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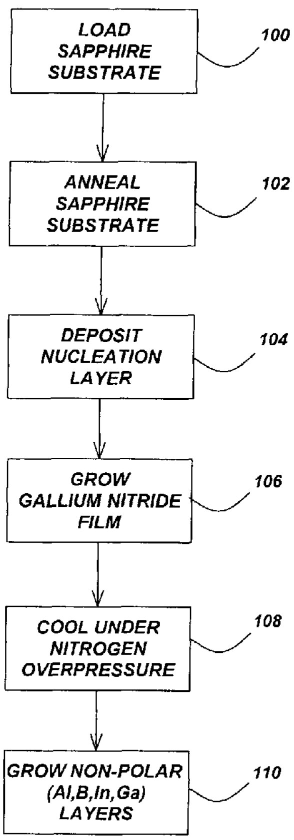
(54) **Title:** NON-POLAR (A1,B,In,Ga) QUANTUM WELL AND HETEROSTRUCTURE MATERIALS AND DEVICES



(57) **Abstract:** A method for forming non-polar (A1,B,In,Ga)N quantum well and heterostructure materials and devices. Non-polar (1120) a-plane GaN layers are grown on an r-plane (1102) sapphire substrate using MOCVD. These non-polar (1120) a-plane GaN layers comprise templates for producing non-polar (A1,B,In,Ga)N quantum well and heterostructure materials and devices.

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NON-POLAR (Al,B,In,Ga)N QUANTUM WELL AND HETEROSTRUCTURE MATERIALS AND DEVICES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit under 35 U.S.C. §119(e) of the following co-pending and commonly-assigned United States Provisional Patent Application Serial No. 60/372,909, entitled "NON-POLAR GALLIUM NITRIDE BASED THIN FILMS AND HETEROSTRUCTURE MATERIALS," filed on April 15, 2002, by Michael D. Craven, Stacia Keller, Steven P. DenBaars, Tal Margalith, James S. Speck, Shuji Nakamura, and Umesh K. Mishra, attorneys docket number 30794.95-US-P1, which application is incorporated by reference herein.

This application is related to the following co-pending and commonly-assigned United States Utility Patent Applications:

Serial No. --/---,---, entitled "NON-POLAR A-PLANE GALLIUM NITRIDE THIN FILMS GROWN BY METALORGANIC CHEMICAL VAPOR DEPOSITION," filed on same date herewith, by Michael D. Craven and James S. Speck, attorneys docket number 30794.100-US-U1; and

Serial No. --/---,---, entitled "DISLOCATION REDUCTION IN NON-POLAR GALLIUM NITRIDE THIN FILMS," filed on same date herewith, by Michael D. Craven, Stacia Keller, Steven P. DenBaars, Tal Margalith, James S. Speck, Shuji Nakamura, and Umesh K. Mishra, attorneys docket number 30794.102-US-U1;

both of which applications are incorporated by reference herein.

1. Field of the Invention.

The invention is related to semiconductor materials, methods, and devices, and more particularly, to non-polar (Al,B,In,Ga)N quantum well and heterostructure materials and devices.

2. Description of the Related Art.

(Note: This application references a number of different patents, applications and/or publications as indicated throughout the specification by one or more reference numbers. A list of these different publications ordered according to these reference numbers can be found below in the section entitled "References." Each of these publications is incorporated by reference herein.)

Current state of the art (Al,B,In,Ga)N heterostructures and quantum well structures employ c-plane (0001) layers. The total polarization of a III-N film consists of spontaneous and piezoelectric polarization contributions, which both originate from the single polar [0001] axis of the wurtzite nitride crystal structure. Polarization discontinuities which exist at surfaces and interfaces within nitride heterostructures are associated with fixed sheet charges, which in turn produce electric fields. Since the alignment of these internal electric fields coincides with the growth direction of the c-plane (0001) layers, the fields affect the energy bands of device structures.

In quantum wells, the "tilted" energy bands spatially separate electrons and hole wave functions, which reduces the oscillator strength of radiative transitions and red-shifts the emission wavelength. These effects are manifestations of the quantum confined Stark effect (QCSE) and have been thoroughly analyzed for GaN/(Al,Ga)N quantum wells. See References 1-8. Additionally, the large polarization-induced fields are partially screened by dopants and impurities, so the emission characteristics can be difficult to engineer accurately.

The internal fields are also responsible for large mobile sheet charge densities in nitride-based transistor heterostructures. Although these large 2D electron gases (2DEGs) are attractive and useful for devices, the polarization-induced fields, and the 2DEG itself, are difficult to control accurately.

Non-polar growth is a promising means of circumventing the strong polarization-induced electric fields that exist in wurtzite nitride semiconductors. Polarization-induced electric fields do not affect wurtzite nitride semiconductors grown in non-polar directions (i.e., perpendicular to the [0001] axis) due to the absence of polarization discontinuities along non-polar growth directions.

Recently, two groups have grown non-polar GaN/(Al,Ga)N multiple quantum wells (MQWs) via molecular beam epitaxy (MBE) without the presence of polarization-induced electric fields along non-polar growth directions. Waltereit et al. grew m-plane $GaN/Al_{0.1}Ga_{0.9}N$ MQWs on γ-$LiAlO_2$ (100) substrates and Ng grew a-plane $GaN/Al_{0.15}Ga_{0.85}N$ MQW on r-plane sapphire substrates. See References 9-10.

Despite these results, the growth of non-polar GaN orientations remains difficult to achieve in a reproducible manner.

SUMMARY OF THE INVENTION

The present invention describes a method for forming non-polar (A1,B,In,Ga)N quantum well and heterostructure materials and devices. First, non-polar $(11\bar{2}0)$ a-plane GaN thin films are grown on a $(1\bar{1}02)$ r-plane sapphire substrate using metalorganic chemical vapor deposition (MOCVD). These non-polar $(11\bar{2}0)$ a-plane GaN thin films are templates for producing non-polar (Al,B,In,Ga)N quantum well and heterostructure materials and devices thereon.

BRIEF DESCRIPTION OF THE DRAWINGS

Referring now to the drawings in which like reference numbers represent corresponding parts throughout:

FIG. 1 is a flowchart that illustrates the steps of a method for forming non-polar (A1,B,In,Ga)N quantum well and heterostructure materials and devices according to a preferred embodiment of the present invention;

FIG. 2 illustrates the photoluminescence (PL) spectra of 5-period a-plane $In_{0.1}GaN/In_{0.03}GaN$ MQW structures with nominal well widths of 1.5 nm, 2.5 nm, and 5.0 nm measured at room temperature;

FIG. 3 illustrates the PL spectra of an a-plane $In_{0.03}Ga_{0.97}N/In_{0.1}Ga_{0.9}N$ MQW structure with a nominal well width of 5.0 nm measured for various pump powers;

FIG. 4(a) shows a 2θ-ω x-ray diffraction scan of the 10-period $Al_{0.4}Ga_{0.6}N$/GaN superlattice, which reveals clearly defined satellite peaks; and

FIG. 4(b) illustrates the PL spectra of the superlattice characterized in FIG. 4(a).

DETAILED DESCRIPTION OF THE INVENTION

In the following description of the preferred embodiment, reference is made to the accompanying drawings which form a part hereof, and in which is shown by way of illustration a specific embodiment in which the invention may be practiced. It is to be understood that other embodiments may be utilized and structural changes may be made without departing from the scope of the present invention.

Overview

The purpose of the present invention is to provide a method for producing non-polar (Al,B,In,Ga)N quantum well and heterostructure materials and devices, using non-polar $(11\bar{2}0)$ a-plane GaN thin films as templates.

The growth of device-quality non-polar $(11\bar{2}0)$ a-plane GaN thin films on $(1\bar{1}02)$ r-plane sapphire substrates via MOCVD is described in co-pending and commonly-assigned United States Provisional Patent Application Serial No. 60/372,909, entitled "NON-POLAR GALLIUM NITRIDE BASED THIN FILMS AND HETEROSTRUCTURE MATERIALS," filed on April 15, 2002, by Michael D. Craven, Stacia Keller, Steven P. DenBaars, Tal Margalith, James S. Speck, Shuji Nakamura, and Umesh K. Mishra, attorneys' docket number 30794.95-US-P1, as well as co-pending and commonly-assigned United States Utility Patent Application Serial No. --/---,---, entitled "NON-POLAR A-PLANE GALLIUM NITRIDE THIN FILMS GROWN BY METALORGANIC CHEMICAL VAPOR DEPOSITION," filed on same date herewith, by Michael D. Craven and James S. Speck, attorneys docket number 30794.100-US-U1, both of which applications are incorporated by reference herein.

The present invention focuses on the subsequent growth of (Al,B,In,Ga)N quantum wells and heterostructures on the $(11\bar{2}0)$ a-plane GaN layers. The luminescence characteristics of these structures indicate that polarization-induced electric fields do not affect their electronic band structure, and consequently, polarization-free structures have been attained. The development of non-polar (Al,B,In,Ga)N quantum wells and heterostructures is important to the realization of high-performance (Al,B,In,Ga)N-based devices which are unaffected by polarization-induced electric fields.

Potential devices to be deposited on non-polar $(11\bar{2}0)$ a-plane GaN layers include laser diodes (LDs), light emitting diodes (LEDs), resonant cavity LEDs (RC-LEDs), vertical cavity surface emitting lasers (VCSELs), high electron mobility transistors (HEMTs), heterojunction bipolar transistors (HBTs), heterojunction field effect transistors (HFETs), as well as UV and near-UV photodetectors.

Process Steps

FIG. 1 is a flowchart that illustrates the steps of a method for forming non-polar (A1,B,In,Ga)N quantum well and heterostructure materials and devices according to a preferred embodiment of the present invention. The steps of this method include the growth of "template" $(11\bar{2}0)$ a-plane GaN layers, followed by the growth of layers with differing alloy compositions for quantum wells and heterostructures.

Block 100 represents loading of a sapphire substrate into a vertical, close-spaced, rotating disk, MOCVD reactor. For this step, epi-ready sapphire substrates with surfaces crystallographically oriented within +/- 2° of the sapphire r-plane $(1\bar{1}20)$ may be obtained from commercial vendors. No ex-situ preparations need be performed prior to loading the sapphire substrate into the MOCVD reactor, although ex-situ cleaning of the sapphire substrate could be used as a precautionary measure.

Block 102 represents annealing the sapphire substrate in-situ at a high temperature (>1000°C), which improves the quality of the substrate surface on the atomic scale. After annealing, the substrate temperature is reduced for the subsequent low temperature nucleation layer deposition.

Block 104 represents depositing a thin, low temperature, low pressure, nitride-based nucleation layer as a buffer layer on the sapphire substrate. Such layers are commonly used in the heteroepitaxial growth of c-plane (0001) nitride semiconductors. In the preferred embodiment, the nucleation layer is comprised of, but is not limited to, 1-100 nanometers (nm) of GaN deposited at approximately 400-900°C and 1 atm.

After depositing the nucleation layer, the reactor temperature is raised to a high temperature, and Block 106 represents growing the epitaxial $(11\bar{2}0)$ a-plane GaN layers to a thickness of approximately 1.5 μn. The high temperature growth conditions include, but are not limited to, approximately 1100°C growth temperature, 0.2 atm or less growth pressure, 30 μmol per minute Ga flow, and 40,000 μmol per minute N flow, thereby providing a V/III ratio of approximately 1300). In the preferred embodiment, the precursors used as the group III and group V sources are trimethylgallium and ammonia, respectively, although alternative precursors could be used as well. In addition, growth conditions may be varied to produce different growth rates, e.g., between 5 and 9 Å per second, without departing from the scope of the present invention.

Upon completion of the high temperature growth step, Block 108 represents cooling the epitaxial $(11\bar{2}0)$ a-plane GaN layers down under a nitrogen overpressure.

Finally, Block 110 represents non-polar (A1,B,In,Ga)N layers, with differing alloy compositions and hence differing electrical properties, being grown on the non-polar $(11\bar{2}0)$ a-plane GaN layers. These non-polar (A1,B,In,Ga)N layers are used to produce quantum wells and heterostructures.

The quantum wells employ alternating layers of different bandgap such that "wells" are formed in the structure's energy band profile. The precise number of layers in the structure depends on the number of quantum wells desired. Upon excitation, electrons and holes accumulate in the wells of the conduction and valence bands, respectively. Band-to-band recombination occurs in the well layers since the density-of-states is highest at these locations. Thus, quantum wells can be engineered according to the desired emission characteristics and available epitaxial growth capabilities.

The nominal thickness and composition of the layers successfully grown on the non-polar $(11\bar{2}0)$ a-plane GaN layers include, but are not limited to:

8 nm Si-doped $In_{0.03}GaN$ barrier
1.5, 2.5, or 5 nm $In_{0.1}GaN$ well

Moreover, the above Blocks may be repeated as necessary. In one example, Block 110 was repeated 5 times to form an MQW structure that was capped with GaN to maintain the integrity of the (In,Ga)N layers. In this example, the layers comprising the MQW structure were grown via MOCVD at a temperature of 825°C and atmospheric pressure.

The luminescence characteristics of this structure indicate that polarization-induced electric fields do not affect the band profiles, and the quantum wells can be considered polarization-free. For example, FIG. 2 illustrates the photoluminescence (PL) spectra of 5-period a-plane $In_{0.1}GaN/In_{0.03}GaN$ MQW structures with nominal well widths of 1.5 nm, 2.5 nm, and 5.0 nm measured at room temperature. The peak PL emission wavelength and intensity increase with increasing well width.

Further, FIG. 3 illustrates the PL spectra of an a-plane $In_{0.03}Ga_{0.97}N/In_{0.1}Ga_{0.9}N$ MQW structure with a nominal well width of 5.0 nm measured for various pump powers. PL intensity increases with pump power as expected while the peak emission wavelength is pump power independent, indicating that the band profiles are not influenced by polarization-induced electric fields.

In addition to (In,Ga)N quantum wells, heterostructures containing (Al,Ga)N/GaN superlattices may also be grown on the non-polar $(11\bar{2}0)$ a-plane GaN layers. For example, heterostructures typically consist of two layers, most commonly

(AlGa)N on GaN, to produce an electrical channel necessary for transistor operation. The thickness and composition of the superlattice layers may comprise, but are not limited to:

9 nm $Al_{0.4}GaN$ barrier
11 nm GaN well

In one example, Block 110 was repeated 10 times to form a 10-period $Al_{0.4}Ga_{0.6}N/GaN$ superlattice that was terminated with a 11 nm GaN well layer. The superlattice was grown via MOCVD at conditions similar to those employed for the underlying template layer: ~1100°C growth temperature, ~0.1 atm growth pressure, 38 μmol/min Al flow, 20 μmol/min Ga flow, and 40,000 μmol/min N flow. The Al flow was simply turned off to form the GaN well layers. Successful growth conditions are not strictly defined by the values presented above. Similar to the (In,Ga)N quantum wells, the luminescence characteristics of the superlattice described above indicate that polarization fields do not affect the structure.

FIG. 4(a) shows a 2θ-ω x-ray diffraction scan of the 10-period $Al_{0.4}Ga_{0.6}N/GaN$ superlattice, which reveals clearly defined satellite peaks, while FIG. 4(b) illustrates the PL spectra of the superlattice characterized in FIG. 4(a). The absence of polarization-induced fields was evidenced by the 3.45 eV (~360 nm) band edge emission of the superlattice. The band edge emission did not experience the subtle red-shift present in c-plane superlattices.

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Conclusion

This concludes the description of the preferred embodiment of the present invention. The following describes some alternative embodiments for accomplishing the present invention.

For example, variations in non-polar (Al,In,Ga)N quantum wells and heterostructures design and MOCVD growth conditions may be used in alternative embodiments. Moreover, the specific thickness and composition of the layers, in addition to the number of quantum wells grown, are variables inherent to quantum well structure design and may be used in alternative embodiments of the present invention.

Further, the specific MOCVD growth conditions determine the dimensions and compositions of the quantum well structure layers. In this regard, MOCVD growth conditions are reactor dependent and may vary between specific reactor designs. Many variations of this process are possible with the variety of reactor designs currently being using in industry and academia.

Variations in conditions such as growth temperature, growth pressure, V/III ratio, precursor flows, and source materials are possible without departing from the scope of the present invention. Control of interface quality is another important aspect of the process and is directly related to the flow switching capabilities of particular reactor designs. Continued optimization of the growth conditions will result in more accurate compositional and thickness control of the integrated quantum well layers described above.

In addition, a number of different growth methods other than MOCVD could be used in the present invention. For example, the growth method could also be molecular beam epitaxy (MBE), liquid phase epitaxy (LPE), hydride vapor phase epitaxy (HVPE), sublimation, or plasma-enhanced chemical vapor deposition (PECVD).

Further, although non-polar a-plan GaN thin films are described herein, the same techniques are applicable to non-polar m-plane GaN thin films. Moreover, non-polar InN, AlN, and AlInGaN thin films could be created instead of GaN thin films.

Finally, substrates other than sapphire substrate could be employed for non-polar GaN growth. These substrates include silicon carbide, gallium nitride, silicon, zinc oxide, boron nitride, lithium aluminate, lithium niobate, germanium, aluminum nitride, and lithium gallate.

In summary, the present invention describes a method for forming non-polar (Al,B,In,Ga)N quantum well and heterostructure materials and devices. First, non-polar $(11\bar{2}0)$ a-plane GaN thin film layers are grown on a $(1\bar{1}02)$ r-plane sapphire substrate using MOCVD. These non-polar $(11\bar{2}0)$ a-plane GaN layers comprise templates for producing non-polar (Al,B,In,Ga)N quantum well and heterostructure materials and devices.

The foregoing description of one or more embodiments of the invention has been presented for the purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed. Many modifications and variations are possible in light of the above teaching. It is intended that the scope of the invention be limited not by this detailed description, but rather by the claims appended hereto.

WHAT IS CLAIMED IS:

1. A method for forming a nitride semiconductor device, comprising:

(a) growing one or more non-polar a-plane GaN layers on an r-plane substrate; and

(b) growing one or more non-polar (Al,B,In,Ga)N layers on the non-polar a-plane GaN layers.

2. The method of claim 1, wherein the substrate is a sapphire substrate.

3. The method of claim 1, wherein the substrate is selected from a group comprising silicon carbide, gallium nitride, silicon, zinc oxide, boron nitride, lithium aluminate, lithium niobate, germanium, aluminum nitride, and lithium gallate.

4. The method of claim 1, wherein the grown non-polar (Al,B,In,Ga)N layers comprise at least one quantum well.

5. The method of claim 4, wherein the quantum well comprises an InGaN quantum well.

6. The method of claim 4, wherein the quantum well is capped with GaN.

7. The method of claim 1, wherein the grown non-polar (Al,B,In,Ga)N layers comprise at least one heterostructure.

8. The method of claim 7, wherein the heterostructure contains an (Al,Ga)N/GaN superlattice.

9. The method of claim 1, wherein the growing step (a) comprises:

(1) annealing the substrate;

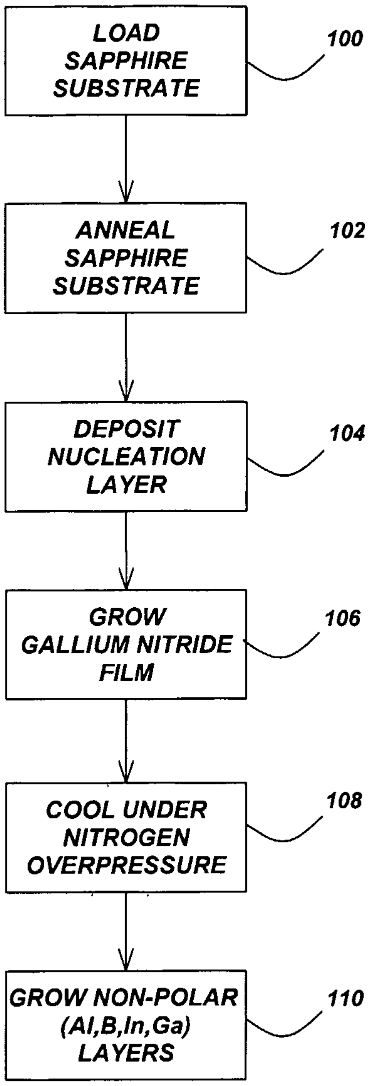
(2) depositing a nitride-based nucleation layer on the substrate;

(3) growing the non-polar a-plane gallium nitride films on the nucleation layer; and

(4) cooling the non-polar a-plane gallium nitride films under a nitrogen overpressure.

10. The method of claim 1, wherein the growing steps are performed by a method selected from a group comprising metalorganic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), liquid phase epitaxy (LPE), hydride vapor phase epitaxy (HVPE), sublimation, and plasma-enhanced chemical vapor deposition (PECVD).

11. A device manufactured using the method of claim 1.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ANNEAL SAPPHIRE SUBSTRATE
102
DEPOSIT NUCLEATION LAYER
104
GROW GALLIUM NITRIDE FILM
106
COOL UNDER NITROGEN OVERPRESSURE
108
GROW NON-POLAR (Al,B,In,Ga) LAYERS
110

FIG. 1

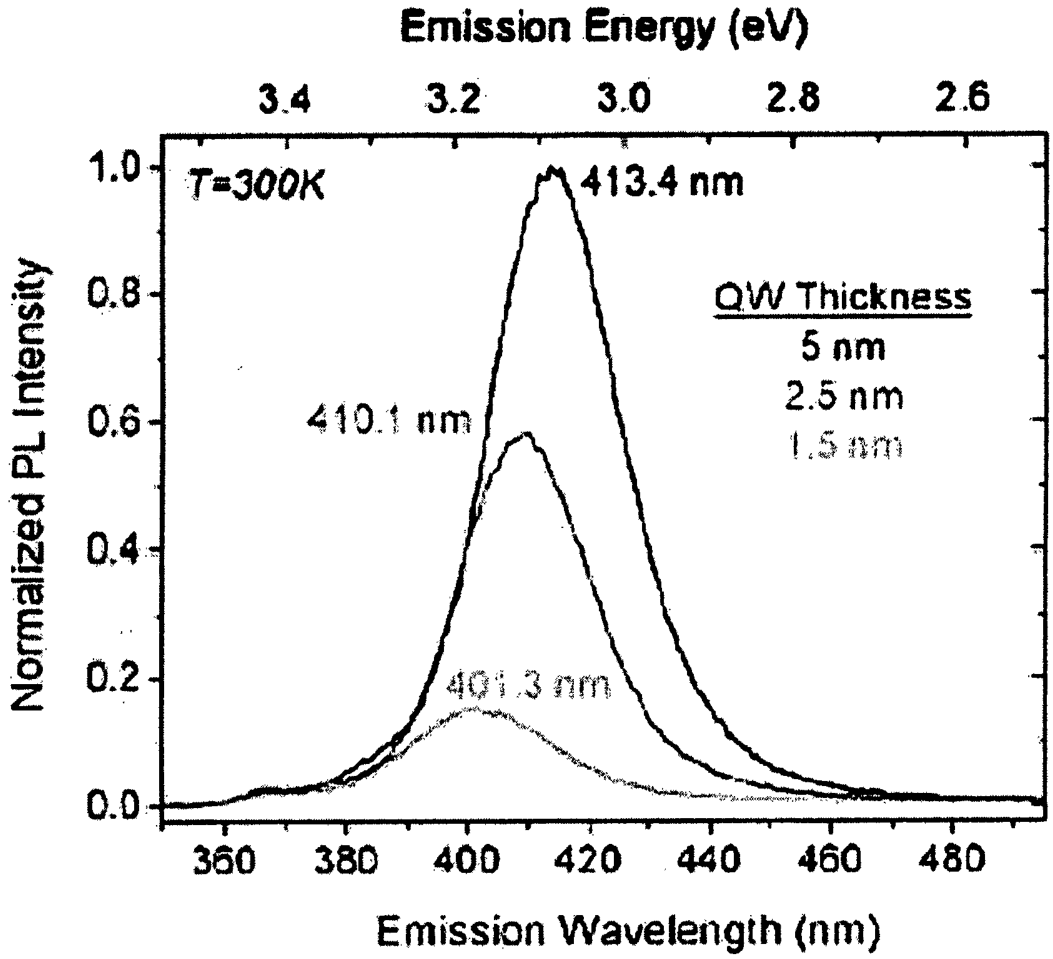
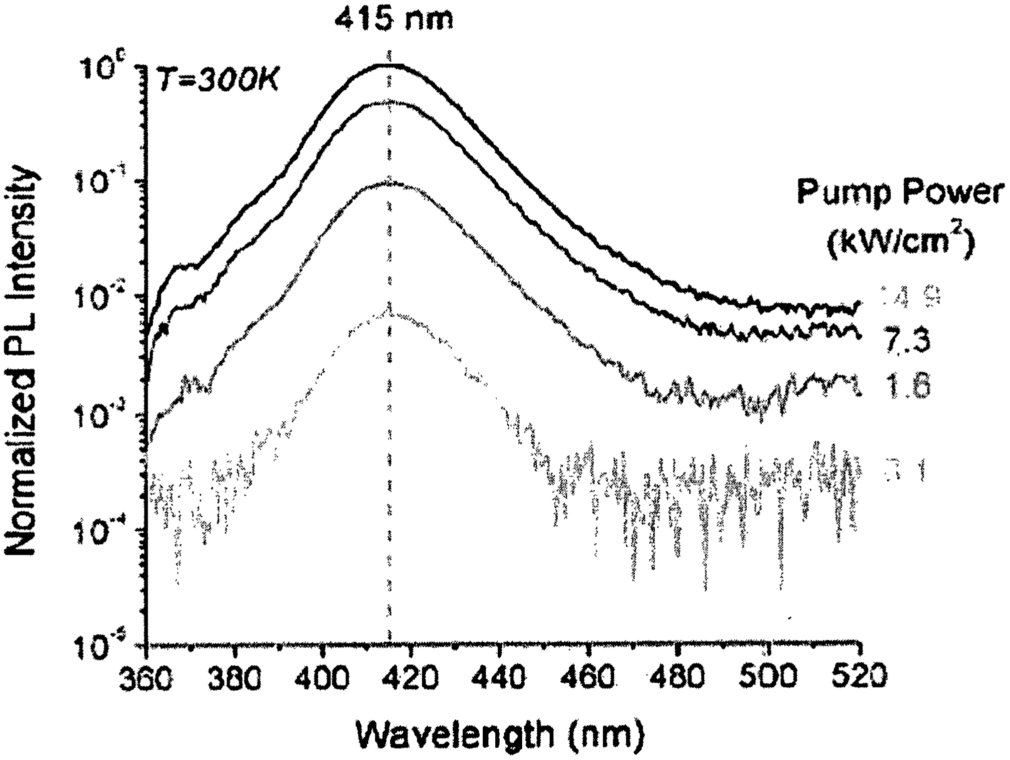

Emission Energy (eV)
3.4
3.2
3.0
2.8
2.6
1.0
0.8
0.6
0.4
0.2
0.0
Normalized PL Intensity
T=300K
413.4 nm
QW Thickness
5 nm
2.5 nm
1.5 nm
410.1 nm
401.3 nm
360
380
400
420
440
460
480
Emission Wavelength (nm)

FIG. 2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T=300K
Normalized PL Intensity
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10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
Pump Power
(kW/cm^2)
7.3
1.6
360 380 400 420 440 460 480 500 520
Wavelength (nm)

FIG. 3

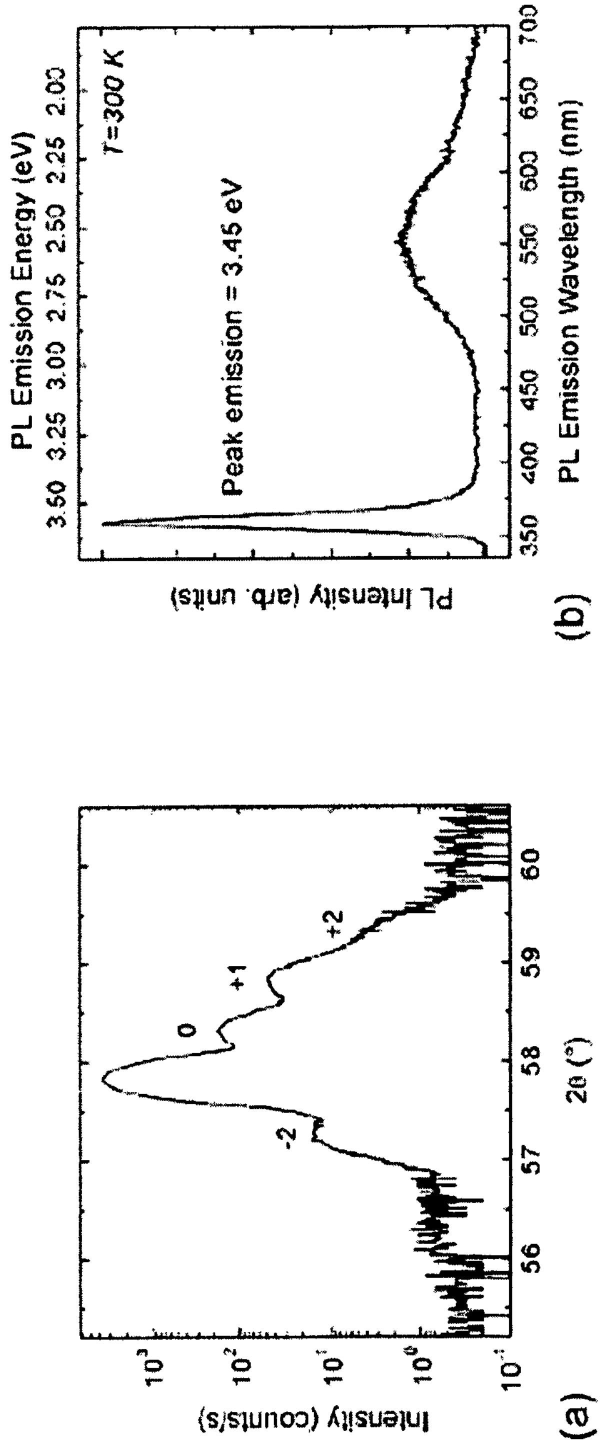
(a)
Intensity (counts/s)
2θ (°)
-2
0
+1
+2
(b)
PL Emission Energy (eV)
PL Intensity (arb. units)
PL Emission Wavelength (nm)
Peak emission = 3.45 eV
T=300 K

FIG. 4

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/11175

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C30B25/02 H01L21/00 H01L21/20 H01L33/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C30B H01L

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

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

PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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[X] Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search	Date of mailing of the international search report
18 August 2003	26/08/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Cook, S

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