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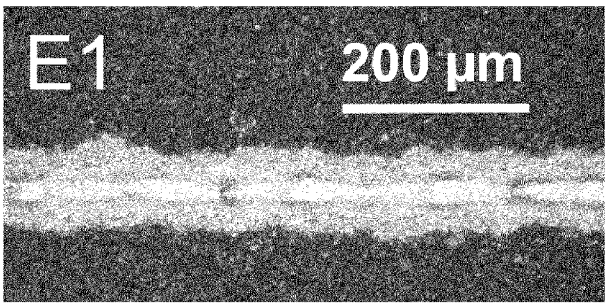


Fig. 1

(57) Abstract: The invention relates to a conductive paste comprising from 30 to 97% by weight of electrically conductive particles, from0 to 20 % by weight of a glass frit, from3 to 70% by weight of an organic medium and from 0.1 to 67% by weight of a silicone oil, each based on the total mass of the paste, wherein the silicone oil hasa boiling pointor a boiling rangein the range between 180 °C and 350 °C.The invention further relates to a use of the conductive paste and a process for producing electrodes on a semicon - ductor substrate using the paste.

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Conductive Paste comprising a silicone oil

The invention relates to a conductive paste comprising from 30 to 97 % by weight of electrically conductive particles, from 3 to 70 % by weight of an organic medium and from 0 to 20 % by weight of a glass frit.

Conductive pastes or inks can be used to form electrodes, such as conductive grid lines, for example silver grid lines, and bus bars on the surface of semiconductor substrates or substrates from an insulating material. A particularly preferred use is screen printing of electrodes on semiconductor substrates for the production of solar cells or photovoltaic cells which convert solar energy to electrical energy when photons from sunlight excite electrons on semiconductors from the valance band to the conduction band. The electrons which flow to the conduction band are collected by the metal electrodes that contact the semiconductors.

Besides printing electrodes on semiconductor substrates for producing solar cells or photovoltaic cells, conductive pastes or inks can be used for printing grid lines on insulating substrates for producing printed electronic circuit boards or hybrid circuits on ceramic substrates.

To print fine lines onto either a semiconductor substrate or an insulating substrate, generally screen printing processes are used for cost efficient mass production. Nevertheless, to generate uniform narrow lines without line interruptions is challenging for screen printing, particularly for high speed screen printing. The industrial printing speed depends on the application requirement. It ranges from 80 mm/s to 800 mm/s, preferably not slower than 150 mm/s, for example in solar cell printing, the printing speed is 150 mm/s to 300 mm/s.

Screens for screen printing are manufactured by covering selected areas in meshes of stainless steel wires with a polymer layer which is called screen emulsion. During the screen printing process the paste can only flow through the areas of the screen which are not covered by the screen emulsion. For this reason the screen printing paste has to show minimum adhesion on the surface of the stainless steel wires and on the surface of the screen emulsion.

When the conductive paste is used for printing on semiconductor substrates, the paste usually comprises electrically conductive particles, which typically are metal powders, an organic medium and optionally a glass frit. The organic medium typically comprises at least one organic liquid, such as organic solvents or organic salts or other organic compounds having liquid form at room temperature. The organic medium comprises optionally a polymeric component. To form metal contacts, the conductive paste is printed onto a substrate. Depending on the type of materials, the substrate is then heated at a temperature in the range from about 150 °C to about 950 °C, where the organic medium is decomposed and the inorganic species form the conductive tracks and electrical contact to the substrate.

Pastes for printing electrodes on semiconductor substrates, for example for producing solar cells, are disclosed for example in JP-A 2010-087251, KR-A 10-2009-0067992 or US-A 2014/0124713.

However, to be used in screen printing processes, a paste has to be released in a quantitative way from the surfaces of the materials the screen is made of and completely transferred to the surface of the substrate. On the other hand, the paste must show sufficient adhesion on the surface of the substrate the paste is printed on to achieve fine lines which have a sufficient thickness and do not show any interruptions.

Therefore it has been an object of the invention to provide a conductive paste which can be printed by screen printing without adhering in a too strong way on the material of the screen and which has a sufficient adhesion to form fine grid lines without seepage on the substrate on which the paste is printed.

This object is achieved by a conductive paste comprising from 30 to 97 % by weight of electrically conductive particles, from 0 to 20 % by weight of a glass frit, from 3 to 70 % by weight of an organic medium and from 0.1 to 67 % by weight of a silicone oil, each based on the total mass of the paste, wherein the silicone oil has a boiling point or a boiling range in the range between 180 °C and 350 °C.

Silicone oils can comprise only one kind of silicone oil molecule or different kinds of silicone oil molecules. Silicone oil molecules contain the elements silicon, oxygen, carbon and hydrogen. In silicone oil molecules silicon atoms are interconnected via one to four oxygen atoms with other silicon atoms. Each silicon atom forms 4 covalent bonds with other atoms, which can be either oxygen atoms or methyl groups.

Silicone oil molecules can be cyclic, branched or linear. Typical examples for cyclic silicone oil molecules are decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane or tetradecamethylcycloheptasilxane. Typical examples for linear silicone oil molecules are decamethyltetrasiloxane, dodecamethylpentasiloxane, tetradecamethylhexasiloxane and hexadecamethylheptasiloxane.

If a silicone oil contains only one single type of molecule then this silicone oil has a defined boiling point at normal pressure of 1013 mbar. Pure hexamethyldisiloxane for example has a boiling point of 100.0 °C. If a silicone oil contains several different types of molecules then this silicone oil exhibits a boiling range which depends on the chemical composition of the silicone oil. At the lower end of a boiling range the most volatile component of a silicone oil changes from the liquid phase of the silicone oil into the gas phase. At the upper end of the boiling range the least volatile component of a silicone oil changes from the liquid phase of the silicone oil into the gas phase. The upper end of the boiling range of a silicone oil can be defined by the least volatile component of a silicone oil which does evaporate but not chemically decompose.

Physical properties of silicone oils depend on the chemical structure of contained silicone oil molecules. In case of linear silicone oils an increase of molecular weight causes an increase of the boiling point, a reduction of vapour pressure at constant temperature, a reduction of diffusion speed in paste formulations, an increase of surface tension and an increase of viscosity.

Copolymers of silicone oil molecules and other chemical species like polyethers are commonly used as surface active components in various applications like defoaming, adhesion control, dispersion and wetting.

Such copolymers of silicone oils and other chemical species are disclosed for example in KR923741B1, JP2010087251A2 and US2014/0124713A1.

At temperatures above 25 °C and ambient pressure silicones either evaporate or decompose. Hexamethyldisiloxane has a boiling point of 100 °C which is the lowest boiling point of all silicone oil molecules. All other silicone oil molecules have a larger molecular weight and therefore a higher boiling point and a lower vapour pressure at constant temperature. When silicone oil molecules are heated from 25 °C to 800 °C then it depends on the heating rate and on the type of silicone oil molecule whether the molecule is evaporated or chemically decomposed.

In complex formulations like metallization pastes which comprise silicone oil molecules it depends also on the total composition of the formulation whether a silicone oil molecule is evaporated or chemically decomposed during heating with a defined heating rate. Vapour pressure and diffusion speed of the silicone oil molecule will determine whether a silicone oil molecule can reach the paste surface and transfer to the gas phase via an evaporation process or whether a silicone oil molecule chemically decomposes inside the paste volume during paste sintering.

During heating from 25 °C to 800 °C chemical decomposition of silicone oil molecules comprises the formation of carbon dioxide, water and silica. Carbon dioxide and water transfer to the gas phase at temperatures above 100 °C. However, silica is a solid even at a temperature as high as 800 °C. Furthermore silica is an electrically nonconductive material which increases the specific resistivity of metal electrodes which are formed via screen printing of metal pastes with subsequent paste drying and firing at elevated temperatures. Therefore addition of silicone oil to formulations of metallization pastes appears to be detrimental for optimum line conductivity.

On the other hand volatile liquid components in metallization pastes can cause fast paste drying during screen printing at 25 °C and ambient pressure. A loss of liquid paste components during screen printing causes a change of paste rheology with detrimental effects on print performance. An increase of paste viscosity due to fast evaporation of liquid components can result in screen prints of interrupted electrodes because of insufficient paste flow through narrow line openings of screen emulsions.

Silicone oils are widely used due to their unique chemical and physical properties. The low polarity of silicone oil molecules enables only weak attractive forces between silicone oil molecules and other chemical species. For this reason silicone oil molecules are part of coatings for reduction of adhesion and used as release agents for thermal molding of rubber, plastics and low-melting metals.

Furthermore silicone oils exhibit a very low surface tension which is the reason for their unique wetting properties of various surfaces. Stainless steel for instance has a very high surface energy. For this reason stainless steel tries to minimize its surface energy by adsorbing any kind of material.

Surprisingly it has been found that a paste which comprises an organic medium and a silicone oil with a boiling point range between 180 °C and 350 °C does significantly improve the print quality during screen printing of conductive pastes on semiconductors, for example for producing solar cells. Said silicone oils significantly improve the release of the conductive paste from the narrow openings of screen emulsions because they wet very efficiently the metal wires of the stainless steel screen mesh. The wetting of the stainless steel wires of the screen mesh with silicone oil molecules during the screen print reduces adhesion of the metallization paste on the stainless steel wires and supports the efficient paste release from the stainless steel surface.

An additional unexpected result was the measurement of equal solids content of two pastes wherein in the second paste only the solvent blend of the first paste has been substituted by silicone oil. This means that silicone oil with a boiling point range between 180 °C and 350 °C does not result in the formation of nonconductive residues of silica as a product of chemical decomposition of silicone oil molecules during paste drying or paste firing at elevated temperatures.

In a preferred embodiment of the present invention the paste contains 0.1 % to 50 % by weight of a silicone oil with a boiling point or a boiling range in the range between 180 °C and 350 °C. Preferred is a boiling point or a boiling range in the range between 190 °C and 300 °C and particularly preferred is a boiling point or a boiling range in the range between 200 °C and 270 °C. The amount of the organic medium in the paste preferably is 3 % to 70 % by weight and the amount of electrically conductive particles preferably is 30 % to 97 % by weight.

In the scope of the present invention the term “boiling range in the range between” is to be understood that the minimum value and the maximum value of the boiling range each are in the range between the temperatures limiting the range but that the minimum value and the maximum value do not necessarily correspond to the temperatures limiting the range in which the boiling range lies.

The silicone oil preferably comprises polydimethylsiloxane molecules.

In one embodiment of the invention, the silicone oil contains linear silicone oil molecules. If linear silicone oil molecules are used then the silicone oil molecules are preferably selected from decamethyltetrasiloxane, dodecamethylpentasiloxane, tetradecamethylhexasiloxane, hexadecamethylheptasiloxane or mixtures thereof.

In another embodiment of the invention, the silicone oil contains cyclic silicone oil molecules. If cyclic silicone oil molecules are used then the silicone oil molecules are preferably selected from decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, tetradecamethylcycloheptasiloxane or mixtures thereof.

Besides the use of linear silicone oil molecules, branched silicone oil molecules or cyclic silicone oil molecules it is also possible to use at least two of the aforementioned types of silicone oil molecules. Independently of the form of the silicone oil molecules, either linear, branched or cyclic or a mixture of at least two thereof, it is particularly preferred when the silicone oil molecules are polydimethylsiloxanes.

The electrically conductive particles present in the electrically conductive paste may be particles of any geometry composed of any electrically conductive material. Preferably, the electrically conductive particles comprise carbon, silver, gold, aluminum, platinum, palladium, tin, nickel, cadmium, gallium, indium, copper, zinc, iron, bismuth, cobalt, manganese, molybdenum, chromium, vanadium, titanium, tungsten, or mixtures or alloys thereof or are in the form of core-shell structures thereof. Preferred as material for the electrically conductive particles are silver or aluminum, particularly silver due to good conductivity and good oxidation resistance.

The mean particle size of the electrically conductive particles preferably is in the range from 10 nm to 100 µm. More preferably, the mean particle size is in the range from 100 nm to 50 µm and particularly preferred, the mean particle size is in the range from 500 nm to 10 µm. The electrically conductive particles may have any desired form known to those skilled in the art. For example, the particles may be in the form of flakes, rods, wires, nodules, spheres or any mixtures thereof. Spherical particles in context of the present invention also comprise particles with a real form which deviates from the ideal spherical form. For example, spherical particles, as a result of the production, may also have a droplet shape or be truncated. Suitable particles which can be used to produce the conductive paste are known to those skilled in the art and are commercially available. Particularly preferably, spherical silver particles are used. The advantage of the spherical particles is their improved rheological behavior compared to irregular shaped particles.

The proportion of electrically conductive particles in the composition is in the range from 30 to 97 % by weight. The proportion is preferably in the range from 70 to 95 % by weight and particularly preferred in the range from 85 to 92 % by weight. This weight percentage of solid particles is often referred as solids content.

The particle shapes and sizes do not change the nature of this invention. Particles can be used as mixtures of different shapes and sizes. It is known to those skilled in the art that the particles with mixtures of different shapes or sizes can result in higher or lower viscosity when they are dispersed in the same organic medium. In such case, it is known to those skilled in the art that the organic medium needs to be adjusted accordingly. The adjustment can be but is not limited to variations of solids content, solvent content, polymer content, thixotrope content and/or surfactant content. As an example, typically when nano-sized particles are used to replace micron-sized particles, the solids content has to be reduced to avoid an increase of the viscosity of the paste, which results in higher contents of organic components.

The electrically conductive particles, especially when made of a metal, generally are coated with organic additives in the course of production. In the course of preparation of the composition for printing conductor tracks, the organic additives on the surface are typically not removed, such that they are then also present in the conductive paste. The proportion of additives for stabilization is generally not more than 10 % by weight, based on the mass of particles. The additives used to coat the electrically conductive particles may, for example, be fatty amines or fatty amides, for example dodecylamine. Further additives suitable for stabilizing the particles are, for example, octylamine, decylamine, and polyethyleneimines. Another embodiment may be fatty acids, fatty acid esters, with or without epoxylation, for example, lauric acid, palmitic acid, oleic acid, stearic acid, or a salt thereof. The coating on the particles does not change the nature of this invention.

In an embodiment, the conductive paste additionally comprises a glass frit. If a glass frit is present in the paste, any glass frit known to a skilled person can be used, either based on lead-containing compositions or on lead-free compositions. The glass frit is not bound to any particular shape or form. The mean particle size of the particles of the glass frit used is in the range from 10 nm to 100 µm. The mean particle size of the glass frit particles is more preferably in the range from 100 nm to 50 µm and particularly preferred in the range from 500 nm to 10 µm. The particles used may have any desired form known to those skilled in the art. For example, the particles may be in the form of flakes, rods, wires, nodules, spheres or any mixture thereof. Spherical particles in this context mean that the real form of the particles deviates from the ideal spherical form, for example, spherical particles, as a result of the production, may also have a droplet shape or be truncated. Suitable particles which can be used as glass frit are known to those skilled in the art and are commercially available. Especially preferred, spherical particles are used. The advantage of spherical particles is their improved rheological behavior compared to irregular shaped particles. According to the invention, the glass frit content is in the range from 0 to 20 % by weight, preferably from 0 to 10 % by weight and most preferably from 1 to 5 % by weight, based on the total mass of the conductive paste.

The organic medium in the conductive paste may comprise at least one solvent. In one embodiment of the invention, the solvent comprises one or more solvents selected from liquid organic components having at least one oxygen atom. The liquid organic component having at least one

oxygen atom is selected from alcohol, ester alcohol, glycol, glycol ether, ketone, fatty acid ester, terpene derivatives and dibasic esters. The liquid organic component for example may be benzyl alcohol, texanol, ethyl lactate, diethylene glycol monoethyl acetate, diethylene glycol monobutylether, diethylene glycol dibutylether, diethylene glycol monobutylether acetate, butyl cellosolve, butyl cellosolve acetate, propylene glycol monometylether, propylene glycol monomethylether acetate, dipropylene glycol monomethylether, propylene glycol monomethylpropionate, ethylether propionate, dimethylamino formaldehyde, methylethylketone, gamma-butyrolactone, ethyl linoleate, ethyl linolenate, ethyl myristate, ethyl oleate, methyl myristate, methyl linoleate, methyl linolenate, methyl oleate, dibutyl phthalate, dioctyl phthalate and terpineol.

The solvent being a liquid organic component having at least one oxygen atom can be used in the conductive paste either as single solvent or as a solvent mix. In case a solvent mix is used, the solvent can additionally comprise 5 to 50 wt% of at least one dibasic ester based on the total mass of the solvent mixture. The dibasic ester preferably is selected from dimethyl esters of adipic acid, glutaric acid, succinic acid or mixtures thereof.

When either a single solvent or a solvent mixture is used, it is necessary that organic binders can be dissolved greater than 2 wt% in the selected single or mixed solvents, such that the organic medium comprises at least 2 wt% dissolved binder based on the total mass of the organic medium.

In an embodiment of the invention, the paste additionally comprises from 0.1 to 20 wt% of at least one additive selected from surfactants, thixotropic agents, plasticizers, solubilizers, defoamers, desiccants, crosslinkers, inhibitors, complexing agents and/or conductive polymer particles. The additives may be used individually or as a mixture of two or more of them.

When a surfactant is used as an additive, it is possible to use only one surfactant or more than one surfactant. In principle, all surfactants which are known to those skilled in the art or are described in the prior art, can be suitable. Preferred surfactants are singular or plural compounds, for example anionic, cationic, amphoteric or nonionic surfactants. However, it is also possible to use polymers with pigment-affinitive anchor groups, which are known to a skilled person as surfactants.

In case the electrically conductive particles are pre-coated with a surfactant, the conductive paste may not comprise an additional surfactant as additive.

Besides the solvent and the further organic additives, the conductive paste also may comprise organic binders in a range from 0.1 to 20 % by weight. The organic binder can be selected from natural or synthetic resins and polymers. As known to those skilled in the art, selections are based on but not limited to solvent compatibility and chemical stability. For example, the common binders as disclosed in the prior art comprise cellulose derivatives, acrylic resin, phenolic resin, urea-formaldehyde resin, alkyd resin, aliphatic petroleum resin, melamine formaldehyde

resin, rosin, polyethylene, polypropylene, polystyrene, polyether, polyurethane, polyvinyl acetate and copolymers thereof.

The inventive paste particularly is used in screen printing processes for producing electrically conductive pattern on a substrate. Particularly preferred, the paste is used to print electrodes on semiconductors for producing solar cells.

The invention further is related to a process for producing electrodes on a semiconductor substrate comprising the steps of:

(a) screen printing a conductive paste as described above on a semiconductor substrate in a predetermined pattern to form a printed semiconductor substrate,

(b) drying the printed semiconductor substrate at a temperature in the range from 100 to 300 °C,

(c) heating the dried printed semiconductor substrate with the printed composition to a sintering temperature in the range from 600 to 900 °C to sinter the electrically conductive particles.

Suitable semiconductor substrates are for example such to produce photovoltaic cells comprising an n-type region, a p-type region, a p-n junction and conductive gridlines. Photovoltaic cells comprise optionally an anti-reflection layer on the surface of substrate. The semiconductor substrate can be mono-crystalline silicon, multi-crystalline silicon, amorphous silicon coated solid substrate, or a substrate whose surface is coated with polycrystalline or amorphous transparent conductive oxides (TCO), such as indium tin oxide (ITO), ZnO based transparent conductive oxides, such as indium gallium zinc oxide (IGZO), indium zinc tin oxide (IZTO), indium zinc oxide (IZO), indium tungsten oxide (IWO), gallium zinc oxide (GZO). The conductive gridlines are formed by the screen printing process from a conductive paste.

The screen printing in step (a) is carried out in any known manner known to a skilled person. The printing process particularly can be an industrial high speed screen printing process. In such a process the printing speed depends on the application requirement. It ranges from 80 mm/s to 800 mm/s, preferably not slower than 150 mm/s, for example in solar cell printing, the printing speed is 150 mm/s to 300 mm/s.

After printing the conductive paste on the semiconductor substrate, the printed semiconductor substrate is dried at a temperature in the range from 100 to 300 °C. The drying step preferably is carried out for a duration in the range from 10 to 50 sec, particularly preferably in the range from 15 to 30 sec.

After drying, the dried printed semiconductor substrate is heated to a sintering temperature in the range from 600 to 900 °C to sinter the electrically conductive particles. In the heating step the printed semiconductor substrate is heated from the drying temperature to the sintering temperature within 5 to 50 sec, preferably within 5 to 35 sec, the sintering temperature is kept for less than 5 sec, and afterwards the printed semiconductor substrate is cooled down to room temperature within 3 to 60 sec, preferably within 3 to 30 sec. The whole heating step is carried out for a duration in the range from 10 to 80 sec, preferably from 15 to 50 sec.

Examples

Conductive pastes according to the compositions in table 1 have been screen printed with the screen parameters as shown in table 3.

Table 1: Paste composition

sample	E1	E2
component	mass %	mass %
silver powder	88.50	88.50
glass frit	3.00	3.00
organic additive blend A	1.25	1.25
organic solvent blend A	7.25	6.45
silicone oil	0.00	0.80
sum	100.00	100.00

In formulation E2 solvent blend A partially has been substituted by silicone oil. Organic additive blend A contains a mixture of a dispersants, polymers and thixotropes. Organic solvent blend A contains a mixture of texanol and dimethyl adipate.

Screen prints have been conducted with the following screen parameters:

Table 2: screen parameters

mesh count [wires/inch]	360
wire thickness [µm]	16
emulsion thickness [µm]	15
fabric thickness [µm]	22
line opening [µm]	36
number of lines	100
busbar type	2 segmented

Table 3: Slip measurement

sample	E1	E2
average rotation speed at 1000 Pa [rpm]	1.89	2.12
standard deviation of rotation speed at 1000 Pa [rpm]	0.014	0.034

Formulation E2 shows less adhesion on the stainless steel surfaces of a rheometer with plate-plate geometry. Therefore in case of formulation E2 the upper plate shows faster rotation speed at constant shear stress.

Results of the printing process are shown in Figures 1 and 2.

Figures 1 and 2 show microscope pictures of printed lines of the paste compositions E1 and E2 after drying at 250 °C and subsequent sintering at 800 °C. By comparison of the lines shown in figures 1 and 2 it can be seen that the line printed with the inventive formulation E2 shows less seepage.

Table 4: characteristics of the printed lines

sample	E1	E2
median shaded line width [µm]	86.1	66.4
median line height [µm]	13.4	16.4

8 multi crystalline wafers have been screen printed with each of pastes E1 and E2. Results of cell efficiency measurements are shown in figure 3. Results of thermal gravimetric analysis are shown in figure 4.

From figure 3 it can be clearly seen, that the paste composition according to the invention which comprises a silicone oil has a higher cell efficiency than a paste composition which does not contain a silicone oil.

Figure 4 shows that the mass reduction during the heating step for both pastes nearly is the same, which shows that during the heating step no silica is formed from the silicone oil which would lead to a reduction of cell efficiency.

Claims

1. A conductive paste comprising from 30 to 97 % by weight of electrically conductive particles, from 0 to 20 % by weight of a glass frit, from 3 to 70 % by weight of an organic medium and from 0.1 to 67 % by weight of a silicone oil, each based on the total mass of the paste, wherein the silicone oil has a boiling point or a boiling range in the range between 180 °C and 350 °C.

2. The conductive paste according to claim 1, wherein the silicone oil contains linear molecules, branched molecules, cyclic molecules or mixtures thereof.

3. The conductive paste according to claim 1 or 2, wherein the silicone oil comprises polydimethylsiloxane.

4. The conductive paste according to claim 2, wherein the linear silicone oil molecule is selected from the group consisting of decamethyltetrasiloxane, dodecamethylpentasiloxane, tetradecamethylhexasiloxane, hexadecamethylheptasiloxane or mixtures thereof.

5. The conductive paste according to claim 2, wherein the cyclic silicone oil molecule is selected from the group consisting of decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, tetradecamethylcycloheptasiloxane or mixtures thereof.

6. The conductive paste according to any of claims 1 to 5, wherein the electrically conductive particles comprise carbon, silver, gold, aluminum, platinum, palladium, tin, nickel, cadmium, gallium, indium, copper, zinc, iron, bismuth, cobalt, manganese, molybdenum, chromium, vanadium, titanium, tungsten, or mixtures or alloys thereof or are in the form of core-shell structures thereof.

7. The conductive paste according to any of claims 1 to 6, wherein the electrically conductive particles are coated with an organic additive.

8. Use of the conductive paste according to any of claims 1 to 7 for printing electrodes on a semiconductor substrate by screen printing.

9. A process for producing electrodes on a semiconductor substrate comprising the steps of:

   (a) screen printing a conductive paste according to any of claims 1 to 7 on a semiconductor substrate in a predetermined pattern to form a printed semiconductor substrate,

   (b) drying the printed semiconductor substrate at a temperature in the range from 100 to 300 °C,

(c) heating the dried printed semiconductor substrate with the printed composition to a sintering temperature in the range from 650 to 900 °C to sinter the electrically conductive particles.

10. The process according to claim 9, wherein the drying step is carried out for a duration in the range from 10 to 50 sec.

11. The process according to claim 9 or 10, wherein in the heating step the printed semiconductor substrate is heated from room temperature to the sintering temperature within 5 to 50 sec, the sintering temperature is kept for 1 to 5 sec and afterwards the printed semiconductor substrate is cooled down to room temperature within 3 to 60 sec.

12. The process according to any of claims 9 to 11, wherein the semiconductor substrate is a semiconductor substrate for a solar cell.

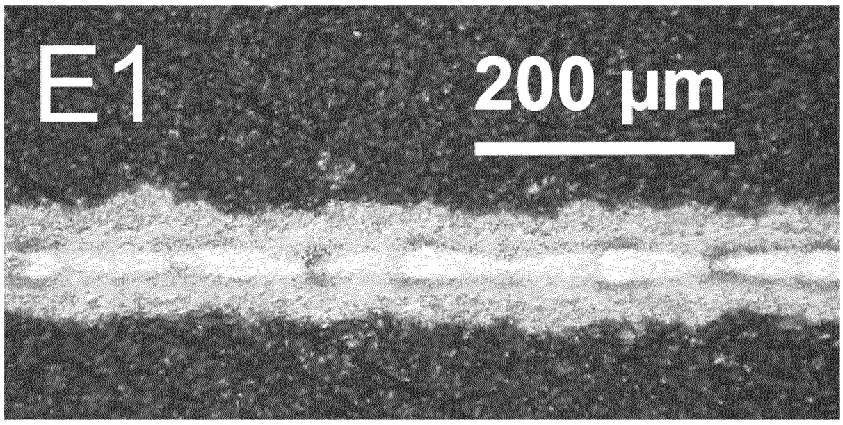


Fig. 1

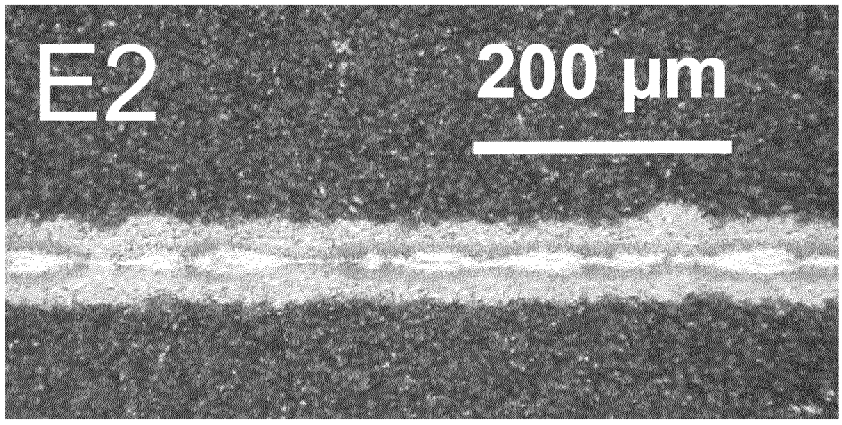


Fig. 2

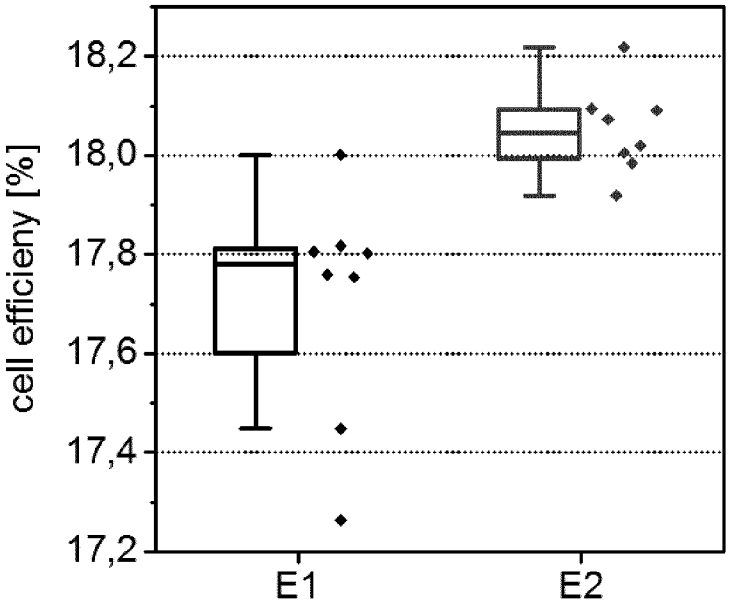

cell efficieny [%]
18,2
18,0
17,8
17,6
17,4
17,2
E1
E2

Fig. 3

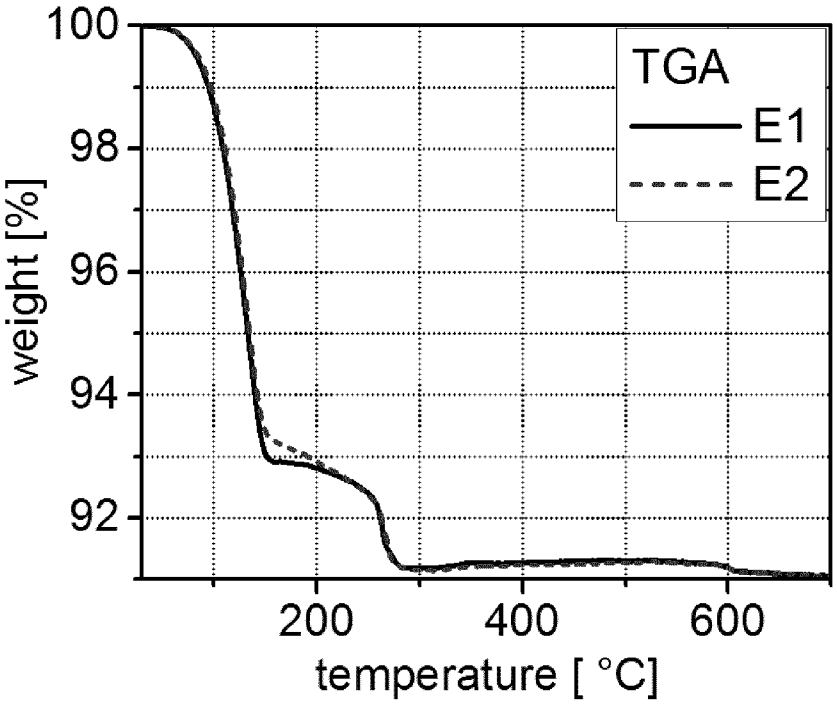

weight [%]
100
98
96
94
92
TGA
E1
E2
200
400
600
temperature [°C]

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/054105

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01B1/02 H01B1/22 H01L31/0224
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01B H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/126797 A1 (LEE SUN MI [KR] ET AL) 23 May 2013 (2013-05-23) paragraphs [0001], [0023] - [0025], [0046] - [0047], [0051]	1-12
X	WO 2011/055995 A2 (LG INNOTEK CO LTD [KR]; KIM SOON GIL [KR]; LEE IN JAE [KR]; KIM SANG G) 12 May 2011 (2011-05-12)	1-9,11, 12
A	paragraphs [0001], [0006] - [0007], [0022], [0034], [0051] - [0068]	10
X	US 2011/083874 A1 (KUROKI MASAKATSU [JP]) 14 April 2011 (2011-04-14) paragraph [0105]; table 2	1-12

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 May 2017	17/05/2017

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Pötzsch, Robert

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/054105

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2010 087251 A (DAINIPPON INK & CHEMICALS; TOYO ALUMINIUM KK) 15 April 2010 (2010-04-15) cited in the application paragraphs [0062] - [0068]	1-12
A	US 2010/090176 A1 (KOSOWSKY LEX [US] ET AL) 15 April 2010 (2010-04-15) paragraphs [0069] - [0073]	1-12
X	EP 0 971 367 A1 (DOW CORNING [US]) 12 January 2000 (2000-01-12)	1-8
A	paragraphs [0044] - [0045], [0065], [0067]	9-12

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2017/054105

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013126797 A1	23-05-2013	CN 103155168 A	12-06-2013
		EP 2599128 A2	05-06-2013
		KR 20120012335 A	09-02-2012
		TW 201213466 A	01-04-2012
		US 2013126797 A1	23-05-2013
		WO 2012015283 A2	02-02-2012
WO 2011055995 A2	12-05-2011	KR 20110049222 A	12-05-2011
		TW 201123464 A	01-07-2011
		WO 2011055995 A2	12-05-2011
US 2011083874 A1	14-04-2011	CN 102549495 A	04-07-2012
		JP 2013507772 A	04-03-2013
		TW 201123215 A	01-07-2011
		US 2011083874 A1	14-04-2011
		US 2012255765 A1	11-10-2012
		WO 2011044196 A1	14-04-2011
JP 2010087251 A	15-04-2010	NONE	
US 2010090176 A1	15-04-2010	CN 102870166 A	09-01-2013
		EP 2513912 A1	24-10-2012
		KR 20120104333 A	20-09-2012
		SG 181777 A1	30-07-2012
		US 2010090176 A1	15-04-2010
		WO 2012030363 A1	08-03-2012
EP 0971367 A1	12-01-2000	DE 69921903 D1	23-12-2004
		DE 69921903 T2	03-11-2005
		EP 0971367 A1	12-01-2000
		JP 2000038510 A	08-02-2000
		US 6017587 A	25-01-2000