

## **GROWTH METHOD FOR GALLIUM NITRIDE COMPOUND SEMICONDUCTOR SINGLE CRYSTAL**

Patent Number: JP2000004045  
Publication date: 2000-01-07  
Inventor(s): SEKI YOJI  
Applicant(s):: JAPAN ENERGY CORP  
Requested Patent: JP2000004045  
Application Number: JP19980167194 19980615  
Priority Number(s):  
IPC Classification: H01L33/00 ; H01L21/205  
EC Classification:  
Equivalents:

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### **Abstract**

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**PROBLEM TO BE SOLVED:** To provide a growth method, wherein a good quality of gallium nitride compound semiconductor single crystal is grown on a rare-earth 13 (3B) group perovskite single-crystal substrate containing one or more kinds of rare earth elements.

**SOLUTION:** This growth method of a gallium nitride compound semiconductor single crystal, having a rare earth 13 (3B) group perovskite single-crystal substrate containing one or more kinds of rare earth elements, contains the first film forming process in which the first gallium nitride layer is grown on the substrate under a first temperature condition, a heat treatment process wherein heat treatment is performed on the substrate by heating up to the prescribed temperature in an inert gas atmosphere, and the second film forming process, where the second gallium nitride layer is grown on the first gallium nitride layer under a second temperature condition, which is higher than the first temperature condition.

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## **GROWTH METHOD OF GALLIUM NITRIDE GROUP SEMICONDUCTOR AND SUBSTRATE FOR GROWING THE GAN GROUP SEMICONDUCTOR**

Patent Number: JP11224856  
Publication date: 1999-08-17  
Inventor(s): AKIMOTO KATSUHIRO; YAMADA AKIYOSHI; KA KOKUHI; MARUYAMA TAKAHIRO  
Applicant(s):: SONY CORP  
Requested Patent: ☐ JP11224856  
Application Number: JP19980024451 19980205  
Priority Number(s):  
IPC Classification: H01L21/203 ; H01L21/205 ; H01L33/00  
EC Classification:  
Equivalents:

### **Abstract**

**PROBLEM TO BE SOLVED:** To provide a method for growing a GaN group semiconductor and a substrate for growing a GaN group semiconductor, wherein a single-crystal GaN group semiconductor of good quality can be grown.

**SOLUTION:** Using a substrate 1 whose surface is made of at least MoS<sub>2</sub>, a GaN group semiconductor 3 is grown on it through molecular beam epitaxy method and the like. Preferably, a buffer layer 2 of GaN group semiconductor is first grown at a temperature lower than the growth temperature for the GaN group semiconductor 3, then the GaN group semiconductor 3 is grown over it. When the GaN group semiconductor 3 or the buffer layer 2 is grown, material supply at the growth of the buffer layer 2 starts with the supplying of a Ga material.

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## EPITAXIAL WAFER COMPOSED OF SINGLE CRYSTAL SUBSTRATE AND GALLIUM NITRIDE-BASED COMPOUND SEMICONDUCTOR CRYSTAL GROWN THEREON

Patent Number: JP11147797  
Publication date: 1999-06-02  
Inventor(s): SAKURAI TETSURO; OKUYAMA MINEO; FUKUDA TSUGUO  
Applicant(s):: SHOWA DENKO KK  
Requested Patent: ☐ JP11147797  
Application Number: JP19970310518 19971112  
Priority Number(s):  
IPC Classification: C30B29/38 ; H01L21/02 ; H01L21/20 ; H01L21/205 ; H01L33/00 ; H01S3/18  
EC Classification:  
Equivalents:

### Abstract

**PROBLEM TO BE SOLVED:** To obtain an epitaxial wafer remarkably reduced in lattice matching properties between the wafer and a single crystal substrate and markedly reduced in crystal defects in an epitaxial film by epitaxially growing a gallium nitride-based compound on a single crystal substrate having a specific structure.

**SOLUTION:** A single crystal substrate is composed of a perovskite type tetragonal crystal containing Al and Sr in an epitaxial wafer composed of the single crystal substrate and the gallium nitride-based compound semiconductor crystal grown thereon. The single crystal substrate has the general structural formula represented in the form of  $A_{1-x}Srx A_1y B_{1-y} O_3$  [ $0 \leq (x) \leq 1$ ;  $0 \leq (y) \leq 1$ ]. The constituent element A is a rare earth element and the constituent element B is a group 5A element. In the formula, the constituent element A is preferably lanthanum(La), neodymium(Nd) or praseodymium(Pr) and the constituent element B is preferably tantalum,(Ta) or niobium(Nb).

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## EPITAXIAL WAFER COMPOSED OF SINGLE CRYSTAL SUBSTRATE AND GALLIUM NITRIDE-BASED COMPOUND SEMICONDUCTOR CRYSTAL GROWN THEREON

Patent Number: JP11147791  
Publication date: 1999-06-02  
Inventor(s): SAKURAI TETSURO; OKUYAMA MINEO; FUKUDA TSUGUO  
Applicant(s):: SHOWA DENKO KK  
Requested Patent: ☐ JP11147791  
Application Number: JP19970310519 19971112  
Priority Number(s):  
IPC Classification: C30B29/28 ; C30B29/22 ; H01L21/20 ; H01L21/205 ; H01L33/00 ; H01S3/18  
EC Classification:  
Equivalents:

### Abstract

**PROBLEM TO BE SOLVED:** To obtain an epitaxial wafer capable of remarkably reducing crystal defects in an epitaxial film and markedly improving device characteristics thereof when used in an electronic device by epitaxially growing a gallium nitride-based compound on a single crystal substrate having a specific structure.

**SOLUTION:** One of the following (1) to (5) is used as a single crystal substrate. (1) a type belonging to an apatite type hexagonal crystal and having the general structural formula represented by  $A_5(PO_4)_3F$  (A is a group 2A element, especially Ca or Sr) or  $X_2Z_8(SiO_4)_6O_2$  (X is a group 2A element, especially Ca or Sr; Z is a group 3A rare earth element, especially La or Y), (2) a type in which  $SiO_4$  is substituted with  $PO_4$  in the  $X_2Z_8(SiO_4)_6O_2$  in (1), (3) an oxide single crystal having the general structural formula represented by  $Li_2B_4O_7$ , (4) an oxide single crystal having the general structural formula represented by  $La_3Nb_{1-x}Ga_xO_{14}$  [ $0 < (x) < 1$ ] and (5) an oxide single crystal having the general structural formula represented by  $LiHo(WO_4)_2$ .

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## VAPOR PHASE GROWTH SYSTEM OF GALLIUM NITRIDE BASED COMPOUND SEMICONDUCTOR

Patent Number: JP11121386  
Publication date: 1999-04-30  
Inventor(s): MANABE KATSUhide; KATO HISAYOSHI; KOIDE NORIKATSU; MABUCHI AKIRA; AKASAKI ISAMU  
Applicant(s):: TOYODA GOSEI CO LTD; UNIV NAGOYA; JAPAN SCIENCE & TECHNOLOGY CORP  
Requested Patent: ☐ JP11121386  
Application Number: JP19980236365 19980807  
Priority Number(s):  
IPC Classification: H01L21/205 ; H01L33/00  
EC Classification:  
Equivalents:

### Abstract

PROBLEM TO BE SOLVED: To improve the crystallinity of a gallium nitride based compound semiconductor.

SOLUTION: A raw gas and a carrier gas are led into a reaction chamber 11 in a reaction tube and the vapor phase of the gallium nitride based compound semiconductor is grown on a substrate mounted on a susceptor 22 in the reaction chamber. The system has a feeding inlet 125 feeding a first gas over the substrate, a leading inlet feeding a second gas to the substrate sideways, and a gas guiding member 12 continuous to the feeding inlet and flowing down the first gas over the substrate by guiding the gas spread out downward.

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## BOARD FOR GALLIUM NITRIDE CRYSTAL GROWTH, AND ITS APPLICATION

Patent Number: JP11103135  
Publication date: 1999-04-13  
Inventor(s): OKAGAWA HIROAKI; OUCHI YOICHIRO; MIYASHITA KEIJI; TADATOMO KAZUYUKI  
Applicant(s):: MITSUBISHI CABLE IND LTD  
Requested Patent: ☐ JP11103135  
Application Number: JP19980005682 19980114  
Priority Number(s):  
IPC Classification: H01S3/18 ; C30B29/38 ; H01L21/205 ; H01L33/00  
EC Classification:  
Equivalents:

### Abstract

**PROBLEM TO BE SOLVED:** To provide a substrate for GaN crystal growth with which a high quality GaN substrate which is thick and moreover does not contain defects such as a transposition, etc., can be obtained, and the manufacture of a GaN semiconductor element using it.

**SOLUTION:** A mask region 12 covered with a mask layer 2 and nonmask region 11, where the base substrate face is exposed, are made at the face of a base substrate 1. A material where crystals will not grow substantially from its own surface is used for the mask layer. In the case of making the upper part of the mask region into low transposition, the mask region is made in such form that at least the outline includes two straight parallel lines y1 and y2 which extend in the direction <1-100>. Furthermore, a width w1 of two parallel straight lines is made smaller than the width of a GaN semiconductor element, and moreover is made larger than the width of the active part of the element. In this case for, dividing the GaN semiconductor element into separate pieces, it is preferable to make use of a nonmask region.

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## VAPOR GROWTH DEVICE OF GALLIUM NITRIDE III-V COMPOUND SEMICONDUCTOR AND GALLIUM NITRIDE III-V COMPOUND SEMICONDUCTOR DEVICE AND ITS MANUFACTURE

Patent Number: JP11074202  
Publication date: 1999-03-16  
Inventor(s): HANAOKA DAISUKE; FURUKAWA MASAKI  
Applicant(s):: SHARP CORP  
Requested Patent: ☐ [JP11074202](#)  
Application Number: JP19970233620 19970829  
Priority Number(s):  
IPC Classification: H01L21/205 ; C23C16/18 ; C23C16/34 ; C30B25/10 ; H01L33/00  
EC Classification:  
Equivalents:

### Abstract

**PROBLEM TO BE SOLVED:** To form a film under ideal growth conditions by lowering the setting temperature of a first heating part being located between a region for mixing a feed gas and a region for placing a substrate, as compared with the setting temperature of a second heating part being located at a region for placing the substrate.

**SOLUTION:** A substrate 7 is placed on a carbon susceptor 8 and is heated by a high-frequency coil 3 from the outside. A second heating body for heating the substrate is formed by the susceptor 8, and the second heating body is constituted of a high-frequency coil 3, a reactor 5, and the susceptor 8. Then, a heater 2 can exist, thus controlling a vapor growth temperature. In this manner, a first heating body for controlling the vapor growth temperature is formed by the heater 2, and the first heating part is formed by the heater 2 and a heating tube 4. While the vapor growth temperature is set to optimum temperature conditions by the first heating part, the substrate temperature is set to a high temperature, without heating the vapor growth temperature around the substrate more than is required by the second heating part.

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## GROWTH OF NITRIDE CRYSTAL AND GROWTH OF GALLIUM NITRIDE

Patent Number: JP11060394  
Publication date: 1999-03-02  
Inventor(s): SHIBATA MASATOMO  
Applicant(s):: HITACHI CABLE LTD  
Requested Patent: ☐ JP11060394  
Application Number: JP19970221628 19970818  
Priority Number(s):  
IPC Classification: C30B29/38 ; C30B9/06  
EC Classification:  
Equivalents:

### Abstract

**PROBLEM TO BE SOLVED:** To easily grow a nitride crystal of a group III element such as GaN, especially a large-size bulk crystal which is not conventionally obtd.  
**SOLUTION:** The growing method of the nitride crystal includes a process to house a nitride crystal powder (source material 6) and a liquid sealing material 5 in a cylinder 7 and to heat the source material and to pressurize it with a piston 3. The GaN crystal is grown by heating a flux and GaN crystal powder under pressure to melt the GaN in the flux, then cooling to grow the GaN crystal. In this method, the flux is heated to  $\geq 800$  deg.C and the flux contains at least one or more of Ga, In, Pd, Sn, Bi and Na.

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## CRYSTAL GROWTH METHOD FOR GALLIUM NITRIDE-BASED SEMICONDUCTOR LAYER CONTAINING INGAN LAYER, GALLIUM NITRIDE-BASED LIGHT-EMITTING ELEMENT, AND MANUFACTURE THEREOF

Patent Number: JP11054847  
Publication date: 1999-02-26  
Inventor(s): KIMURA AKITAKA; SASAOKA CHIAKI  
Applicant(s):: NEC CORP  
Requested Patent: ☐ JP11054847  
Application Number: JP19970213273 19970807  
Priority Number(s):  
IPC Classification: H01S3/18 ; H01L33/00  
EC Classification:  
Equivalents:

### Abstract

**PROBLEM TO BE SOLVED:** To prevent the dissociation of In in an InGaN growth layer and minimize the worsening of crystallinity of a growth layer by sequentially forming the InGaN layer and an AlGaIn layer at a particular substrate temperature, and by specifying the relations among the number of layers of AlGaIn layers, thickness of each layer and Al composition ratio of each layer.

**SOLUTION:** After the growth of an InGaN growth layer and an AlGaIn indium dissociation prevention layer at a substrate temperature of 600 deg.C to 900 deg.C, when the substrate is heated to temperature higher than or equal to 900 deg.C for the growth of GaN or the like, Ga atoms are evaporated from the AlGaIn indium dissociation prevention layer. Because of this, the AlGaIn indium dissociation prevention layer becomes an AlGaIn layer with the aluminum composition being greater than that prior to raising of the temperature, and this layer prevents the slip of In atoms. Here, the relations among the number of layers, thickness of each layer  $d_i$  ( $i=1, \dots, N$ ), aluminum composition  $x_i$  ( $i=1, \dots, N$ ) of each layer of an  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  layer used as the indium dissociation prevention layer are so made so to satisfy the equation.

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## SUBSTRATE FOR GALLIUM NITRIDE BASED CRYSTAL GROWTH AND ITS PRODUCTION AND USE

Patent Number: JP11035396  
Publication date: 1999-02-09  
Inventor(s): OKAGAWA HIROAKI; OUCHI YOICHIRO; MIYASHITA KEIJI; TADATOMO KAZUYUKI  
Applicant(s):: MITSUBISHI CABLE IND LTD  
Requested Patent: ☐ JP11035396  
Application Number: JP19970188775 19970714  
Priority Number(s):  
IPC Classification: C30B29/38 ; C30B33/08 ; H01L33/00  
EC Classification:  
Equivalents:

### Abstract

**PROBLEM TO BE SOLVED:** To provide a substrate for GaN based crystal growth with which a high-quality GaN based crystal substrate of a thick film not contg. defects, such as dislocation, is obtainable and a process for producing the GaN based crystal substrate by using the same.  
**SOLUTION:** A thin film layer a2 of the GaN based crystal is formed directly or via a buffer layer a1 on a base substrate Si and a substrate member S2 which is selectively removable by etching with respect to the GaN based crystal is laminated by joining thereon. The base substrate Si (together with the buffer layer a1, if any) is removed by polishing to expose the one surface all of the thin film layer a2 of the GaN based crystal. This substrate is inverted and is regarded as a fresh base substrate. The exposed surface all is provided with mask regions 12 and non-mask regions 11 partially covering the surface with mask layers 2, by which the substrate for the growth of the GaN based crystal is produced. The thick film of the GaN based crystal is grown by using the same and only the substrate member is etched away, by which the GaN based crystal substrate free of warpage is obtd.

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## CRYSTAL GROWTH OF LOW-MIGRATION GALLIUM NITRIDE

Patent Number: JP11031864  
Publication date: 1999-02-02  
Inventor(s): KIMURA AKITAKA; NIDOU MASA AKI  
Applicant(s):: NEC CORP  
Requested Patent: ☐ JP11031864  
Application Number: JP19970186583 19970711  
Priority Number(s):  
IPC Classification: H01S3/18 ; H01L21/205 ; H01L33/00  
EC Classification:  
Equivalents:

### Abstract

**PROBLEM TO BE SOLVED:** To reduce perforation migration density in a large area region, by forming a mask having openings on the surface of a gallium nitride layer or a single-crystal substrate, selectively forming a gallium nitride layer in the openings of the mask by crystal growth, removing the mask, and heating the substrate at a specific temperature.

**SOLUTION:** A gallium-nitride low-temperature growth buffer layer is formed on a sapphire substrate 101, and an undoped gallium nitride layer 102 having a sapphire surface is formed by MOVPE. A silicon oxide mask 103 having striped openings parallel to a [11-20] direction of the gallium nitride is formed by etching on the surface of the gallium nitride layer 102. An undoped gallium nitride layer 104 is selectively formed in the openings of the mask 103 by MOVPE. The mask 103 is removed by etching using hydrofluoric acid. Further, the substrate is held at a temperature of 900 deg.C for a predetermined period, and the surface of the gallium nitride layer 104 is flattened by mass transport.

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## NITRIDE COMPOUND SEMICONDUCTOR, CRYSTAL GROWTH METHOD THEREOF, AND GALLIUM NITRIDE LIGHT-EMITTING DEVICE

Patent Number: JP11008437  
Publication date: 1999-01-12  
Inventor(s): KIMURA AKITAKA; SUNAKAWA HARUO; NIDOU MASAOKI; SASAOKA CHIAKI  
Applicant(s):: NEC CORP  
Requested Patent: ☐ JP11008437  
Application Number: JP19970156795 19970613  
Priority Number(s):  
IPC Classification: H01S3/18 ; H01L33/00  
EC Classification:  
Equivalents:

### Abstract

**PROBLEM TO BE SOLVED:** To enable a mirror plane to be formed by cleavage by a method, wherein an InGaN layer is formed on the specific surface of a sapphire substrate, and then gallium nitride or indium nitride or aluminum nitride or their mixed crystal is grown.

**SOLUTION:** An  $\text{In}_x\text{Ga}_{1-x}\text{N}$  layer 102 ( $0.894 \leq x < 1$ ) formed on the surface of a sapphire substrate 101 which is a (0001) plane or a plane inclined to form an angle of 5 deg. or less with a (0001) plane and gallium nitride or indium nitride or aluminum nitride or their mixed crystal formed thereon are provided. At this point, the  $\text{In}_x\text{Ga}_{1-x}\text{N}$  layer 102 is grown at a temperature of 400 or higher to 600 deg.C or lower. The cleavage planes of high-temperature growth epitaxial layers 103 to 111 are parallel with that of the substrate 101. Therefore, the mirror plane of a resonator can be formed by cleaving the substrate 101, so that a complicated process such as a dry etching process can be dispensed with, and the mirror plane is superior in smoothness.

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## EPITAXIAL GROWTH OF GALLIUM NITRIDE TYPE COMPOUND SEMICONDUCTOR

Patent Number: JP11001395  
Publication date: 1999-01-06  
Inventor(s): MOTOKI KENSAKU; MATSUSHIMA MASATO  
Applicant(s):: SUMITOMO ELECTRIC IND LTD  
Requested Patent: ☐ JP11001395  
Application Number: JP19970166555 19970609  
Priority Number(s):  
IPC Classification: C30B29/38  
EC Classification:  
Equivalents:

### Abstract

**PROBLEM TO BE SOLVED:** To provide a method of epitaxial growth of a GaN compound semiconductor excellent in homogeneity, on a compound semiconductor substrate by generating a turbulence in the raw material gas.

**SOLUTION:** The turbulence is generated by a trigger action of a counter flow CF containing hydrogen(H<sub>2</sub>) blow out from the inverse direction of the exhaust, and/or down flow gas HF induced by the notch 33 made on the opening 32 of the nozzle 31, when introducing the first gas (GaCl) containing gallium(Ga) and the second gas (NH<sub>3</sub>) containing nitrogen (N), around the compound semiconductor substrate (2A) made of compound semiconductor (GaAs). This turbulence (EF) makes the gas sufficiently mixed and agitated, the gallium nitride(GaN) excellent in homogeneity is capable of epitaxial growing on the substrate (2A). Hydrogen(H<sub>2</sub>) gas is used as the carrier gas.

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## CRYSTAL GROWTH METHOD OF NITRIDE COMPOUND SEMICONDUCTOR AND GALLIUM NITRIDE LIGHT-EMITTING DIODE

Patent Number: JP10341060  
Publication date: 1998-12-22  
Inventor(s): KIMURA AKITAKA; SASAOKA CHIAKI; YAMAGUCHI ATSUSHI; NIDOU MASAOKI  
Applicant(s): NEC CORP  
Requested Patent: ☐ JP10341060  
Application Number: JP19970150761 19970609  
Priority Number(s):  
IPC Classification: H01S3/18 ; H01L21/205 ; H01L33/00  
EC Classification:  
Equivalents:

### Abstract

**PROBLEM TO BE SOLVED:** To manufacture a laser with a low oscillation threshold carrier density by sequentially forming a gallium nitride semiconductor layer with a specific crystal surface as a surface on a sapphire substrate with the specific crystal surface as a surface.

**SOLUTION:** A gallium nitride low-temperature growth buffer layer 102 is grown on a sapphire substrate 101 where a surface that has a tilt angle from (01-01) surface or (01-10) surface within 5 deg. is set to surface. Out it, a process for forming  $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$  layer ( $0 \leq x \leq 1$ ,  $0 \leq y \leq 1$ ,  $0 \leq x+y \leq 1$ ) where the surface that has the tilt angle from (11-22) surface or (11-22) surface within 5 deg. is set to the surface is executed. Then, an n-type gallium nitride contact layer 103, an n-type InGaN layer 104, an n-type AlGaIn cladding layer 105, an n-type gallium nitride light guide layer 106, a multiple-quantum well structure active layer 107 of an InGaIn, a p-type AlGaIn layer 108, a p-type gallium nitride light guide layer 109, a p-type AlGaIn cladding layer 110, and a p-type gallium nitride contact layer 111 are sequentially laminated to form.

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## CRYSTAL GROWTH METHOD FOR GALLIUM NITRIDE BASED COMPOUND SEMICONDUCTOR

Patent Number: JP10294492  
Publication date: 1998-11-04  
Inventor(s): NAKAMURA SHUJI  
Applicant(s):: NICHIA CHEM IND LTD  
Requested Patent: ☐ JP10294492  
Application Number: JP19980029224 19980126  
Priority Number(s):  
IPC Classification: H01L33/00 ; H01L21/205  
EC Classification:  
Equivalents:

### Abstract

**PROBLEM TO BE SOLVED:** To stably grow a gallium nitride based compound semiconductor with a good yield by improving the crystallivity and the surface morphology of the gallium nitride based compound semiconductor grown on a buffer layer to a practical level.

**SOLUTION:** In a reactor in which a gallium nitride based compound semiconductor is grown by an organometallic compound vapor-phase growth method, a buffer layer of  $GaxAl_{1-x}N$  (where  $0.5 \leq x \leq 1$ ) of not more than  $0.2 \mu m$  thick is grown at a temperature lower than the growth temperature of the gallium nitride based compound semiconductor before the gallium nitride based compound semiconductor is grown and then the gallium nitride based compound semiconductor having the same composition as the buffer layer is grown at a growth temperature higher than that of the buffer layer.

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## CRYSTAL GROWTH METHOD FOR GALLIUM NITRIDE-BASED COMPOUND SEMICONDUCTOR

Patent Number: JP10215000  
Publication date: 1998-08-11  
Inventor(s): KOIDE NORIKATSU; KOIKE MASAYOSHI; AKASAKI ISAMU; AMANO HIROSHI  
Applicant(s):: TOYODA GOSEI CO LTD; AKASAKI ISAMU; AMANO HIROSHI  
Requested Patent: ☐ JP10215000  
Application Number: JP19970033178 19970130  
Priority Number(s):  
IPC Classification: H01L33/00 ; H01L21/205 ; H01L27/12  
EC Classification:  
Equivalents:

### Abstract

**PROBLEM TO BE SOLVED:** To form a good-quality gallium nitride-based compound semiconductor layer on a sapphire substrate by a halide vapor growth method.  
**SOLUTION:** A sapphire substrate 1 is cleaned and dried so as to be placed on a susceptor 14 which is installed inside a quartz tube 11 at a halide vapor growth apparatus 10. Then, a substrate temperature is set at 600 deg.C, NH<sub>3</sub> as an N<sub>2</sub> source is supplied at 400 to 800cc/min, HCl which is used to generate GaCl as a Ga source is supplied at 5 to 2cc/min, and N<sub>2</sub> as a carrier gas is supplied at 2l/min. Thereby, GaCl as the reaction product of HCl with Ga placed on a Ga reservoir 12 is obtained so as to be supplied for 30 minutes, and an amorphous buffer layer composed of GaN or a buffer layer having a crystal structure in which an amorphous substance and a fine crystal exist so as to be mixed is grown on the substrate 1 to be a film thickness of about 0.2 $\mu$ m. In succession, the substrate temperature is set at 1,100 deg.C, the above respective gases are supplied for 30 minutes under the same condition as in the formation of the buffer layer, and a GaN layer which is flat and whose crystallinity is good is grown to be a film thickness of about 2 $\mu$ m.

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## GROWTH METHOD OF GALLIUM NITRIDE-BASED SEMICONDUCTOR CRYSTAL

Patent Number: JP8186329  
Publication date: 1996-07-16  
Inventor(s): OKAZAKI HITOSHI; ONIYAMA HIDEYUKI  
Applicant(s):: JAPAN ENERGY CORP  
Requested Patent: ☐ JP8186329  
Application Number: JP19940328222 19941228  
Priority Number(s):  
IPC Classification: H01S3/18 ; C23C16/02 ; C23C16/34 ; C30B29/38 ; H01L21/203 ; H01L21/205 ; H01L33/00  
EC Classification:  
Equivalents:

### Abstract

**PURPOSE:** To obtain a GaN-based semiconductor crystal which is suitable for a blue light-emitting material and which is of good quality by providing a crystal growth method which is improved in such a way that rare-earth 3B perovskite is used as a substrate and that the (c) plane of the GaN-based semiconductor crystal can be grown stably on the 101} plane or the 011} plane of the substrate.  
**CONSTITUTION:** A substrate composed of NdGaO<sub>3</sub> (neodymium gallate) having a plane orientation of (011) is used, a buffer layer which is composed of GaN formed by an MOCVD method at a temperature of 700 deg.C or lower or of ZnO or In<sub>2</sub>O<sub>3</sub> which is formed by an RF sputtering method is formed on the substrate, and a GaN-based semiconductor crystal is grown on it. Consequently, the (c) plane of the GaN-based semiconductor crystal is grown stably via the buffer layer on the 101} plane or the 011} plane of a rare-earth group 3B perovskite substrate which is lattice-matched with the GaN-based semiconductor crystal and which is thermally and chemically stable, and the GaN-based semiconductor crystal which is good as a blue light-emitting semiconductor material is obtained.

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## GROWTH METHOD FOR GALLIUM NITRIDE BASED SEMICONDUCTOR CRYSTAL

Patent Number: JP8186078  
Publication date: 1996-07-16  
Inventor(s): OKAZAKI HITOSHI; ONIYAMA HIDEYUKI  
Applicant(s): JAPAN ENERGY CORP  
Requested Patent: ☐ JP8186078  
Application Number: JP19940328221 19941228  
Priority Number(s):  
IPC Classification: H01L21/205 ; C30B25/18 ; C30B29/42 ; H01L33/00  
EC Classification:  
Equivalents:

### Abstract

**PURPOSE:** To obtain a good quality of GaN based semiconductor crystal suitable for a blue light emitting material by adopting rare earth group 3B perovskite as a substrate and providing a crystal growth method improved so as to be able to stably grow the (c) plane of the GaN based semiconductor crystal on the 101} plane or the 011} plane of the substrate.

**CONSTITUTION:** A substrate comprising NdGaO<sub>3</sub> (neodymium gallate) of a plane orientation 011} is used, and the substrate is exposed under the atmosphere of GaCl in advance for treatment before starting the growth of a GaN based semiconductor crystal. Therefore, relatively good lattice match for the GaN based semiconductor crystal is obtained, and the (c) plane of the GaN based semiconductor crystal is stably grown on the 101} plane or the 011} plane of the substrate of thermally and chemically stable rare earth group 3B perovskite, so that a good quality of GaN based semiconductor crystal suitable for a blue light emitting material may be obtained.

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## METHOD FOR CRYSTAL GROWTH OF N-TYPE GALLIUM NITRIDE COMPOUND SEMICONDUCTOR

Patent Number: JP8070139  
Publication date: 1996-03-12  
Inventor(s): NAKAMURA SHUJI  
Applicant(s):: NICHIA CHEM IND LTD  
Requested Patent: ☐ JP8070139  
Application Number: JP19940227679 19940922  
Priority Number(s):  
IPC Classification: H01L33/00 ; H01S3/18  
EC Classification:  
Equivalents: JP2956489B2

### Abstract

**PURPOSE:** To improve the crystallizability of other nitride semiconductors grown on the surface of an n-type nitride semiconductor layer and to improve the efficiency of a light emitting element and a photoreceptor element by providing a method for growth by reducing the lattice defect of the n-type nitride semiconductor surface.

**CONSTITUTION:** At least one layer of a second n-type nitride semiconductor layer 33 ( $\text{In}_a\text{Al}_b\text{Ga}_{1-a-b}\text{N}$ ,  $0 \leq a$ ,  $0 \leq b$ ,  $a+b \leq 1$ ) whose composition differs from an n-type nitride semiconductor layer 3' is grown in the n-type nitride semiconductor layer 3' growth or the n-type nitride semiconductor layer 3' is grown at least by the thickness of  $5\mu\text{m}$ .

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## GALLIUM NITRIDE CRYSTAL GROWTH

Patent Number: JP9036045  
Publication date: 1997-02-07  
Inventor(s): NAKAO TAKETOSHI  
Applicant(s):: MATSUSHITA ELECTRIC IND CO LTD  
Requested Patent: ☐ JP9036045  
Application Number: JP19950179817 19950717  
Priority Number(s):  
IPC Classification: H01L21/205 ; H01L33/00  
EC Classification:  
Equivalents:

### Abstract

**PROBLEM TO BE SOLVED:** To reduce the temperature for growing gallium nitride crystal and control the growing temperature.

**SOLUTION:** Alkyl gallium hydride provided by replacing the methyl group with hydrogen is used for growing gallium nitride crystal instead of trimethyl gallium which has been used conventionally as gallium source. Thus, transiting energy is reduced in the crystal growing process and gallium nitride is grown at a low temperature.

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## MULTILAYER STRUCTURE AND GROWTH METHOD OF GaN-BASED COMPOUND SEMICONDUCTOR THIN FILM

Patent Number: JP8008185  
Publication date: 1996-01-12  
Inventor(s): IKEDA MASAKIYO; others: 01  
Applicant(s):: FURUKAWA ELECTRIC CO LTD:THE  
Requested Patent: ☐ JP8008185  
Application Number: JP19940156807 19940615  
Priority Number(s):  
IPC Classification: H01L21/203 ; C30B29/38 ; H01L21/205 ; H01L33/00  
EC Classification:  
Equivalents:

### Abstract

**PURPOSE:** To obtain a high quality buffer layer without receiving influence of fluctuation between lots of NH<sub>3</sub> cylinders and thereby to obtain crystal thin film of a GaN based compound semiconductor having the mirror-surface by providing a buffer layer consisting of InGaN of the specified composition on a sapphire substrate and then forming thereon a single crystal thin film of the GaN-based compound semiconductor.

**CONSTITUTION:** The In<sub>x</sub>Ga<sub>1-x</sub>N (0

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## CRYSTAL GROWTH METHOD OF GALLIUM NITRIDE-BASED COMPOUND SEMICONDUCTOR

Patent Number: JP7312350  
Publication date: 1995-11-28  
Inventor(s): NAKAMURA SHUJI  
Applicant(s):: NICHIA CHEM IND LTD  
Requested Patent: ☐ JP7312350  
Application Number: JP19950152676 19950525  
Priority Number(s):  
IPC Classification: H01L21/205 ; C23C16/18 ; H01L33/00  
EC Classification:  
Equivalents:

### Abstract

**PURPOSE:** To obtain a crystal growth method which improves the crystallinity of a gallium nitride-based compound semiconductor to be grown on a buffer layer and in which the gallium nitride-based compound semiconductor is grown stably and at good yield.

**CONSTITUTION:** A reaction gas is supplied into a reaction chamber, and a gallium nitride-based compound semiconductor is grown on a buffer layer by an organometallic compound vapor growth method. Alternatively, both a buffer layer and a gallium nitride-based compound semiconductor are grown by an organometallic compound vapor growth method. Alternatively, before a gallium nitride-based compound semiconductor is grown inside a reaction chamber in which the gallium nitride-based compound semiconductor is grown, a buffer layer whose general expression is  $GaxAl_{1-x}N$  (where X is within a range of  $0.5 \leq X \leq 1$ ) is grown at a growth temperature of 200 deg.C or higher and 900 deg.C or lower.

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## METHOD FOR FORMING GaN MASK FOR SELECTIVE GROWTH

Patent Number: JP6163487  
Publication date: 1994-06-10  
Inventor(s): YOSHIDA KIYOTERU; others: 01  
Applicant(s):: HIKARI GIJUTSU KENKYU KAIHATSU KK  
Requested Patent: ☐ JP6163487  
Application Number: JP19920311614 19921120  
Priority Number(s):  
IPC Classification: H01L21/302 ; C23C8/24 ; C23F4/02 ; H01L21/263 ; H01L21/318  
EC Classification:  
Equivalents: JP2686699B2

### Abstract

**PURPOSE:**To enable patterning of a GaN film without damaging a substrate largely by irradiating a predetermined region of a GaN film formed over the surface of a substrate with electron beams to remove the GaN film of a region irradiated with electron beams.

**CONSTITUTION:**After a GaN film 13 is formed over the surface of a substrate 11, a predetermined region of the GaN film 13 is irradiated with electron beams EB to remove the GaN film 13 of the predetermined region irradiated with electron beams EB. For example, after a GaAs buffer layer 12 is crystal-grown on the GaAs substrate 11 to obtain a clean surface, the temperature of the substrate 11 is heated up to 600 to 630 deg.C while a cracked ammonia gas is introduced to form a GaN film 13 of extremely thin film thickness. Next, a predetermined region of the GaN film 13 is irradiated with electron beams EB under a superhigh vacuum to form an opening 21 by Ga and N desorption. Therefore, with the substrate temperature kept at 500 deg.C, a GaAs layer 22 is selectively grown by simultaneous irradiation with TMG and As<sub>4</sub>.

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## METHOD FOR VAPOR GROWTH OF GALLIUM NITRIDE COMPOUND SEMICONDUCTOR

Patent Number: JP63188938  
Publication date: 1988-08-04  
Inventor(s): MANABE KATSUhide; others: 04  
Applicant(s):: TOYODA GOSEI CO LTD; others: 01  
Requested Patent: ☐ JP63188938  
Application Number: JP19870021126 19870131  
Priority Number(s):  
IPC Classification: H01L21/205 ; H01L33/00  
EC Classification:  
Equivalents: JP1862890C, JP5073252B

### Abstract

**PURPOSE:** To realize the vapor growth of a gallium nitride compound semiconductor thin film by a method wherein a buffer layer composed of aluminum nitride is grown on an a-plane of a sapphire substrate.

**CONSTITUTION:** A single-crystal sapphire substrate 24, which has been cleaned by an organic cleaning method and a heat treatment and whose main plane is an a-plane, is mounted on a susceptor; the sapphire substrate 24 is vapor-etched while H<sub>2</sub> is flowing into a reaction chamber through a first reaction-gas pipe 25 and a second reaction-gas pipe 26. Then, after the temperature has been lowered, the substrate is heat-treated while H<sub>2</sub>, NH<sub>3</sub> and trimethylaluminum are fed through the first reaction-gas pipe 25. During this heat treatment, a buffer layer 30 composed of AlN is formed. Because a gallium nitride compound semiconductor thin film is formed vapor growth on this buffer layer, the crystallinity is improved and it becomes easy to supply the sapphire substrate.

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## VAPOR GROWTH SYSTEM FOR GALLIUM NITRIDE COMPOUND SEMICONDUCTOR

Patent Number: JP63188937  
Publication date: 1988-08-04  
Inventor(s): MANABE KATSUhide; others: 04  
Applicant(s):: TOYODA GOSEI CO LTD; others: 01  
Requested Patent: ☐ JP63188937  
Application Number: JP19870021125 19870131  
Priority Number(s):  
IPC Classification: H01L21/205 ; H01L33/00  
EC Classification:  
Equivalents:

### Abstract

**PURPOSE:** To obtain an type I Al<sub>x</sub>Ga<sub>1-x</sub>N thin film having good crystallinity by a method wherein a dopant gas and another reaction gas are mixed for the first time by a mixing pipe which is situated near a susceptor and a mixed gas is blown toward the susceptor through an opening of the mixing pipe.  
**CONSTITUTION:** A first reaction-gas pipe 25 and a second reaction-gas pipe 26 are installed on the side where a gas flows into a reaction chamber 20; the first reaction-gas pipe 25 is arranged inside the second reaction-gas pipe 26 concentrically with the second reaction-gas pipe 26. The tip part of the first reaction-gas pipe 25 and the second reaction-gas pipe 26 is connected with a spherically shaped mixing pipe 29. A mixed gas composed of a group of NH<sub>3</sub> and trimethylgallium and another group of trimethylaluminum and H<sub>2</sub> flows into the mixing pipe 29 through the first reaction-gas pipe 25; another mixed gas composed of diethylzinc and H<sub>2</sub> flows into the mixing pipe 29 through the second reaction-gas pipe 26. After both kinds of reaction gases have been mixed inside the mixing pipe 29, they are blown toward a sapphire substrate 24 through an opening 29a of the mixing pipe. By this setup, it is possible to grow an type I Al<sub>x</sub>Ga<sub>1-x</sub>N thin film of high quality.

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## VAPOR GROWTH SYSTEM FOR GALLIUM NITRIDE COMPOUND SEMICONDUCTOR

Patent Number: JP63188935  
Publication date: 1988-08-04  
Inventor(s): MANABE KATSUhide; others: 04  
Applicant(s):: TOYODA GOSEI CO LTD; others: 01  
Requested Patent: ☐ JP63188935  
Application Number: JP19870021122 19870131  
Priority Number(s):  
IPC Classification: H01L21/205 ; H01L33/00  
EC Classification:  
Equivalents:

### Abstract

**PURPOSE:** To obtain a gallium nitride compound semiconductor thin film of high quality by a method wherein the main face of a susceptor is tilted at a specified angle with reference to the direction in which a reaction gas flows.

**CONSTITUTION:** A mixed gas composed of a group of  $\text{NH}_3$  and trimethylgallium and another group of trimethylaluminum and  $\text{H}_2$  flows into a reaction chamber 20 through an opening 25a of a first reaction-gas pipe 25; another mixed gas composed of diethylzinc and  $\text{H}_2$  flows into the reaction chamber 20 through an opening 26a of a second reaction-gas pipe 26. By using this vapor growth system an Alx-Ga1-XN thin film was grown while an angle of inclination  $\theta$  of a main face 22a of a susceptor 22 with reference to a direction X in which the reaction gas flows. When its crystallinity was evaluated by referring to a photomicrograph, a locking curve of X-rays and a measured result of photoluminescence, the good crystallinity can be obtained at the angle of inclination ranging from 15-75 deg. as compared with a case where the film was grown at the angle of inclination  $\theta$  of 90 deg..

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## METHOD FOR VAPOR GROWTH OF GALLIUM NITRIDE COMPOUND SEMICONDUCTOR

Patent Number: JP63188933  
Publication date: 1988-08-04  
Inventor(s): MANABE KATSUhide; others: 04  
Applicant(s):: TOYODA GOSEI CO LTD; others: 01  
Requested Patent: ☐ JP63188933  
Application Number: JP19870021120 19870131  
Priority Number(s):  
IPC Classification: H01L21/205 ; H01L33/00  
EC Classification:  
Equivalents: JP2631286B2

### Abstract

**PURPOSE:** To obtain a gallium nitride compound semiconductor thin film having high crystallinity by a method wherein a reaction gas is decomposed into a plasma state at a high frequency and this plasma gas is blown toward a sapphire substrate.

**CONSTITUTION:** A mixed gas composed of a group of NH<sub>3</sub> and trimethylgallium and another group of trimethylaluminum and H<sub>2</sub> flows into a reaction chamber 20 through an opening 25a of a first reaction-gas pipe 25; another mixed gas composed of dimethylzinc and H<sub>2</sub> flows into the reaction chamber 20 through an opening 26a of a second reaction-gas pipe 26. Because the reaction gas and the dopant gas are introduced into a reaction chamber 20a near a sapphire substrate 24 after being separated by the first reaction-gas pipe 25 and the second reaction-gas pipe 26, a good doping process is executed. The reaction gas which has been blown toward the sapphire substrate 24 is transformed into a plasma state by means of a high-frequency coil 42 when it passes through the first reaction-gas pipe 25 and the second reaction-gas pipe 26 and when it remains inside the reaction chamber 20; the reaction gas in the plasma state is blown toward the sapphire substrate 24.

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## GROWTH OF GALLIUM NITRIDE

Patent Number: JP60207332  
Publication date: 1985-10-18  
Inventor(s): KAWABATA TOSHIHARU; others: 02  
Applicant(s):: MATSUSHITA DENKI SANGYO KK  
Requested Patent: ☐ JP60207332  
Application Number: JP19840064039 19840330  
Priority Number(s):  
IPC Classification: H01L21/205 ; H01L33/00  
EC Classification:  
Equivalents:

### Abstract

**PURPOSE:**To enable to obtain a GaN epitaxial layer of 30μm thickness or more having crystallizability of superior quality without generating exfoliation from a substrate by a method wherein growth of the GaN crystal is attained by performing the MOCVD method having small stress at the interface at the first stage, and by performing the CVD method to obtain crystallizability of superior quality at the second stage.

**CONSTITUTION:**A sapphire single crystal substrate 4 on a carbon susceptor 3 is heated at 950 deg.C according to a high-frequency induction heating coil 2 on the outer peripheral part of a quartz reaction tube 1 having a tube wall cooled by passing cooling water, TMG, H<sub>2</sub>, NH<sub>3</sub> are supplied respectively from pipings 5, 6, 7 to make a vapor phase reaction to be performed, and a GaN crystal layer of 5μm thickness is obtained on the substrate 4. Then the GaN crystal layer 14 grown according to the MOCVD method on the tip of a control bar 13 is heated to 950 deg.C according to a heater 12 on the outer peripheral part of a quartz reaction tube 11, and NH<sub>3</sub> and N<sub>2</sub> are supplied from pipings 16, 17. Moreover, GaCl formed by introducing HCl from piping 18, and by making to react with Ga15 heated to be held at 850 deg.C is supplied, and a vapor phase reaction is made to be performed to obtain a GaN epitaxial layer of 30μm thickness in all on a substrate 14.

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