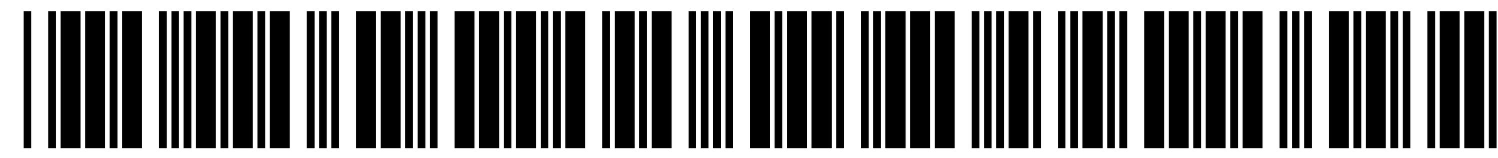

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(54) **METHODS FOR GROWING SEMICONDUCTORS AND DEVICES THEREOF THE ALLOY SEMICONDUCTOR GAINNAS**

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H01L 21/30 (2006.01)

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(58) **Field of Classification Search** 438/45, 438/46, 47, 478; 117/88, 104, 952, 954
See application file for complete search history.

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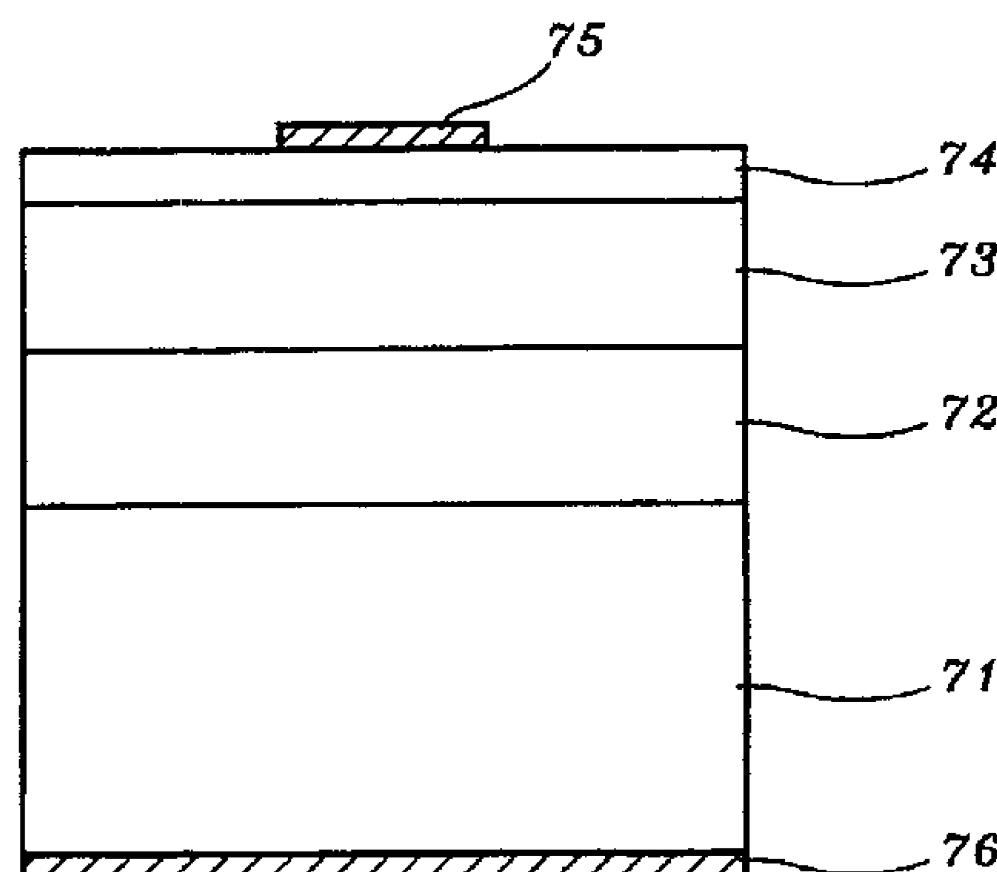
(57) **ABSTRACT**

A method is disclosed for growing a nitrogen-containing III-V alloy semiconductor on a semiconductor substrate such as GaAs, which is formed by MOCVD method using nitrogen containing organic compounds having relatively low dissociation temperatures. The alloy semiconductor has a high nitrogen content which exceeds the contents previously achieved, and has a high photoluminescence intensity.

There are also disclosed fabrications of semiconductor devices comprising the alloy semiconductors, such as heterostructure and homo-junction light emitting devices.

46 Claims, 7 Drawing Sheets



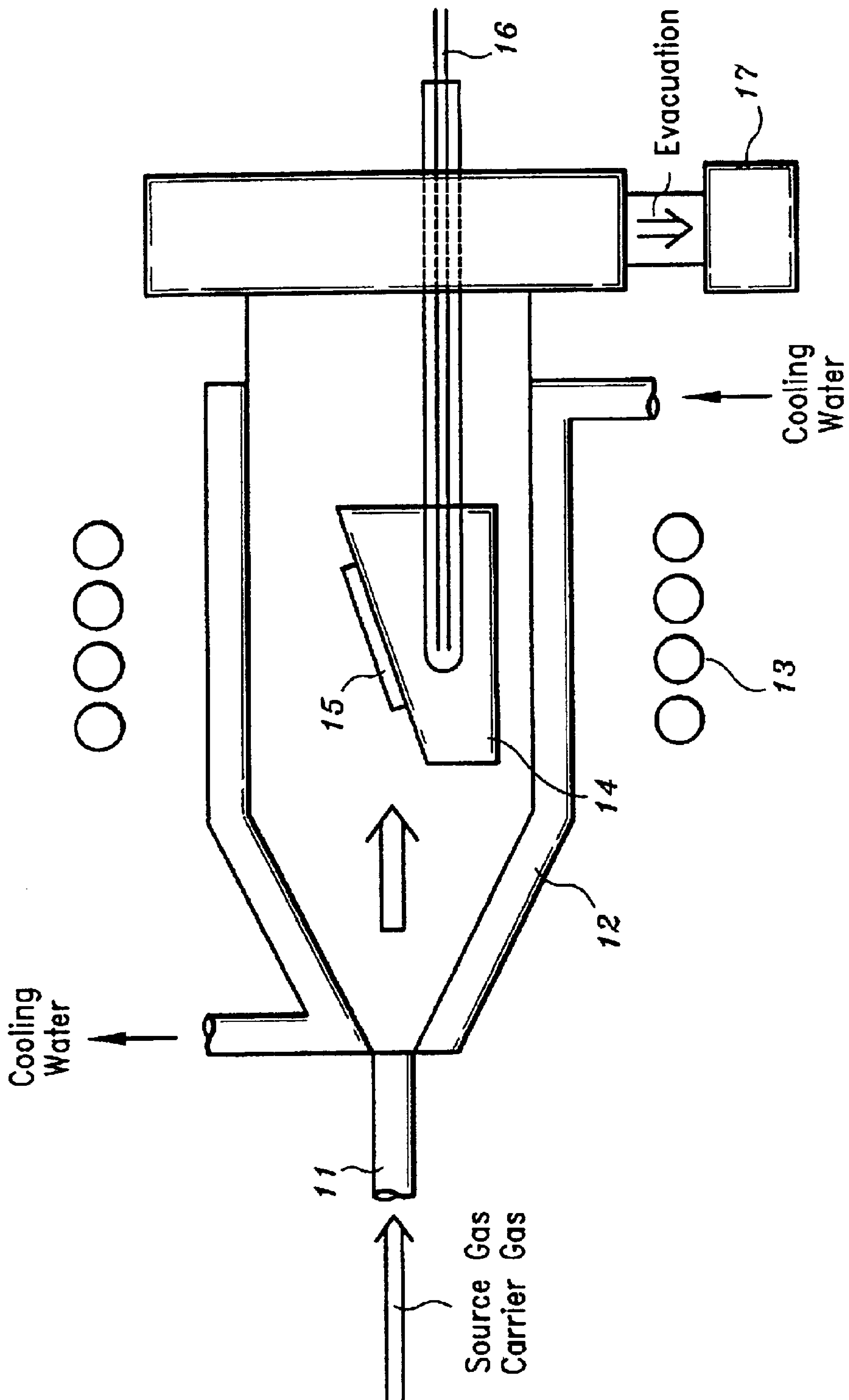


FIG. 1

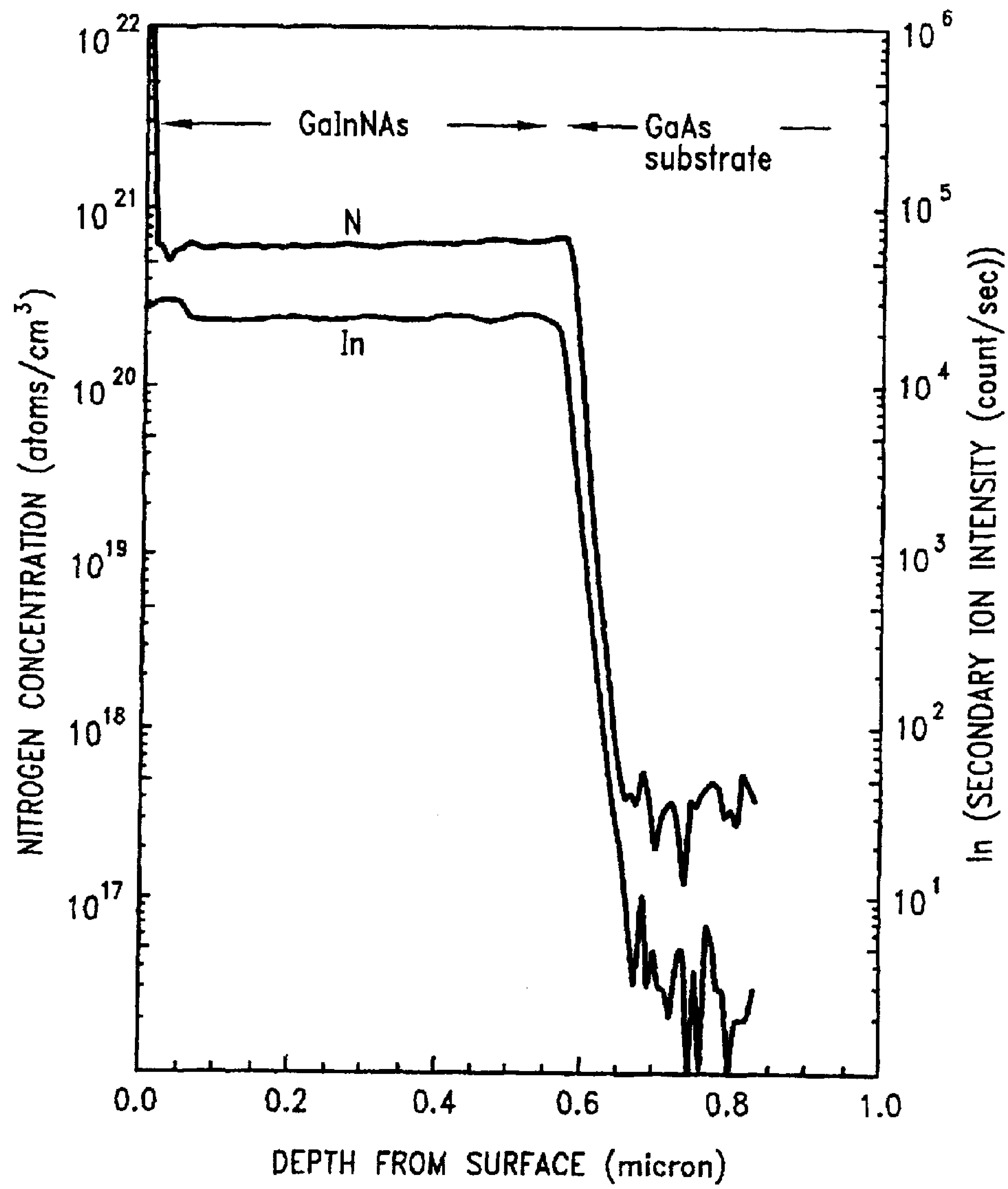


FIG. 2

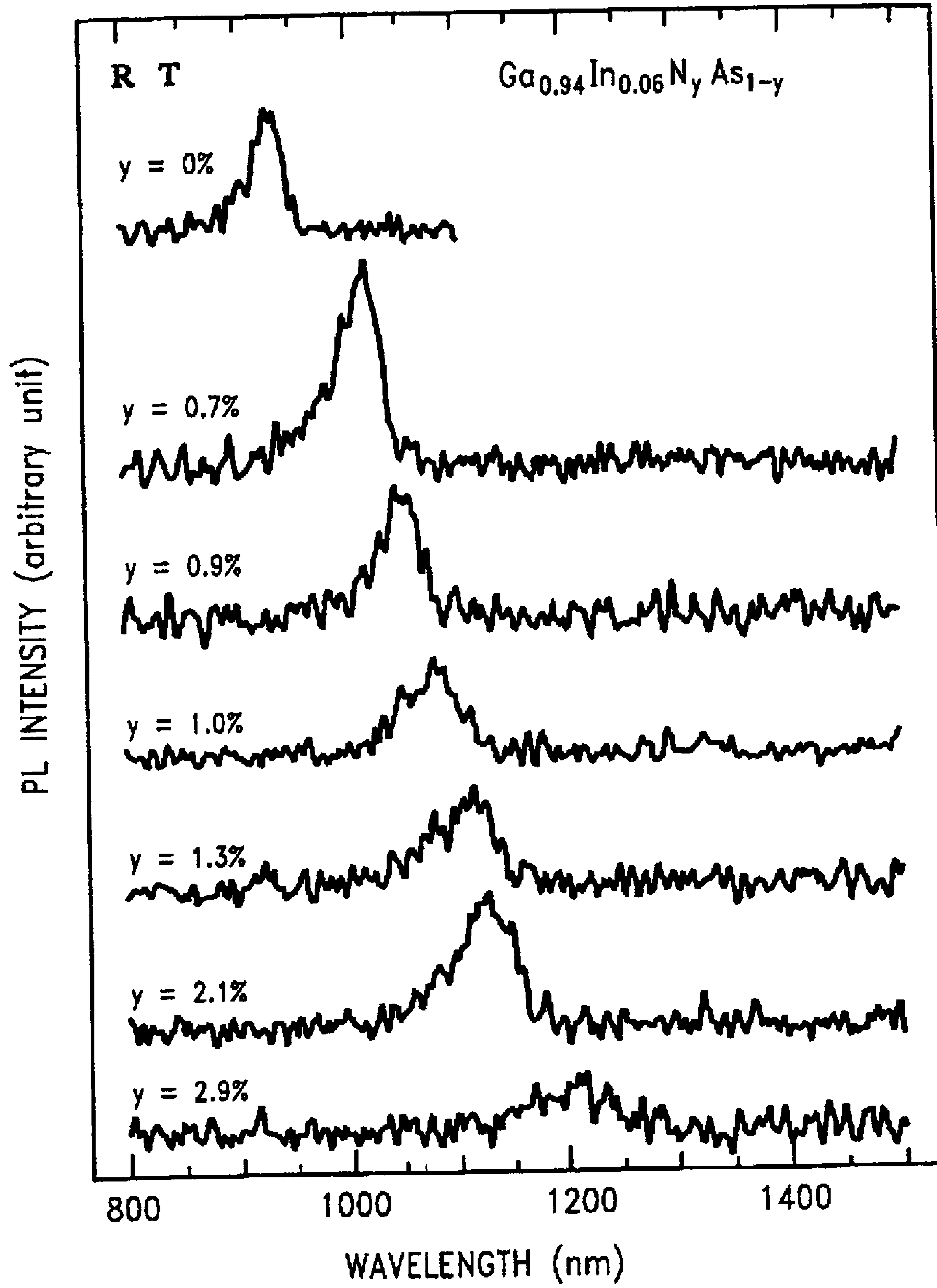


FIG. 3

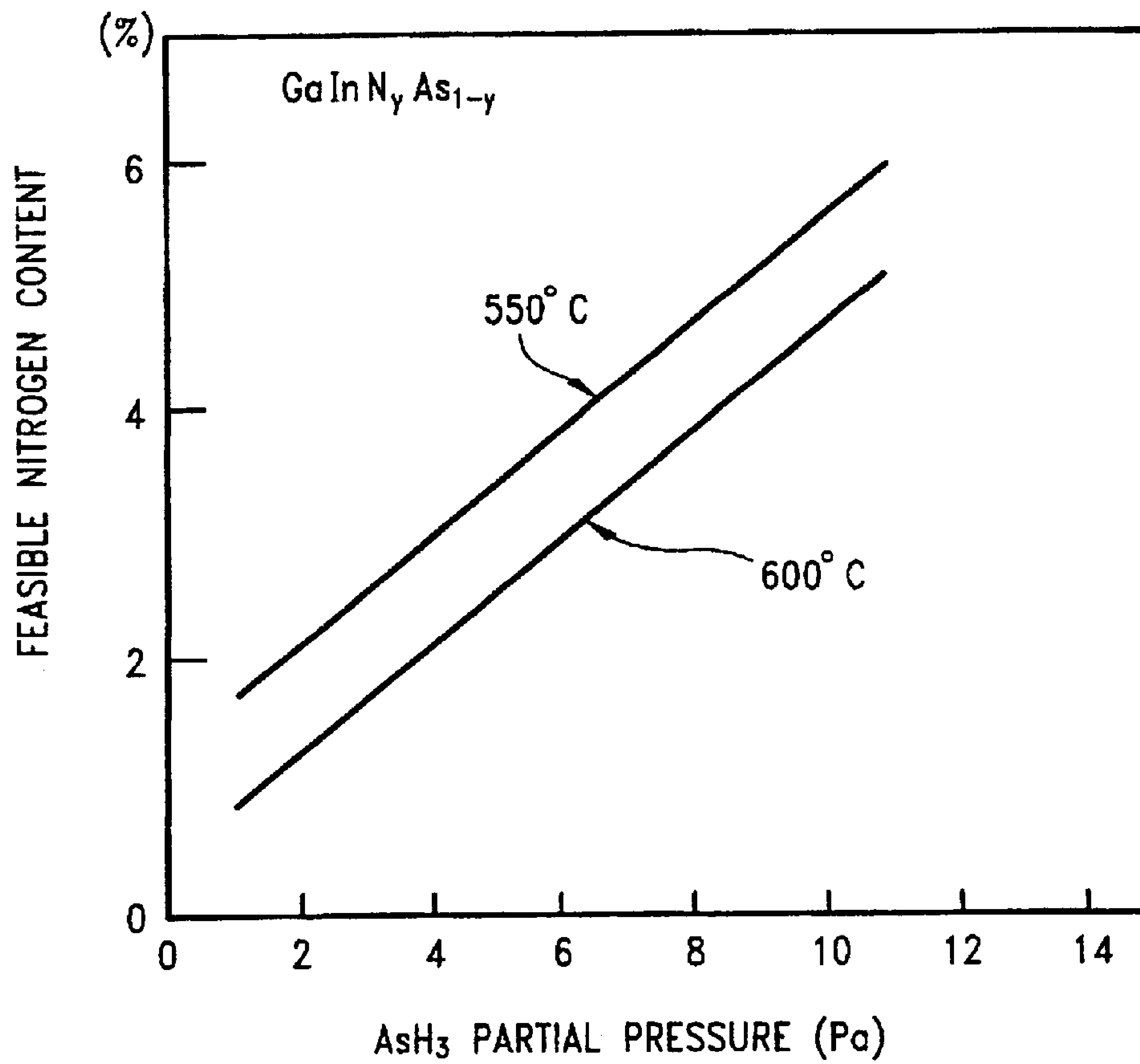


FIG. 4

GROWTH TEMPERATURE (deg C)	< 2	2–10	> 10
650–700	not grown	○	◎
600–650	not grown	○	◎
550–600	△	○	○
500–550	×	△	△
450–500	×	×	×

AsH_3 PARTIAL PRESSURE (Pa)

PL INTENSITY:
- ◎ very strong
- ○ strong
- △ weak
- × very weak

FIG. 5

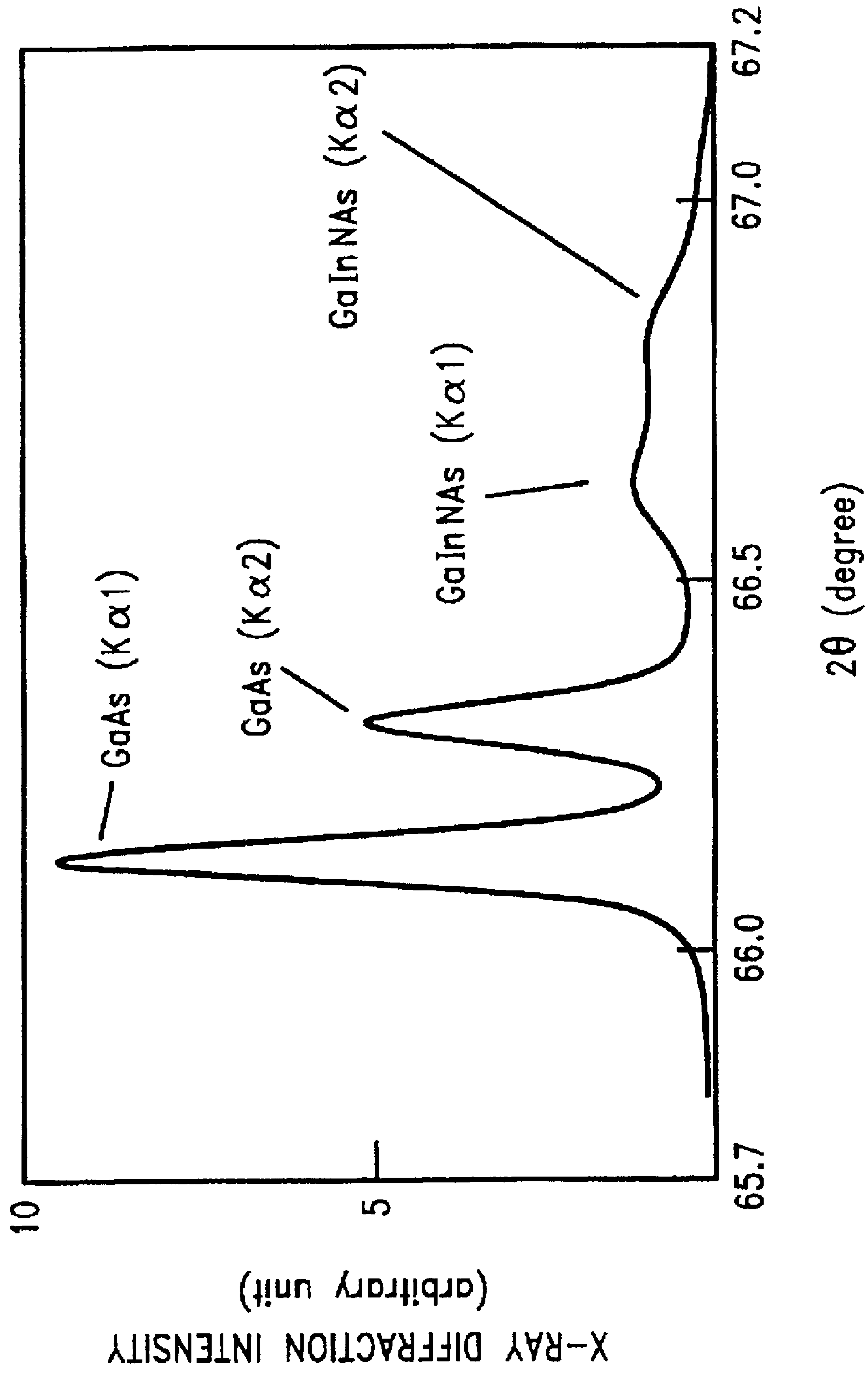


FIG. 6

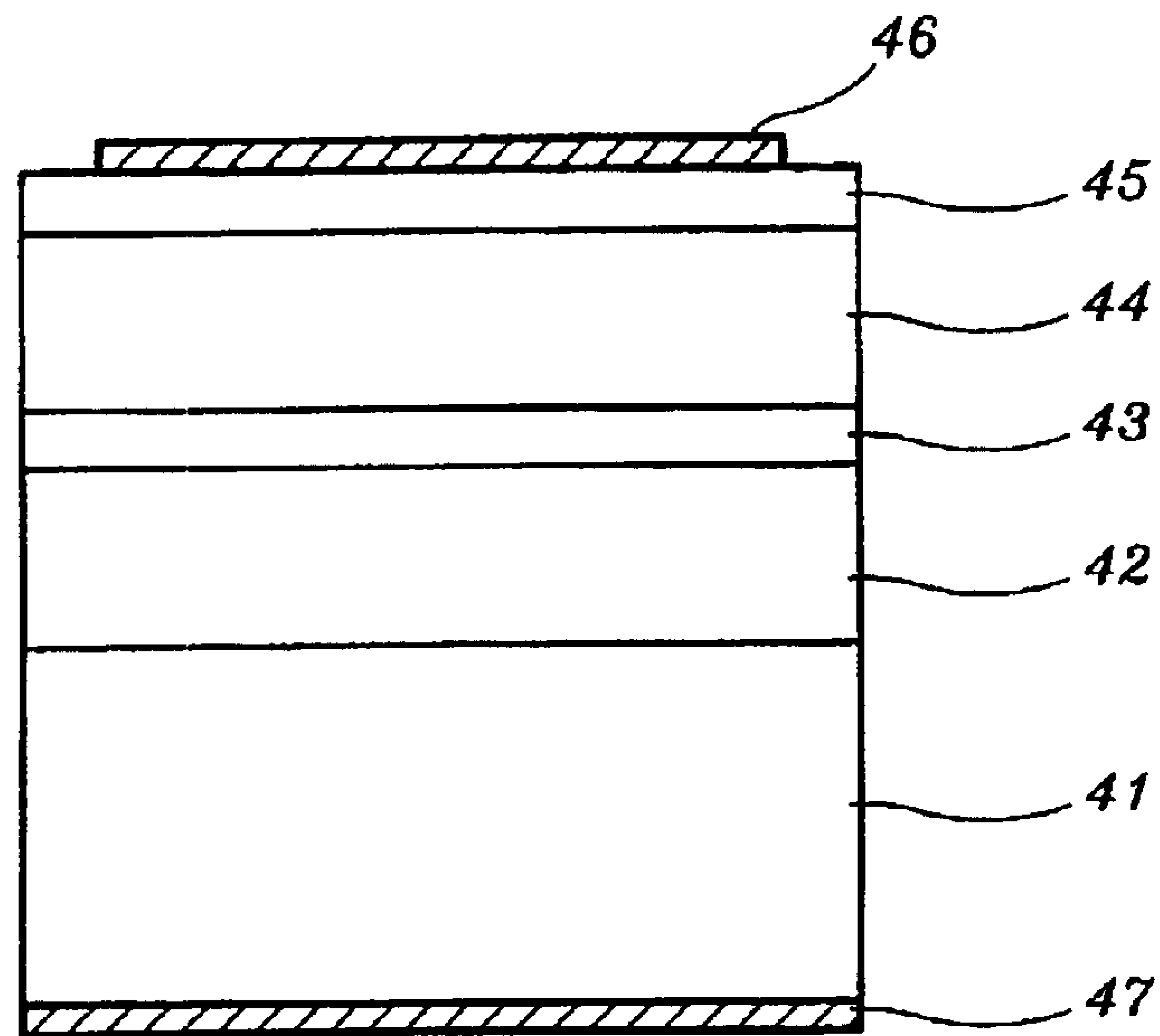


FIG. 7

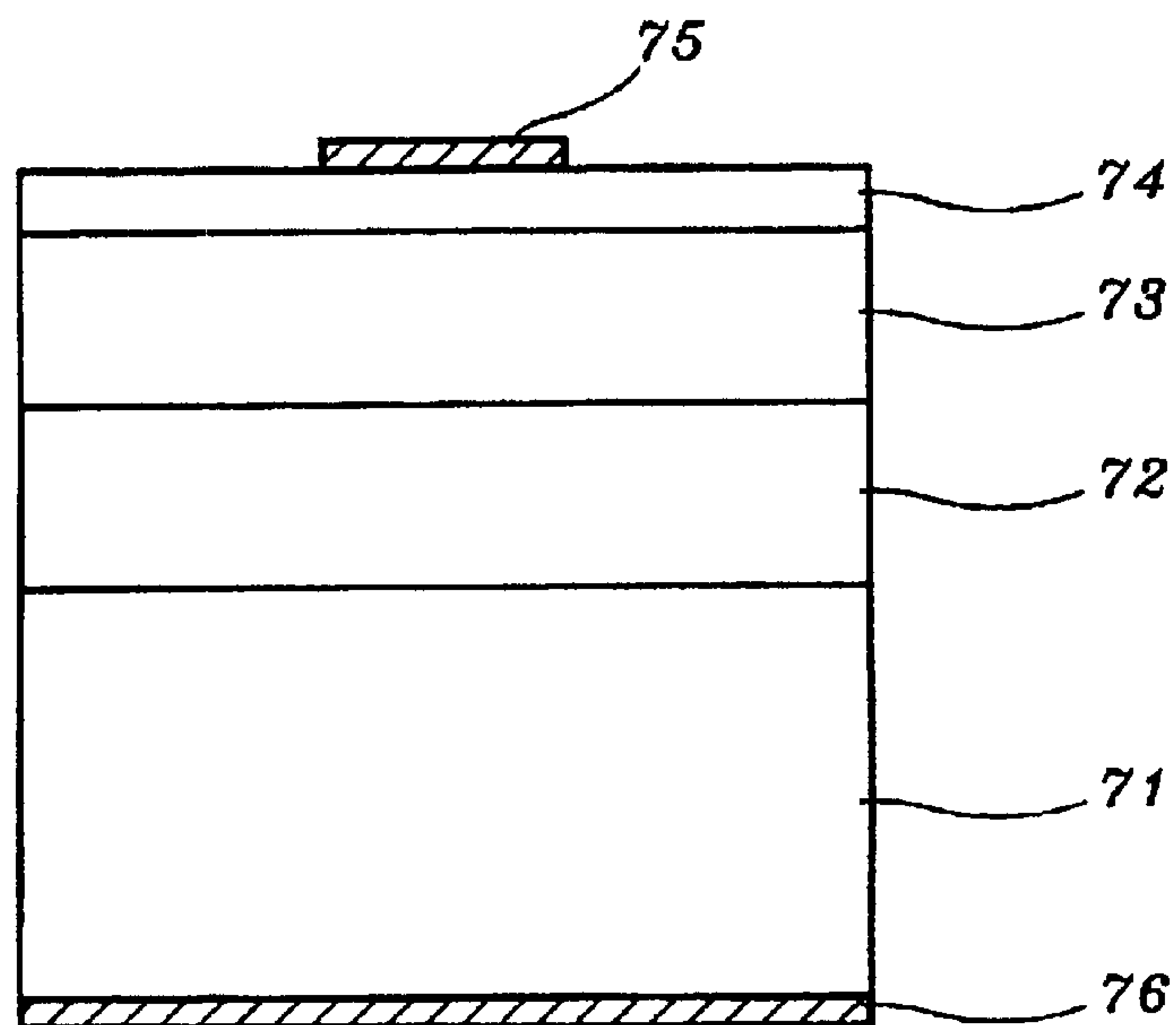


FIG. 8

METHODS FOR GROWING SEMICONDUCTORS AND DEVICES THEREOF THE ALLOY SEMICONDUCTOR GAINNAS

Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

This application, filed May 17, 2001, is an application for reissue of U.S. Pat. No. 5,904,549, issued May 18, 1999, based on U.S. application Ser. No. 08/834,959, filed Apr. 7, 1997, the entire contents of each of which are incorporated by reference herein. In addition, co-pending reissue application Ser. No. 10/603,418, filed Jun. 24, 2003, is a continuation of this reissue application.

BACKGROUND

1. Field of the Invention

This invention relates in general to semiconductors and semiconductor devices and more particularly, to methods for growing nitrogen-containing alloy semiconductors and semiconductor devices such as semiconductor lasers and light emitting diodes comprising the alloy semiconductors.

2. Description of the Related Art

Compound semiconductors in general and nitrogen-containing III-V alloy semiconductors in particular have recently received considerable attention as a group of new semiconductor materials.

As an example of methods for growing a III-V alloy semiconductor, there has been disclosed an epitaxial growth of a nitrogen-containing III-V alloy semiconductor on a silicon substrate (Japanese Laid-Open Patent Application H6-334168). In the disclosure, a nitrogen-containing alloy semiconductor is epitaxially grown without dislocations by the lattice misfit, thereby leading to feasibility of fabricating III-V compound semiconductor devices on silicon.

There are also disclosed nitrogen-containing alloy semiconductors such as GaInNAs, AlGaNAs, and GaNAs, which can be lattice matched to substrates such as GaAs, InP, and GaP (Japanese Laid-Open Patent Application H6-037355). Although it has been previously considered that no known III-V alloy semiconductor is grown, which had a smaller bandgap energy than that of GaAs and lattice matched to GaAs, recent results of the alloy semiconductor growths indicate that the above-mentioned GaInNAs alloy semiconductor, for example, can be grown as a material lattice matched to the GaAs substrate.

Since the GaInNAs compound semiconductor has a smaller bandgap energy than that of GaAs, above growth results of GaInNAs alloy semiconductor may lead to the feasibility of light emitting devices of which wavelength of the light emission is in the range of about 1.5 micron, longer than that from GaAs. As aforementioned, that has been previously conceived not feasible by the devices fabricated on GaAs substrates.

In the growth of the above-mentioned nitrogen-containing III-V alloy semiconductors, a group V element such as arsenic, for example, is desorbed from the surface of a substrate with ease even at relatively low temperatures. Therefore, the alloy semiconductors are preferably grown at temperatures as low as possible.

As a source material for nitrogen, NH_3 has been used conventionally. However, the use of NH_3 is not completely satisfactory, since temperatures for alloy semiconductor growth have to be relatively high because of a relatively high dissociation temperature of NH_3 and an unduly desorption of arsenic results at such temperatures. Therefore, NH_3 is not preferred as a source material for the growth of alloy semiconductors which simultaneously contain both nitrogen and arsenic.

Accordingly, in place of the use of NH_3 as is in conventional growths, active species which are generated by a high frequency plasma excitation of nitrogen, have been used as the source material for nitrogen. These species are used for a growth of nitrogen-containing III-V alloy semiconductors by, for example, molecular beam epitaxy (MBE) which is carried out under very low pressures, or low pressure metalorganic chemical vapor deposition (MOCVD) which is performed at pressures of about 0.1 Torr (13.3 Pa).

As another source material for nitrogen, an organic material such as dimethylhydrazine (DMHy) has been reported for a growth of a GaNAs alloy semiconductor by conventional MOCVD at a reduced pressure of 60 Torr (as described by N. Ohkouchi and others, Proceedings of 12th Symposium on Alloy Semiconductor Physics and Electronics, 1993, pages 337–340)

As aforementioned, nitrogen is desorbed from crystal surfaces with relative ease during the growth. This causes difficulties in obtaining nitrogen-containing III-V alloy semiconductors with a large concentration of nitrogen. In conventional growths of the alloy semiconductors, therefore, previous attention is primarily directed to an increase of the nitrogen content during the crystal growth.

In the above-mentioned method using activated nitrogen species, a partial pressure of nitrogen during the growth had to be relatively low to avoid deactivation of the nitrogen species previously activated. Therefore, for the growth of nitrogen-containing alloy semiconductor such as GaNAs, for example, the low partial pressure of nitrogen necessarily leads to low pressures of another group V element such as arsenic. This results in an undesirable increase in concentrations of arsenic vacancies and makes it difficult to grow nitrogen-containing III-V alloy semiconductor of satisfying quality.

For example, in order to obtain the nitrogen content of about 1%, a crystal growth is carried out under the conditions such as a reactor pressure of 25 Pa, N_2 flow rate of 50 sccm, and AsH_3 flow rate of 10 sccm (as described by M. Sato, Proceedings of 13th Symposium on Alloy Semiconductor Physics and Electronics, 1994, pages 101–101). Although the reactor pressure is once increased to 300 Pa to initiate the plasma discharge in the reactor, a plasma activation of nitrogen is subsequently carried out at 25 Pa, as indicated above. Under the conditions, a partial pressure of AsH_3 of as low as approximately 0.9 Pa results. In addition, other gaseous materials such as triethylgallium (TEG) as a source material for group III element and H_2 as a carrier gas, have to be additionally supplied into the reactor. As a result, the partial pressure of AsH_3 further decreases.

In order to further increase the nitrogen content, it is necessary either to reduce the reactor pressure, increasing the amount of nitrogen source materials, or decreasing the flow rate of AsH_3. The partial pressure of AsH_3 further decreases.

As exemplified as above, previous growth attempts to increase the nitrogen content had led to an increase in the concentration of arsenic(group V element) vacancies, and this gives rise to, in turn, metal (group III element)-rich alloy semiconductors. As a result, these methods are not able to provide nitrogen-containing alloy semiconductors of excellent quality.

As another example of the nitrogen source material, the aforementioned dimethylhydrazine (DMHy) is also used for a growth of a GaNAs alloy semiconductor by conventional low pressure MOCVD operated at a pressure of 60 Torr, resulting in the nitrogen content of about 0.5% or less. This GaNAs growth has been carried out also under conditions of an increased flow rate of DMHy and a decreased flow rate of AsH_3. Because of a decreased AsH_3 partial pressure, a metal-rich alloy semiconductor is obtained similarly to the above example and even under the condition of an increased nitrogen flow rate, it is difficult to increase the nitrogen content and this method also is not be able to provide nitrogen-containing alloy semiconductors of excellent quality.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide methods which overcome the above-noted difficulties.

Another object of the invention is to provide methods for growing III-V alloy semiconductors having a high nitrogen concentration and to provide semiconductor devices comprising the alloy semiconductors.

According to an aspect of the present invention, there is provided a method for growing an alloy semiconductor on a semiconductor substrate, having at least one layer of III-V alloy semiconductor comprised of a plurality of group V elements including at least nitrogen and arsenic simultaneously. The method comprises a step of growing the alloy semiconductor by MOCVD, for example, using source materials such as nitrogen-containing organic compounds for nitrogen, and AsH_3 for arsenic, under conditions of a partial pressure of AsH_3 in a reactor equal to or more than 2 Pa, and a temperature of a semiconductor substrate of more than or equal to 550° C., whereby providing III-V alloy semiconductors of a high nitrogen concentration, which has excellent quality for the use of light emitting devices, of which wavelength of light emission is in a range longer than that from GaAs devices.

According to yet another aspect of the invention, there is provided a method for growing nitrogen-containing III-V alloy semiconductors, using nitrogen-containing organic compounds as source materials for nitrogen, such as dimethylhydrazine (DMHy) and tertiary butyl amine (TBA), which have improved properties such as low dissociation temperatures and high vapor pressures, thereby leading to growths of alloy semiconductors of excellent quality for the use of light emitting devices.

According to another aspect of the invention, there is provided a method for growing nitrogen-containing III-V alloy semiconductors on a semiconductor substrate, and controlling conductive properties of, and carrier concentrations in the alloy semiconductors by adding appropriate dopants such as selenium for n-type, and group II element such as zinc or magnesium for p-type.

By the use of organic materials which contain nitrogen and have a relatively low dissociation temperatures, as the source materials for nitrogen, nitrogen-containing III-V alloy semiconductors can be grown. The alloy semiconductors have a high nitrogen content which exceeds the contents previously achieved by conventional methods, and have excellent crystalline quality and a high photoluminescence efficiency, indicative of promising characteristics for light emitting devices, as well as photodetecting devices.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described hereinbelow with references to the drawings wherein:

FIG. **1** is a schematic drawing of an MOCVD apparatus for growing alloy semiconductors in accordance with the present invention;

FIG. **2** shows results of secondary ion mass spectroscopy (SIMS) on depth profile of nitrogen in GaInNAs layers in accordance with the invention;

FIG. **3** shows room temperature photoluminescence spectra of a plurality of GaInNAs layers in accordance with the invention;

FIG. **4** contains a graph which shows a relationship between the nitrogen content in the alloy semiconductor $Ga_{0.87}In_{0.13}N_yAs_{1-y}$ and growth conditions;

FIG. **5** contains Table 1 which shows a relationship between photoluminescence intensities and AsH_3 partial pressures, of $Ga_{0.94}In_{0.06}N_{0.002}As_{0.98}$ layers in accordance with the invention;

FIG. **6** is an x-ray diffraction pattern of $Ga_{0.92}In_{0.08}N_yAs_{1-y}$ layers in accordance with the invention, from which the nitrogen content of 4.6% is deduced;

FIG. **7** is a section view of a light emitting device in accordance with a second embodiment of the invention; and

FIG. **8** is a section view of a light emitting device in accordance with a third embodiment of the invention.

DESCRIPTION OF THE ILLUSTRATIVE EMBODIMENTS

In the description which follows, specific embodiments of the invention particularly useful in alloy semiconductor growths and light emitting device applications are described. It is understood, however, that the invention is not limited to these embodiments. For example, it is appreciated that the methods for the alloy semiconductor growth and light emitting device fabrication of the present invention are adaptable to any form of semiconductor growths and device fabrications. Other embodiments will be apparent to those skilled in the art upon reading the following description.

Referring to the drawings, the invention will be described.

FIG. **1** represents a section view of a reactor of an MOCVD apparatus used for growing alloy semiconductors in accordance with the present invention. Although a horizontal apparatus is shown in this figure, a vertical apparatus may also be used.

As illustrated in FIG. **1**, the reactor comprises a quartz tube **12** which is operable as a reactor, equipped with a water cooling system around the outer face of the tube, an inlet **11** for feeding gaseous components such as source materials and carrier gas, a substrate **15** placed on a carbon susceptor **14**, a heating coil **13** supplied with high frequency power to heat the carbon susceptor **14** with the substrate **15**, a thermocouple **16** to measure temperatures of the carbon susceptor **14** and the substrate **15**, and an evacuation system **17** to evacuate to and/or maintain an appropriate low pressures. By the use of this apparatus and MOCVD method, growth of alloy semiconductors are carried out.

In the present invention, there is provided a method for growing layers of alloy semiconductors on a semiconductor substrate, having at least one layer of III-V alloy semiconductors comprised of a plurality of group V elements including at least nitrogen and arsenic simultaneously. The method comprises the step of growing the alloy semiconductors by MOCVD, using source materials such as nitrogen-

containing organic compounds for nitrogen and AsH_3 for arsenic, under conditions of a partial pressure of AsH_3 in a reactor equal to or more than 2 Pa, and a temperature of a semiconductor substrate of more than or equal to 550° C.

According to another aspect of the present invention, there is provided a method comprising the step of growing nitrogen-containing III-V alloy semiconductors by MOCVD, using source materials such as nitrogen containing organic compounds under conditions of a partial pressure of AsH_3 in a reactor equal to or more than 10 Pa, and a temperature of a semiconductor substrate of more than or equal to 600° C.

Although NH_3 is conventionally used as a source material for nitrogen, as aforementioned, the dissociation efficiency of NH_3 is relatively low. At temperatures high enough to achieve the nitrogen dissociation, nitrogen as well as other group v element such as arsenic are desorbed from a surface of the semiconductors with relative ease. Therefore, low temperatures are preferred for the growth of layers of nitrogen-containing alloy semiconductors such as GaInNAs. Since these low temperatures are not favorable to the use of NH_3, other nitrogen containing compounds of lower dissociation temperatures are preferred as source materials.

Accordingly, in the present invention, nitrogen containing organic compounds are used such as dimethylhydrazine (DMHy) and tertiary butyl amine (TBA), for example, which have relatively high vapor pressures, thereby leading to lower flow rates of carrier gas such as H_2 used for bubbling and transporting nitrogen source materials. As a result, a fluctuation in transport rates by, for example, temperature change of cylinders of nitrogen source materials, can be reduced and III-V alloy semiconductors can be grown with excellent quality and reproducibility.

Also by the methods of this invention, GaInNAs layers can be grown on a GaAs substrate. By adding indium to GaAs in this layer growth, the lattice constant of the alloy semiconductor increases with decreasing a bandgap energy. By adding nitrogen, by contrast, the lattice constant decreases with decreasing bandgap energy. Accordingly, by adding appropriate amount of nitrogen to $Ga_{1-x}In_xAs$, the lattice constant of resultant alloy semiconductor layers can be matched to that of GaAs, with a decreased band gap energy. It becomes easier, therefore, to grow satisfactory GaInNAs layers which is able to have light emissions at room temperature, of which wavelengths are longer than that from GaAs (approximately 870 nm at room temperature)

The GaInNAs layers can thus be grown with more ease by the method of the present invention, these layers are an improvement over $Ga_{1-x}In_xAs$ layers which are conventionally used for light emitting devices and have a lattice mismatch. By the use of the present GaInNAs layers, it becomes easier to obtain alloy layers having excellent quality and being capable of emitting light with wavelengths of 1.1 μm and above, longer than those by the previous layers.

Also in the layer formation of the present invention, conductive properties and carrier concentrations of the nitrogen-containing III-V alloy semiconductors layers may be controlled by adding appropriate dopants, selenium for n-type, and group II element such as zinc or manganese for p-type, as will be detailed below.

The III-V mixed compound semiconductors grown as mentioned above can be used for fabricating light emitting devices such as light emitting diodes and semiconductor lasers, and photodetecting devices such as photodiodes, having excellent device characteristics.

The following examples are provided further to illustrate preferred embodiments of the invention.

EXAMPLES

Example 1

Layers of a GaInNAs alloy semiconductor of the present invention were grown on a GaAs substrate in accordance with steps which follow.

As source materials for group III element, trimethylgallium (TMG), triethylgallium (TEG), trimethylindium (TMI), or triethylindium (TEI) was used. Also used as source materials were AsH_3 for arsenic, and dimethylhydrazine (DMHy), monomethylhydrazine (MMHy), or tertiary butyl amine (TBA) for nitrogen.

As illustrated in FIG. **1**, gaseous components from these materials were introduced to a water-cooled quartz reactor **12** through a gas inlet **11**. Prior to the introduction of the gaseous species, the reactor was evacuated to a pressure of 1.3×10^4 Pa. A carbon susceptor **14** was heated to an appropriate temperatures by a heating coil **13** fed with high frequency power and a GaAs substrate **15** was subsequently heated by the heat transfer from the susceptor **14**. Source materials were dissociated by heating and resultant gaseous species from the source materials were transported to the GaAs substrate **15** to grow alloy layers by surface reactions on the substrate.

The feeding rates of each source material were from 4.0×10^{-6} to 4.0×10^{5} mol/min for TMG, from 4.4×10^{-7} to 4.4×10^{-6} mol/min for TMI, from 6.0×10^{-5} mol/min (0.4 sccm) to 2.2×10^{-3} mol/min (46.4 sccm) for AsH_3, and from 5.0×10^{-4} to 3.0×10^{-2} mol/min for DMHy. The flow rate of total gaseous species from the source materials together with a carrier gas H_2 was typically 6 l/min. In addition, an AsH_3 partial pressure was from 0.9 to 102 Pa at a temperature for the layer growth ranging from 450° C. to 700° C.

As an example, an alloy semiconductor growth was carried out under conditions such as gas feeding rates of about 2.0×10^{-5} mol/min for TMG, about 2.2×10^{-6} mol/min for TMI, about 3.3×10^{-4} mol/min (7 sccm) for AsH_3, about 6.4×10^{-3} mol/min for DMHy, and an AsH_3 partial pressure of 15.4 Pa. In this example, the AsH_3 partial pressure was higher than the conventional growth condition.

In addition, a feeding rate of DMHy was one order of magnitude higher than that of AsH_3 and a growth temperature was about 630° C. The resulting speed of the layer growth was 1.7 μm/hour.

FIG. **2** represents results of secondary ion mass spectroscopy (SIMS) on the depth profile of nitrogen in GaInNAs layers presently obtained.

From the results, a concentration of nitrogen was deduced to be about 6.5×10^{20} atoms/cm^3, which corresponds to the content of 3%. From the above-mentioned SIMS results together with the lattice constant obtained from x-ray diffraction measurements using Cu $K_\alpha$lines ($K_{\alpha1}$ 0.15405 nm and $K_{\alpha2}$ 0.1544 nm), the indium content was obtained as about 6%, thereby resulting in a composition $Ga_{0.94}In_{0.06}N_{0.03}As_{0.97}$ for the alloy layers. The presently obtained lattice constant of GaInNAs layers was smaller than that of GaAs.

In addition, photoluminescence (PL) spectra from the layers were observed at room temperature with an argon laser excitation and a germanium photodiode as a detector and a peak wavelength of the spectra was obtained at 1.2 μm.

Various GaInNAs alloy layers having the indium content of about 6%, were grown under AsH_3 partial pressures of equal to or more than 4.8 Pa. FIG. **3** shows room temperature photoluminescence spectra from these layers, indicating that

peak wavelengths of the spectra increase with increasing the nitrogen content in the layers. For alloy layers having the nitrogen content of 2.1%, in which the layers are lattice-matched to GaAs, the peak wavelength was about 1.15 μm.

There was also found in the present alloy growths, the nitrogen content increased with decreasing growth temperature at a constant gas feeding rate. In addition, if both of a feeding rate of a nitrogen source material and a growth temperature remained constant, the nitrogen content increased with decreasing an AsH_3 partial pressure. Furthermore, in order to obtain the same nitrogen content under a constant AsH_3 partial pressure, a feeding rate of the DMHy nitrogen source material, had to be increased with increasing growth temperature.

In addition, at such relatively high temperatures as 600° C. or above, $GaInN_yAs_{1-y}$ layers having a high nitrogen content was able to grow without becoming rich in metal (group III) species. FIG. **4** represents a relationship between the nitrogen content and growth conditions, or feasible $Ga_{0.87}In_{0.13}N_yAs_{1-y}$ layers.

As illustrated in FIG. **4**, although maximum nitrogen content in the alloys grown at 600° C. under 2 Pa AsH_3 partial pressure was approximately 1%, the nitrogen content of 4.6% was obtained at 10 Pa AsH_3 partial pressure. Also, even under a AsH_3 partial pressure as low as 2 Pa or less, the desorption of both arsenic and nitrogen was suppressed for the growth at low temperatures such as, for example, between about 450° C. and about 550° C. This results in a high nitrogen content.

For the above-mentioned growth at low temperatures, however, photoluminescence that was observed was considerably weak. Since the light emitting capability of alloy layers manifest itself in the photoluminescence intensity, growth temperatures such as 550° C. and above, and therefore deduced as preferred temperatures for the growth of alloy layers for the light emitting devices.

Furthermore, the photoluminescence intensity becomes approximately unchanged at temperatures of 600° C. and above. It was also observed that, for the layers grown under constant conditions of the growth temperature and the composition of feeding source materials with the exception of changing AsH_3 partial pressure, the photoluminescence intensity increased with increasing the AsH_3 partial pressure, indicative of excellent quality of alloy layers for light emitting devices.

FIG. **5** contains a table which illustrates the relationship between photoluminescence intensity of $Ga_{0.94}In_{0.06}N_{0.02}As_{0.98}$ layers, growth temperatures, and AsH_3 partial pressures. It is shown in the table that, although lower temperatures are advantageous for achieving higher nitrogen contents, photoluminescence intensity decreases at these low temperatures. The results indicates that too low temperatures such as above-mentioned are not preferred for alloy layers to acquire excellent light emitting capability.

As above-mentioned, it is shown that, under AsH_3 partial pressures as low as 2 Pa or less, $GaInN_yAs_{1-y}$ layers are not grown, which have the nitrogen content of 2% or greater and exhibit an excellent photoluminescence characteristics. This is considered due to an accelerated desorption of arsenic and resultant metal-rich alloys. In order to obtain satisfactory growth results under the same conditions, temperatures such as 550° C. or lower are necessary.

By contrast, at temperatures of lower than 550° C. with a decreased AsH_3 flow rate and an increased nitrogen flow rate, GaInNAs layers having a high nitrogen content tend to be formed, resulting in layers of rather insufficient quality caused by too low AsH_3 partial pressures.

Therefore, under conditions such as a AsH_3 partial pressure of 2 Pa or greater and at a temperature of 550° C. or higher, alloy layers can be grown, which have the nitrogen content of about 2%, a high photoluminescence intensity and a high crystallinity.

With a nitrogen concentration of 2%, GaInNAs layers with the indium content of about 6% can be lattice-matched to GaAs substrates. This nitrogen content of 2% is satisfactory for fabricating semiconductor lasers for light signal amplifiers, of wavelengths in the range of about 980 nm.

It has also shown that, if AsH_3 partial pressures were increased to 10 Pa or higher, $GaInN_yAs_{1-y}$ alloy layers were able to grow, even at high temperatures such as 600° C. or above, which had the nitrogen content of 4% or greater and a high photoluminescence intensity. With the nitrogen content of 4.6%, GaInNAs layers having the indium content of about 13%, can be lattice-matched to GaAs. This leads to the feasibility of semiconductor lasers, of which wavelength is 1.3 μm or longer to be used for communication, for example.

$Ga_{0.92}In_{0.08}NAs$ layers having a layer thickness of 0.5 pm were analyzed by x-ray diffraction method. The results of the x-ray analysis are shown FIG. **6** and indicates that the layers have a lattice constant smaller than that of GaAs.

In addition, a Nomarski microscope observation of the layers shows that, since the thickness was less than the critical thickness, no cross-hatching pattern on the surface induced by the lattice relaxation was observed and that the layers were as flat as the surface of GaAs substrate.

As detailed above, by the user of organic materials as the source materials for nitrogen, which contain nitrogen and have a relatively low dissociation temperatures, and also by carrying out the alloy layer growth under AsH_3 partial pressures of as high as at least 2 Pa, there are able to grow nitrogen-containing III-V alloy semiconductors in the present invention.

The alloy layers have the nitrogen content of equal to or more than 0.5%, thereby exceeding the nitrogen content previously achieved by conventional methods which utilize organic nitrogen containing compounds as source materials. Moreover, since the growth was carried out at relatively high temperatures of 550° C. or higher, alloy layers presently grown have excellent crystalline quality and a high photoluminescence efficiency. In addition, under AsH_3 partial pressures of 10 Pa or more and at temperatures of 600° C. or higher, alloy layers can be grown with the nitrogen content of 4% or greater.

With regard to the lattice-match, GaInNAs layers do not have to be completely lattice-matched and may be in the strained-lattice structure as long as the layers are within the critical thickness. Also in the embodiment, although growth methods of nitrogen-containing III-V alloy semiconductors have been described primarily on GaInNAs alloy layers, these methods are not limited to the above examples but also applicable for semiconductor alloys such as, for example, GaNAs, AlNAs, AlInNAs, AlGaNAs, AlGaInNAs, and GaInNPAs.

Example 2

A light emitting device was fabricated using GaInNAs alloy layers for light emitting layers. FIG. **7** represents a sectional view of the device of the present embodiment.

The light emitting device comprises on an n-type (or n-) GaAs substrate **41**, an n-$Al_{0.4}Ga_{0.6}As$ cladding layer **42**, a GaInNAs active layer **43**, a p-$Al_{0.4}Ga_{0.6}As$ cladding layer **44**, and a p-GaAs contact layer **45**, each formed by MOCVD

method from the bottom in the order stated. Additionally provided for the device were a positive electrode **46** on the p-GaAs contact electrode **45** and a negative electrode **47** on the rear side of the n-GaAs substrate **41**, whereby constituting a light emitting device of the broad stripe type construction.

The GaInNAs active layers were grown so as to be lattice-matched to GaAs lattice under the same conditions as those adopted in embodiment 1. As aforementioned, the GaInNAs layers do not have to be completely lattice-matched and may be in the strained lattice structure as long as the layer is within the critical thickness. Also in the present growth, an AsH, partial pressure was 25 Pa, which was higher than that for conventional growths. Under the conditions, GaInNAs active layers were grown with fewer group V vacancies than those conventionally grown and a higher photoluminescence efficiency.

In addition, since a bandgap energy for the GaInNAs is small enough compared with that of GaAs, a strong carrier confinement into the GaInNAs active layer results, thereby constituting a light emitting device which has an improved temperature characteristics and a higher light power output compared with GaInAsP devices which are conventionally used in the relatively long wavelength range.

Although, an $Al_{0.4}Ga_{0.6}As$ layer was used as a cladding layer in the present embodiment, an $Al_xGa_{1-x}As$ ($0 \leqq x \leqq 1$) layer, having different compositions can also be used. Also in the embodiment, although the structure of the layer was described as a rather simple double hetero (DH) structure, other structures such as, for example, a quantum well structure may also be used. Various device structures other than the above-mentioned broad-stripe type may also be adopted. Furthermore, although a GaInNAs layer was described as a active layer, GaInNAs alloys comprised of either aluminum or phosphorus may also be used as long as nitrogen and arsenic are simultaneously included in the alloy.

Also in this embodiment, the device has better temperature characteristics than that of GaInPAs which is conventionally used for the relatively long wavelength region, and also has a higher light power output, as aforementioned. As a result, fabrications of laser devices benign to human eyes, become feasible, which are used for the telecommunication, ranging, and free-space communication. These lasers can be economically operated without auxiliary circuits for automatic power and/or temperature control, for example.

Example 3

Although, there was described in embodiment 2, a light emitting device which was constituted of GaInNAs active layer and had a double heterostructure, a light emitting device comprising also a GaInNAs active layer and having the homo-junction or single heterostructure, may also be fabricated. FIG. **8** represents a sectional view of a light emitting device having a homo-junction structure of embodiment 3.

The light-emitting device comprises, an n-GaInNAs layer **72**, a p-GaInNAs layer **73**, and a p-GaAs contact layer **74**, disposed by MOCVD method on an n-GaAs substrate **71** in the order stated. Additionally provided for the device were a positive electrode **75** on the p-GaAs contact layer **74** and a negative electrode **76** on the rear side of the n-GaAs substrate **71**.

The present GaInNAs layer was grown so as to be lattice-matched to the GaAs lattice under the same conditions as those adopted in embodiment 1. Also in the present growth, an AsH_3 partial pressure was 50 Pa which was higher than that for the conventional growth. This resulted in a GaInNAs active layer with fewer group V vacancies than those in conventionally grown layers and with a higher photoluminescence efficiency.

The control of conductive properties and charge concentration was typically carried out by using dopants such as selenium for n-type, and zinc for p-type. Referring to FIG. **8**, for example, selenium was used as an n-type dopant for the n-GaInNAs layer **72**, and zinc was used as a p-type dopant for the p-GaInNAs layer **73**. As source materials of these dopants, hydrogen selenide for selenium, and dimethylzinc (DMZn) or diethylzinc (DEZn) for zinc were used. Doping efficiencies of these dopants were found satisfactory.

It is generally known that an GaInNAs active layer for DH laser is undoped and, therefore, control of dopants is not necessary. (An exception may be cited here, for the DH LED application, an GaInNAs active layer is often doped, thereby necessitating dopant control.) However, for LEDs having a homo-junction structure such as described in this embodiment, control of, carrier concentrations and a conductive type has to be made, thereby necessitating control of both n-type and p-type dopants. In the present embodiment, selenium and zinc were used for the n-type and p-type dopant, respectively.

It may also be possible to add dopants into a GaInNAs active layer of a DH laser, such as selenium or zinc, for example. This results in a decrease in threshold current for the light emission, since a carrier concentration in the active layer increases, a width of a depletion layer decreases, and a recombinant current decreases.

In addition, a bandgap energy of GaInNAs layers is smaller than that of GaAs, as aforementioned. Because of the smaller bandgap energy, the resultant emission from the GaInNAs layers is transparent for GaAs substrates and GaAs contact layers. Therefore, light emitting devices such as described in the above embodiments 1 and 2 may preferably be used as vertical cavity surface emitting lasers (VCSELs) and surface emitting LEDs.

In addition to above-mentioned selenium and zinc, dopants such as beryllium, magnesium, carbon, silicon, germanium, tin, sulfur, or tellurium may also be used. However, since silicon, carbon, germanium and tin are amphoteric, these dopants have the possibility of occupying either group-III or group-V site to complete the charge compensation. Since neither selenium (group VI) nor zinc (group II) is amphoteric, the above-mentioned difficulty can be obviated. Therefore, it is preferred to use group VI dopants such as selenium for n-type and group II dopants such as zinc for p-type, for example.

In addition, a p-n junction can be formed by diffusing appropriate dopants. Furthermore, although the GaInNAs layer was described as an active layer, GaInNAs layers comprised of both of, or either of aluminum or phosphorus may also be used as long as nitrogen and arsenic are simultaneously included in the alloy.

As described above, nitrogen-containing III-V alloy semiconductors can be grown without increasing concentrations of arsenic vacancies, thereby leading to the fabrication of epitaxial wafers and light emitting devices with noble features, using the wafers. For example, there can be preferably fabricated light emitting devices with better temperature characteristics than that of GaInPAs which has conventionally been used in the long wavelength region, and also have a high light power output.

In addition, the uses of the present nitrogen-containing III-V alloy semiconductors are not limited to the above-

mentioned light emitting devices, and photodetecting devices such as, for example, photodiodes of excellent characteristics also may preferably be fabricated.

Additional modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

What is claimed as new and described to be secured by Letters Patent if the United States is:

1. A method for growing at least one layer of III-V alloy semiconductor on a semiconductor substrate, and including at least nitrogen and arsenic simultaneously, comprising forming said alloy semiconductor by a conventional low pressure MOCVD method, using a nitrogen containing organic compound as a source material for nitrogen and AsH_3 for arsenic, wherein said III-V alloy semiconductor comprises GaInNAs.

2. The method according to claim **1**, wherein said semiconductors substrate comprises GaAs.

3. The method according to claim **1**, wherein said nitrogen containing organic compound is selected from the group consisting of dimethylhydrazine and tertiary butyl amine.

4. The method according to claim **1**, further comprising controlling conductive properties of, and carrier concentrations in said alloy semiconductor by adding a dopant, wherein said dopant is selected from the group consisting of beryllium, magnesium, zinc, carbon, silicon, germanium, tin, sulfur, tellurium, and selenium.

5. A method for growing at least one layer of III-V alloy semiconductor on a GaAs substrate, and including at least nitrogen and arsenic simultaneously, comprising forming said alloy semiconductor by a conventional low pressure MOCVD method under specified conditions of temperatures and pressures, using a nitrogen containing organic compound as a source material for nitrogen and AsH_3 for arsenic, wherein said III-V alloy semiconductor comprises GaInNAs.

6. The method according to claim **5**, wherein said specified conditions are a partial pressure of said AsH_3 in a reactor of equal to or more than 2 Pa and a temperature of said semiconductor substrate of equal to or more than 550° C.

7. The method according to claim **5**, wherein said specified conditions are a partial pressure of said AsH_3 in a reactor of equal to or more than 10 Pa and a temperature of said semiconductor substrate of equal to or more than 600° C.

8. The method according to claim **5**, wherein said nitrogen containing organic compound is selected from the group consisting of dimethylhydrazine and tertiary butyl amine.

9. The method according to claim **5**, further comprising controlling conductive properties of, and carrier concentrations in said alloy semiconductor by adding a dopant, wherein said dopant is selected from the group consisting of beryllium, magnesium, zinc, carbon, silicon, germanium, tin, sulfur, tellurium, and selenium.

10. A method for growing at least one layer of III-V alloy semiconductor on a GaAs substrate, and including at least nitrogen and arsenic simultaneously, comprising:

forming said alloy semiconductor by a conventional low pressure MOCVD method, using a nitrogen containing organic compound as a source material for nitrogen and AsH_3 for arsenic, under conditions such as a partial pressure of said AsH_3 in a reactor of equal to or more than 2 Pa and a temperature of said semiconductor substrate of equal to or more than 550° C., wherein said III-V alloy semiconductor comprises GaInNAs.

11. The method according to claim **10**, wherein said nitrogen containing organic compound is selected from the group consisting of dimethylhydrazine and tertiary butyl amine.

12. The method according to claim **10**, further comprising:

controlling conductive properties of, and carrier concentrations in said alloy semiconductor by adding a dopant, wherein said dopant is selected from the group consisting of selenium, zinc, and magnesium.

13. A method for growing at least one layer of III-V alloy semiconductor on a GaAs substrate, and including at least nitrogen and arsenic simultaneously, comprising:

forming said alloy semiconductor by a conventional low pressure MOCVD method using a nitrogen containing organic compound as a source material for nitrogen and AsH_3 for arsenic, under conditions such as a partial pressure of said AsH_3 in a reactor of equal to or more than 10 Pa and a temperature of said semiconductor substrate of equal to or more than 600° C., wherein said III-V alloy semiconductor comprises GaInNAs.

14. The method according to claim **13**, wherein said nitrogen containing organic compound as said source material for nitrogen is selected from the group consisting of dimethylhydrazine and tertiary butyl amine.

15. The method according to claim **13**, further comprising:

controlling conductive properties of, and carrier concentrations in said alloy semiconductor by adding a dopant, wherein said dopant is selected from the group consisting of beryllium, magnesium, zinc, carbon, silicon, germanium, tin, sulfur, tellurium, and selenium.

16. A method for fabricating a semiconductor device, having at least one layer of a III-V alloy semiconductor on a GaAs substrate, comprised of a plurality of group V elements including at least nitrogen and arsenic simultaneously, comprising:

forming said alloy semiconductor by a conventional low pressure MOCVD method, using a nitrogen containing organic compounds as a source material for nitrogen and AsH_3 for arsenic, under conditions such as a partial pressure of said AsH_3 in a reactor of equal to or more than 2 Pa and a temperature of said semiconductor substrate of equal to or more than 550° C., wherein said III-V alloy semiconductor comprises GaInNAs.

17. The method according to claim **16**, wherein said nitrogen containing organic compound is selected from the group consisting of dimethylhydrazine and tertiary butyl amine.

18. The method according to claim **16**, further comprising:

controlling conductive properties of, and carrier concentrations in said semiconductors by adding a dopant, wherein said dopant is selected from the group consisting of beryllium, magnesium, zinc, carbon, silicon, germanium, tin, sulfur, tellurium, and selenium.

19. A method for fabricating a semiconductor device, having at least one layer of a III-V alloy semiconductor on a GaAs substrate, comprised of a plurality of group V elements including at least nitrogen and arsenic simultaneously, comprising:

forming said alloy semiconductor by a conventional low pressure MOCVD method using a nitrogen containing organic compound as a source material for nitrogen and AsH_3 for arsenic, under conditions such as a partial pressure of said AsH_3 in a reactor of equal to or more than 10 Pa and a temperature of said semiconductor substrate of equal to or more than 600° C.,

wherein said III-V alloy semiconductor comprises at least Ga, In, N and As.

20. The method according to claim **19**, wherein said nitrogen containing organic compound is selected from the group consisting of dimethylhydrazine and tertiary butyl amine.

21. [The] *A* method [according to claim **19**, further] *for fabricating a semiconductor device, having at least one layer of a III-V alloy semiconductor on a GaAs substrate, comprised of a plurality of group V elements including at least nitrogen and arsenic simultaneously,* comprising:

forming said alloy semiconductor by a conventional low pressure MOCVD method using a nitrogen containing organic compound as a source material for nitrogen and AsH_3 for arsenic, under conditions such as a partial pressure of said AsH_3 in a reactor of equal to or more than 10 Pa and a temperature of said semiconductor substrate of equal to or more than 600° C.; and

controlling conductive properties of, and carrier concentrations in said alloy semiconductor by adding a dopant, wherein said dopant is selected from the group consisting of beryllium, magnesium, zinc, carbon, silicon, germanium, tin, sulfur, tellurium, and selenium.

22. A method for growing at least one layer of III-V alloy semiconductor on a semiconductor substrate, and including at least nitrogen and arsenic simultaneously, comprising forming said alloy semiconductor by an MOCVD method at a pressure of at least that of conventional low pressure MOCVD, using a nitrogen containing organic compound as a source material for nitrogen and using a source material for arsenic, wherein said III-V alloy semiconductor comprises at least Ga, In, N, and As.

23. The method according to claim 22, wherein said semiconductors substrate comprises GaAs.

24. The method according to claim 22, wherein said nitrogen containing organic compound is selected from the group consisting of dimethylhydrazine and tertiary butyl amine.

25. The method according to claim 22, further comprising controlling conductive properties of, and carrier concentrations in said alloy semiconductor by adding a dopant, wherein said dopant is selected from the group consisting of beryllium, magnesium, zinc, carbon, silicon, germanium, tin, sulfur, tellurium, and selenium.

26. A method for growing at least one layer of III-V alloy semiconductor on a GaAs substrate, and including at least nitrogen and arsenic simultaneously, comprising forming said alloy semiconductor by an MOCVD method under specified conditions of temperatures and at a pressure of at least that of conventional low pressure MOCVD, using a nitrogen containing organic compound as a source material for nitrogen and using a source material for arsenic, wherein said III-V alloy semiconductor comprises at least Ga, In, N and As.

27. The method according to claim 26, wherein said specified conditions are a partial pressure of said source material for arsenic in a reactor of equal to or more than 2 Pa and a temperature of said semiconductor substrate of equal to or more than 550° C.

28. A method for growing at least one layer of III-V alloy semiconductor on a GaAs substrate, and including at least nitrogen and arsenic simultaneously, comprising forming said alloy semiconductor by an MOCVD method under specified conditions of temperatures and at a pressure of at least that of conventional low pressure MOCVD, using a nitrogen containing organic compound as a source material for nitrogen and using a source material for arsenic, wherein said III-V alloy semiconductor comprises at least N and As, wherein said specified conditions are a partial pressure of said source material for arsenic in a reactor of equal to or more than 10 Pa and a temperature of said semiconductor substrate of equal to or more than 600° C.

29. The method according to claim 26, wherein said nitrogen containing organic compound is selected from the group consisting of dimethylhydrazine and tertiary butyl amine.

30. A method for growing at least one layer of III-V alloy semiconductor on a GaAs substrate, and including at least nitrogen and arsenic simultaneously, comprising forming said alloy semiconductor by an MOCVD method under specified conditions of temperatures and at a pressure of at least that of conventional low pressure MOCVD, using a nitrogen containing organic compound as a source material for nitrogen and using a source material for arsenic, and controlling conductive properties of, and carrier concentrations in said alloy semiconductor by adding a dopant, wherein said dopant is selected from the group consisting of beryllium, magnesium, zinc, carbon, silicon, germanium, tin, sulfur, tellurium, and selenium, wherein said III-V alloy semiconductor comprises at least N and As.

31. A method for growing at least one layer of III-V alloy semiconductor on a GaAs substrate, and including at least nitrogen and arsenic simultaneously, comprising: forming said alloy semiconductor by an MOCVD method at a pressure of at least that of conventional low pressure MOCVD, using a nitrogen containing organic compound as a source material for nitrogen and using a source material for arsenic, under conditions such as a partial pressure of said source material for arsenic in a reactor of equal to or more than 2 Pa and a temperature of said semiconductor substrate equal to or more than 500° C., wherein said III-V alloy semiconductor comprises at least Ga, In, N and As.

32. The method according to claim 31, wherein said nitrogen containing organic compound is selected from the group consisting of dimethylhydrazine and tertiary butyl amine.

33. A method for growing at least one layer of III-V alloy semiconductor on a GaAs substrate, and including at least nitrogen and arsenic simultaneously, comprising:

forming said alloy semiconductor by an MOCVD method at a pressure of at least that of conventional low pressure MOCVD, using a nitrogen containing organic compound as a source material for nitrogen and using a source material for arsenic, under conditions such as a partial pressure of said source material for arsenic in a reactor of equal to or more than 2 Pa and a temperature of said semiconductor substrate equal to or more that 500° C.

controlling conductive properties of, and carrier concentrations in said alloy semiconductor by adding a dopant, wherein said dopant is selected from the group consisting of selenium, zinc, and magnesium,

wherein said III-V alloy semiconductor comprises at least N and As.

34. A method for growing at least one layer of III-V alloy semiconductor on a GaAs substrate, and including at least nitrogen and arsenic simultaneously, comprising: forming said alloy semiconductor by an MOCVD method using a nitrogen containing organic compound as a source material for nitrogen and using a source material for arsenic, under conditions such as a partial pressure of said source material for arsenic in a reactor equal to or more than 10 Pa and a temperature of said semiconductor substrate equal to or more than 600° C., wherein said III-V alloy semiconductor comprises at least Ga, In, N and As.

35. The method according to claim 34, wherein said nitrogen containing organic compound as said source material for nitrogen is selected from the group consisting of dimethylhydrazine and tertiary butyl amine.

36. A method for growing at least one layer of III-V alloy semiconductor on a GaAs substrate, and including at least nitrogen and arsenic simultaneously, comprising forming said alloy semiconductor by an MOCVD method using a nitrogen containing organic compound as a source material

for nitrogen and using a source material for arsenic, under conditions such as a partial pressure of said source material for arsenic in a reactor equal to or more than 10 Pa and a temperature of said semiconductor substrate equal to or more than 600° C., and controlling conductive properties of, and carrier concentrations in said alloy semiconductor by adding a dopant, wherein said dopant is selected from the group consisting of beryllium, magnesium, zinc, carbon, silicon, germanium, tin, sulfur, tellurium, and selenium, wherein said III-V alloy semiconductor comprises at least N and As.

37. A method for fabricating a semiconductor device, having at least one layer of a III-V alloy semiconductor on a GaAs substrate, comprised of a plurality of group V elements including at least nitrogen and arsenic simultaneously, comprising: forming said alloy semiconductor by an MOCVD method at a pressure of at least that of conventional low pressure MOCVD, using a nitrogen containing organic compounds as a source material for nitrogen and using a source material for arsenic, under conditions such as a partial pressure of said source material for arsenic in a reactor equal to or more than 2 Pa and a temperature of said semiconductor substrate equal to or more than 500° C., wherein said III-V alloy semiconductor comprises at least Ga, In, N and As.

38. The method according to claim 37, wherein said nitrogen containing organic compound is selected from the group consisting of dimethylhydrazine and tertiary butyl amine.

39. A method for fabricating a semiconductor device, having at least one layer of III-V alloy semiconductor on a GaAs substrate, comprised of a plurality of group V elements including at least nitrogen and arsenic simultaneously, comprising:

forming said alloy semiconductor by an MOCVD method at a pressure of at least that of conventional low pressure MOCVD, using a nitrogen containing organic compounds as a source material for nitrogen and using a source material for arsenic, under conditions such as a partial pressure of said source material for arsenic in a reactor of equal to or more than 2 Pa and a temperature of said semiconductor substrate equal to or more that 500° C.; and

controlling conductive properties of, and carrier concentrations in said semiconductors by adding a dopant, wherein said dopant is selected from the group consisting of beryllium, magnesium, zinc, carbon, silicon, germanium, tin, sulfur, tellurium, and selenium, wherein said III-V alloy semiconductor comprises at least N and As.

40. A method for fabricating a semiconductor device, having at least one layer of a III-V alloy semiconductor on a GaAs substrate, comprised of a plurality of group V elements including at least nitrogen and arsenic simultaneously, comprising: forming said alloy semiconductor by an MOCVD method at a pressure of at least that of conventional low pressure MOCVD using a nitrogen containing organic compound as a source material for nitrogen and using a source material for arsenic, under conditions such as a partial pressure of said source material for arsenic in a reactor equal to or more than 10 Pa and a temperature of said semiconductor substrate equal to or more than 600° C., wherein said III-V alloy semiconductor comprises at least Ga, In, N and As.

41. The method according to claim 40, wherein said nitrogen containing organic compound is selected from the group consisting of dimethylhydrazine and tertiary butyl amine.

42. A method for fabricating a semiconductor device, having at least one layer of III-V alloy semiconductor on a GaAs substrate, comprised of a plurality of group V elements including at least nitrogen and arsenic simultaneously, comprising:

forming said alloy semiconductor by an MOCVD method at a pressure of at least that of conventional low pressure MOCVD using a nitrogen containing organic compounds as a source material for nitrogen and using a source material for arsenic, under conditions such as a partial pressure of said source material for arsenic in a reactor equal to or more than 10 Pa and a temperature of said semiconductor substrate equal to or more that 600° C.; and

controlling conductive properties of, and carrier concentrations in said alloy semiconductor by adding a dopant, wherein said dopant is selected from the group consisting of beryllium, magnesium, zinc, carbon, silicon, germanium, tin, sulfur, tellurium, and selenium.

43. The method according to any one of claims 1, 5, 10, 13, 16, 19, 22, 26, 31, 34, 37 and 40 comprising the use of a horizontal type MOCVD apparatus to carry out said MOCVD method.

44. A method for growing at least one layer of III-V alloy semiconductor on a GaAs substrate, and including at least nitrogen and arsenic simultaneously, comprising forming said alloy semiconductor by an MOCVD method under specified conditions of at least one of temperatures and at a pressure of at least that of conventional low pressure MOCVD, using a nitrogen containing organic compound as a source material for nitrogen and using a source material for arsenic, wherein said III-V alloy semiconductor comprises at least Ga, In, N and As.

45. A method as in claim 44 wherein the specified conditions comprise conditions of temperatures.

46. A method as in claim 44 wherein the specified conditions comprise conditions of pressures.

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