METHOD OF USING SILICON ALLOY LAYERS IN THIN-FILM PHOTOVOLTAICS

Abstract: A method for making thin-film photovoltaic devices is provided. The devices include a doped microcrystalline semiconductor layer having a high band gap core formed by adding a band gap enhancing element. Crystallinity of the layer is achieved by forming an amorphous doped semiconductor layer, converting the amorphous doped semiconductor layer to a microcrystalline layer using a plasma treatment, and using the microcrystalline layer as a seed layer for forming the rest of the layer. The doped layer formed has a microcrystalline morphology, a high band gap inner portion, and a low band gap outer portion.

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METHOD OF USING SILICON ALLOY LAYERS
IN THIN-FILM PHOTOVOLTAICS

FIELD

[0001] Embodiments described herein generally relate to photovoltaic devices and methods and apparatuses for forming the same. More particularly, the embodiments relate to layer structures in thin-film and crystalline photovoltaic devices.

BACKGROUND

[0002] Crystalline silicon solar cells and thin film solar cells are two types of solar cells. Crystalline silicon solar cells typically use either mono-crystalline substrates (i.e., single-crystal substrates of pure silicon) or multi-crystalline silicon substrates (i.e., poly-crystalline or polysilicon). Additional film layers are deposited onto the silicon substrates to improve light capture, form the electrical circuits, and protect the devices. Thin-film solar cells use thin layers of materials deposited on suitable substrates to form one or more p-n, p-i-n, or n-i-p junctions. Suitable substrates include glass, metal, and polymer substrates.

[0003] To expand the economic uses of solar cells, efficiency must be improved. Solar cell efficiency relates to the proportion of incident radiation converted into useful electricity. To be more cost effective, and for extended applications, there is a significant drive to improve solar cell efficiency. With energy costs rising, there is a need for improved thin film solar cells and methods and apparatus for forming the same in a factory environment.

SUMMARY

[0004] Embodiments described herein provide a method of forming an active layer of a thin-film photovoltaic device by depositing an n-type doped semiconductor layer having an amorphous structure on a photovoltaic substrate, converting at least a portion of the n-type doped semiconductor layer to a microcrystalline structure by exposing the n-type doped semiconductor layer to a plasma comprising hydrogen, and forming a microcrystalline semiconductor layer comprising carbon on the n-type doped semiconductor layer.
[0005] Other embodiments provide a method of forming a thin-film photoelectric conversion layer for a photovoltaic device by forming a p-type doped semiconductor layer on a substrate, forming an intrinsic-type semiconductor layer on the substrate, and forming a microcrystalline n-type doped semiconductor layer having a low band gap outer portion and a high band gap inner portion on the substrate. The high band gap inner portion may have a reduced refractive index relative to the low band gap outer portion.

[0006] Other embodiments provide a thin-film photovoltaic device with a first photoconversion unit and a second photoconversion unit adjacent to the first photoconversion unit, wherein each of the first and the second photoconversion unit has a microcrystalline p-type doped semiconductor layer, an intrinsic type semiconductor layer, and a microcrystalline n-type doped semiconductor layer with a high band gap semiconductor alloy core.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] So that the manner in which the above-recited features of the present invention can be understood in detail, a more particular description of the invention, briefly summarized above, may be had by reference to embodiments, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

[0008] Figure 1 is a flow diagram of a method according to an embodiment.

[0009] Figure 2 is a schematic stack diagram of a solar cell device according to another embodiment.

[0010] To facilitate understanding, identical reference numerals have been used, where possible, to designate identical elements that are common to the figures. It is contemplated that elements disclosed in one embodiment may be beneficially utilized on other embodiments without specific recitation.
DETAILED DESCRIPTION

[0011] Figure 1 is a flow diagram of a method 100 according to an embodiment. The method 100 of Figure 1 may be used in forming one or more doped or un-doped semiconductor layers of a thin-film photovoltaic device. Such devices generally comprise one or more doped semiconductor layers that form a photovoltaic cell. P-type and n-type doped semiconductor layers are generally formed with one or more intrinsic semiconductor layers between them. The intrinsic semiconductor layer collects light to generate free electrons and holes, which migrate toward the p-type and n-type doped semiconductor layers, respectively. The layers may be formed with different morphologies to facilitate capturing different portions of the spectrum. Layers in the device may be microcrystalline to facilitate capturing longer wavelengths of light and to facilitate charge collection, or amorphous to facilitate capturing shorter wavelengths of light. The method 100 of Figure 1 is generally used in forming microcrystalline layers for a thin-film photovoltaic device, and may be practiced using a PECVD 5.7 chamber available from Applied Materials, Inc., of Santa Clara, California. The method may also be practiced using PECVD chambers supplied by other manufacturers.

[0012] At 102, an amorphous doped semiconductor layer is formed on a photovoltaic substrate. The substrate may be a glass substrate, polymer substrate, metal substrate, or other suitable substrate, with thin films, such as conductors, buffer layers, or active layers, formed thereover. The substrate may be any shape and size. In one embodiment, the substrate is a glass substrate that is about 2200mm x 2600mm x 3mm in size. A glass substrate may have a plurality of layers formed thereon prior to using the method 100 of Figure 1.

[0013] The substrate used may be any structural substrate suitable for photovoltaic applications. The substrate may be transparent when desired to admit light into the device, or opaque or reflective if it is to form the back surface of the device. Various types of glasses, such as borosilicate glass (BSG), phosphosilicate glass (PSG), borophosphosilicate glass (BPSG), soda lime glass, and the like, are commonly used. Polymers such as plastics and metal substrates may also be used. Semiconductor substrates such as silicon or germanium may also be used.
The substrate may have a conductor layer formed over the structural substrate. The conductor layer may comprise a transparent dielectric, such as a metal oxide, doped with a conductive material. Oxides of zinc (Zn), tin (Sb), indium (In), aluminum (Al), titanium (Ti), cadmium (Cd), gallium (Ga), or silver (Ag) may be doped with any of those metals to form a transparent conductive oxide layer suitable for use as a conductor. In some embodiments, zinc oxide (ZnO) is doped with aluminum (Al), indium (In), tin (Sb), gallium (Ga), boron (B), or silver (Ag). Indium tin oxide or cadmium stannate may also be used. In some embodiments, a metal doped silicate layer may also be used as a conductor. To improve light absorption by reducing light reflection, the substrate and/or one or more of thin films formed thereover, such as the conductor layer described above, may be textured by wet, plasma, ion, or mechanical processes, or combinations thereof.

In some embodiments, the substrate may comprise a plurality of layers of a photovoltaic device. For example, in one embodiment, the method 100 may be used to form a p-type doped semiconductor layer, which may be an alloy layer, over an intrinsic semiconductor layer of a photovoltaic junction. In another embodiment, the method 100 may be used to form an n-type doped semiconductor layer, which may be an alloy layer, over a p-type doped semiconductor layer in a tandem junction thin-film solar cell. In another embodiment, the method 100 may be used to form an n-type doped semiconductor layer, which may be an alloy layer, over a buffer layer. Any microcrystalline semiconductor layer of a thin-film solar cell may be formed according to the method 100 of Figure 1.

The amorphous doped semiconductor layer may be doped with a p-type dopant such as boron or with an n-type dopant such as phosphorus. P-type dopants are generally derived from groups 12 and 13 of the periodic table, while n-type dopants are generally group 15 or 16 elements. Boron and aluminum are common p-type dopants, while phosphorus, arsenic, or antimony may be used as n-type dopants. Phosphorus is widely used as an n-type dopant. The layer may be formed using a vapor deposition process that may be plasma assisted. A semiconductor source gas and a dopant source gas are generally provided to a processing chamber containing the substrate. The precursors used are generally selected to vaporize easily and react readily under selected processing conditions.
Silicon is widely used as the semiconductor for solar panels. Silicon source compounds for forming the amorphous doped semiconductor layer include silane (Si\(^\text{H}_4\)), substituted silanes, oligo- or poly- silanes, and cyclic silanes. Some other suitable silicon source compounds are disilane (Si\(^2\text{H}_6\)), silicon tetrafluoride (SiF\(_4\)), silicon tetrachloride (SiCl\(_4\)), and dichlorosilane (SiH\(_2\)Cl\(_2\)). Semiconductor materials besides silicon, such as germanium, may be delivered using relatively low-boiling compounds such as germane (GeH\(_4\)) and derivatives thereof. A mixture of any of the above may also be used. Common boron source compounds include trimethylboron (B(CH\(_3\))\(_3\), also "TMB"), diborane (B\(_2\)H\(_6\)) or other lower boranes, BF\(_3\), B(C\(_2\)H\(_3\))\(_3\), and similar compounds. Examples of phosphorus-containing sources include phosphine and similar compounds. The dopant source compounds are typically provided with a carrier gas, such as hydrogen, argon, helium, and other suitable compounds. Hydrogen is also used to control crystal morphology of the deposited layer.

An n-type semiconductor layer having an amorphous structure may be formed by disposing a photovoltaic substrate in a processing chamber and providing a gas mixture comprising silane, phosphine, and hydrogen to the processing chamber. The hydrogen and silane may be provided in a hydrogen to silane volumetric ratio of about 20:1 or less, such as about 5.2:1 or 7.8:1. Normalized to chamber volume, silane gas may be provided at a flow rate between about 0.1 sccm/L and about 10 sccm/L, such as between about 1 sccm/L and about 10 sccm/L, between about 0.1 sccm/L and 5 sccm/L, or between about 0.5 sccm/L and about 3 sccm/L, for example about 1.42 sccm/L or 5.5 sccm/L. Hydrogen gas may be provided at a flow rate between about 1 sccm/L and about 40 sccm/L, such as between about 4 sccm/L and about 40 sccm/L, or between about 1 sccm/L and about 10 sccm/L, for example about 6.42 sccm/L or 27 sccm/L. Phosphine may be provided at a flow rate between about 0.0005 sccm/L and about 0.075 sccm/L, such as between about 0.0005 sccm/L and about 0.0015 sccm/L or between about 0.015 sccm/L and about 0.03 sccm/L, for example about 0.0095 sccm/L or 0.023 sccm/L. If phosphine is provided in a 0.5% molar or volume concentration in a carrier gas, then the dopant/carrier gas mixture may be provided at a flow rate between about 0.1 sccm/L and about 15 sccm/L, such as between about 0.1 sccm/L and about 3 sccm/L, between about 2 sccm/L and about 15 sccm/L, or between about 3 sccm/L
and about 6 sccm/L, for example about 1.9 sccm/L or about 4.71 sccm/L. Applying RF power between about 25 mW/cm² and about 250 mW/cm², such as about 60 mW/cm² or about 80 mW/cm², at a chamber pressure between about 0.1 Torr and about 20 Torr, preferably between about 0.5 Torr and about 4 Torr, such as about 1.5 Torr, will deposit an n-type amorphous silicon layer at a rate of about 100 A/min or more, such as about 200 A/min or more, such as about 300 A/min or about 600 A/min.

[0019] For a substrate larger than about 55,000 cm² (e.g. a 5.7 m² Gen 8.5 substrate) in one embodiment, silane is provided at 2 sLm, hydrogen at 10 sLm, and phosphine at 4.9 sLm, for a total gas flow rate of 16.9 sLm and a hydrogen to silane ratio of 5.2:1. Chamber pressure is maintained at about 1.5 Torr, and temperature at about 225 °C, while RF power of about 1,800 W is coupled into the gas mixture. Exposure of about 10 seconds forms a thin amorphous n-type doped semiconductor layer on the substrate.

[0020] At 104, the amorphous doped semiconductor layer is at least partially crystallized and/or etched, converting at least a portion of it to a microcrystalline structure. Portions of the amorphous doped semiconductor layer may also be removed in the process. Converting portions of the amorphous layer to a microcrystalline structure provides a foundation for forming subsequent microcrystalline layers, which reduces the potential barrier for carriers between the absorber layer and the collector layer, inducing carrier flow to the collector layer. The microcrystallization process is performed by exposing the amorphous doped semiconductor layer to a plasma comprising hydrogen, a noble gas such as helium or argon, or a mixture thereof.

[0021] Not wishing to be bound or limited by theory, it is thought that the plasma induces physical reorganization of the layer structure by energizing atoms within the layer to move to more energetically favored crystal lattice positions, and promotes bonding within the layer by removing hydrogen from the layer. Plasma exposure also restructures the morphology and may remove or etch portions of the amorphous doped and undoped layers. In one embodiment, microcrystalline domains are formed on the surface of the amorphous doped semiconductor layer, the domains being separated at the surface of the layer by amorphous domains. In
this embodiment, the microcrystalline domains form "islands" of microcrystalline material that may serve as seed domains for further microcrystalline layer formation. In another embodiment, a thin surface layer of the amorphous doped semiconductor layer is converted to a microcrystalline structure. In this embodiment, a few monolayers may be converted at the surface. The converted thin surface layer may have a thickness between about 5 Å and about 50 Å, depending on the energy and duration of the plasma exposure. In other embodiments, longer treatment may result in formation of a thicker microcrystalline layer, or effective conversion of the amorphous layer to a microcrystalline layer.

[0022] A plasma treatment may be performed by subjecting a substrate to a hydrogen gas flow between about 0.1 sccm/L and about 1.0 sccm/L at a chamber pressure between about 1 Torr and about 8 Torr, such as between about 3 Torr and about 6 Torr, and RF power between about 50 mW/cm² and about 1,000 mW/cm², such as between about 100 mW/cm² and about 500 mW/cm², for example about 200 mW/cm². Exposure time between about 5 seconds and about 60 seconds, such as between about 15 seconds and about 50 seconds, will result in growth of crystal domains within the layer. Higher RF power and hydrogen gas flow may be advantageous for some embodiments because more hydrogen atoms impact the substrate surface, speeding nucleation of crystal sites. The amorphous doped semiconductor layer protects subjacent layers from plasma attack during the crystallization process. In one embodiment, a substrate such as that described above is treated to a hydrogen flow of 180 sLm at a chamber pressure of about 4.5 Torr and RF power of about 11,000 W for about 30 seconds.

[0023] At 106, a high band gap microcrystalline doped semiconductor layer is formed on the treated amorphous doped semiconductor layer described above. The treated layer, partly or fully microcrystallized, may be used as a seed layer to deposit the high band gap microcrystalline doped semiconductor layer. Use of a seed layer to stimulate deposition of a crystalline morphology generally reduces severity of processing conditions needed to deposit a crystalline morphology. For example, a microcrystalline morphology layer may be deposited using relatively low volumetric ratio of hydrogen to silane of about 500:1 or less, such as about 300:1 or less, for example about 290:1. The high band gap layer is formed by adding a band gap
increasing element to the layer. Elements such as carbon, nitrogen, oxygen, and combinations thereof widen the band gap of silicon and doped silicon materials. Carbon may be added to silicon to form an alloy by including a carbon source with a silicon source in a deposition gas mixture. Carbon sources may be light hydrocarbons, for example \( \text{C}_4 \) hydrocarbons, or organosilanes, organosiloxanes, or organosilanol. The latter group may also be used as sources of both silicon and carbon.

In one embodiment, methane (\( \text{CH}_4 \)) is used as a carbon source in a gas mixture with silane, hydrogen, and phosphine to deposit a high band gap microcrystalline doped semiconductor alloy layer. A ratio of the volumetric flow rate of methane to silane is generally between about 1:10 and about 10:1, such as between about 1:5 and about 5:1, for example about 1:3. Inclusion of band gap increasing elements may reduce crystallinity, so somewhat higher ratio of hydrogen to silane may be used to compensate. In one aspect, a volumetric ratio of hydrogen to silane may be less than about 700:1, such as between about 300:1 and about 600:1, for example about 450:1. In an embodiment featuring a substrate such as that described above, silane is provided at a flow rate of about 0.65 sLm, hydrogen at 290 sLm, phosphine at 4.0 sLm, and methane at 0.25 sLm, with RF power of about 28.5 kW. Chamber pressure may be elevated in some embodiments, due to added partial pressure of methane in the gas mixture, to between about 5 Torr and about 20 Torr, such as between about 10 Torr and about 15 Torr, for example about 11 Torr.

At 108, a low band gap microcrystalline doped semiconductor alloy layer is formed on the high band gap microcrystalline doped semiconductor layer. For the substrate described above with a high band gap microcrystalline doped semiconductor layer formed thereon, a low band gap microcrystalline doped semiconductor layer of the n-type may be formed by disposing the substrate in a processing chamber and providing a gas mixture of about 1 sLm silane, about 290 sLm hydrogen, and about 2 sLm phosphine, and RF power of about 22,000 W for about 10 seconds at a chamber pressure of about 6 Torr.

The high band gap microcrystalline doped semiconductor alloy layer may be formed as a core layer of an overall microcrystalline doped semiconductor layer
for carrier collection. For example, after depositing the high band gap microcrystalline doped semiconductor alloy layer, a low band gap microcrystalline doped semiconductor layer may be deposited to form a composite microcrystalline doped semiconductor layer having a high band gap core. In one embodiment, a low band gap microcrystalline doped semiconductor layer may be deposited on the treated amorphous layer prior to depositing the high band gap microcrystalline doped semiconductor layer. The high band gap component reduces light absorption by the charge collector layer, for example by the n-type collector layer, and lowers refractive index of the n-type layer for increased reflection back into the absorber layer of the photojunction.

[0027] In some embodiments, depositing the amorphous doped semiconductor layer, forming microcrystalline domains therein, and depositing the high and low band gap microcrystalline doped semiconductor layers may be performed in a single processing chamber. In such embodiments, ramping flow rates of gases may be advantageous for maintaining plasma processing. In the examples given above, hydrogen flow rate is about 10 sLm for depositing the amorphous layer and about 180 sLm for the plasma treatment. The hydrogen flow rate may be ramped up at a rate suitable for maintaining plasma processing, while the silane and phosphine are ramped down to zero. While the plasma crystallization process proceeds, hydrogen flow rate may be ramped further to approach conditions for depositing the low band gap layer. In one embodiment, the hydrogen flow rate is ramped to 180 sLm, held for about 10 seconds, ramped to about 260 sLm, held for about 5 seconds, and ramped to about 265 sLm and held for about 15 seconds to complete a hydrogen plasma treatment. The hydrogen is then ramped up to a flow rate of about 290 sLm while the silane and phosphine are ramped to their target flow rates to deposit the low band gap layer.

[0028] In one embodiment, an absorber layer and a composite "sandwich" layer, as described above, may be formed in a single continuous process performed in one processing chamber. An amorphous silicon layer may be formed on the substrate using a hydrogen/silane gas mixture at a volume ratio of about 10:1 hydrogen to silane with 2.5 kW RF power, and then a process similar to that described above
may be performed to form a composite n-type doped semiconductor collector layer with a high band gap core.

[0029] The low band gap and high band gap layers described above may have different refractive indices due to their different compositions. Inclusion of band gap enhancing elements in the high band gap layers may also reduce their refractive index relative to the low band gap layers. Thus, the low band gap layers may be high refractive index layers, while the high band gap layers are low refractive index layers. The difference in refractive index may be useful in forming a reflective interface between the layers to enhance light capture.

[0030] The low band gap microcrystalline doped semiconductor layer comprises a semiconductor element, such as silicon or germanium, or a compound semiconductor such as a group III/VI or group II/VI compound semiconductor, with an n-type or p-type dopant listed above. In one embodiment a low band gap microcrystalline doped semiconductor layer comprises silicon and phosphorus, with a concentration of phosphorus in silicon between about 10^{16} \text{ cm}^{-3} and about 10^{22} \text{ cm}^{-3}, for example between about 10^{18} \text{ cm}^{-3} and about 10^{20} \text{ cm}^{-3}. A p-type microcrystalline semiconductor layer may comprise silicon and boron, with a concentration of boron in silicon between about 10^{16} \text{ cm}^{-3} and about 10^{22} \text{ cm}^{-3}, for example between about 10^{18} \text{ cm}^{-3} and about 10^{20} \text{ cm}^{-3}. A high band gap n-type microcrystalline doped semiconductor layer may comprise silicon, phosphorus, and carbon, with a concentration of phosphorus in silicon between about 10^{16} \text{ cm}^{-3} and about 10^{22} \text{ cm}^{-3}, for example between about 10^{18} \text{ cm}^{-3} and about 10^{20} \text{ cm}^{-3}, and a concentration of carbon in silicon between about 1 atomic percent and about 50 atomic percent, for example between about 1 atomic percent and about 15 atomic percent, for example about 6 atomic percent. A high band gap p-type microcrystalline doped semiconductor layer may comprise silicon, boron, and carbon, with a concentration of boron in silicon between about 10^{16} \text{ cm}^{-3} and about 10^{22} \text{ cm}^{-3}, for example between about 10^{18} \text{ cm}^{-3} and about 10^{20} \text{ cm}^{-3}, and a concentration of carbon in silicon between about 1 atomic percent and about 50 atomic percent, for example between about 1 atomic percent and about 15 atomic percent, for example about 6 atomic percent.
[0031] Figure 2 is a schematic stack diagram of a device 200 according to another embodiment. The device 200 is a tandem junction solar cell having certain layers formed according to methods similar to those described above in connection with Figure 1. Although the device 200 of Figure 2 is a tandem junction solar cell, the layers described above in connection with Figure 1 may be incorporated into a single junction solar cell as well.

[0032] The device 200 has a first structural substrate 202 and a second structural substrate 224, each of which may be any of the structural substrates described above. One of the first or second structural substrates 202/224 will generally be substantially transparent to admit light into the active layers of the device 200, and the other structural substrate will generally be reflective, and will generally have protective properties, such as moisture and oxygen barrier properties. A first conductor layer 226, as described above, may be formed on the structural substrate 202. A first photovoltaic junction 204 may also be formed on the structural substrate 202. For the tandem junction device 200 of Figure 2, a second photovoltaic junction 214 is typically formed over the first photovoltaic junction 204, with one or more optional buffer layers 212 disposed between the first and second photovoltaic junctions 204 and 214. For a single junction device, the second photovoltaic junction 214 would be omitted. A second conductor layer 222 is then typically formed over the second photovoltaic junction 214. The first and second conductor layers 226 and 222 may be essentially the same, or they may be different if desired. One of the first and the second conductor 226 and 222 may have a reflective component such as a metal layer or dielectric mirror incorporated therein to enhance light capture.

[0033] Each of the photovoltaic junctions 204 and 214 separately comprises a p-type doped semiconductor layer, an intrinsic semiconductor layer, and an n-type doped semiconductor layer. The first photovoltaic junction 204 comprises a first microcrystalline n-type doped semiconductor layer 206, a first intrinsic semiconductor layer 208 that may be microcrystalline, amorphous, or a plurality of microcrystalline and amorphous layers, and a first microcrystalline p-type doped semiconductor layer 210. The second photovoltaic junction 214 comprises a second microcrystalline n-type doped semiconductor layer 216, a second intrinsic
semiconductor layer 218, and a second p-type doped semiconductor layer 220. Each of the intrinsic semiconductor layers 208 and 218 may be amorphous or microcrystalline, or some combination thereof. Amorphous intrinsic semiconductor material may be included in the cell to absorb shorter wavelengths of light more efficiently.

[0034] The first microcrystalline n-type doped semiconductor layer 206 generally comprises a plurality of sublayers. In the embodiment of Figure 2, three sublayers, 206A, 206B, and 206C, are shown, but more than three sublayers may be used. The first sublayer 206A may be a microcrystalline semiconductor layer having any of the n-type dopants listed above, for example phosphorus. The second sublayer 206B, which may contact the first sublayer 206A, may be a microcrystalline semiconductor layer having an n-type dopant and a bandgap-enhancing dopant such as carbon. The third sublayer 206C, which may contact the second sublayer 206B, may be a microcrystalline semiconductor layer having an n-type dopant similar to the first sublayer 206A. The broader bandgap of the second sublayer 206B may enhance the transmission of wavelengths of light through the layer, reducing absorption losses. The three sublayers may be formed using a process similar to that described in connection with Figure 1. More than three sublayers may be formed by alternately depositing a layer having carbon, or other bandgap enhancing elements, and a carbon-free layer. The carbon-containing layers increase the overall bandgap of the first microcrystalline n-type doped semiconductor layer 206, reducing absorption of light, and the multiple layers of different refractive index reflect light back into the active layers of the device for improved light capture.

[0035] The first microcrystalline n-type doped semiconductor layer 206 may have a thickness between about 10 nm and about 200 nm, such as between about 50 nm and about 150 nm, for example about 100 nm. Depending on the number of sublayers and the overall thickness of the layer 206, each sublayer may have a thickness between about 10 nm and about 100 nm, such as between about 15 nm and about 50 nm, for example about 30 nm.

[0036] The second sublayer 206B may have up to about 50 atomic percent carbon, or other bandgap enhancing elements, such as between about 1 atomic
percent and about 15 atomic percent, or between about 5 atomic percent and about 10 atomic percent, for example about 6 atomic percent carbon. The addition of carbon to the second sublayer 206B increases the bandgap over microcrystalline silicon by between about 0.01 eV and about 0.20 eV, such as between about 0.05 eV and about 0.15 eV, for example about 0.10 eV. Refractive index is reduced by between about 0.2 and about 1.5, such as between about 0.5 and 1.2, for example about 0.7. Microcrystalline silicon/carbon alloys may have refractive index as low as about 2.3. The difference in refractive index between the sublayers reflects light at the interfaces between the layers to enhance light confinement in the solar cell.

[0037] The first microcrystalline p-type doped semiconductor layer 210 may comprise a plurality of sublayers, similar to the first microcrystalline n-type doped semiconductor layer. In the embodiment of Figure 2, the first microcrystalline p-type doped semiconductor layer 210 has three sublayers 210A, 210B, and 210C. Similar to the first microcrystalline n-type doped semiconductor layer 206, the first and third sublayers 210A and 210C are free of carbon, while the second sublayer 210B is an alloy of silicon and carbon. The carbon reduces light absorption of the first microcrystalline p-type doped semiconductor layer 210 and reflects light back through absorber layers of the solar cell.

[0038] The second microcrystalline n-type doped semiconductor layer 216 may also comprise a plurality of sublayers, for example three sublayers 216A, 216B, and 216C, as shown in Figure 2, and may be similar in many respects to the first microcrystalline n-type doped semiconductor layer 206. The carbon content of the layer 216 may be the same as for the layers 206 and 210, if desired, or the carbon content may vary to achieve incrementally different absorption properties. In general, the second microcrystalline n-type doped semiconductor layer will be formed by a process similar to that described in connection with Figure 1 above.

[0039] The second p-type doped semiconductor layer 220 may be microcrystalline or amorphous depending on the optical properties desired. The second p-type doped semiconductor layer 220 may also have a plurality of sublayers, some of which may be alloys with carbon. If the second p-type doped semiconductor layer 220 is the nearest active layer to the light source, it may be advantageous to use a microcrystalline morphology with carbon to minimize
absorption and reflectivity of light prior to the light reaching the first absorber layer. In many embodiments, one or more amorphous semiconductor layers are included as active layers to absorb wavelengths of light not readily absorbed by microcrystalline semiconductor layers.

[0040] In alternate embodiments, the first sublayers of any of the doped layers 206, 210, 216, and 220, may be amorphous layers having microcrystalline regions. For example, each of the first sublayers 206A, 210A, and 216A, and the first sublayer of the second p-type doped semiconductor layer 220, if any, may individually be an amorphous doped semiconductor layer with microcrystalline portions formed according to embodiments described herein.

[0041] Thin-film photovoltaic panels made according to embodiments described herein may exhibit efficiency between about 9% and about 11.5% with fill factor of about 69-72%, $V_{oc}$ about 141-142, and $I_{sc}$ about 1.35-1.37. A series of seven Gen 8.5 photovoltaic devices was formed using methods described herein. Median CE was 11.2%, with CE ranging from 11.1% to 11.5%. Median $V_{oc}$ per segment was 1.39 V, with Voc ranging from 1.37 V to 1.41 V. Median fill factor was 71.4%, with fill factor ranging from 70.7% to 72.0%. Median $J_{sc}$ was 11.31 mA/cm², with $J_{sc}$ ranging from 11.25 mA/cm² to 11.38 mA/cm².

[0042] While the foregoing is directed to embodiments of the invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof.
What is claimed is:

1. A method of forming an active layer of a thin-film photovoltaic device, comprising:
   
   forming an n-type doped semiconductor layer having an amorphous structure on a photovoltaic substrate;

   converting at least a portion of the n-type doped semiconductor layer to a microcrystalline structure by exposing the n-type doped semiconductor layer to a plasma comprising hydrogen; and

   forming a microcrystalline semiconductor layer comprising carbon on the n-type doped semiconductor layer.

2. The method of claim 1, wherein the microcrystalline semiconductor layer is a silicon and carbon containing layer.

3. The method of claim 2, wherein forming the microcrystalline semiconductor layer comprises:

   providing a gas mixture comprising a silicon source and a carbon source to a processing chamber containing the photovoltaic substrate;

   forming a plasma from the gas mixture; and

   depositing a microcrystalline layer from the plasma onto the n-type doped semiconductor layer.

4. The method of claim 1, further comprising depositing a microcrystalline n-type doped semiconductor layer on the microcrystalline semiconductor layer.

5. The method of claim 1, wherein depositing the n-type doped semiconductor layer comprises:

   positioning the photovoltaic substrate in a processing chamber;
flowing a gas mixture comprising silane and hydrogen at a volumetric flow rate ratio of hydrogen to silane less than about 500:1; and

forming a plasma from the gas mixture.

6. The method of claim 3, wherein depositing the microcrystalline layer from the plasma onto the n-type doped semiconductor layer comprises maintaining a chamber pressure of at least about 5 Torr.

7. The method of claim 6, wherein a volumetric ratio of the silicon source to the carbon source is no more than about 10:1.

8. A method of forming a thin-film photoelectric conversion layer for a photovoltaic device, the method comprising:

   forming a p-type doped semiconductor layer on a substrate;

   forming an intrinsic-type semiconductor layer on the substrate; and

   forming a microcrystalline n-type doped semiconductor layer having a high refractive index outer portion and a low refractive index inner portion.

9. The method of claim 8, wherein the inner portion comprises a band gap increasing element.

10. The method of claim 9, wherein the band gap increasing element is carbon.

11. The method of claim 8, wherein forming the microcrystalline n-type doped semiconductor layer comprises:

   depositing an amorphous n-type doped semiconductor layer;

   converting the amorphous n-type doped semiconductor layer to a first microcrystalline n-type doped semiconductor layer by exposure to a plasma;
depositing a second microcrystalline n-type doped semiconductor layer comprising carbon on the first microcrystalline n-type doped semiconductor layer; and

depositing a third microcrystalline n-type doped semiconductor layer on the second microcrystalline n-type doped semiconductor layer.

12. The method of claim 11, wherein forming the intrinsic-type semiconductor layer and forming the microcrystalline n-type doped semiconductor layer having a low band gap outer portion and a high band gap inner portion are performed in the same chamber under a substantially continuous vacuum.

13. A thin-film photovoltaic device, comprising:

a first photoconversion unit; and

a second photoconversion unit adjacent to the first photoconversion unit, wherein each of the first and the second photoconversion unit comprises a microcrystalline p-type doped semiconductor layer, an intrinsic type semiconductor layer, and a microcrystalline n-type doped semiconductor layer with a high band gap semiconductor alloy core.

14. The thin-film photovoltaic device of claim 13, wherein the first photoconversion unit has an amorphous intrinsic type semiconductor layer and the second photoconversion unit has a microcrystalline intrinsic type semiconductor layer.
100

FORM AN AMORPHOUS DOPED SEMICONDUCTOR
LAYER ON A SUBSTRATE

102

CONVERT PORTIONS OF THE AMORPHOUS DOPED
SEMICONDUCTOR LAYER TO A MICROCRYSTALLINE
STRUCTURE BY EXPOSING THE AMORPHOUS DOPED
SEMICONDUCTOR LAYER TO A PLASMA

104

DEPOSIT A HIGH BAND GAP MICROCRYSTALLINE DOPED
SEMICONDUCTOR ALLOY LAYER ON THE PARTIALLY
MICROCRYSTALLIZED DOPED SEMICONDUCTOR LAYER

106

DEPOSIT A LOW BAND GAP MICROCRYSTALLINE DOPED
SEMICONDUCTOR LAYER ON THE HIGH BAND MICROCRYSTALLINE
DOPED SEMICONDUCTOR LAYER

108

FIG. 1