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(54) Title: SUB-CRITICAL SHEAR THINNING GROUP IV BASED NANOPARTICLE FLUID

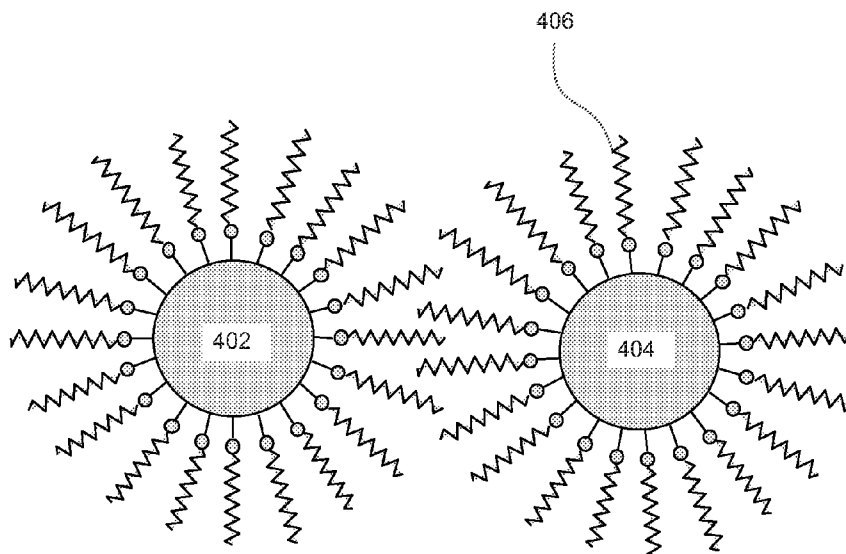


FIG. 4

(57) Abstract: A Group IV based nanoparticle fluid is disclosed. The nanoparticle fluid includes a set of nanoparticles-comprising a set of Group IV atoms, wherein the set of nanoparticles is present in an amount of between about 1 wt% and about 20 wt% of the nanoparticle fluid. The nanoparticle fluid also includes a set of HMW molecules, wherein the set of HMW molecules is present in an amount of between about 0 wt% and about 5 wt% of the nanoparticle fluid. The nanoparticle fluid further includes a set of capping agent molecules, wherein at least some capping agent molecules of the set of capping agent molecules are attached to the set of nanoparticles.

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SUB-CRITICAL SHEAR THINNING GROUP IV BASED NANOPARTICLE FLUID**CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims the benefit of U.S. Provisional Patent Application Serial No. 61/187,731 filed June 17, 2009, and U.S. Non-Provisional Patent Application No. 12/493,946 filed June 29, 2009, the entire disclosures of which are incorporated by reference.

FIELD OF DISCLOSURE

[0002] This disclosure relates in general to semiconductors and in particular to a sub-critical shear thinning nanoparticle fluid and methods thereof.

BACKGROUND

[0003] Semiconductors form the basis of modern electronics. Possessing physical properties that can be selectively modified and controlled between conduction and insulation, semiconductors are essential in most modern electrical devices (e.g., computers, cellular phones, photovoltaic cells, etc.).

[0004] The ability to deposit semiconductor materials using non-traditional semiconductor technologies such as printing may offer a way to simplify and hence reduce the cost of many modern electrical devices (e.g., computers, cellular phones, photovoltaic cells, etc.). Like pigment in paint, these semiconductor materials are generally formed as microscopic particles, temporarily suspended in a matrix, colloidal dispersion, or paste, and later deposited on a substrate.

[0005] For example, it may be desired to form an electrically active thin film (i.e., p-n junction, etc.) on a silicon substrate through the deposition of fluid with electrically active semiconductor particles. In order to have the fluid flow during the deposition process (e.g., inkjet print, aerosol print, screen print, etc.), it generally must have a relatively low viscosity. However, once deposited in a pattern, the same fluid must generally also have a relatively high viscosity in order to retain the pattern during the densification process. Consequently, a shear-thinning or non-Newtonian fluid is desired. That is, the fluid is rigid for shear stress τ , less than a critical value τ_0 . Once the critical shear stress (or "yield stress") is exceeded, the

material flows in such a way that the shear rate, $\frac{\partial u}{\partial y}$ is directly proportional to the amount by which the applied shear stress exceeds the yield stress:

$$\frac{\partial u}{\partial y} = \begin{cases} 0, \tau < \tau_0 \\ (\tau - \tau_0) / \mu, \tau \geq \tau_0 \end{cases} \quad \text{[EQUATION 1]}$$

[0006] Typically, non-Newtonian behavior may be achieved by combining in a suitable solvent, a set of high molecular weight (HMW) molecules, and a certain critical volume fraction of granular material (particles). Below the critical volume fraction, the fluid is Newtonian, whereas above the critical volume fraction, the fluid is non-Newtonian or shear-thinning.

[0007] However, in order to optimize patterned deposition, it is often desired to deposit a fluid with a substantially low volume (typically less than 10 wt%) of granular materials, which may be below the critical volume fraction for shear-thinning behavior. For example, in the deposition of thin films, higher loadings of sub-micron particles tend to form thicker films (> 5 micron) which, in turn, tend to develop stress fractures when the film is densified. Furthermore, in applications where an epitaxy is required, thicker films tend to impede epitaxial growth. An epitaxy is generally a type of interface between a thin film and a substrate and generally describes an ordered crystalline growth on a mono crystalline substrate.

[0008] In view of the foregoing, there is desired a shear thinning Group IV based nanoparticle fluid with a sub-critical volume fraction.

SUMMARY

[0009] The invention relates, in one embodiment, to a Group IV based nanoparticle fluid. The nanoparticle fluid includes a set of nanoparticles-comprising a set of Group IV atoms, wherein the set of nanoparticles is present in an amount of between about 1 wt% and about 20 wt% of the nanoparticle fluid. The nanoparticle fluid also includes a set of HMW molecules, wherein the set of HMW molecules is present in an amount of between about 0 wt% and about 5 wt% of the nanoparticle fluid. The nanoparticle fluid further includes a set

of capping agent molecules, wherein at least some capping agent molecules of the set of capping agent molecules are attached to the set of nanoparticles.

[0010] The invention relates, in another embodiment, to a method for forming a dual-doped emitter on a silicon substrate with a sub-critical shear thinning nanoparticle fluid, the silicon substrate comprising a front surface and a rear surface. The method includes texturing the silicon substrate; cleaning the silicon substrate; and depositing a sub-critical shear thinning nanoparticle fluid on a front surface. The method further includes baking the silicon substrate at a first temperature of between about 150°C to about 800°C and for a first time period between about 1 minute and about 60 minutes. The method also includes exposing the silicon substrate to a dopant source in a diffusion furnace with an atmosphere of POCl_3 , N_2 , and O_2 , at a second temperature of between about 800°C and about 950°C, and for a second time period of between about 30 minutes and about 180 minutes, wherein a PSG layer is formed. The method further includes removing the PSG layer; depositing an anti-reflection coating on the front surface; and depositing a set of front metal contacts on the front surface and a set of rear metal contacts on the rear surface.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] The present invention is illustrated by way of example, and not by way of limitation, in the figures of the accompanying drawings and in which like reference numerals refer to similar elements and in which:

[0012] FIG. 1 shows a simplified diagram comparing viscosity to shear rate for a set of pastes, in accordance with the invention;

[0013] FIG. 2 shows a simplified diagram of the particle size distribution of a substantially dispersed semiconductor nanoparticle dispersion before fluid formulation, in accordance with the invention;

[0014] FIG. 3 shows a simplified diagram comparing viscosity to a set of silicon nanoparticle loadings, in accordance with the invention;

[0015] FIG. 4 shows a simplified diagram of the hydrostatic and electrostatic interaction of substantially dispersed semiconductor nanoparticles, in accordance with the invention; and

[0016] FIG. 5A-B show a simplified method for manufacturing a dual-doped emitter (selective emitter) solar cell with a sub-critical shear thinning nanoparticle fluid, in accordance with the invention.

DETAILED DESCRIPTION

[0017] The present invention will now be described in detail with reference to a few preferred embodiments thereof as illustrated in the accompanying drawings. In the following description, numerous specific details are set forth in order to provide a thorough understanding of the present invention. It will be apparent, however, to one skilled in the art, that the present invention may be practiced without some or all of these specific details. In other instances, well known process steps and/or structures have not been described in detail in order to not unnecessarily obscure the present invention.

[0018] As previously described, it is often difficult to deposit an electrically active thin film by a shear-thinning fluid with a low particle volume fraction. In general, a low (below a critical level) particle volume fraction is preferred for forming a thin film, while a high (above a critical level) particle volume fraction is required for a shear thinning or non-Newtonian behavior that is often required for optimal patterning on a substrate. However, shear thinning behavior is difficult to achieve with a low solid loading.

[0019] In an advantageous manner, a shear thinning Group IV based (silicon, germanium, silicon oxide, etc.) nanoparticle fluid may be formed such that an optimal thin film may be deposited and densified. The inventors believe that, in one configuration, by first substantially dispersing the set of silicon nanoparticles in a colloidal dispersion through the addition of a set of alcohol and ketone capping agents, by next optionally adding of a set of high molecular weight (HMW) molecules, such as cellulose, and then thickening the dispersion by the removal of solvents, an optimal sub-critical shear-thinning fluid may be created. In other configurations, it is further believed that other Group IV based nanoparticle fluids, comprising, for example, germanium nanoparticles and silicon nanoparticles, may yield similar results.

[0020] Nanoparticles are generally microscopic particle with at least one dimension less than 100 nm. In comparison to a bulk material (> 100 nm) which tends to have constant physical properties regardless of its size (e.g., melting temperature, boiling temperature, density, conductivity, etc.), nanoparticles may have physical properties that are size dependent, such as a lower sintering temperature or a wider band gap.

[0021] Nanoparticles may be produced by a variety of techniques such as evaporation (S. Ijima, *Jap. J Appl. Phys.* 26, 357 (1987)), gas phase pyrolysis (K. A Littau, P. J. Szajowski, A. J. Muller, A. R. Kortan, L. E. Brus, *J Phys. Chem.* 97, 1224 (1993)), gas phase photolysis (J. M. Jasinski and F. K. LeGoues, *Chem. Mater.* 3, 989 (1991);), electrochemical

etching (V. Petrova-Koch et al., Appl. Phys. Lett. 61, 943 (1992)), plasma decomposition of silanes and polysilanes (H. Takagi et al, Appl. Phys. Lett. 56, 2379 (1990)), high pressure liquid phase reduction-oxidation reaction (J. R. Heath, Science 258, 1131 (1992)), etc.

[0022] Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand linked glucose units.

[0023] A capping agent or ligand is generally a set of atoms or groups of atoms bound to a central atom in a polyatomic molecular entity. In general, weak hydrostatic and electrostatic interaction between capping agents tend to increase viscosity in non-dynamic force regimes. That is, prior to the addition of a shear force. However, the addition of a relatively small shear force overcomes the hydrostatic interaction and thus tends to reduce the viscosity of the fluid.

[0024] Alcohols such as cyclohexanol, menthol, or terpineol may have an optimal chemical structure in which the terminal alcohol functional group can attach to surface Si element thru Si-O covalent bond formation. However, other alcohols may be used.

[0025] In the case of an alkyl alcohol, the bulky alkyl group generally protrudes to a dispersing medium away from the Si nanoparticles surface. In general, as the nanoparticle surface packing density of a capping agent increases, the dispersability, viscosity, and deglomeration of the nanoparticles also tends to improve. Furthermore, for configurations in which the dispersion fluid or vehicle is the same as the capping agent, dispersability may be enhanced still further since compatibility issues between the capping agent and vehicle are substantially reduced or eliminated altogether.

[0026] For a suspension of low concentration, its viscosity can be calculated by the following equation:

$$\frac{\eta}{\eta_0} = 1 + 2.5\phi + K\phi^2 \quad \text{[EQUATION 2]}$$

where

$$\frac{\eta}{\eta_0} = \text{relative viscosity,}$$

ϕ = particle volumetric concentration, and

K = Hugins coefficient.

In general, K varies with the degree of aggregation and the electrochemical force between particles and $5.0 = K = 15$. It is found after comparison that the measured data of viscosities.

Huaqing Xie, Lifei Chen, and QingRen Wu, *Measurements of the viscosity of suspensions (nanofluids) containing nanosized Al₂O₃ particles*, presented at the 8th Asian Thermophysical Properties Conference, August 21-24, 2007.

[0027] For example, per Equation 2, for fluids with granular materials with a particle size greater than about 100 nm, as K approaches 15 at a shear rate of 1/sec, the value of relative viscosity is estimated to be 1.13. However, in the current invention with a fluid including a sub-critical volume of high-surface area nanoparticles (less than about 100 nm), the measured relative viscosity with the same shear rate (1/sec) has been shown to be about 182, which is more than two orders of magnitude enhancement. Consequently, it has been shown that in comparison to larger particle dispersions, nanoparticle dispersions tend to have higher n/n_0 values, corresponding to a viscosity enhancement because of increased particle-particle interaction as previously described.

[0028] Volume fraction may be calculated using the following equation:

$$\Phi = \frac{\rho_0 \Phi_m}{\rho_0 \Phi_m + \rho_P (1 - \Phi_m)} \quad \text{[EQUATION 3]}$$

where ρ_P and ρ_0 are the densities of the nanoparticles and the base fluid, respectively, Φ and Φ_m are the volume and mass fraction of the powder. However, as previously stated, a critical shear thinning nanoparticle fluid tends to have a substantially smaller volume fraction than typically required for shear-thinning behavior. For example, in comparing the current invention to silver and aluminum paste, commonly used forming the front and rear contacts on a solar cell respectively, a sub-critical shear thinning nanoparticle fluid has a substantially smaller volume fraction.

	Silver (Ag) Paste	Aluminum (Al) Paste	Sub-Critical Shear Thinning Nanoparticle Fluid
Weight fraction	0.8	0.8	0.09
Density of vehicle	0.95	0.95	0.95
Density of powder	10.49	2.70	2.33
Volume fraction	0.27	0.58	0.039

[0029] EXPERIMENT 1

[0030] Referring now to FIG. 1, viscosity is compared to shear rate for a set of pastes, in accordance with the invention. Shear rate in 1/sec 102 is shown along the horizontal axis, while viscosity in KcP 104, is shown along the vertical axis. Viscosity was measured as a function of shear rate to show the influence of silicon nanoparticles.

[0031] All fluids were prepared by dissolving an ethylcellulose binder in a terpeneol (C₁₀H₁₈O) solvent. A first fluid 106 was prepared by dissolving a 1.5 wt% ethylcellulose binder in a terpeneol solvent without silicon nanoparticles. A second fluid 108 and third fluid 110 were prepared, by mixing on a hot-plate at 100°C for 1 hour, a 1.5 wt% ethyl cellulose binder and 8 wt% silicon nanoparticles in a terpeneol solvent. The third fluid 110 was additionally sonicated in a range of about 16-20 kHz for about 3 hrs. During the sonication step, most of agglomerates from the powder production are generally broken down to much smaller with an average size of about 50 to about 150 nm.

[0032] As can be seen, fluid 106 shows a typical Newtonian behavior, where the viscosity of the fluid does not change under a different shear rate, whereas the fluids 308 & 310 show a shear thinning behavior. In addition, in comparison to fluid 308, fluid 310 shows substantial shear thinning behavior, corresponding to a better dispersion and substantial deglomeration as a result of the sonication step as previously described.

[0033] Referring to FIG. 2, a particle size distribution of substantially dispersed semiconductor nanoparticle dispersion before fluid formulation is shown, in accordance with the invention. In general, although the average size of dispersed particles is still much larger than the primary size of silicon nanoparticles (which range from 5 nm to 35 nm), the inventors believe organic groups present on the surface of Si nanoparticles substantially contribute to a shear-thinning fluid behavior as shown in FIG. 1.

[0034] EXPERIMENT 2

[0035] Referring now to FIG. 3, a simplified diagram comparing viscosity to a set of silicon nanoparticle loadings, in accordance with the invention. Silicon nanoparticle loading in mg/ml 302 is shown along the horizontal axis, while viscosity in cP 304, is shown along the vertical axis.

[0036] All fluids were prepared by dissolving silicon nanoparticles in a mixture of alcohol and ketone, and then magnetically stirred at 100°C for 1hr. The dispersions were sonicated by sonic-horn. In one configuration, the ketone may be an alkyl ketone. In contrast to FIG. 1, viscosity values of the fluids are generally lower since binder is not present.

[0037] As can be seen, as loading increases from 20 mg/ml, viscosity substantially increases from about 7 cP to about 14 cP, corresponding to increased electrostatic and hydrophobic interactions between dispersed particles.

[0038] Referring now to FIG. 4, a simplified diagram showing the hydrostatic and electrostatic interaction of substantially dispersed semiconductor nanoparticles. In this configuration, a set of silicon nanoparticles 402 are shown with terpineol capping agent 406. In an advantageous manner, in addition to adding a steric repulsive force that keeps the nanoparticles suspended, hydrophobic set of capping agent 406 tends to also contribute to increase the flow resistance due to the very high electrostatic interaction with other capping agents as well as with other solvents and binders in the dispersion. Furthermore, terpineol capping agent may also serve as a base solvent, and thus allow a high degree of compatibility between the capping agent and the base solvent.

[0039] Consequently, in order to create an optimal sub-critical shear thinning nanoparticle fluid, the silicon nanoparticles should preferably be present in an amount between about 1 wt% and about 20 wt%, more preferably between about 2 wt% and about 15 wt%, and most preferably between about 4 wt% and about 10 wt%. Furthermore, the proportion of HMW molecules should preferably be present in an amount between about 0 wt% and about 10 wt%, more preferably between about 0 %wt and about 4 wt%, and most preferably between about 0.5 wt% and about 2 wt%. The proportion of alcohol present is preferably up to 90 wt% (with the remainder being ketone), more preferably up to 80 wt% (with the remainder being ketone), and most preferably up to 70 %wt (with the remainder being ketone).

[0040] Referring to FIGS. 5A-B, a simplified method is described for manufacturing a dual-doped emitter (selective emitter) solar cell with a sub-critical shear thinning nanoparticle fluid, in accordance with the invention. A selective emitter uses a first lightly doped region optimized for low recombination, and a second heavily doped region pattern (of the same dopant type) optimized for low resistance ohmic contact formation.

[0041] FIG. 5A shows a simplified diagram of a selective emitter as manufactured in accordance with the invention.

[0042] Emitter 506 may be p-type (e.g., boron) or n-type (e.g., phosphorous) and could be formed by various methods, which include but are not limited to gas phase diffusion (such as e.g. using POCl_3 gas as phosphorous source or BBr_3 as boron source), solid source diffusion, or inline processes which typically use liquid dopant sources such as e.g. phosphoric acid.

[0043] Above and in electrical contact with the emitter 506 (which is also typically coated with an antireflection coating 504) is a front metal contact, comprising a set of fingers 505 (here with a width of about 100 μm) and a set of bus bars 503. Typically made out of printed silver paste, the front metal contact is optimized to extract the charge carriers (here electrons) created in the silicon substrate when light is absorbed. The front metal contact is also typically configured with a reduced horizontal surface area (thus minimizing losses due to shading, which tend to reduce the generated current), and an increased cross-sectional aspect ratio (thus reducing the series resistance of the device, which tends to increase the efficiency of the device).

[0044] In general, untreated silicon substrates often reflect more than 30% of incident light. Consequently, in order to reduce this reflected energy and thus directly improve efficiency, the silicon substrate is generally textured and optimized with anti-reflective coatings 504 (e.g., silicon nitride (SiN_x), etc.). In addition, anti-reflective coating 504 also helps passivate the surface of emitter 506, both reducing the impact of contamination of the substrate bulk from external sources, as well as substantially reducing minority carrier recombination caused by dangling Si bonds or imperfections in the doped substrate 508 surface.

[0045] In addition, on the back-side of silicon substrate 508 is often a heavily doped region (of the same type as the substrate) which creates a BSF (back surface field) 510. Minimizing the impact of rear surface recombination, a properly configured BSF tends to repel those minority carriers that are generated closer to the back-side, resulting in higher levels of minority carrier concentrations in the substrate absorber. For example, Al (aluminum) or B (boron) may be added to a p-type substrate to form a BSF layer. In contrast, for an n-type substrate, P (phosphorous) may be added to form a BSF layer. In addition, silver (Ag) pads are generally inserted in the back-side in order to facilitate soldering for interconnection into modules.

[0046] FIG. 5B shows a simplified method for manufacturing a dual-doped emitter of FIG. 5A, in accordance with the invention.

[0047] Initially at 542, the crystalline substrate is pre-cleaned in a sulfuric acid solution and then textured by treating the substrates in a solution of H₂O, IPA, and KOH.

[0048] At 544, the substrate is cleaned and rinsed SC-2 (generally a mixture of H₂O, HCl (hydrochloric acid) and H₂O₂ (hydrogen peroxide)), piranha (generally a mixture of sulfuric acid (H₂SO₄) and H₂O₂), BOE, and H₂O, respectively.

[0049] Next at 546, in an advantageous manner, a sub-critical shear thinning nanoparticle fluid (comprising 8 wt% silicon nanoparticles) is deposited on each textured crystalline silicon substrate. In a common configuration, a screen printer is used. In one configuration, a sub-critical shear thinning nanoparticle fluid may be preferably deposited (as measured prior to step 548) with a fluid mass per unit substrate surface area of between about 0.04 mg/cm² to about 3.0 mg/cm², more preferably between about 0.2 mg/cm² to about 2.0 mg/cm², and most preferably between about 0.4 mg/cm² to about 1.5 mg/cm².

[0050] At 548, the crystalline silicon may be baked at a temperature of between about 150°C to about 800°C for a time period between about 1 minute and about 60 minutes, in order to densify the film. The baking ambient may be one of inert (such as nitrogen), oxidizing (such as air), or a combination of both nitrogen and oxygen. Furthermore, the baking apparatus may be a belt furnace, a tube furnace, or a convection oven.

[0051] At 549, the crystalline silicon substrate is optionally cleaned to remove any possible contaminants accumulated during previous steps. The cleaning options may include HCl, HF/HCl, diluted HF, buffered oxide etch (BOE), SC-1 (generally a mixture of NH₄OH + H₂O₂ + H₂O), SC-2 and other cleaning mixtures.

[0052] At 550, the crystalline silicon substrate is exposed to a dopant source in a diffusion furnace with an atmosphere of POCl₃, N₂, and O₂, at a temperature between about 800°C and about 950°C and for a time period of up to about 3 hours.

[0053] At 552, the crystalline silicon substrate is exposed to a cleaning agent, such as e.g. BOE (generally buffered HF), diluted HF, or mixture of HF and HCl. The degree of removal of the residual PSG layer and the thickness of the densified silicon nanoparticle film may be controlled by varying the period of exposure to the cleaning agent from about 0 minutes to about 60 minutes and by controlling the concentration of the cleaning agent in the cleaning bath. Greater etchant exposure corresponds to a thinner densified silicon nanoparticle film and a more thorough removal of the PSG layer. In addition, typically an etchant exposure greater than 10 minutes substantially removes the thinner densified silicon nanoparticle film.

[0054] At 554, in order to minimize reflection and to optimize surface passivation, an anti-reflection coating and passivation layer of silicon nitride (Si_3N_4 and other non-stoichiometric ratios of Si and N) is deposited on the silicon substrate in an ambient of silane, ammonia, nitrogen, and optionally hydrogen. Here, the reflective index of the Si_3N_4 layer may be between about 1.90 and about 2.10, with a thickness of between about 40 nm and about 120 nm.

[0055] At 556, the front metal contacts (aligned to the deposited sub-critical shear thinning nanoparticle fluid pattern) and rear metal contacts are deposited, forming the solar cell. Specifically, by measuring a ratio of reflectivity within a specific wavelength region between a first highly doped region (formed by the deposition of sub-critical shear thinning nanoparticle fluid) and a second lightly doped diffused region, a set of metal contacts, may be deposited in a manner optimized for each individual solar cell substrate. In one configuration, the front metal contacts are deposited using a screen printer. In another embodiment, a polymer based screen is used in order to avoid metal contamination. This method of metal alignment is further described in U.S. Pat. App. No. 12/468,540 filed May 19, 2009, the entire disclosure of which is incorporated by reference.

[0056] Consequently, the resulting solar cell may have a typical sheet resistance in substrate surface areas where the sub-critical shear thinning nanoparticle fluid was not deposited is between about 90 Ohm/sq. to about 130 Ohm/sq, whereas substrate surface areas underneath the deposited sub-critical shear thinning nanoparticle fluid may be below 60 Ohm/sq.

[0057] The inventions illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms “comprising,” “including,” “containing,” etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed.

[0058] Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification, improvement and variation of the inventions herein disclosed may be resorted to by those skilled in the art, and that such modifications, improvements and variations are considered to be within the scope of this invention. The materials, methods, and examples provided here

are representative of preferred embodiments, are exemplary, and are not intended as limitations on the scope of the invention.

[0059] As will be understood by one skilled in the art, for any and all purposes, particularly in terms of providing a written description, all ranges disclosed herein also encompass any and all possible sub-ranges and combinations of sub-ranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as “up to,” “at least,” “greater than,” “less than,” and the like include the number recited and refer to ranges which can be subsequently broken down into sub-ranges as discussed above. In addition, the terms “dopant or doped” and “counter-dopant or counter-doped” refer to a set of dopants of opposite types. That is, if the dopant is p-type, then the counter-dopant is n-type. Furthermore, unless otherwise dopant-types may be switched. In addition, the silicon substrate may be either mono-crystalline or multi-crystalline. In addition, “undoped” refers to a material with a lack of dopant. As described herein, the ketone molecules and the alcohol molecules may be cyclic, straight, or branched.

[0060] Furthermore, this invention may be applied to other solar cell structures as described in U.S. Pat. App. No. 12/029,838 filed February 12, 2008, the entire disclosure of which is incorporated by reference.

[0061] All publications, patent applications, issued patents, and other documents referred to in this specification are herein incorporated by reference as if each individual publication, patent application, issued patent, or other document were specifically and individually indicated to be incorporated by reference in its entirety. Definitions that are contained in text incorporated by reference are excluded to the extent that they contradict definitions in this disclosure.

[0062] For the purposes of this disclosure and unless otherwise specified, “a” or “an” means “one or more.” All patents, applications, references and publications cited herein are incorporated by reference in their entirety to the same extent as if they were individually incorporated by reference. In addition, the word set refers to a collection of one or more items or objects.

[0063] Advantages of the invention include a substantially uniformly deposited sub-critical shear thinning nanoparticle fluid that is optimized for screen printing.

[0064] Having disclosed exemplary embodiments and the best mode, modifications and variations may be made to the disclosed embodiments while remaining within the subject and spirit of the invention as defined by the following claims.

WHAT IS CLAIMED IS:

1. A silicon nanoparticle fluid comprising:
 - a set of silicon nanoparticles, wherein the set of silicon nanoparticles is present in an amount of between about 1 wt% and about 20 wt% of the silicon nanoparticle fluid;
 - a set of HMW molecules, wherein the set of HMW molecules is present in an amount of between about 0 wt% and about 10 wt% of the silicon nanoparticle fluid; and
 - a set of capping agent molecules, wherein at least some capping agent molecules of the set of capping agent molecules are attached to the set of silicon nanoparticles.
2. The silicon nanoparticle fluid of claim 1, wherein the set of silicon nanoparticles is present in an amount of between about 2 wt% and about 15 wt% of the silicon nanoparticle fluid.
3. The silicon nanoparticle fluid of claim 1, wherein the set of silicon nanoparticles is present in an amount of between about 4 wt% and about 10 wt% of the silicon nanoparticle fluid.
4. The silicon nanoparticle fluid of claim 1, wherein the set of HMW molecules is present in an amount of between about 0 wt% and about 4 wt% of the silicon nanoparticle fluid.
5. The silicon nanoparticle fluid of claim 1, wherein the set of HMW molecules is present in an amount of between about 0.5 wt% and about 2 wt% of the silicon nanoparticle fluid.
6. The silicon nanoparticle fluid of claim 1, wherein the set of capping agent molecules comprises at least one of a set of alcohol molecules and a set of ketone molecules.
7. The silicon nanoparticle fluid of claim 6, wherein the set of alcohol molecules is present in an amount of up to 90 wt% of the silicon nanoparticle fluid.
8. The silicon nanoparticle fluid of claim 6, wherein the set of alcohol molecules is present in an amount of up to 80 wt% of the silicon nanoparticle fluid.

9. The silicon nanoparticle fluid of claim 6, wherein the set of alcohol molecules is present in an amount of up to 70 wt% of the silicon nanoparticle fluid.
10. The silicon nanoparticle fluid of claim 6, wherein the set of alcohol molecules comprises at least one of set of cyclic alcohol molecules, set of straight alcohol molecules, and a set of branched alcohol molecules.
11. The silicon nanoparticle fluid of claim 6, wherein the set of ketone molecules comprises at least one of set of cyclic ketone molecules, set of straight ketone molecules, and a set of branched ketone molecules.
12. The silicon nanoparticle fluid of claim 1, wherein the set of nanoparticles is one of doped and undoped.
13. The silicon nanoparticle fluid of claim 1, wherein the set of nanoparticles is doped with one of boron and phosphorous.
14. The silicon nanoparticle fluid of claim 1, wherein the set of HMW molecules comprises ethyl cellulose.
15. The silicon nanoparticle fluid of claim 1, wherein the silicon nanoparticle fluid has a viscosity of about 5 KcP to about 20 KcP at a shear rate of about 10 sec^{-1} .
16. A Group IV based nanoparticle fluid comprising:
 - a set of nanoparticles-comprising a set of Group IV atoms, wherein the set of nanoparticles is present in an amount of between about 1 wt% and about 20 wt% of the nanoparticle fluid;
 - a set of HMW molecules, wherein the set of HMW molecules is present in an amount of between about 0 wt% and about 5 wt% of the nanoparticle fluid; and
 - a set of capping agent molecules, wherein at least some capping agent molecules of the set of capping agent molecules are attached to the set of nanoparticles.

17. A method for forming a dual-doped emitter on a silicon substrate with a sub-critical shear thinning nanoparticle fluid, the silicon substrate comprising a front surface and a rear surface, the method comprising:
- texturing the silicon substrate;
 - cleaning the silicon substrate;
 - depositing the sub-critical shear thinning nanoparticle fluid on the front surface;
 - baking the silicon substrate at a first temperature of between about 150°C to about 800°C and for a first time period between about 1 minute and about 60 minutes;
 - exposing the silicon substrate to a dopant source in a diffusion furnace with an atmosphere of POCl_3 , N_2 , and O_2 , at a second temperature of between about 800°C and about 950°C, and for a second time period of between about 30 minutes and about 180 minutes, wherein a PSG layer is formed;
 - removing the PSG layer;
 - depositing an anti-reflection coating on the front surface; and
 - depositing a set of front metal contacts on the front surface and a set of rear metal contacts on the rear surface.
18. The method of claim 17, further comprising pre-cleaning the silicon substrate in a sulfuric acid solution prior to texturing the silicon substrate.
19. The method of claim 17, further comprising pre-cleaning the silicon substrate in one of HF/HCl or BOE prior to depositing the sub-critical shear thinning nanoparticle fluid on the silicon substrate.
20. The method of claim 17, wherein the step of texturing the silicon substrate comprises exposing the silicon substrate to a solution comprising H_2O , IPA, and KOH.
21. The method of claim 17, wherein the step of cleaning the silicon substrate comprises exposing the silicon substrate to a solution of SC-2, piranha, BOE, and H_2O .
22. The method of claim 17, further comprising cleaning the silicon substrate with at least one of HF, HF/HCl, BOE, SC-1, SC-2, and HCl before exposing the silicon substrate to the dopant source.

23. The method of claim 17, wherein the step of depositing the sub-critical shear thinning nanoparticle fluid on the front surface comprises using a screen printer.
24. The method of claim 17, wherein baking the silicon substrate at the first temperature is done in one of a belt furnace, a tube furnace, or a convection oven.
25. The method of claim 17 wherein baking the silicon substrate at the first temperature is done in an ambient comprising one of air, a mixture of oxygen and nitrogen, and nitrogen.
26. The method of claim 17 wherein depositing the sub-critical shear thinning nanoparticle fluid includes depositing a mass per unit substrate surface area of about 0.04 mg/cm² to about 3.0 mg/cm².
27. The method of claim 17 wherein depositing the sub-critical shear thinning nanoparticle fluid includes depositing a mass per unit substrate surface area of about 0.2 mg/cm² to about 2.0 mg/cm².
28. The method of claim 17 wherein depositing the sub-critical shear thinning nanoparticle fluid includes depositing a mass per unit substrate surface area of about 0.4 mg/cm² to about 1.5 mg/cm².

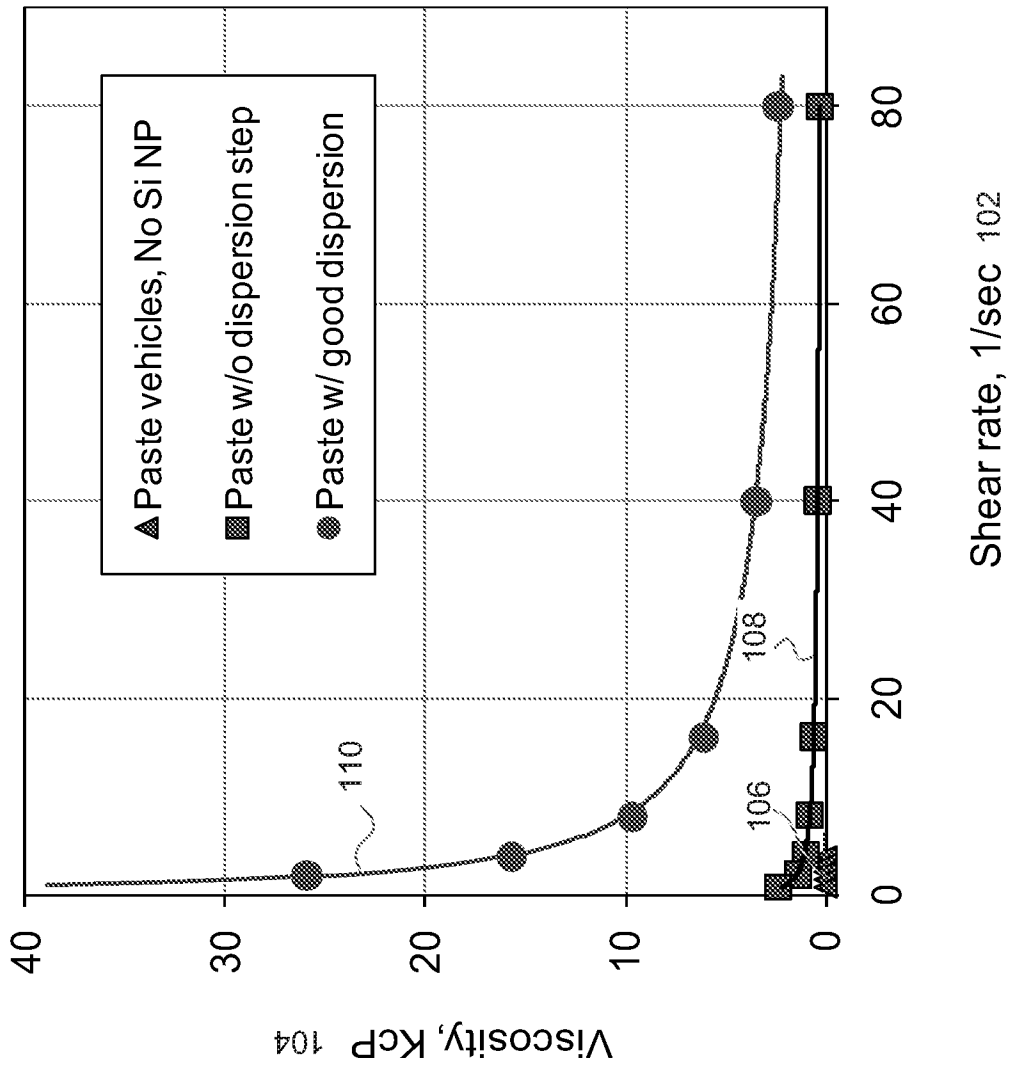


FIG. 1

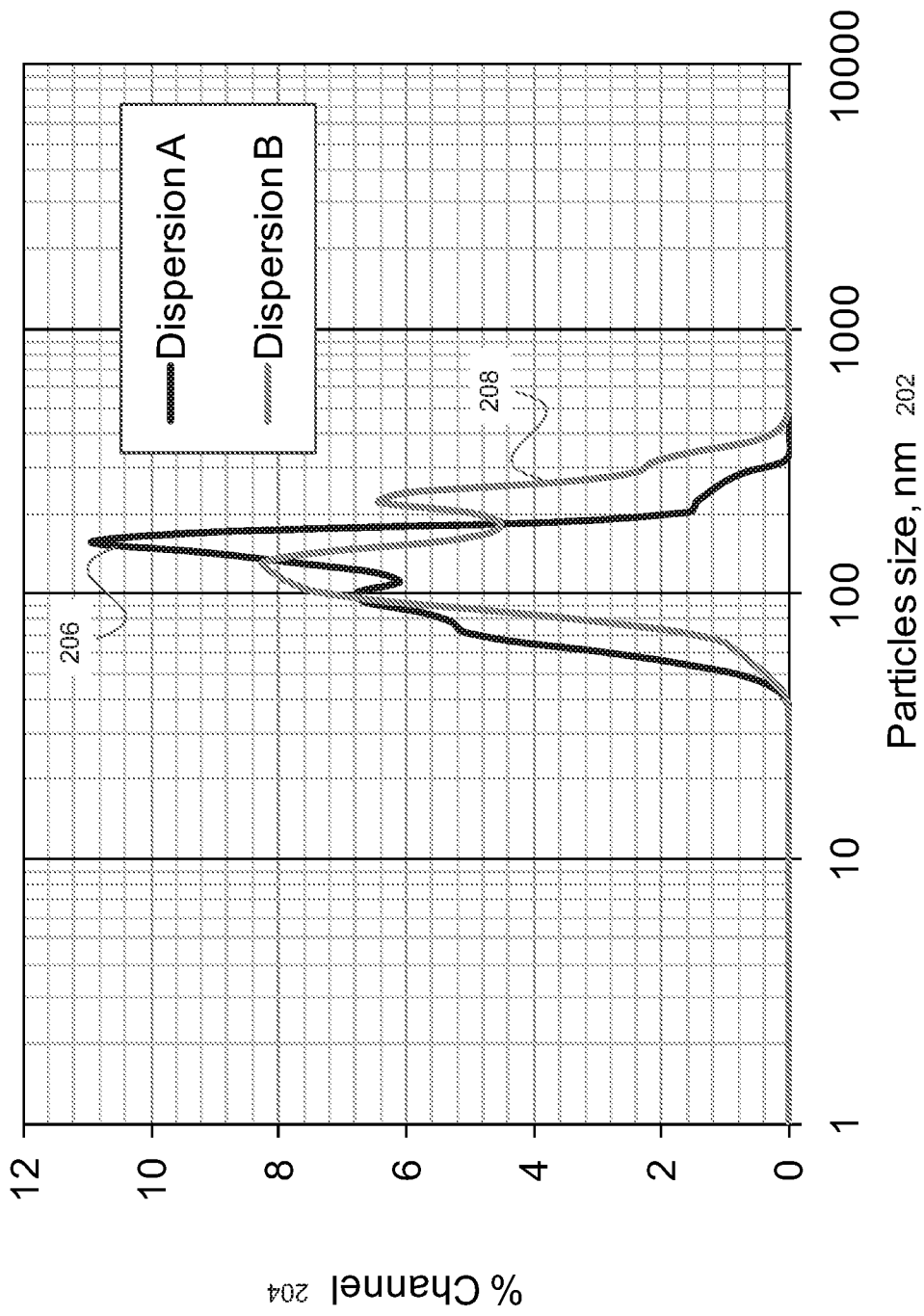


FIG. 2

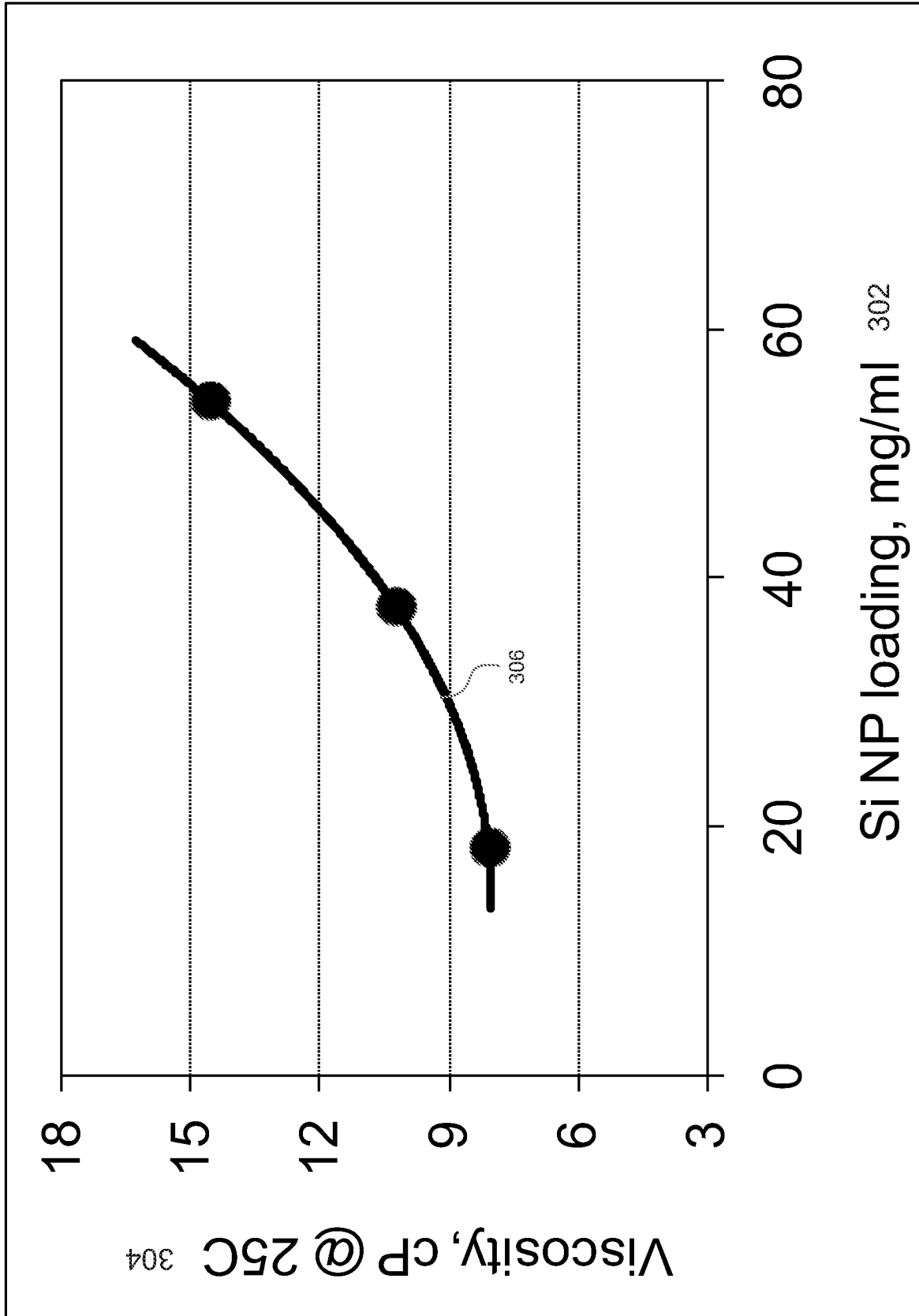


FIG. 3

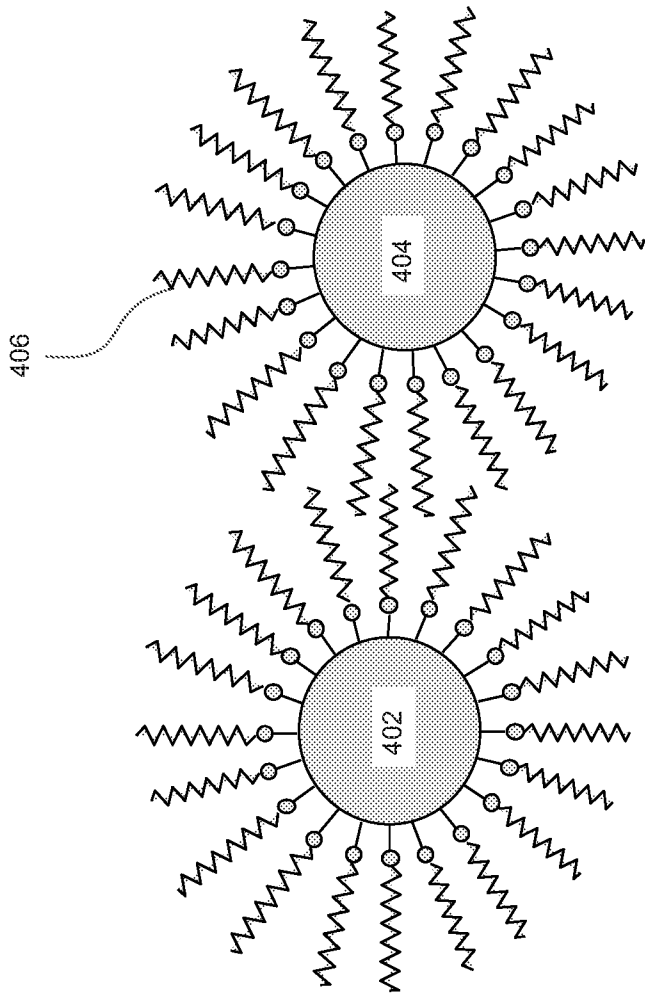


FIG. 4

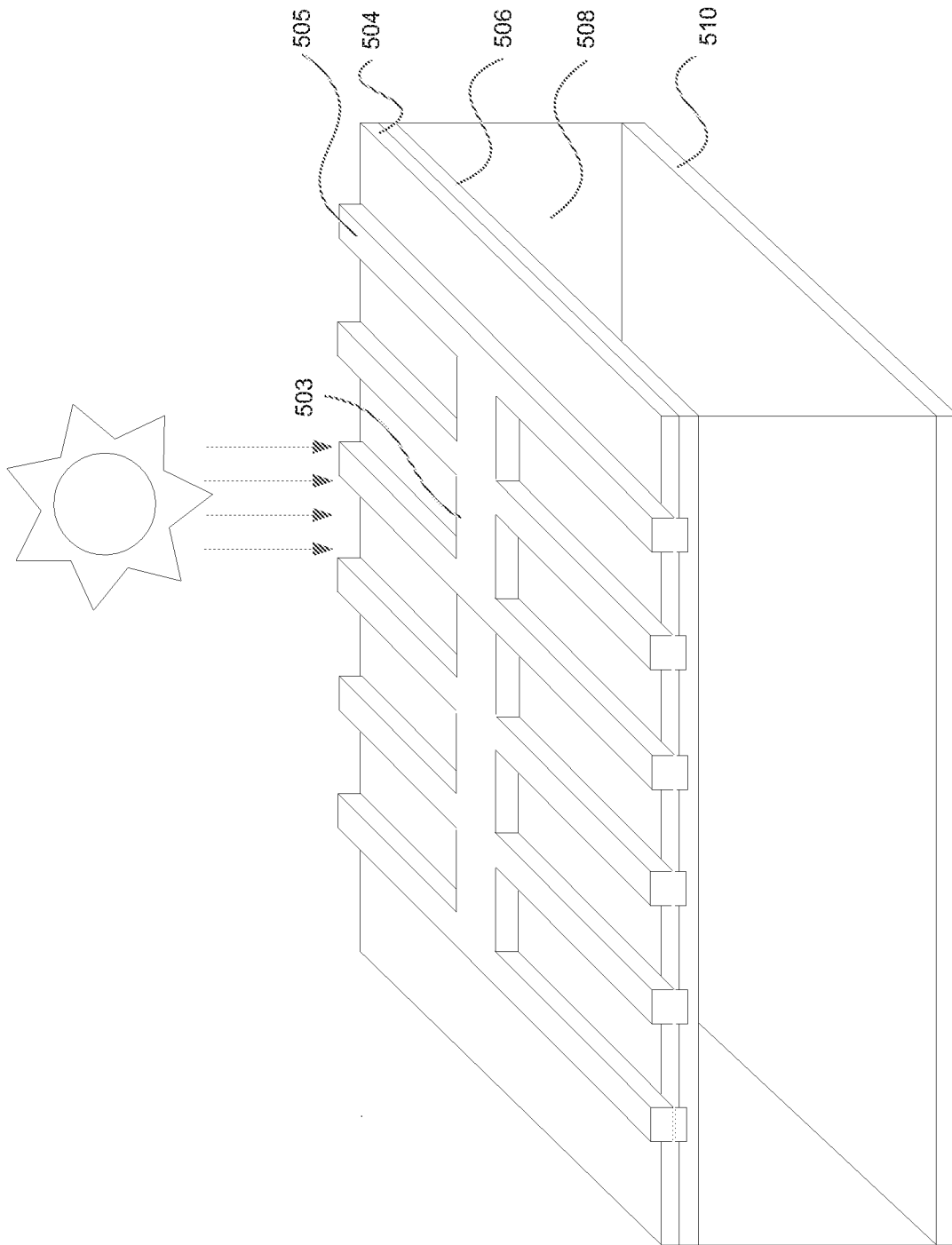


FIG. 5A

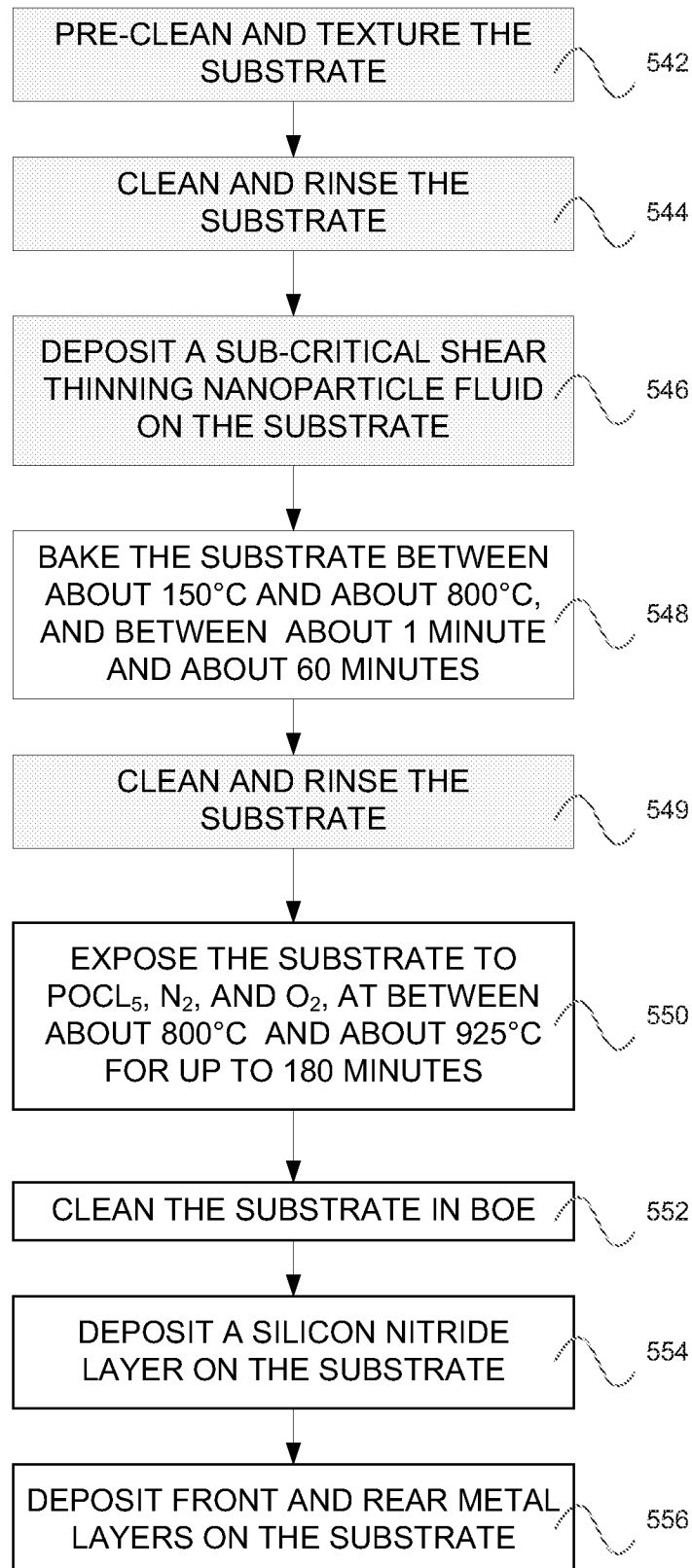


FIG. 5B

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 10/38596

A. CLASSIFICATION OF SUBJECT MATTER IPC(8) - H01B 1/02; H01L 21/208 (2010.01) USPC - 438/501; 252/519.32; 252/521.3 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) IPC(8): H01B 1/02; H01L 21/208 (2010.01) USPC: 438/501; 252/519.32; 252/521.3 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched IPC(8): H01B 1/02; H01L 21/208 (2010.01) USPC: 438/501; 252/519.32; 252/521.3 (keyword delimited) Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) PubWEST (PGPB,USPT,USOC,EPAB,JPAB); Google Scholar (Articles and patents) Search terms used: silicon nanoparticle "ethyl cellulose" alcohol ketone semiconductor shear piranha dopant (PSG OR phosphosilicate glass) oxygen nitrogen (phosphoryl chloride OR phosphorous oxychloride OR "pocl.sub.3") textur\$ clean\$ silicon nitride buffer\$																												
C. DOCUMENTS CONSIDERED TO BE RELEVANT																												
<table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>Y</td> <td>US 2008/0171425 A1 (POPLAVSKYY et al.) 17 July 2008 (17.07.2008), entire document, especially: Abstract, para [0011], [0020]-[0024], [0032]</td> <td>1-16</td> </tr> <tr> <td>Y</td> <td>US 2006/0163744 A1 (VANHEUSDEN et al.) 27 July 2006 (27.07.2006), para [0031], [0169], [0172], [0182], [0192], [0206]</td> <td>1-16</td> </tr> <tr> <td>Y</td> <td>US 5,151,386 A (BOTTARI et al.) 29 September 1992 (29.09.1992), col. 6, ln 13; col. 9, ln 49-65</td> <td>15, 17-28</td> </tr> <tr> <td>Y</td> <td>US 2008/0202576 A1 (HIESLMAIR et al.) 28 August 2008 (28.08.2008), para [0008], [0009], [0030]-[0041], [0050], [0065],</td> <td>17-28</td> </tr> <tr> <td>Y</td> <td>US 3,632,438 A (CARLSON et al.) 04 January 1972 (04.01.1972), col. 4, ln 59-67; col. 5, ln 14-19</td> <td>17-28</td> </tr> <tr> <td>Y</td> <td>US 2008/0078747 A (SAVU et al.) 03 April 2008 (03.04.2008), para [0001], [0004], [0050]</td> <td>18, 19, 21, 22</td> </tr> <tr> <td>Y</td> <td>US 2009/0107545 A1 (MOSLEHI) 30 April 2009 (30.04.2009), para [0015], [0107]</td> <td>20</td> </tr> <tr> <td>Y</td> <td>US 2005/0089748 A1 (OHLSEN et al.) 28 April 2005 (28.04.2005), para [0009]</td> <td>26-28</td> </tr> </tbody> </table>	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	Y	US 2008/0171425 A1 (POPLAVSKYY et al.) 17 July 2008 (17.07.2008), entire document, especially: Abstract, para [0011], [0020]-[0024], [0032]	1-16	Y	US 2006/0163744 A1 (VANHEUSDEN et al.) 27 July 2006 (27.07.2006), para [0031], [0169], [0172], [0182], [0192], [0206]	1-16	Y	US 5,151,386 A (BOTTARI et al.) 29 September 1992 (29.09.1992), col. 6, ln 13; col. 9, ln 49-65	15, 17-28	Y	US 2008/0202576 A1 (HIESLMAIR et al.) 28 August 2008 (28.08.2008), para [0008], [0009], [0030]-[0041], [0050], [0065],	17-28	Y	US 3,632,438 A (CARLSON et al.) 04 January 1972 (04.01.1972), col. 4, ln 59-67; col. 5, ln 14-19	17-28	Y	US 2008/0078747 A (SAVU et al.) 03 April 2008 (03.04.2008), para [0001], [0004], [0050]	18, 19, 21, 22	Y	US 2009/0107545 A1 (MOSLEHI) 30 April 2009 (30.04.2009), para [0015], [0107]	20	Y	US 2005/0089748 A1 (OHLSEN et al.) 28 April 2005 (28.04.2005), para [0009]	26-28	<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/>
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Y	US 2008/0171425 A1 (POPLAVSKYY et al.) 17 July 2008 (17.07.2008), entire document, especially: Abstract, para [0011], [0020]-[0024], [0032]	1-16																										
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<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"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</p> <p>"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</p> <p>"&" document member of the same patent family</p>																												
Date of the actual completion of the international search 27 September 2010 (27.09.2010)	Date of mailing of the international search report 08 OCT 2010																											
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774																											

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 10/38596

Continuation of Box No. III: Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

Two claim groups were found:

Group I: Claims 1-16

Group II: Claims 17-28

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: is directed to a silicon nanoparticle fluid comprising: a set of silicon nanoparticles, wherein the set of silicon nanoparticles is present in an amount of between about 1 wt% and about 20 wt% of the silicon nanoparticle fluid; a set of HMW molecules, wherein the set of HMW molecules is present in an amount of between about 0 wt% and about 10 wt% of the silicon nanoparticle fluid; and a set of capping agent molecules, wherein at least some capping agent molecules of the set of capping agent molecules are attached to the set of silicon nanoparticles.

Group II: is directed to a method for forming a dual-doped emitter on a silicon substrate with a sub-critical shear thinning nanoparticle fluid, the silicon substrate comprising a front surface and a rear surface, the method comprising: texturing the silicon substrate; cleaning the silicon substrate; depositing the sub-critical shear thinning nanoparticle fluid on the front surface; baking the silicon substrate at a first temperature of between about 150C to about 800C and for a first time period between about 1 minute and about 60 minutes; exposing the silicon substrate to a dopant source in a diffusion furnace with an atmosphere of POCh, N₂, and O₂, at a second temperature of between about 800C and about 950C, and for a second time period of between about 30 minutes and about 180 minutes, wherein a PSG layer is formed; removing the PSG layer; depositing an anti-reflection coating on the front surface; and depositing a set of front metal contacts on the front surface and a set of rear metal contacts on the rear surface.

The inventions listed as Groups I-II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Group I does not include the inventive concept of forming a PSG layer, removing the PSG layer, and depositing an anti-reflection coating, as required by group II.

Group II does not include the inventive concept of a set of HMW molecules and a set of capping agent molecules, as required by group I.

Groups I-II therefore lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 10/38596

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Two claim groups were found:
Group I: Claims 1-16
Group II: Claims 17-28

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid

-- please see extra Box

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

- Remark on Protest**
- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
 - The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
 - No protest accompanied the payment of additional search fees.