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Influence of the aluminum paste surface density on the electrical parameters of silicon solar cells

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Abstract

The industrial process of silicon solar cells is mainly based on the aluminum back surface field (Al-BSF) performed by the conventional screen printing and firing in a belt furnace. The goal of this paper is to present the analysis of the influence of the amount of the Al paste on the electrical parameters and on the minority carrier diffusion length. The silicon solar cells were processed in p-type Czochralski solar grade wafers. The amount of Al paste deposited to form the BSF, denominated of Al paste surface density, was ranged from 2.8 mg/cm^2 to 8.8 mg/cm^2. The peak firing temperature for each amount of Al paste was optimized and the depth of the Al-BSF was estimated. The best results were found for the Al paste surface density of 3.5 mg/cm^2 and the peak firing temperature of 840 °C, resulting in the efficiency of the solar cells of (15.0 ± 0.1) %. In this case, the depth of the Al-BSF was (5 ± 1) µm. Taking into account the peak firing temperature obtained for each Al paste surface density, we observed that the short-circuit current increased up to the average Al paste amount of 3.5 mg/cm^2. On the other hand, the fill factor decreased with the increasing of the Al paste surface density. The open circuit voltage was slightly affected by the Al paste amount. The minority carrier lifetime rose from 30 µs to 120 µs after the phosphorus diffusion. A strong improvement in the minority carrier diffusion length was observed after the firing process and depends on the Al paste amount. The measured average values were 500 µm, 1280 µm and 780 µm for the Al paste surface density of about 2.8 mg/cm^2, 3.5 mg/cm^2 and 8.8 mg/cm^2, respectively.

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1. Introduction

The main industrial technology to fabricate silicon solar cells is based on the aluminum back surface field (Al-BSF) performed by the conventional screen printing metallization. The aluminum paste is deposited on the rear face of the p-type Czochralski (Cz-Si) wafers and fired in a belt furnace.

The formation of full-area screen-printed Al-BSF and its effect on the efficiency of the solar cell had been studied. During the firing process, Si diffuses into the Al, with Al then diffusing into the Si [1]. Aluminum spikes are formed in the Si surface. These spikes expand parallel to the silicon surface and join to each other. During cooling, the Al spikes retract and form the Al-BSF [1]. In this process, agglomerations can be formed, leading to a laterally inhomogeneous Si recrystallization and resulting in no homogeneous Al-BSF that reduces the solar cell efficiency [2].

If the firing peak temperature or time of the peak temperature is higher than a critical value, the p^+ region can present thickness variations. This critical temperature is lower for thicker Al layers [3]. Results obtained from float-zone silicon wafers demonstrated that for high peak temperature times more Si dissolves into the molten Al-Si and more Si recrystallizes during the cooling [2]. In a given agglomeration, the thicknesses can range from 15 µm to 40 µm and this variation may be related to large pyramids with height up to 20 µm. Near the agglomeration, the thickness can be lower than 2 µm, where almost no Al-Si eutectic layer was formed, indicating that Al-BSF was no homogeneous. The increasing of the Al paste amount or the decreasing of the peak temperature improves the uniformity in Al-BSF thickness [2].

The formation of the Al-BSF using Al paste deposited by the screen printing technique can produce gettering and improve the minority carrier lifetime. The gettering process is helpful mainly in low quality material as solar grade silicon because reduces the concentration of metal impurities such as iron, copper, nickel and other metals. These impurities act as recombination centers, reducing the minority carrier diffusion length and, consequently, the solar cell efficiency. The Al gettering depends on the segregation coefficient of the metal impurities, the impurity concentration of the Al layer, the impurity concentration in the silicon wafer, the thickness of the Al-Si eutectic layer as well as the firing temperature and time [4]. Results obtained by simulation showed that the thickness of the Al layer is a less important parameter [4].

Silicon solar cells fabricated in Si-Cz wafers with homogeneous high sheet resistance phosphorus emitter (85 Ω/□ – 95 Ω/□) and Al-BSF performed with Al paste fired in a belt furnace achieved the 18.3 % efficiency [5]. Emitter sheet resistance in the range from 65 Ω/□ to 105 Ω/□ was contacted with low average series resistance, resulting in fill factors of 0.789 to 0.768, respectively.

Solar cell processed in FZ-Si wafers with Al-BSF, laser-doped selective emitter and screen-printed metallization reached the efficiency of 19.6 %. When the front contact was formed by light-induced nickel and silver plating, the efficiency obtained was 20.1 %. This cell was modeled with the PC-1D computer program and the minority carrier length of 1150 µm was set [6].

The efficiency in industrial production is lower. Commercial c-Si solar cells, p-type and n-type, have efficiencies in the range from 15 % to 22 % [7]. The high efficiency solar cells, called IBC (interdigitated back contact) and HIT (heterojunction with intrinsic thin layer) were developed by SunPower Corp. and Sanyo, respectively. The average efficiency is around 16.5 % in p-type Cz-Si solar cells with Al-BSF, with the throughput of the lines in between 750 to 2400 pieces per hour [8].

Taking into account that the amount of Al paste and the firing temperature affect the Al-BSF and, consequently, the efficiency of the solar cell, the goal of this paper is to present the analysis of the influence of the amount of the Al paste on the electrical parameters and on the minority carrier diffusion length of the solar cells processed in solar grade Si-Cz wafers by using a typical industrial process.

2. Solar cell process

Solar cells were developed in p-type Cz-Si solar grade wafers with thickness of 200 μm and base resistivity from 1 Ω.cm to 20 Ω.cm. To perform the Al-BSF, the Al paste was deposited by the screen printing technique and fired in a belt furnace. Aluminum was deposited over the whole rear surface, except in the busbar regions, where the Al/Ag paste was screen-printed. The process sequence to produce solar cells is summarized in Fig 1 and it consists of the following steps: texture etching, RCA cleaning, phosphorus diffusion, phosphorus silicate glass (PSG) etching and RCA cleaning, antireflection coating (ARC) deposition, screen printing of the Al and Al/Ag pastes on the rear face and Ag paste on the front side, firing of the metal pastes and laser edge isolation. The amount of Al paste deposited to form the BSF, denominated of Al paste surface density, was ranged from 2.8 mg/cm^2 to 8.8 mg/cm^2. The peak temperature to fire simultaneously the Al, Al/Ag and Ag pastes was independently optimized for each amount of Al paste. Three or four pseudo-square solar cells were processed in each firing temperature.
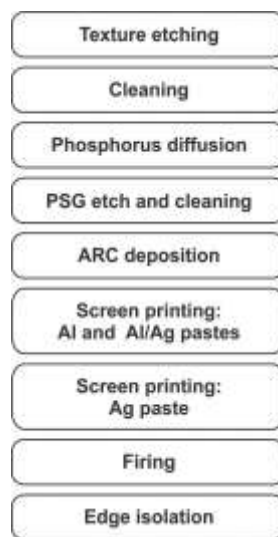
| Texture etching |
| Cleaning |
| Phosphorus diffusion |
| PSG etch and cleaning |
| ARC deposition |
| Screen printing: Al and Al/Ag pastes |
| Screen printing: Ag paste |
| Firing |
| Edge isolation |

Fig. 1. Sequence of the fabrication process used to produce silicon solar cells.

The n$^+$ layer was performed by phosphorus diffusion using POCl$_3$. The sheet resistance of the phosphorus emitter was (45 ± 4) Ω/□ and the junction depth of the emitter, measured with electrochemical capacitance voltage profiling method, was around 0.6 μm. The thickness of the TiO$_2$ antireflection coating, deposited by e-beam technique, was 95 nm.

Solar cells were characterized under standard conditions (100 mW/cm^2, AM1.5G and 25°C) in a solar simulator calibrated with a solar cell previously measured at CalLab - FhG-ISE (*Fraunhofer-Institut für Solare Energiesysteme*), Germany.

The two-dimensional distribution of minority carrier lifetime and diffusion length was measured using the WT-2000PV device of Semilab, by μ-PCD (microwave induced photoconductivity decay) and LBIC (light beam induced current) techniques. These parameters were measured after the phosphorus diffusion, the drying of the metal pastes to remove the solvents and the firing step.

The depth of Al-BSF of the solar cells was estimated taking into account the peak temperature firing and the Al paste surface density [9].

3. Results and discussion

3.1. I-V characteristics and internal quantum efficiency

Table 1 presents the electrical characteristics of the solar cells with the average Al paste surface density of 2.8 mg/cm^2. In this case, the peak firing temperature (T_F) was ranged from 840 °C to 970 °C. As expected, the open circuit voltage (V_{OC}) increases up to T_F of 900 °C - 910 °C because the depth of the Al-BSF was enlarged. The firing temperature of 900 °C produced the depth of the Al-BSF (W_{BSF}) of (5.6 ± 0.9) μm. The highest value of short-circuit current density (J_{SC}) was also found at the temperature of 910 °C. Fill factor (FF) was about 0.76 – 0.77 for all T_F up to 950 °C. The firing temperature of 970 °C causes a reduction in the fill factor, because the Ag paste degrades, affecting also the V_{OC} and J_{SC}. The average efficiency (η) of 14.4 % was obtained for samples fired at peak temperature ranging from 880 °C to 940 °C.

The increase of the Al amount from 2.8 mg/cm^2 to 3.5 mg/cm^2 improved the solar cell efficiency, as shown in Table 2. Fill factor decreased with the increase of the Al paste surface density. The improvement in the efficiency was caused by the increase of J_{SC}. The highest average value rose from 32.1 mA/cm^2 to 33.5 mA/cm^2 when the Al amount was increased from 2.8 mg/cm^2 to 3.5 mg/cm^2. The best average efficiency of 15.0 % was achieved at the firing temperature of 840 °C. In this case, the W_{BSF} was of (5.3 ± 1.0) μm, similar to the value found for the best solar cells with the Al amount of 2.8 mg/cm^2. Again, at firing temperature of 950 °C, the FF fell.

Table 1. Electrical characteristics of the Al-BSF silicon solar cells with average Al paste surface density of 2.8 mg/cm^2 as a function of peak firing temperature.

T_F (°C)	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF	η (%)
840	582 ± 3	30.6 ± 0.4	0.770 ± 0.005	13.7 ± 0.3
850	581.2 ± 2.0	30.87 ± 0.14	0.777 ± 0.006	13.94 ± 0.20
860	584.4 ± 1.0	31.4 ± 0.3	0.777 ± 0.002	14.28 ± 0.20
880	587.9 ± 2.0	31.79 ± 0.03	0.774 ± 0.002	14.46 ± 0.05
900	592.2 ± 1.2	32.02 ± 0.03	0.758 ± 0.002	14.37 ± 0.08
910	595.3 ± 2.0	32.1 ± 0.4	0.756 ± 0.011	14.45 ± 0.11
920	594.1 ± 0.8	31.87 ± 0.06	0.762 ± 0.005	14.44 ± 0.09
940	595.9 ± 0.4	31.54 ± 0.08	0.768 ± 0.001	14.45 ± 0.05
950	596.8 ± 0.3	31.00 ± 0.14	0.764 ± 0.003	14.13 ± 0.10
970	591.9 ± 2.0	30.2 ± 0.6	0.69 ± 0.04	12.4 ± 0.9

Table 2. Electrical characteristics of the Al-BSF silicon solar cells with average Al paste surface density of 3.5 mg/cm^2 as a function of peak firing temperature.

T_F (°C)	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF	η (%)
830	587.7 ± 0.5	33.55 ± 0.08	0.711 ± 0.005	14.02 ± 0.07
840	591.8 ± 1.1	33.50 ± 0.22	0. 756 ± 0.011	15.00 ± 0.10
	594 ± 6	33.4 ± 0.3	0.757 ± 0.007	15.03 ± 0.12
850	589.8 ± 1.0	33.42 ± 0.01	0.746 ± 0.011	14.70 ± 0.24
870	591.3 ± 1.0	33. 45 ± 0.02	0.756 ± 0.010	14.94 ± 0.24
	590.87 ± 0.04	33.1 ± 1.0	0.742 ± 0.013	14.52 ± 0.22
900	591.3 ± 0.6	33.13 ± 0.06	0.741 ± 0.008	14.52 ± 0.13
920	587.9 ± 1.4	32.68 ± 0.07	0.733 ± 0.011	14.09 ± 0.25
950	578.9 ± 1.3	31.71 ± 0.08	0.687 ± 0.013	12.6 ± 0.3

The electrical parameters of the solar cells fabricated with Al paste surface density of 8.8 mg/cm^2 are presented in Table 3. The average efficiency is slightly lower than that presented in Table 2. Then, the augment of Al amount from 3.5 mg/cm^2 to 8.8 mg/cm^2 did not improve the efficiency. The short-circuit current density and fill factor slightly decreased. The best average efficiency was found at firing temperature from 840 °C to 870 °C. For T_F = 840 °C, the estimated W_{BSF} was of (11.2 ± 1.1) μm, approximately twice the value obtained for Al amount of 2.8 mg/cm^2 and 3.5 mg/cm^2. The Al paste surface density of 8.8 mg/cm^2 resulted in a deep W_{BSF}, caused by the high thickness of the Al paste. Fig 2 illustrates the Al paste afterwards the firing process. The average Al thickness was of around 70 μm.

Table 3. Electrical characteristics of the Al-BSF silicon solar cells with average Al paste surface density of 8.8 mg/cm^2 as a function of peak firing temperature.

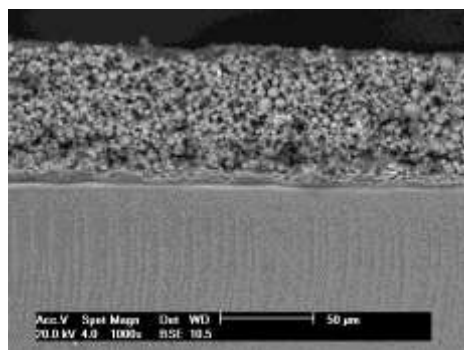| T_F (°C)	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF	η (%)
820	592 ± 3	32.49 ± 0.20	0.591 ± 0.04	11.4 ± 0.9
830	593 ± 3	33.13 ± 0.14	0.67 ± 0.04	13.2 ± 0.8
840	597.0 ± 1.0	33.23 ± 0.07	0.736 ± 0.009	14.60 ± 0.24
850	597.4 ± 0.9	33.19 ± 0.12	0.734 ± 0.006	14.54 ± 0.10
870	596 ± 3	33.21 ± 0.20	0.744 ± 0.013	14.74 ± 0.24
	586.6 ± 1.1	33.7 ± 0.4	0.71 ± 0.04	14.0 ± 1.0
890	592 ± 8	33.23 ± 0.11	0.722 ± 0.011	14.20 ± 0.10
920	583 ± 4	32.71 ± 0.12	0.703 ± 0.012	13.4 ± 0.3

Fig 2. Cross section view of the Al paste and silicon wafer obtained with the scanning electron microscopy. The average Al thickness was of around 70 μm for the Al paste surface density of 8.8 mg/cm^2.

The electric current density as a function of applied voltage (J-V) of solar cells with different Al paste surface density is plotted in Fig 3. We confirmed that the increase of Al amount improved only the J_{SC}. For solar cells with the highest efficiency, the V_{OC} remained around 590 mV, but fill factor diminished from 0.77 to 0.74 with the augment of the thickness of Al amount.

The electrical parameters as a function of the peak firing temperature are plotted in Fig 4. The peak firing temperature that leads to the highest open circuit voltage decreases when the Al paste amount was reduced, as shown in Fig 4-a. The highest values of V_{OC} for solar cells with the Al paste amount of 2.8 mg/cm^2 and 8.8 mg/cm^2 were found at T_F = 950 °C and at T_F = 850 °C, respectively. Concerning the fill factor, in Fig 4-b we noticed that the highest values were obtained for the lowest Al paste surface density independently of the firing temperature. For the Al paste amount of 3.5 mg/cm^2 and 8.8 mg/cm^2, the optimum fill factor was achieved at T_F in the range from 840 °C to 870 °C. Fig 4-c summarizes the results

of the short-circuit current density, that increased strongly with the increase of the Al paste surface density. For this electrical parameter, the optimum values of T_F were 910 °C, 830 °C and 870 °C for the Al paste amount of 2.8 mg/cm^2, 3.5 mg/cm^2 and 8.8 mg/cm^2, respectively.
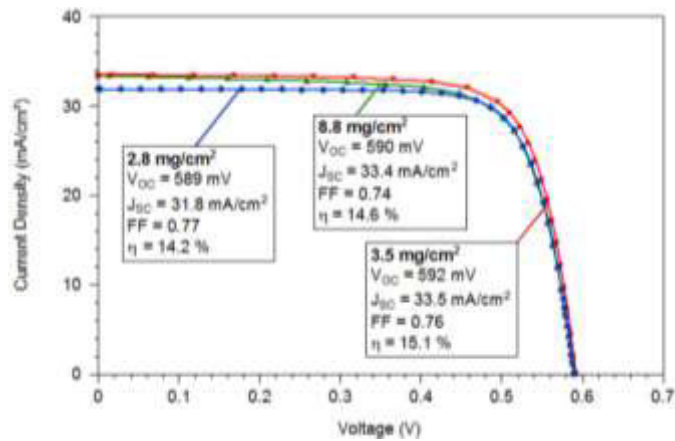

Fig. 3. Electrical characteristics at standard conditions of solar cells processed with Al paste surface density of 2.8 mg/cm^2, 3.5 mg/cm^2 and 8.8 mg/cm^2 and peak firing temperature experimentally optimized.
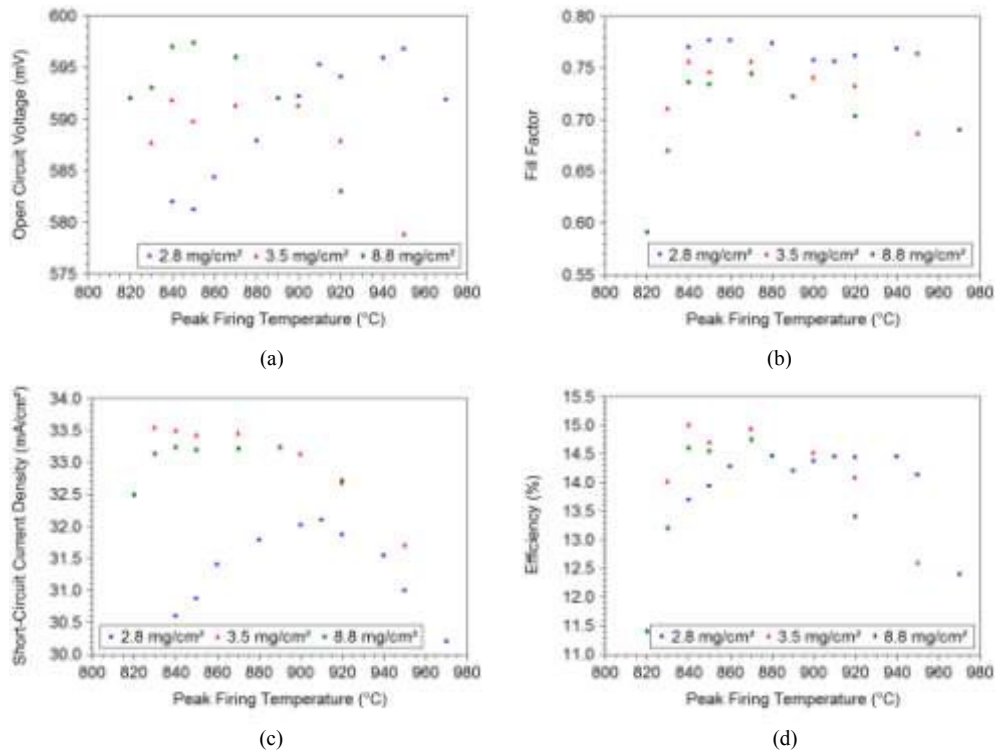
Fig. 4. (a) Open circuit voltage, (b) fill factor, (c) short-circuit current density and (d) efficiency of the solar cells as a function of peak firing temperature and the Al paste surface density.

Concerning V_{OC} and J_{SC}, the optimum peak firing temperature to produce solar cells with Al paste surface density of 2.8 mg/cm^2 was higher than optimum T_F obtained for the other two Al paste amounts evaluated. Consequently, the best efficiency of the solar cells with low Al amount was obtained at higher firing temperature. For the Al paste surface density of 3.5 mg/cm^2 and 8.8 mg/cm^2, the best values of the efficiency were found at T_F in the range from 840 °C to 870 °C. Due to higher J_{SC} obtained for Al paste surface density of 3.5 mg/cm^2, the best average efficiency was achieved at $T_F = 840$ °C, as shown in Fig 4-d.

The internal quantum efficiency (IQE) of solar cells fabricated with different Al paste surface density and optimum peak firing temperature is compared in Fig 5. The Al amount of 3.5 mg/cm^2 is enough to enhance the IQE for wavelengths longer than 700 nm. At short wavelengths, the IQE is low due to the no effective passivation produced by TiO_2 antireflection coating.
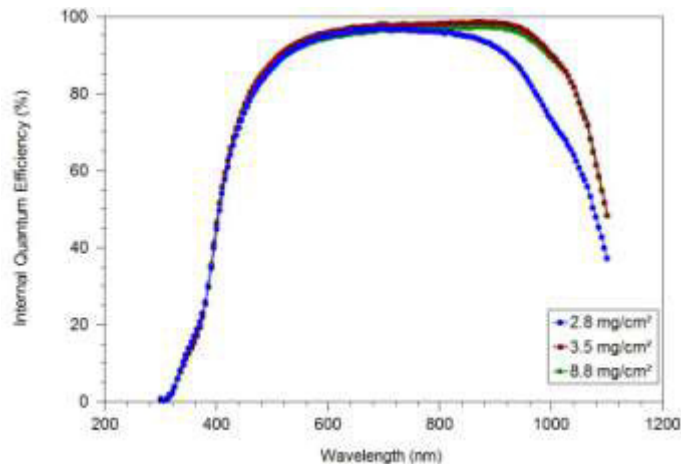

Fig. 5. Internal quantum efficiency of silicon solar cells fired at the optimum peak temperature and with different Al paste surface density.

3.2. Minority carrier lifetime and diffusion length

Fig 6 illustrates the minority carrier lifetime (τ) measurements performed after the phosphorus diffusion, the drying of the metal pastes and the firing in the belt furnace. In the firing step, a wafer without TiO_2 antireflection coating neither metal pastes was submitted to the drying and firing processes to assess the contamination of the belt furnace. Phosphorus emitters (in both faces) were kept during these thermal steps. The initial average minority carrier lifetime measured was of around 30 μs. The phosphorus diffusion produced gettering and τ increased from 30 μs to 120 μs. In this case, the ratio of maximum to minimum τ (R_τ) presented in the μ-PCD map was 1.4. The process of drying the metal pastes in the belt furnace improved the average τ to 200 μs and the R_τ remained similar. The firing step did not degrade the minority carrier lifetime. In this case, the average τ was 190 μs.

Fig 7 compares the two-dimensional distribution of the minority carrier diffusion length (L_D) measured in solar cells processed with the Al amount of 2.8 mg/cm^2 and 8.8 mg/cm^2, at optimum firing temperatures. Increasing the Al paste surface density, the average L_D rose from 510 μm to 780 μm. The ratio of maximum to minimum L_D also increased with the Al amount from 4 to 13, indicating that L_D presented a strong variation for high Al thickness. The highest average value of $L_D = 1280$ μm was measured in solar cells with the Al paste surface density of 3.5 mg/cm^2. In this solar cell the ratio of

maximum to minimum L_D of 19 was higher than that obtained in devices with the Al paste amount of 8.8 mg/cm². For solar cells with Al paste surface density of 3.5 mg/cm² and 8.8 mg/cm², the minimum value of minority carrier diffusion length was similar meanwhile the maximum value was high for solar cells with 3.5 mg/cm² Al amount.
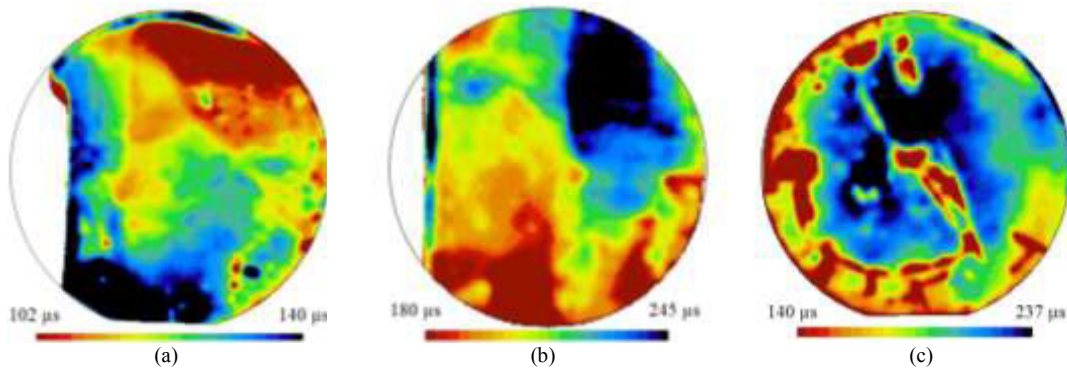

Fig. 6. Two-dimensional distribution of the minority carrier lifetimes measured by μ-PCD technique (WT-2000PV device of Semilab) afterwards (a) the phosphorus diffusion (from 102 μs to 140 μs), (b) the drying of the metal pastes (from 180 μs to 245 μs) and (c) the firing in the belt furnace (from 140 μs to 237 μs).
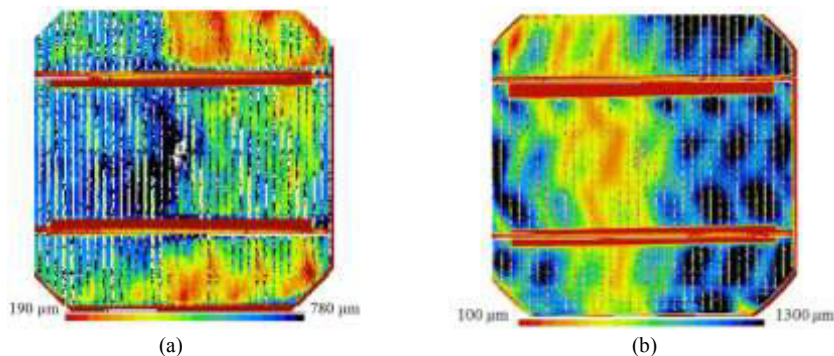

Fig. 7. Minority carrier diffusion length of solar cells with Al amount of (a) 2.8 mg/cm² (from 190 μm to 780 μm) and (b) 8.8 mg/cm² (from 100 μm to 1300 μm).

4. Conclusions

The higher efficiency was found for the Al paste surface density of 3.5 mg/cm² and the peak firing temperature of 840 °C, resulting in the efficiency of the solar cells of (15.0 ± 0.1) %. In these solar cells, the depth of the Al-BSF was (5 ± 1) um.

The optimum open circuit voltage depended on the Al paste amount, as well as the J_{SC} and the FF. The highest values of fill factor were found for the lower Al paste surface density independently of the firing temperature. For the lower Al paste amount, the best efficiency was obtained at higher firing temperature. The increase of the Al paste surface density led to a decrease of the peak firing temperature up to 840 °C.

The short-circuit current density was strongly enhanced by the increase of the Al paste surface density up to the Al paste amount of 3.5 mg/cm². Higher IQE for wavelengths longer than 700 nm explained the

higher J_{SC} obtained. Then, we can conclude that there is a limit to the Al paste surface density of around 3.5 mg/cm^2. Values higher than this can harm the electrical performance of silicon solar cells.

The minority carrier lifetime increased from 30 μs to 120 μs after the phosphorus diffusion. For samples processed with P emitters, but without TiO$_2$ ARC and metal pastes, the drying of the metal paste improved the minority carrier lifetime and the firing process did not contaminate the wafer. The minority carrier diffusion length was high and depended on the Al paste amount. The measured average values were 500 μm, 1280 μm and 780 μm for the Al paste surface density of 2.8 mg/cm^2, 3.5 mg/cm^2 and 8.8 mg/cm^2, respectively.

Acknowledgements

References

[1] Park S, Song J, Tark SJ, Kim YD, Choi C, Kwon S, Yoon S, Son CS, Kim D. Investigation of Al back contacts and BSF formation by in situ TEM for silicon solar cells. *Prog. Photovolt: Res. Appl.* 2012; [DOI: 10.1002/pip.2322].

[2] Rauer M, Schmiga C, Krause J, Woehl R, Hermle M, Glunz SW. Further analysis of aluminum alloying for the formation of p$^+$ regions in silicon solar cells. *Energy Procedia* 2011; **8**: 200-6.

[3] Meemongkolkiat V, Nakayashiki K, Kim DS, Kopecek R, Rohargi A. Factors limiting the formation of uniform and thick aluminum-back-surface fiel and its potential. *Journal of The Electrochemical Society* 2006; **153** (1): G53-8.

[4] Blazek M, Kwapil W, Schön J, Warta, W. Gettering efficiency of backside aluminium layer and Al-Si-eutectic. *Proc. 23rd EU PVSEC*, Valencia, Spain, 2008; p. 1637-43.

[5] Ebong A, Cooper IB, Rounsaville B, Rohatgi A, Borland W, Carroll A, Mikeska K. Overcoming the technological challenges of contacting homogeneous high sheet resistance emitters (HHSE). *Proc. 26th EU PVSEC*, Hamburg, Germany, 2011; p. 1747-9.

[6] Fellmeth T, Mack S, Bartsch J, Erath D, Jäger U, Preu R, Clement F, Biro D. 20.1 % efficient silicon solar cell with aluminum back surface field. *IEEE Electron Device Letters* 2011; **32** (8): 1101-3.

[7] Razykov TM, Ferekides CS, Morel D, Stefanakos E, Ullal HS, Upadhyaya HM. Solar photovoltaic electricity: current status and future prospects. *Solar Energy* 2011; **85**: 1580-1608.

[8] Fath P, Keller S, Winter P, Jooβ W, Herbst W. Status and perspective of Crystalline silicon solar cell production. *Proc. 34th IEEE PVSC*, Philadelphia, USA, 2009; p. 2471-6.

[9] Del Alamo J, Eguren J, Luque A. Operating limits of Al-alloyed high-low junctions for BSF solar cells. *Solid-State Eletronics* 1981; **24**: 415-420.