Flexible n-i-p thin film silicon solar cells on polyimide foils with textured ZnO:Ga back reflector

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Abstract

In thin film silicon solar cells on opaque substrates in n-i-p deposition sequence where the textured transparent conductive oxide (TCO) layer serves as a back reflector, one can independently optimize the morphology of the TCO layer without compromise on transparency and conductivity of this layer and further adjust the electro-optical properties of the back contact by using additional layers on top of the textured TCO. In the present work, we use this strategy to obtain textured back reflectors for solar cells in n-i-p deposition sequence on non-transparent flexible plastic foils. Gallium doped ZnO (ZnO:Ga) films were deposited on polyimide substrates by DC magnetron sputtering at a temperature of 200 °C. A wet-chemical etching step was performed by dipping the ZnO:Ga covered foil into a diluted HCl solution. The textured ZnO:Ga is then coated with a highly reflective Ag/ZnO double layer. On this back reflector, we develop thin film silicon solar cells with a microcrystalline silicon absorber layer. The current density for the cell with the textured ZnO:Ga layer is $\sim 23 \text{ mA/cm}^2$, 4 mA/cm^2 higher than the one without such layer, and a maximum efficiency of 7.5% is obtained for a 1 cm^2 cell.

Keywords

Microcrystalline silicon; Transparent conducting oxide; Light trapping; Polyimide; Flexible substrate; Solar cells

1. Introduction

Flexible thin film silicon solar cells are usually fabricated in the n-i-p deposition sequence in substrate configuration because it allows the use of opaque, light weight substrates, such as plastic sheets or metallic foils [1,2]. The use of such substrates is of interest in thin film silicon solar cell technology because it reduces manufacturing cost by enabling roll-to-roll production [3]. Besides it opens possibilities for applications

like better integration into buildings and textiles. The most used substrate materials for the fabrication of flexible thin film silicon-based solar cells include stainless steel substrates [4,5], polyimide (PI) [6], polyethylene terephthalate and polyethylene naphthalate [7,8]. Among the organic polymer substrates, PI has the advantage of a higher melting point and glass transition temperature, with a smaller thermal shrinkage [9].

For high efficiency of amorphous (a-Si:H) and microcrystalline ($\mu\text{c-Si:H}$) thin film silicon solar cells, light trapping of the incident light within the silicon absorber layers becomes crucial in order to further reduce the cell thickness, which leads to reduction of the light-induced degradation effects for a-Si:H material [10] and higher throughput in production for both a-Si:H and $\mu\text{c-Si:H}$ solar cells [2]. Light scattering at the interfaces is usually achieved by texturing the front transparent conductive oxide (TCO) electrodes and/or the back reflectors [11–14]. Some TCO materials already have a suitable texture in the as-deposited state. On plastic foils, ZnO textured in the as-deposited state obtained by low pressure chemical vapor deposition or 2D periodic structures have been used to provide light trapping in the active layers of n-i-p devices [2,7]. Sputter-deposited ZnO can be textured by a post-deposition wet-chemical etching step [15,16]. For the n-i-p deposition sequence in substrate configuration where the textured TCO serves as a back reflector, this approach has the advantage of using an optimized morphology of the TCO layer, where the electro-optical properties can be adjusted by using additional layers on top of the textured TCO. This technique has been used for solar cells in both p-i-n and n-i-p deposition sequence on transparent glass substrates [11,17]. In the present work, we use this strategy to obtain textured back reflectors for n-i-p solar cells on flexible polyimide foil.

2. Experimental details

Microcrystalline thin film silicon solar cells were prepared on 10x10 cm² and 125 μ m thick PI foils. The substrates for smooth cells were covered with a thermally evaporated 700 nm Ag layer and an 80 nm sputtered ZnO:Ga, both deposited at room temperature. In order to obtain rough cells, an 800 nm ZnO:Ga layer was deposited directly on PI by DC magnetron sputtering at a substrate temperature of 200 °C, using a ZnO:Ga target (99/1 wt.%). The sputtering power density was 100 W. Both, the total gas pressure of 5×10^{-1} Pa as well as the total gas flow rate of 10 sccm were maintained constant during the deposition process. This layer was textured by a post-deposition wet-chemical etching in a 0.5% water diluted HCl solution for 30 seconds. The back contact was finalized with an additional highly reflecting Ag(200 nm)/ZnO(80 nm) sputtered double layer that conformally covers the textured ZnO:Ga surface.

The thin film silicon layers were deposited in n-i-p sequence by plasma enhanced chemical vapor deposition using very high frequency excitation (81.36 MHz). The substrate temperature was 200 °C for intrinsic and doped layers. The power density and chamber pressure for deposition of intrinsic layers were 210 mW/cm² and 100 Pa, respectively. Doped layers were deposited at power densities and pressures of 470 mW/cm² and 300 Pa for n-layers, and 140 mW/cm² and 100 Pa for p-layers. The silane concentration ratio, defined as $[\text{SiH}_4] / ([\text{SiH}_4] + [\text{H}_2])$, was varied between 5% and 7% for intrinsic layers.

The front transparent contacts made of 70 nm thick indium tin oxide (ITO) layers were prepared by radio-frequency (RF) magnetron sputtering at room temperature using a In₂O₃:SnO₂ target (95/5 wt.%) in an argon/oxygen atmosphere with relative oxygen content, defined as $[\text{O}_2] / [\text{O}_2 + \text{Ar}]$, of 0.1%.

The individual solar cells with an area of $1 \times 1 \text{ cm}^2$ were defined by using a shadow mask during ITO deposition on the $10 \times 10 \text{ cm}^2$ substrate. Front metal finger electrodes were prepared by silver evaporation. Finally, standard annealing procedure of finished solar cells was performed in air at 160°C for 30 minutes. The complete device layer sequences were for smooth cells: PI/Ag/TCO/n-i-p/ITO and for rough cells: PI/textured ZnO:Ga/Ag/TCO/n-i-p/ITO. Fig. 1 shows schematics of the solar cells on PI on smooth (Fig. 1.a) and rough (Fig. 1.b) back reflectors.

For comparison solar cells were also deposited on glass substrates with the same layer sequences.

The solar cell parameters open circuit voltage (V_{oc}), fill factor (FF) and short circuit current density (J_{sc}) were determined from current-voltage (I-V) measurements under simulated AM1.5G illumination at 25°C . The external quantum efficiency (EQE) was obtained from spectral response measurements in the range of 300-1100 nm. The integrated current from the EQE curves under short circuit conditions was used to calculate the conversion efficiency in order to avoid possible effects from current collection around the 1 cm^2 solar cells or from imprecision in determination of the cell area.

Raman spectroscopy was used to evaluate the crystalline volume fraction of the intrinsic layers in the solar cells. Raman measurements were performed directly on the solar cells using a Nd:YAG laser with excitation wavelength of 532 nm.

3. Results and discussion

Fig. 2 shows the performance parameters of solar cells deposited on the smooth PI/Ag(700 nm)/ZnO(80 nm) substrate as a function of silane concentration (SC) of the *i*-layer. For reference and in order to assess the effect of the substrate on the

performance of the solar cells, we prepared identical cells on smooth glass covered with a standard Ag/ZnO back reflector, optimized for glass substrate. We observed a similar trend of the performance parameters for the cells on PI when compared to the ones on glass. However, the V_{oc} was around 20-40 mV lower for the cells on PI. A reason for the lower V_{oc} could be the higher *i*-layer crystallinity of the cells deposited on PI as measured by Raman spectroscopy on the solar cells. This is shown in fig. 3. Why the PI substrate possibly promotes the growth of films with higher crystalline volume fraction is not clear at the moment. Despite of the apparent higher crystallinity in the *i*-layer of the solar cells prepared on PI with respect to the ones prepared on glass, the J_{sc} is lower for cells deposited at SC below 6% where one would instead expect higher absorption at higher crystallinity. We speculate that this results from absorption losses in the Ag/ZnO back contact [11], due to the higher roughness of the PI substrate compared to the glass one. The cell deposited with SC of 6.1% showed the highest V_{oc} (505 mV) and FF of 70.7%. For this reason we chose the deposition conditions of this cell for further optimization of the solar cells on PI with rough TCO. Fig. 4 shows the I-V curve of this solar cell on smooth PI and on glass substrate with an *i*-layer thickness of 1.8 μm deposited at SC = 6.1%, which yields a current density of 18.9 mA/cm^2 on PI and 20.7 mA/cm^2 on glass.

To further enhance the current of cells on PI, we developed ZnO:Ga layers for application as textured back reflector [18]. This development was first carried out on glass and later transferred to application on the PI substrate.

Fig. 5 shows the EQE of a solar cell prepared on ZnO:Ga deposited on PI, textured by post-deposition wet-chemical etching in HCl solution for 30 seconds, and covered with a highly reflecting Ag/ZnO double layer. For comparison the EQE of the cell on flat PI is shown. We observe a strong increase in EQE especially above 600 nm for the

cell with the textured ZnO:Ga layer accompanied by efficient reduction of interference fringes. The cell on structured TCO delivers a current density of $\sim 23 \text{ mA/cm}^2$, more than 4 mA/cm^2 higher than the one on flat PI, and an efficiency of 7.5% is achieved for a 1 cm^2 cell. However, the FF decreased from 70.7% to 68%, and the V_{oc} was 30 mV lower. These reductions in FF and V_{oc} are expected and related to the roughness of the substrate [19]. The improvement in current was observed essentially for wavelengths above 650 nm, corresponding to the light trapping region for microcrystalline solar cells [11]. Fig. 6 shows the corresponding IV curve of this cell and, for comparison, the curve of an identical cell deposited on a standard textured TCO/Ag/ZnO back reflector on glass.

Results presented above and summarized in table 1 showed that the well-established technology of post-deposition textured TCO films as a scattering layer to promote light trapping in thin film silicon solar cells can be transferred to application with flexible plastic substrates.

4. Conclusions

We have presented our development of microcrystalline single-junction n-i-p thin film silicon solar cells on flexible polyimide substrate. The results of solar cells on smooth PI showed similar behavior in terms of performance parameters in comparison to cells deposited on smooth glass. The V_{oc} was around 20-40 mV lower for the cells on PI, which is related to higher *i*-layer crystallinity of cells on PI. We developed a textured ZnO:Ga layer to promote light trapping in the solar cells on PI that yield more than 23 mA/cm^2 on absorbers of $1.8 \mu\text{m}$ thickness with cell efficiencies of up to 7.5%.

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References

- [1] A. Banerjee, S. Guha, Study of back reflectors for amorphous silicon alloy solar cell application, *J. Appl. Phys.* 69 (1991) 1030–1035.
- [2] T. Söderström, F.-J. Haug, X. Niquille, C. Ballif, TCOs for nip thin film silicon solar cells, *Prog. Photovoltaics Res. Appl.* 17 (2009) 165–176.
- [3] J. Bailat, V. Terrazzoni-Daudrix, J. Guillet, F. Freitas, X. Niquille, A. Shah, C. Ballif, T. Scharf, R. Morf, A. Hansen, D. Fischer, Y. Ziegler, A. Closset, Recent development of solar cells on low-cost plastic substrates, in: *Proc. 20th Eur. PVSEC*, 2005: pp. 1529–1532.
- [4] J. Yang, A. Banerjee, S. Guha, Triple-junction amorphous silicon alloy solar cell with 14.6 % initial and 13.0 % stable conversion efficiencies, *Appl. Phys. Lett.* 70 (1997) 2975–2977.
- [5] K. Saito, M. Sano, H. Otsoshi, A. Sakai, S. Okabe, K. Ogawa, High efficiency large area solar cells using microcrystalline silicon, in: *Proc. 3rd World PVSEC*, Osaka, 2003: pp. 2793–2798.
- [6] M. Tanda, K. Tabuchi, M. Uno, S. Kato, Y. Takeda, S. Iwasaki, Y. Yokohama, T. Wada, M. Shimosawa, Y. Sakakibara, A. Takano, H. Nishihara, H. Enomoto, T. Kamoshita, Large area, light weight, flexible solar cell production technology-ready for the market entry, in: *Proc. 31st IEEE PVSC*, IEEE, Lake Buena Vista, 2005: pp. 1560–1563.
- [7] F.-J. Haug, T. Söderström, M. Python, V. Terrazzoni-Daudrix, X. Niquille, C. Ballif, Development of micromorph tandem solar cells on flexible low-cost plastic substrates, *Sol. Energy Mater. Sol. Cells.* 93 (2009) 884–887.
- [8] P. Alpuim, G.M. Junior, S.A. Filonovich, P. Roca i Cabarrocas, J.-E. Bouree, E.V. Johnson, Y.M. Soro, Polymorphous and nanocrystalline silicon thin-film solar cells deposited at 150°C on plastic substrates, in: *Proc. 23rd Eur. PVSEC*, 2008: pp. 2455–2458.
- [9] K. Tao, D. Zhang, L. Wang, J. Zhao, H. Cai, Y. Sui, Z. Qiao, Q. He, Y. Zhang, Y. Sun, Development of textured back reflector for n-i-p flexible silicon thin film solar cells, *Sol. Energy Mater. Sol. Cells.* 94 (2010) 709–714.
- [10] D.L. Staebler, C.R. Wronski, Reversible conductivity changes in discharge produced amorphous Si, *Appl. Phys. Lett.* 31 (1977) 292–294.
- [11] J. Müller, B. Rech, J. Springer, M. Vanecek, TCO and light trapping in silicon thin film solar cells, *Sol. Energy.* 77 (2004) 917–930.
- [12] S. Fay, L. Feitknecht, R. Schlüchter, U. Kroll, E. Vallat-Sauvain, A. Shah, Rough ZnO layers by LP-CVD process and their effect in improving performances of amorphous and microcrystalline silicon solar cells, *Sol. Energy Mater. Sol. Cells.* 90 (2006) 2960–2967.
- [13] J. Hüpkens, B. Rech, O. Kluth, T. Repmann, B. Zwaygardt, J. Müller, R. Drese, M. Wuttig, Surface textured MF-sputtered ZnO films for microcrystalline silicon-based thin-film solar cells, *Sol. Energy Mater. Sol. Cells.* 90 (2006) 3054–3060.

- 206 [14] T. Tohsophon, J. Hüpkes, H. Siekmann, B. Rech, M. Schultheis, N. Sirikulrat, High rate
207 direct current magnetron sputtered and texture-etched zinc oxide films for silicon thin
208 film solar cells, *Thin Solid Films*. 516 (2008) 4628–4632.
- 209 [15] O. Kluth, B. Rech, L. Houben, S. Wieder, G. Schöpe, C. Beneking, H. Wagner, A. Löffl,
210 H.W. Schock, Texture etched ZnO:Al coated glass substrates for silicon based thin film
211 solar cells, *Thin Solid Films*. 351 (1999) 247–253.
- 212 [16] W. Böttler, V. Smirnov, J. Hüpkes, F. Finger, Variation of back reflector morphology in
213 n–i–p microcrystalline silicon thin film solar cells using texture-etched ZnO, *J. Non.*
214 *Cryst. Solids*. (2012) 2474–2477.
- 215 [17] W. Böttler, V. Smirnov, A. Lambertz, J. Hüpkes, F. Finger, Window layer development
216 for microcrystalline silicon solar cells in n-i-p configuration, *Phys. Status Solidi C*. 7
217 (2010) 1069–1072.
- 218 [18] M. Warzecha, PhD Thesis, Forschungszentrum Jülich, 2012.
- 219 [19] T. Söderström, F.-J. Haug, V. Terrazzoni-Daudrix, C. Ballif, Optimization of amorphous
220 silicon thin film solar cells for flexible photovoltaics, *J. Appl. Phys.* 103 (2008) 114509–
221 1–114509–8.
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Fig. 1: Structures of the solar cells on PI without (a) and with (b) textured ZnO:Ga layer.

Fig. 2: I-V parameters of solar cells with different *i*-layer silane concentrations deposited on PI/Ag/ZnO (full symbols) and glass/Ag/ZnO (open symbols).

Fig. 3: Raman crystallinity as a function of the *i*-layer silane concentration of solar cells deposited on PI (full symbols) and glass (open symbols). Lines are guides to the eye.

Fig. 4: Comparison of the I-V curves of solar cells on PI/Ag/ZnO (plain curve) and glass/Ag/ZnO (dashed curve).

Fig. 5: Comparison of EQE's of solar cells on PI/Ag/ZnO (dashed line) and PI/textured ZnO:Ga/Ag/ZnO (full line).

Fig. 6: Comparison of the I-V curves of solar cells on PI/textured ZnO:Ga /Ag/ZnO (plain curve) and glass/textured TCO/Ag/ZnO (dashed curve).

Table 1: I-V parameters of solar cells under AM1.5 illumination.

Substrate type	Voc (mV)	Jsc (mA/cm ²)	FF (%)	η (%)
Smooth glass	521	20.7	72.7	7.9
Smooth PI	505	18.9	70.7	6.8
Glass+rough TCO	525	22.8	71	8.5
PI+rough ZnO:Ga	475	23.1	68	7.5