Description

A PHOTOVOLTAIC DEVICE AND METHOD FOR THE PRODUCTION OF A PHOTOVOLTAIC DEVICE

The application relates to a photovoltaic device, such as a solar cell, and methods for the production of a photovoltaic device.

Nanowires have the potential to facilitate a whole new generation of electronic devices. US 7,339,184 B2 discloses methods of harvesting, integrating and exploiting nano-materials, in particular, elongated nanowire materials. Nanowires may be grown by successive growth on a surface to form nanowires which are orientated generally vertically with respect to the surface. Nanowires may then be harvested from this surface by selectively etching a sacrificial layer placed on a nanowire growth substrate in order to remove the nanowires. The harvested nanowires may be integrated into electronic devices such as transistors and photovoltaic devices such as solar cells.

US 7,339,184 B2 also discloses a method in which an outer surface of a cylinder is placed in contact with a fluid suspension of nanowires so that nanowires adhere to the outer surface of the cylinder and can then be deposited onto a device surface by rolling the nanowire coated cylinder onto the device surface. The nanowires are arranged laterally and parallel to the device surface.

However, further device arrangements as well as methods for nanowire harvesting and integration that facilitate mass production, yield consistent nanowire performance characteristics and generate improved device performance are desirable.

A photovoltaic device is provided that comprises a substrate comprising a major surface and a material that is transparent at optical wavelengths. The photovoltaic device further comprises a first metallic electrode arranged on the major surface and a second metallic electrode spaced apart from the first electrode. A first plurality of semiconductive nanowires comprising a longitudinal outer surface and end faces are provided. The plurality of nanowires extends generally parallel to the major surface of the substrate. The photovoltaic device also comprises at least one photovoltaically active material. The plurality of first semiconductive nanowires and the photovoltaically active material are arranged between the first metallic electrode and the second metallic electrode. The longitudinal outer surface of opposing ends of the plurality of first nanowires is embedded in the first metallic electrode.

The nanowires are generally elongated in form and are defined by the longitudinal outer surface that extends orthogonally from and between two opposing end faces. The longitudinal outer surface at regions of opposing ends of the nanowires is embedded within the first metallic electrode. This arrangement is in contrast to an arrangement in which only the end face is in contact with the metallic

electrode as would be the case if the nanowire were grown upwards vertically on the surface of the metallic electrode.

Since the longitudinal outer surface of opposing ends of the plurality of first nanowires is embedded in the first metallic electrode of the photovoltaic device, charge produced in the photovoltaically active material can be conducted along the first nanowires directly into the first metallic electrode. This avoids charge hopping between nanowires as a mechanism for charge conduction within the photovoltaic device and increases the efficiency of charge transfer to the first metallic electrode.

The nanowires comprise a semiconductive material such as ZnO, SnO_2 or Sb-doped SnO_2. The first metallic electrode and the second metallic electrode may comprise the same or different metals or alloys. Suitable metals are aluminum, silver, and gold.

The first metallic electrode and the second metallic electrode of the photovoltaic cell may have different arrangements with respect to one another.

In the first group of embodiments, the second metallic electrode is spaced vertically apart from the first metallic electrode. In this sense vertical is used to define a direction perpendicular to the major surface of the substrate. Such an arrangement of the first metallic electrode and the second metallic electrode enables the photovoltaic device to be build up in a layered fashion on the first major surface of the substrate.

One or more of the first metallic electrode and the second metallic electrode may comprise a ring portion. Ring-shaped electrodes enable the cross-sectional area of the electrode to be increased so as to reduce the contact resistance and increase efficiency of the photovoltaic device.

The area of the photovoltaic device confined by the ring-shaped electrode remains uncovered by metal and is transparent to impinging photons. The photovoltaically active material and the nanowires used to conduct the generated charge are arranged in this region. If both the first metallic electrode and the second metallic electrode are ring-shaped the photovoltaic device may be illuminated from two opposing sides.

In an embodiment, a portion of the longitudinal outer surface at opposing ends of the nanowires is embedded in opposing portions of the ring portion of the first metallic electrode. This provides a short conduction path for the generated charges along the nanowires to the first metallic electrode thus reducing resistance and loss of energy.

The photovoltaic device may further comprise an electrolyte extending between the photovoltaically active material and at least the second electrode. The first plurality of nanowires may comprise a material comprising a first conductivity type and the electrolyte may comprise a material comprising a

second conductivity type which opposes the first conductivity type. For example, the first plurality of nanowires may conduct electrons and the electrolyte may conduct holes or vice versa. The electrolyte can be used to increase the collection and transfer efficiency of the second conductivity type charges within the photovoltaic device. The electrolyte may be a solid and may also have a material in the form of nanoparticles, nanowires, or carbon nanostructures.

In a second group of embodiments, the second metallic electrode is spaced laterally apart from the first metallic electrode. In this sense, laterally is used to denote a plane that is generally parallel to the first major surface. Both the first metallic electrode and the second metallic electrode may be in direct contact with the first major surface of the substrate. Such an arrangement can be used to reduce the height of the photovoltaic device compared with embodiments in which the second metallic electrode is spaced vertically above the first metallic electrode.

In a particular embodiment of the second group of embodiments, the photovoltaic device further comprises a second plurality of nanowires. The second plurality of nanowires are arranged generally parallel to the major surface of the substrate and at an angle θ with respect to the first plurality of nanowires, wherein $0° < \theta \leq 90°$. The second plurality of nanowires may be generally orthogonally orientated with respect to the first plurality of nanowires, i.e. $\theta \approx 90°$.

In an embodiment, the first metallic electrode comprises at least two sub-electrodes spaced laterally apart from one another and the second metallic electrode comprises sub-electrodes spaced laterally apart from one another. The first plurality of nanowires extends between a first sub-electrode and a second sub-electrode providing the first metallic electrode and the second plurality of nanowires extend between a third sub-electrode and a fourth sub-electrode providing the second metallic electrode.

This arrangement of the sub-electrodes allows charge to be conducted along the first plurality of nanowires to a portion of the first metallic electrode arranged at opposing ends of the first plurality of nanowires and likewise for charge to be conducted along the second plurality of nanowires to a portion of the second metallic electrode arranged at opposing ends of the second plurality of nanowires. Therefore, the area over which charge can be created by the photovoltaically active material and collected by the nanowires can be increased whilst still enabling the conduction of the charge along the length of the nanowires to the sub-electrodes to avoid a charge-hopping mechanism between nanowires as the conduction mechanism.

The photovoltaically active material may be provided in different forms. The photovoltaically active material may be provided as a coating on the plurality of first nanowires and the second plurality of nanowires, if present. The photovoltaically active material may have the form of a layer that is arranged between the first plurality of nanowires and the second plurality of nanowires. The layer may be a deposited layer or may be self-supporting in the form of a foil, for example. The photovoltaically

active material may be a dye or a low band gap semiconductor.

A method for producing a photovoltaic device is provided that comprises providing a substrate having a major surface. The substrate comprises a material, which is transparent at optical wavelengths. A plurality of nanowires is provided. Each nanowire comprises a longitudinal outer surface and end faces. The plurality of nanowires is arranged on the major surface of the substrate so that the nanowires extend generally parallel to the major surface of the substrate and a photovoltaically active material is deposited onto the nanowires. A first metallic electrode and a second metallic electrode are deposited on portions of the plurality of nanowires so that a portion of the longitudinal outer surface of opposing ends of the plurality of nanowires is embedded in the first metallic electrode.

This method enables pre-fabricated nanowires to be applied to a major surface of a substrate and the metallic electrodes to be subsequently deposited onto the nanowires so as to embed opposing end portions of the nanowires in the first metallic electrode and provide an electrical connection between the nanowires and the first metallic electrode. This method enables the production of nanowires to be performed separately from the production of the metallic electrodes and enables each production step to be separately optimized. This may lead to a reduction in production costs as lower cost production methods may be used. For example, the nanowires may be pre-fabricated using a lower cost electro-spinning technique rather than a more expensive solid-vapor production technique. Also, the material of the first metallic electrode can be selected to optimize its performance as an electrode as it does not have the dual purpose of acting as a growth surface for the nanowires as is the case for in-situ grown nanowires, for example. This enables lower cost metals such as aluminum to be used for the metallic electrodes. Nanowires may be fabricated by a vapour-liquid-solid technique or electrospinning, for example.

An electrolyte may be deposited onto the first plurality of nanowires if it is desired that the photovoltaic device has a further electrolyte to improve conduction of the charges generated in the photovoltaically active material. The electrolyte may be deposited by coating the nanowires, for example by dip coating or spraying, with a suitable material before application of the nanowires onto the first major surface of the substrate. The electrolyte may also be deposited onto the nanowires after they have been applied to the substrate. The electrolyte may be deposited by a vapour deposition technique, a sputtering technique, a doctor blade process, a spray process, a spin-coating technique, a screen-printing technique or an ink-jet printing technique.

If an electrolyte is provided, the second metallic electrode may be deposited onto the electrolyte and the first metallic electrode may be deposited so as to embed opposing ends of the first plurality of nanowires in the first metallic electrode.

The method may also comprise depositing a second plurality of nanowires onto the first plurality of nanowires so that the second plurality of nanowires are arranged generally parallel to the major sur-

face of the substrate and at and angle θ with respect to the first plurality of nanowires, wherein $0° < \theta \leq 90°$. The second plurality of nanowires may be pre-fabricated and may comprise the same or a different material. For example, the first plurality of nanowires may comprise material that conducts a first charge type, for example, electrons, and the second plurality of nanowires may comprise material that conducts a second charge type, for example holes, that is opposite to the first charge type.

If two pluralities of nanowires are deposited, the photovoltaically active material may be deposited onto the first plurality of nanowires and the second plurality of the nanowires deposited onto the photovoltaically active material to create a layered structure in which the photovoltaically active material is sandwiched between the first plurality of nanowires and the second plurality of nanowires. This arrangement allows the charge generated in the photovoltaically active material to be transferred over a small distance to the first plurality of nanowires and the second plurality of nanowires where it is conducted directly along the nanowires to the first metallic electrode and second metallic electrode, respectively.

The position of the first metallic electrode and the second metallic electrode including sub-electrodes, if present, may be performed by selective deposition of the metal or alloy through a structured mask. In an embodiment, a first sub-electrode is deposited onto first ends of the first plurality of nanowires, a second sub-electrode is deposited onto opposing ends of the first plurality of nanowires, a third sub-electrode is deposited onto first ends of the second plurality of nanowires and a fourth sub-electrode is deposited onto opposing ends of the second plurality of nanowires.

One or more of the first electrode and the second electrode may be deposited by a vapour deposition technique, a sputtering technique, a doctor blade process, a spray process or a solution-based printing technique.

In addition to the materials disclosed above, the following materials may also be used in the photovoltaic device.

The photovoltaically active material may also be described as a conversion material or an absorber. Different classes of material may be used for the photovoltaically active material such as inorganic thin films, organic thin films, dye molecules and quantum dots.

An inorganic thin film may comprise CdS, PbS, ZnS, SnS_2, Ag_2S, FeS_2, SnS, SnS_2, Cu_2S, CuS, Sb_2S_3, CZTS, Sb_2Se_3, CIS, CIGS, CdSe, PbSe, ZnSe, SnSe, Ag_2Se, Sb_2Te_3, CdTe, CdZnTe, PbTe, ZnTe, Ag_2Te, or In_2Te_3.

An organic thin film may comprise Poly(3-hexylthiophene) (P3HT) and other thiophenes, Poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT) and other carbazoles, Pentacene and other acenes, PCBM and other C60

derivatives, vinazenes, Poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl]] (PCPDTBT).

A dye molecule may comprise metal center dyes including but not limited to cis-Bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-di-nonyl-2'-bipyridyl)ruthenium(II), Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II),metal free dyes such as indoline dyes, perylene derivatives, coumarin dyes, porphyrin dyes and cyanine or merocyanine dyes.

Quantum dots may comprise CdS, PbS,ZnS,SnS_2 ,Ag_2S,FeS_2,SnS,SnS_2,Cu_2S,CuS,Sb_2S_3,CZTS, Sb_2Se_3, CIS,CIGS,CdSe,PbSe,ZnSe,SnSe,Ag_2Se, Sb_2Te_3, CdTe, CdZnTe,PbTe,ZnTe,Ag_2Te,In_2Te_3.

If an electrolyte in the form of a hole conductor is provided it may comprise Iodide salts dissolves in appropriate solvents including acetonitrile, valeronitrile, methoxypropionitrile and liquid organic iodide salt 1-propyl-3-methylimidazolium iodide, Spiro-OMTAD, P3HT, PEDOT:PSS and other conductive polymers, solid state electrolytes formed by dissolving lithium,chloride, phosphate and iodide ions in polymers such as PVA,PEO,PVDF and other polymer matrices or polyelectrolyte comprising a single component organic materials including but not limited to Polystyrene sulfonic acid (PSSH) or random copolymer of vinyl phosphonic acid and acrylic acid P(VPAAA) or other groups of polyanions or poly-cations with appropriate counterions including and not limited to I, Cl, OH, Li.

Embodiments will now be described with reference to the accompanying drawings.

Figure 1 illustrates a cross-sectional view of a photovoltaic device according to a first embodiment,

Figure 2 illustrates a further cross-sectional view of the photovoltaic device according to the first embodiment,

Figure 3 illustrates a top view of the photovoltaic device according to the first embodiment,

Figure 4 illustrates a photovoltaic device according to a second embodiment,

Figure 5 illustrates a top view of a photovoltaic cell according to a third embodiment,

Figure 6 illustrates a cross-sectional view of the photovoltaic cell according to the third embodiment,

Figure 7 illustrates a graph of IV-characteristics obtained from dye decorated SnO_2

nanowires,

Figure 8 illustrates a graph of IV-characteristics obtained from dye decorated TiO_2 nanowires, and

Figure 9 illustrates a table of device performances inferred from figure 8.

Figure 1 illustrates a schematic cross-sectional view of a photovoltaic device 1 according to a first embodiment. The photovoltaic device 1 comprises a substrate 2 which comprises a major surface 3 on which the active components of the photovoltaic device 1 are positioned. The substrate 2 comprises a material that is transparent at optical wavelengths, for example glass. The substrate 2 comprises a second major surface 4 which opposes the first major surface 3. The second major surface 4 may provide the surface of the photovoltaic device 1 on which light impinges as schematically illustrated by the arrows 5.

The photovoltaic device 1 comprises a first metallic electrode 6 positioned on the first major surface 3 of the substrate 2. In this embodiment, the first metallic electrode 6 has a ring shape, as illustrated in the top view of Figure 3, which may be also thought of as a rectangular frame. The photovoltaic device 1 comprises a plurality of nanowires 7, of which only one is illustrated in the cross-sectional view of figure 1, which are arranged generally parallel to the first major surface 3 of the substrate 2.

Each nanowire 7 has a generally elongated form comprising end faces 8 and a longitudinal outer surface 9 extending orthogonally from and between the end faces 8. The nanowire may have any shape (e.g. hexagonal, square, etc) cross-section and core can be hollow. Each of the nanowires 7 comprises a semiconductor material such as an oxide or a nitride, for example ZnO, SnO_2 or Sb-doped SnO_2 and nanotube.

The plurality of nanowires 7 extend between opposing portions of the ring shaped first metallic electrode 6 so that the outer longitudinal surface 9 of the opposing ends of the plurality of nanowires 7 is embedded within portions of the ring-shaped first metallic electrode 6 that oppose one another.

Each of the plurality of nanowires 7 is coated with a layer of a photovoltaically active material 10. As used herein, a photovoltaically active material is a material that generates a charged pair that is an electron-hole pair when light having energy bigger than the energy band gap impinges the photovoltaically active material, thus converting optical energy to electrical energy. In this embodiment, the photovoltaic active material 10 is a dye such as a Ruthenium-based dye or a low band-gap semiconductor.

The photovoltaic device 1 further comprises a second metallic electrode 11 which is arranged spaced vertically apart from the first metallic electrode 6. The first metallic electrode 6 may comprise

aluminium and the second metallic electrode 11 may comprise gold.

The photovoltaic device 1 further comprises an electrolyte 12 which extends between the second metallic electrode 11 and the first plurality of nanowires 7. In this embodiment, the plurality of nanowires 7 comprises a semiconductor material such as tin oxide or antimony-doped tin oxide which is able to conduct electrons. The electrolyte 12 comprises a material which conducts holes such as poly (3, 4-ethylenedioxythiophene), polyaniline, poly(3-hexylthiophene), or ion-doped PVDF (polyvinylidene fluoride).

When light impinges the photovoltaic device 1 and the photovoltaically active material 10, an electron-hole pair is formed in the photovoltaically active material 10. The electrons formed within the photovoltaic active coating 10 of the plurality of nanowires 7 are able to be conducted along the length of the nanowires 7 to the first metallic electrode 6 so that charge hopping between nanowires can be avoided, thus increasing efficiency of conduction.

The holes generated in the photovoltaically active coating 10 can be conducted through the electrolyte 12 to the second metallic electrode 11 to produce a voltage between the first metallic electrode 6 and the second metallic electrode 11 and convert optical energy to electrical energy.

Figure 2 illustrates a second cross-sectional view of the photovoltaic device 1 illustrated in figure 1. In the cross-sectional view of figure 2, the plurality of nanowires 7 are illustrated. In this embodiment, only a single layer of nanowires is illustrated. However, the plurality of nanowires may be arranged in several layers and may not necessarily be arranged exactly parallel to one another but also at angles of up to 90° with respect to one another.

Figure 3 illustrates a top view of the photovoltaic device 1 illustrated in figures 1 and 2. In figure 3, the rectangular ring form of the first metallic electrode 6 and of the second metallic electrode 11 can be seen. The plurality of nanowires 7 extend between two opposing sides of the rectangular ring form of the first metallic electrode 6. The first metallic electrode 6 further includes a protruding portion 13 which extends from one side of the first metallic electrode 6 along the major surface 3 of the substrate 2. This extended portion 13 can be used as a contact area for the first metallic electrode 6. The second metallic electrode 11 is arranged vertically above the plurality of nanowires 7. The first metallic electrode 6 may be electrically contacted by means of a bondwire, for example. In further non-illustrated embodiment, the second metallic electrode 11 may also have a protrusion similar to portion 13 for electrical contact.

Figure 4 illustrates a photovoltaic device 14 according to a second embodiment. Similar parts are indicated with the same number as in the first embodiment.

The photovoltaic device 14 of the second embodiment also includes a ring shaped first electrode 6 positioned on a substrate 2 that is optically transparent and a first plurality of nanowires 7 extending between opposing portions of the first metallic electrode 6. Again, the plurality of nanowires 7 is coated with a photovoltaically active material 10 in the form of a ruthenium-based dye or low band gap semiconductor. The plurality of nanowires 7 is embedded in an electrolyte material 12 which has the opposing conductivity as that of the material of the plurality of nanowires 7. Alternatively, the plurality of nanowires 7 itself may absorb the light and play the role of the photovoltaically active material 10.

In the second embodiment, the photovoltaic device 14 further comprises a light scattering layer 15 comprising a second plurality of nanowires 16. A ring shaped second metallic electrode 11 is positioned on the light scattering layer 15, which can comprise nanoparticles so that the second metallic electrode 11 is spaced apart from the first metallic electrode 6.

The light scattering layer 15 serves to prevent shorting between the first metallic electrode 6 and the second metallic electrode 11 and may also provide light scattering so as to reflect light back towards the photovoltaically active material 10 coating the plurality of nanowires 7. This can help to increase the efficiency of the conversion of the optical energy into electrical energy.

Figure 5 illustrates a top view of a photovoltaic cell 17 according to a third embodiment. Figure 6 illustrates a cross-sectional view along the line A-A of the photovoltaic cell 17 of Figure 5. The photovoltaic device 17 comprises a substrate 2 that is optically transparent as in the first and second embodiments. The photovoltaic device 17 comprises, in addition to a first plurality of nanowires 7, a second plurality of nanowires 18 which also extend generally parallel to the major surface 3 of the substrate 2 but generally orthogonally to the first plurality of nanowires 7. The second plurality of nanowires 18 is positioned vertically above or can be intermixed (e.g. like in textiles or clothing) with the first plurality of nanowires 7.

In contrast to the previous embodiments, the first metallic electrode 6 and a second metallic electrode 11 are laterally spaced apart from one another and are both positioned on the major surface 3 of the substrate 2 rather than being vertically spaced apart from one another as is illustrated in the cross-sectional view of figure 6.

Each of the first metallic electrode 6 and the second metallic electrode 11 comprises two sub-electrodes which are spaced apart from one another so that each sub-electrode embeds opposing ends of the respective plurality of nanowires. The photovoltaic device 17 comprises four sub-electrodes, each spaced apart from one another.

A first sub-electrode 19 and a second sub-electrode 20 provide the first metallic electrode 6 and are arranged so as to embed opposing ends of the first plurality of nanowires 7. A third sub-electrode 21

and a fourth sub-electrode 22 provide the second metallic electrode 11 and are arranged so as to embed opposing end portions of the second plurality of nanowires 18. Therefore, the first sub-electrode 19 and second sub-electrode 20 together form the anode and the third sub-electrode 21 and the fourth sub-electrode 22 together form the cathode of the photovoltaic device 17.

A photovoltaically active material is provided in the form of a layer 23 that is positioned between the first plurality of nanowires 7 and the second plurality of nanowires 18.

The material of the first plurality of nanowires 7 and of the second plurality of nanowires 18 is chosen so that the first plurality of nanowires 7 has a complimentary conduction type to that of the second plurality of nanowires 18. For example, the first plurality of nanowires 7 may conduct electrons and the second plurality of nanowires 18 may conduct holes, or vice versa.

When light impinges the lower surface 4 of the substrate 2, or, in the case of discontinuous electrodes, also from the opposing side of the photovoltaic device 17, it passes into the photovoltaically device 17 generating electron-hole pairs in the photovoltaic active layer 23. The electrons are conducted by means of the first plurality of nanowires 7 to the first sub-electrode 19 and to the second sub-electrode 20 which form the anode and the holes generated are conducted by the second plurality of nanowires 18 to the third sub-electrode 21 and to the fourth sub-electrode 22 which form the cathode of the photovoltaic device 17.

The photovoltaically active layer 23 not only generates electron hole pairs under the illumination but can also be used to prevent recombination of the electrons and holes at the junctions where the first plurality of nanowires 7 and the second plurality of nanowires 18 cross. This arrangement of the two pluralities of nanowires also allows for elimination of the photovoltaically active layer 23 from both sides whilst avoiding the use of transparent conductive oxides.

In further embodiments, the photovoltaically active layer 23 can be replaced by a photovoltaically active coating of both the first plurality of nanowires 7 and of the second plurality of nanowires 18.

In further embodiments, the use of additional photoactive layer 23 and of photovoltaically active material in the form of a coating can be avoided by either making the first plurality of the nanowires 7 or the second plurality of nanowires 18 photovoltaically active.

In all of the previously described embodiments, the nanowires are used to collect charges produced in the photovoltaically active material of the photovoltaic device and conduct them directly to the respective metallic electrode or sub-electrode. This avoids the use of charge hopping between separate nano-sized particles as a charge transport mechanism and increases the efficiency of the device.

The nanowires may be configured so as to optimize the efficiency of the device. For example, the density of the nanowires may be optimized. The use of a low-density nanowires results in larger charge collection lengths and lower collection efficiency. However, increasing the nanowire network density above a threshold-level resulted in reduced light transmission since the nanowires themselves are not transparent at optical wavelengths. Therefore, an optimum density of nanowires is required. The density of nanowires is also dependent on the length and in particular the diameter, as well as the electrical resistivity of the nanowires. By using long nanowires of high-quality, that is low electrical resistance, the density of the nanowires may be reduced whilst obtaining sufficient charge collection.

In the embodiments described above, the photovoltaic active material is described as a dye and, in particular, a ruthenium-based dye. However, this dye can be replaced by compounds such as a low bandgap polymer or other inorganic semiconductors.

The photovoltaic devices may be fabricated using pre-fabricated nanowires which are then arranged on the major surface of the device substrate so that they are aligned generally parallel to the major surface of the device substrate. The photovoltaically active material may then be deposited onto the nanowires or the nanowires may be pre-coated with the photovoltaically active material before they are applied to the device substrate. The metallic electrodes and the electrolyte may them be deposited onto the nanowires to build up the device structure. This method enables the photovoltaic device to be fabricated using a wide variety of fabrication techniques and allows different fabrication techniques to be combined. For example, the electrolyte may be deposited using spin-coating and the metallic electrode deposited by evaporation. The method is flexible so that the device structure can be better optimized and the production methods optimized so as to reduce costs.

The photovoltaic devices described above may be fabricated using pre-fabrication nanowires. These pre-fabricated nanowires may be produced using the following methods.

In an embodiment, tin oxide nanowires are synthesised on a silicon (100) substrate comprising a 2 nm thick gold film as a catalyst using a vacuum vapour transport approach. A mixture of tin oxide (SnO_2) and active graphite powder, both having a 99% purity, in a molar ratio of 2 to 1, are used as a source and are loaded in to the centre of quartz tube arranged in a furnace. The temperature is rapidly increased to 900° C and the silicon substrate is placed downstream of the tin oxide and graphite powder source materials in a temperature zone at around 780°C. The peak temperature is held for 15 minutes using argon carrier gas at a flow rate of 120 standard cubic centimetres per minute under pressure of 6.10^{-1} Torr. The system is then cooled to room temperature in vacuum. Tin oxide nanowires grow generally vertically from the silicon substrate. The tin oxide nanowires may also be doped with 5% antimony to increase the conductivity of the nanowires.

In further embodiments, the tin oxide nanowires may also be fabricated by electro-spinning. Whatever, the fabrication method, the prefabricated nanowires are coated with a ruthenium-based dye which acts as the photovoltaically active material.

The pre-fabricated tin oxide nanowires are then transferred to a device substrate, such as a glass substrate, using a contact method so that laterally aligned tin oxide nanowires are formed on the major surface of the device substrate. The nanowires lie parallel to the major surface of the device substrate rather than vertically. The first and second electrodes may be formed by selectively evaporating aluminium using a mask to form electrodes having a thickness of around 100 nm. The shape of mask is chosen so as to provide the desired arrangement of the electrodes with respect to the nanowires.

Figure 7 illustrates a graph of Current-Voltage (IV) characteristics measured for dye decorated SnO_2 nanowire networks under photoillumination. The overall thickness of the nanowire networks was around 100nm. The insert of Figure 7 illustrates a strip electrode used to collect the charges.

Figure 8 illustrates a graph of IV-characteristics measured for dye decorated TiO_2 nanowire networks under photoillumination. The overall thickness of the nanowire networks was around 1 μm (micron). The device performances inferred from figure 8 are summarized in table 1 of figure 9.

The results illustrated in Figures 7 and 8 demonstrate that dye decorated semiconductive and, in particular, oxide nanowires can be successfully used in the production of photovoltaically active devices, such as solar cells.

Claims

1. A photovoltaic device (1; 14; 17), comprising:
a substrate (2) comprising a major surface (3) and a material that is transparent at optical wavelengths,
a first metallic electrode (6) arranged on the major surface (3),
a second metallic electrode (11) spaced apart from the first electrode (6),
a first plurality of nanowires (7) comprising a longitudinal outer surface and end faces, the plurality of nanowires extending generally parallel to the major surface of the substrate and comprising semiconductive material, and
at least one photovoltaically active material (10; 23), the plurality of first nanowires (7) and the photovoltaically active material (10; 23) being arranged between the first metallic electrode (6) and the second metallic electrode (11), the longitudinal outer surface (9) of opposing ends of the plurality of first nanowires (7) being embedded in the first metallic electrode (6).

2. The photovoltaic device (1; 14) according to claim 1, wherein the second metallic electrode (11) is spaced vertically apart from the first metallic electrode (6).

3. The photovoltaic device (1; 14) according to claim 1 or claim 2, wherein one or more of the first metallic electrode (6) and the second metallic electrode (11) comprises a ring portion.

4. The photovoltaic device (1; 14) according to claim 2, wherein a portion of the longitudinal outer surface (9) at opposing ends of the first plurality of nanowires (7) is embedded in opposing portions of the ring portion of the first metallic electrode (6).

5. The photovoltaic device (1; 14) according to one of claims 1 to 4, further comprising an electrolyte (12) extending between the photovoltaically active material (10) and at least the second electrode (11), wherein the first plurality of nanowires (7) comprise a material comprising a first conductivity type and the electrolyte (12) comprises a material comprising a second conductivity type which opposes the first conductivity type.

6. The photovoltaic device (17) according to claim 1, wherein the second metallic electrode (11) is spaced laterally apart from the first metallic electrode (6).

7. The photovoltaic device (17) according to claim 6 further comprising a second plurality of nanowires (18) , the second plurality of nanowires (18) being arranged generally parallel to the major surface (3) of the substrate (2) and at an angle θ with respect to the first plurality of nanowires (7), wherein $0° < \theta \leq 90°$.

8. The photovoltaic device (17) according to claim 7, wherein the first metallic electrode (6) comprises at least two sub-electrodes (19, 20) spaced laterally apart from one another and the second metallic electrode (11) comprises sub-electrodes (21, 22) spaced laterally apart from one another, wherein the first plurality of nanowires (7) extend between a first sub-electrode (19) and a second sub-electrode (20) providing the first metallic electrode (6) and the second plurality of nanowires (18) extend between a third sub-electrode (21) and a fourth sub-electrode (22) providing the second metallic electrode (11).

9. The photovoltaic device (17) according to claim 7 or claim 8, wherein the first plurality of nanowires (7) comprise a material comprising a first conduction type and the second plurality of nanowires (18) comprise a material comprising a second conduction type that opposes the first conduction type.

10. The photovoltaically device (1; 14; 17) according to one of claims 1 to 9, wherein the photovoltaically active material (10) is provided as a coating on the plurality of first nanowires (7) and the second plurality of nanowires (18), if present.

11. The photovoltaic device (17) according to one of claims 6 to 9, wherein the photovoltaically active material (23) has the form of a layer and is arranged between the first plurality of nanowires (7) and the second plurality of nanowires (18).

12. Method for producing a photovoltaic device (1; 14; 17) comprising:
providing a substrate (2) having a major surface (3) that comprises a material that is transparent at optical wavelengths,
providing a plurality of nanowires (7) comprising a longitudinal outer surface (9) and end faces (8),
arranging the plurality of nanowires (7) on the major surface (3) of the substrate (2) so that the plurality of nanowires (7) extend generally parallel to the major surface (3) of the substrate (2),
depositing a photovoltaically active material (10) onto the plurality of nanowires (7), and
depositing a first metallic electrode (6) and a second metallic electrode (11) on portions of the plurality of nanowires (7) so that a portion of the longitudinal outer surface (9) of opposing ends of the plurality of nanowires (7) is embedded in the first metallic electrode (6).

13. The method according to claim 12, wherein the plurality of nanowires (7) are fabricated by a vapour-liquid-solid technique or electrospinning.

14. The method according to claim 12 or claim 13 further comprising depositing an electrolyte (12) onto the first plurality of nanowires (7) .

15. The method according to claim 14, wherein the second metallic electrode (11) is deposited onto the electrolyte (10) and the first metallic electrode (6) is deposited so as to embed opposing ends of the first plurality of nanowires (7) in the first metallic electrode (6).

16. The method according to one of claims 12 to 14 further comprising depositing a second plurality of nanowires (18) onto the first plurality of nanowires (7) so that the second plurality of nanowires (18) are arranged generally parallel to the major surface (3) of the substrate (2) and at and angle θ with respect to the first plurality of nanowires (7), wherein $0° < \theta \leq 90°$.

17. The method according to claim 16, wherein photovoltaically active material (23) is deposited onto the first plurality of nanowires (7) and the second plurality of the nanowires (18) is deposited onto the photovoltaically active material (23).

18. The method according to claim 17 or claim 18, wherein a first sub-electrode (19) is deposited onto first ends of the first plurality of nanowires (7), a second sub-electrode (20) is deposited onto opposing ends of the first plurality of nanowires (7), a third sub-electrode (21) is deposited onto first ends of the second plurality of nanowires (18) and a fourth sub-electrode (22) is deposited onto opposing ends of the second plurality of nanowires (18).

19. The method according to one of claims 12 to 18, wherein
one or more of the first metallic electrode (6) and the second metallic electrode (11) is deposited by a vapour deposition technique, a sputtering technique, a doctor blade process, a spray process or a solution-based printing technique.

20. The method according to one of claims 12 to 19, wherein the electrolyte (12) is deposited by a vapour deposition technique, a sputtering technique, a doctor blade process, a spray process, a spin-coating technique, a screen-printing technique or an ink-jet printing technique.