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METALLISATION TECHNOLOGY OF SILICON SOLAR CELLS USING THE CONVECTIONAL AND LASER TECHNIQUE

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Abstract

The aim of the paper was to optimize the Selective Laser Sintering (SLS) and co-firing in the infrared conveyor furnace parameters in front Screen Printed (SP) contacts. The co-firing in the infrared conveyor furnace was carried out at various temperature. The SLS was carried out at various a laser beam, scanning speed of the laser beam and front electrode thickness. The investigations were carried out on monocrystalline silicon wafers. During investigations was applied a silver powder with the grain size of 40 µm. The contacts parameters are obtained according to the Transmission Line Model (TLM) measurements. Firstly, this paper shows the comparison between the convectional an unconventional method of manufacturing front contacts of monocrystalline silicon solar cells with the different morphology of silicon for comparative purposes. Secondly, the papers shows technological recommendations for both methods in relation to parameters such as: the optimal paste composition, the morphology of the silicon substrate to produce the front electrode of silicon solar cells, which were selected experimentally in order to produce a uniformly melted structure, well adhering to the substrate, with the low resistance of the front electrode-to-substrate joint zone.

Keywords: Silicon solar cells, Screen printing, Selective laser sintering, Transmission line model.

1 Introduction

The research studies in the photovoltaic field are oriented to reduce the costs of electrical energy produced with the use of photovoltaic cells to the level competitive to the costs of energy produced from conventional energy sources. To obtain the above objective it is necessary to eliminate the technological process with expensive and difficult to automate operations and replace them with cheap ones whose production can be automated. One of such emerging production operations of photovoltaic cells is the deposition of electrical contacts. As it has been found by numerous research studies, electrode coating should satisfy different requirements to ensure low resistance between the interface zone of the electrode with the substrate. of particular importance is the proper selection of material (of electrode and substrate), conditions of its fabrication, shape and size of electrode, adhesion of the electrode to the substrate and substrate morphology. In order to improve electrical properties of the front electrode, various fabrication techniques are being analyzed (Figure 1), consisting in different imprint techniques and its final connection with the substrate surface. This paper summarizes recent testing with metallization in the front using a conventional Screen Printing (SP) technique (Figure 2) in comparison with an unconventional Selective Laser Sintering (SLS) technique (Figure 3) [1]-[7].

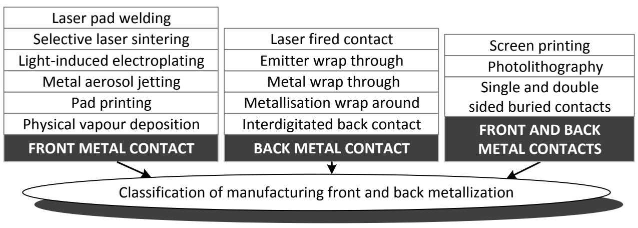


Figure 1: Techniques of producing electrical contacts of solar cells [3].

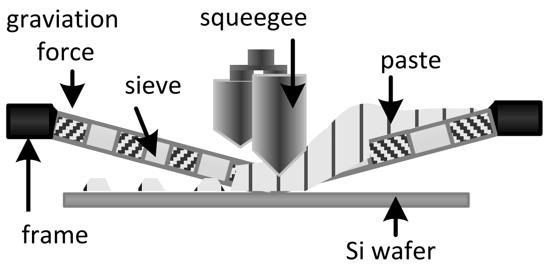


Figure 2: The screen printing method used during printing of silver paste on the front surface of silicon wafer [3]-[6]-[7].

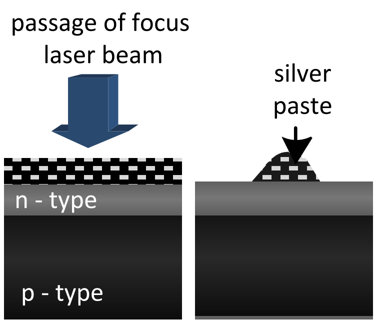


Figure 3: Selective laser sintering of silver paste on the surface of silicon wafer [3]-[5].

2 Material and Methods

The investigations were carried out on monocrystalline (100) silicon wafers. ~330 µm thick wafers were processed with the SLS method, whereas those approx. ~230 µm thick were processed with the SP method and co-fired in the furnace. Table 1 presents the basic parameters of these wafers. During investigations was applied a silver powder about granulation <40 µm (Figure 4). Selection of chemical composition of front contact was carried out by experimental and mixtures were prepared using a mechanical stirrer. In Table 2 is presented the selection of elements in contact layer of solar cell.

Figure 4: SEM micrograph of silver powder.

Table 1: The basic parameters of the two grades of the silicon applied.

Type	p	p
Doped	boron	boron
Thickness	200 ± 30 µm	330 ± 10 µm
Area	5 cm x 5 cm	5 cm x 5 cm
Resistivity	1 ÷ 3 Ω·cm	~1 Ω·cm
Carbon concentration	8x10^{16} at/cm^3	≤1x10^{18} at/cm^3
Oxygen concentration	1x10^{18} at/cm^3	≤2x10^{17} at/cm^3

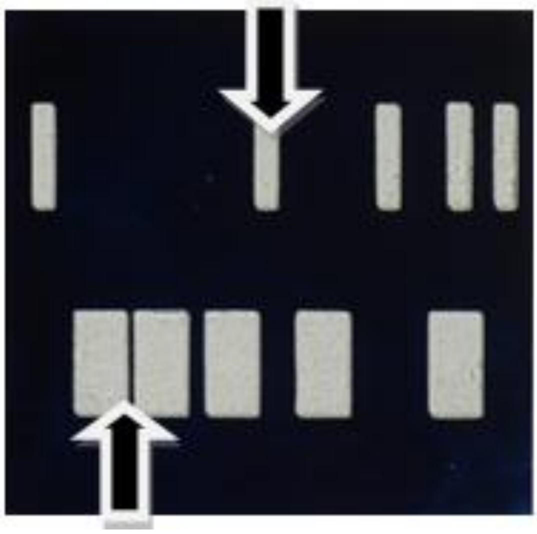
At the Institute of Metallurgy and Materials Science of the Polish Academy of Science in Cracow (Poland) the technology of solar cells has been developed. The solar cells manufacturing process for solar cells with the different morphology of silicon consists of the following steps: 1-chemical etching, 2-formation of p-n junction, 3-formation of parasitic junction, 4-surface passivation of solar cells (SiO2), 5-antireflection coating (TiO_x) deposition, 6 - screen printing of front contacts, 7-co-firing in the furnace front contacts, 8-selective laser sintering of front contacts.

One of the aspects of the paper was to manufacture test electrodes systems (Figure 5) to improve the quality by minimizing the resistance of a joint between the electrode and the substrate. There was prepared a special test electrode system, which was composed of series parallel paths about different distances between them. Test structure was prepared by screen printing method:

I. sizes of front paths were: 2 x 10 mm (wide x length), distances between them were: 20 mm, 10 mm, 5 mm, 2.5 mm,
II. sizes of front paths were: 5 x 10 mm (wide x length), distances between them were: 1 mm, 2 mm, 4 mm, 8 mm.

An initial series for testing the solar wafers was first prepared though laser micro-machining (Tab. 3) in order to achieve the smallest resistance value of the connection zone between the electrode and the silicon substrate of the solar cell and a uniform structure. Next to were selected laser micro-machining conditions for the test electrodes systems (Tab. 4) based on results of metallographic observations.

Test electrodes system I



Test electrodes system II

Figure 5: An overview of test front electrode system.

The basic parameters of the Eosint M 250 Xtended device are laser beam diameter-300 µm, wavelength-10640 nm, the feed rate of passage the laser beam - max. 3.0 m/s, laser beam with an output power-270 W, shielding gas–nitrogen. Table 5 is presented the conditions of co-firing solar cells in the infrared conveyor furnace. The conveyor IR furnace was equipped with tungsten filament lamps, heating both the top and the bottom of the conveyor.

Table 2: The paste properties.

Paste symbol	Surface morphology of the solar cell	Mass concentration of elements, %		
		Basic powder	Organic carrier	Ceramic glaze
UNCONVECTIONAL METHOD				
A	1, 2, 3, 4	88.40	9.60	2
CONVECTIONAL METHOD				
B	1, 2	60.60	39.40	-
C	3, 4	83.33	16.67	-

Comment: 1- Non-textured solar-cells with the deposited TiO_x coating, 2 - Non-textured solar-cells without the deposited TiO_x coating, 3 - Textured solar-cells with the deposited TiO_x coating, 4 - Textured solar-cells without the deposited TiO_x coating.

Table 3: Initial conditions of laser micro-machining for testing electrodes of silicon wafers.

Series	Solar cell surface	Paste symbol	The feed rate of passage the laser beam (v), mm/s	Laser beam, W	The thickness of front electrode, µm
1	Chemical cleaned	A	50 ÷ 200	10,8 ÷ 48,6	40, 60, 80

Table 4: Conditions of laser micro-machining for testing electrodes of solar cells.

Series	Solar cell surface	Paste symbol	The feed rate of passage the laser beam, mm/s	Laser beam, W	The thickness of front electrode, µm
1	1, 2, 3, 4	A	50	21.4; 24.3; 27	60

Comment: 1- Non-textured solar-cells with the deposited TiO_x coating, 2 - Non-textured solar-cells without the deposited TiO_x coating, 3 - Textured solar-cells with the deposited TiO_x coating, 4 - Textured solar-cells without the deposited TiO_x coating.

Table 5: Conditions of co-firing in the infrared conveyor furnace the testing electrodes of silicon solar cells (the front contact thickness of: 15, 40, 60 µm, the conveyor belt feed rate was 200 cm/min).

Series	Paste symbol	Temperature, °C		
		Zone I	Zone II	Zone III
1	B, C	530	570	830
				860
				890
				920
				945

The resistance of the metal-semiconductor connection zone depends on the composition of the conductive paste or metal powder from which the paths were made, as well as on the manufacturing conditions [2]-[3]. The schedule of series resistance (R_s) in a photo element is presented in Figure 6. The electrical parameters such as contact resistance (R_c), specific contact resistance (ρ_c), transfer length (L_T) of a front contact solar cell were measured onto a measuring position at the Institute of Engineering Materials and Biomaterials (Figure 7). It was applied the Transmission Line Model (TLM) method to determine mentioned electrical parameters. TLM consists in a direct current (I) measurement and a voltage (U) measurement between any two separate contacts.

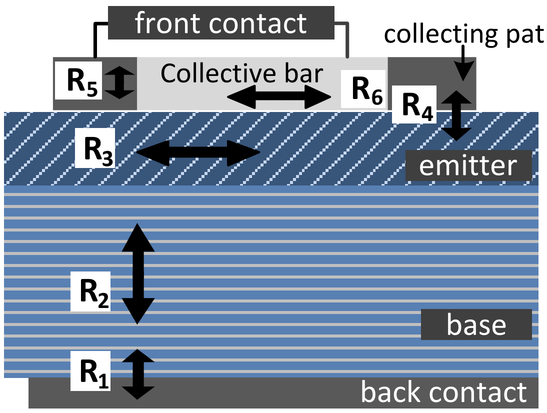


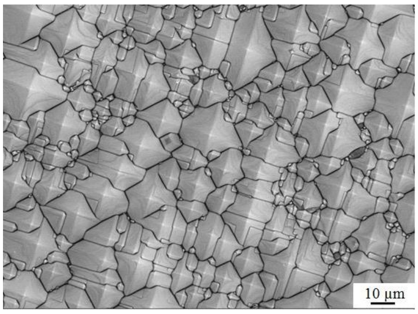
Figure 6: Scheme of series resistance: R_1,R_4 – metal-semiconductor, R_2,R_3-semiconductor material, R_5-the collecting path of front electrode, R_6-collective bar of front electrode [3, 8].

Figure 7: Measuring position of TLM method.

3 Results and Discussion

The topographies of the silicon wafers were observed with texture in the scanning electron microscope (Figure 8 a,b) and atomic force microscope (Figure 8 c). The average thickness of pyramids of 2 µm was determined with the atomic force microscope (Figure 8).

Figure 9 is presented the test front electrodes system I formed with selective laser sintering from the A paste. It was determined through metallographic observations that the grains form numerous spherical agglomerates of silver balls with varied sizes, are present individually on the electrode surface or forms the connected clusters of two or more agglomerates (Figure 19 a,b). The contact layers prepared from the A paste provide many non-homogenous connections with the silicon substrate, the contact points of the contacting particles are included only. Besides, some areas were found where the entire silicon substrate inside the electrode was not covered. It was determined through metallographic observations that the front electrodes prepared from A paste and selective laser sintering with the maximum feed rate of the laser beam (27 mm/s) have their structure more melted, which was created as a result of melting silver powder grains and through melting them together (Figure 9 c,d). Based, the occurrence of some empty areas of the silicon substrate in electrodes were revealed. As a result of the investigations carried out, the authors have withdrawn from applying the A paste for the front side metallization of silicon solar cells with the average thickness of 40 and 80 µm in their further work.



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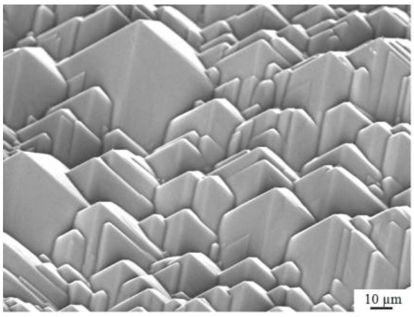

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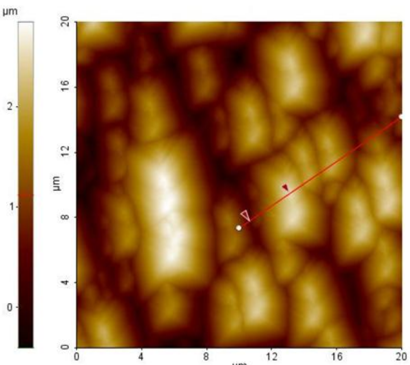

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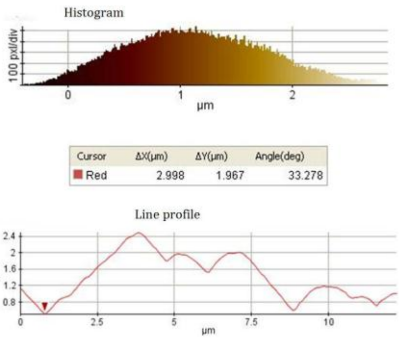
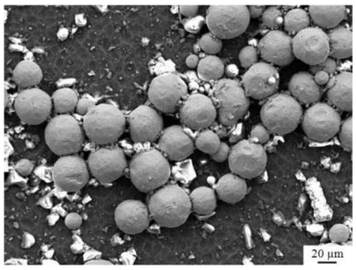


Figure 8: Topography of the textured surface of a solar wafer with the thickness of: a) 200 µm, b) 300 µm (SEM), c) 300 µm (AFM).

Based on electrical properties using the TLM method in the series (Tab. 4) it was found that the smallest specific contact resistance values of the I, II test electrodes system with the average thickness of 60 µm are 0.02÷0.78 Ω·cm², 0.11÷1.01 Ω·cm², properly, for solar cells with different morphology. A minimum specific contact resistance value was obtained for the test electrodes system I, II (0.02 Ω·cm²; 0.11 Ω·cm²) on a substrate without texture and without a TiO_x coating applied with a laser beam of 24.3 W and a laser beam feed rate of 50 mm/s. As a result of SEM investigations, the examined test front electrodes sintered with selective laser reveal the heterogeneity of the deposited metallic layer in form of a columnar structure with pores and a heterogeneous zone of the connection zone between the electrode and silicon of a solar cell (Figure 10).



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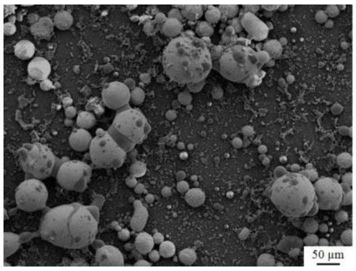

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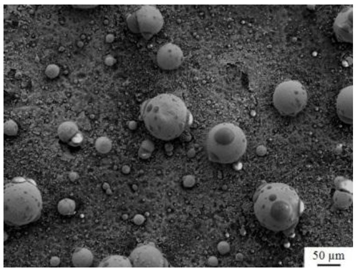

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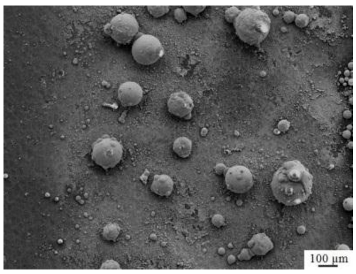


d

Figure 9: Surface layer topography obtained from the A paste on silicon surface by selective laser sintering with the laser beam feed rate of 50 mm/s and a, b) min. laser beam power of 10.8 W, c, d) max. laser beam power of 27 W (SEM). Comment -the front electrode with the average thickness of: 40 µm (a, c); 80 µm (b, d).

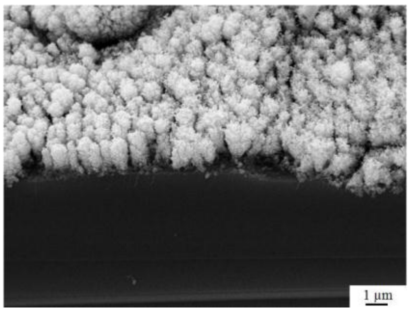


Figure 10: SEM fracture images of the front contact layer (the average thickness of 60 µm) from A paste on an Si substrate without texture and with an ARC layer by selective laser sintering with the laser beam of 24.3 W and the laser beam feed rate of 50 mm/s.

The thickness of the test electrodes was determined by checking the height profile of the three-dimensional surface topography measured using the confocal laser scanning microscope (Figure 11).

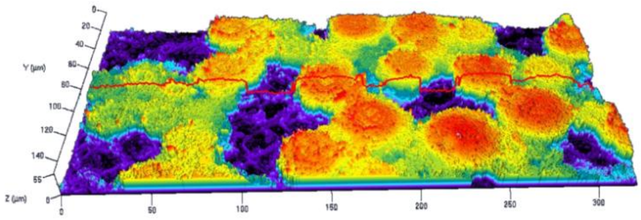


Figure 11: Three-dimensional surface topography (CLSM) of the front electrode prepared from the A paste on a surface without texture and with ARC layer subjected to selective laser sintering with the laser beam of 24.3 W and the laser beam feed rate of 50 mm/s.

The highest range of specific contact resistance was found in the series (Tab. 2.8) for front contacts made of B, C pastes. The minimum specific contact resistance value of the I, II test electrodes system within the temperature of 860 ÷ 945 °C is 0.44÷57.21 Ω·cm² (Figure 12) and 0.45÷38.19 Ω·cm² for solar cells with different morphology. It was found that paste resistance decreases as the electrode co-firing temperature increases by reason of the declining resistance of connection between metallic grains. Contact resistance was found to be growing along with a temperature increase. This can be caused by the molten silver molecules forming huge agglomerates and voids would develop under contacts for a textured surface. A finding was made according to fractographic investigations that the test electrodes made of B, C paste through co-firing in the conveyor furnace method demonstrated that the connection between the electrode and silicon is pointwise, independently of the sintering temperature applied and silicon morphology (Figure 13).

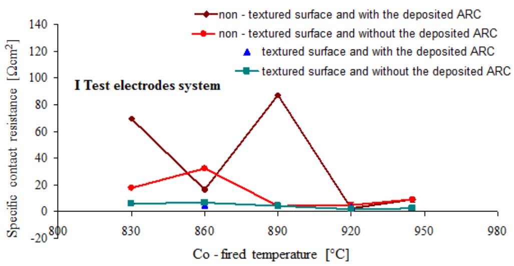
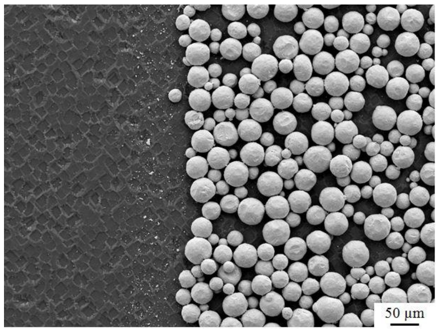


Figure 12: Specific contact resistance depending on co-fired conditions in the furnace with electrodes made from the B, C paste.



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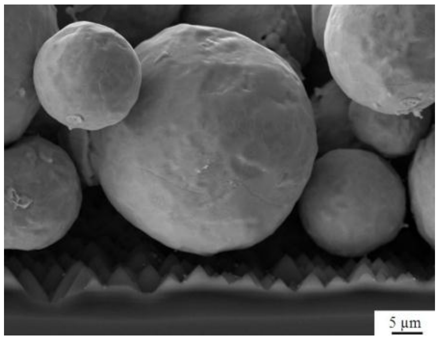

b

Figure 13: SEM images of the front contact layer co-fired in the furnace at the temperature of 830 °C: a) prepared from B paste and deposited on an Si substrate without texture and with an ARC layer, b) prepared from C paste and deposited on an Si substrate with texture and an ARC layer.

4 Conclusions

The paper has confirm that the laser micro-machining of the silicon elements of solar cells made from monocrystalline silicon, including the selective laser sintering of front electrode to its surface using the CO_2 laser improves the quality by minimizing the connection resistance of the front electrode with the surface. The following technology-related recommendations have been proposed as a result of the investigations performed. In a case of the selective laser sintering recommendations relate to the production of the front electrode of silicon solar cells:

- Paste composition–88.40%Ag+2%SiO_2+9.6% of an organic carrier,
- The average thickness of the deposited layer (60 µm),
- Laser micro-machining on two test systems – the laser beam of 24.3 W and the laser beam feed rate of 50 mm/s,
- The surface of a solar cell without texture and an ARC layer.

As a result of SEM investigations, the structure of the test electrode photovoltaic cell prepared from this paste and subjected to selective laser sintering shows columnar forms with pores. Based on the investigations of electrical properties using the TLM method, it was found that the smallest specific contact resistance values of the test electrodes system were obtained in an unconventional method in comparison with a conventional method. As a result of SEM investigations, for electrodes prepared from silver powder (60.60%Ag+39.40% of an organic carrier, 83.33%Ag+16.67% of an organic carrier), the connection between the electrode and silicon is pointwise, independently of the sintering temperature applied and silicon morphology.

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