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
OTHER PUBLICATIONS


* cited by examiner
**FIG. 1**

**FIG. 2**

**FIG. 3**

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>GROUP III</th>
<th>GROUP V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B  Al  Ga  In</td>
<td>N  P  As  Sb</td>
</tr>
<tr>
<td>RADIUS (Å)</td>
<td>0.88  1.26  1.26  1.44</td>
<td>0.70  1.10  1.18  1.36</td>
</tr>
</tbody>
</table>
**FIG. 4**

CUBIC LATTICE CONSTANT (Å)

WURTZITE LATTICE CONSTANT (Å)

GaAs$_{1-x}$N$_x$ COMPOSITION (x)

**FIG. 5**

CUBIC LATTICE CONSTANT (Å)

WURTZITE LATTICE CONSTANT (Å)

InAs$_{1-x}$N$_x$ COMPOSITION (x)
**FIG. 6**

**FIG. 7**
This application is a 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. NASA-33-242 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 is 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 ZnSeS based structure under pulsed current injection at 77 K. More recent advances in this material system using a remote plasma source for the growth of a wurtzite crystal lattice structure 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 AlGaN. 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.

AlGaN materials have so far been grown only on mismatched substrates such as Si, SiC, single crystal Al2O3 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 AlGaN 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 AlGaN 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 AlGaN type material but also has a cubic lattice that induces the growth of a cubic substrate lattice of the AlGaN type material layers. Substrates which have commonly been used for group III-V high bandgap semiconductor, such as basal plane [0001] sapphire (Al2O3) and c-SiC, have the disadvantage of producing the less desirable wurtzite crystal lattice structure.

In U.S. Pat. No. 5,146,645, 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 Al2O3 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 c-ZnO, which falls that of several III-V nitride materials, allowing mixing of those materials in proportions calculated to match the substrate lattice of ZnO, to form AlGaN or AlGaN 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 diode. Similarly, U.S. Pat. No. 5,076,860 to Ohba et al. teaches a compound semiconductor material of GaAl-BNP 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 Hata et al. describes a semiconductor laser formed from alternately stacking BP and GaAIN layers to form GaAlB,_,N,-,NP,-, 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. Feltcher et al. describe gallium arsenide phosphide doped with nitrogen (GaAsP:N) and gallium phosphide doped with nitrogen (GaP:N).


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 lasing 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 accommo- dated 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 than 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,N, material, where x ≤ 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,N, 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 lasers formed from stacking BP and GaAIN layers to form GaAlB,_,N,-,NP,-, material on a GaP substrate.

The monocrystalline material of the present invention formed with 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. InGaAsAIN 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 Al2O3 (sapphire) using either basal plane or r-plane growing surfaces, diamond, Si, Ge, SiC in both wurtzite (c) and zincblende (b) 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 poly crystalline layers with both zincblende and wurtzite crystals result. This miscible 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 concen-
formation 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 (NH₃) may be employed as an N source with catalysts such as arsenic and phosphine used to increase the cracking efficiency of NH₃. 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 NH₃ molecule, resulting in a radical N. Plasma deposition systems can also be used to increase the cracking efficiencies of NH₃.

It is possible to obtain the correct concentration of N relative to As by atomic layer epitaxy, a layered deposition technique where 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 in such a layer. Thus, for example, having two monolayers of Ga interspersed with four layers of Al results in a Ga concentration of approximately 35% and an Al concentration of approximately 65%. 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 LPMOCVD. 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 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 AlGaNAs cubic crystals superposed with the lattice constant of some common substrates.

**FIG. 2** is a graph of the bandgap and lattice constant of AlGaNAs 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 GaAs₁₋ₓNₓ 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 InAs₁₋ₓNₓ 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 GaAs₁₋ₓNₓ for various concentrations (x) of nitrogen.

**FIG. 7** is a graph of the lowest direct bandgap of InAs₁₋ₓNₓ 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 a SiC or GaN substrate.

**FIG. 13** is a side view of an AlGaNAsN 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 AlGaNAs 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 these lines represent the quaternary compounds AlGaNAs 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 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 InSbAs1-xN(x≤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 AlGaNInN 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 Al2O3 (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 ternary compounds. The dashed line 26 represents α-SiC, which has a lattice constant of about 3.08 Å, less than the lattice constant of any AlGaNInN 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 AlGaNAs or GaNAs strained quantum wells. The dashed line 27 represents α-ZnO (SiC and ZnO have both wurtzite (w) and zincblende (z) 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 AlGaNInN 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 (Al2O3) substrates. The basal plane growing surface of the rhombohedral Al2O3 substrate has an equivalent wurtzite lattice constant of about 3.62 Å, which can be seen to be larger than any AlGaNInN 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 (α) and hexagonal wurtzite (αh) lattice constants are related to the bond length (l) by the relations \(a_\alpha = \sqrt[3]{5/3} \ell\) and \(a_{\alpha h} = \sqrt[3]{2/3} \ell\). 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 calculated 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 compound on the line 0.16, 0.3, 0.5 represents a ternary compound on the line 0.16, 0.3, 0.5. 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 Ga\textsubscript{1-x}As\textsubscript{x}N\textsubscript{y} and In\textsubscript{1-x}As\textsubscript{x}N\textsubscript{y} to some common substrates for various concentrations (x) of nitrogen. As shown in FIG. 4, the lattice constant of Ga\textsubscript{1-x}As\textsubscript{x}N\textsubscript{y} 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\textsubscript{2}O\textsubscript{3} 38, In\textsubscript{2}N 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 Ga\textsubscript{1-x}As\textsubscript{x}N\textsubscript{y} materials. The boxed areas represent the approximate nitrogen concentrations which are accessible by means of equilibrium growth techniques, such as MOCVD, namely x≤0.05 and x≥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<0.05), GaAs is a good substrate candidate, while for very high nitrogen concentrations (x>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 In\textsubscript{1-x}As\textsubscript{x}N\textsubscript{y} 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\textsubscript{2}O\textsubscript{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 In\textsubscript{1-x}As\textsubscript{x}N\textsubscript{y} materials. Quaternary GaInAsN compounds would have lattice constants between those of GaAs\textsubscript{1-y}N\textsubscript{y} of FIG. 4 and InAs\textsubscript{1-y}N\textsubscript{y} of FIG. 5, and would allow InP or ZnSe to be used as substrate materials for low nitrogen concentrations (x≤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\textsubscript{1-x}Ga\textsubscript{x}P\textsubscript{0.85}As\textsubscript{0.15}N\textsubscript{0.05}, 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\textsubscript{1-x}N\textsubscript{y} 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≤0.05) or arsenic (x≥0.90) incorporation allowed by adding one or more of the elements boron, aluminum, indium, phosphorus and antimony to the basic GaAs\textsubscript{1-x}N\textsubscript{y} compound to form the more general B\textsubscript{m}Al\textsubscript{n}Ga\textsubscript{1-m-n}P\textsubscript{m}As\textsubscript{n}N\textsubscript{1-m-n} 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\textsubscript{1-x}N\textsubscript{y} and InAs\textsubscript{1-x}N\textsubscript{y}, respectively. The direct bandgap energy for a semiconductor alloy \(E_{g,p}(x)\) may be approximated by the quadratic relationship,

\[
E_g = E_{g,p} (1-x) + E_{g,p} x - C_{g,p} x (1-x),
\]

where \(E_{g,p}\) and \(E_{g,p}\) are the bandgaps of the constituent binary materials and \(C_{g,p}\) is the bandgap bowing parameter. For the Al\textsubscript{1-x}Ga\textsubscript{x}-As system, the bandgap 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\textsubscript{1-x}N\textsubscript{y} is estimated to be approximately 14 eV, while that for InAs\textsubscript{1-x}N\textsubscript{y} 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≤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\textsubscript{1-x}N\textsubscript{y} 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\textsubscript{1-x}N\textsubscript{y} as x increases from 0. For InAs the bandgap is about 0.36 eV, but for InAs\textsubscript{1-x}N\textsubscript{y}, the bandgap is reduced to 0.27 eV. Likewise, for In\textsubscript{0.7}Ga\textsubscript{0.3}As\textsubscript{1-x}N\textsubscript{y}, 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 additions at saturation determined by the temperature within the due to variations in sticking coefficients of the type III-V compound material, and the pressure can range from 0.5 to 10⁻⁶ Torr. The substrate is disposed on a graphite susceptor which has hydrogen gas supplied to it at a rate of 125 sccm. Hydrogen gas saturated with TMB is then supplied to the reaction tube at 190°C at a rate controlled by a seventh flow regulator. Similarly, a third plenum is filled with gaseous ammonia (NH₃) which can be flowed to the reactor tube via another conduit at a rate controlled by a seventh regulator. PH₃ can be provided along with NH₃ to catalyze an NH₃ dissociation reaction, providing more free N for adsorption by the substrate. AsH₃ can similarly be used to catalyze NH₃, both PH₃ and AsH₃ can be combined with NH₃ to cross catalyze an NH₃ dissociation reaction, providing a greater supply of free N. Alternatively, N can be supplied via third plenum being provided with hydrazine (H₂NNH₂). 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-V 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 simultaneously to form III-V semiconductor crystal compounds on the substrate. In other embodiments of the present invention, gases containing Group III atoms are flowed into the reaction tube 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. The alternating growth of single layers of type III and type V atomic species requires that the surface of the substrate upon which growth occurs has an off-axis orientation, such as [111].

For the case of the quaternary 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 AlGaInAsN is grown at a temperature between 500°C and 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 (AlxGa1-x)0.81In0.19As0.10N0.90 layer 336 is grown. The appropriate n-type dopants include Si, Ge, Sn, Se or Te. A layer 337 of nominally undoped (AlxGa1-x)0.81In0.19As0.10N0.90 is grown next, followed by the Ga1-xAlxIn0.22As0.78N0.00 strained layer quantum well active region 338, followed by another layer 339 of nominally undoped (AlxGa1-x)0.81In0.19As0.10N0.90 material. The p-type (AlxGa1-x)0.81In0.19As0.10N0.90 upper cladding layer 340 is grown next, followed by a heavily doped GaIn0.10As0.10N0.90 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. Disassociated 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 NH3, H2, N2, NH2, PH3, and AsH3 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 electroncyclotron resonator, not shown, can be aligned with an NH3 source to crack the NH3 to yield a radical N source. The proviso that each individual layer be of a thickness less than the critical thickness is attached to a servo controlled pivot which can be rotated 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 AlAs0.06N0.94 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. 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 bandgap than indirect bandgap to emit light, which requires that at least 21% of the group III lattice sites are occupied by Al rather than Ga. 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 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 can 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 nm. Both the n-type cladding layer 250 and the p-type cladding layer 260 have low indexes of refraction that are higher than the 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 at Group V lattice sites is chosen to be about 90% and the concentration of Ga is chosen to be about 10% in order to lattice match this layer 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, quantum 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 multi-color 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 present invention, including a p-type window 280 and a n-type window 283, 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 280 is a p-type GaAsN layer 283. 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,Ga,As N 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,Ga,AsN layer 285 is a p-type Al,Ga,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,Ga,AsN layer 287 an n-type Al,Ga,AsN layer 290 having a greater concentration of Al
corresponding to a higher direct bandgap, and lattice matched to the previous layer. The Group III lattice sites of this layer 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 a bandgap corresponding to blue light. Grown on top of the n-type AlGaAsN layer 290 is a p-type AlGaAsN layer 292, 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 291. 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 AlGaAsN layer 285 and p-type AlGaAsN 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 AlGaAsN layer 290 and p-type AlGaAsN layer 293, respectively. The meter leads 310 and 312 are 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 p-type layer 293 or n-type layer 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 formed by combining Group I11 elements which may include Group III-V elements but is doped with Mg such that the material remains p-type or n-type as required.

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 absorbed 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, 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, GaN, GaAs, Ga, and In with Group V atomic species as well, to substantially lattice match, possibly under strain, with various monocrystalline substrates including GaN, GaAs, GaAs, GaP, InP, InN, Si, Ge, Si, ZnO, ZnSe, Al, O, and GaAsN. 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, , should be lattice matched to GaP and Al, GaP, , 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, GaN, InAs, can also be lattice matched to InP. For example, the mid-IR emitting InGaAs material is lattice matched to InP and nitrogen incorporation of up to 5% decreases the lattice constant 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 subject to strain so as to avoid lattice mismatch.

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 AlGa1-xN lower cladding layer 327 are Al0.98Ga0.02As0.44,N0.56 layers 328 and 330 (y>x), in the center of which is placed a GaAs0.71In0.29,N0.08 strained-layer quantum well active region 338, or a p-type upper cladding layer 331 is grown (27k). Finally, a p-type GaAs0.51N0.49 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,Ga1-x)0.83In0.19As0.91,N0.09 lower cladding layer 336 is grown, followed by (Al,Ga1-x)0.83In0.19As0.91,N0.09 layers 337 and 339 (y>x), in the center of which is placed a Ga0.71In0.29As0.44,N0.56 strained layer quantum well active region 338, or a p-type upper cladding layer 334 is then grown, followed by a Ga0.71In0.29As0.44,N0.56 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 approximated 2.8 eV, thus this LED 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 an In0.2G0.8As0.57N0.43 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 NH3 which has been cracked in an electron cyclotron resonator.
10. The method of claim 1 comprising the further step of providing nitrogen from NH3 which has been dissociated in a reaction catalyzed by AsH3 and Ph3.
11. The method of claim 1 wherein the step of depositing the layers includes LPMOCVD.
12. The method of claim 1 wherein the step of depositing 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 of 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 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.

   * * * * *