proposed as an alternative explanation for high-field measurements.

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Search for Novel p^+ materials

Plasma Deposited Boron Phosphides

One component of this project has been a search for novel p^+ materials to act as the window layer for a triple-junction solar cell. The rationale for this research is the argument that the open circuit voltage for wide bandgap cells ($E_T > 1.9$ eV) is limited by the properties of the window layers presently in use (amorphous SiC:H, and microcrystalline Si). For the middle and narrow bandgap cells it is generally accepted that V_{OC} is limited by the properties of the intrinsic layer of *pin* cell.

In the first year of the project we commenced exploring the properties of boron phosphide films. This choice was based on the fact that crystalline BP has been used as a window layer on crystalline Si solar cells (Takenaka, Takigawa, and Shohno, 1978) and that crystalline BP is a fairly wide bandgap material which should have better optical properties than, for example, microcrystalline Si. Our films were deposited using phosphine (PH_3) as the phosphorus precursor, diborane (B_2H_6) or trimethylboron ($B(CH_3)_3$, typically referred to as TMB) as the boron precursors, and hydrogen. Use of TMB as the precursor of course leads to ternary, boron phosphide/carbide films. All the films were prepared using a commercial RF plasma deposition system operating at 13.56 MHz.

We have also demonstrated in this first year a capability to prepare homojunction *nip* a-Si:H solar cells with acceptable open circuit voltages. We infer $V_{OC} = 0.77$ for AM1 conditions based upon intensity-dependence studies for a cell with a fairly opaque top metal contact. The purpose of this effort was simply to develop a baseline capability for preparing *nip* cells, so that promising novel p^+ materials could be assessed in a working cell.

We describe our work in some detail below. There are two principal results:

- We discovered a conducting, transparent film in a remote area of the reactor. We have not produced comparable films in the standard, interelectrode region of the reactor.

- We have prepared amorphous a-BP:H alloys with good optical properties. We have not yet achieved electrical properties in these films which are satisfactory for application as window layers.

The results from about one dozen depositions are presented at Table I. The optical absorption coefficient measured on one specimen is presented in Fig. 1. The absorption coefficient was calculated based on dual-beam transmittance measurements on a Cary, Inc. spectrophotometer and an auxiliary measurement of the thickness using a mechanical profilometer. For comparison purposes we have also shown literature curves (Yang, Chen, Wiedeman, and Catalano, 1993) for the absorption coefficients for several p^+ materials currently used in a-Si:H based cells.

In general the films deposited in the interelectrode area were highly insulating. This insulating behavior is probably an indication that the films have an amorphous structure, and a corresponding tendency to have Fermi energies near the middle of their forbidden gap. We confirmed this speculation by X-ray measurements on one film (noted in Table 1).

Table 1: Summary of BP depositions and properties.

Seq	T_{sub} (°C)	Gas Pressure (mTorr)	Power (W)	$t_{dep.}$ (min)	Thick. (nm)	σ at 293 K $(\Omega.cm)^{-1}$	n	$E_{act.}$ (eV)	Comments
1	15	TMB/H$_2$(2%): 310 PH$_3$/H$_2$(1%): 860	37.4	121	< 100	> 8.2×10^{-6} at 300 K		0.24	Remote only
2	250	PH$_3$/He(3%): 132 B$_2$H$_6$/He(3%): 70	3.3	98	200	< 10^{-12} at 300 K	3.4		
3	250	PH$_3$/He(3%): 213 B$_2$H$_6$/He(3%): 100 SiH$_4$: 4	3.3	110		< 10^{-12} at 300 K			Si doping
4	250	PH$_3$/He(3%): 163 B$_2$H$_6$/He(3%): 87 H$_2$(100%): - 70	3.4	512	1000	9.4×10^{-10} at 404 K	3.4	0.23	X-ray, optical studies.
5	250	PH$_3$/He(3%): 228 TMB/H$_2$(2%): 107	3.7	351	280	< 10^{-12} at 300 K	4.2		
6	250	PH$_3$/He(3%): 100 B$_2$H$_6$/He(3%): 50 H$_2$(100%): 320	4	300		< 10^{-12} at 300 K			
7	250	PH$_3$/H$_2$(1%): 255 TMB/H$_2$(5%): 50	5	328		< 10^{-12} at 300 K			No film found in remote area
8	250	PH$_3$/H$_2$(1%): 320 B$_2$H$_6$/H$_2$(5%): 33	6.3	290		< 10^{-12} at 300 K			Film peeled after 12-hour in air.
9	250	PH$_3$/H$_2$(1%): 320 B$_2$H$_6$/H$_2$(5%): 30	6.5	210	330	8×10^{-10} (mim)			Film peeled after 12-hour in air.
10	250	PH$_3$/H$_2$(1%): 490 TMB/H$_2$(5%): 100	19.6	140		< 10^{-12} at 300 K			
11	15	PH$_3$/H$_2$(1%): 940 TMB/H$_2$(5%): 180	39	132		4×10^{-5} at 300 K			Remote only.
12	300	PH$_3$/H$_2$(1%): 620 TMB/H$_2$(5%): 130	30.5	151		< 10^{-12} at 300 K			Platen center only

The sequence of depositions in Table 1 was designed to search for deposition conditions to yield microcrystalline BP films. We noted in our initial work that no films formed on the platen under relatively high pressure, high power conditions using TMB and PH$_3$ diluted in H$_2$ as precursor gases. Since a thin, conducting film was deposited in a remote area of the reactor (ie. not between the two large plates serving as RF electrodes), we attributed the absence of growth to etching by atomic hydrogen in the discharge. Based on an analogy with growth of microcrystalline Si films, which requires high hydrogen dilution and high RF power, we adjusted our deposition conditions until growth just barely occurred on the platen. Thus in run no. 12 we obtained deposition only near the center of the platen.
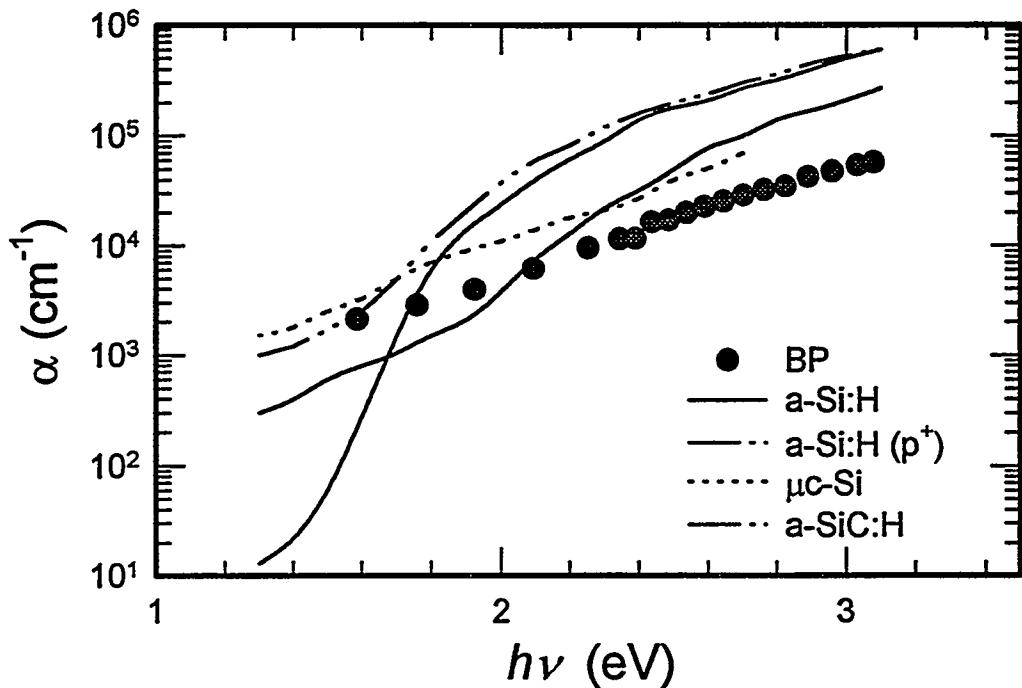
Fig. 1: Absorption coefficient spectra for several materials of interest for window layers to a-Si:H solar cells. BP measurements are from the present report; measurements for the other materials are from Yang, Chen, Wiedeman, and Catalano (1993).

All films deposited in the conventional interelectrode region proved to be highly insulating, even when we achieved very slow deposition due to the concurrent atomic H etching.

Demonstration of a-Si:H based nip cells

An additional task associated with our work to develop improved p^+ materials was to demonstrate a capability to deposit nip a-Si:H based cells which could then serve as the baseline for evaluating cells with novel p layers. We purchased and installed standing doping gas mixtures (PH_3 in SiH_4 and trimethyl-boron in SiH_4), and deposited some very simple nip cells to demonstrate this capability. The cells had a 0.5 µm intrinsic layer; we evaporated fairly reflective top metal Pd contacts. In Fig. 2 below we show a J-V relation measured with such a cell. We infer a value of V_{OC} corresponding to AM1 internal illumination conditions (ie. allowing for the opacity of the top Pd contact) of 0.76 Volts, which we considered to be more than adequate at the present stage of the project.

Fig. 2: *J-V* curve for an a-Si:H nip diode deposited at Syracuse University. The value of V_{OC}
extrapolated to AM1 conditions is 0.76 V.

Electroabsorption Research

One objective of this research project is to improve our understanding of the built-in potentials and fields in amorphous-silicon based solar cells. In particular we seek to establish the conditions for which t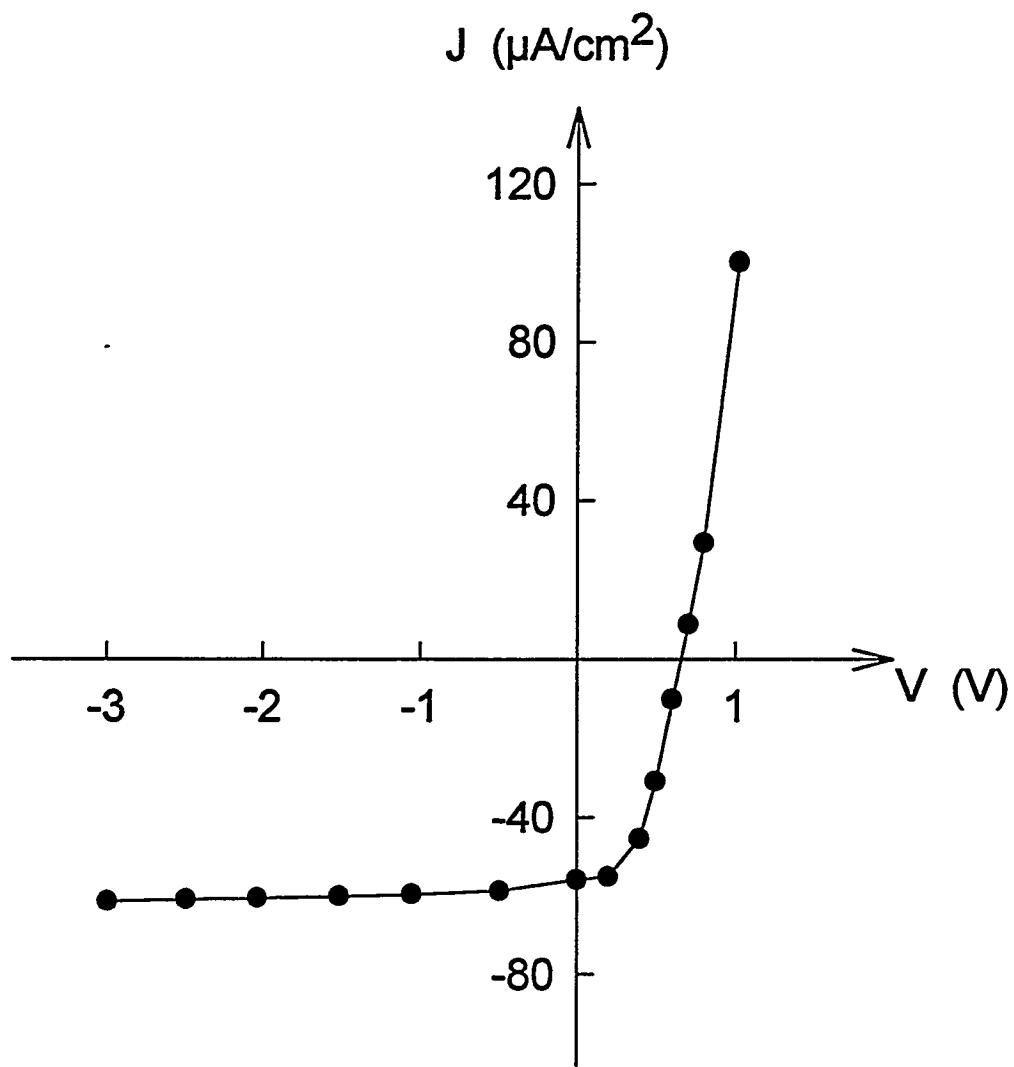he built-in potential limits the open-circuit voltage V_{OC}; at present we believe that this occurs in cells for which $V_{OC} \approx 1.0$ V (Li, 1993; Crandall and Schiff, 1995).

The technical approach we have adopted is to measure the electroabsorption in a-Si based solar cells as a function of the reverse bias voltage across the cell; prior work using this technique is summarized by Wang, Schiff, and Hegedus (1994). We study the electroabsorption modulation signal measured by rapidly modulating the voltage across the cell, and synchronously detecting the the transmittance modulation for a laser beam through the cell. For a true homojunction solar cell it is fairly straightforward to show that the resulting signal $\delta T/T$ yields the built-in potential V_{BI} (Wang, Schiff, and Hegedus, 1994)

$$\delta T/T \propto 2\ \alpha''(\lambda)\ \delta E\ (V\text{-}V_{BI}),$$

where $\alpha''(\lambda)$ is the *electroabsorption coefficient* (the coefficient governing the quadratic dependence of the absorption coefficient upon electric field), δE is the modulation field, and V is the external potential applied to the cell.

In actual measurements we have confirmed a linear dependence $\delta T/T \propto (V\text{-}V_0)$; we denote the fitting parameter which is obtained from the linear fit as V_0. The reason that we distinguish between the built-in potential V_{BI} and the fitting parameter V_0 is that we find that fitting parameter V_0 depends upon the laser wavelength λ; this rules out a simple identification of V_0 with V_{BI}. There are a number of other issues in relating V_0 to V_{BI} involving the modulation frequency, illumination intensity, and corrections for the voltage dependent capacitance of the structure. We have addressed these issues in earlier publications and reports (Wang, Schiff, and Hegedus, 1994; Schiff, Antoniadis, Gu, Lee, Wang, and Zafar, 1994), and shall not repeat this material here.

Some of the measurements exhibiting this wavelength dependence effect are summarized in Fig. 3. We show V_0 for the three laser wavelengths and for five samples obtained from various laboratories, and representing quite different solar cell structures. Some of the properties of the cells are presented in Table 2.

Table 2: Summary of Cells Studied Using Electroabsorption.

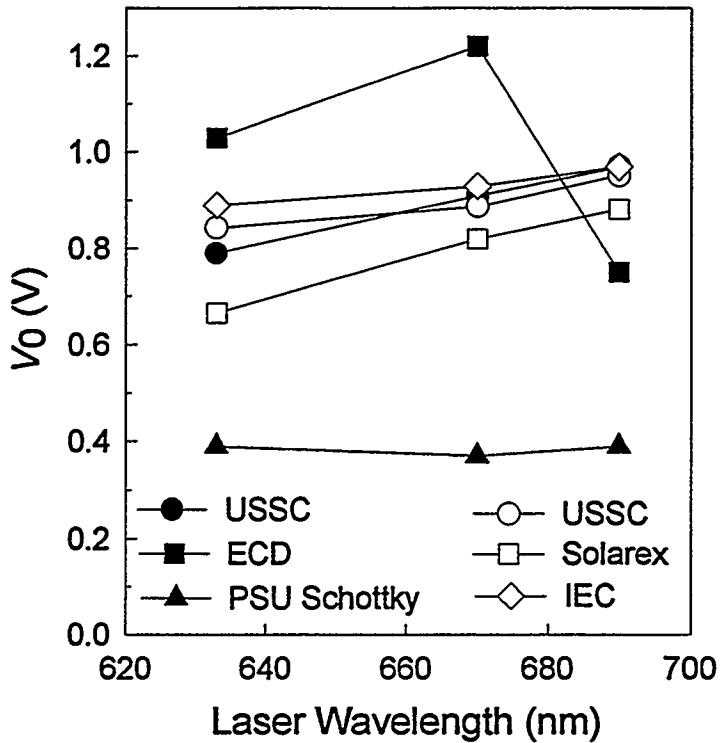| Cell ID	V_{OC} (V)	*p* layer	*i* layer
IEC	0.84	a-SiC (PhotoCVD, no buffer)	a-Si (PhotoCVD)
Solarex	0.85	a-SiC (no buffer)	a-Si
USSC	0.92	μc-Si	a-Si
ECD	1.00	μc-Si	a-Si (wbg)
PSU	--	Pd Schottky	a-Si

Fig. 3: Measurements of the electroabsorption parameter V_0 at several optical wavelengths for *pin* and Schottky barrier solar cells.

We have proposed (Wang, Schiff, and Hegedus, 1994) that the wavelength dependence of V_0 for a given cell is due to a combination of two effects. First, the solar cells are not optically homogeneous: in particular the p window layers of the various cells are optically quite distinct from the intrinsic layers. Second, some of the built-in potential is dropped within the p layer. The importance of this second effect to the electroabsorption measurement is dictated by the ratio of the electroabsorption coefficients of the two layers, which is wavelength dependent and thereby leads to the observed wavelength dependence.

A full analysis of the measurements will thus require independent information about the electroabsorption coefficients for both the p and i layers of the cell. We are currently working to obtain this information; at present we do not consider our information to be definitive. When completed, this interpretation of the measurements should yield two important pieces of information about the quality of a cell's p layer: the built-in potential, which is undoubtedly affected by the location of the Fermi energy within this layer, and the density-of-states in the p layer, which determines how much of the built-in potential is dropped within it. Our best, preliminary analysis indicates a built-in potential of about 1.0 V for the IEC cell, which incorporated photoCVD intrinsic and a-SiC:H p layers. This estimate is consistent with previous electrical studies done at IEC, but is significantly smaller than expected based on rough guesses from the activation energies of the p and n layers and band offsets.

We comment briefly on the fairly large value of V_0 measured for the ECD specimen, which incorporates a wider bandgap intrinsic layer than the remaining cells. The window layer of the cell was comparable to that for the USSC specimen; if electroabsorption were sensitive only to the built-in potential, it would be

surprising to find a significant difference between the cells. We believe that the higher value is simply another reflection of the proposed mechanism for the wavelength dependence.

Fig. 3 also shows measurements on a Schottky barrier solar cell, for which we anticipated a rather low value of V_{BI} and V_0; the latter is confirmed by the figure. We also find a much reduced wavelength-dependence. This result tends to confirm our attribution of the wavelength-dependence effect to the role of the p layer.

Electron Drift Mobility in a-Si:H Prepared by Hot-Wire Deposition

Amorphous silicon-based materials with modified bandgap are of considerable scientific and technical interest. Amorphous silicon-germanium alloys (a-Si$_{1-x}$Ge$_x$:H) have received particulary intensive investigation as narrow bandgap materials. There are many reports on the photogenerated carrier transport in this reduced bandgap material (Karg, Krühler, Möller, and Klitzing, 1986; Bauer, Nebel, Schubert and Schumm, 1989; Wang, Antoniadis, Schiff, and Guha, 1993; Guha, Payson, Agarwal, and Ovshinsky, 1987; Vanderhagen and Longeaud, 1989). The general findings are that electron drift mobility declines with germanium alloying and that hole drift mobility is relatively unaffected by the alloying. The underlying physics is generally interpreted with the exponential bandtail multiple trapping model; the decline of electron mobility is attributed primarily to the broadening of the conduction bandtail width $\mathcal{E}_O$ with alloying. The remaining two parameters, the microscopic mobility μ_0 and the attempt-to-escape frequency ν are apparently relatively unchanged with alloying.

An extensive analysis was done by Wang, *et al* (1993) on the electron transport in silicon-germanium alloys. Wang was able to fit essentially all the electron drift mobility data from different laboratories around the world using only the bandtail broadening effect, and assuming a bandgap-independent attempt-to-escape frequency $\nu = 5 \times 10^{11}$ Hz and a microscopic mobility $\mu_0 = 1$ cm^2/Vs,. The conclusion was that ν and μ_0 change little with alloying: the electron drift mobility of a material is determined adequately by the broadening of the bandtail which accompanies narrowing of the bandgap.

The bandgap of a-Si:H can also be varied solely by varying the concentration of hydrogen; less hydrogen reduces the bandgap. Maruyama, Yoshimine, Terakawa, Sayama, Ninomiya, Hishikawa, Tarui, Tsuda, Nakano, and Kuwano (1993) have discussed how germanium alloying and hydrogen concentration determine the bandgap in a-SiGe:H alloys. a-Si:H material produced by the "hot-wire" (HW) deposition technique combines reduced hydrogen content and bandgap with the remarkable property that the material is apparently more stable under light exposure than conventional plasma deposited a-Si:H (Mahan and Vanecek, 1991; Crandall, 1992). This property is clearly of potential importance in designing solar cells using a-Si based materials.

In the present paper we present a first account of the electron drift mobility in HW a-Si:H. The data fairly clearly violate the empirical rule of Wang, *et al* (1993) governing the effects of bandgap narrowing on the electron drift mobility. The measurements in low H-content HW material suggest that the attempt frequency ν increased *vis a vis* conventional plamsa deposited material. The fundamental microscopic mobility μ_0 is apparently affected neither by Ge alloying nor by changes in H concentratiuon.
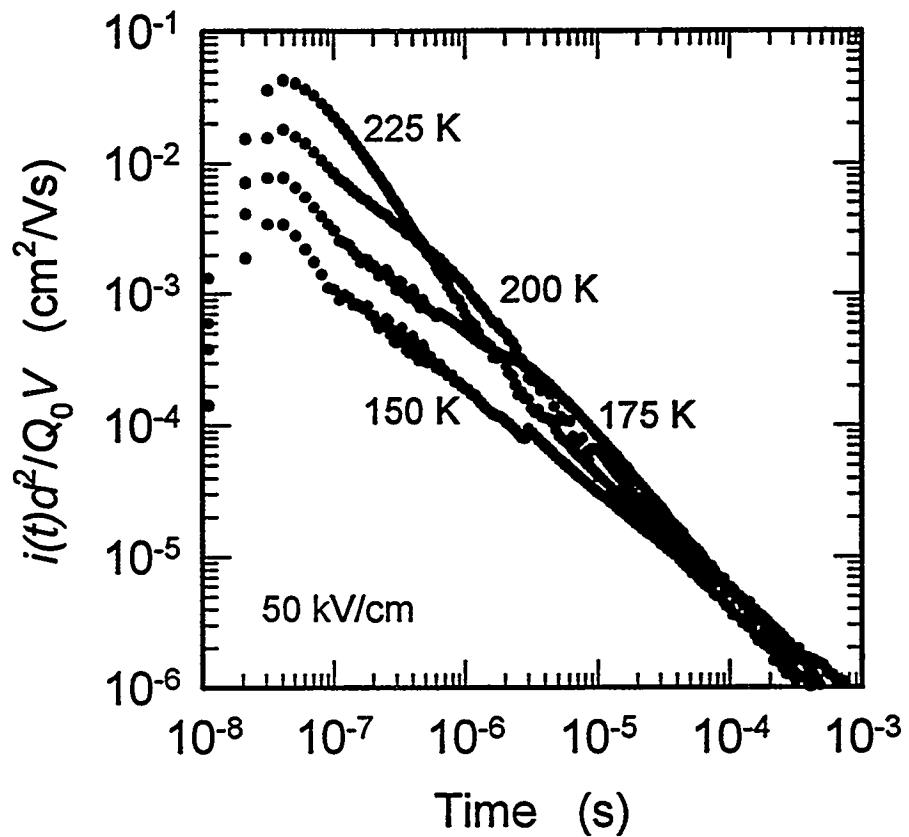
Fig. 4: Normalized transient photocurrents $i(t)d^2/Q_0V$ for electrons measured at 570 nm for the indicated temperatures. Electron sweepout is clearest at high temperatures. The charge Q_0 used to normalized these currents was measured at a higher field.

Electron Drift Mobility Measurements

The sample in which we did electron drift mobility measurements was a *pin* diode with a *i*-layer thickness of 4 μm. The structure, which was prepared at NREL, is $SS/n^+/i/p^+/Pd$; SS stands for "stainless steel." The *p*-layer and *n*-layer are each about 40 nm thick. The *p*-layer is a wide bandgap amorphous silicon-carbon alloy. The sample has about 2% hydrogen concentration in the intrinsic layer, which is significantly lower than the hydrogen concentration of about 10% in most device-grade, plasma deposited a-Si:H. The bandgap for our test sample is 1.60 eV, down 0.15 eV from about 1.75 eV of conventional plasma-deposited a-Si:H.

The experiment was carried out by using photocarrier time-of-flight (TOF). A fairly detailed discussion of our apparatus and procedures has been published previously (Wang, *et al*, 1993). In the present experiment, we used a pulsed laser wavelength of 570 nm; for the 1.60 eV bandgap of the sample we estimated that the electrons and holes were generated within 100 nm of the p^+/i interface. We obtained useful measurements from 150 K to 225 K.

In Fig. 4, we present the normalized photocurrent $i(t)d^2/Q_0V$ (essentially a transient mobility $\mu(t)$) at 50 kV/cm for four temperatures; d is sample thickness, V is applied bias, and Q_0 is the total photocharge generated in the specimen. For each of the transients, there is a transition from a shallow decay to a deep decay which occurs at a typical transit time for photogenerated carriers. It is clear that raising the temperature increases the magnitude of the transients and decreases the transit times. Both of the effects

correspond to the increase with temperature in electron drift mobility. The early-time "lumps" in the low temperature transients can be attributed to the RC time constant of the specimen.

In Fig. 5, we show the time integral $Q(t)d^2/Q_0V$ of normalized photocurrent from Fig. 4. We used these measurements to estimate the typical transit times t_T at different temperatures. In particular, we are interested in obtaining estimates of t_T which correspond to a specific ratio L/E of the mean electron displacement L to the bias electrical field E. In previous work we found that a value 2×10^{-9} cm^2/V was a satisfactory choice; the detailed procedure has been given by Wang et al (1993). In Fig. 5 we have drawn a corresponding horizontal line at 2×10^{-9} cm^2/V; the horizontal readings of the four intersections are the transit time estimates. The average drift mobility μ_D is calculated as $\mu_D = (L/E)/t_T = 2\times10^{-9}/t_T$. We note that there is a slight, logarithmic increase in the photocharge discernible at longer times in Fig. 5; we do not know the origin of this effect.

We show the resulting electron drift mobility as a function of temperature in Fig. 6. The present measurements for a HW specimen are represented by the solid circles. In the figure, we also include (as the squares) the electron drift mobilities obtained on a series of a-Si$_{1-x}$Ge$_x$:H with germanium concentrations x = 0.0, 0.1, and 0.5; the corresponding bandgaps are 1.72, 1.60, 1.47 eV, respectively. The two specimens with $E_G = 1.60$ eV are of special interest, and are highlighted using solid symbols. For each specimen, the data can be fit with a straight line which indicates simple activation of the drift mobility. It is useful to note that, for multiple-trapping, the intercept on the vertical axis is v (L/E), and hence determines the multiple trapping parameter v.

Discussion
The dashed lines in Fig. 6 show that the plasma-deposited, silicon-germanium alloys can be fit using the multiple trapping model assuming that only the bandtail width $\mathcal{E}_0$ changes with bandgap, while the other
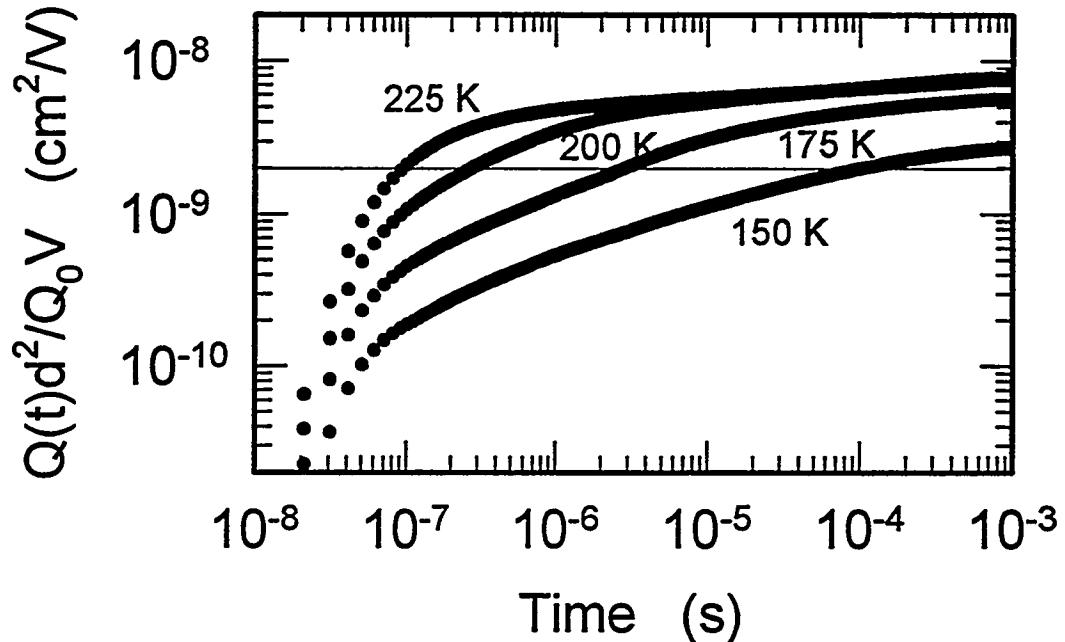

Fig. 5: Time integral $Q(t)d^2/Q_0V$ of $i(t)d^2/Q_0V$. The intersection of the transients with the horizontal line at 2×10^{-9} cm^2/V were used to determine electron transit times

two parameters, μ_0 and ν, remain unaffected by the alloying.

The solid line is a linear regression of the current data. It is clear that the solid line intercepts the vertical axis at a significantly higher value than obtained for the plasma deposited specimens, implying that hot wire deposited a-Si:H has a much higher attempt-to-escape frequency than the plasma-deposited a-SiGe:H alloys. In the Table below we give the 3 multiple-trapping parameters for the two specimens with E_G = 1.60 eV. For the HW specimen our data were insufficient to independently determine both $\mathcal{E}_0$ and μ_0, and we arbitrarily chose μ_0 = 1.0 cm^2/Vs to agree with the analysis from Wang, et al (1993), from which the parameters for plasma-deposited a-Si:H were taken. Nonetheless it is most interesting that the same values for $\mathcal{E}_0$ and μ_0 are consistent with measurements for both the 1.60 eV germanium alloy and HW material.
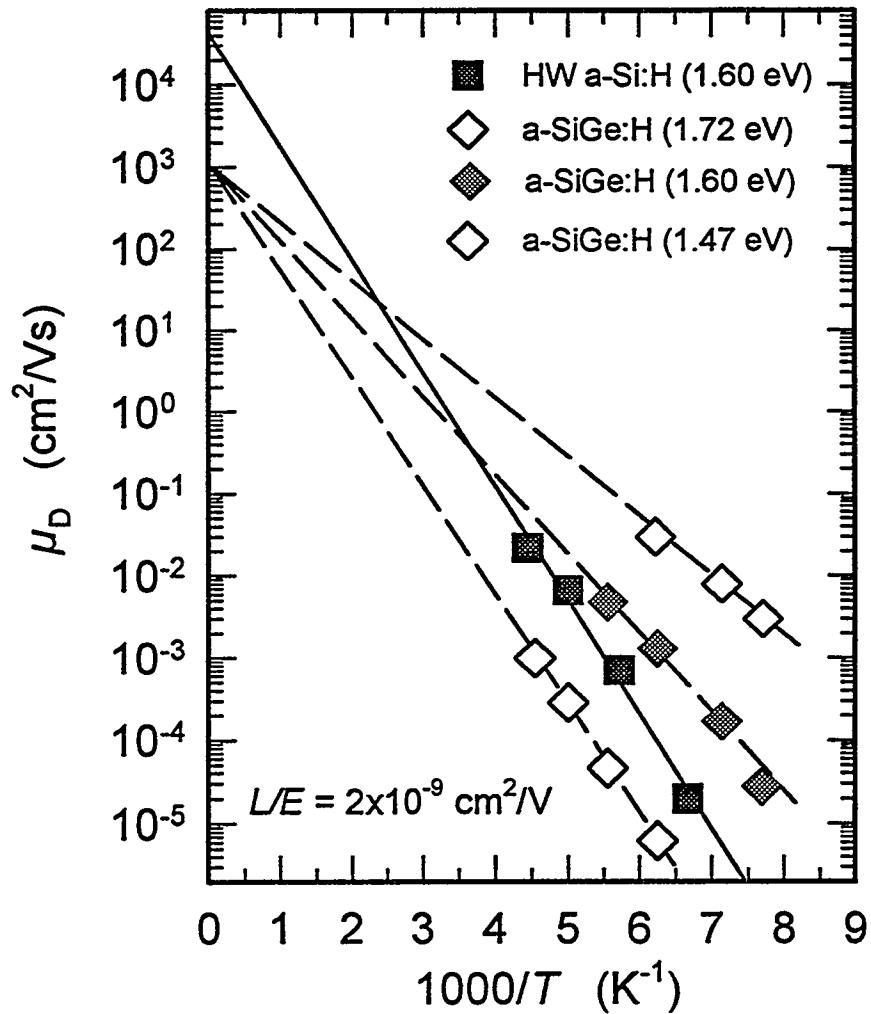
Fig. 6: Semilogarithmic plot of electron drift mobility μ_D as a function of reciprocal temperature $1/T$ for a hot-wire a-Si:H specimen and three plasma-deposited a-SiGe:H specimens; the optical bandgaps are indicated in the legend; the displacement/field ratio L/E = 2×10^{-9} cm^2/V. Solid squares are the present work on hot-wire a-Si:H. The dashed lines indicate multiple trapping fits with ν= 5×10^{11} s^{-1}; all the a-Si$_{1-x}$Ge$_x$:H specimens fit adequately. The solid line is a multiple trapping fit to the HW specimen for ν = 2.2×10^{13} s^{-1}.

Fig. 7: Schematic density-of-states diagram. The right most curve represents ordinary a-Si:H with a bandgap of 1.75 eV. The left most curve is valence band. In middle is a curve represent the two materials with 1.60 eV bandgap. The "+" shows that HW a-Si:H has a higher density of states at mobility edge than a-Si$_{1-x}$Ge$_x$:H (assuming the same bandgap).

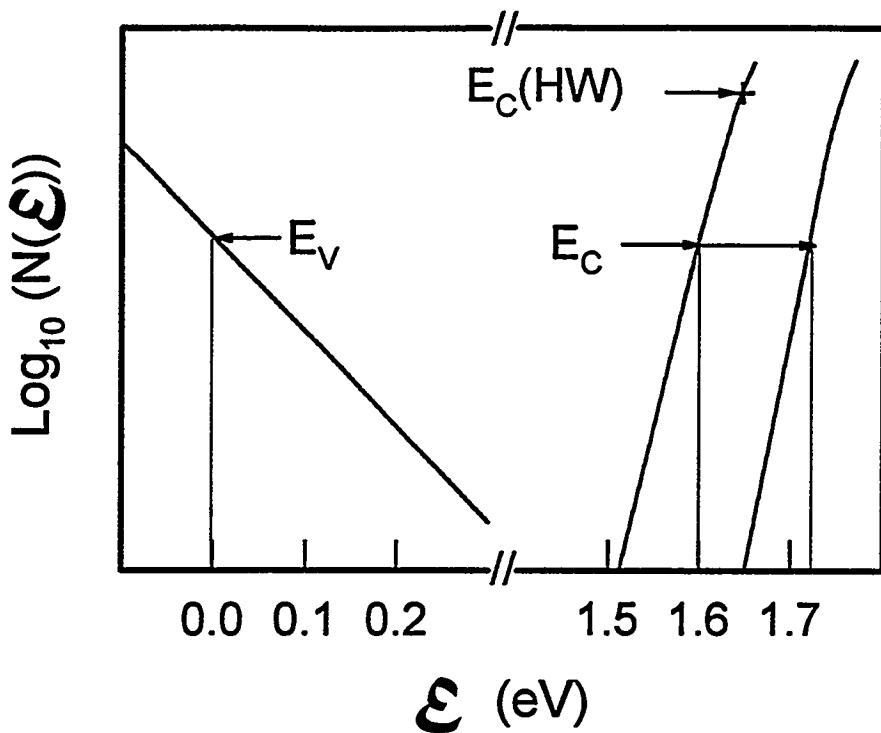| Sample	Bandgap (eV)	μ_0 (cm^2/Vs)	$\mathcal{E}_0$ (meV)	ν (s^{-1})
HW a-Si:H	1.60	1	25.8	2.2×10^{13}
a-Si$_{1-x}$Ge$_x$:H	1.60	1	25	5×10^{11}

The limited data we have obtained prevent us from asserting that this interesting trend — the large increase in ν *vis a vis* a-SiGe:H alloys with comparable bandgap — is a necessary consequence of narrowing the bandgap in a-Si:H alloys using hydrogen depletion. We nonetheless briefly speculate as to possible models.

For the plasma-deposited specimens, Wang, *et al* (1993) claimed that bandtail broadening alone was sufficient to explain the decline in electron drift mobility as the bandgap narrows in a series of plasma deposited a-SiGe:H alloys. This claim first implies that the microscopic mobility $\mu_0 \approx 1$ cm^2/Vs, and hence the fundamental transport process, was unaffected by alloying.

The second implication is that the attempt frequency ν was also unaffected. We suggest that ν be viewed as follows. We associate electrical transport in a-Si based materials with a *transport edge*, as illustrated in Fig. 7. The underlying character of this edge is not established: plausible microscopic models include a mobility-edge separating localized from extended states as well as pure hopping models involving only localized states. The microscopic mobility μ_0 is a property of this edge, but so too is ν. In particular we expect that a detailed balance relation $\nu = N_C b_T$ holds connecting ν with *(i)* the density-of-states N_C at the transport edge and *(ii)* the trapping coefficient b_T which governs electron capture into the bandtail. No specific model for b_T has been established, but the simplest viewpoint is to assume that it is *diffusion-limited*: $b_T = 4\pi D_0 R$, where D_0 is a microscopic diffusion coefficient and R is a capture radius. Since the

mobility μ_0 changes little as a-Si:H is modified, it seems reasonable to guess that b_T is similarly unaffected. Hence ν primarily reflects the transport-edge density-of-states N_C.

For the plasma-deposited a-SiGe:H alloys, we therefore suggest that the constancy of ν indicates that the transport edge occurs at essentially the same value of N_C in the alloys, as also indicated in Fig. 7. We further speculate that narrowing the bandgap of a-Si:H by reducing the density of hydrogen incorporated into it increases the value of N_C. This effect is in addition to the conventional attribution of drift-mobility declines to bandtail broadening. We have illustrated this idea in Fig. 7, where we indicate that the transport edge in the hot-wire material lies at different positions in a conduction bandedge which is common to the 1.60 eV alloys.

Diffusion-controlled bimolecular recombination in a-Si

In this section we review a fundamental difficulty in understanding recombination of electrons and holes in a-Si:H; the work itself was a contribution to a memorial issue of *Journal of Non-Crystalline Solids* honoring Marvin Silver's career.

Marvin Silver delighted in posing scientific riddles for his colleagues. Of these perhaps his favorite was a mobility paradox (Ries, Bäßler, Schönherr, Silver, and Snow, 1984). In brief, direct measurements of carrier drift mobilities in hydrogenated amorphous silicon (a-Si:H) yield fairly low values: the electron drift mobility is at most 2 cm^2/Vs near room temperature (Schiff, Devlen, Grahn, Tauc, and Guha, 1989; Devlen, Tauc, and Schiff, 1989), and holes are far less mobile. For such low mobilities the recombination of electrons and holes should be diffusion-controlled, which means that the recombination rate is limited by the time required for electrons and holes to diffuse close enough to annihilate each other. There are two straightforward consequences expected for diffusion-controlled recombination (Silver and Jarnagin, 1968): geminate (or Onsager) recombination of an electron and hole pair immediately following their photogeneration, and Langevin recombination for electrons and holes which manage to escape the geminate process. Both of these consequences are well documented in a variety of low-mobility materials.

The paradox is that neither of these consequences of low mobilities is found in experiments on a-Si:H. Geminate recombination is essentially negligible near room-temperature (Carasco and Spear, 1983), and estimates of the non-geminate, bimolecular recombination rate for electrons and holes are much lower than expected from the Langevin theory (Juska, Kocka, Viliunas, and Arlauskas, 1993). These problems cannot be explained away by adding new recombination mechanisms such as Auger processes: the geminate and Langevin recombination processes in principle represent lower bounds to recombination rates, and it is extremely disturbing to find that measurements yield recombination rates orders of magnitude lower than expected.

Silver and his collaborators suggested several possible mechanisms which might resolve both aspects of the mobility paradox (Ries, *et al*, 1984; Silver and Jarnagin, 1968). The fundamental mobility of photocarriers might be much higher than the drift mobility measurements suggest, and thus recombination is not diffusion-limited. The internal potential fluctuations due to the disorder of a-Si:H might be so large as to require modifications to the standard low-mobility calculations. There may be barriers which impede the final recombination process for electrons and holes.

In the present work we comment on the second, bimolecular recombination aspect of the mobility paradox for a-Si:H. In particular, the analyses of bimolecular recombination in a-Si:H have apparently all been restricted to mean field theories, which (by definition) largely ignore the role of fluctuations in the electron and hole densities. Incorporating such fluctuations can lead to qualitatively different conclusions regarding bimolecular recombination, as has become increasingly clear in theoretical work on diffusion-controlled

bimolecular recombination in the last decade (Ovchinnikov and Zeldovich, 1978; Toussaint and Wilczek, 1983; Kang and Redner, 1984).

It seems surprising that the results in a-Si:H have not (to our knowledge) been compared with the predictions of the fluctuation-dominated model. Kang and Redner (1984) suggested that this be done in their 1984 paper on these recombination models. We shall show here that these models do indeed provide a more satisfactory account for several picosecond domain experiments on a-Si:H than the mean field theories.

Incorporating fluctuation effects into the analysis of bimolecular recombination in a-Si:H does not explain the surprisingly small magnitude for geminate recombination in a-Si:H near room temperature. However, fluctuation-dominated models assume an initial spatial distribution of electrons and holes which is random to some degree. In particular we estimate that the initial thermalization radius r_0 (the typical separation of a photogenerated electron and hole following their photogeneration as a pair) must obey $r_0 > 12$ nm. This magnitude for r_0, although difficult to explain, is consistent with the small magnitude for geminate recombination.

a-Si:H appears almost unique as a material which satisfies two criteria for observation of the fluctuation-dominated regime: it has a modest electron mobility, so that diffusion control is plausible, but it also has a reasonably large thermalization radius, which is necessary to produce observable fluctuations in the first place. On the other hand, charged pair systems such as electrons and holes have, in the past, been considered unlikely candidates for observation of fluctuation-dominated behavior because of their large electrostatic interactions; we shall return to this problem at the end of this paper.

Langevin Recombination

The standard rate equation for bimolecular recombination in a bulk, homogeneous semiconductor is:

$$\frac{dN}{dt} = -b_R N(t) P(t)$$

where $N(t)$ is the density of electrons and $P(t)$ is the density of holes. b_R is the recombination coefficient governing the rate of bimolecular recombination.

This rate equation is an example of a *mean field* theory for recombination: we neglect correlations between the electron and hole densities and random fluctuations in the densities.

This approach seems completely reasonable in crystalline semiconductors, for which the charge carriers have long mean free paths: the fluctuations and correlations are smoothed over length scales of the order of the mean free path.

For materials in which both the electrons and holes have low mobilities, the assumption that the mean densities of electrons and holes is uncorrelated is clearly invalid: the Coulomb attraction of the electrons and holes modifies the mean electron density $N(r)$ near the hole. Assuming for simplicity that holes are immobile, one can solve for $N(r)$ and for the recombination current $j(r)$ as a boundary condition problem involving the drift/diffusion equation. The remarkable consequence is that the recombination coefficient b_R has the simple, Langevin form $b_L = e\mu/\varepsilon\varepsilon_0$, where e is the electronic charge, and $\varepsilon\varepsilon_0$ is the dielectric constant of the material.
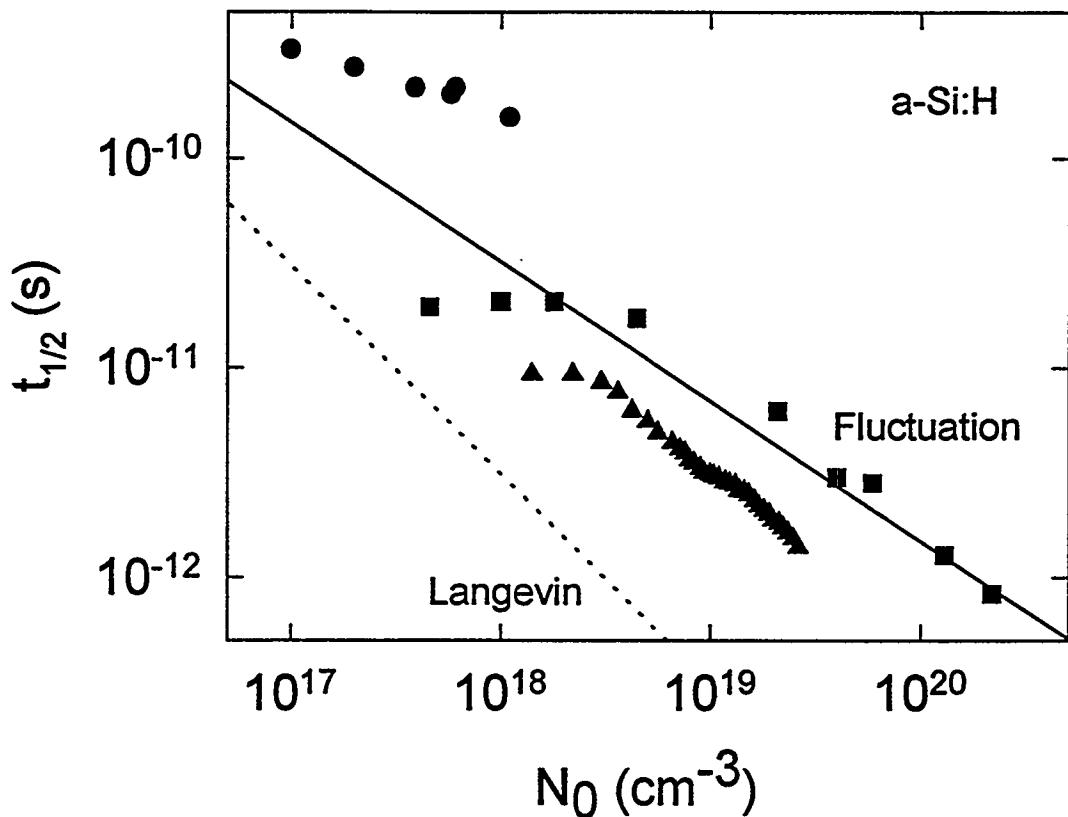
Fig. 8: Plot of decay time $t_{1/2}$ for photoinduced absorption as a function of the volume photoexcitation density N_0. The points refer to: circles-Devlen, Schiff, and Tauc (1989)), squares-Esser, et al (1990), triangles- Fauchet, et al (1992). The solid and dotted lines are the theoretical predictions of the Langevin and fluctuation-dominated models assuming a diffusion constant of 0.05 cm^2/s.

Picosecond Domain Studies of Bimolecular Recombination in a-Si:H

Optical techniques using pulsed lasers are almost ideal for exploring bimolecular recombination in a-Si:H. A very short "pump" pulse (typically 1 ps or less) from the laser photogenerates electrons and holes. The evolution of the density is then probed after a short delay (typically 1 - 1000 ps) by measuring the transmittance or reflectance for a second optical pulse. Since the delay between the pulses can be varied readily, one measures the time-dependent change in the material's optical properties induced by the pump pulse.

For a-Si:H these optical pump and probe experiments have now been done by several groups. A consensus has emerged (Fauchet, Hulin, Vanderhagen, Mourchid, and Nighan, 1992; Tauc and Vardeny, 1991) that the signals are primarily sensitive to the time-dependent decay of the density of electrons (and holes) as they recombine.

In Fig. 8 the results from several of these experiments at room temperature are summarized. Specifically, the characteristic response times $t_{1/2}$ (essentially the time for the optical response to decay to half its initial value) have been plotted as a function of the initial volume excitation density N_0.

The solid line in Fig. 8 is the prediction of the Langevin model described in section 2, for which:
$$t_{1/2} = 1/b_L N_0 = \varepsilon\varepsilon_0/e\mu N_0 \quad .$$
The values in Fig. 8 correspond to $\mu = 2$ cm^2/Vs, which is the measured value for the electron drift mobility in a-Si:H in the picosecond domain (Schiff, *et al*, 1989; Devlen, *et al*, 1989). Hole motion is neglected, since the hole mobility is much lower than the electron's (Gu, Wang, Schiff, Li, and Malone, 1994, and references therein).

It is clear from Fig. 8 that Langevin recombination provides a poor account for the measured response times. It is important to note that the measured times are longer than predicted. A recombination channel which competed with Langevin recombination would decrease $t_{1/2}$ below the Langevin value. In addition to the difficulty in accounting for the magnitudes of $t_{1/2}$ with Langevin recombination, the scaling of $t_{1/2}$ with N_0 is weaker than the expected dependence N_0^{-1}. The discrepancy has generally been attributed to competition between a "monomolecular" recombination process (dominating at low intensities) and a bimolecular process at high intensities, as proposed by Jackson (1989).

A Fluctuation Dominated Model

In Fig. 8 we have also shown a prediction based upon a fluctuation-dominated, bimolecular recombination model, which apparently agrees better with the measurements than the mean field form. The characteristic result of the fluctuation dominated models is that, for longer times, the density of carriers decays as
$$N(t) \propto N_0^{1/2} (Dt)^{-d/4}$$
where $d < 4$ is the dimensionality of the system and D is the diffusion coefficient of the mobile carrier (Ovchinnikov and Zeldovich, 1978; Toussaint and Wilczek, 1983). This form should be compared to the prediction of the mean-field, diffusion-controlled model
$$N(t) \propto (Dt)^{-1}$$
where it is important to emphasize that, unlike the fluctuation-dominated result, this long-time form is independent of the initial density N_0 and of the dimensionality d.

The effects anticipated from the electrostatic attraction of electrons and holes also fail to appear in electrical measurements at longer times in at least two experiments. Juska , *et al* (1994) have estimated the parameter b_R of the mean field, monomolecular + bimolecular recombination model using subnanosecond resolution electrical measurements of photoinduced transient space-charge limited currents. Most of their measurements are sensitive to the long time tail of recombination, since for higher intensities most carriers recombine on the picosecond scale. The authors obtain reasonable agreement with the mean field model's expected independence of intensity at long times and high intensities.

A mean field form seems reasonable, since both the thermalization radius and Coulombic effects lead to crossover from fluctuation-dominated to mean field behavior at long times. However, the authors conclude that recombination is slower than that predicted by the Langevin model by some orders of magnitude.

A similar conclusion can also be reached using the measurements of Conrad and Schiff (1986), who reported the transient photocurrent in coplanar electrode structures as a function of laser intensity at still longer times than Juska , et al (1994). Langevin, bimolecular recombination has a staggeringly simple long-time prediction for the photoconductivity:
$$\sigma_p(t) = N(t)e\mu = e\mu/b_R t = \varepsilon\varepsilon_0/t$$

At 1 μs this relationship predicts $\sigma_p \approx 10^{-6} \; \Omega^{-1} \, cm^{-1}$, which is nearly 1000 times smaller than the observed photoconductivities for high laser intensities in this work. On the other hand, the prediction of a t^{-1} decay and of temperature-independence are roughly confirmed in the measurements.

As Marvin Silver had surmised over ten years ago, the effects expected from the Langevin and Onsager views on diffusion-controlled recombination incorporating electrostatic interaction of electrons and holes are not found in a-Si:H. Either of the two assumptions of the analysis -- diffusion-control, or electrostatic attraction -- might fail in a-Si:H. However, it would appear from the picosecond measurements that a diffusion-controlled model does apply for a-Si:H -- at least if fluctuation effects are included. This statement is the main conclusion which can be drawn from the present work. But accepting the validity of diffusion-control leaves us with a conundrum, since the remaining assumption -- the electrostatic attraction of electrons and holes -- would seem to be beyond challenge. If we were allowed one final speculation, it would be to suggest that intrinsic potential fluctuations in a-Si:H may affect the recombination physics as significantly as the extrinsic photocarrier density fluctuations discussed here.

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13. ABSTRACT (Maximum 200 words)

This report describes work performed with three broad objectives: (1) To seek a deeper understanding of the open-circuit voltage (V_{oc}) in amorphous silicon (a-Si)-based solar cells and, in particular, for cells employing wide-band-gap modification of a-Si as the absorber layer. (2) To improve V_{oc} in wide-band-gap cells by searching for superior materials for the p-type "window layer" of the cell. (3) To seek to improve the understanding of the fundamental electron and hole photocarrier transport processes in the materials used for a-Si-based solar cells. A summary of accomplishments for this reporting period include the following: (1) We conducted a survey of thin BP:H and BPC:H films prepared by plasma deposition using phosphine, diborane, trimethyl boron, and hydrogen as precursor gases. (2) We found an interesting, conductive, and transparent BPC:H film in a remote deposition region of the reactor but were unable to transfer deposition of this film to the standard interelectrode region. (3) We developed our capability to deposit n-i-p sequence a-Si-based solar cells and demonstrated a V_{oc} greater than 0.7 V. (4) We continued our studies of built-in potential in a-Si-based solar cells using the electroabsorption technique, extending our measurements to include cells with wider-band-gap intrinsic layers and Schottky barrier test structures. (5) We made the first time-of-flight drift mobility measurements on a-Si:H prepared by hot-wire deposition. (6) We performed some theoretical work that addresses a difficulty in understanding photocarrier recombination in a-Si:H first identified by M. Silver. (6) We worked on high field electron drift mobilities in a-Si:H and on the validity of the Einstein relation connecting the diffusion and drift of holes in a-Si:H.

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