substrate is partially masked and the III-nitride layer is coerced to grow laterally over the mask. The epitaxial film over the mask has a greatly reduced dislocation density. However, the epitaxial film in the open regions still have the same high dislocation density as achieved on a non-masked substrate. In addition, further defects are generated where adjacent laterally overgrown regions meet. To further reduce the dislocation density, one can perform multiple ELO steps. It is clear that this is a very expensive and time consuming process, and in the end produces a non-homogeneous substrate, with some areas of low dislocation density and some areas with high dislocation density.

The most successful approach to date to reducing defect densities is to grow very thick layers of the III-nitride material. Because the dislocations are not oriented perfectly parallel with the growth direction, as growth proceeds, some of the dislocations meet and annihilate each other. For this to be effective one needs to grow layers on the order of 300 to 1000μm. The advantage of this approach is that the layer is homogeneous across the substrate. The difficulty is finding a growth chemistry and associated equipment that can practically achieve these layer thicknesses. MOVPE or MBE techniques have growth rates on the order of less than 1 to about 5 μm/hour and thus are too slow, even for many of the ELO techniques discussed above, which require several to tens of microns of growth. The only growth technique that has successfully achieved high growth rates is hydride vapor phase epitaxy (HVPE).

In summary, the current state of the art in producing low dislocation Group III nitride material is to use HVPE to produce very thick layers. However the current HVPE process and equipment technology, while able to achieve high growth rates, has a number of disadvantages. Embodiments of t~~T~~he present invention now seek to overcomes these disadvantages and provides relatively low cost, high quality Group II nitride lead to new, innovative applications, e.g., in residential and commercial lighting systems.

SUMMARY OF THE INVENTION

According to an aspect of the present invention, there is provided a high volume manufacturing process for depositing gallium nitride on a substrate by delivering a gaseous form of gallium trichloride to a reaction zone, comprising: providing a carrier gas selected from the group consisting of: hydrogen, nitrogen, helium, argon and mixtures thereof at a pressure above atmospheric pressure; heating the carrier gas to a temperature of at least 110°C; heating gallium trichloride in a solid form held in a container, so as to create a bath of a liquid form of gallium trichloride; injecting the carrier gas into said bath of a liquid form of the gallium trichloride, the gallium trichloride in the bath being heated in the temperature range of 110°C to 130°C; and conveying the carrier gas and any entrained gallium trichloride from the bath to a reaction zone at a controlled temperature such that the temperature does not decrease from the source to the reaction zone, at a controllable mass flow of gallium of at least 50g per hour for a time of at least 48 hours without requiring interruption of said high volume manufacturing process for synthesizing said gallium nitride.

~~The invention relates to a method for providing a gaseous Group III precursor for forming a monocrystalline Group III - V semiconductor material. The method comprises continuously providing the precursor at a mass flow of at least 50g Group III element/hour for a time of at least 48 hours to facilitate high volume manufacture of the semiconductor material. Advantageously, the method further comprises controlling the mass flow of the gaseous Group III precursor to deliver the desired amount to form the semiconductor material.~~

One preferred gaseous Group III precursor is a gallium compound that is continuously provided as a mass flow that continuously delivers at least 5kg gallium. In particular, this gallium compound is gallium trichloride and it is provided by heating solid gallium trichloride. When the solid gallium trichloride is heated to a liquid, the method may include encouraging increased evaporation of the gallium trichloride during the heating to provide a mass flow rate of gaseous gallium trichloride of at least 100g gallium/hour. Preferably, the solid gallium trichloride is initially heated to a temperature sufficient to induce a low viscosity liquid state on the order of ambient temperature water, such as by heating the solid gallium trichloride to a temperature of 110 to 130°C. Advantageously, a carrier gas is bubbled into the liquid gallium trichloride during the heating to generate the gaseous gallium trichloride. The carrier gas may be hydrogen, helium, neon, argon or mixtures thereof.

Alternatively, the gaseous precursor may be a Group III halide, with the method further comprising heating the halide to a temperature below its melting point but sufficiently high to generate a vapor pressure that achieves the mass flow. In addition to a gallium halide, this embodiment is useful for providing gaseous indium chloride or aluminum chloride precursors.

According to another aspect of the present invention, there is provided a system for facilitating a high volume manufacturing process for depositing gallium nitride on a substrate, which comprises a source of gaseous gallium trichloride, characterized in that said gallium trichloride source is capable of holding at least 25 kg of gallium trichloride and in that said source comprises: a container holding a solid form of said gallium trichloride, said container having a corrosion resistant inner surface for holding a liquid form of the gallium trichloride; a container heater for heating the container to a temperature sufficient to melt a solid form of the gallium trichloride in the temperature range of 110°C to 130°C; a source of a carrier gas and a carrier gas heater for heating the carrier gas to a temperature of at least 110°C; a dip tube in the container with an outlet for bubbling said carrier gas through a liquid in the container; a valve controlled container inlet leading to the dip tube; and a valve controlled container outlet leading to a delivery line; the delivery line for carrying the carrier gas and a gaseous form of the gallium trichloride to a reaction zone for conversion of the gallium trichloride into gallium nitride, the delivery line being configured to control the temperature such that the temperature does not decrease from the container to the reaction zone; such that said gallium trichloride source is able to provide a controllable mass flow of gallium of at least 50g per hour for a time of at least 48 hours without requiring interruption of the high volume manufacturing process.

~~Another embodiment of the invention relates to a system for providing a gaseous Group III precursor for forming a monocrystalline Group III – V semiconductor material, which comprises a source of sufficient amounts of the precursor for continuously providing the precursor at a mass flow of at least 50g Group III element/hour for a time of at least 48 hours to facilitate high volume manufacture of the semiconductor material. In this system, the source of Group III precursor typically comprises a container for holding the precursor.~~

Advantageously, the source of Group III precursor is operatively associated with a mass flow controller to deliver the desired amount to form the semiconductor material. Generally, the source of Group III precursor further includes a heating arrangement for heating the precursor and for generating a gas flow of the precursor. In addition, the container may be operatively associated with a source of carrier gas and a related conduit that introduces the carrier gas into the container in a manner which facilitates formation of the gas flow of the precursor. When the gaseous Group III precursor is a gallium compound, the system is capable of providing it in a mass flow that continuously delivers at least 5kg gallium.

Containers of various sizes may be used, as desired for the high volume manufacture of the semiconductor material. Generally, the container may initially hold at least 10 to 60 Kg of a solid Group III halide with the heating arrangement is configured and dimensioned to heat the solid halide sufficiently to provide the gaseous precursor. The container can hold at least

25Kg of solid halides such as indium trichloride or aluminum trichloride, with the heating arrangement configured and dimensioned to heat the trichloride sufficiently to provide the gaseous precursor. Also, the heating arrangement may be configured and dimensioned to heat the trichloride to provide a mass flow rate of at least 75g Group III element/hour. For further extended manufacture, a plurality of container can be connected in series to facilitate delivery of the gaseous precursor for a longer time than if a single container is used.

A preferred Group III halide is gallium trichloride, with the container and heating arrangement configured and dimensioned to heat the solid gallium trichloride to a liquid. This can be achieved by heating solid gallium trichloride to a temperature sufficient to induce a low viscosity liquid state on the order of ambient temperature water with the container further including a mechanism for encouraging increased evaporation of the gallium trichloride during the heating to provide a mass flow rate of gaseous gallium trichloride of at least 100g gallium/hour. The solid gallium trichloride is typically heated to a temperature of 110 to 130°C while the mechanism for encouraging increased evaporation includes a source of carrier gas and a conduit associated with the container for bubbling the carrier gas into the liquid gallium trichloride during the heating to generate the gaseous gallium trichloride. The source of carrier gas may be any supply of hydrogen, helium, neon, argon or mixtures thereof.

There are also disclosed~~In a further preferred embodiment, the invention provides~~ systems that facilitate high volume manufacturing of a Group III - V semiconductor material and includes a source of a gaseous Group III precursor at a controllable mass flow of Group III element of at least 50g per hour for a time of at least 48 hours without requiring interruption of the high volume manufacturing process. Specifically, the controllable mass flow of the Group III element is sufficient to enable deposition rates of the Group III-V semiconductor material equivalent to at least 100 µm/hour on a 200mm substrate during the time that the precursor is provided.

The precursor source can include a container having a corrosion resistant inner surface for holding a liquid form of the Group III precursor, a dip tube in the container with an outlet for bubbling a carrier gas through a liquid in the container, a valve controlled container inlet leading to the dip tube; and a valve controlled container outlet leading to a delivery line;, the delivery line for carrying the carrier gas and a gaseous form of the Group III precursor to a reaction zone for conversion of the Group III precursor into a Group III - V semiconductor material. Also disclosed is~~Aspects of this embodiment include~~ a purifier capable of removing moisture from the carrier gas down to no more than 5 parts per billion; or a carrier gas filter downstream of the carrier gas purifier; or a container heater for heating the container to a temperature sufficient to melt a solid form of the Group III precursor; a source of a carrier gas and a carrier

gas heater for heating the carrier gas to a temperature of at least 110°C; or a carrier gas line configured with sinusoidal bends for providing increased heat exchange surface proximate to the carrier gas heater; or the carrier gas being hydrogen, helium, neon, argon or mixtures thereof and heated to a temperature of 110°C to 130°C; or a mass flow controller for controlling the mass flow of the carrier gas; or an insulating outer portion for the container; or a delivery line further includes a coaxial portion having an inner line conveying the carrier gas and the Group III precursor and an enclosing coaxial line providing an annular space for containing a heating medium.

TAspects of this embodiment include that the container, or the delivery line, or the valved inlet, the valved outlet and the valves in such inlet and outlet include stainless steel, Hastelloy, Monel, or combinations thereof; that the valves or the inner surface of the container include polytetrafluoroethylene seats; and that at least one of the container, the valved inlet, the valved outlet, the inlet valves, the outlet valves, or the delivery line further include a material selected from a group consisting of a nickel-based alloy, tantalum, a tantalum-based alloy, silicon carbide, boron nitride, boron carbide, aluminum nitride, fused silica layer, bonded amorphous silicon layer, and other known chlorine resistant materials.

There are also disclosedIn a further preferred embodiment, the invention provides processes for delivering a gaseous form of a Group III precursor to a reaction zone for synthesizing gallium nitride that include the steps of providing a carrier gas selected from the group consisting of: hydrogen, nitrogen, helium, argon and mixtures thereof at a pressure above atmospheric pressure; heating the carrier gas to a temperature of at least 110°C; injecting the carrier gas into a bath of a liquid form of the Group III precursor; and conveying the carrier gas and any entrained Group III precursor from the bath to a reaction zone for synthesizing a Group III nitride delivering. TIn aspects of this embodiment, the carrier gas and entrained Group III precursor is delivered to the reaction zone at a temperature of at least 110°C; or the carrier gas is purified by removal of moisture to no more than 5 parts per billion; or the carrier gas is provided at a flow rate of 5 to 15 liters per minute; or the Group III precursor in the bath is heated to a temperature in the range of 110°C to 130°C; or the Group III precursor includes gallium trichloride.

Further aspects and details and alternate combinations of the elements of this invention will be apparent from the appended drawings and following detailed description and these are also within the scope of the invention.

CLAIMS:

1. A metal halide system for facilitating a high volume manufacturing process for forming a Group III - V semiconductor material which comprises a source of a gaseous Group III precursor at a controllable mass flow of Group III element of at least 50g per hour for a time of at least 48 hours without requiring interruption of the high volume manufacturing process, wherein the precursor source further comprises:

a metallic container having a corrosion resistant inner surface for holding a liquid form of the Group III precursor;

a dip tube in the container with an outlet for bubbling a carrier gas through a liquid in the container;

a valve controlled container inlet leading to the dip tube; and

a valve controlled container outlet leading to a delivery line;

the delivery line for carrying the carrier gas and a gaseous form of the Group III precursor to a reaction zone for conversion of the Group III precursor into a Group III - V semiconductor material.

2. The system of claim 1 further comprising a purifier capable of removing moisture from the carrier gas down to no more than 5 parts per billion.

3. The system of claim 2 further comprising a carrier gas filter downstream of the carrier gas purifier.

4. The system of claim 1 further comprising a container heater for heating the container to a temperature sufficient to melt a solid form of the Group III precursor.

5. The system of claim 1 further comprising a source of a carrier gas and a carrier gas heater for heating the carrier gas to a temperature of at least 110°C.

6. The system of claim 5 further comprising a carrier gas line configured with sinusoidal bends for providing increased heat exchange surface proximate to the carrier gas

heater, wherein the carrier gas is hydrogen, helium, neon, argon or mixtures thereof and is heated to a temperature of 110°C to 130°C.

7. The system of claim 1 wherein the container further comprises an insulating outer portion.

8. The system of claim 1 wherein the delivery line further comprises a coaxial portion having an inner line conveying the carrier gas and the Group III precursor and an enclosing coaxial line providing an annular space for containing a heating medium.

9. The system of claim 1 wherein container further comprises stainless steel, Hastelloy, Monel, or combinations thereof.

10. The system of claim 1 wherein the delivery line further comprises stainless steel, Hastelloy, Monel or combinations thereof.

11. The system of claim 1 wherein the valved inlet, the valved outlet and the valves in such inlet and outlet further comprise stainless steel, or hastaloy, or monel, or mixtures thereof.

12. The system of claim 11 wherein the valves further comprise polytetrafluoroethylene seats.

13. The system of claim 1 wherein the inner surface of the container comprises polytetrafluoroethylene.

14. The system of claim 1 wherein at least one of the container, the valved inlet, the valved outlet, the inlet valves, the outlet valves, or the delivery line further comprise a material selected from the group consisting of a nickel-based alloy, tantalum, a tantalum-based alloy, silicon carbide, boron nitride, boron carbide, aluminum nitride, fused silica layer, bonded amorphous silicon layer, and other known chlorine resistant materials.

15. The system of claim 1 wherein the controllable mass flow of the Group III element is sufficient to enable deposition rates of the Group III-V semiconductor material equivalent to at least 100 μm/hour on a 200mm substrate during the time that the precursor is provided.

16. The system of claim 1 further comprising a mass flow controller for controlling the mass flow of the carrier gas.

Claims:

1. A system for facilitating a high volume manufacturing process for depositing gallium nitride on a substrate, which comprises a source of gaseous gallium trichloride, characterized in that said gallium trichloride source is capable of holding at least 25 kg of gallium trichloride and in that said source comprises:

a container holding a solid form of said gallium trichloride, said container having a corrosion resistant inner surface for holding a liquid form of the gallium trichloride;

a container heater for heating the container to a temperature sufficient to melt a solid form of the gallium trichloride in the temperature range of 110°C to 130°C;

a source of a carrier gas and a carrier gas heater for heating the carrier gas to a temperature of at least 110°C;

a dip tube in the container with an outlet for bubbling said carrier gas through a liquid in the container;

a valve controlled container inlet leading to the dip tube; and

a valve controlled container outlet leading to a delivery line;

the delivery line for carrying the carrier gas and a gaseous form of the gallium trichloride to a reaction zone for conversion of the gallium trichloride into gallium nitride, the delivery line being configured to control the temperature such that the temperature does not decrease from the container to the reaction zone;

such that said gallium trichloride source is able to provide a controllable mass flow of gallium of at least 50g per hour for a time of at least 48 hours without requiring interruption of the high volume manufacturing process.

2. System according to claim 1, characterised in that the controllable mass flow of gallium is sufficient to enable deposition rates of the gallium nitride equivalent to at least 100 µm/hour on a 200mm substrate during the time that the gallium trichloride is provided.

3. System according to any of claims 1 or 2, characterised in that it comprises a mass flow controller for controlling the mass flow of the carrier gas.

4. System according to any of claims 1 to 3, characterised in that it comprises a carrier gas line configured with sinusoidal bends for providing increased heat exchange surface proximate to

the carrier gas heater, wherein the carrier gas is hydrogen, helium, neon, argon or mixtures thereof and is heated to a temperature of 110°C to 130°C.

5. System according to any of claims 1 to 4, characterised in that the delivery line further comprises a coaxial portion having an inner line conveying the carrier gas and the Group III trichloride precursor and an enclosing coaxial line providing an annular space for containing a heating medium.

6. System according to any of claims 1 to 5, characterised in that the container, and/or the delivery line, and/or the valved inlet, the valved outlet and the valves in such inlet and outlet comprise stainless steel, Hastelloy, Monel, or combinations thereof.

7. A high volume manufacturing process for depositing gallium nitride on a substrate by delivering a gaseous form of gallium trichloride to a reaction zone, comprising:

providing a carrier gas selected from the group consisting of: hydrogen, nitrogen, helium, argon and mixtures thereof at a pressure above atmospheric pressure;

heating the carrier gas to a temperature of at least 110°C;

heating gallium trichloride in a solid form held in a container, so as to create a bath of a liquid form of gallium trichloride;

injecting the carrier gas into said bath of a liquid form of the gallium trichloride, the gallium trichloride in the bath being heated in the temperature range of 110°C to 130°C; and

conveying the carrier gas and any entrained gallium trichloride from the bath to a reaction zone at a controlled temperature such that the temperature does not decrease from the source to the reaction zone, at a controllable mass flow of gallium of at least 50g per hour for a time of at least 48 hours without requiring interruption of said high volume manufacturing process for synthesizing said gallium nitride.

8. Process according to claim 7, characterised in that the carrier gas and entrained gallium trichloride is delivered to the reaction zone at a temperature of at least 110°C.

9. Process according to any of claims 7 or 8, characterised in that it comprises purifying the carrier gas by removal of moisture to no more than 5 parts per billion.

10. Process according to any of claims 7 to 9, characterised in that the carrier gas is provided at a flow rate of 5 to 15 litres per minute.