(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
5 August 2004 (05.08.2004)

PCT

(10) International Publication Number
WO 2004/066346 A2

(51) International Patent Classification[7]: H01L

(21) International Application Number: PCT/CA2004/000076

(22) International Filing Date: 22 January 2004 (22.01.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/441,413	22 January 2003 (22.01.2003)	US
60/441,485	22 January 2003 (22.01.2003)	US
60/450,661	3 March 2003 (03.03.2003)	US

(71) Applicant *(for all designated States except US)*: **GROUP IV SEMICONDUCTOR INC.** [CA/CA]; 540 Brierwood Avenue, Ottawa, Ontario K2A 2H5 (CA).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **HILL, Steven, E.** [US/US]; 1765 Foxfield Drive, Castle Rock, CO 80104 (US).

(74) Agent: **SMART & BIGGAR**; 900 - 55 Metcalfe Street, P.O Box 2999, Station D, Ottawa, Ontario K1P 5Y6 (CA).

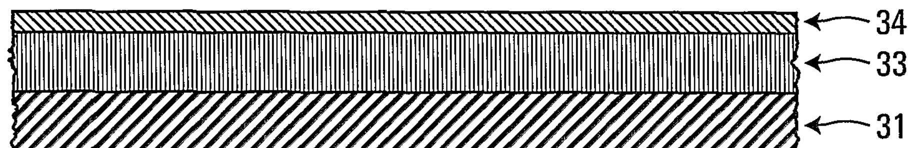
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DOPED SEMICONDUCTOR NANOCRYSTAL LAYERS, DOPED SEMICONDUCTOR POWDERS AND PHOTONIC DEVICES EMPLOYING SUCH LAYERS OR POWDERS



(57) **Abstract:** The present invention relates to a doped semiconductor nanocrystal layer comprising (a) a group IV oxide layer which is free of ion implantation damage, (b) from 30 to 50 atomic percent of a semiconductor nanocrystal distributed in the group IV oxide layer, and (c) from 0.5 to 15 atomic percent of one or more rare earth element, the one or more rare earth element being (i) dispersed on the surface of the semiconductor nanocrystal and (ii) distributed substantially equally through the thickness of the group IV oxide layer. The present invention also relates to a semiconductor structure comprising the above semiconductor nanocrystal layer and to processes for preparing the semiconductor nanocrystal layer. Furthermore, photonic devices employing the new materials are also provided. The invention provides a doped semiconductor powder comprising nanocrystals of a group IV semiconductor and a rare earth element, the rare earth element being dispersed on the surface of the group IV semiconductor nanocrystals. The invention also provides processes for the preparation of the above doped semiconductor powder, a composite material comprising the a matrix in which is dispersed a doped semiconductor powder, and photonic devices comprising doped semiconductor powders and doped semiconductor layers.

WO 2004/066346 A2

DOPED SEMICONDUCTOR NANOCRYSTAL LAYERS, DOPED SEMICONDUCTOR POWDERS AND PHOTONIC DEVICES EMPLOYING SUCH LAYERS OR POWDERS

FIELD OF THE INVENTION

The present invention relates to semiconductor nanocrystal layers and powders doped with rare earth elements, to semiconductor structures comprising these semiconductor nanocrystal layers, to processes for preparing the semiconductor nanocrystal layers doped with rare earth elements, and to photonic devices employing these materials.

BACKGROUND OF THE INVENTION

Silicon has been a dominant semiconductor material in the electronics industry, but it does have a disadvantage in that it has poor optical activity due to an indirect band gap. This poor optical activity has all but excluded silicon from the field of optoelectronics. In the past two decades there have been highly motivated attempts to develop a silicon-based light source that would allow one to have combined an integrated digital information processing and an optical communications capability into a single silicon-based integrated structure. For a silicon-based light source (silicon Light Emitting Diode (LED)) to be of any practical use, it should (1) emit at a technologically important wavelength, (2) achieve its functionality under practical conditions (e.g. temperature and pump power), and (3) offer competitive advantage over existing technologies.

One material that has gathered much international attention is erbium (Er) doped silicon (Si). The light emission from Er-doped Si occurs at the technological important 1.5 micron (μm) wavelength. Trivalent erbium in a proper host can have a fluorescence of 1540 nm due to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ intra-4f transition. This 1540 nm fluorescence occurs at the minimum absorption window of the silica-base telecommunication

fiber optics field. There is great interest in Er doping of silicon as it holds the promise of silicon based optoelectronics from the marriage of the vast infrastructure and proven information processing capability of silicon
5 integrated circuits with the optoelectronics industry. Theoretical and experimental results also suggest that Er in Si is Auger-excited via carriers, generated either electrically or optically, that are trapped at the Er-related defect sites and then recombine, and that this process can be very efficient due
10 to strong carrier-Er interactions. However, if this strong carrier-Er interaction is attempted in Er-doped bulk Si, the efficiency of the Er^{3+} luminescence is reduced at practical temperature and pump powers.

Recently, it has been demonstrated that using
15 silicon-rich silicon oxide (SRSO), which consists of Si nanocrystals embedded in a SiO_2 (glass) matrix, reduces many of the problems associated with bulk Si and can have efficient room temperature Er^{3+} luminescence. The Si nanocrystals act as classical sensitizer atoms that absorb incident photons and
20 then transfer the energy to the Er^{3+} ion, which then fluoresce at the 1.5 micron wavelength with the following significant differences. First, the absorption cross section of the Si nanocrystals is larger than that of the Er^{3+} ions by more than 3 orders of magnitude. Second, as excitation occurs via Auger-
25 type interaction between carriers in the Si nanocrystals and Er^{3+} ions, incident photons need not be in resonance with one of the narrow absorption bands of Er^{3+}. However, existing approaches to developing such Si nanocrystals have only been successful at producing concentrations of up to 0.3 atomic
30 percent of the rare earth element, which is not sufficient for practical applications. A schematic of the energy mechanisms of erbium doped silicon-rich silicone oxide is shown in Figure 13.

In general, manufacture of type IV semiconductor nanocrystals doped with a rare earth element is done by ion implantation of silicon ions into a silicon oxide layer, followed by high temperature annealing to grow the silicon nanocrystals and to reduce the ion implantation damage. The implantation of Si ions is followed by an ion implantation of the rare earth ions into the annealed silicon nanocrystal oxide layer. The resulting layer is again annealed to reduce the ion implant damage and to optically activate the rare-earth ion.

There are several problems with this method: i) it results in a decreased layer surface uniformity due to the ion implantation; ii) it requires an expensive ion implantation step; iii) it fails to achieve a uniform distribution of group IV semiconductor nanocrystals and rare-earth ions unless many implantation steps are carried out; and iv) it requires a balance between reducing the ion implant damage by thermal annealing while trying to maximise the optically active rare-earth.

To diminish the above drawbacks, Plasma Enhanced Chemical Vapor Deposition (PECVD) has been utilised to make type IV semiconductor nanocrystal layers. The prepared layers are then subjected to a rare-earth ion implantation step and a subsequent annealing cycle to form the IV semiconductor nanocrystals, and to optically activate the rare-earth ions that are doped in the nanocrystal region. Unfortunately, the layers prepared with this method are still subjected to an implantation step, which results in a decrease in surface uniformity.

Another PECVD method that has been used to obtain a doped type IV semiconductor crystal layer consists of co-sputtering together both the group IV semiconductor and rare-earth metal. In this method, the group IV semiconductor and a rare-earth metal are placed into a vacuum chamber and exposed

to an Argon ion beam. The argon ion beam sputters off the group IV semiconductor and the rare-earth metal, both of which are deposited onto a silicon wafer. The film formed on the silicon wafer is then annealed to grow the nanocrystals and to optically activate the rare-earth ions. As the rare earth metal is in solid form, the argon ion beam (plasma) is only able to slowly erode the rare earth, which leads to a low concentration of rare earth metal in the deposited film. While higher plasma intensity could be used to more quickly erode the rare earth metal and increase the rare earth concentration in the film, a higher intensity plasma damages the film or the group IV semiconductor before it is deposited. The plasma intensity is therefore kept low to preserve the integrity of the film, therefore limiting the rare earth concentration in the film. The doped group IV semiconductor nanocrystal layers made through this method have the drawbacks that: i) the layer does not have a very uniform distribution of nanocrystals and rare-earth ions, ii) the layer suffers from upconversion efficiency losses due to rare-earth clustering in the film, and iii) the concentration of rare earth metal in the layer is limited by the plasma intensity, which is kept low to avoid damaging the layer.

The concentration of the rare earth element in semiconductor nanocrystal layers is preferably as high as possible, as the level of photoelectronic qualities of the film, such as photoluminescence, is proportional to the concentration. One problem encountered when a high concentration of rare earth element is present within the semiconductor layer is that when two rare earth metals come into close proximity with one another, a quenching relaxation interaction occurs that reduces the level of photoelectronic dopant response observed. The concentration of rare earth element within a semiconductor film is thus balanced to be as

high as possible to offer the most fluorescence, but low enough to limit the quenching interactions.

In the past history of the semiconductor development silicon has been considered unsuitable for the optoelectronic applications. This is from the indirect nature of its energy band gap, bulk silicon is indeed a highly inefficient light emitter. There have been different approaches developed to overcome this problem, quantum confinement in silicon nanostructures and rare earth doping of crystalline silicon have received a great deal of attention. Of particular interest is silicon nanoclusters (NC) embedded in SiO_2 in recent years attracted interest of the scientific community as a promising new material for the construction of visible Si-based Light Emitting Diodes (LED).

The telecommunications industry commonly uses optical fibers to transmit large amounts of data in a short time. One common light source for optical-fiber communications systems is a laser formed using erbium-doped glass. One such system uses erbium-doped glass fibers to form a laser that emits at a wavelength of about 1.536 micrometer and is pumped by an infrared source operating at a wavelength of about 0.98 micrometer. One method usable for forming wave guides in a substrate is described in U.S. Pat. No. 5,080,503 issued Jan. 14, 1992 to Najafi et al., which is hereby incorporated by reference. A phosphate glass useful in lasers is described in U.S. Pat. No. 5,334,559 issued Aug. 2, 1994 to Joseph S. Hayden, which is also hereby incorporated by reference. An integrated optic laser is described in U.S. Pat. No. 5,491,708 issued Feb. 13, 1996 to Malone et al., which is also hereby incorporated by reference.

There is a need in the art for an integrated optical system, including one or more high-powered lasers along with routing and other components that can be inexpensively mass-

produced. The system should be highly reproducible, accurate, and stable.

In the area of opto-electronic packages, it is generally accepted that the most time consuming and costly component of the package is the alignment of the optical fiber, or wave guide, to the semiconductor emitter or receiver. The traditional approach to this alignment requires that the two parts be micromanipulated relative to each other while one is operating and the other is monitoring coupled light. Once the desired amount of coupled light is attained, the two parts must be affixed in place in such a way as to maintain this alignment for the life of the product. This process, commonly referred to as active alignment, can be slow and given to poor yields stemming from the micromanipulation and the need to permanently affix the two objects without causing any relative movement of the two with respect to each other.

To alleviate this problem, opto-electronic package designs have been suggested which incorporate passive alignment techniques. These designs do not require activation of the opto-electronic device. Generally, they rely on some mechanical features on the laser and the fiber as well as some intermediate piece for alignment. By putting the pieces together with some adhesion mechanism, alignment can be secured and maintained for the life of the component. Typical of this technology is the silicon optical bench design. In this design, the laser is aligned via solder or registration marks to an intermediate piece, a silicon part, which has mechanical features--"v-grooves" --which facilitate alignment of an optical fiber. The drawbacks to this design are the number of alignments in the assembly process and the cost of the intermediate component. Additionally, these designs can be difficult to use with surface emitting/receiving devices

because of the need to redirect the light coupled through the system.

Other approaches have been suggested which do not incorporate a silicon intermediate structure. Swirhun et al.
5 (U.S. Pat. No. 5,631,988) suggests that defined features in a surface emitting laser array could be used as an alignment means for a structure that holds embedded optical fibers. This third structure adds complexity and adds to the overall tolerance scheme for the alignment system.

10 In other prior art, attempts have been made to cope with the dilemma of adding intermediate parts and their associated costs and tolerances. Matsuda (U.S. Pat. No. 5,434,939) suggests a design that allows direct fiber coupling to a laser by way of a guiding hole feature in the backside of
15 the actual laser substrate. The precision with which such guiding holes can be manufactured is not currently adequate for reliable coupling. Additionally, the process of making a hole in the actual laser substrate can weaken an already fragile material. Furthermore, this design is not appropriate when it
20 is desired to have light emit from the top surface of the opto-electronic device, commonly called a top emitter in the vernacular of the industry. In contrast, a bottom emitter is a photonic device wherein the emitted light propagates through the substrate and out the bottom surface of the device.

25 What is needed is a photonic device that allows direct passive alignment and attachment of an optical signal carrying apparatus, such as an optical fiber for example, via robust guide features formed integrally on the surface of the photonic device. This photonic device would enable precise
30 positioning of the fiber relative to the active region with the potential for sub-micron alignment accuracy without the addition of interfacial alignment components. Furthermore, it

would be advantageous if the fabrication method for the above is compatible with standard semiconductor processing equipment.

Optical combiner devices are generally known. Such devices may be used to receive multiple pump signals via 5 respective input ports and to combine the pump signals into an pump source. The input signals may have different operational wavelengths. The combined signal may be used to energize an optical amplifier, for example.

It has been suggested to locate fiber gratings 10 upstream from the input ports of the combiner device to control and/or stabilize the wavelengths of the respective optical sources. One problem with this approach, however, is that it can be difficult to match the wavelength characteristics of the fiber gratings to the acceptance bandpass characteristics of 15 the input ports. The spectral misalignment can be caused by normal manufacturing variations, by temperature variations, and by other factors. Any misalignment between the spectral characteristics of the gratings and the input ports of the combiner device can result in a loss of optical efficiency. 20 This also has the caveat that the pump sources are coherent i.e. lasers.

In general, a fiber type light amplifier including an optical fiber having a core doped with a rare earth element such as erbium (Er) or the like is used as a light amplifier 25 used in an optical communication system.

In a typical arrangement of a fiber type light amplifier, a signal light with a wave-length of 1.53 μm passing through an optical fiber is input to a wave synthesizer. The wave synthesizer synthesizes a pumping light with a wavelength 30 of 1.48 μm supplied from a pumping light output unit and the signal light and supplies the same to an Er-doped optical fiber. The Er-doped optical fiber absorbs the pumping light

and amplifies the signal light. A wave separator separates the amplified signal light from the pumping light which has not been absorbed by the Er-doped light fiber and outputs only the signal light to an optical fiber.

5 Nevertheless, this fiber type light amplifier has a drawback in that the attachment of the wave synthesizer and wave separator to the Er-doped optical fiber and the adjustment thereof is time consuming. Further, the miniaturization of the amplifier as a whole is difficult because a lower limit exists 10 in the winding radius of the long Er-doped optical fiber and an extra length is needed to the portion of the Er doped optical fiber to be connected to the wave synthesizer and wave separator.

To overcome the above drawback, there is recently 15 proposed a planar type optical amplifier including an amplifying core, a core having a function as a wave synthesizer, and a core having a function as a wave separator formed thereto, these cores being made by etching a glass film obtained by doping with a type IV semiconductor nanocrystal 20 with a rare earth element such as erbium (Er) or the like on a silicon substrate or quartz glass substrate.

SUMMARY OF THE INVENTION

According to one broad aspect, the invention provides a doped semiconductor powder comprising nanocrystals of a group 25 IV semiconductor and a rare earth element, the rare earth element being dispersed on the surface of the group IV semiconductor nanocrystals.

According to another broad aspect, the invention provides a photonic device comprising at least one integral 30 formed from a REDGIVN (rare earth doped group iv nanocrystal) material.

According to another broad aspect, the invention provides a photonic device comprising: an amplification medium comprising REDGINV; a plurality of light sources; a combiner adapted to combine light from the plurality of light sources to produce a broadband optical pump source which pumps light into the amplification medium.

According to another broad aspect, the invention provides a method of manufacturing a planar type optical amplifier comprising: forming a bar-shaped core on a plane substrate; forming a groove to the core which extends to the longitudinal direction thereof; filling the groove with a filler containing REDGIVN; and solidifying the filler.

According to another broad aspect, the invention provides a method of preparing a photonic device with an integral guide formed from a type IV semiconductor nanocrystal doped with rare earth ion material.

According to another broad aspect, the invention provides a method of preparing a REDGIVN wave guide on a photonic device comprising the steps of applying a resist, transferring an image to the resist, and developing the image.

According to another broad aspect, the invention provides a method of preparing a plated REDGIVN guide on a photonic device comprising the steps of applying a resist, transferring an image to the resist, developing the image, plating the resist, and removing the resist.

According to another broad aspect, the invention provides a photonic device comprising an LED comprising REDGIVN (rare earth doped group IV nanocrystal) material.

According to another broad aspect, the invention provides a photonic device comprising an optical laser comprising REDGIVN material.

According to another broad aspect, the invention provides a photonic device comprising a laser component comprising: a thin film containing REDGIVN and having a plurality of wave guides defined by channels within the substrate; one or more feedback elements for providing optical feedback to the wave guides to form a respective laser-resonator cavity in each wave guide with a distinct resonance characteristic to provide lasing action at a selected wavelength when pumped, wherein injection of pump light at one or more suitable wavelengths into the laser-resonator cavity causes output of laser light at the selected wavelength in accordance with a longitudinal cavity mode of the cavity.

The above and other objects, features and advantages of the present invention will become apparent from the following description when taken in conjunction with the accompanying figures which illustrate preferred embodiments of the present invention by way of example.

BRIEF DESCRIPTION OF THE FIGURES

Embodiments of the invention will be discussed with reference to the following Figures:

Figure 1 is a diagram of a semiconductor structure comprising a substrate, a doped semiconductor nanocrystal layer, and a current injection layer;

Figure 2 is a diagram of a superlattice semiconductor structure comprising a substrate and alternating doped semiconductor nanocrystal layers and dielectric layers;

Figure 3 is a diagram of a Pulse Laser Deposition apparatus;

Figure 4 displays a schematic of a gas pyrolysis apparatus suitable for the production of a group IV semiconductor powder doped with a rare earth element;

Figure 5 is a schematic diagram of a first LED which uses Group IV semiconductor nanocrystals doped with rare-earth ions, provided by an embodiment of the invention;

Figure 6 is a schematic diagram of another LED
5 provided by an embodiment of the invention, adapted to produce white light;

Figure 7 is a schematic of an array of LEDs provided by an embodiment of the invention;

Figure 8 is a schematic diagram of a Fabry-Perot
10 Cavity laser provided by an embodiment of the invention;

Figure 9 is a schematic diagram of a distributed feedback laser provided by an embodiment of the invention;

Figure 10 is a schematic diagram of an array of DFB lasers provided by an embodiment of the invention;

15 Figure 11 is a schematic diagram of an array of v-grooved lasers;

Figure 12 is a schematic diagram of an electrically pumped SRSO laser provide by another embodiment of the invention;

20 Figure 13 is a schematic of energy mechanisms of erbium doped SRSO;

Figure 14 is a perspective view of an example planar optical circuit provided by an embodiment of the invention;

Figure 15 is a side view of a broadband optical pump
25 provided by an embodiment of the invention;

Figure 16 is a cross section of the broadband optical pump of Figure 15; and

Figure 17 is a side view of a planar optical amplifier provided by an embodiment of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Doped Semiconductor Nanocrystal Layer

5 The doped semiconductor nanocrystal layer of the invention comprises a group IV oxide layer in which is distributed semiconductor nanocrystals. The group IV element used to prepare the layer is preferably selected from silicon, germanium, tin and lead, and the group IV semiconductor oxide 10 layer is more preferably silicon dioxide. The group IV oxide layer preferably has a thickness of from 1 to 2000 nm, for example of from 80 to 2000 nm, from 100 to 250 nm, from 30 to 50 nm, or from 1 to 10 nm.

The semiconductor nanocrystals that are dispersed 15 within the group IV semiconductor oxide layer are preferably the nanocrystal of a group IV semiconductor, e.g. Si or Ge, of a group II-VI semiconductor, e.g. ZnO, ZnS, ZnSe, CaS, CaTe or CaSe, or of a group III-V semiconductor, e.g. GaN, GaP or GaAs. The nanocrystals are preferably from 1 to 10 nm in size, more 20 preferably from 1 to 3 nm in size, and most preferably from 1 to 2 nm in size. Preferably, the nanocrystals are present within the group IV semiconductor oxide layer in a concentration of from 30 to 50 atomic percent, more preferably in a concentration of 37 to 47 atomic percent, and most 25 preferably in a concentration of from 40 to 45 atomic percent.

The one or more rare earth element that is dispersed on the surface of the semiconductor nanocrystal can be selected to be a lanthanide element, such as cerium, praseodymium, neodymium, promethium, gadolinium, erbium, thulium, ytterbium, 30 samarium, dysprosium, terbium, europium, holmium, or lutetium, or it can be selected to be an actinide element, such as thorium. Preferably, the rare earth element is selected from

erbium, thulium, and europium. The rare earth element can, for example, take the form of an oxide or of a halogenide. Of the halogenides, rare earth fluorides are preferred as they display more intense fluorescence due to field distortions in the rare earth-fluoride matrix caused by the high electronegativity of fluorine atoms. Most preferably, the rare earth element is selected from erbium oxide, erbium fluoride, thulium oxide, thulium fluoride, europium oxide and europium fluoride.

The one or more rare earth element is preferably present in the group IV semiconductor oxide layer in a concentration of 0.5 to 15 atomic percent, more preferably in a concentration of 5 to 15 atomic percent and most preferably in a concentration of 10 to 15 atomic percent. While such a high concentration of rare earth element has led to important levels of quenching reactions in previous doped semiconductor materials, the doped semiconductor nanocrystal layer of the present invention can accommodate this high concentration as the rare earth element is dispersed on the surface of the semiconductor nanocrystal, which nanocrystal offers a large surface area. The reduced amount of quenching reactions between the rare earth element and the proximity of the rare earth element to the semiconductor nanocrystal provide the basis for a doped semiconductor nanocrystal layer that offers improved optoelectronic properties.

Semiconductor Layer Structure

Using the doped semiconductor nanocrystal layer described above, a multitude of semiconductor structures can be prepared. For example, a semiconductor structure is shown in Figure 1, in which one or more layers 33 of the doped semiconductor nanocrystal layer are deposited on a substrate 31.

The substrate on which the semiconductor nanocrystal layer is formed is selected so that it is capable of withstanding temperatures of up to 1000°C. Examples of suitable substrates include silicon wafers or poly silicon layers, either of which can be n-doped or p-doped (for example with $1x10^{20}$ to $5x10^{21}$ of dopants per cm^3), fused silica, zinc oxide layers, quartz and sapphire substrates. Some of the above substrates can optionally have a thermally grown oxide layer, which oxide layer can be of up to about 2000nm in thickness, a thickness of 1 to 20 nm being preferred. The thickness of the substrate is not critical, as long as thermal and mechanical stability is retained.

The semiconductor structure can comprise a single or multiple doped semiconductor nanocrystal layers, each layer having an independently selected composition and thickness. By using layers having different rare earth elements, a multi-color emitting structure can be prepared. For example, combining erbium, thulium and europium in a single semiconductor structure provides a structure that can fluoresce at the colors green (erbium), blue (thulium), and red (europium).

When two or more doped semiconductor nanocrystal layers are used in a single semiconductor structure, the layers can optionally be separated by a dielectric layer. Examples of suitable dielectric layers include silicon dioxide, silicon nitrite and silicon oxy nitrite. The silicon dioxide dielectric layer can also optionally comprise semiconductor nanocrystals. The dielectric layer preferably has a thickness of from 1 to 10 nm, more preferably of 1 to 3 nm and most preferably of about 1.5 nm. The dielectric layer provides an efficient tunnelling barrier, which is important for obtaining high luminosity from the semiconductor structure.

The semiconductor structure can also have an Indium Tin Oxide (ITO) current injection layer (34) overtop the one or more doped semiconductor nanocrystal layers. The ITO layer preferably has a thickness of from 150 to 300 nm. Preferably, 5 the chemical composition and the thickness of the ITO layer is such that the semiconductor structure has a conductance of from 30 to 70 ohms cm.

The thickness of the semiconductor structure is preferably 2000 nm or less, and the thickness will depend on 10 the thickness of the substrate, the number and thickness of the doped semiconductor nanocrystal layers present, the number and the thickness of the optional dielectric layers, and the thickness of the optional ITO layer.

One type of preferred semiconductor structure 15 provided by an embodiment of the present invention is a superlattice structure, shown by way of example in Figure 2, which structure comprises multiple layers of hetero-material 60 on a substrate 51. Multiple doped semiconductor nanocrystals layers having a thickness of from 1 nm to 10 nm are deposited 20 on the substrate 52 and 54, and the doped semiconductor nanocrystals layers can comprise the same or different rare earth elements. Optionally, the doped semiconductor nanocrystal layers are separated by dielectric layers 53 of about 1.5 nm in thickness, and an ITO current injection layer 25 (not shown) can be deposited on top of the multiple layers of the superlattice structure. There is no maximum thickness for the superlattice structure, although a thickness of from 250 to 2000 nm is preferred and a thickness of from 250 to 750 nm is more preferred.

30 *Preparation of the Doped Semiconductor Nanocrystal Layer*

The preparation of the doped semiconductor nanocrystal layer comprises the following two general steps:

(a) the simultaneous deposition of a semiconductor rich group IV oxide layer and of one or more rare earth element; and

(b) the annealing of the semiconductor rich group IV oxide layer prepared in (a) to form semiconductor nanocrystals.

The semiconductor rich group IV oxide layer comprises a group IV oxide layer, which group IV oxide is preferably selected from SiO_2 or GeO_2, in which group IV oxide layer is dispersed a rare earth element and a semiconductor, which semiconductor can be the same as, or different than, the semiconductor that forms the group IV oxide layer.

By "semiconductor rich", it is meant that an excess of semiconductor is present, which excess will coalesce to form nanocrystals when the semiconductor rich group IV oxide layer is annealed. Since the rare earth element is dispersed within the oxide layer when the nanocrystals are formed, the rare earth element becomes dispersed on the surface of the semiconductor nanocrystals upon nanocrystal formation.

Since the semiconductor rich group IV oxide layer and the one or more rare earth element are deposited simultaneously, ion implantation of the rare earth element is avoided. As such, the group IV oxide layer surface is free of the damage associated with an implantation process. Also, since the rare earth element is deposited at the same time as the semiconductor rich group IV oxide layer, the distribution of the rare earth element is substantially constant through the thickness of the group IV oxide layer.

The deposition of the semiconductor rich group IV oxide layer doped with one or more rare earth elements is preferably carried out by Plasma-Enhanced Chemical Vapor Deposition (PECVD) or by Pulse Laser Deposition (PLD). The above two methods each have their respective advantages for

preparing the semiconductor rich group IV oxide layer doped with one or more rare earth elements, and the methods are described below.

5

Pulse Laser Deposition

Pulse laser deposition is advantageous for the deposition of the semiconductor rich group IV oxide layer doped with one or more rare earth elements as it permits the
10 deposition of a wide variety of semiconductors and a wide variety of rare earth elements.

Referring now to Figure 3, which shows by way of a diagram a typical set up of a pulse laser deposition apparatus, the pulse laser deposition apparatus consists of a large
15 chamber 41, which can be evacuated down to at least 10^{-7} bars or pressurized with up to 1 atmosphere of a gas such as oxygen, nitrogen, helium, argon, hydrogen or combinations thereof. The chamber has at least one optical port 42 in which a pulse laser beam 45 can be injected to the chamber and focused down onto a
20 suitable target 44. The target is usually placed on a carrousel 43 that allows the placement of different target samples into the path of the pulse laser focus beam. The carrousel is controlled so that multiple layers of material can be deposited by the pulse laser ablation of the target. The flux of the
25 focused pulse laser beam is adjusted so that the target ablates approximately 0.1 nm of thickness of material on a substrate 47, which can be held perpendicular to the target and at a distance of 20 to 75 millimetres above the target. This flux for instance is in the range of 0.1 to 20 joules per square cm
30 for 248 nm KrF excimer laser and has a pulse width of 20 - 45 nanosecond duration. The target can be placed on a scanning platform so that each laser pulse hits a new area on the

target, thus giving a fresh surface for the ablation process. This helps prevent the generation of large particles, which could be ejected in the ablation plume 46 and deposited on to the substrate. The substrate is usually held on a substrate holder 48, which can be heated from room temperature up to 1000°C and rotated from 0.1 to 30 RPM depending on the pulse rate of the pulse laser, which in most cases is pulsed between 1-10 Hz. This rotation of the substrate provides a method of generating a uniform film during the deposition process. The laser is pulsed until the desired film thickness is met, which can either be monitored in real time with an optical thickness monitor or quartz crystal microbalance or determined from a calibration run in which the thickness is measured from a given flux and number of pulses. Pulse laser deposition can be used for depositing layers of from 1 to 2000nm in thickness.

For the preparation of a semiconductor rich group IV oxide layer doped with one or more rare earth elements, the target that is ablated is composed of mixture of a powdered group IV binding agent, a powdered semiconductor that will form the nanocrystal, and a powdered rare earth element. The ratio of the various components found in the doped semiconductor nanocrystal layer is decided at this stage by controlling the ratio of the components that form the target. Preferably, the mixture is placed in a hydraulic press and pressed into a disk of 25mm diameter and 5mm thickness with a press pressure of at least 500 Psi while being heated to 700°C. The temperature and pressure can be applied, for example, for one hour under reduced pressure (e.g. 10^{-3} bars) for about one hour. The press pressure is then reduced and the resulting target is allowed to cool to room temperature.

The group IV binding agent can be selected to be a group IV oxide (e.g. silicon oxide, germanium oxide, tin oxide or lead oxide), or alternatively, it can be selected to be a

group IV element (e.g. silicon, germanium, tin or lead). When the group IV binding agent is a group IV oxide, the binding agent, the semiconductor and the rare earth element are combined to form the target, and the pulse laser deposition is carried out in the presence of any one of the gases listed above. If a group IV element is used as the group IV binding agent instead, the pulse laser deposition is carried out under an oxygen atmosphere, preferably at a pressure of from $1x10^{-4}$ to $5x10^{-3}$ bar, to transform some or all of the group IV element into a group IV oxide during the laser deposition process. When the semiconductor element which is to form the nanocrystals is selected to be a group II-VI semiconductor (e.g. ZnO, ZnS, ZnSe, CaS, CaTe or CaSe) or a group III-V semiconductor (e.g. GaN, GaP or GaAs), the oxygen concentration is kept high to insure that all of the group IV element is fully oxidized. Alternatively, if the nanocrystals to be formed comprise the same group IV semiconductor element that is being used as the binding agent, the oxygen pressure is selected so that only part of the group IV element is oxidized. The remaining non-oxidized group IV element can then coalesce to form nanocrystals when the prepared semiconductor rich group IV oxide layer is annealed.

The powdered rare earth element that is used to form the target is preferably in the form of a rare earth oxide or of a rare earth halogenide. As mentioned above, the rare earth fluoride is the most preferred of the rare earth halogenides.

Pulse laser deposition is useful for the subsequent deposition of two or more different layers. Multiple targets can be placed on the carrousel and the pulse laser can be focussed on different targets during the deposition. Using this technique, layers comprising different rare earth elements can be deposited one on top of the other to prepare semiconductor structures as described earlier. Different

targets can also be used to deposit a dielectric layer between the semiconductor rich group IV oxide layers, or to deposit a current injection layer on top of the deposited layers. Pulse laser deposition is the preferred method for preparing the
5 superlattice semiconductor structure described above.

Preparation of the semiconductor rich group IV oxide layer doped with one or more rare earth elements can of course be carried out with different pulse laser deposition systems that are known in the art, the above apparatus and process
10 descriptions being provided by way of example.

Plasma Enhanced Chemical Vapor Deposition

PECVD is advantageous for the deposition of the semiconductor rich group IV oxide layer doped with one or more rare earth element, as it permits the rapid deposition of the
15 layer. The thickness of the semiconductor rich group IV oxide layer doped with one or more rare earth element prepared with PECVD is 10 nm or greater, more preferably from 10 to 2000 nm.

Formation of a non-doped type IV semiconductor nanocrystal layer through chemical vapor deposition has been
20 described, for example, by J. Sin, M. Kim, S. Seo, and C. Lee [*Applied Physics Letters*, (1998), Volume 72, 9, 1092-1094], the disclosure of which is hereby incorporated by reference.

In this embodiment, the doped semiconductor nanocrystal layer is prepared by incorporating a rare-earth
25 precursor into the PECVD stream above the receiving heated substrate on which the semiconductor film is grown. PECVD can be used to prepare the doped semiconductor nanocrystal layer where the semiconductor nanocrystal is a silicon or a germanium nanocrystal, and where the rare earth element is a rare earth
30 oxide.

In the PECVD process, a group IV element precursor is mixed with oxygen to obtain a gaseous mixture where there is an atomic excess of the group IV element. An atomic excess is achieved when the ratio of oxygen to group IV element is such 5 that when a group IV dioxide compound is formed, there remains an excess amount of the group IV element. The gaseous mixture is introduced within the plasma stream of the PEVCD instrument, and the silicon and the oxygen are deposited on a substrate as a group IV dioxide layer in which a group IV atomic excess is 10 found. It is this excess amount of the group IV element that coalesces during the annealing step to form the group IV nanocrystal. For example, to prepare a silicon dioxide layer in which silicon nanocrystals is dispersed, a silicon rich silicon oxide (SRSO) layer is deposited on the substrate.

15 The group IV element precursor can contain, for example, silicon, germanium, tin or lead, of which silicon and germanium are preferred. The precursor itself is preferably a hydride of the above elements. A particularly preferred group IV element precursor is silane (SiH_4).

20 The ratio (Q) of group IV element precursor to oxygen can be selected to be from 3:1 to 1:2. If an excess of group IV element precursor hydride is used, the deposited layer can contain hydrogen, for example up to approximately 10 atomic percent hydrogen. The ratio of the flow rates of the group IV 25 element precursor and of oxygen can be kept, for example, between 2:1 and 1:2.

Also introduced to the plasma stream is a rare earth element precursor, which precursor is also in the gaseous phase. The rare earth precursor is added to the plasma stream 30 at the same time as the group IV element precursor, such that the rare earth element and the group IV element are deposited onto the substrate simultaneously. Introduction of the rare earth precursor as a gaseous mixture provides better dispersion

of the rare earth element within the group IV layer. Preferably, presence of oxygen in the plasma stream and in the deposited layer leads to the deposition of the rare earth element in the form of a rare earth oxide.

5 The rare earth element precursor comprises one or more ligands. The ligand can be neutral, monovalent, divalent or trivalent. Preferably, the ligand is selected so that when it is coordinated with the rare earth element, it provides a compound that is volatile, i.e. that enters the gaseous phase 10 at a fairly low temperature, and without changing the chemical nature of the compound. The ligand also preferably comprises organic components that, upon exposure to the plasma in the PECVD apparatus, will form gaseous by-products that can be removed through gas flow or by reducing the pressure within the 15 PECVD apparatus. When the organic components of the ligand are conducive to producing volatile by-products (e.g. CO_2, O_2) less organic molecules are incorporated into the deposited layer. Introduction of organic molecules into the deposited layer is generally not beneficial, and the presence of organic molecules 20 is sometimes referred to as semiconductor poisoning.

Suitable ligands for the rare earth element can include acetate functions, for example 2,2,6,6-tetramethyl-3,5-heptanedione, acetylacetonate, flurolacetonate, 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione, i-25 propylcyclopentadienyl, cyclopentadienyl, and n-butylcyclopentadienyl. Preferred rare earth metal precursor include tris(2,2,6,6-tetramethyl-3,5-heptanedionato) erbium(III), erbium (III) acetylacetonate hydrate, erbium (III) flurolacetonate, tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-30 3,5-octanedionate)erbium (III), tris(i-propylcyclopentadienyl)erbium (III), Tris(cyclopentadienyl)erbium (III), and tris(n-butylcyclopentadienyl)erbium (III). A particularly preferred

rare earth element precursor is tris(2,2,6,6-tetramethyl-3,5-heptanedionato) erbium(III) ($Er^{+3}[(CH_3)_3CCOCH=COC(CH_3)_3]_3$), which is also referred to as $Er^{+3}(THMD)_3$.

If the rare earth element precursor is not in the
5 gaseous phase at room temperature, it must be transferred to the gaseous phase, for example, by heating in an oven kept between 80°C and 110°C. The gaseous rare earth element precursor is then transferred to the plasma stream with an inert carrier gas, such as argon. The gaseous rare earth
10 element precursor is preferably introduced to the plasma at a position that is below a position where the group IV element containing compound is introduced to the plasma. Use can be made of a dispersion mechanism, for example a dispersion ring, to assist in the dispersion of the gaseous rare earth element
15 precursor in the plasma.

In order to obtain a more even deposition of the doped type IV oxide layer, the substrate can be placed on a sceptre that rotates during deposition. A circular rotation of about 3rpm is suitable for increasing the uniformity of the
20 layer being deposited.

An Electron Cyclotron Resonated (ECR) reactor is suitable for producing the plasma used in the PECVD method described above. ECR is a particular method of generating plasma, where the electrons have a spiral motion caused by a
25 magnetic field, which allows a high density of ions in a low-pressure region. The high ion density with low pressure is beneficial for deposition, as the rare earth metal precursor can be stripped of its organic components and incorporated uniformly and in a high concentration. The plasma used in the
30 PECVD method can comprise, for example, argon, helium, neon or xenon, of which argon is preferred.

The PECVD method is carried out under a reduced pressure, for example $1x10^{-7}$ torr, and the deposition temperature, microwave power and scepter bias can be kept constant. Suitable temperature, microwave and scepter bias values can be selected to be, for example, 300°C, 400W and $-200V_{DC}$, respectively.

The semiconductor rich group IV oxide layer doped with one or more rare earth element can be grown at different rates, depending on the parameters used. A suitable growth rate can be selected to be about 60 nm per minute, and the semiconductor rich group IV oxide layer can have a thickness of from 10 to 2000 nm, more preferably of from 100 to 250 nm.

Preparation of the semiconductor rich group IV oxide layer doped with one or more rare earth elements can of course be carried out with different plasma enhanced chemical vapor deposition systems that are known in the art, the above apparatus and process descriptions being provided by way of example.

Annealing Step

After the semiconductor rich group IV oxide layer doped with one or more rare earth element has been prepared, the doped type IV oxide layer is annealed, optionally under flowing nitrogen (N_2), in a Rapid Thermal Anneal (RTA) furnace, at from about 600°C to about 1000°C, more preferably from 800°C to 950°C, from 5 minutes to 30 minutes, more preferably from 5 to 6 minutes. It is during the annealing step that the atomic excess of semiconductor is converted into semiconductor nanocrystals.

When PECVD is used to prepare the semiconductor rich group IV oxide layer doped with one or more rare earth element, the annealing step can also be carried out under an oxygen

atmosphere to insure oxidation of the rare earth element, or under a reduced pressure in order to facilitate the removal of any volatile by-products that might be produced.

The amount of excess semiconductor in the group IV oxide layer and the anneal temperature dictate the size and the density of the semiconductor nanocrystal present in the final doped semiconductor nanocrystal layer.

Since the rare earth element is well dispersed through the deposited group IV semiconductor oxide layer, when the nanocrystals are formed during the annealing step, the rare earth element becomes localised on the surface of the nanocrystals. Since the nanocrystals provide a large surface area on which the rare earth element can be dispersed, the concentration of the rare earth element can be quite elevated, while retaining good photoelectronic properties.

Doped Semiconductor Powder

The present invention also teaches the simple manufacturing of a doped semiconductor powder, which semiconductor powder comprises nanocrystals of a group IV semiconductor and a rare earth element.

The doped semiconductor powder comprises as a major component nanocrystals of a group IV semiconductor. The group IV semiconductor can be selected, e.g., from silicon, germanium, tin or lead, of which silicon and germanium are preferred. Combinations of these semiconductors can also be used, as well as multi-element semiconductors that comprise the above semiconductors. Preferably, the nanocrystals have an average diameter of from 0.5 to 10 nm, for example of about 3 nm.

The rare earth element that is dispersed on the surface of the semiconductor nanocrystals is preferably

selected from cerium, praseodymium, neodymium, promethium, gadolinium, erbium, thulium, ytterbium, samarium, dysprosium, terbium, europium, holmium, lutetium, and thorium, of which erbium, thulium and europium are most preferred. The rare earth element is preferably in the form of a complex comprising a rare earth and one or more ligands. The nature of the one or more ligands is dictated by the process used to prepare the doped semiconductor powder. The doped semiconductor powders of the invention can also comprise more than a single rare earth element.

Since the rare earth element is dispersed on the surface of the group IV semiconductor nanocrystal, reduced photoactivity due to aggregation of the rare earth element is reduced. The concentration of the rare earth element in the doped semiconductor powder is preferably from 0.5 to 10 atomic percent, more preferably from 0.5 to 5 atomic percent, and most preferably from 0.5 to 2 atomic percent. The atomic percent values are calculated on the basis of the number of rare earth atoms relative the total number of atoms in the doped semiconductor powder.

Gas Pyrolysis

A gas pyrolysis process can be utilised to prepare the doped semiconductor powder of the invention. In this process, a group IV semiconductor precursor and a rare earth element complex are mixed in the gaseous phase, and the mixture is first heated, and then cooled to obtain the desired product. The gas pyrolysis reaction consists of the thermal treatment of a gaseous group IV element, in the presence of a gaseous rare earth element, to such a temperature that the gaseous group IV element forms a nanocrystal. When the formed nanocrystal is cooled down in the presence of a rare earth element, the rare earth element goes form the gaseous state to the solid state and it deposits itself on the surface of the nanocrystal.

Gas pyrolysis can be carried out, for example, in a gas pyrolysis apparatus, a schematic of which is provided in figure 4. In the apparatus shown in figure 1, a carrier gas, a gaseous group IV semiconductor precursor and a gaseous rare 5 earth element complex are introduced via entry ports 10, 12 and 14. The carrier gas is preferably an inert gas, such as argon.

As the group IV semiconductor is in the gaseous phase during reaction, a group IV semiconductor precursor is used. The group IV semiconductor precursor is chosen so that the 10 precursor is volatile at room temperature, or so that it can be volatilized at a fairly low temperature, e.g., from 80 to 120°C. Preferably, the group IV semiconductor precursor is selected so that the by-products obtained after nanocrystal formation are themselves volatile compounds that will be 15 removed with the gas flow. The group IV semiconductor is preferably selected from silicon, germanium, tin or lead, of which silicon and germanium are preferred. The precursor is preferably a hydride of the above elements. A particularly preferred group IV semiconductor precursor is silane (SiH_4).

20 Similarly, as the rare earth element is in the gaseous phase during reaction, a rare earth element complex that is volatile or that can be volatilized is used. The rare earth element complex comprises one or more ligands, which ligands can be neutral, monovalent, divalent or trivalent. 25 Preferably, the ligand is selected so that when it is coordinated with the rare earth element, it provides a compound that is volatile, i.e. that enters the gaseous phase at a fairly low temperature, and without changing the chemical nature of the compound. Suitable ligands for the rare earth 30 element complex include acetate functions, for example 2,2,6,6-tetramethyl-3,5-heptanedione, acetylacetonate, flurolacetonate, 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione, i-propylcyclopentadienyl, cyclopentadienyl, and n-

butylcyclopentadienyl. Preferred rare earth element complex include tris(2,2,6,6-tetramethyl-3,5-heptanedionato) erbium(III), erbium (III) acetylacetonate hydrate, erbium (III) flurolacetonate, tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-
5 3,5-octanedionate)erbium (III), tris(i-propylcyclopentadienyl)erbium (III), Tris(cyclopentadienyl)erbium (III), and tris(n-butylcyclopentadienyl)erbium (III). A particularly preferred rare earth element complex is tris(2,2,6,6-tetramethyl-3,5-
10 heptanedionato) erbium(III), which is also referred to as $Er^{+3}(THMD)_3$.

When the rare earth element complex or the group IV semiconductor precursor are not volatile at room temperature, use can be made of a temperature-controlled oven 16 to bring
15 the precursor or complex into the gaseous phase. The temperature controlled oven, which can be kept. E.g., between 110°C and 120°C, controls the concentration of rare earth metal that is present in the gaseous phase. The temperature control oven can be fitted with a carrier gas inlet 26 to transfer the
20 gaseous rare earth element complex to the furnace through the mass-flow controllers 18.

The ratio of the carrier gas, the group IV semiconductor precursor and the rare earth element complex is controlled by mass-flow controllers 18, which control the
25 introduction of each gaseous component in the apparatus. The flow of the combined three mass-flow controllers is controlled to obtain a flow through the furnace that is preferably between 20 and 30 standard cubic centimetres per minute. The flow through the apparatus can be assisted with a mechanical vacuum
30 pump 24 at the end of the gas pyrolysis apparatus.

Once introduced in the apparatus, the gaseous components flow into a short, temperature controlled furnace 20 (also referred to as a flow-through furnace). The flow-through

furnace 20 is preferably a small tubular furnace having a length between 3cm and 9cm, the furnace being temperature controlled to be at a temperature where the gaseous group IV semiconductor precursor reacts to form nanocrystals. Temperatures of from 600°C to 1000°C have been found to be suitable for carrying out this reaction, although specific temperatures, which may be within or outside of this range, can be determined by non-inventive experimentation. Heating of the furnace can be carried out by any suitable method, such as electric heating or microwave heating. The tubular furnace can have an inside diameter that ranges, for example, from 6 to 20mm, with an inside diameter of 12 mm being preferred. Selection of the length of the furnace, its inside diameter and the furnace temperature can be used to control the size of the nanocrystals obtained, as these parameters control the thermodynamics of the system. The parameters can be monitored so as to permit computer control of the gas pyrolysis process.

As the group IV semiconductor precursor and the rare earth element complex are heated in the furnace, the group IV semiconductor precursor forms semiconductor nanocrystals, and the rare earth element complex deposits on the surface of the nanocrystals when the gaseous stream is cooled. The deposited rare earth element complex is preferably not part of the nanocrystal lattice but is deposited principally on the surface of the nanocrystals. The organic components are preferably transformed into gaseous by-products that are removed along with the carrier gas.

The gaseous stream containing the doped semiconductor nanocrystals can be allowed to cool within a cooling zone (not shown). The cooling zone can be from 10 cm to a few meters, and active cooling methods, such as mechanical refrigeration, an acetone/dry ice environment or a liquid nitrogen environment can be utilised.

The prepared doped semiconductor nanocrystals are then recovered from the carrier gas, for example by passing the carrier gas through one or more bubblers 22 that contain a solvent, such as ethylene glycol, in which the doped semiconductor nanocrystals display some solubility. The solvent can then removed from the bubblers and is vacuum dried to recover the doped type IV semiconductor nanocrystals.

Solution saturation

A second method for preparing the doped semiconductor powder of the invention uses solution oversaturation of the rare earth element to deposit the rare earth element onto the nanocrystal surface. In this method, a solution comprising an undoped group IV semiconductor nanocrystal powder, a rare earth element complex and a solvent which is a good solvent for the rare earth element complex and a poor solvent for the undoped group IV semiconductor nanocrystal powder is heated to dissolve the rare earth element complex. Upon cooling of the solution, the solution becomes oversaturated with the rare earth element complex and the complex precipitates from solution to be deposited on the surface of the group IV semiconductor nanocrystals.

By "good solvent" is meant a solvent in which the rare earth complex is poorly soluble at low temperature, e.g. room temperature, but in which the rare earth complex is well dissolved at higher temperature. By "poor" solvent is meant a solvent in which the undoped group IV semiconductor nanocrystal powder displays little or no solubility, at both low and high temperatures. Examples of suitable solvent include ethanol, ethylene glycol, toluene, and benzene.

The first step of this process requires the preparation of an undoped group IV semiconductor nanocrystal

powder, which preparation can be effected, for example, by (A) solution chemistry or (B) gas pyrolysis.

(A) Solution chemistry:

In the solution chemistry process, two complementary semiconductor complexes are combined to form the semiconductor nanocrystal and a salt, which nanocrystal and salt are subsequently separated. The undoped semiconductor nanocrystals are prepared by mixing a group IV semiconductor salt, such as a magnesium, sodium or iodine salt of silicon or germanium, with a halogenated group IV semiconductor compound such as silicon or germanium tetrachloride. The mixture is solubilised in a suitable solvent, for example ethylene glycol or hexane, and the mixture is refluxed. Filtration or centrifugation can be used to remove any insoluble salts formed, and the semiconductor nanocrystals are formed upon cooling of the solution.

The process for preparing the undoped semiconductor nanocrystal is preferably carried out in an inert atmosphere, and the reaction vessel used must be inert to the presence of silicon, such as a Teflon vessel, or a silonated glass vessel.

(B) Gas pyrolysis

The gas pyrolysis process used to prepare the undoped group IV semiconductor nanocrystal powder is similar to the gas pyrolysis process described above for preparing *doped* semiconductor powders, but where the gaseous rare earth element complex is omitted.

Preparation of the doped type IV semiconductor nanocrystals is achieved by mixing undoped nanocrystals and a rare earth complex in a solvent which is a good solvent for the rare complex and a poor solvent for the type IV semiconductor nanocrystals, for example ethanol. Suitable rare earth

complexes include, for example, erbium acetate hydrate and erbium (III) acetylacetonate hydrate. The heterogeneous mixture can be refluxed, for example, for about 90 to about 180 minutes, after which time the solution is cooled to obtain the doped nanocrystals. As the solution cools, the rare earth element complex precipitates out of solution and it deposits on the surface of the nanocrystals in the solution. The rare earth element that is deposited on the surface of the nanocrystal is in the form of a rare earth element complex.

Materials comprising doped semiconductor powders

An important advantage of the doped semiconductor powder over the doped layers traditionally prepared is that the doped semiconductor powder above can be incorporated into a variety of different hosts, and that these hosts can represent a liquid or a solid phase. The host or matrix is preferably chosen so that it does not interfere with the photoluminescence of the doped nanocrystals.

Examples of a suitable host or support matrix for the doped semiconductor powders of the invention include, for example, polymers, silica sol-gels, and spin-on-glass (SOG). Spin-on-glass can be comprised, for example, of a mixture of silicates that are dissolved in alcohol. Examples of suitable polymers include, for example, poly(2-methoxy-5-(2 -ethyl-hexyloxy)-1,4-phenylene-vinylene) (PPV), polymethylmethacrylate (PMMA), and polyphenylene ether (PTE). When the host or support matrix is in a liquid or semi-liquid state, the doped semiconductor powder can be formed into specific shapes or patterns. These specific shapes can include layers that are prepared by spin-coating a liquid solution comprising the doped semiconductor powder. Patterns can also be prepared by combining a liquid polymer comprising the doped semiconductor powder with printing technology such as ink jet technology.

Another advantage of the doped semiconductor powder over the doped layers rests in the fact that they can be used to prepare thicker layers. It also allows the combination of different nanocrystal types to form hybrid systems, such as
5 Si_{nc}+PbS or Si_{nc}+CdS.

The materials comprising doped semiconductor powders of the invention also have the advantage that the components of the materials, such as the host or support matrix, and any additional components such as a base substrate, are not
10 required to be resistant to high temperatures. In traditional doped layer processes, the nanocrystals are formed by the high temperature annealing of amorphous silicon clusters, which requires that the other components present during annealing, such as the substrates, be temperature resistant. Components
15 that are not temperature resistant can be used with the doped semiconductor powders of the invention, as the nanocrystals are formed prior to being incorporated in the materials.

However, when the components used to prepare the materials comprising semiconductor nanocrystal powders are
20 temperature resistant, the materials can be subsequently annealed. This can prove beneficial for the preparation, for example, of semiconductor layers comprising semiconductor nanocrystals and a rare earth element. For example, a doped semiconductor powder of the invention can be incorporated into
25 a silica sol-gel, which silica sol-gel is then formed into a layer. Annealing the sol-gel/nanocrystal powder mixture leads to the removal of the organic components of the mixture, leaving a silicon oxide layer in which the doped semiconductor nanocrystal powder is dispersed. Annealing can be carried out,
30 for example, in a Rapid Thermal Anneal (RTA) furnace at from about 600°C to about 1000°C. The annealing process can be carried out under an oxygen atmosphere to insure the removal of the organic components, and to promote the oxidation of the

rare earth element. The annealing step can also be carried out under a reduced pressure in order to facilitate the removal of any volatile organic by-products that might be produced.

Examples of devices that can be prepared with the materials comprising doped semiconductor powders include, for example, optical amplifiers, lasers, optical displays, optical planar circuits, and organic light emitting diodes (OLED).

The following examples are offered by way of illustration and not by way of limitation.

EXAMPLES

Example 1

Silane (SiH_4) and Oxygen (O_2) are added to an argon plasma stream produced by an Electron Cyclotron Resonated (ECR) reactor via dispersion ring. The ratio (Q) of silane to oxygen has been varied between 3:1,1.7:1,1.2:1,1:1.9, and 1:2. An erbium precursor (Tris(2,2,6,6-tetramethyl-3,5-heptanedionato) erbium(III) [$Er^{+3}(THMD)_3$]) is placed in a stainless steel oven held between 90 and 110 °C.

A carrier gas of Ar is used to transport the Er precursor from the oven through a precision controlled mass-flow controller to a dispersion ring below the Silane injector and above the heated substrate. The instrument pressure is kept at about $1x10^{-7}$ torr. The substrates used are either fuse silica or silicon wafers on which is thermally grown an oxide layer of 2000nm thickness. The deposition temperature, the microwave power and the sceptre bias are kept constant at 300°C, 400W and $-200V_{DC}$. The SiH_4, Ar flow rates were adjusted while keeping the O_2 flow rate at 20 militorr sec^{-1} for the various excess silicon content. The Er/Ar flow rate was adjusted to

the vapor pressure generated by the temperature controlled oven for the desired erbium concentration. The film is grown at a rate of 60 nm per minute and thickness has been grown from 250 nm to 2000nm thick. The scepter was rotated at 3rpm during the
5 growth to help in uniformity of film. After deposition, the samples are annealed at 950°C -1000°C for 5-6 minutes under flowing nitrogen (N_2) in a Rapid Thermal Anneal (RTA) furnace.

Example 2

An ablation target is fabricated by combining
10 powdered silicon, powdered silicon dioxide and powdered erbium oxide, the prepared powder mixture comprising 45% silicon, 35% silicon oxide and 20% erbium oxide. Each powder component has a size of about 300 mesh. The mixture is placed into a ball mill and ground for approximately 5 to 10 minutes. The mixture
15 is then placed into a 25 mm diameter by 7mm thick mould, placed into a hydraulic press, and compressed for 15 minutes at 500psi. The obtained target is then placed into an annealing furnace and heated to 1200°C in a forming gas atmosphere of 5% H_2 and 95% N_2 for 30 minutes. The Target is cooled down to room
20 temperature and then reground in a ball mill for ten minutes. The mixture is then again placed in a mould, compressed and annealed as described above. The obtained target is placed onto a target holder inside a vacuum chamber. A silicon substrate [n-type, <110> single crystal, 0.1-0.05 Ωcm
25 conductivity] of 50 mm diameter and 0.4 cm thickness is placed on a substrate holder parallel to and at a distance of 5.0 cm above the surface of the target. The substrate is placed onto a substrate support that is heated at 500°C, and the substrate is rotated at a rate of 3 rpm during the deposition. The
30 vacuum chamber is evacuated to a base pressure of $1x10^{-7}$ torr and then back filled with $20x10^{-3}$ torr of Ar. An excimer laser (KrF 248 nm) is focused on to the target at an energy density of about $10Jcm^{-2}$ and at a glancing angle of 40° to the vertical

axis, such that a 0.1 nm film is generated per pulse. The target is rotated at 5 rpm during deposition in order to have a fresh target surface for each ablation pulse. After a 100 nm layer is deposited on the substrate, the newly deposited film
5 is annealed at temperature of from 900°C to 950°C for 5 minutes to form silicon nanocrystals in the Silicon Rich Silicon Oxide (SRSO).

The substrate is reintroduced in the vacuum chamber, and the target is replaced with an Indium Tin Oxide (ITO)
10 target. The atmosphere inside the vacuum chamber is set to $2x10^{-3}$torr of O_2, and the substrate is heated to 500°C and rotated at 3 rpm. A 100 nm ITO layer is deposited on top of the annealed rare earth doped SRSO film.

Example 3

15

A gas pyrolysis apparatus was fitted with a small tubular furnace having a length of 3 cm and an interior diameter of 12 mm. While the furnace temperature was held between 900 and 950°C, an argon carrier gas, silane (SiH_4), and
20 $Er^{+3}(THMD)_3$ were introduced to the furnace by way of precision mass-flow controllers. The $Er^{+3}(THMD)_3$ was transferred to the gaseous phase through the use of a temperature controlled oven. The flow through the apparatus was assisted by a mechanical vacuum pump at the end of the apparatus. Once through the
25 furnace, the gaseous stream was allowed to pass through a cooling zone and then to pass through a two-stage bubbler of ethylene glycol. The ethylene glycol solution was removed from the bubbler and it was vacuum dried to recover Er doped Si nanocrystals having an average diameter of about 3 nm.

30 Example 4

A doped semiconductor powder was prepared through a saturated solution process. The process was carried out in an

inert atmosphere glove box, and the glassware used was first silonated by washing for one hour in a 2% toluene solution of $(CH_3)_2SiCl_2$, followed by repeated washes with hexane and methanol.

5 400mg of magnesium silicide (MgSi) was added to 100ml of dried ethylene glycol, stirred and refluxed for 12 hours in a glove box. 3ml of $SiCl_4$ was added, and the mixture was again refluxed for another 12 hours. After this time, the mixture was filtered, cooled and dried under vacuum. 100ml of ethanol 10 was added to the dried Si nanocrystals, and 230 mg of dehydratated erbium acetate was added to the solution while stirring, followed by a 3 hour reflux. Upon cooling, the Er doped Si nanocrystals were obtained.

Further embodiments of the invention provide a number 15 of photonic devices which make use of the above described materials. In what follows, rare earth doped Group IV semiconductor nanocrystal material, hereinafter REDGIVN material, will refer to any of the above discussed materials.

Light Emitting Diode

20 Figure 5 shows an example structure of an LED that is formed by a Metal Oxide Semiconductor (MOS) structure provided by an embodiment of the invention. This structure uses a p silicon substrate 100 which might for example have a resistivity of 0.001. Any other suitable bottom layer could 25 alternatively be used, for example Zinc Oxide, or Diamond. Preferably the substrate is conductive. On top of the substrate 100 there is a REDGIVN layer 102, for example in the form of an Er:SRSO film. On top of the REDGIVN layer 102 is a conductive, transparent layer 108. This might for example be 30 polysilicon, but other materials may alternatively be used. A bottom first contact 106 is shown below the substrate 100, and a second top contact 104 is shown on top of the conductive

transparent layer 108. Also shown is an opening 107 in the top contact layer 104 to allow light to escape.

In operation, the REDGIVN layer 102 is activated by applying a voltage across the two contacts 104,106. The substrate 10 and the transparent conductive layer 108 serve to spread the field created between the two contacts such that substantially all of the REDGIVN layer 102 is activated. The electric field excites the nanocrystals in the REDGIVN layer 102 which in turn excite the rare earth dopants, which then emit at the characteristic wavelengths of the rare earth element.

There are several ways of making the device of Figure 5. The incorporated applications in particular teach a number of ways of forming the REDGIVN layer 102. In an example process of making the device of Figure 5 that assumes that silicon nanocrystals are employed in the REDGIVN layer 102, the p silicon substrate 100 is cleaned and etched to remove any oxide on the silicon substrate. This cleaned and etched substrate is placed into an ECR PECVD reactor and then exposed to argon plasma for 3 min after pump down to do a final clean off the silicon substrate. During the plasma clean the substrate is brought up to 300°C. silicon substrate, which might for example be n-type with a conductivity of 0.05-0.001 cm, is kept at this temperature during the Silicon Rich Silicon Oxides (SRSO) film growth. A rare-earth precursor is also turned on during the SRSO growth to dope the silicon nanocrystals. The doped SRSO film is grown, preferably from 10 nm to 1000 nm and more preferably from 100 nm - 250 nm in thickness. The refractive index of this film can be measured with a ellispometer during the deposition and the silane flow adjusted to have the index of refraction be 1.85 to 1.9. This allows the SRSO film to have a Si content on the order of 42-45 at%. This is to insure high conductivity of the SRSO film and small Si

nanocrystals on the order of 1 nm diameter. Other values can be employed. The rare earth precursor and oxygen are turned off and a doped p^+ poly-silicon layer 108 of 10nm-50nm thickness and a conductivity of 0.001 for example is grown on top of the SRSO film. An element may be introduced into semiconductor to establish either p- type (acceptors) or n- type (donors) conductivity; common dopants in silicon: p-type, boron, B; n-type phosphorous, P, arsenic, As, antimony, Sb. This is to make sure of a good transparent current sheet for a top electrode. The grown structure is then placed in a RTA furnace and annealed at 950°C for 5 minutes to form the nanocrystals and optically activate the rare earth ions into it's 3+ or 2+ valance states. The result is an erbium doped SRSO film 102. After the anneal step a top contact Aluminum film 104 for example of 250nm - 1000nm thick is deposited on top of the doped p^+ poly-silicon-Er:SRSO film 102. More generally any of the conductive metals can be employed. Aluminum has a good work function energy level so that an ohmic conductor can be made with the boron doped p^+ poly-silicon layer. Gold would work but may need to have a chrome layer applied first or else it will peel and flake off the surface. The bottom contact 106 is also deposited on to the silicon substrate of a thickness of 500nm-2500nm thickness. An anneal of 450°C for 5 minutes is performed to form a ohmic contact on the back side of the n^+ silicon substrate. In one embodiment, the small aperture 107 is etched through the top Aluminum contact 104 to allow emitted light 109 out. In another embodiment, a serpent top front contact can be employed to allow light exit. More generally, in so far as the making of the REDGIVN material, any of the previously disclosed methods may be employed.

An appropriate selection of the rare earth ion can be used to tailor the colour of the emitted light 109 from the prepared LED. For a blue light emitting diode, the rare earth metal precursor can be selected from Tetrakis(2,2,6,6-

tetramethyl-3,5-heptanedionato)cerium(IV) and $Ce(TMHD)_4$. For a green light emitting diode, the rare earth metal precursor can be selected to be Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)erbium (III) $Er^{+3}(THMD)_3$. For a red light
5 emitting diode, the rare earth metal precursor can be selected from Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium (III) and $Eu(TMHD)_3$. This selection of rare earth metal ion precursors is not meant to be limiting.

In another embodiment, in order to extract light also
10 from the bottom of the LED, the layer below the REDGIVN layer 102 is also transparent (but still conductive), and an appropriately shaped bottom contact is employed.

Figure 6 is an example of a white light LED structure based on the structure of Figure 5 but with the REDGIVN layer
15 102 replaced with a REDGIVN layer 110 doped with three different rare earth ions, one for each of blue, red and green light to generate three different types of light which collectively produce a white light emission 111. The layer 110 can be formed by simultaneously doping using different rare
20 earth ions. In a preferred embodiment, a separate layer is used for each dopant. In some embodiments a buffer layer, for example of p^+ poly silicon, is provided between each rare earth layer. In one example, the active region consists of a layer of REDGIVN doped with a first rare earth ion, a buffer layer of
25 p^+ polysilicon, a second layer of REDGIVN doped with a second rare earth ion, a buffer layer of p polysilicon, and a third layer of REDGIVN doped with a third rare earth ion, with the three layers containing respective dopants to produce red, green and blue. More generally any combination of dopants may
30 be employed.

Referring now to Figure 7, shown is an array of LEDs provided by an embodiment of the invention. In the illustrated

example, there are twelve LEDs 112,…,123 each based on the above described embodiment. LEDs 112,115,118,121 are blue LEDs; LEDs 113,116,119,122 are green LEDs, and LEDs 114,117,120,123 are red LEDs, the colour of each LED being
5 determined by the appropriate selection of the rare earth dopant. The LEDs are also shown in four groups 124,125,126,127 of three LEDs, each group containing a respective LED of each of the three primary colours. Each such set of three LEDs can be used to form a white light LED. In one embodiment, each of
10 the colours making up the group of three is individually actuatable so as to produce a desired colour. In another embodiment, all three LEDs in a group turn on together to produce white light at a point a distance from the device where substantial combination of light has taken place. The
15 arrangement of Figure 7 can be made using a single layered process by applying the three rare earth dopants in three separate stages while masking the remaining areas. While specific examples of different colours are shown in Figure 7, it is to be understood that an arbitrary array of LEDs is
20 contemplated.

Optical Laser

Another embodiment of the invention provides a planar optical laser that is manufactured by using IV semiconductor nanocrystals that are doped with rare-earth ions such as
25 Scandium, Yttrium and the Lanthanides. The purpose of this technology is to allow one to develop an inexpensive method of manufacturing planar optical lasers for use in the telecommunication industry but is not limited to just that field. This technology is also applicable in advanced high
30 speed back-planes and other high speed hybrid optoelectronic circuits.

Preferably the planar optical laser is fabricated on a flat substrate such as fuse silica and or silicon and other

such suitable substrate material. The substrate could also be of a flexible nature assuming that the nanocrystal layer did not crack or peel due to the flexible nature of the substrate. By using silicon wafers as the substrate one then gains access
5 to well-established process and fabricating manufacturing facilities throughout the world. Also by developing the flexible substrate technology one would be able to exploit roll-web processes, which would allow one to print the Planar Optical Circuits, as one would do for newspaper, magazines and
10 other such printing technologies.

One embodiment provides optical structures and methods for producing tunable wave guide lasers. In one embodiment, a wave guide is defined within a glass substrate doped with a rare-earth element or elements by PECVD. Feedback
15 elements such as mirrors or reflection gratings in the wave guide further define a laser-resonator cavity so that laser light is output from the wave guide when pumped optically or otherwise. The wavelengths reflected by the reflection gratings can be varied and the effective length of the
20 resonator cavity can be varied to thereby tune the laser to a selected wavelength. For example, having a Bragg reflector as one of the feedback mirrors would allow the cavity to have a preferential high Q for the resonate of the Bragg reflector which then would re-enforce the laser frequency. The Bragg
25 grating could be made to have a varying frequency response by having the grating tuned, for example by thermal or mechanical stressor a combination of these.

Another embodiment provides apparatus and methods for integrating rare-earth doped lasers and optics on glass
30 substrates. The invention includes a laser component formed from a glass substrate with REDGIVN regions defining a plurality of wave guides defined by channels within the substrate. The laser component may constitute a monolithic

array of individual wave guides in which the wave guides of the array form laser resonator cavities with differing resonance characteristics. The channels defining the wave guides may for example be created by exposing a surface of the substrate to 5 which a photo resist is spin on and a mask having a plurality of line apertures corresponding to the channels, which are to be formed. Other processes may be employed.

Another embodiment provides a laser component that includes a thin film doped with one or more optically active 10 rare earth (preferably lanthanide) species and type IV nanocrystals and having a plurality of wave guides defined by channels within the film. As used herein, a "channel within the film" is meant to broadly include any channel formed on or in the substrate, whether or not covered by another structure 15 or layer of substrate. Each substrate wave guide (or "channel") is defined within the substrate as a region of increased index of refraction relative to the substrate. The semiconductor nanocrystal glass film is doped with one or more optically active rare earth species which can be optically 20 pumped (typically a rare-earth element such as Er, Yb, Nd, or Pr and or other lanthanide elements or a combination of such elements such as Er and Yb) to form a laser medium which is capable of lasing at a plurality of frequencies. Again, any of the layered structures of the incorporated embodiments may be 25 used to form a suitable laser medium. Mirrors or distributed Bragg reflection gratings may be located along the length of a wave guide for providing feedback to create a laser-resonator cavity. One or more of the mirrors or reflection gratings is preferably made partially reflective for providing laser 30 output.

An example of a wave guide laser based Fabry-Perot Cavity laser is shown in Figure 8. This example shows a substrate 130 which may for example be silica, but could be any

other appropriate substrate material. On top of this is a cladding layer 132, a core wave guiding layer 134, and a top cladding layer 136. The wave guiding layer 134 also contains REDGIVN. Also shown is an HR (high reflectivity) mirror 138
5 and an OC (output coupler) mirror 140. The arrangement of Figure 8, when pumped, spontaneously emits a light which resonates and eventually exits as output light source 142 through the OC mirror 140 which is partially reflective to allow some light to escape. The laser of Figure 8 is
10 preferably optically pumped.

In the arrangement of Figure 8, the feedback components employed are in the form of the pair of mirrors 138,140. This produces a Fabry-Perot Cavity. The laser component may constitute a monolithic array of individual wave
15 guides in which the wave guides of the array form laser resonator cavities with differing resonance characteristics (e.g., resonating at differing wavelengths). The component may thus be used as part of a laser system outputting laser light at a plurality of selected wavelengths.

20 The frequency response of the arrangement of Figure 8 is generally indicated at 143 where it has been assumed that Erbium was used as the rare earth dopant. The size of the cavity (distance between HR mirror 138 and OC mirror 140) is tuned to resonate near the active frequencies for Er. This
25 results in the lasing to occur at the active frequencies for Er which include a dominant frequency and several other nearby frequencies which are emitted with less power as shown. In general, the cavity size is preferably substantially matched to the peak in the fluorescence response for the particular rare
30 earth dopant to achieve peak efficiency.

In certain embodiments of the invention, the resonance characteristics of a wave guide cavity are varied by

adjusting the width of the channel formed in the film, which thereby changes the effective refractive index of the wave guide. The effective refractive index can also be changed by modifying the diffusion conditions under which the wave guides are formed as described below. A diffraction Bragg reflector (DBR) grating formed into or close to the wave guide is used, in some embodiments, to tune the wavelength of light supported in the wave guide cavity. Changing the effective refractive index thus changes the effective wavelength of light in the wave guide cavity, which determines the wavelengths of the longitudinal modes supported by the cavity. In another embodiment, the resonance characteristics of the wave guide cavities are individually selected by varying the pitch of the DBR reflection gratings used to define the cavities that, along with the effective refractive index for the propagated optical mode, determines the wavelengths of light reflected by the gratings. In still other embodiments, the location of the gratings on the wave guide is varied in order to select a laser-resonator cavity length that supports the desired wavelength of light.

In one embodiment, a surface-relief grating forming a distributed Bragg reflection grating is fabricated on the surface of the wave guide, for example by coating the surface with photo resist, defining the grating pattern in the photo resist holographically or through a phase mask, developing the photo resist pattern, and etching the grating pattern into the wave guide with a reactive ion system such as an argon ion mill. In certain embodiments, a more durable etch mask allowing more precise etching and higher bias voltages is obtained by depositing chromium on the developed photo resist pattern using an evaporation method which causes the chromium to deposit on the tops of the grating lines. This forms a much more durable mask for the reactive ion system allowing a deeper etch which would be required for a thicker active volume.

An example of a distributed feedback laser based on the above embodiment is shown in Figure 9. This embodiment shows a substrate 152, bottom cladding 160, core 162 and top cladding 164. The reflecting components consist of an HR
5 mirror 150 and an OC mirror 154. In this embodiment, the core is in the form of a distributed Bragg reflection grating which might for example have been formed as described above. The shape used to show the core is illustrative of the Bragg grating characteristic that concerns an oscillating index of
10 refraction, and is not necessarily indicative of the physical shape of the core. The core also contains rare-earth doped nanocrystals. The OC mirror 154 in this example is slightly less reflective than the HR mirror resulting in light 166 exiting the arrangement and forming the output of the laser.
15 In this embodiment, the cavity again defines the wavelength of the laser and this needs to be substantially set near the active wavelengths of the rare earth dopants. Preferably, the grating 162 is also tuned to one of these wavelengths. This causes the arrangement to lase substantially at the single
20 frequency for which the arrangement is tuned. Thus, the frequency response of this arrangement, shown generally at 155 has a single peak.

A first example of an array of lasers will now be described with reference to Figure 10. In this example, there
25 are four lasers generally indicated by 210,212,214,216. Each laser 210,212,214,216 has a respective first Bragg grating 170,172,174,176 (although other reflective elements may alternatively be employed) a respective core area 178,180,182,184 forming a laser cavity and a respective second
30 Bragg grating 188,190,192,194 (although other output reflective elements can be employed. In the illustrated example, one set of gratings 170,172,174,176 is almost completely reflective for example having 99% reflectivity. The other set of gratings 1788,180,182,184 is slightly less reflective to allow some

light through as an output signal. In the illustrated example, the second set has 96% reflectivity.

The lasers have outputs 200,202,204,206 which generate wavelengths λn, $\lambda 3$, $\lambda 2$, $\lambda 1$ respectively. It is of
5 course to be understood that any number of lasers can be included in an array such as the array of Figure 10. Four are shown simply by way of example. Here, the characteristics of each laser in the array are tuned to generate the respective wavelength. This can be done by adjusting the first and second
10 Bragg gratings of a given laser and/or by adjusting the length of the cavity. As in previous embodiments, the core region of each laser is constructed using SRSO doped with rare-earth ions. The array of lasers of Figure 10 can be formed in a single layered structure with the four lasers being side by
15 side in a respective channel within the substrate for example. The frequency response of the arrangement of Figure 10 is generally indicated at 201, and shows a respective frequency for each laser. In this case, by tuning the Bragg gratings a narrow frequency response can be generated for each laser
20 output.

An individual laser can also be formed using the embodiment of Figure 10. Furthermore, in another embodiment, the arrangement of Figure 10 is provided, but oriented orthogonally to the arrangement shown. This consists of a
25 substrate, a first layer containing a Bragg grating, a second layer containing the core/cavity, and a third layer containing a second partially reflective Bragg grating. This arrangement produces a laser that emits light out the top of the device.

Figure 11 is another example of an array of lasers
30 provided by an embodiment of the invention. Again, the array is shown to include four separate lasers 350,352,354,356, but any appropriate number of lasers could alternatively be provided. In this embodiment, each laser has an HR mirror

300,302,304,306, and an active SRSO segment 310,312,314,316. The active SRSO segment of each laser is followed by an output coupler 360,362,364,368. The arrangement thus far is substantially similar to the arrangement of Figure 10, which was a perspective view whereas the view of Figure 11 is a top view. The output couplers 360,362,364,368 couple the output of the active SRSO segments 310,312,314,316 into a v groove section 320,322,324,326 that in turn is coupled to output fibers 330,332,334,336 connected to output couplers 340,342,344,346.

In a variant of the above described embodiment, the output fibers can be attached to a single a ferrule having a plurality of spaced-apart attachment sites.

The embodiments above have assumed optical pumping. More generally several examples of methods of pumping REDGIVN are provided in the further photonic devices described below with respect to Figures 13-17. Those applications involve pumping for the purpose of amplification. However, the same principles are applicable here for pumping in the context of lasers. Optical pumping and electrical pumping are disclosed and contemplated for these laser applications.

When electrical pumping is used instead of optical pumping the substrate is conductive, for example an n^+ silicon substrate, to which a transparent conductive cladding buffer such as zinc oxide (ZnO) film, for example of from 2000 to 6000 nm, is applied. A REDGIVN film, for example having a thickness of from 100 to 500nm, is deposited on transparent conductive layer and annealed. A top electrical contact, for example 500-1000nm of Indium Tin Oxide (ITO), is deposited on top of the REDGIVN film. Alternatively, a p^+ poly-silicon layer can also be used as well as a cadmium oxide CdO film and other metal oxides. One would make the choice based on whether the REDGIVN film is a positive (hole) donor or negative (electron) donor.

This is then masked and etched to form a active wave guide in which HR mirror and output coupler placed at each end of the wave guide to form the resonating cavity.

Figure 12 shows an example featuring electrical pumping. Shown is an n+ silicon substrate 400 having a bottom electrical contact 402. Shown is a ZnO film 406 on top of the n+ silicon substrate 400. On top of the ZnO film there is a layer of rare-earth doped SRSO film 408 to which is applied a top contact layer 404 which might for example be Indium Tin Oxide as in the above example. As in some previous embodiments, shown is an HR mirror 410 and an output coupler 412 through which an output light signal 414 passes. More generally, the electrical pumping can be used for any of the embodiments described herein with appropriate modifications.

Planar Optical Circuits using IV semiconductor nanocrystals doped with rare-earth ions.

Another embodiment of the present invention relates to the use of type IV semiconductor nanocrystals doped with rare earth ions, i.e. any of the above summarized REDGIVN materials, especially a silicon rich silicone oxide (SRSO), in the manufacturing of guide structures on photonic semiconductor wafers.

This embodiment provides a planar optical circuit that is manufactured by using IV semiconductor nanocrystals that are doped with rare-earth ions, and more generally any material generated/described in the above referenced incorporated applications, i.e. REDGIVN.

This technology provides an inexpensive method of producing planar optical circuits that could be used in the telecommunications field but not limited to just that field. This technology could also be used in advanced high speed back-planes and other high speed hybrid optoelectronic circuits.

The planar optical circuits are fabricated on flat substrates such as fused silica and or silicon and other such suitable substrate materials. The substrate could also be of a flexible nature assuming that the nanocrystal layer did not crack or peel due to the flexible nature of the substrate. By using silicon wafers as the substrate one then gains access to well-established process and fabrication manufacturing facilities throughout the world. Also by developing the flexible substrate technology exploit roll-web processes, which can be exploited allow one to print the planar optical circuits, as one would do for newspaper, magazines and other such printing technologies.

In a preferred embodiment, the use of the above described nanocrystals is employed in conjunction with a more conventional broadband light source to pump the Si nanocrystals rather than an expensive laser to pump one of the narrow absorption bands of the Er^{3+} ions. In a preferred embodiment, inexpensive long life visible wavelength LEDs are used which might have a broadband emission wavelength of about 20 nm for example compared to typical narrow band optical sources having emissions focussed within about 2 nm. This reduces the cost of the planar circuit greatly and also allows for a much easier assembly of the circuit. In a preferred embodiment, the planar circuit is pumped transversely from a top surface rather than trying to couple the pump light coaxial as is done with the pump laser EDFA and EDWA. The sensitizer Si nanocrystals also provide the refractive index contrast necessary for the wave guiding. One observes gain in the 1.54 μm wavelength that is coupled into the wave guide when the wave guide is pumped from the top, and demonstrates that such a wave guide satisfies all of the three aforementioned conditions necessary for a practical device.

An example is shown in Figure 14. Shown is a substrate 510, for example a fused silica substrate on top of which is located a REDGIVN layer, for example erbium doped SRSO. Depending on the substrate, a separate bottom cladding layer (not shown) may also be required. Also shown is an etched rib channel structure 514, for example formed using SOG (spin on glass). Pump light 516 is shown, for example originating from an LED (not shown). This pump light is shown pumping the planar circuit transversely from the top surface. Also shown is an input optical signal beam 518.

The etched ribbed channel 514 results in some lateral confinement of the optical modes in a particular region of the REDGIVN layer 512 below the channel. Other features may alternatively be employed for achieving this lateral confinement, referred to herein as optical confinement features. More generally, all that is required is that confinement to a channel of interest is achieved.

The example of Figure 14 shows a very specific structure being implemented by the planar structure which includes a pump light source to thereby form an optical amplifier, namely a rib channel wave guide structure. It is to be understood that more generally any suitable structure can be formed in the planar arrangement. Other structures may alternatively be employed within the overall planar arrangement to result in confinement which achieves other functions such as Mach Zehnder interferometers and optical splitters to name a few examples, by appropriate definition of the lateral confinement features.

In the example of Figure 14, the pump light is transversely pumped into the core. This has the advantage over co-axial pumping that light can more or less be uniformly applied throughout the length of the amplification medium. A co-axial pump source may alternatively be employed, but

efficiency will be compromised due to losses along the amplification medium. The transverse pumping is an option in these embodiments because of the capacity to use a broadband pump, at lower pump power, all because of the increased
5 activity of the REDGIVN material compared to conventional amplification mediums.

Preferably, the pump light is a broadband optical pump source, for example in the form of a broadband LED. In other words, in contrast to conventional EDFAs for example
10 which require a very precise frequency pump source to activate the Erbium, with the use of the REDGIVN, the nanocrystals have a sensitivity to a much broader range of frequencies and as such a broad band pump source can be used. A single or multiple LEDs can be used as a pump source. Other pump sources
15 are also contemplated. For example, silicon nanocrystals respond to 500 nm to 320 nm.

Various coupling mechanisms can be used in conjunction with the embodiment of Figure 14. For example, one or both ends may be substantially flat so as to allow abutment
20 up against another optical component to achieve efficient coupling of light to the input of the amplifier and from the output of the amplifier. Alternatively, free space optics may be employed at the input and/or the output to provide the necessary coupling of light. In the context of measuring
25 signal strength using a tap detector, the output of the amplifier is fed to a sensor which detects the signal strength after amplification.

More generally, another embodiment of the invention provides a photonic device with an integral guide formed of
30 REDGIVN. The arrangement of Figure 14 provides but one example.

Another embodiment provides a method of preparing a photonic device with an integral guide formed from REDGIVN. The REDGIVN material is fabricated for example using methods taught in any of the incorporated applications. The remainder of the device can be fabricated using any appropriate method, many such methods being well known.

One method of preparing a guide on a photonic device involves the steps of applying a resist, transferring an image to the resist, and developing the image. Another method of preparing a plated guide on a photonic device involves applying a resist, transferring an image to the resist, developing the image, plating the resist, and removing the resist.

Broad Band Optical Pump

Another aspect of the invention relates generally to optical devices and systems, especially to telecommunications systems, optical amplifier systems, and/or wavelength division multiplexing systems. The present invention also relates to devices for combining multiple optical pump sources into one or more combined pump sources.

This embodiment of the invention provides a broad band optical pump source that is used to excite IV semiconductor nanocrystals that are doped with rare-earth ions. The purpose of this technology is to allow one to develop an inexpensive method of pumping planar optical amplifiers that could be used in the telecommunication field but not limited to just that field. This technology could also be used in advanced high speed back-planes and other high speed hybrid optoelectronic circuits.

The broad band optical pump sources are preferably LEDs that are mounted on flat or curve substrates such as fused silica and/or silicon and other such suitable substrate materials. The substrate could also be of a flexible nature

assuming that the LEDs did not crack or peel due to the flexible nature of the substrate. The LEDs are arranged so that the maximum amount of light is directed to the REDGIVN material that is being used in the optical amplifier and or optical amplifiers. This might for example include micro-lens and or micro-reflectors to direct the LEDs light to the type IV semiconductor nanocrystals. In the preferred embodiment light is transversely pumped into the gain medium but is not strictly limited to this geometry of pumping.

Each LED can be of a single or multiple wavelengths that cover the particular absorption band of the type IV semiconductor nanocrystals. For example, he pump wavelength of choice for silicon nanocrystals in the near UV and blue region running from about 320 nm to 500 nm, although one could use other LED sources for example a source with light output at 670 nm at a reduction in pump efficiency. The pump source can be a single or multiple emitter source configured to illuminate the optical active gain media by being in close proximity to the gain media and/or by using micro-optics to gather and redirect the pump source to the gain media by refraction or reflective and/or diffractive means.

Referring now to Figure 15, shown is a side view of a broadband optical pump provided by the embodiment of the invention. In this example, shown are a set of LEDs, five in this particular case, 530,532,534,536,538, although more generally any number can be employed. Each LED has a respective coupling optics 542,544,546,548,550 for coupling the light signal generated by the respective LED to the planar structure 540 below, and in particular for focussing the light into the REDGIVN layer 554. In one embodiment, the coupling optics can be a microlens. Other coupling optics can alternatively be employed. The planar structure 540 comprises a substrate 552 on top of which is defined the REDGIVN 554

containing at least one doped nanocrystal wave guide. More generally, a wave guide doped with any of the materials of the incorporated embodiments can be employed. The LEDs may all be the same, or they may be different. Advantageously, as
5 described previously, these can be broadband LEDs. Specific single wavelength sources may also be employed, but this would increase cost significantly with no real advantage. A larger number of LEDs will increase the amount of pumping energy available. Also shown is a micro-reflector 553 which contains
10 light within the arrangement.

The arrangement of Figure 15 efficiently combines the pump light signals within the amplification medium.

A cross section of the LED pump chamber of Figure 15 is shown in Figure 16. Here, one of the LEDs 530 is shown
15 together with the coupling optics 540 in the form of a microlens, substrate 552 within which four doped Si nanocrystal wave guides are defined. More generally, at least one channel is defined, either in or on the substrate. The reflection chamber, or micro-reflector 553 is more easily seen in this
20 view. This keeps light in the arrangement. It might for example be an aluminized piece of glass, or polished metal. The arrangement can be implemented without this component, but with reduced efficiency.

The example of Figure 15 and Figure 16 assumes five
25 LEDs, and four wave guides. More generally, an arbitrary number of LEDs, and an arbitrary number of wave guides which do not necessarily need to be parallel are defined.

Referring now to Figure 17 shown is a planar optical amplifier provided by an embodiment of the invention. This
30 embodiment features a silicon substrate 560. Upon this is formed a wave guide structure comprising a bottom cladding layer 562, a core REDGIVN layer 564 for example consisting of

doped SRSO film, and a top cladding layer 566. More generally, any suitable substrate can be employed and the core contains group IV semiconductor nanocrystals that are doped with rare-earth ions. Also shown is an input fiber 570 interfacing with
5 a first end of the arrangement, and an output fiber 572 interfacing with a second end of the arrangement. More generally any optical coupling means can be employed for an input and output to the device. Also shown is a set of LEDs 568. With LEDs, the arrangement of Figure 17 is not that
10 different from the arrangement of Figure 15. However, in another embodiment, the pump source 568 is an electrical pump source. This requires that the top and bottom cladding be conductive, and the substrate if present also be conductive such that electric field can be applied across the layer 569.
15 For example, the cladding might be ZnO or AlN, and the substrate might be n+ or p+ doped silicon.

Another embodiment provides a method of efficiently combining input light signals into a combined light signal, the combined light signal then being used as an optical pump source
20 for the REDGIVN. The method operates without any fiber gratings or other spectral filtering devices between the sources and the combiner device. Instead of gratings in the input fibers, the invention provides wavelength selection by the LED broadband sources. The method operates to self-align
25 the operational wavelengths of the LED sources to the acceptance angle characteristics of the input lens, the lens functioning as a combiner. The lens may for example have a Plano-convex aspherical cylindrical design that has a small F# and short focal length to re-image the LED source and or
30 sources to a planar output plane where the amplifying medium is located.

In a preferred embodiment of the invention such as shown by way of example in Figures 15 and 16, a single or

multiple micro-reflectors are employed to efficiently combine input light signals into a combined light signal. The method operates without any fiber gratings or other spectral filtering devices between the sources and the combiner device. Instead of gratings in the input fibers, the invention provides wavelength selection by the LED broadband sources. The method operates to self-align the operational wavelengths of the LED sources to the acceptance angle characteristics of the micro-reflectors. The micro-reflector is a convex aspherical cylindrical design that has a small F# and short focal length to re-image the LED source and or sources to a planar output plane where the amplifying median is located

In a preferred embodiment of the invention, a combiner is provided in the form of a single or multiple broadband Holographic Optical Element (HOE)'s are located after (downstream from) the LED source and or sources. Thus, the combiner device is located between the pump LED and or LEDs and the optical amplifying element. The diffraction of the combiner device (through the respective input ports) determine the wavelengths of the broadband light provided by the LED and or LEDs, such that the LED wavelengths are at the minimum loss wavelengths associated with the combiner device. Thus, efficient diffraction concentration can be obtained independent of operating temperatures, age of the system, etc.

Another embodiment provides a method of manufacturing the planar type optical amplifier which comprises the steps of (1) forming a bar-shaped core on a plane substrate, (2) forming a groove to the core which extends to the longitudinal direction thereof, (3) filling the groove with a filler doped with a rare earth element, and (4) solidifying the filler.

All publications, patents and patent applications cited in this specification are herein incorporated by

reference as if each individual publication, patent or patent application were specifically and individually indicated to be incorporated by reference. The citation of any publication is for its disclosure prior to the filing date and should not be construed as an admission that the present invention is not entitled to antedate such publication by virtue of prior invention.

Although the foregoing invention has been described in some detail by way of illustration and example for purposes of clarity of understanding, it is readily apparent to those of ordinary skill in the art in light of the teachings of this invention that certain changes and modifications may be made thereto without departing from the spirit or scope of the appended claims.

It must be noted that as used in this specification and the appended claims, the singular forms "a", "an", and "the" include plural reference unless the context clearly dictates otherwise. Unless defined otherwise all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this invention belongs.

We claim:

1. A doped semiconductor powder comprising nanocrystals of a group IV semiconductor and a rare earth element, the rare earth element being dispersed on the surface of the group IV
5 semiconductor nanocrystals.

2. A doped semiconductor powder according to claim 1, wherein the rare earth element is present in a concentration of from 0.5 to 10 atomic percent.

3. A doped semiconductor powder according to claim 1,
10 wherein the rare earth element is present in a concentration of from 0.5 to 5 atomic percent.

4. A doped semiconductor powder according to claim 1, wherein the rare earth element is present in a concentration of from 0.5 to 2 atomic percent.

15 5. A doped semiconductor powder according to claim 1, wherein the nanocrystals have an average diameter of from 0.5 to 10 nm.

6. A doped semiconductor powder according to claim 1, wherein the nanocrystals have an average diameter of about 3
20 nm.

7. A doped semiconductor powder according to claim 1, wherein the group IV semiconductor is selected from Si, Ge, Sn and Pb.

8. A doped semiconductor powder according to claim 1,
25 wherein the rare earth element is selected from cerium, praseodymium, neodymium, promethium, gadolinium, erbium, thulium, ytterbium, samarium, dysprosium, terbium, europium, holmium, lutetium, and thorium.

9. A doped semiconductor powder according to claim 1, wherein the rare earth element is selected from erbium, thulium and europium.

10. A group IV semiconductor nanocrystal powder according to claim 1, wherein the rare earth element is in the form of an oxide.

11. A process for preparing a doped semiconductor powder as claimed in claim 1, the process comprising:

(a) heating a gaseous mixture comprising a gaseous group IV semiconductor precursor and a gaseous rare earth element complex at a temperature suitable for forming group IV semiconductor nanocrystals,

(b) cooling the gaseous mixture to obtain the doped semiconductor powder.

12. A process according to claim 11, wherein the temperature is from 600 to 1000°C.

13. A process according to claim 11, wherein the gaseous mixture is cooled to room temperature.

14. A process according to claim 11, wherein the gaseous group IV semiconductor precursor comprises silicon, germanium, tin or lead.

15. A process according to claim 11, wherein the gaseous group IV semiconductor precursor is a hydride of a group IV element.

16. A process according to claim 11, wherein the gaseous group IV semiconductor precursor is silane.

17. A process according to claim 11, wherein the gaseous rare earth element complex comprises a rare earth element

selected from cerium, praseodymium, neodymium, promethium, gadolinium, erbium, thulium, ytterbium, samarium, dysprosium, terbium, europium, holmium, lutetium, and thorium.

18. A process according to claim 11, wherein the gaseous
5 rare earth element complex comprises erbium, thulium or europium.

19. A process according to claim 11, wherein the gaseous rare earth element complex comprises a ligand selected from 2,2,6,6-tetramethyl-3,5-heptanedione, acetylacetonate,
10 flurolacetonate, 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione, i-propylcyclopentadienyl, cyclopentadienyl, and n-butylcyclopentadienyl.

20. A process according to claim 11, wherein the gaseous rare earth element complex is selected from tris(2,2,6,6-
15 tetramethyl-3,5-heptanedionato) erbium(III), erbium (III) acetylacetonate hydrate, erbium (III) flurolacetonate, tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate)erbium (III), tris(i-propylcyclopentadienyl)erbium (III),
20 Tris(cyclopentadienyl)erbium (III), and tris(n-butylcyclopentadienyl)erbium (III).

21. A process according to claim 11, wherein the gaseous mixture is heated in a flow-through furnace.

22. A process for preparing a doped semiconductor powder
25 as claimed in claim 1, the process comprising:

(a) mixing an undoped group IV semiconductor nanocrystal powder, a rare earth element complex and a solvent, the solvent being a good solvent for the rare earth element complex and a poor solvent for the undoped
30 group IV semiconductor nanocrystal powder, to form a heterogeneous mixture

(b) heating the heterogeneous mixture to dissolve the rare earth complex in the solvent, and

(c) cooling the heterogeneous mixture to obtain the doped semiconductor powder.

5 23. The process according to claim 22, wherein the undoped group IV semiconductor nanocrystal powder comprises silicon, germanium, tin or lead.

24. The process according to claim 22, wherein the undoped group IV semiconductor nanocrystal powder has an

10 average nanocrystal diameter of from 0.5 to 10 nm.

25. The process according to claim 22, wherein the rare earth complex comprises a rare earth element selected from the group consisting of cerium, praseodymium, neodymium, promethium, gadolinium, erbium, thulium, ytterbium, samarium,

15 dysprosium, terbium, europium, holmium, lutetium, and thorium.

26. The process according to claim 22, wherein the rare earth complex comprises erbium, europium or thulium.

27. The process according to claim 22, wherein the rare earth complex is selected from erbium acetate hydrate and

20 erbium (III) acetylacetonate hydrate.

28. The process according to claim 22, wherein the solvent is ethanol.

29. The process according to claim 22, wherein the concentration of the rare earth complex in the heterogeneous

25 solution if from 0.03 to 30 atomic percent.

30. The process according to claim 22, wherein the heterogeneous solution is heated for a duration of from 90 to 180 minutes.

31. The process according to claim 22, wherein the heterogeneous solution is cooled to room temperature.

32. A composite material comprising a support matrix and a doped semiconductor powder according to claim 1, the doped semiconductor powder being coated on or embedded in the support matrix.

33. A composite material according to claim 32, wherein the doped semiconductor powder is embedded in the support matrix.

34. A composite material according to claim 32, wherein the support matrix comprises spin-on-glass, a silica sol-gel or a polymer.

35. A composite material according to claim 32, wherein the support matrix is in the form of a layer prepared by spin-coating.

36. A composite material according to claim 32, wherein the support matrix comprises silicon dioxide obtained by annealing a silica sol-gel.

37. A composite material according to claim 32, wherein the support matrix is in the form of a printed pattern.

38. A photonic device comprising at least one integral formed from a REDGIVN (rare earth doped group iv nanocrystal) material.

39. A photonic device according to claim 38 wherein the wave guide has a planar structure.

40. A photonic device according to claim 39 comprising a substrate and/or bottom cladding, a layer containing the REDGIVN material, and a lateral containment element adapted to laterally confine light to a region within the layer containing

the REDGIVN material where the at least one wave guide is to be defined.

41. A photonic device according to claim 38 wherein the at least one wave guide is arranged to form a Mach Zehnder 5 interferometer.

42. A photonic device according to claim 38 wherein the at least one wave guide are arranged to form an optical splitter.

43. A photonic device according to claim 38 further 10 comprising:

a pump source adapted to activate the nanocrystals in the wave guide which in turn activate the rare earth element in the REDGIVN.

44. A photonic device according to claim 43 adapted to 15 perform an amplification function upon an input optical signal to produce an amplified output optical signal.

45. A photonic device according to claim 44 comprising a substrate and/or bottom cladding, a layer containing the REDGIVN material, and a lateral containment element adapted to 20 laterally confine light to a region within the layer containing the REDGIVN material where the at least one wave guide is to be defined.

46. A photonic device according to claim 44 wherein the pump source comprises an optical pump source.

25 47. A photonic device according to claim 46 wherein the optical pump source comprises a broadband optical pump source.

48. A photonic device according to claim 47 wherein the broadband optical pump source is arranged to transversely pump light into the at least one wave guide.

49. A photonic device according to claim 48 comprising a substrate and/or bottom cladding, a layer containing the REDGIVN material, and a lateral containment element adapted to laterally confine light to a region within the layer containing
5 the REDGIVN material where the at least one wave guide, wherein the lateral containment element comprises an etched ribbed channel of spin on glass.

50. A photonic device according to claim 47 wherein the broadband source comprises at least one broadband LED (light
10 emitting diode).

51. A photonic device according to claim 50 wherein the at least one broadband LED comprises a plurality of broadband LEDs arranged to collectively transversely pump the at least one wave guide.

15 52. A photonic device according to claim 50 further comprising coupling optics between each LED and the wave guide to focus light from the LED into the wave guide.

53. A photonic device according to 52 further comprising a reflection chamber surrounding the device to contain light
20 within the device.

54. A photonic device according to claim 38 comprising an optical signal receiving surface through which light is received into the wave guide.

55. A photonic device according to claim 51 wherein said
25 at least one wave guide comprises a plurality of wave guides, and wherein each LED pumps the plurality of wave guides.

56. A photonic device according to claim 38 further comprising an optical signal conveying surface through which the output signal is coupled to another optical element either
30 directly or through free space optics.

57. A photonic device according to claim 38 wherein the wave guide is a plated wave guide formed in an opening in a resist prior to the resist being removed.

58. A photonic device according to claim 46 wherein optical pump source comprises an LED of a single or multiple wavelengths that cover a particular absorption band of the type IV semiconductor nanocrystals.

59. A photonic device according to claim 46 further comprising an optical taper used to transmit the combined light signal away from the broadband optical source, the taper using Total Internal Reflection (TIR) to direct the broadband source to the wave guide.

60. A photonic device according to claim 59 wherein the optical taper is an optical prism.

61. A photonic device according to claim 46 further comprising:

at least one Holographic Optical Element (HOE) located after (downstream from) the optical pump source.

62. A photonic device comprising:

an amplification medium comprising REDGINV;

a plurality of light sources;

a combiner adapted to combine light from the plurality of light sources to produce a broadband optical pump source which pumps light into the amplification medium.

63. A photonic device according to claim 62 wherein the plurality of light sources comprise a plurality of LEDs.

64. A photonic device according to claim 63 wherein the combiner comprises an lens, wherein there is self-alignment of

the operational wavelengths of the LED sources to the acceptance angle characteristics of the input lens.

65. A photonic device according to claim 64 wherein the lens is a Plano-convex aspherical cylindrical design that has a
5 small F# and short focal length to re-image the LED source and or sources to a planar output plane where the amplifying median is located.

66. A photonic device according to 62 wherein the combiner comprises a single or multiple micro-reflectors to
10 efficiently the light signals into the broadband optical pump source.

67. A method of manufacturing a planar type optical amplifier comprising:

forming a bar-shaped core on a plane substrate;

15 forming a groove to the core which extends to the longitudinal direction thereof;

filling the groove with a filler containing REDGIVN; and

solidifying the filler.

20 68. A method of preparing a photonic device with an integral guide formed from a type IV semiconductor nanocrystal doped with rare earth ion material.

69. A method of preparing a REDGIVN wave guide on a photonic device comprising the steps of applying a resist,
25 transferring an image to the resist, and developing the image.

70. A method of preparing a plated REDGIVN guide on a photonic device comprising the steps of applying a resist, transferring an image to the resist, developing the image, plating the resist, and removing the resist.

71. A photonic device comprising an LED comprising REDGIVN (rare earth doped group IV nanocrystal) material.

72. A photonic device according to claim 71 comprising in sequence:

5 a conductive substrate and/or bottom cladding;

the REDGIVN in a REDGIVN film;

a conductive and transparent layer on top of the REDGIVN film;

a first contact on top of the conductive and
10 transparent layer and a second contact on the substrate;

wherein the LED is turned on by applying a voltage across the first contact and the second contact.

73. A photonic device according to claim 72 wherein:

the substrate is selected from a group consisting of:
15 comprises p or n silicon substrate or Transparent metal oxide semiconductors such as Zinc Oxide and III V compound semiconductor substrates, and diamond substrate;

the REDGIVN layer is a silicon rich silicon oxide (SRSO) film containing silicon nanocrystals doped with a rare-
20 earth precursor,;

the conductive and transparent layer comprises a poly-silicon layer.

74. A photonic device according to claim 73 further comprising a small aperture is etched through the first contact
25 to allow emitted light out.

75. A photonic device according to claim 73 wherein the first contact is a serpent contact to allow emitted light out.

76. A photonic device according to claim 71 comprising additional rare earth dopants in the REDGIVN layer so as to produce multiple colours.

77. A photonic device according to claim 76 comprising
5 rare earth dopants for red, green and blue so as to produce white light.

78. A photonic device according to claim 71 comprising a plurality of layers of REDGIVN each separated by a buffer layer, and each containing a respective rare earth dopant.

10 79. A photonic device according to claim 78 wherein said plurality of layers of REDGIVN comprise three layers, one each for red, blue and green light.

80. A photonic device according to claim 79 wherein the rare earth ion are selected from a group consisting of: for
15 blue light: Tetrakis(2,2,6,6 tetramethyl-3,5-heptanedionato)cerium(IV) and $Ce(TMHD)_4$; for a green light: Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)erbium (III) $Er^{+3}(THMD)_3$; for a red light: Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium (III) and $Eu(TMHD)_3$.

20 81. A photonic device according to claim 71 wherein the conductive substrate and/or bottom cladding are also transparent so as to allow some light to exit out the bottom of the device.

82. A photonic device comprising an array of LEDs each in
25 accordance with claim 71.

83. A photonic device according to claim 82 wherein different rare earth dopants are used in respective subsets of the array.

84. A photonic device according to claim 82 wherein the
30 LEDs are arranged in groups of three, each group of three

including a red light LED, a green light LED and a blue light LED so as to produce an overall white light LED.

85. A photonic device according to claim 82 wherein each LED is individually actuatable.

5 86. A photonic device comprising a group of three LEDs according to claim 71 wherein each of the three LEDs has a respective different rare earth dopant so as to produce one of red, green and blue light.

87. A photonic device according to claim 86 wherein each
10 of the three LEDs is individually actuatable.

88. A photonic device according to claim 86 wherein the group of LEDs is collectively actuatable.

89. A photonic device comprising an optical laser comprising REDGIVN material.

15 90. A photonic device according to claim 89 comprising:

at least one wave guide comprising a REDGIVN channel;

at least one feedback element(s) defining a laser-laser-resonator cavity in the wave guide so that laser light is output from the wave guide when pumped;

20 a pump source.

91. A photonic device according to claim 90 wherein the pump source is a broadband optical pump source.

92. A photonic device according to claim 90 wherein the pump source is an electrical pump source.

25 93. A photonic device according to claim 90 comprising a substrate and/or bottom cladding below the wave guide and a top cladding.

94. A photonic device according to claim 90 wherein the laser cavity has a size, which is tuned to an excitation wavelength of the rare earth dopant.

95. A photonic device according to claim 90 wherein the
5 at least one feedback element(s) comprise a first highly reflective mirror, and a second output coupler mirror which is partially reflective.

96. A photonic device according to claim 90 wherein the at least one feedback element(s) comprise a first Bragg grating
10 which is highly reflective, and a second Bragg grating which is which is partially reflective.

97. A photonic device according to claim 90 wherein the feedback elements are frequency selective, and are tuned to be most reflective near a resonant frequency of the cavity.

15 98. A photonic device according to claim 90 further comprising means for varying the wavelength(s) reflected by the feedback element(s) and varying the effective length of the resonator cavity to thereby tune the laser to a selected wavelength.

20 99. A photonic device comprising an array of lasers according to claim 90 formed on a common substrate.

100. A photonic device according to claim 99 wherein each laser of the array of lasers has resonant characteristics and dopants selected to produce a respective different wavelength.

25 101. A photonic device according to claim 100 wherein each laser has a respective laser cavity having a different length.

102. A photonic device according to claim 90 further comprising a Diffraction Bragg reflector (DBR) grating formed

into or close to the wave guide is used to tune the wavelength of light supported in the wave guide cavity.

103. A photonic device according to claim 90 wherein the resonance characteristics of the wave guide cavities are individually selected by varying the pitch of the reflection gratings used to define the cavities which, along with the effective refractive index for the propagated optical mode, determines the wavelengths of light reflected by the gratings.

104. A photonic device according to claim 90 comprising a surface-relief grating forming a distributed Bragg reflection grating fabricated on a surface of the wave guide.

105. A photonic device according to claim 90 comprising:

a conductive substrate having a first electrical contact;

a transparent conductive cladding buffer;

a layer comprising the wave guide,

a second electrical contact on top of the REDGIVN channel;

an electrical pump source.

106. A photonic device according to claim 105 wherein the at least one feedback element(s) comprise a high reflecting mirror and output coupler at opposite each end of the wave guide to form the resonating cavity.

107. A photonic device comprising a laser component comprising:

a thin film containing REDGIVN and having a plurality of wave guides defined by channels within the substrate;

one or more feedback elements for providing optical feedback to the wave guides to form a respective laser-resonator cavity in each wave guide with a distinct resonance characteristic to provide lasing action at a selected
5 wavelength when pumped, wherein injection of pump light at one or more suitable wavelengths into the laser-resonator cavity causes output of laser light at the selected wavelength in accordance with a longitudinal cavity mode of the cavity.

108. A photonic device according to claim 107 further
10 comprising:

a ferrule having a plurality of spaced-apart attachment sites; and

a plurality of optic fibers attached to the ferrule at a respective one of the plurality of spaced-apart attachment
15 sites, each optical fiber also being connected to receive light from a respective one of the resonator cavities.

109. A photonic device according to claim 107 wherein the laser-resonator cavities have a plurality of widths on a substrate surface to thereby define a plurality of effective
20 indices of refraction for the cavities, the wavelength of a longitudinal cavity mode being dependent thereon.

110. A photonic device according to any one of claims 71 - 109 wherein the REDGIVN material comprises:

a doped semiconductor powder comprising nanocrystals
25 of a group IV semiconductor and a rare earth element, the rare earth element being dispersed on the surface of the group IV semiconductor nanocrystals.

111. A photonic device according to claim 110 wherein the rare earth element is present in a concentration of from 0.5 to
30 10 atomic percent.

112. A photonic device according to claim 110, wherein the rare earth element is present in a concentration of from 0.5 to 5 atomic percent.

113. A photonic device according to claim 110, wherein the
5 rare earth element is present in a concentration of from 0.5 to 2 atomic percent.

114. A photonic device according to claim 110, wherein the nanocrystals have an average diameter of from 0.5 to 10 nm.

115. A photonic device according to claim 110, wherein the
10 nanocrystals have an average diameter of about 3 nm.

116. A photonic device according to claim 110, wherein the group IV semiconductor is selected from Si, Ge, Sn and Pb.

117. A photonic device according to claim 110, wherein the rare earth element is selected from cerium, praseodymium,
15 neodymium, promethium, gadolinium, erbium, thulium, ytterbium, samarium, dysprosium, terbium, europium, holmium, lutetium, and thorium.

118. A photonic device according to claim 110, wherein the rare earth element is selected from erbium, thulium and
20 europium.

119. A photonic device according to claim 110, wherein the rare earth element is in the form of an oxide.

120. A photonic device according to claim 110 wherein the REDGIVN comprises a support matrix, wherein the doped
25 semiconductor powder is coated on or embedded in the support matrix.

121. A photonic device according to claim 110, wherein the doped semiconductor powder is embedded in the support matrix.

122. A photonic device according to claim 110, wherein the support matrix comprises spin-on-glass, a silica sol-gel or a polymer.

123. A photonic device according to claim 110, wherein the support matrix is in the form of a layer prepared by spin-coating.

124. A photonic device according to claim 110, wherein the support matrix comprises silicon dioxide obtained by annealing a silica sol-gel.

125. A photonic device according to claim 110, wherein the support matrix is in the form of a printed pattern.

126. A photonic device according to any one of claims 71 - 109 wherein the REDGIVN material comprises:

a doped semiconductor nanocrystal layer comprising (a) a group IV oxide layer which is free of ion implantation damage, (b) from 30 to 50 atomic percent of a semiconductor nanocrystal distributed in the group IV oxide layer, and (c) from 0.5 to 15 atomic percent of one or more rare earth element, the one or more rare earth element being (i) dispersed on the surface of the semiconductor nanocrystal and (ii) distributed substantially equally through the thickness of the group IV oxide layer.

127. A photonic device according to claim 126, wherein the group IV oxide layer comprises silicon dioxide or germanium dioxide.

128 A photonic device according to claim 126 or 127, wherein the group IV oxide layer has a thickness of from 1 to 2000 nm.

129. A photonic device according to claim 126 or 127, wherein the group IV oxide layer has a thickness of from 80 to 2000 nm.

130. A photonic device according to claim 126 or 127,
5 wherein the group IV oxide layer has a thickness of from 100 to 250 nm.

131. A photonic device according to claim 126 or 127, wherein the group IV oxide layer has a thickness of from 1 to 10 nm.

10 132. A photonic device according to any one of claims 126 to 131, wherein the semiconductor nanocrystal is a group IV semiconductor, a group II-VI semiconductor or a group III-V semiconductor.

133. A photonic device according to claim 132, wherein the
15 group IV semiconductor is selected from Si, Ge, Sn and Pb.

134. A photonic device according to claim 132, wherein the group II-VI semiconductor is selected from ZnO, ZnS, ZnSe, CaS, CaTe and CaSe.

135. A photonic device according to claim 132, wherein the
20 group III-I semiconductor is selected from GaN, GaP and GaAs.

136. A photonic device according to any one of claims 126 to 135, wherein the concentration of semiconductor nanocrystals in the group IV oxide layer is from 37 to 47 atomic percent.

137. A photonic device according to any one of claims 126
25 or 135, wherein the concentration of semiconductor nanocrystals in the group IV oxide layer is from 40 to 45 atomic percent.

138. A photonic device according to any one of claims 126 or 137, wherein the semiconductor nanocrystals are from 1 to 10 nm in size.

139. A photonic device according to any one of claims 126 or 137, wherein the semiconductor nanocrystals are from 1 to 3 nm in size.

140. A photonic device according to any one of claims 126
5 or 137, wherein the semiconductor nanocrystals are from 1 to 2 nm in size.

141. A photonic device according to any one of claims 126 or 140, wherein the rare earth element is selected from cerium, praseodymium, neodymium, promethium, gadolinium, erbium,
10 thulium, ytterbium, samarium, dysprosium, terbium, europium, holmium, lutetium, and thorium.

142. A photonic device according to any one of claims 126 or 141, wherein the rare earth element is selected from erbium, thulium and europium.

15 143. A photonic device according to any one of claims 126 or 142, wherein the rare earth element is in the form of an oxide or a halogenide.

144. A photonic device according to any one of claims 126 or 143, wherein the halogenide is a fluoride.

20 145. A photonic device according to any one of claims 126 or 144, wherein the rare earth concentration is from 5 to 15 atomic percent.

146. A photonic device according to any one of claims 126 or 145, wherein the rare earth concentration is from 10 to 15
25 atomic percent.

147. A photonic device according to any one of claims 38 to 66 and claims 71 to 110 wherein the REDGIVN material comprises a doped semiconductor nanocrystal layer comprising (a) a group IV oxide layer which is free of ion implantation
30 damage, (b) a semiconductor nanocrystal distributed in the

group IV oxide layer, and (c) one or more rare earth element, the one or more rare earth element being dispersed on the surface of the semiconductor nanocrystal.

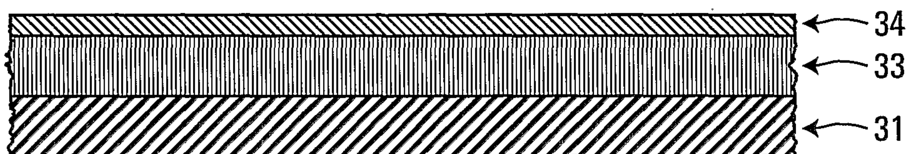


FIG. 1

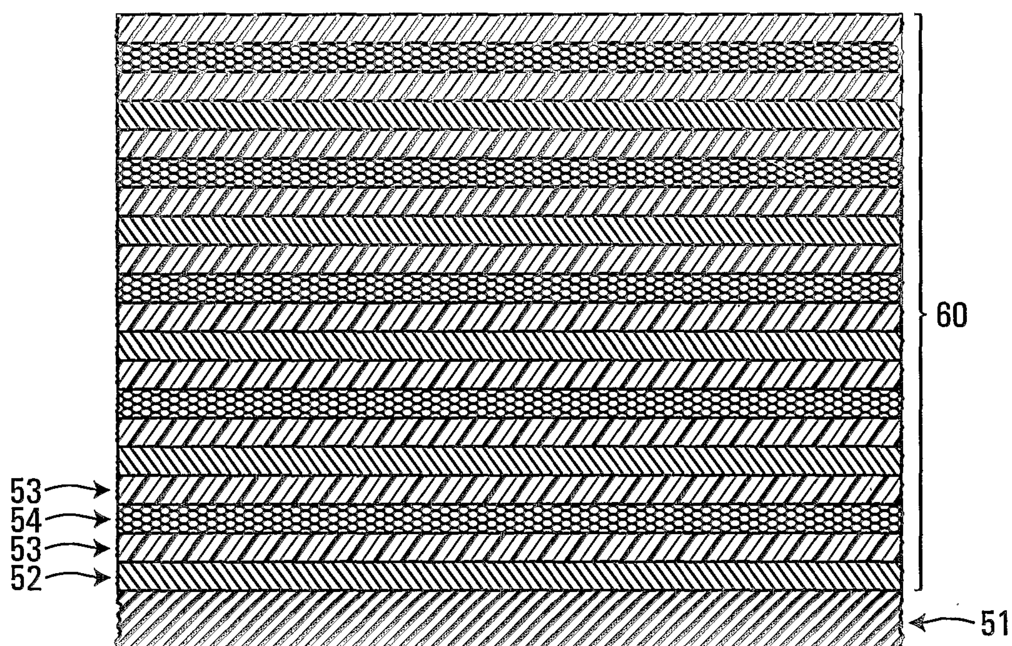


FIG. 2

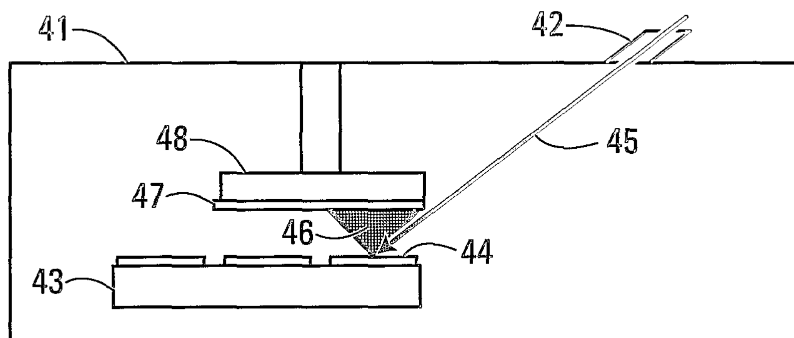


FIG. 3

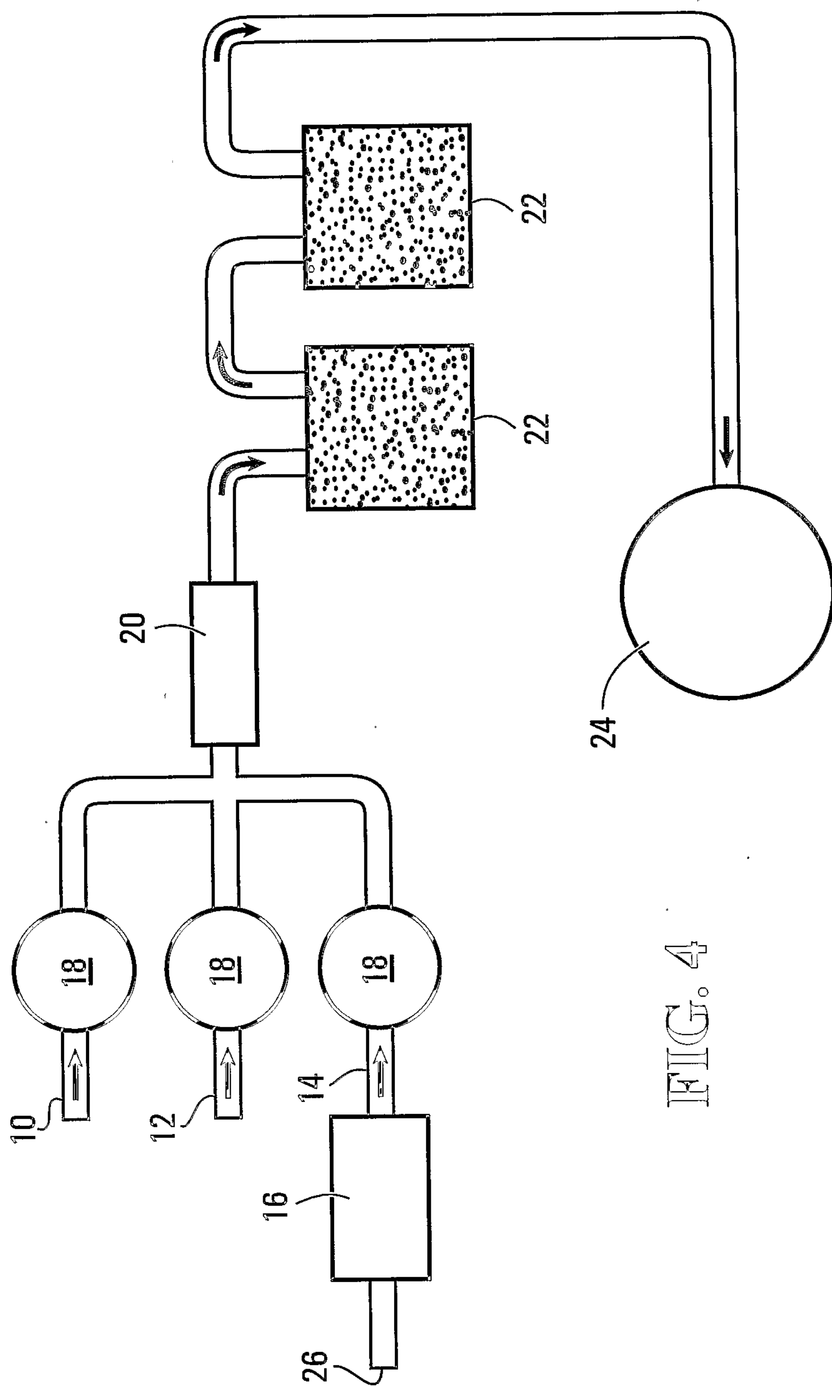


FIG. 4

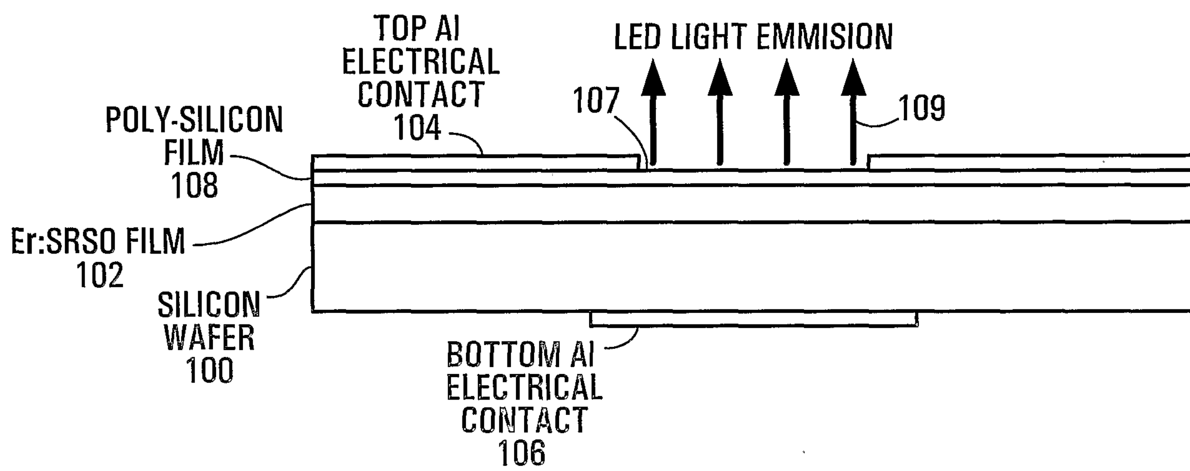


FIG. 5

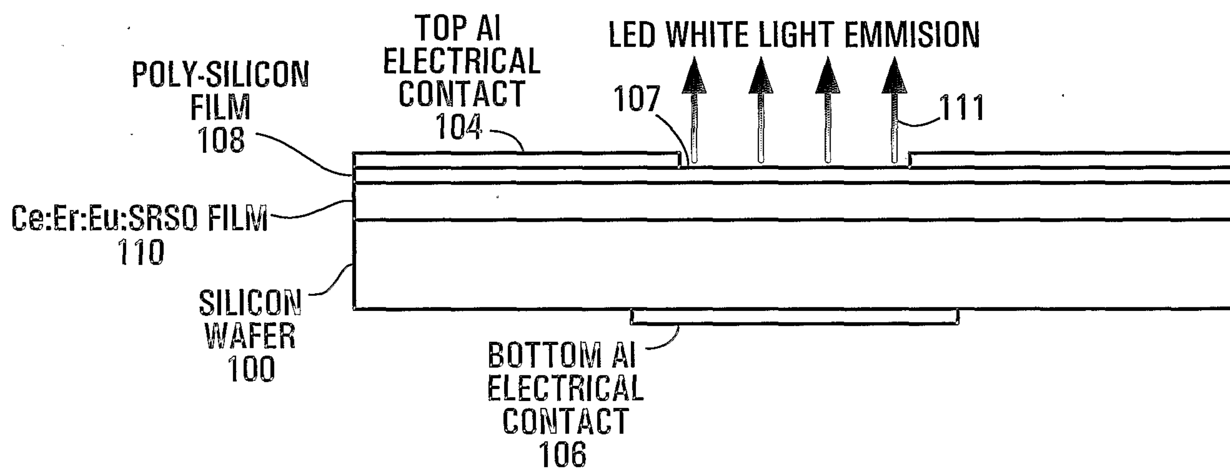


FIG. 6

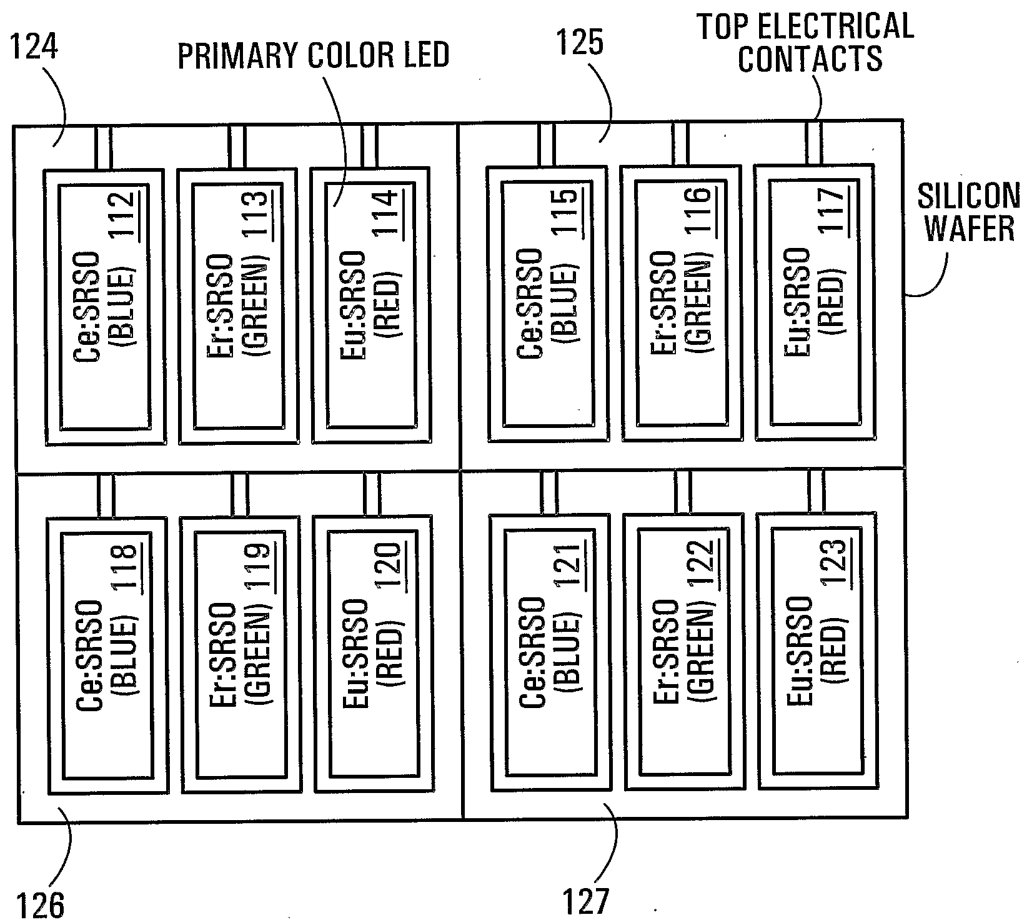


FIG. 7

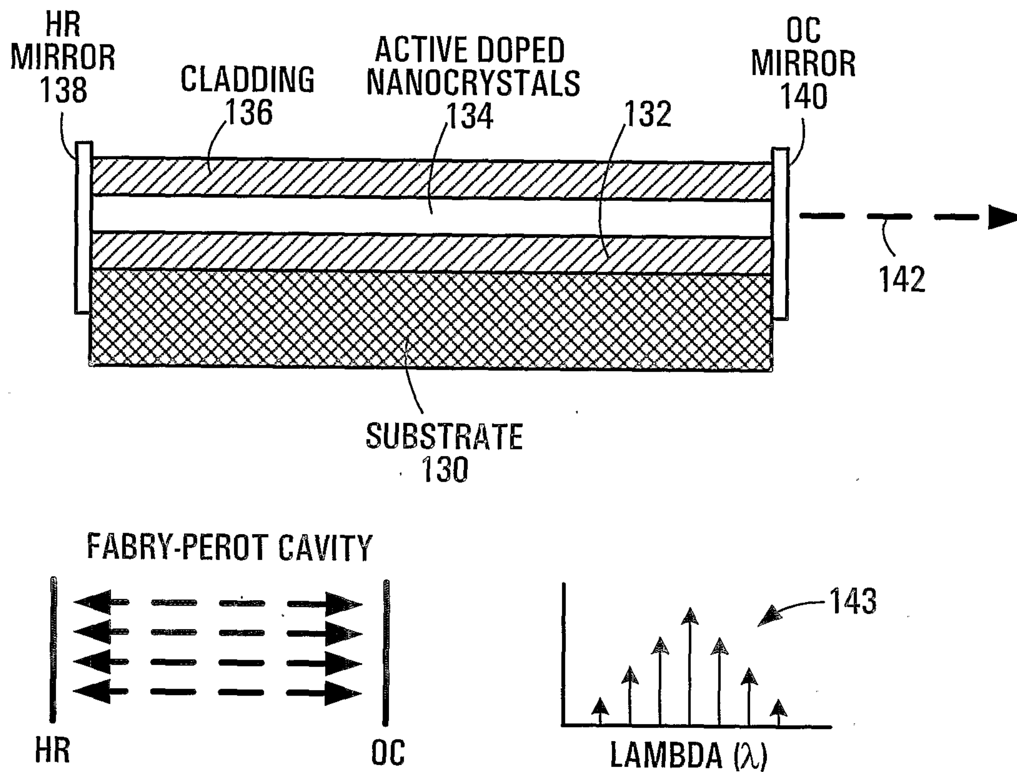


FIG. 8

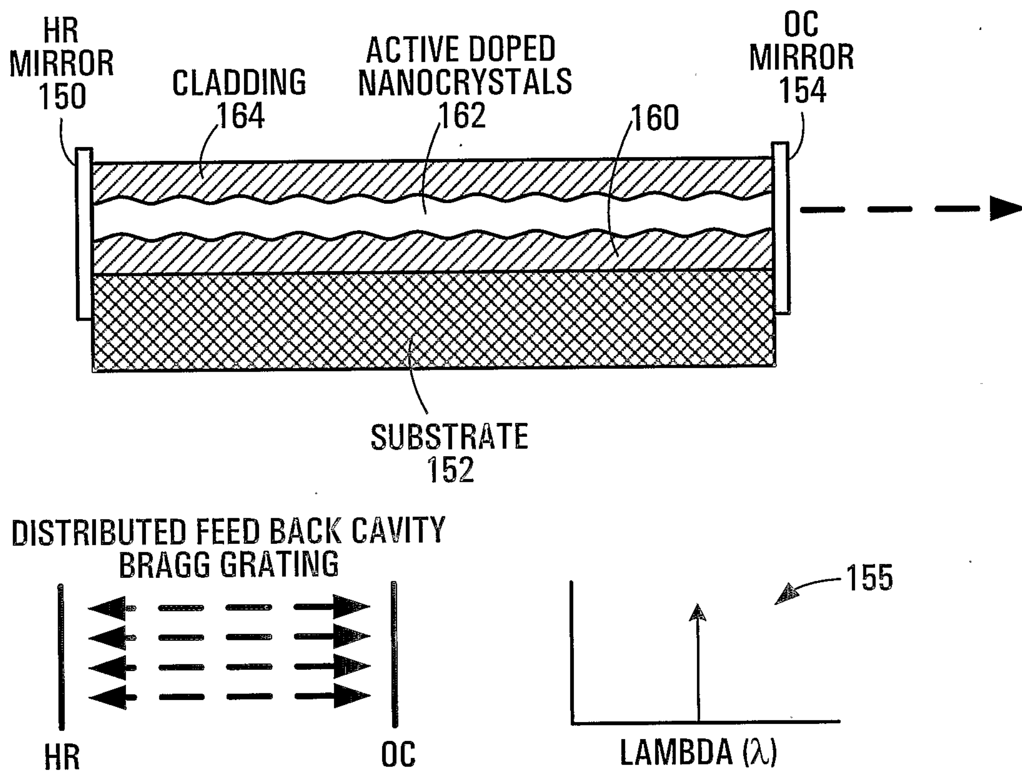


FIG. 9

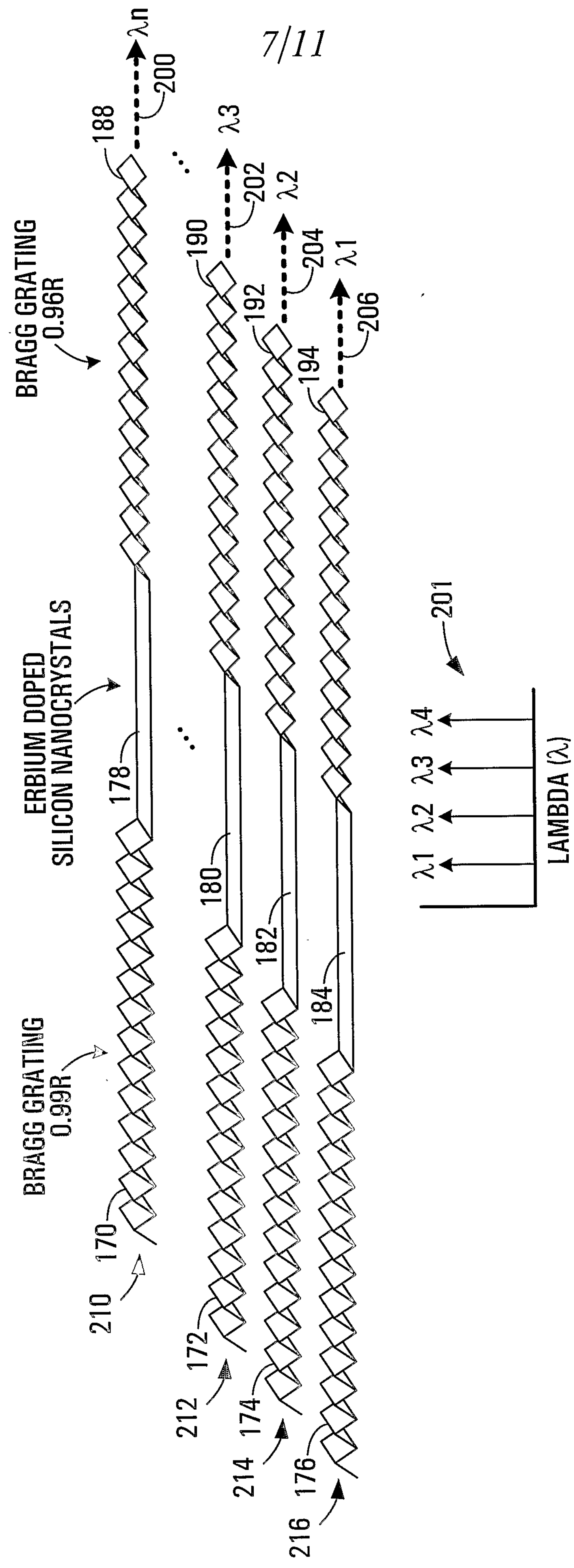


FIG. 10

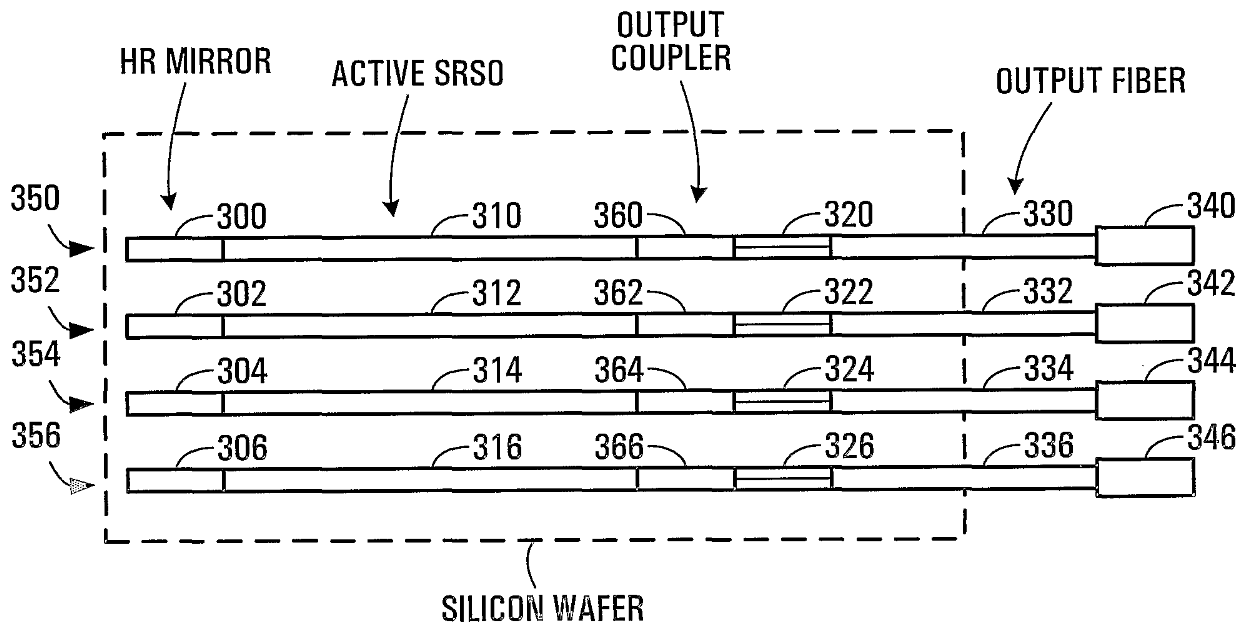


FIG. 11

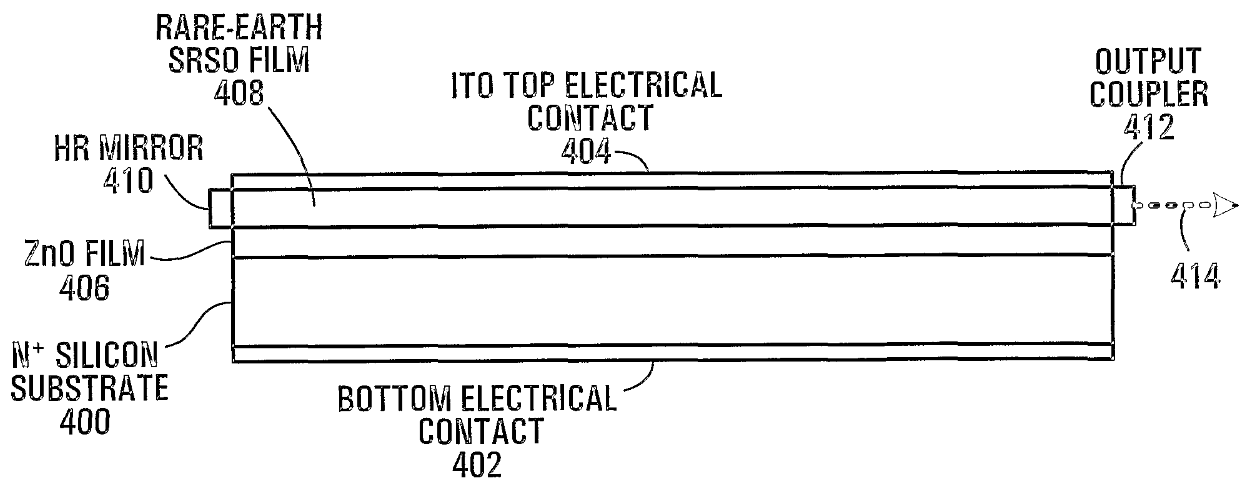


FIG. 12

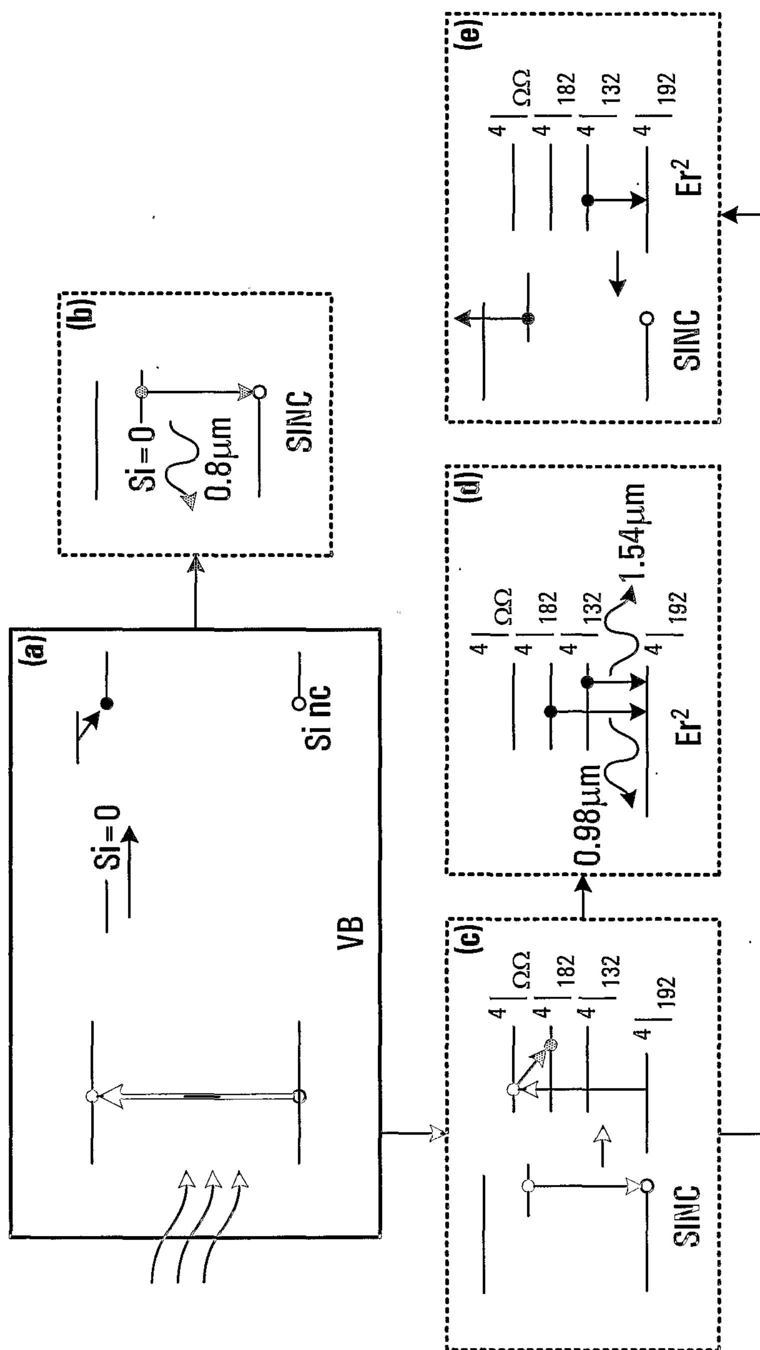


FIG. 13

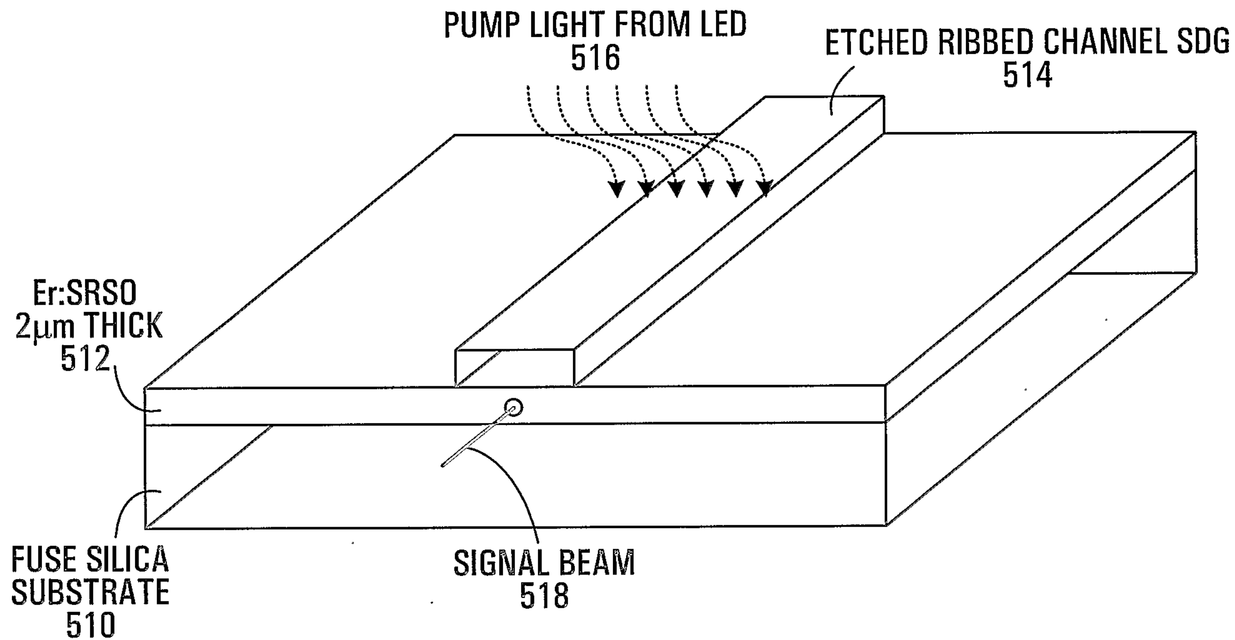


FIG. 14

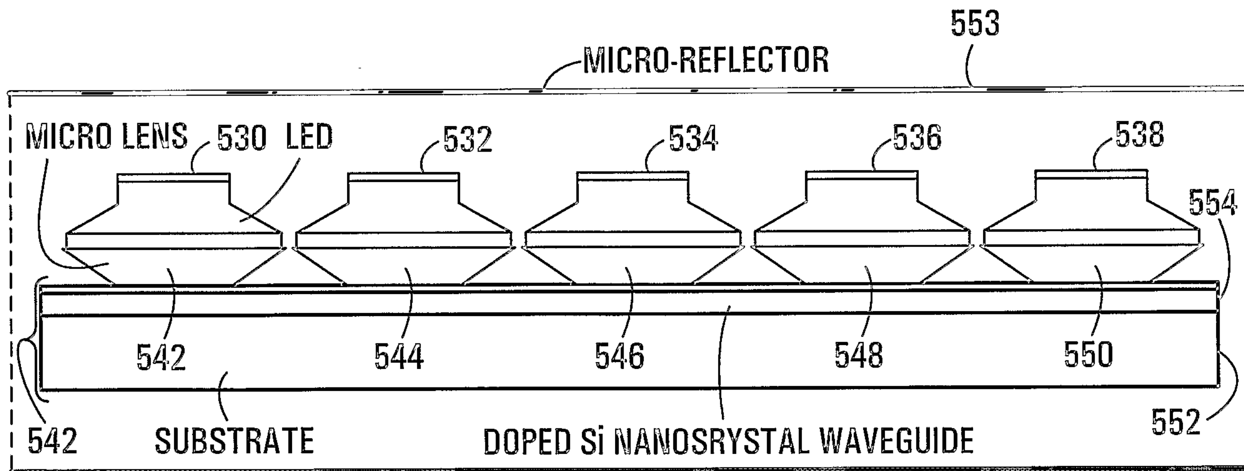


FIG. 15

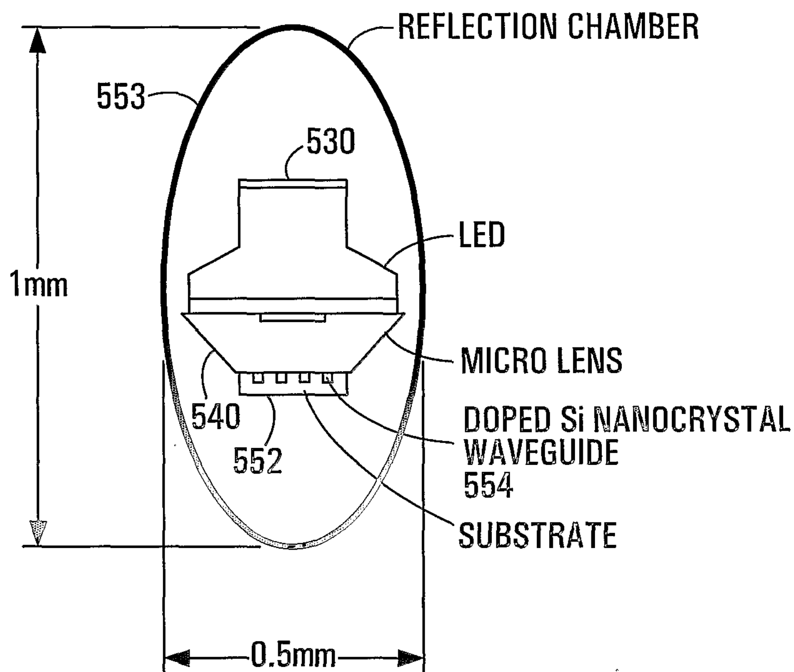


FIG. 16

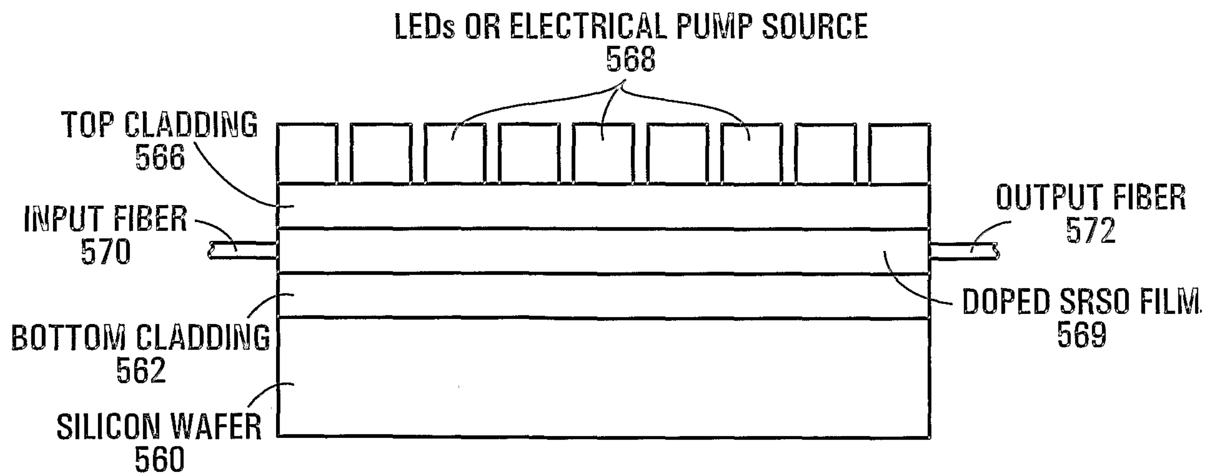


FIG. 17