(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
28 January 2010 (28.01.2010)

PCT

(10) International Publication Number
WO 2010/011719 A1

(51) International Patent Classification:
C08K 3/08 (2006.01) *C08L 71/00* (2006.01)
H01L 31/0224 (2006.01)

(21) International Application Number: PCT/US2009/051357

(22) International Filing Date: 22 July 2009 (22.07.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/082,524 22 July 2008 (22.07.2008) US

(71) Applicant *(for all designated States except US)*: **E. I. du Pont de Nemours and Company** [US/US]; 1007 Market Street, Wilmington, Delaware 19898 (US).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **DORFMAN, Jay, Robert** [US/US]; 507 Stinhurst Drive, Durham, North Carolina 27713 (US).

(74) Agent: **SIEGELL, Barbara, C.**; E. I. du Pont de Nemours and Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, Delaware 19805 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) **Title**: POLYMER THICK FILM SILVER ELECTRODE COMPOSITION FOR USE IN THIN-FILM PHOTOVOLTAIC CELLS

(57) **Abstract**: The invention is directed to a polymer thick film silver composition comprising: (a) conductive silver flake (b) organic medium comprising (1) phenoxy organic polymeric binder and (2) organic solvent. The composition may be processed at a time and energy sufficient to remove all solvent. The invention is further directed to method(s) of grid formation on top of Thin-Film photovoltaic cells.

WO 2010/011719 A1

TITLE OF INVENTION

POLYMER THICK FILM SILVER ELECTRODE COMPOSITION FOR USE IN THIN-FILM PHOTOVOLTAIC CELLS

FIELD OF THE INVENTION

The invention is directed to a polymer thick film (PTF) silver conductor composition for use in Thin-Film photovoltaic cells. In one embodiment, the PTF silver composition is used as a screen-printed grid on top of a Transparent Conductive Oxide (TCO) such as Indium Tin Oxide.

SUMMARY OF THE INVENTION

The invention is directed to a polymer thick film composition comprising: (a) silver flake (b) organic medium comprising (1) organic polymeric binder; (2) solvent; and (3) printing aids. The composition may be processed at a time and temperature necessary to remove all solvent. The silver flakes may be 76.0-92.0 weight percent of the total composition, the phenoxy resin may be 2.0 to 6.5 weight percent of the total composition, and the organic medium may be 8.0-24.0 weight percent of the total composition.

The invention is further directed to method(s) of electrode grid formation on Thin-Film Photovoltaic Cells using such compositions and to articles formed from such methods and/or compositions.

DETAILED DESCRIPTION OF INVENTION

The invention describes a polymer thick film silver composition for use in Thin-Film Photovoltaic (PV) cells. It is typically used so as to improve the electrical efficiency of the cell. A grid-like pattern of Ag is printed on top of the Transparent Conductive Oxide (TCO). Thin-film PV cells are usually characterized by a light-absorbing semiconductor such as amorphous silicon, Copper Indium Gallium Diselenide (CIGS), or Cadmium Telluride. This distinguishes them from the traditional crystalline silicon-based PV cells. Thin-film refers to the thickness of the semiconductor which is typically 2 microns or so for the Thin-Film cells as opposed to 30-50 microns for crystalline silicon. Another difference between Thin-Film and c-Silicon PV cells is the temperature limitations involved. Thin-Film cells must be processed at less than 200 °C as the semiconductor and/or the substrate used in Thin-Film cannot withstand high temperatures. The traditional c-Silicon PV cells may be processed at temperatures up to 800 °C. Thus, the use of a PTF Ag composition as the top electrode grid is required as PTF compositions themselves are only stable up to approximately 200 °C.

Generally, a thick film composition comprises a functional phase that imparts appropriate electrically functional properties to the composition. The functional phase comprises electrically functional powders dispersed in an organic medium that acts as a carrier for the functional phase. Generally, the composition is fired to burn out the organics and to impart the electrically functional properties. However, in the case of polymer thick film, the organics remain as an integral part of the composition after drying. Prior to firing, a processing requirement may include an optional heat treatment such as drying, curing, reflow, and others known to those skilled in the art of thick film technology. “Organics” comprise polymer or resin components of a thick film composition.

The main components of the thick film conductor composition are a conductive powder dispersed in an organic medium, which includes polymer resin and solvent. The components are discussed herein below.

A. Conductive Powder

In an embodiment, the conductive powders in the present thick film composition are Ag conductor powders and may comprise Ag metal powder, alloys of Ag metal powder, or mixtures thereof. Various particle diameters and shapes of the metal powder are contemplated. In an embodiment, the conductive powder may include any shape silver powder, including spherical particles, flakes (rods, cones, plates), and mixtures thereof. In an embodiment, the conductive powder may include silver flakes.

In an embodiment, the particle size distribution of the conductive powders may be 1 to 100 microns; in a further embodiment, 2-10 microns.

In an embodiment, the surface area/weight ratio of the silver particles may be in the range of 0.1-2.0 m^2/g. In a further embodiment, the surface area/weight ratio of the silver particles may be in the range of 0.3-1.0 m^2/g. In a further embodiment, the surface area/weight ratio of the silver particles may be in the range of 0.4-0.7 m^2/g.

Furthermore, it is known that small amounts of other metals may be added to silver conductor compositions to improve the properties of the conductor. Some examples of such metals include: gold, silver, copper, nickel, aluminum, platinum, palladium, molybdenum, tungsten, tantalum, tin, indium, lanthanum, gadolinium, boron, ruthenium, cobalt, titanium, yttrium, europium, gallium, sulfur, zinc, silicon, magnesium, barium, cerium, strontium, lead, antimony, conductive carbon, and combinations thereof and others common in the art of thick film compositions. The additional metal(s) may comprise up to about 1.0 percent by weight of the total composition.

In an embodiment, the silver flakes may be present at 76 to 92 wt %, 77 to 88 wt %, or 78 to 83 wt % of the total weight of the composition.

B. Organic Medium

The powders are typically mixed with an organic medium (vehicle) by mechanical mixing to form a paste like composition, called "pastes", having suitable consistency and rheology for printing. A wide variety of inert liquids can be used as organic medium. The organic medium must be one in which the solids are dispersible with an adequate degree of stability. The rheological properties of the medium must be such that they lend good application properties to the composition. Such properties include: dispersion of solids with an adequate degree of stability, good application of composition, appropriate viscosity, thixotropy, appropriate wettability of the substrate and the solids, a good drying rate, and a dried film strength sufficient to withstand rough handling.

The polymer resin may include a phenoxy resin which allows high weight loading of silver flake and thus helps achieve both good adhesion to Indium Tin Oxide substrates and low contact resistivity, two critical properties for silver electrodes in Thin-Film Photovoltaic Cells. In an embodiment, the phenoxy resin may be 2.0 to 6.5 wt %, 2.2 to 5.9 wt %, or 2.5 to 5.7 wt % of the total weight of the composition. In an embodiment, the phenoxy resin may be 1.5 to 6 weight percent of the total composition.

Solvents suitable for use in the polymer thick film composition are recognized by one of skill in the art and include acetate and terpenes such as alpha- or beta-terpineol or mixtures thereof with other solvents such as kerosene, dibutylphthalate, butyl carbitol, butyl carbitol acetate, hexylene glycol and high boiling alcohols and alcohol esters. In an embodiment, the solvent may include one or more components selected from the group consisting of: Diethylene Glycol Ethyl Ether Acetate (carbitol acetate), DiBasic Ester, and C-11 Ketone. In addition, volatile liquids for promoting rapid hardening after application on the substrate may be included in the vehicle. In many embodiments of the present invention, solvents such as glycol ethers, ketones, esters and other solvents of like boiling points (in the range of 180°C to 250°C), and mixtures thereof may be used. The preferred mediums are based on glycol ethers and β-terpineol. Various combinations of these and other solvents are formulated to obtain the viscosity and volatility requirements desired.

Although screen-printing is expected to be a common method for the deposition of polymer thick film silver, any other conventional methods including stencil printing, syringe dispensing or other deposition or coating techniques may be utilized.

In an embodiment, the organic medium may be present at 8.0 to 24.0 wt %, 10.0 to 22.0 wt %, or 12.0 to 21.0 wt % of the total weight of the composition.

In an embodiment, the ratio of Ag to phenoxy resin may be between 13:1 and 35:1. In a further embodiment, the ratio of Ag to phenoxy resin may be between 15:1 and 30:1.

Application of Thick Films

The polymer thick film silver composition also known as a "paste" is typically deposited on a substrate, such as sputtered polyester, that is impermeable to gases and moisture. The substrate can also be a sheet of flexible material, such as an impermeable plastic such as polyester, for example polyethylene terephthalate, or a composite material made up of a combination of plastic sheet with optional metallic or dielectric layers deposited thereupon. In one embodiment, the substrate can be a build-up of layers with metalized (stainless steel) polyester followed by the semiconductor layer (CIGS, for example), followed by a thin CdS layer, followed by sputtered Indium Tin Oxide. In another embodiment, Zinc Oxide may be used in place of Indium Tin Oxide as the Transparent Conductive Oxide (TCO) of the Thin-Film Solar Cell.

The deposition of the polymer thick film silver composition is performed preferably by screen printing, although other deposition techniques such as stencil printing, syringe dispensing or coating techniques can be utilized. In the case of screen-printing, the screen mesh size controls the thickness of deposited thick film.

The deposited thick film is dried by exposure to heat for typically 10-15 min at 140 °C, thus forming a thin-film solar cell.

The present invention will be discussed in further detail by giving practical examples. The scope of the present invention, however, is not limited in any way by these practical examples.

EXAMPLE 1

The PTF silver electrode paste was prepared by mixing silver flake with an average particle size of 7 μm (range was 2-15 microns) with an organic medium composed of polyhydroxyether resin (also known as Phenoxy resin) available from Phenoxy Associates, Inc. The molecular weight of the resin was approximately 20,000. A solvent was used to dissolve the phenoxy resin completely prior to adding the silver flake. That solvent was Carbitol Acetate (Eastman Chemical).

The composition silver conductor C is given below:

81.55 wt % Flaked Silver
15.53 wt % Organic Medium (23.0 wt % phenoxy resin/77.0 wt % solvent)
2.92 wt % Carbitol Acetate Solvent

This composition was mixed for 30 minutes on a planetary mixer. The composition was then transferred to a three-roll mill where it was subjected to two passes at 100 and 200 psi. At this point, the composition was used to screen print a silver grid pattern on top of Indium Tin Oxide (80 ohm/sq resistivity) sputtered polyester. Using a 280 mesh stainless steel screen, a series of lines were printed, and the silver paste was dried at 150C for 15 min. in a forced air box oven. The contact resistivity was then measured as 2 x 10 -3 ohm cm2. As a comparison, a standard composition such as silver conductor A could not be measured as it has poor adhesion to ITO. Another standard product such as silver conductor B showed 3 x 10 -1 ohm cm2. This unexpected large improvement in contact resistivity for silver conductor C, a key property for Thin-Film PV silver compositions, enables it to be used for most applications and improves PV cell efficiency. A summary table appears below:

Table 1

Silver Composition	Adhesion to ITO	Contact Resistivity
Silver conductor A	1	3 x 10 -1 ohm cm2
Silver conductor B	1	Cannot be Measured
Silver Conductor C	5	2 x 10 -3 ohm cm2

Comparative Example 2

PTF silver electrode paste D was prepared by mixing silver flake with an average particle size of 7 um with an organic medium composed of polyhydroxyether (Phenoxy resin) as per example 1. The solvent used was the same as in Example 1 (Carbitol Acetate). The composition of D is given below:

70.0 wt % Flaked Silver
29.0 wt % Organic Medium (19.0 wt% phenoxy resin/81 wt % solvent)
1.0 wt % Carbitol Acetate Solvent

The composition was mixed and roll-milled as per Example 1. The paste was screen-printed and dried exactly the same as indicated in Example 1. The contact resistivity measured was 8 x 10 -1 ohm cm2 almost two orders of magnitude worse than silver conductor C. Adhesion to ITO was measured as clearly inferior to silver conductor C.

Additional compositions made and tested as described herein are shown in Table 2.

Table 2

wt % Ag	wt % Resin	Ag/Resin	Contact R (mohm cm2)	Adhesion (To ITO)
70.0	5.51	12.70	8 x 10 -1	1
73.0	6.75	10.81	2 x 10 -1	3
77.5	5.12	15.14	2 x 10 -3	5
81.5	3.57	22.83	1 x 10 -3	5
87.0	2.99	29.10	1 x 10 -3	5

In the examples herein, adhesion to ITO was measured using an ASTM Tape method. A 600 grade Tape was applied to a printed/dried pattern of silver ink. The tape was removed in a continuous fashion and the amount of silver ink material removed was estimated based upon an arbitrary scale of 1 to 5 with 5 representing no material removal (i.e. excellent adhesion).

In the examples herein, contact resistivity was measured by printing a series of silver lines on a Transparent Conductive Oxide

(Indium Tin Oxide) of varying spacing. The silver ink was dried under standard conditions. The Transmission Line Method was used to calculate the Contact R by plotting the Resistance of the lines vs. the spacing. The y-intercept then represents 2 x the Contact R.

CLAIMS

What is claimed is:

1. A composition comprising:

(a) a conductive composition comprising silver flakes, wherein the silver flakes are 76.0-92.0 weight percent of the total composition; dispersed in

(b) organic medium comprising (i) phenoxy resin, wherein the phenoxy resin is 2.0 to 6.5 weight percent of the total composition, dissolved in (ii) an organic solvent.

2. The composition of claim 1, wherein the organic medium is 8.0-24.0 weight percent of the total composition.

3. The composition of claim 1, wherein the phenoxy resin is 2.2-5.9 weight percent of the total composition.

4. The composition of claim 1, wherein the organic solvent comprises one or more components selected from the group consisting of: Diethylene Glycol Ethyl Ether Acetate (carbitol acetate), DiBasic Ester, and C-11 Ketone.

5. A composition comprising:

(a) a conductive composition comprising silver flakes,

(b) organic medium comprising (i) phenoxy resin, an (ii) an organic solvent,

wherein the ratio of silver to phenoxy resin is between 13:1 and 35:1.

6. A method of forming a silver grid on a thin-film photovoltaic cell, comprising the steps of:

(a) applying the composition of claim 1 to a substrate, wherein the substrate is sputtered polyester;

(b) drying the composition on the substrate.

7. The method of claim 6, wherein the polyester is sputtered with indium tin oxide.

8. A thin-film photovoltaic cell comprising a silver grid line comprising the composition of claim 1.

9. A thin-film photovoltaic cell formed by the method of claim 6.

10. The method of Claim 6, wherein the polyester is sputtered with zinc oxide.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/051357

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K3/08 H01L31/0224
ADD. C08L71/00

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)
C08K H01L C09D C09J

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 practical, 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.
A	US 5 051 208 A (BOWNS RICHARD E [US] ET AL) 24 September 1991 (1991-09-24) claims 1,3,8; example 2	1,5
A	EP 1 541 654 A (NAMICS CORP [JP]; SUGANUMA KATSUAKI [JP]) 15 June 2005 (2005-06-15) page 6, line 15; examples 7,8; table 2	1,5
A	US 5 006 575 A (CHAN MAN-SHEUNG [US]) 9 April 1991 (1991-04-09) column 5, line 48 - line 59; claims 1,6-10,12; examples 1,2	1,5,6
A	US 5 049 313 A (FRENTZEL RICHARD L [US]) 17 September 1991 (1991-09-17) column 4, line 36 - line 68; tables 1-3	1,5,6
X	claims 1-6,17,18	5

-/--

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

[X] 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

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 November 2009	02/12/2009

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	Engel, Hermann

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/051357

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 454 005 A (DU PONT [US]) 30 October 1991 (1991-10-30) page 3, line 5 - line 6 page 3, line 18 - line 52; claims 1,6 -----	1,5

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2009/051357

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
US 5051208	A	24-09-1991	NONE			
EP 1541654	A	15-06-2005	AU	2002330479	A1	29-03-2004
			CN	1665899	A	07-09-2005
			WO	2004022663	A1	18-03-2004
			US	2005230667	A1	20-10-2005
US 5006575	A	09-04-1991	NONE			
US 5049313	A	17-09-1991	NONE			
EP 0454005	A	30-10-1991	CA	2041295	A1	27-10-1991
			DE	69105597	D1	19-01-1995
			DE	69105597	T2	11-05-1995
			JP	2589892	B2	12-03-1997
			JP	4227782	A	17-08-1992