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Dependence of open-circuit voltage in hydrogenated protocrystalline silicon solar cells on carrier recombination in p/i interface and bulk regions

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Contribution of carrier recombination from the p/i interface regions and the bulk to the dark current–voltage $(J_D - V)$ and short-circuit current–open-circuit voltage $(J_{sc} - V_{oc})$ characteristics of hydrogenated amorphous-silicon (*a*-Si:H) p-i-n and n-i-p solar cells have been separated, identified, and quantified. Results are presented and discussed here which show that a maximum 1 sun V_{oc} for a given bulk material can be validly extrapolated from bulk dominated $J_{sc}-V_{oc}$ characteristics at low illumination intensities. © 2000 American Institute of Physics. [S0003-6951(00)01445-5]

Significant progress has been made in increasing opencircuit voltages (V_{oc}) in p-i-n and n-i-p hydrogenated amorphous-silicon (a-Si:H) solar cells with values over 1 V being obtained,¹ however, there are also still unanswered questions regarding the physical phenomena that underlie their magnitude and stability. Even though it is known that the band gap of the intrinsic layers and the p/i interface regions play very important roles in determining $V_{\rm oc}$, their contributions as yet have not been sufficiently separated and quantified so as to allow the limitations imposed by the bulk *i* layer to be evaluated.² This is in part because in such studies both the p/i interface regions and the bulk *i* layer were changed.^{2,3} Such absence of reliably quantified information about the individual contributions of the bulk and interface seriously limits the ability of systematically (rather than empirically) improving the $V_{\rm oc}$. In addition, it does not allow any meaningful predictions to be made regarding the maximum attainable value of $V_{\rm oc}$ under 1 sun illumination, for a given intrinsic material. To overcome these limitations a study was carried out in which the contributions of highquality protocrystalline Si:H intrinsic layers were held constant and the p/i interface regions and p layers were systematically changed. This was carried out by fabricating p-i-nsolar cells with 200 Å regions adjacent to the p a-SiC:H having different H₂ dilution as well as fabricating n-i-p cell structures with p- μc Si:H. Because of the high quality of the intrinsic material, even good p/i interface regions have significant effects on both the dark current voltage $(J_D - V)$ and $V_{\rm oc}$ characteristics. This allows the contributions to the $V_{\rm oc}$ of different p/i interface regions as well as that of the bulk to be quantified for cell structures that exhibit both high V_{oc} and high fill factors (0.72 for 4000 Å i layers).

The protocrystalline solar cells were fabricated with intrinsic Si:H by rf plasma-enhanced chemical-vapor deposition with SiH₄ diluted with hydrogen with a dilution ration $R \equiv [H_2]/[SiH_4] = 10$ under conditions previously described.⁴ The p-i-n structures consisted of specular SnO₂/p a-SiC:H (250 Å)/*i* a-Si:H(4000 Å)/ $n\mu c$ -Si:H(250 Å)/Cr and the n-i-p structures were stainless-steel/n a-Si:H(250 Å)/*i* a-Si:H(400 Å)/ $p\mu c$ -Si:H/ITO with the $p\mu c$ -Si:H and ITO contacts being deposited by United Solar.⁵ In the p-i-n cells the 200 Å p/i interface regions were systematically improved⁷ by increasing their R from 10 to 40. To minimize possible contributions of shunts to the dark J-V at low forward bias, small areas (0.02 cm²) were defined by reactive ion etching of the $n\mu c$ -Si:H layers. The J_D-V and $J_{sc}-V_{oc}$ characteristics were measured at 25 °C with the latter being obtained with illuminations between $\sim 10^7$ and ~ 50 suns. Results were obtained on cells in the annealed state (4 h at 170 °C) as well as the 1 sun degraded steady state (DSS) obtained after 100 h of illumination.⁶

In the annealed state the 1 sun V_{oc} in the p-i-n cells systematically improved from 0.872 to 0.933 V as R at the p/i interface increased from 10 to 40 and the n-i-p cells were 0.941 V. There were no indications that any of these voltages were limited by the built-in potentials since V_{oc} well over 1 V were obtained at low temperatures and higher illuminations.⁷ the p-i-n cells with R < 40 exhibited virtually no change in V_{oc} after 1 sun exposure to the DSS, whereas the R = 40 p - i - n and the n-i-p cells both degraded to 0.92 V. This result is remarkable due to the vastly different p/i interfaces and p layers of the two cells. The observed stability of the 1 sun V_{oc} strongly suggests their values are limited by the recombination processes in the p/i interface regions since they are unaffected by the light-induced defects created in the bulk.

The effect of the improved p/i interface regions on the recombination of carriers is evident in the difference in the J_D-V characteristics of the R=10 and R=40 p/i interface cells in the annealed state. These are shown in Fig. 1 and it can be seen that the presence of the R=40 interface reduces the forward-bias current densities by over an order of magnitude. In this case, the improvement is sufficient to allow the currents to now be determined by the recombination in the bulk rather than the p/i interface. This is clearly indicated

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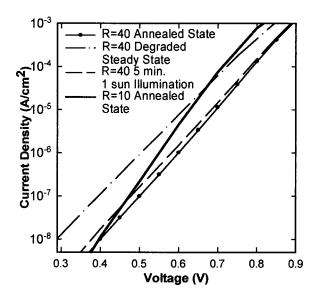


FIG. 1. $J_D - V$ characteristics of the p-i-n solar cells with R = 10 p/i interface in the annealed state and with an R = 40 p/i interface in the annealed state, after 5 min of 1 sun illumination, and in the degraded steady state.

by fast changes in the $J_D - V$ characteristics also shown Fig. 1 after light-induced defects are crated in the bulk *i* layer after 5 min of 1 sun illumination. These fast changes in the p-i-n cell are synonymous with those observed in the films of identical material.⁸ On the other hand, the R = 10 interface cell's $J_D - V$ characteristic is not affected by short light exposures.

The exponential dependence of the current on voltage seen in Fig. 1 can be expressed as

$$J_D = J_0 [\exp(qV/mkT) - 1],$$
(1)

where *m* is an operational diode quality factor and J_0 is the reverse saturation current density. J_0 is determined by the number of charge carriers *generated* in the bulk (J_{OB}) plus those in the p/i interface region (J_{OI}), when there is no voltage applied. The values of *m*, which are determined by the voltage dependence of recombination of *injected* carriers and their values, depend on *i* layer thickness as well as their densities and distributions of recombination centers, also have a bulk and interface recombination component. The increasing of *m* from 1.3 to 1.6, is in part a reflection of the interface recombination having a higher-voltage dependence than the bulk, however, it should be noted that even bulk values of *m* are not unique for high-quality *a*-SiH.

Contributions to V_{oc} of the p/i interface and the bulk could be identified from its dependence on illumination covering a wide range in the intensities. Since in these cells the short-circuit current densities (J_{sc}) have a linear dependence on intensity this is also illustrated by the corresponding $J_{sc}-V_{oc}$ characteristics such as those shown in Fig. 2. Figure 2(a) shows the results for the annealed state of the R=10, R=40 interface p-i-n cells and the n-i-p cells for a range of illuminations from 10^{-7} to 1 sun $(J_{sc}=10^{-9}-10^{-2}$ mA/cm²) as well as the J_D-V characteristic for the R $=40 \ p/i$ interface cell of Fig. 1. The characteristics in Fig. 2(a) can also be represented by an equation of the same form as Eq. (1), where J_D and V are replaced by J_{sc} and V_{oc} . In the case of the two p-i-n cells, the $J_{sc}-V_{oc}$ characteristics exhibit two distinct reactions; one with $m_B=1.6$ and the

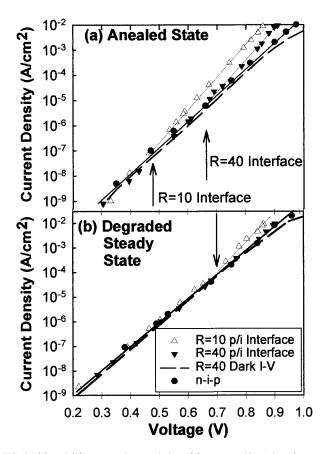


FIG. 2. (a) and (b): $J_D - V$ characteristics of for an R = 40 p/i interface cell superimposed on the $J_{sc} - V_{oc}$ characteristics for three cells: an R = 10 p/i interface p-i-n cell, an R = 40 p/i interface p-i-n cell, and an n-i-p cell in the annealed state. (b) illustrates the same characteristics as in (a) in the degraded steady state

other with $m_I = 1.35$. The n-i-p cell, on the other hand, exhibits $m = m_B = 1.6$ over the entire range of illumination up to 1 sun (10^{-2} A/cm^2) , which is the same value as that for the exponential region of the $J_D - V$ for the R = 40 interface cell. The overlap at low intensities of the current–voltage regions with an m_B of 1.6 clearly implies that these values are associated with recombination dominated by the bulk, and the m_I values with that in the p/i interface region. It can also be seen in Fig. 2(a) that the significant lowering of carrier recombination by the R = 40 p/i interface region in the p-i-n cells results in an extension of their superposition on the n-i-p cell characteristics from 10^{-7} A/cm² (0.45 V) to 1×10^{-3} A/cm² (0.8 V).

The corresponding results for the DSS are shown in Fig. 2(b) where the $J_{sc}-V_{oc}$ characteristics are now composed of virtually unchanged short-circuit currents and lower opencircuit voltages for any given intensity except in the region indicted by m_I =1.3. These characteristics reflect the contribution of the light-induced defects in the *i* layer that, as shown in Fig. 1, significantly increase the dark currents and change the values of *m* from m_B =1.6 to m_B^* =1.8 (in the DSS). Despite the changes in V_{oc} there is clear superposition of the $J_{sc}-V_{oc}$ characteristics for the three cells as well as overlap with the J_D-V results, as implied by Sakai *et al.*² and in contrast to claims made by Hegedus, Salzman, and Fagen.³ It is important to note that this superposition is now significantly more extensive than in the annealed state and that it occurs with m_B^* =1.8, which is the same as for the

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 $J_D - V$ characteristics. In the case of the R = 10 interface cell, the $m_B^* = 1.8$ region now extends to an illumination intensity of 10^{-2} suns ($J_{sc} = 10^{-4}$ A/cm², $V_{oc} = 0.7$ V indicated by the arrow) before the stable V_{oc} regime of Fig. 2(a) sets in. In the case of the R = 40 interface cell, this regime extends now all the way up to an illumination of 1 sun illumination. Such an extension of superposition and the concomitant degradation in V_{oc} are a clear indication that the results in these cells with $m_B^* = 1.8$ correspond to the V_{oc} values that are determined predominantly by the bulk in the DSS.

Several points can be made here without the detailed discussion that will be carried out elsewhere. We have shown that it is possible to separate, identify, and quantify the bulk and interface contributions to the $J_D - V$ and $J_{sc} - V_{oc}$ characteristics and how to establish the maximum 1 sun $V_{\rm oc}$ for a non-contact-limited cell for any given bulk material. The values of m_B found for Eq. (1) are specific to the particular properties of this intrinsic layer and its thickness, as is the overlap of the $J_{sc}-V_{oc}$ with bulk-dominated J_D-V characteristics. Such overlaps are not primarily limited only by series resistance² but also by the range of illumination intensities whose photogenerated carriers do not seriously affect the recombination of injected charge carriers with forward bias. The results presented here on cells in the annealed and the DSS indicate that providing there exists an extended region of superposition between shunt-free, bulk-dominated $J_D - V$ characteristics and the corresponding $J_{sc}-V_{oc}$ characteristics with the same values of m_B , m_B^* , and J_0 , it is valid to extrapolate these results to obtain the maximum $V_{\rm oc}$ at 1 sun illumination that is attainable for that bulk material.

For the cells consisting of this protocrystalline bulk material, which has a Cody optical gap of 1.7 eV and a mobility gap of 1.86 eV determined by internal photoemission,⁹ the limit imposed by the bulk on the 1 sun V_{oc} for the DSS is 0.92 V [n-i-p and p-i-n (R=40) cells]. These results show that the creation of $\sim 10^{17}$ cm⁻³ light-induced defects in the bulk¹⁰ leads to a 22 meV decrease in V_{oc} at 1 sun illumina-

tion. This drop occurs because m_B^* , being larger than m_B , decreases more rapidly as the intensity of illumination is lowered and the split in the quasi-Fermi levels is reduced by the lower generation of carriers. This underscores the very limited information that has been obtained only from 1 sun illumination studies and their analysis. Finally, since the results presented here have quantified bulk and p/i interface contributions to carrier recombination, they allow realistic analysis to be carried out on cell characteristics without the arbitrary assumptions being made about the properties of the p/i interface regions.¹¹

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