United States Patent

Major et al.

[34] III-V ARSENIDE-NITRIDE SEMICONDUCTOR

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[ abstract ]

III-V arsenide-nitride semiconductor are disclosed. 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 materials 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 material can be accomplished by growing thin layers of elements or compounds in sequences that result in the overall lattice match and bandgap desired.
OTHER PUBLICATIONS


FIG. 1

![Graph showing lattice constant vs. energy gap for different elements.](image1)

FIG. 2

![Graph showing lattice constant vs. energy gap for different elements.](image2)

FIG. 3

<table>
<thead>
<tr>
<th>Element</th>
<th>Group III</th>
<th>Group V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
<td>Al</td>
</tr>
<tr>
<td>Radius (Å)</td>
<td>0.88</td>
<td>1.26</td>
</tr>
</tbody>
</table>
FIG. 4

FIG. 5
FIG. 6

FIG. 7
FIG. 9

FIG. 12

<table>
<thead>
<tr>
<th>Layer</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>332</td>
<td>GaAs$<em>{0.1}$N$</em>{0.9}$</td>
</tr>
<tr>
<td>331</td>
<td>Al$<em>z$Ga$</em>{1-z}$N</td>
</tr>
<tr>
<td>330</td>
<td>Al$<em>x$Ga$</em>{1-x}$N</td>
</tr>
<tr>
<td>329</td>
<td>Al$<em>x$Ga$</em>{1-x}$N</td>
</tr>
<tr>
<td>328</td>
<td>Al$<em>y$Ga$</em>{1-y}$N</td>
</tr>
<tr>
<td>327</td>
<td>AlGaN</td>
</tr>
<tr>
<td>326</td>
<td>SiC or Al$_2$O$_3$</td>
</tr>
<tr>
<td>325</td>
<td>---</td>
</tr>
</tbody>
</table>
FIG. 13

\[
\begin{align*}
341 & \sim \text{Ga}_{0.81}\text{In}_{0.19}\text{As}_{0.1}\text{N}_{0.9} \\
340 & \sim (\text{Al}_{z}\text{Ga}_{1-z})_{0.81}\text{In}_{0.19}\text{As}_{0.1}\text{N}_{0.9} \\
339 & \sim (\text{Al}_{x}\text{Ga}_{1-x})_{0.81}\text{In}_{0.19}\text{As}_{0.1}\text{N}_{0.9} \\
338 & \sim (\text{Al}_{x}\text{Ga}_{1-x})_{0.81}\text{In}_{0.19}\text{As}_{0.1}\text{N}_{0.9} \\
337 & \sim (\text{Al}_{y}\text{Ga}_{1-y})_{0.81}\text{In}_{0.19}\text{As}_{0.1}\text{N}_{0.9} \\
336 & \sim (\text{Al}_{y}\text{Ga}_{1-y})_{0.81}\text{In}_{0.19}\text{As}_{0.1}\text{N}_{0.9} \\
335 & \sim \text{ZnO}
\end{align*}
\]

FIG. 14

\[
\begin{align*}
349 & \sim \text{p-type SiC} \\
348 & \sim \text{In}_{0.2}\text{Ga}_{0.8}\text{As}_{0.1}\text{N}_{0.9} \\
347 & \sim \text{n-type SiC} \\
345 & \sim \text{SiC}
\end{align*}
\]
III-V ARSENIDE-NITRIDE SEMICONDUCTOR

CROSS-REFERENCE TO RELATED APPLICATION

This is a continuation of patent application, Ser. No. 08/724,321, filed Oct. 1, 1996, now U.S. Pat. No. 5,689,123, which is a continuation of patent application, Ser. No. 08/373,362, filed Jan. 17, 1995, now abandoned, which is a continuation-in-part of U.S. patent application 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. NASS-32442 awarded by the National Aeronautics and Space Administration (NASA) and under Contract No. N00014-93C-0130 awarded by the Department of the Navy. The government has certain rights in the invention.

TECHNICAL FIELD

The present invention relates to monocrystalline III-V arslenide-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, comprising III-V compound semiconductors GaAsN, GaInAs, and InAsN, 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 ZnSeS 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 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 wurzite, 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 semiconductors, such as basal plane [0001] sapphire (Al2O3) and c-SiC, have the disadvantage of producing the less desirable wurzite 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 Al2O3 substrate. Kahn et al. appear to overcome some of the difficulties inherent in the wurzite 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 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 AlGaN or AlGaN layers. The resultant crystal lattice appears to be wurzite in form.

In U.S. Pat No. 4,862,471, Pankove describes the growth on a gallium phosphide (GaP) substrate of gallium nitride...
Letters, phosphide doped with nitrogen (GaP:N). To the basic GaAsN composition allows somewhat independent growth. R. M. Fletcher et al. describe gallium arsenide phosphide doped with nitrogen (GaAsP:N) and gallium such as boron, aluminum, indium, phosphorus and indium, whenever possible, that the substrate promotes growth in the r-plane growing surfaces, diamond, Si, Ge, SiC in both crystalline and amorphous forms.

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$_x$N$_{1-x}$ 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. observed a red shift in emission spectra from GaP:N nitrogen (N) concentration is increased in “Band gap Bowing in GaP$_x$N$_{1-x}$ 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$_x$N$_{1-x}$ for x=0.4 in an article entitled “Metalorganic vapor phase epitaxy of GaP$_x$N$_{1-x}$ 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 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 than 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$_{N_{1-x}}$ 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$_{N_{1-x}}$ material 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, in 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$_x$N$_{1-x}$ active regions, where x≤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 is 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. 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 Al$_2$O$_3$ (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 metal-organic 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 AlGaAsSn semiconductor material allows a greater concentration of N to be incorporated in the crystal. It is possible
Ammonia (NH₃) may be employed as an N source with when used with cladding layers of GaN, AlGaN or AlGaAsN lines connecting these points represent the various ternary materials lattice matched to Si, SiC or GaP. 60 materials. The points

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 example, 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 well formed layers of the layer order of the electron wave-lengths (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 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 AlGaInAs heterostructure of the present invention matched to an SiC or Al₂O₃ 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.

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION**

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 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 mismatch of about 4%. These substrates have been used to grow AlGaAs 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 InAs$_{1-x}$Sb$_x$ and InSb$_{1-x}$As$_x$ (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 AlGaN 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 [001] surface of a hexagonal substrate or on the [111] surface of a cubic substrate. In the case of rhombohedral Al$_2$O$_3$ (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 correspondingly 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 AlGaN 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 AlN, GaN and InN, respectively, while the lines connecting 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 ($a_z$) and hexagonal wurtzite ($a_h$) lattice constants are related to the bond length ($l$) by the relations:

$$a_z = \frac{4}{3\sqrt{3}} l,$$

and

$$a_h = \frac{2}{\sqrt{6}} l.$$

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$_{0.9}$N$_{0.1}$ has a bond length of 0.17 (1.96 Å)+0.03 (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 6.06 Å and the wurtzite lattice constant for GaN ($x=1.0$) 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$_2$O$_3$ 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 GanInAsN 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 ($x$≤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$_{1-x}$Ga$_x$N$_{1-x}$P$_{0.52}$As$_{0.1}$ 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 L- 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 ($x$≤0.05) or arsenic ($x$≥0.90) incorporation allowed by adding one 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$_m$Al$_n$Ga$_{1-m-n}$In$_p$N$_{1-p}$P$_y$N$_{1-y}$ 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 $1_{1-x}$ may be approximated by the quadratic relationship,

$$E_{gap} = E_{gap,0} (1-x)^2 + E_{gap,2} x (1-x) + E_{gap,0,2} (1-x),$$

where $E_{gap,0}$ and $E_{gap,2}$ are the bandgaps of the constituent binary materials and $E_{gap,0,2}$ is the bandgap bowsing parameter. For the Al$_{1-x}$Ga$_x$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 bowsing coefficient is sufficiently great that, instead of increasing as expected for negligible bowsing, 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 ($x$≤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$_x$.

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$_2$O$_3$ 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 GanInAsN 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 ($x$≤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$_{1-x}$Ga$_x$N$_{1-x}$P$_{0.52}$As$_{0.1}$ 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 L- 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 ($x$≤0.05) or arsenic ($x$≥0.90) incorporation allowed by adding one 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$_m$Al$_n$Ga$_{1-m-n}$In$_p$N$_{1-p}$P$_y$N$_{1-y}$ 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 $1_{1-x}$ may be approximated by the quadratic relationship,

$$E_{gap} = E_{gap,0} (1-x)^2 + E_{gap,2} x (1-x) + E_{gap,0,2} (1-x),$$

where $E_{gap,0}$ and $E_{gap,2}$ are the bandgaps of the constituent binary materials and $E_{gap,0,2}$ is the bandgap bowsing parameter. For the Al$_{1-x}$Ga$_x$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 bowsing coefficient is sufficiently great that, instead of increasing as expected for negligible bowsing, 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 ($x$≤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 In\(\text{As}_x\text{N}_y\), as \(x\) increases from 0. In\(\text{As}_x\text{N}_y\) the bandgap is about 0.36 eV, but for In\(\text{As}_x\text{N}_{0.01}\) the bandgap is reduced to 0.27 eV. Likewise, for In\(\text{As}_x\text{N}_{0.23}\text{As}_{0.77}\), 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 (using a GaAs or InP substrate), the increase in emission energy due to strain will be decreased, so the actual emission wavelength for the 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 is shown. The substrate is disposed on a graphite susceptor for heating although, as will be discussed below, the heating is less than 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 and susceptor are housed in a quartz reactor tube which is ringed by a set of conductive coils. A radio frequency alternating current that contain the aforementioned group \(III\) and group \(V\) elements and gases containing group \(V\) atoms are flowed through 65 as \([\text{III}]\). Oligomeric metallic compounds that are used to introduce the group III materials are contained in separate constant temperature baths. In a first constant temperature bath is a bubbler of trimethylgallium (TMGa) through which hydrogen gas from a hydrogen gas supply is flowed, the flow controlled by a first flow regulator. As the hydrogen gas bubbles through the TMGa, the gas becomes saturated with the oligomeric vapor, the gaseous concentrations at saturation determined by the temperature within the first bath. A conduit controlled by a first shut-off valve connects the TMGa bubbler with the reactor tube. By controlling the temperature in the first bath and the mass flow of hydrogen gas through the regulator, the mass flow of TMGa to the reactor tube can be precisely controlled.

A second constant temperature bath houses bubbler of trimethylaluminum (TMAI) which is supplied with hydrogen gas from the hydrogen gas supply at a rate controlled by a second flow regulator. In combination with the temperature of the second bath, the flow of hydrogen gas through valve controls the flow of TMAI that can be allowed by a second shut-off valve through conduit to enter reactor tube. Similarly, a third constant temperature bath contains a bubbler of trimethylindium (TMI) which is provided with hydrogen gas at a rate controlled by a third flow regulator. Hydrogen gas saturated with TMI can then be flowed to the reactor tube via conduit, which flow switched on and off by a third shut-off valve. A fourth constant temperature bath likewise contains a trimethylboron (TMB) bubbler which has hydrogen gas supplied to it at a rate determined by a fourth regulator. Flow to the reactor tube of hydrogen gas saturated with TMB is then provided by conduit, controlled by a fourth shut-off valve.

Alternative metal-organic compounds may be used for the column \(III\) pre-cursors. For 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 of separate carriers. A first plenum contains phosphine (PH\(_3\)) gas which can be supplied to the reactor tube at rate controlled by a fifth mass flow regulator. A second plenum contains arsine (AsH\(_3\)) gas which can be flow to the reactor tube at a rate controlled by a sixth flow regulator. Similarly, a third plenum is filled with gaseous ammonia (NH\(_3\)) which can be flowed to the reactor tube at a rate controlled by a seventh regulator. PH\(_3\) can be provided along with NH\(_3\) to catalyze an NH\(_3\) disassociation reaction, providing for adsorption by the substrate. AsH\(_3\) can similarly be used to catalyze NH\(_3\). Both PH\(_3\) and AsH\(_3\) can be used 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 being provided with hydrazine (H\(_2\)NNH\(_2\)). Alternative sources may also be used for the column \(V\) elements, phosphorus, arsenic and antimony.

In addition to the above described bobbler and plenums that contain the aforementioned group \(III\) and group \(V\) elements, other bobbler 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 bobbler 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 \(III\) and \(V\) 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 elements 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 [\(\text{III}\)].

For the case of the quineterary system AlGaInAsN lattice matched to ZnO, as shown in FIG. 13, the actual growth of...
the material proceeds from a ZnO substrate. The initial buffer layer of AlGaAs is grown at a temperature between 500–550 °C. Following the growth of the buffer layer, the reactor temperature is raised to the growth temperature between 750–800 °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 lower initial buffer layer, a cladding layer, comprising n-type (Al,Ga),In,As,(N), (Al,Ga,In,As,N), layer 336 is grown. The appropriate n-type dopants include Si, Ge, Sn, Se or Te. A layer 337 of nominally undoped (Al,Ga,In,As,N), is grown next, followed by the GaAs,In,As,N, strained layer quantum well active region 338, followed by another layer 339 of nominally undoped (Al,Ga,In,As,N), material. The p-type (Al,Ga,In,As,N), upper cladding layer 340 is grown next, followed by a heavily doped p-type GaAs,N, contact layer.

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 gas such as N₂, H₂, NH₃, 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 electron-cyclotron resonator, not shown, can be aligned with an NH₃ source to crack the NH₃ to yield a radical N source. The group V elements can be produced in independently heated effusion ovens which are enclosed in liquid nitrogen cooled shrouds. The group III elements can be housed in introducing dislocations due to the strain from adjacent mismatched layers. In some material systems with a large concentration of N, it is similarly possible to provide the relative concentrations of N relative to Ga generally raises the material accumulated in 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.

An example of an arrangement for manufacturing a heterostructure laser of AlGaAs/N is shown in FIG. 9. In this case the substrate 210 might be ZnO, for which AlGaAs/N 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 10⁻¹⁰ to 10⁻¹⁴ 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 Se 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 to provide the 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 on 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 AlAs₀₋₀₅,N₀₋₀₂ 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 is formed of the desired thickness.

On top of the n-type cladding layer 250 an active layer 255 is grown. In order to grow a defect free active layer, the group V lattice sites are again proportioned such that As occupies about 80% of those sites, and N occupies the remaining 20%. 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 nm. If desired, the active layer 255 can be incorporated along with a GaN monolayer to enhance n-type AlAsN layer to be somewhat electrically conductive.

The active layer 255 is grown as a p-type cladding layer of AlAsN 260, followed by growth of 111-V materials. This sequence is repeated to achieve the approximately 210, 248, 275, 300, 338, 370, 408, 438, 468, 498, 528, 558, 588, and 618 periods of growth of AlGaAsN materials on a ZnO substrate.

While the light emitting device 248 is described 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 multicolor light emitting diode may 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 transparent 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 previous device 248 in a converse fashion, that of receiving photons and emitting electrons. On a n-type GaN substrate 278 is grown an n-type GaAs 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 GaAs 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 GaAs layer to be somewhat electrically conductive. On top of the n-type GaAs layer 280 is grown a p-type GaAs 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 GaAs layers 280 and 283 have a direct band gap of about 1.9 eV, corresponding to red or yellow light.

Atop the p-type GaAs layer 283 is grown a lattice matched, zincblende, n-type Al,Ga1-xAsN 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 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. Growth on the n-type Al,Ga1-xAsN layer 285 is a
p-type $\text{Al}_x\text{Ga}_{1-x}\text{AsN}$ 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 $\text{Al}_x\text{Ga}_{1-x}\text{AsN}$ layer 287 an n-type $\text{Al}_x\text{Ga}_{1-x}\text{AsN}$ 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 $\text{Al}_x\text{Ga}_{1-x}\text{AsN}$ layer 290 is a p-type $\text{Al}_x\text{Ga}_{1-x}\text{AsN}$ 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 $\text{GaAsN}$ 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 287 is a second lead 297. The leads 295 and 297 are fed to a voltage or current meter which can detect voltage differences and current between the leads 295 and 297. Another pair of leads 303 and 305 are similarly attached to the n-type $\text{Al}_x\text{Ga}_{1-x}\text{AsN}$ layer 285 and p-type $\text{Al}_x\text{Ga}_{1-x}\text{AsN}$ 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 $\text{Al}_x\text{Ga}_{1-x}\text{AsN}$ layer 290 and p-type $\text{Al}_x\text{Ga}_{1-x}\text{AsN}$ 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 and converted to electricity. The high-bandgap lattice-matched materials system of the present invention can be used as a green light detector. 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.

A third photon 320 impinging upon surface 317 has an energy corresponding to red light and thus passes through layers 293, 290, 287, and 285. The third photon 320 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.
an example, GaP_{x,76}As_{x,24}N_{0.04}, should be lattice matched to GaP and Al_{x,5}Ga_{1-x}P_{0.94}N_{0.06} 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-x}In_{x}As_{1-x}N_{x} can also be lattice matched to InP. For example, the mid-IR emitting In_{0.55}Ga_{0.45}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 thickness and structure such that 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=3.5 Å) or Si (3.11 Å) substrate. 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_{x}Ga_{1-x}N lower cladding layer 327 are Al_{x}Ga_{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_{x}Ga_{1-x}N p-type upper cladding layer 331 is grown (27 k). Finally, a p-type Ga_{x}As_{0.9}N_{0.1} cap 332 is grown to provide a low-resistance ohmic contact. If 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), a n-type (Al_{x}Ga_{1-x}) lower cladding layer 336 is grown, followed by (Al_{x}Ga_{1-x})_N lower cladding layer 337 and 339 (y>x), in the center of which is placed a GaAs_{0.1}N_{0.9} strained-layer quantum well active region 338. A p-type (Al_{x}Ga_{1-x})_N upper cladding layer 340 is then grown, followed by a Ga_{x}As_{0.1}N_{0.9} 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 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 cladding layer 347, a GaAsN, GaPN, or GaSbN active layer 348 and a p-type SiC upper cladding layer 349. This LED has utility when the bandgap of the active region 348 is less than the bandgap of the SiC cladding 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 GaAs_{0.1}N_{0.9} strained-layer quantum well.

We claim:
1. A Group III-As_{1-x}N_{x} semiconductor comprising: a semiconductor substrate; at least one region formed on said substrate comprising one or more monolayers substantially of N with at least one Group III element interspersed with one or more monolayers comprised substantially of As with at least one Group III element; said region providing a bandgap bowing portion when a molecular factor x of Group III-As_{1-x}N_{x} in said layer is varied from between 0 and 1 where x is not 0 or 1; selection of the molecular factor x for said group layers providing materials with different emission wavelengths within the lightwave spectrum from UV to IR wavelengths.
2. The Group III arsenide-nitride semiconductor of claim 1 wherein said Group III arsenide-nitride compound comprises GaAs_{1-x}N_{x} or InAs_{1-x}N_{x}, InGaAs_{1-x}N_{x} or AlGaAs_{1-x}N_{x}.
3. The Group III arsenide-nitride semiconductor of claim 1 wherein said layer group is lattice matched to substrate under strain.
4. The Group III arsenide-nitride semiconductor of claim 1 wherein said layer group is lattice matched to said substrate.
5. The Group III arsenide-nitride semiconductor of claim 1 wherein some of said layers are doped p-type, others doped n-type and remaining layers are undoped and formed in said bandgap bowing portion where the material is semiconductive.
6. A III-V semiconductor single crystal composite material comprising:
   a series of layers having nitrogen and at least one other Group V atomic species disposed at Group V lattice sites in said series of layers, said series of layers at least partially containing nitrogen in one set of said layers and at least partially containing one other Group V atomic species in another set of said layers, said layers being sufficiently thin in the monolayer regime to avoid formation of defects, said layer sets arranged with their overall nitrogen to the other Group V atomic species ratio providing an overall direct bandgap for the combined series of layers.
7. The composite material of claim 6 where in said layer sets are alternated groups of said layer series comprising first layers having nitrogen disposed at Group V lattice sites and second layers having another Group V atomic species disposed at Group V lattice sites.
8. The composite material of claim 7 wherein the Group V atomic species in said second layers is As.
9. The composite material of claim 7 wherein said layer sets arranged with their overall nitrogen to the other Group V atomic species ratio substantially provide lattice match of said composite material layers to a crystalline substrate.
10. The composite material of claim 9 wherein said substrate is selected from the group consisting of GaP, Si, GaAs, Ge, InN, SiC, ZnSe, ZnO and diamond.
11. The composite material of claim 6 wherein at least one layer of said composite material has a direct bandgap.
12. The composite material of claim 6 wherein said thin layers are composed of In_{x}Al_{1-x}Ga_{1-y}N and In_{x}Al_{1-x}Ga_{1-y}As.
13. The composite material of claim 6 wherein at least one of said layers in said series of layers is a monolayer.
14. A compound semiconductor having a zinc blend crystal lattice and an overall composition with at least one element from the group consisting of B, Al, Ga and In disposed at Group III lattice sites, and also including a
of the ratio of bowing parameter.

20.

15. The compound semiconductor of claim 14 wherein said material forming a layer that is strained and is sufficiently thin to avoid defect formation.

16. The Group III arsenide-nitride semiconductor of claim 1 wherein the substrate is selected from the group consisting of Al₂O₃, MgO, GaP, Si, GaAs, Ge, SiC, ZnSe, ZnO and diamond.

17. The group III arsenide-nitride semiconductor of claim 1 wherein the As-to-N ratio in said Group III-Nₓ is selected to be substantially lattice match with the substrate.

18. The Group III arsenide-nitride semiconductor of claim 17 wherein the lattice match is due to strain.

19. The Group III arsenide-nitride semiconductor of claim 17 wherein the substrate is selected from the group consisting of Al₂O₃, MgO, GaP, Si, GaAs, Ge, SiC, ZnSe, ZnO and diamond.

20. The Group III arsenide-nitride semiconductor of claim 1 wherein the Group III arsenide-nitride semiconductor is included in a device comprising a light emitting diode or a laser diode.

21. The compound semiconductor of claim 14 wherein the compound semiconductor material exhibits a bandgap bowing parameter allowing for different composition of the alloy with adjustment of the ratio of As to N in the deposit of the material.

22. The compound semiconductor of claim 21 wherein said bandgap bowing parameter is approximated by the quadratic relationship,

\[ E_{gap} = E_{gap,As}x + E_{gap,N}y - C_{b}(1-x) \]

where \( E_{gap,As} \) and \( E_{gap,N} \) are the bandgaps of the constituent binary materials and \( C_{b} \) is the bandgap bowing parameter.

23. The compound semiconductor of claim 21 wherein said bandgap bowing parameter is in excess of 1 eV.

24. The compound semiconductor of claim 14 wherein said material exhibits a bandgap bowing parameter, adjustment of the ratio of As to N in said alloy provides for a reduction of its direct bandgap resulting in higher electrical conductivity in the semiconductor alloy due to said bandgap bowing parameter.

25. The compound semiconductor of claim 14 wherein concentration of N to As in the compound semiconductor material is either about 5% or less or about 90% or more.

26. The compound semiconductor of claim 14 wherein low levels of N (±0.05) or As (±0.05) permit an additional amount of one or more of B, Al, In or P to the compound semiconductor material thereby reducing the bandgap bowing of the compound semiconductor material as compared to a GaAs, Nₓ compound semiconductor material.

27. The compound semiconductor of claim 14 wherein the compound semiconductor material is utilized as a semiconductor layer in a semiconductor device.

28. The compound semiconductor of claim 27 wherein the semiconductor layer is an ohmic contact layer.

29. The compound semiconductor of claim 27 wherein the semiconductor device is a light emitting device.

30. The compound semiconductor of claim 27 wherein the semiconductor device is a laser.

31. The compound semiconductor of claim 27 wherein in the semiconductor device has an emission wavelength within the infrared wavelength range.

32. The compound semiconductor of claim 27 wherein the semiconductor device has an emission wavelength greater than 440 nm.

33. The compound semiconductor of claim 27 wherein selection of the molecular factors, w, x, y and z, for the semiconductor layer as well as other layers in the device providing for different emission wavelengths within the lightwave spectrum from UV to IR wavelengths.

34. The compound semiconductor of claim 27 wherein the semiconductor layer is deposited employing atomic layer epitaxy.

35. The compound semiconductor of claim 14 wherein the substrate is selected from the group consisting of Al₂O₃, MgO, GaP, Si, GaAs, Ge, SiC, ZnSe, ZnO and diamond.

36. The compound semiconductor of claim 14 wherein the compound semiconductor material is lattice matched to a substrate due to strain.

37. The compound semiconductor of claim 36 wherein the substrate is selected from the group consisting of Al₂O₃, MgO, GaP, Si, GaAs, Ge, SiC, ZnSe, ZnO and diamond.

38. The compound semiconductor of claim 14 wherein the compound semiconductor material is a strained layer quantum well.