TITLE OF THE INVENTION

NITRIDE-BASED SEMICONDUCTOR EPITAXIAL SUBSTRATE, METHOD OF MANUFACTURING THE SAME, AND HEMT SUBSTRATE

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a nitride-based semiconductor epitaxial substrate, a method of manufacturing the same, and a high electron mobility transistor (HEMT) substrate.

Description of the Background Art

Light emitting diodes such as a light emitting diode, a laser diode, and the like, each of which uses a gallium nitride-based semiconductor, have recently attracted attention as illumination or display devices or next-generation optical recording light sources because short-wavelength light in the region from ultraviolet light to blue-green light can be emitted. GaN single crystal substrates each having lattice constants coinciding with those of an epitaxially grown GaN layer preferably are used as epitaxial substrates for these semiconductor devices. However, it has conventionally been considered difficult to manufacture a GaN single crystal substrate, so chemically stable sapphire substrates having lattice constants close to GaN have been used.

However, a GaN single crystal substrate suitable

G00002

for forming a gallium nitride-based semiconductor layer recently has been developed. For example, the patent reference 1 described below discloses a technique for forming a GaN epitaxially grown layer having few defects by so-called lateral growth using a mask having apertures. Epitaxial growth of GaN on a GaN single crystal substrate can produce an epitaxially grown layer in which the number of defects is significantly decreased, as compared with the use of a sapphire substrate.

The GaN-based semiconductor has a high saturated electron velocity under a high electric field, and high breakdown voltage. Therefore, the GaN single crystal substrate is expected to be applied to high-power high-speed semiconductor devices such as a field effect transistor (FET), a heterojunction bipolar transistor (HBT), and a high electron mobility transistor (HEMT), and the like.

Also, a GaN layer is known to exhibit strong n-type conductivity without being intentionally doped with an impurity, and thus GaN is expected as a blue light emitting element. However, it was previously said that improvements in characteristics such as emission efficiency and operating voltage were limited because p-type conductivity or high resistance could not be realized with GaN. However, the quality of the

GaN layer was improved drastically by the growth of the GaN layer at high temperature after the growth of a buffer layer on a sapphire substrate at low temperature, and consequently an undoped GaN layer which does not exhibit strong n-type was obtained. As a result of further studies on GaN, a technique for realizing a GaN layer having p-type conductivity or a GaN layer having high resistance has been developed, in which Mg is added to GaN by using organometallic sources like biscyclopentane dienyl magnesium (Cp_2Mg) as a dopant. GaN is then irradiated with a low-energy electron beam or heat-treated in a hydrogen-free atmosphere (for example, refer to non-patent reference 1). This technique for controlling conductivity significantly increases the possibility of realizing an actual device using GaN.

[Patent reference 1]

International Publication No. 99/23693 pamphlet

[Non-patent reference 1]

Shuji Nakamura, "Japanese Journal of Applied Physics", 1991, Vol. 30, L1705

For application to a field-effect transistor device, when the GaN single crystal substrate is conductive, the substrate must be insulated from a device layer formed thereon in order to prevent deterioration of element characteristics due to a

current leakage from the device layer to the GaN single crystal substrate. A conceivable method for ensuring such an insulation state is to dope GaN with Mg to compensate the n-type conductivity originally possessed by GaN, to obtain a gallium nitride-based semiconductor layer with high resistivity.

However, the inventors found that in forming a single crystal substrate comprising a GaN layer having high resistivity by an Mg doping process, Mg diffuses to a device layer formed on the substrate to deteriorate the performance of a device such as HEMT or the like.

SUMMARY OF THE INVENTION

The present invention has been achieved for solving the above problem, and it is an object of the present invention to provide a nitride-based semiconductor epitaxial substrate capable of ensuring electrical insulation between a device layer and a GaN single crystal substrate, and capable of suppressing the diffusion of Mg added for controlling conductivity to the device layer side, to provide a method of manufacturing the substrate, and an HEMT substrate.

(1) In order to achieve the object, a nitride-based semiconductor epitaxial substrate of the present invention comprises a GaN single crystal substrate, an Mg-doped first layer epitaxially grown on one side of

the GaN single crystal substrate and composed of $Al_xGa_yIn_{1-x-y}N$ ($y > 0$), and an undoped insulating second layer epitaxially grown on one side of the first layer and composed of $Al_xGa_yIn_{1-x-y}N$ ($y > 0$).

A device layer is formed on such a nitride-based semiconductor epitaxial substrate to obtain a semiconductor device such as HEMT or the like. In the present invention, the Mg-doped first layer has high resistivity or p-type conductivity, and thus a current leakage from the device layer formed on the nitride-based semiconductor epitaxial substrate to the GaN single crystal substrate can be suppressed. Also, the undoped second layer is provided between the first layer and the device layer, and thus Mg diffusion from the first layer to the device layer can be suppressed. Furthermore, the second layer is insulating, and thus a current leakage from the device layer to the GaN single crystal substrate can be suppressed.

In the present invention, the second layer may be characterized by a resistivity of 900 Ωcm or more. When the second layer has this level of resistivity, a current leakage from the device layer to the GaN single crystal substrate can be sufficiently suppressed. The inventors also found that even if a dopant for compensating conductivity is not introduced, a gallium nitride-based semiconductor layer having high

resistivity can be obtained by epitaxial growth while a ratio (hereinafter referred to as "V/III ratio") of a molar concentration of ammonia gas to a molar concentration of group-III raw material gas containing Ga is maintained at 1875 or more. This technique for maintaining a high V/III ratio can be used for forming the undoped insulating second layer. It was found from experiments that when the second layer is formed with a V/III ratio of 1875, the resistivity of the second layer is 900 Ωcm.

In the present invention, the second layer preferably has a thickness of 2.5 μm or more. The inventors found that the dopant Mg of the first layer diffuses by about 2.5 μm in the thickness direction of the substrate. Therefore, with the second layer having a thickness of 2.5 μm or more, Mg diffusion to the device layer can be more effectively suppressed.

In the present invention, the first layer may have p-type conductivity. When the Mg-doped first layer has p-type conductivity, the first layer functions as a barrier against electrons in the device layer, thereby suppressing a current leakage to the GaN single crystal substrate.

In the present invention, an undoped underlying layer composed of $Al_xGa_yIn_{1-x-y}N$ ($y > 0$) is preferably inserted between the GaN single crystal substrate and

the first layer.

By providing such an underlying layer, layers formed above the first layer can be provided with a flat morphology. Consequently, the characteristics of a semiconductor device using the nitride-based semiconductor epitaxial substrate of the present invention can be improved.

(2) An HEMT substrate according to the present invention comprises the above-described nitride-based semiconductor epitaxial substrate of the present invention, a channel layer composed of $Al_xGa_yIn_{1-x-y}N$ ($y > 0$) and formed on the nitride-based semiconductor epitaxial substrate, and an electron supplying layer composed of $Al_xGa_yIn_{1-x-y}N$ ($y > 0$) and formed on the channel layer.

In the HEMT substrate of the present invention, as described above, Mg diffusion from the nitride-based semiconductor epitaxial substrate to the channel layer can be suppressed, thereby improving the electron mobility of HEMT. By forming a source electrode, a gate electrode, and a drain electrode on the HEMT substrate of the present invention, an HEMT can be obtained.

(3) A method of manufacturing a nitride-based semiconductor epitaxial substrate of the present invention comprises the steps of epitaxially growing,

on one side of a GaN single crystal substrate, an Mg-doped first layer composed of $Al_xGa_yIn_{1-x-y}N$ ($y > 0$), and epitaxially growing an undoped insulating second layer composed of $Al_xGa_yIn_{1-x-y}N$ ($y > 0$) on one side of the first layer in a growth reactor.

In the thus-obtained nitride-based semiconductor epitaxial substrate, the Mg-doped first layer has high resistivity or p-type conductivity, and thus a current leakage form a device layer formed on the nitride-based semiconductor epitaxial substrate to the GaN single crystal substrate can be suppressed. Also, the undoped second layer is provided between the first layer and the device layer, and thus Mg diffusion from the first layer to the device layer can be suppressed. Furthermore, the second layer is insulative, and thus a current leakage from the device layer to the GaN single crystal substrate can be suppressed.

In the manufacturing method of the present invention, the insulating second layer is preferably epitaxially grown by supplying to the growth reactor group-III raw material gas containing Ga and ammonia gas while maintaining a ratio of the molar concentration of the ammonia gas to the molar concentration of the group-III raw material gas of 1875 or more. As described above, when the second layer is formed with a V/III ratio of 1875, the resistivity of

the second layer is 900 Ωcm, thereby effectively suppressing a current leakage from the device layer to the GaN single crystal substrate.

In the manufacturing method of the present invention, after the first layer is grown, the growth reactor preferably is heated with the substrate being removed from the growth reactor, and then the second layer is epitaxially grown on the first layer.

Although Cp_2Mg can be used as a dopant source for forming the first layer, Cp_2Mg tends to be deposited on the wall of the growth reactor and various members such as a substrate tray, and the like. Also, when an intermediate product of Cp_2Mg and NH_3 supplied in GaN growth deposited on the wall of the growth reactor and various members, are heated to high temperature, Mg is easily released. The present invention further comprises the step of heating the growth reactor before the undoped second layer is formed, for the purpose of removing an Mg releasing source to improve the purity of the layer to be then epitaxially grown.

The manufacturing method of the present invention preferably further comprises the step of heating the growth reactor with the substrate being removed from the reactor after the second layer is formed, and the step of epitaxially growing an undoped insulating third layer composed of $Al_xGa_yIn_{1-x-y}N$ ($y > 0$) on the second

layer.

Although Mg diffuses as an impurity from the first layer to the second layer, the Mg concentration at the surface of the second layer is apparently lower than that at the interface between the first layer and second layer. When the third layer is formed after the growth reactor is heated for removing the Mg releasing source, the concentration of Mg diffusing from the second layer to the third layer is lower than the concentration of Mg diffusing from the first layer to the second layer. Therefore, in the resultant nitride-based semiconductor epitaxial substrate, the Mg concentration at its surface becomes extremely low.

In the manufacturing method comprising forming the third layer, the thickness of the second layer may be 0.5 μm or more. Also, the thickness of the third layer may be 0.5 μm or more. Since the remaining Mg is removed by heating before each of the second and third layers is formed, and Mg diffusion is prevented in the two steps, i.e., the second and third layers, Mg diffusion to the device layer side can be sufficiently suppressed by the two layers each having the above-descried thickness. Namely, the nitride-based semiconductor epitaxial substrate and a device formed by epitaxially growing a semiconductor layer on the substrate can be thinned.

In the manufacturing method of the present invention, an undoped underlying layer composed of $Al_xGa_yIn_{1-x-y}N$ ($y > 0$) is preferably epitaxially grown on the GaN single crystal substrate before the epitaxial growth of the first layer, and then the first layer is formed on the underlying layer. By providing such an underlying layer, layers formed above the first layer can be provided with a smooth morphology. As a result, the characteristics of a semiconductor device using the nitride-based semiconductor epitaxial substrate of the present invention can be improved.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a side view schematically showing a nitride-based semiconductor epitaxial substrate according to an embodiment of the present invention;

Figure 2 is a drawing showing an HEMT using the epitaxial substrate shown in Fig. 1;

Figure 3 is a flowchart showing a method of manufacturing a nitride-based semiconductor epitaxial substrate according to the present invention;

Figure 4 is a drawing showing an OMVPE apparatus for manufacturing a nitride-based semiconductor epitaxial substrate;

Figure 5 is a drawing showing a nitride-based semiconductor epitaxial substrate according to another embodiment of the present invention;

Figure 6 is a drawing showing a test wafer used in an example carried out for determining a relation between a V/III ratio and resistivity of a GaN layer;

Figure 7 is a graph showing the relation between the V/III ratio and resistivity in an example;

Figure 8 is a profile showing an Mg concentration distribution in an example of the present invention; and

Figure 9 is a profile showing an Mg concentration distribution in a comparative example.

DETAILED DESCRIPTION OF THE INVENTION

Preferred embodiments of the present invention will be described in detail below with reference to the attached drawings. In the description, the same elements are denoted by the same reference numerals to avoid duplication.

Figure 1 is a side view showing a nitride-based semiconductor epitaxial substrate 10 according to an embodiment of the present invention. The epitaxial substrate 10 comprises a GaN single crystal substrate 11, an undoped GaN (hereinafter referred to as "u-GaN") layer (underlying layer) 12 epitaxially grown on the substrate 11, an Mg-doped, high-resistivity GaN layer (first layer) 13 epitaxially grown on the u-GaN layer 12 (i.e., on one side of the GaN single crystal substrate 11), and an undoped, high-resistivity u-GaN

layer (second layer) 14 epitaxially grown on one side of the high-resistivity GaN layer 13. By forming a device layer comprising a plurality of semiconductor layers on the epitaxial substrate 10, various semiconductor devices such as field effect transistor (FET), heterojunction bipolar transistor (HBT), high electron mobility transistor (HEMT), etc., can be obtained.

In this embodiment, an n-type conductive substrate is used as the GaN single crystal substrate 11. The n-type GaN single crystal substrate 11 can be obtained by, for example, a hydride vapor phase epitaxy process (HVPE process). In this process, the GaN single crystal substrate 11 having high crystallinity can be manufactured by a so-called lateral growth technique. The GaN single crystal substrate 11 is polished by an appropriate method according to demand, and has a thickness of, for example, about 400 μm to 500 μm.

The u-GaN layer (underlying layer) 12 is formed to a thickness of about 0.1 μm to 1.0 μm. The u-GaN layer 12 can provide a smooth morphology to the layers which are then grown on the layer 12. Although the u-GaN layer 12 is not necessarily provided, the u-GaN layer 12 is preferably provided for improving crystallinity and smoothness of the high-resistivity GaN layer 13 and the layers formed thereon, and the device layer.

The high-resistivity GaN layer (first layer) 13 is doped with Mg for compensating the n-type conductivity originally possessed by GaN, and has high resistivity, i.e., insulation. The thickness of the high-resistivity GaN layer 13 is about 0.1 μm to 1.0 μm.

The high-resistivity GaN layer (second layer) 14 is epitaxially grown to a thickness of about 0.5 μm to 5 μm on the high-resistivity GaN layer 13. The GaN layer 14 has high resistivity in spite of no doping with an impurity for compensating conductivity. More specifically, the high-resistivity GaN layer 14 has a resistivity of, for example, 900 Ωcm or more, and such a degree of insulation can sufficiently suppress a current leakage from the device layer to the GaN single crystal substrate 11. A method of forming such a layer will be described below.

The nitride-based semiconductor epitaxial substrate 10 having the above-described configuration has the following effect. In this embodiment, the Mg-doped high-resistivity GaN layer 13 is provided to suppress a current leakage from the device layer formed on the epitaxial substrate 10 to the GaN single crystal substrate 11. Also, the undoped high-resistivity GaN layer 14 formed on the high-resistivity GaN layer 13 functions as a barrier for suppressing Mg diffusion from the high-resistivity GaN layer 13 to the device

layer. Furthermore, the high-resistivity GaN layer 14 is insulative (resistivity of, for example, 900 Ωcm or more, as described above), thereby further suppressing a current leakage from the device layer to the GaN single crystal substrate 11.

In this embodiment, the high-resistivity GaN layer 14 preferably has a thickness of 2.5 μm or more. The inventors found from an experiment that an Mg dopant in the high-resistivity GaN layer 13 diffuses by about 2.5 μm in the thickness direction (the upward direction in a drawing) of the substrate (refer to the experimental results described below in examples). Therefore, the high-resistivity GaN layer 14 having a thickness of 2.5 μm or more can more effectively suppress Mg diffusion to the device layer.

Beside GaN, the u-GaN layer (underlying layer) 12, the high-resistivity GaN layer (first layer) 13, and the high-resistivity GaN layer (second layer) 14 can be made of AlGaN, InGaN, AlInGaN, or the like, which is specified by $Al_xGa_yIn_{1-x-y}N$ ($y > 0$).

Figure 2 is a side view schematically showing a High Electron Mobility Transistor (HEMT) 70 using the epitaxial substrate 10 shown in Fig. 1.

The HEMT 70 comprises an HEMT substrate 60 of this embodiment, which comprises the epitaxial substrate 10 and a device layer 50, a gate electrode 55, a source

electrode 56, and a drain electrode 57. The device layer 50 comprises a channel layer 51 composed of u-GaN formed on the epitaxial substrate 10, and an electron supplying layer 52 formed on the channel layer 51. The gate electrode 55 is made of, for example, Au, and the source electrode 56 and the drain electrode 57 are made of, for example, Ti/Al. When the HEMT is operated, a two-dimensional electron gas layer is formed in an upper layer of the channel layer 51 to achieve a high-speed electron transfer.

As described above, the HEMT substrate 60 of the HEMT 70 uses the epitaxial substrate 10, and thus Mg diffusion from the substrate 10 to the channel layer 51 can be suppressed. Therefore, the purity of the channel layer 51 can be kept high to realize a high electron mobility in the HEMT 70.

Next, a method of manufacturing the nitride-based semiconductor epitaxial substrate 10 shown in Fig. 1 will be described with reference to a flowchart of Fig. 3.

The manufacturing method of this embodiment comprises the following steps (A) to (F):

(A) First, the GaN single crystal substrate 11 is prepared (S101).

(B) The GaN single crystal substrate 11 is set in an OMVPE apparatus, and then heat-treated to smooth the

substrate surface (S102).

(C) The u-GaN layer 12 is epitaxially grown on the GaN single crystal substrate 11 (S103).

(D) The Mg-doped high-resistivity GaN layer 13 is formed on the u-GaN layer 12 (S104).

(E) The substrate is removed from the growth reactor after the above growth, and the growth reactor is heated (S105).

(F) The undoped, insulating high-resistivity GaN layer 14 is formed on the high-resistivity GaN layer 13 (S106).

Each of the steps will be described below.

First, a description will be made of the step (A) (S101) of preparing the GaN single crystal substrate 11. The GaN single crystal substrate 11 can be formed by any one of various known methods. For example, International Publication No. 99/23693 pamphlet discloses that the GaN single crystal substrate 11 having few defects can be formed by so-called lateral growth using an SiO_2 mask having apertures formed therein. The surface of the thus-grown GaN single crystal substrate 11 is polished by an abrasive, and then cleaned with a liquid such as pure water or the like.

Next, the heat treatment step (B) (S102) will be described. First, the GaN single crystal substrate 11

prepared as described above is set in the OMVPE apparatus 20 schematically shown in Fig. 4. The OMVPE apparatus 20 is adapted for epitaxially growing a gallium nitride-based semiconductor by an OMVPE process, but the substrate 11 is heat-treated in this apparatus before the epitaxial growth.

The OMVPE apparatus 20 comprises a vertical growth reactor 22 in which a raw material gas is injected to the surface of the substrate 11 from a direction vertical to the substrate surface. The growth reactor 22 mainly comprises raw material supply pipes 21a to 21e to which raw material gas and carrier gas are respectively supplied, an exhaust pipe 23o for evacuating the reactor and exhausting gases during growth, a wafer tray 32 on which a plurality of substrates 11 is set, and a heater 33 for heating the wafer tray 32 from below. Also, a water-cooling jacket 34 is provided in an upper portion of the inside of the growth reactor 22, for the purpose of preventing a reaction of a raw material gas due to heating before reaching the substrate 11.

Furthermore, a driving mechanism 44 is provided below the growth reactor 22, for rotating the wafer tray 32. The driving mechanism 44 comprises a motor 41, and a rotational shaft 43 to which rotation of the motor 41 is transmitted through a belt 42. The

rotational shaft 43 is introduced into the growth reactor 22 through a magnetic fluid seal 44, the upper end of the rotational shaft 43 being connected to the bottom of the wafer tray 32. The magnetic fluid seal 44 is provided around the rotational shaft 43 to close a through hole of the growth reactor 22 through which the rotational shaft 43 is passed. As the wafer tray 32, a carbon material coated with SiC can be used, and can be rotated at a high speed of, for example, about 1000 rpm by the driving mechanism 40.

In the OMVPE apparatus 20, the GaN single crystal substrate 11 is heat-treated by maintaining for about 15 minutes at a substrate temperature of about 1020°C under a reactor pressure of about 26.7 kPa while supplying, for example, 11 slm of NH_3 or 5 slm of N_2. In this heat treatment step, abrasive flaws remaining on the surface of the substrate 11 are removed to planarize the surface.

Next, a description will now be made of the step (C) (S103) of epitaxially growing the u-GaN layer 12 on the GaN single crystal substrate 11. After the heat treatment step (B) is completed, epitaxial growth is preferably started without removal of the substrate 11 from the growth reactor 22, for preventing contamination of the surface of the substrate 11.

In epitaxially growing the u-GaN layer 12,

trimethylgallium (TMG) as a group-III raw material gas containing Ga, hydrogen gas (H_2) for carrying trimethylgallium toward the substrate 11, and ammonia gas (NH_3) are supplied to the growth reactor 22 under a condition in which the substrate temperature is decreased to about 1000°C after the heat treatment, and the pressure in the growth reactor is set to about 26.7 kPa (200 Torr).

Next, a description will be made of the step (D) (S104) of forming the Mg-doped high-resistivity GaN layer 13. In this step, 11 slm of ammonia gas, 175 μmol/min of trimethylgallium, and 4.5 μmol/min of biscyclopentane dienyl magnesium (Cp_2Mg) serving as a dopant for compensating conductivity are supplied to the growth reactor under a condition in which the substrate temperature is about 1020°C, and the pressure in the growth reactor is set to about 26.7 kPa (200 Torr). As the doping gas for compensating conductivity, alkylated cyclopentadienyl magnesium such as methylcyclopentadienyl magnesium, ethylcyclodienyl magnesium, or the like may be used in place of Cp_2Mg.

The high-resistivity layer 13 formed as the first layer on the u-GaN layer 12 may have p-type conductivity. In this case, after growth, heat treatment may be performed at 600 to 800°C in a hydrogen-free atmosphere such as an N_2 atmosphere or

air. When the Mg-doped first layer 13 has p-type conductivity, the first layer 13 functions as a barrier against electrons in the device layer 50, thereby suppressing a current leakage to the GaN single crystal substrate 11.

A description will now be made of the step (E) (S105) of heating the growth reactor. In forming the high-resistivity GaN layer 13, Cp_2Mg or the like is used as a dopant source, but it tends to be adsorbed or deposited on the wall of the growth reactor 22, and on various members such as the wafer tray 32, and the like. Also, when an intermediate product of Cp_2Mg and NH_3 supplied in GaN growth deposited on the wall of the growth reactor and various members, are heated to a high temperature, Mg is easily released. Therefore, the substrate 11 is removed from the growth reactor 22 after the high-resistivity GaN layer 13 is formed in the course of production, and the growth reactor 22 is heated for the purpose of removing an Mg releasing source, improving the purity of the layer to be then epitaxially grown.

Next, a description will be made of the step (F) (S106) of forming the high-resistivity GaN layer 14. In epitaxially growing the high-resistivity GaN layer 14, trimethylgallium (TMG) serving as a group-III raw material gas containing Ga, hydrogen gas (H_2) for

carrying trimethylgallium to the substrate 11, and ammonia gas (NH_3) are supplied to the growth reactor under a condition in which the substrate temperature is about 1020°C, and the pressure in the growth reactor is set to about 26.7 kPa (200 Torr).

In this embodiment, a gas flow rate is controlled so that the ratio (i.e., the "V/III ratio") of the molar concentration of ammonia gas to the molar concentration of trimethylgallium is 1875 or more. For example, when the flow rate of ammonia gas is 11 slm, and the flow rate of trimethylgallium is 262 μmol/min, the V/III ratio is 1875. By setting the V/III ratio to 1875 or more, an insulating GaN layer having a resistivity of 900 Ωcm or more can be obtained without intentional doping for compensating conductivity.

When the high-resistivity GaN layer comprises, for example, an InGaN layer as the second layer trimethylgallium (TMG) and trimethylindium (TMI) are supplied as group-III raw material gases to the growth reactor 22, and the ratio of the molar concentration of ammonia gas to the total of the molar concentrations of trimethylgallium and trimethylindium is set to 1875 or more. In this case, an insulating InGaN layer can be obtained without doping for compensating conductivity.

On the other hand, when trimethylgallium and trimethylaluminum (TMA) are supplied as group-III raw

material gases to the growth reactor 22, and the ratio of the molar concentration of ammonia gas to the total of the molar concentrations of trimethylgallium and trimethylaluminum is set to 1875 or more, a high-resistivity AlGaN layer can be obtained without doping for compensating conductivity.

The above-described steps can ensure electrical insulation between the device layer 50 and the GaN single crystal substrate 11, and can achieve the epitaxial substrate 10 capable of suppressing diffusion of Mg for controlling conductivity to the device layer 50.

Another embodiment of the present invention will be described below with reference to Fig. 5. In this embodiment, a substrate is removed from a growth reactor 22 after a high-resistivity GaN layer 14 is formed, and then the growth reactor 22 is again heated. In this heating process, Mg remaining in the growth reactor 22 can again be removed. A high-resistivity GaN layer (third layer) 15 is then, epitaxially grown by the same method as that used for the high-resistivity GaN layer 14. In this method, the concentration of Mg diffusing from the high-resistivity GaN layer 14 to the high-resistivity GaN layer 15 is lower than the concentration of Mg diffusing from the high-resistivity GaN layer 13 to the high-resistivity

GaN layer 14. Therefore, the resultant nitride-based semiconductor epitaxial substrate 10 has an extremely low Mg concentration at its surface.

In these manufacturing steps, the high-resistivity GaN layer 14 and the high-resistivity GaN layer 15 can be made thin. Namely, remaining Mg is removed by heating before each of the high-resistivity GaN layer 14 and the high-resistivity GaN layer 15 is formed, and the two layers function as barriers for preventing Mg diffusion, thereby achieving thinning of each of the layers. Specifically, the high-resistivity GaN layer 14 and the high-resistivity GaN layer 15 each having a thickness of 0.5 μm or more can sufficiently suppress Mg diffusion to the device layer. Also, thinning of the high-resistivity GaN layer 14 and the high-resistivity GaN layer 15 enables thinning of the entire device such as an HEMT 70 or the like.

Examples

The effect of the present invention will be described in detail below with reference to examples.

[Undoped high-resistivity GaN layer]

Experiments were carried out for obtaining an insulating high-resistive GaN layer without doping. The experiments will be described with comparative examples.

In an example, an experiment was performed for

determining a relationship between a V/III ratio and resistivity of a GaN layer epitaxially grown on a substrate 11. In determining the resistivity of the high-resistivity GaN layer, the test wafer 80 shown in Fig. 6 was prepared. This test wafer 80 was prepared by forming, on the n-type conductive GaN single crystal substrate 11, a first epitaxially grown layer 72 in which the resistivity was increased by Mg doping, and then epitaxially growing a second epitaxially grown layer 74 (the high-resistivity GaN layer 14 shown in Fig. 1). The first epitaxially grown layer 72 was provided for ensuring insulation between the GaN single crystal substrate 11 and the second epitaxially grown layer 74 (high-resistivity GaN layer) to enable the measurement of the resistivity of the second epitaxially grown layer 74. This process will be described in detail below.

First, the n-conductive GaN single crystal substrate 11 was set in the OMVPE apparatus 20 shown in Fig. 4, and then heat-treated as pre-treatment under the conditions shown in Table I.

Table I

	Pretreatment	First epilayer	Second epilayer
Flow rate of NH_3	11SLM	11SLM	11 SLM
Flow rate of TMG	-	175 μmol/min	174 - 491 μmol/min
Flow rate of H_2	5 SLM	5 SLM	5 SLM

Flow rate of Cp_2Mg	-	4.5 μmol/min	-
Treatment temperature	1020°C	1000°C	1000°C
Treatment time	15 min.	20 min.	45 - 95 min.
Pressure of reactor chamber	200 Torr	200 Torr	200 Torr
Layer thickness	-	0.4 μm	2 μm

Next, 11 slm of ammonia gas, 175 μmol/min of trimethylgallium, 4.5 μmol/min of biscyclopentanedienyl magnesium (Cp_2Mg) serving as a dopant for compensating conductivity were supplied to the growth reactor 22 under a condition in which the substrate temperature was 1000°C, and the pressure in the growth reactor was about 26.7 kPa (200 Torr). As a result, the first epitaxially grown layer 72 having a thickness of 0.4 μm was formed on the GaN single crystal substrate 11. The steps up to the steps of forming the first epitaxially grown layer 72 were the same in the examples and comparative examples described below.

Next, in order to prevent dopant Mg adhering to the inside of the reactor from being mixed with the second epitaxially grown layer 74, the wafer was removed from the growth reactor 22, and the reactor was heated to a high temperature to remove remaining Mg.

Next, the second epitaxially grown layer (high-resistivity GaN layer) 74 was formed without the supply of the conductivity compensating dopant under a

condition in which the substrate temperature was 1000°C, and the pressure in the growth reactor was about 26.7 kPa (200 Torr). As shown in Table I, in forming the second epitaxially grown layer 74, the flow rate of trimethylgallium was changed from the range of 175 to 491 μmol/min to a constant flow rate of 11 slm of ammonia gas to obtain a total of five V/III ratio patterns.

The resistivity of each of the thus-formed second epitaxially grown layers 74 was measured by a so-called four-probe method. The measured resistivity values are shown in Table II and Fig. 7.

In comparative example 1, the flow rate of trimethylgallium was 491 μmol/min, and the V/III ratio was 1000. In comparative example 1, the V/III ratio was determined by $11/22.4/(491 \times 10^{-6})$ in consideration of the unit "slm" of the flow rate of ammonia gas. In comparative example 2, the flow rate of trimethylgallium was 393 μmol/min, and the V/III ratio was 1250. Table II and Fig. 7 indicate that the resistivity values are 1.1 and 1.3 Ωcm, respectively, in comparative examples 1 and 2. Insulation between the device layer and GaN single crystal substrate cannot be ensured with these resistivity values.

In example 1, the flow rate of trimethylgallium was 262 μmol/min, and the V/III ratio was 1875. In

example 2, the flow rate of trimethylgallium was 210 μmol/min, and the V/III ratio was 2337. In example 3, the flow rate of trimethylgallium was 175 μmol/min, and the V/III ratio was 2800. Table II and Fig. 7 indicate that the resistivity values are 900, 1300, and 2300 Ωcm, respectively, in examples 1, 2, and 3. It was thus found that the second epitaxially grown layer 74 has sufficient resistivity for ensuring insulation between the device layer and the GaN single crystal substrate 11.

Table II

	Flow rate of NH_3 (SLM)	Flow rate of TMG (μmol/min)	V/III ratio	Resistivity (Ωcm)
Comparative Example 1	11	491	1000	1.1
Comparative Example 2	11	393	1250	1.3
Example 1	11	262	1875	900
Example 2	11	210	2337	1300
Example 3	11	175	2800	2300

As described above, it was confirmed in these examples that with a V/III ratio of 1875 or more, a high-resistivity GaN layer having a resistivity of 900 Ωcm or more can be obtained without doping for compensating conductivity.

[Suppression of Mg diffusion]

It was also confirmed that Mg diffusion to the device layer can be effectively prevented by providing

an undoped, insulating high-resistivity GaN layer (second layer) on the Mg-doped high-resistivity GaN layer (first layer).

In example 4, a GaN layer has an undoped underlying layer, an Mg-doped high-resistivity GaN layer, and an undoped high-resistivity GaN layer which are laminated in that order on a substrate to obtain an epitaxial substrate. An undoped GaN layer corresponding to a channel layer of an HEMT was then, formed on the epitaxial substrate.

In further detail, a sapphire substrate was used as the substrate in place of a GaN single crystal substrate. The crystallinity of a grown layer is lower with the use of the sapphire substrate than with the use of the GaN single crystal substrate, but there is no effect on the degree of Mg diffusion to the device layer. The substrate was heated at 1000°C in a hydrogen atmosphere, and then a GaN buffer layer was grown after the substrate temperature was decreased to 500°C. Then, the substrate temperature was increased to 1000°C, and an undoped GaN layer was formed to a thickness of about 1.0 μm.

Furthermore, an Mg-doped high-resistivity GaN layer was grown to a thickness of about 0.3 μm, and then the substrate was removed from the growth reactor. The growth reactor was then, heated at 1050°C in a

hydrogen atmosphere for 1 hour. Thereafter, an undoped high-resistivity GaN layer was formed to a thickness of about 3.0 μm at a V/III ratio of 2800 to obtain an epitaxial substrate. Then, an undoped GaN layer corresponding to a channel layer of an HEMT was formed to a thickness of 3.2 μm on the epitaxial substrate.

On the other hand, in comparative example 3, a GaN layer as an undoped underlying layer, and an Mg-doped high-resistivity GaN layer were formed on a GaN single crystal substrate to prepare an epitaxial substrate, and an undoped GaN layer corresponding to a channel layer was formed on the epitaxial substrate. Namely, a device layer was grown without an undoped high-resistivity GaN layer for preventing Mg diffusion from the Mg-doped GaN layer.

In further detail, the GaN single crystal substrate was annealed at 1020°C in a mixed atmosphere of hydrogen and NH_3, and then the undoped GaN layer was grown to a thickness of about 0.45 μm. Furthermore, the Mg-doped high-resistivity GaN layer was grown to a thickness of 0.45 μm to obtain the epitaxial substrate. The substrate was then, removed from the growth reactor, and the growth reactor was heated at 1050°C in a hydrogen atmosphere for 1 hour. Furthermore, an undoped GaN layer corresponding to a channel layer was formed to a thickness of about 2.75 μm on the epitaxial

substrate.

For each of the epitaxial substrates obtained in example 4 and comparative example 3, an Mg concentration distribution was determined by secondary ion mass spectrometry (SIMS). Figure 8 shows a profile of example 4, and Fig. 9 shows a profile of comparative example 3.

Figure 8 shows that in example 4, the undoped high-resistivity GaN layer functions as a barrier, sufficiently suppressing Mg diffusion from the Mg-doped high-resistivity GaN layer to the channel layer. Also, Mg diffuses by about 2.5 μm from the Mg-doped high-resistivity GaN layer in the thickness direction of the substrate, and thus the Mg concentration at a distance of about 2.5 μm or more from the Mg-doped high-resistivity GaN layer decreases to a detection limit (1 x 10^{14} cm^{-3}) or less. As described above, considering the fact that Mg diffuses by about 2.5 μm, Mg diffusion to the channel layer can be effectively suppressed by the undoped high-resistivity GaN layer having a thickness of 2.5 μm or more.

On the other hand, Fig. 9 shows that the Mg concentration of the channel layer becomes a high value without the undoped high-resistivity GaN layer. Also, the Mg concentration near the surface of the channel layer reaches about 7 x 10^{15} cm^{-3}.

It was confirmed by the experiment that Mg diffusion to the device layer can be effectively prevented by providing an undoped insulating high-resistivity GaN layer (second layer) on an Mg-doped high-resistivity GaN layer (first layer).

As described above, in a nitride-based semiconductor epitaxial substrate and HEMT substrate of the present invention, electrical insulation can be ensured between a device layer and the GaN single crystal substrate, and diffusion of Mg for controlling conductivity to the device layer side can be suppressed.

CLAIMS

1. A nitride-based semiconductor epitaxial substrate comprising:

a GaN single crystal substrate;

an Mg-doped first layer which is epitaxially grown on one side of the GaN single crystal substrate and which is composed of $Al_xGa_yIn_{1-x-y}N$ ($y > 0$); and

an undoped insulating second layer which is epitaxially grown on one side of the first layer and which is composed of $Al_xGa_yIn_{1-x-y}N$ ($y > 0$).

2. A nitride-based semiconductor epitaxial substrate according to claim 1, wherein the second layer has a resistivity of 900 Ωcm or more.

3. A nitride-based semiconductor epitaxial substrate according to claim 1 or 2, wherein the second layer has a thickness of 2.5 μm or more.

4. A nitride-based semiconductor epitaxial substrate according to claim 1, wherein the first layer has p-type conductivity.

5. A nitride-based semiconductor epitaxial substrate according to any one of claims 1 to 4, further comprising an undoped underlying layer composed of $Al_xGa_yIn_{1-x-y}N$ ($y > 0$) provided between the GaN single crystal substrate and the first layer.

6. An HEMT substrate comprising:

a nitride-based semiconductor epitaxial substrate

according to any one of claims 1 to 5;

a channel layer composed of $Al_xGa_yIn_{1-x-y}N$ ($y > 0$) and formed on the nitride-based semiconductor epitaxial substrate; and

an electron supplying layer composed of $Al_xGa_yIn_{1-x-y}N$ ($y > 0$) and formed on the channel layer.

7. A method of manufacturing a nitride-based semiconductor epitaxial substrate comprising the steps of:

epitaxially growing, on one side of a GaN single crystal substrate, an Mg-doped first layer composed of $Al_xGa_yIn_{1-x-y}N$ ($y > 0$) in a growth reactor; and

epitaxially growing an undoped insulating second layer composed of $Al_xGa_yIn_{1-x-y}N$ ($y > 0$) on one side of the first layer.

8. A method of manufacturing a nitride-based semiconductor epitaxial substrate according to claim 7, wherein the insulating second layer is epitaxially grown by supplying a group-III raw material gas containing Ga and an ammonia gas to the growth reactor while maintaining a ratio of the molar concentration of the ammonia gas to the molar concentration of the group-III raw material gas of 1875 or more.

9. A method of manufacturing a nitride-based semiconductor epitaxial substrate according to claim 7 or 8, wherein after the first layer is grown, the

growth reactor is heated with the substrate being removed from the growth reactor, and then the second layer is epitaxially grown on the first layer.

10. A method of manufacturing a nitride-based semiconductor epitaxial substrate according to any one of claims 7 to 9, further comprising the step of:

heating the growth reactor with the substrate being removed from the reactor after the second layer is formed; and

epitaxially growing an undoped insulating third layer composed of $Al_xGa_yIn_{1-x-y}N$ ($y > 0$) on the second layer.

11. A method of manufacturing a nitride-based semiconductor epitaxial substrate according to claim 10, wherein the thickness of the second layer is 0.5 μm or more.

12. A method of manufacturing a nitride-based semiconductor epitaxial substrate according to claim 10 or 11, wherein the thickness of the third layer is 0.5 μm or more.

13. A method of manufacturing a nitride-based semiconductor epitaxial substrate according to any one of claims 7 to 12, wherein an undoped underlying layer composed of $Al_xGa_yIn_{1-x-y}N$ ($y > 0$) is epitaxially grown on the GaN single crystal substrate before epitaxial growth of the first layer, and the first layer is then

formed on the underlying layer.