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Major et al.

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(54) **METHODS FOR FORMING GROUP III-ARSENIDE-NITRIDE SEMICONDUCTOR MATERIALS**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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Related U.S. Application Data

(60) Division of application No. 08/908,766, filed on Aug. 7, 1997, now Pat. No. 6,100,546, which is a continuation of application No. 08/724,321, filed on Oct. 1, 1996, now Pat. No. 5,689,123, which is a continuation of application No. 08/373,362, filed on Jan. 17, 1995, now abandoned, which is a continuation-in-part of application No. 08/224,027, filed on Apr. 7, 1994, now abandoned.

(51) **Int. Cl.**^{7} **H01L 21/00**

(52) **U.S. Cl.** **438/46**

(58) **Field of Search** 438/22, 46, 47, 438/48, 57, 73, 93, 94, 478, 503, 507, 936, 938, 956; 117/2, 84, 88, 89, 952, 954; 372/43, 44, 45, 50; 257/14, 15, 17, 18, 22, 28, 76, 184, 185, 190, 196, 200, 201

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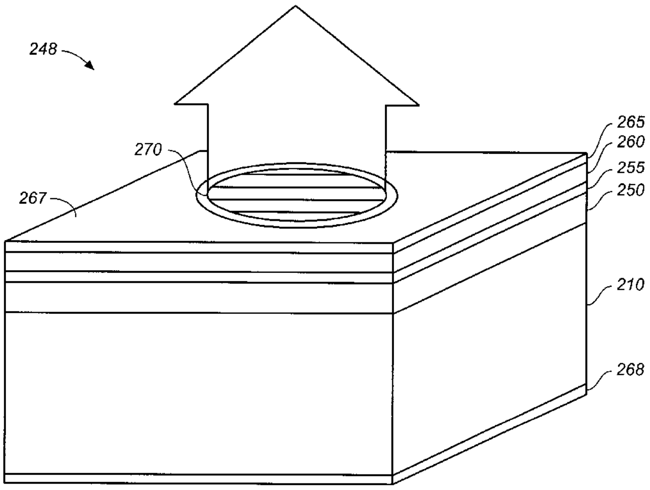
Primary Examiner—Charles Bowers
Assistant Examiner—K Christianson
(74) *Attorney, Agent, or Firm*—W. Douglas Carothers, Jr.

(57) **ABSTRACT**

Methods are disclosed for forming Group III-arsenide-nitride semiconductor materials. Group III elements are combined with group V elements, including at least nitrogen and arsenic, in concentrations chosen to lattice match commercially available crystalline substrates. Epitaxial growth of these III-V crystals results in direct bandgap materials, which can be used in applications such as light emitting diodes and lasers. Varying the concentrations of the elements in the III-V crystals varies the bandgaps, such that materials emitting light spanning the visible spectra, as well as mid-IR and near-UV emitters, can be created. Conversely, such material can be used to create devices that acquire light and convert the light to electricity, for applications such as full color photodetectors and solar energy collectors. The growth of the III-V crystals can be accomplished by growing thin layers of elements or compounds in sequences that result in the overall lattice match and bandgap desired.

22 Claims, 8 Drawing Sheets



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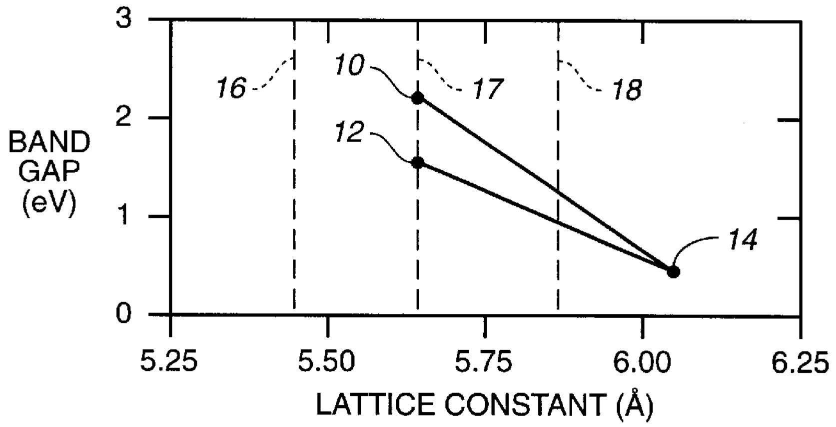


FIG._1

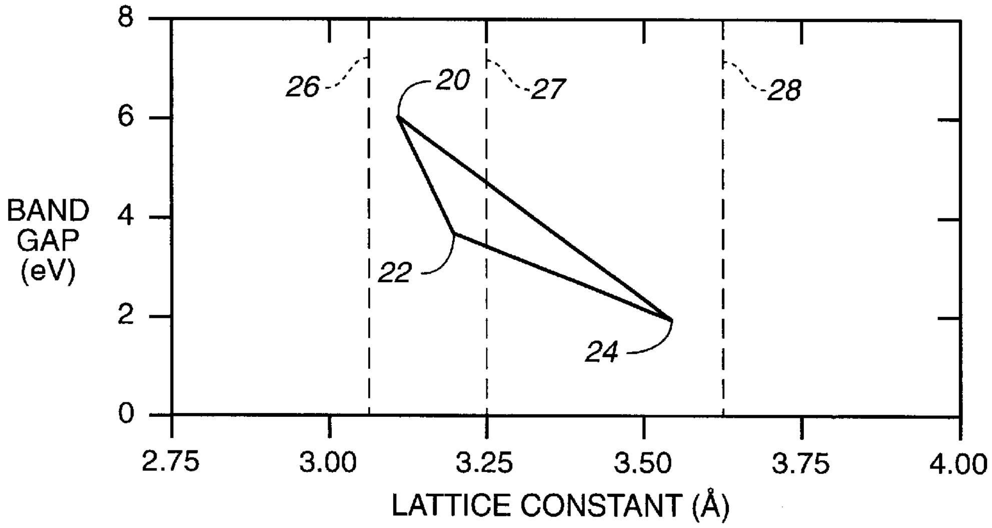


FIG._2

	GROUP III				GROUP V			
ELEMENT	B	Al	Ga	In	N	P	As	Sb
RADIUS (Å)	0.88	1.26	1.26	1.44	0.70	1.10	1.18	1.36

FIG._3

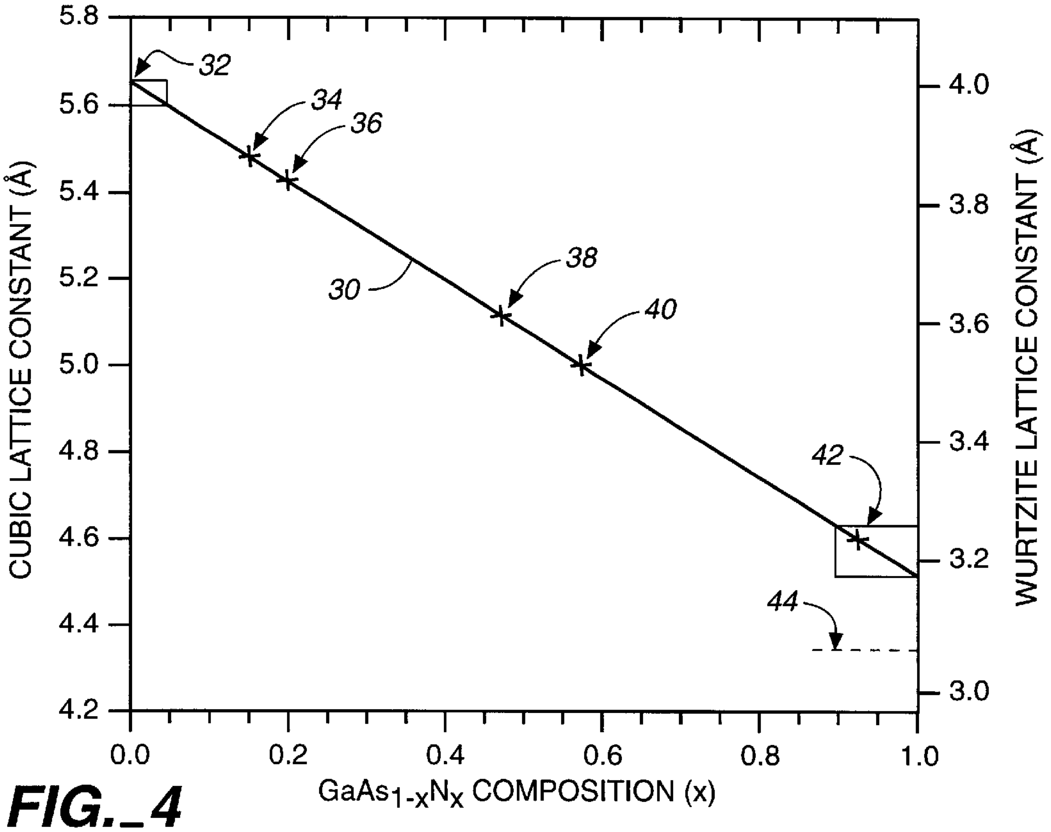

5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
CUBIC LATTICE CONSTANT (Å)
4.0
3.8
3.6
3.4
3.2
3.0
WURTZITE LATTICE CONSTANT (Å)
0.0
0.2
0.4
0.6
0.8
1.0
GaAs$_{1-x}$N$_x$ COMPOSITION (x)
30
32
34
36
38
40
42
44

FIG._4

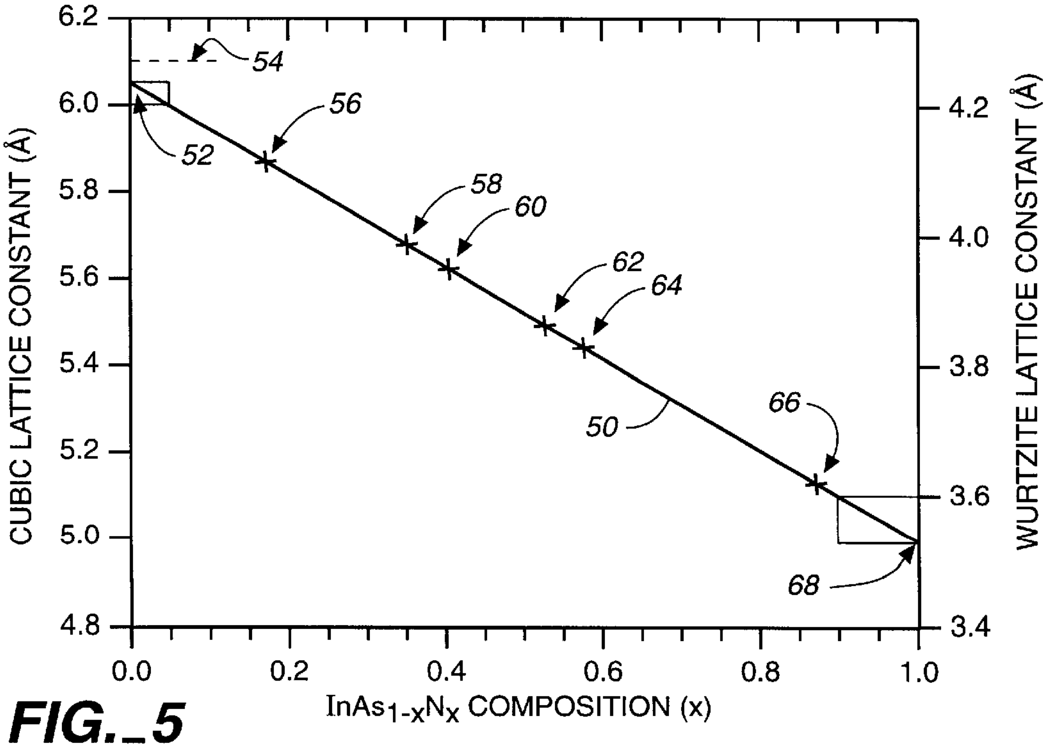

6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
CUBIC LATTICE CONSTANT (Å)
4.2
4.0
3.8
3.6
3.4
WURTZITE LATTICE CONSTANT (Å)
0.0
0.2
0.4
0.6
0.8
1.0
InAs$_{1-x}$N$_x$ COMPOSITION (x)
50
52
54
56
58
60
62
64
66
68

FIG._5

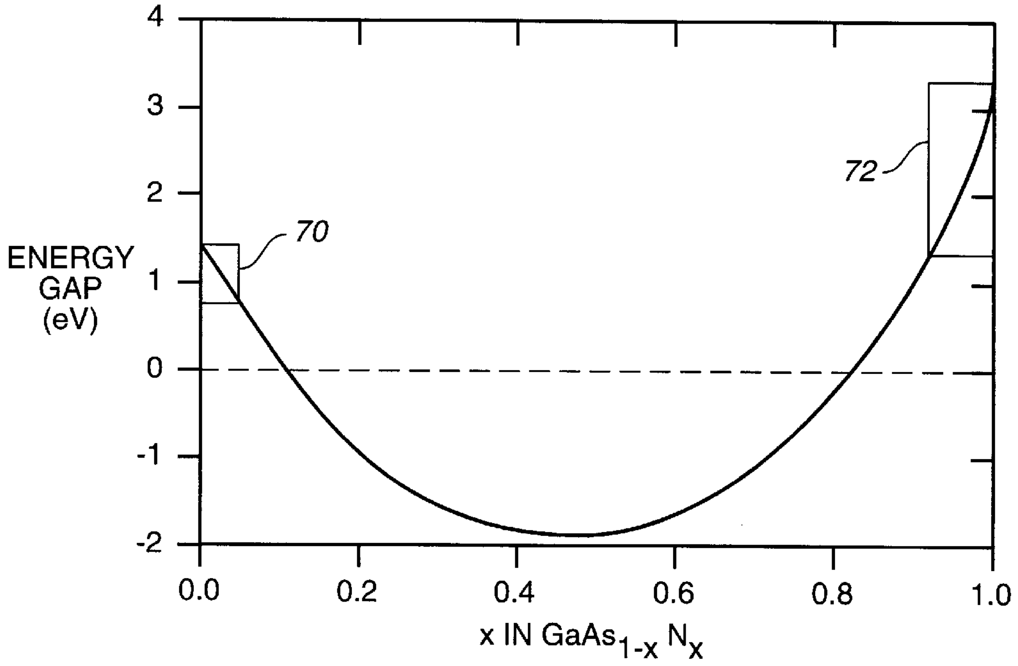

4
3
2
1
0
-1
-2
ENERGY GAP (eV)
70
72
0.0
0.2
0.4
0.6
0.8
1.0
x IN $GaAs_{1-x}N_x$

FIG._6

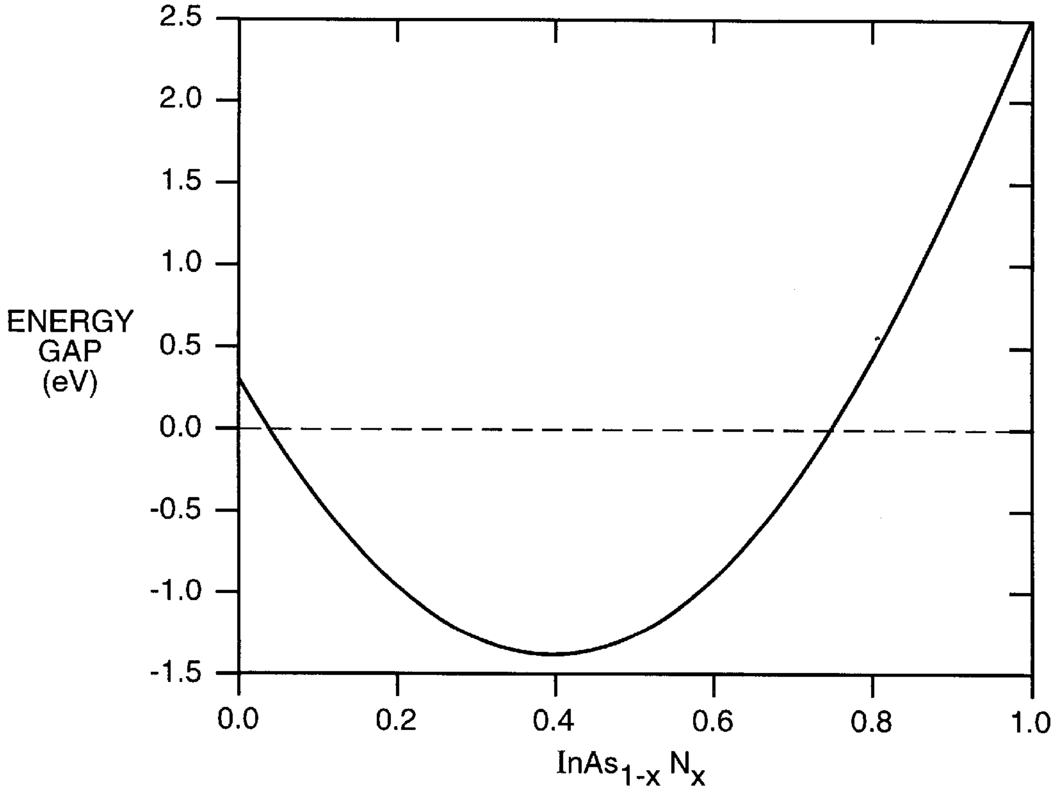

2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
ENERGY GAP (eV)
0.0
0.2
0.4
0.6
0.8
1.0
$InAs_{1-x}N_x$

FIG._7

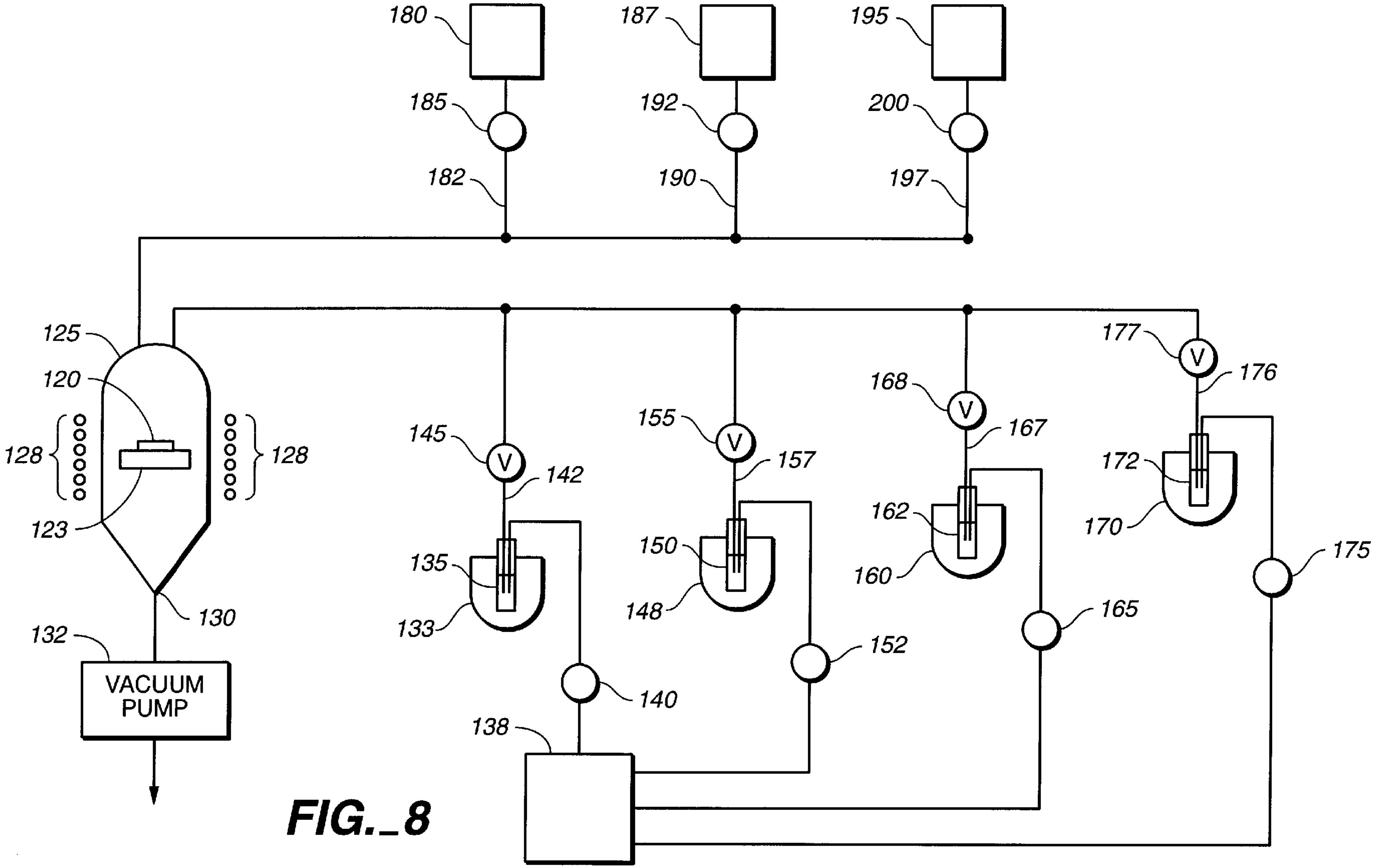

180
187
195
185
192
200
182
190
197
125
120
128
128
123
130
132
VACUUM PUMP
145
142
135
133
140
138
155
157
150
148
152
168
167
162
160
165
177
176
172
170
175

FIG._8

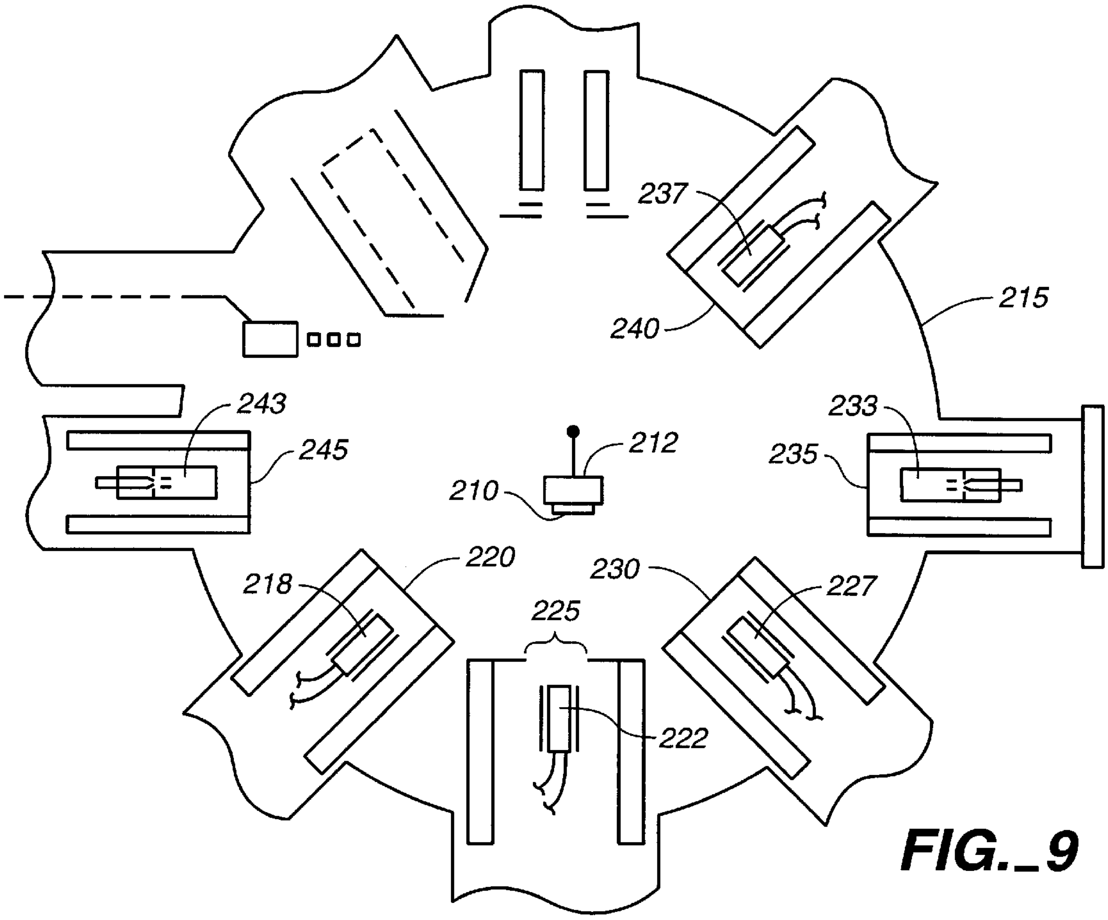
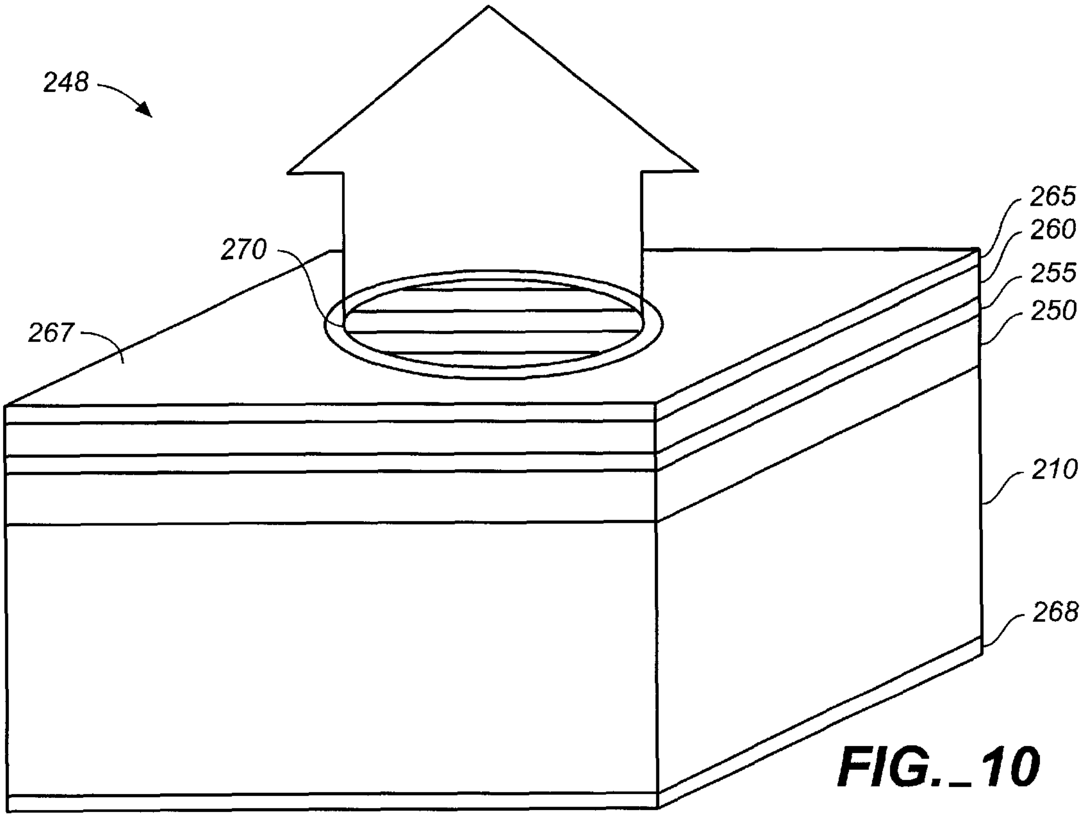
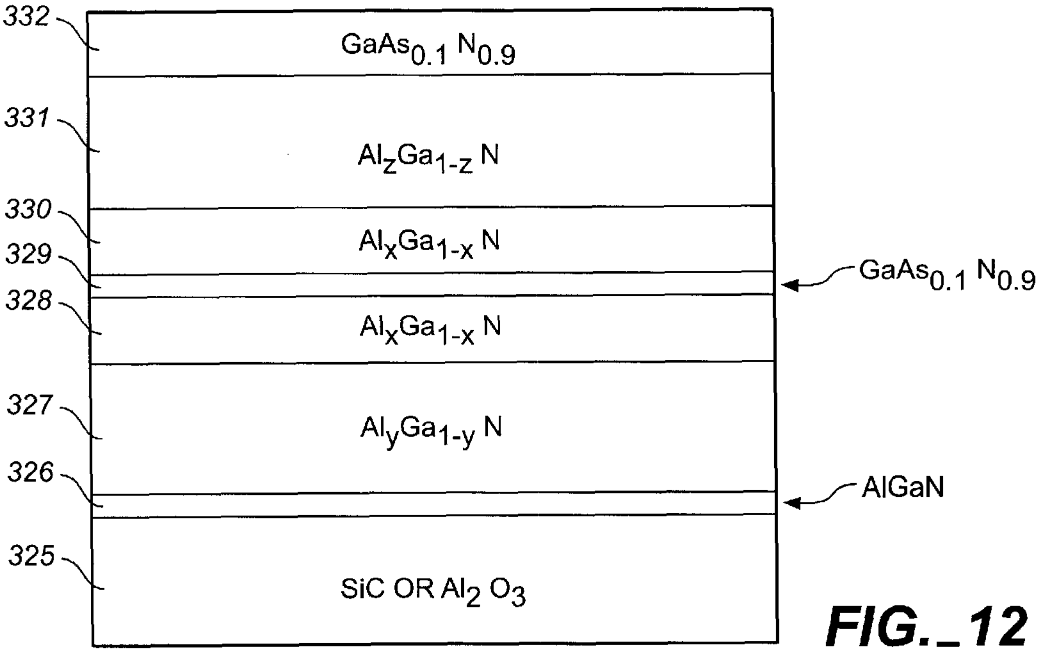


FIG._9



248
270
267
265
260
255
250
210
268

FIG._10



332
$GaAs_{0.1} N_{0.9}$
331
$Al_zGa_{1-z} N$
330
$Al_xGa_{1-x} N$
329
$GaAs_{0.1} N_{0.9}$
328
$Al_xGa_{1-x} N$
327
$Al_yGa_{1-y} N$
326
AlGaN
325
SiC OR $Al_2 O_3$

FIG._12

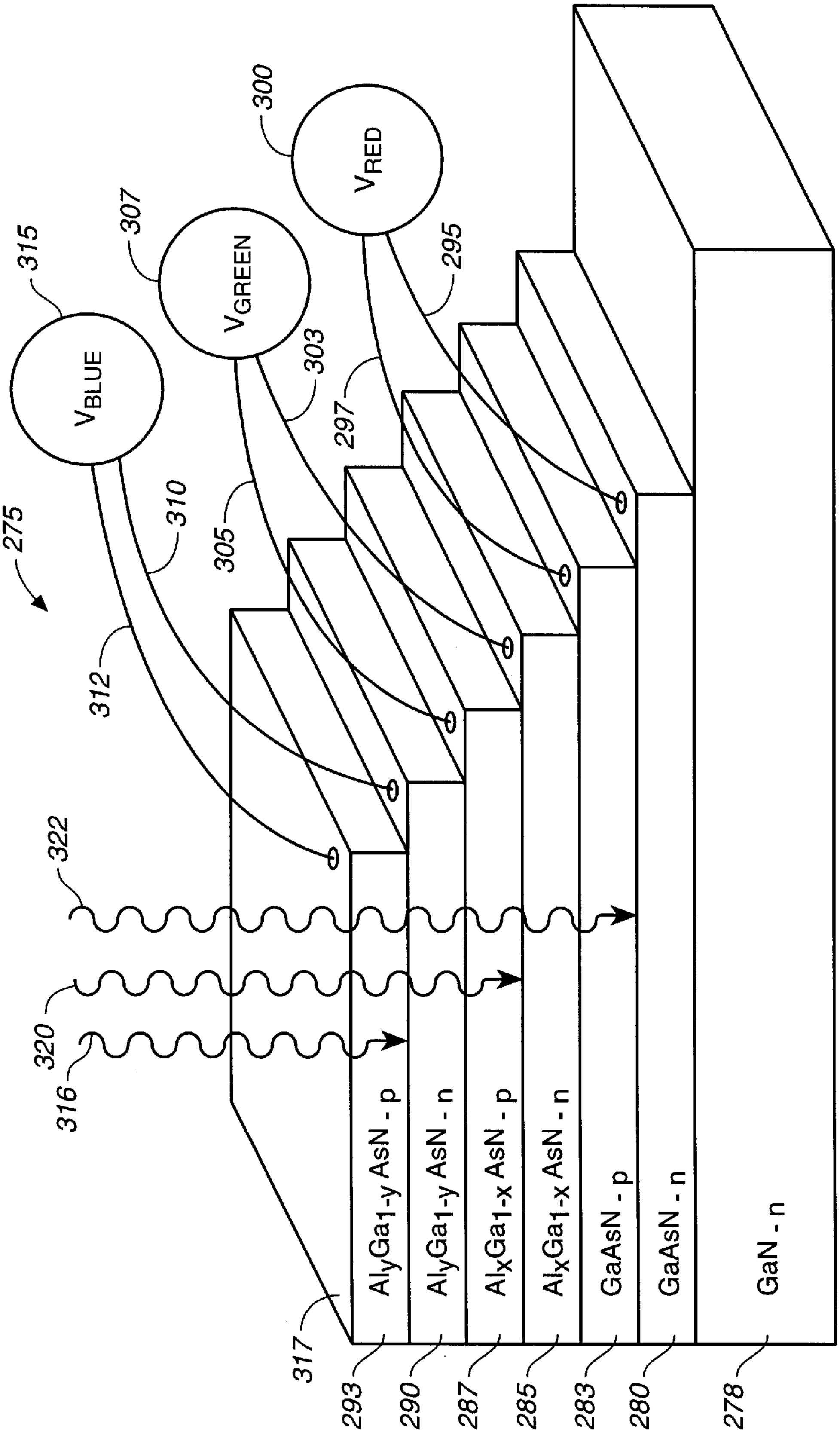

275
315
V_{BLUE}
307
V_{GREEN}
300
V_{RED}
295
297
303
305
310
312
322
320
316
317
$Al_yGa_{1-y}AsN$ - p
$Al_yGa_{1-y}AsN$ - n
$Al_xGa_{1-x}AsN$ - p
$Al_xGa_{1-x}AsN$ - n
GaAsN - p
GaAsN - n
GaN - n
293
290
287
285
283
280
278

FIG._11

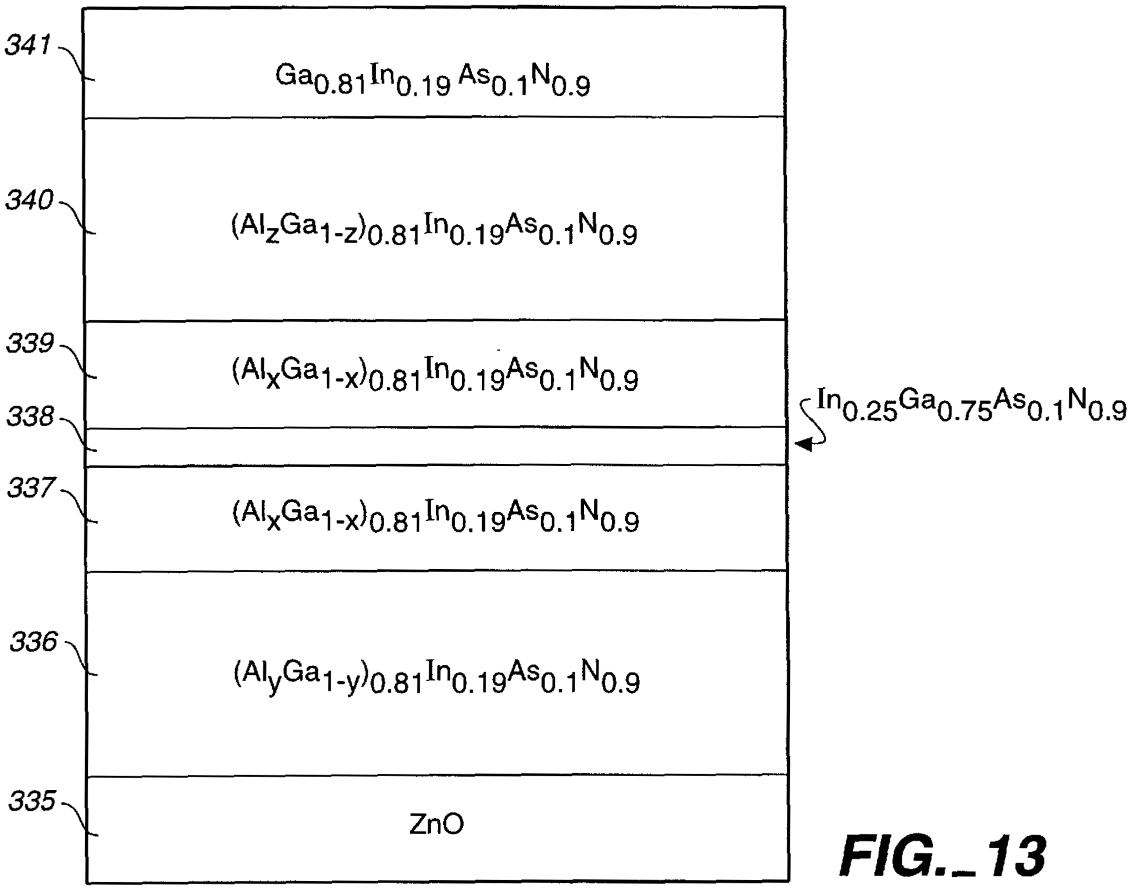

341
$Ga_{0.81}In_{0.19}As_{0.1}N_{0.9}$
340
$(Al_zGa_{1-z})_{0.81}In_{0.19}As_{0.1}N_{0.9}$
339
$(Al_xGa_{1-x})_{0.81}In_{0.19}As_{0.1}N_{0.9}$
338
$In_{0.25}Ga_{0.75}As_{0.1}N_{0.9}$
337
$(Al_xGa_{1-x})_{0.81}In_{0.19}As_{0.1}N_{0.9}$
336
$(Al_yGa_{1-y})_{0.81}In_{0.19}As_{0.1}N_{0.9}$
335
ZnO

FIG._13

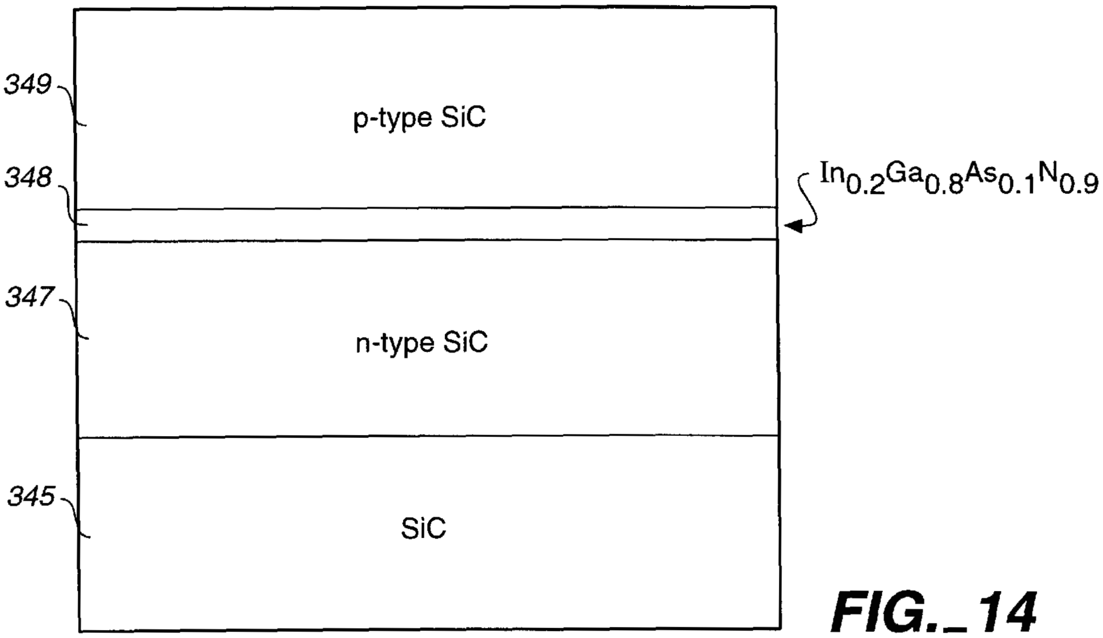

349
p-type SiC
348
$In_{0.2}Ga_{0.8}As_{0.1}N_{0.9}$
347
n-type SiC
345
SiC

FIG._14

METHODS FOR FORMING GROUP III-ARSENIDE-NITRIDE SEMICONDUCTOR MATERIALS

CROSS-REFERENCE TO RELATED APPLICATION

This application is divisional application of patent application, Ser. No. 08/908,766 filed Dec. 7, 1997, now U.S. Pat. No. 6,100,546 which is a continuation of patent application Ser. No. 08/724,321, filed Oct. 1, 1996 now U.S. Pat. No. 5,689,123, issued Nov. 18, 1997, which is a continuation of U.S. patent application Ser. No. 08/373,362, filed Jan. 17, 1995, now abandoned, which is a continuation-in-part of Ser. No. 08/224,027 filed Apr. 7, 1994, now abandoned.

STATEMENT AS TO RIGHTS TO INVENTIONS MADE UNDER FEDERALLY-SPONSORED RESEARCH AND DEVELOPMENT

This invention was made with government support under Contract No. NAS5-32442 awarded by the National Aeronautics and Space Administration (NASA) and under Contract No. N00014-93-C-0130 awarded by the Department of the Navy. The government has certain rights in the invention.

TECHNICAL FIELD

The present invention relates to methods for forming monocrystalline III-V arsenide-nitride semiconductor materials, especially those materials having a high bandgap (greater than 2.0 eV). More particularly it relates to direct bandgap light emitting materials, preferably those with cubic crystal lattices, which can be used to make devices such as semiconductor lasers that emit light with frequencies in a range that more than span the visible spectra.

BACKGROUND ART

Semiconductor lasers that emit light in the long wavelength visible (red) and near infrared spectra have been known for many years. To date, however, it has been difficult to produce such lasers that emit light in the short wavelength, blue region of the visible spectra. A wide variety of applications await such "blue" lasers, should they become commercially available.

Certain II-VI semiconductor compounds such as zinc selenide sulphide (ZnSeS) have been considered promising candidates for blue lasers. In an article entitled "Blue-green laser diodes", *Applied Physics Letters,* v. 59, Sep. 9, 1991, M. A. Haase et al. describe achieving lasing action at a wavelength of 490 nm with a ZnSe based structure under pulsed current injection at 77 K. More recent advances in this material system using a remote plasma source for the introduction of radical nitrogen (N) atoms have resulted in the demonstration of pulsed laser operation at room temperature at a wavelength of 480 nm.

The ZnSeS based structures have several limitations, however, due to conduction band alignment and the activation energy of defects. The confinement energy of the cladding layers limits efficient operation of the ZnSeS system to a wavelength of 530 nm, as the electron confinement is too small for efficient operation of laser diodes at 480 nm or shorter wavelengths. The low activation energy of defects in the crystal lattice of such a material limits the processing and growth temperature of the structure to no more than a few hundred degrees Celsius.

The ZnSeS materials are further complicated by the problems associated with growth on a gallium arsenide (GaAs) substrate. The interface between the ZnSeS and GaAs results in a cross doping of the compounds. The Ga and As act as dopants in the ZnSeS and the Zn, Se and S act as dopants in the GaAs. As a result the interface between the two compounds becomes quite resistive. Laser diodes fabricated with this interface require operating voltages in excess of 20 V. The heat dissipated from this is also high, preventing continuous wave (CW) operation at room temperature.

An alternative to the II-VI compounds for blue light emission are the III-V semiconductor compounds, such as AlGaInN. The advantages of the III-V material systems are several. First, they include materials having large direct bandgaps ranging from 2 eV to 6 eV. Second, large energy differences between the valleys of the lowest direct bandgaps and those of the lowest indirect bandgaps exist. Third, electrons and holes can be satisfactorily confined in heterostructures, including quantum well structures, due to large confinement energies. Fourth, production of these materials is compatible with metal organic chemical vapor deposition (MOCVD) growth reactors. Fifth, the materials typically have low resistance to n-type and p-type doping. Finally, the III-V materials can avoid the cross doping and defect creation and propagation problems that plague the II-VI materials.

AlGaInN materials have so far been grown only on mismatched substrates such as Si, SiC, single crystal Al_2O_3 and MgO. Mismatched crystal lattices tend to have defects that absorb light, lowering the efficiency of light generation and reducing lasing potential. Defects also tend to propagate through crystals, lowering the useful life of the crystals.

Another difficulty is that AlGaInN type materials typically have a native wurtzite, or generally hexagonal, crystal lattice, which has few convenient cleavage planes to form mirrored facets for Fabry-Perot reflection and which cannot be easily grown to exactly layered depths for quantum wells or other cladding confined structures. For laser diodes, it is desirable that the heterostructure material have a generally cubic zinc-blende crystal lattice. While in AlGaInN materials the cubic structure is metastable at typical production temperatures, and thus not impossible to form in principle, to actually produce such a cubic crystal lattice material by epitaxial growth techniques appears to require a substrate that is not only lattice matched to the AlGaInN type material but also has a cubic lattice that induces the growth of a cubic substrate lattice of the AlGaInN type material layers. Substrates which have commonly been used for group III-V high bandgap semiconductors, such as basal plane $\{0001\}$ sapphire (Al_2O_3) and α-SiC, have the disadvantage of producing the less desirable wurtzite crystal lattice structure.

In U.S. Pat. No. 5,146,465, Kahn et al. describe growing layers of AlGaN with alternating concentrations of Al and Ga on an AlN buffer layer which, in turn, was grown on an Al_2O_3 substrate. Kahn et al. appear to overcome some of the difficulties inherent in the wurtzite lattice by polishing walls of the device and adding mirrors. However, cleaved facets, when available, are inherently better mirror surfaces than etched or polished surfaces because of their lower defect density. In U.S. Pat. Nos. 5,173,751 and 5,274,251, Ota et al. take advantage of the lattice constant of α-ZnO, which falls between that of several III-V nitride materials, allowing mixing of those materials in proportions calculated to match the substrate lattice of ZnO, to form AlGaInN or AlGaNP layers. The resultant crystal lattice appears to be wurtzite in form.

In U.S. Pat. No. 4,862,471, Pankove describes the growth on a gallium phosphide (GaP) substrate of gallium nitride (GaN). Indium nitride (InN) or aluminum nitride (AlN) layers are similarly grown to form a quantum well light emitting device. Similarly, U.S. Pat. No. 5,076,860 to Ohba et al. teaches a compound semiconductor material of GaAlBNP with a zincblende (cubic) crystal lattice, grown on a GaP substrate. Ohba et al. describe several different materials, including a GaAlN semiconductor grown on a BP substrate and the growth of group III-V materials having ordered bonds but non-lattice matched crystals. U.S. Pat. No. 5,042,043 to Hatano et al. describes a semiconductor laser formed from alternately stacking BP and GaAlN layers to form $Ga_xAl_yB_{1-x-y}N_zP_{1-z}$ material on a GaP substrate. In all of these cases, the use of GaP as a substrate results in a severe lattice mismatch with the nitride material layers (about 20% mismatch for GaN). In an article entitled "High-Efficiency Aluminum Indium Gallium Phosphide Light-Emitting Diodes," Hewlett-Packard Journal, August 1993, pp. 6–14, R. M. Fletcher et al. describe gallium arsenide phosphide doped with nitrogen (GaAsP:N) and gallium phosphide doped with nitrogen (GaP:N).

In an article entitled "Luminescence quenching and the formation of the $GaP_{1-x}N_x$ alloy in GaP with increasing nitrogen content", *Applied Physics Letters,* Vol. 60, No. 20, May 18, 1992, pp. 2540–2542, J. N. Baillargeon et al. teach N doping in GaP of up to 7.6% using molecular beam epitaxy (MBE), and note that increasing nitrogen content tends to shift emission spectra lower above a certain nitrogen concentration. Similarly, X. Liu et al. describe observing a red shift in emission spectra from GaP:N as nitrogen (N) concentration is increased in "Band gap Bowing in $GaP_{1-x}N_x$ alloys", *Applied Physics Letters,* Vol. 63, No. 2, Jul. 12, 1993, pp. 206–210. Difficulties are encountered when mixed compounds having significant amounts of both nitrogen and other group V elements are attempted. Miyoshi et al. describe a miscibility gap for growth of $GaP_{1-x}N_x$ for $x \geqq 0.04$ in an article entitled "Metalorganic vapor phase epitaxy of $GaP_{1-x}N_x$ alloys on GaP", *Applied Physics Letters,* Vol. 63, No. 25, Dec. 20, 1993, pp. 3506–3508.

Of primary concern to reliable visible laser diode operation is the optimization of the substrate and growth buffer layers. To form a semiconductor material having desirable lacing properties, it is advantageous to grow such a material on a lattice matched substrate in order to avoid the promulgation of defects that absorb light. It is also desirable, whenever possible, that the substrate promote growth in the semiconductor material of a cubic crystal lattice that facilitates the relatively easy formation of cleaved reflective facets for defining resonant laser cavities.

SUMMARY OF THE INVENTION

The present invention involves formation of monocrystalline III-V compound semiconductor materials having at least nitrogen and arsenic at group V lattice sites of the crystal material. Other group V elements, such as phosphorus and antimony, can also be present at group V lattice sites in addition to the nitrogen and arsenic. The group III atomic species can be any combination of boron, aluminum, gallium and indium.

The exact composition of a particular material to be produced, that is, the relative concentration of each of the group III and group V elements in the III-V compound, is generally selected so as to substantially lattice match with the selected substrate's growing surface. Some lattice strain due to lattice mismatch greater that 1% can be accommodated provided the mismatched layer is sufficiently thin to avoid formation of lattice defects. In addition, for light emitting devices, such as laser diodes and LEDs, the desired emission wavelength determines the required semiconductor bandgap for the material and hence plays a major role in the choice of material composition and of a suitable substrate. For emission wavelengths shorter than about 620 nm, a bandgap greater the 2 eV is required. The III-V compound arsenide-nitride materials of the present invention are characterized by a large bandgap bowing parameter which must be taken into account when matching up the desired semiconductor bandgap with a possible material composition. $GaAs_xN_{1-x}$ material, where $x \leqq 0.10$, has a bandgap greater than 2.0 eV. Laser diodes further require that the selected material be a direct bandgap material, that is, one where the energy of the lowest direct bandgap is below that of the lowest indirect bandgap, while LEDs are capable of operating using either direct or indirect bandgap materials. The $GaAs_xN_{1-x}$ noted above is a direct bandgap material. The addition of other group III and group V elements, such as boron, aluminum, indium, phosphorus and indium, to the basic GaAsN composition allows somewhat independent adjustment of the lattice constant and bandgap, allowing different materials with different emission wavelengths to be lattice matched to the same substrate. For LIDAR systems, laser diodes using strained $InGaAs_{1-y}N_y$ active regions, where $y \leqq 0.04$, can produce light emissions in the 2.0 μm to 2.5 μm range. It is also possible to produce electronic devices, such as transistors, which are capable of high temperature operation, using the high bandgap semiconductor material of the present invention.

The monocrystalline material of the present invention if formed by epitaxial growth on a monocrystalline substrate. Depending on the choice of substrate material and the orientation of the substrate's crystal lattice with respect to the substrate's surface, that is, the choice of crystal lattice plane for the growing surface, the resulting III-V compound arsenide-nitride material layers may have either a cubic zincblende crystal structure or a hexagonal wurtzite crystal structure. InGaAlAs materials have a native zincblende structure, but with the appropriate choice of substrate can be induced to grow in the metastable wurtzite structure. InGaAsAlN materials, on the other hand, have a native wurtzite structure, but with the appropriate choice of substrate can be induced to grow in the metastable zincblende structure. Substrates can be selected from the group consisting of Al_2O_3 (sapphire) using either basal plane or r-plane growing surfaces, diamond, Si, Ge, SiC in both wurtzite (α) and zincblende (β) forms, InN, GaP, GaAsP, GaAs, InP, ZnO, ZnS, and ZnSe.

The arsenide-nitride materials of the present invention generally favor growth of cubic zincblende crystal structures when arsenic is the majority component in the group V lattice sites, up to about 4 or 5 percent nitrogen and favor growth of hexagonal wurtzite crystal structures when nitrogen is the majority component in the group V lattice sites, up to about 20 percent arsenic. When growth techniques, such as metalorganic chemical vapor deposition (MOCVD), are used to attempt growth of material with between 5 and 90 percent nitrogen, mixed polycrystalline layers with both zincblende and wurtzite crystals result. This immiscible region for the arsenide-nitride material of the present invention necessitates the use of growth techniques further away from thermodynamic equilibrium, such as atomic layer epitaxy, to obtain defect-free monocrystalline material with the required composition.

It has been found that lowering the growth rate of the AlGaAsN semiconductor material allows a greater concentration of N to be incorporated in the crystal. It is possible to increase the availability of N for incorporation by epitaxial growth using low-pressure metal organic vapor deposition (LP-MOCVD) utilizing N sources including hydrazine, phenol-hydrazine and metal-organic N sources. Ammonia (NH_3) may be employed as an N source with catalysts such as arsine and phosphine used to increase the cracking efficiency of NH_3. Alternatively, the N source can be pre-cracked. For example, in molecular beam epitaxy (MBE) an electron cyclotron resonator can be used to crack the NH_3 molecule, resulting in a radical N. Plasma deposition systems can also be used to increase the cracking efficiencies of NH_3.

It is possible to obtain the correct concentration of N relative to As by atomic layer epitaxy, a sequenced layering technique in which the growth monolayers containing N is interspersed with the growth of other monolayers containing As. The monolayers are thin enough to avoid defects due to mismatched lattices, as differing lattice constants between the monolayers tend to compensate for each other to produce a desired lattice match. For instance, five monolayers of GaAs can be grown for every monolayer of GaN, resulting in an overall Group V lattice site N concentration of approximately 17% and As concentration of about 83%. It is similarly possible to provide the relative concentrations of Al compared to Ga with such layering. Thus, for example, having two monolayers of Ga interspersed with four layers of Al results in a Ga concentration of approximately 33% and an Al concentration of approximately 67%. This process can be continued to form, for example, alternating quarter wavelength (115 nm) optically reflective layers or quantum wells formed of layers on the order of the electron wavelengths (5 nm) and other heterostructure lasing devices for which the exact depth of the layers is important.

The previous discussion has centered upon the growth techniques for alloys with N as the minority element on the Group V sublattice. Similar growth technology may be employed to grow alloys where N is the majority element on the Group V sublattice. However, the growth conditions themselves must be changed. Experiments have shown that the solubility of As in GaN is significantly greater than the solubility of N in GaAs; transmission electron microscopy has shown greater than 10% incorporation of As in GaN grown by conventional LP-MOCVD. Thus, for alloys with As content equal to or less than 10% MOCVD, either atmospheric or low-pressure, growth can be used with the ratio between N and As in the gas phase adjusted to provide the required As content. For alloy compositions greater than 10% As, multiple layer growth, as previously outlined, will be employed. For example, the layer structure required for the case of 10% As would employ nine layers of GaN, followed by a single layer of GaAs, etc.

Such materials can be used in a variety of applications. Semiconductor lasers and diodes can be created that emit light of frequencies that more than span the visible spectra, from infrared to ultraviolet. Conversely, photodetectors and solar detectors can be fashioned that utilize the wide range of available bandgaps to collect light of all colors. High temperature transistors, diode rectifiers and other electronic devices can also be produced using the high direct bandgap materials lattice matched to Si, SiC or GaP.

Thus, active layers of the direct bandgap material GaAsN, when used with cladding layers of GaN, AlGaN or AlGaAsN in a diode heterostructure, are prime candidates for optical emission which can be placed under biaxial compressive strain, a visible analog to the InGaAs strained layer technology currently employed in the AlGaAs material system for diode lasers or LED's. At a border between two of the semiconductor materials, a p-n junction is formed by doping the respective materials with p-type and n-type dopants. Introducing dopants, both acceptors, such as C, Mg, and Zn, and donors, such as Si, Se, or Ge, into the GaAsN can be used to fabricate p-type and n-type doping, respectively. A cubic crystal lattice provides for easy formation of cleaved mirror and waveguide structures that feedback the emitted light to cause laser amplification. The resulting devices can efficiently emit coherent light spanning the visible spectra, including the blue region.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a graph of the bandgap and lattice constant of AlGaInAs cubic crystals superposed with the lattice constant of some common substrates.

FIG. **2** is a graph of the bandgap and lattice constant of AlGaInN wurtzite crystals superposed with the lattice constant of some common substrates.

FIG. **3** is a table of tetrahedral covalent radii of group III and group V elements used to estimate nearest neighbor bond lengths in the crystal lattices of materials of the present invention.

FIG. **4** is a graph of the cubic and wurtzite lattice constants of $GaAs_xN_{1-x}$ for various concentrations (x) of N superposed with the lattice constants of various substrates.

FIG. **5** is a graph of the cubic and wurtzite lattice constants of $InAs_xN_{1-x}$ for various concentrations (x) of N superposed with the lattice constants of various substrates.

FIG. **6** is a graph of the lowest direct bandgap of $GaAs_{1-x}N_x$ for various concentrations (x) of nitrogen.

FIG. **7** is a graph of the lowest direct bandgap of $InAs_{1-x}N_x$ for various concentrations (x) of nitrogen.

FIG. **8** is a diagram of a LP-MOCVD apparatus used for manufacturing materials and devices of the present invention.

FIG. **9** is a diagram of an MBE apparatus used for manufacturing materials and devices of the present invention.

FIG. **10** is a perspective view of a light emitting device of the present invention.

FIG. **11** is a cutaway perspective view of a light receiving device of the present invention.

FIG. **12** is a side view of an AlGaAsN heterostructure of the present invention matched to an SiC or Al_2O_3 substrate.

FIG. **13** is a side view of an AlGaInAsN heterostructure of the present invention matched to a ZnO substrate.

FIG. **14** is a side view of an LED with an active region made from material of the present invention sandwiched between SiC layers.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

With reference to FIG. **1**, the lattice constants and bandgap of AlGaInAs semiconductor materials are plotted along with the lattice constants of several common substrate materials. The points **10**, **12** and **14** represent the binary compounds AlAs, GaAs and InAs, respectively, while the lines connecting these points represent the various ternary compounds AlGaAs, AlInAs and GaInAs and the triangular region enclosed by those lines represent the quaternary compounds AlGaInAs with various proportions of Al, Ga and In. All of these materials have a native cubic zincblende crystal structure. AlAs has a large bandgap of about 2.2 eV and a cubic lattice constant of about 5.66 Å. However, the binary compound AlAs, represented by point **10**, as well as the ternary and quaternary compounds with a large proportion of aluminum, in the region near point **10**, are indirect bandgap materials. GaAs has a direct bandgap of about 1.4 eV and a cubic lattice constant of about 5.65 Å. Thus, AlAs and GaAs are structural isomorphs, allowing free substitution of aluminum and gallium in solid solution without any significant change in the lattice constant. InAs is also a direct bandgap material with a bandgap energy of about 0.4 eV, but with a substantially larger lattice constant of about 6.06 Å. The introduction of indium can be used to produce strain so as to alter the bond structure in a layer and its neighboring layers of a heterostructure, most notably affecting the heavy hole valence bond in a way that can reduce laser threshold and improve operating efficiency of a laser diode.

The lattice constants of several common substrates are also seen in FIG. **1**. The dashed line **16** represents both silicon and GaP substrates. Silicon has a diamond-type (cubic) crystal structure with a lattice constant of about 5.43 Å, while GaP has a zincblende (also cubic) crystal structure with a lattice constant of about 5.45 Å. Both of these substrates have a smaller crystal lattice than AlAs and GaAs, with a lattice mis-match of about 4%. These substrates have been used to grow AlGaAsP layers (although such compounds are indirect bandgap materials for large proportions of either aluminum or phosphorus), but attempts to grow AlGaAs layers on silicon or GaP have generally been unsuccessful, with the mismatch-strain causing unacceptable defect concentrations in the resulting material. The dashed line **17** represents both germanium and GaAs. As noted previously, GaAs has a lattice constant of about 5.65 Å making it an ideal substrate for AlGaAs materials, as well as AlGaInP, AlGaAsP and InGaAs material layers. Germanium, like silicon, has a diamond-type structure, and also has a cubic lattice constant of about 5.66 Å, nearly identical to GaAs. The dashed line **18** represents InP. It has a zincblende structure with a lattice constant of about 5.87 Å and is commonly used as a substrate for long emission wavelength materials (with emissions longer than 1100 nm) with a large proportion of indium, such as InGaAs and InGaAsP. Due to its relatively large lattice, InP is considered to be a potential substrate only for the mid-IR and far-IR emitting InAs1−xNx and $InSb_yAs1_{-x-y}\,N_x$ ($x \leqq 0.05$) materials of the present invention, the other arsenide-nitride materials of the present invention having too small a lattice for an InP substrate.

FIG. **2** shows another plot corresponding to FIG. **1**, but for AlGaInN semiconductor materials. These nitride materials have a native hexagonal wurtzite crystal structure, but can also be induced to grow in a metastable cubic zincblende crystal structure with a suitable choice of substrate material and growth surface. That is, growth of a zincblende structure is generally favored on the [001] surface of a cubic substrate, while the active wurtzite structure generally results from growth on the [0001] surface of a hexagonal substrate or on the [111] surface of a cubic substrate. In the case of rhombohedral Al_2O_3 (sapphire) substrates, growth of a wurtzite structure is favored when the basal plane surface is used, while growth of a zincblende structure is favored when the r-plane surface is used. The plot in FIG. **2** assumes wurtzite growth for these materials, and so the corresponding wurtzite lattice constants are used.

The points **20**, **22** and **24** represent the binary compounds AlN, GaN and InN, respectively, while the lines connecting those points represent the various ternary compounds AlGaN, AlInN and GaInN and the triangular region enclosed by those lines represent the quaternary compounds AlGaInN with various proportions of Al, Ga and In. It can be seen that AlN has a very high bandgap of about 6.0 eV and a relatively small lattice constant of about 3.11 Å. GaN can be seen to have a lower bandgap of about 3.4 eV and a slightly larger lattice constant of about 3.19 Å. InN has a still lower bandgap of about 2.0 eV and a considerably larger lattice constant of about 3.53 Å.

Superposed on the plot of FIG. **2** are the lattice constants of some common substrates. The dashed line **26** represents α-SiC, which has a lattice constant of about 3.08 Å, less than the lattice constant of any AlGaInN compound. The lattice mismatch with this substrate is about 1% for AlN and about 3.5% for GaN, and so α-SiC is a useful substrate for growing AlGaN layers, but less suitable for most of the arsenide-nitride materials of the present invention, since the lattice mismatch becomes worse as arsenic is incorporated into the lattice. However, the substrate could be used in AlGaN heterostructures that include AlGaAsN or GaAsN strained quantum wells. The dashed line **27** represents α-ZnO. (SiC and ZnO have both wurtzite (α) and zincblende (β) forms, although the α-form is more common.) It can be seen that α-ZnO has a lattice constant of about 3.25 Å, which nearly matches GaN (with a mismatch of only 1.9%) and which corresponds to a wide range of AlGaInN compounds, as seen by the dashed line **27** intersecting the triangular region. α-ZnO is thus a promising substrate. Its use has been limited so far by the relatively poor quality of available ZnO crystals, but the quality is expected to improve. The dashed line **28** represents basal plane sapphire (Al_2O_3) substrates. The basal plane growing surface of the rhombohedral Al_2O_3 substrate has an equivalent wurtzite lattice constant of about 3.62 Å, which can be seen to be larger than any AlGaInN material. However, sapphire substrates are considered promising for the arsenide-nitride semiconductor compounds of the present invention, since the lattice size increases as arsenic is added.

Because the arsenide-nitride materials of the present invention can have either a zincblende structure or a wurtzite structure, with the zincblende structure being the native crystal phase for those compounds with arsenic as the majority element and nitrogen as a minority element at the group V lattice sites, and with the wurtzite structure being the native crystal phase for those compounds with nitrogen as the majority element and arsenic as a minority element at the group V lattice sites of the crystal, it is more convenient to use nearest neighbor bond length rather than lattice constant in order to select suitable substrate materials and to determine the approximate compositions of materials which substantially match the crystal lattice at the growing surface of the selected substrate.

For this purpose, the method of tetrahedral covalent bonding radii of Pauling is used to estimate the nearest neighbor bond length. This method is applicable for tetrahedrally bonded semiconductors with bonds of a primarily covalent nature, as is the case for the wurtzite and zincblende-type III-V compound semiconductors of the present invention, as well as diamond-type (cubic) group IV semiconductor substrates, such as silicon and germanium, and both wurtzite and zincblende-type II-VI and IV—IV compound semiconductor substrates, such as ZnO and SiC. The set of values used for this composition is given in FIG. **3** for the group III and group V elements in the materials of the present invention. For example, the approximate nearest neighbor bond lengths for GaN and GaAs are 1.96 Å and 2.44 Å, respectively, determined by adding the corresponding pair of radii obtained from FIG. **3**.

The cubic zincblende (a_c) and hexagonal wurtzite (a_h) lattice constants are related to the bond length (l) by the relations $a_c=\frac{4}{3}\sqrt{3}1$: and $a_h=\frac{2}{3}\sqrt{6}1$. A comparison of the estimated bond lengths derived from the table with the actual lattice constants for the various binary compounds shows that, although the method tends to underestimate the bond lengths and corresponding lattice constants for heavier compounds and tends to overestimate them for the lighter compounds, none of the estimated values differ by more than 3% from the actual values and most are within 1% of the actual values. In addition to the values calculable from the table in FIG. **3**, the following substrates have equivalent bond lengths: diamond 1.54 Å, SiC 1.88 Å, ZnO 1.99 Å, basal plane sapphire 2.22 Å, ZnS 2.34 Å, Si 2.35 Å, Ge 2.45 Å and ZnSe 2.45 Å.

The bond lengths are used to calculate approximate compositions of materials that lattice match with a particular substrate. For example, using the previously estimated lengths for GaN and GaAs, and estimating the bond length for a GaP substrate as 2.36 Å, we find that a ternary composition of $GaAs_{0.83}N_{0.17}$ has a bond length of 0.17 (1.96 Å)+0.83 (2.44 Å)=2.36 Å, that substantially lattice matches with GaP. The calculated values may be confirmed by growing a sample of the determined material on the selector substrate, and then, using known techniques, measuring the actual lattice constants of the material. Any deviations from the estimated value can then be ascertained and used to make slight modifications to the approximate composition calculated by the bond length method.

FIGS. **4** and **5** provide graphic illustration of the lattice matching of $GaAs_{1-x}N_x$ and $InAs_{1-x}N_x$ to some common substrates for various concentrations (x) of nitrogen. As seen in FIG. **4**, the lattice constant of $GaAs_{1-x}N_x$, shown by line **30**, decreases as the nitrogen concentration increases, since nitrogen is a smaller element than arsenic. The cubic lattice constant for GaAs (x=0.0) is about 5.65 Å and the wurtzite lattice constant for GaN (x=1.0) is about 3.19 Å. The marked locations on the line **30** represent the lattice constants for various substrates, including Ge or GaAs 32, GaP 34, Si 36, Al_2O_3 38, InN 40, and ZnO 42. The dashed line **44** represents the lattice constant for SiC, which can be seen to be smaller than any of the $GaAs_{1-x}N_x$ materials. The boxed areas represent the approximate nitrogen concentrations which are accessible by means of equilibrium growth techniques, such as MOCVD, namely $x \leqq 0.05$ and $x \geqq 0.90$, while the portion of the line **30** between the boxed regions represent the MOCVD immiscible region, approximately $0.05<x<0.90$, which require a nonequilibrium growth technique, such as the atomic layer epitaxy technique described below. It can be seen that for low nitrogen concentrations ($x \leqq 0.05$), GaAs is the ideal substrate, indicated by reference numeral **32** on the graph, while for very high nitrogen concentrations ($x \geqq 0.90$), ZnO is a likely choice of substrate, indicated by reference numeral **42** on the graph, as is pure bulk GaN (x=1.0) and possibly even SiC (dashed line **44**).

In FIG. **5**, it can be seen that the lattice constant of $InAs_{1-x}N_x$, shown by line **50**, also decreases as the nitrogen concentration (x) increases. The cubic lattice constant for InAs (x=0.0) is about 6.06 Å and the wurtzite lattice constant for InN (x=1.0) is about 3.53 Å. Again the marked locations on the line **50** represent the lattice constants for various substrates, including InAs 52, InP 56, ZnSe 58, Ge or GaAs 60, GaP 62, Si 64, Al_2O_3 66 and InN 68. The dashed line **54** represents the lattice constant for GaSb, which can be seen to be larger than any of the $InAs_{1-x}N_x$ materials. Quaternary GaInAsN compounds would have lattice constants between those of $GaAs_{1-x}N_x$ of FIG. **4** and $InAs_{1-x}N_x$ of FIG. **5**, and would allow InP or ZnSe to be used as substrate materials for low nitrogen concentrations ($x \leqq 0.05$) in the MOCVD miscible region.

Further, the introduction of other group III and group V elements, including boron, aluminum, phosphorus and antimony, allows achieving a lattice match to silicon (with $Al_xGa_{1-x}P_{0.852}As_{0.108}N_{0.04}$, for example) and other substrates without having to resort to atomic layer epitaxy, since the proportions of arsenic and nitrogen can then be made compatible with standard LP-MOCVD or atmospheric pressure MOCVD growth techniques. Note, for example, that the ternary compound $GaAs_{1-x}N_x$ requires about 20% nitrogen to lattice match to silicon, whereas with sufficient phosphorus incorporated into the compound, the match can be achieved with less than 5% nitrogen at the group V lattice sites. Further, as discussed below, the more modest levels of nitrogen ($x \leqq 0.05$) or arsenic ($x \geqq 0.90$) incorporation allowed by adding one or more of the elements boron, aluminum, indium, phosphorus and antimony to the basic $GaAs_{1-x}N_x$ compound to form the more general $B_mAl_nGa_{1-m-n-p}In_pSb_zAs_{1-x-y-z}P_yN_x$ compound (where m, n, p, y and z can range from 0 to 1) reduces the amount of bandgap bowing that is seen in the arsenide-nitride semiconductor compounds, since the effect is most pronounced for nitrogen levels between 5% and 90%.

With reference to FIGS. **6** and **7**, this bandgap bowing effect is clearly seen by graphing bandgap energy versus nitrogen concentration (x) for $GaAs_{1-x}N_x$ and $InAs_{1-x}N_x$, respectively. The direct bandgap energy for a semiconductor alloy I_xII_{1-x} may be approximated by the quadratic relationship,

$$E_{gap}=E_{gap,I}\ (1-x)+E_{gap,II}\ (x)-C_{I,II}\ (x)\ (1-x),$$

where $E_{gap,I}$ and $E_{gap,II}$ are the bandgaps of the constituent binary materials and $C_{I,II}$ is the bandgap bowing parameter. For the $Al_xGa_{1-x}As$ system, the bowing parameter is negligible and can be ignored. This is also the case for many other III-V compound semiconductor materials. However, this is not the case for materials incorporating nitrogen as a constituent. In fact for the arsenide-nitride compounds, the experimental results obtained to date suggest that the bandgap bowing coefficient is sufficiently great that, instead of increasing as expected for negligible bowing, the lowest direct bandgap actually decreases as nitrogen is added. Based on the limited experimental data obtained to date and theoretical models, the bowing parameter for $GaAs_{1-x}N_x$ is estimated to be approximately 14 eV, while that for $InAs_{1-x}N_x$ is estimated to be about 11 eV.

The graphs in FIGS. **6** and **7** show the calculated bandgap energies for these material systems based on the estimates. The boxed areas **70** and **72** in FIG. **6** enclose those portions of the curve representing materials obtainable with growth techniques like MOCVD. The area **72** in particular ($x \geqq 0.90$) shows that GaAsN materials with direct bandgaps greater than 2.0 eV are obtainable for light emission in the green, blue and near UV portions of the spectrum. Note that the model also predicts a closing of the bandgap in $GaAs_{1-x}N_x$ for $0.16<x<0.71$. Materials with negative bandgaps are no longer semiconductors, but are metallic instead.

A similar reduction in bandgap occurs in $InAs_{1-x}N_x$ as x increases from 0. For InAs the bandgap is about 0.36 eV, but for $InAs_{0.99}N_{0.01}$ the bandgap is reduced to 0.27 eV. Likewise, for $In_{0.75}Ga_{0.25}As_{1-x}N_x$, the bandgap reduces from 0.62 eV (corresponding to 2.0 μm emission) for x=0 to 0.53 eV (corresponding to 2.34 μm emission) for x=0.01.

Taking into account the fact that strain for such a quantum well layer will also be reduced when nitrogen is added (when using a GaAs or InP substrate), the increase in emission energy due to strain will be decreased, so the actual emission wavelength for the 1% N material will be longer (about 2.5 μm). These materials are useful for LIDAR systems, which require emission in the mid-IR region of the spectrum.

In all of these material systems GaAsN, InGaAsN and InAsN, the addition of aluminum to the composition is known to increase the bandgap energy. Likewise, the addition of phosphorus to the composition is known to increase the bandgap energy when arsenic is the dominant group V element. Either or both of these compositional variations can be used to create carrier confining heterostructures for more efficient light emission and cw laser operation.

Before providing examples of devices that can be created with these materials, a discussion of the process used for creating the materials is in order. Referring now to FIG. **8**, a LP-MOCVD system that can be used to grow the III-V arsenide-nitride semiconductor compound materials of the present invention lattice matched to a selected substrate **120** is shown. The substrate **120** is disposed on a graphite susceptor **123** for heating although, as will be discussed below, the heating is less than is typical for LP-MOCVD, in order to encourage sufficient N concentration in the lattice matched material, and the pressure can range from 0.5 to 10^{-3} Torr. The substrate **120** and susceptor **123** are housed in a quartz reactor tube **125** which is ringed by a set of conductive coils **128**. A radio frequency alternating current is adjustably applied to the coils **128** to produce heat in the susceptor **123**, thereby heating the substrate **120** to a desired temperature. Connected to an outlet **130** of the tube **125** is a vacuum pump **132** which is used to evacuate the tube **125** of gases as is needed.

Organometallic compounds that are used to introduce the group III materials are contained in separate constant temperature baths. In a first constant temperature bath **133** is a bubbler of trimethylgallium (TMGa) **135** through which hydrogen gas from a hydrogen gas supply **138** is flowed, the flow controlled by a first flow regulator **140**. As the hydrogen gas bubbles through the TMGa, the gas becomes saturated with the organometallic vapor, the gaseous concentrations at saturation determined by the temperature within the first bath **133**. A conduit **142** controlled by a first shut-off valve **145** connects the TMGa bubbler **135** with the reactor tube **125**. By controlling the temperature in the first bath **133** and the mass flow of hydrogen gas through the regulator **140**, the mass flow of TMGa to the reactor tube **125** can be precisely controlled.

A second constant temperature bath **148** houses a bubbler of trimethylaluminum (TMAl) **150** which is supplied with hydrogen gas from the hydrogen gas supply **138** at a rate controlled by a second flow regulator **152**. In combination with the temperature of the second bath **148**, the flow of hydrogen gas through valve **152** controls the flow of TMAl that can be allowed by a second shut-off valve **155** through conduit **157** to enter reactor tube **125**. Similarly, a third constant temperature bath **160** contains a bubbler of trimethylindium (TMIn) **162** which is provided with hydrogen gas at a rate controlled by a third flow regulator **165**. Hydrogen gas saturated with TMIn can then be flowed to the reactor tube **125** via conduit **167**, that flow switched on and off by a third shut-off valve **168**. A fourth constant temperature bath **170** likewise contains a trimethylboron (TMB) bubbler **172** which has hydrogen gas supplied to it at a rate determined by a fourth regulator **175**. Flow to the reactor tube **125** of hydrogen gas saturated with TMB is then provided by conduit **176**, controlled by a fourth shut-off valve **177**.

Alternative metal-organic compounds may be used for the column III precursors. As an example, triethylgallium (TEGa) may be used in place of trimethylgallium (TMGa) as the gallium source. Similarly, alternative compounds exist for boron, aluminum and indium which may be used for the growth of these III-V compounds.

The group V components used for III-V crystal growth are supplied to the reaction tube **125** from separate containers. A first plenum **180** contains phosphine (PH_3) gas which can be supplied to the reactor tube **125** via conduit **182** at rate controlled by a fifth mass flow regulator **185**. A second plenum **187** contains arsine (AsH_3) that can be flowed to the reactor tube **125** via conduit **190** at a rate controlled by a sixth flow regulator **192**. Similarly, a third plenum **195** is filled with gaseous ammonia (NH_3) which can be flowed to reactor tube **125** via another conduit **197** at a rate controlled by a seventh regulator **200**. PH_3 can be provided along with NH_3 to catalyze an NH_3 disassociation reaction, providing more free N for adsorption by the substrate **120**. AsH_3 can similarly be used to catalyze NH_3. Both PH_3 and AsH_3 can be combined with NH_3 to cross catalyze an NH_3 disassociation reaction, providing a greater supply of free N. Alternatively, N can be supplied via third plenum **195** being provided with hydrazine (H_2NNH_2). Alternative sources may also be used for the column V elements, phosphorus, arsenic and antimony.

In addition to the above described bubblers and plenums that contain the aforementioned group III and group V elements, other bubblers and plenums, which have been left out for ease of illustration, may be provided in a given LP-MOCVD system, in order to provide inputs of other molecules. For example, it may be desirable to provide plenums containing silicon (Si), magnesium (Mg) or other elements for doping the crystal. On the other hand, not all of the above delineated bubblers and plenums may be needed for a given application.

In order to form a crystal having desired concentrations of elements using this LP-MOCVD system, gases are flowed into the reaction tube at precisely controlled rates and time periods. The rates and time periods can vary considerably due to variations in sticking coefficients of the type III elements being adsorbed and other factors. In some embodiments of the present invention, mixtures of gases containing type III atoms and gases containing type V atoms are flowed into the reaction tube **125** simultaneously to form III-V semiconductor crystal compounds on the substrate **120**. In other embodiments of the present invention, gases containing Group III atoms are flowed into the reaction tube **125** separately from gases containing type V atomic species, to form a semiconductor crystal from alternating single atomic layers of group III and type V on the substrate **120**. The alternating growth of single layers of type III and type V atomic species requires that the surface of the substrate **120** upon which growth occurs has an off-axis orientation, such as [111].

For the case of the quinternary system AlGaInAsN lattice matched to ZnO, as shown in FIG. **13**, the actual growth of the material proceeds from a ZnO substrate **335**. The initial buffer layer of AlGaN is grown at temperature between 500° C.–900° C. Following the growth of the buffer layer, the reactor temperature is raised to the growth temperature between 750° C. and 1100° C. The constraints of growth temperature are (1) the growth temperature must be low enough to incorporate both In and As, and (2) the growth temperature must be high enough to allow the growth of high-quality crystal. The growth precursors are as previously mentioned. However, the relative ratio of As to N in the gas phase is adjusted to be N-rich so as to grow compounds with a majority of N of the Group V sublattice.

Following the growth of the initial buffer layer, a lower cladding layer, the n-type $(Al_yGa_{1-y})_{0.81}In_{0.19}As_{0.10}N_{0.90}$ layer **336** is grown. The appropriate n-type dopants include Si, Ge, Sn, Se or Te. A layer **337** of nominally undoped $(Al_xGa_{1-x})_{0.81}In_{0.19}As_{0.10}N_{0.90}$ is grown next, followed by the $Ga_{0.75}In_{0.25}As_{0.1}N_{0.90}$ strained layer quantum well active region **338**, followed by another layer **339** of nominally undoped $(Al_xGa_{1-x})_{0.81}In_{0.19}As_{0.10}N_{0.90}$ material. The p-type $(Al_zGa_{1-z})_{0.81}In_{0.19}As_{0.10}N_{0.90}$ upper cladding layer **340** is grown next, followed by a heavily doped $GaIn_{0.19}As_{0.10}N_{0.90}$ contact layer **341**.

A molecular-beam epitaxy device for manufacturing semiconductor compounds of the present invention is shown in FIG. **9**. A substrate **210** is attached to a molybdenum (Mo) block **212** used for heating the substrate **210**. The block **212** is attached to a servo controlled pivot which can be rotated to face the substrate **210** in different directions within an ultrahigh vacuum chamber **215**. Disposed at various angles around the substrate **210** and block **212** are sources of the group III and group V elements. The group V sources can be provided to the chamber **215** via gases such as NH_3 or H_2NNH_2, PH_3 and AsH_3 that have been disassociated in a manner similar to that discussed under LP-MOCVD. Alternatively, the type V elements can be produced in high pressure ovens for improved disassociation. An electron-cyclotron resonator, not shown, can be aligned with an NH_3 source to crack the NH_3 to yield a radical N source. The group V elements can be produced in independently heated effusion ovens which are enclosed in liquid nitrogen enclosed shrouds. The group III elements can be housed in similar effusion ovens. Group III-V compounds may also be provided in separate effusion ovens, for those applications in which it is desired to provide binary molecules to the substrate. The choice of the means for supplying elements and compounds to the chamber, including the geometric arrangement of the various sources of elements and compounds, depends upon the semiconductor material to be grown on the substrate **210**.

An example of an arrangement for manufacturing a heterostructure laser of AlGaAsN is shown in FIG. **9**. In this case the substrate **210** might be ZnO, for which AlGaAsN can be lattice matched provided that N atoms occupy approximately 92% of the Group V lattice sites and As atoms occupy about 8% of the Group V lattice sites. At a first angle of the chamber **215** is a GaN source **218** comprising a liquid nitrogen cooled effusion oven containing GaN. A GaN shutter **220** is closed, and the substrate **210** is facing away from the GaN source **218**, indicating that GaN is not being grown on the substrate at this time. Adjacent to the GaN source **218** at a second angle is a GaAs source **222** comprising a liquid nitrogen cooled effusion oven containing GaAs. A pair of GaAs shutters **225** are open and the substrate is facing the GaAs **222** source, indicating that a thin layer of GaAs is being grown. Due to the ultra high vacuum maintained in the chamber, which may be 10^{-7} to 10^{-4} Torr, the GaAs emitted from the GaAs source **222** shoots out of the open shutters **225** as a molecular beam that impinges upon and sticks to the substrate and any monolayers already present on the substrate **210**. Adjacent to the GaAs source **222** at a third angle is a AlN source **227** housed in a cooled effusion oven and shuttered by ALN shutters **230** which are shown closed. At a fourth angle, an AlAs source **233** is located, contained within AlAs shutters **235** that are closed. Adjacent to the AlAs source **233** at a fifth angle is a silicon (Si) source **237** which is similarly contained in an effusion oven cooled by liquid nitrogen. A Si shutter **240** is shown closed, restricting the Si from the substrate **210**. The Si source **237** is provided for n-type doping of the III-V material, which can be accomplished by opening the Si shutters when one of the III-V layers is being grown and the substrate is facing somewhat away from the Se source **237**. The concentration of Si being incorporated into the III-V material can be lowered to dopant levels by lowering the temperature of the Si effusion oven, so that less Si molecules are provided to the substrate **210**. On the other side of the chamber **215** adjacent to the GaN source **218** is a magnesium (Mg) source **243** which can be used for incorporation of a p-type dopant into the III-V material. The Mg source **243** is shown separated from the chamber by a closed Mg shutter **245**. The amount of Mg provided to the substrate **210** is kept at dopant levels by facing the substrate somewhat away from the Mg source **243** and by maintaining the Mg effusion oven at a lower temperature. Although Si and Mg are provided as dopants in the above example, other dopants can alternatively be used.

It is possible to obtain the correct concentration of N relative to As by a sequenced layering technique in which approximately one monolayer containing N is grown for every five containing As. In the examples which follow, atomic monolayers are described, where each monolayer is one layer of atoms on the order of 2.5 Å thick. However, this method can be generalized to include layers of increased thickness, i.e., more than one atomic layer thick, with the proviso that each individual layer be of a thickness less than the so-called critical thickness. The critical thickness is defined as the maximum layer thickness possible without introducing dislocations due to the strain from adjacent mismatched layers. In some material systems with a sequence of relatively closely matched crystal layers, the layer thicknesses can be as much as several hundred angstroms, while in more severely mismatched systems, such as GaAs/GaN layer sequences, the critical thickness is just a few atomic layers.

As an example, five monolayers of GaAs can be grown for every monolayer of GaN, resulting in an N concentration of approximately 17% and an As concentration of about 83%, which is known to lattice match with a GaP substrate. It is similarly possible to provide the relative concentrations of Al compared to Ga with such layering. Thus, for example, having two monolayers of Ga interspersed with four layers of Al results in a Ga concentration of approximately 33% and an Al concentration of approximately 67%. Having an increased concentration of Al relative to Ga generally raises the bandgap, however, for Ga concentrations below about 21% and Al concentrations above about 79% of the Group V lattice sites, the lowest bandgap is indirect. Al also has a lower index of refraction than Ga, making a material having a high Al concentration favorable as a cladding material.

Thus, a simple light emitting device **248** as shown in FIG. **10** can be formed on an n-type, ZnO substrate **210** as follows. Initially, an n-type cladding layer **250** made of $AlAs_{0.08}N_{0.92}$ can be grown to a thickness of about 0.2 μm. This layer can be formed by growing one monolayer of AlAs doped with Se, followed by eleven monolayers of AlN, upon which another monolayer of AlAs doped with Se is grown, etc. The pattern of growing a monolayer of Se doped AlAs followed by eleven monolayers of AlN is then repeated until a crystal lattice cladding layer **250** of the desired thickness is formed.

On top of the n-type cladding layer **250** an active layer **255** is grown. In order to grow a defect free active layer **255** the group V lattice sites are again proportioned such that As occupies about 8% of those sites and N occupies the remaining 92% or so. If desired, the active layer **255** can have a lattice constant that is slightly mismatched with that of the cladding layer **250**. This mismatch, formed for example by the addition of indium or a reduction of nitrogen concentration, produces a strain between the layers **250** and **255** that can reduce the threshold current required for light emission. The active layer **255** also must have a lower direct than indirect bandgap to emit light, which requires that at least 21% of the group III lattice sites are occupied with Ga rather than Al. The active layer **255** also has dimensions of a quantum well, in this example having a thickness of about 240 angstroms. This active layer **255** can be formed by sequential growth of a monolayer of GaN, followed by growth of a two monolayers of AlN, followed by one monolayer of GaN, which is followed by two more monolayers of AlN, etc. This sequence is repeated to achieve the approximately 240 angstrom thick active layer.

On top of the active layer **255** is grown a p-type cladding layer of AlAsN **260**. Once again, the active layer **255** and the p-type cladding layer **260** can have lattice constants that are closely matched or mismatched to produce strain between the layers **255** and **260**. This layer is formed in much the same way as the n-type cladding layer **250**, except that Mg is incorporated as a dopant rather than Se. The Mg may be supplied along with the GaN layer in order to enhance the sticking of N. The p-type cladding layer of AlAsN **260** is formed to a thickness of about 0.2 μm. Both the n-type cladding layer **250** and the p-type cladding layer **260** have lower indexes of refraction than the active layer **255**, causing light that is generated in the active layer **255** to be reflected. Both the n-type cladding layer **250** and the p-type cladding layer **260** have higher bandgaps than the active layer **255**, forming a potential well in the active layer **255** which encourages electron-hole recombination in the active layer **255**.

Grown atop the p-type cladding layer **260** is a p-type contact layer of GaAsN **265**. As before, the ratio of N to As is chosen at about eleven to one in order to lattice match this layer **265** with the previous layer **260**. Again the Mg dopant can be incorporated along with a GaN monolayer to enhance sticking of the N. A surface **267** of p-type window **265** can be annealed in N so that N replaces As in a thin layer of a thickness of about 10 Å–100 Å at that surface **267**, forming a translucent window and a potential barrier against surface recombination.

Attached to the substrate **210** on a face opposite to the surface on which the n-type cladding layer **250** is grown is affixed a metallic contact **268** used for providing a negative voltage to the device **248**. At an opposite end of the device **248**, on top of the GaAsN window **265** is affixed an interdigitated metallic contact **270** that is used to provide a positive voltage to the device **248**. The interdigitated contact **270** has spaces between metal strips that allow light to pass through the contact **270**. Alternatively, a contact can be made with the GaAsN window **265** that conducts electricity and is translucent.

During use, the metallic contact **268** is provided with a negative voltage and the interdigitated contact is provided with a positive voltage, together causing electrons from the n-type substrate **210** and n-type cladding layer **250** to move into the active layer **255**, and causes holes from the p-type cladding layer **260** and p-type window **265** to move into the active layer **255**. In the active layer **255** the electrons and holes combine, encouraged by the potential well, and since the active layer is a direct bandgap material, light is emitted. This light is emitted through the interdigitated contact **270**.

While the light emitting device **248** is described in terms of growth of AlGaAsN materials on a ZnO substrate **210**, it should be realized that similar devices can be formed from the many other III-V compounds previously described by growth on any of the several substrates previously described. In addition, while the foregoing description has been limited for ease of description to a simple light emitting device **248**, other light emitting devices employing multiple quantum wells, quarter wavelength layers for Bragg reflection, edge emitting laser bars and lasers or diodes that emit light through the substrate can all be created by means of the present invention. It is also possible to remove the substrate by selective etching after formation of the layers of III-V materials.

In the preceding example, the light emitting diode **248** was constructed for blue light emission. However, as previously described, this materials technology is useful for the fabrication of light-emitting devices for emission throughout the visible spectrum. Further, a multi-color light emitting diode may easily be fabricated by sequentially growing a series of light emitting diodes. If all of the materials on top of any given light emitting diode are translucent to the light emanating from that diode, then the emission from all of the light emitting diodes is visible, allowing monolithic multicolor operation. If all of the diodes are operated simultaneously, additive color synthesis is possible. In the following text, the operation of such a "stacked" structure useful for the detection of radiation is described.

FIG. **11** shows an optoelectronic apparatus **275** employing materials of the previous device **248** in a converse fashion, that of receiving photons and emitting electrons. On an n-type GaN substrate **278** is grown an n-type GaAsN layer **280**. For short visible light detection, N atoms occupy at least 90% of the Group V lattice sites, while As atoms occupy the remaining 10% or less of the Group V sites. The n-type GaAsN layer **280** can be grown as described above in a series of monolayers or layers of minimal thickness in order to obtain the desired ratio of N to As, and the layer **280** can be doped with Si during GaAs monolayer growth to form the n-type doping. The Si doping is fairly heavy to cause the n-type GaAsN layer to be somewhat electrically conductive. On top of the n-type GaAsN layer a p-type GaAsN layer **283** is grown. This layer **283** is much the same as the previous layer **280** except that Mg is added to the material during GaN monolayer growth to cause p-type doping rather than Si being added for n-type doping. Both of these GaAsN layers **280** and **283** have a direct band gap of about 1.9 eV, corresponding to red or yellow light.

Atop the p-type GaAsN layer **283** is grown a lattice matched, zincblende, n-type $Al_xGa_{1-x}AsN$ layer **285** by methods described earlier. As before, the concentration of N atoms at Group V lattice sites is chosen to be about 90% and the concentration of As atoms at those sites is chosen to be about 10% in order to lattice match to the previous layer **283**. Al and Ga are structural isomorphs in an AlGaAsN crystal, with AlN having only a slightly smaller lattice constant than GaN. Grown on the n-type $Al_xGa_{1-x}AsN$ layer **285** is a p-type $Al_xGa_{1-x}AsN$ layer **287**. The p-type doping is accomplished as described before with Mg. The concentration of Al is chosen to be about 30% and the concentration of Ga about 70% at group III lattice sites, to produce a direct bandgap corresponding to green light.

Atop the p-type $Al_xGa_{1-x}AsN$ layer **287** an n-type $Al_yGa_{y-y}AsN$ layer **290** having a greater concentration of Al corresponding to a higher direct bandgap, and lattice matched to the previous layer **287**. The group III lattice sites of this layer **290** are about 60% Al and about 40% Ga, and the Group V lattice sites are again about 10% As and 90% N, giving the layer **290** a bandgap corresponding to blue light. Grown on top of the n-type $Al_yGa_{1-y}AsN$ layer **290** is a p-type $Al_yGa_{1-y}AsN$ layer **293**, which has similar concentrations of Group III and V elements but is doped with Mg rather than Si of the n-type layer **290**.

Affixed to the n-type GaAsN layer **280** is an electrically conductive first lead **295**. The first lead wraps around the layer **280** to provide electrical contact around a perimeter of the layer **280**. Similarly affixed to the p-type GaAsN layer is a second lead **297**. The leads **295** and **297** are fed to a voltage or current meter **300** which can detect voltage differences and current between the leads **295** and **297**. Another pair of leads **303** and **305** are similarly attached to n-type $Al_xGa_{1-x}AsN$ layer **285** and p-type $Al_xGa_{1-x}AsN$ layer **287**, respectively, the pair of leads **303** and **305** also being connected to a second voltage or current meter **307**. A third pair of leads **310** and **312** are affixed to the n-type $Al_yGa_{1-y}AsN$ layer **290** and p-type $Al_yGa_{1-y}AsN$ layer **293**, respectively, the pair of leads being connected at opposite ends to a third voltage or current meter **315**.

A photon **316** having an energy corresponding to blue light impinging upon a top surface **317** of the apparatus **275** will be absorbed within p-type layer **293** or n-type layer **290**. The energy of the photon **316** will likely be absorbed by an electron moving from a valence band to a conduction band within either layer **290** or layer **293**, which requires an energy at least that of the direct bandgap of the materials comprising layers **290** and **293**. Those carriers generated within approximately an ambipolar diffusion length of the depletion region between layers **290** and **293** will lead to a measurable photocurrent or photovoltage, dependent upon the biasing of the device. Thus, a measuring apparatus attached to leads **310** and **312** will register a signal when blue light impinges upon layers **290** and **293**.

At a p-n junction between layers **290** and **293**, electrons flow from n-type layer **290** into p-type layer **293**, reaching a lower energy state by occupying holes in the p-type layer. Similarly, holes flow from the p-type region **293** to the n-type region **290**. This process continues until an equilibrium voltage builds up across the p-n junction that counterbalances the reduction in energy achieved by crossing the border. This voltage creates a diode across the p-n junction that allows electrical current to flow across the junction from the p-layer to the n-layer but not the reverse. Similar p-n junctions can be found at a junction between layers **285** and **287** and at a junction between layers **280** and **283**. Reverse p-n junctions exist at a boundary connecting layers **290** and **287**, and at a boundary connecting layers **283** and **285**.

A second photon **320** impinging upon surface **317** has an energy corresponding to green light. The second photon **320** does not have sufficient energy to boost an electron from a conduction to a valence band in layer **290** or layer **293**, and travels through those layers unabated. The resulting photon will likely be absorbed within the p-type layer **287** or the n-type layer **285** since its energy matches that needed to boost an electron from a filled valence band to a conduction band of layers **285** and **287**. Photogenerated carriers that diffuse to the p-n junction depletion region lead to photocurrent. Measurable current flows through leads **303** and **305**, being detected as current or voltage by meter **307**, which acts as a green light detector.

A third photon **322** impinging upon surface **317** has an energy corresponding to red light and thus passes through layers **293**, **290**, **287**, and **285**. The third photon **322** is then absorbed in layer **280** or layer **283**, leading to current flow through leads **295** and **297** through meter **300**, where it is detected as voltage or current corresponding to red light.

Apparatus **275** has been limited for ease of illustration to three meters **300**, **307** and **315** for detecting three frequencies of light. Expansion of light detection capabilities of such a system can be made by adding more p-n junctions between layers of materials having bandgaps that are stacked in increasing energy. Apparatus **275** has also been limited in this example to AlGaAsN compounds lattice matched to a GaN substrate. As discussed previously, many other arsenide-nitride compounds and several other substrates can be used to create other similar optoelectronic apparatuses. In addition, an apparatus similar to that described above can instead be made to receive light through the substrate, provided that the substrate is translucent, and that the bandgaps of the materials forming the p-n junctions are highest adjacent the substrate and lowest furthest from the substrate. Alternatively, the substrate can be removed by selective etching to allow light to enter this reverse-stacked apparatus unobstructed. Apparatus **275** shows metal contacts for the leads **295**, **297**, **303**, **305**, **310** and **312** located on the top surfaces of the layers **280**, **283**, **285**, **287**, **290** and **293**. Access to these surfaces is generally formed by etching through the various layers in a staircase or mesa arrangement so that contact with each of the layers can be made from the top of the structure.

Thus, optoelectronic apparatus **275** presents a photodetector capable of acquiring and differentiating light of frequencies spanning the visible spectrum. Such an apparatus **275** can also function as an efficient solar cell, as light of frequencies spanning the visible spectrum can be collected and converted to electricity. The high-bandgap lattice-matched materials system of the present invention can improve the performance of electronic devices which are required to operate at elevated temperatures. In particular, the high degree of crystallinity of these lattice-matched materials will lead to the improved performance of minority carrier devices, since the performance of minority carrier devices is substantially impaired in materials of inferior crystallinity. Thus, transistors and diode rectifiers required to operate at elevated temperatures will be enhanced by the materials technology described herein.

Other embodiments of the present invention can be formed by combining Group III elements which may include Al, Ga, B and In with Group V elements including at least N and As, and possibly other Group V atomic species as well, to substantially lattice match, possibly under strain, with various monocrystalline substrates including GaN, GaAs, GaAsP, GaP, InP, InN, Si, Ge, SiC, ZnO, ZnSe, Al_2O_3 (basal-plane and r-plane sapphire) and diamond, using the crystal template provided by the substrate to epitaxially grow III-V semiconductor compounds. Due to the large number of possible combinations of the above III-V elements that can be lattice matched to the above substrates, and the various concentration ranges of the III-V elements that can be lattice matched to a given substrate, a wide variety of useful materials and devices can be fabricated. As an example, $GaP_{0.764}As_{0.196}N_{0.04}$ should be lattice matched to GaP and $Al_{1-x}Ga_xP_{0.764}As_{0.196}N_{0.04}$ should also be lattice matched to GaP, so that layers of these materials could be grown to form a laser or light emitting diode. In addition, $Ga_{1-w}In_wAs_{1-y}N_y$ can also be lattice matched to InP. For example, the mid-IR emitting $In_{0.53}Ga_{0.47}As$ material is lattice matched to InP and nitrogen incorporation of up to 5% decreases the lattice constant only slightly.

The inclusion of As, P, or Sb in a GaN active region is useful for decreasing the bandgap of the active region of a light-emitting device. The addition of As, P or Sb into the active region may also introduce strain into the active region, thus, the GaAsN, GaSbN or GaPN active region can be a coherently strained active region under biaxial compression. Note that unstrained layers may also be grown by a proper choice of substrate, grown layer compositions or a thin layer composition and thickness such layers being sufficiently thin so as to avoid defect generation.

FIG. **12** shows an embodiment of this system. An AlGaN heterostructure **326**–**332** is grown upon a sapphire (a=3.6 Å) or SiC (a=3.0865 Å) substrate **325**, standard non-lattice-matched substrates currently used for nitride growth, with n- and p-type doping in the lower and upper cladding layers **327** and **331**, respectively. Following an AlGaN buffer layer **326** and the n-type $Al_yGa_{1-y}N$ lower cladding layer **327** are $Al_xGa_{1-x}N$ layers **328** and **330** (y>x), in the center of which is placed a $GaAs_{0.1}N_{0.9}$ strained-layer quantum well active region **329**. Subsequently, an $Al_zGa_{1-z}N$ p-type upper cladding layer **331** is grown (27 k). Finally, a p-type $GaAs_{0.1}N_{0.9}$ cap **332** is grown to provide a low-resistance ohmic contact. In this example, As has been substituted in the GaN active and capping layers, however, P or Sb also provides for compressive strain and a diminution of the bandgap of GaN, which also provides low contact resistance. Appropriate dopants in this system are Mg, Zn or C for the p-dopant and Si, Ge, Sn, Se or Te for the n-dopant.

The application of this effect to the growth of a lattice-matched structure **335**–**341** is shown in FIG. **13**. Starting with the ZnO substrate **335** (a=3.25 Å), an n-type $(Al_yGa_{1-y})_{0.81}In_{0.19}As_{0.10}N_{0.90}$ lower cladding layer **336** is grown, followed by $(Al_xGa_{1-x})_{0.81}In_{0.19}As_{0.10}N_{0.90}$ layers **337** and **339** (y>x), in the center of which is placed a $Ga_{0.75}In_{0.25}As_{0.10}N_{0.90}$ strained layer quantum well active region **338**. A p-type $(Al_zGa_{1-z})_{0.81}In_{0.19}As_{0.10}N_{0.90}$ upper cladding layer **340** is then grown, followed by a $Ga_{0.81}In_{0.19}As_{0.10}N_{0.90}$ contact layer **341**. This example uses a lattice-matched active region **338**. However, further increases of As, Sb, or P or the inclusion of In in the active region **338** can introduce strain into the active region. Appropriate dopants in this system are Mg, Zn or C for the p-dopant and Si, Ge, Sn, Se or Te for the n-dopant.

One final application of interest is the construction of an LED, shown in FIG. **14**, formed by the growth in a SiC substrate **345** of an n-type SiC lower confining layer **347**, a GaAsN, GaPN, or GaSbN active layer **348** and a p-type SiC upper confining layer **349**. This LED has utility when the bandgap of the active region **348** is less than the bandgap of the SiC confining layers. The bandgap of SiC is approximately 2.8 eV, thus this LED configuration would have utility for photon emission less than 2.8 eV or, equivalently, wavelengths greater than 440 nm, allowing access to the entire range of visible emission. For example, the active layer **348** may be a $In_{0.2}G_{a0.8}As_{0.1}N_{0.9}$ strained layer quantum well.

What is claimed is:

1. A method of incorporating larger concentrations of N relative to As at group V lattice sites in a III-V compound semiconductor crystal without experiencing defects due to lattice mismatch comprising the steps of:

providing a crystalline substrate;

epitaxially depositing on the substrate at least one set of a plurality of alternating groups of one or more layers comprising a first group having Group V atoms of all or a majority of nitrogen atoms at Group V lattice sites with at least one Group III element at Group III lattice sites and a second group having Group V atoms of all or a majority of arsenic atoms at Group V lattice sites with at least one Group III element at Group III lattice sites; and

depositing the layers in the first and second groups as monolayers so that the formation of defects due to lattice mismatch is avoided.

2. The method of claim **1** wherein at least one of said layers has a crystal lattice that is maintained in strained relation with an adjoining layer.

3. The method of claim **1** wherein some of the layers are comprised of binary semiconductor compounds.

4. A method of incorporating significant concentrations of at least N and As at group V lattice sites in a III-V compound semiconductor crystal comprising:

providing a crystalline substrate;

depositing at least one layer of a III-V semiconductor compound on the substrate having at least one element from Group III elements of Al, B, Ga and In disposed at group III lattice sites and having at least one element from Group V elements of As, N, P and Sb disposed at group V lattice sites;

the improvement comprising the step of

depositing said Group III element and said Group V element as separate and alternate monolayers of at least one Group III element absent of a Group V element and at least one Group V element absent of a Group III element sequentially on a [111] crystalline substrate to form the III-V compound semiconductor layer so that desorption of the Group III element is averted during deposition.

5. The method of claim **1** further comprising the step of annealing the as-grown layers causing, at least in part, interlayer diffusion.

6. The method of claim **1** comprising the step of depositing the layers at a temperature below 600° C.

7. The method of claim **1** comprising the further step of providing nitrogen from molecules including hydrazine.

8. The method of claim **1** comprising the further step of providing nitrogen from organometallic molecules containing N atoms.

9. The method of claim **1** comprising the further step of providing nitrogen from dissociated NH_3 which has been cracked in an electron cyclotron resonator.

10. The method of claim **1** comprising the further step of providing nitrogen from NH_3 which has been dissociated in a reaction catalyzed by AsH_3 and PH_3.

11. The method of claim **1** wherein the step of depositing of the layers includes LP-MOCVD.

12. The method of claim **1** wherein the step of depositing of the layers includes MBE.

13. The method of claim **1** comprising the further step of adding dopants during the deposition of at least some of the layers either of the first or second group or both groups.

14. The method of claim **1** wherein the one other Group V atoms are arsenic.

15. The method of claim **1** wherein the Group III elements are selected from the group consisting of one or more of B, Al Ga and In.

16. The method of claim **1** comprising the further step of arranging the number of layers in the groups of the set such that the overall ratio of nitrogen atoms to the one other Group V atoms providing substantial lattice match with the crystalline substrate.

17. The method of claim **15** wherein the first group of the layer or layers comprise GaN, GaAsN or InAsN and the second group of the layer or layers comprise GaAs, AlGaAs or InGaAs.

18. The method of claim **1** wherein, in the second group, arsenic is the majority component in the Group V sites with above about 5% nitrogen at the Group V sites.

19. The method of claim **1** wherein, in the first group, nitrogen is the majority component in the Group V sites with up to about 20% arsenic at the Group V sites.

20. The method of claim **1** wherein at least one layer in the series of layers is a monolayer.

21. The method of claim **1** wherein the substrate is selected from the group consisting of GaP, Si, GaAs, Ge, SiC, ZnSe, ZnO and diamond.

22. A method of incorporating significant concentrations of at least N and As at group V lattice sites in a III-V compound semiconductor crystal comprising:

providing a crystalline substrate;

depositing at least one layer of a III-V semiconductor compound on the substrate having a first group of at least one element from Group III elements of Al, B, Ga and In disposed at group III lattice sites and having a second group of at least one element from Group V elements of As, N, P and Sb disposed at group V lattice sites;

the improvement comprising the steps of

depositing semiconductor monolayers of first and second groups with the first group having N atoms at a majority of such atoms at Group V lattice sites with at least one Group III element at the group III lattice sites, and with the second group having As atoms at a majority of such atoms at Group V lattice sites with at least one Group III element at the Group III lattice sites; and

depositing said first and second groups as alternate monolayers of the Group III element absent of a Group V element and the Group V element absent of a Group III element so that desorption of Group III elements is averted during deposition of the layer.

* * * * *