ITO/SiO_x:H Stacks for Silicon Heterojunction Solar Cells

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ABSTRACT

A method of reducing optical losses in the transparent conductive oxides (TCO) used in silicon heterojunction solar cells without compromising with series resistance is described. In the method the thickness of a TCO is reduced two-three times and a hydrogenated dielectric is deposited on top to form a double layer antireflection coating. The conductivity of a thin TCO is increased due to the effect of hydrogen treatment supplied from the capping dielectric during the post deposition annealing. The optimized cells with ITO/SiO_x:H stacks achieved more than 41 mA/cm² generation current on 120-micron-thick wafers while having approximately 100 Ohm/square sheet resistance. The paper also considers integration of ITO/SiO_x:H stacks with Cu plating and using ITO/SiN_x/SiO_x triple layer antireflection coatings.

Keywords: silicon heterojunction solar cells, transparent conductive oxides

1. INTRODUCTION

Silicon heterojunction (SHJ) technology can achieve very high solar cell efficiency and potentially provide low cost in high volume manufacturing [1]. In conventional SHJ cells doped a-Si films are deposited on both sides of the wafer to form p- and n-type carrier collectors. Usually a transparent conductive oxide (TCO) is formed on top of the doped a-Si films to achieve lateral conductivity and good ohmic contact with metal electrodes. On the front side of the cell TCO also serves as an antireflection coating, while at the rear side it can be optimized in conjunction with a corresponding metal layer to form an infrared reflector.

Optimization of TCO layers in SHJ solar cells is a subject of multiple tradeoffs between optical, recombination and series resistance losses. The TCO requirements usually include, but not limited to the following: (1) refractive index close to 2.0 to serve as an antireflection coating on top of silicon wafer; (2) transparency in the entire ‘silicon solar’ range from 350 to 1200 nm for the front layer [2], transparency in the approximately 800 and 1200 nm to avoid parasitic absorption of the IR light for the rear layer [3]; (3) TCO on the front side should provide a necessary lateral conductivity, which is determined by the design of the front grid and is usually in 50-100 Ω/□ range; (4) both TCOs should achieve a good ohmic contact with the corresponding metal electrodes and doped a-Si films, where Schottky barriers can be formed [4]; (5) deposition of the TCO should not damage the underlying a-Si film [5] and should not induce a change in the a-Si/c-Si heterojunction reducing the performance of a SHJ solar cell [6]; (6) the TCO should not cause reliability issues not to contribute to the degradation and failures in the field.

It is often the case, that material properties favorable for certain design requirements are harmful to the others. As a result of the tradeoffs between the listed requirements most SHJ cells including record cells usually have lower J_{SC} compared to diffused junction cells (for most reported cells <40 mA/cm²) with a characteristic low response of the external

quantum efficiency (EQE) in 350-600 nm range. This is partly due to the absorption in the front a-Si films, but also due to the absorption in the front TCO. Also, if not optimized, rear TCO/metal stack can cause significant absorption in IR part of the spectrum leading to additional J_{SC} losses.

In this paper we report using ITO/SiO_x:H stacks on the front and on the rear sides of SHJ cell to reduce optical losses without compromising with series resistance or recombination. The idea behind this structure is that SiO_x:H on the front can serve as a second antireflection coating to allow thinner TCO absorbing less light [7]. At the same time conductivity of a thin TCO can be maintained at a sufficient level due to the effect of hydrogen treatment, where hydrogen is supplied from SiO_x:H during post-deposition annealing. At the rear side thin-ITO/SiO_x:H/Ag stack can be a superior rear mirror compared to a conventional thick-TCO/Ag stack with less parasitic absorption in 800-1200 nm range.

The effect of hydrogen doping of ITO from hydrogenated PECVD films was recently reported by Ritzau et al., where the observed increase of ITO conductivity during a post deposition annealing in a standard SHJ cell was attributed to hydrogen effusion from underlying a-Si films [8]. Hydrogen was also reported to promote crystallinity of certain TCOs, for example, IO and ICO, if supplied to the chamber during their deposition [9][10]. Thus, it can be expected that hydrogen treatment of post deposited ITO films not only increases free carrier density, but can also improve mobility. In our approach the starting ITO films have the thickness of 30-50-nm and a relatively high oxygen content with very low carrier density. Such films with 150-200 nm thickness would normally be used at the rear side of the cell as IR mirrors. The conductivity of these films is increased after SiO_x:H deposition and annealing. This approach allowed us to achieve 41-41.3 mA/cm² generation current (J_{gen}) on 120- μ m-thick double side textured wafer, while keeping the sheet resistance ($R_{\square}$) of the front ITO film equal to 100 $\Omega/\square$.

In this study SHJ cells with metal electrodes deposited on ITO were simply coated with a PECVD SiO_x:H film. Although not preventing probing the cells, this approach would make soldering Cu ribbons to the busbars challenging. Thus, in the actual solar cell with ITO/SiO_x:H stack an additional patterning process would need to be used in order to form a front metal grid. In this paper we report one method, where SiO_x:H is patterned by the lift off of the screen printed resist and Cu is plated in the openings by light induced plating.

2. EXPERIMENTAL DETAILS

To optimize ITO/SiO_x:H stacks we only used J_{gen} and $R_{\square}$ measured on complete SHJ solar cells. SHJ cells with the junction on the front side were used. Therefore sheet conductivity between metal fingers on the front was only due to the ITO film. SHJ cells were made on n-type CZ wafers with 3-4 Ω -cm resistivity. The thickness of the wafers after texturing was approximately 120 μ m. A-Si films were deposited on both sides of the wafers followed by ITO sputtering and sputtering of the rear Ag contact. Front metal grid was either formed by screen printing of Ag paste to make 10x10 cm² cells or by photolithographic patterning of the sputtered Ag film to make 1x4 cm² cells. Screen printed cells had three 1-mm-wide busbars and approximately 100- μ m-wide fingers. Photolithographically patterned cells had 20- μ m-wide fingers and featured a busbar around the perimeter of the cell defining its area. Finally, the cells were capped with dielectric layers and annealed in a muffle furnace at 200 °C for 30 min. More details of ASU SHJ solar cell process can be found elsewhere [11]-[12].

ITO films were reactively sputtered at room temperature using MRC 944 tool with a DC power supply. ITO target with 90/10 In₂O₃/SnO₂ ratio was used. Oxygen flow and deposition pressure were varied. A-Si and SiO_x:H films were deposited using Applied

Materials P-5000 PECVD tool. $\text{SiO}_x\text{:H}$ films were previously measured by RBS to have approximately 25% hydrogen by the number of atoms [13]. The thickness of $\text{SiO}_x\text{:H}$ and ITO films was measured using Woollam M-2000 ellipsometer. Optical modelling was done using Opal 2 and Ray Tracer software developed by PVLighthouse [14]. In simulations we used optical constants of hydrogenated ITO and $\text{SiO}_x\text{:H}$ films measured by ellipsometry. The results of the modelling suggested the optimum combination of ITO and $\text{SiO}_x\text{:H}$ to be 40-50 nm and 90-110 nm respectively (providing that this ITO achieves the conductivity required for a particular grid design). IV curves of the cells were measured on a flash IV tester from Sinton Instruments using an NREL certified cell as a reference.

3. RESULTS AND DISCUSSION

3.1. EQE and $R_{\square}$ of SHJ cells with ITO/ $\text{SiO}_x\text{:H}$ stacks

Figure 1(left) compares $R_{\square}$ measured on p-side-up SHJ solar cells having 80-nm-ITO with $R_{\square}$ measured on the cells having 50-nm-ITO/100-nm- $\text{SiO}_x\text{:H}$ stack on the front side. On the rear side the cells had a thick-ITO/Ag stack optimized to work as an IR mirror. It follows that capping ITO with $\text{SiO}_x\text{:H}$ can increase its conductivity 2-3 times depending on the initial oxygen content in ITO film and sputtering pressure. The same effect was observed, if ITO was capped by $\text{SiN}_x\text{:H}$ and a-Si:H films. Thus, our results are in agreement with the data obtained by Ritzau et al, for the films doped from underlying a-Si:H films. Similarly we observed 20-40% increase of ITO conductivity after annealing when it is sputtered on a-Si:H films versus being sputtered on glass or crystalline silicon.

FIG. 1. $R_{\square}$ and J_{gen} as a function of oxygen flow and sputtering pressure varied during ITO sputtering for the front emitter SHJ cells having 80-nm-ITO and 50-nm-ITO/100-nm- $\text{SiO}_x\text{:H}$ stacks.

Figure 1(right) shows J_{gen} measured on p-side-up SHJ cells prepared for this study. 50-nm-thick ITO films capped with $\text{SiO}_x\text{:H}$ demonstrated a superior optical performance when sputtered with high oxygen dilution. The cells with the optimum ITO film (for example, sputtered at 5 mTorr pressure and 2 sccm O_2 flow), achieved $40.5 \text{ mA}/\text{cm}^2$ J_{gen} and 90-100 $\Omega/\square$ $R_{\square}$, which is approximately $1 \text{ mA}/\text{cm}^2$ higher than the cells with a single optimized 80-nm-thick ITO layer with almost no loss in sheet resistance. Such $R_{\square}$ would be sufficient for use with most front grid designs with an acceptable series resistance loss.

It is possible that a similar performance could be achieved by using a conventional low oxygen ITO film normally having about $50 \Omega/\square$ $R_{\square}$ (being 80 nm thick) capped with a low index dielectric not containing hydrogen. This can be, for example, thermally evaporated MgO or RF sputtered SiO_x . In this case ITO is not excessively doped by hydrogen and can provide the necessary transparency. A better understanding of the effect of hydrogen

treatment on material properties of ITO can help to guide the design of ITO/dielectric stacks.

Further improvement of the optical response of SHJ cells is possible providing reducing parasitic IR absorption at the rear side of the cell. In this study we replaced a conventional 200-nm-ITO/Ag stack with a 20-nm-ITO/200-nm-SiO_x:H/Ag stack. To make a contact with Ag, SiO_x:H was immersed in HF solution prior to Ag sputtering. This process presumably created local openings in PECVD SiO_x:H due to its porous structure and was sufficient to make a contact to the sputtered Ag for EQE measurement. Thus, EQE data represents mostly ITO/SiO_x:H/Ag structure with some fraction of ITO/Ag. Note that such structures were prepared only for EQE measurement, which is done at short circuit with minor influence of the series resistance. It is expected that the used method can lead to the additional lateral and contact resistance effecting a FF of the solar cell. A better patterning method would need to be implemented to produce functional solar cells with ITO/SiO_x:H/Ag stacks at the rear side.

Figure 2 compares EQE of a conventional SHJ cell with the EQE of the cells having ITO/SiO_x:H stacks on the front and on both front and rear sides of the cell. It follows that a thinner ITO together with a lower reflectance double layer antireflection coating allows better response in 300-500 nm and 700-1050 nm wavelength ranges. In its turn improving rear IR mirror allowed better IR response in 1000-1200 nm range and added another 0.7 mA/cm² to the overall J_{gen}. Interestingly, improving a rear mirror in this study was equivalent to using a thicker wafer. For example, SHJ cells with 20-nm-ITO/SiO_x rear mirror made on a 120-μm-thick wafer had a similar IR performance (~60%-70% EQE at 1100 nm) to a 230-μm-thick cell having a conventional 200-nm-ITO/Ag stack.

FIG. 2. EQE of p-side-up 120-μm-thick SHJ cells having three different optical structures.

3.2. Simulation of SHJ cells with ITO/SiN_x/SiO_x stacks.

For some cell designs optical losses can be further reduced by using even thinner ITO films. For example, in the cells with 10-μm-wide fingers the spacing between the fingers can be less than 1 mm, which allows using TCOs with 200-300 Ω/□ R_□. Such fingers can be produced, for example, by laser patterning and Cu plating. Another example is the cells with a rear emitter, where lateral conductivity between the fingers is increased by the conductivity of the bulk of the wafer [15]. In SHJ cells at maximum power point operation the bulk can have 1×10¹⁵-3×10¹⁵ cm⁻³ excess carrier density, which provides approximately 100-300 Ω/□ lateral conductivity in 120-μm-thick wafers.

Thus, the thickness of ITO can be reduced even more, down to 10-20 nm. The limit for the thickness reduction will depend on the interaction between metal grid and doped a-Si and other considerations such as metal contact adhesion and reliability. In the extreme design TCO can be eliminated altogether and completely excluded from optical losses.

However the cells with a very thin ITO (<50 nm) films will require using dielectrics with higher index in addition to SiO_x to complete antireflection properties. For example a transparent low temperature SiN_x can be used. Figure 3 shows simulated EQE curves for the structures with 10-nm-ITO/ SiN_x / SiO_x stacks. Simulation suggests that J_{gen} of such structures can reach 42 mA/cm^2 .

FIG. 3. Simulated EQE of p-side-up SHJ cells comparing optical response in 50-nm-ITO/ SiO_x and 20-nm-ITO/ SiN_x / SiO_x structures.

3.3. Solar cells performance

Table I summarizes the performance of the best SHJ solar cells having ITO/ SiO_x :H stacks on the front side. No effect of capping ITO with SiO_x :H on the cell performance besides reducing sheet resistance and improving optical response discussed above was observed. The full potential of the stack was realized in $1 \times 4 \text{ cm}^2$ cells having 20- μm -wide photolithographically patterned fingers. The front grid shading in these cell comprised approximately 2% allowing $>40 \text{ mA/cm}^2$ J_{SC} . Note also that these cells had optimized a-Si films on the front side allowing a better response in visible range. The rear side of the cells had a conventional 200-nm-ITO/Ag stack.

TABLE I. The parameters for the record SHJ cells, which were using ITO/ SiO_x stacks.

Cell type	V_{oc} (mV)	J_{gen} (mA/cm^2)	J_{sc} (mA/cm^2)	pFF (%)	FF (%)	η (%)
$10 \times 10 \text{ cm}^2$, screen printing	727	40.6	37.9	81.6	78.2	21.5 ¹
$1 \times 4 \text{ cm}^2$ photolith., floating busbar	739	41.3	40.6	82.0	78.0	23.4 ²

¹confirmed at NREL, ²in-house measurement

3.4. Integration with Cu plating

This study reported solar cells with a SiO_x :H layer deposited after the formation of the front metal grid, which would make soldering the cells problematic. To resolve this issue we have developed a process flow, which is using SiO_x as a mask for Cu plating. To pattern SiO_x a resist grid was screen printed on ITO followed by the deposition of SiO_x on top of the resist. Next the resist was lifted using an alkaline solution to make openings in dielectric. Thus, a dielectric mask for Cu plating was formed. Then, for example, a Ni/Cu/Sn could be plated in the openings using light or field induced plating. In this study

we used an alternative seeding method, which allowed direct Cu/Sn plating on ITO with a superior adhesion. The cells processed this way in our lab achieved 20% efficiency on 153 cm² area with parameters: 729 mV V_{OC} , 36.1 mA/cm² J_{SC} and 75.9% FF.

4. CONCLUSION

We reported a new method to improve optical response of SHJ cells by using ITO/SiO_x:H stacks and described a method to integrate these stacks with Cu plating. It was demonstrated that conductivity of the sputtered ITO films can be increased by treating them with hydrogen supplied from PECVD dielectrics. SHJ cells with the optimized ITO/SiO_x stacks on both sides of the cells produced up to 41 mA/cm² J_{gen} with 100 $\Omega/\square$ sheet resistance while the best structures achieved 41.3 mA/cm². Modelling suggested that further reducing the thickness of ITO and using it in ITO/SiN_x/SiO_x stacks with advanced cell designs allowing 300 $\Omega/\square$ can further increase J_{gen} to 42 mA/cm². However, to fully realize the potential of ITO/SiO_x:H stacks, more work is required to understand the mechanism of increasing conductivity in ITO films capped with hydrogenated dielectrics.

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Figure 1
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