THE ROLE OF PHASE TRANSITIONS BETWEEN AMORPHOUS AND MICROCRYSTALLINE SILICON ON THE PERFORMANCE OF PROTOCRYSTALLINE Si:H SOLAR CELLS

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ABSTRACT

A systematic study has been carried out to quantify the effect of microcrystallite nucleation in the intrinsic layer of protocrystalline Si:H p-i-n solar cells prepared by rf plasma enhanced chemical vapor deposition (PECVD). Real-time spectroscopic ellipsometry (RTSE) results that have previously identified the transitions from amorphous to microcrystalline phase were confirmed with atomic force microscopy (AFM) images. The effects of the phase transitions in the bulk intrinsic layer, as well as near the p/i interface of p-i-n cells, have been evaluated as a function of film thickness and H₂-dilution ratio (R=[H₂]/[SiH₄]). Illuminated and dark J-V characteristics are correlated with the microstructural evolution of the Si:H films yielding insight into the “sharpness” of the transition. Evidence of abrupt changes in the mobility gap is obtained from the selfconsistent numerical modeling of cell characteristics.

INTRODUCTION

Significant progress has been made in improving the performance and stability of a-Si:H based p-i-n and n-i-p solar cells using customized cell structures and protocrystalline intrinsic layers prepared with hydrogen dilution of silane [1,2,3,4,5]. The distinguishing characteristics of protocrystallinity, a term used to describe a-Si:H prepared close to the amorphous-microcrystalline phase boundary in deposition parameter space, are materials with improved stability under illumination and increased ordering [2,6,7]. The effects of the transition from the amorphous to microcrystalline phase within the Si:H layers of p-i-n solar cells have been previously observed and insights have been obtained into the properties of some structurally graded materials [3,4]. Real-time spectroscopic ellipsometry studies have also indicated that the way to optimize protocrystalline Si:H p-i-n cell structures is to exploit a microstructurally engineered p/i interface region obtained by a two-step variation of the i-layer H₂-dilution ratio R=[H₂]/[SiH₄] [2]. However, there has been no quantitative correlation between the evolving microstructure of the Si:H films and the physical mechanisms responsible for the corresponding effects on solar cell performance.

EXPERIMENTAL DETAILS

The Si:H films studied by RTSE were deposited in a single-chamber reactor on R=0 a-Si:H films which in turn were deposited on c-Si. This structure is used to simulate i-layer growth on the amorphous p-type SiC:H layers used in fabricating the p-i-n cells. Crystalline Si was used as the substrate material due to its inherent smoothness that enables the features of even small crystallites to be clearly discerned in the amorphous matrix using AFM. A rotating compensator multichannel ellipsometer was used for the RTSE measurements [8]. The specular SnO₂/p-a-SiC:H:B/i-a-Si:H/n-μc-Si:H:P/Cr cells were deposited in a multi-chamber rf-PECVD system with all film and cell depositions carried out at 200°C under previously described conditions [1]. AFM was carried out in the tapping mode on a Digital Instruments multi-mode scanning probe microscope or in non-contact mode with a Park Scientific M5. The J-V characteristics of the p-i-n cells were measured with a Keithley 236 Source/Measure unit at 25°C both with and without 1 sun illumination from an Oriel 6258 solar simulator.

RESULTS AND DISCUSSION

An example of the evolution of the surface roughness thickness (dₛ) versus the bulk layer thickness (dₖ) obtained from RTSE measurements of a Si:H film deposited with R=20 is shown in Fig. 1. The key feature in Fig. 1b is the abrupt increase in dₛ, which indicates the onset of an amorphous to mixed-phase amorphous + microcrystalline transition in the material, that occurs at a film thickness of approximately 900 Å. Such a transition is confirmed not only by a corresponding change in the dielectric function but also by the AFM images that are obtained for films of different thickness. Fig. 1a illustrates the rapid increase in the density of microcrystalline nuclei from only 4 nuclei/μm² at 880 Å to what appears to be the onset of nuclei coalescence at 3500 Å, where the corresponding AFM images are shown in Fig. 2. The discrepancy between the RTSE-determined roughness and the rms roughness from AFM can be attributed to changes in the volume fraction of Si within the roughness layer, which are not included in the optical model used to interpret the RTSE data.
The results in Fig. 1 and 2 not only corroborate the interpretation of the RTSE data that identifies the phase transition and defines an evolutionary phase diagram [2,6], but also provide a means for assessing the effect that the nuclei in the intrinsic layers have on p-i-n cell characteristics. This was carried out by comparing the initial fill factor (FF) of p-i-n solar cells with i-layers (1100 Å to 4000 Å) which were deposited under similar conditions but with R=0, 10, and 20. The results are shown in Fig. 3 where it can be seen that at a thickness of 1100 Å, the initial FF of all of the cells is similar irrespective of dilution. With R=0 and R=10, where no microcrystals are formed within the 4000 Å, there are the expected decreases in FF with thickness due to the changes in the electric field distribution and carrier collection. However, these are significantly smaller than those in the R=20 cell [3,4], which already shows a significant decrease at 2000 Å thickness, and a very large one at 4000 Å where the AFM results indicate the onset of coalescence. These observed decreases are not related to any adverse effects in the p/i interface region since insertion of a 200 Å R=20 p/i interface region into cells with bulk R=10 i-layers leads to improved performance. Therefore, the large decrease in the R=20 FF is a bulk effect that can be attributed to the increase in carrier recombination in the microcrystalline region of the i-layer whose bandgap is narrower than that of the initial 900 Å amorphous material. Because these transitions are close to the n/i contact they affect only the FF in p-i-n cells [3,4]. However, there is a large effect on both the FF and open-circuit voltage (V\text{oc}) when these transitions occur in the p/i interface region [5,9]. Accordingly, customized cells were fabricated in which different thickness R=40 Si:H layers were inserted into cells having 4000 Å, R=10 i-layers. The light J-Vs of cells having 100, 200, 300, and 400 Å thick R=40 layers in the p/i interface region are shown in Fig. 4.
The corresponding AFM images of the R=40 i-layers are shown in Fig. 5 and the results of both measurements are listed in Table 1.

The introduction of the R=40 p/i interface regions of 100 Å and 200 Å thicknesses increases the $V_{oc}$ from the 0.88V baseline value obtained without an interface region to 0.92V and 0.93V, respectively, without altering the FF. Subsequent increase in the thickness of the R=40 layer to 300 Å and 400 Å significantly reduces both the $V_{oc}$ as well as the FF.

These changes can be related to the AFM results. As seen in Table 1, for a 100Å R=40 interface layer the film has an rms roughness of $\sim$3 Å with the microcrystalline nuclei having heights of over 50 Å. At 200 Å there is a marked increase in the density of these nuclei but their lateral size remains $\sim$ 50 Å. This change has a relatively small effect on the cell characteristics. However, when the thickness is increased to 300 Å there is an increase not only in the density of the nuclei but also in their lateral size which allows them to come into contact. This has a profound effect on the cell characteristics reducing $V_{oc}$ from 0.93 to 0.85 V and the FF from 0.73 to 0.60. This onset of coalescence is also marked by an increase in the height of the microcrystals from $\sim$90 Å to $\sim$125 Å. The coalescence of the microcrystalline nuclei is completed in the interface layer of 400 Å. This final stage in the progressive transition from an amorphous to a microcrystalline phase further decreases the FF and $V_{oc}$ to 0.46 and 0.79, respectively.

<table>
<thead>
<tr>
<th>R=40 layer Thickness(Å)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>rms roughness (Å)</th>
<th>R(p-v) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.92</td>
<td>0.73</td>
<td>3.3</td>
<td>53</td>
</tr>
<tr>
<td>200</td>
<td>0.93</td>
<td>0.73</td>
<td>11</td>
<td>89</td>
</tr>
<tr>
<td>300</td>
<td>0.85</td>
<td>0.60</td>
<td>17.2</td>
<td>124</td>
</tr>
<tr>
<td>400</td>
<td>0.79</td>
<td>0.46</td>
<td>28</td>
<td>190</td>
</tr>
</tbody>
</table>

Table 1. Quantitative effect of microstructural evolution on p-i-n cell performance. (R$_{p-v}$ indicates average peak-to-valley distance.)

Insight into the nature of the phase transition and the electronic properties that affect solar cell operation was obtained from the corresponding dark J-V characteristics. Under forward bias, the current density, $J$, in the exponential region can be expressed as:

$$J = J_o \left( e^{\frac{qV}{nkT}} - 1 \right)$$

where $J_o$ is the reverse saturation current density and $n$ is the diode quality factor, both of which are dependent on the dominant transport mechanism. These J-V characteristics are determined by the generation-recombination currents in the cell which depend on the states near midgap but are even more sensitive (exponentially) on the bandgap [10]. P-i-n diodes with high-quality interfaces and intrinsic layers have typical $J_o$ values of $\sim 10^{-9}$ mA/cm$^2$ and $n$ factors of $\sim 1.6$. Studies on p-i-n cells with R=10 bulk layers but different p/i regions have shown that p-i-n cells fabricated with thin ($\leq 200Å$) R=40 interface layers used in this study exhibit dark currents that are not limited by the p/i interface but are completely dominated by generation-recombination in the bulk i-layer in both the annealed and degraded steady states [11].

Evidence for increased recombination in the vicinity of the phase transition region in the i-layer material can be seen from the successive increase of the room temperature dark currents in the exponential region with increase in the thickness of the R=40 Si:H layers. The dark J-V results for the four p-i-n cells of Fig. 4 are shown in Fig. 6. As the R=40 Si:H layer increases from 100 Å to 400 Å and traverses the amorphous-to-microcrystalline phase boundary, the room temperature value of $J_o$ increases from $3\times 10^{-9}$ to $2.5\times 10^{-7}$ mA/cm$^2$, clearly indicating a large increase in generation-recombination currents.
layers having different thickness p/i interface layers. (Experimental results shown as solid lines.)

Fig. 6. Dark J-V characteristics of p-i-n solar cells fabricated with customized two-step i-layers having different thickness p/i interface layers.

The characteristics of p-i-n cells of Figs. 4-6 with the evolving interface layer were modeled using the transport simulation code AMPS (Analysis of Microelectronic and Photonic Structures) [12]. A gap state distribution was used for the a-Si:H that includes charged defects, similar to that used in the analysis of results of detailed studies on thin a-Si:H films [13]. The transition from the amorphous to microcrystalline phase in the i-layer was modeled as an abrupt change in mobility gap from the value of 1.86 eV, determined by internal photoemission for the a-Si:H, to a value of 1.2 eV, characteristic of microcrystalline Si:H. Since the exact nature of the band discontinuities are not determined from the microstructure results on films. More detailed results on the effects of changes in bandgap on different solar cell characteristics will be discussed elsewhere.

These simulation results, similar to the experimental ones in Fig. 6 (illustrated as solid lines in Fig. 7), clearly show large increases in the exponential region of the dark current, and hence $J_0$, which are attributed to the increased recombination in the narrow gap microcrystalline region. Simulation of the 1 sun J-V characteristics also shows a dramatic drop in both the FF and $V_{oc}$ to values of 0.43 and 0.73 V, respectively, in good agreement with the values listed in Table I for the cell having a 400 Å R=40 Si:H interface layer.

CONCLUSIONS

New insights into the effect that the phase transitions between amorphous and microcrystalline Si:H have on the performance of p-i-n and n-i-p solar cells have been obtained from the results reported here. The effects of transitions near both the p and n contacts have been identified, quantified, and correlated with changes in microstructure. The coalescence of microcrystals has been identified as the mechanism that gives rise to the large changes in electronic properties and device performance. Numerical simulation of the cell characteristics of the different structures confirmed an abrupt change in mobility gap at the thicknesses determined from the microstructure results on films. More detailed results on the effects of changes in bandgap on different solar cell characteristics will be discussed elsewhere.

REFERENCES