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(54) Title: ELECTRONICALLY CONDUCTIVE COMPOSITION FOR USE AN ELECTRONICALLY CONDUCTIVE ADHESIVE FOR MECHANICALLY AND ELECTRICALLY CONNECTING ELECTRICAL CONDUCTORS TO ELECTRICAL CONTACTS OF SOLAR CELLS

(57) Abstract: Electrically conductive composition comprising (A) 2 to 35 vol.-% of silver particles having an average particle size in the range of 1 to 25 µm and exhibiting an aspect ratio in the range of 5 to 30 : 1, (B) 10 to 63 vol.-% of non-metallic particles having an average particle size in the range of 1 to 25 µm, exhibiting an aspect ratio in the range of 1 to 3 : 1, (C) 30 to 80 vol.-% of a thermoplastic polymer system (D) 0 to 25 vol.-% of at least one additive, wherein the sum of the vol.-% of particles (A) and (B) totals 25 to 65 vol.-%.



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Electrically conductive composition

for use as an electrically conductive adhesive for mechanically and electrically connecting electrical conductors to electrical contacts of solar cells

5 The invention relates to an electrically conductive composition

for use as an electrically conductive adhesive for mechanically and electrically connecting electrical conductors to electrical contacts of solar cells.

Solar cells can convert light, such as sunlight, into electrical energy. It is possible to collect the electrical energy from one single solar cell. In order to increase the voltage
10 delivered by individual solar cells to a suitable level, a plurality of solar cells is conventionally electrically connected together in series to form an array of solar cells which can be incorporated into a photovoltaic module. Collection of the electrical energy and electrical connection of solar cells is typically made via electrical conductors which are mechanically and at the same time electrically connected to the emitter and
15 collector contacts of the solar cells. The mechanical and at the same time electrical connection of the electrical conductors to the cell contacts is typically made by soldering or by adhesive bonding, in the latter case making use of an electrically conductive adhesive.

The term "electrical conductor" used herein means conventional electrical conductors
20 like, for example, conventional wire, tape, ribbon or conductive backsheet foil (back contacting foil).

The term "emitter contact" used herein means an electrical contact connecting the emitter of a solar cell to an electrical conductor, whereas the term "collector contact" used herein means an electrical contact connecting the collector of a solar cell to an
25 electrical conductor. The electrical contacts take the form of metallizations.

In most of today's photovoltaic modules, the solar cells have emitter contacts and collector contacts located on opposite sides of the cells. The emitter contacts are located on the front surface, i.e. the surface exposed to the sunlight, whereas the collector contacts are on the back side. An example are H-type cells, typically having
30 two emitter contacts known as emitter busbars on their frontface and two collector

contacts also known as collector busbars on their backface. A skilled person will recognize that emitter contacts and collector contacts are of opposite polarity.

New cell types have been developed in which the emitter contacts have been moved from the front face to the back face of the solar cell in order to free up an additional portion of front surface and increase the amount of electrical energy that can be produced by the cell. Such solar cells, in which both emitter and collector contacts are located on the back side of the cell, are known under the common designation "back-contact cells", which designation includes metallization wrap-through (MWT) cells, back-junction (BJ) cells, integrated back-contact (IBC) cells and emitter wrap-through (EWT) cells. In the case of these back-contact cells, the emitter contacts are the so-called "vias", or "back emitter contacts", located on the backface of the cells, while the collector contacts are also located there.

Most of today's solar cells are silicon solar cells.

Conventional electrically conductive adhesives comprise a huge portion of silver particles with an order of magnitude of about 80 wt.-% (weight-%). Because of the high silver price so-called low-silver alternatives have been developed in terms of replacing a considerable portion of the silver particles by silver-coated particles, for example, silver-coated copper particles. However, there are concerns to use such type of copper containing electrically conductive adhesive for the adhesive bonding of electrical conductors to solar cell contacts, in particular in the case of silicon solar cells. The reasoning is that solar cells are intended for long-term use which enlarges the risk that during a solar cell's service life copper diffuses into the solar cell bulk material and hence forms undesired efficiency reducing recombination centers or even destroys the p-n or n-p transition of the solar cell. This is in particular a concern in the case of silicon solar cells. However, said concerns do not only apply in case of copper but also in case of other elements having a similar effect like copper. Examples of such elements include phosphorus, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, zirconium, niobium, molybdenum, tantalum and tungsten, see "Energy research Centre of the Netherlands, Gianluca Coletti, Sensitivity of crystalline silicon solar cells to metal impurities, September 14, 2011" or "J.R. Davis in IEEE Trans El. Dev. ED-27, 677 (1980)".

The invention prevents said risk by using a specific electrically conductive low-silver type adhesive for mechanically and at the same time electrically connecting the contacts of a solar cell with electrical conductors. In an embodiment, the elements copper, phosphorus, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, zirconium, niobium, molybdenum, tantalum, aluminum and tungsten in elemental or metal form or in the form of an alloy are essentially or completely avoided in the electrically conductive adhesive.

Hence, the invention relates to an electrically conductive composition useful as an electrically conductive adhesive for mechanically and at the same time electrically connecting at least one contact of a solar cell, preferably a silicon solar cell, with an electrical conductor, wherein said at least one contact is selected from the group consisting of emitter contacts and collector contacts, characterized in that the electrically conductive composition comprises

- (A) 2 to 35 vol.-% (volume-%) of silver particles having an average particle size in the range of 1 to 25 μm and exhibiting an aspect ratio in the range of 5 to 30 : 1,
 - (B) 10 to 63 vol.-% of non-metallic particles having an average particle size in the range of 1 to 25 μm , exhibiting an aspect ratio in the range of 1 to 3 : 1,
 - (C) 30 to 80 vol.-% of a thermoplastic polymer system, and
 - (D) 0 to 25 vol.-% of at least one additive,
- wherein the sum of the vol.-% of particles (A) and (B) totals 25 to 65 vol.-%.

In the description and the claims the term "solar cell" is used. It shall not mean any limitation as to a certain type of solar cell. It includes any type of solar cell including in particular silicon solar cells. The cells may be of the afore mentioned H- or back-contact cell type, for example.

In an embodiment, the sum of the vol.-% of (A), (B), (C) and, if present, (D) may total 100 vol.-% of the electrically conductive composition.

The vol.-% disclosed in the description and the claims refer to the electrically conductive composition or, to be even more precise, to the electrically conductive composition prior to its application or use according to the invention.

In the description and the claims the term "average particle size" is used. It shall mean the mean primary particle diameter (d_{50}) determined by means of laser diffraction. Laser diffraction measurements can be carried out making use of a particle size analyzer, for example, a Mastersizer 3000 from Malvern Instruments.

5 In the description and the claims the term "aspect ratio" is used with regard to the shape of the particles (A) and (B) included in the electrically conductive composition. The aspect ratio means the ratio of the largest dimension to the smallest dimension of a particle and it is determined by SEM (scanning electron microscopy) and evaluating the electron microscopical images by measuring the dimensions of a statistically meaningful
10 number of individual particles.

The electrically conductive composition comprises 2 to 35 vol.-%, preferably 2 to 30 vol.-% and most preferably 2 to 20 vol.-% of silver particles (A) having an average particle size in the range of 1 to 25 μm , preferably 1 to 20 μm , most preferably 1 to 15
15 μm and exhibiting an aspect ratio in the range of 5 to 30 : 1, preferably 6 to 20 : 1, most preferably 7 to 15 : 1. The silver particles (A) may have a coating comprising at least one organic compound, in particular a C8 to C22 fatty acid or derivative thereof like salts or esters. The vol.-% values include the volume contribution of said coatings on the silver particles (A).

The silver particles (A) include particles of silver and silver alloys; i.e. the term "silver
20 particles" used herein shall mean particles of pure silver and/or of silver alloy. In case of silver alloy the total proportion of alloying metals is, for example, >0 to 5 wt.-%, preferably >0 to 1 wt.-%. The silver alloys may comprise binary alloys of silver and one other metal or alloys of silver with more than one metal other than silver. Examples of
25 metals which can be used as alloying metals for the silver include in particular zinc, rhodium, palladium, indium, tin, antimony, rhenium, osmium, iridium, platinum, gold, lead and bismuth. In an embodiment, copper, phosphorus, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, zirconium, niobium, molybdenum, tantalum, aluminum and tungsten are excluded as alloying elements.

The silver particles (A) exhibit an aspect ratio in the range of 5 to 30 : 1, preferably 6 to
30 20 : 1, most preferably 7 to 15 : 1. Said aspect ratio shall express that the silver particles (A) are, for example, acicular particles (needles) or flakes (platelets) as

opposed to, for example, particles having a spherical, an essentially spherical, an elliptical or an ovoid shape.

The electrically conductive composition may comprise one type of silver particles (A) or a combination of two or more different types of silver particles (A). In any case, all types of silver particles (A) contained in the electrically conductive composition meet the afore-
5 mentioned average particle size and aspect ratio conditions. To illustrate this, the following theoretical example may be envisaged: An electrically conductive composition may comprise two different types of silver particles as the only particles (A), namely X
10 vol.-% of silver particles having a d50 value of $x \mu\text{m}$ and an aspect ratio of $y : 1$, and Y vol.-% of silver particles having a d50 value of $v \mu\text{m}$ and an aspect ratio of $w : 1$, with $X+Y$ lying in said 2 to 35 vol.-% range, x and v independently lying in said 1 to 25 μm range and y and w independently lying in said 5 to 30 : 1 range.

Silver particles of type (A) are commercially available. Examples of such silver particles include SF-3, SF-3J from Ames Goldsmith; Silver Flake #80 from Ferro; RA-0101, AA-
15 192N from Metalor.

In an embodiment, the electrically conductive composition may comprise a portion, for example, 10 to 30 vol.-% of silver particles other than those of type (A), in particular, silver particles having an aspect ratio in the range of, for example, 1 to $< 5 : 1$ or 1 to 3 : 1. One commercially available example of such silver particles is FA-3162 from Metalor.
20 The electrically conductive composition comprises 10 to 63 vol.-%, preferably 15 to 63 vol.-% and most preferably 15 to 60 vol.-% of non-metallic particles (B) having an average particle size in the range of 1 to 25 μm , preferably 1 to 20 μm , most preferably 1 to 15 μm and exhibiting an aspect ratio in the range of 1 to 3 : 1, preferably 1 to 2 : 1, most preferably 1 to 1.5 : 1. Examples of useful particles of the (B) type include graphite
25 particles and electrically non-conductive non-metallic particles, in each case meeting said average particle size and aspect ratio conditions. The term "electrically non-conductive non-metallic particles" used herein shall mean non-metallic particles of a material having an electrical conductivity of $< 10^{-5} \text{ S/m}$. Examples of such materials include glass, ceramics, plastics, diamond, boron nitride, silicon dioxide, silicon nitride,
30 silicon carbide, aluminosilicate, aluminum oxide, aluminum nitride, zirconium oxide

calcium carbonate, barium sulfate, talc, silica, polymer microspheres and titanium dioxide.

The non-metallic particles (B) exhibit an aspect ratio in the range of 1 to 3 : 1, preferably 1 to 2 : 1, most preferably 1 to 1.5 : 1. Said aspect ratio shall express that the particles (B) have a true spherical or essentially spherical shape as opposed to particles like, for example, acicular particles or flakes. The individual particles (B) when looked at under an electron microscope have a ball like or near-to-ball like shape, i.e., they may be perfectly round or almost round, elliptical or they may have an ovoid shape.

The electrically conductive composition may comprise one type of particles (B) or a combination of two or more different types of particles (B). In any case, all types of particles (B) contained in the electrically conductive composition meet the aforementioned average particle size and aspect ratio conditions.

Particles of type (B) are commercially available. Examples include AE9104 from Admatechs; EDM99,5 from AMG Mining; CL4400, CL3000SG from Almatiss; Glass Spheres from Sigma Aldrich; Spheromers® CA6, CA10, CA15 from Microbeads®.

In a preferred embodiment, the silver particles (A) have an average particle size in the range of 0.2 to 2 times the average particle size of the non-metallic particles (B).

The sum of the vol.-% of silver particles (A) and non-metallic particles (B) totals 25 to 65 vol.-%.

The electrically conductive composition comprises 30 to 80 vol.-%, preferably 30 to 75 vol.-% and most preferably 30 to 70 vol.-% a thermoplastic polymer system (C).

The thermoplastic polymer system (C) comprises those constituents of the electrically conductive composition which after the application embed the (A) and (B) particles.

The thermoplastic polymer system (C) comprises one or more thermoplastic polymers.

The thermoplastic polymer system of the invention exhibits a melting temperature in the range of 100 °C - 350 °C.

A distinction between oligomeric and polymeric materials can be defined by the weight average molar mass determined by gel permeation chromatography (GPC; divinylbenzene-crosslinked polystyrene as the immobile phase, tetrahydrofuran as the

liquid phase, polystyrene standards). Oligomeric materials have a weight average molar mass of ≤ 500 , while the weight average molar mass of polymeric materials is > 500 .

Examples of useful thermoplastic polymers include acrylonitrile butadiene styrene (ABS), amorphous Poly-alpha-olefins (APAO), ethylene-vinyl acetate (EVAC), ethylene
5 acrylic acid copolymer (EAA), polylactic acid (polylactide), polyamides (PA),
polybenzimidazole (PBI), polycarbonate (PC), polycaprolactone (PCL), polyether
sulfone (PES), poly ether ether ketone (PEEK), polyetherimide (PEI), polyethylene (PE),
polyphenylene oxide (PPO), polyphenylene sulfide (PPS), polypropylene (PP),
polypyrrole (PPY), polystyrene (PS), polyvinyl chloride (PVC), polyvinylpyrrolidone
10 (PVP), thermoplastic polyesters (TPE-E), thermoplastic polyurethanes (TPE-U).

The electrically conductive composition comprises 0 to 25 vol.-% of at least one additive (D).

Examples of additives include non-polymeric tackifying resins (e.g. terpenes, aliphatic, cycloaliphatic and aromatic resins, hydrogenated hydrocarbon resins, terpene-phenol-
15 resins), adhesion promoters (e.g. organosilanes, organosulfides, organoamines) ,
waxes (e.g. microcrystalline waxes, Fischer-Tropsch waxes), plasticizers (e.g.
benzoates such as 1,4-cyclohexane dimethanol dibenzoate, glyceryl tribenzoate, or
pentaerythritol tetrabenzoate, phthalates, paraffin oils, polyisobutylene), antioxidants
(sterically hindered phenols as N,N'-di-2-butyl-1,4-phenylenediamine, phosphites,
20 hindered aromatic amines) UV stabilizers (e.g. benzophenones, sterically hindered
amines as N,N'-di-2-butyl-1,4-phenylenediamine), antistatic agents (aliphatic amines
and amides, quaternary ammonium salts, polyethylene glycol, esters of phosphoric
acid, polyols, indium tin oxide, ethoxylated amines, glycerol esters, long-chain alkyl
phenols), metal powders others than those in A,

25 The electrically conductive composition can be made by mixing components (A), (B),
(C) and, optionally, (D). After completion of the mixing the so-produced electrically
conductive composition can be stored until its use according to the invention.

The electrically conductive composition is used according to the invention, i.e. it is used
as an electrically conductive adhesive for mechanically and – at the same time -
30 electrically connecting at least one contact of a solar cell with an electrical conductor,

wherein the at least one contact is selected from the group consisting of solar cell emitter contacts and solar cell collector contacts.

To this end, the electrically conductive composition is applied to the contact surface of the at least one contact of the solar cell and/or to the contact surface of the electrical conductor to be adhesively bonded to the at least one contact of the solar cell. Typically, the contact surface of a solar cell's contact is a metallization as has already been aforementioned in the paragraph explaining emitter and collector contacts. The contact surface of an electrical conductor may be a terminal and/or other suitable place of a wire, tape or ribbon. In case of an electrical conductor in the form of a conductive backsheet foil the contact surface thereof is typically in the form of a pattern designed to fit the at least one contact of the solar cell.

The electrically conductive composition may be applied by various applications methods. Application of the electrically conductive composition may be performed, for example, by printing, e.g. screen printing or stencil printing, by jetting, by dispensing or by extruding. The typical thickness of the applied electrically conductive composition lies in the range of, for example, 20 to 500 μm .

The thermoplastic polymer system may be present in the electrically conductive composition in melted state, dissolved or dispersed.

After the application of the electrically conductive composition the one or more solar cell contacts and the electrical conductor(s) to be adhesively bonded thereto are put together with their contact surfaces having the electrically conductive composition in between.

After the application and prior to or after putting together the one or more solar cell contacts and the electrical conductor(s), an optional drying step may be performed in order to remove eventually present volatile compounds like, for example, organic solvent, from the electrically conductive composition. If such drying step is performed, the drying parameters are for example, 1 to 120 minutes at an object temperature of, for example, 60 to 160 $^{\circ}\text{C}$.

The so formed assembly comprising the electrically conductive composition is then solidified.

After application of the electrically conductive composition the solar cell with the electrical conductors attached to its contacts or the array of solar cells connected to each other by electrical conductors may be used for the production of electrical energy, or, in particular, it may be incorporated into a conventional photovoltaic module. To this end, a photovoltaic stack or photovoltaic module may be assembled, for example, by placing a conventional back encapsulant layer on a conventional back sheet, placing the solar cell or the array of solar cells on top of the back encapsulant layer, placing a conventional front encapsulant layer on top of the one or more solar cells and then placing a conventional front sheet on top of the front encapsulant layer. Typically, a so-assembled photovoltaic stack is then consolidated in a laminating device by heating the stack and subjecting the heated photovoltaic stack to a mechanical pressure in a direction perpendicular to the plane of the stack and decreasing the ambient pressure in the laminating device. The heating allows the front and back encapsulants to soften, flow around and adhere to the one or more solar cells. Finally the photovoltaic stack is cooled to ambient temperature and the mechanical pressure is released and atmospheric pressure is reestablished in the laminating device.

Examples

Example 1a (Preparation of an electrically conductive thermoplastic):

High density Polyethylene (HDPE) was introduced into a heated sigma-bladed mixer. The device was heated to 160 °C. When the polymer is molten, AA-192N silver particles from Metalor (particles of (A) type and 31 vol.-% (40 wt.-%) of AE9104 Al₂O₃ from Admatechs (particles of (B) type) were introduced into the mass over the course of 15 min and then, the further additives were added. The composition was mixed for additional 10 min. After the composition cooled to room temperature and solidified. The grinded solid composition was remelted on a heatable roll mill and milled at a roll temperature of 150 °C.

Example 1b (Preparation of an electrically conductive thermoplastic):

Ethylene-vinyl acetate was introduced into a heated sigma-bladed mixer. The device was heated to 130 °C. When the polymer is molten, AA-192N from Metalor (particles of

(A) type and 31 vol.-% (40 wt.-%) of AE9104 from Admatechs (particles of (B) type) were introduced into the mass over the course of 15 min and then, the further additives were added. The composition was mixed for additional 10 min. After the composition cooled to room temperature and solidified. The grinded solid composition was remelted
5 on a heatable roll mill and milled milled at a roll temperature of 140 °C.

Example 2 (Production of a photovoltaic stack):

The electrically conductive composition of Example 1 was applied in liquid state to the backside emitter and collector contacts of a MWT solar cell (JACP6WR-0 from JA
10 Solar) via stencil printing in a thickness of 400 µm.

Meanwhile a punched Ebfoil® dielectric layer from Coveme was placed on a conductive backsheet foil (Ebfoil® Backsheet Back-contact from Coveme) to form a stack.

Thereafter the solar cell was placed with its backside provided with the electrically conductive composition facing the punched Ebfoil® dielectric layer of the stack. On top
15 of the solar cells frontside a sheet of a Solar Encapsulant Film EVA9100 from 3M™ was placed. A glass sheet (vsol from vetro solar™) was placed on top of the encapsulant film.

The entire stack was then laminated under application of heat and mechanical pressure. First, temperature was increased to 150 °C at a rate of 13 °C/min. At 80 °C a
20 mechanical pressure of 1 bar was applied gently and homogeneously on the top and bottom face of the stack. After 9 minutes at 150 °C the stack was cooled at a rate of 25 °C/min until the stack reached 20 °C. After reaching 80 °C the mechanical pressure was reduced to zero.

Claims

1. Electrically conductive composition comprising
 - 5 (A) 2 to 35 vol.-% of silver particles having an average particle size in the range of 1 to 25 μm and exhibiting an aspect ratio in the range of 5 to 30 : 1,
 - (B) 10 to 63 vol.-% of non-metallic particles having an average particle size in the range of 1 to 25 μm , exhibiting an aspect ratio in the range of 1 to 3 : 1,
 - (C) 30 to 80 vol.-% of a thermoplastic polymer system
 - 10 (D) 0 to 25 vol.-% of at least one additive,wherein the sum of the vol.-% of particles (A) and (B) totals 25 to 65 vol.-%.

2. Electrically conductive composition of claim 1,
wherein the sum of the vol.-% of (A), (B), (C) and, if present, (D) totals 100 vol.-%
15 of the electrically conductive composition.

3. Electrically conductive composition of claim 1 or 2,
wherein the silver particles (A) are particles of pure silver and/or of silver alloy.

- 20 4. Electrically conductive composition of any one of the preceding claims,
wherein the non-metallic particles (B) are selected from the group consisting of graphite particles, glass particles, ceramics particles, plastics particles, diamond particles, boron nitride particles, silicon dioxide particles, silicon nitride particles, silicon carbide particles, aluminosilicate particles, aluminum oxide particles,
25 aluminum nitride particles, zirconium oxide particles titanium dioxide particles., calcium carbonate particles, barium sulfate particles, talc particles and polymer microspheres.

5. Electrically conductive composition of any one of the preceding claims,
wherein the silver particles (A) have an average particle size in the range of 0.2 to
5 2 times the average particle size of the non-metallic particles (B).
6. Electrically conductive composition of any one of the preceding claims,
wherein thermoplastic polymer system (C) comprises those constituents of the
electrically conductive composition which after the application embed the particles
10 (A) and (B).
7. Electrically conductive composition of any one of the preceding claims,
wherein the electrically conductive composition is applied to the contact surface of
the at least one contact of the solar cell and/or to the contact surface of the
15 electrical conductor to be adhesively bonded to the at least one contact of the
solar cell.
8. Electrically conductive composition of any one of the preceding claims,
wherein the application of the electrically conductive composition is performed by
20 printing, jetting, dispensing or extruding.
9. Electrically conductive composition of any one of the preceding claims,
wherein after the application of the electrically conductive composition the one or
more solar cell contacts and the electrical conductor(s) to be adhesively bonded
25 thereto are put together with their contact surfaces having the electrically
conductive composition in between to form an assembly.

10. Use of an electrically conductive composition of any one of the preceding claims as an electrically conductive adhesive for mechanically and electrically connecting at least one contact of a solar cell with an electrical conductor, wherein said at least one contact is selected from the group consisting of emitter contacts and collector contacts.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/062826

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01B1/22
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

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. |
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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| Date of the actual completion of the international search 19 July 2017 | Date of mailing of the international search report 27/07/2017 |
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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