

Polymer conductive paste for heterojunction solar cells

Pertinent art

This invention pertains to thick-film microelectronics, namely to the materials used to produce screen-printed electrically conductive contact layers, and it can be used to form solar cell grids.

Related art

Semiconductor solar cells are made of semiconducting materials, for example, of silicon. Contacts on surface of a silicon substrate can be produced by applying electrically conductive liquid slurry (hereinafter called as the “paste”) using the screen-printing technique.

The paste composition usually contains an electrically conductive component which is a fine metal powder, a structure-forming agent, an organic solvent, and functional additives of miscellaneous purpose for the specified printing performance of the thick-film material.

At present time, one of the main trends of thick-film solar cells manufacturing is the conductive paste based contact grid width reduction and, as a result, solar cell efficiency enhancement through the reduction of conductor linear resistance. This is obtained by an integrated approach implementation when developing the conductive paste composition, namely the usage of fine metal powder having the specified grain size parameters that ensures stable printing performance of the paste; a solvent or a mixture of solvents that ensures the required solid phase and substrate wettability and, as a result, relative monodispersity of the final product; a polymer component with specified range of molecular weight and functional groups; one or more functional additives.

Composition of a conductive paste can contain the following components:

- (A) at least one conductive filler,
- (B) a structure-forming agent,
- (C) at least one functional additive.

The term “conductive” means ability to conduct heat and/or electrical current.

As the conductive filler (A), powders of silver, platinum, palladium, nickel, copper, and/or various compositions thereof can be used. Shape of the metal powder particles can be spherical, flaked or mixture thereof.

As the structure-forming agent (B), a thermoset and/or thermoplastic resin-based component may be used. Polyester resins, phenol resins, phenol formaldehyde resins, epoxy resins, acrylate resins, and various compositions thereof may be used as the structure-forming agent.

As the functional additive, dispersing agents, emulsifiers, slip agents, adhesive agents, thickeners, defoamers, rheology agents, and various compositions thereof may be used, which provide the required range of printing and technical performance of the paste.

The composition of the conductive paste can also contain a solvent (D).

As solvents, dihydric alcohols (such as diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, propylene glycol monomethyl ether and propylene glycol monoethyl ether), esters (such as 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, 2,2,4-trimethyl-1,3-pentanediol diisobutyrate, etc.), ketones (such as cyclohexanone and isophorone, terpeneol) can be used. It is preferable to use high-boiling solvents to avoid problems arising during the processes of screen printing and baking. Such preferable high-boiling solvents include diethylene glycol monoethyl ether acetate, diethylene glycol monobutyl ether acetate, tripropylene glycol monomethyl ether, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, terpeneol, etc.

The conductive paste is produced by mixing with the subsequent homogenization of components (A), (B), and (C) in a certain proportion, using a mixer, three-roller mill or gyroscopic mixer.

Brief description of drawings and other materials

Fig. 1 shows a schematic drawing of a solar cell (SC) front surface area with a section of electroconductive grid in the form of two parallel conductors; the geometrical characteristics are specified as follows: L – conductor length, h – conductor height, d – conductor width.

Fig. 2 shows an absolute efficiency value dependence on relative conductor width d decrease when the conductor cross-section area S_{sec} remains constant.

Fig. 3 shows an absolute efficiency value dependence on relative conductor width d decrease when the conductor height h remains constant.

Fig. 4 shows a schematic view of velocity distribution profile within the metallization paste volume across the screen opening in case of turbulent flow: a) paste penetrates through the screen mesh, b) subsequent screen and substrate separation.

Fig. 5 shows a schematic view of velocity distribution profile within the metallization paste volume along the screen opening in case of laminar flow: a) paste penetrates through the screen mesh, b) subsequent screen and substrate separation.

Fig. 6 shows top view of the conductor patterns produced using screens with various opening width: a – opening width is 60 μm ; b – opening width is 40 μm .

Fig. 7 shows conductor linear resistance R_{line} [Ohm·cm] vs. screen opening width [μm] dependence.

Fig. 8 shows viscous flow curves of metallization pastes characterized by different interaction behavior with screen printing equipment: sample A is highlighted with red, sample B is highlighted with green.

Fig. 9 shows conductive fingers top view for the paste samples from Examples 1-4.

Fig. 10 shows finger width measurements results for the paste samples from Examples 5-7.

Fig. 11 shows current-voltage measurement results for the paste samples from Examples 5-7.

Fig. 12 shows solar cell cross-section microphotographs with paste samples from Examples 8-12 after drying (a – 8, b – 9, c – 10, d – 11, e – 12) and curing (a1, b1, c1, d1, e1).

Fig. 13 shows the specific electrical resistance measurement results for the paste samples from Examples 8-12 after drying (ρ_1) and curing (ρ_2).

Fig. 14-15 show current-voltage measurement results for the paste samples from Examples 8-12.

Disclosure of the invention

Design of solar-to-electrical power converters (solar cells, photovoltaic converters) includes one or more electroconductive contacts. For most types of modern solar cells (mono/multi/amorphous Si, OPV, thin-film) electroconductive contact typically is situated on a surface that absorbs solar radiation (front surface, front side). In this case, the electric charge carriers collection and transfer from generation region to an external circuit is provided by electroconductive contact which is made in form of thin parallel conductors grid (Fig. 1). This design is the most commonly used, since it provides a significant cost reduction in the mass production of solar cells, despite the partial shadowing of the front side by the contact located on it.

With the development of the technology, the electroconductive contact design optimization has become an increasingly significant factor of the solar cell efficiency increase. Fig. 1 shows a schematic drawing of a solar cell front surface area with a section of electroconductive contact grid in the form of two parallel conductors.

A portion of the solar cell surface non-occupied with the electroconductive contact is characterized by the effective area S_{eff} . For example, for a solar cell front contact grid containing 5 busbars and about 100 parallel conductors, the S_{eff} value comprises more than 95 % of total front surface area. Increase of S_{eff} improves the solar cell efficiency because of higher photon amount absorbed by the front side and, consequently, higher amount of charge carriers generated. As it follows from Fig. 1, S_{eff} increase is possible by reducing conductor width d . In this case, depending on a ratio between the final conductor width d and height h , the conductor linear electrical resistance value of R_{line} changes as follows

$$\mathbf{R_{line}} \sim \boldsymbol{\rho} \cdot \mathbf{L} / \mathbf{S_{sec}}, \quad (1)$$

where $\boldsymbol{\rho}$ is the specific resistance of conductor material, [Ohm·cm];

$\mathbf{L}$ is the conductor length, [cm];

$\mathbf{S_{sec}} \sim \mathbf{d} \cdot \mathbf{h}$ is the conductor cross section area, [cm²].

The $\mathbf{R_{line}}$ parameter characterizes the electroconductive contact, and being a part of solar cell series resistance it affects the final efficiency value in combination with other parasitic resistances. The contribution of the width $\mathbf{d}$ to the value of efficiency coefficient, achieved to date, subject to the conductor constant cross section $\mathbf{S_{sec}}$ and, respectively, the constant $\mathbf{R_{line}}$, is shown in the graph in Fig. 2, according to which the decrease of $\mathbf{d}$ by 5% results in the increase of absolute value of the efficiency coefficient by 0.04% by means of the effect of larger number of generated charge carriers described above. When $\mathbf{d}$ is decreasing, the condition to keep the values $\mathbf{S_{sec}}$ and, respectively, $\mathbf{R_{line}}$ constant is realized by means of proportional increase of the conductor height $\mathbf{h}$. In the case, when decreasing $\mathbf{d}$ the conductor height $\mathbf{h}$ remains unchanged (or decreases), then due to the increase of $\mathbf{R_{line}}$ (in accordance with formula 1), the dependence $\Delta\text{Eff}(\mathbf{d})$ will demonstrate negative trends and cancel in full the effect of excessive generation of the carriers (Fig. 3). Therefore, when developing and producing the highly effective solar cells, it is necessary to ensure a balance between the value of cross section area $\mathbf{S_{sec}}$ and the value of conductor linear resistance $\mathbf{R_{line}}$ as accurately as possible. This fact poses strict requirements to stability and repeatability of the conductive contact manufacturing method.

Nowadays, silk-screen printing is the most commonly used metallization technology as the most compliant with the criteria of mass production industry. During the screen printing process, geometrical parameters of a conductor are determined by the opening width in the screen emulsion layer. During the process, the metallization paste is pressed through the screen opening using the pressure from an elastic squeegee, and the conductor is formed in this way. In general, a distribution profile of velocities of the paste thin layers in its volume along the cross section of the screen opening is of the form shown schematically in Fig. 4, in this case the pattern of the paste flow along the opening walls is rather turbulent. In this context, the turbulence means the presence of intense interaction between the opening wall and the thin layer of the paste that has a direct contact to the wall. This interaction results in non-regular distribution of the velocities in the paste's volume both when the paste is been pressing through and when separating the substrate and the screen, which results in defects in the form of splashes, drops, and halo on the edges of the conductor to be formed; the presence of such defects results in significant variation of the conductor local values $\mathbf{S_{sec}}$. Step-by-step narrowing of the opening width during the process of optimization of the conductive contact geometry enhances the contribution of the paste turbulent flow to variability of the conductor producing process. For screen openings 50 μm and less wide it is preferable to use metallization paste

that is characterized by mainly laminar pattern flow along the walls of the opening (Fig. 5). In the case of laminar flow, the force of interaction between the opening wall and the contacting thin layer of paste is rather less; in such event the thin layer of the paste slips along the opening wall that results in smoothing the velocity distribution profile. As a result, defects in the form of splashes, drops and halo do not occur, the shape of the conductor reproduces the shape of the screen opening more precisely, and the conductor has a stable and repeatable cross section S_{sec} .

In addition to interaction between the paste and the screen opening walls, which affects the conductor linear resistance R_{line} through the local variations of its cross section S_{sec} , there are some processing factors that impact on the value R_{line} during the silk-screen printing process. The basis of the structure of the most commonly used type of screen printing tools (the stencil screen) is a grid in the form of interlaced strands forming a strongly regular array of fixed size cells. The paste flows to the opening area directly through these cells separated from each other by the distance of the strand width. When optimizing the geometry of the conductive contact with reducing of the opening width up to 50 μm and less, the structure of the conductor to be made starts to reproduce the periodic structure of the screen grid as illustrated by the pictures below. Fig. 6.a shows a picture of a section of the conductor produced using a screen opening 60 μm wide. This conductor is characterized by a pronounced linear structure while the form of a conductor made using a screen opening 40 μm wide (Fig. 6.b) is not linear, but is characterized by alternating local thickenings and narrowings (necks) that have additional impact on the conductor linear resistance R_{line} . Dependence of R_{line} on a width of the screen opening used during the production process is shown in Fig.7. As it appears from the graph, when the opening width decreases to a value less than 50 μm , the relative increase of the conductor linear resistance becomes exponential. To eliminate the effect of local thickenings/narrowings, metallization paste shall be characterized by its ability to pass rapidly through small and ultra small size cells and fill uniformly the screen opening area, which is also facilitated by the laminar flow mechanism described above.

A metallization paste is a liquid high-solid slurry, which, in addition to a conductive filler, contains organic solvents and polymer compounds of various three-dimensional structure with a broad range of molecular number. To study the properties of liquid systems, macroscopic properties of which are determined by intermolecular and interparticle interaction, rheological methods are used widely. The qualitative measurement of the nature of interaction between a metallization paste silk-screen printing tools can be made using a standard CR rheometer. The flow curves of metallization paste samples A and B, constructed in the coordinates “shear velocity $\dot{\gamma}$ [c^{-1}] – shear stress τ [Pa]” (Fig. 8), are characterized by areas of linear increase in shear stress I, conditioned by gradual failure of the structural framework of interlaced polymer chains in the bulk of the sample during the test. The change of the curves slope after the shear velocity of 40 c^{-1} has been achieved, shows the process

of polymer molecules disentanglement is completed, and the molecules are mainly oriented in the rotor spinning direction. The fact that the flow curve area II of A sample is near parallel to X axis, shows a weak dependence of the shear stress on the shear velocity beyond 40 c^{-1} . At the microlevel, this means that the rotor spinning mechanical energy under further increase in the shear velocity transfers in full to the immediately adjacent paste layer by means of interparticle forces and disperses in the bulk of the sample when the conductive filler particles encounter. Therefore, the nature of flow curve of A sample having area II parallel to X axis gives an indication of occurrence of a strong pronounced interaction of this metallization paste sample with the parts of the rheometer. As for B sample, the nature of the flow curve, showing a negative slope beyond 40 c^{-1} , indicates the presence of specific interaction causing a weakening of the sample response to the rotor force when a certain threshold value of shear velocity has been reached. At the microlevel, this effect is due to exfoliation of the sample of metallization paste, when an interlayer of polymer molecules, acting as a lubricant, releases in the thin layer between the paste and the rheometer tool surface as the shear velocity is further increasing.

Therefore, a metallization paste for high-performance solar cells, which is suitable to give narrow current conductive conductors having stable local S_{sec} value and low R_{line} value using the silk-screen printing technique, when measuring its rheological properties in the coordinates “shear velocity $\dot{\gamma} [\text{c}^{-1}]$ – shear stress $\tau [\text{Pa}]$ ”, is characterized by a negative slope of the flow curve when the shear velocity threshold value of 40 c^{-1} is exceeded.

To implement the described slipping motion mechanism promoting the laminar flow of metallization paste along the parts of tools during the silk-screen printing process, some functional additives are included in the paste composition, which can be siloxanes.

There are known application WO2009035453 (published on 19.03.2009) and US20180163063 (published on 14.06.2018) for current conducting composition having polysiloxane as its component, where this material can act as one of components of organic binding agent along with other thermoplastic and thermosetting polymers. But these patent applications do not explain a mechanism, by which polysiloxane provides advantages to the current conducting compositions based on it.

The compositions of current conducting materials in applications US20030107026 (published on 12.06.2003) and CA2461011 (published on 03.04.2003) contain polyorganosiloxane as a principal component of organic binding agent, but at the same time these described materials are not intended to manufacture a current conducting contact analogous to this invention.

To minimize specific resistance, it is necessary to use submicron powder, it is better when sintering at low temperatures around 200°C . But as the particle size decreases, the forces, which result in agglomeration due to surface area S_{BET} increase, are increasing.

As the powder surface area S_{BET} increases, the processes resulting in oxide coating on silver particles surface run more actively, and the subsequent surface treatment of the powder to prevent oxidation and agglomeration becomes more necessary.

As a surface treatment, fatty acids of boiling points at 350-400°C can be used, which also prevent agglomeration of the powder particles at 200°C (the maximum possible temperature of HJT process) and thereby increase the specific resistance of the sintered conductor.

When minimizing the specific resistance for more effective sintering of the particles, it is necessary to determine some chemical agents that will remove the oxides and fatty acids residues from the surface and promote the surface, reducing the energy of particles coalescence. These chemical agents shall escape easily from the conductor layer during the process of sintering and not disrupt the ITO structure.

As a technical solution in this case, some polymers stabilized with halogenids can be used. Namely, halogenic polymers with a softening temperature of below 200°C. Particularly, chlorine-containing polymers, in which the chlorine atoms are hypermobile. There is a known chlorine-containing polymer, the melting temperature of which is 165-170°C, but, when being heated to a temperature over 35°C, some damage processes occur in it, which followed by atomic chlorine removal with subsequent occurrence of chlorine hydride resulting in intense macrochains disruption.

The object of the invention is to ensure required technical, printing, and thermal performance of the paste, complying with the actual trends in the field of “thin” printing. Namely, to retain a set of rheological properties of the paste when decreasing the screen opening width, by means of the best mixture ratio and introduction of additives ensuring the flow nature described above during the screen printing process. As well as use of halogenic polymers with low onset temperature, ensuring effective sintering of silver powder even at the stage of the conductive contacts soft baking.

The technical result consists in enhancement of performance of a solar converter through decrease of the conductor linear resistance by means of reduction of the finger width on the one hand, and decrease of the conductor specific resistance by means of more effective sintering of fine silver powder on the other hand.

This technical result can be achieved that the polymer conductive paste for HJ solar cells contains a silver powder, an organic binding agent that contains a structure-forming agent as a component of the solvent, and a functional additive, wherein a halogenic polymer with softening temperature of below 200°C is used as the structure-forming agent, and a polymer organic-silicon compound with a number of siloxane units less than 3000 is used as the functional additive, whereby the mixture ratio (% wt) is as follows: silver powder – 80-95; organic binding agent – 4-18; functional additive – 0.1-2.0.

The average size of the silver powder particles may be D50 0.5-5.0 μm .

The quantity of the structure-forming agent in the organic binding agent may be 5-10 % wt.

The functional additive may contain some additional components.

When measuring rheological properties of the conductive paste in the coordinates “shear velocity $\dot{\gamma}$ [c-1] – shear stress τ [Pa]”, the flow curve is characterized by a negative slope if the threshold value of the shear velocity of 40 c-1 is exceeded.

The conductive paste contains fine silver powder, a structure-forming agent in the solvent, and a rheological additive, which ensures the best topology of the finger. The average size of the fine silver powder particles is $D_{50}=0.5-5.0$ μm , $D_{50}=1.0-3.0$ μm is preferable. The content of silver powder can vary from 80 to 95 % wt., the preferable content of silver is 85-92 % wt. The structure-forming agent can be a polyvalent epoxy resin with two or more epoxy groups in the same molecule. For example, they may be epichlorohydrin and phenolic novolac, cresylic novolac, polyatomic phenols, ethylene glycol and bisphenol A, hydrogenated bisphenol A, bisphenol F, bisphenol AD, and resorcin. These epoxy resins can be used both individually and combined. As a rheological additive, it is possible to use a polyamide, namely, a non-polar polyamide modified with urea; a polyolefine, in particular, a polyethylene emulsion with molar weight of 1000-3000; fatty acid esters with preferable carbon number value of 26-30. Also, as an additive improving the printing properties, some polymer organic-silicon compounds can be used, silicone fluids with siloxane unit number of less 3000 are preferable. It is the additive from the series of organic-silicon compounds that provides the required rheological behavior, decreasing the surface tension at the boundary between the paste and screen and providing the paste with “slipping” ability (decrease of friction of the conductive paste against the screen opening walls), that results in uniform prints in the process of screen printing with no “exfoliation” effect, which is particularly important for the modern printing of fingers of up to 30 μm in width. This rheological additive is essentially nonreactive, i.e. it has no material effect on electrical and physical and mechanical properties of solar converter, but it significantly improves a process of pass of the paste through the screen and minimizes occurrence of any possible defects. As the structure-forming agent, it is preferable to use a halogenic polymer with low decomposition temperature, namely, a chlorine-containing polymer. A macromolecule of this polymer type dissociates at a comparably low temperature that results in additional energy output promoting the thermal catalysis of silver particles sintering in the conductor layer and, as a consequence, reduction of a level of the conductor specific resistance. Therefore, the technical performance is provided by presence of two key factors of this invention: a siloxane rheological additive and a halogenic polymer with low decomposition temperature.

The present invention uses fine silver powder with the average particle size of D_{50} 0.5 — 5.0 μm . When the average size of silver powder particles D_{50} is more than 5.0 μm , then there is a tendency towards decreasing the paste dynamic viscosity, that in its turn results in deterioration of

printing performance and spreading of a finger of the conductor. Otherwise, when the average size of particles D50 is less than 0.5 μm , the dynamic viscosity increases that can also lead to deterioration of printing performance due to non-uniform distribution of paste, occurrence of gaps in the conductor fingers. When the dynamic viscosity is decreased by reducing the polymer, a trend towards adhesive power deterioration can occur.

The organic binding agent contains a mixture of high-boiling solvents and a structure-forming agent. As the structure-forming agent, this invention uses a halogenic thermoplastic polymer with softening point of less than 200°C. If the concentration of the structure-forming agent is more than 10% of the organic binding agent composition, the viscosity of paste increases, and its printing performance deteriorates consequently. Alongside this, when the structure-forming agent concentration is increased, there is a tendency towards the linear resistance rise in the solar cell. When maintaining the concentration of structure-forming agent less than 5% of the organic binding agent, deterioration of the conductive paste printing performance due to loss of its ductility can be observed.

Furthermore, the conductive paste of this invention contains a functional rheological additive that provides the paste surface tension reduction and therefore enhances passage of the paste through the screen during the printing process to obtain the best possible topology of conductive contacts. This rheological additive is one of polymer organic silicon compounds with a number of siloxane units less than 3000. It is preferable to use 0.1-2.0% of this additive in this invention. When concentration of the additive is less than 0.1%, the required printing performance cannot be obtained. When the concentration of siloxane additive is over 2.0%, it results in increase of the specific resistance.

The principal characteristic of the conductive paste of this invention is the use a halogenic polymer as the structure-forming component, which provides effective sintering of silver particles that results in increase of the current conducting layer conductivity, and the adding of a functional additive based on polymer siloxane organic compounds, which enhances printing performance of the paste.

The optimality of the paste quantitative composition is confirmed by the fact that when adding the components in the amounts above or below the limits specified, the required operating and rheological performance can not be provided.

The analysis of the prior art shows that the combination of essential features set out in the invention patent claim is unknown. This suggests that the claimed technical solution complies with the “novelty” criterion.

The comparative analysis shows that the prior art has no solutions having any properties coincident with the properties of the claimed invention, and anticipation of the influence of such

properties over the technical result is not confirmed. Therefore, the claimed technical solution meets the “inventive step” patentability criterion.

Embodiment of the invention.

The current conductive paste should be prepared in the following manner. All the ingredients stated above are mixed in the established quantity in the mixer tank using a planetary mixer. Further, the paste is homogenized using a three-roll paste mill to obtain the degree of grinding required.

A degree of grinding is measured using a Hegman gauge. The device consists of a gauge block with a V-shaped groove and a scraper. A test portion of the paste in the amount sufficient to fill the entire groove is put beyond the upper limit of the scale. The scraper is set perpendicular to the gauging face and moved at 90° for a few seconds from the scale ceiling beyond the zero.

The dynamic viscosity is measured using a cone-and-plate spindle viscometer. Its mode of operation is based on dependence of torque on a viscosity initiating the sample shear strength.

Example 1

To prepare the conductive paste, the following components are used: silver powder with the average particle size of 0.5-5.0 μm in the quantity of 80-95 % wt., an organic binding agent containing a structure-forming agent and solvent, a functional additive A based on a polyacrylic resin solution in the quantity of 0.1-2.0 % wt.

Example 2

To prepare the conductive paste, the following components are used: silver powder with the average particle size of 0.5-5.0 μm in the quantity of 80-95 % wt., an organic binding agent containing a structure-forming agent and solvent, a functional additive B based on polydimethyl siloxane modified with polyester in the quantity of 0.1-2.0% wt.

Example 3

To prepare the conductive paste, the following components are used: silver powder with the average particle size of 0.5-5.0 μm in the quantity of 80-95 % wt., an organic binding agent containing a structure-forming agent and solvent, a functional additive C based on polydimethyl siloxane modified with polyester in the quantity of 0.1-2.0% wt.

Example 4

To prepare the conductive paste, the following components are used: silver powder with the average particle size of 0.5-5.0 μm in the quantity of 80-95 % wt., an organic binding agent containing a structure-forming agent and solvent, a functional additive D based on polydimethyl siloxane in the quantity of 0.1-2.0% wt.

Investigation of properties of the samples described above was carried out as a part of heterojunction solar cells. The basis of HJT technology is a substrate made of n-type crystalline

silicon, on which thin amorphous silicon films are applied through plasma-chemical vapor deposition followed by heterojunction formation; the next stage is ITO film coating, on which current collecting contacts with silver paste are printed.

The current collecting contacts with the above mentioned samples were applied on the structures through silk-screen printing technique using EKRA E2 semi-automatic printer. Soft baking was carried out using “JRT” DT-040-Rk-X conveyor dryer, hard baking was carried out using “Heraeus” D-6450 cabinet dryer at 210°C within 15 minutes. The width of conductive fingers was measured using “Olympus” microscope. The height of conductive fingers was measured using “Leitz” 512761-20 microscope.

Printing and technical and electrophysical parameters of the prepared conductive pastes from Examples 1-4 are stated in Table 1.

Table 1. Printing and technical performance of conductive pastes

Sample No.	Functional additive	Composition	Conditional coefficient of surface tension*	Degree of grinding, um	Dynamic viscosity, Pa*s	Width of conductive finger, um	Height of conductive finger, um	Conductor cross section area S_{sec} , cm ²	Specific resistance ρ , Ohm*cm	Conductor length, cm	Linear resistance R_{lin} , Ohm
1	A	Polyacrylic additive	0.79	5	103	63	14	0.0000088	5.17E-06	1.55E+01	9.09E+00
2	B	Polydimethyl siloxane modified with polyester	0.88	6	109	58	16	0.0000093	5.30E-06	1.55E+01	8.86E+00
3	C	Polydimethyl siloxane modified with polyester	0.98	6	111	53	18	0.0000095	5.41E-06	1.55E+01	8.78E+00
4	D	Polydimethyl siloxane	1.00	5	122	52	19	0.0000099	5.49E-06	1.55E+01	8.62E+00

* - degree of paste surface tension reduction

As Table 1 shows, the samples of conductive pastes from Examples 1-4 have a sufficient degree of grinding and dynamic viscosity, therefore, the required printing and operating performance is provided. Besides, a direct dependence of the conductive finger width on the surface tension conditional coefficient can be observed. Therefore, the sample from Example 4 with the functional

additive D based on polydimethyl siloxane has the highest surface tension conditional coefficient thereby reducing a degree of friction of the conductive paste against the screen opening walls and providing the best topological contact grid. Moreover, the sample from Example 4 has the lowest value of linear resistance that confirms the theoretical part described above.

Fig. 9 shows the photographs of the conductive fingers from the examples above. The improvement of the conductive finger profile can be clearly observed, both reduction of its width and reduction of the edge “blots” (Fig. 9).

Example 5

To prepare the conductive paste, silver powder with the average particle size of 0.5-5.0 μm in the quantity of 80-95% wt., an organic binding agent containing a structure-forming agent and solvent, were used.

Example 6

To prepare the conductive paste, silver powder with the average particle size of 0.5-5.0 μm in the quantity of 80-95% wt., an organic binding agent containing a structure-forming agent and solvent, and a functional additive based on polymer siloxane organic compounds in the quantity of 0.25% wt., were used.

Example 7

To prepare the conductive paste, silver powder with the average particle size of 0.5-5.0 μm in quantity of 80-95% wt, an organic binding agent containing a structure-forming agent and solvent, and a functional additive based on polymer siloxane organic compounds in the quantity of 0.50% wt., were used. Investigation of properties of the samples from Examples 5-7 was carried out in the same manner as for the samples from Examples 1-4.

Fig. 10 shows the measurement results of the conductive finger width for the samples from Examples 5-7.

Fig. 11 shows the measurement results of current-voltage characteristics for the samples from Examples 5-7.

As is seen from the results presented in Fig. 6, the sample from Example 5 without a functional additive has the widest conductive finger. When increasing the content of a functional additive, a tendency towards reduction of the finger width can be observed (Example 6 and Example 7). The achieved results correlate to the Vac measurement data (Fig. 11). Addition of a functional additive, which reduces spread of paste, makes it possible to increase the short-circuit current and reduce the value of series resistance in the solar cell.

Example 8

To prepare the conductive paste, silver powder with the average particle size of 0.5-5.0 μm in the quantity of 80-95% wt., an organic binding agent containing a structure-forming agent based on

halogenic thermoplastic polymer in the quantity of 5-10% wt. of the organic binding agent volume, and a solvent were used.

Example 9

To prepare the conductive paste, silver powder with the average particle size of 0.5-5.0 μm in the quantity of 80-95% wt., an organic binding agent containing a structure-forming agent based on phenoxy resin in the quantity of 5-10% wt. of the organic binding agent volume, and a solvent were used.

Example 10

To prepare the conductive paste, silver powder with the average particle size of 0.5-5.0 μm in the quantity of 80-95% wt., an organic binding agent containing a structure-forming agent based on acrylate resin in the quantity of 5-10% wt. of the organic binding agent volume, and a solvent were used.

Example 11

To prepare the conductive paste, silver powder with the average particle size of 0.5-5.0 μm in the quantity of 80-95% wt., an organic binding agent containing a structure-forming agent based on epoxy resin in the quantity of 5-10% wt. of the organic binding agent volume, and a solvent were used.

Example 12

To prepare the conductive paste, silver powder with the average particle size of 0.5-5.0 μm in the quantity of 80-95% wt., an organic binding agent containing a halogenic thermoplastic polymer in the quantity of 5-10% wt. of the organic binding agent volume, and a solvent were used.

Investigation of properties of the samples from Examples 8-12 was carried out in the same manner as for the samples from the Examples mentioned above.

The halogenic thermoplastic polymer-based samples from Examples 8 and 12 have the reduce specific resistance after the soft baking stage (Fig. 3) that confirms a theory of silver particle catalytical sintering through halogenic polymer thermal decomposition at low temperature. This theory is also indirectly confirmed by the presented photographs (Fig. 12), which show silver powder partial agglomeration of samples a) and d) (Examples 8 and 12 respectively) even at the soft baking stage.

The samples from Examples 8, 10, 11, 12 show a comparable efficiency level as a part of solar cells, meanwhile the samples from Examples 10 and 11 do not have sufficient adhesion to substrate that has effected on the results of short-circuit current measurement for these samples. The sample from Example 9 has a high linear resistance level and, as a consequence, is low efficient (Fig. 14-15).

Industrial applicability

The polymer conductive paste for heterojunction solar cells in accordance with the present invention contains silver powder with the average particle size D50 of 0.5-5.0 μm in the quantity of 80-95% wt. of the paste volume, a polymer organic-silicon additive, which reduces a degree of paste surface tension and therefore improves the silk-screen printing process and the current conducting contact topology, and, as result, reduces the linear resistance of conductor, a structure-forming agent based on a halogenic polymer, which reduces the specific resistance of conductor and improves its conductivity through the process of silver particle thermocatalytic sintering. This composition implies the uniqueness of its formulation as compared to other existing analogues.

The conductive paste of the present invention can be used as a part of solar cells with the sintering temperature of below 210°C.

Claims

1 The polymer conductive paste for heterojunction solar cells, containing silver powder, an organic binding agent, which contains a structure-forming agent as a part of the solvent, and a functional additive, wherein a halogenic polymer with the softening temperature of below 200°C is used as the structure-forming agent, and a polymer organic-silicon compound with the number of siloxane units of less than 3000 is used as the functional additive, the mixture ratio is the following (% wt.):

Silver powder – 80-95

Organic binding agent – 4-18

Functional additive – 0.1-2.0

2 The conductive paste of claim 1 is different in that the average size of silver powder is D50 of 0.5-5.0 μm .

3 The conductive paste of claim 1 is different in that the quantity of structure-forming agent as a component of the organic binding agent is 5-10% wt.

4 The conductive paste of claim 1 is different in that the functional additive contains additional components.

5 The conductive paste of claim 1 is different in that when measuring its rheological properties in the coordinates “shear velocity $\dot{\gamma}$ [c^{-1}] – shear stress τ [Pa]”, the flow curve is characterized by a negative slope when the threshold value of shear velocity of 40 c^{-1} is exceeded.