ANTI-REFLECTION LAYER AT THE TCO/Si INTERFACE FOR HIGH EFFICIENCY THIN-FILM SOLAR CELLS DEPOSITED ON ROUGH LP-CVD FRONT ZnO

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ABSTRACT: ZnO layers with a wide range of surface roughness and morphologies can be deposited by low pressure chemical vapor deposition (LP-CVD). In this paper, we investigate the effect of a low-resistivity TiO_2-ZnO bi-layer incorporated as an anti-reflection coating between the rough ZnO front transparent conductive oxide (TCO) and the silicon layer, for thin film p-i-n microcrystalline silicon solar cells. The TiO_2 layers are deposited by reactive rf-sputtering from a Ti target with a H_2O/Ar gas mixture. We study the potential of this coating with respect to TCO surface roughness and morphology and we show that with a TiO_2 layer of 55 nm, having a refractive index of ~2.5 at 550 nm we can decrease the reflectance of typical μc-Si:H solar cell at 550 nm down to 6 %, corresponding to reflectance at the glass interfaces only. Depending on the TCO properties, increases in short-circuit current density ranging from 1.7 to of 3.8 % are obtained, the latter value is obtained for a ZnO layer particularly suitable for the growth of microcrystalline silicon solar cells.
Keywords: Antireflection Coating, TiO_2, Micro Crystalline Si

1 INTRODUCTION

Light shining onto a thin film solar cell is partially reflected at the interfaces between different materials before reaching the photo-active layers. This effect reduces the current generated by the cell and therefore has to be minimized. The reflections, due to abrupt changes of the refractive index at the interfaces, can be reduced by two different means: by inserting additional layers with intermediate refractive indices (index matching) [1] or by roughening the interface with surface structures having sizes comparable to the light wavelength (index grading) [2].

In a typical thin-film p-i-n microcrystalline silicon (μc-Si:H) solar cell, the incident light is partially reflected at the air/glass, glass/ZnO and ZnO/silicon interfaces before it is mostly absorbed in the photo-active silicon layer. Using the Fresnel equations, the approximate refractive indices of 1/1.5/2/4 for air/glass/ZnO/silicon at 550 nm, assuming flat interfaces and neglecting interference effects, a primary reflection of 4 % at the air/glass interface, 2 % at the glass/ZnO interface and 11 % at the ZnO/Si interface is obtained. The first two reflections can be minimized with industry standard anti-reflection coatings (ARC) on glass [1]. The reflection at the ZnO/Si interface is reduced due to the index grading caused by the roughness of the front TCO layer, primarily used to improve light trapping in p-i-n μc-Si:H solar cells.

In our study, a rough as-grown ZnO deposited by low-pressure chemical vapor deposition (LP-CVD) is used as front transparent conductive oxide (TCO). A surface treatment (ST) is then used to modify the morphology, which has been shown to significantly improve open-circuit voltage (Voc) and fill-factor (FF) of μc-Si:H solar cells [3,4]. This treatment, however, reducing the root-mean-square (RMS) roughness (σ_{RMS}) of the ZnO surface, and changing the surface morphology from V- to U-shape, increases the reflection loss at the TCO/Si interface. This trade-off between electrical characteristics and optical absorbance is limiting the efficiency of our μc-Si:H solar cells. We therefore introduce a TiO_2/ZnO bi-layer ARC between the ZnO and the p-layer, as proposed by Matsui [5] to decrease reflection losses while keeping TCO morphology favorable for high Voc and FF.

2 EXPERIMENTAL

Boron-doped ZnO, deposited by LP-CVD on Schott AF45 glass, is used as front TCO. The rough ZnO layer is modified by a surface treatment procedure as shown in Fig. 1 [3,4]. The TiO_2 layers are deposited on the ZnO layer by reactive rf-sputtering of a Ti target at 3 W/cm^2, with a H_2O/Ar gas mixture containing less than 10 % H_2O, resulting in a deposition rate of ~2 nm/min. Compared to sputtering of a ceramic TiO_2 target, as reported by Matsui [5], reactive sputtering has the advantage that the stoichiometry of the film can be controlled by adjusting the H_2O/Ar gas mixture. This allows us to produce sub-stoichiometric layers with lower resistivity as compared to pure TiO_2 layers [6]. A thin ZnO layer (~10 nm) is then added in the same deposition system by rf-sputtering of a ZnO:Al target to ensure a good electrical contact to the p-layer and avoid the reduction of TiO_2 [5].

The microcrystalline silicon (μc-Si:H) p-i-n solar cells are deposited in the p-i-n configuration by plasma enhanced chemical vapor deposition, at very high frequencies (50-150 MHz) [7].
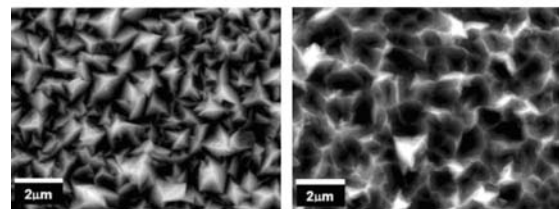

Fig. 1: SEM images of LP-CVD ZnO front contact rough as-grown (left) and after long surface treatment (right).

The σ_{RMS} of the different TCO surfaces is calculated from non-contact AFM measurements. The optical constants of the TiO_2 layer are obtained from spectroscopic ellipsometry measurements. Optical reflectance is measured between 320 nm and 2000 nm with a Perkin-Elmer photo-spectrometer, type lambda 900. The absorbance of the cell is calculated by subtracting the measured reflectance from unity, because the transmittance is zero due to the opaque back reflector used for the solar cells. The short-circuit current density (J_{sc}) of the solar cells is calculated from the measurement

of the external quantum efficiency (EQE) curve, by integrating, over the wavelength range from 350 to 1100 nm, the product of EQE times the incoming photon flux of the AM1.5g solar spectrum. The internal quantum efficiency (IQE) is obtained from the division of the EQE by the absorbance. The current-voltage curves are measured under a dual lamp WACOM solar simulator in standard test conditions (25 °C, AM1.5g spectrum, 1000 W/m^2).

3 RESULTS AND DISCUSSION

3.1 Optical and electrical properties of TiO$_2$ layers

The optical constants of the TiO$_2$ layers are plotted in Fig. 2. The layers deposited under the aforementioned conditions have negligible absorption for wavelengths above 400 nm, avoiding thereby absorption losses in the useful part of the solar spectrum. Below 400 nm, the absorption of the light by the TiO$_2$ layer has negligible effect since most of the light is absorbed by the front TCO. The refractive index of 2.47 at 550 nm is close to 2.76, the geometrical average of the refractive indices of ZnO and Si, necessary to minimize the reflection losses. For ~ 100 nm thick TiO$_2$ layers deposited on glass, in-plane resistivities between 10^4 and 10^6 Ωcm are measured.
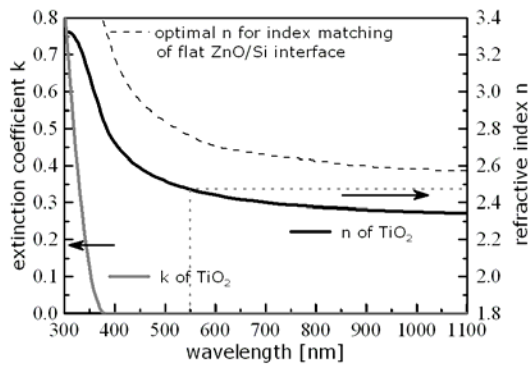

Fig. 2: Optical constants of TiO$_2$ layer determined by spectroscopic ellipsometry measurements

3.2 Reflection at the TCO/Si interface

To evaluate the potential of TiO$_2$ ARC for thin-film silicon solar cells we deposited μc-Si:H cells on a variety of different TCOs with different surface roughness and morphologies with and without TiO$_2$ ARC. Figure 3 shows the reflectance at 550 nm of these cells vs. the σ_{RMS} of the TCO surface. Light with the wavelength of 550 nm shows only little absorption in the front TCO, but is fully absorbed in the Si layer and is thus used hereafter to study the reflection originating from the TCO/Si interface. A lower limit for the reflectance of μc-Si:H cells deposited on a ZnO front contact can be fixed at 5.9 %, which is the calculated Fresnel reflection for the flat air/glass/ZnO interfaces (dashed line), which remain unchanged in this study. The deposited ZnO layers are relatively thick (1 - 4 μm) and we assume therefore that there are no interference effects. The calculated Fresnel reflection for flat air/glass/ZnO/Si and air/glass/ZnO/TiO$_2$/Si interfaces is shown by the open square and the open triangle respectively.

At 550 nm, an increase of the reflectance above 5.9 % can be assumed to originate from the ZnO/Si interface, since the transmitted light with this wavelength is entirely absorbed in the active layer. From Figure 3 it appears clearly, that the reflection at the ZnO/Si interface is

negligible for the rough as-grown ZnO having a σ_{RMS} of 190 nm. Adding the TiO$_2$ ARC does not change the reflectance in this case. The in-plane feature size (δ) of this ZnO is ~ 1 μm. With increasing ST time the surface changes from V- to U-shaped morphology and the σ_{RMS} decreases from 190 to 110 nm, but the bulk properties of the TCO do not change [3,4]. The surface morphology obtained after the longest ST is the most desirable for improving the electrical properties of μc-Si:H cells, but it increases the reflectance at the ZnO/Si interface to 2.3 %, thus decreasing the J_{sc} of the cell. With the TiO$_2$ ARC the reflectance at the ZnO/Si interface can be reduced to nearly zero and the total reflectance is brought back to ~ 6 % for all the treated surfaces, while conserving the desired surface roughness and morphology.
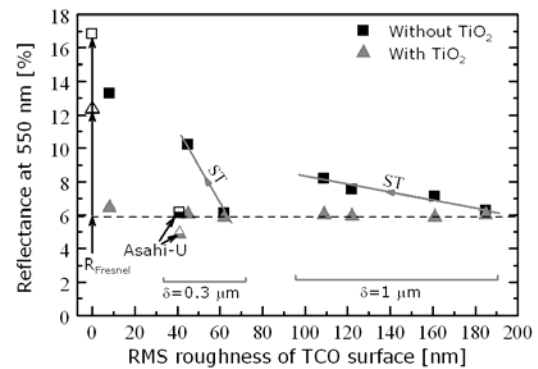

Figure 3: Reflectance at 550 nm of a μc-Si:H cell deposited on different ZnO layers with different surface roughness and morphology with (■) and without (▲) TiO$_2$ ARC. SnO$_2$ Asahi-U (half symbols) and calculated Fresnel reflection due to the flat interfaces (empty symbols) are also plotted. R$_{Fresnel}$ for the flat air/glass/ZnO interfaces is shown by the dashed line.

Reflectance for a LP-CVD ZnO with smaller feature size ($\delta \approx 300$ nm) is also shown in Fig. 3. The reflectance at the TCO/Si interface is negligible for the ZnO as deposited. With the surface treatment, the σ_{RMS} is here decreased from 62 to 45 nm and the reflectance increases from 6.1 to 10.2 %, but can still be offset with the ARC. On a relatively flat ZnO deposited by sputtering ($\delta \approx 100$ nm) the reflectance reaches 13.2 %, but can be reduced to 6.4 % with the TiO$_2$ ARC. For comparison, the same measurement has been conducted on a SnO$_2$ TCO (Asahi U-type) with an in-plane feature size of ~ 300 nm. The reflectance at 550 nm without TiO$_2$ is 6.2 % and is reduced to 4.9 % with the TiO$_2$ ARC. Such a low value for the reflectance is most likely linked to interference effects in the SnO$_2$ layer, which is a factor 2 to 3 thinner than the LP-CVD ZnO layers.

The proposed TiO$_2$ ARC decreases the reflectance at the ZnO/Si for the entire useful part of the solar spectrum, but reaches minimal values only for the wavelengths between 500 and 600 nm. The reflectance at the rough TCO/Si interface is influenced by the surface feature size and its shape. To predict the exact behavior of such optical interfaces is not yet possible, because it would require a full solving of the Maxwell equations for highly complicated systems, which is at the limit of what current computer can achieve. On the contrary, reflectance measurement is an easy tool to characterize the TCO's impact on solar cell performance and evaluate the potential current gain with a TiO$_2$ ARC.

3.3 Optical effects of the TiO$_2$ layers in µc-Si:H cells

Figure 4 shows the reflectance of four cells fabricated in one deposition run. Two standard cells without ARC (black lines) are deposited on LPCVD-ZnO with different surface morphologies, obtained after a short (dotted lines) and a long (solid lines) surface treatment. The long surface treatment decreases the σ_{RMS} of the ZnO from 180 to 91 nm with respect to the short ST, leading to an increase in reflectance from 7.0 to 10.2 % at 550 nm. The grey lines show the reflectance of the same cells deposited on the same TCOs, but with a TiO$_2$ ARC added between the ZnO and the Si layer. The TiO$_2$ layer of ~55 nm decreases the reflectance at 550 nm from 7.0 to 6.0 % and from 10.2 to 6.4 % for the TCO prepared with a short and long surface treatment, respectively. The primary reflectance due the flat air/glass/ZnO interfaces calculated form the Fresnel equation is shown on the same graph (dashed line) and fixes a lower limit for the reflectance of the entire solar cell, if no other ARCs are used on the glass interfaces. Between 500 and 600 nm, the grey lines touch the dashed line, meaning that the reflection at the ZnO/Si interface is nearly zero in this range. The reflectance of the cell increases strongly from 600 to 1100 nm due to the portion of the light reflected at the opaque back reflector and leaving the cell without being absorbed. For wavelengths above 1100 nm the reflectance decreases again due to increasing free carrier absorption in the ZnO layers.
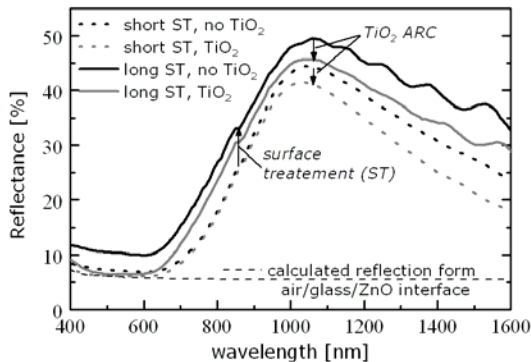

Fig. 4: Reflectance of four cells fabricated in one run deposited on a TCO prepared with a short and a long surface treatment, with and without TiO$_2$ ARC.

Figure 5 shows the EQEs and IQEs of the same four cells as in Fig. 4. The good superposition of the two IQE curves for the cells deposited on the same TCO demonstrates that the presented results are free from artifacts caused by possible layer inhomogeneities. For the TCO prepared with a short ST, the EQE at 550 nm increases from 86 to 87 % due to the insertion of the TiO$_2$ ARC. For the TCO exposed to a long ST the EQE increases from 82 to 86 %. Integrated over the whole solar spectrum, this leads to an increase in J_{sc} from 25.06 to 25.48 mA/cm^2 and from 23.38 to 24.27 mA/cm^2, which represents a relative current gain of 1.7 % and 3.8 %, respectively.

On the best cell that showed a relative increase in J_{sc} of at least 2%, we measured an increase in series resistance of 0.2 Ωcm^2. From such an increase in series resistance we can expect an absolute loss in FF of 0.6 % [8] and thus a final relative increase in efficiency of 1.5-2 % for a µc-Si:H solar cell. For tandem micromorph cells with twice less current this series resistance effect will be negligible.
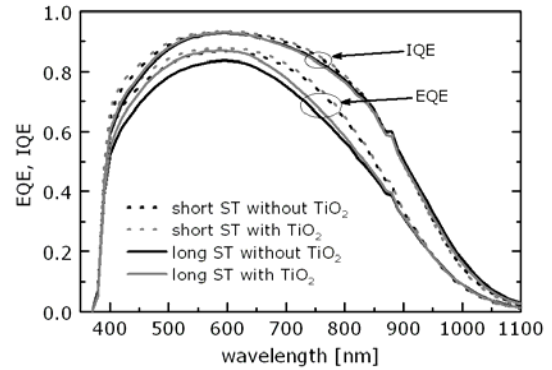

Fig. 5: EQE and IQE of four cells fabricated in one run deposited on a TCO prepared with a short and a long ST, with and without TiO$_2$ ARC.

4   CONCLUSION

Optical measurements reveal that the reflection at the ZnO/Si interface in a typical p-i-n µc-Si:H solar cell as produced in our laboratory contributes to the total reflectance of the cell and therefore decreases its current density. With a TiO$_2$ layer deposited by reactive sputtering of a Ti target, we can reduce the reflection at this interface to nearly zero for a wide variety of different interface roughness and morphologies. For µc-Si:H deposited on a ZnO exposed to a long surface treatment, the total reflectance at 550 nm decreases from 10.2 % to 6.4 % by adding the TiO$_2$ ARC, increasing this way the J_{sc} by 3.8 % from 23.38 to 24.27 mA/cm^2.

For the thin-film silicon solar cells deposited on LP-CVD ZnO exposed to a surface treatment the ARC seems promising to overcome the limitations imposed by the trade-off between electrical characteristics and optical absorbance, opening new ways to a further increase of solar cell efficiencies.

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