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(54) **FORMATION OF COMPOUND FILM FOR PHOTOVOLTAIC DEVICE**

(75) Inventors: **Matthew R. Robinson**, East Palo Alto, CA (US); **Chris Eberspacher**, Palo Alto, CA (US)

Correspondence Address:
JOSHUA D. ISENBERG
JDI PATENT
809 CORPORATE WAY
FREMONT, CA 94539 (US)

(73) Assignee: **Nanosolar, Inc.**, Palo Alto, CA (US)

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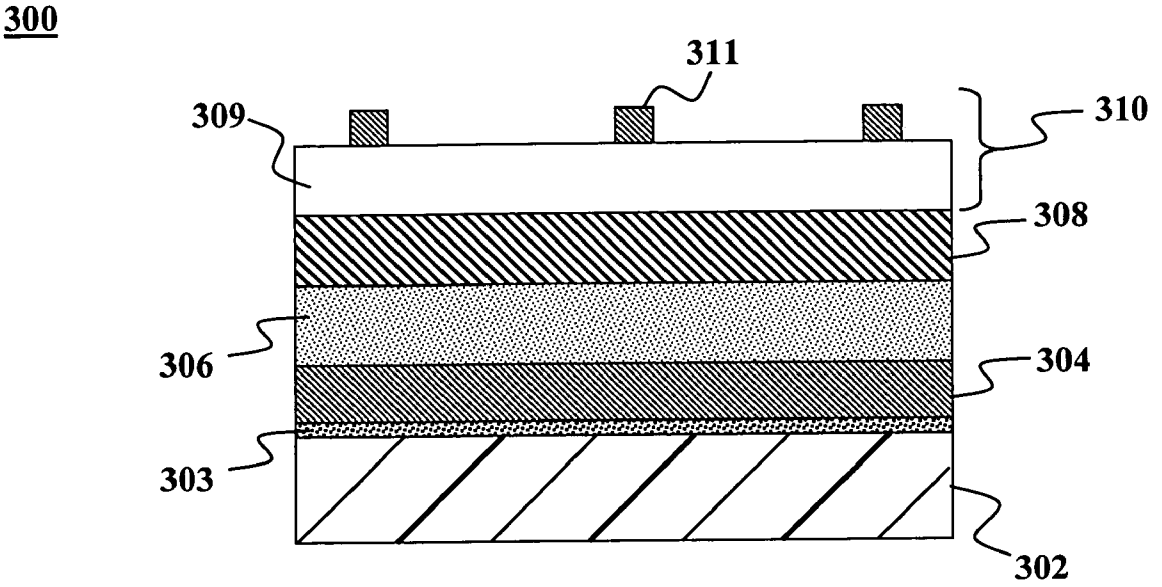
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(57) **ABSTRACT**

A compound film for an active layer of a photovoltaic device may be formed in two or more sub-layers. A first sub-layer having a first component of the active layer may be formed on a substrate with a first process. A second sub-layer including a second component of the active layer may then be formed using a second process such that the first sub-layer is disposed between the second sub-layer and the substrate. The second component has a different chemical composition than the first component. The first and/or second sub-layer may comprise one or more components in the form of particles and/or globules. This procedure may be repeated any number of times for any number of sub-layers so that active layer can be built up sequentially. The different chemical compositions of the components in the sub-layers can provide the active layer with a graded bandgap. The components of the sub-layers may include elements of group IB, and/or group IIIA. One or more elements of group VIA can be incorporated into the components of the sub-layers before, during or after formation of the layers.



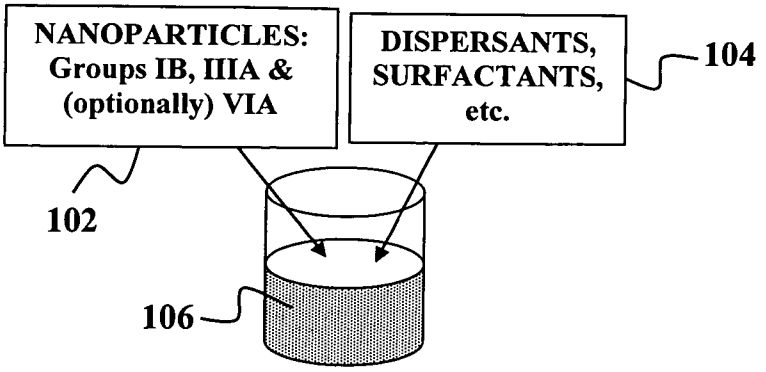


FIG. 1A

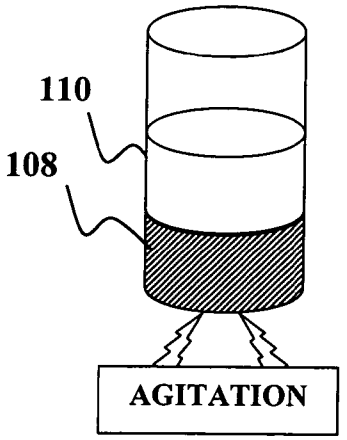


FIG. 1B

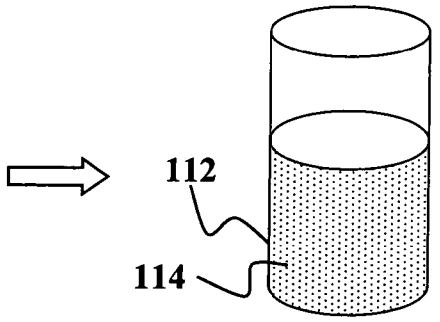


FIG. 1C

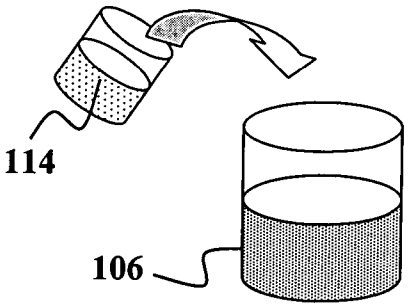


FIG. 1D

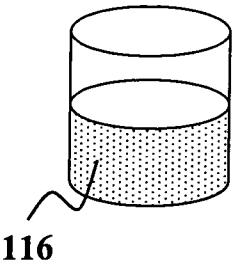


FIG. 1E

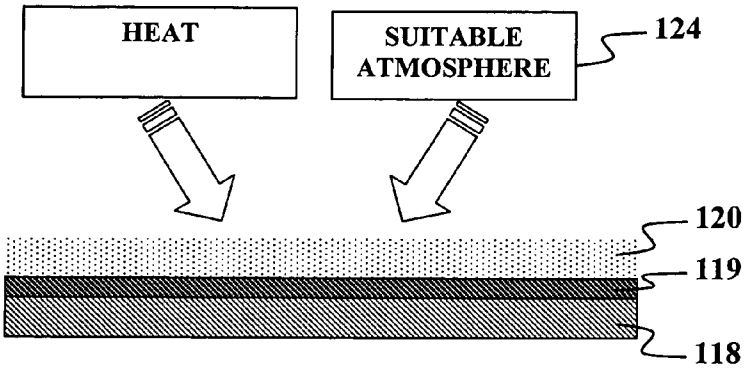


FIG. 2A

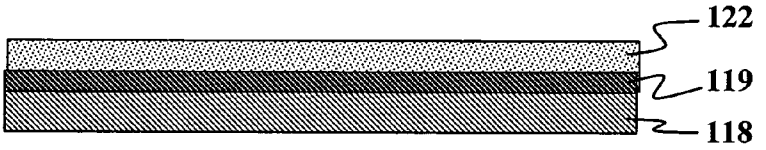


FIG. 2B

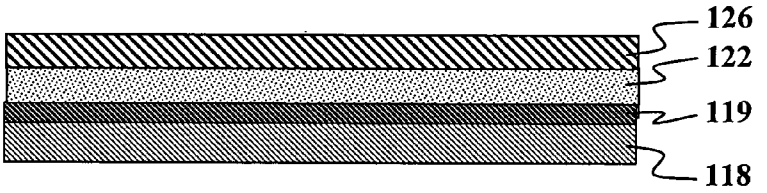


FIG. 2C

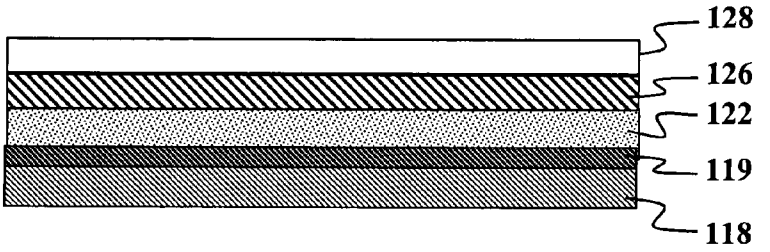


FIG. 2D

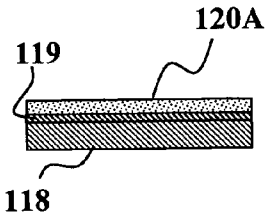


FIG. 2E

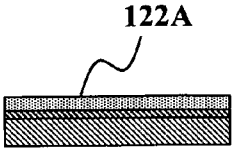


FIG. 2F

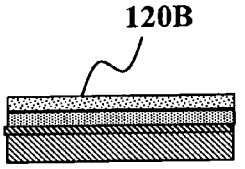


FIG. 2G

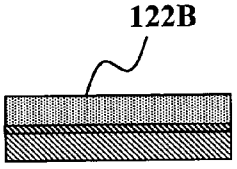


FIG. 2H

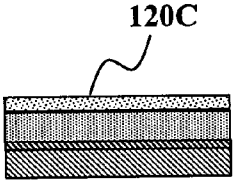


FIG. 2I

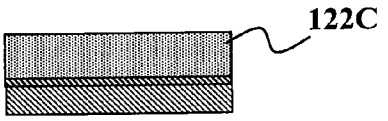


FIG. 2J

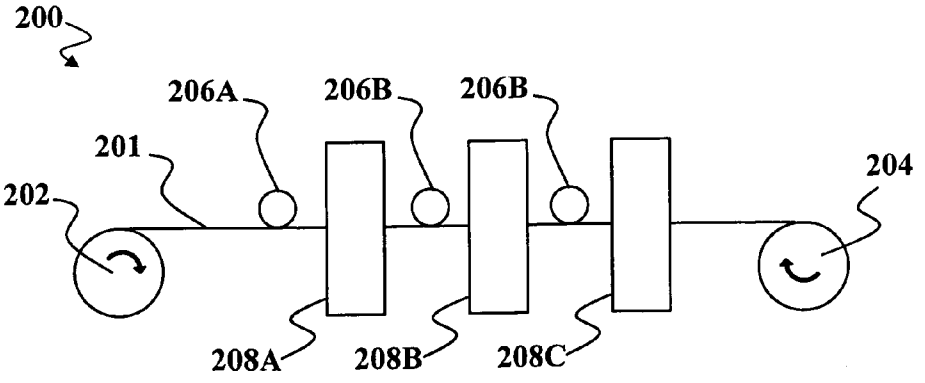


FIG. 2K

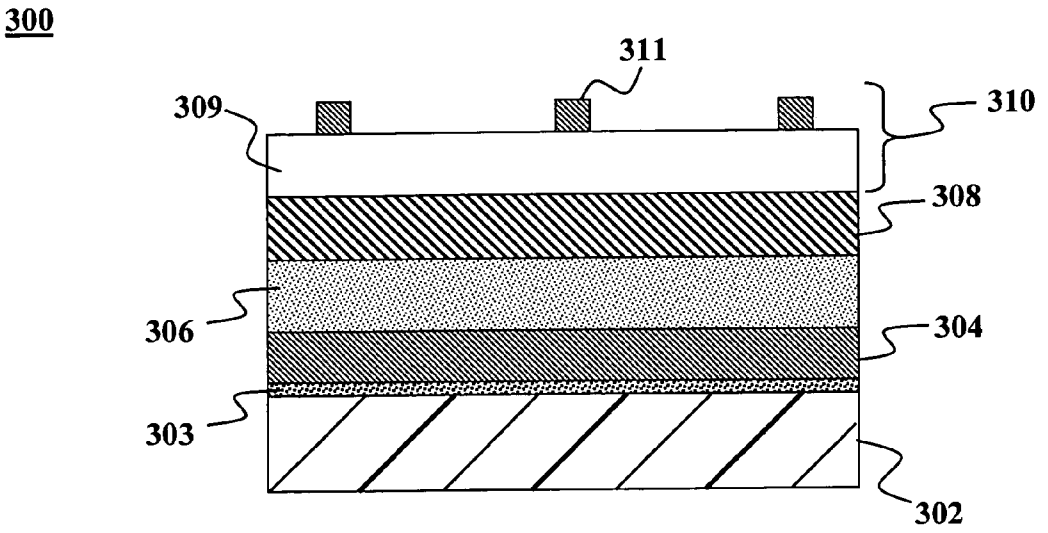

300
311
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303
302

FIG. 3

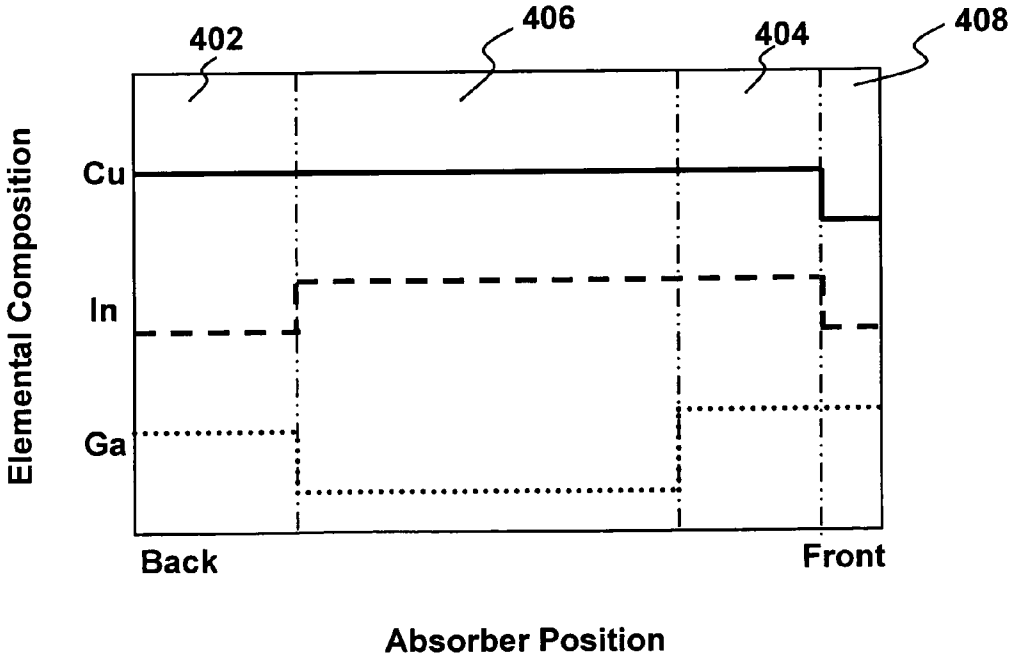

402
406
404
408
Cu
In
Ga
Elemental Composition
Back
Front
Absorber Position

FIG. 4

FORMATION OF COMPOUND FILM FOR PHOTOVOLTAIC DEVICE

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is a continuation-in-part of commonly-assigned, co-pending application Ser. No. 11/081,163, entitled "METALLIC DISPERSION", which was filed on Mar. 16, 2005, the entire disclosures of which are incorporated herein by reference. This application is also related to commonly-assigned, co-pending application Ser. No. 10/782,017, entitled "SOLUTION-BASED FABRICATION OF PHOTOVOLTAIC CELL" which was filed Feb. 19, 2004 and published as US Patent Application Publication 20050183767, and to commonly-assigned, co-pending application Ser. No. 10/943,658 entitled "FORMATION OF CIGS ABSORBER LAYER MATERIALS USING ATOMIC LAYER DEPOSITION AND HIGH THROUGHPUT SURFACE TREATMENT," which was filed Sep. 18, 2004 and published as US Patent Application Publication 20050186342, the entire disclosures of both of which are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] This invention is related to formation of nanoparticles and more particularly to formation of photovoltaic cells using nanoparticle inks for the fabrication of IB-IIIA-VIA absorber layers and where the absorber layers have a graded bandgap.

BACKGROUND OF THE INVENTION

[0003] Solar cells convert sunlight into electricity. These electronic devices have been traditionally fabricated using silicon (Si) as a light-absorbing, semiconducting material in a relatively expensive production process. To make solar cells more economically viable, solar cell device architectures have been developed that can inexpensively make use of thin-film, light-absorbing semiconductor materials such as copper-indium-gallium-sulfo-selenide, $Cu(In,Ga)(S,Se)_2$, also termed CI(G)S(S). Solar cells of this class typically have an absorber layer sandwiched between an electrode layer and a junction partner layer. The electrode layer is often Mo, while the junction partner is often CdS or ZnS. A transparent conductive oxide (TCO) such as zinc oxide (ZnO) is formed on the junction partner layer is typically used as a transparent electrode. CIGS-based solar cells have been demonstrated to have power conversion efficiencies exceeding 19%.

[0004] A central challenge in constructing a CIGS-based solar cell is that the components of the CIGS layer must be within a narrow stoichiometric ratio in order for the resulting cell to be highly efficient. Achieving precise stoichiometric composition over relatively larger substrate areas is however difficult using traditional vacuum-based deposition processes. For example, it is difficult to deposit compounds and/or alloys containing more than one element by sputtering or evaporation. Both techniques rely on deposition approaches that are limited to line-of-sight and limited-area sources, tending to result in poor surface coverage. Line-of-sight trajectories and limited-area sources can result in the non-uniform three-dimensional distribution of elements in all three dimensions and/or poor film-thickness uniformity over large areas. These non-uniformities can occur over the nano-meso, and/or macroscopic scales. Such non-uniformity also alters the local stoichiometric ratios of the absorber layer, decreasing the potential power conversion efficiency of the complete device.

[0005] Alternative approaches to vacuum-based deposition techniques such as sputtering and evaporation have been developed. In particular, production of solar cells on flexible substrates using semiconductor printing technologies provides a highly cost-efficient alternative to conventional vacuum-deposited solar cells. For example, T. Arita and coworkers [20th IEEE PV Specialists Conference, 1988, page 1650] described a screen printing technique that involved mixing and milling pure Cu, In and Se powders in the compositional ratio of 1:1:2 and forming a screen printable paste, screen printing the paste on a substrate, and sintering this film to form the compound layer. They reported that although they had started with elemental Cu, In and Se powders, after the milling step the paste contained the $CuInSe_2$ phase. However, solar cells fabricated using the sintered layers had very low efficiencies because the structural and electronic quality of these absorbers were poor.

[0006] Screen-printed $CuInSe_2$ deposited in a thin-film was also reported by A. Vervaet et al. [9th European Communities PV Solar Energy Conference, 1989, page 480], where a $CuInSe_2$ powder was used along with Se powder to prepare a screen printable paste. Layers formed by screen printing were sintered at high temperature. A difficulty in this approach was finding an appropriate fluxing agent for dense $CuInSe_2$ film formation. Solar cells made in this manner also had poor conversion efficiencies.

[0007] U.S. Pat. No. 5,985,691 issued to B. M. Basol et al describes another particle-based method to form a Group IB-IIIA-VIA compound film. The described method includes the steps of preparing a source material, depositing the source material on a base to form a precursor, and heating the precursor to form a film. In that method the source material includes Group IB-IIIA containing particles having at least one Group IB-IIIA phase, with Group IB-IIIA constituents present at greater than about 50 molar percent of the Group IB elements and greater than about 50 molar percent of the Group IIIA elements in the source material. The powder is milled to reduce its particle size and then used in the preparation of an ink which is deposited on the substrate in the form of a precursor layer. The precursor layer is then exposed to an atmosphere containing Group VIA vapors at elevated temperatures to convert the film into the compound. The precursor films deposited using this technique were porous and they yielded porous $CuInSe_2$ layers with small-grain regions as reported by G. Norsworthy et al. [Solar Energy Materials and Solar Cells, 2000, vol. 60, page 127]. Porous solar cell absorbers yield unstable devices because of the large internal surface area within the device, and small grains limit the conversion efficiency of solar cells. Another key limitation of this method was the inability to effectively incorporate gallium into the material. The properly-distributed presence of gallium in a CIS film serves to potentially broaden the bandgap of the semiconductor material, thereby increasing the open circuit voltage of the solar cell, and to promote the adhesion of the CIGS layer to a (Mo) electrode, providing a back surface electric field which can improve the collection of carriers. The absence of gallium decreases the potential power conversion

efficiency of the solar cell. In practice, while gallium oxide particles can easily be produced, it is very difficult to reduce gallium oxide, even at relatively high temperatures, and in the absence of reduction, gallium oxide cannot be effectively used as a precursor material for gallium in the final film. Accordingly, in addition to poor stability, solar cells made using the approach of Basol et al. had sub-optimal power conversion efficiency.

[0008] Eberspacher and Pauls in U.S. Pat. No. 6,821,559 describe a process for making phase-stabilized precursors in the form of fine particles, such as sub-micron multinary metal particles, and multi-phase mixed-metal particles comprising at least one metal oxide. The preparation of particulate materials was described using a range of methods including laser pyrolysis, atmospheric arc evaporation, solution precipitation, chemical vapor reactions, aerosol pyrolysis, vapor condensation, and laser ablation. In particular, aerosol pyrolysis was used to synthesize mixed-metal particulates comprising metal oxides formed as substantially solid and spherical particulates. These particulate precursor materials were then deposited onto large-area substrates in thin layers using any of a variety of techniques including slurry spraying methods such as pneumatic spraying with a pressurized gas nozzle, hydraulic spraying with a pressurized slurry expelled through an orifice, and ultrasonic spraying with a rapidly vibrating atomization surface. A disadvantage of solar cell devices comprised of thin-film absorber layers formed in this manner was the poor reproducibility of the resulting device performance, and the porous form of the absorber layer, which tends to result in poor device stability.

[0009] Bulent Basol in U.S. Published Patent application number 20040219730 describes a process of forming a compound film including formulating a powder material with a controlled overall composition and having particles of one solid solution. The powder material is deposited on a substrate to form a layer on the substrate, and this layer is reacted in at least one suitable atmosphere to form the compound. According to one preferred embodiment of that process, the compound film has a Cu/(In+Ga) compositional range of 0.7-1.0 and a Ga/(In+Ga) compositional range of 0.05-0.3. Due to the improved process window made available by the phase space of a solid solution, the use of nanoparticles comprised of a solid solution may improve the repeatability and the overall yield of the thin-film deposition and solar cell production process.

[0010] Using the solid-solution approach, gallium can be incorporated into the metallic dispersion in non-oxide form—but only with up to approximately 18 relative atomic percent (Subramanian, P. R. and Laughlin, D. E., in *Binary Alloy Phase Diagrams* 2nd *Edition*, edited by Massalski, T. B. 1990. ASM international, Materials Park, Ohio, pp 1410-1412; Hansen, M., *Constitution of Binary Alloys.* 1958. 2nd Edition, McGraw Hill, pp. 582-584.). The lack of a means to incorporate additional Ga beyond that possible through a solid-solution (containing either Cu+ Ga or In+Ga) restricts the potential performance of a device constructed by this method. In particular, since the presence of additional gallium in the light absorbing film can serve both to widen the bandgap of the semiconductor material and to increase the open circuit voltage of the solar cell, a lack of additional gallium in the light-absorbing thin film tends to decrease the potential power conversion efficiency of solar cells created in this manner. Efficient CIGS solar cells benefit from achieving a gallium ratio of up to 40 relative atomic percent. Furthermore, it would be simpler to directly work with elemental metallic nanoparticles rather than solid-solution metallic nanoparticles in that the elements can be optimized individually and they are more readily available in elemental form. However, no technique was known in the prior art to create gallium nanoparticle powders sufficient and adequate for semiconductor applications, in part because gallium is molten near room temperature and therefore does not lend itself to common techniques for creating nanoparticles in the form of powders that are then dispersed in solution (as is commonly done with the other elements). As a result, it was not possible to directly incorporate gallium (or incorporate gallium in a high percentage) into a metallic dispersion used to print the CIG precursor of a CIGS solar cell.

[0011] Robinson and Roscheisen, in commonly-assigned, co-pending, prior U.S. patent application Ser. No. 11/081,163, recently developed a technique to incorporate any desired amount of gallium into a nanoparticulate mixture used to form a compound film in a photovoltaic device. In this approach, a mixture of elemental nanoparticles composed of the IB, the IIIA, and, optionally, the VIA group of elements is combined with a suspension of nanoglobules of gallium to form a dispersion. The dispersion may be deposited onto a substrate to form a layer on the substrate. The layer may then be reacted in a suitable atmosphere to form the compound film that can be used as a light-absorbing layer in a photovoltaic device. However, this approach results in a compound film without an intentionally graded bandgap.

[0012] It would be highly desirable to grade the bandgap of a CIGS absorber layer by varying its composition as a function of depth, since there are numerous advantages to varying the relative concentrations of the components of the CIGS absorber layer. These advantages include (1) improved open circuit voltage; (2) improved short circuit current density; and (3) improved optoelectronic quality in the absorber layer. A detailed discussion of these and other advantages may be found in Olle Lundberg in "Band Gap Profiling and High Speed Deposition of Cu(In, Ga)Se_2 for Thin Film Solar Cells", *Comprehensive Summaries of Uppsala Dissertations From the Faculty of Science and Technology* 903, Acta Universitatis Upsaliensis, Uppsala, Sweden 2003, which is incorporated herein by reference.

[0013] In particular, the presence of higher concentrations of Ga at the back of the absorber layer can also act as a carrier reflector, directing carriers forward to the junction at the front of the absorber layer. In addition, higher amounts of Ga deposited at or near the back contact (e.g. near the Mo interface) of the CIGS cell tend to improve device function by forming smaller grains in the presence of Ga near the back contact region, where these smaller grains are less-mechanically stressed, thus improving the mechanical stability of the cell.

[0014] Further, a relatively high level of Ga in the middle of the CIGS absorber layer tends to negatively impact device function, as small $CuGaSe_2$ grains form. These small grains tend to have a high defect density and may act as sites for charge recombination in the absorber layer.

[0015] Finally, high amounts of Ga deposited at or near the front contact (e.g. near the TCO layer) of the CIGS cell promote improved device function in two ways: (1) a higher

bandgap (e.g. about 1.35 eV) near the front contact sets the voltage of the cell at a relatively higher value than would otherwise exist, allowing the absorption of more photons than would otherwise be possible, thus further increasing the efficiency of light harvesting, and (2) such a higher voltage couples with a lower current, resulting in fewer I^2R losses.

[0016] In the prior art, graded bandgap devices with graded concentration profiles have been prepared using co-evaporation in a vacuum from elemental and/or alloy sources, and have produced the best performing CIGS solar cells recorded to date. For example, Ramanathan and coworkers at the National Renewable Energy Laboratory showed a cell having a 19.2% conversion efficiency with a fill factor of 78.12%, Jsc=35.71 mA/cm^2, and an open-circuit voltage of 0.69 V using this approach (see K. Ramanathan et al., "Properties of 19.2% Efficiency ZnO/CdS/CuInGaSe$_2$ Thin-Film Solar Cells", *Progress in Photovoltaics: Research and Applications*. Vol. 11 2003, pp. 225-230). However, this device was formed on a relatively small substrate, and the compound film was formed over a relatively long time. This fabrication method does not provide an efficient approach for high-volume solar cell production.

[0017] Further, as described above, there are several challenges and disadvantages associated with evaporation or other vacuum-based deposition techniques for the CIGS absorber layer, including but not limited to (a) relatively high production cost, (b) relatively poor spatial and chemical uniformity of deposited compound films, and (c) relatively low throughput, limiting the potential for high-volume production. Moreover, the creation of a bandgap graded absorber layer using evaporative sources requires a relatively expensive real-time monitoring system to assess the relative composition of the absorber layer as it is being constructed.

[0018] Thus, there is a need in the art for a method of forming a material comprised of gallium-containing nanoparticulate CIGS precursor materials, where the precursor materials can be reproducibly, uniformly, and densely printed over large substrate areas to form the absorber layer of a thin-film CIGS solar cell, and where the absorber layer has a graded bandgap.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] The teachings of the present invention can be readily understood by considering the following detailed description in conjunction with the accompanying drawings, in which:

[0020] **FIGS. 1A-1E** are a sequence of schematic diagrams depicting the formation of a composition of matter according to an embodiment of the present invention.

[0021] **FIGS. 2A-2B** are a sequence of cross-sectional schematic diagrams illustrating the formation of a compound film using the composition of matter according to an embodiment of the present invention.

[0022] **FIGS. 2C-2D** are a sequence of cross-sectional schematic diagrams illustrating the fabrication of a photovoltaic device using the compound film according to an embodiment of the present invention.

[0023] **FIGS. 2E-2J** are a sequence of cross-sectional schematic diagrams illustrating formation of an absorber layer with an iterative sequence according an alternative embodiment of the present invention.

[0024] **FIG. 2K** is a schematic diagram illustrating roll-to-roll manufacturing of photovoltaic devices according to an embodiment of the present invention.

[0025] **FIG. 3** is a schematic diagram of a photovoltaic cell according to an embodiment of the present invention.

[0026] **FIG. 4** is a graph illustrating concentration profiles for a CIGS absorber layer that may be obtained according to embodiments of the present invention.

DESCRIPTION OF THE SPECIFIC EMBODIMENTS

[0027] Although the following detailed description contains many specific details for the purposes of illustration, anyone of ordinary skill in the art will appreciate that many variations and alterations to the following details are within the scope of the invention. Accordingly, the examples of embodiments of the invention described below are set forth without any loss of generality to, and without imposing limitations upon, the claimed invention.

[0028] According to embodiments of the present invention, a compound film for an active layer of a photovoltaic device may be formed in two or more sub-layers. A first sub-layer having a first component of the active layer may be formed on a substrate with a first process.

[0029] A second sub-layer including a second component of the active layer may then be formed using a second process such that the first sub-layer is disposed between the second sub-layer and the substrate. The second component has a different chemical and/or physical composition than the first component. This procedure may be repeated any number of times for any number of sub-layers so that active layer can be built up sequentially. The different chemical compositions of the components in the sub-layers can provide the active layer with a graded bandgap. The components of the sub-layers may include elements of group IB, and/or group IIIA. One or more elements of group VIA can be incorporated into the components of the sub-layers before, during or after formation of the layers. Although, for the sake of example, the active layer is described as having first and second sub-layers, the active layer may be made with any number of additional sub-layers and corresponding components.

[0030] There are a number of different processes for forming the any or all of the sub-layers. Many of these processes involve "printing" a precursor film. Such precursor films may be made, e.g., using particle-based inks. As used herein, the term particle generally refers to a relatively small discrete portion of some substance having a defined chemical composition. The term particle is intended to encompass both discrete quantities of solid matter and discrete quantities of liquid matter. The term "globule" is often used herein to refer to particles of matter in the liquid state. In addition, the expressions "nanoparticles" and "nanoparticulates" as used herein refer to particles (in either the liquid or solid state) characterized by nanometer-scale dimensions, e.g. sizes ranging from about 1 nm to about 1000 nm. Nanoparticles are discrete entities sized less than about 1000 nm, more preferably less than about 500 nm, and still more preferably less than about 250 nm. When the

nanoparticles are sized less than about 10 nm, their chemical, physical, electronic, and optical properties often change relative to that of bulk material, and at about the 10 nm or less size scale, nanoparticles are also called "quantum dots". As used herein, the expression "nanoglobule" similarly refers to globules (as that term is defined above) characterized by nanometer-scale dimensions, e.g., sizes ranging from about 1 nm to about 1000 nm.

[0031] The use of particles in forming such inks is useful in that the particle sizes and compositions can be controlled to adjust the properties of the ink and the resulting film. For example, decreased particle size can significantly lower both the melting point and the sintering temperature required (see e.g., C R M Wronski, "*The Size Dependence of the Melting point of Small Particles of Tin*" in the *British Journal of Applied Physics* vol. 18. No. 12, (December 1967) pp 1731-1737, IOP Publishing, Bristol, UK; L. H. Allen, "Nanocalorimetry Studies of Materials: Melting Point Depression and Magic Nanostructures" NNUN Abstracts 2002/Materials, Physics, Processes & Characterization, pp 40; Zhang et al., 2000. "Size-dependent melting point depression of nanostructures: Nanocalorimetric measurements." Phys. Rev. B 62 (15): 548-557; Lisecki et al. 2000. "Annealing Process of Anisotropic Copper Nanocrystals." 2. Rods. Langmuir 16: 8807-8808). Generally, reduction in the melting point is inversely proportional to the particle radius, i.e., the smaller the nanoparticles, the lower the melting point.

[0032] Smaller particles also tend to pack closer together and make better contact with each other.

[0033] Reduction in size from bulk material to particles in about the 500 nm regime can already show significant differences in melting point and other altered physical and chemical properties. With much smaller particle sizes, e.g. in the nanometer size range, the surface area of particles will increase and nanoparticles will be in intimate contact with each other. In addition, in the nanometer size range, the reactivity of the particles and interaction between nanoparticles will be enhanced. This can help particles fuse together more easily, thereby enhancing the cohesion of the resulting CIGS layer (W. H. Qi, et al. in "China—EU Forum on Nanosized Technology" Beijing, P. R. China. December 2002. pp 86-92). This promotes coalescence between neighboring particles during sintering.

[0034] By way of example, nanopaticulate-based inks containing elements and/or solid solutions from groups IB, IIIA and optionally VIA may be formed as described in commonly-assigned US Patent Application publication 20050183767, which has been incorporated herein by reference. A film of the liquid ink can be spread onto the substrate and annealed to form the first or second layer. By way of example the liquid ink can be made by forming and non-oxide nanoparticles containing elements from group IB, group IIIA and, optionally, group VIA and intermixing these nanoparticles and adding them to a liquid to from an ink.

[0035] In one embodiment any or all of the sub-layers may be formed by depositing a source material on the substrate to form a precursor, and heating the precursor to form a film. The source material may include Group IB-IIIA containing particles having at least one Group IB-IIIA phase, with Group IB-IIIA constituents present at greater than about 50 molar percent of the Group IB elements and greater than about 50 molar percent of the Group IIIA elements in the source material. Additional details of this technique are described in U.S. Pat. No. 5,985,691 to Basol, which is incorporated herein by reference.

[0036] In another embodiment any or all of the sub-layers may be made from a precursor film containing one or more phase-stabilized precursors in the form of fine particles comprising at least one metal oxide. The oxides may be reduced in a reducing atmosphere. In particular single-phase mixed-metal oxide particles with an average diameter of less than about 1 micron may be used for the precursor. Such particles can be fabricated by preparing a solution comprising Cu and In and/or Ga as metal-containing compounds; forming droplets of the solution; and heating the droplets in an oxidizing atmosphere. The heating pyrolyzes the contents of the droplets thereby forming single-phase copper indium oxide, copper gallium oxide or copper indium gallium oxide particles. These particles can then be mixed with solvents or other additives to form a precursor material which can be deposited on the substrate, e.g., by screen printing, slurry spraying or the like, and then annealed to form the sub-layer. Additional details of this technique are described in U.S. Pat. No. 6,821,559 to Eberspacher, which is incorporated herein by reference.

[0037] In another embodiment, the sub-layers may be deposited using a precursor in the form of a nano-powder material formulated with a controlled overall composition and having particles of one solid solution. The nano-powder material precursor may be deposited to form the first, second layer or subsequent sub-layers, and reacted in at least one suitable atmosphere to form the corresponding component of the active layer. The precursor may be formulated from a nano-powder, i.e. a powdered material with nano-meter size particles. Compositions of the particles constituting the nano-powder used in precursor formulation are important for the repeatability of the process and the quality of the resulting compound films. The particles making up the nano-powder are preferably near-spherical in shape and their diameters are less than about 200 nm, and preferably less than about 100 nm. Alternatively, the nano-powder may contain particles in the form of small platelets. The nano-powder preferably contains copper-gallium solid solution particles, and at least one of indium particles, indium-gallium solid-solution particles, copper-indium solid solution particles, and copper particles.

[0038] Alternatively, the nano-powder may contain copper particles and indium-gallium solid-solution particles. The nano-powder may additionally contain Group VIA particles, e.g., particles of Se, S and Te or their alloys or solid solutions.

[0039] The nano-powder may be mixed with well known solvents, carriers, dispersants etc. to prepare an ink or a paste that is suitable for deposition onto a substrate. Alternatively, nano-powder particles may be prepared for deposition on a substrate through dry processes such as dry powder spraying, electrostatic spraying or processes which are used in copying machines and which involve rendering charge onto particles which are then deposited onto substrates. After precursor formulation, the precursor, and thus the nano-powder constituents are deposited onto a substrate in the form of a micro-layer, e.g., using dry or wet processes. Dry processes include electrostatic powder deposition

approaches where the prepared powder particles may be coated with poorly conducting or insulating materials that can hold charge. Examples of wet processes include screen printing, ink jet printing, ink deposition by doctor-blading, reverse roll coating etc. In these approaches the nano-powder may be mixed with a carrier which may typically be a water-based or organic solvent, e.g., water, alcohols, ethylene glycol, etc. The carrier and other agents in the precursor formulation may be totally or substantially evaporated away to form the micro-layer on the substrate. The micro-layer can subsequently be reacted to form the sub-layer. The reaction may involve an annealing process, such as furnace-annealing, RTP or laser-annealing, microwave annealing, among others. Annealing temperatures may be in 350-600° C. and preferably between 400-550° C. If the micro-layer contains Group VIA particles, the annealing atmosphere may be inert. Alternatively, reaction step may employ an atmosphere with the vapors of at least one of Group VIA elements (Se,S,Te) to provide a desired level of Group VIA elements in the sub-layer. Further details of this technique are described in US Patent Application Publication 20040219730 to Bulent Basol, which is incorporated herein by reference.

[0040] In some embodiments, the group IIIA element may be provided in molten form. For example, an ink may be made starting with a molten mixture of Gallium and/or Indium (commercially available, e.g., from Alfa Aesar of Ward Hill, Mass.). Copper nanoparticles may then be added to the mixture, which may then be used as the ink/paste. Copper nanoparticles are available commercially, e.g., from Materials Modification Inc., of Fairfax, Va.

[0041] Alternatively, the temperature of the Cu—Ga—In mixture may be adjusted (e.g. cooled) until a solid forms. The solid may be ground at that temperature until small nanoparticles (e.g., less than about 100 nm) are present. Selenium may be added to the ink and/or a film formed from the ink by exposure to selenium vapor, e.g., before, during, or after annealing.

[0042] The nanoparticles may be in a desired particle size range of between about 0.1 nm and about 500 nm in diameter, preferably between about 0.1 nm and about 10 nm in diameter. For each element, a majority of the mass of the non-oxide quantum nanoparticles may range in size from no more than about 40% above or below an average particle size, or, if the average particle size is less than about 5 nanometers, from no more than about 2 nanometers above or below the average particle size. Methods to make nanoparticles of the desired materials having the desired narrow particle size distribution include controlling the reaction conditions under which the nanoparticles are made or using size-selective precipitation and other techniques (such as ultrafiltration and membrane emulsification) to separate out particles in the desired size range.

[0043] In other embodiments of the invention, the first or second layer may be fabricated by forming a molten mixture of one or more metals of group IIIA and metallic nanoparticles containing elements of group IB and coating the substrate with a film formed from the molten mixture. The molten mixture may include a molten group IIIA element containing nanoparticles of a group IB element and (optionally) another group IIIA element. By way of example nanoparticles containing copper and gallium may be mixed with molten indium to form the molten mixture. The molten mixture may also be made starting with a molten mixture of Indium and/or Gallium (commercially available, e.g., from Alfa Aesar of Ward Hill, Mass.). Copper nanoparticles may then be added to the molten mixture. Copper nanoparticles are available commercially, e.g., from Materials Modification Inc., of Fairfax, Va. Alternatively, such nanoparticles can be produced using any of a variety of well-developed techniques, including but not limited to (i) electro-explosion of copper wire, (ii) mechanical grinding of copper particles for a sufficient time so as to produce nanoparticles, or (iii) solution-based synthesis of copper nanoparticles from organometallic precursors. Alternatively, the temperature of a molten Cu—Ga—In mixture may be adjusted (e.g. cooled) until a solid forms. The solid may be ground at that temperature until small nanoparticles (e.g., less than 5 nm) are present. Selenium and/or sulfur may optionally be added to the molten mixture, and/or a coating formed from the molten mixture before, during or after coating the substrate. Additional details of this technique are described in commonly assigned US Patent Application publication 2005183768, which is incorporated herein by reference.

[0044] Alternatively the first or second layer may be fabricated using coated nanoparticles as described in commonly-assigned U.S. patent application Ser. No. 10/943,657, which is incorporated herein by reference. Various coatings could be deposited, either singly, in multiple layers, or in alternating layers, all of various thicknesses. Specifically, core nanoparticles containing one or more elements from group IB and/or IIIA and/or VIA may be coated with one or more layers containing elements of group IB, IIIA or VIA to form coated nanoparticles. Preferably at least one of the layers contains an element that is different from one or more of the group IB, IIIA or VIA elements in the core nanoparticle. The group IB, IIIA and VIA elements in the core nanoparticle and layers may be in the form of pure elemental metals or alloys of two or more metals. By way of example, and without limitation, the core nanoparticles may include elemental copper, or alloys of copper with gallium, indium, or aluminum and the layers may be gallium, indium or aluminum. Using nanoparticles with a defined surface area, a layer thickness could be tuned to give the proper stoichiometric ratio within the aggregate volume of the nanoparticle. By appropriate coating of the core nanoparticles, the resulting coated nanoparticles can have the desired elements intermixed within the size scale of the nanoparticle, while the stoichiometry (and thus the phase) of the coated nanoparticle may be tuned by controlling the thickness of the coating(s).

[0045] In certain embodiments of the invention, the sub-layers may be annealed, either sequentially or simultaneously. According to embodiments of the present invention, the sub-layer(s) may be annealed by rapid heating from an ambient temperature to a plateau temperature range of between about 200° C. and about 600° C. The temperature is maintained in the plateau range for a period of time ranging between about a fraction of a second to about 60 minutes, and subsequently reduced. Alternatively, the annealing temperature could be modulated to oscillate within a temperature range without being maintained at a particular plateau temperature. This technique (referred to herein as rapid thermal annealing or RTA) is particularly suitable for forming photovoltaic active layers (sometimes called "absorber" layers) on metal foil substrates, such as

aluminum foil. Additional details of this technique are described in U.S. patent application Ser. No. 10/943,685, which is incorporated herein by reference.

[0046] Other alternative embodiments of the invention utilize techniques other than printing processes to form the absorber layer. For example, a group IB, group IIIA and/or group VIA elements can be deposited onto the top surface of a substrate and/or onto the top surface of one or more of the sublayers of the active layer by atomic layer deposition (ALD). For example a thin layer of Ga may be deposited by ALD at the top of a stack of sub-layers formed by printing techniques. By use of ALD, copper, indium, gallium, and selenium can be deposited in a precise stoichiometric ratio that is intermixed at or near the atomic level.

[0047] Furthermore, by changing sequence of exposure pulses for each precursor material, the relative composition of C, I, G and S within each atomic layer can be systematically varied as a function of deposition cycle and thus depth within the absorber layer. Such techniques are described in US Patent Application Publication 20050186342, which is incorporated herein by reference. Alternatively, the top surface of a substrate could be coated by using any of a variety of vacuum-based deposition techniques, including but not limited to sputtering, evaporation, chemical vapor deposition, physical vapor deposition, electron-beam evaporation, and the like.

[0048] In another embodiment, the various sub-layers of a IB-IIIA-VIA compound film for use as a light-absorbing layer in a photovoltaic device, may be formed using a composition of matter in the form of a dispersion containing a mixture of elemental nanoparticles of the IB, the IIIA, and, optionally, the VIA group of elements, dispersed with a suspension of nanoglobules of Gallium. Based on the relative ratios of input elements, the gallium nanoglobule-containing dispersion can then have a Cu/(In+Ga) compositional ratio ranging from 0.01 to 1.0 and a Ga/(In+Ga) compositional ratio ranging from 0.01 to 1.0. This technique is described in commonly-assigned U.S. patent application Ser. No. 11/081,163, which has been incorporated herein by reference.

[0049] As illustrated in **FIG. 1A** a mixture **106** of elemental nanoparticles **102** of the IB, the IIIA, and, optionally, the VIA group of elements is formed by combining nanoparticles **102** comprised of the element of the IB group of elements (e.g. Copper) with nanoparticles comprised of the element of the IIIA group of elements (e.g. indium) and optionally nanoparticles comprised of the VIA group of elements (e.g. Selenium, Sulfur and/or Tellurium).

[0050] The mixture of elemental nanoparticles **102** may optionally include Aluminum, Tellurium, or Sulfur. For example, any or all of these classes of nanoparticles may be optionally doped with one or more inorganic materials. Examples of such inorganic materials include but are not limited to Aluminum (Al), Sulfur (S), Sodium (Na), Potassium (K), or Lithium (Li). The nanoparticles **102** typically have average diameters ranging from 10 nm to 1000 nm, more preferably from 10 nm to 500 nm, and most preferably, from 10 nm to 100 nm. Preferably, the nanoparticles are less than about 500 nm in diameter, more preferably less than about 100 nm and even more preferably less than about 50 nm. Various techniques may be used for making such nanoparticles, including but not limited to dry-synthesis techniques such as evaporation-condensation (Granqvist and Buhrman, 1976, "Ultrafine metal particles", J. Applied Physics 47 (5): 220-2219, which is incorporated herein by reference) and the electro-explosion of wire (Tepper, "Nanosized Alumina Fibers", Advanced Materials, American Ceramic Society Bulletin, Vol. 80, No. 6, June 2001, which is incorporated herein by reference), and wet chemical techniques, including but not limited to thermal decomposition of organometallic precursors (Hambrock et al, 2002, Chem. Commun. 68-69, which is incorporated by reference) and metal salt reduction (Cai et al., 2004. Applied Surface Science 226: 422-426; Capek, 2004. Adv. In Colloid and Interface Science 110: 49-74, both of which are incorporated by reference). In addition, nanoparticles of certain elements, such as copper are commercially available from a variety of vendors in the form of nano-powders.

[0051] The nanoparticles **102** are mixed together and with one or more chemicals **104** including but not limited to surfactants (surface active agents such as dispersants, anti-flocculants, wetting agents and the like), polymers, binders, cross-linking agents, emulsifiers, anti-foaming agents, dryers, solvents, fillers, extenders, thickening agents, film conditioners, anti-oxidants, flow agents, leveling agents, and corrosion inhibitors.

[0052] Dispersants are used to prevent ultrafine flocculating particles from coalescing, thus facilitating the suspension of solid materials in a liquid medium and stabilizing the dispersion thereby produced. If particle surfaces attract one another, then flocculation occurs, resulting in aggregation and decreasing stability and/or homogeneity. If particle surfaces repel one another, then stabilization occurs, where fine particles do not aggregate and tend not to settle out of solution as fast.

[0053] An efficient dispersing agent can typically perform pigment wetting, dispersing, and stabilizing. Dispersing agents are different depending on the nature of the ink/paint. Polyphosphates, styrene-maleinates and polyacrylates are often used for aqueous formulations whereas fatty acid derivatives and low molecular weight modified alkyd and polyester resins are often used for organic formulations.

[0054] Wetting agents lower the surface tension of the solvent in which they dissolve, and keep the surface tension of an (aqueous) medium low so that an ink interacts with a substrate surface. Certain types of wetting agents are also used as dispersing agents. Wetting agents typically contain both a hydrophobic carbon chain and a hydrophilic polar group. The polar group can be non-ionic. If the polar group is ionic, the charge can be either positive or negative, resulting in cationic or anionic surfactants. Zwitterionic surfactants contain both positive and negative charges within the same molecule; one example is N-n-Dodecyl-N, N-diemthyl betaine. Certain surfactants are often used as dispersant agents for aqueous solutions. Representative classes include acetylene diols, fatty acid derivatives, phosphate esters, sodium polyacrylate salts, polyacrylic acids, soya lecithin, trioctylphosphine (TOP), and trioctylphosphine oxide (TOPO).

[0055] Binders and resins are often used to hold together proximate particles in a nascent or formed dispersion. Examples of typical binders include acrylic monomers (both as monofunctional diluents and multifunctional reactive agents), acrylic resins (e.g. acrylic polyol, amine synergists,

epoxy acrylics, polyester acrylics, polyether acrylics, styrene/acrylics, urethane acrylics, or vinyl acrylics), alkyd resins (e.g. long-oil, medium-oil, short-oil, or tall oil), adhesion promoters such as polyvinyl pyrrolidone (PVP), amide resins, amino resins (such as melamine-based or urea-based compounds), asphalt/bitumen, butadiene acrylonitriles, cellulosic resins (such as cellulose acetate butyrate (CAB)), cellulose acetate proprionate (CAP), ethyl cellulose (EC), nitrocellulose (NC), or organic cellulose ester), chlorinated rubber, dimer fatty acids, epoxy resin (e.g. acrylates, bisphenol A-based resins, epoxy UV curing resins, esters, phenol and cresol (Novolacs), or phenoxy-based compounds), ethylene co-terpolymers such as ethylene acrylic/methacrylic Acid, E/AA, E/M/AA or ethylene vinyl acetate (EVA), fluoropolymers, gelatin (e.g. Pluronic F-68 from BASF Corporation of Florham Park, N.J.), glycol monomers, hydrocarbon resins (e.g. aliphatic, aromatic, or coumarone-based such as indene), maelic resins, modified urea, natural rubber, natural resins and gums, rosins, modified phenolic resins, resols, polyamide, polybutadienes (liquid hydroxyl-terminated), polyesters (both saturated and unsaturated), polyolefins, polyurethane (PU) isocyanates (e.g. hexamethylene diisocynate (HDI), isophorone diisocyanate (IPDI), cycloaliphatics, diphenylmethane disiocyanate (MDI), toluene diisocynate (TDI), or trimethylhexamethylene diisocynate (TMDI)), polyurethane (PU) polyols (e.g. caprolactone, dimer-based polyesters, polyester, or polyether), polyurethane (PU) dispersions (PUDs) such those based on polyesters or polyethers, polyurethane prepolymers (e.g. caprolactone, dimer-based polyesters, polyesters, polyethers, and compounds based on urethane acrylate), Polyurethane thermoplastics (TPU) such as polyester or polyether, silicates (e.g. alkyl-silicates or water-glass based compounds), silicones (amine functional, epoxy functional, ethoxy functional, hydroxyl functional, methoxy functional, silanol functional, or cinyl functional), styrenes (e.g. styrene-butadiene emulsions, and styrene/vinyl toluene polymers and copolymers), or vinyl compounds (e.g. polyolefins and polyolefin derivatives, polystyrene and styrene copolymers, or polyvinyl acetate (PVAC)).

[0056] Emulsifiers are dispersing agents that blend liquids with other liquids by promoting the breakup of coalescing materials into small droplets and therefore stabilize the suspension in solution. For example, sorbitan esters are used as an emulsifier for the preparation of water-in-oil (w/o) emulsions, for the preparation of oil absorption bases (w/o), for the formation of w/o type pomades, as a reabsorption agent, and as a non toxic anti-foaming agent. Examples of emulsifiers are sorbitan esters such as sorbitan sesquioleate (Arlacel 60), sorbitan sesquioleate (Arlacel 83), sorbitan monolaurate (Span 20), sorbitan monopalmitate (Span 40), sorbitan monostearate (Span 60), sorbitan tristearate (Span 65), sorbitan mono-oleate (Span 80), and sorbitan trioleate (Span 85) all of which are available, e.g., from Uniqema of New Castle, Del. Other polymeric emulsifiers include polyoxyethylene monostearate (Myrj 45), polyoxyethylene monostearate (Myrj 49), polyoxyl 40 stearate (Myrj 52), polyoxyethylene monolaurate (PEG 400), polyoxyethylene monooleate (PEG 400 monoleate) and polyoxyethylene monostearate (PEG 400 monostearate), and the Tween series of surfactants including but not limited to polyoxyethylene sorbitan monolaurate (Tween 20), polyoxyethylene sorbitan monolaurate (Tween 21), polyoxyethylene sorbitan monopalmitate (Tween 40), polyoxyethylene sorbitan monostearate (Tween 60), polyoxyethylene sorbitan tristearate (Tween 61), polyoxyethylene sorbitan mono-oleate (Tween 80), polyoxyethylene sorbitan monooleate (Tween 81), and polyoxyethylene sorbitan tri-oleate (Tween 85) all of which are available, e.g., from Uniqema of New Castle, Del. Arlacel, Myrj, and Tween are registered trademarks of ICI Americas Inc. of Wilmington, Del.

[0057] Foam may form from the release of various gases during the coating/printing process, especially if the printing process takes place at high speeds. Surfactants may adsorb on the liquid-air interface and stabilize it, accelerating foam formation. Anti-foaming agents prevent foaming from being initiated, while defoaming agents minimize or eliminate previously-formed foam. Anti-foaming agents include hydrophobic solids, fatty oils, and certain surfactants, all of which penetrate the liquid-air interface to slow foam formation. Anti-foaming agents also include silicate, silicone and silicone-free materials. Silicone-free materials include microcrystalline wax, mineral oil, polymeric materials, and silica- and surfactant-based materials.

[0058] Solvents can be aqueous (water-based) or non-aqueous (organic). While environmentally friendly, water-based solutions carry the disadvantage of a relatively higher surface tension than organic solvents, making it more difficult to wet substrates, especially plastic substrates. To improve substrate wetting with polymer substrates, surfactants are added to lower the ink surface tension (while minimizing surfactant-stabilized foaming), while the substrate surfaces are modified to enhance their surface energy (e.g. by corona treatment). Typical organic solvents include acetate, acrylates, alcohols (butyl, ethyl, isopropyl, or methyl), aldehydes, benzene, dibromomethane, chloroform, dichloromethane, dichloroethane, trichloroethane, cyclic compounds (e.g. cyclopentanone or cyclohexanone), esters (e.g. butyl acetate or ethyl acetate), ethers, glycols (such as ethylene glycol or propylene glycol), hexane, heptane, aliphatic hydrocarbons, aromatic hydrocarbons, ketones (e.g. acetone, methyl ethyl ketone, or methyl isobutyl ketone), natural oils, terpenes, terpinol, toluene.

[0059] Additional components may include fillers/extenders, thickening agents, rheology modifiers, surface conditioners, including adhesion promoters/bonding, anti-gelling agents, anti-blocking agents, antistatic agents, chelating/complexing agents, corrosion inhibitors, flame/rust inhibitors, flame and fire retardants, humectants, heat stabilizers, light-stabilizers/UV absorbers, lubricants, pH stabilizers, and materials for slip control, anti-oxidants, and flow and leveling agents.

[0060] To provide gallium for the composition, gallium nanoglobules **114** are formed by initially creating an emulsion **112** of liquid gallium **108** in a solution **110** as shown in **FIGS. 1B-1C**. In particular, gallium metal or gallium metal in a solvent with or without emulsifier is heated to liquefy the metal, which is then sonicated and/or otherwise mechanically agitated in the presence of a solvent and optionally an emulsifier. Agitation can also be carried out either mechanically or electromagnetically in the presence of a solvent with or without a surfactant, dispersant, and/or emulsifier. As gallium emulsifies, nanoglobules **114** are formed in this environment. The emulsion **112** containing liquid gallium nanoglobules **114** may be added to the mixture **106**. In some embodiments, the gallium nanoglob-

ules **114** may first be manipulated to form a solid-particulate, e.g., by quenching in an environment either at or below room temperature. When quenched, liquid gallium nanoglobules are converted to solid gallium nanoparticles. In addition, the dispersion of liquid gallium in solution may be modified. Techniques to modify the dispersion of liquid gallium in a solution include stirring, quenching, sonication, and/or the addition of melting point modifiers which can be used separately or in concert to reduce the size and/or narrow the size distribution of the Ga globules into a particular range within any of several spatial scales including but not limited to the nanoscale, sub-micron scale, and/or micron scale. Roughly spheroidal nanoglobules can be formed with average diameters ranging from about 10 nm to about 1000 nm. The gallium nanoglobules are then mixed with the nanoparticle mixture **106** as shown in **FIG. 1D**, forming a dispersion **116** as shown in **FIG. 1E**. Based on the relative ratios of the input elements, the gallium nanoglobule-containing dispersion **116** can then have a Cu/(In+Ga) compositional ratio ranging from 0.01 to 1.0 and a Ga/(In+Ga) compositional ratio ranging from 0.01 to 1.0.

[**0061**] To form one of the sub-layers of a light-absorbing layer, the dispersion **116** may then be deposited onto a substrate **118** with a contact layer **119** to form a layer **120** as shown in **FIG. 2A**, using any of a variety of coating methods including but not limited to dip coating, spin coating, web coating, doctor blade coating, cup coating, spray coating, printing, and the like. These coating methods may also be used for deposition of nano-particle based inks formulated using any of the other techniques described above. The uniformity of film thickness of the layer **120** can be improved by use of any of a variety of printing techniques including but not limited to microgravure, reverse microgravure, comma, slot/die coating, lip coating, and the like. The substrate **118** may be flexible, in the form of a metal foil (e.g. Al, Mo, Ti, or stainless steel), a plastic foil, or a metallized plastic foil, or the substrate may be rigid, e.g. a glass plate or other rigid surface. Where the substrate **118** is made of a metal such as aluminum, a contact layer **119** comprised of a different metal must be also present, e.g., molybdenum, which may be disposed between the substrate **118** and the film **120**.

[**0062**] The layer **120** is then reacted in a suitable atmosphere to form a compound film **122**. For example, upon printing, the layer **120** is then heated to remove any solvent and other added organic or volatile materials from the dispersion **116** and to anneal it into a compound film **122** as shown in **FIG. 2B**. During this step, in the case of a metal foil, the contact layer **119** inhibits the diffusion of metal or other contaminants from the substrate **118** into the compound film **122**. Either during or after this heating step, the layer **120** (if during the heating step) or compound film **122** (if after the heating step) may be reacted in at least one suitable atmosphere **124**. By way of example, the suitable atmosphere **124** may contain at least one of selenium, sulfur, or tellurium, and/or hydride gases comprising Se and/or S and/or Te, or mixtures of these gases.

[**0063**] One of the advantages of the use of nanoparticle-based inks is that it is possible to vary the concentration of the elements within the absorber layer by varying the relative elemental concentrations of the nanoparticles that make up the ink. Thus, for example, the concentration of gallium within the absorber layer may be varied as a function of depth within the absorber layer. For example, as depicted in **FIGS. 2E-2J**, the steps of **FIGS. 2A-2B** may be repeated using inks with different relative concentrations gallium and/or indium and/or copper. For example, as shown in **FIGS. 2E-2F** first compound film **122**A may be formed from an initial sub-layer **120**A as described above with respect to **FIGS. 2A-2B**. The first compound film may have a Cu:In:Ga ratio of 92:0:100 (i.e., 92 parts copper to 0 parts indium to 100 parts gallium). A second sub-layer **120**B may be then be formed from a nanoparticle ink having a Cu:In:Ga ratio of 92:70:30 as shown in **FIG. 2G**. The second sub-layer **120**B may be annealed as shown in **FIG. 2H** to become part of a modified compound film. A third sub-layer **120**C may be formed from a nanoparticle ink having a Cu:In:Ga ratio of 52:20:80 as shown in **FIG. 2I**. Third layer **120**C may be annealed as shown in **FIG. 2J** to become part of a final compound film **122**C. The annealing process may be RTA, as discussed above. Furthermore, the annealing process may also involve exposure of the compound film to a gas such as H_2, N_2, H_2Se or Se vapor.

[**0064**] Not all of the sub-layers need to be deposited using nanoparticulate-based inks. In some embodiments, the third layer **120**C or one or more of the other sub-layers may be deposited using any of a variety of alternative deposition techniques including but not limited to vapor deposition techniques such as ALD, evaporation, sputtering, CVD, PVD, electroplating and the like. Such techniques may also be used to deposit additional sub-layers between the printed layers, e.g., between the first sub-layer **120**A and the second sub-layer **120**B or between the second sub-layer **120**B and the third sub-layer **120**C.

[**0065**] Embodiments of the invention are compatible with roll-to-roll manufacturing, as depicted in **FIG. 2K**. Specifically, in a roll-to-roll manufacturing system **200** a flexible substrate **201**, e.g., aluminum foil travels from a supply roll **202** to a take-up roll **204**. In between the supply and take-up rolls, the substrate **201** passes a number of applicators **206**A, **206**B, **206**C, e.g. microgravure rollers and heater units **208**A, **208**B, **208**C. Each applicator deposits a precursor for a sub-layer of a photovoltaic device active layer, e.g., as described above. The heater units are used to anneal the different sub-layers. In the example depicted in **FIG. 2K**, three different sub-layers may be applied and each sub-layer may be annealed before the next sub-layer is deposited. Alternatively, all three sub-layers may be annealed at the same time.

[**0066**] The result of these steps is an absorber layer **122**C having a gallium concentration that increases with distance from the substrate **118**. In the embodiments depicted with respect to **FIGS. 2E-2J** selenium may be incorporated within the absorber layer in between thin film depositions (e.g., by exposure of the film to Selenium vapor and/or H_2Se gas in conjunction with the annealing) or after the last thin film deposition, or both.

[**0067**] The total number of printing steps can be modified to construct absorber layers with bandgaps of differential gradation. For example, additional films (fourth, fifth, sixth, and so forth) can be printed (and optionally annealed between printing steps) to create an even more finely-graded bandgap within the absorber layer. Alternatively, fewer films (e.g. double printing) can also be printed to create a less finely-graded bandgap.

[0068] Referring again to **FIGS. 2A-2D**, the compound film **122** may be used as the light-absorbing layer in a photovoltaic device. For example, as shown in **FIG. 2C** a window layer **126** may be deposited onto the compound film **122** as a junction partner between the compound film **122** and a transparent conducting layer **128** as shown in **FIG. 2D**. By way of example, the window layer **126** (sometimes referred to as a junction partner layer) may include inorganic materials such as cadmium sulfide (CdS), zinc sulfide (ZnS), zinc hydroxide, zinc selenide (ZnSe), n-type organic materials, or some combination of two or more of these or similar materials, or organic materials such as n-type polymers and/or small molecules. Layers of these materials may be deposited, e.g., by chemical bath deposition (CBD) or chemical surface deposition, to a thickness ranging from about 2 nm to about 1000 nm, more preferably from about 5 nm to about 500 nm, and most preferably from about 10 nm to about 300 nm.

[0069] The transparent conductive layer **128** may be inorganic, e.g., a transparent conductive oxide (TCO) such as indium tin oxide (ITO), fluorinated indium tin oxide, zinc oxide (ZnO) or aluminum doped zinc oxide, or a related material, which can be deposited using any of a variety of means including but not limited to sputtering, evaporation, CBD, electroplating, sol-gel based coating, spray coating, chemical vapor deposition (CVD), physical vapor deposition (PVD), atomic layer deposition (ALD), and the like. Alternatively, the transparent conductive layer may include a transparent conductive polymeric layer, e.g. a transparent layer of doped PEDOT (Poly-3,4-Ethylenedioxythiophene), carbon nanotubes or related structures, or other transparent organic materials, either singly or in combination, which can be deposited using spin, dip, or spray coating, and the like. Combinations of inorganic and organic materials can also be used to form a hybrid transparent conductive layer. Examples of such a transparent conductive layer are described e.g., in commonly-assigned US Patent Application Publication Number 20040187917, which is incorporated herein by reference.

[0070] **FIG. 3** depicts an example of an optoelectronic device **300**, e.g., a photovoltaic cell, incorporating a compound film fabricated as described above. The device **300** includes a base substrate **302**, an optional adhesion layer **303**, a base electrode **304**, an absorber layer **306** incorporating a compound film of the type described above, a window layer **308** and a transparent electrode **310**. By way of example, the base substrate **302** may be made of a metal foil, a polymer such as such as polyimides (PI), polyamides, polyetheretherketone (PEEK), Polyethersulfone (PES), polyetherimide (PEI), polyethylene naphtalate (PEN), Polyester (PET), related polymers, or a metallized plastic. The base electrode **304** is made of an electrically conducive material. By way of example, the base electrode **304** may be of a metal layer whose thickness may be selected from the range of about 0.1 micron to about 25 microns. An optional intermediate layer **303** may be incorporated between the electrode **304** and the substrate **302**. The transparent electrode **310** may include a transparent conductive layer **309** and a layer of metal (e.g., Al, Ag or Ni) fingers **311** to reduce sheet resistance.

[0071] As described with respect to **FIGS. 2E-2J**, the concentrations of group IB, group IIIA and group VIA elements in the IB-IIIA-VIA absorber layer **306** vary with respect to depth to achieve a graded bandgap. For the purposes of the following discussion, the base electrode **304** and/or adhesion layer **303** is sometimes referred to as the "back" contact of the device **300**. Similarly, the transparent electrode **310** is sometimes referred to as the "front" contact of the device **300**. It is also noted that the base electrode **304** and adhesion layer **303** are sometimes referred to as being at or near a "back end" of the device **300**. Consequently, regions of the absorber layer **306** that are close to the base electrode **304** and adhesion layer **303** are sometimes referred to as a "back region" of the absorber layer **306**. Similarly, the window layer **308** and transparent electrode **310** are sometimes referred to as being at the "front end" of the device **300** and regions of the absorber layer **306** proximate the window layer **308** are sometimes referred to as a "front region." A portion of the absorber layer **306** intermediate the front and back regions is referred to herein as a "central region".

[0072] As described above, the sequential printing of discrete nanoparticulate inks or paints where each ink has different elemental and/or alloy concentrations can be used to form an aggregate stack of compound films where, for example, the Ga content is higher at and near both the front and back contacts of the absorber layer **306**, but minimized in the central region of the absorber layer **306**, resulting in a "saddle" profile for Ga concentration as a function of depth within the absorber layer **306**, e.g., as shown in the graph depicted in **FIG. 4**. In the example depicted in **FIG. 4**, an absorber layer may include a first Ga-rich region **402** in the vicinity of the back end, a second Ga-rich region **404** in the vicinity of the front end, a relatively Ga-deficient central region **406** between the first and second Ga-rich regions **402**, **404** in the vicinity of the front end. By way of example, the first Ga-rich region **402** may be characterized by a thickness of up to about 500 nm and a Ga to In+Ga ratio of between about 10% and about 90%. The second Ga-rich region **404** may between about 5 nm and about 50 nm thick and have a ratio of Ga to In+Ga of between about 20% and about 80%. The central region **406** has a ratio of Ga to In+Ga of less than about 5%. The central region **406** may be up to about 1000 nm thick.

[0073] Furthermore, as described above, the sequential printing of discrete nanoparticulate inks or paints where each ink has different elemental and/or alloy concentrations can be used to form an aggregate stack of compound films where the indium and/or copper concentration varies as a function of depth within the aggregate absorber stack. For example, the indium concentration in the absorber layer may be characterized as a ratio of indium to copper. In the first and second Ga-rich regions **402**, **404**, the ratio of In to Cu may be roughly three parts indium to one part copper. The overall indium level in the first gallium-rich region **402** and the selenium-rich region **408** is typically less than in other regions of the absorber layer. In the central region **406** the In:Cu ratio is roughly 0.88-0.92 parts Cu to one part In. The concentration of Cu may be measured as an atomic ratio of Cu to the group IIIA elements (e.g., In and Ga). This ratio may be as large as 90%. The ratio of Se to Cu may be roughly constant over most of the absorber layer but may be slightly higher in a Se-rich region **408** near the front of the device that overlaps partly with the second Ga-rich region **404** as a result of a slightly lower concentration of Cu.

[0074] The thicknesses and concentration ratios set forth above are presented for the purpose of example and in no

way limit the invention. Those of skill in the art will recognize that the particular concentrations and thicknesses may be adjusted to optimize power conversion efficiency, open circuit voltage, short-circuit current density, fill factor, grain size, charge mobility and other functional and/or structural parameters of the device **300**.

[**0075**] Although in part of the preceding section the absorber layer **306** is described as including copper, indium and gallium, those of skill in the art will recognize that the advantages of varying the stoichiometric concentration as a function of depth may be extended more generally to absorber layers of the IB-IIIA-VIA type. As such, embodiments of the invention should not be limited to absorber layers containing copper, indium and gallium. For example, by varying their concentrations in discretely formed and sequentially applied inks or paints, materials such as aluminum, tellurium, sulfur, and/or other elements or alloys or compounds can also be incorporated into the absorber layer where any or all of these elements or alloys or compounds is tuned to have a varying concentration as a function of depth in the absorber layer.

[**0076**] While the above is a complete description of the preferred embodiment of the present invention, it is possible to use various alternatives, modifications and equivalents. Any feature, whether preferred or not, can be combined with any other feature, whether preferred or not. Therefore, the scope of the present invention should be determined not with reference to the above description but should, instead, be determined with reference to the appended claims, along with their full scope of equivalents. In the claims that follow, the indefinite article "A", or "An" refers to a quantity of one or more of the item following the article, except where expressly stated otherwise. The appended claims are not to be interpreted as including means-plus-function limitations, unless such a limitation is explicitly recited in a given claim using the phrase "means for."

What is claimed is:

1. A method of forming a compound film for an active layer of a photovoltaic device comprising the steps of:

forming a first sub-layer including a first component of the active layer on a substrate with a first process;

forming a second sub-layer including a second component of the active layer using a second process, wherein the second component has a different chemical composition than the first component and wherein the first sub-layer is disposed between the second sub-layer and the substrate

wherein the first and/or second component includes particles.

2. The method of claim 1, further comprising, forming one or more additional sub-layers including one or more additional components of the active layer.

3. The method of claim 1 wherein the particles include nanoparticles and/or nanoglobules.

4. The method of claim 1 wherein the first and/or second process is a printing process.

5. The method of claim 1, further comprising depositing a one or more addition sub-layers by a vapor deposition technique.

6. The method of claim 5 wherein the vapor deposition technique is selected from the group of ALD, evaporation, sputtering, CVD, PVD, electroplating and the like.

7. The method of claim 1 wherein the different chemical compositions of the first and second components in the first and second sub-layers provide the active layer with a graded bandgap.

8. The method of claim 1 wherein the first and/or second components include elements of group IB, and/or group IIIA.

9. The method of claim 8, further comprising the step of incorporating an element of group VIA into the first and/or second component.

10. The method of claim 1 wherein forming the first and/or second sub-layer includes making one or more phase-stabilized precursors in the form of fine particles, particles comprising at least one metal oxide and reducing the metal oxides in a reducing atmosphere.

11. The method of claim 1 wherein forming the first and/or second sub-layer includes making single-phase mixed-metal oxide particles with an average diameter of less than about 1 micron by preparing a solution comprising Cu and In and/or Ga as metal-containing compounds; forming droplets of the solution; and heating the droplets in an oxidizing atmosphere to pyrolyze the contents of the droplets to form single-phase copper indium oxide, copper gallium oxide or copper indium gallium oxide particles.

12. The method of claim 1 wherein forming the first and/or second sub-layer includes preparing a source material, depositing the source material on the substrate to form a precursor, and heating the precursor to form a film, wherein the source material includes Group IB-IIIA containing particles having at least one Group IB-IIIA phase, with Group IB-IIIA constituents present at greater than about 50 molar percent of the Group IB elements and greater than about 50 molar percent of the Group IIIA elements in the source material.

13. The method of claim 1 wherein forming the first and/or second sub-layer includes formulating a nano-powder material with a controlled overall composition and having particles of one solid solution, depositing the nano-powder material to form the first or second sub-layer, and reacting in at least one suitable atmosphere to form the first or second component.

14. The method of claim 1 wherein forming the first and/or second sub-layer includes forming a liquid ink containing elements from groups IB, IIIA and optionally VIA, spreading a film of the liquid onto the substrate, and annealing the film to form the first or second sub-layer.

15. The method of claim 14 wherein forming the liquid ink includes

forming non-oxide quantum nanoparticles containing elements from group IB; and forming non-oxide quantum nanoparticles containing elements from group IIIA; and optionally forming non-oxide quantum nanoparticles containing elements from group VIA;

intermixing the non-oxide quantum nanoparticles from groups IB and IIIA and optionally VIA wherein the non-oxide quantum nanoparticles are in a desired particle size range of between about 0.1 nm and about 10 nm in diameter, wherein, for each element, a majority of the mass of the non-oxide quantum nanoparticles range in size from no more than about 40% above or

below an average particle size, or, if the average particle size is less than about 5 nanometers, from no more than about 2 nanometers above or below the average particle size, and

mixing the non-oxide nanoparticles to form a liquid that serves as the ink

16. The method of claim 14 wherein forming the liquid ink includes:

forming nanoparticles from group IB; and

intermixing the nanoparticles from group IB with elements from group IIIA, wherein the elements from group IIIA are in molten form, wherein the nanoparticles from group IB comprise particles in a desired particle size range of between about 0.1 nm and about 500 nm in diameter, wherein a majority of the mass of the nanoparticles range in size from no more than about 40% above or below an average particle size, or, if the average particle size is less than about 5 nanometers, from no more than about 2 nanometers above or below the average particle size; and

mixing the nanoparticles with the molten elements to form a liquid that serves as the ink.

17. The method of claim 14 wherein forming the liquid ink includes:

forming nanoparticles containing elements from groups IB, and IIIA and optionally VIA, wherein the particles are in a desired particle size range of between about 0.1 nm and about 500 nm in diameter, wherein a majority of the mass of the nanoparticles range in size from no more than about 40% above or below an average particle size, or, if the average particle size is less than about 5 nanometers, from no more than about 2 nanometers above or below the average particle size; and

mixing the nanoparticles to form a liquid that serves as the ink.

18. The method of claim 1 wherein forming the first or second sub-layers includes:

forming a molten mixture of one or more metals of group IIIA and metallic nanoparticles containing elements of group IB; and

coating a substrate with a film formed from the molten mixture.

19. The method of claim 1 wherein forming the first or second sub-layers includes:

obtaining core nanoparticles containing one or more elements from group IB and/or IIIA; and

coating the core nanoparticles with one or more layers of metal from group IB, IIIA or an element from group VIA in a controlled fashion such that the resulting film of coated nanoparticles have a desired stoichiometric ratio of elements

forming an ink, paste, or paint containing the nanoparticles;

forming a thin film of the ink, paste or paint on the substrate; and

annealing the thin film.

20. The method of claim 1 wherein the substrate is an aluminum foil substrate.

21. The method of claim 1, further comprising rapidly heating the first and/second sub-layer and/or substrate from an ambient temperature to a plateau temperature range of between about 200° C. and about 600° C.; maintaining the first and/or second sub-layer and/or substrate in the plateau temperature range for between about a fraction of a second and about 60 minutes; and reducing the temperature of the first and/or second sub-layer and/or substrate.

22. The method of claim 1, further comprising: performing atomic layer deposition of a group IB element and/or a group IIIA element and/or a group VIA element onto the substrate, the first sub-layer or the second sub-layer.

23. The method of claim 1, wherein forming the first and/or second sub-layer includes formulating a dispersion of IB and IIIA elemental nanoparticles, wherein a group IIIA element is incorporated into the dispersion in the form of a suspension of nanoglobules; depositing said dispersion onto a substrate to form a film on the substrate; and reacting the film in a suitable atmosphere.

24. The method of claim 23, further comprising iteratively repeating said formulating, depositing and reacting steps two or more times to form said compound film.

25. The method of claim 24 wherein, for at least one iteration, the formulating step includes changing a relative concentration of the IB, IIIA or VIA elemental nanoparticles such that a concentration of the IB, IIIA or VIA elements within the compound film varies as a function of depth.

26. The method of claim 24 wherein iteratively repeating said formulating, depositing and reacting steps produces a concentration of group IIIA elements that is relatively higher at and near a front region and a back region of the compound film, and relatively lower in a central region of the compound film, resulting in a "saddle" profile for the concentration of the one or more group IIIA elements as a function of depth within the compound film.

27. The method of claim 26 wherein the group IIIA elemental nanoparticles include Gallium and/or Indium.

28. The method of claim 27 wherein iteratively repeating said formulating, depositing and reacting steps produces a Gallium concentration that is relatively high at or near the back region.

29. The method of claim 26 wherein a Gallium concentration is relatively lesser in the central region.

30. The method of claim 26 wherein the group IB element is copper (Cu).

31. The method of claim 23, wherein the IIIA elemental nanoparticles include Gallium

32. The method of claim 23 wherein the IIIA elemental nanoparticles include Indium.

33. The method of claim 23 wherein the IIIA elemental nanoparticles include Aluminum.

34. The method of claim 23 wherein the group IB elemental nanoparticles include Copper.

35. The method of claim 23 further comprising, incorporating a group VIA elemental material into the compound film.

36. The method of claim 35 wherein incorporating a group VIA elemental material into the compound film includes exposing the compound film to vapor and/or gas containing the group VIA elemental material in conjunction with annealing.

37. The method of claim 35 wherein incorporating the group VIA elemental material into the compound film

includes the use of nanoparticles containing a VIA group element in step of formulating the dispersion.

38. The method of claim 35 wherein the group VIA elemental material includes Selenium.

39. The method of claim 35 wherein the group VIA elemental material includes Sulfur

40. The method of claim 35 wherein the group VIA elemental material includes Tellurium.

41. The method of claim 1 wherein the compound film includes an alloy of Copper and Gallium, wherein a ratio of Gallium to Copper varies as a function of depth within the compound film.

42. The method of claim 1 wherein the compound film includes an alloy of Copper and Indium wherein a ratio of Indium to Copper varies as a function of depth within the compound film.

43. The method of claim 1 wherein the substrate is a flexible substrate and printing the first and/or second sub-layers includes the use of roll-to-roll manufacturing on the flexible substrate.

44. A photovoltaic device having a light-absorbing layer, wherein the light-absorbing layer is a compound film formed by the method of claim 1.

45. The device of claim 44 wherein the light-absorbing layer contains elements of groups IB, IIIA and VIA.

46. The device of claim 44 wherein a concentration of the IB, IIIA or VIA elements within the light-absorbing layer varies as a function of depth

47. The device of claim 44 wherein the light-absorbing layer is disposed between a base electrode and a transparent electrode.

48. The device of claim 47, further comprising a junction partner layer between the active layer and the transparent electrode.

49. The device of claim 48 wherein the junction partner layer includes cadmium sulfide (CdS), zinc sulfide (ZnS), or zinc selenide (ZnS) or some combination of two or more of these.

50. The device of claim 48 wherein the junction partner layer includes an organic n-type polymer or small molecule.

51. The device of claim 48 wherein the base electrode includes a layer of molybdenum proximate the junction partner layer.

52. The device of claim 47 wherein the transparent electrode includes a layer of a transparent conductive oxide.

53. The device of claim 52 wherein the transparent conductive oxide is indium tin oxide, fluorinated indium tin oxide, zinc oxide or aluminum doped zinc oxide or a related material.

54. A method of forming a compound film comprising the steps of:

formulating a dispersion of IB and IIIA elemental nanoparticles, wherein a group IIIA element is incorporated into the dispersion in the form of a suspension of nanoglobules; depositing said dispersion onto a substrate to form a layer on the substrate; and reacting the layer in a suitable atmosphere; and iteratively repeating said formulating, depositing and reacting steps two or more times to form said compound film, wherein, for at least one iteration, the formulating step includes changing a relative concentration of the IB, IIIA or VIA elemental nanoparticles such that a concentration of the IB, IIIA or VIA elements within the compound film varies as a function of depth.

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