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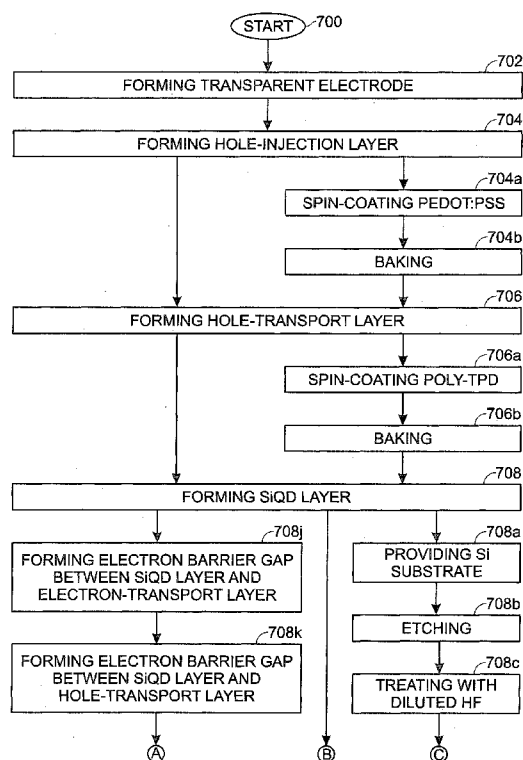
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(54) Title: A METHOD MANUFACTURING COLLOIDAL SILICON QUANTUM DOT VISIBLE SPECTRUM LIGHT-EMITTING DIODE, AND COLLOIDAL SILICON QUANTUM DOT VISIBLE SPECTRUM LIGHT-EMITTING DIODE

FIG. 7A



(57) Abstract: A method for manufacturing a colloidal silicon quantum dot visible spectrum light-emitting diode includes the steps of forming a transparent first electrode; forming a hole-injection layer overlying the first electrode; forming a hole-transport layer overlying the hole-injection layer; forming a silicon quantum dot layer overlying the hole-transport layer; forming an electron-transport layer overlying the silicon quantum dot layer; and forming a second electrode overlying the electron-transport layer, wherein the silicon quantum dot layer includes a plurality of silicon quantum dots having a diameter of less than 6 nanometers.



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[Description]

[Title of Invention]

A METHOD MANUFACTURING COLLOIDAL SILICON QUANTUM DOT
VISIBLE SPECTRUM LIGHT-EMITTING DIODE, AND COLLOIDAL
5 SILICON QUANTUM DOT VISIBLE SPECTRUM LIGHT-EMITTING DIODE

[Technical Field]

The present invention generally relates to organic light-emitting diodes (OLEDs) and, more particularly, to an OLED fabricated using silicon quantum dots (SiQDs). The present application claims priority from United States
10 Provisional Application Serial Number 13/094,262, filed on April 26, 2011.

[Background Art]

Colloidal inorganic semiconductor quantum dots (QDs) with size-tunable band gaps, high photoluminescence (PL) quantum yield, and narrow emission line widths are good candidates for solution-processable chromophores in a
15 hybrid QD-organic light-emitting diode (QD-OLED) structure. Visible electroluminescence (EL) from the hybrid structure has been reported in group II-VI semiconductor QD systems, such as CdSe, CdZnSe, ZnSe, or CdZnS cores with single or multiple shells. High luminance and high efficiency QD-OLEDs using these II-VI QDs have been recently demonstrated in a display
20 with an active matrix drive backplane.

[Summary of Invention]

[Technical Problem]

There has been significant development in synthesis and characterization regarding group IV colloidal semiconductor QDs. However, there has not

been any demonstration of visible EL from these nanomaterials. It would be advantageous if OLEDs fabricated with silicon QDs (SiQDs) could produce EL across the entire visible spectrum.

[Solution to Problem]

- 5 Silicon QDs (SiQDs) exhibit tunable band gaps due to quantum confinement effect when the dot sizes are within the Bohr exciton radius of bulk Si (around 4.9 nanometers (nm)). Thus, a visible red to blue spectrum can be achieved for electroluminescence (EL) and photoluminescence (PL) applications by adjusting QD radius from approximately 6 nm to 1 nm.
- 10 Compared to conventional II-VI QDs, SiQDs are heavy-metal-free, potentially compatible with well-established Si processing technologies, and can be synthesized from almost inexhaustible starting materials in the earth crust. A substantial number of the device layers can be fabricated using solution-processing methods, including spin-coating and drop-casting. Therefore, the
- 15 Si QD-OLEDs are potentially low-cost and suitable for large area application, such as flat-panel displays.

- (1) An aspect of a method for manufacturing a colloidal silicon quantum dot visible spectrum light-emitting diode includes: a first step of forming a transparent first electrode; a second step of forming a hole-injection layer
- 20 overlying the first electrode; a third step of forming a hole-transport layer overlying the hole-injection layer; a fourth step of forming a silicon quantum dot layer overlying the hole-transport layer; a fifth step of forming an electron-transport layer overlying the silicon quantum dot layer; and, a sixth step of forming a second electrode overlying the electron-transport layer. Here, the
- 25 silicon quantum dot layer includes a plurality of silicon quantum dots having a diameter of less than 6 nanometers.

(2) The above method may be configured as follows: the fourth step further includes the steps of: providing a silicon substrate; etching the silicon substrate through exposure to a first mixture including hydrofluoric acid, methanol, hydrogen peroxide, and polyoxometalates; treating the silicon
5 substrate to diluted hydrofluoric acid in a second mixture including water and methanol; immersing, in a nitrogen filled environment, the silicon substrate in a hexane/1-octene mixture with a catalytic amount of chloroplatinic acid; ultra-sonicating the silicon substrate in hexanes; and forming a suspension of silicon quantum dots.

10 (3) The above method may be configured as follows: the fourth step further includes the steps of: filtering the suspension of silicon quantum dots to remove a particle having a diameter of larger than 6 nanometers; spin-coating the suspension of silicon quantum dots at 300 revolutions per minute for 30 seconds; and vacuum drying the suspension of silicon quantum dots.

15 (4) The above method may be configured as follows: the second step further includes the steps of: spin-coating a layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) at 4000 revolutions per minute for 40 seconds, to a thickness of 100 nanometers; and baking the layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) in a nitrogen-filled
20 environment at 120° C for 30 minutes.

(5) The above method may be configured as follows: the third step includes the steps of: spin-coating a layer of poly(N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl) benzidine at 2000 revolutions per minute for 30 seconds, to a thickness of 50 nanometers; and, baking the layer of poly(N,N'-bis(4-
25 butylphenyl)-N,N'-bis(phenyl) benzidine in a nitrogen-filled environment at 110° C for 30 minutes.

(6) The above method may be configured as follows: the fifth step includes the steps of: preparing a titanium oxide precursor sol-gel, in a ratio of 1.56 milliliters titanium isopropoxide to 12 mL of 2-methoxyethanol; spin-coating the titanium oxide precursor sol-gel at 3000 revolutions per minute for 40 seconds, to a thickness of 65 nanometers; and heating the titanium oxide precursor sol-gel at 80° C in an ambient air environment.

(7) The above method may be configured as follows: the first step further includes a step of forming an indium tin oxide electrode; and the sixth step further includes a step of forming an aluminum electrode.

(8) The above method may be configured as follows: the fourth step further includes the steps of: forming an electron energy barrier gap between the electron-transport layer and the silicon quantum dot layer, of less than or equal to 0.4 electron volts; and forming an electron energy barrier gap between the silicon quantum dot layer and the hole-transport layer, of greater than or equal to 1.2 electron volts.

(9) The above method may be configured as follows: the fourth step further includes the steps of: forming a hole energy barrier gap between the hole-transport layer and the silicon quantum dot layer, of less than or equal to 0.9 electron volts; and forming a hole energy barrier gap between the silicon quantum dot layer and the electron-transport layer, of greater than or equal to 1.5 electron volts.

(10) The above method may be configured as follows: the fourth step further includes the steps of: using a plurality of silicon quantum dots having a diameter in a range between 3 nanometers and 6 nanometers; forming an electron energy barrier gap between the electron-transport layer and the silicon

quantum dot layer, of less than or equal to 0.2 electron volts; and forming an electron energy barrier gap between the silicon quantum dot layer and the hole-transport layer, of greater than or equal to 1.4 electron volts.

(11) The above method may be configured as follows: the fourth step
5 further includes the steps of: using a plurality of silicon quantum dots having a diameter in a range between 1 nanometers and 2 nanometers; forming an electron energy barrier gap between the electron-transport layer and the silicon quantum dot layer, of less than or equal to 0.4 electron volts; and forming an electron barrier gap between the silicon quantum dot layer and the hole-
10 transport layer, of greater than or equal to 1.2 electron volts.

(12) The above method may be configured as follows: the fourth step further includes the steps of: using a plurality of silicon quantum dots having a diameter in a range between 3 nanometers and 6 nanometers; forming a hole energy barrier gap between the hole-transport layer and the silicon quantum dot
15 layer, of less than or equal to 0.4 electron volts; and forming a hole energy barrier gap between the silicon quantum dot layer and the electron-transport layer, of greater than or equal to 2 electron volts.

(13) The above method may be configured as follows: the fourth step further includes the steps of: using a plurality of silicon quantum dots having a
20 diameter in a range between 1 nanometers and 2 nanometers; forming a hole energy barrier gap between the hole-transport layer and the silicon quantum dot layer, of less than or equal to 0.9 electron volts; and forming a hole energy barrier gap between the silicon quantum dot layer and the electron-transport layer, of greater than or equal to 1.5 electron volts.

25 (14) The above method may further include the steps of applying a voltage potential between the first electrode and the second electrode; and

emitting blue-colored light. Here, the fourth step further includes the step of using a plurality of particles having a diameter in a range of 1 nanometers to 2 nanometers.

(15) The above method may further include the steps of applying a
5 voltage potential between the first and second electrodes; and emitting red-colored light. Here, the fourth step further includes the step of using a plurality of particles having a diameter in a range of 3 nanometers to 6 nanometers.

(16) The above method may be configured as follows: the fifth step
10 further includes the step of forming an electron energy barrier gap between the electron-transport layer and the second electrode, of 0.2 electron volts or less. In addition, the second step further includes the step of forming a hole energy barrier gap between the hole-injection layer and the first electrode, of 0.5 electron volts or less.

15 (17) The above method may be configured as follows: the fourth step further includes the step of forming a plurality of core/shell silicon quantum dots including a silicon as a core.

(18) Incidentally, a colloidal silicon quantum dot visible spectrum light-emitting diode according to an aspect of the present invention includes: a first
20 transparent electrode; a hole-injection layer overlying the first electrode; a hole-transport layer overlying the hole-injection layer; a silicon quantum dot layer overlying the hole-transport layer; an electron-transport layer overlying the silicon quantum dot layer, and a second electrode overlying the electron-transport layer. Here, the silicon quantum dot layer includes a plurality of
25 silicon quantum dots having a diameter of less than 6 nanometers.

(19) The above colloidal silicon quantum dot visible spectrum light-emitting diode may be configured as follows: the hole-injection layer includes poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate).

5 (20) The above colloidal silicon quantum dot visible spectrum light-emitting diode may be configured as follows: the hole-transport layer includes poly(N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl) benzidine).

(21) The above colloidal silicon quantum dot visible spectrum light-emitting diode may be configured as follows: the electron-transport layer includes titanium oxide.

10 (22) The above colloidal silicon quantum dot visible spectrum light-emitting diode may further include: an electron energy barrier gap between the electron-transport layer and the silicon quantum dot layer, of less than or equal to 0.4 electron volts; and an electron energy barrier gap between the silicon quantum dot layer and the hole-transport layer, of greater than or equal to 1.2
15 electron volts.

(23) The above colloidal silicon quantum dot visible spectrum light-emitting diode may further include: a hole energy barrier gap between the hole-transport layer and the silicon quantum dot layer, of less than or equal to 0.9 electron volts; and a hole energy barrier gap between the silicon quantum dot
20 layer and the electron-transport layer, of greater than or equal to 1.5 electron volts.

(24) The above colloidal silicon quantum dot visible spectrum light-emitting diode may further include: the first electrode includes indium tin oxide; and the second electrode includes aluminum.

Additional details of the above-described method, and a colloidal SiQD visible spectrum LED, are provided below with reference to the attached diagrams.

[Advantageous Effects of Invention]

5 According to the above configurations, OLEDs fabricated with silicon QDs (SiQDs) can produce EL across the entire visible spectrum.

[Brief Description of Drawings]

[Fig. 1]

Fig. 1 is a partial cross-sectional view of a colloidal silicon
10 quantum dot (SiQD) visible spectrum light-emitting diode (LED).

[Fig. 2]

Fig. 2 is a graph depicting photoluminescence (PL) intensity as a function of wavelength.

[Fig. 3A]

15 Fig. 3A is an energy band diagram of an LED of Fig. 1 with blue SiQDs used as an emissive layer.

[Fig. 3B]

Fig. 3B depicts EL spectra of an LED of Fig. 1 with blue SiQDs used as an emissive layer.

20 [Fig. 4]

Fig. 4 depicts an I-V curve associated with EL spectra measurements of Fig. 3B.

[Fig. 5A]

Fig. 5A is an energy band diagram of an LED of Fig. 1 with red SiQDs used as an emissive layer.

[Fig. 5B]

5 Fig. 5B depicts EL spectra of an LED of Fig. 1 with red SiQDs used as an emissive layer.

[Fig. 6]

Fig. 6 depicts a PL spectra of an (ITO/PEDOT:PSS/poly-TPD) reference device.

10 [Fig. 7A]

Fig. 7A is a flowchart illustrating a method for fabricating a colloidal SiQD visible spectrum LED.

[Fig. 7B]

15 Fig. 7B is a flowchart illustrating a method for fabricating a colloidal SiQD visible spectrum LED.

[Fig. 7C]

Fig. 7C is a flowchart illustrating a method for fabricating a colloidal SiQD visible spectrum LED.

[Description of Embodiments]

20 Hereinafter, an embodiment of the present invention is described with reference to Figs. 1 to 7B.

Fig. 1 is a partial cross-sectional view of a colloidal silicon quantum dot (SiQD) visible spectrum light-emitting diode (LED) 100. The LED 100 comprises a first transparent electrode 102, a hole-injection layer 104 overlying the first electrode 102, and a hole-transport layer 106 overlying the hole-injection layer 104. A SiQD layer 108 overlies the hole-transport layer 106, where each SiQD has a diameter of less than about 6 nanometers (nm). An electron-transport layer 110 overlies the SiQD layer 108, and a second electrode 112 overlies the electron-transport layer 110.

According to an aspect of the present embodiment, the first electrode 102 is indium tin oxide (ITO), and the hole-injection layer 104 is poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). In addition, the hole-transport layer 106 is poly(N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine (poly-TPD). The electron-transport layer 110 is titanium oxide (TiO₂), and the second electrode 112 is aluminum (Al).

According to an aspect of the present embodiment, the SiQD layer 108 may include an electron energy barrier gap between the electron-transport layer 110 and the SiQD layer 108, of less than or equal to 0.4 electron volts (eV). There is an electron energy barrier gap between the SiQD layer 108 and the hole-transport layer 106, of greater than or equal to 1.2 eV. In addition, there is a hole energy barrier gap between the hole-transport layer 106 and the SiQD layer 108, of less than or equal to 0.9 eV. Further, there is a hole energy barrier gap between the SiQD layer 108 and the electron-transport layer 110, of greater than or equal to 1.5 eV. Additional details of the energy barrier gaps are provided below.

The SiQDs may be synthesized by electrochemical etching of a Si wafer, followed by surface passivation through hydrosilylation and ultra-sonication for

dispersion of the QDs in solvents. In the electrochemical etching reaction, a *p*-type boron-doped Si wafer with (100) orientation and 5-20 ohm-cm resistivity was etched by stirring in a mixture of hydrofluoric acid (HF), methanol, hydrogen peroxide (H₂O₂) and polyoxometalates (POMs). Hydrogen peroxide (H₂O₂) and polyoxometalates (POMs) function as catalysts. Alternatively, an *n*-doped or intrinsic Si substrate may be used. A mild etching recipe, e.g., etching current density = 10 mA/cm², etching time = 2 hours, and a small amount of H₂O₂, may be used to avoid the formation of micro-size pores on the wafer surface. After the electrochemical etching, the wafers are treated with diluted HF in water/methanol mixture for further removal of oxide residues and the formation of purely hydride termination on the surface. Then, in a nitrogen-filled glove box, the wafers are immersed in a hexane/1-octene mixture with a catalytic amount of chloroplatinic acid as catalysts for hydrosilylation reaction. Unsaturated double bonds of 1-octenes form stable covalent bonds with hydrides on the Si surface. With surface passivation by alkyl-ligands, the wafers are ultra-sonicated briefly in hexanes.

Fig. 2 is a graph depicting photoluminescence (PL) intensity as a function of wavelength. The resulting nearly transparent suspension shows bright red PL under 350 nm UV excitation with a peak at 612 nm and a much smaller minor peak in the short wavelength region, as shown in Fig. 2. Passing the red PL suspension through a syringe filter (polypropylene membrane and pore size of 0.2 μm), a clear suspension of SiQDs is obtained, which show blue PL with a narrow line width and a peak at 430 nm. The QD diameter is around 2 nm. The removal of the red peak by simply passing the SiQDs through the syringe filter is likely due to the following two reasons. First, during the electrochemical etching, the red PL SiQDs are mostly formed on and attached to micro-size structures which are then dispersed into solvents

together with SiQDs. Second, the red PL SiQDs tend to form aggregates and get retained when passing through pores of the syringe filter.

According to an aspect of the present embodiment, the multi-layered light-emitting device of Fig. 1 comprises indium-tin-oxide (ITO)/poly(3,4-
5 ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, 100 nm)/poly(N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl) benzidine (poly-TPD, 50 nm)/SiQDs/titanium dioxide (TiO₂, 65 nm)/Al (100 nm). First, the ITO substrates 102 are sequentially cleaned by ultra-sonication in de-ionized water, isopropanol and acetone, and then treated with oxygen plasma for removing
10 organic residues and enhancing surface hydrophilic property. The hole-injection-layer 104 PEDOT:PSS (2.8 wt % dispersion in H₂O) may be spin-coated at 4000 rpm for 40 seconds and baked in a nitrogen-filled glove box at 120 °C for 30 minutes. Subsequently, the hole-transport-layer 106 poly-TPD (1.5 wt % in chlorobenzene) may be spin-coated at 2000 rpm for 30 seconds
15 and baked in the same glove box at 110 °C for 30 minutes. The emissive layer of SiQDs 108 may be spin-coated at 300 rpm for 30 seconds, followed by vacuum drying.

For the electron-transport layer 110, a TiO₂ precursor sol-gel may be prepared (1.56 mL titanium isopropoxide in 12 mL 2-methoxyethanol) and spin-
20 coated at 3000 rpm for 40 seconds, followed by heating at 80 °C in air. The moisture in air facilitates the precipitation and formation of the amorphous TiO₂ thin film. Finally, a thin film of Al may be RF-sputtered through a shadow mask that defines the active area. Immediately after metallization, fabricated QD-OLEDs 100 may be packaged with glass slides and high vacuum
25 silicone grease. The following I-V curves and EL spectra measurements were performed in an ambient condition.

Fig. 3A is an energy band diagram of an LED of Fig. 1 with blue SiQDs used as an emissive layer. Fig. 3B depicts EL spectra of an LED of Fig. 1 with blue SiQDs used as an emissive layer. The EL spectra were measured with current densities of 34.6, 46.2, 57.7, and 69.3 mA/cm². The optical
5 power increases almost linearly as the current density increases. At the highest input current density, the optical power density of the blue SiQD-OLED was measured to be around 150 nW/cm², which corresponds to an external quantum efficiency (EQE) of around 1×10^{-5} %.

Fig. 4 depicts an I-V curve associated with the EL spectra measurements
10 of Fig. 3B. The I-V curve follows a diode rectifying characteristic.

Fig. 5A is an energy band diagram of an LED of Fig. 1 with red SiQDs used as an emissive layer. Fig. 5B depicts EL spectra of an LED of Fig. 1 with red SiQDs used as an emissive layer. In order to verify the role of oxygen in red emission SiQDs and observe their EL response, another QD-
15 OLED device was fabricated with the same structure, but using red PL SiQDs (the red PL spectrum in Fig. 2) as the emissive layer. The EL spectra at current densities = 46.2, 69.3 and 115.5 mA/cm² of the red SiQD-OLED are depicted in Fig. 5B. The I-V characteristics are similar to the blue SiQD-OLED. However, the quantum efficiency is lower as a result of not only
20 nanocrystalline SiQDs, but also some micro-size Si particles being embedded in the emissive layer. The micro-size particles generate no EL but can absorb the emission from SiQDs.

Second, the EL peak at 618 nm is close to the red SiQD PL peak at 612 nm. Therefore, the “orangish” EL likely comes from carrier recombination in
25 the core quantum confinement states of SiQDs, considering poly-TPD has only blue emission. Furthermore, since the energy band gap of red SiQDs (612 nm)

is smaller than the energy difference between electron and hole trap states (590 nm), the oxide states have negligible effect on the EL or PL spectra.

Consequently, only one EL peak is observed at 618 nm, rather than multiple peaks in the case of the blue Si QD-OLED. Finally, at the poly-TPD/SiQDs interface, the CB (C band) energy barrier of the red SiQD-OLED (1.4 eV) is larger than that of the blue SiQD-OLED (1.2 eV). The VB (V band) energy barrier of the red SiQD-OLED (0.4 eV) is smaller than that of the blue SiQD-OLED (0.9 eV). Therefore, there is better electron-stop and hole-transport at the poly-TPD/SiQDs interface, which leads to much less carrier recombination in the poly-TPD layer for the red SiQD-OLED.

Fig. 6 depicts the PL spectra of an (ITO/PEDOT:PSS/poly-TPD) reference device. In the EL spectra of Fig. 3B, there are three peaks at all current densities, which are 430 nm, 488 nm and 606 nm. The 430 nm EL peak, consistent with the blue PL peak in Fig. 2, is likely due to carrier recombination in the core quantum confinement states of the blue emission SiQDs. The PL spectrum of a reference device (ITO/PEDOT:PSS/poly-TPD) was measured and a peak was observed at 486 nm as shown in Fig. 6. As a result, the 488 nm EL peak can likely be attributed to carrier recombination in the poly-TPD layer. The “orangish” 606 nm peak is likely due to carrier recombination through the surface trap states of the oxidized blue emission SiQDs. The oxidization may occur as the device is heated in air after the TiO₂ coating and/or during the measurement. The trap states located in the energy band gap lower the radiative recombination energy and thus shift the emission toward longer wavelengths. Similar results in the PL study have been found with SiQDs on porous silicon surface prepared by electrochemical etching of *p*-type Si wafers. (See Wolkin et al., *Electronic States and Luminescence in Porous Silicon Quantum Dots: The Role of Oxygen*.) Upon oxidation, SiQDs

with blue or green PL showed a large Stokes shift and the upper limit of the emission energy was 2.1 eV (590 nm) due to localized states in the Si = O bonds, which is close to the 606 nm observed in the above-described EL measurements. However, for the SiQDs that display orange or red emission,
5 the oxide states have a negligible impact on the PL spectrum.

Figs. 7A, 7B, and 7C are flowcharts illustrating a method for fabricating a colloidal SiQD visible spectrum LED. Although the method is depicted as a sequence of numbered steps for clarity, the numbering does not necessarily dictate the order of the steps. It should be understood that some of these steps
10 may be skipped, performed in parallel, or performed without the requirement of maintaining a strict order of sequence. Generally however, the method follows the numeric order of the depicted steps. The method starts at Step 700.

Step 702 forms a transparent first electrode. For example, the first
15 electrode may be ITO. Step 704 forms a hole-injection layer overlying the first electrode. Step 704a may spin-coat a layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) at about 4000 RPM for about 40 seconds, to a thickness of about 100 nm. Step 704b bakes in a nitrogen-filled environment at about 120° C for about 30 minutes. Step
20 706 forms a hole-transport layer overlying the hole-injection layer. Step 706a may spin-coat a layer of poly(N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine (poly-TPD) at about 2000 RPM for about 30 second, to a thickness of about 50 nm. Step 706b bakes in a nitrogen-filled environment at about 110° C for about 30 minutes. Steps 704a, 704b, 706a, and 706b are optional steps
25 which may be performed in an aspect of the present embodiment.

Step 708 forms an SiQD layer overlying the hole-transport layer, where each SiQD has a diameter of less than about 6 nanometers (nm). Step 708 may form the SiQD layer using core/shell SiQDs, where the cores are Si. Examples of a shell include ZnS, ZnO, and Cu_xS . Typically, the shell diameter is less
5 than 2 nm.

Step 708a may provide a silicon substrate. Step 708b etches the Si substrate through exposure to a stirred mixture of hydrofluoric acid (HF), methanol, hydrogen peroxide (H_2O_2), and polyoxometalates (POMs). Step 708c treats the Si substrate with diluted hydrofluoric acid (HF) in a mixture of
10 water and methanol. In a nitrogen filled environment, Step 708d immerses the Si substrate in a hexane/1-octene mixture with a catalytic amount of chloroplatinic acid. Step 708e ultra-sonicates the Si substrate in hexanes, and Step 708f forms a suspension of SiQDs. Step 708g filters the suspension of SiQDs to remove particles larger than 6 nm. Step 708h spin-coats the
15 suspension of SiQDs at about 300 revolutions per minute (RPM) for about 30 seconds. Step 708i vacuum dries the spin-coated SiQD. Steps 708a through 708i are optional steps which may be performed in an aspect of the present embodiment.

Step 710 forms an electron-transport layer overlying the SiQD layer.
20 Step 710a may prepare a TiO_2 precursor sol-gel, in a ratio of about 1.56 milliliters (mL) titanium isopropoxide to about 12 mL of 2-methoxyethanol. Step 710b spin-coats at about 3000 RPM for about 40 seconds, to a thickness of about 65 nm. Step 710c heats at about 80° C in an ambient air environment. Steps 710a through 710c are optional steps which may be performed in an
25 aspect of the present embodiment.

Step 712 forms a second electrode overlying the electron-transport layer. The second electrode may be Al. Alternatively, the LED may be fabricated in reverse order, from Step 712 to Step 702.

According to an aspect of the present embodiment, Step 710 may include
5 the step of forming an electron energy barrier gap between the electron-transport and second electrode of 0.2 eV, or less. Further, Step 704 may include the step of forming a hole energy barrier gap between the hole-injection layer and the first electrode of 0.5 eV, or less.

According to an aspect of the present embodiment, Step 708 may include
10 the following substeps 708j through 708m. Step 708j forms an electron energy barrier gap between the electron-transport layer and the SiQD layer, of less than or equal to 0.4 electron volts (eV). Step 708k forms an electron energy barrier gap between the SiQD layer and the hole-transport layer, of greater than or equal to 1.2 eV. Step 708l forms a hole energy barrier gap between the
15 hole-transport layer and the SiQD layer, of less than or equal to 0.9 electron volts (eV). Step 708m forms a hole energy barrier gap between the SiQD layer and the electron-transport layer, of greater than or equal to 1.5 eV.

More specifically, Step 708 forms the SiQD layer using SiQDs having a diameter in a range between 3 and 6 nm. Then, Step 708j forms an electron
20 energy barrier gap between the electron-transport layer and the SiQD layer, of less than or equal to 0.2 eV. Step 708k forms an electron energy barrier gap between the SiQD layer and the hole-transport layer, of greater than or equal to 1.4 eV. Step 708l forms a hole energy barrier gap between the hole-transport layer and the SiQD layer, of less than or equal to 0.4 eV. Step 708m forms a
25 hole energy barrier gap between the SiQD layer and the electron-transport layer, of greater than or equal to 2 eV.

Alternatively, if Step 708 forms the SiQD layer using SiQDs having a diameter in a range between 1 and 2 nm, then Step 708j may form an electron energy barrier gap between the electron-transport layer and the SiQD layer, of less than or equal to 0.4 eV. Step 708k forms an electron energy barrier gap
5 between the SiQD layer and the hole-transport layer, of greater than or equal to 1.2 eV. Step 708l forms a hole energy barrier gap between the hole-transport layer and the SiQD layer, of less than or equal to 0.9 eV. Step 708m forms a hole energy barrier gap between the SiQD layer and the electron-transport layer, of greater than or equal to 1.5 eV.

10 According to another aspect of the present embodiment, Step 708 may form the SiQD layer using particles having a diameter in a range of about 1 to 2 nm. Then, Step 714 may apply a voltage potential between the first and second electrodes. In Step 716, the LED emits blue-colored light. Alternatively, if Step 708 forms the SiQD layer using particles having a
15 diameter in a range of about 3 to 6 nm, the LED may emit red-colored light in Step 718.

A SiQD LED device and a method for manufacturing a SiQD LED device have been described above. The specific materials and steps presented in the above embodiments are exemplary. The present invention is not limited by
20 any of the above examples. Various alterations and combinations of the embodiments may be made as long as they do not deviate from the gist of the present invention.

[Industrial Applicability]

The present invention may be applied to hybrid QD-organic light-
25 emitting diode (QD-OLED) structure.

[Reference Signs List]

	100	Colloidal SiQD visible spectrum LED
	102	First Electrode
	104	Hole-Injection Layer
5	106	Hole-Transport Layer
	108	SiQD Layer
	110	Electron-Transport Layer
	112	Second Electrode

[Claims]

[Claim 1]

A method for manufacturing a colloidal silicon quantum dot visible spectrum light-emitting diode, the method comprising:

5 a first step of forming a transparent first electrode;

a second step of forming a hole-injection layer overlying the first electrode;

a third step of forming a hole-transport layer overlying the hole-injection layer;

10 a fourth step of forming a silicon quantum dot layer overlying the hole-transport layer;

a fifth step of forming an electron-transport layer overlying the silicon quantum dot layer; and,

15 a sixth step of forming a second electrode overlying the electron-transport layer, wherein

the silicon quantum dot layer comprises a plurality of silicon quantum dots having a diameter of less than 6 nanometers.

[Claim 2]

The method according to claim 1, wherein the fourth step further
20 comprises the steps of:

providing a silicon substrate;

etching the silicon substrate through exposure to a first mixture comprising hydrofluoric acid, methanol, hydrogen peroxide, and polyoxometalates;

treating the silicon substrate to diluted hydrofluoric acid in a second
5 mixture comprising water and methanol;

immersing, in a nitrogen filled environment, the silicon substrate in a hexane/1-octene mixture with a catalytic amount of chloroplatinic acid;

ultra-sonicating the silicon substrate in hexanes; and

forming a suspension of silicon quantum dots.

10 [Claim 3]

The method according to claim 2, wherein the fourth step further comprises the steps of:

filtering the suspension of silicon quantum dots to remove a particle having a diameter of larger than 6 nanometers;

15 spin-coating the suspension of silicon quantum dots at 300 revolutions per minute for 30 seconds; and

vacuum drying the suspension of silicon quantum dots.

[Claim 4]

The method according to claim 1 wherein the second step further
20 comprises the steps of:

spin-coating a layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) at 4000 revolutions per minute for 40 seconds, to a thickness of 100 nanometers; and

baking the layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) in a nitrogen-filled environment at 120° C for 30 minutes.

[Claim 5]

The method according to claim 4, wherein the third step comprises the steps of:

spin-coating a layer of poly(N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine at 2000 revolutions per minute for 30 seconds, to a thickness of 50 nanometers; and,

baking the layer of poly(N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine in a nitrogen-filled environment at 110° C for 30 minutes.

[Claim 6]

The method according to claim 5 wherein the fifth step comprises the steps of:

preparing a titanium oxide precursor sol-gel, in a ratio of 1.56 milliliters titanium isopropoxide to 12 mL of 2-methoxyethanol;

spin-coating the titanium oxide precursor sol-gel at 3000 revolutions per minute for 40 seconds, to a thickness of 65 nanometers; and

heating the titanium oxide precursor sol-gel at 80° C in an ambient air environment.

[Claim 7]

The method according to claim 5 wherein:

the first step further comprises a step of forming an indium tin oxide electrode; and

5 the sixth step further comprises a step of forming an aluminum electrode.

[Claim 8]

The method according to claim 1, wherein the fourth step further comprises the steps of:

forming an electron energy barrier gap between the electron-transport
10 layer and the silicon quantum dot layer, of less than or equal to 0.4 electron volts; and

forming an electron energy barrier gap between the silicon quantum dot layer and the hole-transport layer, of greater than or equal to 1.2 electron volts.

[Claim 9]

15 The method according to claim 1, wherein the fourth step further comprises the steps of:

forming a hole energy barrier gap between the hole-transport layer and the silicon quantum dot layer, of less than or equal to 0.9 electron volts; and

forming a hole energy barrier gap between the silicon quantum dot layer
20 and the electron-transport layer, of greater than or equal to 1.5 electron volts.

[Claim 10]

The method according to claim 1, wherein the fourth step further comprises the steps of:

using a plurality of silicon quantum dots having a diameter in a range between 3 nanometers and 6 nanometers;

5 forming an electron energy barrier gap between the electron-transport layer and the silicon quantum dot layer, of less than or equal to 0.2 electron volts; and

forming an electron energy barrier gap between the silicon quantum dot layer and the hole-transport layer, of greater than or equal to 1.4 electron volts.

10 [Claim 11]

The method according to claim 1, wherein the fourth step further comprises the steps of:

using a plurality of silicon quantum dots having a diameter in a range between 1 nanometers and 2 nanometers;

15 forming an electron energy barrier gap between the electron-transport layer and the silicon quantum dot layer, of less than or equal to 0.4 electron volts; and

forming an electron barrier gap between the silicon quantum dot layer and the hole-transport layer, of greater than or equal to 1.2 electron volts.

20 [Claim 12]

The method according to claim 1, wherein the fourth step further comprises the steps of:

using a plurality of silicon quantum dots having a diameter in a range between 3 nanometers and 6 nanometers;

forming a hole energy barrier gap between the hole-transport layer and the silicon quantum dot layer, of less than or equal to 0.4 electron volts; and

5 forming a hole energy barrier gap between the silicon quantum dot layer and the electron-transport layer, of greater than or equal to 2 electron volts.

[Claim 13]

The method according to claim 1, wherein the fourth step further comprises the steps of:

10 using a plurality of silicon quantum dots having a diameter in a range between 1 nanometers and 2 nanometers;

forming a hole energy barrier gap between the hole-transport layer and the silicon quantum dot layer, of less than or equal to 0.9 electron volts; and

forming a hole energy barrier gap between the silicon quantum dot layer
15 and the electron-transport layer, of greater than or equal to 1.5 electron volts.

[Claim 14]

The method according to claim 1, the method further comprising the steps of

applying a voltage potential between the first electrode and the second
20 electrode; and

emitting blue-colored light,

wherein

the fourth step further comprises the step of using a plurality of particles having a diameter in a range of 1 nanometers to 2 nanometers.

[Claim 15]

The method according to claim 1, the method further comprising the
5 steps of:

applying a voltage potential between the first and second electrodes; and
emitting red-colored light,

wherein

the fourth step further comprises the step of using a plurality of particles
10 having a diameter in a range of 3 nanometers to 6 nanometers.

[Claim 16]

The method according to claim 1, wherein

the fifth step further comprises the step of forming an electron energy
barrier gap between the electron-transport layer and the second electrode, of
15 0.2 electron volts or less; and

the second step further comprises the step of forming a hole energy
barrier gap between the hole-injection layer and the first electrode, of 0.5
electron volts or less.

[Claim 17]

20 The method according to claim 1, wherein the fourth step further
comprises the step of forming a plurality of core/shell silicon quantum dots
comprising a silicon as a core.

[Claim 18]

A colloidal silicon quantum dot visible spectrum light-emitting diode comprising:

a first transparent electrode;

5 a hole-injection layer overlying the first electrode;

a hole-transport layer overlying the hole-injection layer;

a silicon quantum dot layer overlying the hole-transport layer;

an electron-transport layer overlying the silicon quantum dot layer, and

a second electrode overlying the electron-transport layer, wherein

10 the silicon quantum dot layer comprises a plurality of silicon quantum dots having a diameter of less than 6 nanometers.

[Claim 19]

The colloidal silicon quantum dot visible spectrum light-emitting diode according to claim 18, wherein the hole-injection layer comprises poly(3,4-
15 ethylenedioxythiophene):poly(styrenesulfonate).

[Claim 20]

The colloidal silicon quantum dot visible spectrum light-emitting diode according to claim 18, wherein the hole-transport layer comprises poly(N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl) benzidine.

20 [Claim 21]

The colloidal silicon quantum dot visible spectrum light-emitting diode according to claim 18, wherein the electron-transport layer comprises titanium oxide.

[Claim 22]

5 The colloidal silicon quantum dot visible spectrum light-emitting diode according to claim 18, further comprising:

an electron energy barrier gap between the electron-transport layer and the silicon quantum dot layer, of less than or equal to 0.4 electron volts; and

10 an electron energy barrier gap between the silicon quantum dot layer and the hole-transport layer, of greater than or equal to 1.2 electron volts.

[Claim 23]

The colloidal silicon quantum dot visible spectrum light-emitting diode according to claim 18, further comprising:

15 a hole energy barrier gap between the hole-transport layer and the silicon quantum dot layer, of less than or equal to 0.9 electron volts; and

a hole energy barrier gap between the silicon quantum dot layer and the electron-transport layer, of greater than or equal to 1.5 electron volts.

[Claim 24]

20 The colloidal silicon quantum dot visible spectrum light-emitting diode according to claim 18, wherein:

the first electrode comprises indium tin oxide; and

the second electrode comprises aluminum.

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FIG. 1

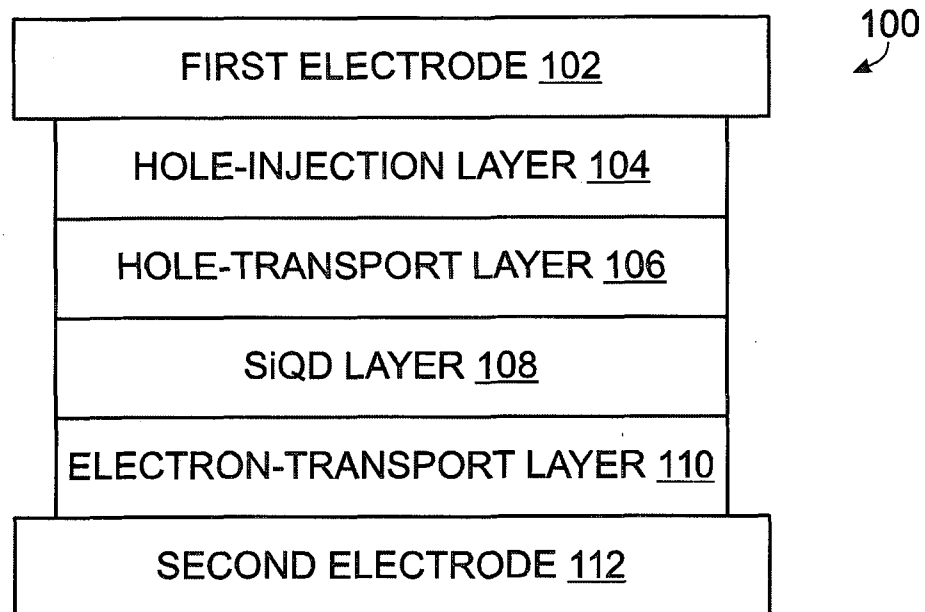
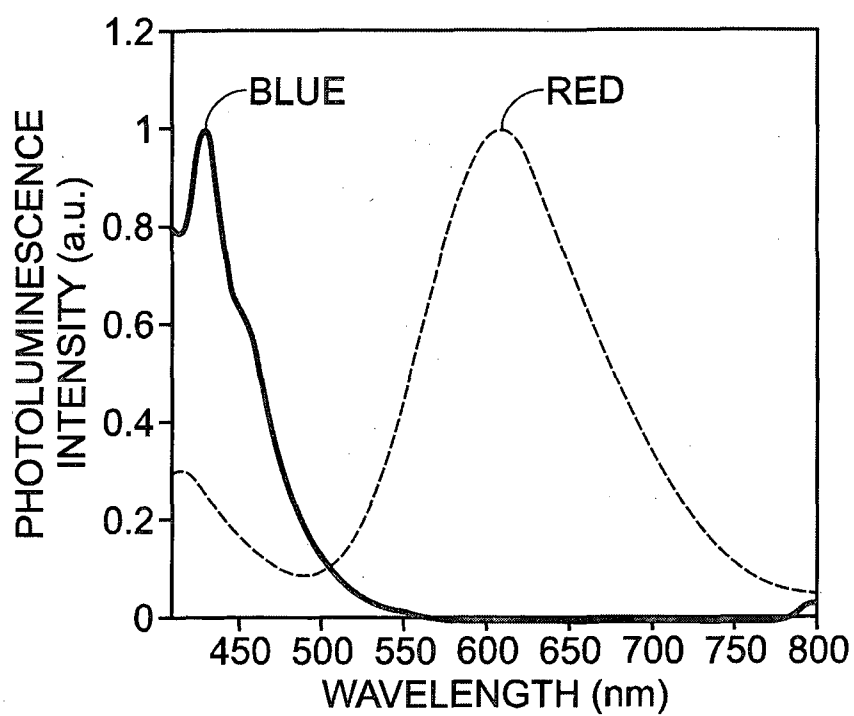


FIG. 2



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FIG. 3 A

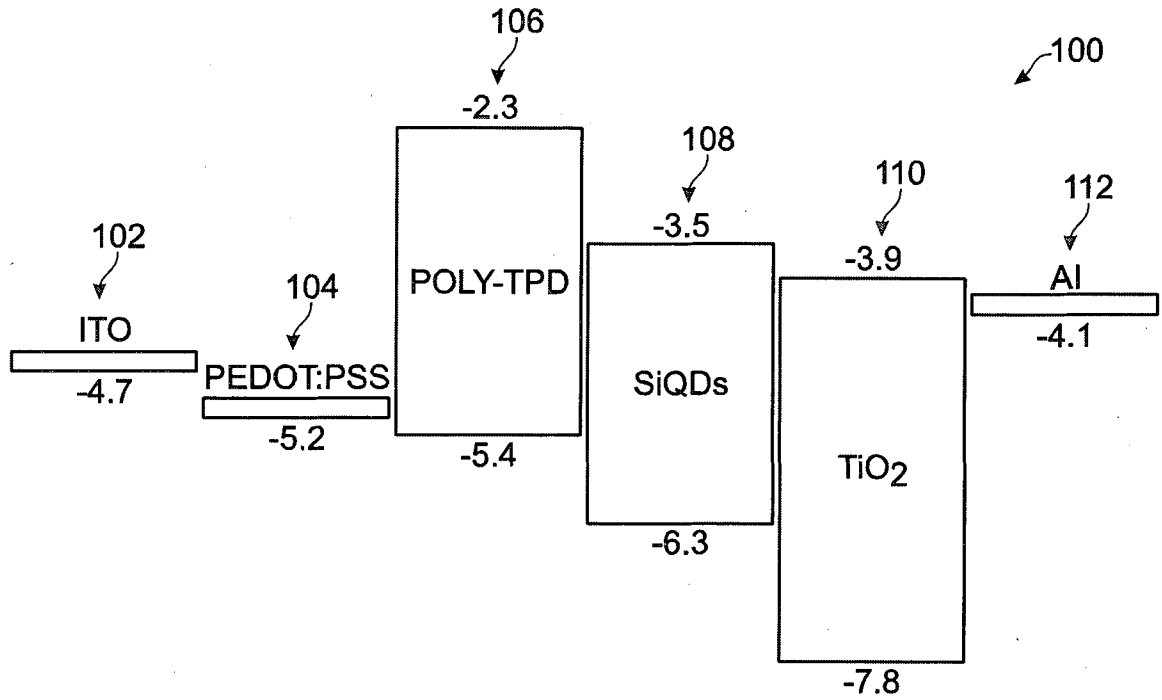
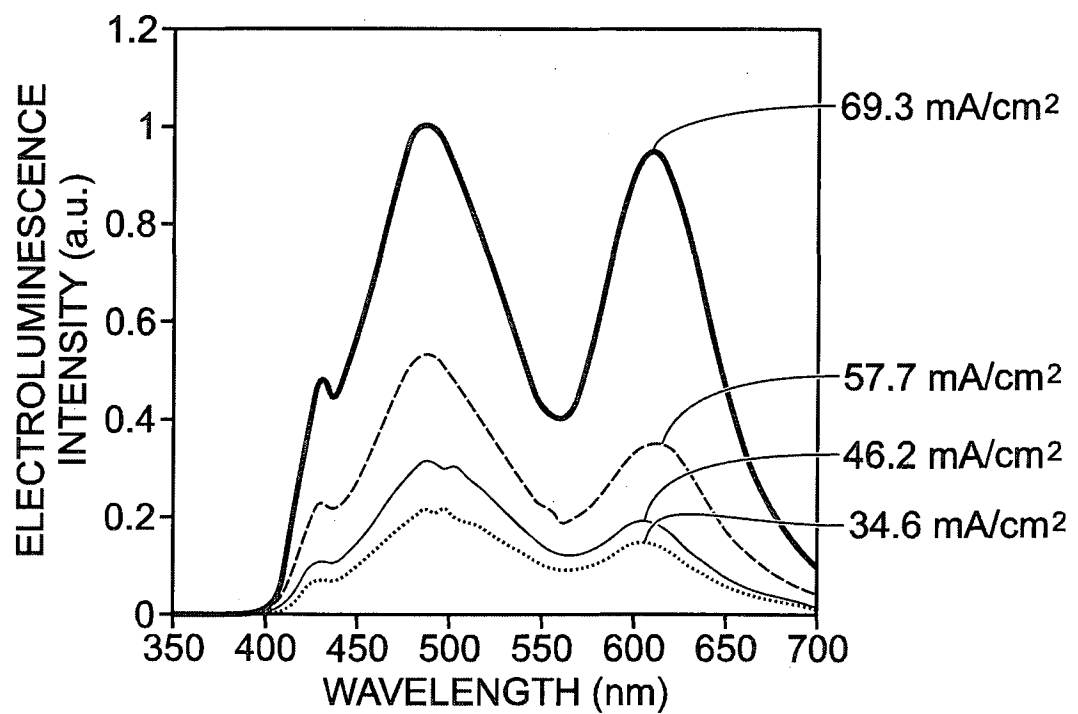
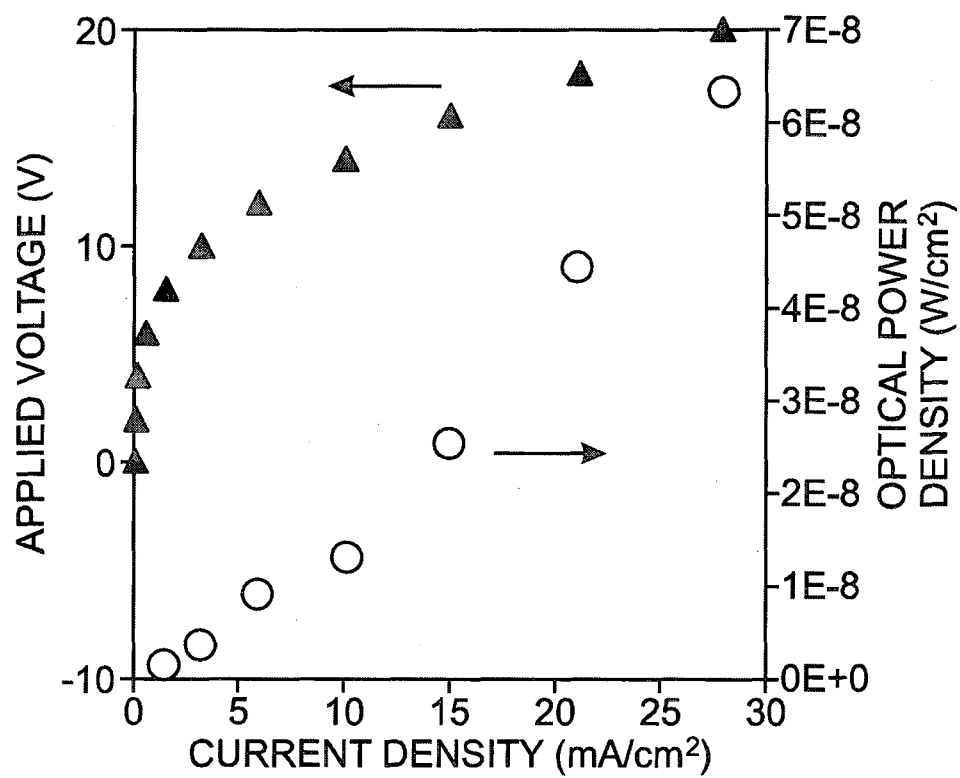


FIG. 3 B



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FIG. 4



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FIG. 5A

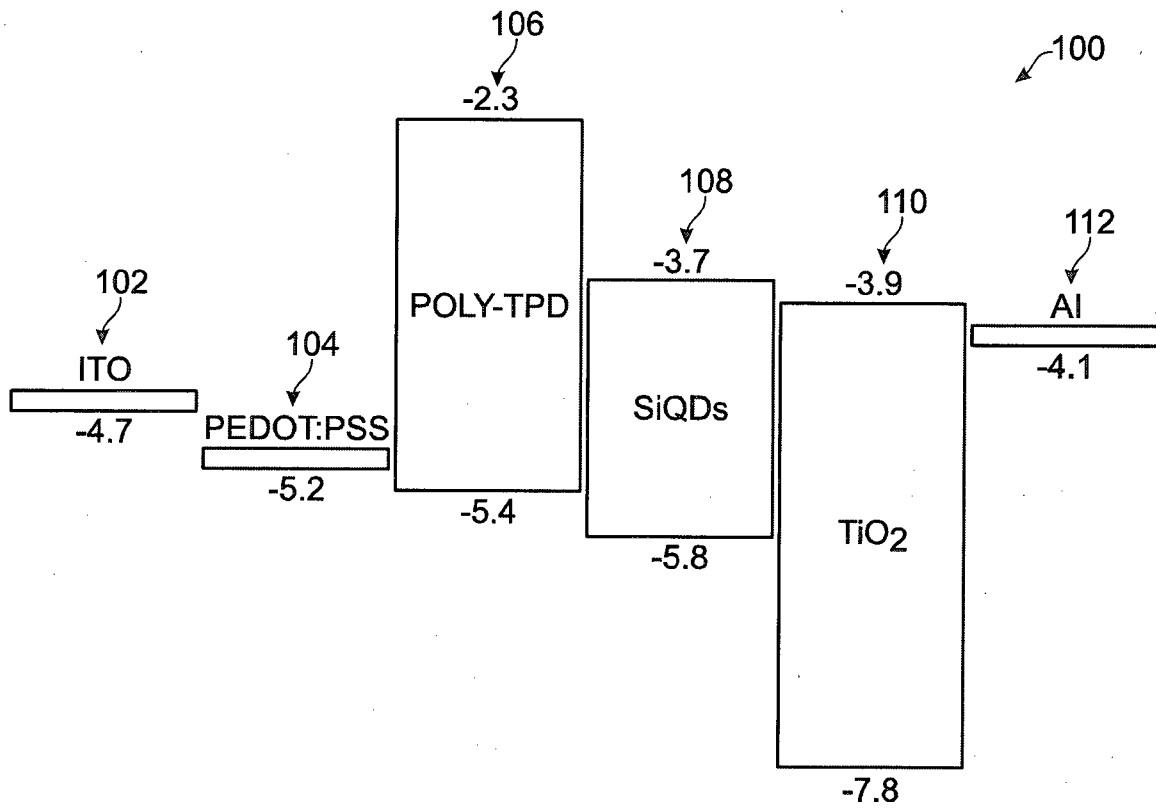
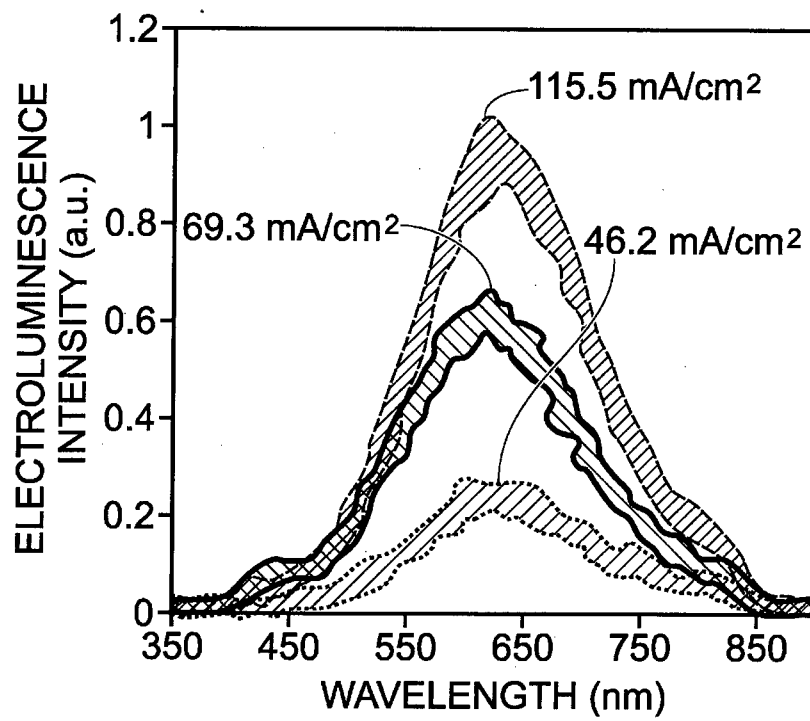
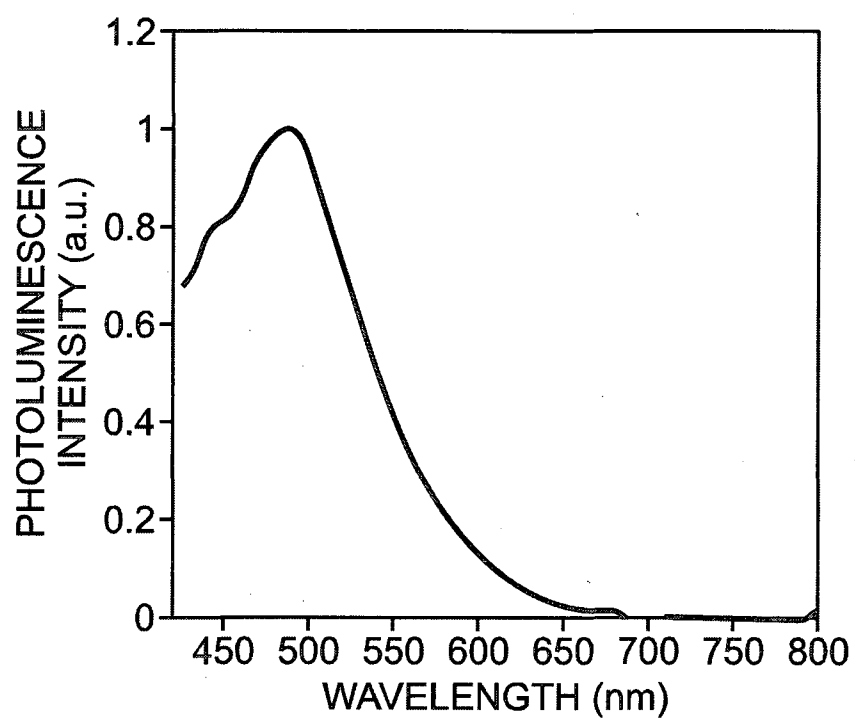


FIG. 5B



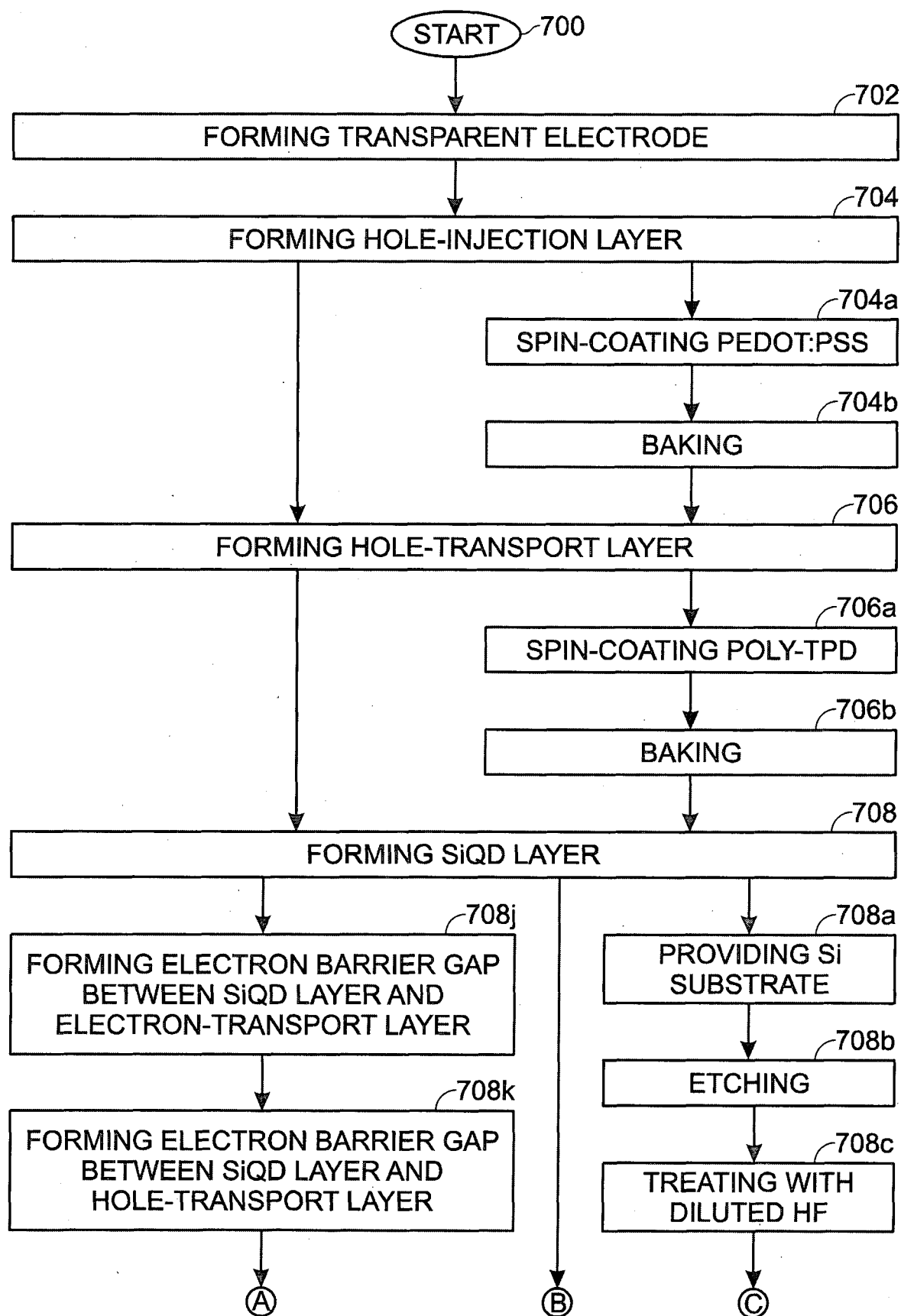
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FIG. 6



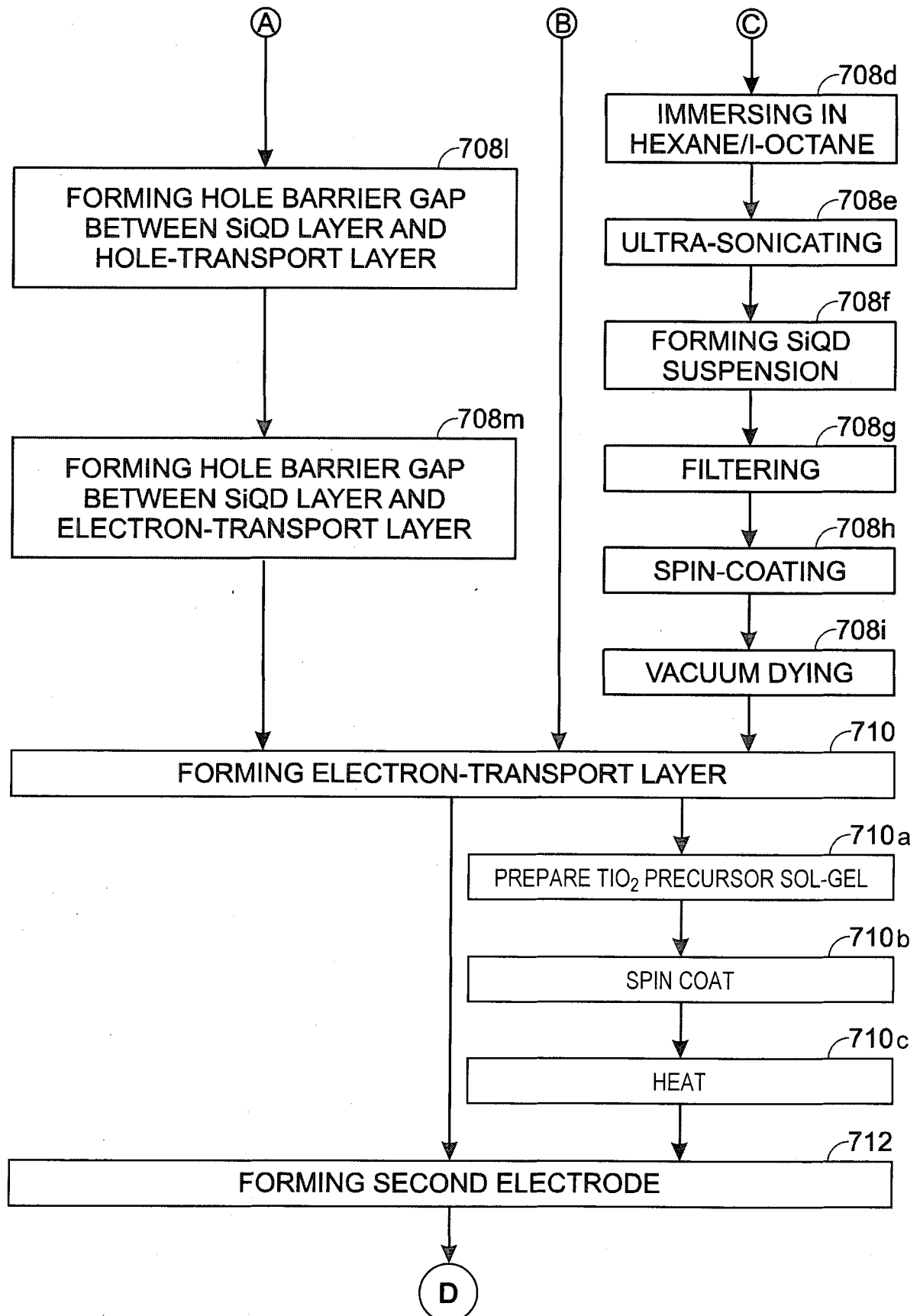
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FIG. 7A



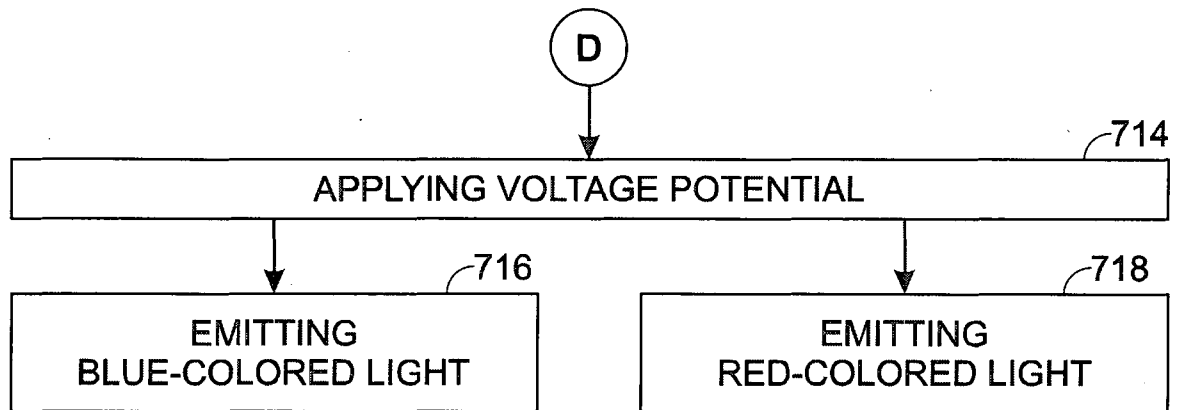
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FIG. 7B



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FIG. 7C



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/061500

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. H05B33/10 (2006.01) i, H01L51/50 (2006.01) i, H05B33/14 (2006.01) i,
B82Y20/00 (2011.01) n, B82Y40/00 (2011.01) n

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. H05B33/10, H01L51/50, H05B33/14, B82Y20/00, B82Y40/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2012
Registered utility model specifications of Japan 1996-2012
Published registered utility model applications of Japan 1994-2012

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Cheng et al., High-Efficiency Silicon Nanocrystal Light-Emitting Devices, Nano Letters, 2011.04.04, Vol.11, No.5, pp.1952-1956	1, 4, 5, 7-10, 12, 15, 16, 18-20, 22-24
Y		2, 3, 6, 11, 13, 14, 17, 21
Y	Tu et al., Solution-processed photodetectors from colloidal silicon nano/micro particle composite, OPTICS EXPRESS, 2010.10.11, Vol.18, No.21, pp.21622-21627	2, 3



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

31.07.2012

Date of mailing of the international search report

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2905

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/061500

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2008/0238299 A1 (SAMSUNG ELECTRONICS CO., LTD.) 2008.10.02, [0049], [0050] & JP 2008-177168 A & KR 10-2008-0069085 A	6, 21
Y	JP 2010-9995 A (SEIKO EPSON CORPORATION) 2010.01.14, 【0012】 , 【0025】 , 【0032】 (No Family)	11, 13, 14, 17
P, X	Tu et al., Visible electroluminescence from hybrid colloidal silicon quantum dot-organic light-emitting diodes, APPLIED PHYSICS LETTERS, 2011.05.23, Vol.98, No.21, pp.213102-1-3	1-24
A	Puzzo et al., Visible Colloidal Nanocrystal Silicon Light-Emitting Diode, Nano Letters, 2011.03.28, Vol.11, No.4, pp.1585-1590	1-24