CORRELATION OF LIGHT-INDUCED CHANGES IN a-Si:H FILMS WITH CHARACTERISTICS OF CORRESPONDING SOLAR CELLS

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ABSTRACT

For the first time direct correlations are obtained between the light induced changes under 1 sun illumination in the properties of a-Si:H and those in the characteristics of p-i-n cells incorporating identically-prepared i-layers. These correlations were obtained after account was taken of the effects that the location of the electron and hole quasi-Fermi levels have on the carrier recombination that occurs through the different gap states. The changes in midgap state density, as measured on the films and reflected in the subgap absorption at 1.2 eV, are directly correlated with changes in the dark I-V characteristics under low forward bias. In this case small quasi-Fermi level splitting is present so the recombination of the injected carriers is determined by the midgap states in the bulk of the i-layer. In addition, the changes in the electron mobility-lifetime products as measured on the films are correlated with changes in the fill factor measured on cells under the same conditions as long as large quasi-Fermi level splitting is present and recombination occurs through states spanning a wide region of the gap, such as occurs under 1 sun illumination. The results explain (i) the failure of numerous attempts to correlate the degradation of solar cells reliably with the creation of dangling bond defects and (ii) the inadequacy of the large number of modeling results that assume such correlations.

INTRODUCTION

There remains great interest in improving materials for more stable, high performance hydrogenated amorphous silicon (a-Si:H) based solar cells. However, there have been very few studies to date in which the results on thin films have been directly related to those on cells having identically-prepared i-layer materials. This is particularly true for results in which both films and cells are degraded under 1 sun illumination so that the kinetics and the degraded steady state (DSS) under solar cell operating conditions can be directly correlated. Previous attempts to connect the light induced changes in a-Si:H to the degradation in solar cells have focused on the creation of dangling bonds, D0, near midgap in relation to the changes in efficiencies (fill factors) of cells. This has been done in spite of the reported lack of such correlations by von Roedern [1] and Yang et al. [2]. Attempts by Wyrsch et al. [3] at correlating the light induced changes in effective mobility-lifetime products, representing the transport of both holes and electrons in films with the changes in cells, had somewhat better success but still left many unanswered questions. The serious limitations of such approaches derive from their restriction to the widely held viewpoint proposed by Stutzmann et al. [4] that the carrier recombination in a-Si:H materials is determined solely by the D0 defects located at midgap. From this viewpoint, the degradation of solar cell efficiencies, primarily due to changes in fill factors (FF), could be directly related to the increase in the D0 density.

However, there is extensive evidence from results on thin film materials that indicates the other types of defects have a large effect on carrier recombination. In the case of the annealed state, this includes, for example, the orders of magnitude differences in electron mobility-lifetime products (µτ) for films with virtually the same subgap absorption at 1.2 eV (α(1.2)), the latter commonly used as the measure of the densities of states at midgap. In addition, large decreases in µτ are observed with carrier generation rates (illumination intensity) [5,6] in contrast to the constant lifetimes predicted by Stutzmann et al. [4]. In the case of light induced changes, the predicted direct correlation between the changes in µτ with those in α(1.2) [7] is absent, as is the $t^{\alpha(1.2)}$ time dependence in the degradation kinetics under 1 sun illumination [8,9]. In addition, the inability to fit the kinetics of the light induced changes with a single rate equation and the dependence of the kinetics on temperature is clearly inconsistent with the creation and annealing of the D0 defects alone [9,10]. There is also evidence of other types of defects from results obtained on solar cells. For example, the rate of defect creation in cells is found to be approximately proportional to the square of the intensity (I) rather than to the predicted $I^{0.6}$. This discrepancy also occurs in the kinetics of both annealing [11] and degradation under 1 sun illumination [10]. However, all of these results on cells are found to be consistent with the creation of multiple defects in SWE.

This paper addresses (i) the effects of gap states other than those located at midgap on carrier recombination and (ii) the correlation between light induced changes in thin film materials and those in solar cells. The paper also addresses the question as to whether the rates at which
defects are created under 1 sun illumination are the same in thin films as in the identically-prepared i-layers of the corresponding solar cells. This is accomplished by studying the kinetics of the characteristics of films and cells during illumination to a degraded steady state (DSS). The approach adopted here is to take into account the relative contributions of the different states to the carrier recombination. The recombination depends on the quasi-Fermi level splitting that occurs in the films and corresponding solar cells. The light induced changes in recombination obtained for small quasi-Fermi level splitting (~0.4 eV) at low forward bias in the cells were then compared to those observed in the densities of midgap states obtained from \( \alpha(1.2) \). The light induced changes obtained in \( \mu\tau \) with quasi-Fermi level splitting present under cell operating conditions (~0.9 eV) were compared to the 1 sun FF. In the present studies, the protocrystalline Si:H p-i-n cells incorporated i-layers thick enough so that their contribution to the cell characteristics could be clearly identified [12].

**EXPERIMENTAL DETAILS**

This study was carried out on intrinsic protocrystalline Si:H films from 0.5 to 1.2 \( \mu \)m thick and on p(a-Si:C:H)-i(a-Si:H)-n(µc-Si:H) solar cells with corresponding i-layers from 0.2 to 1.0 \( \mu \)m thick. The intrinsic materials were deposited by PECVD at 200°C with dilution ratios of hydrogen to silane, \( R=\frac{[H_2]}{[SiH_4]}=10 \), under conditions described previously [13]. The films were characterized by their \( \alpha(1.2) \) values, measured using dual beam photoconductivity (DBP), and their electron \( \mu\tau \) products, obtained with carrier generation rates (G) \( \sim 10^{19} \text{cm}^{-3}\text{s}^{-1} \), corresponding to 1 sun illumination [15]. The cells were characterized by their forward bias I-V characteristics and their fill factors, obtained from light I-Vs under 1 sun illumination using an Oriel solar simulator. The light induced changes both in cells under open circuit conditions and in films were characterized at temperatures between 25°C and 100°C. The degradations to the DSS were carried out with 1 sun illumination using either ELH lamps with cutoff filters or an Oriel solar simulator. The starting annealed states were obtained after heating at 170°C for four hours.

**RESULTS AND DISCUSSION**

In spite of the evolutionary nature of the protocrystalline Si:H materials, they can exhibit uniform bulk properties over extended regions of thickness [10]. For the protocrystalline Si:H material used in these studies, the amorphous phase extends to more than 1\( \mu \)m thickness. This is illustrated in Fig 1 with results obtained from transmission electron microscopy on films having thickness of 0.4\( \mu \)m and 1.0\( \mu \)m. It can be seen that the amorphous phase is present in both films without any transition to a mixed (a+µc)-Si:H phase [13,14] even after 1\( \mu \)m. This conclusion is in agreement with spectroscopic ellipsometry and AFM results. The characterization of \( \mu\tau \) and \( \alpha(E) \) on the films was carried out with films of different thickness to ensure that bulk properties were measured and to avoid any contributions from a mixed-phase transition layer. The thickness independence of these results clearly indicated that the film properties are sufficiently uniform that the nature of these film materials and their light induced changes can be characterized with confidence.

No correlation is found between the FF and the commonly used \( \alpha(1.2) \) when comparing the kinetics of degradation at all temperatures investigated below 100°C. Furthermore as pointed out by Gunes and Wronski [7], there is no such correlation between \( \alpha(1.2) \) and \( \mu\tau \) products measured at high values of G on the same film. It should also be noted here that a striking similarity is found between the FF and \( \mu\tau \), when comparing the significant improvements that occur with annealing temperature after degradation to a 1 sun DSS. This indicates that in cell structures in which carrier recombination is dominated within the i-layer, the creation of defects under open circuit conditions is similar to that in the corresponding film.

![Fig. 1 Cross sectional TEM images of R=10 i-layer material deposited on c-Si/SiO_2/Cr substrates at thicknesses of (a) 0.4\( \mu \)m and (b) 1.0\( \mu \)m.](image)
The absence of correlations between $\alpha (1.2)$ and the electron $\mu \tau$ products at high $G$ is a result of the difference in quasi-Fermi level splitting. Large quasi-Fermi level splitting introduces defect states that are located away from midgap and thus act as recombination centers. This has been addressed by including defects other than $D_0^0$ [6,7] and is not discussed further here. A similar problem exists in relating $\alpha (1.2)$ to the FFs because the recombination, which is solely through the midgap defect states, occurs only with relatively small quasi-Fermi level splitting, and not under 1 sun illumination. Under 1 sun, the splitting is approximately equal to the open circuit voltage ($V_{oc}$), and thus it extends over a wide fraction of the gap. In solar cells as in the films, the small quasi-Fermi splitting limits the carrier recombination to midgap states and occurs only at very low illumination intensities.

However, small quasi-Fermi level splitting and the associated recombination through midgap states in the bulk of the i-layer can also be obtained under carrier injection with small forward biases [15]. The forward bias I-V characteristics of a 0.4$\mu$m p-i-n cell in the annealed state are shown in Fig. 2 along with its subsequent changes under 1 sun illumination at 25$^\circ$C. These currents exhibit monotonic increases under 1 sun illumination, reaching a DSS in the same time as the $\mu \tau$ products and $\alpha (1.2)$, and as a result are a direct measure of the increase in the density of midgap states. In this case, direct correlations can indeed be obtained between the light induced changes in $\alpha (1.2)$ for the film and the changes in the currents at 0.4 V for the corresponding cell, as illustrated in Fig. 3. Fig. 3, both results have been normalized to their initial values (AS). The excellent agreement found here between the degradation kinetics of $\alpha (1.2)$ and those of a cell characteristic associated with recombination in the bulk layer (although not the FF), is a clear indication that the rate at which midgap defects are created under 1 sun illumination are the same in both cases.

Next the light induced changes in the FF under 1 sun illumination, controlled by carrier recombination in the i-layer, will be correlated with the changes in the corresponding film. In order to do this, it is necessary to ensure that both are characterized with comparable quasi-Fermi level splitting. Since the FF’s are determined by both electron and hole transport, it is somewhat surprising that direct correlations are found between the FF’s and the electron $\mu \tau$ products, the latter obtained with $G=10^{19}\ \text{cm}^{-3}\text{s}^{-1}$ corresponding to 1 sun illumination. Indeed, such correlations are found not only for cells having different thicknesses, in which case the FF’s are directly related to the i-layer, but also for degradations carried out at different temperatures between 25$^\circ$C and 100$^\circ$C. This is illustrated by plotting $1/\mu \tau$ versus FF as in Figs. 4 and 5. The quantity $1/\mu \tau$ is proportional to the densities of defects that act as recombination centers [16].
In Fig. 4, results are shown for the FF for cells with 0.2, 0.4, 0.7 µm i-layers obtained under 1 sun illumination at 25°C. There are clear linear relationships between FF and $1/\mu\tau$ in all three cases, and the difference in the slopes here is due to the fact that a given increase in the density of defects has a larger effect on the FF for larger i-layer thicknesses.

![Graph showing FF vs. Time for different temperatures](image)

In Fig. 5 a similar plot is shown for a cell with a 0.7 µm i-layer in which case the 1 sun degradation is carried out at 25, 50, and 75°C. Here again a direct correlation is evident for all three temperatures. In this case, the difference in slopes reflects the changes in the creation and annealing of defects that occurs as the degradation temperature is increased above 25°C [10].

**CONCLUSIONS**

For the first time, the light induced changes under 1 sun illumination in thin film material properties have been successfully correlated with corresponding changes in the characteristics of cells having identically-prepared i-layers. These correlations (i) explain the inability to relate changes in the densities of midgap states to changes in the cell FF and (ii) confirm the key role that non-D states have on the recombination kinetics in both films and solar cells. Also highly significant is the correlation found between the electron recombination in films with a similar quasi-Fermi level splitting to that in solar cells when illuminated under 1 sun. Apart from establishing another long-sought correlation between the results on thin films and corresponding solar cells, this study points to the importance of further addressing the many unanswered questions that remain concerning the nature and energy distribution of the different light induced defect states in a-Si:H. Furthermore, the correlations reported here offer additional probes to characterize and establish mechanisms responsible for SWE. This research demonstrates clearly the inadequacy of the many predictions for the performance and stability of single and multijunction cells that have been performed with modeling assuming a simple distribution of states associated solely with dangling bonds.

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**REFERENCES**


