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Thin-film silicon triple-junction solar cell with 12.5% stable efficiency on innovative flat light-scattering substrate

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Several thin-film solar cell technologies require light-trapping schemes that are predominantly based on depositing the solar cells on rough surfaces. While this approach efficiently increases the density of photo-generated carriers, open-circuit voltage and fill factor generally decrease. Substrates that decouple the growth interface from the light-scattering interface were previously proposed as a solution to this dilemma, and proof-of-concepts were demonstrated in thin film-silicon solar cells. In this contribution, we review as an introduction the problematic of rough versus smooth interface for n-i-p single-junction µc-Si:H cells. Then, the benefits of the newly developed substrate that decouples the growth and scattering interfaces are investigated in n-i-p triple-junction a-Si:H/µc-Si:H/µc-Si:H solar cells for the first time. Conversion efficiencies of 13.7% (initial) and 12.5% (stabilized) are obtained, which are among the highest ever reported for such devices. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4768272]

I. INTRODUCTION

In thin-film photovoltaic devices, such as organic and silicon (Si) based solar cells, the active layer thickness is restricted because of stability issues and/or the limited diffusion length of photo-generated carriers. Therefore, intelligent light management schemes are necessary to trap light and efficiently absorb the solar spectrum. Since the pioneering work of Deckman et al.1 and Tiedje et al.,2 who successfully introduced light scattering at rough interfaces to increase the light path length inside devices, numerous contributions have addressed this problem. In general, textured electrodes or substrates on which cells are deposited are used to improve the short-circuit current density ($J_{sc}$).3–15 However, most of the time, a rough surface induces structural defects in the device grown on top of it, leading to reduced open-circuit voltage ($V_{oc}$) and fill factor (FF).12,14–18 Therefore, a compromise between roughness for efficient light scattering (high $J_{sc}$) and smoothness for high $V_{oc}$ and FF has to be made. A different approach is to decouple the growth interface from the scattering interface. In this case, the growth interface is designed to be flat, leading to devices with high $V_{oc}$ and FF. Efficient light scattering is instead achieved through a buried, optically rough interface leading to high $J_{sc}$. Previous studies have demonstrated proofs of concept,19–21 but no high-efficiency multi-junction device using this substrate architecture has been presented yet. In a previous report,18 we described a type of substrate with a specific choice of materials that can be used for the fabrication of thin-film Si solar cells grown by plasma-enhanced chemical vapor deposition (PE-CVD).

In this contribution, three sets of experiments are presented and discussed: First, single-junction microcrystalline ($µc$-Si:H) solar cells are used to study (1) the importance of a smooth growth interface on the $V_{oc}$ and FF of a solar cell in the n-i-p configuration and (2) the importance of adding a buried, optically rough interface when the cell is grown on a smooth texture. Second, we show the potential of newly developed substrates that combine an optically rough interface with a physically flat growth interface by comparing triple-junction cells deposited on this substrate and on a standard rough substrate. Finally, we demonstrate an n-i-p triple-junction amorphous silicon (a-Si:H)/µc-Si:H/µc-Si:H solar cell grown on the newly developed substrate which exhibits efficiencies among the highest reported both in the initial state (13.7%) and after degradation (12.5%).

II. SUBSTRATES DETAILS

Fig. 1 presents schematics drawings of the substrates used in this work. Substrates A–E were used in single-junction µc-Si:H cells, whereas substrates F and E were used in triple-junction a-Si:H/µc-Si:H/µc-Si:H solar cells. Substrates A–D consist of a silver (Ag) layer (flat Ag in A and B and rough Ag in C and D) which plays the role of the buried back reflector interface. A thin layer of sputtered aluminum doped zinc oxide (ZnO:Al) followed by approximately 4 µm (Z4) of non intentionally doped (NID) ZnO grown by low-pressure (LP) CVD were then grown. Two surface treatment times22 were applied to the LP-CVD ZnO to smoothen the pyramidal features: substrates A and C were treated for a shorter time (35 min) than substrates B and D (90 min) and are, therefore, rougher. Substrate E is a Hot Ag reference substrate which consists of a rough Ag back reflector sputtered onto a substrate held at approximately 300 °C, which is then further covered by 60 nm of ZnO:Al. Finally, substrate F is the newly developed substrate that decouples the growth interface from the light-scattering interface. It consists of a flat Ag layer covered with 20 nm of sputtered ZnO:Al and untreated 2.5- or 5-µm-thick layer of NID LP-CVD ZnO.
The optically rough interface was created by growing a dummy undoped a-Si:H layer that buries the pyramidal ZnO features. As a result, light scattering at the pyramidal features is ensured by the difference in refractive index of the two materials \((n_{a-Si:H} \cong 4, n_{ZnO} \cong 2)\). The final flat interface on which cells were grown was subsequently obtained by chemical mechanical polishing.23 Further details on these substrates can be found in Ref. 19.

III. SINGLE-JUNCTION SOLAR CELLS

Single-junction \(\mu\)c-Si:H solar cells with total thicknesses of 1.36 \(\mu\)m were obtained with a low deposition rate (approximately 3 \(\AA/s\)) to obtain \(\mu\)c-Si:H material of high quality.18 Small amounts of carbon dioxide (CO\(_2\)) were added to the precursor gases of the \(n-\) and \(p-\) doped layers to incorporate oxygen during layer growth. These silicon oxide (SiO\(_x\)) doped layers are known to have two predominant effects in doped layers: first, the incorporation of these layers leads to less parasitic absorption.24,25 An extended study of the material quality as a function of the growth conditions and oxygen content of the doped layers of \(p-i-n\) solar cells can be found in Ref. 18. The front contact was a 2.5-\(\mu\)m-thick boron-doped LP-CVD ZnO layer. The solar cells with an area of 0.35 \(cm^2\) were characterized as follows: current-voltage measurements were done using a dual-beam spectrophotometer equipped with an integrating sphere (Lambda 900, Perkin Elmer). The cells were attached externally to the integrating sphere during these measurements. 

Fig. 2 and Table I present the results of the single-junction \(\mu\)c-Si:H solar cells grown on substrates \(A-E\). The similar EQE and absorption measurements (Fig. 2) of cells grown on substrates \(A\) and \(C\) indicate that the buried, optically rough Ag interface yields a marginal \(J_{sc}\) enhancement since the growth Si/ZnO interface is rough enough to efficiently scatter the incoming light. However, when this Si/ZnO growth interface is smoother, as is the case for substrates \(B\) and \(D\), it is beneficial for light that is transmitted through the ZnO to be scattered on a rough buried Ag layer. This results in higher EQE and absorption for the cell grown on substrate \(D\) compared to the cell grown on substrate \(B\). Still, the \(J_{sc}\) of substrate \(D\) is lower than those given by the roughest substrates \((A\) and \(C\)) as Table I reveals. This can be attributed to a larger primary reflection at the Si/ZnO growth interface in substrates \(B\) and \(D\). Nevertheless, the real figure of merit is the cell efficiency and is shown in Table I. Despite the SiO\(_x\) doped layers, the \(V_{oc}\) and FF exhibit a large decrease for the rougher substrates \(A\) and \(C\). These losses are not counterbalanced by the increase in \(J_{sc}\) given by the rough Si/ZnO interface. A relative efficiency increase of 9% is hence obtained using the smoother substrates \(B\) and \(D\). Furthermore, an even higher FF can be obtained using the smoothest substrate of this series, i.e., the reference Hot Ag substrate \(E\). The high \(V_{oc}\) of 560 mV and FF of 78% show that growth of \(\mu\)c-Si:H materials on this substrate is of very high quality with few structural defects. These \(n-i-p\) cells show that a smooth interface for \(\mu\)c-Si:H cell growth is of first and foremost importance for the cell efficiency.

![Fig. 1. Schematics of the various types of substrates.](image)

**TABLE I. Characteristics of \(n-i-p\) single-junction \(\mu\)c-Si:H solar cells grown on various substrates.**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>(V_{oc}) (mV)</th>
<th>FF (%)</th>
<th>(J_{sc}) (mA/cm(^2))</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Flat Ag Z4-medium treatment</td>
<td>529</td>
<td>70.3</td>
<td>24.3</td>
<td>9.0</td>
</tr>
<tr>
<td>B: Flat Ag Z4-long treatment</td>
<td>559</td>
<td>77.1</td>
<td>22.7</td>
<td>9.8</td>
</tr>
<tr>
<td>C: Rough Ag Z4-medium treatment</td>
<td>522</td>
<td>70.3</td>
<td>24.6</td>
<td>9.0</td>
</tr>
<tr>
<td>D: Rough Ag Z4-long treatment</td>
<td>550</td>
<td>76.6</td>
<td>23.3</td>
<td>9.8</td>
</tr>
<tr>
<td>E: Hot Ag reference</td>
<td>560</td>
<td>78.0</td>
<td>22.3</td>
<td>9.7</td>
</tr>
</tbody>
</table>
IV. TRIPLE-JUNCTION SOLAR CELLS

In the remainder of this work, we present triple-junction a-Si:H/μc-Si:H/μc-Si:H solar cells. The bottom μc-Si:H cell is 3.5 μm thick and has a μc-Si:H n-doped layer that does not contain oxygen to ensure sufficient lateral conductivity (see Ref. 19 for more details), while the p-doped layer is alloyed with oxygen to increase its transparency. The μc-Si:H middle cell has a total thickness of 1.86 μm and contains SiOx doped layers. The a-Si:H top cell is approximately 270 nm thick and incorporates a recently developed highly transparent p-SiOx doped layer, contributing to high Voc.27 The front contact is a 2.5-μm-thick boron-doped LP-CVD ZnO layer. As previously explained, EQE measurements were used to determine the Jsc. However, here the EQE measurement of each sub-cell requires the saturation of the other sub-cells with light: as a consequence, the sub-cells which are saturated with light apply a negative voltage to the cell under measurement.26 To best reproduce short-circuit conditions, we, therefore, applied an external positive electrical bias of 0.7 V for the EQE measurement of the a-Si:H top cell and of 1 V for the μc-Si:H bottom and middle cells. The cells were subsequently measured after being exposed to 1000 h in a class AAA degradation system at 50°C and in open-circuit conditions.

Fig. 3 presents the EQEs of co-deposited triple-junction a-Si:H/μc-Si:H/μc-Si:H solar cells grown on a Hot Ag reference substrate (E) and on a polished substrate (F) that decouples the growth interface from the scattering interface. The corresponding electrical parameters are reported in Table II. This comparison reveals the gains that can be obtained with the newly developed polished substrate F.

We conclude that the substrate F clearly outperforms substrate E in terms of light-management for wavelength > 700 nm. The efficient light scattering was also corroborated by an additional experiment in which polished substrates grown on either a flat Ag or a rough Ag layer were compared. No significant EQE differences (below 1% variation of Jscbottom + Jscmiddle) were observed (not shown), suggesting that the first back scattering interface “dummy” a-Si:H/ZnO is sufficiently rough that the cell does not benefit from an additional underlying rough Ag layer. This is similar to the observation made by comparing cells grown on substrates A and C in the first part of this contribution.

As demonstrated in single-junction cells (Voc and FF shown in Table I), substrate E allows for the growth of high-quality μc-Si:H material without structural defects. Similarly, the comparable electrical performances of the triple-junction cells grown on substrates E and F (Table II) show that the latter substrate provides an equivalently good surface for the growth of μc-Si:H material. As Table II shows, the Voc of cells grown on both substrates is similar, and even a slight gain in FF is obtained on substrate F. As the difference in current mismatch between both substrates is minor, the higher FF obtained on substrate F proves that the material quality is similar to or even slightly better than that of the material grown on substrate E.

The Jsc gain and the similar Voc and FF values hence demonstrate that substrate F combines efficient light management and an interface suitable for the growth of high-quality materials. This is further supported by the higher initial and post-degradation efficiencies obtained on substrate F compared to substrate E.

Finally, Fig. 4 and the last cell shown in Table II present the EQE and electrical parameters of an optimized triple-junction a-Si:H/μc-Si:H/μc-Si:H solar cell grown on substrate F. This cell differs from the previous triple-junction cells shown in Fig. 3 in that the top cell, especially its p-layer, was optimized. The doping in the p-layer was increased and as a result, both the Voc and FF improved while a slight loss in Jsc can be observed. The substrate was also slightly different as the dummy a-Si:H layer was grown on a Z2.5 compared to a Z5 for the unoptimized cell. This cell, thus, reaches efficiencies among the highest reported both in the

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Voc (V)</th>
<th>FF (%)</th>
<th>Jsc top (mA/cm²)</th>
<th>Jsc middle (mA/cm²)</th>
<th>Jsc bottom (mA/cm²)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot Ag (E)</td>
<td>1.89</td>
<td>71.3</td>
<td>9.3</td>
<td>8.7</td>
<td>9.0</td>
<td>11.7</td>
</tr>
<tr>
<td>After degradation</td>
<td>1.84</td>
<td>66.7</td>
<td>9.1</td>
<td>8.7</td>
<td>8.8</td>
<td>10.7</td>
</tr>
<tr>
<td>Polished (F)</td>
<td>1.88</td>
<td>74.6</td>
<td>9.4</td>
<td>9.1</td>
<td>9.5</td>
<td>12.8</td>
</tr>
<tr>
<td>After degradation</td>
<td>1.85</td>
<td>69.9</td>
<td>9.2</td>
<td>8.9</td>
<td>9.4</td>
<td>11.5</td>
</tr>
<tr>
<td>Optimized cell on polished (F)</td>
<td>1.96</td>
<td>77.7</td>
<td>9.2</td>
<td>9.1</td>
<td>9.2</td>
<td>13.7</td>
</tr>
<tr>
<td>After degradation</td>
<td>1.93</td>
<td>72.7</td>
<td>9.0</td>
<td>8.9</td>
<td>9.1</td>
<td>12.5</td>
</tr>
</tbody>
</table>
V. CONCLUSION

To conclude, we first showed the necessity of growing the \( \mu \text{-Si:H} \) layers on a smooth surface for achieving high-quality material and high-efficiency in single-junction solar cells. Second, we demonstrated the efficient light management of a newly developed substrate and its suitability for \( \mu \text{-Si:H} \) growth, by comparing co-deposited triple-junction a-Si:H/\( \mu \text{-Si:H}/\mu \text{-Si:H} \) solar cells grown on it and on a reference Hot Ag substrate. Finally, we presented a triple-junction cell with high efficiency which profits from the decoupling of the growth interface from the scattering interface. This solar cell exhibits efficiencies of 13.7% in the initial state and 12.5% after degradation. The efficiency after degradation is among the highest reported to this date for purely silicon based \( n-i-p \) thin film solar cells.

ACKNOWLEDGMENTS

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