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ABSTRACT

We present measurements on the decline of the open-circuit voltage V_{OC} in a-Si:H solar cells during extended illumination (light-soaking) at 295 K. We used a near-infrared laser that was nearly uniformly absorbed in the intrinsic layer of the cell. At the highest photogeneration rate (about 2×10^{21} cm^{-3}), a noticeable decline (0.01 V) occurred within about 10 minutes; V_{OC} stabilized at 0.04 V 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. The version of the hydrogen-collision model that we used assumes that only bandtail recombination drives the hydrogen collision processes. Within this picture, the crossover between bandtail and defect recombination occurs on the same timescale as the "light-induced annealing" process that accounts for stabilization of the optoelectronic properties for long light-soaking times.

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 for a single light-soaking 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 degradation by 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-dependent degradation 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 have been 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 implication of this perspective on metastability that deserves further investigation. It appears that there is a coincidence of two time-scales: (i) the time at which

crossover between bandtail and defect recombination occurs, and (ii) the time at which a stabilized state of the sample is achieved. The coincidence suggests that defect recombination may mediate light-induced annealing.
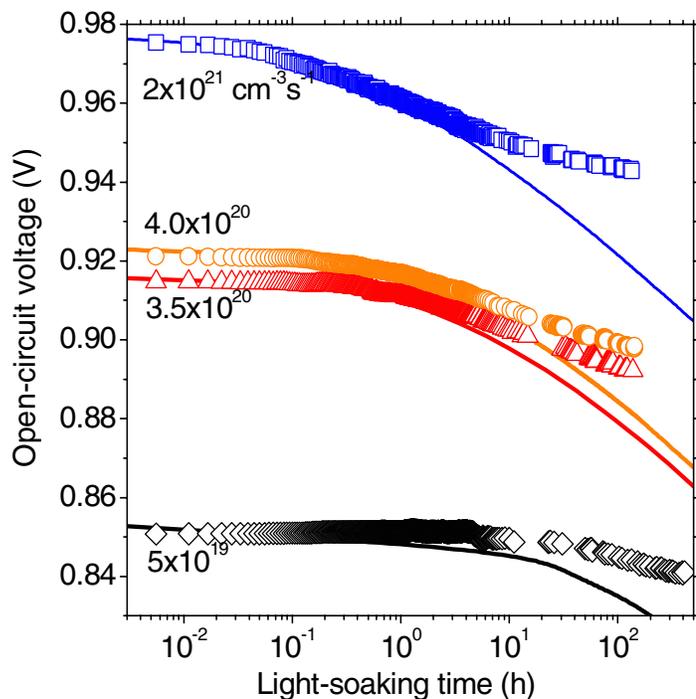
MEASUREMENTS

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 intrinsic layer thicknesses from 185 nm to 893 nm. 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 0.98 V and the white-light fill factors averaged 0.66.

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

Further studies were done using a 30 mW, 685 nm 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 $V = -2$ V using the expression $G = J_p(V)/ed$, 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; the photocurrent density was 18 mA/cm^2 with the laser (and -2 V), and was about 15 mA/cm^2 with the solar simulator (short-circuit). We maintained the sample holder temperature at 294.5 K to within better than 0.1 K.

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 0.01 V, 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 [5,6].

A MODIFIED H-COLLISION MODEL

In another paper [1] we presented temperature-dependent measurements on the open-circuit voltage for a-Si:H cells from the same substrate used for Fig. 1. These measurements for the as-deposited and the light-soaked states are consistent with the following model. 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 [3,5,6,7] is that the defect density increases as about the 1/3 power of the light-soaking time: $N_d \propto t^{1/3}$ from shortly after the onset of illumination until a saturated state is achieved. The original "SJT" explanation [3] for the $t^{1/3}$ form made two assumptions. First, recombination traffic through the bandtails R_t generated defects:

$$\frac{dN_d}{dt} \propto R_t \ . \tag{1}$$

Second, for times at which the $t^{1/3}$ form applied, most recombination traffic went through defects $R_d \approx G$. The particular model that was proposed had the property that the recombination traffic R_t through the tails obeyed:

$$R_t \propto \left(G/N_d\right)^2 , \qquad \text{(SJT recombination)} \tag{2}$$

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:

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

At least for the samples we have studied, SJT-recombination does not apply over a significant time-regime. Recombination traffic mostly passes through the bandtail states ($R_t \approx G$) in the as-deposited state, and falls only modestly even for the saturated, light soaked state. Although we have not studied the growth of the defect density during light-soaking with these particular samples, the near-universality of the observation of the $t^{1/3}$ form for $N_d(t)$ suggests that we seek another explanation than SJT-recombination for the kinetics of light-soaking. A similar situation also applies to light-soaking with intense pulses, or at very low sample temperatures. Bandtail recombination is completely dominant, but defect growth nonetheless shows a sublinear dependence on illumination time [8,9].

The principal alternative to the SJT approach is the "hydrogen-collision" model [2], which assumes the existence of an illumination-induced mobile hydrogen density H_m obeying:

$$H_m \propto G_H / N_d \ . \tag{4}$$

G_H is the rate at which light generates mobile hydrogen, and it has been assumed that the

recombination traffic of hydrogen mostly flows through dangling bonds (density N_d). Rarely, mobile hydrogens "collide" to form a metastable, paired hydrogen complex. Such a collision leaves 2 metastable dangling bonds that are not present in the initial state; the defect generation rate obeys the "hydrogen-collision" proportionality:

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

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

The assumption $G_H \propto G$ needs to be consistent with several experiments [10] that suggest that defect generation is mediated by photocarrier recombination, and most probably by the tail state recombination $G_H \propto R_t$. This identity is broadly consistent with the conclusion for our samples that R_t / G is of order unity through most of the light-soaking process in our samples, and we therefore use the more direct form for the hydrogen-collision model:

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

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

$$\frac{dN_d}{dt} = C_{SW} \left(\frac{R_t(N_d)}{N_d}\right)^2 \qquad (6)$$

R_t depends upon the defect density. The equation $R_t = G$ applies as long as the defect density is sufficiently small that it doesn't significantly that its effect on recombination remains small. For this condition, the "$G^{2/3} t^{1/3}$" form obtains.

BANDTAIL+DEFECT CALCULATIONS

In another paper in these proceedings [1] 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). In Fig. 1 we have presented (as the four
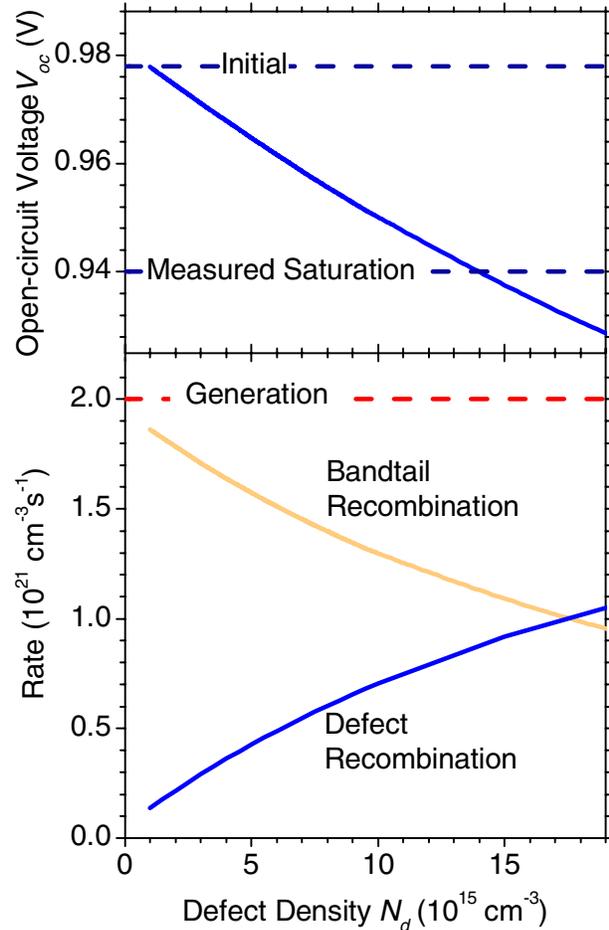
Figure 2. Bandtail recombination rate R_t and open-circuit voltage V_{OC} calculated as a function of defect density N_d using the bandtail+defect code for uniform photogeneration $G = 2 \times 10^{21}$ cm^{-3}s^{-1}. The photogeneration rate and defect recombination rate are also shown. The initial experimental value of V_{OC} corresponds to $N_d = 1 \times 10^{15}$ cm^{-3}, and we have suggested a saturation value. Note that bandtail recombination is comparable to G throughout this range of defect densities.

lines) the corresponding calculations for $V_{OC}(t)$ based on eq. (6). We used the following procedure for these calculations. Assuming a spatially uniform defect density N_d, we used the bandtail+defect calculation to calculate the open-circuit voltage V_{OC} as a function of N_d for each of the four generation rates; the results are illustrated in Fig. 2 for $G = 2 \times 10^{21}$ cm^{-3}s^{-1}, along with the associated rates of bandtail recombination R_t and defect recombination R_d evaluated at the middle of the cell.

We used the function $R_t(N_d)$ to numerically integrate eq. (6) to obtain $N_d(t)$; we used the value $C_{SW} = 10$ cm^{-3}s that is typical of direct studies of the defect generation during light-soaking [5,6]. We arbitrarily chose $N_d(0) = 1.0 \times 10^{15}$ cm^{-3}. Once $N_d(t)$ has been computed, $V_{OC}(t)$ is obtained from Fig. 2, and plotted in Fig. 1 for the four different generation rates. This procedure is certainly approximate, in that it assumes a uniform defect density across the cell at all stages of light-soaking; we have not explored the error associated with this approximation.

Experimentally, V_{OC} only declines about 0.04 V (to the value denoted "measured saturation") when $G = 2 \times 10^{21}$ cm^{-3}s^{-1}. As indicated in Fig. 2, a decline by 0.04 V implies that most of the photocarrier recombination traffic still flows through the bandtails even in the saturated, light-soaked state.

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. (6). Experimentally, defect densities also saturate for sufficiently extended light-soaking. The saturation effect is usually attributed to a combination of thermal and "light-induced" annealing of defects [2,6,11]; we have not included the annealing processes in the present work.

DISCUSSION

The H-collision model, in conjunction with the bandtail+defect recombination model, predicts deviations from the $t^{1/3}$ form for the dependence of the defect density when the light-soaking time exceeds the time required for crossover from bandtail recombination to defect recombination. In Fig. 3 we show the predictions for the defect density obtained from numerical integration of eq. (6), and using the highest photogeneration rate (2×10^{21} cm^{-3}s^{-1}) of our 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 to the 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, as can be shown using eq. (6) and the
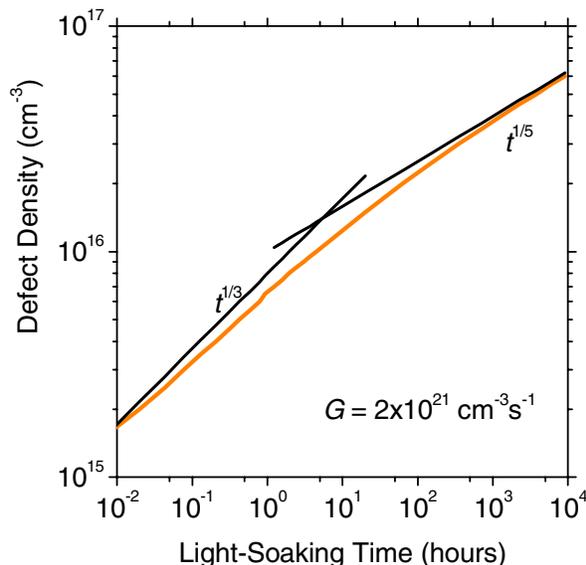

Fig. 3: Calculated growth of the defect density during light-soaking (photogeneration rate 2×10^{21} cm^{-3}s^{-1}); the calculation was based on the hydrogen-collision model of defect generation ($C_{SW} = 10$ cm^{-3}s) and the bandtail+defect recombination model. The calculation shows a cross-over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

assumption $R_t \propto 1/N_d$.

Experimentally, after about 10 hours V_{OC} begins to show saturation behavior (cf. Fig. 1), which we attribute to light-induced annealing. At least for the present samples, it appears that the long-time saturation would obscure direct observation of the $t^{1/5}$ regime.

It is an interesting coincidence that two apparently independent time scales must be fairly similar to account for the measurements in Fig. 1. The two times are (i) the crossover time at which recombination traffic switches between the bandtail and defects, and (ii) the "light-induced annealing" time. 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 $k_B T/e = 0.025$ V), 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. Of course, it is unlikely that two entirely independent processes would appear on the same timescale, but we do not presently have a satisfactory explanation for it.

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