US007098058B1

(12) **United States Patent**
Karpov et al.

(10) **Patent No.:** US 7,098,058 B1
(45) **Date of Patent:** Aug. 29, 2006

(54) **PHOTOVOLTAIC HEALING OF NON-UNIFORMITIES IN SEMICONDUCTOR DEVICES**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 78 days.

(21) Appl. No.: **11/035,170**

(22) Filed: **Jan. 13, 2005**

Related U.S. Application Data

(60) Provisional application No. 60/536,673, filed on Jan. 15, 2004.

(51) **Int. Cl.**
H01L 21/00 (2006.01)
(52) **U.S. Cl.** **438/22**; 257/79
(58) **Field of Classification Search** 438/4, 438/22, 88, 95, 96; 257/79, 80, 113
See application file for complete search history.

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(57)   **ABSTRACT**

A method of making a photovoltaic device using light energy and a solution to normalize electric potential variations in the device. A semiconductor layer having nonuniformities comprising areas of aberrant electric potential deviating from the electric potential of the top surface of the semiconductor is deposited onto a substrate layer. A solution containing an electrolyte, at least one bonding material, and positive and negative ions is applied over the top surface of the semiconductor. Light energy is applied to generate photovoltage in the semiconductor, causing a redistribution of the ions and the bonding material to the areas of aberrant electric potential. The bonding material selectively bonds to the nonuniformities in a manner such that the electric potential of the nonuniformities is normalized relative to the electric potential of the top surface of the semiconductor layer. A conductive electrode layer is then deposited over the top surface of the semiconductor layer.

28 Claims, 10 Drawing Sheets
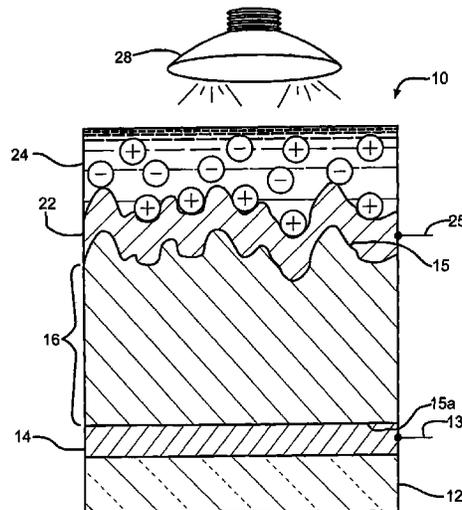
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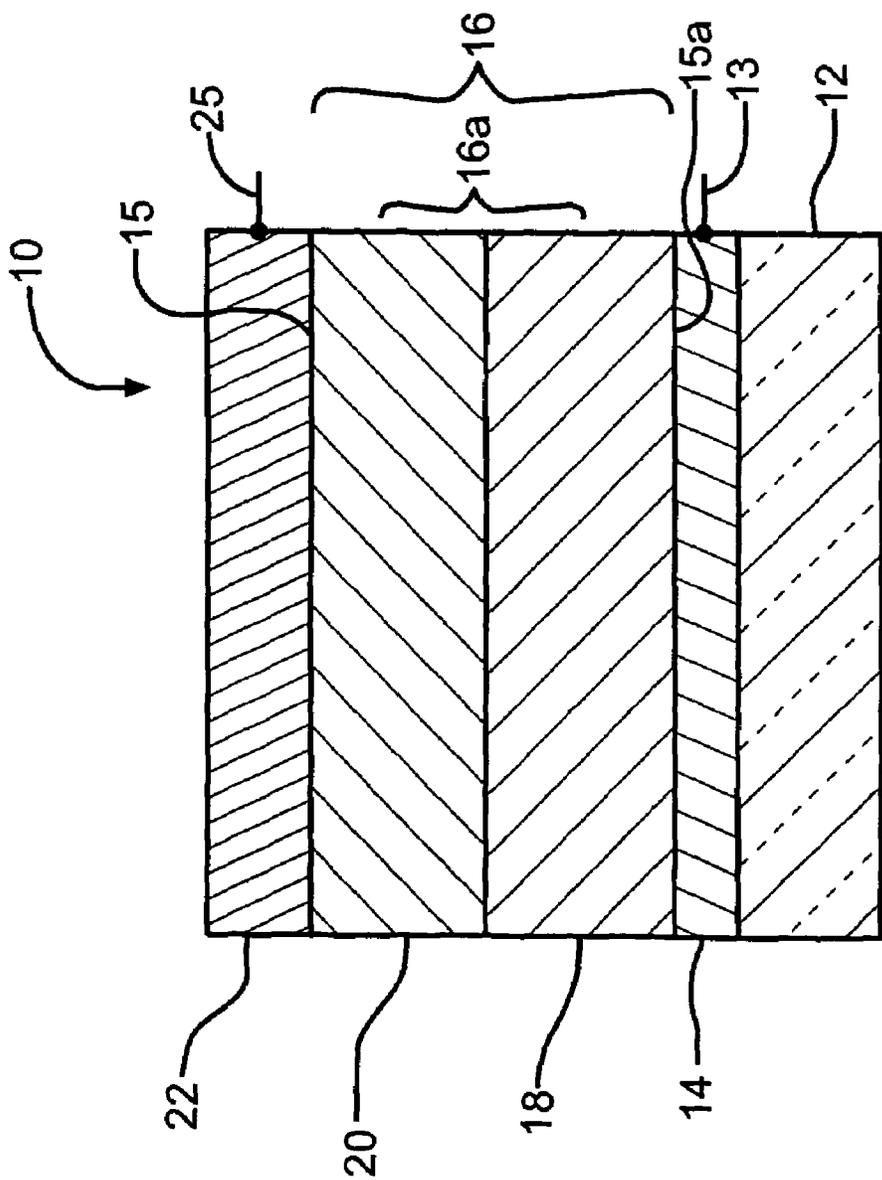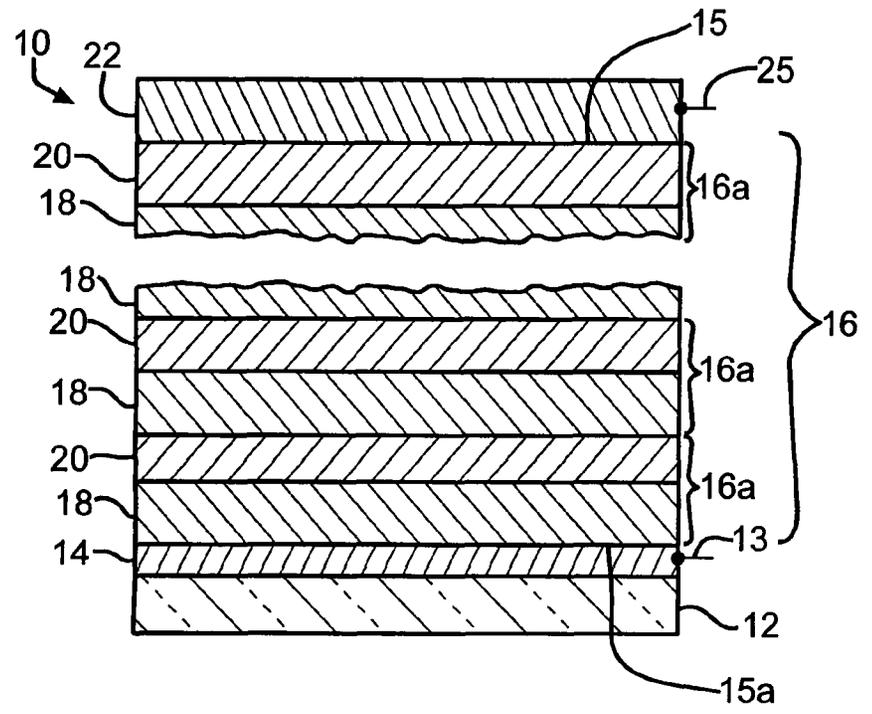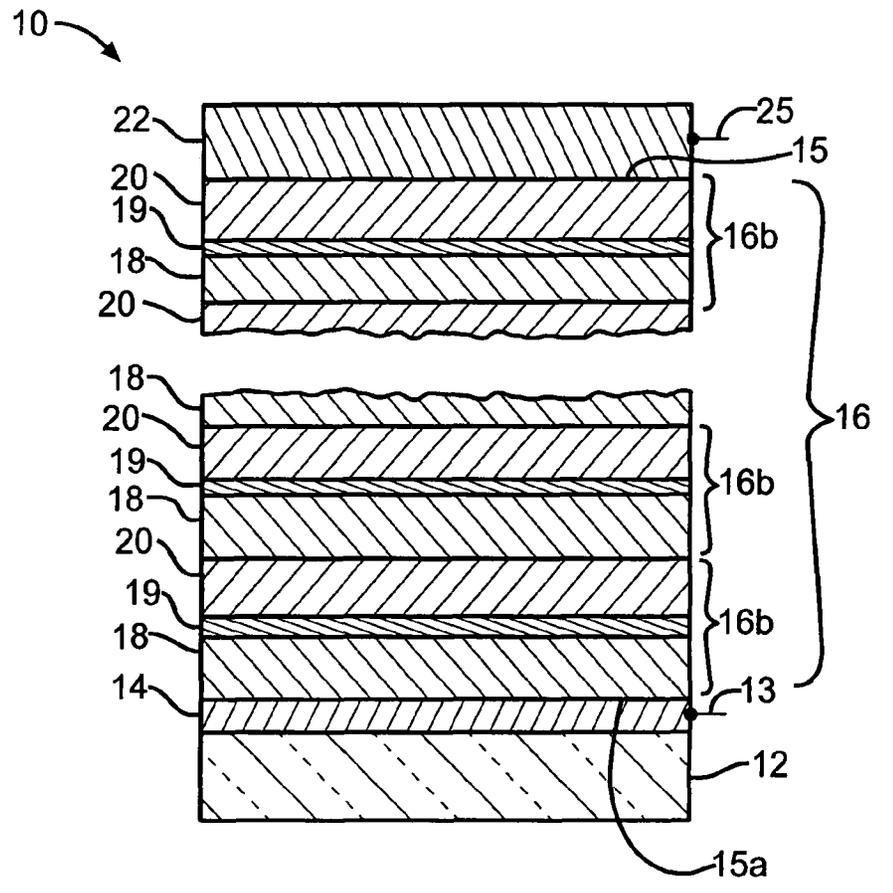
* cited by examiner

FIG. 1

FIG.2

FIG.3
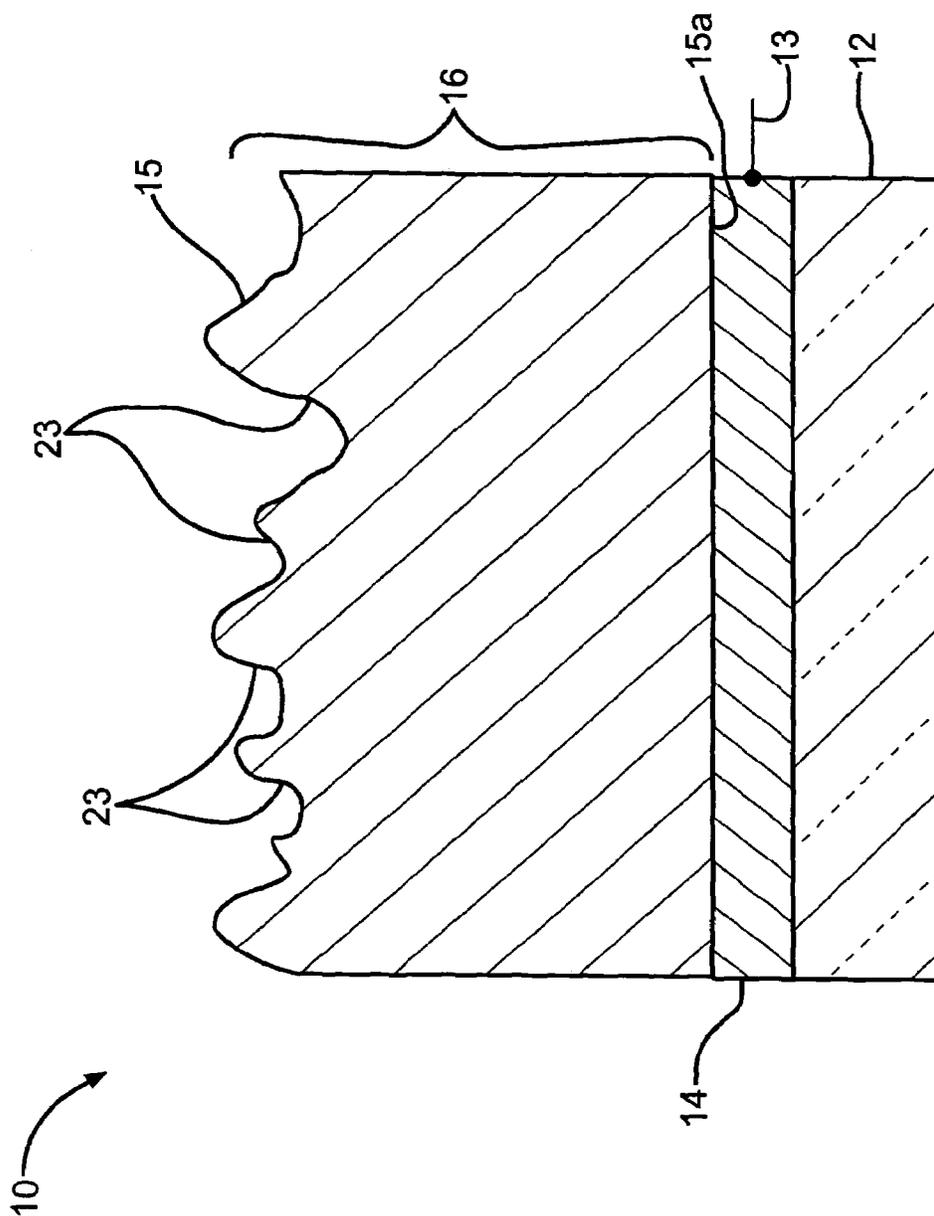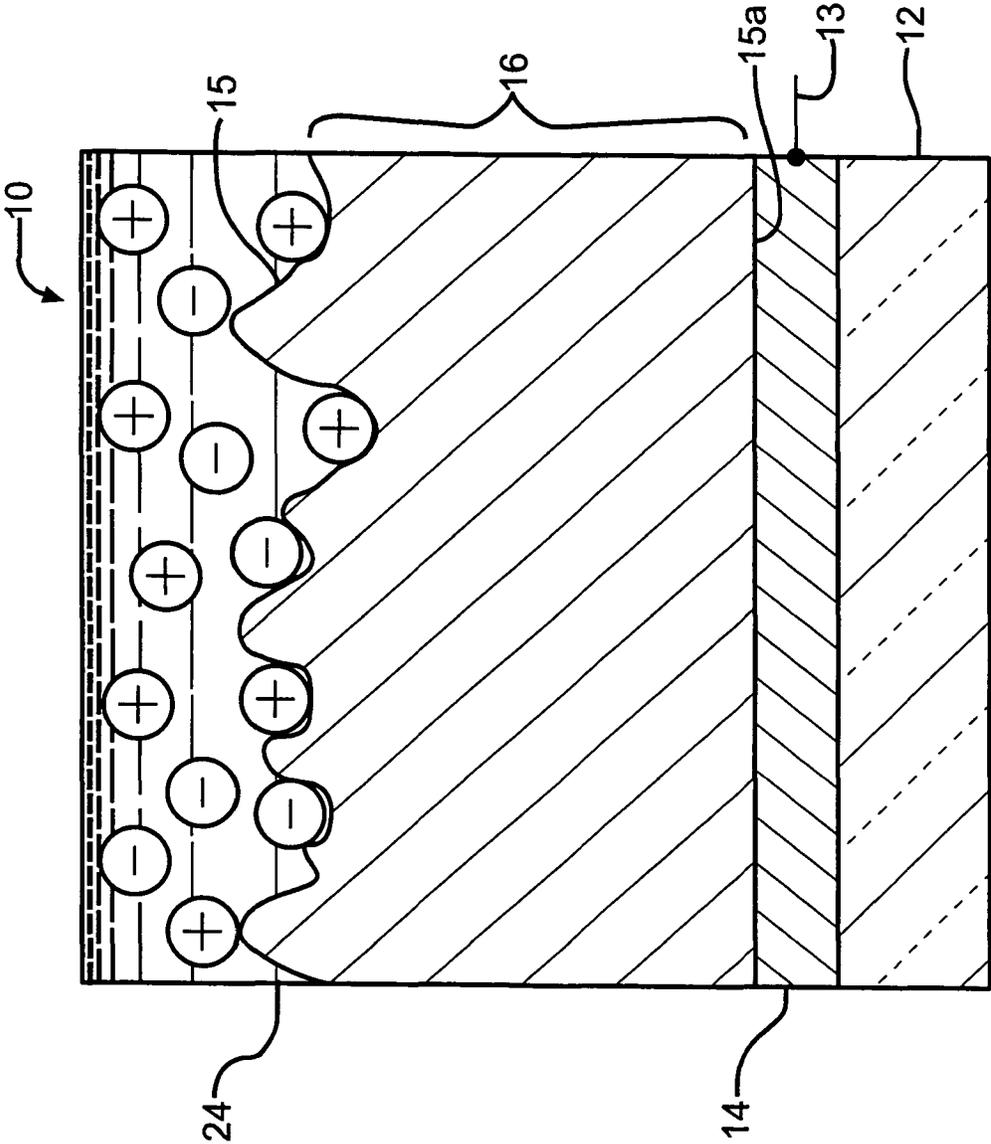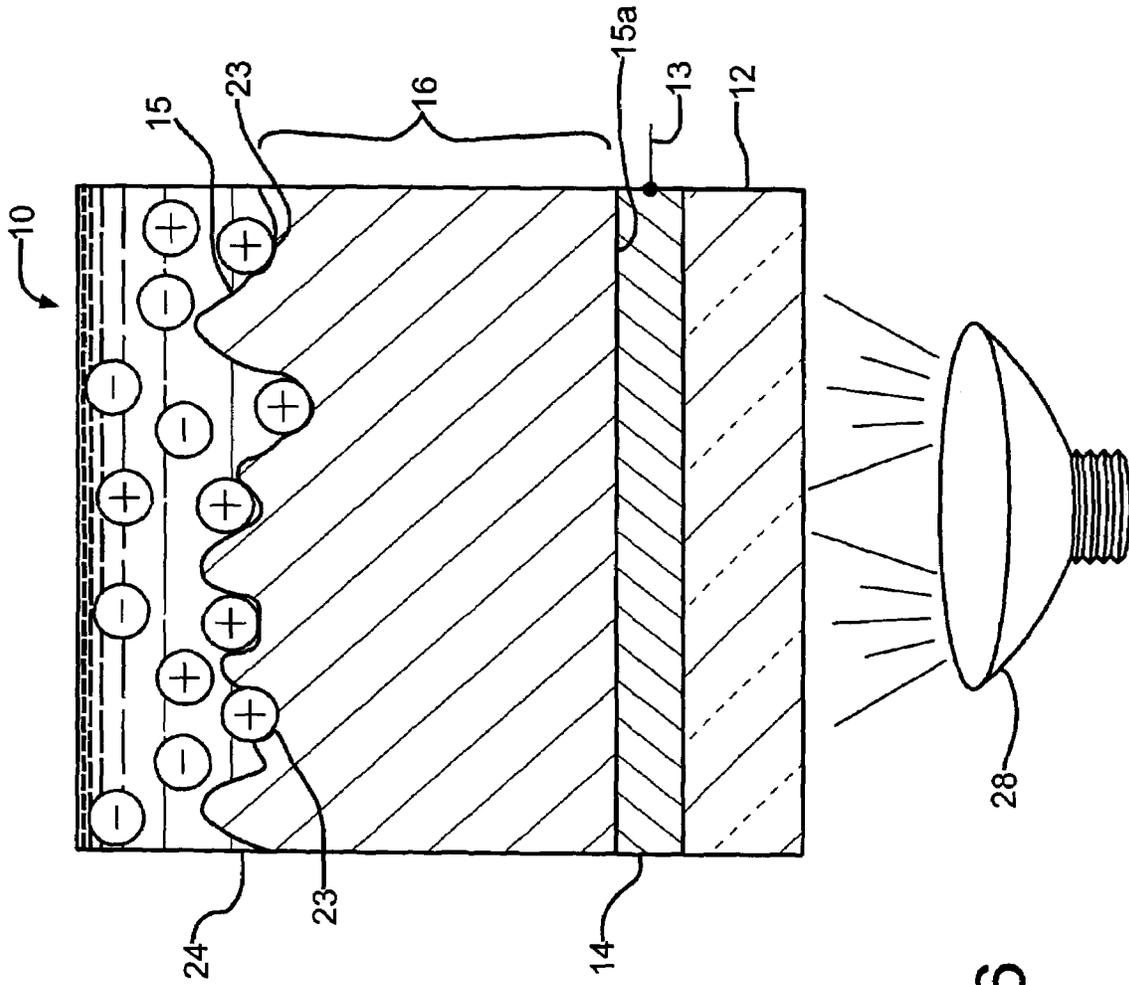
FIG.4

FIG. 5

FIG.6

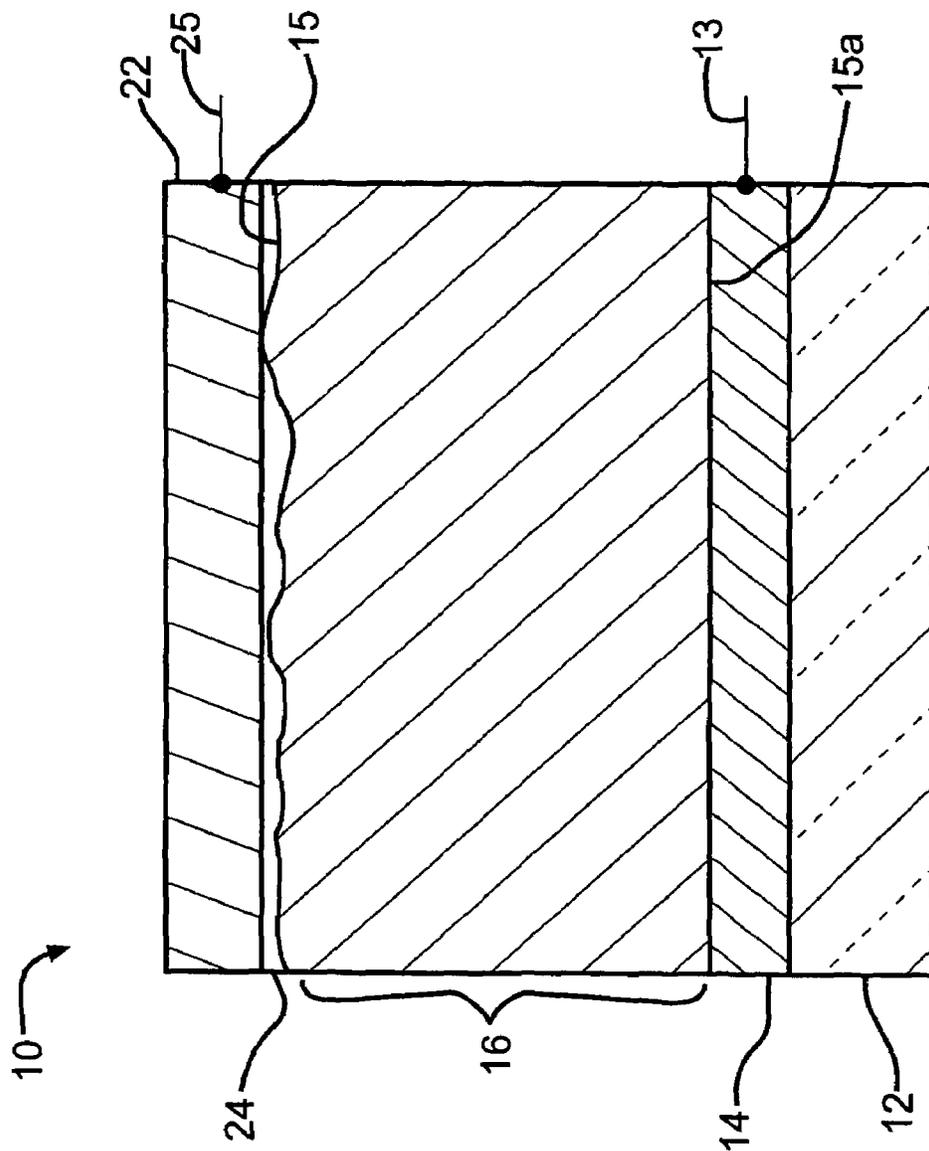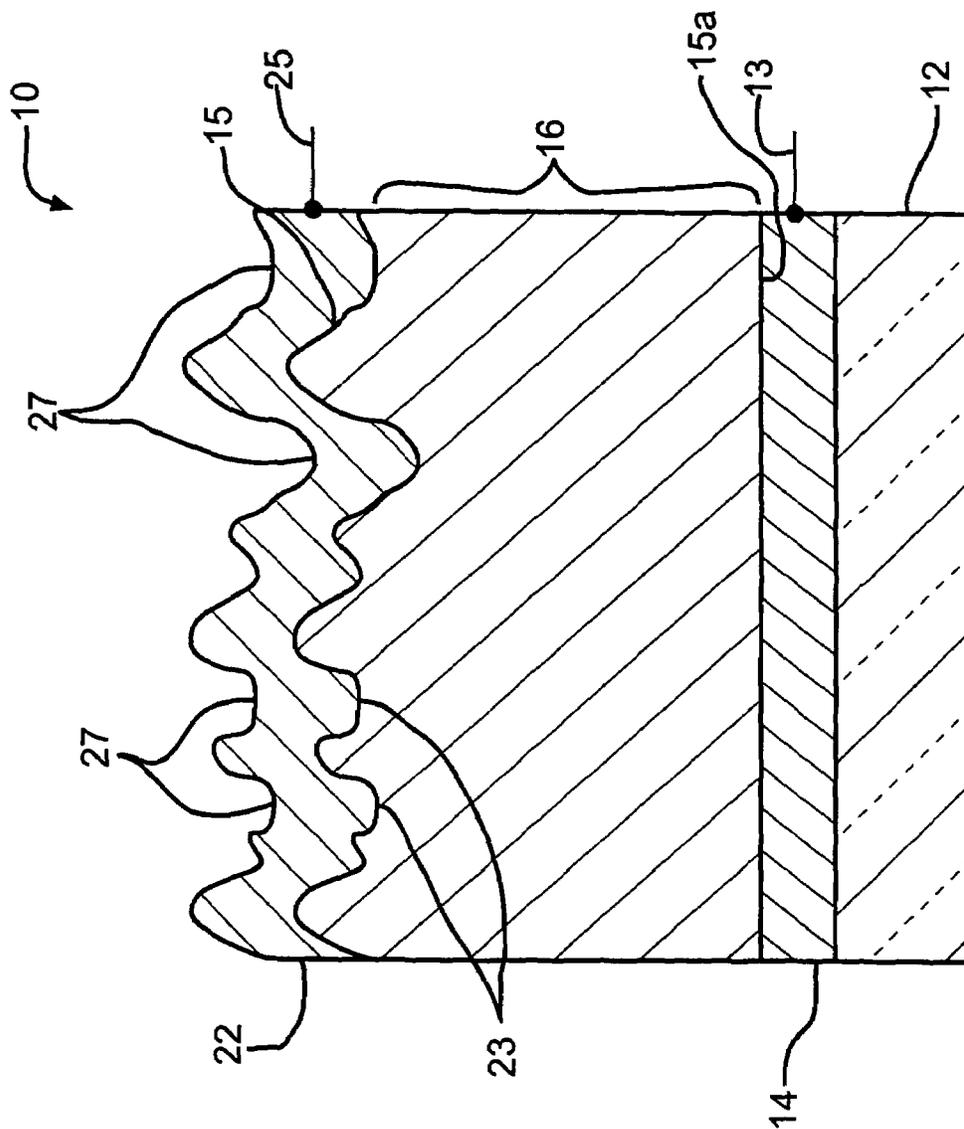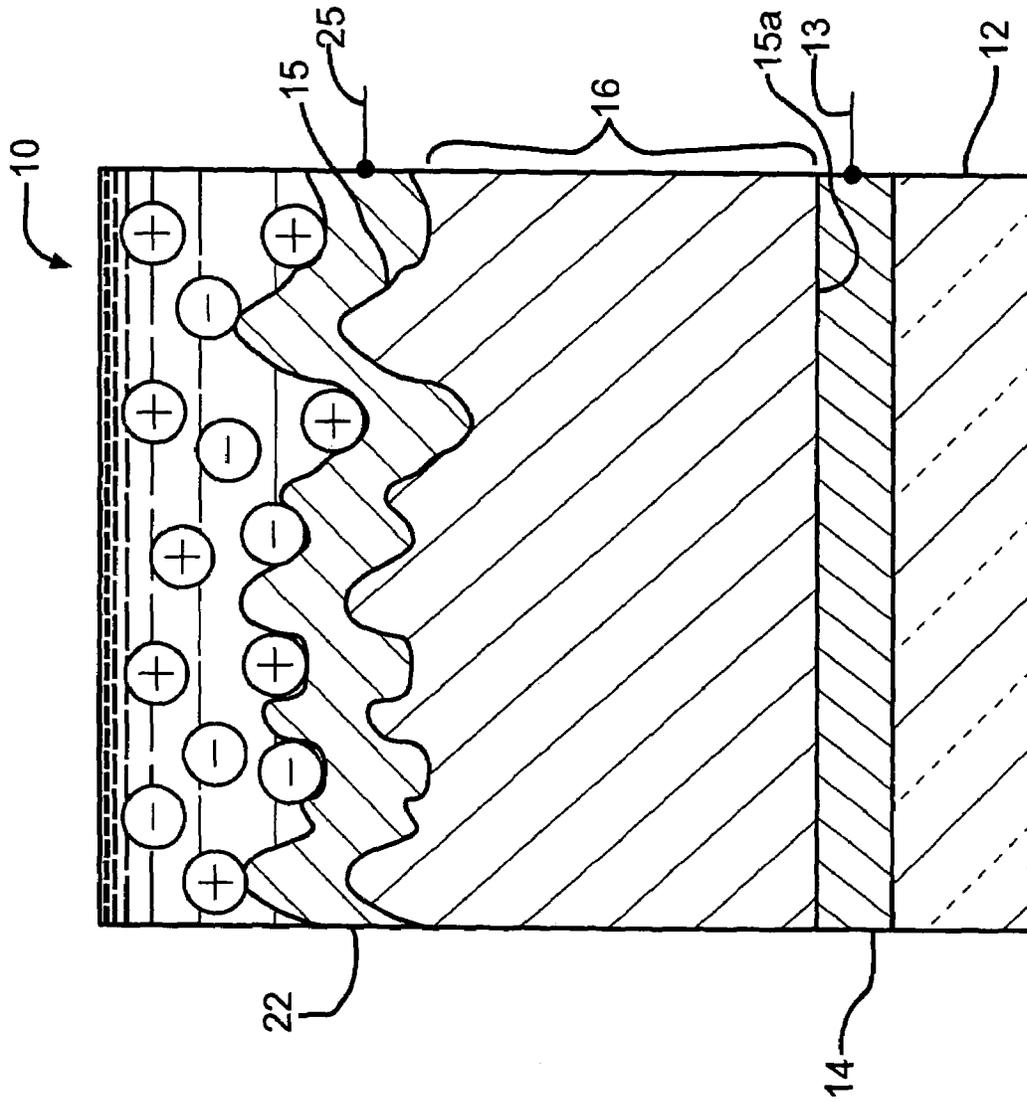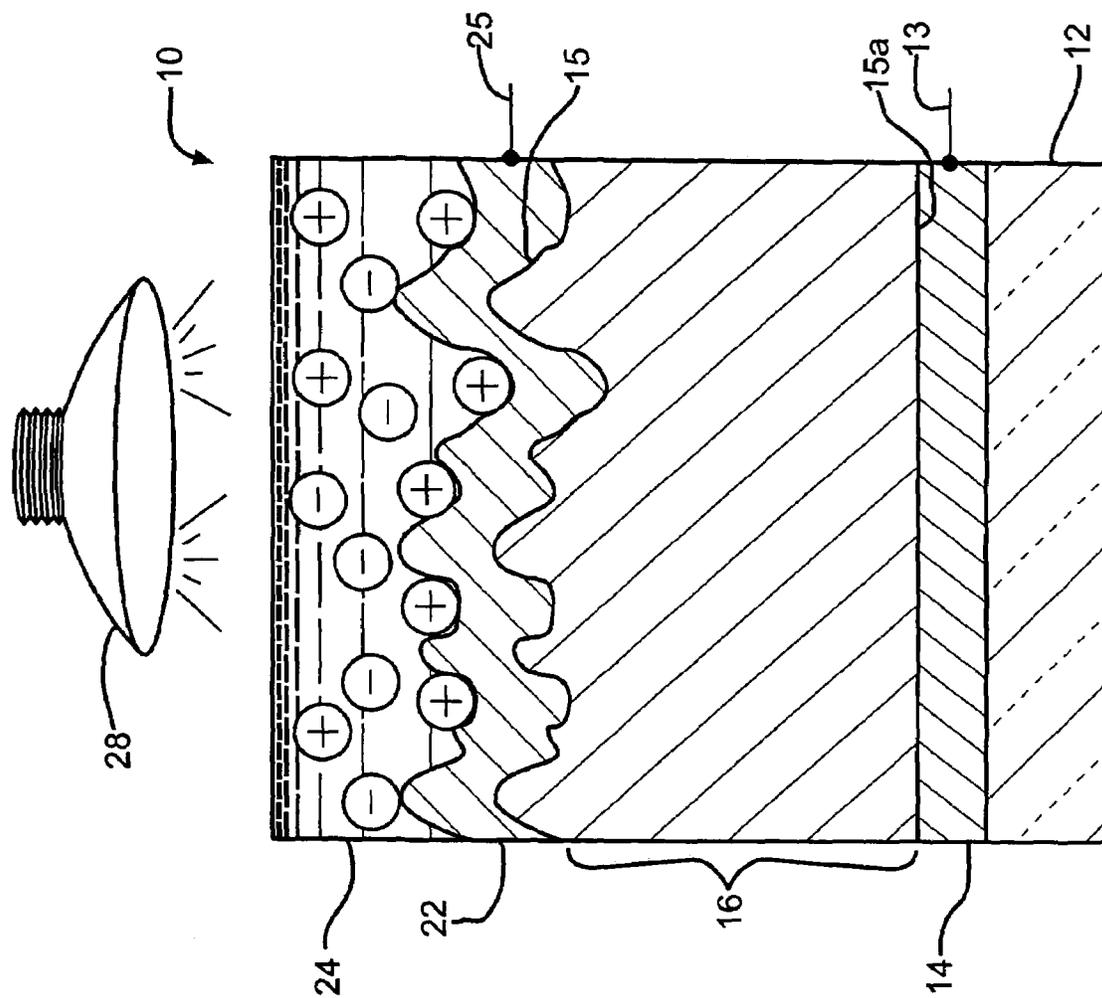FIG. 7

FIG.8

FIG.9

FIG. 10

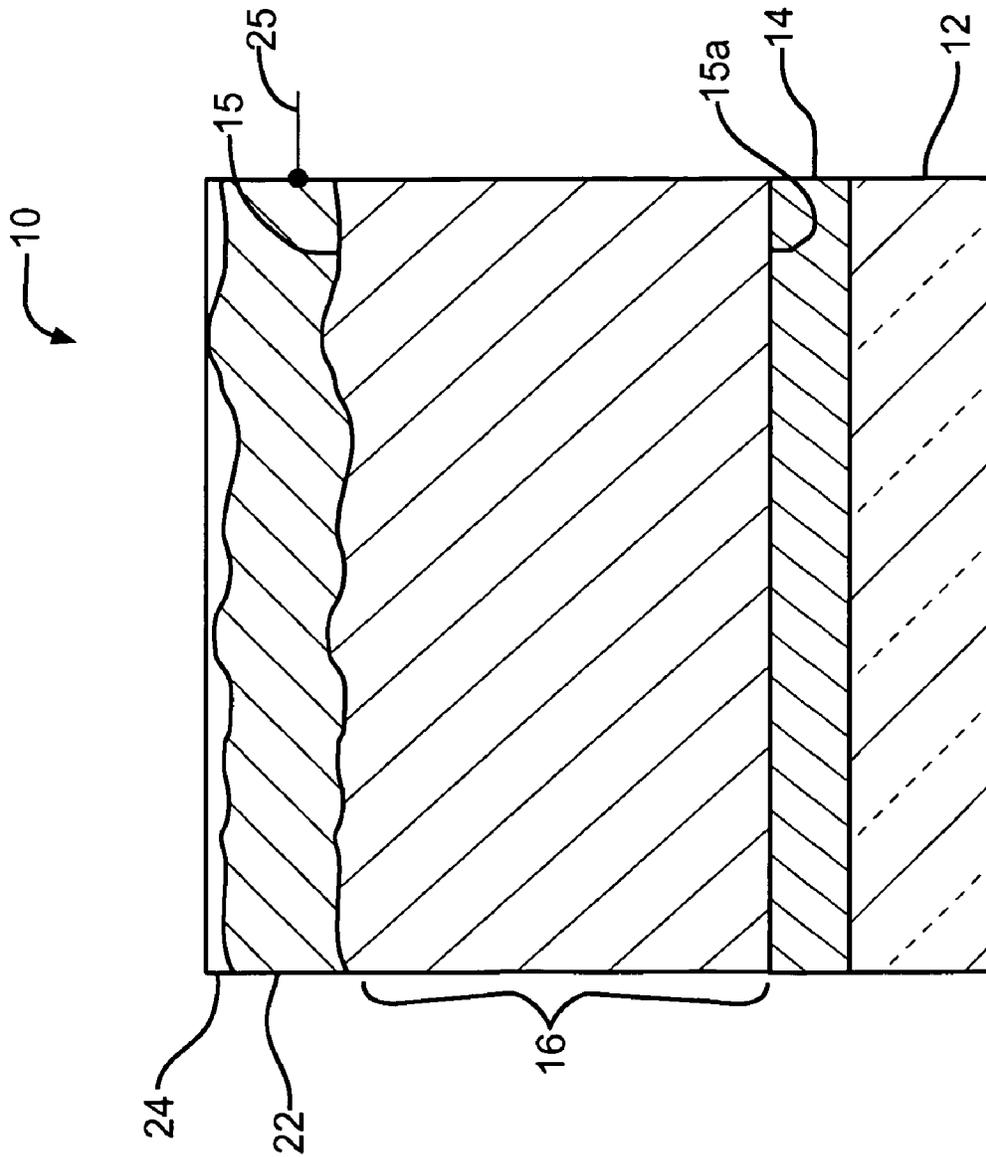FIG. 11

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PHOTOVOLTAIC HEALING OF NON-UNIFORMITIES IN SEMICONDUCTOR DEVICES

CROSS REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. Provisional Application No. 60/536,673, filed Jan. 15, 2004, the disclosure of which is incorporated herein by reference.

GOVERNMENT INTERESTS

The United States Government has certain rights in this invention pursuant to Contract No. NERL-NDJ-1-30630-02 awarded by the U.S. Department of Energy.

TECHNICAL FIELD

The present invention concerns semiconductor devices and a method of manufacturing semiconductor devices. More particularly, this invention relates to a method of manufacturing a semiconductor junction structure that includes selectively creating an electrically modified layer over areas of aberrant electric potential that deviate from the average electric potential in a semiconductor or electrode layer of a semiconductor device.

BACKGROUND OF THE INVENTION

Thin film semiconductor structures have recently found increasing popularity in industries requiring large active area semiconductor devices, such as the terrestrial photovoltaic, light emitting panel, and liquid crystal display driver fields. All of the above fields may incorporate devices having a photovoltaic cell type structure that generates a photovoltaic effect by generating voltage in response to absorbed light energy.

A typical photovoltaic (PV) cell includes a substrate layer for mounting the cell and two ohmic contacts or conductors for passing current to an external electrical circuit. The cell also includes an individual multi-layer semiconductor cell or several semiconductor cells connected in series. The cells operate by having readily excitable electrons that can be energized by solar energy to higher energy levels, thereby creating positively charged holes and negatively charged electrons at the interface of various semiconductor layers. The creation of these positive and negative charge carriers applies a net voltage across a base electrode layer and a top electrode layer positioned on either side of the semiconductor layer of the PV cell, which can force a current of electricity when the device is connected to a proper electric circuit.

The application of semiconductor devices in industries such as those mentioned above has created a need for semiconductor devices having active area requirements extending up to approximately one square meter. Due to these size requirements, the use of polycrystalline or amorphous thin film semiconductor material layers has become increasingly popular in semiconductor device design, as opposed to known crystalline semiconductor structures, which are both limited in size and expensive to manufacture. However, inherent in such polycrystalline or amorphous thin film layer semiconductor device configurations is the presence of various structural nonuniformities. Where a PV cell structure is used, these structural nonuniformities can cause lateral fluctuations in the electric potential at the surfaces of

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the various layers of the PV device (areas of low electric resistance are often referred to as shunts) as well as cause forward current leakage paths (often referred to as weak diodes). The structural nonuniformities can result from either defects within various semiconductor layers of the device or from morphological irregularities in the deposition surface of the substrate material. These defects lead to an overall decrease in the efficiency of the semiconductor device.

In order to minimize the negative impact such structural nonuniformities have on the performance of a PV device, there are a number of known treatment or minimization methods that effectively disable the semiconductor defect regions by destroying or isolating the corresponding defect region present in one of the electrode layers of the PV device. For example, U.S. Pat. No. 5,084,400 to Nath et al. discloses a method of using an activated conversion reagent to alter the physical properties of a top metal electrode layer to make highly resistive the areas of the top metal electrode layer surrounding low resistance current paths of the PV device caused by the surface nonuniformities of the semiconductor layer. Another known method, disclosed by U.S. Pat. No. 4,385,971 to Swartz, involves electrolytically etching or removing the corresponding top metal electrode material surrounding the semiconductor nonuniformity regions. Japanese Patent 60085576 to Fuse discloses a method of anodizing areas of a base metal electrode layer exposed through defects in the semiconductor layer to a non-conductive state prior to the application of the top electrode layer to prevent short circuit paths in the PV cell.

Another known method for minimizing the effects of nonuniformities in PV cells is the application of a barrier layer over a semiconductor surface containing surface nonuniformities. The application of such a barrier layer blocks the undesired electrical contact with the defect areas and minimizes electrical path failures to improve the overall operating efficiency of the PV cell. For example, U.S. Pat. No. 4,598,306 to Nath et al. discloses a continuous transparent barrier layer disposed between the semiconductor region and one of the electrode layers of the PV device. The barrier layer is disposed across the entire surface of the semiconductor and is formed from a specific group of materials designed to increase the resistivity of shunt (low resistance) regions on the semiconductor surface, which limits the flow of current through the short circuit current path of the shunt.

Even in light of the known methods for minimizing the effects of structural nonuniformities in PV cells utilizing thin-film semiconductor devices, there remains a continuing need for a more efficient, less expensive, and longer lasting thin-film semiconductor device. Thus, it would be advantageous to develop an improved method for treating structural nonuniformities in semiconductor devices that modifies the electric potential of localized defect areas within the semiconductor device to create a more uniform distribution of the electric potential generated by the semiconductor device.

SUMMARY OF THE INVENTION

The above objects as well as other objects not specifically enumerated are achieved by a method for treating structural nonuniformities in semiconductor devices that modifies the electric potential of localized defect areas within the semiconductor device to create a more uniform distribution of electric potential generated by the semiconductor device.

A typical photovoltaic (PV) device structure is a PV cell. A typical PV cell generally includes a substrate layer having

a base electrode material deposited thereon. An individual multi-layer semiconductor cell or several semiconductor cells connected in series is deposited over the base electrode layer. A conductive electrode layer is then placed over the semiconductor layer. The cells of the semiconductor layer operate to create a net voltage across the base electrode layer and conductive electrode layer positioned on either side of the semiconductor layer of the PV cell.

Thin film semiconductor devices generally contain a plurality of structural nonuniformities within the semiconductor layer. These structural nonuniformities effect the performance of the PV cell because areas of aberrant electric potential corresponding to these nonuniformities are created at the top surface of the semiconductor layer. The areas of aberrant electric potential deviate from the average electric potential of the remainder of the top surface of the semiconductor layer, which can lead to a decrease in the performance of the PV cell due to the variations in electric potential at the top surface of the semiconductor layer.

According to the method of this invention, a combination of light energy and a chemical solution is used to normalize the electric potential variations caused by surface nonuniformities in the semiconductor layer of the PV device. In a first embodiment of the invention, the top surface of the semiconductor layer is treated prior to the application of the conductive electrode layer. A solution is applied to the top surface of the semiconductor layer. The solution is generally comprised of an electrolyte and one or more bonding materials. Preferably, the solution has electrochemical properties, and more preferably includes a combination of an aniline material, p-toluenesulphonic acid, and sodium chloride (NaCl) in a deionized water base. The electrolyte component of the solution provides positive and negative ions within the solution. These positive ions can act as carriers for the non-ionic bonding material during the treatment process, as the non-ionic bonding material attaches to the positive and negative ions within the solution.

In a next step of the method, light energy is applied to the semiconductor layer of the PV device. The light energy generates a photovoltage in the semiconductor layer. The photovoltage enhances the deviation in the electric potential of the aberrant electric potential areas caused by the nonuniformities of the semiconductor layer. The generation of the photovoltage also causes an electrochemical reaction between the semiconductor layer and the solution. This electrochemical reaction causes a redistribution of the positive and negative ions of the solution, which carry the bonding material of the solution to the areas of aberrant electric potential caused by the nonuniformities in the semiconductor layer. The electrochemical reaction then causes the bonding material to bond to the top surface of the semiconductor layer. The resultant bonding is selective bonding of the bonding material to the areas of aberrant electric potential. This selective bonding of the bonding material normalizes the electric potential of the nonuniformities relative to the average electric potential of the remainder of the top surface of the semiconductor layer. A conductive electrode layer is then deposited over the treated top surface of the semiconductor layer to complete the PV device.

The net result of the selective deposition of the bonding material is the normalization of the overall average surface photovoltage of the semiconductor layer. This normalization of the surface photovoltage of the semiconductor layer can increase the performance of the PV device. Additionally, the normalization of the surface photovoltage increases the stability of the PV device. Stability is increased by reducing

the stresses caused by the nonuniformities in the semiconductor layer, which slows nonuniform degradation of the PV device.

In a second embodiment of the invention, the PV device can be treated after the application of the conductive electrode layer to the top surface of the semiconductor layer. Where treatment is applied to the conductive electrode layer, the conductive electrode layer must generally be formed from a transparent conductive electrode material. When a transparent conductive electrode layer is applied to an untreated semiconductor layer, the areas of aberrant electric potential at the top surface of the semiconductor cause corresponding defect areas of aberrant electric potential in the conductive electrode layer.

According to the second embodiment of the method, a solution is applied over the transparent conductive electrode layer. The solution used preferably has the same chemical parameters and characteristics as the solution used in the first embodiment of the invention. Following the application of the solution, light energy is applied to the semiconductor layer. The light energy enhances the deviation in the electric potential of the aberrant electric potential areas in both the semiconductor layer and the transparent conductive electrode layer. The enhancement of the deviations prompts an electrochemical reaction between the solution and transparent conductive electrode layer. As in the first embodiment, the electrochemical reaction causes a redistribution of the positive and negative ions of the solution. The electrochemical reaction also causes the bonding material carried by the positive and negative ions to bond to the top surface of the transparent conductive electrode layer. The resultant bonding is selective bonding of the bonding material to the areas of aberrant electric potential of the transparent conductive electrode layer. This selective bonding of the bonding material normalizes the electric potential of the defect areas relative to the average electric potential of the remainder of transparent conductive electrode layer.

Various objects and advantages of this invention will become apparent to those skilled in the art from the following detailed description of the preferred embodiment, when read in light of the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic elevational view of a photovoltaic cell having a single junction semiconductor layer.

FIGS. 2 and 3 are schematic elevational views of a tandem photovoltaic cell having a multi-junction semiconductor layer formed from a plurality of individual semiconductor cells that may be treated using the method of the present invention.

FIG. 4 is a schematic elevational view of a portion of a photovoltaic cell illustrating nonuniformities present in the semiconductor layer.

FIG. 5 is a schematic elevational view illustrating the application of a solution to the semiconductor layer in accordance with the method of the present invention.

FIG. 6 is a schematic elevational view illustrating the application of light energy to the photovoltaic cell in accordance with the method of the present invention.

FIG. 7 is a schematic elevational view of a completed photovoltaic cell treated in accordance with the method of the present invention.

FIG. 8 is a schematic elevational view of a portion of a photovoltaic cell illustrating nonuniformities present in both the semiconductor layer and the transparent conductive electrode layer.

FIG. **9** is a schematic elevational view illustrating the application of a solution to the transparent conductive electrode layer in accordance with a second embodiment of the method of the present invention.

FIG. **10** is a schematic elevational view illustrating the application of light energy to the photovoltaic cell in accordance with a second embodiment of the method of the present invention.

FIG. **11** is a schematic elevational view of a completed photovoltaic cell treated in accordance with a second embodiment of the method of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Referring now to the drawings, there is shown in FIGS. **1** through **3** photovoltaic cell configurations, indicated generally at **10**, having semiconductor device and semiconductor junction structures that may be manufactured according to the method of the present invention. The illustrated configurations for the photovoltaic cells **10** are, in large measure, conventional in the art and are intended merely to illustrate general photovoltaic cell configurations in which this invention may be used. It will also be appreciated that the method of the present invention may be utilized in the manufacture of any apparatus that includes a semiconductor device used to generate voltage in response to absorbed light energy, such as light emitting diode arrays or liquid crystal display drivers. Thus, the scope of this invention is not intended to be limited to either photovoltaic cells in general or to the specific structures for the photovoltaic cells **10** illustrated in FIGS. **1** through **3**.

The photovoltaic cell **10** includes a substrate layer **12**. Preferably this substrate layer **12** is a transparent material, such as glass, but it will be appreciated that other transparent materials can also be used. It will also be appreciated that an opaque substrate material, such as metal, may also be used. A base electrode layer **14** is applied to the substrate layer **12**. The base electrode layer **14** can be composed of either a transparent conductive material, such as a transparent conductive oxide, or a non-transparent conductive material, such as a metallic material. Where a transparent conductive material is used, preferably a transparent conductive oxide material such as a fluorine-doped tin oxide (SnO2:F) is used. It will also be appreciated that any suitable transparent conductive oxide material may also be used. This base electrode layer **14** forms one of the two ohmic contacts or electrodes for the photovoltaic cell **10**, and contains a conductive lead **13** for conducting current through an electric circuit (not shown).

The semiconductor layer, indicated generally at **16**, is applied over the base electrode layer **14**. The semiconductor layer **16** is comprised of at least one individual semiconductor cell, which may be configured in any suitable manner. FIG. **1** illustrates a simple PV cell design including a semiconductor cell **16a**, which is comprised of two layers (often referred to as a single junction semiconductor cell). The first layer of the semiconductor cell **16a** is comprised of an n-type semiconductor material **18**. In a preferred embodiment of the invention this n-type semiconductor material is cadmium sulfide (CdS), although it will be appreciated that any suitable n-type semiconductor material may also be used. The next layer of the semiconductor cell **16a** is comprised of a p-type semiconductor material **20**. In a preferred embodiment of the invention this p-type semiconductor material is cadmium telluride (CdTe), although it will be appreciated that any suitable p-type semiconductor mate-

rial may also be used. FIGS. **2** and **3** illustrate tandem PV cells having a multi-junction semiconductor layer **16**, which is comprised of a plurality of individual semiconductor cells **16a**, **16b**. As shown in FIG. **2**, the individual semiconductor cells may be of the single junction, two-layer cell type **16a** described above with reference to FIG. **1**. Alternatively, FIG. **3** shows a multi-junction semiconductor layer **16** comprised of a plurality of three-layer (often referred to as double junction) cells **16b**. The individual three-layer semiconductor cells **16b** are comprised of an n-type semiconductor layer **18**, a p-type semiconductor layer **20**, and also include an intrinsic (i-type) semiconductor layer **19** disposed between the p-type semiconductor layer **20** and the n-type semiconductor layer **18**. It will also be appreciated that the simple PV cell **10** illustrated in FIG. **1** may also be constructed using an individual double-junction type semiconductor cell **16b** shown in FIG. **3**. The individual thin-film layers of the semiconductor layer **16** may be applied to the substrate layer **12** using any suitable application method, such as by vapor transport deposition or by sputtering techniques.

To complete the PV cells **10** shown in FIGS. **1** through **3**, a conductive electrode layer **22** is deposited onto the top surface **15** of the semiconductor layer **16**. The top surface **15** of the semiconductor layer **16** is the surface of the semiconductor layer **16** disposed opposite the surface **15a** of the semiconductor layer **16** applied to the base electrode layer **14**. The conductive electrode layer **22** serves as the second of the two ohmic contacts or electrodes for the photovoltaic cell **10**. The conductive electrode layer **22** contains a conductive lead **25** for conducting current through the electric circuit (not shown). The conductive electrode layer **22** can be composed of either a transparent conductive material, such as a transparent conductive oxide, or a non-transparent conductive material, such as a metallic material. Generally, only one of the base electrode layer **14** or the conductive electrode layer **22** is formed from a transparent conductive material, with the remaining electrode layer being formed from a non-transparent material. Therefore, in a preferred embodiment where a transparent conductive material is used for the base electrode layer **14**, a non-transparent material is used for the conductive electrode layer **22**. Examples of such suitable non-transparent materials for the conductive electrode layer **22** include nickel, titanium, chromium, or aluminum. It will be appreciated, however, that the base electrode layer **14** and the conductive electrode layer **22** may be formed using any suitable materials that allow for light to be absorbed into the semiconductor layer **16** through at least one of the electrode layers **14**, **22**. Both the base electrode layer **14** and the conductive electrode layer **22** may be applied to the PV cell **10** using any suitable thin-film application method, such as sputtering techniques.

In both simple and multi-junction PV cell designs, a number of structural nonuniformities or defects exist throughout the semiconductor layer **16** of the PV cell **10**. These defects can occur for numerous reasons, and can include such defects as irregularities caused by the deposition process used to form the various semiconductor layers or defects caused by morphological irregularities in the deposition surface of the substrate material **12**. As shown in FIG. **4**, the defects throughout the various semiconductor cells **16a**, **16b** result in nonuniformities **23**, which cause areas of aberrant electric potential in the top surface **15** of the semiconductor layer **16**. The areas of aberrant electric potential caused by the nonuniformities **23** deviate from the average electric potential of the remainder of the top surface **15** of the semiconductor layer **16**. These areas of aberrant electric potential caused by the nonuniformities **23** can cause

a decrease in the performance of the PV cell **10**. It will be appreciated that the peaks and valleys illustrated on the top surface **15** of FIGS. **4** through **6** and **8** through **9** illustrate these areas of aberrant electric potential caused by the nonuniformities **23** and do not represent an actual variation in the thickness of the semiconductor layer **16** or conductive electrode layer **22**. It will further be appreciated that the areas of aberrant electric potential caused by the nonuniformities **23** in FIGS. **4, 5, 8,** and **9** have been exaggerated to show the enhancement of the variations in electric potential that occurs by the application of light energy to the semiconductor layer **16**. Prior to the application of light energy, the areas of aberrant electric potential caused by the nonuniformities **23**, although present, are generally less pronounced. The application of light energy to the semiconductor layer **16** will be explained in greater detail below.

During operation of the PV cell **10**, light in the visible spectrum that is applied through the transparent electrode layer **14** or **22** travels to the semiconductor layer **16**, where the light is largely absorbed. For example, where the base electrode layer **14** is comprised of a transparent conductive material, light is applied through the base electrode layer **14** and travels to the semiconductor layer **16**; conversely, where the base electrode layer **14** is comprised of a non-transparent material, light is applied through the conductive electrode layer **22**, which is formed from a transparent conductive material, and travels to the semiconductor layer. The fields created at the semiconductor junctions within the semiconductor layer **16** causes a voltage to be applied across the two electrode layers **14** and **22**, thereby causing a current to flow through the external circuit. The nonuniformities **23** of the top surface **15** of the semiconductor layer **16** compromise the flow of current through the circuit, as areas of decreased electric potential can cause short circuit and forward current leakage paths in the PV cell **10**, as discussed above. Similarly, areas of fluctuating electric potential (increasing and decreasing) create localized stresses within the semiconductor layer **16**, which can cause non-uniform degradation of the PV cell **10**.

As shown in FIGS. **5** through **7**, the method of the present invention uses a combination of light energy **28** and the application of a solution **24** containing both an electrolyte and at least one bonding and/or etching material to normalize, or level out, the surface potential variations caused by the nonuniformities **23** in the top surface **15** of the semiconductor layer **16**. The application of light energy **28** is needed to generate a surface photovoltage in the semiconductor layer **16**. This surface photovoltage causes a redistribution of the ions in the solution **24**. The redistribution of the ions carries the bonding material of the solution **24** to the areas of aberrant electric potential on the top surface **15** of the semiconductor layer **16** and causes an electrochemical reaction between the semiconductor layer **16** and the solution **24**. Depending upon the chemicals in the solution **24**, the electrochemical reaction causes the selective deposition of the bonding material over the areas of aberrant electric potential caused by the nonuniformities **23** in the top surface **15** of the semiconductor layer **16**. This selective deposition may include selectively etching and/or depositing local surface "clogs" of bonding material at the areas of aberrant electric potential of the semiconductor layer **16**. These surface modifications can be electrically insulating or otherwise active (electric double layer, etc.), which causes a blockage (passivation) of the areas of aberrant electric potential. The blockage of the areas of aberrant electric potential blocks the effects of the nonuniformities **23** on device performance after subsequent deposition of the con-

ductive electrode layer **22**. This process can be described generally as a "self-healing" process of the nonuniformities **23** of the semiconductor layer **16** to reflect the fact that the process selectively acts to deposit the bonding material over only the weak spots of the PV device **10**.

The process for normalizing the surface potential variations described above requires applying the solution **24** prior to the application of the conductive electrode layer **22**. As shown in FIGS. **8** through **11**, the process may also be used after the deposition of the conductive electrode layer **22** to selectively deposit the bonding material over defect areas **27** of aberrant electric potential in the conductive electrode layer **22**. These defect areas **27** correspond to the surface nonuniformities **23** of the semiconductor layer **16**. Treatment following the application of the conductive electrode layer **22** is generally possible only when the sheet resistance of the conductive electrode **22** is high enough to keep the surface potential nonuniformities **23** electrically isolated. In order to meet this resistance criterion, the conductive electrode layer **22** is generally comprised of a transparent conductive oxide material.

The treatment of the semiconductor layer **16** according to the first embodiment of the invention will now be described in more detail. FIGS. **4** through **7** illustrate the treatment of the semiconductor layer **16** with the solution **24** prior to the application of the conductive electrode layer **22**. The configuration of the PV cell **10** to be treated is shown in FIG. **4**. When the semiconductor layer **16** is treated prior to the application of the conductive electrode layer **22**, preferably both the substrate layer **12** and the base electrode layer **14** are composed of transparent materials to allow for the application of light energy to the semiconductor layer **16** through the substrate **12** and the base electrode layers **14**. More preferably, a glass substrate layer **12** coated with a fluorine-doped tin oxide (SnO_2:F) base electrode layer **14** is used. However, it will also be appreciated that either or both of the substrate layer **12** and the base electrode layer **14** may be comprised of an opaque material, such as a metallic material. Where an opaque material is used, light energy is applied directly to the top surface **15** of the semiconductor layer **16** during the treatment process, as will be explained in greater detail below.

As shown in FIG. **5**, a solution **24** containing an electrolyte and one or more bonding materials is applied to the top surface **15** of the semiconductor layer **16**. Preferably, the solution **24** has electrochemical properties, and more preferably includes a combination of an aniline material, p-toluenesulphonic acid, and sodium chloride (NaCl) in a deionized water base. Aniline material is used based on its ability to electropolymerize in acidic media at low electric potentials that are comparable to the surface photovoltage fluctuations caused by the areas of aberrant electric potential of the semiconductor layer **16**. It will be appreciated that the solution **24** may also be formed from any suitable alternate chemical formulations that contain a material with electrochemical properties.

The electrolyte component of the solution **24** provides positive and negative ions within the solution **24**. It will be appreciated, however, that the term "ion" as used throughout the application may refer to both simple ions provided by the electrolytic media portion of the solution **24** alone as well as electrolyte ions that carry the non-ionic bonding material(s) included within the solution **24**. For example, the term "ion" as used in the preferred embodiment refers to the combination of the sodium chloride (NaCl) electrolyte ion having the aniline material of the solution **24** attached thereon. The

importance of the positive and negative ions and their distribution within the solution **24** will be explained in greater detail below.

The electrolytic media component provides a solution resistivity to the solution **24**. This resistivity of the solution **24** is preferably of a magnitude sufficient to cause the redistribution of the positive and negative ions of the solution **24** during the electrochemical reaction between the solution **24** and the semiconductor layer **16**. This redistribution of ions is necessary to carry the bonding material to the areas of aberrant electric potential corresponding to the nonuniformities **23** on the top surface **15** of the semiconductor layer **16**. Preferably, the resistivity of the solution **24** is within the range of from about 0.1 to about 2000 Ωcm, and is more preferably within the range of from about 0.1 to about 10 Ωcm, depending upon the NaCl content of the solution **24**. The solution **24** is preferably applied to the semiconductor layer **16** in a liquid form, although it will be appreciated that any other suitable application form may also be used.

FIG. **6** illustrates the application of light energy **28** to the semiconductor layer **16** following the application of the solution **24**. Where a transparent substrate layer **12** and a transparent base electrode layer **14** are used, the light energy **28** is applied through the substrate layer **12**. Alternatively, an opaque substrate **12** and/or opaque base electrode layer **14** may be used, which requires light energy **28** to be applied through the solution **24** at the top surface **15** of the semiconductor layer **16**. In a preferred embodiment of the invention, a tungsten-halogen lamplight is used as the source of light energy **28**. It will be appreciated, however, that the light energy **28** can be supplied using any suitable source having sufficient intensity and spectrum for the light energy **28** to be absorbed into the semiconductor layer **16** and generate an electrochemical response between the solution **24** and the semiconductor layer **16**. For proper absorption of the light energy into the semiconductor layer **16**, the intensity of the light energy **28** is preferably within the range of from about 0.1 to about 5.0 sun, and is most preferably around 1.0 sun. A single (1.0) unit sun is the equivalent of 0.1 Watt/cm^2; therefore, the intensity of the light energy **28** may also be restated in alternative units as preferably within the range of from about 0.01 to about 0.5 Watt/cm^2, and most preferably around 0.1 Watt/cm^2.

FIGS. **5** through **7** illustrates the electrochemical response of the solution **24** and the semiconductor layer **16** with the application of light energy **28**. FIG. **5** shows the solution **24** prior to the application of light energy **28** to the semiconductor layer **16**. Prior to the application of light energy **28**, the solution **24** contains a generally random distribution of the positive and negative ions. FIG. **6** shows the application of light energy **28** to the semiconductor layer **16**. When the light energy **28** is applied to the semiconductor layer **16**, photovoltage is generated in the semiconductor layer **16**. This photovoltage enhances the areas of aberrant electric potential caused by the nonuniformities **23** at the top surface **15** of the semiconductor layer **16**. The pronounced peaks and valleys in FIG. **6** illustrate this enhancement of the deviations of electric potential in the aberrant areas from the average electric potential of the remainder of the top surface **15** of the semiconductor layer **16**.

The activation using light energy **28** to generate photovoltage in the semiconductor layer **16** causes an electrochemical reaction between the semiconductor layer **16** and the solution **24**. As shown in FIG. **6**, this electrochemical reaction causes the ions within the solution **24**, which carry the bonding material, to redistribute and selectively bond the

bonding material to the areas of aberrant electric potential caused by the nonuniformities **23** on the top surface **15** of the semiconductor layer **16**. This bonding of the bonding material to the areas of aberrant electric potential can occur by any suitable bonding method, such as electropolymerization, etching, or double electric layer deposition, depending upon the chemical composition of the solution **24**. FIG. **7** illustrates the net result of this electrochemical reaction. The redistribution of ions from the solution **24** causes a selective deposition of bonding material to the areas of aberrant electric potential caused by the nonuniformities **23** in the semiconductor layer **16**. This selective deposition subsequently causes the average electric potential across the surface of the semiconductor layer **16** to normalize, or level out. The selectively deposited bonding material may also be characterized as either a resistive or a dipole "double electric" layer of material, as the deposited material functions similar to an electric capacitor by modifying the areas of weakened/increased electric potential to normalize the overall average surface photovoltage of the semiconductor layer **16**.

The leveling of the surface photovoltage of the semiconductor layer **16** provides several advantages. A first advantage is an overall increase in PV cell efficiency, as the deposition of the bonding material blocks or passivates only those areas of aberrant electric potential coinciding with the nonuniformities **23** of the semiconductor layer **16**. Another advantage is increased stability of the PV cell **10**. By normalizing the surface photovoltage of the semiconductor layer **16**, stresses caused by the nonuniformities **23** of the semiconductor layer **16** that normally lead to the nonuniform degradation of the PV cell **10** are minimized. The minimization of stresses caused by the nonuniformities **23** increases the stability and operational life of the PV cell **10**.

Following the bonding of the bonding material to the top surface **15** of the semiconductor layer **16**, the PV cell **10** is completed by the application of the conductive electrode layer **22**. FIG. **7** illustrates the completed PV cell **10** including the conductive electrode layer **22**. As previously discussed, generally only one of the base electrode layer **14** or the conductive electrode layer **22** is comprised of a transparent material. Therefore, where a transparent electrode material is used for the base electrode layer **14**, the conductive electrode layer **22** is preferably formed from any suitable opaque, metallic material. However, where an opaque material is used for the base electrode layer **14**, the conductive electrode layer **22** is then preferably comprised of any suitable transparent conductive material. Examples of such suitable transparent and opaque metallic materials include those materials previously discussed. Similarly, the application of the conductive electrode layer **22** may be achieved using any suitable application method, such as the application techniques previously discussed.

FIGS. **8** through **11** illustrate a second embodiment of the invention where treatment of the semiconductor layer **16** occurs after the application of the conductive electrode layer **22**. The general configuration of the PV cell **10** for this embodiment is shown in FIG. **8**. Where the semiconductor layer **16** is treated following the application of the conductive electrode layer **22**, it is necessary that the conductive electrode layer **22** be composed of a transparent electrode material. Preferably, the transparent electrode material is a transparent conductive oxide material, such as fluorine-doped tin oxide (SnO$_2$:F), although any suitable transparent conductive oxide material may be used. A transparent material is necessary to allow the light energy **28** to penetrate the conductive electrode layer **22** and be absorbed into the

semiconductor layer **16**. Because the conductive electrode layer **22** is formed from a transparent electrode material, it is preferable that the base electrode layer **14** is composed of an opaque metallic material. It will also be appreciated that the substrate layer **12** may be formed from an opaque material as well, although a transparent material may also be used.

When the transparent conductive electrode layer **22** is applied to a semiconductor layer **16** having untreated surface nonuniformities **23**, defect areas **27** corresponding to the nonuniformities **23** on the top surface **15** of the semiconductor layer **16** occur within the transparent conductive electrode layer **22**. FIG. **8** illustrates the defect areas **27** of the transparent conductive electrode layer **22**, which are generally characterized by areas of aberrant electric potential that deviate from the average electric potential of the remainder of the surface of the transparent conductive electrode layer **22**. The defect areas **27** of the transparent conductive electrode layer **22** coincide with the underlying nonuniformities **23** of the semiconductor layer **16**.

As shown in FIG. **9**, a solution **24** containing an electrolyte and one or more bonding materials is applied to the transparent conductive electrode layer **22**. The solution **24** preferably has the same chemical parameters and characteristics as the solution used in the first embodiment of the invention. The preferred chemical parameters and characteristics have been previously described in detail herein with respect to the first embodiment and may also be considered the requirements for the solution **24** used in this second embodiment of the invention.

FIG. **10** illustrates the application of light energy **28** to the transparent conductive electrode layer **22** following the application of the solution **24**. In this embodiment, the light energy **28** is applied through the solution **24** placed on the surface of the transparent conductive electrode layer **22**. The application of light energy **28** through the transparent conductive electrode layer **22** is required because, as previously discussed, generally one or both of the substrate layer **12** and the base electrode layer **14** are composed of an opaque material that prohibits the passage of light energy **28** through the opaque layer. The light intensity and spectrum requirements are the same as those required in the first embodiment of the invention, which have been described in detail herein.

FIG. **11** illustrates the selective deposition of the bonding material that occurs as a result of the electrochemical response between the solution **24** and the transparent conductive electrode layer **22**. As in the first embodiment, when the light energy **28** is applied to the semiconductor layer **16**, photovoltage is generated in the semiconductor layer **16**. This photovoltage enhances the areas of aberrant electric potential caused by the nonuniformities **23** at the top surface **15** of the semiconductor layer **16**, which subsequently results in defect areas **27** of aberrant electric potential within the transparent conductive electrode layer **22**. The pronounced peaks and valleys in FIG. **10** illustrates this enhancement of the deviations of electric potential caused by the nonuniformities **23** of the semiconductor layer **16** that in turn result in the defect areas **27** of aberrant electric potential in the transparent conductive electrode layer **22**.

The activation using light energy **28** to generate photovoltage in the semiconductor layer **16** causes an electrochemical reaction between the transparent conductive electrode layer **22** and the solution **24**. As shown in FIG. **10**, this electrochemical reaction causes the ions within the solution **24**, which carry the bonding material, to redistribute and selectively bond the bonding material to the defect areas **27** of aberrant electric potential caused by the nonuniformities

23 on the top surface **15** of the semiconductor layer **16**. This bonding of the bonding material to the areas of aberrant electric potential can occur by any suitable bonding method, such as electropolymerization, etching, or double electric layer deposition, depending upon the chemical composition of the solution **24**. FIG. **11** illustrates the net result of this electrochemical reaction. The redistribution of ions from the solution **24** causes the selective deposition of material to the defect areas **27** of aberrant electric potential caused by the nonuniformities **23** in the semiconductor layer **16**. This selective deposition subsequently causes the average electric potential across the surface of the transparent conductive electrode layer **22** to normalize, or level out. The selectively deposited bonding material may also be characterized as either a resistive or a dipole "double electric" layer of material, as the deposited bonding material functions similar to an electric capacitor by modifying the areas of weakened/increased electric potential to normalize the overall average surface photovoltage of the transparent conductive electrode layer **22**.

The leveling of the photovoltage of the transparent conductive electrode layer **22** yields the same advantages of increased PV cell performance and increased stability and wear of the PV cell **10**. Additionally, treatment of PV cell **10** following the application of the transparent conductive electrode layer **22** provides an additional advantage in that operational mode failure defects, or defects that arise subsequent to the manufacture of the PV cell **10**, may also be treated.

The principle and mode of operation of this invention have been described in its preferred embodiments. However, it should be noted that this invention may be practiced otherwise than as specifically illustrated and described without departing from its scope.

What is claimed is:

1. A method of making a photovoltaic device comprising:
   providing a substrate having a base electrode layer;
   depositing a semiconductor layer onto the substrate layer, with a bottom surface of the semiconductor layer being deposited onto the base electrode layer, and a top surface of the semiconductor layer containing a plurality of nonuniformities, wherein the nonuniformities comprise areas of aberrant electric potential deviating from the average electric potential of the remainder of the top surface of the semiconductor layer;
   applying a solution over the top surface of the semiconductor layer, wherein the solution is comprised of an electrolyte and at least one additional bonding material, and wherein the solution contains positive and negative ions;
   applying light energy to the semiconductor layer to enhance the deviation in the electric potential of the aberrant electric potential areas, thereby causing a redistribution of the positive and negative ions of the solution, and also causing the bonding material to bond to the top surface of the semiconductor layer, wherein the resultant bonding is selective bonding of the bonding material to the areas of aberrant electric potential in a manner such that the electric potential of the nonuniformities is normalized relative to the average electric potential of the remainder of the top surface of the semiconductor layer; and
   depositing a conductive electrode layer over the top surface of the semiconductor layer.

2. The method of claim **1** wherein the positive and negative ions include a non-ionic bonding material carried with the positive and negative ions of the solution.

3. The method of claim **1** wherein the bonding of the bonding material to the nonuniformities occurs by any one of electropolymerization, etching, or double electric layer deposition.

4. The method of claim **1** wherein the solution includes a combination of an aniline material, p-toluenesulphonic acid, and NaCl in a deionized water base.

5. The method of claim **1** wherein the solution has sufficient resistivity to cause the redistribution of the positive and negative ions of the solution.

6. The method of claim **5** wherein the resistivity of the solution is within the range of from about 0.1 to about 2000 Ωcm.

7. The method of claim **1** wherein the substrate layer is formed from a transparent material and the base electrode layer is formed from a transparent conductive electrode material.

8. The method of claim **7** wherein the conductive electrode layer is formed from an opaque metallic material.

9. The method of claim **7** wherein the light energy is applied to the device through the substrate layer.

10. The method of claim **7** wherein the transparent conductive electrode material is a transparent conductive oxide.

11. The method of claim **1** wherein the base electrode layer is formed from an opaque metallic material.

12. The method of claim **11** wherein the conductive electrode layer is formed from a transparent conductive electrode material.

13. The method of claim **11** wherein the light energy is applied to the device through the solution applied to the top surface of the semiconductor layer.

14. The method of claim **1** in which the source of light energy is a tungsten-halogen lamp light.

15. The method of claim **1** wherein the intensity and spectrum of the light energy is sufficient to be absorbed into the semiconductor layer of the device and cause the redistribution of the positive and negative ions of the solution.

16. The method of claim **15** wherein the intensity of the light energy is within the range of from about 0.1 to about 5.0 sun.

17. A method of making a photovoltaic device comprising:

provising a substrate having a base electrode layer;

depositing a semiconductor layer onto the substrate layer, with a bottom surface of the semiconductor layer being deposited onto the base electrode layer, and a top surface of the semiconductor layer containing a plurality of nonuniformities, wherein the nonuniformities comprise areas of aberrant electric potential deviating from the average electric potential of the remainder of the top surface of the semiconductor layer;

depositing a transparent conductive electrode layer over the top surface of the semiconductor layer, the transparent conductive electrode layer containing a plurality of defect areas corresponding to the nonuniformities of the semiconductor layer, wherein the defect areas com-

prise areas of aberrant electric potential deviating from the average electric potential of the remainder of the transparent conductive electrode layer;

applying a solution over the transparent conductive electrode layer, wherein the solution is comprised of an electrolyte and at least one additional bonding material, and wherein the solution contains positive and negative ions; and

applying light energy to the semiconductor layer to enhance the deviation in the electric potential of the aberrant electric potential areas of the semiconductor layer and the transparent conductive electrode layer, thereby causing a redistribution of the positive and negative ions of the solution, and also causing the bonding material to bond to the top surface of the transparent conductive electrode layer, wherein the resultant bonding is selective bonding of the bonding material to the areas of aberrant electric potential of the transparent conductive electrode layer in a manner such that the electric potential of the defect areas is normalized relative to the average electric potential of the remainder of the transparent conductive electrode layer.

18. The method of claim **17** wherein the positive and negative ions include a non-ionic bonding material carried with the positive and negative ions of the solution.

19. The method of claim **17** wherein the bonding of the bonding material to the defect areas occurs by any one of electropolymerization, etching, or double electric layer deposition.

20. The method of claim **17** wherein the solution includes a combination of an aniline material, p-toluenesulphonic acid, and NaCl in a deionized water base.

21. The method of claim **17** wherein the solution has sufficient resistivity to cause the redistribution of the positive and negative ions in the solution.

22. The method of claim **21** wherein the resistivity of the solution is within the range of from about 0.1 to about 2000 Ωcm.

23. The method of claim **17** wherein the light energy is applied through the solution placed over the transparent conductive electrode layer.

24. The method of claim **17** in which the source of light energy is a tungsten-halogen lamp light.

25. The method of claim **17** wherein the intensity and spectrum of the light energy is sufficient to be absorbed into the semiconductor layer of the device and cause the redistribution of the positive and negative ions of the solution.

26. The method of claim **25** wherein the intensity of the light energy is within the range of from about 0.1 to about 5.0 sun.

27. The method of claim **17** wherein the transparent conductive electrode layer is formed from a transparent conductive oxide material.

28. The method of claim **17** wherein the base electrode layer is formed from an opaque metallic material.

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