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PREFACE

This annual report covers the work performed at Syracuse University for the period February 20, 1991 to February 19, 1992 under National Renewable Energy Laboratory Subcontract XG-1-10063-7. Byron Stafford and Bolko von Roedern were technical monitors of this project. Several of the research projects discussed here were commenced under an earlier subcontract XB-6-06005-2 (John Benner, technical monitor). The principal contributors to this report and their present institutions were:

Dr. Homer Antoniadis, University of Rochester, Rochester, New York

Dr. Jung-Keun Lee, Iowa State University, Ames, Iowa

Dr. Eric A. Schiff (principal investigator), Syracuse University, Syracuse, New York

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We have benefitted from collaborations with Dr. Rob Devlen (Max Planck Institut, Stuttgart), Dr. Sergei Esipov (Syracuse University and University of Illinois at Urbana-Champaign), Dr. Subhendu Guha (United Solar Systems Corp.), Mr. Douglas Melcher (Syracuse University), Prof. Jan Tauc (Brown University), and Dr. Sufi Zafar (University of Chicago). Dr. Richard Crandall (National Renewable Energy Laboratory) arranged for us to receive a specimen from Chronar, Inc..

SUMMARY OF PRINCIPAL RESULTS

1. Effects of Light-Soaking on Electron Drift Mobility in a-Si:H.

The solar conversion efficiency of a-Si:H declines significantly following extended illumination (light-soaking); understanding and reducing this effect is a high priority of a-Si:H materials research. Most scientists associate the effect with an increase in midgap defect states under illumination, but the effects of light-soaking on the photocarrier mobilities may also be important. We studied the effects of light-soaking on the electron drift mobility for three specimens. The mobility effects were not larger than the 20 % reproducibility error. Sizable changes in electron deep-trapping due to light-soaking were observed.

2. Modulated Electron Spin Resonance and Defect Correlation Energies in a-Si:H.

Defect mediated recombination significantly limits conversion efficiency in current a-Si:H solar cells. An understanding of these defects requires that their typical charge state be established. We pursued recent proposals that most defects in undoped a-Si:H are charged due to small electronic correlation energies by performing temperature-dependent electron spin resonance measurements. The measured temperature-dependence was smaller than predicted from these models, and appears consistent with the view that most defects are electrically neutral in undoped a-Si:H.

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1. INTRODUCTION

In this annual report we describe at some length the results from research on two research topics:

- The effects of light-soaking on the electron drift mobility in a-Si:H.
- Modulated electron spin resonance measurements and their relationship to the electronic correlation energy of the D-center in a-Si:H.

Both of these projects were undertaken to better determine where the "standard" model for a-Si:H breaks down. In this model only a single defect, the D-center, dominates the deep level density of undoped a-Si:H. The D-center is hypothesized to have a significant *positive* electronic correlation energy U. By this we mean that the D-center's correlation energy is envisioned to exceed both the disorder-induced broadening of the level as well as the thermal energy k_BT. This standard model is reasonably successful in accounting for the most elementary "deep-trapping" aspects of electron and hole transport in a-Si:H, and it accounts adequately for the sub-bandgap optical properties. However, it is much less clear whether it provides a sufficient basis for understanding several effects which are crucial in operating solar cells: electron and hole mobilities and recombination in the presence of light-bias and of space-charge.

We therefore examined more carefully the two topics noted above. In the standard model one would not expect significant effects on drift-mobilities due to light-soaking, which would be envisioned as simply increasing the D-center density. Similar, in the standard model one would not anticipate a significant temperature-dependence to electron spin resonance, since essentially all spins are already detected.

Although one can find fragmentary discussion of both of these issues in the literature, the evidence regarding both effects was inconclusive. The work reported here sets considerably more stringent constraints on the magnitude of the two effects. It seems unlikely that light-soaking affects the electron drift mobility by more than 10 - 20 % . We also found only a very small temperature-dependence to the spin density. Neither set of measurements significantly challenges the standard model. We are currently planning experiments to look more directly at electron and hole drift under the presence of optical bias; this topic was explored by our group in preliminary work between 1982 and 1985.

We have also performed some research which will not be described at length here; some of this work is in print or in press, as noted below.

- High-field effects on the electron and hole drift mobility in a-Si:H [1-3]. At room-temperature nonlinearity is only observable above 10^5V/cm, but the field threshold declines with temperature.
- Thermal metastability of the spin density in a-Si:H [4,5]; this effect is attributed to atomic rearrangement, and not to the correlation energy effects just described. We also studied hydrogen-based models for these effects.
- Techniques for optical detection of photocarrier transport. We contributed to a review of these techniques, which we believe may contribute to future transport work in a-Si:H [6].
- Transient photocharge measurements in a-Si:H. We have been able to follow the transient photocharge in a-Si:H between 10 ns and 100 s. The transients nicely show the effects expected from the re-emission of electrons from deep traps in the millisecond

domain [3,7,8].

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2. EFFECTS OF LIGHT SOAKING ON THE ELECTRON DRIFT MOBILITY IN a-Si:H

For many years it has been known that light-soaking modifies the drift of photocarriers in hydrogenated amorphous silicon (a-Si:H). Staebler and Wronski first observed the effect in dark and photoconductivity measurements, which were substantially and reversibly affected by prior illumination history of an annealed specimen [1]. Later work on drift-mobilities in annealed and light-soaked material [2-4] clearly showed that light-soaking also accelerates "deep-trapping" of photogenerated electrons and holes in proportion to the increase in the deep-level density. It has been presumed that light-soaking does not affect the fundamental transport mechanism, which is usually accepted to involve bandtail states. However, the experimental limits on the magnitude of bandtail effects established by the early work [2] are relatively crude, and there are some preliminary reports suggesting that such an effect may exist [5-7].

Since the performance of a-Si:H solar cells is determined by the light-soaked state, a clear understanding of this issue is crucial for operating solar cells. A convincing demonstration of an effect of light-soaking on bandtail transport would also significantly change theoretical views of the mechanisms limiting mobilities in a-Si:H [8]. We have performed studies of the electron drift mobility using photocarrier "time-of-flight" techniques for optimized, undoped a-Si:H specimens from three different laboratories. We studied these effects between 130 K and 300 K. A preliminary account of parts of this work [7] and the description of instrumentation [9] were given elsewhere. We find very little effect of light-soaking on the bandtail-limited transport of electrons in a-Si:H under the "near dark" conditions used for time-of-flight techniques. This result is consistent with recent work by Wyrsch and Shah [10].

We first discuss measurements in an a-Si:H p-i-n diode fabricated at Chronar, Inc. (i-layer thickness of 10 μm). For this specimen our normal procedure of simply contacting the top layer with a circular metal electrode was unsuccessful; the very conductive top n-layer led to significant displacement current and photocurrent from regions of the film which were not under the electrode. We isolated the structure from the rest of the specimen by scribing around the electrode and through the film, leaving a narrow bridge to the rest of the film. We made the electrode by applying silver paint to the "island" in the film a few millimeters past this bridge. The laser illumination was through the bottom SnO_2 electrode and the p-layer. Fig. 1 was measured with 700 nm, for which the absorption length (4.3 μm) is comparable to the specimen thickness. Measurements at 610 nm were anomalous, which we attributed to inhomogeneity of the specimen's drift-mobility: the region near the top of the specimen apparently had a larger drift-mobility than the region near the back. Measurements at 700 nm essentially give the spatial average of the drift-mobility (cf. Appendix of ref. 9).

We measured a family of transient photocurrent responses for varying bias voltages at four different temperatures. Two light-soaking states were examined: the annealed state (obtained by heating the specimen at 180 C for 90 minutes) and a light-soaked state (obtained by 2 hours of illumination using a 250 W tungsten halogen illuminator (type ENH) at 30 cm from the specimen); the intensity of illumination was about 250 mW/cm^2. There was no significant attenuation of this intensity by the SnO_2 electrode.

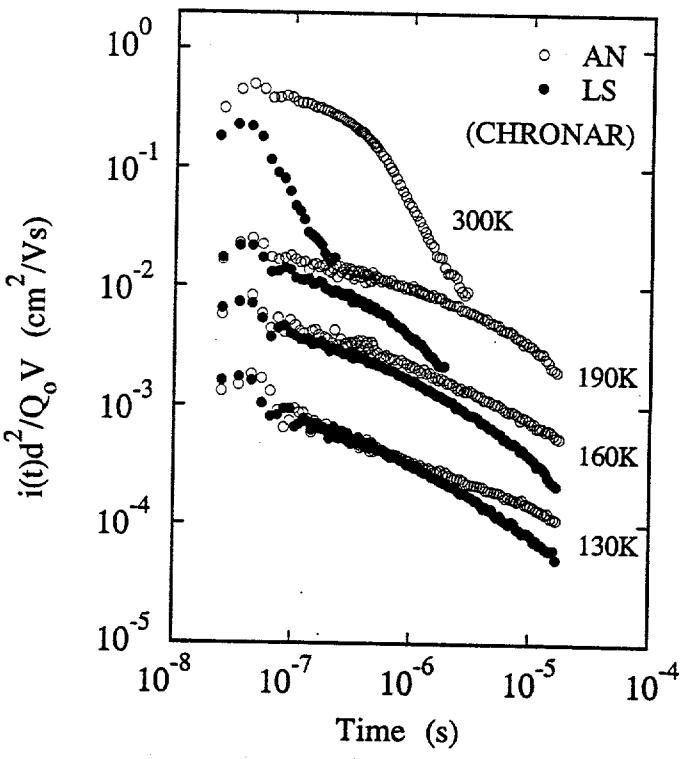

Fig. 1. Mobility-normalized transient photocurrents for a 10 μm thick a-Si:H *p-i-n* diode prepared at Chronar, Inc.. Two specimen states are illustrated: AN - annealed, LS - light-soaked. See Table I for details.

In Fig. 1 we present logarithmic plots of the normalized transient photocurrent: $i(t)(d^2/Q_0V)$. V is the reverse bias voltage applied to the diode 18 μs before the laser pulse. d is the thickness of the undoped layer of the diode. Q_0 is the total charge of mobile electrons in the diode (assuming quantum efficiency η is independent of temperature [11]). The procedure used to determine Q_0 will be discussed shortly; note that the normalized photocurrent has the dimensions of mobility. The rather slow rise of $i(t)$ (about 30 ns) for this specimen is due to diode series resistance effects remaining after our scribing procedure. The particular transients presented in Fig. 1 were measured with bias voltages chosen so that neither internal field effects nor the effects of electron transit across the specimen are apparent. We have shown in previous work that hole photocurrents are negligible in a-Si:H under the conditions of Fig. 1 despite the use of weakly absorbed illumination [9].

Fig. 1 is thus a highly condensed representation of the measurements; however, for brevity we shall not present complete families of transient photocurrents measured with varying bias. The families exhibited the well understood effects of photocarrier transit for larger voltages, and we integrated these higher voltage transients at 300 K to obtain Q_0. The measurements illustrated are typical of an "Ohmic" regime for the transient photocurrents. At voltages significantly lower than those used for Fig. 1 the transient photocurrent is nearly independent of voltage due to internal fields in the p-i-n diode structure.

With these precautions, the curves in Fig. 1 may be interpreted as measurements of an electron "transient drift mobility" $\mu(t) = v(t)/E$, where $v(t)$ is the speed of the mean

Table I. Electron deep-trapping mobility lifetime product $\mu\tau_{e,t}$ in several a-Si:H specimens for the annealed and the indicated light-soaking states. The left column gives the structure (sequence from top to glass substrate (denoted gl)), thickness, and source of each specimen.

Specimen	Illumination Time (hour)	$\mu\tau_{e,t}$ (cm^2/V)
Pd/nip/SnO_2/gl	0	2.9×10^{-7}
10 μm	2	2.8×10^{-8}
(CHRONAR)		
Al/i/Cr/gl	0	2.1×10^{-7}
4.8 μm	72[a]	6.3×10^{-8}
(SU)		
Pd/pin/Cr/gl	0	4×10^{-8}
2.65 μm	20	1.8×10^{-8}
(ECD)		

[a]Light soaked through semitransparent upper electrode.

position $x(t)$ of the photocarrier distribution. We have checked in several specimens that $\mu(t)$ can be used to predict transit times observed at higher voltages; see also ref. [9]. We first discuss the annealed state data. At 300 K the initial electron mobility is just below 1 cm^2/Vs, as usual for electrons in a-Si:H near room-temperature. The steep decline in $i(t)(d^2/Q_0V)$ after about 300 ns is the signature of "deep-trapping." We estimated the deep-trapping mobility-lifetime product $\mu\tau_{e,t}$ at 300 K using the standard, "Hecht" procedure of graphing the charge collected up to 10 μs as a function of voltage. For the annealed state charge collection due to internal fields was about 0.3 Q_o; we used the slope of the Q vs. V relation near $V = 0$ to estimate $\mu\tau_{e,t}$. For the light-soaked state deep-trapping occurred much earlier; the initial mobilities were probably comparable at 300 K, but these data are inconclusive because of the slow risetime. The value of $\mu\tau_{e,t}$ for the light-soaked state is reported in Table I; note that light-soaking reduced this value by nearly tenfold.

In Fig. 1 we see that the low-temperature transients for the two light-soaking states tend to converge at the earlier times, and diverge significantly at the longest times in the transient. These measurements may be interpreted as follows. Below 300 K the electron

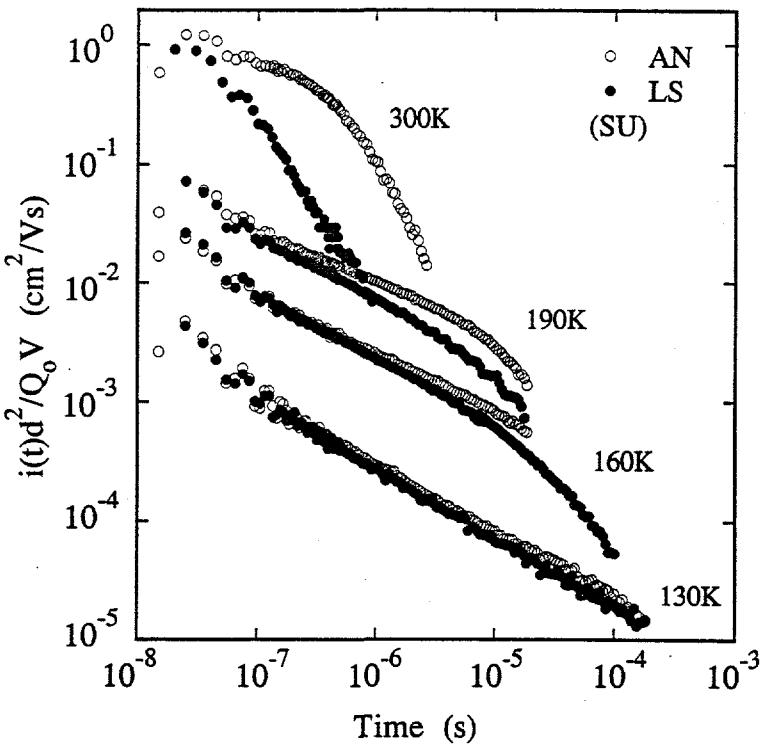

Fig. 2. Mobility-normalized transient photocurrents for a 4.8 μm thick a-Si:H diode prepared at Syracuse University (SU). Two specimen states are illustrated: AN - annealed, LS - light-soaked. See Table I for details.

mobility in a-Si:H declines with time as a power-law (with exponent between 0 and -1) because of bandtail trapping effects (i.e. multiple-trapping) [12]. This "dispersion" effect occurs earlier than deep-trapping and is apparently unrelated to it. At later times deep-trapping accelerates the decay of the transients; as expected the light-soaked state shows deep-trapping effects earlier than the annealed state.

We can therefore constrain the effect of light-soaking on the bandtail transport by examining the earliest times in the transients; at 190 K the difference between the light-soaked and annealed states is about 20% at 10^{-7} s. This difference is comparable to the absolute reproducibility of the measurements.

In Fig. 2 we present similar measurements (using 610 nm laser wavelength) for a 4.8 μm diode prepared at Syracuse University (SU). This specimen was light-soaked through a top electrode, which attenuated the illumination approximately tenfold. The specimen was illuminated for 72 hours with a filter which cut off wavelengths shorter than 665 nm. We measured a threefold drop in the value of $\mu\tau_{e,t}$ (cf. Table I). The effects of light-soaking are clearly shown in the accelerated onset of deep-trapping at 300 K.

In Fig. 3 we present the measurements (using 610 nm laser wavelength) for a 2.65 μm diode prepared at Energy Conversion Devices, Inc. (ECD). This specimen was clearly different than either the Chronar or Syracuse specimens. In the annealed state the electron deep-trapping mobility lifetime product $\mu\tau_{e,t}$ was signficantly smaller; however, the *hole* deep-trapping mobility lifetime product $\mu\tau_{h,t}$ was essentially equal to the electron $\mu\tau_{e,t}$.

For most undoped specimens previously reported $\mu\tau_{e,t} \simeq 10\,\mu\tau_{h,t}$ (cf. Fig. 7 of ref. 9).

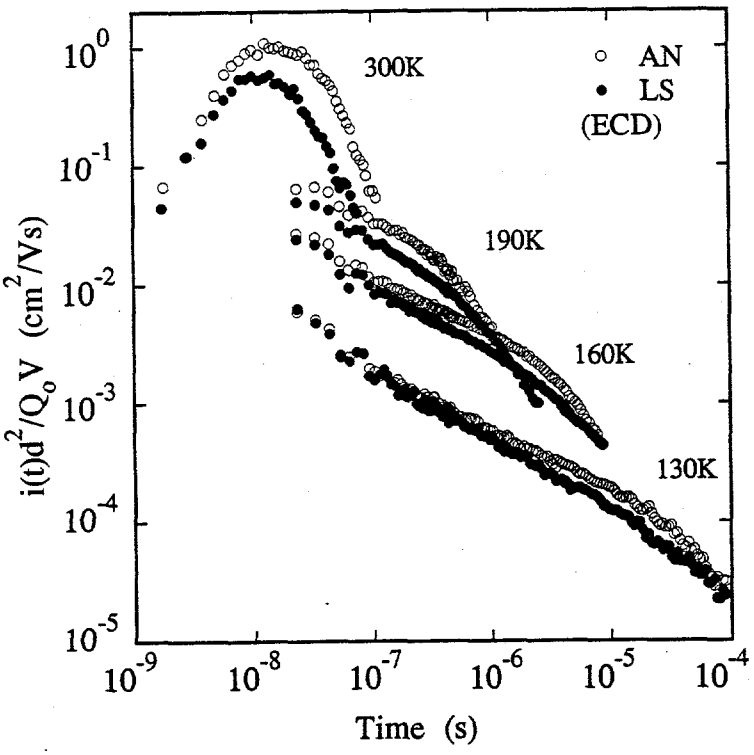

Fig. 3. Mobility-normalized transient photocurrents for a 2.65 μm thick a-Si:H *p-i-n* diode prepared at Energy Conversion Devices, Inc. (ECD). Two specimen states are illustrated: AN - annealed, LS - light-soaked. See Table I for details.

The absolute magnitude of the electron drift-mobility at lower temperatures is comparable to that of the Chronar specimen down to 130 K. Light-soaking was performed prior to deposition of the top electrode to prevent attenuation of the illumination; nonetheless $\mu\tau_{e,t}$ declined relatively little under light-soaking for this specimen.

As for the Chronar specimen, the risetime of the transient photocurrent tends to obscure the initial bandtail region at 300 K for light-soaked state. For this specimen we analyzed the short-time region fairly carefully. We found that the light-soaked transient was interpretable as a simple exponential; the extrapolated initial mobility was 1.0 cm^2/Vs. This value is the same as directly measured for the annealed state. The 190 K data suggest a small difference in bandtail mobility, but this effect is not apparent at 160 K and 130 K. We therefore conclude that the effects of light-soaking are again no larger than 20% for the drift-mobility of this specimen.

Some data for the Syracuse and ECD specimens are previously published [7]. For the ECD specimen we previously reported a factor 2 difference between the light-soaked diode and an annealed diode below 200 K. The light-soaked diode was prepared by first light-soaking and then deposited the top Pd electrode; the annealed one was a "sister" diode at a different location on the substrate. We did not find comparably large effects when the same diode was used for both states, and it thus seems probable that differences between the diodes were interpreted as evidence for a light-soaking effect.

The authors thank S. Guha for providing the ECD specimen, R. Crandall for help with obtaining the Chronar specimen, Sufi Zafar for depositing the SU specimen, Philip

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3. MODULATED ELECTRON SPIN RESONANCE MEASUREMENTS AND DEFECT CORRELATION ENERGIES IN a-Si:H

Ever since the discovery that defects in chalcogenide glasses such as Se and As_2Se_3 can have *negative* effective correlation energies U - that is, ever since the discovery that charge exchange between identical defects

$$D^0 + D^0 + U \rightarrow D^+ + D^-$$

can be *exothermic* - it has been clear that experimental constraints on U are crucial to the interpretation of defect experiments [1-4]. The original puzzle in chalcogenides was that the large densities of gap states detected electrically gave no corresponding signal in electron spin resonance (ESR) measurements. The puzzle is neatly solved by a negative correlation energy: only neutral defects are detected by ESR, but with a negative U essentially all defects are charged in equilibrium (half positively, and half negatively).

The discovery of negative U in chalcogenide glasses was probably delayed by the absence of experimental techniques which directly address its value and sign. Research on hydrogenated amorphous silicon (a-Si:H) benefitted from a novel, depletion width modulated ESR technique developed in 1982 by Cohen, Harbison, and Wecht [5] to probe correlation energies. These "DWM-ESR" measurements were done on phosphorus-doped a-Si:H. Initially, the D-centers were negatively charged due to doping; spins were created by "depleting" the specimen of electrons, thereby creating spins (neutral D^0 defects). The measurements were consistent with a substantial, positive correlation energy $U > 0.2$eV.

One might expect that the properties of D-centers in doped a-Si:H and intrinsic (not intentionally doped) a-Si:H should be the same, and indeed some early experimental estimates of U were based on this premise. However, it now appears that the optical [6,7] and spin-relaxation [8] properties of the D-center vary significantly between specimens, presumably reflecting the relatively large range of configurations possible for a given type of defect in a non-crystalline material. A systematic difference between doped and intrinsic a-Si:H is possible and even probable. The first DWM-ESR measurements in intrinsic a-Si:H were reported only fairly recently [9]. They were interpreted as evidence for a zero correlation energy, thereby suggesting that most defects in intrinsic a-Si:H are charged and undetected by ESR. A summary of the evidence favoring the generalized "charged-defect" view for a-Si:H has been given recently [10]. Specifically at issue are the microscopic interpretation of the defect density-of-states, and the use of ESR measurements for absolute calibration of optical and electrical defect spectroscopies.

In this paper we first discuss further the general relationship of modulated electron spin resonance measurements and effective correlation energies. We evalute both thermal-modulated and depletion-modulated ESR for a conventional model of defects in amorphous semiconductors. The model incorporates both the correlation energy of the defects and also the Fermi level, which may be affected by dopants or by other defects not included in the model. As expected from previous work [5,9], depletion modulated ESR is quite sensitive to the correlation energy, but it proves to be quite sensitive to the Fermi level as well. Thermal modulation is primarily sensitive to the correlation energy, and is remarkably independent of the Fermi level. We therefore propose that temperature-dependent ESR

should be used to estimate U in amorphous semiconductors, and that depletion modulation should be used in conjunction to gauge the doping level.

We then present temperature-dependent ESR measurements for intrinsic a-Si:H prepared under a wide range of conditions. These appear to be the first such measurements to be published [11]; we believe that our measurements are sufficiently accurate to detect 1% deviations from Curie-law behavior in the temperature range 77 K - 350 K. We interpret these measurements as indicating a correlation energy of 0.3 eV for the D-center in intrinsic a-Si:H, and we reinterpret the DWM-ESR data as indicating essentially no inadvertent doping of the specimen.

The principle of the two modulation techniques is illustrated in Fig. 1 for a conventional model [6,7,9] of defects in a-Si:H. The density-of-states $g(E)$ corresponding to the transition $D^+ + e^- \rightarrow D^0$ is illustrated in the top panel. The density of spins N_s is determined in this model using the probability $f_1(E)$ that a defect is singly-occupied: $N_s = \int g(E) f_1(E)\, dE$. $f_1(E)$ is evaluated using textbook statistical mechanics for sites D^+, D^0, and D^- charge states [12]:

$$f_1(E) = \left(1 + 1/2\exp(\beta(E-\mu)) + 1/2\exp(-\beta(E-\mu+U))\right)^{-1} \quad . \tag{1}$$

μ is the electronic chemical potential (or Fermi level) determined by the total density of electrons n; $\beta \equiv 1/k_B T$. We assume that defects have a common correlation energy U despite the distribution of level positions E. The solid curve in the middle panel of Fig. 1 illustrates the function obtained for $\mu = 0.0$ eV and $U = +0.3$ eV. The upper cutoff in this curve is at μ, as for ordinary Fermi statistics. The lower cutoff is at $\mu - U$. Levels lying deeper than $\mu - U$ are doubly occupied, and hence f_1 declines to zero.

In an ideal depletion modulation experiment, the chemical potential μ would be lowered by depleting the total density of electrons n. The new function $f_1(E)$ which might result is illustrated by the dashed curve of the middle panel; there is of course a corresponding change in spin density. Lowering the specimen temperature can also affect the spin density; the lower panel of Fig. 1 illustrates the effects of changing temperature while leaving the electron density n constant. The cutoffs in f_1 become sharper at lower temperature. There is also a change in μ, although this effect is not obvious in the illustration.

We found it simplest to study the depletion and thermal effects in this model using numerically evaluated partial derivatives of $N_s(n,T)$. We define the depletion modulation of the spin density $DM \equiv \frac{\partial N_s}{\partial n}$, and we define the thermal modulation $TM \equiv \frac{\partial N_s}{\partial T}/N_s$. We used the density of states illustrated in Fig. 1:

$$g(E) = (N_D/\pi\Delta E)\mathrm{sech}((E-E_0)/\Delta E) \quad . \tag{2}$$

N_D is the total density of defects; note that TM and DM are independent of N_D. We chose a value for ΔE which yields a FWHM width of 0.3 eV; this value is consistent with the optical measurements [6,7], and was used in the previous work on depletion modulation [9].

In Fig. 2 we illustrate how DM and TM depended upon the density of electrons $(n-N_D)/N_D$ near 360 K. If no dopants or other defects are present, the ratio $(n-N_D)/N_D$ is zero; doping or other defects cause $(n-N_D)/N_D$ to vary between -1 and +1. Consider

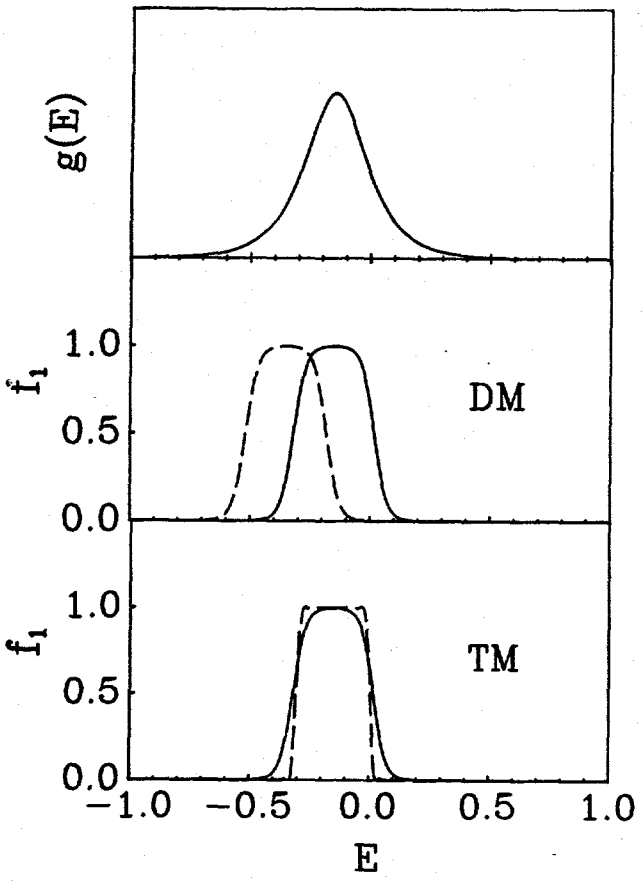

Fig. 1: Calculation of spin densities for a density-of-states model. The upper panel illustrates the density of states $g(E)$. The function $f_1(E)$ in the middle and lower panels is the probability that a defect labeled by E is occupied by one electron for an effective correlation energy $U_{eff} = +0.3$eV. The middle panel illustrates $f_1(E)$ for two values of the total electron density n; the lower panel illustrates $f_1(E)$ for two temperatures and a constant value of n.

first an empty defect system with $(n - N_D)/N_D = -1$. When $U = 0.3$, adding an electron increases the mean number of spins by almost 1.0 ($DM = 0.9$). As the electron density n increases, DM declines to zero because of the increasing population of D^- states. DM is an odd function of $(n - N_D)/N_D$; for a nearly full system ($(n - N_D)/N_D = +1$), adding an electron decreases the spin density. As illustrated, DM also falls substantially as U decreases; for negative U essentially no spins are present for any Fermi level.

Thermal modulation TM exhibits a dependence upon U which is nicely complementary to that of depletion modulation. For $U = 0.0$ TM is of order $1/T$, and it declines to nearly zero for $U = 0.3$. On the other hand, *TM hardly depends upon the Fermi level at all.* This feature makes TM simpler to use than DM when doping levels are poorly known.

We now discuss experimental determination of TM in a-Si:H. In Fig. 3 we have presented temperature-dependent measurements of the product $S(T) \cdot T$ of the absorption susceptibility $S(T)$ (measured using electron spin resonance) and the specimen tempera-

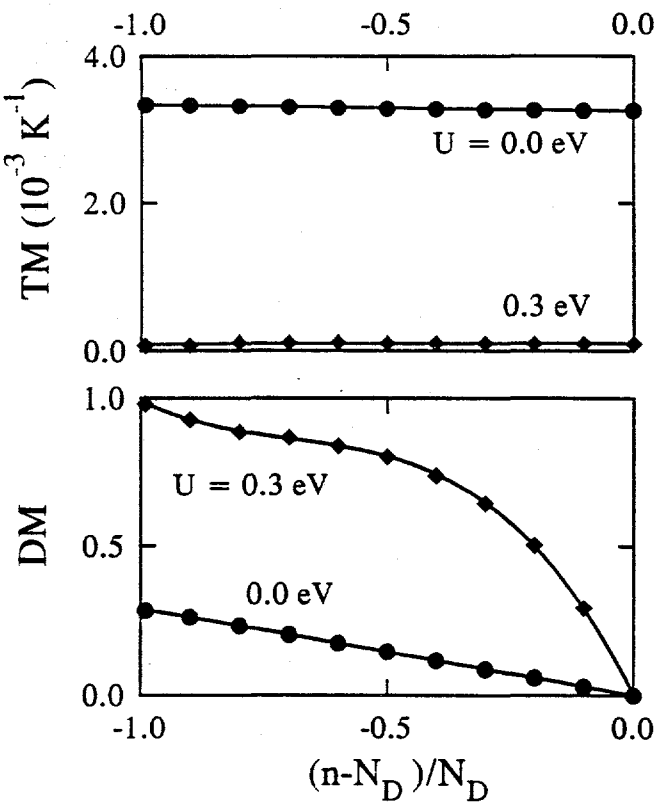

Fig. 2: Dependence of depletion-modulated ESR $DM \equiv \frac{\partial N_s}{\partial n}$ and thermal modulated ESR $TM \equiv \frac{\partial N_s}{\partial T}/N_s$ upon the excess electron occupancy $(n - N_D)/N_D$ due to doping effects. The points were computed numerically from the defect model of Fig. 1; the curves are guides. Results for two correlation energies U are plotted.

ture T. This product eliminates the $1/T$ Curie-law temperature dependence of the susceptibility anticipated for isolated spin = 1/2 defects, and hence is interpretable as the temperature-dependent spin density $N_s(T)$. Since we are only interested in the form of $N_s(T)$, we have normalized the data so that the apparent $T = 0$ K intercept is 1.0.

The various symbols correspond to different a-Si:H specimens, as explained in the caption. The specimens were deposited using a commercial plasma deposition system (Plasma Technology, Inc. "Plasmalab") operating with 200 mTorr of SiH_4. Specimens with widely varying spin densities were obtained by varying the substrate temperature during deposition, and by subsequent thermal quenching and annealing treatments in some cases. ESR measurements were done with a commercial spectrometer (Varian, Inc. model E-9; 100 kHz magnetic field modulation). Temperature-dependent measurements were performed with the specimen inside a quartz insert in the microwave cavity; only the insert and the specimen were cooled using flowing nitrogen gas. We determined the effects of changing the insert temperature upon the cavity Q using a a high-sensitivity microwave reflectivity technique. We found about a 4% change in Q as the insert temperature changed between 300 and 77 K. We checked this calibration using a ruby (0.1% Cr^{3+}), which exhibited a 2% deviation from Curie behavior between 77 K and 300 K. Further details of our procedures are given elsewhere [13].

It is crucial to use low microwave power for temperature-dependent measurements

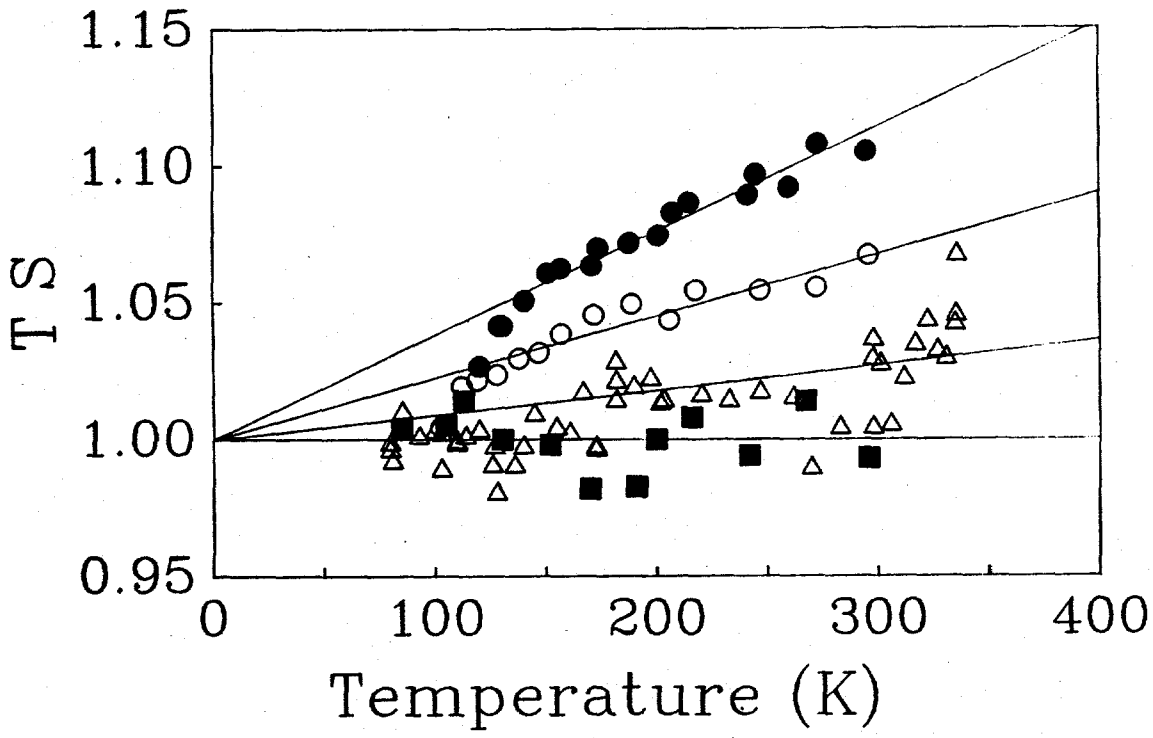

Fig. 3: Temperature-dependent measurements of the resonant absorption susceptibility $S(T)$ for four specimens of a-Si:H. The vertical axis is the product $S(T) \cdot T$, which compensates for the Curie-law dependence of $S(T)$; the measurements for each specimen were normalized so that the $T = 0$ K limit is 1.0. The average spin densities and the thicknesses of the specimens were [$\bullet : 1.4 \times 10^{19}$ cm^{-3}, $8.1\mu m$]; [$\circ : 1.2 \times 10^{18}$ cm^{-3}, $8.1\mu m$]; [$\triangle : 5 \times 10^{16}$ cm^{-3}, $3.0\mu m$]; [$\sqcup : 1.1 \times 10^{16}$ cm^{-3}, $1.6\mu m$].

to avoid microwave saturation effects. We chose a power of 0.004 mW, based on previous studies [8,14]. We subsequently discovered that the uppermost curve of Fig. 3 was slightly saturated below 150 K, which accounted for the deviation from linear behavior for this curve. This specimen was deposited at 150 C; the anomalous saturation behavior largely disappeared upon annealing at 220 C (data presented as open circle symbols).

We also explored the role of interface states on these Curie-law deviations by studying the effects of specimen thickness for specified deposition and annealing conditions. For the two upper curves in Fig. 3 the areal spin density (spins per cm^2 of specimen) was accurately proportional to the specimen thickness, confirming that these data are characteristic of the specimen bulk. For better specimens we measured an interfacial spin density of 2×10^{12} cm^2. The lowest curve in Fig. 3 is thus entirely due to interfacial states, and we concluded from these data that there is no significant non-Curie behavior for interfacial spins.

We estimated the thermal modulation parameter $TM = \frac{\partial N_s}{\partial T}/N_s$ from the slopes of the linear temperature-dependence, as indicated in Fig. 3. For specimens with areal spin densities comparable to the interfacial density of 2×10^{12} cm^{-2} we calculated the slopes after subtracting a (temperature-independent) interfacial spin density 2×10^{12} cm^{-2} to estimate the bulk spin density N_B. We did not explicitly measure the temperature-dependence of the entire thickness series in these specimens.

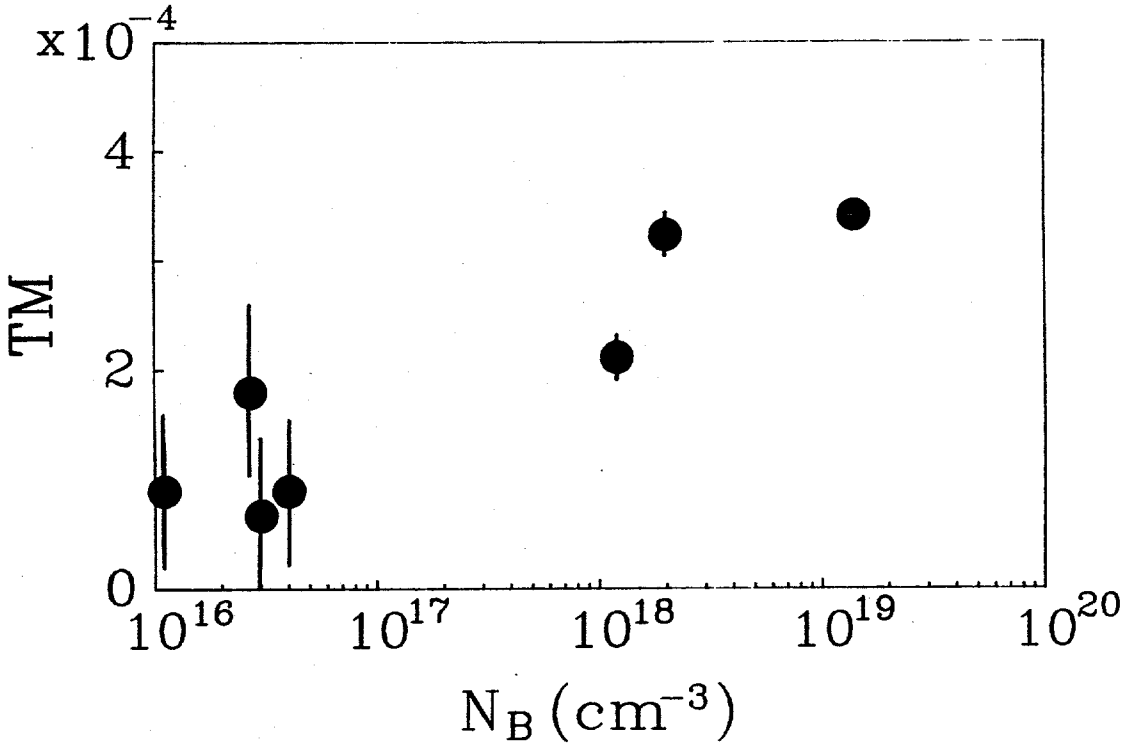

Fig. 4: Correlation of the thermal modulation TM of the spin density with the bulk spin density N_B for seven specimens of a-Si:H. TM was evaluated using straight line fits such as shown in Fig. 3; a correction for interfacial spins was applied to the specimens with $N_B < 10^{17}$ cm^{-3}. The error bars indicate the standard deviation of independent thermal cycles.

In Fig. 4 we show the correlation of TM with the bulk spin density N_B; the error bars indicate the statistical uncertainties in the slope estimates. We estimate that "bulk spins" in a-Si:H of typical device quality exhibit a thermal modulation of $1-2\times10^{-4}$ K^{-1}, which corresponds to a deviation from Curie-dependence of 2 - 4% between 100 and 300 K. Poorer specimens exhibit a thermal modulation of nearly 4×10^{-4} K^{-1}. Such a systematic variation appears compatible with other inhomogeneities in D-center effects noted in the introduction; a microscopic interpretation is probably premature. It surprised us that interfacial spins gave no detectible Curie-law deviation, since we might assume that these spins should be characteristic of "poor" a-Si:H. Presumably the surface and bulk microstructures in a-Si:H leading to defects in the two regions are different.

We shall interpret these measurements using the conventional model presented in figures 1 and 2. A "device-grade" material with TM of 10^{-4}K^{-1} corresponds to $U = 0.3$ eV; this fitting is essentially independent of the measurement temperature between 77 K and 400 K. "Poor-quality" a-Si:H corresponds to a lower value $U = 0.2$ eV. A better way to describe the implications of the TM data is to estimate the ratio N_s/N_D of the spin density to the total defect density N_D. This ratio depends less strongly on the particular parameters of $g(E)$; we obtained $N_s/N_D \sim 0.75$ when $TM = 10^{-4}$K^{-1}. Thus these temperature-dependent ESR data agree broadly with earlier estimates of U based on interpretations of infrared absorption measurements [6,7], and they support the widespread

use of the spin density N_s as an estimate for the total density of deep levels in a-Si:H.

We now discuss the relationship of these TM measurements and the earlier DWM-ESR work. Essick and Cohen [9] reported a depletion effect $\Delta N_s/\Delta n \sim 0.14$ for the five different "light-soaking" states of the specimen. They proposed that $U \sim 0.0$ eV using a similar correlation energy model and density-of-states to that used here. Their estimate for U reflects their assumption about the Fermi level. They chose the value $(n - N_D)/N_D = -0.5$ [15], corresponding to a nominal degree of inadvertent doping of the specimen. Equating $\Delta N_s/\Delta n = +0.14 = DM$, their value $U = 0.0$ eV obtains from Fig. 2. Essick and Cohen argued that, if the specimen were truly undoped and had a larger U, it would be unlikely that the five light-soaking states (with five different spin densities) should have yielded essentially the same value for $\Delta N_s/\Delta n$. Light-soaking presumably modifies $(n - N_D)/N_D$, and thereby DM.

We interpret these measurements as follows. The temperature-dependent measurements establish U fairly unambiguously given a basic density-of-states model. DWM-ESR can then be used to estimate the inadvertent doping level in intrinsic a-Si:H; for $U \sim 0.25$ eV we found [16] that $(n - N_D)/N_D$ is indistinguishable from zero based on Essick and Cohen's data.

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16. Abstract (Limit: 200 words)

This report describes the results from research on two topics: (1) the effects of light-soaking on the electron drift mobility in a-Si:H, and (2) modulated electron spin resonance measurements and their relationship to the electronic correlation energy of the D center in a-Si:H. Both of these projects were undertaken to better determine where the "standard" model for a-Si:H breaks down. The standard model is reasonably successful in accounting for the most elementary "deep trapping" aspects of electron and hole transport in a-Si:H, and it accounts adequately for the sub-band-gap optical properties. However, it is much less clear whether it provides a sufficient basis for understanding several effects which are crucial in operating solar cells: electron and hole mobilities and recombination in the presence of light-bias and space-charge. In the standard model, one would not expect significant effects on drift mobilities due to light-soaking, which would be envisioned as simply increasing the D-center density. Similarly, in the standard model one would not anticipate a significant temperature dependence to electron spin resonance, because essentially all spins are already detected. Discussions in the available literature on the evidence regarding both effects were inconclusive. The work reported here sets considerably more stringent constraints on the magnitude of the two effects.

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