Solar Energy Materials & Solar Cells 117 (2013) 537–543

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Using hydrofluoric acid to reduce the contact resistance of screen-printed silicon solar cells – Its recombination impact and a method to eliminate it

Kee Soon Wang*, Alison J. Lennon, Budi S. Tjahjono, Ashraf Uddin, Stuart R. Wenham

School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Sydney, NSW 2052, Australia

ARTICLE INFO

Article history:
Received 18 September 2012
Received in revised form
10 June 2013
Accepted 11 June 2013
Available online 15 August 2013

Keywords:
Screen-printing
Solar cell
Silver paste
Contact resistance
Recombination
Ideality factor

ABSTRACT

Using hydrofluoric acid (HF) to improve the contact resistance of a screen-printed silicon solar cell with a high sheet resistance emitter was found to concurrently reduce its pseudo-fill factor. By treating the cell in phosphoric acid, this impact was found to be significantly reduced or eliminated. In the solar cell presented in this work, the pseudo-fill factor reduced from 82.1% to 79.9% after treating the cell in HF, but increased to 81.8% after a subsequent phosphoric acid treatment. Similar effects were found in three other screen-printed solar cells that were fired at different peak furnace temperatures and belt speeds. It was also shown that the phosphoric acid treatment alone does not affect the pseudo-fill factor of a cell. HF treatment can now be used to reduce the contact resistance of a screen-printed silicon solar cell with a high sheet resistance emitter without suffering from a lower pseudo-fill factor so that the full benefit of a HF treatment on a screen-printed silicon solar cell can be realized. This combination of HF and phosphoric acid treatments can potentially be a useful failure analysis method for screen-printed silicon solar cells in the production line and the laboratory.

1. Introduction

In commercial screen-printed silicon solar cells, low contact resistance ($R_{contact}$) is essential for high fill factors (FF) and efficiencies [1]. The $R_{contact}$ of a screen-printed silver (Ag) conductor is determined by a number of factors, one of which is the thickness of the insulating oxide layer that forms between the screen-printed Ag conductor and the emitter surface [2–7]. When the oxide is too thick, it retards the conduction of current into the Ag fingers [2,8]. This can be circumvented by using dilute hydrofluoric acid (HF) to thin or possibly eliminate such oxides. It was previously demonstrated that this HF treatment can lower the $R_{contact}$ of such screen-printed cells, thus raising their FF and efficiencies [9–11]. With increasing interest in high sheet resistance emitters, the positive impact of an HF treatment on the FF of screen-printed cells with 100 Ω/□ emitters was reported [10]. However, no negative electronic impacts were mentioned. This research reports that HF treatments on screen-printed silicon solar cells with such high sheet resistance emitters can increase recombination in the cell and reduce its pseudo-FF (pFF) [12]. Furthermore, a method to reduce or eliminate this impact is also presented.

2. Experimental

A screen-printed silicon solar cell, Cell 1, was fabricated on a 2 in. square, ~200 μm thick mono-crystalline 1 Ωcm (100) planar silicon wafer. After saw damage etch and alkaline texturing, the wafer was cleaned in RCA1 and RCA2 [13] before undergoing $POCl_3$ diffusion to produce an ~100 Ω/□ emitter. A subsequent dilute HF treatment was used to remove the phosphosilicate glass layer. Approximately 75 nm of silicon nitride with a refractive index of 2.0 was deposited on the emitter surface using a remote plasma-enhanced chemical vapor deposition system. The wafer was then screen-printed with aluminum (Al) paste on the rear side, dried at 150 °C for 15 min, screen-printed with a commercial Ag paste DuPont PV145 [14] on the emitter side, dried at 150 °C for 15 min, before being fired at a peak furnace-set temperature of 810 °C and a belt speed of 6200 mm/s in a Centrotherm 6-zone belt furnace. The cell was then edge-isolated by using a laser with an emission wavelength of 1064 nm to partially-cleave the wafers from the rear side before the redundant side pieces were manually snapped off. The final cell dimension was ~2.9 × 2.8 cm^2. Cell 1 was then characterized using its light current voltage (*IV*) curve (at standard testing conditions of 100 mW/cm^2 of an AM1.5G spectrum at 25 °C), dark *IV* curve, Suns–Voc curve and its pFF [12], and photoluminescence series resistance (PL Rs) spatial image [15] using a BTi imaging tool [16]. Cell 1 was then immersed in a 1% HF solution (thereafter referred as "HF treatment") for 5 s before being

* Corresponding author. Tel.: +61 2 93856782.
E-mail address: wangkeesoon@gmail.com (K.S. Wang).

0927-0248/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.solmat.2013.06.017

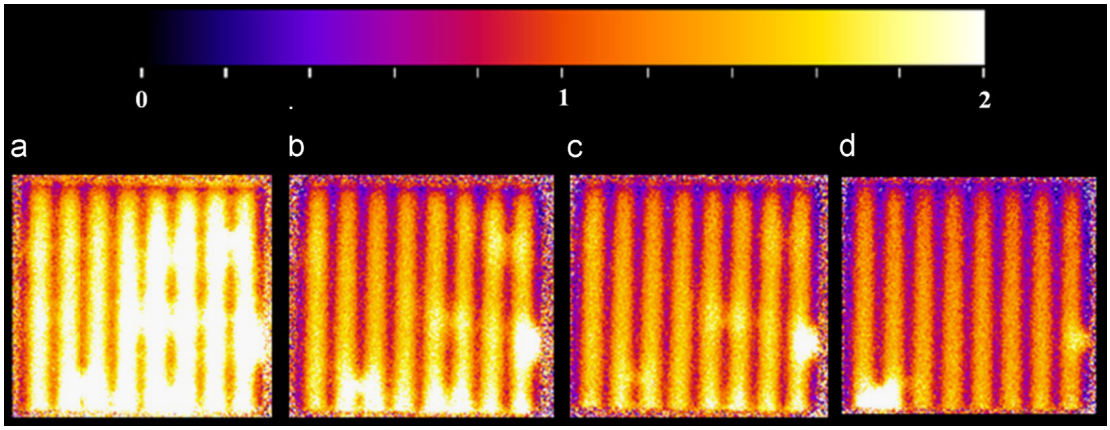

Fig. 1. Photoluminescence series resistance (PL Rs) images of Cell 1 (a) as-fired, (b) after 5 s, (c) after 10 s, and (d) after 20 s of treatment in a 1% HF solution. The resistance color scale is 0–2 Ωcm^2. In (d), the Ag finger at the lower left corner peeled off due to prolonged HF treatment, resulting in higher local resistance.

rinsed in de-ionized (DI) water (~18 MΩ) for 10 min and dried in nitrogen (N_2) gas. It was again characterized as described above. This cycle continued until the cumulative duration of the HF treatment was 25 s.

After undergoing 25 s of the HF treatment, Cell 1 was subsequently immersed in an 85% (w/v) phosphoric acid (H_3PO_4) solution (thereafter referred as "H_3PO_4 treatment") for 10 s. The cell was then characterized with the same methods as described before. This cycle continued until the cumulative H_3PO_4 treatment duration was 30 s.

To check the cross-sectional profile of the Ag fingers after the HF treatments, another cell, Cell 1A, was fabricated with the same process condition as that of Cell 1. Cell 1A was then cleaved from the rear Al side in a direction perpendicular to the orientation of the Ag fingers before the two half pieces were manually snapped off in the same way that edge-isolation of Cell 1 was done. In this way, the Ag finger cross-sections are exposed. A cross-sectional SEM image for the as-fired sample was taken from one of the cleaved Ag fingers. Subsequently, one of the halved pieces underwent the same cumulative 25 s of the HF treatment that was done to Cell 1. After cleaving another randomly-picked spot along the same Ag finger, another cross-sectional SEM image was taken for same Ag finger.

In this work, the front Ag grid pattern had a finger pitch of 3.5 mm. Such a non-optimally wide pitch was used because the objective of the research was to fabricate laser-doped (LD) semiconductor fingers (SCF) silicon solar cells [17], although no LD SCF were incorporated into any of the cells presented in this work. Therefore, high series resistance and low FF levels should be expected, although they did not affect the analyses presented here.

3. Results and discussions

3.1. Impact of hydrofluoric acid treatment

Fig. 1 shows the PL Rs images of Cell 1 for different cumulative durations of the HF treatment. The vertical dark lines are the Ag fingers and the busbar is the top horizontal line. Fig. 1(a) shows that the local series resistance was not uniform across the cell as-fired. Fig. 1(b)–(d) shows increasingly lower and improved uniformity of local resistance from longer HF treatments. As a result, the slope of the *IV* curve (see Fig. 2) at voltage >0.45 V became steeper after 25 s of the HF treatment, which indicates that the series resistance in Cell 1 has reduced. This is supported by the cell data shown in Table 1, where the series resistance

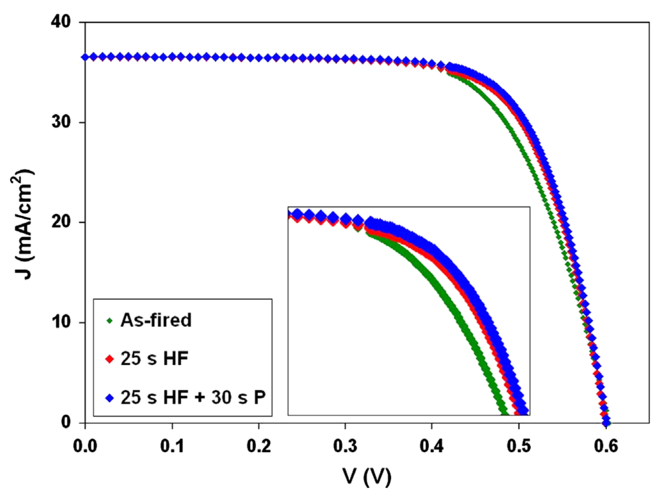

Fig. 2. Light *IV* curves of Cell 1 as-fired, after a 25 s 1% HF treatment ("25 s HF") and after a subsequent 30 s of 85% phosphoric acid treatment ("25 s HF+30 s P"). Inset: magnified view of the "knee" of the *IV* curves between 0.35–0.55 V.

Table 1
The 1-Sun power conversion output data of Cell 1: as-fired, after a cumulative of 25 s of HF treatment in a 1% (w/v) HF solution ("25 s HF"), and after different cumulative durations of treatments in 85% (w/v) phosphoric acid ("+P"). The Suns–Voc [12] pseudo-FF (pFF) and local ideality factor [18] at the maximum power point (SunsVoc m_{MPP}), and the series resistance (R_{series}) are also shown.

Cell 1 treatments	Voc (mV)	Jsc (mA/cm^2)	FF (%)	Eff. (%)	pFF (%)	SunsVoc m_{MPP}	R_{series} (Ωcm^2)
As-fired	603.2	36.5	68.4	15.0	82.1	1.2	2.7
25 s HF	599.6	36.0	71.7	15.5	79.9	1.5	1.6
25 s HF +10 s P	600.0	36.0	72.3	15.6	81.7	1.2	1.6
25 s HF +20 s P	600.0	36.1	72.6	15.7	81.7	1.2	1.6
25 s HF +30 s P	600.6	35.9	72.7	15.7	81.9	1.2	1.5

reduced from 2.7 Ωcm^2 to 1.6 Ωcm^2 after 25 s of the HF treatment, and as a result the FF increased from 68.4% to 71.7%.

It can also be observed in Fig. 1(d) that the Ag finger at the lower left corner of Cell 1 has a higher local resistance compared to adjacent fingers. This is because the Ag finger in this section has peeled off, thus causing electrons generated in its vicinity to travel