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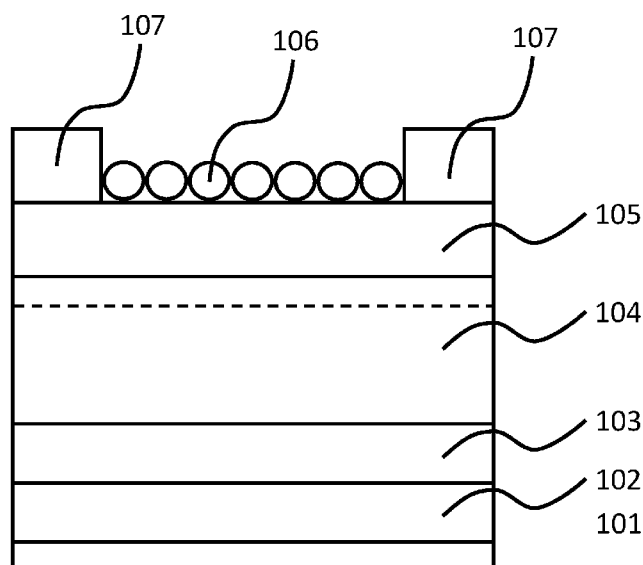


FIG. 1

(57) Abstract: An improved optoelectronic device is described, which employs optically responsive nanoparticles and utilises a non-radiative energy transfer mechanism. The nanoparticles are disposed in proximity to a window layer of the device in order to extract light energy absorbed by the window layer and recycle it to an energy absorbing region of the device electronic structure. The energy is transferred from the window layer to the nanoparticles non-radiatively through non-contact dipole-dipole interaction and is emitted luminescently by the nanoparticles at a longer wavelength that can be absorbed in the energy absorbing region. The technique finds particular application in light harvesting devices, such as photovoltaic (solar) cells.

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AN OPTICAL DEVICE

Field of the Invention

The present invention relates to optoelectronic devices which employ optically-
5 responsive nanoparticles and utilise a non-radiative energy transfer mechanism,
particularly for improved efficiency of operation in light collecting devices, such as
photovoltaic (solar) cells and imaging devices and detectors.

Background to the Invention

10 In view of depletion of non-renewable energy sources and the associated impact
on the environment there is need to develop green, renewable energy
technologies, and increase the wall plug efficiency of existing technologies. One
such technology is solar energy harvesting devices, which commonly utilize the
15 photovoltaic effect to harness solar energy by converting sunlight to electricity
with minimal expense to greenhouse gases, production of major pollutants or
depletion of non-renewable sources.

However, for so-called photovoltaics (PVs) to become the preferred solution for
generating clean energy, the production cost has to be comparable to that of
20 alternative sources and the environmental impact of fabrication should not exceed
the energy payback, as described by K. Knapp and T. Jester in Sol. Energy 71,
165 (2001) and G. Peharz, and F. Dimroth in Prog. Photovoltaics 13, 627 (2005).
These requirements raise the demand for PVs of ever higher light-to-current
conversion efficiency. Solar cells have evolved over three technology
25 generations and we now briefly review the state of the art in this field.

First generation Solar (PV) Cells

First generation solar cells consist of a P type semiconductor material in contact
with an N type semiconductor material, typically doped monocrystalline Silicon. A
30 junction region then exists between the n- and p-doped semiconductor materials.
First generation solar cells had a single P-N junction region. Photons impinging
on the surface penetrate some distance into the top semiconductor layer of the
device.

Absorption of a photon (with energy larger than the semiconductor material band gap energy) causes electrons (negative charge) to become promoted from the valance band to the conduction band of the semiconductor in the top layer of the device, leaving behind a hole (positive charge) in the valance band. The two
5 charged particles (electron and hole) are initially bound together and are commonly known as an exciton. The region where this process occurs is therefore the 'light absorbing' region.

After a short period of time (known as the lifetime) the electron will collapse back
10 to the valance band, releasing energy. This process is known as recombination, and energy can be released in the form of heat (phonons) or under special conditions light (photons). For a solar cell radiative recombination is not desirable and is inhibited by choice of materials. The exciton has a finite lifetime, which is dependent upon the mobility of the semiconductor material.

15 An electric field exists across the junction region of the device due to lack of electrons in the P type material, and excess electrons in the N type material. This imposes a force on electrons close to the junction region in the N type material, causing electrons within the vicinity of the junction region to be attracted towards
20 the junction region. Hence electrons generated within a certain distance to the junction region will tend to drift towards and across the junction region. Once across the junction region electrons will rapidly recombine with holes as these are the majority carrier. Movement of electrons across the junction region by diffusion then constitutes an electric current. Continuous movement of electrons
25 across the junction region is only possible when the P and N sides of the device are electrically connected, as is the case within an electrical circuit.

For the avoidance of doubt, we note that 'junction region' is here defined to be the volume of space close to the P-N junction over which electrons diffuse under the
30 influence of the electric field, and so is not limited to the actual position of the interface between P and N type materials.

Provided the generated electron-hole pairs (excitons) are able to cross the junction region before recombination (within their lifetime), they will gives rise to
35 an electrical current. Collection efficiency is therefore dependent upon carrier

lifetime which relates to recombination distance, and mobility in the material. Metal contacts are arranged as inter-digitated arrays to conduct the current away from the cell.

5 *Second Generation Solar Cells*

Second generation solar cells utilise improved thin film semiconductor materials such as Cadmium Telluride, Copper Indium Gallium Selenide (CIGS), Amorphous Silicon and Micro-Amorphous Silicon to reduce cost of manufacture.

- 10 Currently, the preferred routes to mass scale fabrication are single crystal (1st generation) or polycrystalline (2nd generation) silicon-based PVs with power conversion efficiency ranging from 10-18%, whereas recent advances in multi-junction p-i-n PVs (3rd generation) have reached lab-reported efficiencies approaching 40%, as detailed in R. R. King et al., Appl. Phys. Lett. 90, 183516
15 (2007).

Third Generation Solar Cells

- Third generation solar cells utilise a range of advanced technologies to increase efficiencies. These include direct bandgap semiconductor materials and multi-
20 junction solar cell configurations.

- GaAs based semiconductor solar cells can exhibit very high PCEs, with demonstrated values in excess of 40% (W. Guter, J. Schöne, S. P. Philipps, M. Steiner, G. Siefert, A. Wekkeli, E. Welser, E. Oliva, A. W. Bett, F. Dimroth, Appl. Phys. Lett. 2009, 94, 223504) and even reaching 44.7% (Press Release, World
25 Record Solar Cell with 44.7% Efficiency, Fraunhofer Institute for Solar Energy Systems ISE, 2013).

- These solar cells are typically triple-junction devices consisting of multi-layer
30 stack of P-N junctions fabricated from different semiconductor materials, each with a slightly different band gap energy. Each junction region is tuned to absorb a slightly different portion of the solar spectrum. The highest band gap energy material is placed towards the top (light receiving surface) of the structure such

that photons with energy below that band gap penetrate further to underlying junctions, which then have successively smaller band gaps.

Material sequences such as GaInP, GaAs, and Ge are typical. In this case the
5 Ge bottom cell absorbs mostly near-infrared photons between 0.65 eV and 1.4 eV, a middle InGaAs cell principally absorbing red photons in the 1.4-1.86 eV range and an InGaP top cell harvesting blue and UV photons above 1.86 eV. Such devices have achieved a practical efficiency of 40.8%.

10 Fabrication of triple junction solar cells is extremely difficult due to the requirement for precise lattice matching between successive material layers during epitaxial growth procedures. This also affects choice of substrate materials and in practice Germanium is a suitable substrate material for GaInP, GaAs and InGaAs. InP substrates are under investigation. In addition, as
15 electrical contact between the junction regions is in series, the current through all junction regions must be equal. There are therefore issues associated with differing maximum power handling capabilities for the successive junction regions which reduce maximum attainable efficiency.

20 *Optical Loss Mechanisms*

The spectral mismatch between the response of a solar cell and the solar spectrum represents the largest loss factor for all photovoltaic technologies. Efficiency is limited by the fact that absorption only occurs efficiently over a limited spectral range for photons with energies above the semiconductor band
25 gap energy.

While photons with energy smaller than the band-gap energy of the semiconducting materials simply cannot be absorbed in a beneficial way, excess energy possessed by photons with larger energy than the band gap energy
30 becomes lost via non-radiative relaxation of the carriers in the form of heat via indirect' phonon 'transitions.

These fundamental losses limit the theoretical maximum photon conversion efficiencies (PCE) efficiency to 34% for an optimal 1.34eV band-gap

semiconductor material. The best experimental single junction solar cells achieve conversion efficiencies around 30% under one sun illumination (Press release, Alta Devices Achieves 30.8% Efficiency Record with New Generation Solar Cell Technology, Alta Devices, 2013). These high experimental efficiencies are typically achieved through advanced front surface optimization of the solar cells, to maximize the collection efficiency of the high energy photons absorbed at the surface of the devices.

Such optimization techniques prove in many cases too costly for large-scale industrial production, and typical mass-produced solar modules only reach conversion efficiencies of around 20% (E. Klampaftis, D. Ross, K. R. McIntosh, B. S. Richards, Sol. Energy Mater. Sol. Cells 2009, 93, 1182–1194). Better use of high energy photons thus remains a limiting factor for commercial solar cells.

A general issue for all PV solar technologies is the reduction of optical loss arising from reflection. First to third Generation PV solar devices are all based on Semiconductor materials, which are relatively high refractive index materials, and so give rise to Fresnel reflection loss at the air/semiconductor interface upon incidence of a photon. Random surface texturing is commonly used to reduce the effect of Fresnel loss or rather to increase the acceptance cone angle of the material. Optical collectors are also used to concentrate incident light onto solar cells and thereby increase their efficiency.

Conventional semiconductor solar cells have a thin window layer at the surface which serves the purpose to passivate surface states at the top surface of the cell. Without the window layer, efficiency of the device is reduced, as excitons (electron – hole pairs) generated by absorption of photons in the P-N junction region of the cell would otherwise recombine at surface states (at the top of the cell) in a way which does not contribute to extracted electrical power. Hence surface states greatly reduce the efficiency of a solar cell.

A thin window layer of AlInP is typically deposited above the top cell of a triple junction cell to act as a passivation layer. This layer minimizes non-radiative surface recombination of the excitons created near the surface of the top cell by creating an energy barrier for the minority carriers (see Figure 1b).

Although the window layer reduces recombination at surface states it does not completely eliminate them, as carriers created in the window layer can still recombine through surface states at the interface between the semiconductor and window layer (A. Luque, S. Hegedus, Handbook of Photovoltaic Science and Engineering, Wiley, Hoboken, NJ, USA 2011). This effect lowers the quantum efficiency of the solar cell in the high energy region of the solar spectrum. The benefit of the window layer is to reduce the quantity of surface states, and thereby the associated loss.

Moreover, although the window layer improves the overall efficiency of the solar cell, the window layer contributes a new loss mechanism to the cell (in addition to loss via surface state recombination mentioned in the previous paragraph). Specifically, light (photons) with short wavelength become absorbed in the bulk of the window layer (not just the interface region), thereby creating electron-hole pairs in an excited state within the window layer, rather than in the junction region.

After a short period of time the electron will relax back to the valence band releasing its gained energy. As the window layer is usually made of an indirect band gap material (typically AlInP with a band-gap around 2.2 eV), recombination of electron-hole pairs in the window layer preferentially gives rise to the generation of phonons rather than photons. Phonons release their energy to their surroundings in the form of heat. Hence energy absorbed in the window layer gets converted to non-useful heat (via phonon process) rather than useful electricity.

Hence, while improving the extraction efficiency in the top cell, the window layer also acts as an absorber for high energy photons. Indeed, a typical 30nm window layer can induce a loss of more than 5% of the incident solar power.

Dye Sensitized (LDS) Solar Cells

An alternative approach to the triple junction configuration for achieving a better utilization of high energy photons is the use of luminescent down-shifting (LDS) of

the solar spectrum. In this scheme, short wavelength (high energy) photons are absorbed by a luminescent material which re-emits at a more favorable higher wavelength.

- 5 Organic dyes and colloidal quantum dots (QDs) have been considered as LDS materials for a wide range of photovoltaic technologies. The high absorptivity at shorter wavelengths, narrow emission spectral range, good absorption and emission tunability, high absorption cross-section and high photoluminescence quantum yield of colloidal QDs make them ideal candidates for LDS layers.
- 10 Large scale LDS films can be readily deposited using low-cost techniques such as spray coating and do not significantly add to the cost of the final modules, thus maintaining the cost competitiveness of the modules.

- Dye-sensitized and nanocrystal quantum dot (NQD)-sensitized PVs provide
- 15 alternative solar power technologies with the benefit of: simpler fabrication, high absorption, widely tunable spectral absorption, and low-cost synthesis.

Non-Radiative Energy Enhanced Solar Cells

- An alternative way to bypass the inefficiencies and limitations associated with
- 20 electrical extraction in PV cells, is to engineer devices that utilize alternative electrical transport schemes, making use of high absorption, and widely tuneable spectral range of organic dyes and NQDs. Although the thermodynamic limit of single band gap photovoltaic cells restrict the cell efficiency to 31%, an efficiency for colloidal NC photovoltaic cells of up to 60% is possible.

- 25 Resonance Energy Transfer (RET), or Förster RET (FRET), provides such a non-radiative mechanism. As first studied by Förster (T. Förster, Annalen der Physik 2, 55 (1948), no 9) in nature, transfer of energy between chromophores predominantly occurs through a non-radiative dipole-dipole coupling mechanism
- 30 (where donor emission overlaps with acceptor absorption), which does not involve charge transfer or emission and absorption of photons between donor and acceptor, and which can exceed the radiative energy transfer routinely used in phosphor light emitting devices.

Experimental evidence of the non-radiative energy transfer process has been observed in hybrid semiconductor heterostructures under excitation between carriers in a single semiconductor quantum well and a vicinal layer of colloidal semiconductor quantum dots [M. Achermann et al., Nature 429, 642 (2004), and
5 Š. Kos, et al, Physical Review B 71, 205309 (2005)] or organic molecules [G. Heliotis et al., Adv. Mater. (Weinheim, Ger.) 18, 334 (2006), and S. Blumstengel et al., Phys. Rev. Lett. 97, 237401 (2006)]. Energy transfer efficiencies as high as 60% have been achieved [S. Rohmoser et al., Appl. Phys. Lett. 91, 092126 (2007)], thereby exceeding that of traditional radiative energy transfer where the
10 donors emit photons and the photons are subsequently absorbed by the acceptors.

Non-radiative energy transfer rate (k_{ET}) scales linearly with spectral overlap and is proportional to R^{-C} where R is donor-acceptor distance and C is a constant.
15 For example, $C = 2$ and 6 describes energy transfer in layer-layer and isolated dipole-dipole systems, respectively [S. Coe et al., Nature 420, 800 (2002) no. 4, and Q. Sun et al., Nat. Photon. 1, 717 (2007) no. 5]. To increase the energy transfer rate, the donor-acceptor separation distance has to be minimised. Ideally this should be of the order of magnitude of the Forster distance, which is the
20 distance at which the rate of non-radiative energy transfer equals the rate of radiative energy transfer.

Non-radiative energy transfer mechanisms can be applied to a solar energy collection device (photovoltaic cell). In this case materials must be chosen such
25 that the electronic band gap energy of the nanoparticle is larger than that of the proximal epitaxial heterostructure. In the conventional configuration the phosphor or quantum dot behaves as a light absorbing material, generating an electron-hole pair upon absorption of an incoming photon. The electron-hole pair is then transferred back to the epitaxial structure where it induces an electrical current.
30 The light emitting particles can again be a mixture of various sized phosphor or quantum dots, whose overall absorption spectrum can be tuned to that of the solar spectrum by size, shape and mixture selection.

However, notwithstanding these developments, a practical issue limiting efficient
35 light harvesting devices employing non-radiative energy transfer processes is the

requirement to bring the light collecting particle into close proximity to the heterostructure, while still providing suitable conduction channels to the energy transfer region. For example, in the case of a colloidal NQDs/multiple quantum well LED configuration, the current received wisdom is that the quantum well barrier and the top contact layer must be as thin as possible, while remaining thick enough in order to minimise surface recombination of injected carriers and to allow for uniform spreading of the injected carriers over the active layers (current spreading). As a consequence, an undesirable trade-off exists between these requirements.

Thus, as will be appreciated by those skilled in the art, there is a need for improved optoelectronic devices and device configurations which overcome the problems described above and facilitate more efficient operation.

Summary of the Invention

According to a first aspect of the present invention there is provided an optical device having a surface for receiving light energy from a light source, the optical device comprising:

- an electronic structure having an energy absorbing region, wherein the electronic structure exhibits an electronic band gap with an associated band gap energy;

- a window layer comprising a material which exhibits an electronic band gap with an associated band gap energy; and

- a plurality of optically responsive particles which exhibit an electronic band gap with an associated band gap energy that is smaller than the band gap energy of the window layer material,

- wherein the optically responsive particles are adapted to mediate:

- a first energy transfer process involving non-radiative energy transfer, whereby light energy absorbed by the window layer is transferred from the window layer to the optically responsive particles via non-radiative dipole-dipole interaction; and,

- a second energy transfer process involving luminescent energy emission, whereby light energy transferred from the window layer to the optically responsive particles is re-emitted as longer wavelength lower energy light which can be absorbed by the energy absorbing region,

and wherein the optically responsive particles are located in proximity to the window layer and the energy absorbing region such that the first and second energy transfer processes may occur simultaneously or sequentially, whereby energy transferred to the optically responsive particles from the window layer via the first energy transfer process is re-emitted via the second energy transfer process for absorption by the light absorbing region.

In this way light energy absorbed by the window layer is extracted and recycled to the energy absorbing region by the optically responsive particles via a combination of resonant energy transfer (RET) and luminescent energy transfer. It is noted that this involves an abnormal direction of energy transfer as compared to conventional devices and energy transfer processes therein.

It is noted here that the light receiving surface defined here need not be the final outer surface of the device through which light enters the device. The surface merely relates to refractive index boundary in the device. Thus, a passivation layer, antireflection coating, electrical contacts, or the like may be formed on top of the surface in question.

In many embodiments it is preferred that the optically responsive particles are further adapted to mediate:

a third energy transfer process involving luminescent energy absorption, whereby some light energy received from the light source is absorbed directly by the optically responsive particles; and

the second energy transfer process involving luminescent energy emission, whereby light energy absorbed directly by the optically responsive particles is re-emitted as longer wavelength lower energy light which can be absorbed by the energy absorbing region,

wherein the optically responsive particles are located in proximity to the window layer and the energy absorbing region such that the first, second and third energy transfer processes may occur simultaneously or sequentially, whereby energy absorbed directly by the optically responsive particles via the third energy transfer process is also re-emitted via the second energy transfer process for absorption by the light absorbing region.

In this way, light at wavelengths that may otherwise not be absorbed in the device may be absorbed directly by the optically responsive particles and then re-emitted luminescently as longer wavelength lower energy light which can be absorbed by the energy absorbing region of this device. This provides a further improvement in device efficiency. Preferably, the optically responsive particles are adapted to absorb one or more of blue and ultraviolet optical radiation via the third energy transfer process, as such wavelengths are less likely to be absorbed directly by either the window layer or the energy absorbing layer.

10 In some embodiments the optically responsive particles are discrete particles. In some other embodiments the optically responsive particles are contained or embedded within a host matrix, which may provide a hybrid function.

15 Preferably, the optically responsive particle(s) comprises a direct band gap semiconductor material and has a well-defined shape. In some preferred embodiments, the optically responsive particle comprises a quantum dot or a quantum rod. Such particles cooperate well with an electronic structure comprising one or more quantum wells, or P-N junctions.

20 The optically responsive particle may take other forms and may comprise a phosphor. For example, the optically responsive particle may be spherical in shape and/or may comprise a tetrapod. In this case, the optically responsive particle may comprise a spherical core of a given semiconductor material and a spherical shell of another semiconductor of smaller or larger band gap.

25 Alternatively, the optically responsive particle may comprise a spherical core of a given semiconductor material and an elongated rod-shaped shell of another semiconductor of smaller or larger band gap. In another embodiment the optically responsive particle may comprises a spherical shell of a given semiconductor material and four extensions of a different semiconductor of smaller or larger band gap comprising a tetrapod.

30 In some embodiments the optically responsive particles have a refractive index with a magnitude that is between that of the refractive indices of materials on either side of the optically responsive particles, whereby to provide a degree of refractive index matching between said materials and reduce Fresnel reflection of

incident light. Such matching occurs most effectively when the refractive index (magnitude) of a layer approaches the geometric mean of the refractive indices of the material layers between which it is disposed, and also when the layer thickness approaches odd multiples of a quarter of the wavelength of the incident
5 light.

In some embodiments the distribution of the optically responsive particles is non-uniform, as it has been found that local aggregation of the particles can induce internal light scattering in the structure, which can significantly improve the
10 performances of devices.

In some embodiments, the window layer comprises an indirect bandgap semiconductor material. However, the window layer may also comprise a direct bandgap semiconductor material.
15

In some embodiments the window layer is preferably disposed between the optically responsive particles and the energy absorbing region of the electronic structure. Typically, the window layer is disposed closer to the light receiving surface than is the energy absorbing region. In such arrangements light energy
20 absorbed by the window layer is first transferred via the first energy transfer process to the optically responsive particles on one side of the window layer and then re-emitted via the second energy transfer process as longer wavelength lower energy light to travel back through the window layer and be absorbed by the energy absorbing region on the other side.

25 In some embodiments it is preferred that the optically responsive particles are disposed such that their distance from a surface of the window layer is less than twice the Forster distance. Such a configuration can optimise the first (non-radiative) energy transfer process. In some embodiments the optically
30 responsive particles are disposed on a surface of the window layer such that they are in physical contact with said surface. In other embodiments there may be one or more intervening layers. In some embodiments the optical device may comprise one or more additional window layers.

In many embodiments it is preferred that the energy absorbing region comprises at least one electronic junction region. It is noted that the energy absorbing region defined here is the volume of space within which impinging photons become absorbed, and this may include, but is not limited to, a junction region.

5

The junction region may include a P-N junction, which may comprise an indirect bandgap material, such as Si, or a direct bandgap material, such as CIGS or GaAs. Of course, other suitable material systems may be used. In some embodiments the energy absorbing region comprises at least one quantum well.

10 Thus, the junction region is the volume of space close to a P-N junction (or quantum well) over which electrons diffuse under the influence of an electric field, and so is not constrained to the actual position of the interface between P and N type materials (or quantum well).

15 Preferably, the electronic structure comprises an epitaxial structure. In some embodiments the electronic structure comprises at least one p-n junction having a depletion region in the vicinity of the energy transfer region. In other embodiments, the electronic structure comprises a semiconductor heterostructure including one or more quantum wells.

20

The electronic structure may comprise a direct band gap semiconductor material, or alternatively an indirect band gap semiconductor material.

25 According to a second aspect of the present invention there is provided a light harvesting device comprising an optical device as described above, wherein light energy absorbed by the energy absorbing region of the electronic structure generates an electric potential therein. A light harvesting device of the present invention may simply be used to harvest light in order to generate electricity. However, the device has equal application in imaging devices and detectors,
30 including charge-coupled devices (CCDs).

According to a third aspect of the present invention, a method of fabricating a device according to the first or second aspect comprises the steps of:

35 providing the electronic structure having the energy absorbing region;
forming the window layer; and,

providing the plurality of optically responsive particles located in proximity to the window layer and the energy absorbing region.

5 Preferably, the optically responsive particles are deposited using a suitable deposition technique.

As will be appreciated, the present invention relates to device configurations which optimise light collection per unit surface area via improvement of the efficiency of overall energy absorption by reducing losses associated with the window layer. Crucially, and in contrast to known devices, a multi-step energy transfer/conversion process is invoked, which involves extraction of energy from the solar cell via non-contact dipole-dipole energy transfer mechanism (RET). This is counter intuitive in the art as extraction of energy would normally reduce the efficiency of the device. Extracted energy is converted to a wavelength more easily absorbed by the junction region, and then re-injected back into the device.

As will be described, the device configuration in combination with specific material properties of the constituent parts, allows energy to be efficiently transferred from an 'indirect' bandgap material to a direct bandgap material. This has previously not been considered possible or viable in the art. The invention overcomes this limitation by invoking a configuration that breaks the translation symmetry. The invention is applicable to all types of inorganic (semiconductor based), and hybrid (combination of semiconductor and organic material) solar cells.

25 We now describe two particular broad embodiments of the invention. In the first embodiment of the invention, the optical device comprises a light harvesting device including a substrate, and other functional layers. In particular, the device may comprise a non-transparent electrical contact layer disposed over the surface of the device. This facilitates very good local electrical connection.

30

Optically responsive particles are placed on the surface of a solar cell window layer. Energy associated with electron hole pairs created in the window layer couple back to the optically responsive particles by a process called resonant energy transfer (RET).

35

RET is a direct energy transfer mechanism which does not involve generation of photons and can be utilised in both direct and indirect band gap semiconductor materials. Forster radius (a common term in the field) is the distance at which the rate of resonant energy transfer equals the radiative rate. RET can occur over a distance several times the Forster distance, but is most efficient up to a distance of twice the Forster radius. RET can occur between an indirect and direct band gap semiconductor, as well as between two direct band gap semiconductor materials.

- 10 The device configuration proposed as a first embodiment of the invention, allows energy to be extracted back to the optically responsive particles by RET process from a volume of space within the structure some distance below the surface upon which the particles are disposed. In this configuration RET competes with radiative energy transfer and thermal relaxation in the window layer.
- 15 Consequently, a portion of the energy associated with photons absorbed in the window layer is no longer lost as thermal energy (as is the case in a conventional LDS solar cell) , but is instead transferred out of the window layer back to the optically responsive particles. In this way, energy which would normally be lost as heat is extracted out of the cell to optically responsive particles.

20

- Energy transferred back from the window layer to the optically responsive particles by RET is then released in the form of a new photon. The wavelength of the newly generated photon is dependent upon the properties of the optically responsive particles. Properties of the optically responsive particles are chosen such that photons are generated predominantly at a wavelength that is not absorbed by the window layer, and can be easily absorbed by the junction region.

25

- Overall, in this configuration, energy which would normally be lost as heat in the window layer becomes absorbed as photons in the junction region, and so contributes to useful generated electrical power.

30

- In addition to providing a mechanism for energy extraction from the window layer, the optically responsive particles perform a secondary function known as Luminescent Down Shifting (as is utilised in current third generation solar cells).
- 35 Solar light at wavelength which is not easily absorbed by the energy absorbing

region incident on the structure, becomes absorbed directly by the optically responsive particles, and converted to a photon at a new wavelength which can penetrate the window layer and be absorbed by the junction region.

- 5 Further benefit is provided by matching the refractive index of the optically responsive particles to the refractive index of the underlying layer of the solar cell. Photons generated in the optically responsive particles, are then able to transfer to the underlying layer with minimal loss due to Fresnel reflection at the interface.
- 10 Overall, the first broad embodiment recycles light energy that would otherwise be lost as heat in the solar cell through RET. Light energy absorbed by the window layer is transferred through RET to the responsive particles. The responsive particle transfers this energy to back the useful area of the solar cell. The recycling of the light energy absorbed by the window layer comprises one of the
- 15 inventive steps. Thus, the device configuration simultaneously allows recycling of heat energy from the window layer by RET and LDS.

- In a second broad embodiment of the invention, it is preferred that the window layer is composed of an indirect bandgap semiconductor material, and a light
- 20 absorbing junction region a direct bandgap material. Example materials for the window layer and light absorbing region for this embodiment could be AlInP, Si, doped InGaP, but are not limited to these.

- Resonance energy transfer of excitons from an indirect bandgap material window
- 25 layer to a direct band-gap material junction region is completely forbidden by requirements for 'momentum conservation'. Radiative recombination of carriers generated in the window layer is therefore not possible in an indirect bandgap material preventing luminescent down-shifting occurring in the window layer.

- 30 In this embodiment of the invention energy is transferred by RET in the reverse direction, from the indirect band-gap window layer to the optically responsive particles which in this case may be partly comprised of a direct bandgap semiconductor material. Quantum confinement in the optically responsive particles breaks the translational symmetry invariance, relaxing the constraints
- 35 imposed by momentum conservation allowing the RET energy transfer process to

occur from the indirect bandgap window layer to direct bandgap material of the optical responsive particles.

As will be appreciated by those skilled in the art, the present invention provides for significant efficiency enhancements in light harvesting or collecting optoelectronic devices. The use of optically responsive particles for a hybrid non-radiative energy transfer (RET) and luminescent downshifting (LDS) mode of operation permits the recycling of energy that would otherwise not be usefully harvested or collected by the device.

10

Brief Description of the Drawings

Examples of the present invention will be described in detail with reference to the accompanying drawings, in which:

Figure 1 shows a simplified depiction of the first configuration of the first and second embodiment of the invention that includes a bottom metal contact (101), a GaAs substrate (102), a back-surface field layer (103), an InGaP p-n junction (104), an AlInP window layer (105), a nanoparticle epilayer (106) and a top metal contact (107);

Figure 2 shows the photoluminescence (201) and absorption (202) spectra of the nanoparticles used in the first and second embodiment;

Figure 3 shows the valence and conduction levels of the top-most part of the invention according to the first and second embodiment, and includes a back-surface layer (301), an InGaP p-n junction (302), an AlInP window layer (303) and a nanoparticle epilayer (304);

Figure 4 shows the absorptivity of the bare (401) and hybridized (402) devices according to the first and second embodiment of the invention;

Figure 5 shows the current-voltage characteristics of the bare (501) and hybridized (502) devices according to the first and second embodiment of the invention;

Figure 6 shows the external quantum efficiency spectra of the bare (601) and hybridized (602) devices according to the first and second embodiment of the

invention, along with a simulated spectrum assuming non-absorbing nanoparticles (603);

Figure 7 shows the internal quantum efficiency spectra of the bare (701) and hybridized (702) devices according to the first and second embodiment of the invention;

Figure 8 shows the photoluminescence rise-time of nanoparticles used in the first and second embodiment deposited on glass (801) and on an AlInP thin-film (802) as a function of the excitation wavelength;

Figure 9 shows a simplified depiction of the second configuration of the first and second embodiment of the invention, where an anti-reflective coating (908) is deposited above the NQDs;

Figure 10 shows a simplified depiction of the first configuration of the third embodiment of the invention that includes a bottom metal contact (1001), an absorbing layer (1002), a window layer (1003), a plurality of NQDs (1004), a top contact (1005), and a solid substrate (906);

Figure 11 shows a simplified depiction of the second configuration of the third embodiment of the invention, where the NQDs are inserted between the absorbing layer and the window layer;

Figure 12 shows a simplified depiction of the third configuration of the third embodiment of the invention, where the NQDs are embedded into the window layer;

Figure 13 shows a simplified depiction of the fourth configuration of the third embodiment of the invention, where the NQDs are embedded into the top contact layer;

Figure 14 shows a simplified depiction of the fifth configuration of the third embodiment of the invention, where the NQDs are embedded within the absorbing layer;

Figure 15 shows a simplified depiction of the first configuration of the fourth embodiment of the invention that includes a substrate (1501), a bottom metal contact (1502), an absorbing region (1503), window layer (1504), a plurality of

NQDs (1505), a top continuous contact (1506) and a patterned metallic contact (1507);

Figure 16 shows a simplified depiction of the second configuration of the fourth embodiment of the invention, where the NQDs are inserted between the
5 absorbing layer and the window layer;

Figure 17 shows a simplified depiction of the third configuration of the fourth embodiment of the invention, where the NQDs are embedded into the window layer;

Figure 18 shows a simplified depiction of the fourth configuration of the fourth
10 embodiment of the invention, where the NQDs are embedded into the top contact layer;

Figure 19 shows a simplified depiction of the fifth configuration of the fourth embodiment of the invention, where the NQDs are embedded within the absorbing layer; and,

Figures 20A to 20H illustrate the steps of an example fabrication process flow for
15 fabricating devices according to the present invention.

Detailed Description

The present invention relates to device configurations which optimise collection
20 per unit surface area via improvement of efficiency of non-radiative energy transfer, and thereby increase the number of exciton pairs actively involved in the light collection process. We illustrate this with four broad embodiments, which in turn may be implemented in a range of configurations. Although the invention is primarily illustrated using nanocrystal quantum dots (NQDs) as the optically
25 responsive particles, other types of optically responsive particles may be used, as described above

First and Second Embodiments of the Invention

For the purpose of illustration we now discuss in detail the practical
30 implementation and demonstration of the first and second embodiments of the present invention as a light harvesting device with reference to the figures. The

primary difference between the first and second embodiments is that, in the second embodiment, the window layer of the structure comprises an indirect semiconductor.

5 GaAs based semiconductor solar cells can exhibit very high PCEs, with demonstrated values in excess of 40% and even reaching 44.7%. These solar cells are typically triple-junction devices, with a Ge bottom cell absorbing mostly near-infrared photons between 0.65 eV and 1.4 eV, a middle InGaAs cell principally absorbing red photons in the 1.4-1.86 eV range and an InGaP top cell
10 harvesting blue and UV photons above 1.86 eV. A thin window layer of AlInP is typically deposited above the top cell to act as a passivation layer. The photons absorbed in this layer are typically hard to extract, which lowers the conversion efficiency of the devices. LDS has been found to be a potential solution to circumvent this issue.

15

As shown by E. Klampaftis et al., Sol. Energy Mater. Sol. Cells **93**, 1182 (2009), nanocrystals can be used to implement luminescent down-shifting in existing technologies. In this case, nanocrystals are deposited on top of the device to absorb high energy photons. The photons are then re-emitted below the band-
20 gap of the window layer, which limits parasitic light absorption. The necessity of an optically thick nanoparticle layer increases reabsorption losses in the LDS film which limits its performance.

In contrast, the proposed invention utilizes a thin (~10-50nm) film of nanocrystal
25 in proximity or near the window layer, strongly suppressing reabsorption issues in the film. While such a film would only weakly radiatively couple to the incoming light, the use of RET between the window layer and the nanocrystals allows the activation of an efficient pumping channel at the nano-scale which transfer excitons from the window layer to the thin LDS layer.

30

Figure 1 illustrates the hybrid structure introduced in this embodiment of the invention. A 50nm $\text{Al}_{0.7}\text{Ga}_{0.3}\text{As}$ back-surface-field (BSF) layer (103), a 1500nm InGaP p-n junction (104) and a 30nm AlInP window layer (105) are consecutively grown on a GaAs substrate (102). The samples were grown using molecular
35 beam epitaxy. Gold continuous (101) and digitated (107) contacts were

deposited using electron beam evaporation at the bottom and top of the device, respectively, and the final devices were microbonded to circuit boards for analysis. The active area of the devices is 16.24 mm^2 . A nanocrystal quantum dot (NQD) epilayer (106) was deposited on top of the device using dynamic spincoating at 1500RPM. The film thickness was estimated to be 10nm using ellipsometry.

Figure 2 presents the photoluminescence (201) and absorption (202) spectra of the NQDs. The NQDs are oleic acid capped $\text{CdS}_x\text{Se}_{1-x}/\text{ZnS}$ core/shell colloidal semiconductor quantum dots, with 1s emission wavelengths of $585 \pm 15 \text{ nm}$ and $665 \pm 15 \text{ nm}$, respectively, and 1s absorption peaks of 560 nm and 660 nm , respectively, indicating a respective Stokes shift of 9.5 meV and 1.4 meV .

The band diagram of the hybrid solar cell is depicted in Figure 3. It depicts the valence and conduction bands of the BSF layer (301), the p-n junction (302), the window layer (304) and the NQD epilayer (304). To harness the carriers captured in the window layer, an epilayer of colloidal semiconductor NQDs was deposited and resonance energy transfer (RET) was utilized to funnel excitons from the window layer (303) to the NQD epilayer (304). High energy photons (305) are absorbed by the window layer and create excitons that non-radiatively transfer to the NQDs through RET. The NQDs are tuned to emit below the band-gap of the window layer (306), optically pumping the p-n junction (302), where the photogenerated carriers can be efficiently extracted. Since AlInP has a much higher refractive index than air ($n_{\text{AlInP}}=3.00$ at 585 nm), most of the NQD emission couples into the cell.

Figure 4 presents the absorptivity of the device before (401) and after (402) hybridization with the NQDs. Absorptivity is found to drastically increase after hybridization. The effect is especially pronounced in the UV, where the NQDs are strong absorbers, with a 22% relative increase in absorptivity at 325 nm . The enhancement remains significant across the $350\text{-}1100 \text{ nm}$ wavelength range under consideration, even for energies below the band-gap of the NQDs. This indicates that the NQD film acts as a refractive index matching layer between the air and the window layer, enhancing the overall light coupling efficiency across the spectral range. The optimal value for a refractive index matching layer at

normal incidence can be approximated to the geometric average of the refractive indices of the materials above and beneath it. In our case, using a value of $n=3.00$ for AlInP and $n=1$ for air at 585nm, the optimal value is found to be $n=1.73$. This is indeed close to the refractive index of the NQDs, with a value of
 5 1.61 at 585 nm.

Figure 5 presents the current-voltage (I-V) characteristics of the device before (501) and after (502) hybridization with the NQDs. As expected from the absorptivity data, the short-circuit current (J_{sc}) of the hybridized device is strongly
 10 enhanced, increasing from $13.31\text{mA}/\text{cm}^2$ to $15.21\text{mA}/\text{cm}^2$. The PCE is found to increase from 13.6% to 15.6%, indicating a relative enhancement of 14.6%. The open-circuit voltage (V_{oc}) and fill-factor (FF) are mostly unchanged, as expected for an LDS driven enhancement.

Figure 6 presents the external quantum efficiency (EQE) spectra of the devices, both before (601) and after (602) the NQD deposition. The EQE of the hybrid device is significantly improved compared to the bare case across the wavelength range, with a maximum relative enhancement of 127% at 320 nm. The 1s
 15 absorption peak of the NQDs is clearly visible as a negative dip in the EQE spectrum of the hybrid device at 560nm. To separate the effects of light coupling enhancement and of NQD absorption, the EQE after hybridization can be estimated for a non-absorbing film as follows:
 20

$$EQE_{calc} = EQE_{bare} * (1 + \Delta A_{Fresnel})$$

where EQE_{bare} is the EQE of the device before hybridization and $\Delta A_{Fresnel}$ is the relative absorption enhancement for a non-absorbing layer. The calculated EQE,
 25 presented in Figure 6 as 603, corresponds to the EQE of a device coated with a non-absorbing material of the same refractive index as the NQDs. Below 382nm, the EQE of the hybrid device is largely enhanced compared to EQE_{calc} . This indicates that the enhancement is not only due to refractive index matching, but that the absorption properties of the NQDs activate efficient photon conversion
 30 channels that increase the EQE. Above this crossing point, the EQE of the hybrid solar cell remains significantly lower than the calculated values. The presence of a dip in the EQE spectrum of the hybrid device at the 1s absorption wavelength of the NQDs clearly shows the detrimental effect of NQD absorption in this

wavelength range. Above 600nm, the NQDs are only weakly absorbing and EQE_{calc} matches the values measured for the hybrid device.

To explain the EQE variations after hybridization, two NQD-mediated pumping mechanisms are considered. On the one hand, the NQD film acts as a LDS layer, such that NQDs are optically excited, radiatively relax and the resulting photoluminescence is transmitted through the window layer into the InGaP p-n junction, where it is absorbed to create efficiently extractable carriers. The second mechanism involves RET of excitons photogenerated in the AlInP window layer to the NQD epilayer that consequently luminesce, resulting in a RET mediated LDS process. Since both LDS processes involve the absorption of the NQD luminescence by the p-n junction, their overall PCEs are proportional to the spectral overlap between the emission of the NQDs and the EQE of the bare solar cell. The emission wavelength of the NQDs was chosen so close to the maximum EQE of the bare device, with a value of 70% at 585nm.

Figure 7 presents the Internal Quantum Efficiency (IQE) before (701) and after (702) hybridization. The IQE of the hybridized device is found to be significantly higher than the IQE of the bare device below 385nm. Hybridization proves to be detrimental to the IQE above 385nm. This crossing point confirms the presence of a competition between LDS mechanisms and direct radiative excitation of the InGaP p-n junction, due to radiative coupling losses and non-radiative recombination channels intrinsic to the NQDs. For lower wavelengths, LDS is efficient enough compared to direct pumping of the p-n junction to beneficially contribute to the IQE of the hybrid device. The absorptivity of both the NQDs and the window layer increases rapidly towards the UV, which enhances the impact of LDS. Above the crossing point, LDS cannot compete with direct radiative pumping of the p-n junction and the hybridized IQE is lower than in the bare case. Getting closer to the InGaP band-gap, the NQDs become non-absorbing and the hybridized and bare IQEs match.

The IQE of the hybrid structure was modelled to separate the contributions of LDS and of direct optical pumping of the p-n junction, as follows:

$$IQE_{Hybrid}(\lambda) = IQE_{direct}(\lambda) + IQE_{LDS}(\lambda) + IQE_{RET}(\lambda)$$

where IQE_{direct} , IQE_{LDS} and IQE_{RET} are the contributions of direct optical pumping of the p-n junction, of LDS due to direct optical pumping of the NQD film and of RET mediated LDS to the overall IQE, respectively. These contributions are described as follows:

$$IQE_{direct}(\lambda) = (1 - \alpha_{QD}(\lambda)) * (1 - A(\lambda)) * IQE_{InGaP}(\lambda)$$

$$IQE_{LDS}(\lambda) = \alpha_{QD}(\lambda) * QY * IQE_{Bare}(\lambda_{PL-QD})$$

$$IQE_{RET}(\lambda) = (1 - \alpha_{QD}(\lambda)) * A_{AllnP}(\lambda) * \eta_{RET} * QY * IQE_{bare}(\lambda_{PL-QD})$$

- 5 where IQE_{Hybrid} and IQE_{Bare} are the IQEs of the hybrid and bare devices, IQE_{InGaP} is the IQE of the InGaP p-n junction, α_{QD} and QY are the absorptivity and quantum yield of the NQDs, λ_{PL-QD} is the emission wavelength of the NQDs, A_{AllnP} is the absorptivity of the AllnP window layer and η_{RET} is the efficiency of resonance energy transfer between the window layer and the NQDs. For zero
10 extraction efficiency of excitons photogenerated in the window layer, the bare IQE is calculated as:

$$IQE_{Bare} = (1 - A(\lambda)) * IQE_{InGaP}(\lambda)$$

- For simplicity, the quantum yield and the resonance energy transfer efficiency are assumed independent of the excitation wavelength. The absorptivity of a 30nm thin film of AllnP was calculated using the complex refractive index of the
15 material. The absorptivity of the NQD film on the solar cell was assumed to be the same as for the NQDs on glass, measured in an ultraviolet-visible spectrometer. The RET mediated LDS contribution was initially neglected and the RET efficiency was set to zero. A least squares technique was used to fit the measured data by varying the QY, which yielded an unrealistic value of QY of
20 66%. This value is much higher than the QY of 40% which was measured for NQDs deposited on glass in an integrating sphere and higher than the QY of the NQDs in solution (50%). Next, the data was fitted by setting the NQDs QY to 40%, as measured on glass, and by using the RET efficiency as a fitting parameter. The analysis yielded a value of 71% for the RET efficiency.

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The contributions of the various IQE components to the generated photocurrent can be estimated using the following equation:

$$\frac{I_X}{I_{SC}} = \frac{\int IQE_X(\lambda) * A_{hybrid}(\lambda) * \Phi_{AM1.5}(\lambda) d\lambda}{\int EQE_{hybrid}(\lambda) * \Phi_{AM1.5}(\lambda) d\lambda}$$

where I_X and IQE_X are respectively the contributions of each pumping channel to the I_{SC} and to the IQE of the solar cell, A_{hybrid} is the absorptivity of the hybrid structure and $\Phi_{AM1.5}$ is the photon flux of the AM1.5 direct spectrum (ASTMG173). RET mediated LDS is found to account for 3.5% of the total photocurrent, while direct LDS from the NQD film is found to amount to 5.2% of the total photocurrent, resulting in an 8.7% overall contribution of LDS to the total photocurrent.

The PCE variations can be correlated to the EQE data, since the PCE is proportional to the integral of the product of the EQE and of the AM1.5 photon flux:

$$PCE \propto \int EQE * \Phi_{AM1.5} d\lambda$$

where $\Phi_{AM1.5}$ is the AM1.5 photon flux spectrum (NREL ASTM G173-03 Direct + Circumsolar) and where the integration is done from 300nm to 750nm. Calculating these values for the bare and hybrid cases, the relative PCE enhancement is found to be 13.3%. The slight discrepancy between the values measured and calculated from the EQE is attributed to the difference in power density between the monochromatic source used for the EQE measurements and the AM1.5 solar spectrum. The enhancement is even more pronounced if the AM0 solar spectrum (ASTM E490 Air Mass Zero) is used instead. This spectrum describes the solar spectrum outside the earth's atmosphere, and is of interest for space applications. The PCE is found to increase in this case by 17.6% after hybridization with the NQDs, which further underlines the usefulness of RET luminescent down-shifting for space applications, where costly III-V multi-junction solar cells are typically used.

Further evidence of RET between the AlInP window layer and an epilayer of NQDs was obtained using time-resolved spectroscopy, by exciting the NQDs with a femtosecond laser and monitoring the photoluminescence rise time of the NQDs as a function of excitation wavelength using time-correlated single photon counting. The photoluminescence rise dynamics was fitted with a single exponential for the first 200 ps.

Figure 8 presents the PL rise-time of NQDs on glass (801) and on AlInP (802) as a function of the excitation wavelength. In the case of 801, the spheres represent the data point while the dashed curve is a guide for the eye. In the case of 802, the triangles represent the data point while the dotted curve is a guide for the eye. The rise dynamics of the NQDs on glass is found to be only weakly dependent on the excitation wavelength. On the contrary, the rise time of the NQDs on AlInP is found to vary strongly with excitation wavelength, with a rapid acceleration below 400nm and a 25% decrease at 355nm compared to the value on glass. Excitons photogenerated in the AlInP window layer can rapidly relax (~100fs) and transfer non-radiatively through RET to the overlying NQDs. The transferred excitons are relatively cold (~2.2eV) and can quickly relax to the ground state of the NQD (~2.1eV), thus accelerating the average rise time of the NQDs population. As the excitation wavelength decreases, the exciton population in the window layer increases, which enhances the RET contribution to the rise time of the NQDs. This provides strong evidence of the presence of RET between the AlInP window layer and the NQD epilayer in hybrid InGaP solar cells.

Figure 9 illustrates another configuration of the first embodiment, in which the structure previously shown in Figure 1 is encapsulated with an anti-reflective coating to lower reflections at the top surface of the device and to increase the absorption of the device. In this configuration, the NQDs are placed in between the window layer (905) and the anti-reflective coating (908).

Third Embodiment of the Invention

In this embodiment of the invention, the structure consists of a superstrate hybrid NQD thin-film solar cell. The different configurations relate to different positions of light responsive particles (in this embodiment NQDs) within the layer stack of the device. In the first configuration, as shown in Figure 10, the structure consists of a bottom metal contact (1001), an absorbing layer (1002), such CdTe or CIGS, a window layer (1003), such as CdS or ZnO, a plurality of NQDs (1004), a top contact (1005), such as a transparent conductive oxide, and a transparent solid substrate (1006), such as glass or polyimide. The thickness of the absorbing layer is typically several microns thick, while the window layer is typically 10-200nm thick. In such a device, the incoming solar radiation penetrates first through the

transparent substrate, the top contact and the window layer before reaching the absorbing region. In this structure, the depletion field is mostly created within the absorbing region (1002). As in the previous embodiments, carriers absorbed in the window layer are difficult to extract which creates a loss mechanism. In this scheme, the carriers generated in the window layer are transferred through RET to NQDs deposited between the top contact and the absorbing region. The NQDs are tuned to emit photoluminescence at energies lower than the band-gap of the window layer, which allows the emitted light to penetrate through the window layer and to be absorbed in the absorbing region to generate extractable charges.

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Figure 11 illustrates a second configuration of the third embodiment of the invention. In this configuration, the NQDs (1103) are placed in between the window layer (1104) and the absorbing layer (1102). This allows the emitters to be placed in direct contact with the absorbing layer, which enhances the efficiency of the luminescent transfer between the NQDs and the absorbing layer.

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Figure 12 illustrates a third configuration of the third embodiment of the invention. In this configuration, a plurality of NQDs (1203) is embedded into a window layer material (1204) to form a hybrid window layer. This minimizes the distance between the NQDs and the excitons generated in the window layer, which enhances RET between the window layer and the NQDs.

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Figure 13 illustrates a fourth configuration of the third embodiment of the invention. In this configuration, a plurality of NQDs (1304) is embedded into a conductive material (1305) to form a hybrid top contact. By placing the NQDs within the top contact, this configuration minimizes the resistive losses at the interface between the top contact and the window layer.

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Figure 14 illustrates a fifth configuration of the third embodiment of the invention. In this configuration, a plurality of NQDs (1403) is embedded within the absorbing material (1402) and positioned in close proximity (less than 2 Foster radii) of the window layer (1404) to form a hybrid absorbing layer. This allows the NQDs to be placed within the absorbing material, which optimizes the efficiency of the luminescent transfer between the NQDs and the absorbing layer.

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Fourth Embodiment of the Invention

In this embodiment of the invention, the structure consists of a substrate hybrid NQD thin-film solar cell. In the first configuration, as illustrated in Figure 15, the structure consists of a substrate (1501), such as stainless steel or plastic, a bottom metal contact (1502), such as Mo, an absorbing region (1503), such as CdTe or CIGS, a window layer (1504), such as CdS, a plurality of NQDs (1505), a top continuous contact (1506), such as a transparent conductive oxide, and a patterned metallic contact (1507), such as a digitated gold contact. In such a device, the incoming solar radiation is transmitted through the top transparent conductive oxide and the window layer before being absorbed in the absorbing region. In contrast with the third embodiment, the fourth embodiment allows the use of non-transparent substrates. The thickness of the absorbing layer is typically several microns thick, while the window layer is typically 10-200nm thick. As in the third embodiment, the depletion field is mostly created within the absorbing region (1503), which induces absorptive losses.

Figure 16 illustrates a second configuration of the fourth embodiment of the invention, analogous to the second configuration of the third embodiment. In this configuration, the NQDs (1604) are placed in between the window layer (1605) and the absorbing layer (1603). This allows the emitters to be placed in direct contact with the absorbing layer, which enhances the efficiency of the luminescent transfer between the NQDs and the absorbing layer.

Figure 17 illustrates a third configuration of the fourth embodiment of the invention, analogous to the third configuration of the third embodiment. In this configuration, a plurality of NQDs (1704) is embedded into a window layer material (1705) to form a hybrid window layer. This minimizes the distance between the NQDs and the excitons generated in the window layer, which enhances RET between the window layer and the NQDs.

Figure 18 illustrates a fourth configuration of the fourth embodiment of the invention, analogous to the fourth configuration of the third embodiment. In this configuration, a plurality of NQDs (1805) is embedded into a conductive material (1806) to form a hybrid top contact. By placing the NQDs within the top contact,

this configuration minimizes the resistive losses at the interface between the top contact and the window layer.

Figure 19 illustrates a fifth configuration of the fourth embodiment of the invention, analogous to the fifth configuration of the third embodiment. In this configuration, a plurality of NQDs (1904) is embedded within the absorbing material (1903) and positioned in close proximity (less than 2 Foster radii) of the window layer (1905) to form a hybrid absorbing layer. This allows the NQDs to be placed within the absorbing material, which optimizes the efficiency of the luminescent transfer between the NQDs and the absorbing layer.

Methods of Fabrication

All embodiments of the present invention can currently be realised through conventional semiconductor processing techniques. Fabrication methods for conventional photovoltaic (solar) cells, photodetectors and single photon devices are well known and so will not be described in detail here. NQDs can be deposited on a large scale using a variety of techniques, including spin-coating, pulsed-spray deposition and inkjet printing.

Figure 20A to 20G illustrate the steps of an example fabrication process flow for fabricating devices according to the present invention, starting from a bare epitaxial Si-deposited GaAs substrate, as show in Figure 20A.

With reference to Figure 20B, a 500nm GaAs buffer (2002), a n⁺⁺/p⁺⁺ GaAs tunnel diode (2003), a 50 nm Al_{0.7}Ga_{0.3}As back surface field layer (2004), a 1500 nm In_{0.5}Ga_{0.5}P p-n junction (2005) and a 30 nm Al_{0.5}In_{0.5}P window layer (2006) are consecutively deposited on top of the substrate using a method such as molecular beam epitaxy or metal organic chemical vapour deposition. The GaAs buffer (2002) provides an atomically flat surface for the growth of the device, while the tunnel diode (2003) allows a good electrical connexion between the p-n junction (2005) and the underlying substrate.

As shown in Figure 20C, a mask (2007) may then be deposited on top of the contact layer. Such a mask could consist of a light or electron sensitive layer (resist), such as poly(methyl methacrylate) or poly(methyl glutarimide) and may

be deposited using techniques such as spin-coating or evaporation. This layer is patterned by means of a suitable technique, such as conventional optical lithography, nano-imprint lithography, or electron beam lithography, and developed to form shaped voids (2008) at predefined positions, as shown in
5 Figure 20D.

As shown in Figure 20E, a top metal contact (2009) stack, can subsequently be deposited using a technique such as thermal evaporation or magnetron sputtering so as to fill the shaped voids (2008). The remaining resist mask can then be
10 removed by acid or solvent wash or oxygen plasma ashing, leaving a patterned metal structure as shown in Figure 20F. The contact stack may comprise a single layer of metal such as gold, or may comprise a multi-layer stack including adhesion layers, as well as other materials as appropriate to provide a good ohmic contact. A common process for this step is known as 'metal lift off'.

15 The remaining patterned metal layer then forms an electrical contact allowing efficient collection of charge at the top-surface of the device. As shown in Figure 20G, a continuous metallic layer (2010), such as gold, may finally be deposited onto the bottom side of the substrate using the techniques used for the top
20 electrical contact deposition to form a bottom electrical contact.

As shown in Figure 20H, optically responsive particles (2011) are then deposited above the window layer in between the top metal features by a suitable method, such as drop casting, inkjet deposition, spray deposition, and the like.

25

Method of Design

All proposed embodiments of the invention can be designed utilising Finite difference time domain simulation techniques, whereby the model incorporates isolated dipole emitters, and also measures to prevent coherence effects within
30 the simulation. Electrical characteristics can be modelled using commercially available software such as Silvaco.

Applications

As indicated, the optical device of the present invention may be used as a single photon absorbing or multi-photon absorbing device. The device can find application in solar cell technologies, photodetectors and imaging devices such as Charged Coupled Devices (CCDs).

5

Claims

1. An optical device having a surface for receiving light energy from a light source, the optical device comprising:
- 5 an electronic structure having an energy absorbing region, wherein the electronic structure exhibits an electronic band gap with an associated band gap energy;
- a window layer comprising a material which exhibits an electronic band gap with an associated band gap energy; and
- 10 a plurality of optically responsive particles which exhibit an electronic band gap with an associated band gap energy that is smaller than the band gap energy of the window layer material,
- wherein the optically responsive particles are adapted to mediate:
- a first energy transfer process involving non-radiative energy
- 15 transfer, whereby light energy absorbed by the window layer is transferred from the window layer to the optically responsive particles via non-radiative dipole-dipole interaction; and,
- a second energy transfer process involving luminescent energy emission, whereby light energy transferred from the window layer to the
- 20 optically responsive particles is re-emitted as longer wavelength lower energy light which can be absorbed by the energy absorbing region,
- and wherein the optically responsive particles are located in proximity to the window layer and the energy absorbing region such that the first and second energy transfer processes may occur simultaneously or sequentially, whereby
- 25 energy transferred to the optically responsive particles from the window layer via the first energy transfer process is re-emitted via the second energy transfer process for absorption by the light absorbing region.
2. An optical device according to claim 1, wherein the optically responsive
- 30 particles are further adapted to mediate:
- a third energy transfer process involving luminescent energy absorption, whereby some light energy received from the light source is absorbed directly by the optically responsive particles; and
- the second energy transfer process involving luminescent energy
- 35 emission, whereby light energy absorbed directly by the optically responsive

particles is re-emitted as longer wavelength lower energy light which can be absorbed by the energy absorbing region,

wherein the optically responsive particles are located in proximity to the window layer and the energy absorbing region such that the first, second and
5 third energy transfer processes may occur simultaneously or sequentially, whereby energy absorbed directly by the optically responsive particles via the third energy transfer process is also re-emitted via the second energy transfer process for absorption by the light absorbing region.

10 3. An optical device according to claim 2, wherein the optically responsive particles are adapted to absorb one or more of blue and ultraviolet radiation via the third energy transfer process.

4. An optical device according to any preceding claim, wherein the first
15 energy transfer process involves resonance energy transfer (RET).

5. An optical device according to any one of claims 1 to 4, wherein the optically responsive particles are discrete.

20 6. An optical device according to any one of claims 1 to 4, wherein the optically responsive particles are contained within a host matrix.

7. An optical device according to any preceding claim, wherein the optically responsive particles comprise a direct band gap material.
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8. An optical device according to any preceding claim, wherein the optically responsive particles comprise at least one of a type-II semiconductor, a molecular absorber, an organic semiconductor, and a phosphor.

30 9. An optical device according to any preceding claim, wherein the optically responsive particles have a regular shape.

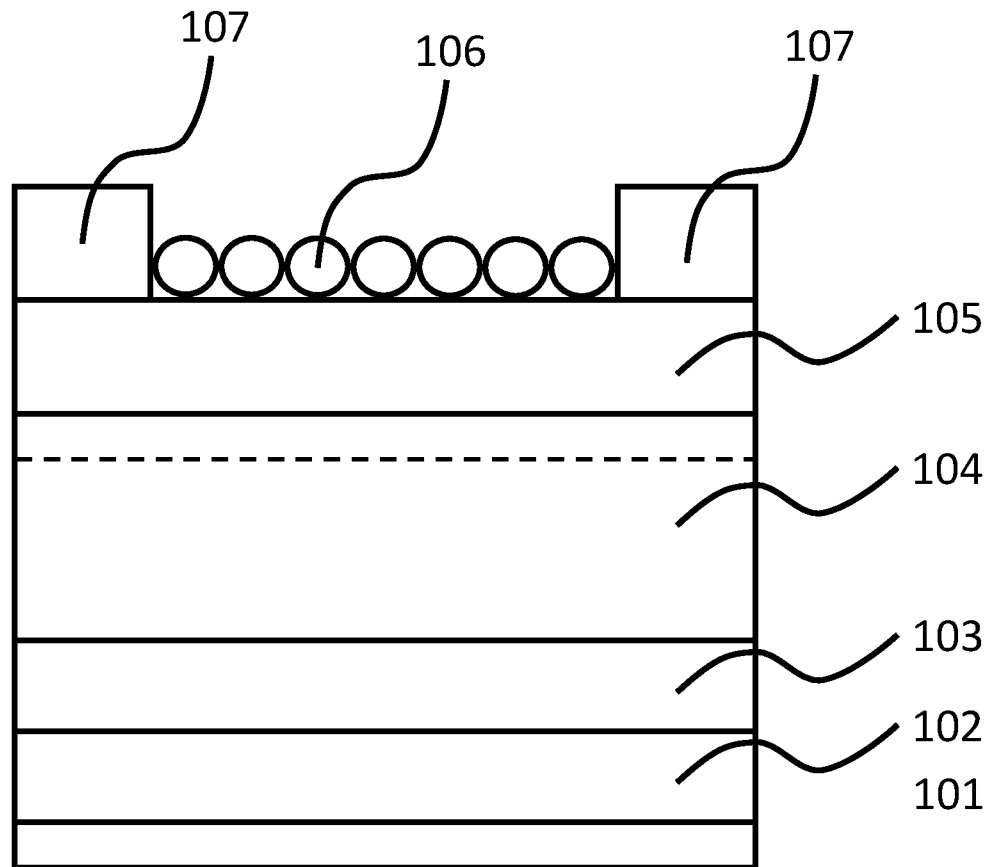
10. An optical device according to claim 9, wherein the shape of the optically responsive particles includes one or more of spherical, elongate rod and tetrapod.
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11. An optical device according to any preceding claim, wherein the optically responsive particles have a core-shell structure.
12. An optical device according to any preceding claim, wherein the optically responsive particles comprise at least one of quantum dots and quantum rods.
13. An optical device according to any preceding claim, wherein the optically responsive particles have a refractive index with a magnitude that is between that of the refractive indices of materials on either side of the optically responsive particles, whereby to provide a degree of refractive index matching between said materials and reduce Fresnel reflection of incident light.
14. An optical device according to any preceding claim, wherein the window layer comprises an indirect bandgap semiconductor material.
15. An optical device according to any preceding claim, wherein the window layer comprises a direct bandgap semiconductor material.
16. An optical device according to any preceding claim, wherein the window layer is disposed between the optically responsive particles and the energy absorbing region of the electronic structure.
17. An optical device according to any preceding claim, wherein the window layer is disposed closer to the light receiving surface than is the energy absorbing region.
18. An optical device according to any preceding claim, wherein the optically responsive particles are disposed such that their distance from a surface of the window layer is less than twice the Forster distance.
19. An optical device according to any preceding claim, wherein the optically responsive particles are disposed such that their distance from the energy absorbing region is more than twice the Forster distance.

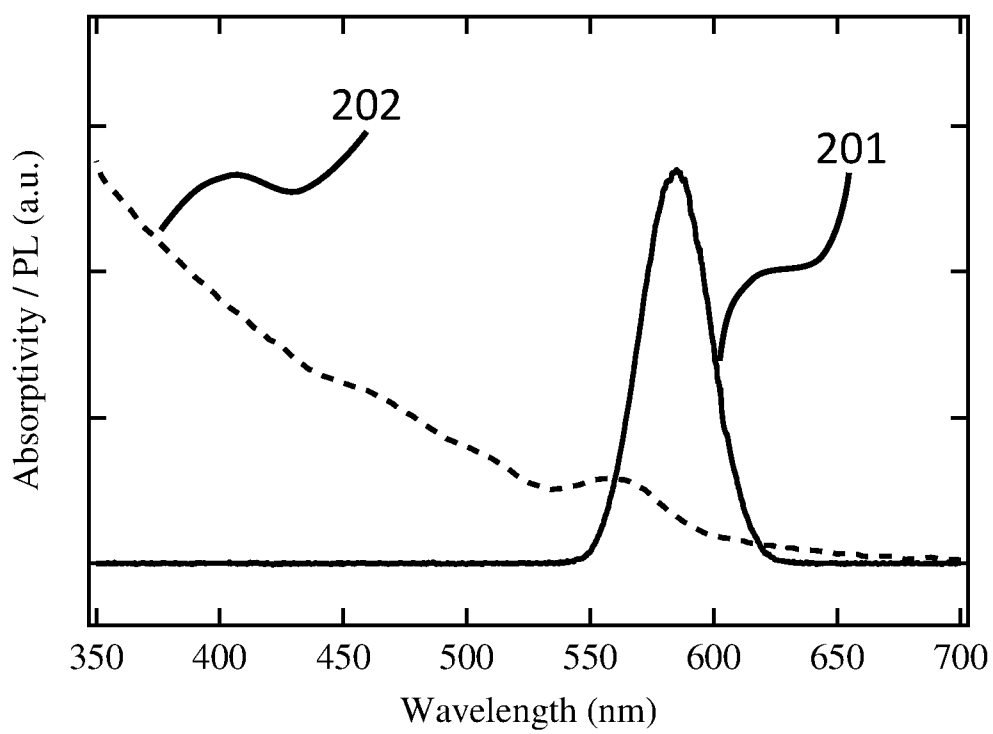
20. An optical device according to any preceding claim, wherein the optically responsive particles are disposed on a surface of the window layer such that they are in physical contact with said surface.
- 5 21. An optical device according to any preceding claim, comprising one or more additional window layers.
22. An optical device according to any preceding claim, wherein the energy absorbing region comprises at least one electronic junction region.
- 10 23. An optical device according to claim 22, wherein the at least one electronic junction region includes a P-N junction.
24. An optical device according to claim 23, wherein the P-N junction
15 comprises an indirect bandgap material.
25. An optical device according to claim 23, wherein the P-N junction comprises a direct bandgap material.
- 20 26. An optical device according to any preceding claim, wherein the energy absorbing region comprises at least one quantum well.
27. An optical device as hereinbefore described.
- 25 28. An optical device as hereinbefore described with reference to the accompanying drawings.
29. A light harvesting device comprising an optical device according to any preceding claim, wherein light energy absorbed by the energy absorbing region of
30 the electronic structure generates an electric potential therein.
30. A method of fabricating an optical device according to any preceding claim, the method comprising the steps of:
providing the electronic structure having the energy absorbing region;
35 forming the window layer; and,

providing the plurality of optically responsive particles located in proximity to the window layer and the energy absorbing region.

1/23

**FIG. 1**

2/23

**FIG. 2**

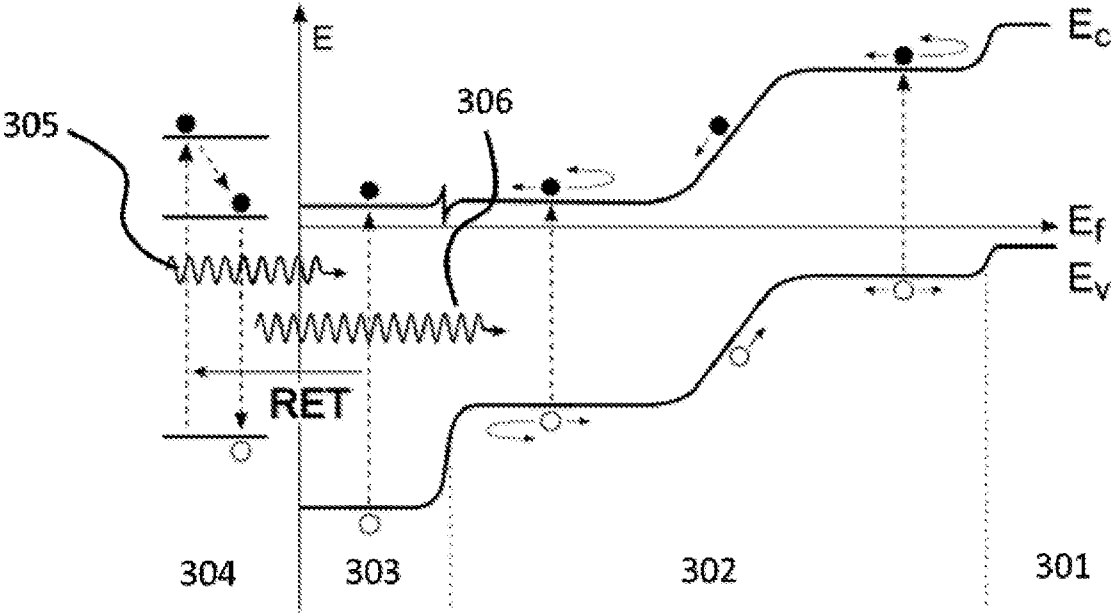
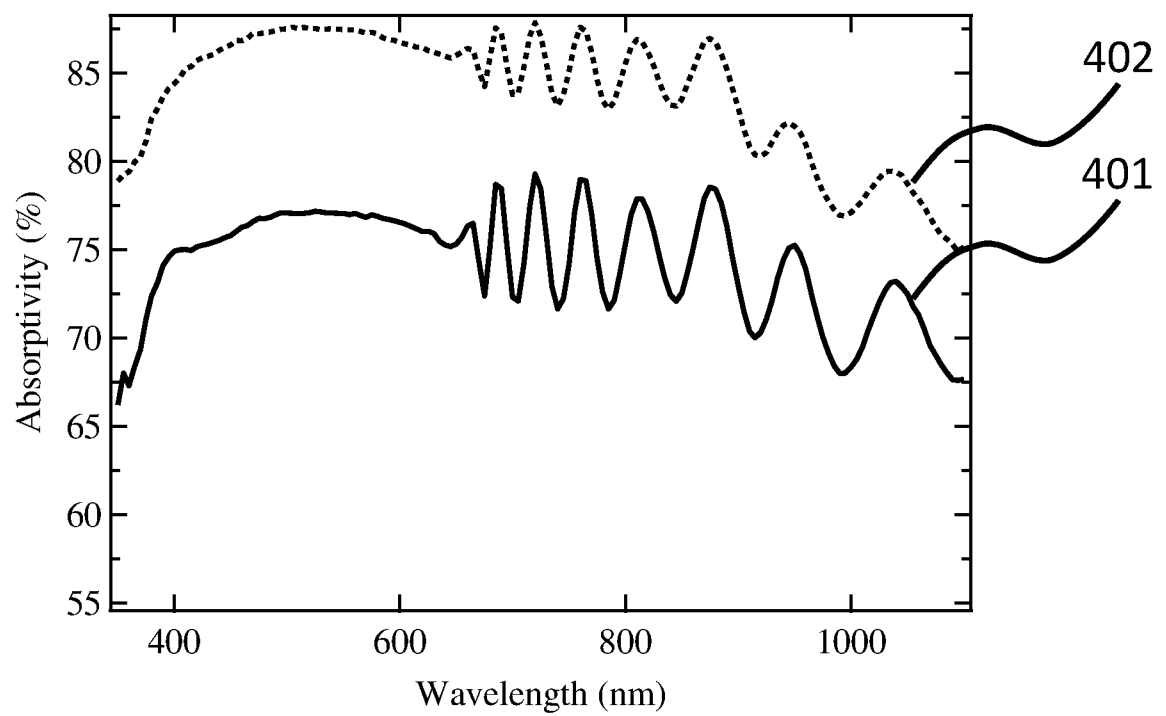
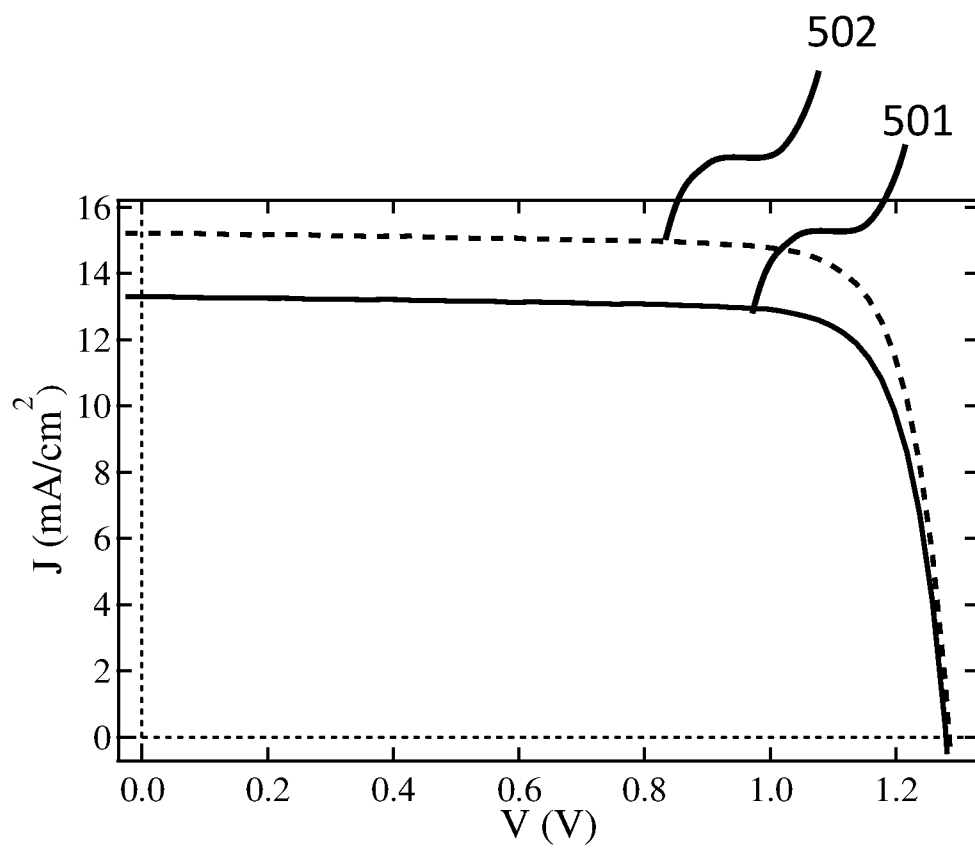


FIG. 3

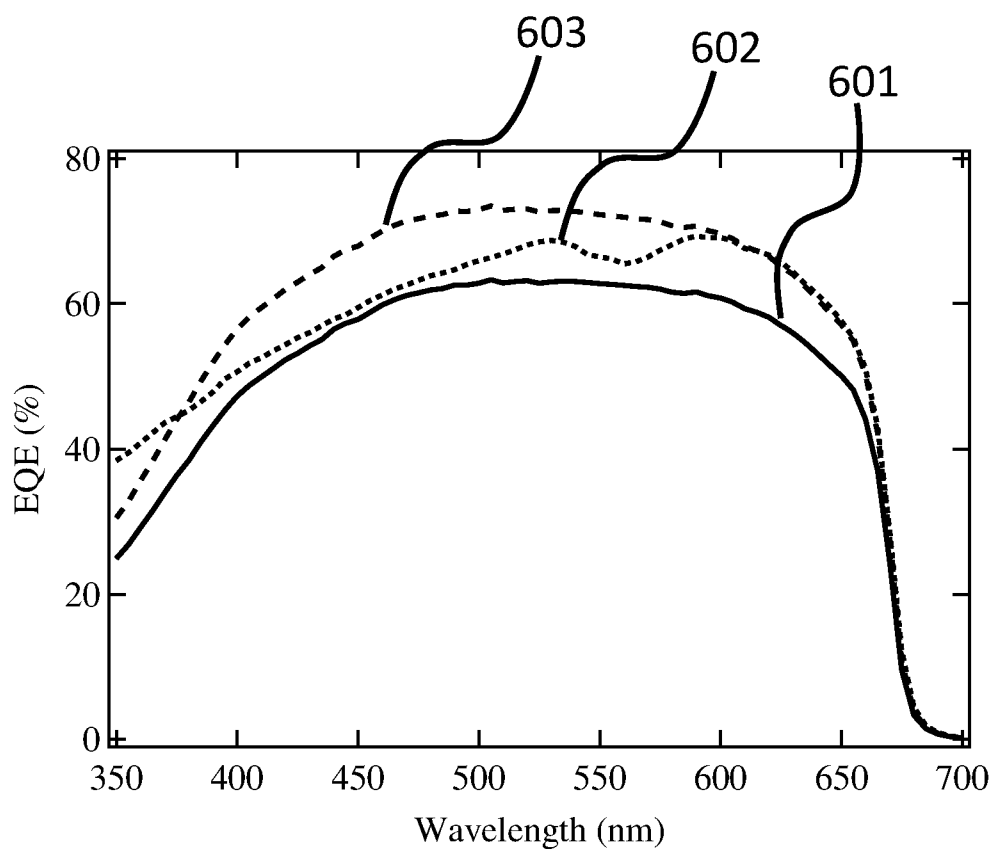
4/23

**FIG. 4**

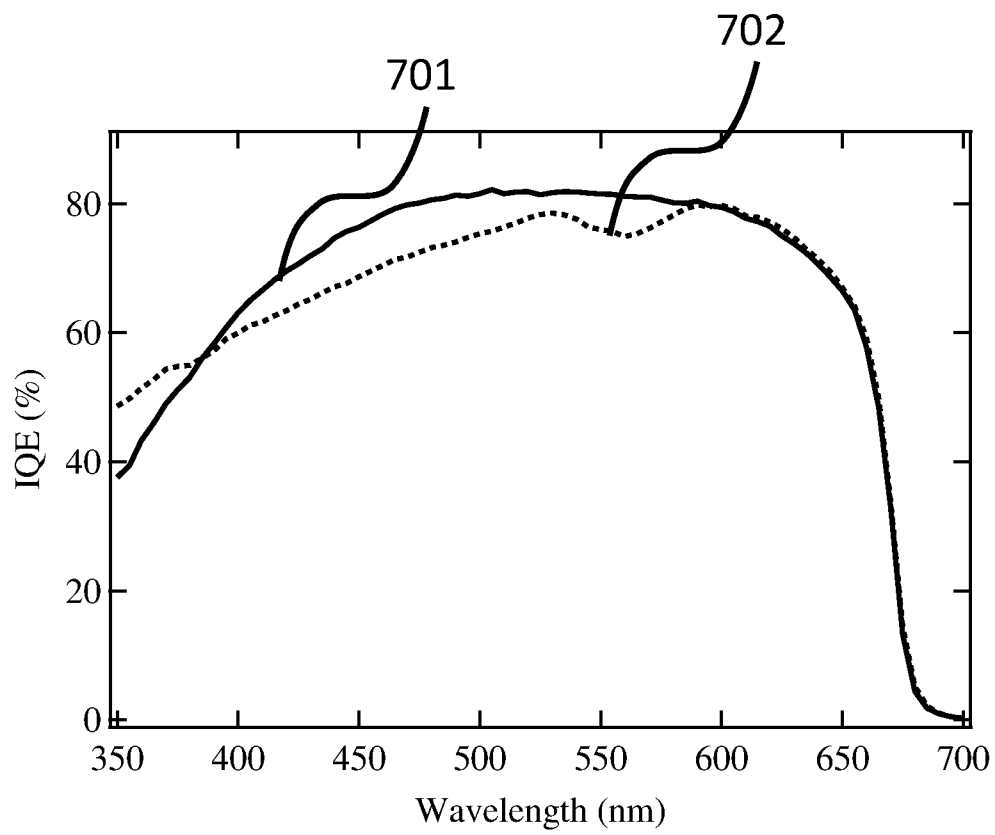
5/23

**FIG. 5**

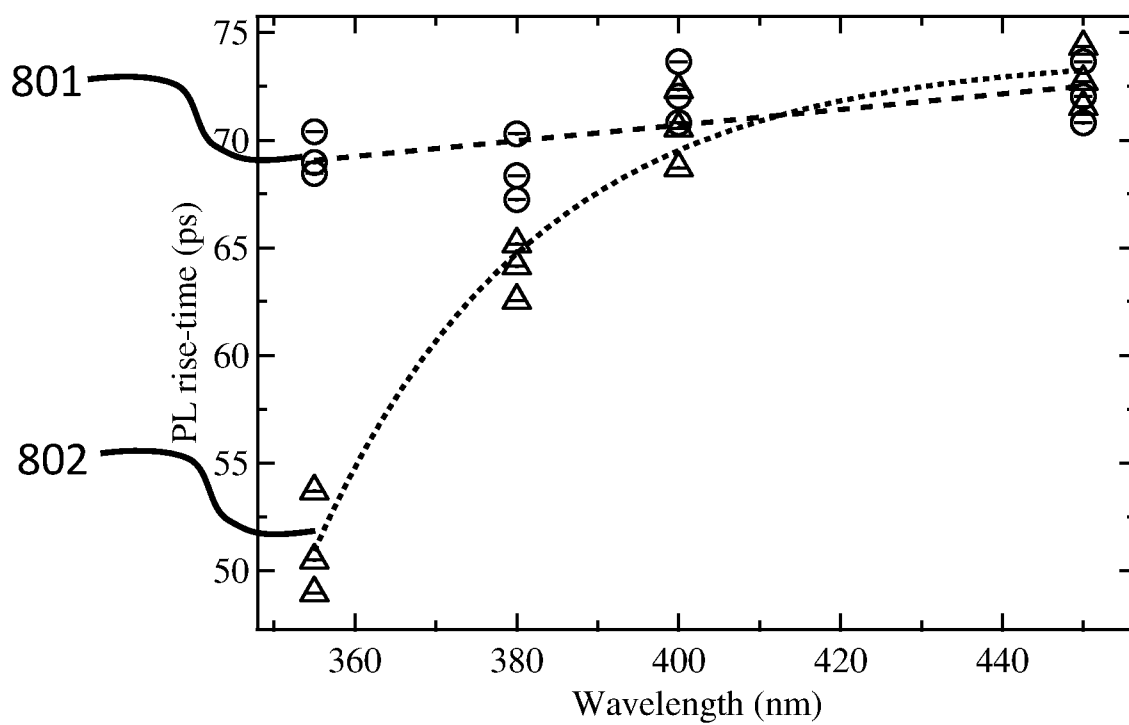
6/23

**FIG. 6**

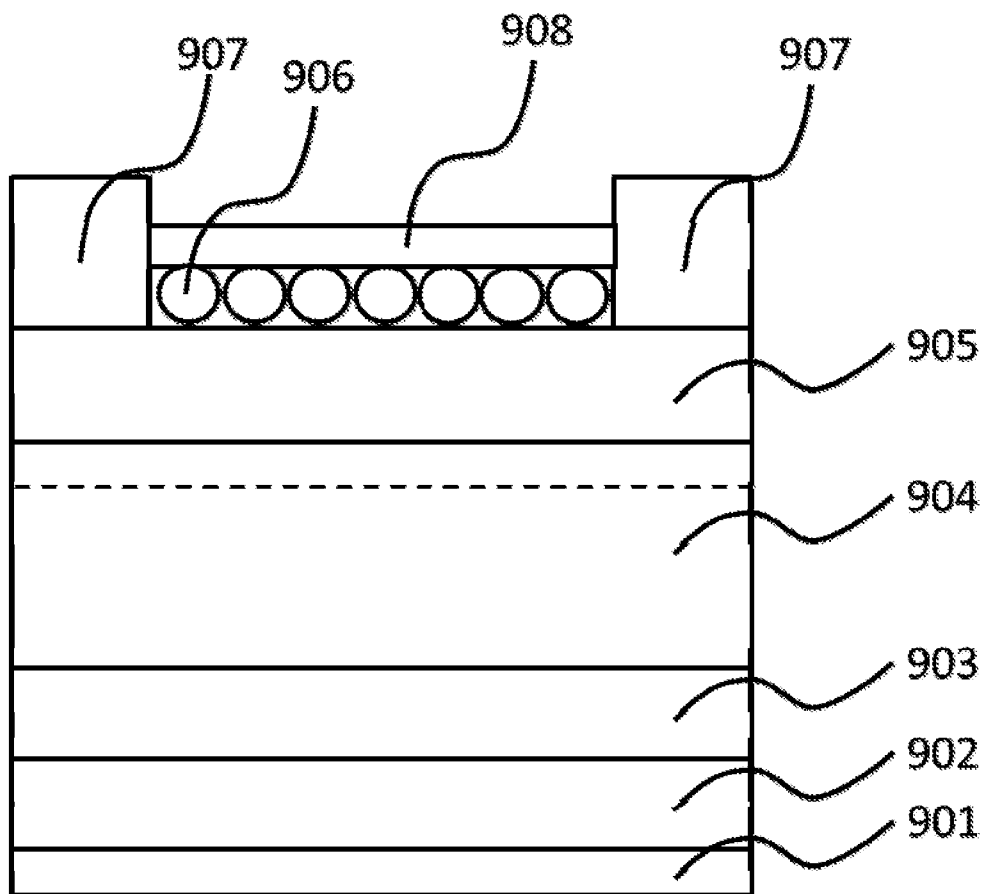
7/23

**FIG. 7**

8/23

**FIG. 8**

9/23

**FIG. 9**

10/23

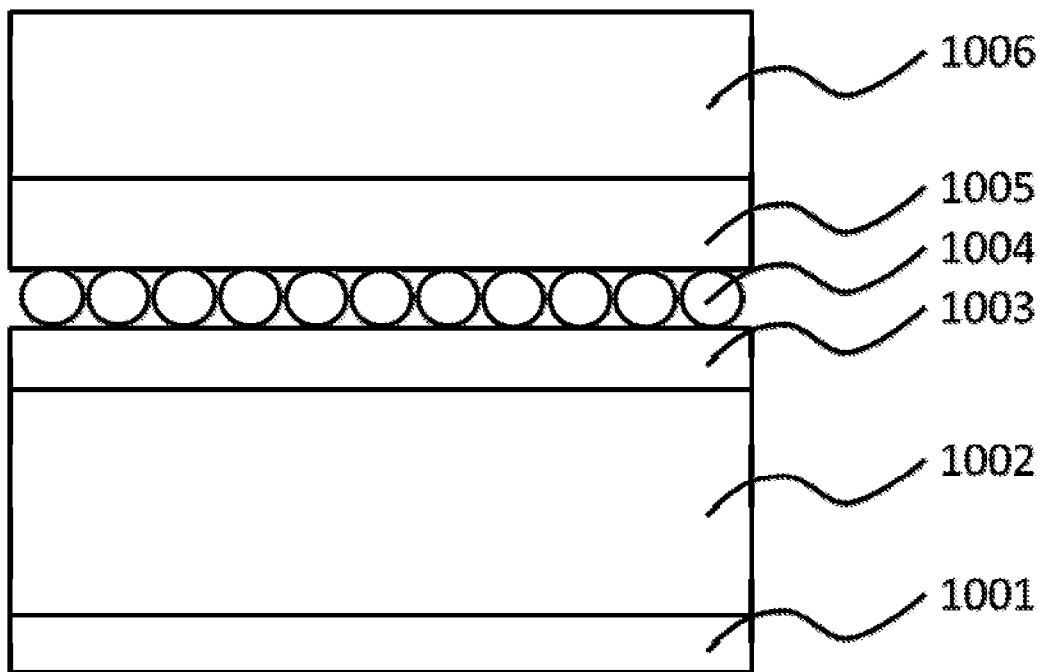


FIG. 10

11/23

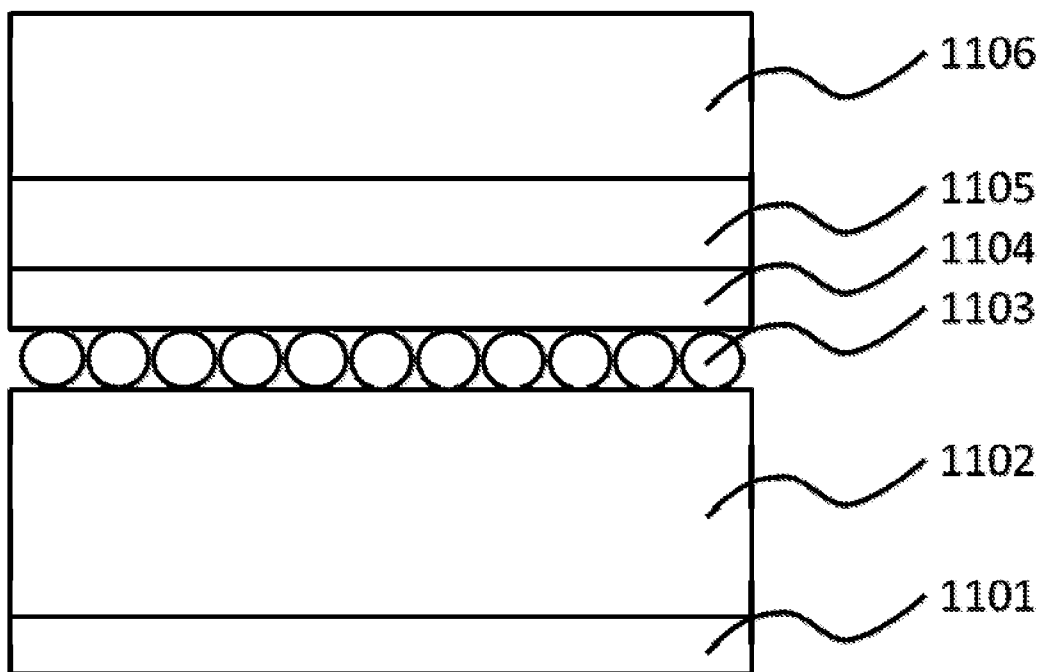
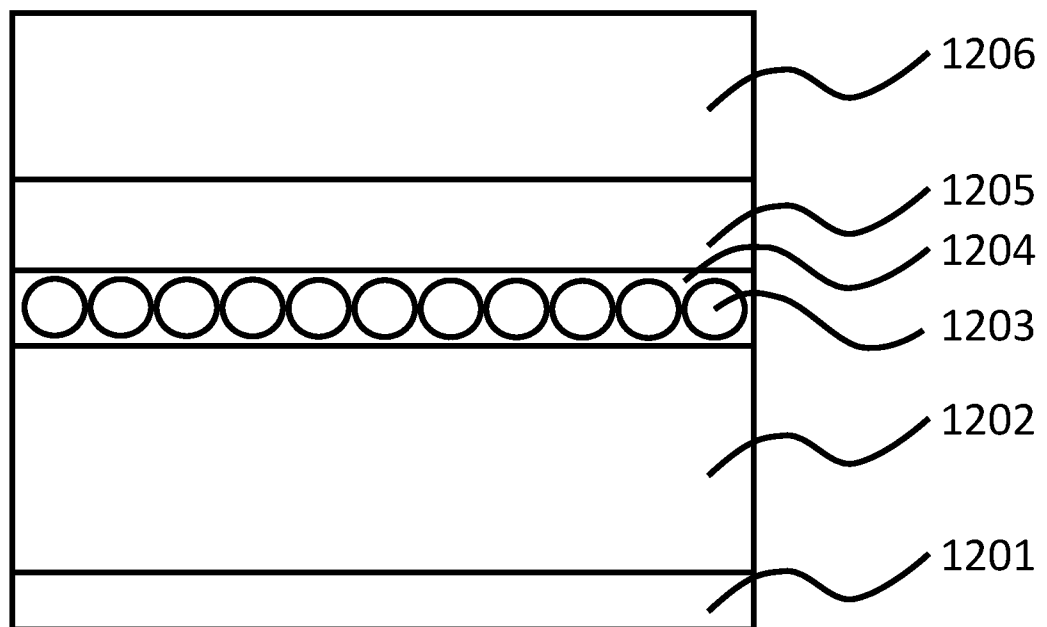
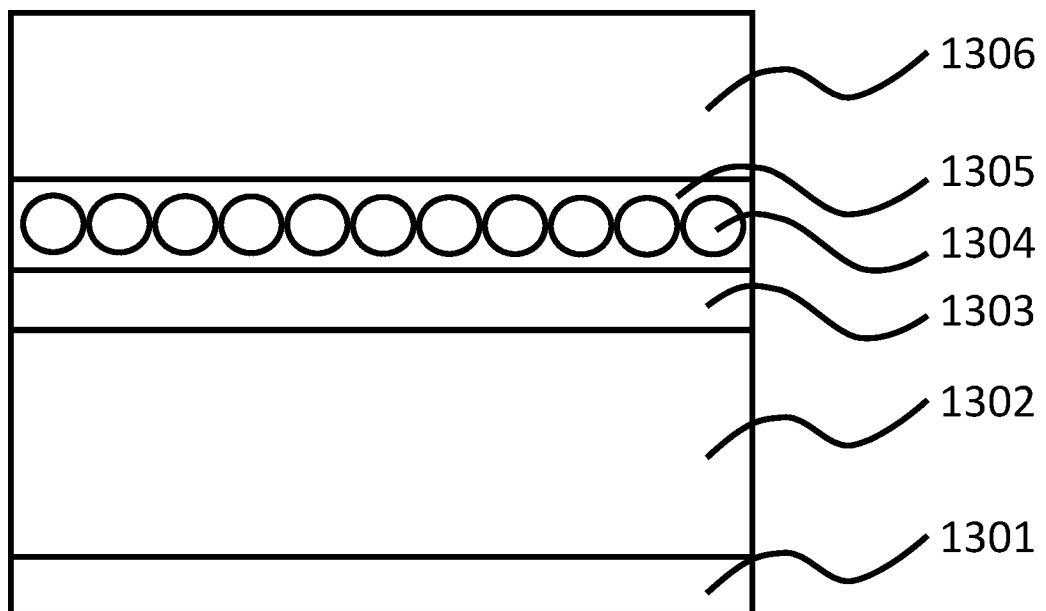


FIG. 11

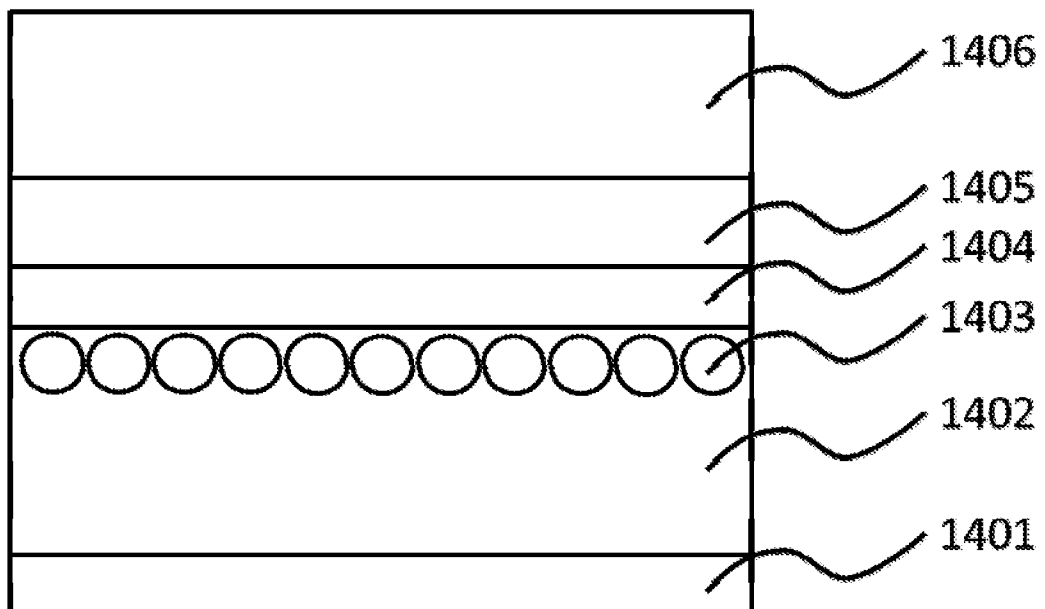
12/23

**FIG. 12**

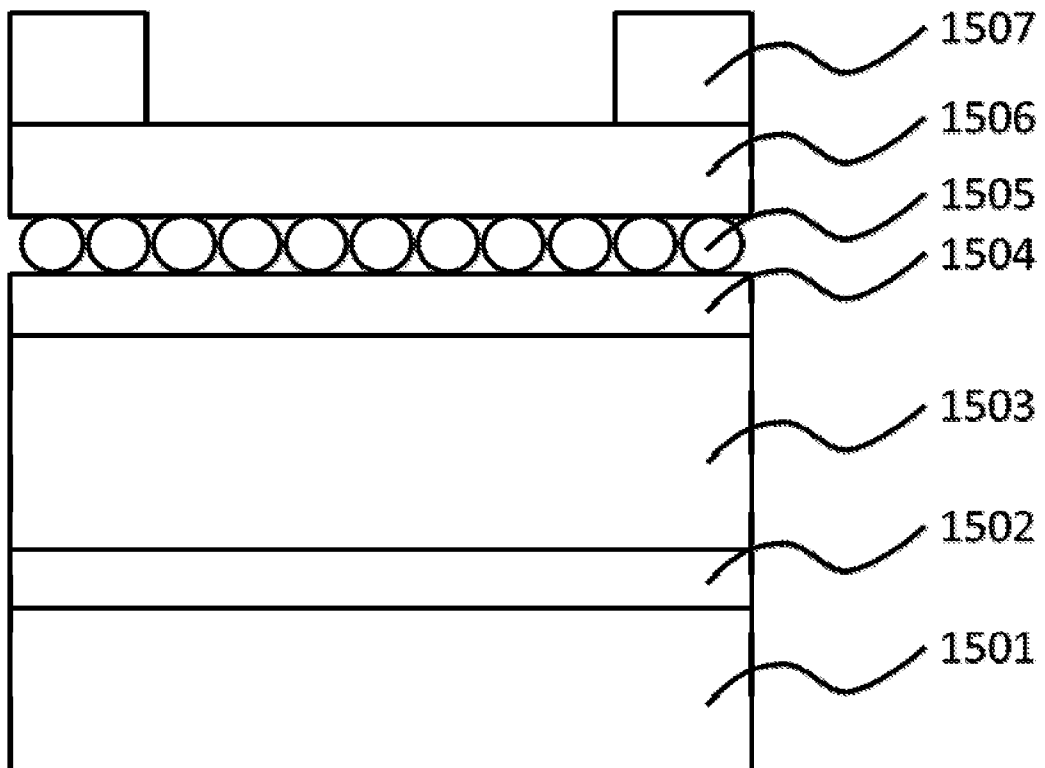
13/23

**FIG. 13**

14/23

**FIG. 14**

15/23

**FIG. 15**

16/23

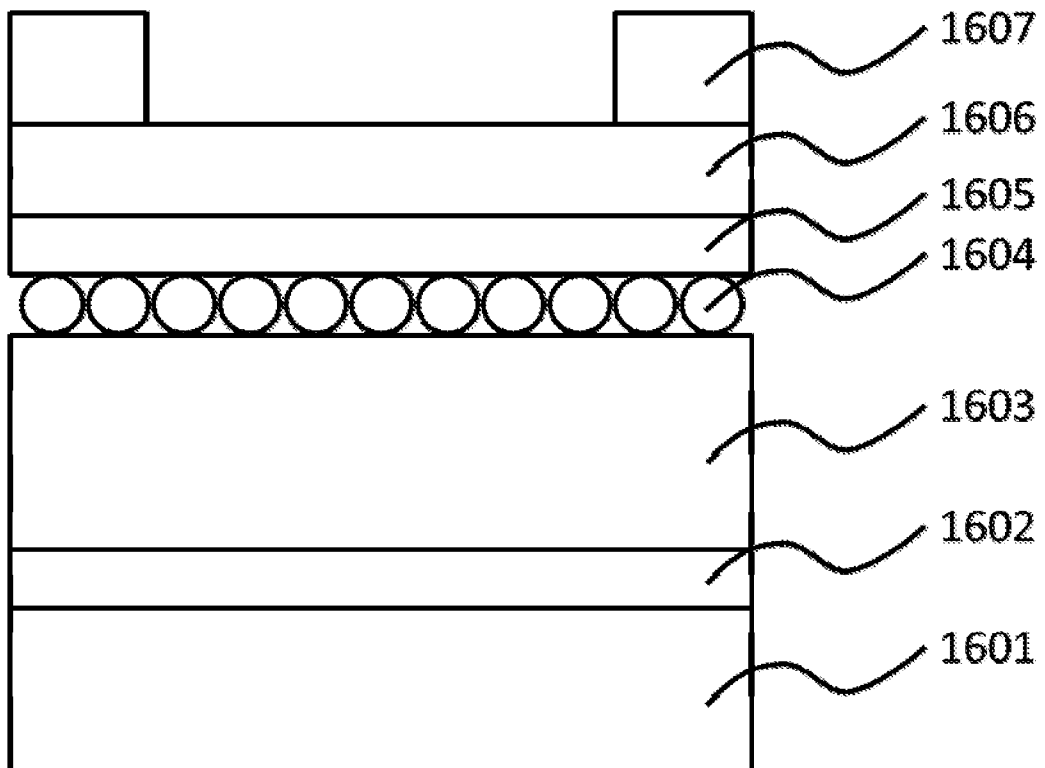


FIG. 16

17/23

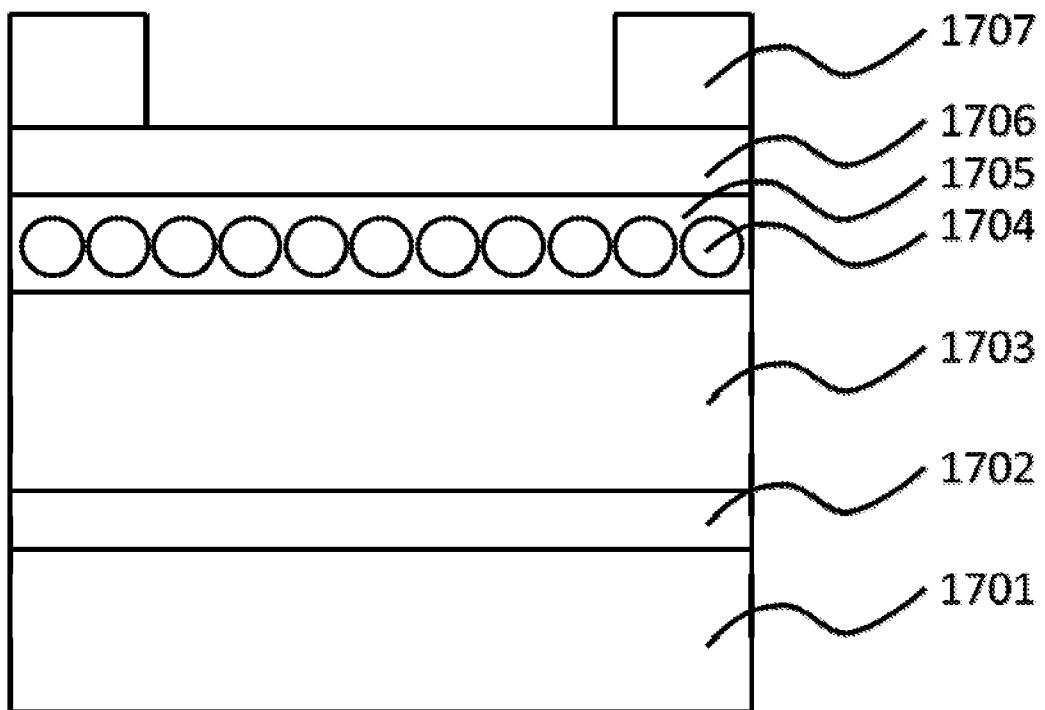


FIG. 17

18/23

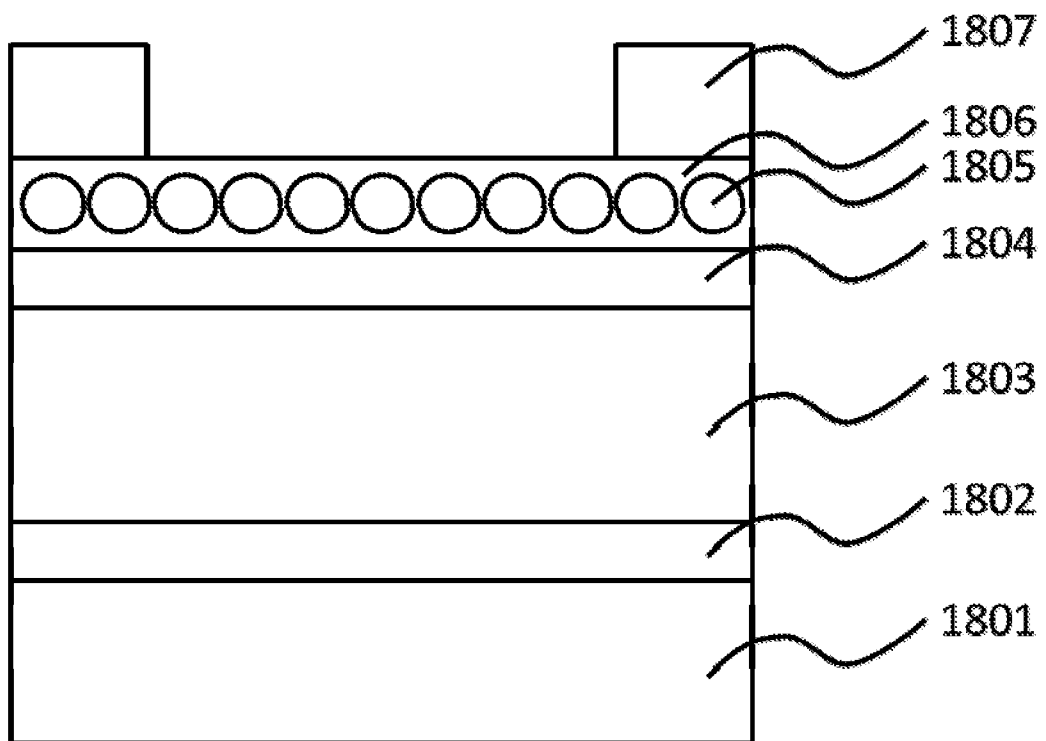


FIG. 18

19/23

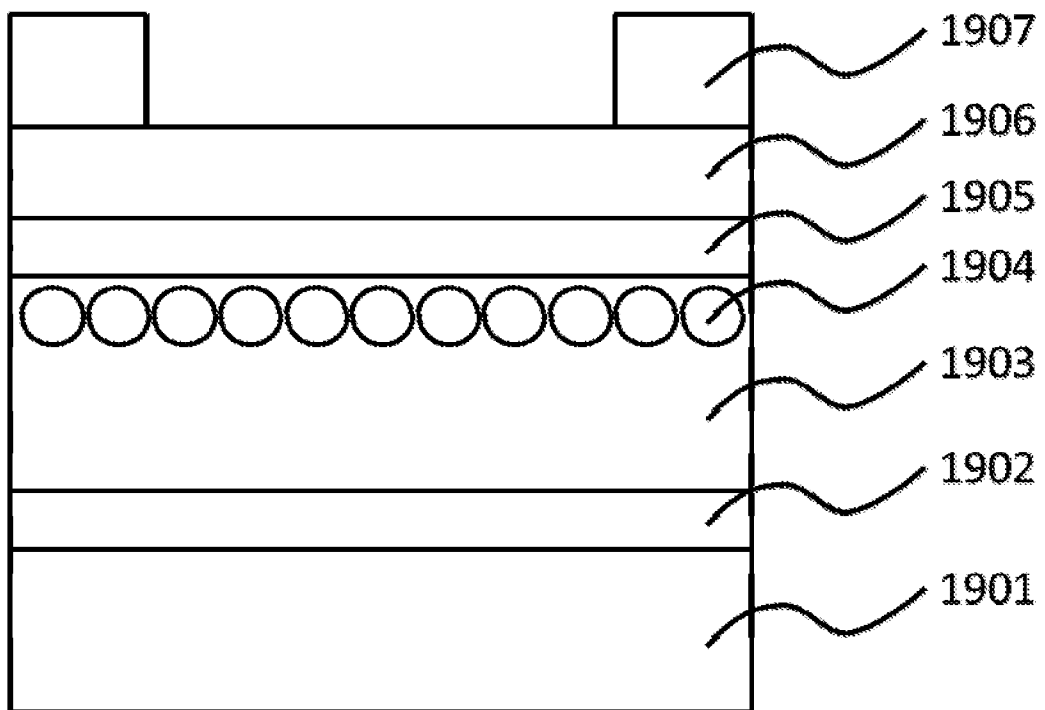


FIG. 19

20/23

FIG. 20A

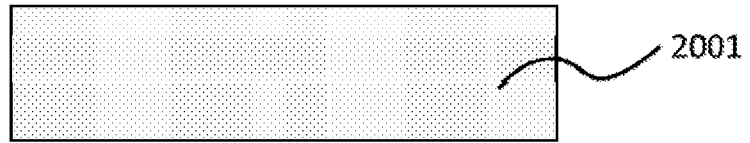


FIG. 20B

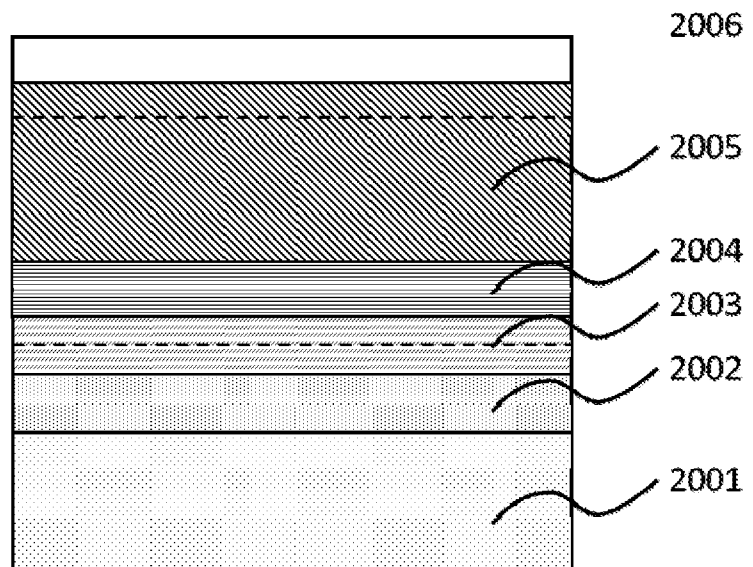


FIG. 20C

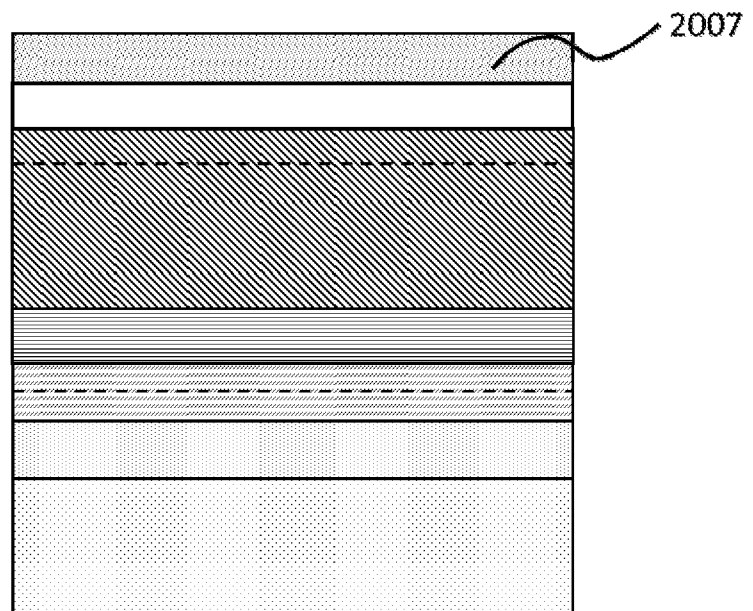


FIG. 20D

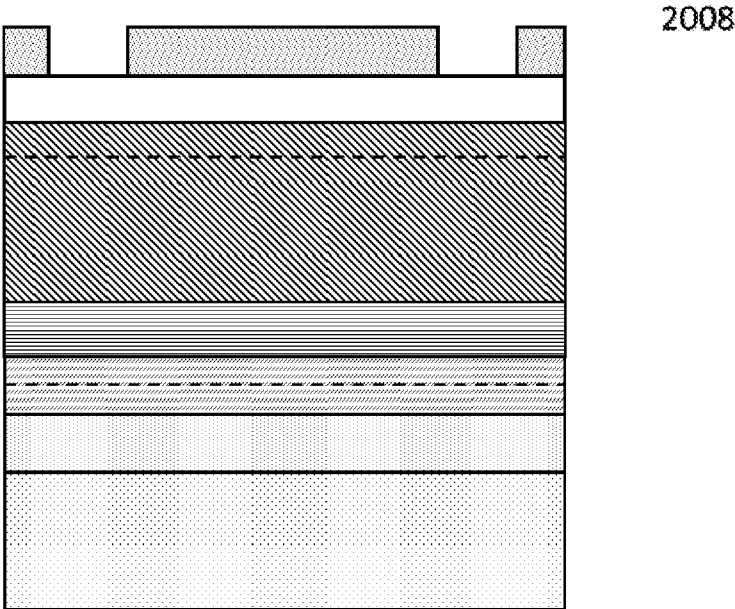


FIG. 20E

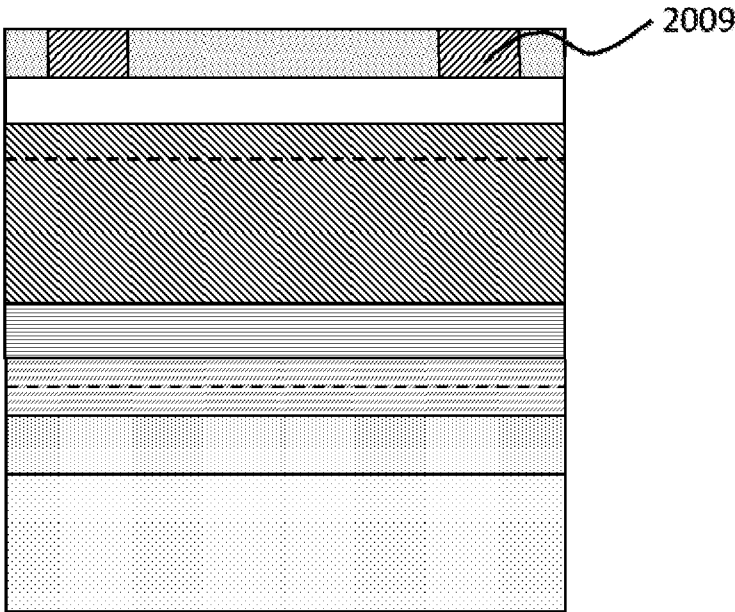


FIG. 20F

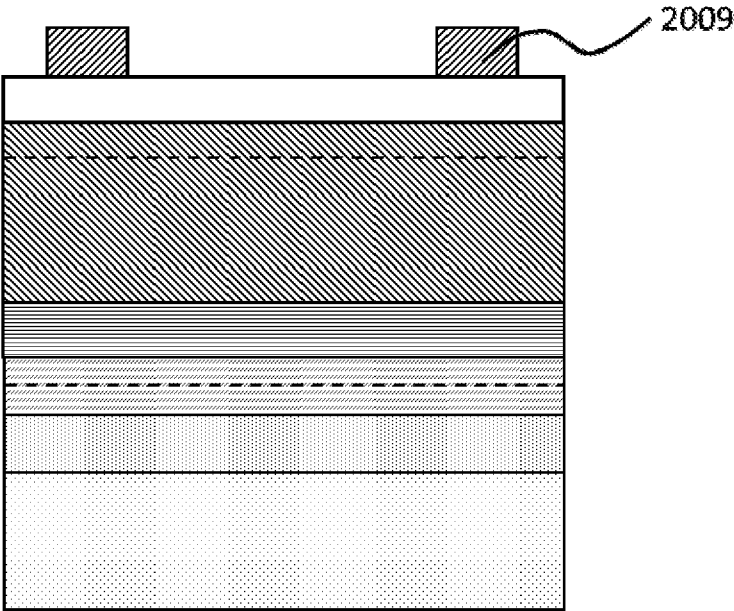
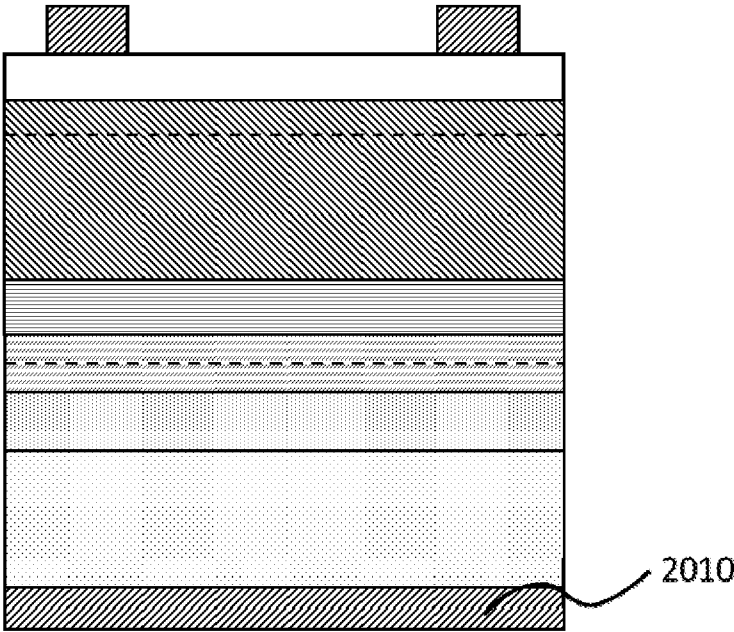
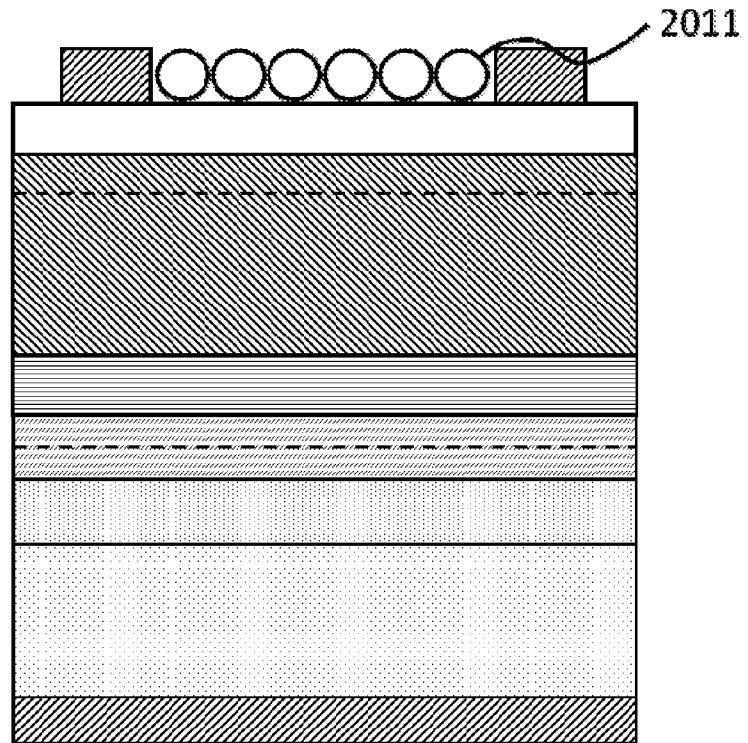


FIG. 20G



23/23

FIG. 20H



INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2015/053730

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L31/0352
ADD.

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)
H01L

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	JP 2013 229388 A (NAT INST OF ADV IND & TECHNOL) 7 November 2013 (2013-11-07) abstract; figure 5 paragraphs [0015], [0016], [0042] -----	1-30
X	US 2012/112165 A1 (CHARLTON MARTIN DAVID BRIAN [GB] ET AL) 10 May 2012 (2012-05-10) abstract; figures 1,2A paragraphs [0020], [0133] ----- -/-	1,27-30



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

11 January 2016

Date of mailing of the international search report

18/01/2016

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Fax: (+31-70) 340-3016

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Favre, Pierre

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2015/053730

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 2010/264333 A1 (OFFERMANS PETER [NL] ET AL) 21 October 2010 (2010-10-21) abstract; figure 1 paragraphs [0017], [0077] -----	1,27-30

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Information on patent family members

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