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Characteristics of a-Si:H Solar Cell Under Extended Illumination Condition Using NIR Laser

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In this work, characteristics of a-Si:H solar cell under extended illumination condition, using an NIR laser diode, were studied. These characteristics were introduced by calculations of recombination rate, open-circuit voltage and defect growth rate as functions of illumination time. Stabilized open-circuit voltage of 0.04V and photogeneration rate of ~2x10^{21}cm^{-3} were observed. We present measurements on the decline of the open-circuit voltage V_{OC} in a-Si:H solar cells during extended illumination (light-soaking). We used a near-infrared laser that was nearly uniformly absorbed in the intrinsic layer of the cell. At the highest photogeneration rate (about 2x10^{21}cm^{-3}), a noticeable decline (0.01V) occurred within about 10 minutes; V_{OC} stabilized at 0.04V below its initial value after about 200 hours. We found that both the kinetics and the magnitudes of V_{OC} are reasonably consistent with the predictions of a calculation combining a bandtail+defect picture for recombination and a hydrogen-collision model for defect generation.

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1. Introduction

The metastable degradation of the optoelectronic properties of a-Si:H has been actively studied for more than 25 years. Important progress has been made by many researchers, but a fully satisfactory picture for the effect has never emerged. The difficulty of the metastability problem may, at least in part, be ascribed to the fact that there are probably two difficult, linked problems that must be understood simultaneously. First, it is likely that photocarrier recombination drives metastability, but - even in a single state of an a-Si:H sample - no consensus viewpoint on these recombination processes has emerged. Second, even if one accepts the role of recombination in mediating metastability, there is no consensus viewpoint about how recombination leads to metastable defect generation (or other metastabilities).

The present paper exploits the close connection between the open-circuit voltage V_{OC} measured in an nip solar cell and photocarrier recombination in the bulk, intrinsic-layer material. In particular we report a series of measurements of the time-dependence of V_{OC} in United Solar cells under near-solar illumination. In recent work [1] we reported the temperature-dependence of V_{OC} at solar illumination intensities. We concluded from these studies that, for their as-deposited state, the recombination traffic in our samples flowed predominantly through the valence bandtail states. For the stabilized, light-soaked state recombination traffic appears to be split fairly evenly between the valence bandtail and defects. We emphasize that these conclusions apply to our materials, under near-solar illumination, and near room-temperature; these are, of course, the conditions of greatest practical significance for solar cells.

Using this recombination model as the starting point, we report here that we are able to account for the time-dependent decay of V_{OC} using a straightforward extension of the hydrogen-collision model [2] for defect generation; the extension assumes that mobile hydrogen is generated by bandtail recombination. For our materials, we can also exclude the best known alternative model [3].

There is at least one implications of this perspective on metastability that deserves further investigation. It appears that there is a coincidence of the time-scales at which crossover between bandtail and defect recombination occurs, and at which a stabilized state of the sample is achieved. The coincidence suggests that defect recombination may mediate light-induced annealing.

2. Measurements

For these experiments, six depositions of nip solar cells on stainless steel substrates were done at United Solar Ovonic Corp.. The n and p layers were the same in all depositions; the deposition time for the intrinsic layer was chosen to give

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intrinsic layer thicknesses from 185nm to 893nm. The cells were not optimized for solar conversion efficiency, but the individual layers are comparable to those used in high-efficiency cells. Details of the deposition procedures have been given elsewhere [4]. As-deposited properties of the cells were measured under a solar simulator. This paper emphasizes results for the thickest cells, for which the white-light V_{OC} averaged 0.98V and the white-light fill factors averaged 0.66.

Further studies were done using a 30mW, 685nm wavelength near-infrared laser. We chose to use this laser because its wavelength is absorbed fairly uniformly throughout the intrinsic layer of the cells, which substantially simplifies modeling of the measurements. We were able to achieve photocurrent densities in the cells that were comparable to solar illumination.

Measurements of the decline of the open-circuit voltage V_{OC} are presented in Fig. (1). The different symbols indicate measurements for four different laser intensities. We used four different cells on the same substrate for these measurements; the cells had very similar initial properties under white-light. The average photogeneration rates G for each experiment are indicated in the figure; these were calculated from the measured photocurrent density J_p at $V_r = -2V$ using the expression $G=J_p(-V_r)/ed$, where e is the electronic charge and d is the thickness of the intrinsic layer. The measurements for the highest intensity are most comparable to solar illumination (saturated photocurrent density was 18mA/cm^2 with the laser, and about 15mA/cm^2 with the solar simulator). The sample temperature was maintained at 294.5K to within better than 0.1K.

An interesting feature of the measurements is that the onset of degradation occurs for later times at lower photogeneration rates. If we define an "onset time" when V_{OC} has declined by 0.01V, it is evident in Fig. 1 that this onset time increases by more than 1000 over the range of photogeneration rates in the figure. For the largest photogeneration rate it appears that V_{OC} is approaching a saturation value within this time window; saturation at longer times is fairly well-established in earlier work on solar cell parameters, defect density, and other optoelectronic properties of a-Si:H.

3. A Modified H-Collision Model

In another paper [1] we presented temperature-dependent measurements on the open-circuit voltage for a-Si:H in its light-soaked and as-deposited states. These measurements are consistent with the model that, for the as-deposited states of a-Si:H, the photocarrier recombination traffic is predominantly through the valence bandtail (through the process of electron capture by a bandtail-trapped hole). Light-soaking then has a surprisingly modest effect: the defect-density rises until recombination traffic is fairly evenly split between the bandtails and the defects.

One important fact that has been established in several light-soaking experiments [3,5-6] is that the defect increases as about the 1/3 power of the light-soaking time: $N_d \propto t^{1/3}$ essentially from the onset of illumination until a saturated state is achieved. The original "SJT" explanation [3] for the $t^{1/3}$ form assumed that recombination traffic through the bandtails R_t generated defects:

$$\frac{dN_d}{dt} \propto R_t \qquad (1)$$

The $t^{1/3}$ form then emerged from a particular recombination model based on the assumption that most recombination traffic went through defects. The particular model that was proposed had the property that the fraction of the recombination traffic through the tails obeyed:

$$\frac{R_t}{G} \propto \frac{1}{N_d^2} \qquad \text{(SJT recombination)} \qquad (2)$$

where G is the carrier photogeneration rate and N_d is the density of defects. With this assumption, one obtains the form usually found by experiment:

$$N_d(t,G) = 3C_{SW}G^{2/3}t^{1/3} \qquad (3)$$

The assumed recombination model appears to be inconsistent with the $V_{OC}(T)$ measurements, in particular in its assumption that the defect recombination traffic R_d is predominant (i.e. that $R_d \approx G$), and thus is unlikely to be the correct explanation for the empirical form (2). The principal alternative to this model is the "hydrogen-collision" model [2], which assumes the existence of a mobile hydrogen density H_m obeying:

$$H_m \propto \frac{G_H}{N_d} \qquad (4)$$

where G_H is the rate at which light generates mobile hydrogen. A mobile hydrogen is assumed to recombine by attaching itself to the density of dangling bond defects N_d. The rate at which new defects are generated obeys the "hydrogen-collision" proportionality:

$$\frac{dN_d}{dt} \propto H_m^2 \qquad \text{(hydrogen-collision)} \qquad (5)$$

The empirical "$t^{1/3}$" form (2) obtains if we assume that $G_H \propto G$.

An interesting alternative to the assumption $G_H \propto G$ is $G_H \propto R_t$. It has often been noted that the large energies dissipated by bandtail recombination of photocarriers make it attractive as an originating event for defect metastability; the energy dissipated is nearly equal to the bandgap E_g, and is certainly larger than

dissipation from recombination through defect levels lying near the center of the gap. One might envision that tail-state recombination might occasionally lead to a peculiar "hydrogen-Auger" process that liberates hydrogen from a nearby, saturated dangling bond. However, the $G_H \propto R_t$ model looks undesirable if one assumes that the SJT recombination model $R_t/G \propto 1/N_d$ is valid. It leads to the behavior $N_d \propto t^{1/5}$, and is thus largely excluded by experiment.

Our measurements of the temperature-dependence of the open-circuit voltage experiments have led us to suggest that R_t/G is of order unity through most of the light-soaking process, which suggests that we reconsider the following, alternative version of the hydrogen-collision equations:

$$\frac{dN_d}{dt} \propto H_m^2 \propto \left(\frac{G_H}{N_d}\right)^2 \propto \left(\frac{R_t}{N_d}\right)^2 \qquad (6)$$

or, collecting several proportionality constants together as C_{SW}:

$$\frac{dN_d}{dt} = C_{SW}\left(\frac{R_t(N_d)}{N_d}\right)^2 \text{ (modified H-collision)} \quad (7)$$

We have indicated that R_t depends upon the defect density; of course, for R_t=G the usual behavior of Eq. (3) obtains.

4. Bandtail+Defect Calculations

In another paper we present the parameters and procedures of a "bandtail+defect" calculation of the open-circuit voltage; the calculation used the AMPS-1D computer program (©Pennsylvania State University).

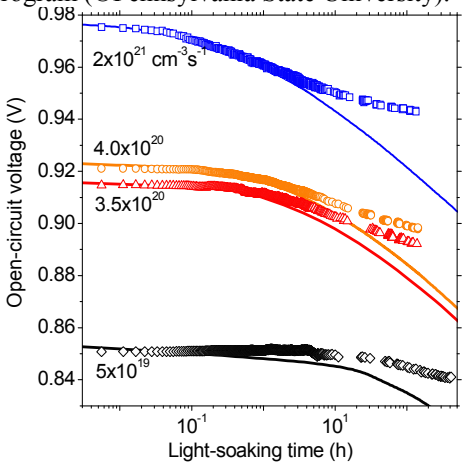

Fig. (1) Decay of the open-circuit voltage with time at four different intensities. The symbols denote the experimental measurements in four cells (893nm i-layer thickness, laser wavelength 685nm) on the same substrate. The lines represent calculations for the "extended hydrogen-collision model" described in the text

In Fig. (1), we have presented (as the four lines) the corresponding calculations for $V_{OC}(t)$ based on Eq. (7), and using the value $C_{SW} = 10^1 cm^{-3}s$ that is typical of direct studies of the defect generation during light-soaking [5,6].

We first used the bandtail+defect calculation to obtain the dependence of the bandtail recombination rate R_t upon the defect density N_d; we assumed a spatially uniform density N_d. The results are illustrated in Fig. (2) (lower panel). We then used this function $R_t(N_d)$ to numerically integrate Eq. (7) to obtain $N_d(t)$; note that Eq. (7) implies that defect generation depends upon the square of R_t. The bandtail+defect calculation also yields V_{OC} as a function of N_d (upper panel of Fig. 2), from which we finally obtained $V_{OC}(t)$.

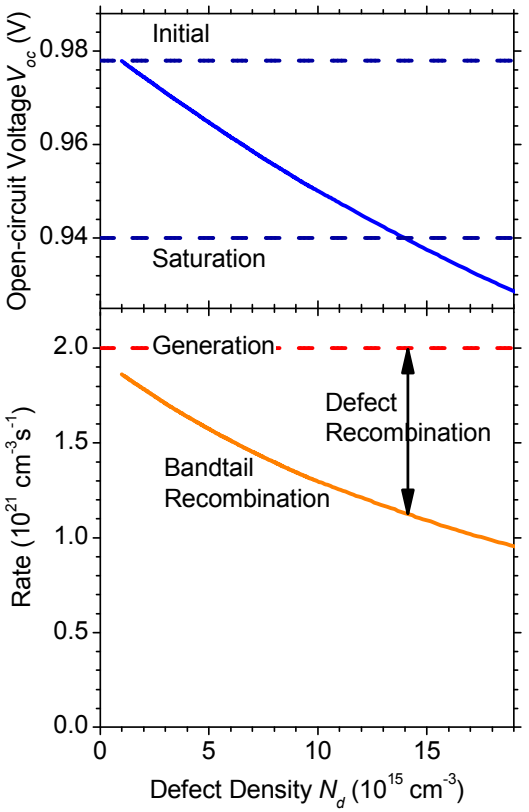

Fig. (2) Bandtail recombination rate R_t and open-circuit voltage V_{OC} calculated as a function of defect density N_d using the bandtail+defect code. The photogeneration rate and defect recombination rate are also shown. The initial experimental value of V_{OC} corresponds to N_d=1x10^{15}cm^{-3}, and we have suggested a saturation value. Note that bandtail recombination is comparable to G throughout this range of defect densities

Experimentally, V_{OC} only declines about 0.04V (to the value denoted "measured saturation"). Fig. (2) indicates that this decline corresponds to a fairly small difference between R_T and G. For the four intensities, the agreement between the experimental measurements and the calculations is fairly good through the initial stages of the decay of V_{OC}. For longer times the measured values for V_{OC} fall much more slowly than predicted by Eq. (7), which undoubtedly corresponds to the onset of the "light-induced"

annealing effects reported previously for defect-density measurements [7].

For our experiments, we used laser illumination that was nearly uniformly absorbed; this choice was part of an effort to simplify modeling and to avoid a non-uniform density of defects. Nonetheless, our assumption of a spatially uniform value for N_d as it grew under light-soaking was not self-consistent with the spatial profiles of R_t that were calculated. For the larger values of the density N_d, the bandtail recombination traffic was reduced in a zone about 100-200nm from the p/i interface compared to values in the middle of the cell. We used R_t values from the middle to do the numerical integration of Eq. (6). For full self-consistency we would have needed to allow for a profile of N_d. The profile would have a reduced density of defects as the p/i interface was approached from the middle. A rough analysis indicates that inclusion of this effect would improve the agreement between the calculations and the measurements slightly, but we have not pursued non-uniform distributions for N_d further.

5. Results and Discussion

As noted earlier, the modified H-collision model, in conjunction with the bandtail+defect recombination model, predicts some deviations from the $t^{1/3}$ form for the dependence of the defect density upon the light-soaking time. We did not do simultaneous measurements of the defect density during light-soaking of the present solar cells. In Fig. (3), we show the predictions of the defect density from numerical integration of Eq. (7) that corresponds to the highest photogeneration rate we used for experiments.

The calculations show the expected $t^{1/3}$ form for the earlier times. There is a softening that occurs around 10 hours, which corresponds well to a change in the recombination mechanism. For lower defect density, the majority of the recombination traffic goes through the bandtail; for larger densities, the majority goes through defects. A $t^{1/5}$ form is a good fit at longer times. Experimentally, after about 10 hours V_{OC} begins to show saturation behavior (cf. Fig. 1), which we attribute to some "light-induced annealing" process. At least for the present samples, it appears that the long-time saturation effect would obscure direct observation of the $t^{1/5}$ regime.

6. Conclusions

It is an interesting coincidence that the crossover time between the two recombination regimes and the time at which light-induced annealing sets in are so similar in the present sample. This apparent coincidence is the reason offered by the present viewpoint for the fact that open-circuit voltages decline only modestly during light soaking (roughly by the thermal voltage k_BT/e=0.025V), as well as for the fact that most direct experiments on the kinetics of the defect density are reasonably consistent with the $t^{1/3}$ form.

It is unlikely that two entirely independent processes would appear on the same timescale. We therefore speculate that the mechanism underlying light-induced annealing is photocarrier recombination through defects.

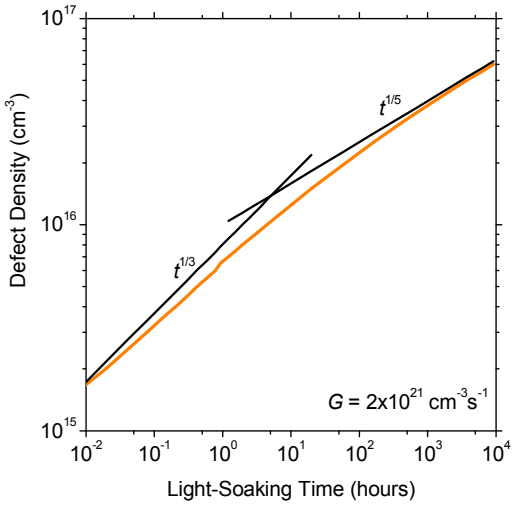

Fig. (3) Calculated growth of the defect density during light-soaking (photogeneration rate $2x10^{21}cm^{-3}s^{-1}$); the calculation was based on the hydrogen-collision model of defect generation (C_{sw}=10cm^{-3}s) and the bandtail+defect recombination model. The calculation shows a cross-over from $t^{1/3}$ to $t^{1/5}$ kinetics when recombination traffic switches from the bandtails to the defects

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