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Selective laser sintering method of manufacturing front electrode of silicon solar cell

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Properties

ABSTRACT

Purpose: The aim of the paper is to demonstrate a laser method of micro-machining front contacts of monocrystalline solar wafers. This means forming front electrodes in order to decrease their resistance. It was demonstrated, that laser processing is a promising technique for selective laser sintering (SLS) solar cell contacts compared conventional forming front grid methods.
Design/methodology/approach: The topography of laser micro-machining contact formations and screen-printing were investigated using ZEISS SUPRA 25 scanning electron microscope. The materials used in the present invention are different granulation silver powders. The grain size analysis were used in order to determine their size. The transmission line model (TLM) patterns were fabricated by selective laser sintering.
Findings: This work presents an initial analysis of a new selective laser sintering/melting process to contact crystalline silicon solar cells. The seed layer was created using both silver pastes and powders by a selective laser sintering, do not use up to now in Poland. These contact structures were investigated microscopically to gain a better understanding of the method and select laser micro-machining parameters, which will influence on electrical parameters of formed front side grids.
Practical implications: SLS can produce parts from a relatively wide range of commercially available powder materials. The physical process can be full melting, partial melting, or liquid-phase sintering and depending on the material. The thickness of silicon solar wafer can cause some difficulties connected with adhesion electrode during contact formation process.
Originality/value: In pursuing the purpose of increasing the efficiency η of industrial crystalline solar cells to reduce costs of PV electricity, a measure to improve the front side grid is interesting – decreasing contact resistance and increasing efficiency in this way.
Keywords: Electrical properties; Solar cells, Photovoltaics; Laser micro-machining, Selective laser sintering, Transmission line model

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1. Introduction

Selective Laser Sintering consist on integration of a powder layers using a laser beam (for instance: Nd-YAG or CO_2) and it is designed for manufacturing models of tools and prototypes. The selection of adequate parameters allows to melt or sinter a metal powder particles in precisely definite areas. A whole process (processing or mirco-processing) is controlled by program [1, 5-9].

1.1. Description of the SLS method

The forming a front electrode with SLS can be realized according to the following (Fig. 1) stages [1-6]:

1. Before laser processing a silicon wafer is located in a chamber to sintering, where a special drift fender deposits uniformly a metal powder (for example: W, Mn, Pd, Ag, Al or their mixtures) on it's surface (Fig. 1a). The excess of the powder is moved into a container, so the rest of the powder is recovered and can be utilized once again.
2. A laser beam scans a surface of powder layer onto silicon wafer according to introduced before data, which concerned next layers of cross-section of a spatial picture object (Fig. 1b).
3. A table is lowering below determined before height in the programme and another powder layer is deposited by drift fender (then a bonding of grains takes place). There are used a few short and intensive laser impulses, delivering especially for a connecting material and accurate location repeated actions of sintering or melting, which are a typical feature of this method. The cycle is repeated until a front electrode on the surface of the solar cell with desirable properties is obtained (Fig. 1c).

The description of application of this method for the front side metallization of silicon solar cell will be presented. The aim of the present paper is to optimize co-firing parameters of LMS front contacts obtaining procedure.

2. Experimental procedure

The investigations were done on circular wafers from monocrystalline silicon (100) produced by Deutsche Solar (Germany). The basic parameters of these wafers are:

- type: p
- doped: boron
- thickness: 300 ± 10 μm
- the diameter about 8 cm
- resistivity: 1 Ωcm
- carbon concentration: $1x10^{18}$ atoms/cm^3
- oxygen concentration: $2x10^{17}$ atoms/cm^3

The baseline process for the fabrication of monocrystalline solar cells consisted only of the chemical etching. The chemical procedure for cleaning the wafers is given in Table 1.

Two different granulations silver powders were used in the investigations:

- <40 μm (Ag) (Fig. 2a),
- <40 nm (nAg) (Fig. 2b).

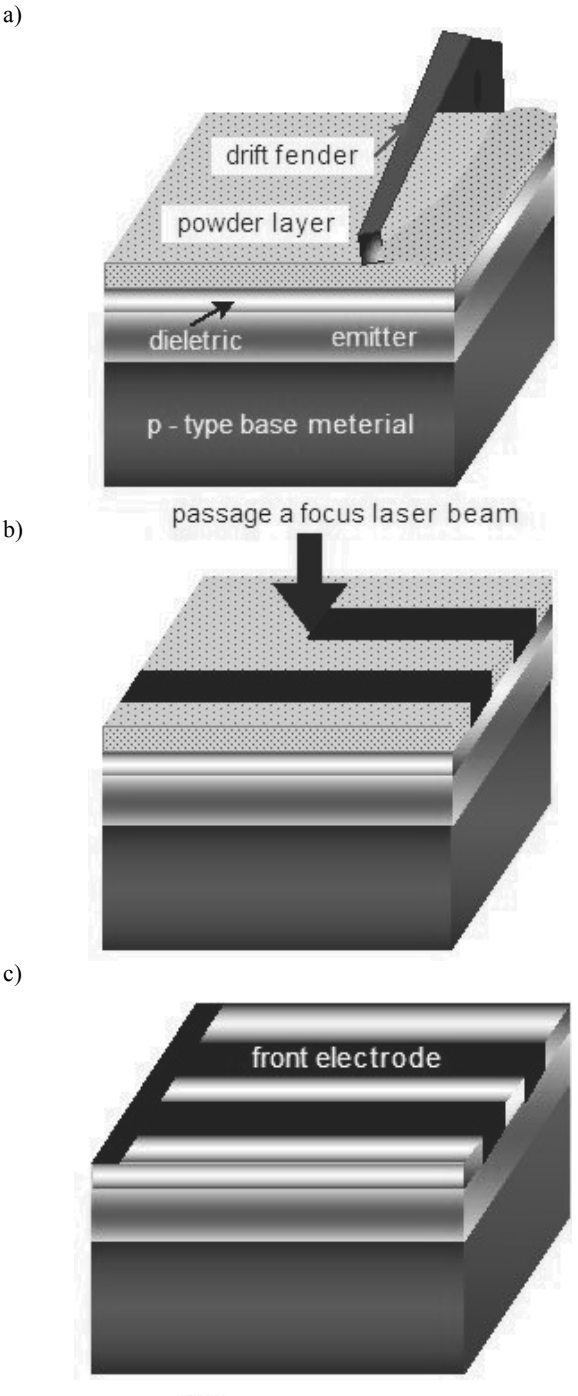


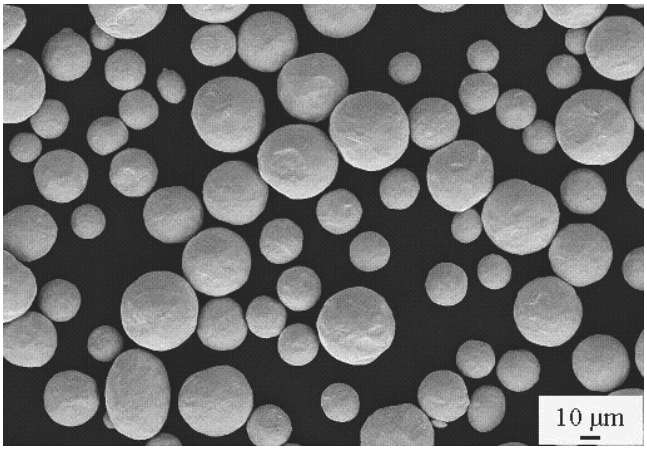
Fig. 1. Scheme of laser sintering process: a) deposition of powder of metal on the surface of the silicon wafer, b) scanning a powder layer by laser beam, c) forming front electrode

There was used also a ceramic glaze (SiO_2) during experiments, in order to increase a wettability of silicon. It was added into silver pastes. The powders were offered by Stanchem company.

Table 1.
Chemical processing of silicon wafers

Chemical process	Chemical recipe	Time (min)	Temp. (°C)
Washing in acetone	CH_3COCH_3	10	56
Rinsing	DIH_2O	0.5	21
Distorted layer removing	30% KOH	3	81
Rinsing	DIH_2O	1	50
Metallic contamination removing	2%HCl	10	25
Native oxide removing	10%HF	10	25
Rinsing	DIH_2O	10	25

a)



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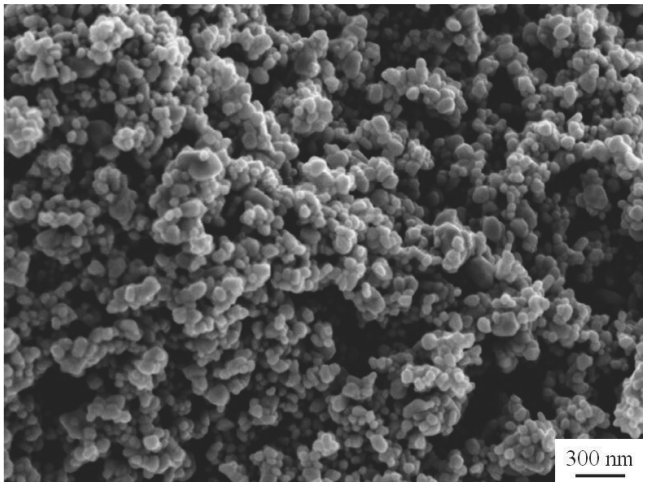


Fig. 2. SEM micrographs of base powders: a) Ag, b) nAg

Grain fractions analysis of Ag samples were performed using the Analbaliysette 22 - Fritsch company, according to a standard PN-ISO 9276-1. The Zetasizer S90 – Malvern laser analyser was used for NAg, according to a standard PN-ISO 13321.

Selective laser sintering is performed by machines called SLS systems, which gives a possibility to easily make very complex geometries directly from digital CAD data. The formula of row parallel lines were designed in a *stl file on the basis on 3D model in CAD – AUTODESK Inventor Professional 2010 x 64 programme. The testing structure was performed on silicon wafer. The testing structure consisted of five identical contacts (in a shape of thin paths, width equals about 2 mm and length equals about 10 mm, each pair of contacts being separated by a variable distance namely: d_1=20 mm, d_2=10 mm, d_3=5 mm, d_4=2.5 mm.

The applied laser is a medium energy CO_2 laser, which is used to sinter metal powders and their alloys in a serial and elementary production. The basic characteristic data of device are presented in Table 2.

Table 2.
The technical specification of CO_2 laser [5]

Scanning speed:	3,0 m/s
Thickness of putting on powder layers	20 – 60 µm
Accuracy of obtaining subjects	+/- 0.05 mm
Laser output power	270 W
The diameter of laser beam	300 µm
The maximal dimension of building element	250 x 250 x 200 mm
Activation method	electric energy
A system of putting on a gas shroud, integrated generator of nitrogen in a device	gas shroud - nitrogen

Table 3.
Technological conditions of laser micro-machining

Symbol of sample	Thickness of layer [µm]	Scanning speed [mm/s]	Laser energy [W]	Distance between lines in filled area of path [mm]
A1	60	100	135	0.45
A2		200	135	
A3		100	202.5	
A4			256.5	
A5	20	100	121.5	0.3
A6			162	
A7			135	
B1	40	100	54	0.2
B2			81	
B3	60		54	
B4			81	
B5			54	
B6			81	
C1	60	100	135	0.2
C2			135	
C3			202.5	
D1	60	100	54	0.2
D2			67.5	
D3			45.9	

There were performed numerous tests to select proper conditions of laser micro-machining and form front contacts on the surface of silicon solar cells (Fig. 3).

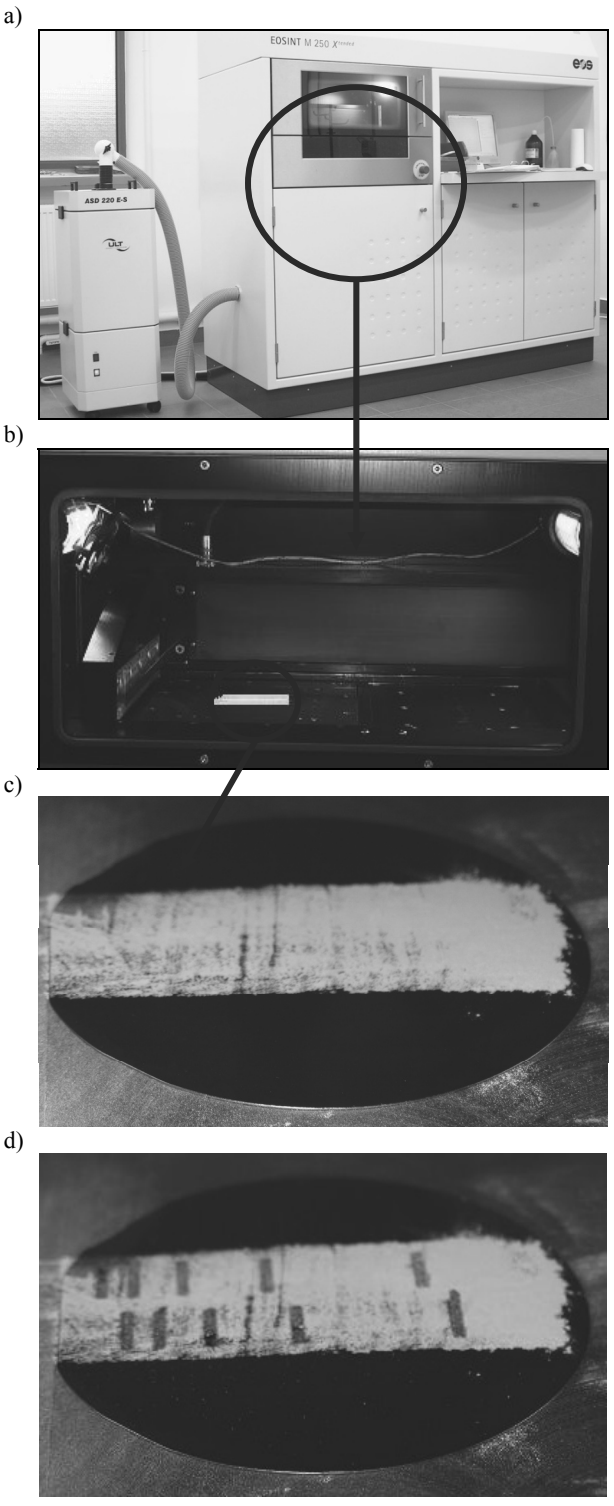


Fig. 3. The laser micro-machining system: a) the EOSINT M 250 Xtended device, b) a working chamber, c) a surface of powder layer onto silicon wafer before SLS, d) front electrodes obtained on the monocrystalline wafer after SLS

In order to select proper proportion of mixture or paste elements different combinations of theirs contents were used:

- only powder: 100%Ag and 100%nAg - samples A1 - A6,
- powder and ceramic glaze: 90%Ag/10%SiO_2 - samples B1 - B6,
- powder and organic element and ceramic glaze: 73.33%Ag/16.67% org. el./10% SiO_2 - samples C1 -C3,
- powder and organic element and ceramic glaze: 71%nAg/15% org. el./6% SiO_2 - samples D1 - D3.

Tests were performed for different scanning speeds, thickness of electrode and power of laser (Table 3).

3. Results and discussion

As result of etching in a solution of 30% KOH, approximately 7.07 μm of material on both sides of the wafers was removed.

Qualitative and quantitative chemical composition of mixtures and pastes is presented in Table 4.

Table 4.
Chemical composition (wt.%) of wafers determined using energy dispersive spectrometry (SEM/EDS)

No	Symbol	Element	Wt. [%]
1	B3	C	3
		O	21
		Na	1
		Al	1
		Si	7
		Ag	64
2	B4	Al	2
		Si	97
3	C1	C	4
		O	9
		Si	9
		Ag	76
4	D1	O	15
		Na	2
		Al	4
		Si	44
		P	1
		Ag	23
		Ca	6
5	D3	C	6
		O	5
		Na	1
		Si	22
		Ag	64

Figures 4 and 5 present the results of grain size analysis of Ag and nAg powders.

It was found that the average grain size of Ag grains was higher (for example, in the last class grain range from 229 to 2 it was found 0.61% medium grain size molecules (247.06 μm) than specified by manufacturer (<40μm).

The histogram of nAg grain distribution (Fig. 4) shows that investigated sample has multimodal distribution. This is confirmed by high value of PI parameter (PI - polydispersity index determined in a range from 0.2-0.5; dimensionless measure of width

distribution size molecule), which is equal 0.45. Some agglomerates of nAg were observed, but their amount was slight and the size of silver molecules was close to specified by manufacturer.

On the basis on microscopic and macroscopic observations of formed front electrodes, it was found that:

- Ag powder was well distributed on the surface of silicon wafer by drift fender,
- nAg was badly distributed powder on the surface of silicon wafer by drift fender, because it slid on the wafer surface,
- in a case of samples: A1 and A2 - Ag powder was melted on the surface of Si wafer, but electrodes completely got unstuck,
- in a case of both samples: A3 and A4 - Ag powder was melted on the surface of Si wafer, but electrodes were very weakly held to a Si surface,
- samples A5 - A7 cracked under the effect of thermal shock, what was caused a weak wettability of silicon surface,
- in a case of both samples: B1 and B2 a mixture was melted on the surface of Si wafer, but electrodes partly got unstuck,
- there were observed on Si surface of sample B3 some single agglomerates (islands) of silver, however on the surface of electrode on sample B4 were observed numerous cracks and vestigial quantity of silver,
- in a case of B5 and B6 samples most of electrodes completely or partly came unstuck from Si substrate, the similar situation was in a case of both C2 and C3 samples,
- in a case of sample C1 a paste was melted on the surface of Si wafer, but there were still found some cracks on electrodes,
- in a case of sample D1 a nano - paste was locally melted on the surface of Si wafer, but there were visible very small cracks on the electrodes ,
- in a case of sample D2 a nano - paste was melted on the surface of Si wafer, but there were visible very big cracks on the electrodes, there were visible significant amount of silicon rather than silver in melted electrodes,
- in a case of sample D3 a nano - paste was melted on the surface of Si wafer, but there were visible sparse cracks and SiO_2 coated a top surface of electrodes, what completely has a negative influence on electric parameters of front electrodes.

SEM images of a path of contact layer prepared by LMS using some pastes or mixture elements are presented in Figures 6-10.

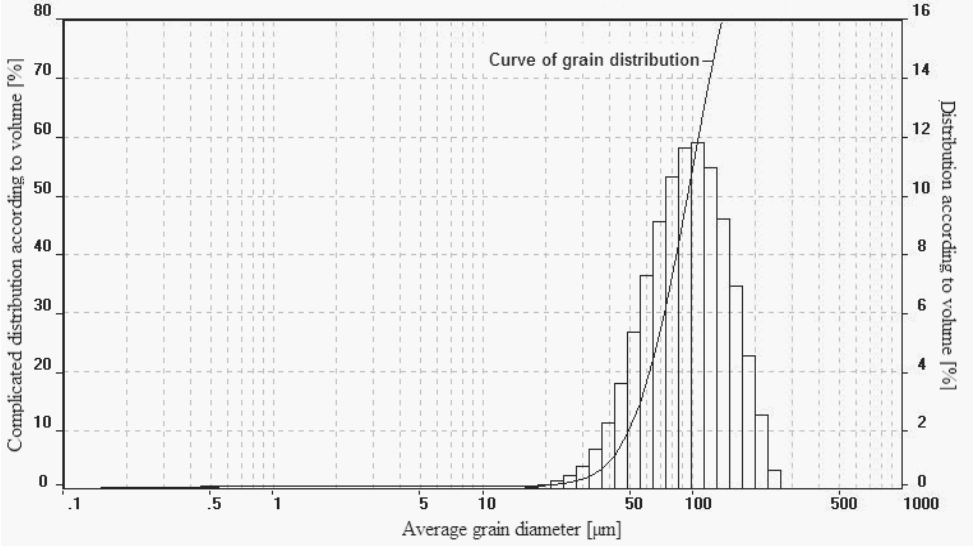


Fig. 4. Grain distribution according to volume for Ag powder, determined using the Analbaliysette 22 - Fritsch company, according to a standard PN-ISO 9276-1

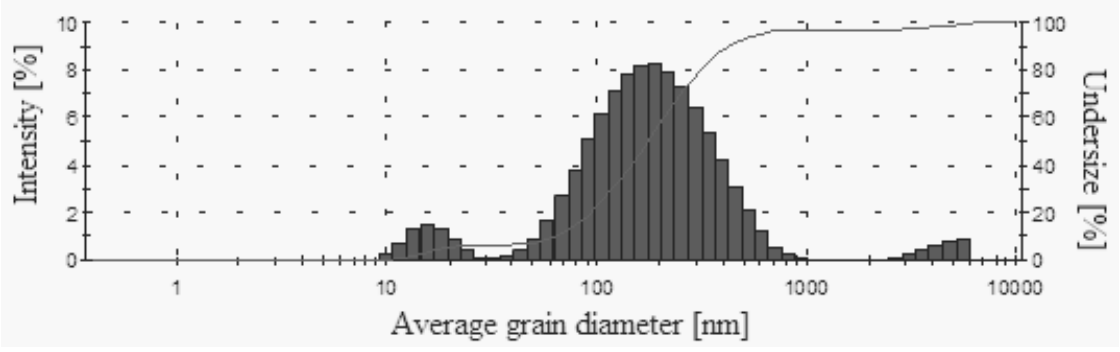


Fig. 5. Grain distribution according to volume for nAg powder determined using the Zetasizer S90 - Malvern laser analyser, according to a standard PN-ISO 13321

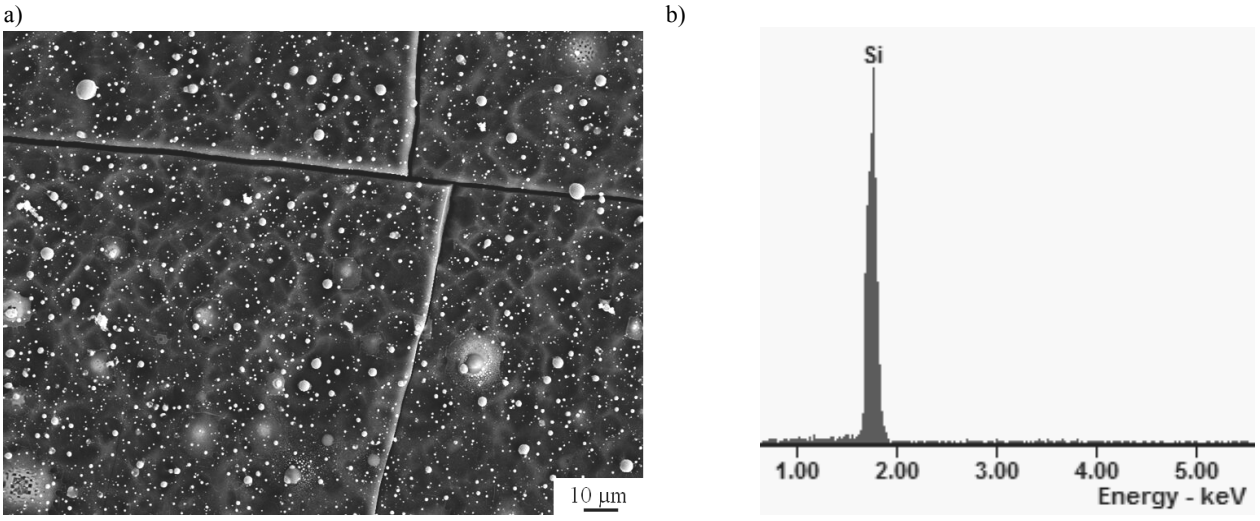


Fig. 6. SEM images of a path of nAg contact layer prepared by LMS (A1), a) topography image, b) EDS spectrum from X1 area

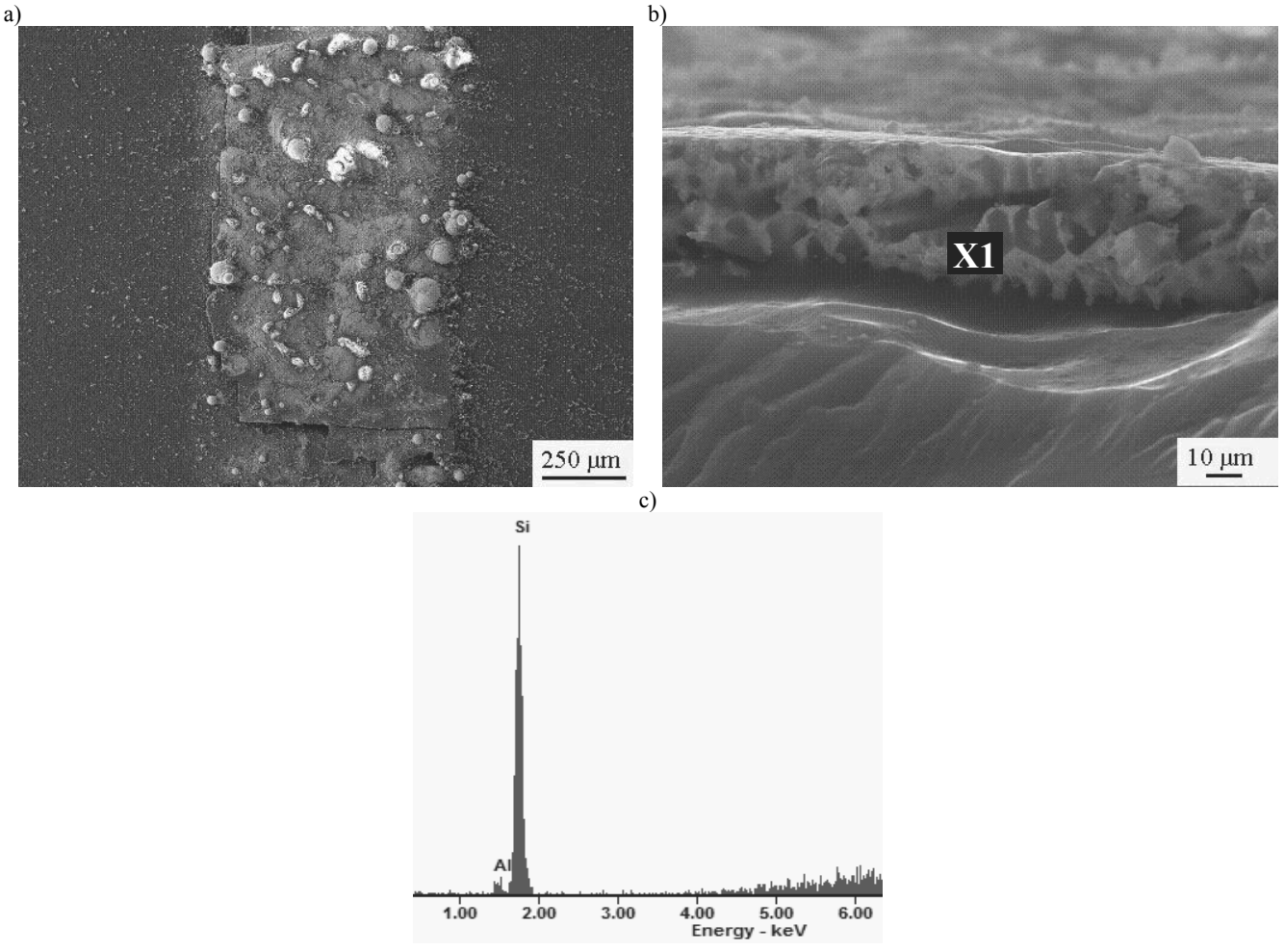


Fig. 7. SEM images of a path of one contact layer prepared by LMS (B4 sample), a) topography image, b) fracture image, c) EDS spectrum from X1 area

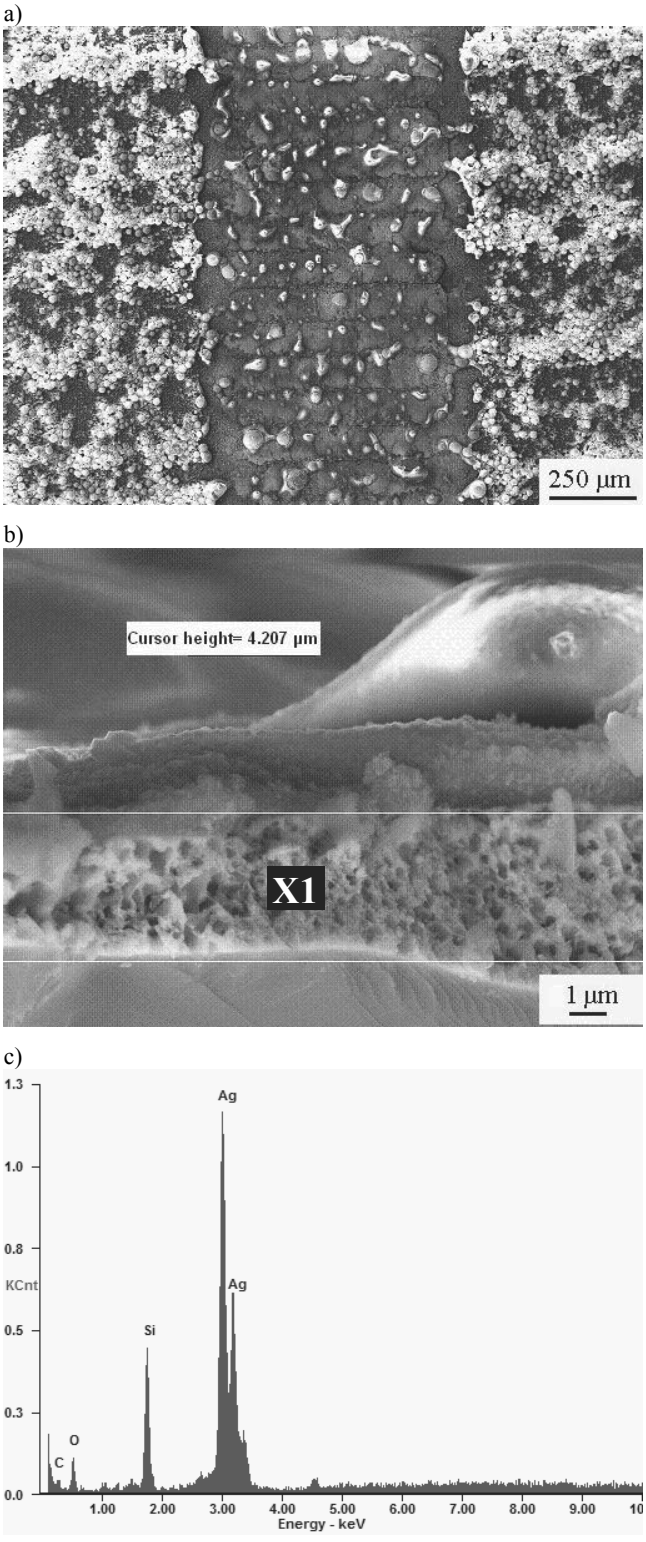


Fig. 8. SEM images of a path of one contact layer prepared by LMS (C1 sample), a) topography image, b) fracture image, c) EDS spectrum from X1 area

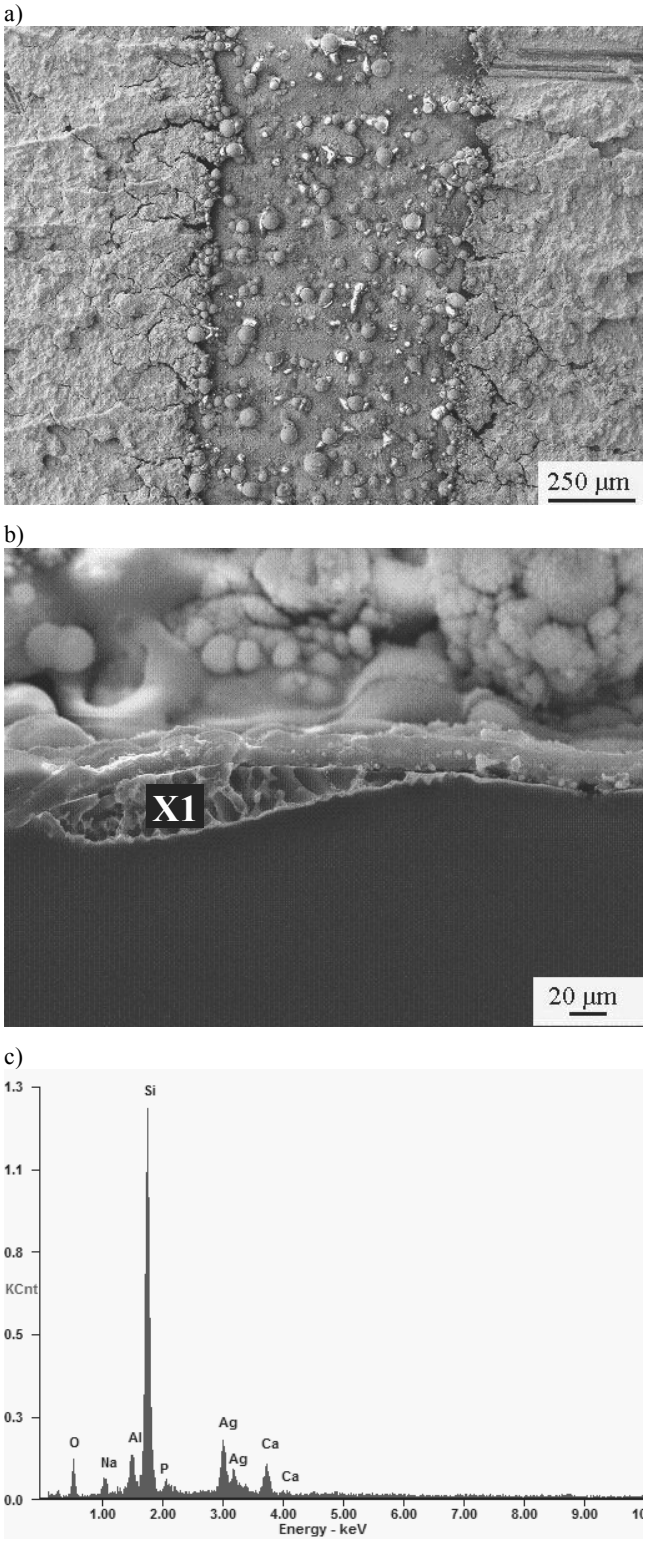
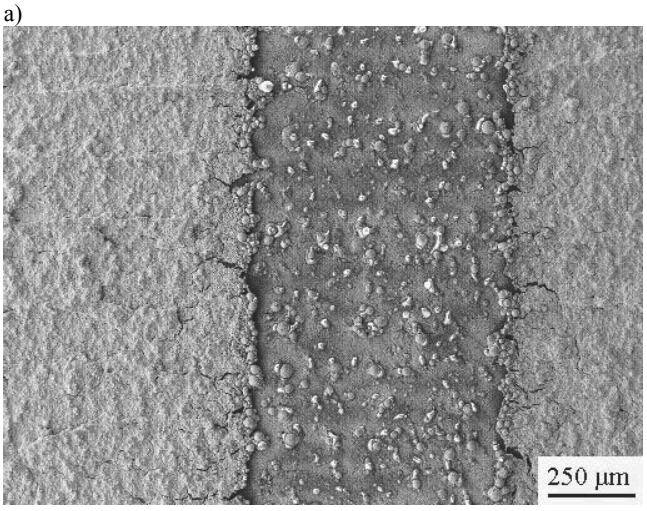


Fig. 9. SEM images of a path of one contact layer prepared by LMS (D1 sample), a) topography image, b) fracture image, c) EDS spectrum from X1 area

a)



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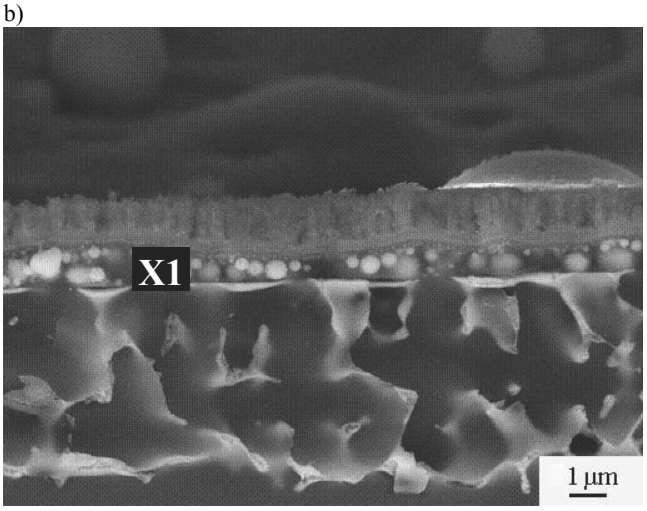

c)

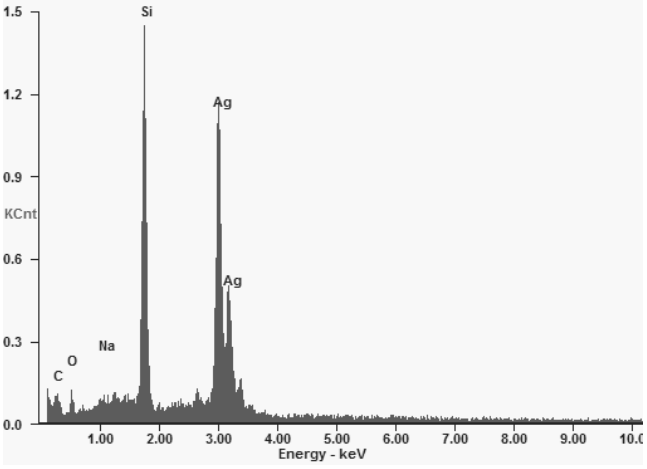

Fig. 10. SEM images of a path of one contact layer prepared by LMS (D3 sample), a) topography image, b) fracture image, c) EDS spectra from X1 area

4. Summary

Obtained results confirmed that grain size of NAg powder is close to specified by manufacturer while the average grain size of Ag grains is higher than value given by manufacturer.

As a result of performed experiments parameters of LMS procedure were established. The amount of SiO_2 added to silver paste should be smaller than 6%, otherwise the sintered electrode on the surface of solar cell will not conduct. Silver powder cannot be used without SiO_2 for contact layer preparation, because obtained layers on silicon wafers have numerous cracks.

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Additional information

Selected issues related to this paper are planned to be presented at the 16th International Scientific Conference on Contemporary Achievements in Mechanics, Manufacturing and Materials Science CAM3S'2010 celebrating 65 years of the tradition of Materials Engineering in Silesia, Poland and the 13th International Symposium Materials IMSP'2010, Denizli, Turkey.

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