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SPIN DEPENDENT PHOTOCURRENTS IN RIBBON SOLAR CELLS

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ABSTRACT

Spin Dependent Transport (SDT) is a method of identifying recombination centers which employs a microwave resonance condition to affect the recombination rate of minority carriers in a device. When this technique is used to analyze the diffusion-limited currents produced by long-wavelength optical excitation, it has the potential to chemically identify the major recombination sites in solar cells. We have used this resonance technique to analyze short circuit photocurrents in Edge-defined film-Fed Growth (EFG) ribbon silicon solar cells. At room temperature, our observed photocurrent resonances have zero-crossing g values and linewidths which are similar to SDT observations made on the trans-barrier currents in silicon bicrystals, and electron spin resonance signals seen in damaged silicon, and polycrystalline silicon. These dangling-bond-like SDT signals depend on cell illumination levels in a way that suggests that the values of recombination velocity at electrically active linear boundaries decrease with illumination intensity. Hydrogen processed cells show markedly smaller SDT response, consistent with the passivation of Si dangling bond defects. While most of our SDT observations have been made on n^+/p EFG cells, we suggest that measurements made at low temperatures on other cell structures might uncover resonances due to other recombination centers in this material.

INTRODUCTION

Identifying the recombination centers which control minority carrier lifetime is an important step in the process of optimizing the performance of low-cost photovoltaic devices. Techniques like Electron Beam Induced Current (EBIC)¹ and its light beam counterpart, LBIC¹, can reveal spatially localized defect arrays such as grain boundaries or dislocations, but do not provide information about the chemical identity of the actual recombination centers. Deep Level Transient Spectroscopy (DLTS) can sense deep electron or hole trap levels in the depletion region of a junction device², but literally hundreds of different trap energies have been catalogued in materials like Si and GaAs, so identification of the specific contaminant may prove difficult.

Beginning in the early 1970's, a spin resonance-based transport technique variously identified as SDT (spin dependent transport) or SDC (spin dependent conductivity) has been demonstrated in single crystal silicon^{3,4}, silicon

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bicrystals^{5,6}, and Si transistors^{7,8}. In this measurement the photoconductivity, trans-barrier current, or dark junction current is measured as a resonance condition is established for paramagnetic defects which control the sample current. Because the (usually unique) magnetic resonance properties of the transport controlling defect are probed, this measurement has a high degree of chemical specificity.

Our work will demonstrate the use of this technique to probe the nature of minority carrier recombination in silicon ribbon solar cell structures. The results show that one relatively well understood recombination center, the silicon dangling bond, is present in these devices, and that the density of dangling bonds can be substantially reduced by hydrogen in-diffusion. We show that our SDT signal-to-noise ratio at 300K is close to that necessary to detect any spin-saturable recombination center which obeys the simple model first proposed by Lepine³; At 76K our signal to noise ratio should easily permit us to observe SDT resonances which obey this model. Despite this fact, we see only resonances associated with the dangling bond at these lower temperatures. These studies represent the first application of this method to understanding recombination mechanisms in a production photovoltaic device made from crystalline silicon.

EXPERIMENTAL

The cells measured here were cut from large EFG ribbon Si n⁺/p solar devices⁹. Edge-fed film-defined growth silicon is a high purity, solar grade material obtained by pulling a continuous liquid ribbon from a carbon crucible through a carbon die. Because of the high stress levels present during the cooling process, coherent or higher order twin boundaries with associated dislocation arrays form along the growth axis of the ribbon. Many of these structures are active recombination planes and are easily observed in EBIC analyses¹⁰. Hydrogen passivation¹⁰ of these structures greatly reduces this EBIC activity and produces increases in ribbon solar cell short circuit currents of ~4-6%. In ribbon cells with minority carrier diffusion lengths, X_L , of 50-60 μm , the average spacing of EBIC active boundaries is typically 10 per cm. Given these parameters, we estimate that ~5 - 10% of short circuit cell currents are lost at grain boundaries, assuming that all photocarriers generated within X_L are swept into these defects and undergo non-radiative recombination. While this estimate makes the H passivation results¹⁰ seem sensible, it has also been noted that the bulk diffusion length, measured away from active boundaries, shows significant improvement as well.

Small (~3 X 3 mm) scribed and broken pieces of fabricated cells (with no AR coating) were inserted into a TE102 X-band microwave cavity located in a standard electron spin resonance apparatus. The cavity and sample could be cooled to 76K. The available microwave power was 150-250 mW. Illumination was provided by a quartz halogen source with spectral selection via Corning glass filters. Short circuit photocurrent was monitored with a Keithley 427

current amplifier; its output was lock-in detected at the 0.2-3 KHZ magnetic field modulation frequencies used for standard derivative detection.

RESULTS

Figure 1 shows the photoconductivity derivative spectra obtained at 300K for a non-hydrogen-processed EFG cell with red light (Corning 2-58 filter, $\lambda_{\text{min}} = 600 \mu\text{m}$) illumination. Because of the fairly small signal size, a 4 Gauss p-p magnetic field modulation was employed; recent experience¹¹ with SDT in Si bicrystals leads us to believe that this signal may be seriously overmodulated at this p-p value. At this modulation level the derivative of the current resonance is symmetric about $g = 2.003 \pm .001$, has a ~ 10 G p-p width, and corresponds to a decrease in the photocurrent; it closely resembles the Si dangling bond resonances seen in a-Si:H¹², damaged¹³, and polycrystalline Si¹⁴.

Under these signal conditions $\Delta I_{\text{sc}}/I_{\text{sc}} = -4 \times 10^{-6}$, an estimate which is uncertain by perhaps a factor of 2 due to our ignorance of the true lineshape. Cooling the sample to 76K reduces the short circuit photocurrent by a factor of 3, but the value of $\Delta I_{\text{sc}}/I_{\text{sc}}$ at $g=2.003$ remains roughly equal to its 300K value. No other resonances were observed at either temperature despite many field scans at other H values.

Table 1 shows ΔI_{sc} at 300K versus microwave power for several samples. No attempt was made to control sample temperature during these measurements and full microwave power does raise the cell an estimated 5-15°C above the ambient dewar temperature. We see that, while ΔI_{sc} is a sublinear function of power at the highest power levels, we are not able to saturate the spin system in any of our samples. Thus, our above estimate of $\Delta I_{\text{sc}}/I_{\text{sc}}$ is only a lower bound to the infinite power value. We also note that there is almost no modulation frequency dependence of ΔI_{sc} .

We observe that the spectral composition of the incident light has a large effect on the SDT signal. Using a Corning (blue) 2-60 filter we were able to generate photocurrent from carriers produced in the n+ emitter. When we compare the signal produced by blue light with that produced at equal I_{sc} levels by red light, we find no observable blue-light-SDT response within the noise levels ($\sim \pm 15\%$) present at the rather small photocurrents employed. We also observe no dark SDT signal with small forward or reverse junction biases; in addition, the light-induced SDT response did not seem to be a noticeable function of cell bias. All of these observations indicate that the SDT response is primarily due to resonance induced variations of the minority carrier lifetime in the p-type base of the cell.

While our observed photocurrents were (within a few %) linear in the illumination intensity (not shown), a noticeable dependence on I_{sc} is observed when the normalized value of the resonance induced current decrease, $\Delta I_{\text{sc}}/I_{\text{sc}}$, is plotted, as illustrated in Figure 1. This is particularly true for EFG cells that have been hydrogen passivated. Figure 1 shows that this treatment not only reduces the SDT response, but also enhances the dependence

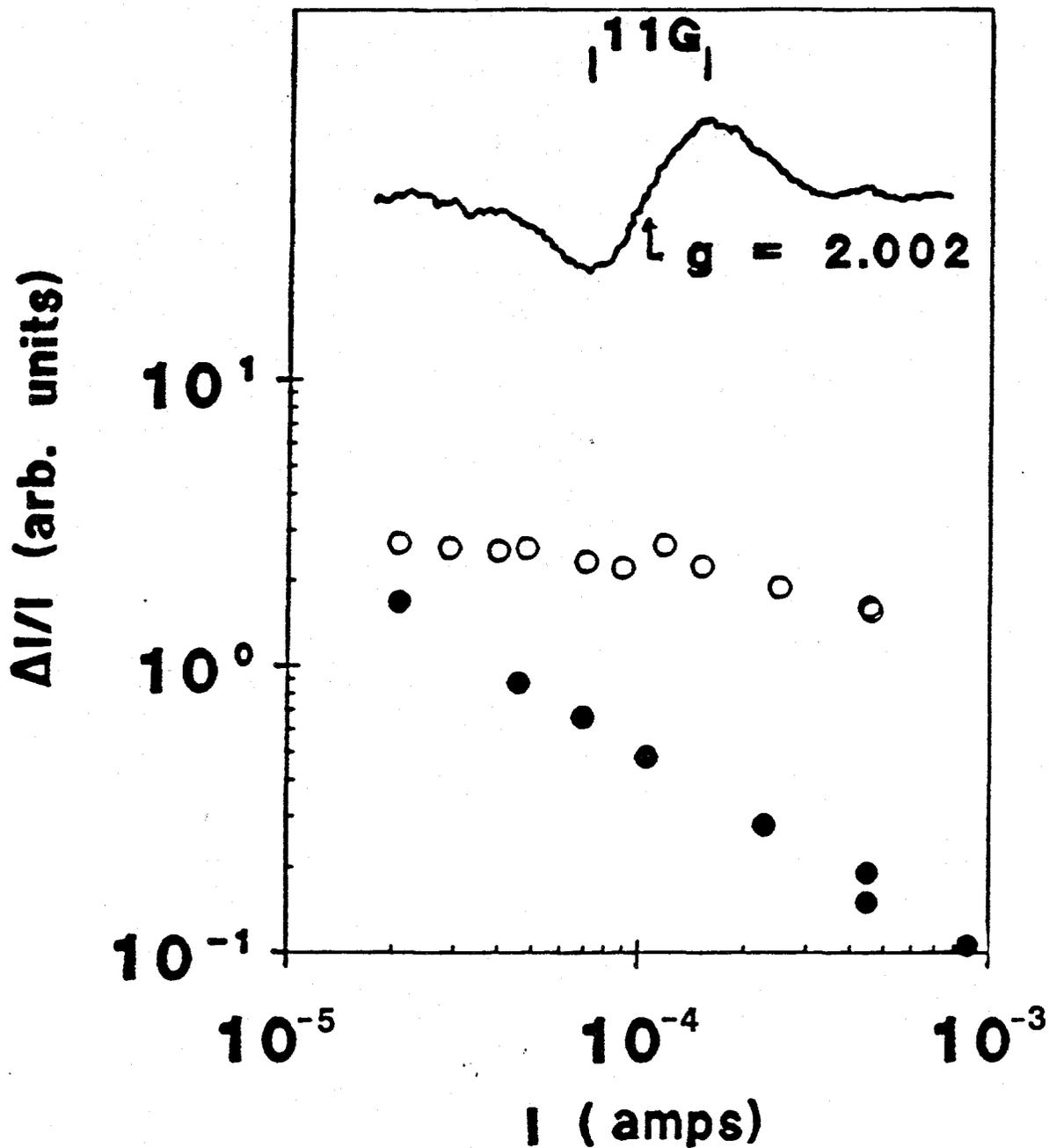


Figure 1. The peak to peak values of the resonance induced variation of short circuit photocurrent, ΔI_{sc} , normalized by I_{sc} and plotted versus I_{sc} . Open circles are for an untreated EFG ribbon silicon solar cell; closed circles; a hydrogenated EFG cell. The inset shows a derivative ΔI_{sc} spectra recorded for an untreated cell with red light illumination and 4 G p-p magnetic field modulation.

of $\Delta I_{sc}/I_{sc}$ on cell current. Since these cells were passivated before being scribed and broken, the difference in response between baseline and H passivated cells indicates that dangling bonds at the broken edges are probably not an important source of our SDT signals. The data shown in Figure 1 were replicated by other virgin and H passivated cells.

DISCUSSION

Previous treatments¹⁵⁻¹⁷ of minority carrier recombination at grain boundaries suggest that the recombination velocity, S , is typically an exponential function of the barrier height, i.e.:

$$S \propto \sigma_n e^{\phi_B/kT} \quad (1)$$

where σ_n is the capture cross-section for an electron at a positively charged boundary in p-type material, and ϕ_B is the potential barrier height. This expression is generally valid for $\phi_B < 0.25$ eV. For parallel grain boundaries with average separation X_B , it is not hard to show, using the formalism of reference (17), that the spatially averaged minority carrier population is:

$$n_{ave} = n_{\infty} (1 - (2X_L/X_B)(S/(S+1))), \quad (2)$$

where n_{∞} is the steady state minority density far away from a boundary, and S (now dimensionless) is expressed in units of (D_n/X_L) where D_n is the minority carrier diffusion coefficient. If $S = S + \Delta S$ at resonance, and n_{∞} does not change, we find that:

$$\frac{\Delta I_{sc}}{I_{sc}} = - \frac{2X_L}{X_B} \frac{S}{(S+1)^2} \frac{\Delta S}{S}, \quad (3)$$

where we have assumed that $\Delta I_{sc}/I_{sc}$, the fractional change in diode photocurrent, $= \Delta n_{ave}/n_{ave}$. It is reasonable to assume that the only term in Equation (1) that varies at resonance is σ_n , so that $\Delta S/S$ in Equation (3) may be replaced with $\Delta \sigma_n/\sigma_n$. To explain the variation of $\Delta I_{sc}/I_{sc}$ seen in Figure 1 we remind the reader that, above some threshold light intensity, S starts to drop and eventually becomes a linearly decreasing function¹⁷⁻¹⁹ of

illumination level (or equivalently of I_{sc}). We now refer to a plot of the S dependence of equation (3) shown in Figure 2. We suppose that in unhydrogenated EFG material a distribution of boundaries exists with S values both above and below $S = 1$ (corresponding to $\approx 10^4$ cm/sec). This distribution is outlined with a solid rectangle in the figure. Under these conditions, any decrease in S caused by illumination (shown by dashed lines) does not shift the average value of $\Delta I_{sc}/I_{sc}$ very much, since the RHS of Equation (3) is relatively constant for $0.2 < S < 5$. At large I_{sc} values, however, the center of gravity of the distribution of S values will shift to the left of $S = 1$, and some decrease in $\Delta I_{sc}/I_{sc}$ will be seen, as experimentally observed.

Previous studies have shown^{10,20} that hydrogenation reduces grain boundary S values by 1-2 decades, presumably by rendering boundary trap states electrically inactive. We see from Figure 2 that when most boundary S values lie below 1, decreases of S with illumination will lead to almost linear decreases in $\Delta I_{sc}/I_{sc}$ with increasing illumination ($\propto I_{sc}$), as observed (Figure 1).

Equation (3) predicts that the magnitude of $\Delta I_{sc}/I_{sc}$ will be:

$$\frac{\Delta I_{sc}}{I_{sc}} < \frac{2X_L}{X_B} \frac{1}{4} \cdot \frac{\Delta\sigma_n}{\sigma_n} \quad (4)$$

for the distribution of S values shown in Figure (1) for unhydrogenated cells. Recent studies of SDT in silicon bicrystals have inferred that $\Delta\sigma_n/\sigma_n \geq 2 \times 10^{-3}$ for carrier recombination at Si dangling bonds²¹. This rather large value may be associated with recombination of correlated e-h pairs at dangling bond arrays found at dislocation or grain boundary cores and has been predicted theoretically by Kaplan et al.²¹. Using $X_L = 50 \mu\text{m}$ and $X_B = 0.1 \text{ cm}$, Equation (4) yields $\Delta I_{sc}/I_{sc} < 5 \times 10^{-5}$. This upper limit is consistent with the experimental values that we observe. We note that these fractional alterations of the photocurrent are well above the prediction of the Lepine model ($\sim 7 \times 10^{-6}$) at 300K. Note that this model applies to uncorrelated recombination at isolated impurities. In the present case we anticipate that both electrons and holes may be simultaneously trapped at higher order twin boundaries giving rise to pair recombination.

An alternative explanation for the increased dependence of $\Delta I_{sc}/I_{sc}$ on I_{sc} seen for hydrogenated cells may lie in the mechanism for the light sensitivity of grain boundary potential barriers. It has been shown that these barriers begin to decrease when the captured minority carrier currents become comparable to the steady state flux of majority carriers which are captured and emitted by unfilled majority carrier traps¹⁷. If some process (hydrogenation in this case) substantially reduces this trap state density, essentially all of the majority carrier traps may be filled in the dark state, leaving boundaries which are very light sensitive, despite their rather low barrier heights. At present experimental bicrystal studies which bear on this issue have not been carried out.

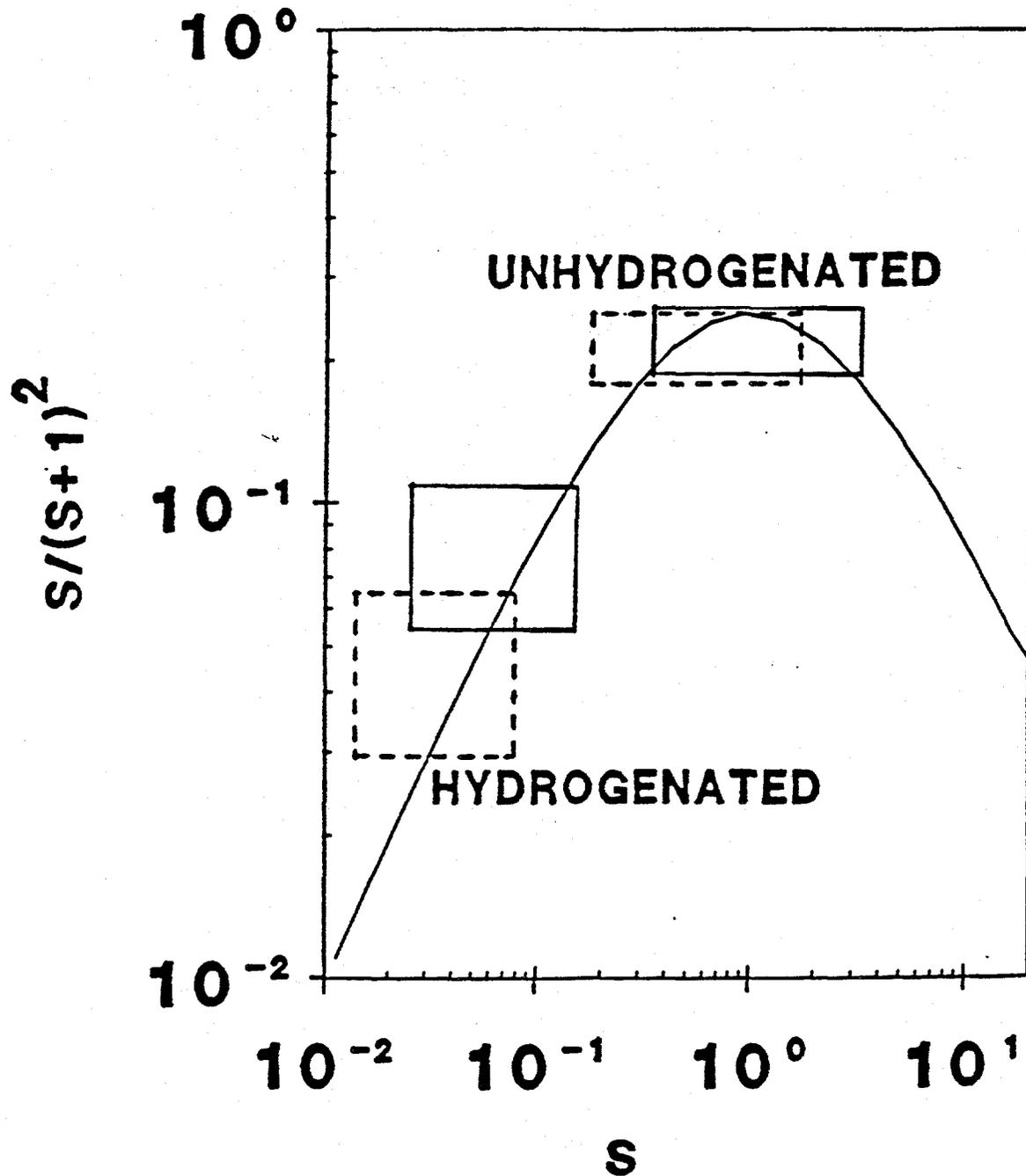


Figure 2. The S variation of Equation 3 plotted versus S . The upper solid rectangle shows a hypothesized range of S values for unhydrogenated EFG cells in the dark; the upper dashed rectangle shows the range of S values at an arbitrary illumination level. The rectangles at the lower left show possible S ranges for dark and illuminated EFG cells which have been hydrogenated.

Because of the uncertainty in boundary parameters for EFG material, these arguments must be, by necessity, somewhat qualitative. In our view, they are reasonably consistent with the hypothesis that our SDT signals arise from Si dangling bonds at higher order twin boundaries, and that this loss mechanism represents only a small fraction of e-h recombination in this material. What can be said about the remaining recombination events? We have scanned other regions of magnetic field to search for defects having responses above and below those shown in Figure (1). No other detectable SDT resonances were found at 300K or 76K. For p-p SDT linewidths in the 5-15 Gauss range, Lepine-like signals (from uncorrelated e-h recombination) would be near to our 300K noise level, but well above our 76K resolution assuming that spin relaxation times are long enough for us to reach microwave spin saturation. These observations do not rule out the presence of recombination at other centers, such as transition metal impurities. For a Lepine-like signal to be present, it is necessary that the impurity be paramagnetic before minority carrier capture. It is conceivable that this paramagnetic state could only exist for Fermi level positions in the upper half of the forbidden gap. To check for this possibility we are beginning measurements on EFG cells with n-type bases.

CONCLUSIONS

We have observed SDT resonances in the short circuit current from EFG ribbon silicon solar cells. These signals represent a microwave-induced decrease of the diffusion current collected in the p-type base region, and have g values similar to spin resonance data attributed to dangling silicon bonds in silicon bicrystals, damaged and polycrystalline silicon. Hydrogenation strongly affects the magnitude and current dependence of these signals in a fashion that appears consistent with prior studies which indicate that this process reduces the number of electrically active dangling bonds at grain boundaries. These and other studies indicate that dangling bond defects at electrically active boundaries are responsible for less than 10% of the recombination losses in untreated ribbon cells. While SDT signatures of other defects controlling recombination have not been detected, we suggest that experiments with n-type base solar cells could result in the identification of Lepine-like SDT signals arising from uncorrelated e-h recombination at other sites in these materials. Of course, it is also possible that the silicon dangling bond is the only major recombination center in these materials. This would be consistent with observations of H passivation of isolated dislocations in the bulk of EFG ribbon cells and the generally large increases in bulk lifetime seen after hydrogenation.

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TABLE I

Values of the SDT variation, ΔI_{sc} , at various microwave power densities and short circuit current levels for unhydrogenated and hydrogenated ribbon Si solar cells.

CELL#	TYPE	I_{sc} ($\times 10^{-4}$ A)	PWR(arb. units)	ΔI_{sc} (arb. units)	$\Delta I_{sc}/PWR$
2	unhyd.	4.5	1.0	7.4	7.4
"	"	"	0.5	4.9	9.8
"	"	"	0.25	2.3	9.2
"	"	"	0.10	1.03	10.3
"	"	0.48	1.0	1.28	1.28
"	"	"	0.5	0.7	1.4
3	hydrog.	1.0	1.0	1.60	1.60
"	"	"	0.5	1.23	2.46
"	"	"	0.25	.60	2.40
"	"	8.8	1.0	3.00	3.00
"	"	"	0.5	1.97	3.93
"	"	"	0.25	1.27	5.07

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