

New kind of Cu based paste for Si solar cells front contact formation

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Potential impact of copper replacing silver in the paste used for the front electrode fabrication in crystalline silicon solar cells was investigated. The copper was applied as a new CuXX component with about 2 wt.% to 6 wt.% share of XX modifier. The generated CuXX molecules were analyzed using transmission microscopy. Based on the commercial Du Pont PV19B paste, CuXX and XX materials, the new PV19B/CuXX paste with 51 wt.% share of Cu and the PV19B/XX paste with 51 wt.% share of XX only were developed. Comparative studies of the effect of the commercial PV19B paste made by DuPont Company, and the pastes with the CuXX component and with the modifier XX alone on the electrical parameters of solar cells produced on crystalline silicon were carried out. The solar cells were characterized by the current-voltage technique. As a final result, the Cz-Si solar cell with the 51 wt.% share of Cu in the front electrode having a series resistance of $0.551 \Omega \cdot \text{cm}^2$, an efficiency of 14.08 % and, what is more important, the fill factor of 0.716, was obtained. It is the best result ever obtained concerning direct Cu application for solar cells fabricated in thick-film technology.

Keywords: *Cu based paste; front contact electrode; silicon solar cells*

1. Introduction

The research studies in the photovoltaics field are oriented to reducing the cost of electrical energy produced with the use of photovoltaic cells to the level competitive to the cost of energy produced from conventional energy sources. To obtain this objective, it is necessary to eliminate the technological processes including expensive and difficult to automate operations. Deposition of electrical contacts of photovoltaic cells is one of such production operations. Conventional screen-printing method combined with burning-out in a furnace is currently commonly used for the front electrode production. As it has been found by numerous research studies [1–4], electrode coating should satisfy different requirements to ensure low resistance at the interface zone between the electrode and substrate.

Savings in silver paste by replacement of Ag by copper or other metals is one of the challenges

for the research investigations due to the fact that approximately 30 % of the non-base material related costs of crystalline Si solar cells are contributed by Ag in the paste used for the front electrode fabrication [5]. Copper prices equate to only 1 % of silver prices and are less susceptible to fluctuation of the final solar cell fabrication costs. The average consumption of Ag paste deposited using screen-printing method for production of crystalline silicon-based solar cells is between 70 mg/Wp and 110 mg/Wp. Assuming an annual solar cells production on the level of 50 GW and a lower consumption of Ag paste to produce 1 Wp of power of solar cell, it results in a yearly consumption of Ag in the photovoltaic industry at the level of 3500 tons. With an annual production of silver, according to 2010 data, at the level of 28,600 tons, this translates into more than 10 % of photovoltaics sector in silver consumption [6]. Replacing the Ag-based paste with the paste containing Cu, would bring measurable economic benefits. The problem of replacing

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the Ag-based paste with the paste based on Cu in solar cells is now the latest innovative concept in photovoltaic research [7].

A lot of studies concern electroplating of nickel-copper contacts, which offer many advantages and prospects for the metallization of the solar cells, but their industrial applications are limited [8].

The development and application of a Cu-based paste causes many problems associated with the influence of copper atoms on the material properties of the cell layers.

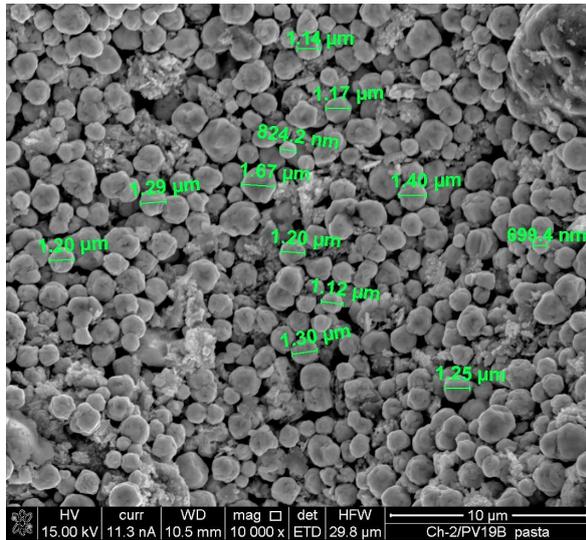
Cu is a fast diffusing element in Si, where an intrinsic diffusion length of the order of 1 mm is reached after 3 h at room temperature. Cu diffuses towards areas of higher chemical potential, such as extended defects and surfaces, and consequently significant degradation of electrical properties of the solar cell occurs [9]. The copper dopant in Si semiconductor is amphoteric, reveals base and interstitial diffusion, so its appearance in the spatial charge area of the solar cell, located in the relation to the active surface at a depth of about 0.3 μm to 0.5 μm , may significantly reduce its parallel resistance, whose value above 1 $\text{k}\Omega\cdot\text{cm}^2$ is required to obtain a solar cell with a fill factor bigger than 0.75. With a diffusion coefficient values of 1.0×10^{-9} m/s, at 600 °C, the solubility of Cu in the solid phase Si reaches 10^{21} atoms per cubic meter, which causes that the metallization process of the front electrode contacts must be performed in a narrow temperature range [10]. This paper presents the CuXX copper-based component which was obtained by chemical treatment of copper powder and can partly substitute silver in the pastes used for screen-printing of electrical paths in silicon solar cells [11]. The XX modifier can also be taken into account as a material for Ag and Cu replacement, but its price and electrical conductivity is not so low and appropriate as those of Cu.

2. New Cu-based component and commercial pastes

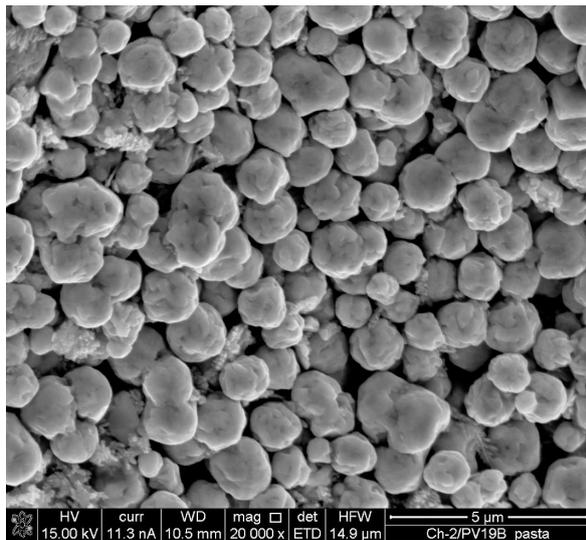
The CuXX component was made using chemical method, which allows for mass production

which is essential for industrial application [12]. The CuXX particles were mixed with the commercial Du Pont PV19B silver paste, which gave a new paste presented in Fig. 1. The SEM images indicate a homogeneous distribution of mixed CuXX and Ag particles which are undistinguished and do not exhibit agglomeration tendency. The average particle diameter in the prepared paste is 1.2 ± 0.3 μm . This particle size has a direct impact on the bulk resistance of Ag contact ρ_{con} , which is lower for smaller particles. In the case of average particle size between 0.7 μm and 2.0 μm the ρ_{con} is between 3.094×10^{-5} $\Omega\cdot\text{cm}$ and 4.302×10^{-5} $\Omega\cdot\text{cm}$ [13]. Smaller Ag particles, with a larger specific surface area and higher specific surface energy, result in greater solubility in melted glass and thus higher densification of Ag contact after the high-temperature metallization process [13]. The original Ag and the new CuXX particles exhibit spherical shape and processing does not change their morphology. Considering the shape and dimension, such spherical shape of the particles results in a lower specific surface area and residual stress, causing lower densification of the contact when compared to flaky shape particles [11, 13]. On the other hand, the production of repetitive and controlled morphology of spherical particles does not cause as many problems as the flaky particles, which is important for mass industrial production.

A commercially used paste, besides metallic particles which is usually silver in the amount of 70 wt.% to 90 wt.%, the mixture contains glass frits and organic binder. The glass frit is usually added in the amount of about 2 wt.% to 5 wt.% into the paste and its composition can contain such oxides as PbO, SiO₂, B₂O₃, Al₂O₃, CaO and ZnO [14]. A very important role in the contact formation during the high-temperature firing stage plays PbO which wets and dissolves silver particles at low temperatures, etches and dissolves the anti-reflection coating, and enhances the formation of silver crystallites [15]. The raw materials of the paste are mixed with an organic binder, which is ethyl cellulose (5 wt.%) dissolved in terpineol and dibutyl phthalate [16].



(a)



(b)

Fig. 1. SEM micrographs presenting the mixed CuXX component with Du Pont PV19B silver paste (a) at magnification of 10 000 \times with marked diameters of particles and (b) at magnification of 20 000 \times .

In our study, by replacing 51 wt.% of the original paste with CuXX component, we reduced the glass frit and organic binder simultaneously by more than 50 %, which had a negative impact on the final parameters of the solar cell.

The morphology of the copper components was analyzed by dual beam high-resolution scan-

ning electron microscopy (SEM) FEI Quanta 3D FEG integrated with an EDAX Trident system. A TECNAI G2 F20-200 kV FEG transmission electron microscope (TEM) with an energy dispersive spectrum (EDS) detector was used to observe the distribution of elements in CuXX particles after the chemical process.

Fig. 2 shows the homogenous distribution of Cu and XX modifier in one selected particle. In Fig. 3a, the result of a linear analysis of radiation intensity change for individual elements, carried out on a section of CuXX particle with a diameter of 1100 nm is shown. The Cu distribution shows greater changes compared to the XX modifier distribution, but this does not degrade the utility characteristics of the component produced. The modifier XX itself has a very uniform distribution which fully prevents Cu atoms diffusion from the CuXX molecule. It is the most important feature of the final product of the chemical method developed for CuXX fabrication. The developed chemical method is inexpensive and suitable for high volume mass production, appropriate for the industry. The resulting CuXX particle has a homogeneous crystal structure, which is confirmed by the high-resolution analysis performed by the TEM method (Fig. 3b). This is important in terms of material stability as well as behavior of high-temperature metallization of the contacts of the solar cell.

3. Experimental

The new PV19B/CuXX paste with 51 wt.% share of Cu was made based on the CuXX component. In addition, the PV19B/XX paste with 51 wt.% share of XX only was prepared. As the third one, the PV19B original paste was applied to make the reference solar cell. The solar cells were fabricated on 1 Ω -cm p-type 160 μ m thick, Cz-Si (1 0 0) wafers. The cell had the dimension of 5 cm² \times 5 cm² and a textured surface. The diffusion process was carried out in a quartz tube furnace from POCl₃ donor source at a temperature of 835 $^{\circ}$ C for 30 min. The sheet resistance of the final emitter was kept within 50.5 \pm 1.9 Ω / \square . The edge isolation was performed

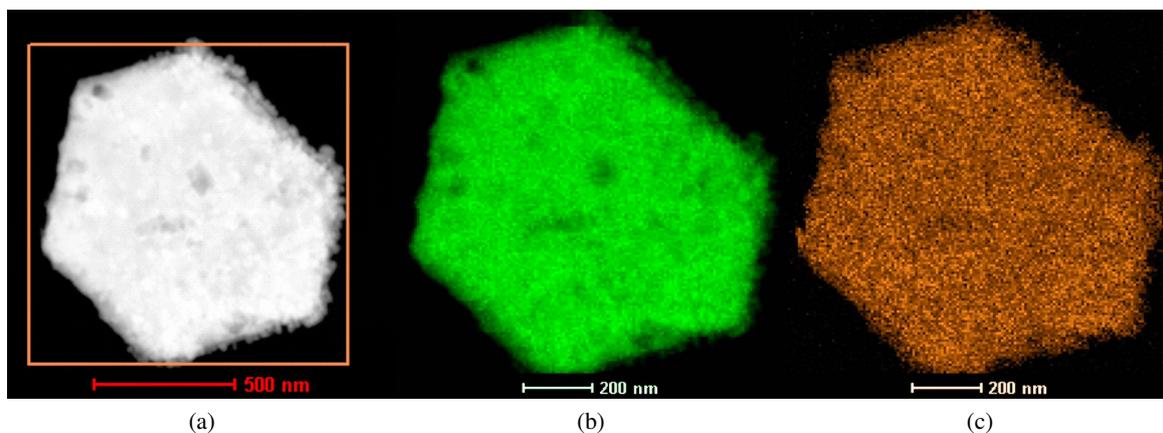


Fig. 2. (a) TEM image of CuXX single particle with a diameter of 1.1 μm , and the respective element distribution maps of (b) Cu, and (c) XX modifier.

by the chemical method, and then the phosphosilicate glass was removed by immersion in a bath of $\text{HF}:\text{H}_2\text{O}$ (1:9) solution for 2 min. The surface passivation was achieved by the growth of 12 nm thick SiO_2 grown at 800 $^\circ\text{C}$ in dry air for 10 min. The 70 nm thick titanium dioxide layer was deposited by CVD method using $\text{Ti}(\text{C}_2\text{H}_5\text{O})_4$ as a source, to assure the anti-reflective coating (ARC) front layer. On the rear side, the PV505 and PV381(AI) pastes were screen-printed. Finally, the PV19B, PV19B/CuXX and PV19B/XX pastes were printed on the front. After drying in air at 150 $^\circ\text{C}$ the printed pastes were co-fired in the IR belt furnace at a belt speed of 200 cm/min.

4. Results

The fabricated solar cells were characterized by the current-voltage (I-V) measurements using a Solar Simulator SS200 AAA class EM Photo Emission Tech., Inc., with solar cell I-V curve tracer SS I-V CT-02 PV. The data were obtained under AM1.5 global spectrum at 1000 W/m^2 light intensity at a temperature of 25 $^\circ\text{C}$, and the final data are collected in Table 1. For the proper determination of other parameters, especially the series resistance, the I-V characteristics of the cells were numerically fitted with the double diode exponential relationship (DEM) [17]. The fitting was done under the assumption that the diode quality

coefficients were $A_1 = 1$ and $A_2 = 2$, and the final results are summarized in Table 2. The match factor value ϵ ranges from 1.340×10^{-8} to 5.536×10^{-8} . The ϵ factor determines the accuracy of the fitting of the experimental I-V curve in respect to the theoretical one in the DEM model; it is equal to the difference in surface area between the experimental and theoretical curves in respect to the surface defined by the experimental curves between axes I and V. The obtained value of the match factor ϵ confirms the high quality of fitting for the performed calculations.

Electrical properties of solar cells co-fired in a furnace in the temperature range from 915 $^\circ\text{C}$ to 930 $^\circ\text{C}$ determined from I-V curves prove that the highest efficiency is equal to $E_{\text{ff}} = 14.93 \%$ for cell number PV19B-1 with the electrode obtained from the PV19B paste. The difference in the short-circuit current of all solar cells does not exceed 16 mA, and similarly, the V_{oc} difference is within 5 mV, except for the PV19B/CuXX-4 solar cell, whose metallization process was performed at temperature of 930 $^\circ\text{C}$, inadequate for this paste composition. For this solar cell, the metallic material from the contact path diffused under the p-n junction, resulting in an increase in the density of the saturation current up to 493.96 nA/cm^2 , a drastic decrease in the shunt resistance to value of 200 $\Omega\cdot\text{cm}^2$, and as a consequence, low $\text{FF} = 0.632$ and poor photoconversion efficiency. In the case

Table 1. Current-voltage (I-V) parameters of 25 cm², p-type, Cz-Si, textured wafers solar cells fabricated by application of the original PV19B paste, and pastes: PV19B with XX and CuXX components used for the deposition of the electrical front contact.

Cell	T _M [°C]	I _{sc} [A]	V _{oc} [V]	I _m [A]	V _m [V]	P _m [W]	FF	E _{ff} [%]
PV19B-1	915	0.814	0.601	0.740	0.501	0.370	0.757	14.93
PV19B/XX -1	915	0.826	0.600	0.744	0.483	0.359	0.725	14.38
PV19B/CuXX-1	890	0.820	0.596	0.734	0.469	0.344	0.705	13.79
PV19B/CuXX-2	900	0.823	0.597	0.729	0.482	0.352	0.716	14.08
PV19B/CuXX-3	915	0.810	0.596	0.727	0.478	0.348	0.720	13.92
PV19B/CuXX-4	930	0.808	0.566	0.668	0.433	0.289	0.632	11.59

where: I_{sc} – short circuit current, V_{oc} – open circuit voltage, I_m – current at optimum power point, V_m – voltage at optimum power point, P_m – optimum power point, FF – fill factor, E_{ff} – conversion efficiency.

Table 2. Parameters of solar cells fabricated by application of original PV19B paste, and pastes: PV19B with XX and CuXX components, numerically fitted with the double diode exponential relationship.

Cell	j _{ph} [mA]	r _s [Ω·cm ²]	r _{sh} [kΩ·cm ²]	j _{s1} [pA/cm ²]	j _{s2} [nA/cm ²]	E _{ff} [%]
PV19B-1	32.57	0.331	1.70	1.430	101.35	14.93
PV19B/XX -1	33.04	0.656	3.15	1.070	156.86	14.38
PV19B/CuXX-1	32.79	0.834	2.05	0.938	197.54	13.79
PV19B/CuXX-2	32.90	0.551	1.11	1.000	181.57	14.08
PV19B/CuXX-3	32.42	0.704	1.20	1.280	158.04	13.92
PV19B/CuXX-4	32.39	0.485	0.20	0.025	493.96	11.59

j_{ph} is density of photocurrent generated by electromagnetic radiation; r_s is specific series resistance; r_{sh} is specific shunt resistance; j_{s1} is density of saturation current of dark current diffusion component; j_{s2} is density of saturation current of dark current generation-recombination component.

of the other solar cells for which E_{ff} is higher by almost 2 %, the difference between their two most important parameters, namely the fill factor and conversion efficiency, is solely due to the mutual relation of r_s and r_{sh}. For all the solar cells, r_{sh} is over 1 kΩ·cm², which is particularly important for solar cells PV19B/CuXX-1, XX-2 and XX-3 with 51 wt.% copper in the paste. The obtained values of r_{sh} confirm unequivocally the absence of Cu diffusion into the p-n junction region and the efficiency of the new CuXX component. The solar cell made exclusively from commercial PV19B paste has the lowest r_s value of 0.331 Ω·cm². This is a typical value of commercially produced cells [18]. This value is higher than mentioned in the literature. For solar cells manufactured with the use of CuXX component and the modulator XX only, the increase in r_s value ranged from 0.551 Ω·cm² to

0.843 Ω·cm², but there was no definite degradation of the parameter, as it did not exceed the value of 1 Ω·cm². The problem remains with the increase in the r_s value of the solar cells containing CuXX or the modulator XX. It was explained by TEM investigations, the results of which are shown in Fig. 4. Nevertheless, as a final result, the solar cell with an efficiency above 14 % and with the fill factor of 0.716 was obtained for the front electrode deposited from the PV19B/CuXX paste.

The lower fill factors of the cells with CuXX and XX share is related to higher series resistance than that of the PB19B-1 cell, caused partially by a change of physical parameters of the PV19B paste, higher viscosity and consequently, lower quality of screen-printing deposition. The image shown in Fig. 4a presents a typical, very regular path

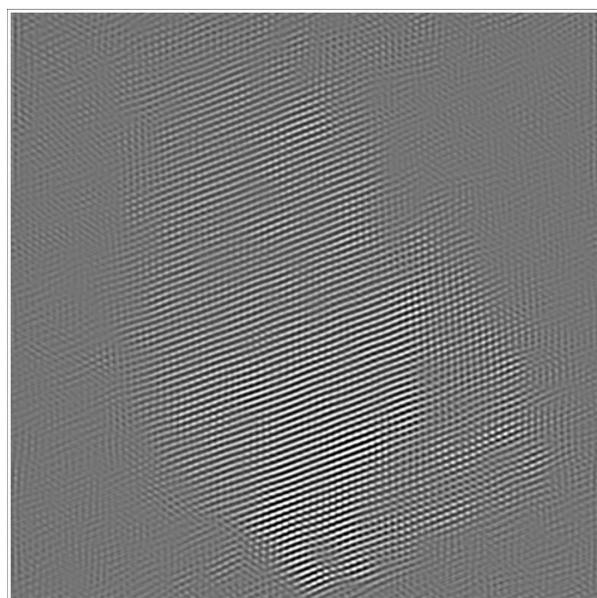
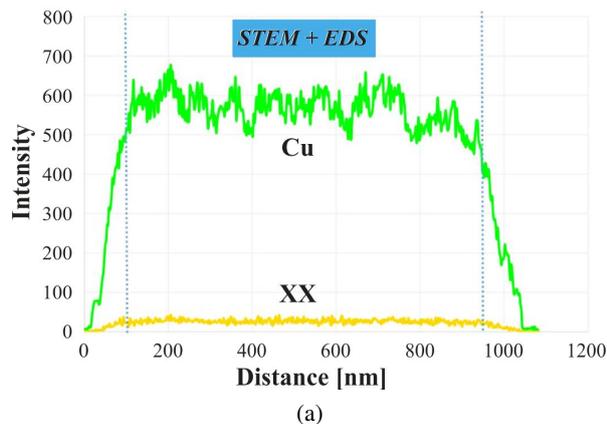


Fig. 3. Distribution of Cu and XX elements extracted by scanning transmission electron microscopy (STEM) for (a) CuXX single particle, and (b) TEM high resolution image of a single particle CuXX.

of the front electrode of the solar cell with a width of about 100 μm , deposited on the textured surface of the Cz-Si wafer. An accurate slice analysis of the cross section is shown in Fig. 4b. It shows the existence of empty areas in the track of material. The presence of the mentioned defects is attributable to 50 % glass frit and organic binder reduction in the PV19B paste, which directly affected the r_s value of the solar cells made from the PV19B/CuXX paste and the PV19B/XX paste.

Elimination of the deficiency should reduce r_s value, which would directly cause an increase of fill factor of the solar cell.

In Fig. 5, the dark curves of selected solar cells demonstrate the usefulness of the CuXX component and the XX modifier. The differences in the dark I-V curves of the solar cells with CuXX and XX in relation to the solar cell made from commercial PV19B paste occurs only in conductivity direction, which results from the increase of their r_s value, while the parallel passage towards the barrier for all solar cells indicates the absence of Cu atoms in the p-n junction area, further confirming the obtained values of shunt resistance of solar cells above 1000 $\Omega\cdot\text{cm}^2$.

5. Conclusions

The research results lead to the conclusion that the paste with the 51 wt.% share of Cu can be used for solar cells production by the commonly applied screen-printing process. The copper was applied as a new and patented CuXX component [11]. Copper prices equate to only 1 % of silver prices and are less susceptible to fluctuation in the final solar cell price, which makes the presented results very attractive for photovoltaic industry. Therefore, taking into account that the presented studies were not focused on the optimization of solar cell efficiency but the contact formation, the CuXX component allows for fabrication of the solar cell with fill factor 0.72, what is the best result for screen-printed copper paste. In the case of copper paste, it is possible to obtain the efficiency of 14.08 % with the series resistance equal to 0.551 $\Omega\cdot\text{cm}^2$, which confirms good quality of the metal-silicon contact. This value is higher than that mentioned in the literature, but improving this parameter is planned by the authors in the next stage of this study. Applying the same modifier XX as a paste ingredient is also reasonable, but not as cost-effective as using the CuXX component. It is worth noting that the Ag price amounts to about 8 % of the price of the whole solar cell [19]. Reducing the cost of material for electrodes of solar cells can contribute to a significant reduction of the price of entire solar cell. In the experimental works, replacing 51 wt.%

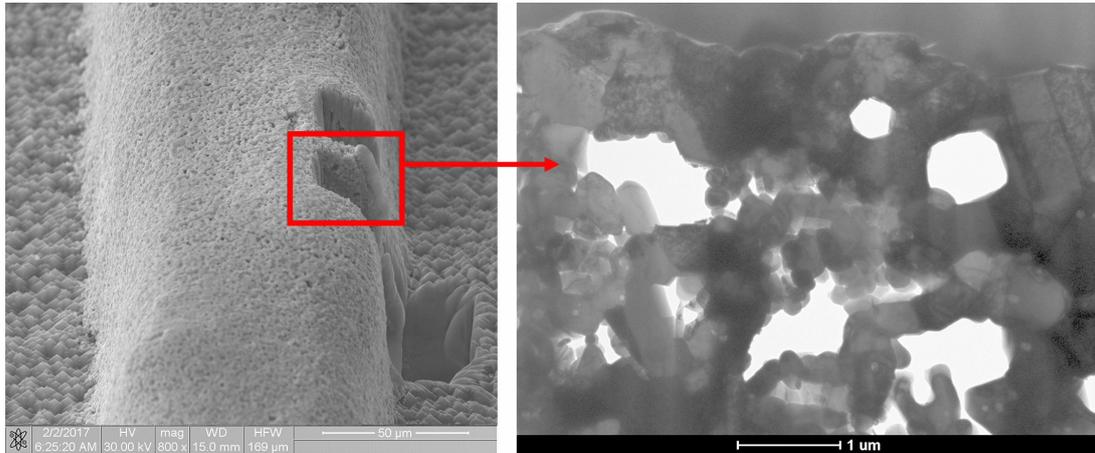


Fig. 4. (a) TEM image of front line electrode deposited from PV19B/CuXX paste; the red rectangle marks the area selected for analysis, (b) high resolution cross-section TEM image showing the front line electrode after metallization process.

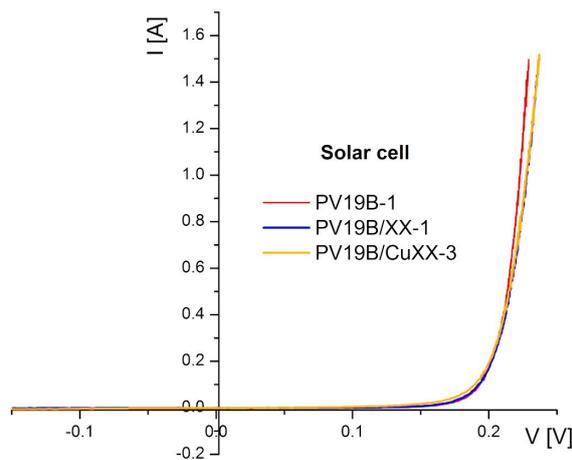


Fig. 5. Black I-V characteristics of the solar cells made from three kinds of paste used for front electrode deposition.

of the original PV19B paste with the CuXX component, glass frit and the organic binder in the PV19B paste were reduced by more than 50 %, which negatively affected the distribution of molecules in the front electrode path and consequently, altered the series resistance of the solar cells. Taking this into account, the current research aim is producing a completely new paste with the CuXX component at the level of 55 wt.% to 65 wt.%: a paste with the right share of a glass frit and organic binder.

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References

- [1] DOBRZAŃSKI L.A., MUSZTYFAGA M., *JAMME*, 48 (2011), 115.
- [2] BURGELMAN M., *MicroTherm*, 1998 (1998), 129.
- [3] GAUTERO L., HOFMANN M., RENTSCH J., LEMKE A., MACK S., SEIFFE J., NEKARDA J., BIRO D., WOLF A., BITNAR B., SALLESE J.M., PREU R., *PVSC*, 34 (2009), 1888.
- [4] ALEMÁN M., STREEK A., REGENFUB P., METTE A., EBERT R., EXNER H., GLUNZ S.W., WILLEKE G., *PVSEC*, 21 (2006), 705.
- [5] RUDOLPH D., OLIBET S., HOORNSTRA J., WEEBER A., CABRERA E., CARR A., KOPPES M., KOPECEK R., *Energy Procedia*, 43 (2013), 44.
- [6] GREEN M. A., *Prog. Photovoltaics*, 19 (2011), 911.
- [7] POORTMANS J., PIETERS P., BAERT K., *Photovolt. Int.*, 3 (2011), 102.
- [8] BARTSCH J., BRAND A., EBERLEIN D., MONDON A., VÖLKER C., TRANITZ M., GRAF M., NEKARDA J., EITNER U., PHILIPP D., GLATTHAAR M., *Photovolt. Int.*, 3 (2014), 49.
- [9] GASPAR G., MODANESE C., SCHØN H., SABATINO M. D., ARNBERG L., ØVRELID E. J., *Energy Procedia*, 77 (2015), 586.
- [10] JÜRGEN R., *Science*, 313 (2006), 1057.
- [11] PANEK P., SOCHA R., PUTYNKOWSKI G., SLAOUI A., *Energy Procedia*, 92 (2016), 962.
- [12] PANEK P., SOCHA PR., DRABCZYK K., *Polish Patent Office*, Warsaw, 2014, No. P409794.

- [13] ZHOU J., XU N., YANG H., ZHANG Q., *Procedia Eng.*, 94 (2014), 1.
- [14] HONG KK., CHO SB., YOU JS., JEONG JW., BEA SM., HUH JY., *Sol. Energ. Mat. Sol. C.*, 93 (2009), 898-904.
- [15] KALIO A., LEIBINGER M., FILIPOVIC A., KRÜGER K., GLATTHAAR M., WILDE J., *Sol. Energ. Mat. Sol. C.*, 106 (2012), 51.
- [16] REINHARDT K., SCHMIDT U., KÖRNER S., JURK R., PARTSCH U., EBERSTEIN M., *Energy Procedia*, 55 (2014), 702.
- [17] ENEBISH N., AGCHBAYAR D., DORJKHAND S., BAATAR D., YLEMJ I., *Sol. Energ. Mat. Sol. C.*, 29 (1993), 201.
- [18] LEE J. H., LEE Y. H., AHN J. Y., JEONG J. W., *Sol. Energ. Mat. Sol. C.*, 95 (2011), 22.
- [19] SCHULER S., I. LUCK, *Photovolt. Int.*, 23 (2014), 46.

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