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Electrical investigation of ITO films in Al-doped crystalline silicon solar cells

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Abstract

Low temperature processing of crystalline Si solar cells is attractive due to lower wafer and manufacturing costs. For thinner silicon wafers, thermal mismatch between Al and Si at high temperatures leads to thermal stress and wafer bowing. In this paper, replacement of back surface Al BSF contact by ITO films has been investigated as a function of Al-doping level. ITO films were deposited on back Si surfaces with sheet resistances in ~16–48Ω/□ range. ITO/Si contact resistance increases slightly as sheet resistance is reduced, however, the variation is not significant. At sheet resistance of 25Ω/□, solar cell performance comparable to conventional AL BSF configuration. Even at sheet resistance ~50Ω/□, it is possible to form high quality ITO/Si contact. The role of surface defects has been deemed to be critical. Without etching of Al-doped surface, surface quality is poor due to defects originating from the Al-alloy formation. As these defects are removed with controlled etching, a more pristine surface emerges that forms superior contacts with ITO film.

1. Introduction

Crystalline silicon (c-Si) solar cells dominate the photovoltaic (PV) market. The c-Si wafer accounts for almost 40% of the production cost of the PV module[1]. Therefore, systematic reduction in wafer thickness, and thus the amount of crystalline material used, has been used to reduce PV module production cost. At present, the thickness of industrially produced Si wafers in solar cells is approximately 200 μm and research efforts have been focused on achieving 120-μm thick wafer solar cells in production in next decade[2].

In industrially-produced, monofacial, c-Si solar cells, an Al-doped region, known as the back surface field (BSF), located on the rear surface is used to enhance electrical and optical performance of the solar cell[3]. This BSF region is formed screen printing and high temperature sintering of aluminum (Al) paste in an infra red belt furnace[4]. In c-Si solar cells, the optimised device configuration requires base thickness of ~300 μm[5]. This thickness requirement is relaxed to enable comparable efficiencies at significantly lower thickness reducing surface recombination velocity (SRV) and creating an electric field in the high-low BSF junction configuration[6].

However, another problem arises when applying the Al BSF layer to thin wafer c-Si solar cells which is bowing phenomenon[7]. Typically, bowing and residual stress occurs during the fabrication of c-Si solar cells; back-surface field (BSF) formation. The degree of wafer bowing strongly depends on the thermal conditions during Al paste sintering[8]. This phenomenon arises from mismatch of the thermal coefficient of expansion (TCE) between the silicon and the rear contact aluminum layers[9, 10]. Figure 1 shows an example of severe bowing in 6-inches diameter Si wafers with 100% Al paste coverage on the rear side. Under identical thermal processing conditions, the thinner (~200 μm) suffers from severe bowing almost to the breaking point, which for the thicker (~600 μm), the bowing is acceptable. Therefore, a low temperature process is required to overcome wafer bowing in p+p back back surface field solar cells.
Indium tin oxide (ITO) layers are widely used as contact layers in thin film solar cells and heterojunction with intrinsic thin layer (HIT) solar cells due to their high conductivity, high refractive index, low contact resistance, and transparency in the visible range of the solar spectrum \cite{11, 12}. The most significant feature of HIT solar cells relates to photo-generated charge carrier collection by transition through intrinsic hydrogenated amorphous-Si (i-a-Si:H), doped a-Si:H film and ITO layers before collection by metal electrodes \cite{13, 14}. Due to low conductivity of these i-a-Si:H and doped a-Si:H films, metal electrodes alone, as in a conventional cell, are insufficient to collect all charge carriers \cite{15}. Therefore, the higher conductivity of ITO film plays a dominant role in HIT solar cells.

In HIT solar cells, the doping of a-Si thin films requires toxic gases such as phosphine (PH$_3$) and diborane (B$_2$H$_6$) for n- and p-type doping respectively \cite{16–19}. For long-term environmental sustainability it is important to have completely non-toxic processing approach. The ITO/Al-doped contact offers that potential for both non-toxic and low-temperature processing. This concept can also be applied to TOPCon solar cells \cite{20}.

Even though, conventional, high temperature processes have been applied to form Al BSF in this paper, same results can be achieved using room temperature pulsed laser processing \cite{21}. Lasers are attractive due to their spectral, temporal, and spatial characteristics and have been extensively used for many solar cells processing applications including diffusion \cite{22, 23}.

In literature, vacuum-deposited ITO films on a-Si surfaces have been investigated in extensive detail, however, there is significant lack of fundamental research on electrical characteristics of ITO films deposited on Al-doped (ITO/p$^+$-Si) surfaces. In order to achieve performance comparable with conventional Al BSF solar cells, contact resistance between the ITO/p$^+$Si layer needs to be $\sim$1.3 $\Omega$ \cite{24}.

The aim of this paper is to investigate electrical properties of ITO films deposited on p$^+$ (Al doped) back surfaces on p-type wafers in solar cell configuration.

2. Material and methods

For this study, we used solar grade silicon wafers grown by the Czochralski method, p-type, boron doped, resistivity of 1–3 $\Omega$cm and 100 orientation. The thickness of the wafers was approximately 200 $\mu$m. Figure 2 describes the four solar cell configurations, which have been described below.

i. Figure 2(a) describes conventional monofacial solar cell with front Ag contact and back side Al BSF contact,

ii. Figure 2(b) describes monofacial solar cell with identical front surface as in figure 2(a) but with Al-doped, p$^+$ back surface coated with ITO film and low temperature screen-printed, polymer-based conductive Ag paste,
iii. Figure 2(c) describes monofacial solar cell with identical front surface as in figure 2(a) but with Al-doped, p\textsuperscript{+} back surface coated with ITO film only, and

iv. Figure 2(d) describes monofacial solar cell with identical front surface as in figure 2(a) but with Al-doped, p\textsuperscript{+} back surface coated polymer-based conductive Ag paste.

Conventional solar cell fabrication details have been described elsewhere [25]. For the rear surface ITO and coated polymer Ag solar cells, following procedures were implemented.

i. Al paste was etched off in HCl solution at room temperature in order to retain the BSF layer since this etching solution does not etch the Si [26],

ii. Back surfaces with varying doping levels were subsequently formed by controlled etching in HF:HNO\textsubscript{3} solution,

iii. ITO films were rf sputter-deposited in Applied Films Corporation System 3 equipped with 34 inches target consisting of In\textsubscript{2}O\textsubscript{3}:SnO\textsubscript{2} in 90:10 concentration In\textsubscript{2}O\textsubscript{3}:SnO\textsubscript{2} using 5.0 UHP Argon with partial pressure 4.3 of UHP Oxygen; ITO thickness was ∼147 nm with sheet resistance of ∼15 ohm/square, and

iv. The rear blanket metal based on LF33-750 (Ferro) was screen-printed and baked at 150 °C for 10 min [27].

Figure 3(a) shows cross-sectional field emission view of the ITO film deposited on the Si surface indicating uniform coverage and thickness of ∼150 nm. Figure 3(b) shows EDX analysis of the film demonstrating elemental concentrations typical of ITO films [28].

All solar cells were characterized using an automated current voltage-measurement system with a custom-designed, 100 mW cm\textsuperscript{−2} illumination based on Xenon arc lamps [29]. Figure 4 shows LIV measurements from four types of solar cells with varying rear surface Al-doped sheet resistances. Succinct features of LIV measurements in figure 4 are summarized below.

i. Figure 4(a) plots LIV measurements of back surface with sheet resistance of ∼16.45Ω/□ along with the series resistances for the three solar cell configurations. Red line plot represents LIV measurements with polymer Ag paste on ITO film, black line represents LIV measurement without Ag, and blue line represents LIV measurement with Ag paste without the ITO film. Notice that at this sheet resistance, ITO film response with and without Ag paste is comparable. In contrast, the Ag paste without ITO film leads to significantly higher resistance,

ii. Figure 4(b) plots LIV measurements of back surface with sheet resistance of ∼19.35Ω/□ along with the series resistances for the three solar cell configurations. Red line plot represents LIV measurements with polymer Ag paste on ITO film, black line represents LIV measurement without Ag, and blue line represents
Figure 3. Fields emission scanning electron microscope (SEM) picture (a) and energy dispersive x-ray (EDX) analysis of sputter-deposited ITO on solar cell.

Figure 4. LIV data as a function of p-layer sheet resistance.
LIV measurement with Ag paste without the ITO film. Notice that for this sheet resistance, ITO film response with & without Ag paste is significantly different, and Ag paste without ITO film has lower resistance than the ITO only case,

iii. Figure 4(c) plots LIV measurements of back surface with sheet resistance of $\sim 24.9\Omega/\square$ along with the series resistances for the three solar cell configurations. Red line plot represents LIV measurements with polymer Ag paste on ITO film, black line represents LIV measurement without Ag, and blue line represents LIV measurement with Ag paste without the ITO film. Notice that for this sheet resistance, ITO film response with & without Ag paste is again significantly different, and Ag paste without ITO film has higher resistance than the ITO only case, and

iv. Figure 4(d) plots LIV measurements of back surface with sheet resistance of $\sim 48\Omega/\square$ along with the series resistances for the three solar cell configurations. Red line plot represents LIV measurements with polymer Ag paste on ITO film, black line represents LIV measurement without Ag, and blue line represents LIV measurement with Ag paste without the ITO film. Notice that at this high sheet resistance, ITO film response with & without Ag paste is slightly different, and Ag paste without ITO film has extremely high resistance.

For a baseline comparison, figure 5 plots LIV response from conventional Al BSF solar cell. Open circuit voltage ($V_{oc}$) obtained from the device was 586 mV. The current density is $\sim 35.5 \text{ mA cm}^{-2}$ with 61.5% fill factor and overall efficiency of approximately 12.75%.

3. Result and discussion

In order to understand the results, an approach based on solar cell series resistances has been developed. Total series resistance $R_1$ of Al BSF solar cell (figure 2(a)) can be modelled by

$$R_1 = R_2 + R_3 + R_4$$

(1)

where $R_2$ is Ag/n-Si contact resistance, $R_3$ combined grid and bus bar resistance, and $R_4$ Al/p-Si contact resistance. Similarly, the total series resistance $R_5$ of ITO solar cell (figure 2(b)) can be described by

$$R_5 = R_2 + R_3 + R_6$$

(2)

where $R_6$ is the ITO/p$^+$-Si contact resistance. The total series resistance $R_7$ of polymer Ag/ITO solar cell (figure 2(c)) can be described by

$$R_7 = R_2 + R_3 + R_6 + R_8$$

(3)

where $R_8$ represents the contact resistance of Ag/ITO interface. Finally, the total series resistance $R_9$ of polymer Ag/p$^+$-Si solar cell (figure 2(d)) is given by

$$R_9 = R_2 + R_3 + R_{10}$$

(4)

where $R_{10}$ represents the contact resistance of Ag/p$^+$-Si interface.
Since both Ag and ITO films are highly conductive, the resistance term $R_8$ is negligible. This is demonstrated through TLM-based contact measurements of Ag/ITO interface described in figure 6 \([30]\). The contact resistivity measurement of 75 mcm$^2$ is in reasonable good agreement with literature \([31]\).

By subtracting equations (1) from (2), $R_6$ can be represented by

$$R_6 (ITO/p^+ - Si) = R_5 + R_4 - R_1$$  \(5\)

Similarly, by subtracting equations (1) from (4), $R_{10}$ can be represented by

$$R_{10}(Ag/p^+ - Si) = R_9 + R_4 - R_1$$  \(6\)

In order to determine $R_6$ and $R_{10}$, accurate measurements of $R_4$ are required. Therefore, a series of experiments were carried out in two configurations illustrated in figure 7. Screen-printed Al paste was deposited on both surfaces of p-Si wafer in figure 7(a) and annealed at peak temperatures varying in 750 °C to 1000 °C in order to vary the concentration of Al-doped p$^+$-layer. Contact resistances between top and bottom surfaces were measured with a digital multimeter as a function of temperature and have been plotted in figure 8. It is noted that there is rapid variation in Al-doped p$^+$-layer contact resistance at low $< 750^\circ$C, while at higher temperatures, the contact variation is relatively negligible in 0.2–0.7 range. The Al-paste was subsequently removed in order to measure the sheet resistance using a four-point probe with current source and two voltage.
measurement sensors. Figure 8 also plots the sheet resistance as a function of annealing temperature exhibiting large, rapid variations at lower annealing temperatures. These two measurements allow a reasonably accurate estimate of R4 for R6 and R10 measurements in equations (5) and (6) respectively.

Based on measured series resistance values, resistance of ITO/ p+ -Si interface has been calculated in table 1, its variation with sheet resistance has been plotted in figure 9. The ITO/ p+ -Si contact increases slightly at low sheet resistances reaching a maximum at \( \sim 20 \Omega/\square \), it then reduces slowly as sheet resistances increases. Almost comparable values of ITO/Si contact resistances have been observed for both heavily and lightly doped p+ surfaces. Finally, an independent confirmation of high contact resistance of polymer Ag contact on p+ -doped surfaces is determined by screen printing polymer Ag paste on p+ -doped surfaces (figure 7(b)) and plotting contact resistances in figure 10(a). An extremely large variation in contact resistance of Ag/p+ -Si surfaces is observed especially for shallow-doped surfaces. The calculated resistances of Ag/p+ -Si contacts as a function of

Table 1. Calculated R_{ITO/p+}-Si resistance measurement.

| Sheet resistance (\( \Omega/\square \)) | R6, calculated R_{ITO/p+}-Si | R1, series resistance of Al/BSF solar cell (\( \Omega \)) | R4, Al/Si contact resistance (\( \Omega \)) | R5, series resistance of ITO/Si solar cell (\( \Omega \)) |
|----------------------------------------|------------------------------|-----------------------------------------------|-----------------------------------|-----------------------------------|
| 16.45                                  | 2.45                         | 1.26                                          | 0.10                              | 3.61                              |
| 19.35                                  | 7.18                         | 1.26                                          | 0.10                              | 8.54                              |
| 24.90                                  | 4.51                         | 1.26                                          | 0.15                              | 5.67                              |
| 48.00                                  | 2.55                         | 1.26                                          | 0.30                              | 3.71                              |

Figure 8. Measured variations of Al-doped layer contact resistance with annealing temperature and sheet resistance variation of Al-doped p+ -layer with temperature.

Figure 9. Calculated contact resistance measurements of ITO/p+ -Si as a function of sheet resistance.
sheet resistance using equation (6) has been plotted in figure 10(b). As expected, contact resistances are very high for lightly doped p⁺ surfaces.

4. Conclusion

Experimental investigation and series resistance analysis of four solar cell configurations has been carried out. In all four cases, the front surface configuration was kept identical, only the rear surface contact was varied. For baseline comparison, conventional solar cell with Al BSF was chosen. Back surface sheet resistance was varied in approximately 16–48/Ω range in order to understand variation of ITO contact doping level. It has been observed that the lowest ITO/p⁺-Si contact resistance is with un-etched, Al-doped back surface formed after removal of excess Al without nitric: HF etching. As Al-doped surface is etched, the contact resistance increases slightly before decreasing back to a value comparable to un-etched surface. With the polymer Ag/ITO solar cells, the series resistance is approximately comparable except at sheet resistance of ∼25Ω/□, for this value, LIV responses of AL BSF and Ag/ITO solar cells are almost identical (figure 11). The work reported here indicates that good electrical contact can be made over a wide range of Al-doped surfaces. The role of surface passivation is critical. Without etching of Al-doped surface, surface quality has defects based on Al-alloy formation, these defects are removed with etching resulting in superior contact of ITO/Si surface as indicated in progressive improvement of LIV response in figure 4.
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