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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
13 September 2012 (13.09.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/122403 A1

(51) International Patent Classification:
B22F 1/00 (2006.01) *B22F 9/24* (2006.01)

(21) International Application Number:
PCT/US2012/028341

(22) International Filing Date:
8 March 2012 (08.03.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/450,259 8 March 2011 (08.03.2011) 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) Inventors; and
(75) Inventors/Applicants *(for US only)*: **IRIZARRY, Roberto** [US/US]; 5801 Valley Mist Court, Raleigh, North Carolina 27613 (US). **YANG, Haixin** [CA/US]; 402 New Parkside Drive, Chapel Hill, North Carolina 27516 (US).

(74) Agent: **HAAS, Charles, W.**; 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, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, 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, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, 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, RS, 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**: PROCESS FOR MAKING SILVER POWDER PARTICLES WITH SMALL SIZE CRYSTALLITES

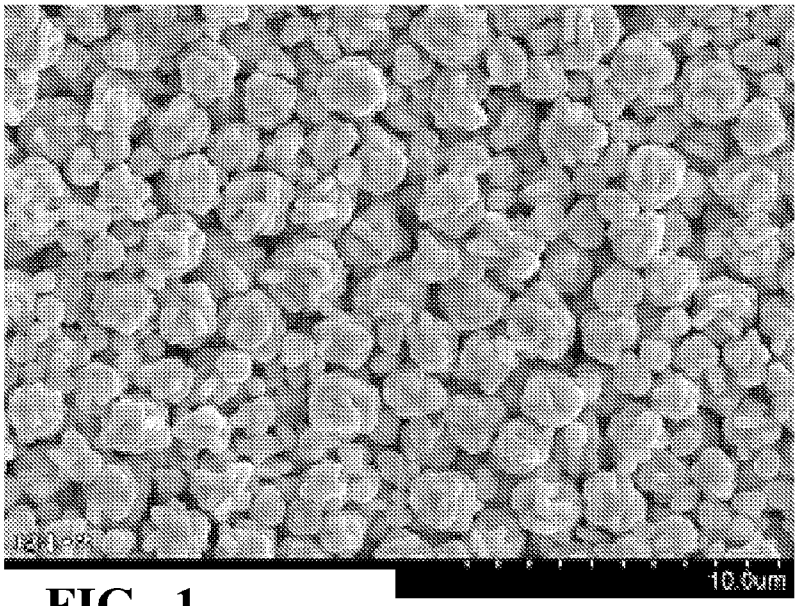


FIG. 1

(57) **Abstract**: The process for making silver powder particles with small size crystallites uses a combination of gum arabic and maleic acid with the reduction of a silver salt with ascorbic acid. Silver thick film paste containing these silver powder particles can be used in electronic applications to form electrodes for semiconductor devices and, in particular, solar cells..

WO 2012/122403 A1

TITLE

PROCESS FOR MAKING SILVER POWDER PARTICLES WITH SMALL SIZE CRYSTALLITES

FIELD OF THE INVENTION

The invention is directed to a process for making silver powder particles with small size crystallites. These silver powder particles are particularly useful in electronic applications.

BACKGROUND OF THE INVENTION

Silver powder is used in the electronics industry for the manufacture of conductor thick film pastes. The thick film pastes are screen printed onto substrates forming conductive circuit patterns. These circuits are then dried and fired to volatilize the liquid organic vehicle and sinter the silver particles.

Many processs currently used to manufacture metal powders can be applied to the production of silver powders. For example, thermal decomposition processes, electrochemical processes, physical processes such as atomization or milling and chemical reduction processs can be used. Thermal decomposition processes tend to produce powders that are spongy, agglomerated, and very porous whereas electrochemical processes produce powders that are crystalline in shape and very large. Physical processes are generally used to make flaked materials or very large spherical particles. Chemical precipitation processes produce silver powders with a range of sizes and shapes.

Silver powders used in electronic applications are generally manufactured using chemical precipitation processes. Silver powder is produced by chemical reduction in which an aqueous solution of a soluble salt of silver is reacted with an appropriate reducing agent under conditions such that silver powder can be precipitated. Inorganic reducing agents including hydrazine, sulfite salts and formate salts can produce powders which are very coarse in size, are irregularly shaped and have a large particle size distribution due to aggregation. Organic reducing agents such as alcohols, sugars or aldehydes are used with alkali hydroxides to reduce silver nitrate. The reduction reaction is very fast; hard to control and produces a powder contaminated with residual alkali ions. Although small in size (<1 μm), these powders tend to have an

irregular shape with a wide distribution of particle sizes that do not pack well. It is difficult to control the sintering of these types of silver powders and they do not provide adequate line resolution in thick film conductor circuits.

Therefore, there is a need for a process to produce silver powder spherical particles comprising small size crystallites and having a d_{50} paricle size in the range of 0.5 to 3.5 μm to provide silver thick film paste with improved sintering properties.

SUMMARY OF THE INVENTION

This invention provides a process for making silver powder particles, the process comprising:

(a) preparing an acidic aqueous silver salt solution comprising a water soluble silver salt dissolved in deionized water;

(b) preparing an acidic aqueous reducing and particle modifier solution comprising:

(i) a reducing agent selected from the group consisting of ascorbic acid, ascorbates and mixtures;

(ii) nitric acid;

(iii) gum arabic;

(iv) maleic acid; and

(v) deionized water;

(c) maintaining the acidic aqueous silver salt solution and the acidic reducing and particle modifier solution at the same temperature, wherein the temperature is in the range of 10°C to 65°C, while stirring each the solution during and after preparation;

(d) adding the acidic aqueous silver salt solution to the acidic aqueous reducing and particle modifier solution while stirring to make a reaction mixture and and maintaining the temperature of the reaction mixture at the temperature of (c), wherein the silver powder particles precipitate and are contained within the resulting final aqueous solution; and

(e) increasing the temperature of the final aqueous solution to a temperature in the range of 65°C to 80°C while continuing stirring;

the silver powder particles comprising crystallites of between 30 and 47 nm in size as determined by X-ray diffraction and the Scherrer formula; and the silver powder particles having d_{50} in the range of 0.5 to 3.5 μm.

Also provided is the above process further comprising:

(f) separating the silver powder particles from the final aqueous solution;

(g) washing the silver powder particles with deionized water; and

(h) drying the silver powder particles.

Also provided are the silver powder particles made by the above process, silver thick film paste made with the silver powder particles and a semiconductor device, e.g., a solar cell, comprising an electrode that prior to firing comprises the silver thick film paste.

BRIEF DESCRIPTION OF THE FIGURES

Figure1 is a scanning electron microscope image at a magnification of 5,000 of the silver powder particles made in Example 1. The d_{50} particle size is 2.8 μm.

Figure 2 is a scanning electron microscope image at a magnification of 10,000 of the silver powder particles made in Example 2. The d_{50} particle size is 2.2 μm.

Figure 3 is a scanning electron microscope image at a magnification of 10,000 of the silver powder particles made in Example 3. The d_{50} particle size is 1.6 μm.

Figure 4 is a scanning electron microscope image at a magnification of 10,000 of the silver powder particles made in Comparative Experiment 1. The d_{50} particle size is 10.1 μm.

Figure 5 is a scanning electron microscope image at a magnification of 10,000 of the silver powder particles made in Comparative Experiment 2. The d_{50} particle size is 8.7 μm.

DETAILED DESCRIPTION OF THE INVENTION

This invention provides a process for making spherically-shaped silver powder particles with small size crystallites. A combination of gum arabic and maleic acid is used with the reduction of a silver salt with ascorbic acid to control the crystallite size. The process is a reductive process in which silver particles comprising crystallites between 30 and 47 nm in size as determined by X-ray diffraction and the Scherrer formula are precipitated by adding together an acidic aqueous solution of a water soluble silver salt and an acidic aqueous reducing and particle modifier solution containing a reducing agent, nitric acid, gum arabic and maleic acid.

The acidic aqueous silver salt solution is prepared by adding a water soluble silver salt to deionized water. Any water soluble silver salt, e.g.,silver nitrate, silver phosphate, and silver sulfate, can be used. Silver nitrate is preferred. No complexing agents are used which could provide side reactions that affect the reduction and type of particles produced. Nitric acid can be added to increase the acidity.

The process can be run at concentrations up to 1.2 moles of silver per liter of final aqueous solution. It is preferred to run the process at concentrations of 0.47 to 0.8 moles of silver per liter of final aqueous solution. It is especially preferred to run the process at concentrations of 0.47 to 1.0 moles of silver per liter of final aqueous solution. These relatively high concentrations of silver make the manufacturing process cost effective.

The acidic aqueous reducing and particle modifier solution is prepared by adding the various components, i.e., a reducing agent, gum arabic, maleic acid and nitric acid, to deionized water. Suitable reducing agents for the process are ascorbic acids such L-ascorbic acid and D-ascorbic acid and related ascorbates such as sodium ascorbate. Ascorbic acid is preferred.

In one embodiment, the acidic aqueous reducing and particle modifier solution also contains a metal colloid selected from the group consisting of gold colloid and silver colloid. A suitable metal colloid is gold colloid or silver colloid. Gold colloid is preferred.

The components can be added to the deionized water in various orders. In one embodiment, gum arabic is the first component added to the deionized water. The gum arabic is added to the deionized water and then stirred for a period of time before adding the other components. In the Examples, 14 g of gum arabic was added to 375 g or 750 g of deionized water and the mixture was stirred for an hour before adding the other components. Times for stirring smaller or larger quantities could be adjusted accordingly. Nitric acid, maleic acid, ascorbic acid and gold colloid solution were then added in that order. Stirring for a time as indicated above should occur following addition of the gum arabic no matter the order of adding the components.

The order of preparing the acidic aqueous silver salt solution and the acidic reducing and particle modifier solution is not important. The acidic aqueous silver salt solution can be prepared before, after, or contemporaneously with the acidic reducing and particle modifier solution. The acidic aqueous silver salt solution is added to the acidic reducing and particle modifier solution. The addition is carried out slowly. For example, with the quantities used in the Examples, i.e.,125 and 250 g of deionized water for the acidic aqueous silver salt solution and 375 and 750 g of deionized water for the acidic aqueous reducing and particle modifier solution, the acidic aqueous silver salt solution was added to the acidic reducing and particle modifier solution over a period of one hour. Smaller quantities could be mixed over a shorter time interval and larger quantites over a longer time period. The reaction mixture is stirred during the addition.

In this process the acidic aqueous silver salt solution and the acidic reducing and particle modifier solution are both maintained at the same temperature, i.e., a temperature in the range of 10°C to 65°C and each solution is stirred until they are mixed. In some emdodiments the solutions are maintained at a temperature in the range of 10°C to 35°C. In one such embodiment the solutions are maintained at 25°C. When the two solutions are mixed to form the reaction mixture, the reaction mixture is maintained at that same temperature.

The mixture of the acidic aqueous silver salt solution and the acidic reducing and particle modifier solution results in the precipitation of the silver particles that are contained within the resulting final aqueous solution. Following precipitation, the temperature of the final aqueous solution is heated to a temperature in the range of 65°C to 80°C. In some embodiments the a temperature is in the range of 65°C to 75°C. In one such embodiment the temperature is 70°C. The final aqueous solution containing the silver particles is maintained at this temperature for about an hour and is stirred during that time.

The silver particles are then separated from the final aqueous solution by filtration or other suitable liquid-solid separation operation and the solids are washed with deionized water until the conductivity of the wash water is 100 microSiemans or less. The silver particles are then dried.

The silver powder particles made by the process of the invention have a particular set of physical characteristics. The silver particles are described herein as spherically-shaped. It can be seen from the scanning electron microscope (SEM) images of Figures 1-3 that the particles are generally spherical in shape but are not perfect spheres. The average particle size determined from the SEM images is in the range of 1 to 2.5 μm. The silver powder particles are comprised of crystallites between 30 and 47 nm in size as determined by X-ray diffraction and the Scherrer formula. In one group of embodiments the crystallites are between 30 and 39 nm in size. The silver powder particles have a d_{50} in the range of 0.5 to 3.5 μm and a size distribution such that $(d_{90}-d_{10})/d_{50} < 2.2$. The quantity $(d_{90}-d_{10})/d_{50}$ is a measure of the size distribution of the particles. Since $(d_{90}-d_{10})/d_{50} < 2.2$, it is an indication of the narrow size distribution of the particles, i.e., the uniformity of particle size and the correspondly highly dispersible nature of the silver powders comprising these particles. The silver particles have a solids content of in excess of 99% as determined by thermogravimetric analysis. Thermomechanical analysis (TMA) is used herein as an indicator of sinterabilty. A pellet was formed from the silver particles and subjected to a temperature regime. The observed per cent

shrinkage, i.e., the dimensional change of the pellet, is a measure of the sinterability of the particles. The results are presented herein as TMA equal to the percent dimensional change, a negative per cent change since it represents a shrinkage. The silver particles of the invention showed TMA dimensional changes, i.e., shrinkages, of at least -10%.

The silver powder particles made by the process of this invention can be used in thick film paste applications, including thick films for front side metallization of photovoltaic solar cells and thick films for other semiconductor devices.

This invention also provides the silver powder particles made by the process of this invention. These silver powder particles can be used in thick film paste. The structure of these silver particles will lend them to be more readily sintered and provide improved thick film conductors. Also provided is a semiconductor device, e.g., a solar cell, comprising an electrode that prior to firing comprises the silver thick film paste.

Silver Thick Film Paste

This invention also provides a silver thick film paste comprised of the silver powder particles made by the process of this invention and glass frit dispersed in an organic medium. As used herein, "thick film paste" refers to a composition which after being deposited on a substrate and fired has a thickness of 1 to 100 μm.

The glass frit compositions are described herein as including percentages of certain components. The percentages are the percentages of the components used in the starting material that was subsequently processed as described herein to form a glass composition. The composition contains certain components and the percentages of those components are expressed as a percentage of the corresponding oxide or fluoride form. The weight percentages of the glass frit components are based on the total weight of the glass composition. A certain portion of volatile species may be released during the process of making the glass. An example of a volatile species is oxygen.

Various glass frit compositions are useful in the silver thick film pastes of the invention. The glass frit used has a softening point of 300 to 600°C The glass frit compositions described herein are not limiting. Minor

substitutions of additional ingredients can be made without substantially changing the desired properties of the glass composition. For example, substitutions of glass formers such as 0-3 wt% P_2O_5, 0-3 wt% GeO_2 and 0-3 wt% V_2O_5 can be used either individually or in combination to achieve similar performance.

The glass frit compositions can also contain one or more fluorine-containing components such as salts of fluorine, fluorides and metal oxyfluoride compounds. Such fluorine-containing components include, but are not limited to BiF_3, AlF_3, NaF, LiF, KF, CsF, PbF_2, ZrF_4, TiF_4 and ZnF_2.

Exemplary lead free glass compositions contain one or more of SiO_2, B_2O_3, Al_2O_3, Bi_2O_3, BiF_3, ZnO, ZrO_2, CuO, Na_2O, NaF, Li_2O, LiF, K_2O, and KF. In various embodiments the compositions comprise the following oxide constituents in the compositional ranges, the SiO_2 is 17 to 26 wt%, 19 to 24 wt%, or 20 to 22 wt%; the B_2O_3 is 2 to 9 wt%, 3 to 7 wt %; or 3 to 4 wt%; the Al_2O_3 is 0.1 to 5 wt%, 0.2 to 2.5 wt%, or 0.2 to 0.3 wt%; the Bi_2O_3 is 0 to 65 wt%, 25 to 64 wt%, or 46 to 64 wt%; the BiF_3 is 0 to 67wt%, 0 to 43 wt%, or 0 to 19 wt%; the ZrO_2 is 0 to 5 wt%, 2 to 5 wt%, or 4 to 5 wt%; the TiO_2 is 1 to 7 wt%, 1 to 5 wt%, or 1 to 3 wt%; CuO is 0 to 3 wt% or 2 to 3 wt%; Na_2O is 0 to 2 wt% or 1 to 2 wt%; NaF is 0 to 3 wt% or 2 to 3 wt%; Li_2O is 0 to 2 wt% or 1 to 2 wt%; and LiF is 0 to 3 wt% or 2 to 3 wt%. Some or all of the Na_2O or Li_2O can be replaced with K_2O and some or all of the NaF or LiF can be replaced with KF to create a glass with properties similar to the compositions listed above.

In other embodiments, the glass frit compositions can include one or more of a third set of components: CeO_2, SnO_2, Ga_2O_3, In_2O_3, NiO, MoO_3, WO_3, Y_2O_3, La_2O_3, Nd_2O_3, FeO, HfO_2, Cr_2O_3, CdO, Nb_2O_5, Ag_2O, Sb_2O_3, and metal halides (e.g. NaCl, KBr, NaI).

Exemplary lead containing glass compositions comprise the following oxide constituents in the compositional range of 0-36 wt% SiO_2, 0-9 wt% Al_2O_3, 0-19 wt% B_2O_3, 16-84 wt% PbO, 0-4 wt% CuO, 0-24 wt% ZnO, 0-52 wt% Bi_2O_3, 0-8 wt% ZrO_2, 0-20 wt% TiO_2, 0-5 wt% P_2O_5, and 3-34 wt% PbF_2. In other embodiments relating to glasses containing bismuth oxide, the glass frit composition contains 4-26 wt% SiO_2, 0-1 wt% Al_2O_3, 0-8 wt% B_2O_3, 20-52 wt% PbO, 0-4 wt% ZnO, 6-52 wt% Bi_2O_3, 2-7

wt% TiO_2, 5-29 wt% PbF_2, 0-1 wt% Na_2O and 0-1 wt% Li_2O. In still other embodiments relating to glasses containing 15–25 wt% ZnO, the glass frit comprises 5-36 wt% SiO_2, 0-9 wt% Al_2O_3, 0-19 wt% B_2O_3, 17-64 wt% PbO, 0-39 wt% Bi_2O_3, 0-6 wt% TiO_2, 0-5 wt% P_2O_5 and 6-29 wt% PbF_2. In various of these embodiments containing ZnO, the glass frit compositions comprises 5-15 wt% SiO_2 and/or 20-29 wt% PbF_2 and/or 0-3 wt% ZrO_2 or 0.1–2.5 wt% ZrO_2. Embodiments containing copper oxide and/or alkali modifiers comprise 25-35 wt% SiO_2, 0-4 wt% Al_2O_3, 3-19 wt% B_2O_3, 17-52 wt% PbO, 0-12 wt% ZnO, 0-7 wt% Bi_2O_3, 0-5 wt% TiO_2, 7-22 wt% PbF_2, 0-3 wt% CuO, 0-4 wt% Na_2O and 0-1 wt% Li_2O.

An exemplary method for producing the glass frits described herein is by conventional glass making techniques. Ingredients are weighed then mixed in the desired proportions and heated in a furnace to form a melt in platinum alloy crucibles or other suitable metal or ceramic crucibles. As indicated above, oxides as well as fluoride or oxyfluoride salts can be used as raw materials. Alternatively, salts, such as nitrate, nitrites, carbonate, or hydrates, which decompose into oxide, fluorides, or oxyfluorides at temperature below the glass melting temperature can be used as raw materials. Heating is conducted to a peak temperature of typically 800-1400°C and for a time such that the melt becomes entirely liquid, homogeneous, and free of any residual decomposition products of the raw materials. The molten glass is then quenched between counter rotating stainless steel rollers to form a 10-15 mil thick platelet of glass. The resulting glass platelet was then milled to form a glass frit powder with its 50% volume distribution set between to a desired target (e.g. 0.8 – 1.5 μm). Alternative synthesis techniques such as water quenching, sol-gel, spray pyrolysis, or others appropriate for making powder forms of glass can be employed.

The organic medium used in the silver thick film paste is a solution of a polymer in a solvent. The organic medium can also contain thickeners, stabilizers, surfactants and/or other common additives. In one embodiment, the polymer is ethyl cellulose. Other exemplary polymers include ethylhydroxyethyl cellulose, wood rosin, mixtures of ethyl cellulose and phenolic resins, polymethacrylates of lower alcohols, and monobutyl

ether of ethylene glycol monoacetate, or mixtures thereof. The solvents useful in the organic medium of the silver thick film paste compositions include ester alcohols 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. The organic medium can also contain volatile liquids for promoting rapid hardening after application on the substrate.

The thick film silver composition is adjusted to a predetermined, screen-printable viscosity with the organic medium.

The inorganic components, i.e., the silver powder particles and the glass frit are typically mixed with the organic medium by mechanical mixing to form a viscous paste composition.

The ratio of organic medium in the silver thick film paste composition to the inorganic components in the dispersion is dependent on the method of applying the paste and the kind of organic medium used, and it can vary. The dispersion will typically contain 70 to 95 wt% of inorganic components and 5 to 30 wt% of organic medium in order to obtain good wetting. The weight percents (wt%) used herein are based on the total weight of the silver thick film paste composition. Typically, the polymer present in the organic medium is in the range range of 8 wt% to 11 wt% of the weight of the total composition.

In one embodiment, the silver thick film paste contains 65 to 90 wt% silver powder, 0.1 to 8 wt% glass frit and 5 to 30 wt% organic medium. In another embodiment the silver thick film paste contains 70 to 85 wt% silver powder, 1 to 6 wt% glass frit and 10 to 25 wt% organic medium. In still another embodiment the silver thick film paste contains 78 to 83 wt% silver powder, 2 to 5 wt% glass frit and 13 to 20 wt% organic medium.

Semiconductor Device; Solar Cell

The invention also provides a method of making a semiconductor device, e.g., a solar cell or a photodiode. The semiconductor device has an electrode, e.g., a front side electrode of a solar cell or a photodiode, wherein prior to firing the electrode is comprised of a silver thick film paste of the invention.

The method of manufacturing a semiconductor device, comprises the steps of:

(a) providing a semiconductor substrate, one or more insulating films, and the silver thick film paste of the invention ;

(b) applying the insulating film to the semiconductor substrate,

(c) applying the silver thick film paste to the insulating film on the semiconductor substrate, and

(d) firing the semiconductor substrate, the insulating film and the silver thick film paste composition.

Exemplary semiconductor substrates useful in the methods and devices described herein include, but are not limited to, single-crystal silicon, multicrystalline silicon, and ribbon silicon. The semiconductor substrate may be doped with phosphorus and boron to form a p/n junction.

The semiconductor substrates can vary in size (length x width) and thickness. As an example, the thickness of the semiconductor substrate is 50 to 500 μm; 100 to 300 μm; or 140 to 200 μm. The length and width of the semiconductor substrate are each 100 to 250 mm; 125 to 200 mm; or 125 to 156 mm.

Typically an anti-reflection coating is formed on the front side of a solar cell. Exemplary anti-refection coating materials useful in the methods and devices described herein include, but are not limited to: silicon nitride, silicon oxide, titanium oxide, SiN_x:H, hydrogenated amorphous silicon nitride, and silicon oxide/titanium oxide film. The coating can be formed by plasma enhanced chemical vapor deposition (PECVD), CVD, and/or other known techniques known. In an embodiment in which the coating is silicon nitride, the silicon nitride film can be formed by PECVD, thermal CVD, or physical vapor deposition (PVD). In an embodiment in which the insulating film is silicon oxide, the silicon oxide film can be formed by thermal oxidation, thermal CVD, plasma CVD, or PVD.

The silver thick film paste of the invention can be applied to the anti-reflective coated semiconductor substrate by a variety of methods such as screen-printing, ink-jet printing, coextrusion, syringe dispensing, direct writing, and aerosol ink jet printing. The paste can be applied in a

pattern and in a predetermined shape and at a predetermined position. In one embodiment, the paste is used to form both the conductive fingers and busbars of the front-side electrode. In such an embodiment, the width of the lines of the conductive fingers are 20 to 200 μm, 40 to 150 μm, or 60 to 100 μm and the thickness of the lines of the conductive fingers are 5 to 50 μm, 10 to 35 μm, or 15 to 30 μm.

The paste coated on the ARC-coated semiconductor substrate can be dried, for example, for 0.5 to 10 minutes during which time the volatile solvents and organics of the organic medium are removed.

The dried paste is fired by heating to a maximum temperature of between 500 and 940°C for a duration of 1 second to 2 minutes. In one embodiment, the maximum silicon wafer temperature reached during firing ranges from 650 to 80°C for a duration of 1 to 10 seconds. In a further embodiment, the electrode formed from the silver thick film paste is fired in an atmosphere composed of a mixed gas of oxygen and nitrogen. In another embodiment, the electrode formed from the conductive thick film paste is fired above the organic medium removal temperature in an inert atmosphere not containing oxygen. This firing process removes any remaining organic medium and sinters the glass frit with the silver powder and any metal oxide present to form an electrode. Typically, the burnout and firing is carried out in a belt furnace. The temperature range in the burnout zone, during which time the remaining organic medium is removed, is between 500 and 700°C. The temperature in the firing zone is between 860 and 940°C

During firing, the fired electrode, preferably the fingers, reacts with and penetrates the anti-reflective oating, thereby making electrical contact with the silicon substrate.

In a further embodiment, prior to firing, other conductive and device enhancing materials are applied to the back side of the semiconductor device and cofired or sequentially fired with the paste compositions of the invention. The materials serve as electrical contacts, passivating layers, and solderable tabbing areas.

In one embodiment, the back side conductive material contains aluminum or aluminum and silver.

In a still further embodiment the materials applied to the opposite type region of the device are adjacent to the materials described herein due to the p and n region being formed side by side. Such devices place all metal contact materials on the non illuminated back side of the device to maximize incident lignt on the illuminated front side.

Measurements

The particle size distribution numbers (d_{10}, d_{50}, d_{90}) used herein are based on a volume (mass) distribution. The particle sizes were measured using a Microtrac® Particle Size Analyzer from Leeds and Northrup. The d_{10}, d_{50} and d_{90} are the equivalent diameters that represent the 10th percentile, the median or 50th percentile and the 90th percentile of the particle sizes, respectively, as measured by volume. That is, the d_{50} (d_{10}, d_{90}) is a value on the distribution such that 50 volume% (10 volume%, 90 volum%) of the particles have an equivalent diameter of this value or less.

The solids content of the silver particles was determined by thermogravimetric analysis, i.e., by a weight loss method after heating at 850°C for 10 minutes.

The size of the crystallites making up the silver powder particles was determined by X-ray diffraction and the Scherrer formula. The X-ray diffractometer used was a Rigaku Rint RAD-rb. The Cu target provided awavelength of 0.15405 nm. The Bragg plane was the (111). In the Scherrer formula:

$$L(111) = 0.94\,\lambda/(\beta\cos\theta),$$

L is the crystallite size, λ is the wavelength, β is the line broadening at half the peak maximum intensity (full width – half maximum) in radians and θ is the Bragg angle.

The TMA was carried out as follows. A pellet was formed by pouring 0.9-1.1 g of silver powder into a die and onto a cylindrical metal insert serving as the bottom. A second cylindrical metal is inserted into the die on top of the silver powder so that the powder is sandwiched between the the cylindrical metal inserts. The top insert is then firmly tapped 6 times with a mallet. The pellet is placed in a Bargal TMA:Q400

analyzer which measured the dimensional change as a function of temperature. The temperature was raised from room temperature at a rate of 10°C/min to 650°C and the pellet is maintained at that temperature for 10 minutes. The final per cent dimensional change is reported as the TMA for that powder pellet. A negative value indicates shrinkage and a positive value expansion of the pellet.

EXAMPLES

The following Examples and discussion are offered to further illustrate, but not limit the process of this invention.

Example 1

The acidic aqueous silver salt solution was prepared by dissolving 80 g of silver nitrate in 250 g of deionized water. This solution was kept at 25°C while continuously stirring.

The acidic reducing and particle modifier solution was prepared by adding 14 g of gum arabic to 750 g of deionized water in a separate container from the silver nitrate solution. This solution was kept at 25°C while continuously stirring for an hour. 20 g of nitric acid (70% w/w), 5 g maleic acid, 45 g ascorbic acid and 1 g of gold colloid solution was then added to the solution still maintained at 25°C and stirred.

The acidic aqueous silver salt solution was slowly added to the acidic reducing and particle modifier solution over a period of one hour to form a reaction mixture that was intensely stirred during the addition. The reaction mixture was maintained at 25°C. Silver particles precipitated and were contained within the final aqueous solution. The final aqueous solution was then heated to 70 °C for one hour and stirring continued during the heating.

As shown in the scanning electron microscope image of Figure 1, the silver powder was comprised of spherically-shaped silver particles. The size L of the crystallites in the particles was 37.4 nm. d_{10}, d_{50}, and d_{90} were 1.8 μm, 2.8 μm and 4.8 μm, respectively. The silver particles were 99.2% solids. The TMA = -12%

Example 2

Example 2 was carried out using the process described in Example 1 except that 125 g of deionized water was used in preparing the acidic

aqueous silver salt solution and 375 g of deionized water was used in preparing the acidic reducing and particle modifier solution

As shown in the scanning electron microscope image of Figure 2, the silver powder was comprised of spherically-shaped silver particles. The size L of the crystallites in the particles was 38.2 nm. d_{10}, d_{50}, and d_{90} were 1.2 μm, 2.2 μm and 3.9 μm, respectively. The silver particles were 99.8% solids. The TMA = -16%

Example 3

Example 3 was carried out using the process described in Example 2 except that 3 g of nitric acid (70% w/w), 1 g maleic acid and 5 g of gold colloid solution was used in preparing the acidic reducing and particle modifier solution.

As shown in the scanning electron microscope image of Figure 3, the silver powder was comprised of spherically-shaped silver particles. The size L of the crystallites in the particles was 35.2 nm. d_{10}, d_{50}, and d_{90} were 0.8 μm, 1.6 μm and 3.4 μm, respectively. The silver particles were 99.7% solids. The TMA = -14

Comparative Experiment 1

Comparative Experiment 1 was carried out using the process described in Example 1 except that no gum arabic was added in preparing an acidic reducing and particle modifier solution.

As shown in the scanning electron microscope image of Figure 4, the silver powder was comprised of irregular-shaped large silver particles that appear to be highly crystalline. The size L of the crystallites in the particles was 72.0 nm. d_{10}, d_{50}, and d_{90} were 4.6 μm, 10.1 μm and 15.1 μm, respectively. The TMA = -9.8%

Comparative Experiment 2

An acidic aqueous silver salt solution was prepared by adding 14 g of gum arabic to 250 g of deionized water. This solution was kept at 25°C while continuously stirring for an hour. Then 80 g of silver nitrate was added. This solution was kept at 25°C while continuously stirring.

An acidic reducing and particle modifier solution was prepared by adding 5 g of nitric acid (70% w/w), 5 g maleic acid, 45 g ascorbic acid and

1 g of gold colloid solution to 750 g of deionized water in a separate container from the silver nitrate solution. This solution was kept at 25°C while continuously stirring.

The acidic aqueous silver salt solution was slowly added to the acidic reducing and particle modifier solution over a period of one hour to form a reaction mixture that was intensely stirred during the addition. The reaction mixture was maintained at 25°C. Silver particles precipitated and were contained within the final aqueous solution. The final aqueous solution was then heated to 70 °C for one hour and stirring continued during the heating.

The silver particles were recovered as described in Example 1.

As shown in the scanning electron microscope image of Figure 5, the silver powder was comprised of very irregular-shaped relatively large silver particles. The size L of the crystallites in the particles was 47.6 nm. d_{10}, d_{50}, and d_{90} were 5.4 μm, 8.7 μm and 14.0 μm, respectively. The TMA = -7.5%

Comparative Experiment 3

An acidic aqueous silver salt solution was prepared by dissolving 80 g of silver nitrate in 250 g of deionized water. This solution was kept at 25°C while continuously stirring.

An acidic reducing and particle modifier solution was prepared by adding 12 g of gum arabic to 750 g of deionized water in a separate container from the silver nitrate solution. This solution was kept at 25°C while continuously stirring for an hour. 20 g of nitric acid (70% w/w), 3 g K_2SO_4, 45 g ascorbic acid and 0.1 g of gold colloid solution was then added to the solution still maintained at 25°C and stirred.

The acidic aqueous silver salt solution was slowly added to the acidic reducing and particle modifier solution over a period of one hour to form a reaction mixture that was intensely stirred during the addition. The reaction mixture was maintained at 25°C. Silver particles precipitated and were contained within the final aqueous solution. The final aqueous solution was then heated to 70 °C for one hour and stirring continued during the heating.

The silver particles were recovered as described in Example 1.

The size L of the crystallites in the particles was 60.0 nm. d_{10}, d_{50}, and d_{90} were 2.0 μm, 3.5 μm and 6.3 μm, respectively. The TMA = -6%

Comparative Experiment 4

Comparative Experiment 1 was carried out using the process described in Comparative Experiment 3 except that 5 g of gold colloid solution was used in preparing the acidic reducing and particle modifier solution

The size L of the crystallites in the particles was 56.2 nm. d_{10}, d_{50}, and d_{90} were 0.9 μm, 1.6 μm and 2.9 μm, respectively. The TMA = -6%.

Claims

What is claimed is:

1. A process for making silver powder particles, said process comprising:

(a) preparing an acidic aqueous silver salt solution comprising a water soluble silver salt dissolved in deionized water;

(b) preparing an acidic aqueous reducing and particle modifier solution comprising:

(i) a reducing agent selected from the group consisting of ascorbic acid, ascorbates and mixtures thereof dissolved in deionized water;

(ii) nitric acid;

(iii) gum arabic;

(iv) maleic acid; and

(v) deionized water;

(c) maintaining said acidic aqueous silver salt solution and said acidic reducing and particle modifier solution at the same temperature, wherein said temperature is in the range of 10°C to 65°C, while stirring each said solution during and after preparation;

(d) adding said acidic aqueous silver salt solution to said acidic aqueous reducing and particle modifier solution while stirring to make a reaction mixture and maintaining the temperature of said reaction mixture at said temperature of (c), wherein said silver powder particles precipitate and are contained within the resulting final aqueous solution; and

(e) increasing the temperature of said final aqueous solution to a temperature in the range of 65°C to 80°C while continuing stirring;

said silver powder particles comprising crystallites between 30 and 47 nm in size as determined by X-ray diffraction and the Scherrer formula; and said silver powder particles having d_{50} in the range of 0.5 to 3.5 μm.

2. The process of claim 1, further comprising:

(f) separating said silver powder particles from said final aqueous solution;

(g) washing said silver powder particles with deionized water; and

(h) drying said silver powder particles.

3. The process of claim 1, wherein said water soluble silver salt is silver nitrate and wherein said reducing agent is ascorbic acid.

4. The process of claim 1, said acidic aqueous reducing and particle modifier solution further comprising a metal colloid selected from the group consisting of gold colloid and silver colloid.

5. The process of claim 1, wherein the temperature in step (c) is in the range of 10°C to 35°C and the temperature in step (e) is in the range of 65°C to 75°C

6. The process of claim 1, wherein said silver powder particles have a size distribution such that $(d_{90}-d_{10})/d_{50} < 2.2$.

7. The process of claim 1, wherein said silver powder particles have a solids content in excess of 99% as determined by thermogravimetric analysis.

8. The silver powder particles made by the process of claim 1

9. A silver thick film paste comprising said silver powder particles of claim 8.

10. A solar cell comprising an electrode, said electrode, prior to firing, comprising said silver thick film paste of claim 9.

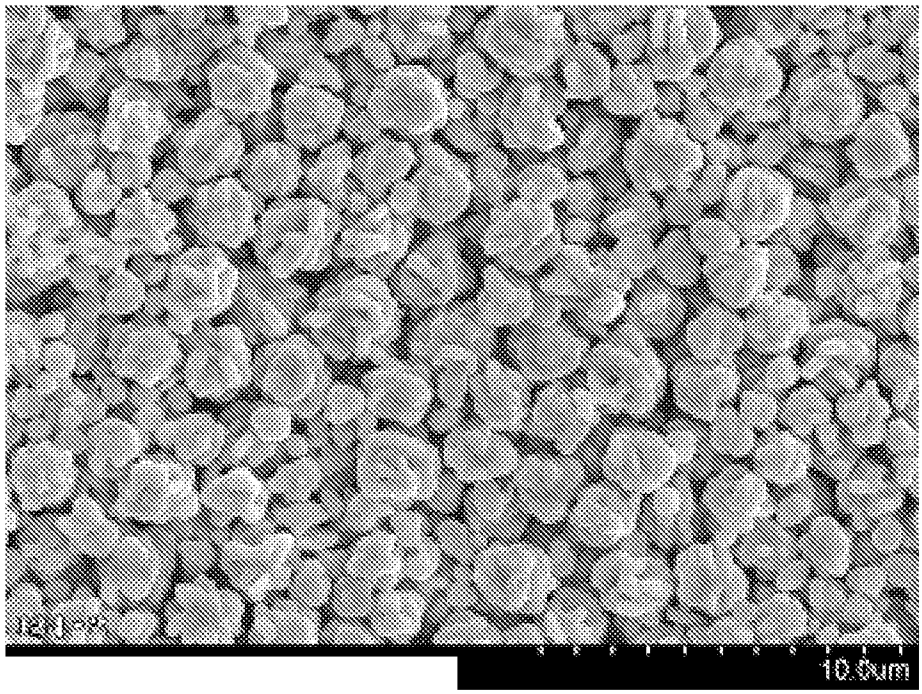


FIG. 1

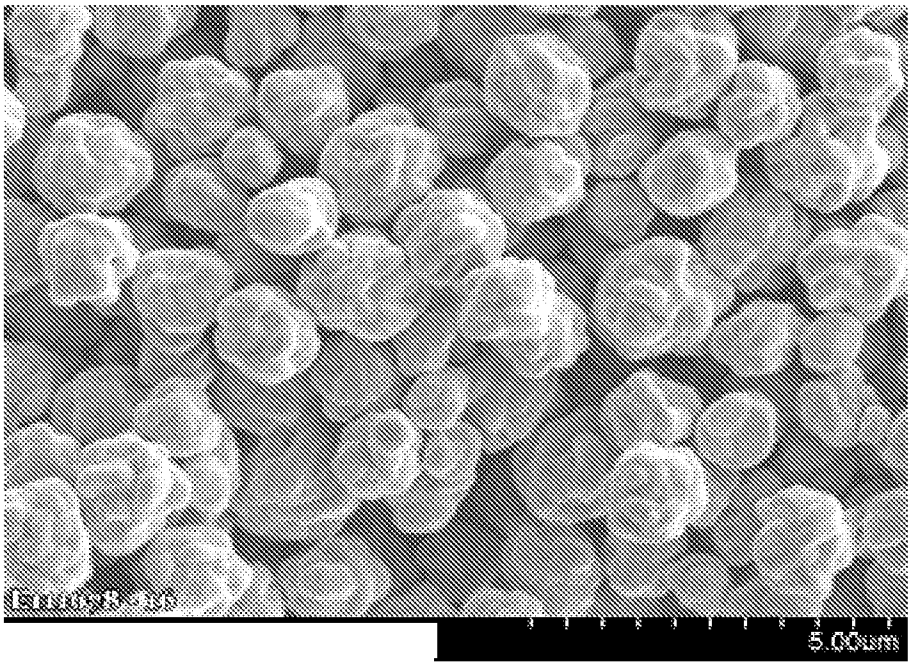


FIG. 2

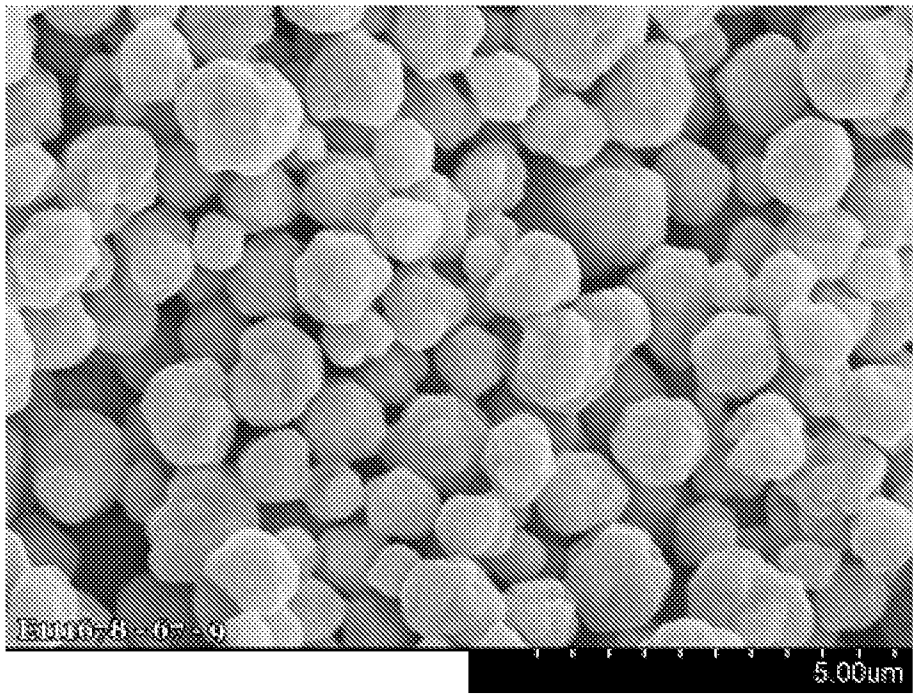


FIG. 3

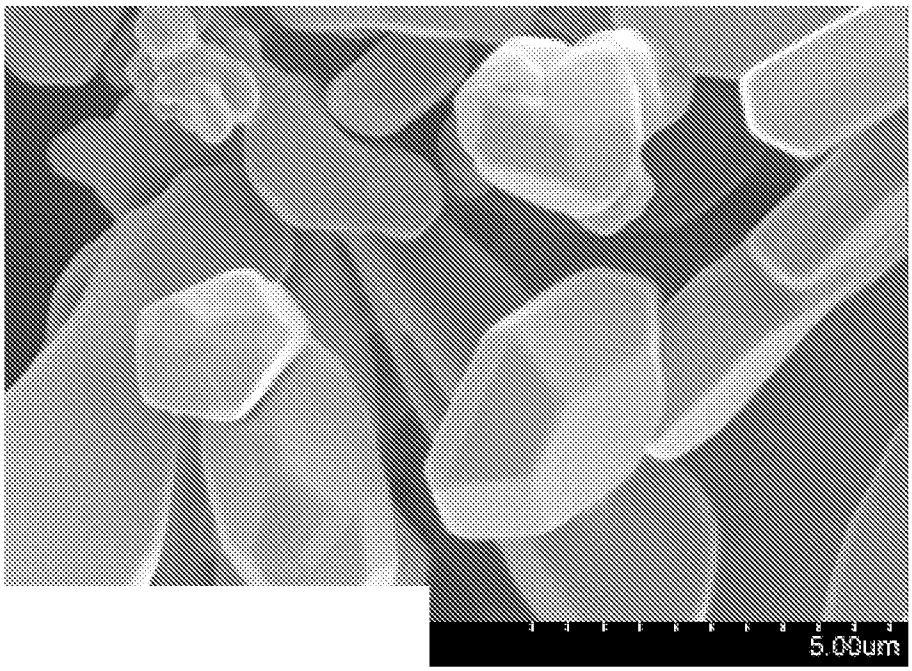


FIG. 4

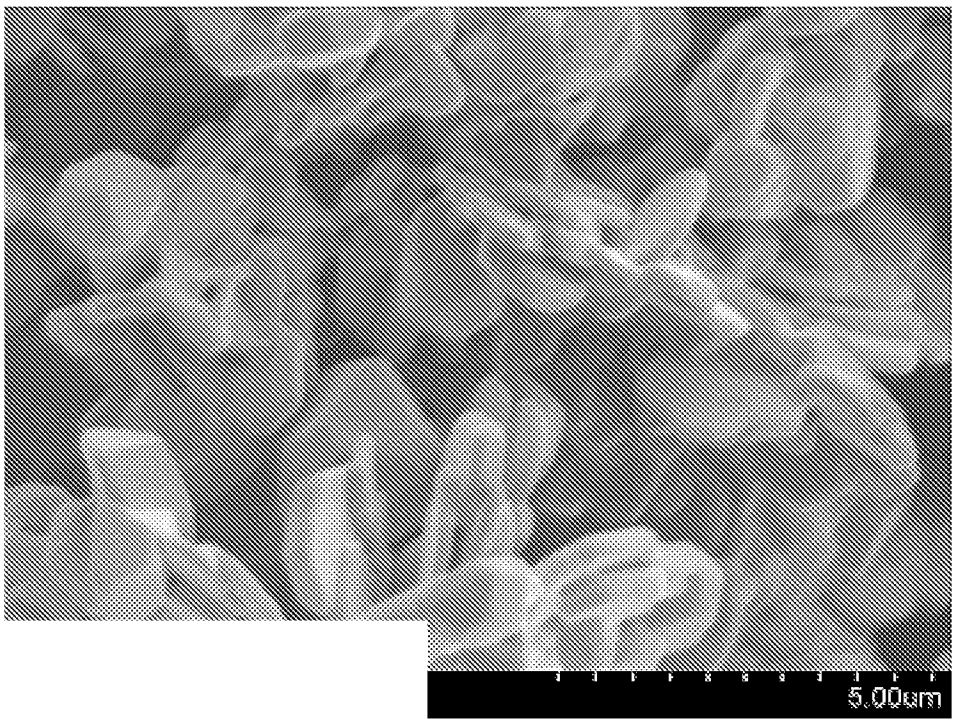


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/028341

A. CLASSIFICATION OF SUBJECT MATTER
INV. B22F1/00 B22F9/24
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)
B22F

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	WO 2007/143125 A2 (DU PONT [US]; IRIZARRY-RIVERA ROBERTO; GLICKSMAN HOWARD DAVID [US]; AL) 13 December 2007 (2007-12-13) examples 21-22; tables 1-2 -----	1-10
X	JP 2006 225760 A (SHOEI CHEMICAL IND CO) 31 August 2006 (2006-08-31) abstract; claims 1-4; examples 1-7 -----	1-10

☐ 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

"E" earlier application or patent 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
18 July 2012	25/07/2012

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	Liu, Yonghe

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2012/028341

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2007143125 A2	13-12-2007	CN 101460271 A	17-06-2009
		EP 2026924 A2	25-02-2009
		JP 2009540111 A	19-11-2009
		KR 20090018178 A	19-02-2009
		TW 200808471 A	16-02-2008
		US 2008028889 A1	07-02-2008
		WO 2007143125 A2	13-12-2007
JP 2006225760 A	31-08-2006	JP 4301247 B2	22-07-2009
		JP 2006225760 A	31-08-2006