

SLS: One of the Modern Technologies of Laser Surface Treatment

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Abstract Photovoltaic cells are one way of achieving solar energy. One of the stages of their fabrication is the production of front electrode. The application of an unconventional method of selective laser sintering using the CO₂ laser for the fabrication of front electrode of silicon photovoltaic cell was a real challenge. The most notable research results yielded by the research indicate what should be the focus of further investigation. The main objective of the paper is to work out the guidelines to be applied to laser micromachining of the front electrode of the photovoltaic cell concerning the selection of parameters such as the laser beam and laser beam feed rate, which give the possibility to assure its proper quality and suitable operating properties (including also its electrical properties). The investigation results obtained should yield the precise assessment of the laser micromachining conditions for the fabrication of front electrode of photovoltaic cells to improve their quality by the minimization of the Ag–Si interface resistance.

Keywords CO₂ laser · Front electrode · Selective laser sintering · Silicon solar cell

1 Introduction

Using the photovoltaic cells is one way to get solar energy. They allow the direct conversion of solar energy into electricity. Monocrystals are expensive in mass production but have very good properties and cell efficiency. The polycrystalline solar cells are less expensive, and therefore, are applied in the industry sector more frequently due

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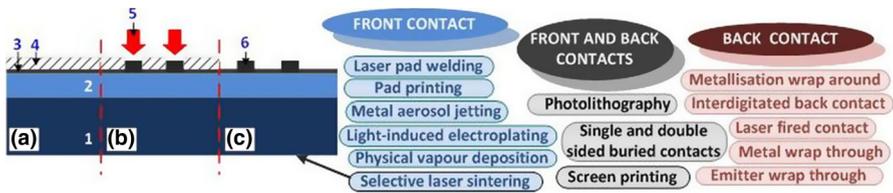


Fig. 1 Methods of producing contacts of solar cells with specification of SLS technology, which consist of the following stages: (a) metallic powder is deposited on wafer, (b) laser processing of front side metallization, (c) excess metallic powder from wafer (1—p-type base material, 2—n-type emitter, 3—dielectric layer, 4—powder layer, 5—passage of focus laser beam, 6—laser processing seed layers on the Si surface) [6–9]

to lower energy consumption during their production, but are a less efficient alternative to solar cells fabricated from the monocrystalline silicon. This is why, research studies are being carried out currently to find new solutions involving the production technology and the indispensable tools used for that purpose, aiming to raise their efficiency with the minimum reduction of material consumption [1,2]. It is anticipated that laser technology [3–5] will considerably simplify the fabrication of PV cells. One of the stages of their fabrication is the production of the front electrode. The electrode coating should meet specific requirements to guarantee the low resistance between the electrode and substrate, like its material and manufacturing technology, the geometrical quantity of the electrode, and substrate morphology. Different manufacturing methods are considered and analysed to improve the electrical properties of the front contacts, see Fig. 1 [6–9].

2 Experimental Procedures

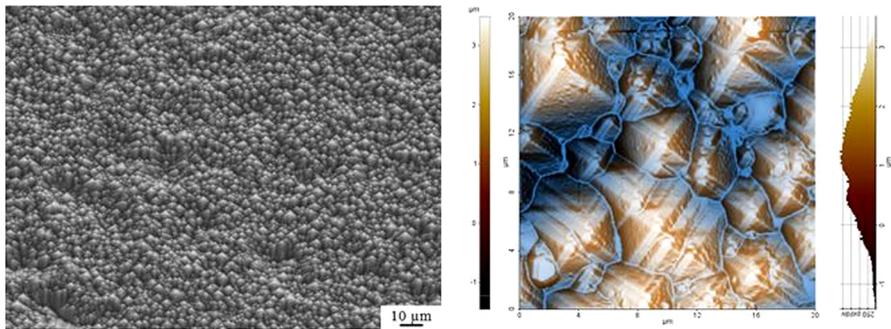
2.1 Specimens and Their Purity

Material properties of monocrystalline silicon used in this paper are as follows: conductivity—p-type (Si-doped boron), resistivity: $1 \div 3 \Omega\text{-cm}$, cross section: $50 \times 50 \pm 0.5 \text{ mm}$, thickness: $300 \pm 20 \mu\text{m}$, $200 \pm 30 \mu\text{m}$. The manufacturing process steps for the monocrystalline solar cells included: wafer surface degreasing process, removal of highly defective layer of the wafer surface, chemical processing, p-n junction formation, parasitic junction formation, surface passivation (SiO_2), antireflection coating deposition (TiO_x), overprinting of the front and back contacts, selective laser sintering of the front contacts.

Based on the preliminary metallographic investigations of the front electrode manufactured using the SLS method, silver powders were used of about $40 \mu\text{m}$ and 40 nm granulation (denoted Ag; nAg). The mechanical mixer was used to prepare mixtures. Selection of the contents to form the front electrode of the photovoltaic cell was as follows: $83\% \text{ nAg} + 2\% \text{ SiO}_2 + 15\% \text{ organic carrier}$ —A paste, $8.40\% \text{ Ag} + 2\% \text{ SiO}_2 + 9.60\% \text{ organic carrier}$ —B paste. The photovoltaic cells were produced on a textured surface with a coated anti-reflexive layer most commonly

Table 1 Conditions of laser micro-treatment testing electrodes of silicon solar cells

Series	Morphology	Paste symbol	Laser beam feed rate (ν), (mm/s)	Laser beam (P), (W)	Thickness of front electrode, μm
1	Textured with deposited antireflection coating	A	50	37.8; 40.5; 43.2	15; 35
2		B	50	21.6; 24.3; 27	60

**Fig. 2** Topography of the textured surface of monocrystalline solar wafer with thickness 200 μm SEM (on the right), AFM (on the left)

applied in practice, since such a coating, among others, ensures the highest efficiency of the photovoltaic conversion.

Front electrodes were elaborated to determine the suitability of the particular pastes, applying the micromachining technology to produce the required batch of silicon solar cells. One aspect of the work was the manufacture of the test electrodes systems on the surface of the solar cell using this technology. Based on the theoretical analysis and practical verification, the model was adopted in the work in which two custom made test electrode systems (denoted 1; 2) were prepared with the conventional method: sizes of the front paths were (width \times length): (1) 2×10 mm, (2) 5×10 mm; spacing between them was: (1) 20 mm, 10 mm, 5 mm, 2.5 mm, (2) 1 mm, 2 mm, 4 mm, 8 mm. The semi-automatic screen printer (made by de Haart IMMS ST/8/198) was applied to deposit these electrodes. Next, the printed silicon wafers were dried in a dryer (KBC-2W type). Finally, the electrodes were put to the selective laser sintering process (Table 1) (see Fig. 2) with the following selected parameters: laser beam output power—270 W, laser beam feed rate—max. $3.0 \text{ m}\cdot\text{s}^{-1}$, wavelength 10640 nm, laser beam diameter—300 μm .

2.2 Description of the Experimental Technique

The following work agenda was employed to carry out the present research objectives:

1. Elaboration of the metallization method of front electrodes of the photovoltaic cell to determine the applicability of particular pastes using the SLS technology;
2. Laser processing of the test electrodes' system to its face applying EOSINT M 250 Xtended device equipped with a CO₂ laser [10];
3. Testing of electrical properties of the front electrode using the transmission line method TLM at the research stand, in which the particular component elements were designed and worked out by the author of this paper to determine the minimal resistivity value of the contact area silicon-front electrode of the solar cell;
4. Testing the topography of the textured surface of the monocrystalline silicon wafer using the metallographic methods (scanning electron microscopy, atomic force microscopy) to determine average height of pyramids of the textured surface;
5. Testing the topography of the surface and cross-section of the produced electrode and Ag–Si interface with the use of metallographic methods (scanning electron microscopy methods, confocal microscopy) to determine the quality of the obtained structure.

3 Results

It can be found that the most popular conventional method to do metallization is the silk-screen printing. It is confirmed by the available literature studies [11–14], and author's experience [7,8], The analysed literature data and own research carried out on front electrodes indicate that the best properties (electrical and structural) are demonstrated by the test system burnt out in the furnace and obtained from the commercial paste. The coating process of silicon layer using the silk-screen printing is time-consuming and difficult to automate. It seems to be grounded that further experimental research involving the initial phases of the process should be carried out—taking into account the material factors and fabrication conditions (having the impact on quality, in particular with the application of pastes and powders) as well as economic factors. Such approach is also confirmed by some examples involving the fabrication of the front metallization with the use of laser methods presented in the available literature [7,8,15–18]. In the literature review, the author came across not that many publications relating to undertaking this problem. In the paper, most of all, attention was devoted to investigations on the development of the conditions for manufacturing of the front electrode employing silver powders with different granulations (being the paste component) using the laser technology.

To assess the impact of the agreed micro-treatment conditions, including mainly the laser power, laser beam feed rate, layer thickness and the type of the silver paste on the electrical properties of solar cells, two series of test electrode systems of the front electrode were selected for testing. For the first batch, the silver paste based on powder with granulation A was applied, in the second batch, the paste was applied with the nanometric granulation B. The electrical properties of the test front electrode systems of photovoltaic cells were analysed in this study. The minimum range of the specific contact resistance (minimum, maximum) of the solar cell was the criterion for selection of the operating conditions.

It was found that in the first batch, the smallest specific contact resistance values of test electrodes system for the first batches I, II were $1.03 \div 12.28 \Omega \cdot \text{cm}^2$, $1.12 \div 2.20 \Omega \cdot \text{cm}^2$; $0.04 \div 0.09 \Omega \cdot \text{cm}^2$, $0.79 \div 0.99 \Omega \cdot \text{cm}^2$ and for the second series $0.12 \div 0.15 \Omega \cdot \text{cm}^2$, $1.01 \Omega \cdot \text{cm}^2$, suitable for the photovoltaic cells with the textured surface and the antireflection coating deposited. Based on the obtained investigation results, the following micro-treatment conditions of the front electrode were found: laser beam $P = 48.6 \text{ W}$ and laser beam feed rate $v = 50 \text{ mm/s}$, as well as recommendations for the optimal technology for the manufacturing of the front side metallization: the composition of paste (a), the average thickness of applied electrode layer ($35 \mu\text{m}$). Based on these batches, it was found that electrical properties of an electrode are greatly dependent on the participation of the particular components of pastes from which are prepared. Granulation - the geometrical shape of powder—has a significant impact on paste conduction. The ceramic glaze (SiO_2) gives the paste a proper viscosity and combines base material particles between each other and with a substrate. The following parameters: an antireflection coating, surface morphology, and thickness of depositing paste also has an influence on obtaining the electrical properties of the electrode. In a case of an antireflection coating, it ensures the good protective properties of solar cells surface and prevents reflecting of energy loss. The textured surface results in improved performance to an increase in the short-circuit current. The textured surface of silicon wafers was observed in two microscopes. The medium textured surface was equal to $3 \mu\text{m}$. The repeatability of the obtained measurement resistance results and better morphology of the electrode structure (without cracks, for example) and the Ag–Si interface, complete in the paste composition the powder granulation. Based on the metallographic observations of structures, it was found that laser processing testing of the front metallization with the medium thickness of $35 \mu\text{m}$ appear to be well concentrated, without pores, discontinuities, also adhering well to the silicon substrate (see Fig.3). However, testing of the front contacts with the thickness of about $15 \mu\text{m}$ revealed areas of the totally uncoated silicon substrate and damages of their coat in the form of micro-burst, which can possibly be caused by laser micro-treatment, in some places, a distinct granular structure is visible (see Fig. 4). In a case of the front side metallization obtained from paste B and with laser processing, it shows columnar forms with pores (see Fig. 5).

4 Conclusions

The results of the author's research have yielded the answers to the following research questions (the answers which might be the basis for the determination of the optimal fabrication technology of photovoltaic cells due to the minimum resistivity of the electrode):

1. What is the optimal granularity of the applied silver powder and optimal composition of silver paste for the acquisition of front electrode of solar silicon cell using the method of selective laser sintering?

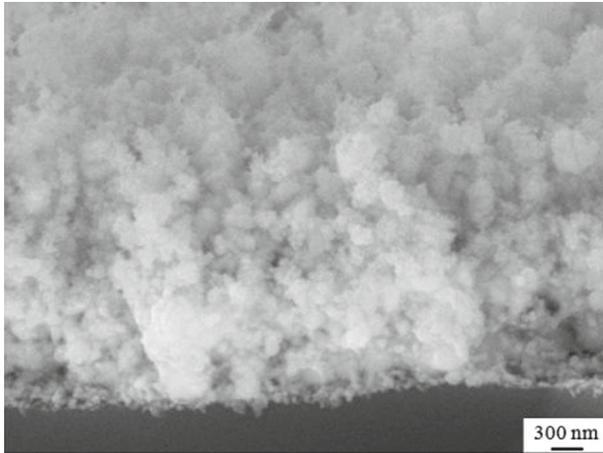


Fig. 3 SEM fracture image obtained from paste A on silicon surface SLS with the laser beam feed rate 50 mm/s and minimum laser beam power 48.6 W

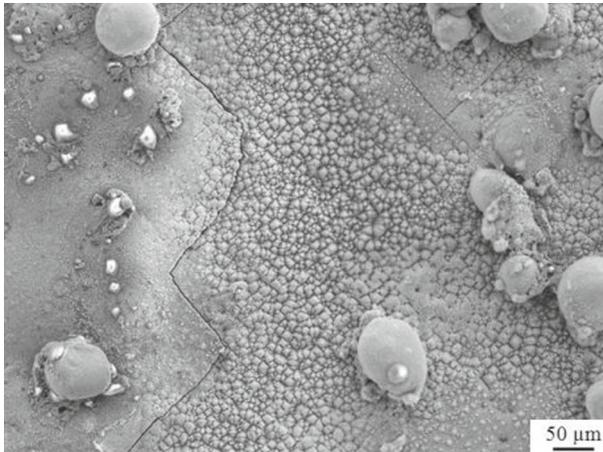


Fig. 4 Surface layer topography obtained from paste A on silicon surface SLS the laser beam feed rate 50 mm/s and minimum laser beam power 40.5 W

The optimal granularity of the applied silver powder is 40 nm, and the optimal composition of silver paste for the acquisition of front electrode of solar silicon cell using the method of selective laser sintering is A paste.

2. Do the electrical properties of the front metallization closely depend on the share of components of pastes or powders from which they are made?

Yes, they do. The conductivity of the tested silver paste depends on particle shape and size, powder content of the composition.

3. What is the impact of the condition of silicon substrate surface (its morphology and anti-reflexive layer) as well as the thickness of the deposited metallic coating on the resistance value of Si–Ag interface?

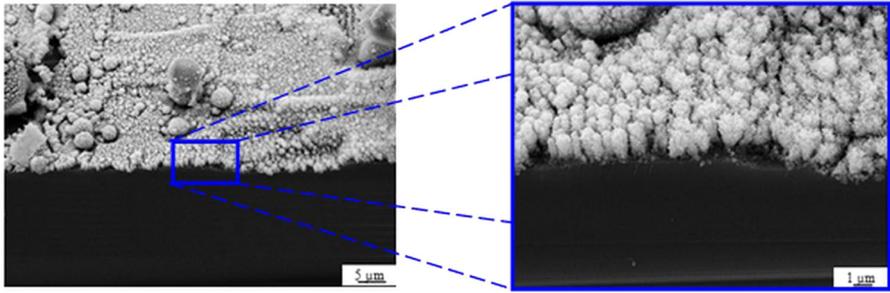


Fig. 5 SEM fracture image obtained from paste B on silicon surface SLS with the laser beam feed rate 50 mm/s and minimum laser beam power 24.3 W

In the case of the silicon substrate morphology, it has an important impact on obtaining the minimal resistance value of electrodes made by laser processing from the silver paste. It is bigger for textured surface rather than for the one without it; probably this is because of the empty places under the contacts. In a case of the antireflection coating, it creates a barrier into the connection zone, which has an influence on the increase of resistance between the electrode and substrate. The deposited thickness layer has an impact on electrode structure and its resistance value.

4. Does the laser micromachining of silicon elements of photovoltaic cells from monocrystalline silicon, including the selective laser sintering of front electrode to its surface, using CO₂ laser have an influence on the quality improvement of the cell through minimising the resistance of front electrode interface with the substrate?

Yes, it does. Laser processing improves the quality by minimization the connection resistance of the front electrode with the surface.

The application of an unconventional method of the selective laser sintering for the fabrication of front electrode of silicon photovoltaic cell was a real challenge since this problem has not been investigated to date, and the author of the project is the first to have undertaken this problem in Poland. The most notable research results yielded by the study indicate on what the further investigation studies should be focused. These are, among others:

1. The acquisition of lower resistance of the front electrode interface made from silver nano paste using laser micromachining method with the silicon substrate as compared to burning out in a furnace.
2. The selection of optimal conditions of laser micromachining of the electrode testing system, including the intensity of laser beam and scanning speed of the beam.
3. The elaboration of optimal composition of silver nano paste and thickness of the coated layer.

The work carried out so far has brought to light new problems and also indicated new potential perspectives which should also be taken care of. In the already completed

research, Si inserts with the textured surface and without texture were applied to find out the influence of substrate type on electrical properties of the obtained front electrodes. Although the application of Si inserts without the anti-reflexive coating (ARC) prior to the metallization process is somehow in contrast with the process engineering, which results from the fact that the ARC layer protects the Si layer against pollution during the metallization process of front electrode, yet nobody has carried out such research in Poland using this method. Therefore the research carried out has the undoubtedly informative value. Technical limitations of the apparatus in the investigations carried out, including mainly the scanning speed of laser beam (min. 50 mm/s), made it impossible to fabricate a structure of the front electrode of regular shape, without cracks or micropores. This somehow critical approach should give an impulse for further studies. The investigation studies on the elaboration of fabrication conditions of front electrode with the use of silver powders of various granulation and silver pastes (including nano pastes) with the application of laser technique, which has currently become an indispensable element of modern photovoltaic technology, will have an innovative contribution to the solution of present photovoltaic problems and will become a challenge of some sort since the problem is relatively new in Poland. Hence the results of the work on that problem may provide a guideline for other research workers what to focus on in the further research.

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