METHOD AND APPARATUS FOR GROWTH OF III-NITRIDE SEMICONDUCTOR EPITAXIAL LAYERS

A metalorganic-hydride vapor phase epitaxy (MOHVPE) system is generally disclosed, along with methods of forming epilayers on a substrate utilizing the MOHVPE system. The system includes a reaction chamber, a nitrogen source gas, a HVPE-like system, and a MOCVD-like system. The metal source of the HVPE-like system is located outside of the reaction chamber. The MOHVPE system is particularly well suited for use in nitride-based devices, such as group III-nitride based devices. The presently disclosed methods and systems combine the advantages of the well known MOCVD, pulsed atomic layer epitaxy (PALE), and HVPE techniques, while minimizing the disadvantages. Additionally, both techniques can be utilized to grow layers on the same substrate without removing the substrate from the reaction chamber.
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METHOD AND APPARATUS FOR GROWTH OF HI-NITRIDE SEMICONDUCTOR EPITAXIAL LAYERS

Priority Information

The present application claims priority to U.S. Provisional Patent Application Nos. 60/861,828 filed on November 30, 2006, titled "Method and Apparatus for Producing III-Nitride Semiconductor Epitaxial Layers" and 60/861,886 filed on November 30, 2006, titled "Method, Apparatus and Growth for Producing III-Nitride Semiconductor Epitaxial Layers", both naming M. Asif Khan, Qhalid Fareed, and Jinwei Yang as inventors. Both of these provisional applications are incorporated by reference herein in their entirety.

Background of the Invention

Wide bandgap semiconductor materials (with $E_g > 2$ eV) such as silicon carbide (SiC) or Group III nitride compound semiconductors (e.g., gallium nitride GaN) are very attractive for use in high-power, high-temperature, and/or radiation resistant electronics. SiC power rectifiers and RF transistors are now commercially available, and SiC power switches as well as GaN microwave transistors are expected to appear in the commercial market in the near future.

Group III nitride semiconductors possess a band gap of a direct transition type of energy corresponding to the visible light through the ultraviolet light region and permit highly efficient light emission and have been consequently reduced to commercial products, such as light emitting diodes (LED) and laser diodes (LDs). A currently favored prior art technique for the growth of relatively thick layers (e.g., of GaN) is Hydride Vapour Phase Epitaxy (HVPE). In this process, growth proceeds due to the high-temperature vapor-phase reaction between gallium mono-chloride (GaCl) and ammonia. The ammonia is supplied from a standard gas source, while the GaCl is produced by passing hydrogen chloride (HCl) gas over a liquid gallium supply. Using this method, GaN can be grown relatively quickly and inexpensively. Further, GaN grown at a fast rate (i.e., greater than 100$\mu$m/hour) may produce layers with less defect densities.

Another prior art of producing Group III-nitride layers is metal-organic chemical vapor deposition (MOCVD). In this technique, ammonia gas ($\text{NH}_3$) is
reacted with a metallo-organic compound containing aluminum or gallium or indium. The reaction occurs at high temperatures in the vicinity of a substrate (i.e., within the growth chamber), and a solid product (GaN or AIN) is deposited on the substrate. However, this technique is not only expensive, but is also slow. In particular, the metallo-organic source materials are costly, and they can only be delivered to the substrate for reaction at low rates.

However, the low growth rates in MOCVD (as well as molecular beam epitaxy or MBE) make it easy to grow abrupt and sharp interface layers with compositional control for ternary and quaternary layers. Thus, the possibility of using these techniques for forming thick or bulk low defect density III-nitride substrates or layers suitable for optoelectronic and electronic device structures is limited.

As such, a need exists for a growth method and system that combines the advantages of the MOCVD technique (namely the controlled growth rates allowing greater composition control and sharp abrupt interfaces) and the HVPE technique (the high growth rates for thick layers). Such a method and system would facilitate the development of high power, reliable and stable III-nitride optoelectronic and electronic devices as seen by the commercial applications.

**Summary of the Invention**

Objects and advantages of the invention will be set forth in part in the following description, or may be obvious from the description, or may be learned through practice of the invention.

In one embodiment, a metalorganic-hydride vapor phase epitaxy (MOHVPE) system is generally disclosed. The system includes a reaction chamber, a nitrogen source gas, a HVPE-like system, and a MOCVD-like system. The reaction chamber includes a rotatable platform configured to support a substrate (such as in a vertical arrangement). The rotatable platform can include a heating element. The nitrogen source gas is configured to flow to the reaction chamber via a nitrogen source line, such that the flow rate of the nitrogen source gas is controllable by a nitrogen source valve.

The HVPE-like system includes a carrier gas and a metallic source located outside of the reaction chamber, and is configured such that the carrier gas
transports the metallic source into the reaction chamber. The flow rate of the metallic source to the reaction chamber is controllable by a carrier gas valve. The metallic source can be gallium, aluminum, indium, or a combination thereof. In this case, the system further includes a halide reactant gas configured to react with the metallic source outside of the reaction chamber to form a metal halide and then transport the metal halide to the reaction chamber via the carrier gas. Alternatively, the metal source can be a metal halide that is transported to the reaction chamber via the carrier gas.

The MOCVD-like system includes a MOCVD carrier gas and a metalorganic source, such that the MOCVD carrier gas is configured such that the MOCVD carrier gas transports the metalorganic source to the reaction chamber, wherein the flow rate of the metalorganic source to the reaction chamber is controllable by a MOCVD carrier gas valve.

In one particular embodiment, a purge gas source is also included in the MOHVPE system, such that the purge gas source is configured to provide an ambient gas to the reaction chamber. Also, in one embodiment, no metallic source is contained within the reaction chamber.

This system can be utilized in a method of growing a group III-nitride epilayer on a substrate, wherein the group III-nitride epilayer comprises \( \text{Al}_x\text{In}_y\text{Ga}_{1-x-y}N \), wherein \( 0<x<1 \), \( 0<y<1 \) and \( 0<x+y\leq1 \). For example, one method of growing epilayers on a substrate includes first positioning a substrate on a platform within a reaction chamber. A first group III-nitride layer can be formed on the substrate, wherein the first group III-nitride layer comprises \( \text{Al}_x\text{In}_y\text{Ga}_{1-x-y}N \), wherein \( 0<x<1 \), \( 0<y<1 \) and \( 0<x+y<1 \). The first group III-nitride layer can be formed by reacting a nitrogen source gas with a metalorganic source.

Also, a second group III-nitride layer on the substrate can be formed on the substrate. The second group III-nitride layer can be formed by reacting the nitrogen source gas and a metal source positioned outside of the reaction chamber. For example, when the metallic source comprises gallium, aluminum, indium, or a combination thereof, the second group III-nitride layer can be formed by reacting a halide reactant gas with the metallic source outside of the reaction chamber to form a metal halide. Then, the metal halide can be transferred to the
reaction chamber via a carrier gas. Alternatively, the metal source can be a metal halide that is simply transported to the reaction chamber via a carrier gas.

Of course, the order of the formation of these layers can be reversed, repeated, etc.

In one embodiment, the nitrogen source and the metalorganic source are sequentially pulsed into the reaction chamber to form the first group III-nitride layer. Similarly, the nitrogen source and the metal source can be sequentially pulsed into the reaction chamber to form the second group III-nitride layer.

Other features and aspects of the present invention are discussed in greater detail below.

**Brief Description of the Figures**

A full and enabling disclosure of the present invention, including the best mode thereof to one skilled in the art, is set forth more particularly in the remainder of the specification, which includes reference to the accompanying figure, in which:

Figure 1 shows an exemplary MOHVPE system according to one embodiment of the present invention.

Figures 2a-2d are diagrams showing the operation of the MOHVPE system during exemplary HVPE-like pulse modes.

Figure 3 is a diagram showing the operation of the MOHVPE system during an exemplary MOCVD-like pulse mode, such as Pulse Atomic Layer Epitaxy (PALE) or Pulsed Lateral Overgrowth (PLOG).

Figure 4 is scanning electron microscopy image of an exemplary AIN layer grown according to the MOHVPE method of the present invention.

Figure 5 is an atomic force microscopic image of an exemplary AIN layer grown according to the MOHVPE method of the present invention.

Figure 6 are dark field transmission electron microscopic images of an exemplary AIN layer grown according to the MOHVPE method of the present invention. The images are taken to show screw-type and the edge-type threading dislocations: (a) \( g = 0002 \) and (b) \( g = \frac{1}{120} \).

Figure 7 is a cathodoluminescence spectrum of the exemplary AIN layer of Figure 1, with a CL image taken at 210nm emission (inset).
Figure 8 is a cathodoluminescence spectra of deep UVLED LED grown on MOHVPE AIN with emission peaks at 260nm and 285 corresponds to AlGaN:Si and MQW layers; (inset) CL image of AlInGaN multiple quantum well taken at 285 nm emission.

Repeat use of reference characters in the present specification and drawings is intended to represent the same or analogous features or elements of the present invention.

**Detailed Description of the Preferred Embodiments**

Reference now will be made to the embodiments of the invention, one or more examples of which are set forth below. Each example is provided by way of an explanation of the invention, not as a limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the invention without departing from the scope or spirit of the invention. For instance, features illustrated or described as one embodiment can be used on another embodiment to yield still a further embodiment. Thus, it is intended that the present invention cover such modifications and variations as come within the scope of the appended claims and their equivalents. It is to be understood by one of ordinary skill in the art that the present discussion is a description of exemplary embodiments only, and is not intended as limiting the broader aspects of the present invention, which broader aspects are embodied exemplary constructions.

Generally speaking, the present invention is directed to methods and systems for the deposition of materials on substrates. The present invention is particularly well suited for use in nitride-based devices, such as group III-nitride based devices. Although the present invention is not specifically limited to group III-nitride based devices, the following discussion focuses on group III-nitride based devices due to their particular compatibility with the present invention.

"Group III nitride" refers to those semiconducting compounds formed between elements in Group III of the periodic table and nitrogen. More preferably the Group III element is selected from the group consisting of aluminum (Al), gallium (Ga), and indium (In). Ternary and quaternary compounds (e.g., AlGaN and AlInGaN) are particularly preferred. As is well understood in the art, the Group III elements can combine with nitrogen to form binary compounds (e.g., GaN, AIN
and InN), ternary compounds (e.g., AlGaN, AlInN, and GaInN), and quaternary compounds (i.e., AlInGaN).

The group III nitride epilayer can be composed of any combination of group III elements (e.g., Al, In, and Ga) and nitride. In one particular embodiment, the group III-nitride epilayer can be represented by the formula $\text{Al}_x\text{In}_y\text{Ga}_{-x-y}\text{N}$, wherein $0<x<1$, $0<y<1$ and $0<x+y<1$. In employing growth techniques to grow the group III nitride epilayer, the precursor sources typically include a metal-organic source (e.g., trimethyl aluminum, trimethyl gallium, triethyl gallium, trimethyl indium), a nitrogen source (e.g., ammonia), a carrier gas (e.g., hydrogen and/or nitrogen), and an optionally doping source (e.g., silane, disilane, bis(cyclopentadienyl) magnesium, etc.). Of course, other materials can be utilized to grow the group III nitride epilayer, and the present invention is not intended to be limited by the above listed materials. For example, another type of a metal-organic source and/or a nitrogen source can be utilized to grow the group III nitride epilayer.

The present inventors have termed their combination methods and systems "metalorganic-hydride vapor phase epitaxy" (MOHVPE). The presently disclosed methods and systems combine the advantages of the well known MOCVD, pulsed atomic layer epitaxy (PALE), and HVPE techniques, while minimizing the disadvantages. Additionally, both techniques can be utilized to grow layers on the same substrate without removing the substrate from the reaction chamber. Thus, III-Nitride device structures with multilayers grown with different growth mode can be formed without removing the substrate from the chamber. For example, a buffer layer can be grown on a substrate formed by Pulsed HVPE and PALE without removing the substrate from the reactor. Also, a buffer layer can be grown on an epitaxial layer with thin buffer layer grown by PALE, an epitaxial layer grown by MOCVD and thick III-Nitride layer by HVPE without removing the substrate from the reactor. Thus, the MOHVPE system can grow a high quality sharp and abrupt interface superlattice layer in pulse atomic layer epitaxy mode and a thick buffer layer in a HVPE mode without removing the substrate from the reactor.

According to the MOHVPE methods and systems described herein, the growth rate of the III-Nitride semiconductor can be controlled with thickness from 1Å to few hundred microns in a single reactor. Additionally, the reaction rate of the metal source can be controlled by controlling the source temperature. Also, pre-
reaction or adduct formation in the gas phase can be controlled (e.g., limited) by pulsing the precursor source independently.

Through the use of the presently disclosed system and methods, a layer or layers can be grown on a substrate with improved composition control. The substrate can be any suitable substrate for the growth of the epitaxial layer, including but not limited to, sapphire, silicon carbide, silicon, gallium arsenide, zinc oxide, magnesium oxide, lithium aluminate, lithium gallate, gallium nitride, aluminum nitride, aluminum gallium nitride, indium gallium nitride, aluminum indium gallium nitride, diamond, glass, and the like. Of course, any other suitable substrate can be used as the base layer to grow the group III nitride epilayer. These substrates include polar (e.g., c-plane) or non-polar (e.g., a-plane, r-plane, or m-plane) or semi-polar substrates and epilayers. Likewise, the substrate can be patterned or non-patterned, porous or nonporous, made in-situ or ex-situ. The substrate can have any suitable size, such as from about 1 mm to about 300 mm, or any suitable shape, such as a square, rectangle, triangle, circle, cylindrical, or a random shape.

Referring to Fig. 1, an exemplary MOHVPE system 10 is generally shown. A substrate 12 is shown positioned on the rotatable platform 14 in the reaction chamber 16. In one embodiment, the rotatable platform 14 can be configured to hold more than one substrate. The rotatable platform 14 is configured to rotate from about 1 rotation per minute to about 100,000 rotations per minute. The vertical configuration of the reaction chamber 16 allows the rotatable platform 14 to be rotated, since a support axis 15 can easily be positioned underneath the rotatable platform. The reaction chamber 16 is defined by chamber walls 18. As is known in the art, an inert gas (e.g., nitrogen gas (N₂), argon, helium) can be provided to purge the reaction chamber 16 from purge gas tank 20. The inert gas can be supplied from the purge gas tank 20 to the reaction chamber 16 via purge gas line 22. Purge gas valve 24 is configured to allow a user to control the flow of the inert gas from the purge gas tank 20 through the purge gas line 22 to the reaction chamber 16.

According to the present invention, the MOHVPE system 10 can be utilized to selectively grow layers using either or both of the HVPE and MOCVD techniques. As such, layers can be grown on the substrate 12 without having to
remove the substrate 12 from the reaction chamber, which can expose the substrate 12 to oxygen and other chemicals. For example, the MOHVPE system 10 shown in Fig. 1 has a HVPE-like system 26 and a MOCVD-like system 28 included. Both the HVPE-like system 26 and the MOCVD-like system 28 share the nitrogen source 32, although this tank is not shown to be included within either of the systems.

According to the exemplary embodiment shown in Fig. 1, the HVPE-like system 26 has a nitrogen source tank 32 configured to provide the nitrogen source gas to the reaction chamber 16 via nitrogen source line 34. The flow of the nitrogen source gas from the nitrogen source tank 32 to the reaction chamber can be selectively controlled by the nitrogen source valve 36. In one particular embodiment, the nitrogen source gas can be ammonia (NH₃). However, any nitrogen source suitable for formation of an group III-nitride layer on the substrate may be used.

In order to form the group III-nitride layer on the substrate in a conventional HVPE process, the nitrogen source gas reacts with a metallic source located within a reaction chamber (or at least a section of the reaction chamber) having heated walls. Then, the metal source (e.g., Ga, Al, In) reacts with the nitrogen source to grow the group III-nitride layer on the substrate. In a conventional HVPE system, hydride or chloride precursors are used for growth of IM-V semiconductors in a hot walled chamber. The epitaxial growth that takes place is a nearly thermodynamically equilibrium condition. The opportunity this process offers is to efficiently manufacture thick and pure semiconductor structures. However, one of the disadvantages of hot wall reactor geometry is homogeneous reactions (parasitic reactions) prior to the deposition. The device structure with sharp abrupt interface are difficult due to high reaction rates. In case of metalorganic source, the decomposition temperature is very low and it will decompose prior to reaching the surface of the substrate. Hence it is impossible to grow epitaxial layers using metalorganic source in a hot wall geometry. Thus, if the reaction chamber is a hot walled reaction chamber, the heat generated within the reaction chamber will decompose the metalorganic source of the MOCVD-like system 28, rendering this MOCVD-like system 28 inoperable.
However, in the MOHVPE system 10 of the present invention (and contrary to the conventional HVPE systems), the present inventors have discovered that the metallic source of the HVPE-like system 26 can have a metallic source 30 located outside of the reaction chamber 16, while still forming the group III-nitride layer with HVPE-like speed. For example, the HVPE-like system 26 can grow an group III-nitride layer at a rate of from about 1 μm/hour to about 500 μm/hour (measured in the thickness of the layer).

According to the MOHVPE system 10 of Fig. 1, a metallic source 30 is provided outside of the reaction chamber 16. Metallic source heaters 31 are configured to heat the metallic source 30 to the desired temperature. Although the metallic source heaters 31 can be any suitable heating device, a resistance heater is particularly suitable for heating the metallic source 30. The metallic source 30 can be heated, for instance, to temperatures from about 50°C to about 900°C, such as from about 400°C to about 700°C, depending on the actual composition of the metallic source 30. Generally, the metallic source 30 is heated to a temperature that vaporizes the metallic source to enable the carrier gas to transport the metallic source 30 to the reaction chamber 16. A carrier gas is provided to the metallic source 30 from the carrier gas tank 38 via carrier gas line 40, and is controlled by carrier gas valve 42.

In one embodiment, the metallic source 30 can be a metal halide, such as in powder form. Particularly suitable metal halides include, but are not limited to, gallium chloride (GaCl₃), aluminum chloride (AlCl₃), and indium chloride (InCl₃), where x ranges from 0.1 to 3. In one particular embodiment, x is 3. In this embodiment, the carrier gas simply functions as a true carrier, transferring the metal halide from the metallic source 30 to the reaction chamber 16. Suitable carrier gases include, but are not limited to nitrogen (N₂), hydrogen (H₂), helium, argon, and other inert gases.

In an alternative embodiment, the metallic source 30 can be, a group III metal (gallium, aluminum, indium, etc.). In this embodiment, a reactant gas (not shown) is supplied to the metallic source 30 (which can be the same setup as the carrier gas). The reactant gas reacts with the metal to form a metal halide MX₃, where M is the group III metal and X is a halide (e.g., chloride, bromide, iodide, fluoride, etc.). For example, the reactant gas can be hydrogen chloride (HCl),
hydrogen fluoride (HF), hydrogen bromide (HBr), etc. In this embodiment, the heating of the metallic source 30 is from about 50° C to about 900° C to ensure that the reaction of the halide reactant gas and the metallic source 30 (forming the metal halide) occurs. Then, the formed metal halide is vaporized at these temperatures for transport to the reaction chamber 16.

The carrier gas 38 (e.g., nitrogen (N₂), hydrogen (H₂), helium, argon, and other inert gases) then transports the vaporized metal halide to the reaction chamber 16 via the metallic source gas line 33. This metallic source gas line 33 is heated to a temperature of greater than about 50° C to ensure that the metal halide does not condense on the inside of the metallic source gas line 33. However, due to limitations of the couplings of the line, the metallic source gas line 33 cannot be overheated, leaving the upper temperature limit of the metallic source gas line 33 from 400° C to about 500° C. Thus, the metallic source gas line 33 is heated from about 50° C to about 500° C, such as from about 200° C to about 400° C.

When released into the reaction chamber 16, the metallic source gas line 33 can be positioned directly over the substrate 12 and in close proximity (e.g., from about 0.1 mm to about 300 mm away from the surface of the substrate 12). This configuration inhibits the metal halide from condensing on the cooler chamber walls 18 (such as having a temperature of less than about 200° C) of the reaction chamber 16. In one embodiment, the HVPE-like system 26 can grow the group III-nitride epilayer even with chamber walls 18 at room temperature (e.g., from about 20 °C to about 25° C).

In order to grow the group III-nitride layer via the HVPE-like system 26, both the nitrogen source and the metallic source can be provided simultaneously to the reaction chamber 16. The growth rate of the epilayer formed through use of the HVPE-like system depends on the flow rate of the nitrogen source gas and the metallic source (through the flow of the carrier gas), the temperature of the substrate 12 in the reaction chamber 16, the temperature of the metallic source 30, and the length of time that the nitrogen source gas and the metallic source are exposed to the reaction chamber 16. Thus, one of ordinary skill in the art would be able to precisely control the growth rate of the III-nitride epilayer on the substrate.
Alternatively, the nitrogen source and the metallic source can be sequentially provided to the reaction chamber 16. For example, referring to Figs. 2a-2d, exemplary diagrams showing different possibilities of pulsing of the components of the HVPE-like system 26 are generally shown. In Fig. 2, the on/off position of the gas flow from each of the gas components (controllable by their respective valves) is shown plotted against time. In each diagram, the upper bar of each line is on, while the lower bar is off. For example, in Fig. 2c, the carrier gas (N$_2$, H$_2$, etc.) is first allowed to flow from the carrier gas tank 38 via carrier gas line 40 (e.g., the carrier gas valve 42 is opened). Also, a reactant gas (HCl in this example) is allowed to flow to the metallic source 30 and reacts with the metal source to form the metal chloride (MCI$_x$), which flows to the reaction chamber 16 with the carrier gas. Next, the carrier gas valve 42 is closed and the flow of the carrier gas (HCl) is stopped, and the flow of the reactant gas (HCl) is also stopped. However, the nitrogen source (NH$_3$ in this example) is allowed to flow to the reaction chamber via the nitrogen source gas line 34 (e.g., the nitrogen source valve 36 is opened).

In another embodiment shown in Fig. 2a, the carrier gas (N$_2$, H$_2$, etc.) and the reactant gas (e.g., HCl) can be allowed to constantly flow to the reaction chamber 16, while the nitrogen source (e.g., NH$_3$) is pulsed. In yet another embodiment, such as shown in Fig. 2b, the carrier gas (N$_2$, H$_2$, etc.) can be allowed to constantly flow to the reaction chamber 16, while the reactant gas (HCl in this example) and the nitrogen source (e.g., NH$_3$) are sequentially pulsed (i.e., while the reactant gas flows, the nitrogen source does not flow and vice versa). In still another embodiment, the nitrogen source (e.g., NH$_3$) can be allowed to constantly flow to the reaction chamber 16, while the carrier gas (N$_2$, H$_2$, etc.) and the nitrogen source (e.g., NH$_3$) are simultaneously pulsed to the reaction chamber 16. Any of these processes can be repeated any number of times to form an epilayer having the desired thickness. The control of these source gases through their respective valves can be manually controlled or digitally controlled (e.g., by a computer program).

Pulse HVPE allows accurate control of the quaternary layer composition and thickness by simply changing the number of aluminum, indium, and gallium pulses in a unit cell and the number of unit cell repeats. By controlling the pulse time,
pulse condition, flow rate, and therefore chemical availability, the systematic growth provides a layer with significantly control of the composition, thickness and crystalline quality.

In one particular embodiment, multiple metallic sources 30 can be provided in the HVPE-like system 26. Through control of the carrier gas flow to each metallic source, the composition of the group III-nitride layer(s) formed from the HVPE-like system 26 can be precisely controlled. Thus, the use of multiple metallic sources 30 enables an epilayer to be formed having the formula $A_\mu_1I_nG_a_\mu_1$. $x_\gamma N$, wherein $0<x<1$, $0<y<1$ and $0<x+y<1$, where the precise stoichiometric amounts of each metal is controlled.

In addition to the HVPE-like system 26 (or multiple HVPE-like systems 26), the MOHVPE system 10 contains a MOCVD-like system 28. This MOCVD-like system 28 can be used to form relatively thin group III-nitride layers, since the growth rate is lower than with the HVPE-like system 26. For example, the MOCVD-like system 28 can be used to grow an group III-nitride layer at a rate of from about $0.1 \mu m/hour$ to about $10 \mu m/hour$ (measured in the thickness of the layer), such as from about $1 \mu m/hour$ to about $5 \mu m/hour$. The low growth rates in MOCVD make it easier to grow abrupt and sharp interface layers with compositional control for ternary and quaternary layers.

The MOCVD-like system 28 of the exemplary embodiment shown in Fig. 1 includes a MOCVD carrier gas tank 44 configured to carrier the metalorganic source 46 to the reaction chamber 16. Any suitable metalorganic source can be utilized, including without limitation gallium-R, indium-R, aluminum-R, boron-R, magnesium-R, zinc-R, iron-R, etc., where R is any suitable organic compound (e.g., $CH_3$, $C_2H_5$, etc.). The carrier gas is transferred from the MOCVD carrier gas tank 44 to the metalorganic source 46 via the MOCVD carrier gas line 48, and controlled via MOCVD carrier gas valves 50a, 50b. Then, the metalorganic source 46 can be carried to the reaction chamber 16 via metalorganic source line 52.

In the reaction chamber 16, the metalorganic source 46 is combined with the nitrogen source, from nitrogen source tank 32, in order to grow the III-nitride epilayer. As with the HVPE-like system 26, growth of the group III-nitride layer via the MOCVD-like system 28 can be controlled by varying the flow rate of the MOCVD carrier gas (and thus the metalorganic source 46) and the nitrogen source.
32, the temperature of the substrate 12 in the reaction chamber 16, the temperature of the metalorganic source 46, and the length of time that the nitrogen source gas and the metalorganic source 46 are exposed to the reaction chamber 16. Thus, one of ordinary skill in the art would be able to precisely control the growth rate of the III-nitride epilayer on the substrate.

Alternatively, the nitrogen source and the metalorganic source 42 can be sequentially provided to the reaction chamber 16. For example, referring to Fig. 3, an exemplary diagram showing the pulsing of the components of the MOCVD-like system 28 is generally shown. In Fig. 3, the on/off position of the gas flow from each of the gas components (controllable by their respective valves) is shown plotted against time. In the diagram, the upper bar of each line is on, while the lower bar is off. For example, in the shown diagram, the carrier gas (H$_2$ or N$_2$ in this example) is first allowed to flow from the MOCVD carrier gas tank 44 via MOCVD carrier gas line 48 (e.g., the MOCVD carrier gas valves 50a, 50b are opened). The carrier gas transports the metalorganic source 46 to the reaction chamber 16. Next, the MOCVD carrier gas valves 50a, 50b are closed to stop the flow of the carrier gas, while the nitrogen source (NH$_3$ in this example) is allowed to flow to the reaction chamber via the nitrogen source gas line 34 (e.g., the nitrogen source valve 36 is opened). This process can be repeated any number of times to form an epilayer having the desired thickness. The control of these source gases through their respective valves can be manually controlled or digitally controlled (e.g., by a computer program).

Pulse MOCVD or Pulse atomic layer epitaxy (PALE) allows accurate control of the quaternary layer composition and thickness by simply changing the number of aluminum, indium, and gallium pulses in a unit cell and the number of unit cell repeats. By controlling the pulse time, pulse condition, flow rate, and therefore chemical availability, the systematic growth provides a layer with significantly control of the composition, thickness and crystalline quality.

Pulsed lateral overgrowth (PLOG) is a technique wherein a Group III comprising material (e.g., triethyl gallium or trialkly aluminum) and a nitrogen material (e.g., ammonia) are supplied in a vapor phase for deposition of the Group III-nitride. With pulsed lateral overgrowth the flow rate of the Group III material is maintained at a constant rate whereas the flow rate of the nitrogen compound is
systematically altered, preferable from full flow to off, in a predetermined sequence as set forth in "Vertically Faceted Lateral Overgrowth of GaN on SiC with Conducting Buffer Layers Using Pulsed Metalorganic Chemical Vapor Deposition", Fareed et al., Applied Physics Letters, Vol. 77, Number 15, 9 October 2000, page 2343-5, which is incorporate by reference herein. By controlling the flow rate, and therefore chemical availability, of the nitrogen systematic growth of select crystallographic planes can be accomplished. The systematic growth provides a layer which significantly mitigates transfer of dislocations caused by lattice mismatches through the layer.

In one particular embodiment, multiple metalorganic sources 46 can be provided in the MOCVD-like system 28. Through control of the carrier gas flow to each metalorganic source 46, the composition of the group III-nitride layer(s) formed from the MOCVD-like system 28 can be precisely controlled. Thus, the use of multiple metalorganic sources 46 enables an epilayer to be formed having the formula $A_1^x In_y Ga_{1-x-y}N$, wherein $0 \leq x \leq 1$, $0 \leq y \leq 1$ and $0 < x + y < 1$, where the precise stoichiometric amounts of each metal is controlled.

Of course, all of the gas lines (purge gas line 22, nitrogen source line 34, carrier gas line 40, MOCVD carrier gas line 48, and metalorganic source line 52) can be heated as is known in the art.

In the reaction chamber 16, the substrate 12 is positioned on a rotatable platform 14, as stated above. In one particular embodiment, the reaction chamber 16 can be a cold wall reaction chamber, where chamber walls 18 are not significantly heated (e.g., less than about 200° C). As discussed above, the use of a hot walled reaction chamber would decompose the metalorganic source 46 and inhibit the growth of the III-nitride epilayer on the substrate. In order to heat the substrate 12, heaters can be provided in conjunction with the rotatable platform 14. Thus, the substrate can be heated, through conduction, via contact with the rotatable platform 14. For example, referring to Fig. 1, a heating element 54 is located on the rotatable platform 14 in order to heat the substrate and allow growth of the epilayer of via the MOCVD-like system 28. Alternatively, an external heat source 60 can be utilized to heat the substrate without substantially heating the chamber walls 18. Suitable external heat sources 60 can include, for instance, radio frequency (rf) heating coil, a resistive heating element, a lamp, etc.
However, the present inventors have discovered that the use of the cold walled reaction chamber can be also used in conjunction with the HVPE-like system 26 of the MOHVPE system 10, without sacrificing the growth rate typically expected with conventional hot wall HVPE systems.

As shown, the reaction chamber 16 is set up in a vertical arrangement, such that the source gases enter the reaction chamber above the substrate 12 (through source gas openings 56(a-d), pass over and around the substrate 12, and out the exit passage 58. The use of a vacuum pump (not shown) drawing the gases out of the reaction chamber 16 at exit passage 58 can further control the reaction time of the source gases in the reaction chamber 16.

Through rotation of the substrate 12 on the rotatable platform 14, the III-nitride epilayers can be more uniformly grown.

**Examples**

The MOHVPE system of the present invention was utilized to combine metalorganic chemical vapor deposition (MOCVD) and hydride vapor phase epitaxy (HVPE) in a single growth chamber to deposit 20 µm thick, crack-free single crystal AlN films over grooved basal plane sapphire substrates with lateral growth rates in excess of 2 µm/hr. The combination of MOCVD and HVPE in the same reactor affords the flexibility to grow buffer and device layers at growth rates ranging from 0.1 - 10 µm/hr without removing the substrate. It is therefore ideal for the deposition of thick AlN buffers and deep UV light emission devices over substrates such as sapphire with excellent optical properties but a low thermal conductivity. In addition, the viability of the MOHVPE process for fast lateral epitaxy of AlN and a subsequent growth of high-quality UVC LED epilayers is demonstrated.

First, a high quality 0.1 µm thick AlN layer was grown on basal plane sapphire using pulsed low-pressure MOCVD followed by a 2 µm thick Al_{x}Ga_{1-x}N layer with conventional MOCVD. For these growths the MOHVPE system was operated in the MOCVD mode. Trimethyl-aluminum, trimethyl-gallium and ammonia were used as the precursors and the growth temperature and pressure were 1050° C and 76 torr respectively. The AlGaN layer was then grooved using standard photolithography and inductively coupled plasma assisted reactive ion
etching (ICPRIE). The grooves were oriented along the AIN $[\bar{1}00]$ directions and their widths ranged from 4 to 10 µm with a period of 6 to 12 µm. The grooved template was then reloaded in the MOHVPE system. A 0.1 µm thick AIN layer was then re-grown operating the MOHVPE reactor in the MOCVD mode. This was followed by lateral overgrowth of an AIN layer with thicknesses up to 20 µm while operating the MOHVPE system in the HVPE mode. For the HVPE step, the growth temperature and pressure were 1200°C and 150 torr and we used AlCl$_3$ and ammonia as the precursors and hydrogen as the carrier gas for all the precursors. The growth rate for AIN was about 5 µm/hour. In addition to yielding AIN layers with thicknesses in excess of 20 µm, the MOHVPE method also resulted in an extremely smooth surface morphology and dislocation densities as low as $10^7$cm$^{-2}$ in the lateral overgrown regions.

In Figure 4, a cross-section scanning electron micrograph (SEM) image of a 17 µm thick MOHVPE AIN/sapphire template grown for 180 min is shown. The width of trenches in this particular sample was 9.1 µm. Evidence of lateral growth from the 2 µm wide pillars (10 µm wide trenches) of the template is clearly visible. It gives rise to triangular shaped air pockets before a complete coalescence of the lateral growth fronts. The vertical to lateral growth-rate ratio was approximately 1.7. The MOHVPE growth mode resulted in a complete coalescence over the entire 2 inch substrate. An additional 1 µm growth was carried out after the coalescence of the lateral growth fronts.

The surface morphology was then studied using an atomic force microscope scan. These data for a 2 µm x 2 µm scan are included in Figure 5. The scan area was over the laterally grown region. As seen the surface of the wafer is extremely smooth with an RMS roughness of only 0.2 nm. The well defined steps clearly imply that the growth mode is dominated by two-dimensional step flow growth. The laterally overgrown material has long parallel atomic steps without step termination indicating a reduced threading dislocation (TD) density. Height difference of 2.8 Å corresponds to approximately 1 ML of (0001) AIN (c/2 = 2.5 Å). The step termination marked by an arrow, corresponds to either pure screw or mixed screw-edge character. The on axis (002) and the off-axis (102) X-ray spectra for the MOHVPE AIN layer were then measured. The linewidths for these X-ray peaks were respectively 150 and 290 arc seconds. It is well established that
for the Hf-N material system the off-axis X-ray peak line-width is a direct reflection of the film quality and can be used for estimating the number of the edge dislocations. The 290 arcsec off-axis X-ray linewidth for the MOHVPE AIN layer clearly indicates it to be of a very high crystalline quality.

To confirm this, the layers were analyzed using cross-section transmission electron microscopy (TEM). The TEM thin film was pre-thinned to ~20µm by mechanical polishing and then thinned to electron transparency by using a dual-beam focused ion beam (FIB) system with a liquid Ga⁺ source. The diffraction contrast TEM analysis was performed in a FEI CM-200 FEG transmission electron microscope. In Fig. 6, the bright-field TEM micrographs show the cross-section view of a lateral overgrown AIN stripe along a <U00> direction. The images are taken under different two-beam conditions to show the edge-type and screw-type threading dislocations (a) \( g = \frac{1}{3} \langle 20 \rangle \); (b) \( g = 002 \). Threading dislocations are only observed in the region above mesa and has a density of about \( 10^8 \text{cm}^{-2} \). Most of them are pure-edge type. In the lateral growth region, the density of threading dislocations reduces significantly to less than \( 10^8 \text{cm}^{-2} \). In this sense, the lateral overgrowth method is very efficient in reduction of threading defects in the laterally overgrown AIN films. In addition, parasitic growth in the trench does not create any problems for the merger of the AIN lateral overgrown stripes.

The improved material quality for the MOHVPE AIN layers is further confirmed using monochromatic cathodoluminescence imaging, as shown in Fig. 7. For these measurements the electron beam from a SEM (Scanning Electron Microscope) was used as the pump source. The CL spectra were collected using a GATAN Mono CL3 system with enhanced UV sensitivity. Cross section CL image of near band edge emission from a lateral overgrown AIN is shown in Fig. 4(inset). The brighter area corresponds to higher intensity of the 210nm light emission. Stronger emission from the lateral overgrown region material and a relatively weaker intensity from the mesa region are observed. The CL spectra from the spots located on the laterally overgrown and the vertically grown regions show a strong band-edge emission peak at 210 nm, clearly indicating a high optical quality for the MOHVPE grown AIN layer. Furthermore, the intensity of the emission signal from the laterally overgrown material was about a factor of 20
higher than that from the vertically grown region. It was approximately a factor of 40 higher than our best MOCVD grown AlN films. These data clearly show that the quality of the MOHVPE AlN material to be much superior in the lateral overgrown region. These CL data are in very good agreement with the conclusions derived from the cross-section TEM and the off-axis X-ray data.

The viability of the combination growth reactor and the MOHVPE growth approach for thick-lateral epitaxy of AlN buffers and deep UV LED devices in a single run was confirmed. First, the 17 µm thick AlN buffer layer growth was followed by depositing an Al_xGa_{1-x}N multiple quantum well (MQW) based p-n junction LED structure. The AlGaN compositions in the active layers were selected for emission at 285 nm. The LED epilayer structure was similar to the one discussed in an earlier report. Surface CL emission spectrum of the LED epilayer and a cross-section CL image taken at 285 nm (inset) are included in Figure 8. As seen the emission signal at 285 nm from the device structure on the MOHVPE template is clearly distinct and of a high intensity. The bright cross-section CL image at 285nm confirms the high quality of the MQW layer. This clearly establishes the viability of using the MOHVPE technique for depositing high-quality laterally grown thick-buffer and device quality heterostructures in a single run and within the same reactor.

In summary the MOHVPE approach for lateral epitaxy of high-quality AlN layers over sapphire with thicknesses in excess of 20 µm and growth rates over 5 µm/hr followed by the deposition of high-quality UVC LED structures is shown. Structural and optical characterization data are presented to support the high-quality of the MOHVPE deposited Al_xGa_{1-x}N layers. This represents the first report of combining MOCVD and HVPE growths in a single chamber for lateral epitaxy of extremely high-quality AlN buffers followed by the deposition of a deep UV LED device structure in the same run.

These and other modifications and variations to the present invention may be practiced by those of ordinary skill in the art, without departing from the spirit and scope of the present invention, which is more particularly set forth in the appended claims. In addition, it should be understood the aspects of the various embodiments may be interchanged both in whole or in part. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of
example only, and is not intended to limit the invention so further described in the appended claims.
IN THE CLAIMS:

1. A metalorganic-hydride vapor phase epitaxy system comprising
   a reaction chamber, wherein the reaction chamber comprises a rotatable
   platform configured to support a substrate;
   a nitrogen source gas configured to flow to the reaction chamber via a
   nitrogen source line, wherein the flow rate of the nitrogen source gas is
   controllable by a nitrogen source valve;
   an hydride vapour phase epitaxy system comprising a carrier gas and a
   metallic source located outside of the reaction chamber, wherein the hydride
   vapour phase epitaxy system is configured such that the carrier gas transports the
   metallic source into the reaction chamber, wherein the flow rate of the metallic
   source to the reaction chamber is controllable by a carrier gas valve; and
   a metal-organic chemical vapor deposition system comprising a MOCVD
   carrier gas and a metalorganic source, wherein the MOCVD carrier gas is
   configured such that the MOCVD carrier gas transports the metalorganic source to
   the reaction chamber, wherein the flow rate of the metalorganic source to the
   reaction chamber is controllable by a MOCVD carrier gas valve.

2. A system as in claim 1, further comprising a purge gas source
   configured to provide an ambient gas to the reaction chamber.

3. A system as in claim 1, wherein the rotatable platform comprises a
   heating element.

4. A system as in claim 1, wherein the reaction chamber is vertically
   arranged.

5. A system as in claim 1, wherein the reaction chamber is defined by
   chamber walls, wherein the chamber walls are configured to have a temperature of
   less than about 200° C.

6. A system as in claim 1, wherein the metal source is configured to be
   heated between about 50° C to about 900° C.
7. A system as in claim 1, wherein the rotatable platform is configured to rotate from about 1 rotation per minute to about 100,000 rotations per minute.

8. A system as in claim 1, wherein no metallic source is contained within the reaction chamber.

9. A system as in claim 1, wherein the metallic source comprises gallium, aluminum, indium, or a combination thereof, and the system further comprises a halide reactant gas configured to react with the metallic source outside of the reaction chamber to form a metal halide and then transport the metal halide to the reaction chamber via the carrier gas.

10. A method of growing a group III-nitride epilayer on a substrate comprising

   utilizing the system of claim 1 to form the epilayer, wherein the group III-nitride epilayer comprises Al\textsubscript{x}In\textsubscript{y}Ga\textsubscript{1-x-y}N, wherein 0≤x≤1, 0≤y≤1 and 0≤x+y<1.

11. A method of growing epilayers on a substrate, the method comprising

   positioning a substrate on a platform, wherein the substrate and the platform are within a reaction chamber;

   forming a first group III-nitride layer on the substrate, wherein the first group III-nitride layer comprises Al\textsubscript{x}In\textsubscript{y}Ga\textsubscript{1-x-y}N, wherein 0<x≤1, 0<y<1 and 0≤x+y<1, wherein the first group III-nitride layer is formed by reacting a nitrogen source gas with a metalorganic source; and

   forming a second group III-nitride layer on the substrate, wherein the second group III-nitride layer comprises Al\textsubscript{x}In\textsubscript{y}Ga\textsubscript{1-x-y}N, wherein 0<x≤1, 0<y<1 and 0<x+y≤1, wherein the second group III-nitride layer is formed by reacting the nitrogen source gas and a metal source, wherein the metal source is positioned outside of the reaction chamber,

12. A method as in claim 11, wherein the reaction chamber is defined by chamber walls having a temperature of less than about 200° C.
13. A method as in claim 11 further comprising rotating the platform to a rotation speed of from about 1 rotation per minute to about 100,000 rotations per minute.

14. A method as in claim 11, wherein the nitrogen source gas comprises ammonia.

15. A method as in claim 11, wherein the metal source comprises a metal halide.

16. A method as in claim 11, wherein the metallic source comprises gallium, aluminum, indium, or a combination thereof, and wherein the second group III-nitride layer is formed by reacting a halide reactant gas with the metallic source outside of the reaction chamber to form a metal halide and then transporting the metal halide to the reaction chamber via a carrier gas.

17. A method as in claim 11, wherein the nitrogen source and the metalorganic source are sequentially pulsed into the reaction chamber to form the first group III-nitride layer.

18. A method as in claim 11, wherein the nitrogen source and the metal source are sequentially pulsed into the reaction chamber to form the second group III-nitride layer.

19. A method of growing epilayers on a substrate, the method comprising
   positioning a substrate on a platform, wherein the substrate and the platform are within a reaction chamber;
   forming a first group III-nitride layer on the substrate, wherein the first group III-nitride layer comprises $\text{Al}_x\text{In}_y\text{Gai}_{x-y}N$, wherein $0<x<1$, $0<y<1$ and $0<x+y<1$, wherein the first group III-nitride layer is formed by reacting the nitrogen source gas and a metal source, wherein the metal source is positioned outside of the reaction chamber; and
   forming a second group III-nitride layer on the substrate, wherein the second group III-nitride layer comprises $\text{Al}_x\text{In}_y\text{Gai}_{x-y}N$, wherein $0<x<1$, $0<y<1$ and
0 < x + y ≤ 1, wherein the second group III-nitride layer is formed by reacting a nitrogen source gas with a metalorganic source.

20. A method as in claim 19, wherein the reaction chamber is defined by chamber walls having a temperature of less than about 200° C.

21. A method as in claim 19 further comprising rotating the platform to a rotation speed of from about 1 rotation per minute to about 100,000 rotations per minute.

22. A method as in claim 19, wherein the nitrogen source gas comprises ammonia.

23. A method as in claim 19, wherein the metallic source comprises gallium, aluminum, indium, or a combination thereof, and wherein the first group III-nitride layer is formed by reacting a halide reactant gas with the metallic source outside of the reaction chamber to form a metal halide and then transporting the metal halide to the reaction chamber via a carrier gas.

24. A method as in claim 19, wherein the metal source comprises a metal halide.

25. A method as in claim 19, wherein the nitrogen source and the metal source are sequentially pulsed into the reaction chamber to form the first group III-nitride layer.

26. A method as in claim 19, wherein the nitrogen source and the metalorganic source are sequentially pulsed into the reaction chamber to form the second group III-nitride layer.

27. A semiconductor device made according to the method of any of claims 11 - 26.
**FIG. 2A**

**FIG. 2B**
FIG. 8