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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,[19] 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 E and F 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 times[22] 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.

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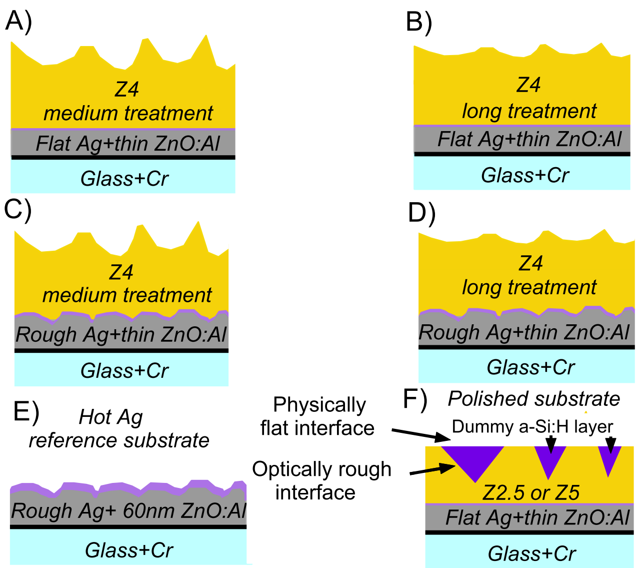

FIG. 1. Schematics of the various types of substrates.

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 μc-Si:H solar cells with total thicknesses of 1.36 μm were grown with a low deposition rate (approximately 3 Å/s) to obtain μc-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 *p-i-n* solar cells: first, the incorporation of these layers leads to cells with V_{oc} and *FF* values that are more tolerant to rough substrates and, second, these layers are more transparent than standard doped layers and therefore lead 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-μm-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-lamp solar simulator (Wacom WXS-220S-L2) in standard test conditions (25 °C, AM 1.5 G spectrum and 1000 W/m^2) and were used to extract the V_{oc} and *FF* values of the solar cells. The J_{sc} values were obtained by convolution of external quantum efficiency (EQE) and the AM1.5 G solar spectrum. Total absorption was derived from reflection measurements measured using a dual-beam spectrophotometer equipped with an integrating sphere (Lambda 900, Perkin Elmer). The cells

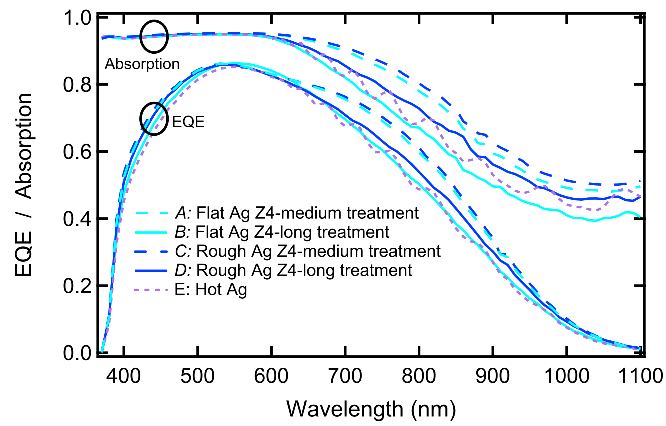

FIG. 2. EQE and absorption of *n-i-p* single-junction μc-Si:H solar cells grown on various substrates.

were attached externally to the integrating sphere during these measurements.

Fig. 2 and Table I present the results of the single-junction μc-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 μc-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 μc-Si:H cell growth is of first and foremost importance for the cell efficiency.

TABLE I. Characteristics of *n-i-p* single-junction μc-Si:H solar cells grown on various substrates.

Substrate	V_{oc} (mV)	*FF* (%)	J_{sc} (mA/cm^2)	Efficiency (%)
A: Flat Ag Z4-medium treatment	529	70.3	24.3	9.0
B: Flat Ag Z4-long treatment	559	77.1	22.7	9.8
C: Rough Ag Z4-medium treatment	522	70.3	24.6	9.0
D: Rough Ag Z4-long treatment	550	76.6	23.3	9.8
E: *Hot Ag* reference	560	78.0	22.3	9.7

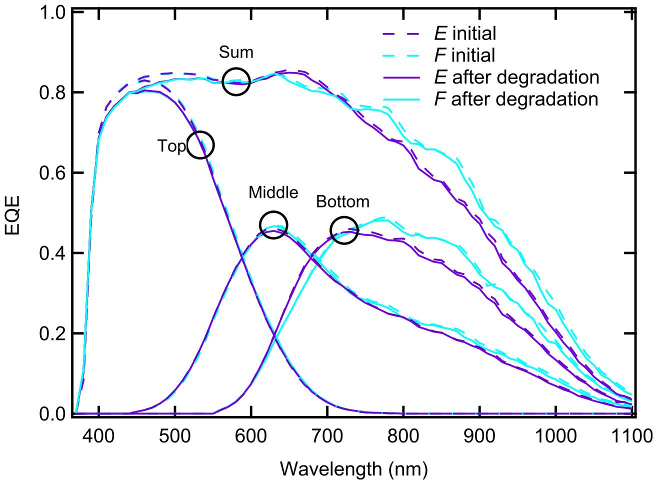

FIG. 3. Comparison of EQE of *n-i-p* triple-junction a-Si:H/μc-Si:H/μc-Si:H solar cells co-deposited on substrates *E* and *F*.

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 SiO_x doped layers. The a-Si:H top cell is approximately 270 nm thick and incorporates a recently developed highly transparent *p*-SiO_x doped layer, contributing to high V_{oc}.[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 J_{sc}. 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 $J_{sc_{bottom}} + J_{sc_{middle}}$) 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 (V_{oc} 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 V_{oc} 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 J_{sc} gain and the similar V_{oc} 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 V_{oc} and *FF* improved while a slight loss in J_{sc} 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 II. Characteristics of *n-i-p* triple-junction a-Si:H/μc-Si:H/μc-Si:H solar cells. The first two cells are co-deposited on substrate *E* and *F*. The last cell which is presented was optimized on substrate *F*.

Substrate	V_{oc} (V)	*FF* (%)	J_{sc} top (mA/cm^2)	J_{sc} middle (mA/cm^2)	J_{sc} bottom (mA/cm^2)	Efficiency (%)
Hot Ag (*E*)	1.89	71.3	9.3	8.7	9.0	11.7
After degradation	1.84	66.7	9.1	8.7	8.8	10.7
Polished (*F*)	1.88	74.6	9.4	9.1	9.5	12.8
After degradation	1.85	69.9	9.2	8.9	9.4	11.5
Optimized cell on polished (*F*)	1.96	77.7	9.2	9.1	9.2	13.7
After degradation	1.93	72.7	9.0	8.9	9.1	12.5

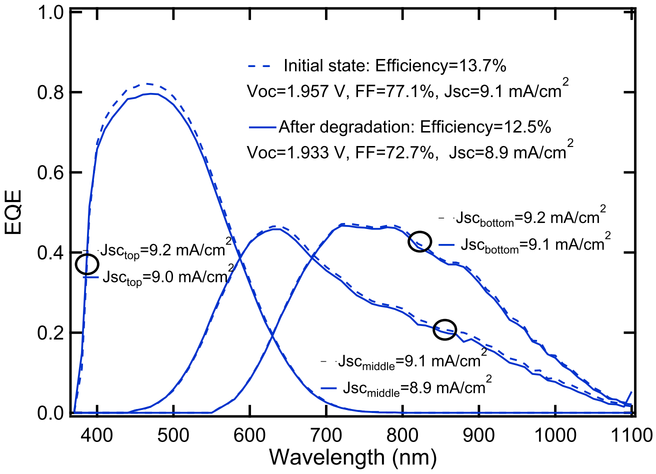

FIG. 4. EQE and electrical parameters of optimized triple-junction a-Si:H/μc-Si:H/μc-Si:H solar cells grown on substrate *F*.

initial state (13.7%) and after degradation (12.5%) for *n-i-p* thin-film Si cells without germanium content. The efficiency after degradation is similar to the certified record reported by United Solar in *n-i-p* configuration with indium tin oxide (ITO) as front contact.[28,29] The table of record efficiencies presented in Ref. 29 will have to be modified as, recently, LG electronics reported a new stable record efficiency of 13.4% using *p-i-n* triple-junction solar cells (presented at the 27th European photovoltaics solar energy conference held in Francfurt in 2012).

Here, we used thick μc-Si:H layers as proof of concept and future developments should aim at decreasing the layer thicknesses (e.g., by increased crystallinity) and decreasing the process time (e.g., by higher growth rates) for the absorber layers. Indeed, on the flat substrates of type *F*, the formation of defective porous areas in the μc-Si:H layer is significantly reduced. This, in turn, avoids losses in *FF* and V_{oc} which are often observed for high crystallinity or high growth rates.[18] Other routes for process time and layer thicknesses reduction could be the incorporation of an a-SiGe:H middle cell.[28,30] Finally, reflection and absorption losses due to the front contact can still be improved, either by reducing doping in the LP-CVD ZnO:B used in this contribution or using an ITO front contact coupled with double anti-reflection layers. In both cases, the deposition of a small contact metal grid becomes necessary in order to guarantee sufficient conduction of the front contact.

V. CONCLUSION

To conclude, we first showed the necessity of growing the μc-Si:H layers on a smooth interface 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 μc-Si:H growth, by comparing co-deposited triple-junction a-Si:H/μc-Si:H/μc-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.

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