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EP 2 575 161 B1

Description

TECHNICAL FIELD

[0001] The present invention relates to a semiconductor crystal growing technology, and more particularly to a technique for growing Group III nitride crystals on an SiC surface.

BACKGROUND ART

[0002] Hexagonal SiC has a very high heat conductivity, and both electrically conductive and insulating substrates are available. Its lattice constant and coefficient of thermal expansion are relatively close to those of AlN and GaN-based Group III nitrides. Another characteristic of hexagonal SiC is that it is a hexagonal crystal and possesses polarities, as to Group III nitrides.

[0003] There are high expectations for the realization of a technology for growing high-quality crystals of Group III nitrides on SiC for applications relating to a buffer layer for the formation of a GaN-based device structure on an SiC substrate, or relating to Group III nitride/SiC hetero-junction devices. It has been difficult to grow a high-quality Group III nitride layer on SiC because of the mismatch of the stacked structure of SiC and Group III nitrides in the c-direction, or the so-called polytype mismatch. Namely, 4H-SiC and 6H-SiC, which are representative of hexagonal SiC, have structures with 4-and 6-monolayer periods, respectively, in the c-axis direction, while AlN and GaN, which are Group III nitrides, have 2-monolayer periods in the c-axis direction in a structure referred to as the wurtzite structure.

[0004] In order to solve this problem, it has been proposed to make the SiC substrate surface a flat plane without any steps, or to control the height of the steps on the SiC substrate surface to be common multiples of the stacking periods of SiC and the Group III nitride. For example, a technology has been proposed whereby a SiC substrate surface is subjected to HCl gas etching so as to form a SiC surface with the aforementioned features, which is followed by the growing of an AlN layer (see Non-patent Document 1: Norio Onojima, Jun Suda, and Hiroyuki Matsunami, "Molecular-beam epitaxial growth of insulating AlN on surface-controlled 6H-SiC substrate by HCl gas etching," Applied Physics Letters, Vol. 80, No. 1, (2002) p.76-78, for example).

[0005] Jeganathan et al. (Phys. Stat. Sol. (c) 0, No. 1 143-137, 2002) describe the growth of strain free GaN layers on 6H-SiC (0001) substrate by plasma-assisted molecular beam epitaxy, using a double-step AlN buffer process grown at two different high temperatures with a difference of 30-50°C.

[0006] Jeganathan et al. (Journal of Crystal Growth 244 2002 33-38) describe the preparation of GaN layers directly grown on 6H-SiC (0001) substrates that have been surface-modified by Ga-metal deposition and flash-off at high temperature.

[0007] Jeganathan et al. (Surface Science 527 2003 L197-L202) describe the initial nucleation kinetics of GaN growth on SiC(0001) substrates.

[0008] Stevens et al. (J. Vac. Sci. Technol. B, Vol. 12, No. 2, 1994 1186-1189) describe the growth of GaN and InGaN on Si(111) substrates.

DISCLOSURE OF THE INVENTION

[0009] While it is expected that the inconsistency in stacked structures can be resolved by the method in Non-patent Document 1, there are two additional problems in the crystal growth of Group III nitride on SiC surfaces. One is that the SiC surface is chemically and thermally stable, and it is difficult to control the SiC surface condition unless a high-temperature environment, such as one exceeding 1200°C, is used. Such high-temperature environment, however, is difficult to realize via conventional Group III nitride growth apparatuses.

[0010] The second problem is that because the interface of crystal growth is an interface of substances with different chemical bonds, namely IV-IV and III-V, there would be either an excess or a lack of electrons in the formation of covalent bonding, such as in the cases of IV-III or IV-V, at the interface. As a result, the interface could be destabilized and the mode of crystal growth tends to be that of three-dimensional island growth. Thus, it has been difficult to achieve high-quality Group III nitride crystal growth.

[0011] It is an object of the invention to provide a technique for growing high-quality Group III nitride crystals on SiC by controlling the surface of SiC and/or through sequence control at the beginning of growth.

[0012] The invention provides a crystal growing method comprising the steps of: forming a flat and clean SiC surface; growing AlN under high vacuum by feeding Al and N atoms, wherein feeding of Ga or In as surface control element for controlling the mode of crystal growth of said AlN is started before starting said growing; and wherein feeding of Ga or In for controlling the mode of crystal growth of said AlN is terminated after said growing is started.

[0013] By thus feeding Al and nitrogen after the feeding of the surface control element, the formation of a nitride layer of Si or the like on the SiC surface can be prevented regardless of the order of feeding of Al and nitrogen. As a result, a good interface can be formed and the need to control the order of feeding of Al and nitrogen can be eliminated.

[0014] Preferably in the crystal growing method of the invention said SiC surface has an offset angle of 0 to 15° with respect to the (0001)_{Si} or (000-1)_C plane.

[0015] Preferably in the crystal growing method of the invention the step of growing said Group III nitride is performed under a vacuum of 10⁻² to 10⁻⁴ Pa.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016]

Fig. 1 shows the steps of crystal growth in accordance with the invention.

Fig. 2 shows a step of forming a clean substrate surface.

Fig. 3 shows a sequence chart regarding the timing (which is controlled by turning on or off of a shutter, for example, in the case of MBE) of feeding of a growth element before and after the growth of a AlN crystal.

Fig. 4(A) to (D) shows examples of structures grown by the crystal growing method according to the invention.

Fig. 5(A) shows an example of the cross-sectional structure of a MISFET in which the band discontinuity and the difference in electron affinity between SiC and AlN are utilized and in which a two-dimensional electron gas layer is used as a channel layer. Fig. 5(B) shows an energy band structure in a SiC-AlN junction structure.

Fig. 6 shows a cross section of a laser structure, illustrating an example in which the crystal growing technique according to an embodiment of the invention is applied to an optical device.

Fig. 7 shows a cross section of a GaN/SiC-based HBT, illustrating an example in which the crystal growing technique according to an embodiment of the invention is applied to an HBT (heterojunction bipolar transistor).

BEST MODES FOR CARRYING OUT THE INVENTION

[0017] The technique for growing Group III crystals on SiC according to the invention will be described with reference to the drawings. The term "SiC surface" herein includes both the surface of a SiC substrate and the surface of a SiC layer deposited on different types of materials, such as a Si substrate and a sapphire substrate. The term "SiC substrate" also includes substrates on the surface of which SiC exists.

[0018] Hereafter, a crystal growing method according to the invention is described with reference to the drawings. Fig. 1 shows the steps of the crystal growing method according to the present embodiment, and Fig. 3 shows a sequence chart regarding the timing of feeding of growth elements (which is controlled by turning on and off of a shutter, for example, in the case of MBE) before and after the crystal growth of a Group III nitride.

[0019] In the following, the crystal growth steps in accordance with the present embodiment will be described with reference to Figs. 1, 2 and 3. As shown in Fig 1(A), initially a washed 4H-SiC(0001)Si substrate 21 is prepared. Then a clean surface 25 is formed on the surface of the substrate 21, as shown in Fig. 2. The surface of the SiC substrate 21 taken out into the atmosphere was

treated with aqua regia, hydrochloric acid, and hydrofluoric acid sequentially. By the hydrofluoric acid process, a minute amount of silicon oxide film formed on the surface of the SiC substrate 21 can be removed. On the surface of the substrate, there is formed a clean surface 25 of SiC.

[0020] Thereafter, as shown in Fig. 1(B) and Fig. 3, at a certain time (time t20), the Ga irradiation is first carried out. Near the growth temperature of AlN, the vapor pressure of Ga is higher than the vapor pressure of Al, so that the components of the Ga atoms that are adsorbed on the surface 25 of the SiC substrate 21 and the components that are evaporated from the surface are substantially equal, whereby a kind of equilibrium is achieved. As a result, a state 25a is created in which Ga in a state of equilibrium is adsorbed on the surface.

[0021] The growth of AlN is initiated by feeding Al and N simultaneously at a certain time (time t22), as shown in Fig. 1(C) and Fig. 3. Because the Ga irradiation is performed for the purpose of controlling the mode of AlN crystal growth at the beginning thereof, the feeding of Ga is terminated after the beginning of AlN growth at time t24.

[0022] Because Al and Ga are fed during the period t24 and t22, an $Al_xGa_{1-x}N$ layer 25b is formed at the interface of the AlN layer 35 and the SiC substrate 21, as shown in Fig. 1(D). If the presence of an AlGaN layer between SiC and AlN is not preferable for the given purpose, such as when an AlN/SiC MIS structure is to be prepared, it would be necessary to reduce the period t24 to t22 to be sufficiently shorter than the growth time for a monolayer of the AlGaN layer. For example, if the Ga irradiation were to be stopped simultaneously with the start of feeding of Al and N (t22 = t24), there would be only a minute amount of Ga at the interface, and the formation of the AlGaN layer could be virtually disregarded. On the other hand, if there are no restrictions as to the SiC/AlN interface structure, such as when a buffer layer for a GaN laser structure is to be prepared, the timing of feeding of Al can be given a certain degree of freedom. Specifically, Al could be fed at t21 prior to the feeding of N at t22, or Al could be fed at t23 following the feeding of N at t22. If feeding were to be started at t21, excess Al could be aggregated on the SiC surface if the preceding irradiation time t22 to t21 is too long, resulting in a poor crystallinity. On the other hand, if feeding were to be started at t23, a GaN layer would be formed because Ga and N would be fed during t23 and t21, whereby a SiC/GaN/AlN structure would be formed. After the AlN layer with a desired thickness is formed, the feeding of Al and N is terminated so as to terminate the growth of the AlN layer.

[0023] By thus the irradiation of Ga atoms 27, which re-evaporate and do not become aggregated, first, the formation of an SiN film or excess Si-N bond can be prevented and the mode of AlN crystal growth can be easily rendered into the layer-to-layer growth, even without carrying out the preceding irradiation of the Al atoms 31. In the present invention, where the Ga atoms 27, which are more easily evaporated than Al, are used, and the equi-

librium state between adsorption and separation of the Ga atoms is utilized, timing adjustment of preceding irradiation of Al is advantageously not required.

[0024] Instead of Ga, In, which is similarly easily re-evaporated, may be used. In this case, too, the possibility of the rf-plasma excited active nitrogen 33 directly reacting with the SiC surface 25 can be reduced, so that the formation of a SiN layer or the like on the SiC surface 25 can be prevented and, as a result, the state of interface between the SiC surface 25 and the AlN layer 35 can be maintained in a good condition. The feeding of N may be carried out in an intermittent manner. When the growth method involves a gas source for feeding Ga, such as in the case of CBE (chemical beam epitaxy) or MOVPE (metal organic vapor phase epitaxy), an organic metal containing Ga, such as trimethyl gallium or triethyl gallium, would be fed, thereby substantially feeding Ga. The same applies to N, namely, by feeding a nitrogen-containing gas, such as ammonia or hydrazine, N is substantially fed.

[0025] Fig. 4 shows example structures grown by the crystal growing method according to the invention. In the structure shown in Fig. 4(A), there are only Ga atoms on the ppm order remaining between the SiC substrate 1 and the AlN layer 53. In the structure shown in Fig. 4(B), there is formed a thin $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layer 55 ($x = 0$ to 1) between the SiC substrate 51 and the AlN layer 53. This is a layer formed by the growth of the AlN layer following the feeding of Ga as shown in Fig. 3. When In is used instead of Ga, In atoms 58 remain between the SiC substrate 51 and the AlN layer 53, as shown in Fig. 4(C). If In on the percentage order is mixed, a thin $\text{Al}_x\text{In}_{1-x}\text{N}$ layer 59 ($x = 0$ to 1) is formed between the SiC substrate 51 and the AlN layer 53, as shown in Fig. 4(D). This is a layer formed by the growth of the AlN layer following the feeding of Ga or In as shown in Fig. 3. If any of the illustrated structures is present, it can be presumed that the crystal growing method of the invention has been used.

[0026] Fig. 5 shows examples of device structures according to the crystal growing method according to the invention. Fig. 5(A) shows an example of the cross-sectional structure of an MISFET in which the band discontinuity between SiC and AlN is utilized and the two-dimensional electron gas layer at the interface is used as a channel. Fig. 5(B) shows an energy band structure in the junction structure of SiC and AlN.

[0027] As shown in Fig. 5(A), a heterojunction MISFET comprises a substrate 61 with a SiC surface; a high-quality AlN layer 66 grown on the substrate 61 by the crystal growing technique according to the present embodiment; a gate electrode 68 formed on the AlN layer 66; a source layer 63 and a drain layer 65 that are formed on either side of the gate electrode 68 within SiC and in which high concentrations of impurities are doped; a source electrode 67a formed for the source layer 63; and a drain electrode 67b formed for the drain layer 65.

[0028] As shown in Fig. 5(B), between the AlN layer 66 (with a bandgap of approximately 6.2 eV) and the SiC

(with a bandgap of approximately 3.4 eV) surface, there is a large band offset. As a result, when the gate electrode is formed on the AlN layer 66, the concentration of two-dimensional electron gas induced at the interface can be controlled by the voltage at the gate electrode, whereby transistor operation can be realized.

[0029] An improved AlN crystallinity can be obtained in the above-described AlN/SiC-based MISFET due to the use of the crystal growing technique of the present embodiment, whereby a high-performance MISFET with good gate insulating property and high channel electron mobility can be realized.

[0030] In the following, an example where the crystal growing technique of the present embodiment is applied to an optical device will be described with reference to the drawings. Fig. 6 shows a cross section of a laser structure to which the crystal growing technique has been applied. As shown, a semiconductor laser employing the crystal growing technique of the invention comprises: a substrate 71 with a SiC surface; an AlN buffer layer 73 formed on the substrate 71; an AlGaIn (n-type) cladding layer 75; a GaN/InGaIn multiquantum well (MQW) structure 77; and an AlGaIn (p) cladding layer 78. On top of the AlGaIn (p) cladding layer 78, there is formed a first electrode E1. On top of the AlGaIn (n-type) cladding layer 75, there is formed a second electrode E2. In this laser structure, too, a good AlN crystal can be formed on the SiC substrate 71, so that the characteristics of the laser operation prepared thereon can be greatly improved, thus contributing to the reduction of the threshold current density of laser and to the increase in the life of the device.

[0031] The structure shown in Fig. 6 can be modified by changing the SiC 71 to an n-type and making the AlN layer 73 to be thin enough that a tunnel current can be expected, such as on the order of 10 nm or less. In such a modification, current can be caused to flow vertically. In this case, the second electrode may be formed on a back surface E2' of SiC 71, which would make it possible to omit the step for forming a mesa structure of a Group III nitride. Alternatively, in the structure shown in Fig. 6, SiC 71 may be changed to an n-type, and an n-type AlGaIn layer may be used as a buffer layer instead of the AlN layer 73, so that current can be caused to flow vertically.

[0032] Fig. 7 shows an example of the structure of a heterojunction bipolar transistor (HBT) manufactured by the crystal growing method of the present embodiment. As shown, the HBT has a vertically stacked structure that comprises: a n-SiC substrate 81; a p-SiC layer 83 formed on the substrate; and a n⁺-GaIn layer 85 formed on the p-SiC layer 83. An emitter electrode 91 is formed for the n⁺-GaIn layer 85, a base electrode 93 is formed on the p-SiC layer 83, and a collector electrode 95 is formed on the back surface of the n-SiC substrate 81, thereby forming an HBT. In accordance with the crystal growing method of the present embodiment, a good interface can be obtained between the n⁺-GaIn (Group III nitride) and p-SiC, so that the interface recombination can be prevented

and the current amplification factor β , which is an important performance indicator in HBT, can be increased.

[0033] As described above, in accordance with the crystal growing technique of the invention, an AlN layer can be formed on the SiC surface through the layer-by-layer growth or step-flow growth immediately after the start of the crystal growth. As a result, the introduction of defects that would be caused in the case of an island growth can be reduced, and a thin film can be grown highly accurately. Thus, improved properties can be obtained by applying the invention to electronic devices utilizing the wide bandgap of SiC or to light-emitting optical devices utilizing a Group III nitride.

[0034] While the invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood that various changes in form and details can be made.

Industrial Applicability

[0035] The crystal growing technique of the invention, whereby a Group III nitride is formed on an SiC surface through a layer-by-layer growth or a step-flow growth, makes it possible to reduce the introduction of defects and to grow a thin film highly accurately. Therefore, improved device properties can be obtained by applying the invention to the production of electronic devices or optical devices in which the wide bandgap of SiC or a Group III nitride is utilized.

Claims

1. A crystal growing method comprising the steps of:

forming a flat and clean SiC surface;
growing AlN under high vacuum by feeding Al and N atoms, wherein feeding of Ga or In as surface control element for controlling the mode of crystal growth of said AlN is started before starting said growing; and **characterized in that** feeding of Ga or In for controlling the mode of crystal growth of said AlN is terminated after said growing is started.

2. The crystal growing method according to claim 1, wherein said SiC surface has an offset angle of 0 to 15° with respect to the (0001)_{Si} or (000-1)_C plane.

3. The crystal growing method according to claim 1 or claim 2, wherein the step of growing said AlN is performed under a vacuum of 10⁻² to 10⁻⁴ Pa.

Patentansprüche

1. Verfahren zum Züchten eines Kristalls, welches die folgenden Schritte umfasst:

Bilden einer flachen und sauberen SiC-Oberfläche;

Züchten von AlN unter hohem Unterdruck durch Zuführen von Al- und N-Atomen, wobei das Zuführen von Ga oder In als Oberflächensteuerungselement zum Steuern des Modus des Kristallwachstums des AlN vor dem Starten des Züchtens gestartet wird; und **dadurch gekennzeichnet, dass** das Zuführen von Ga oder In zum Steuern des Modus von Kristallwachstum des AlN nach Starten des Züchtens beendet wird.

2. Verfahren zum Züchten eines Kristalls nach Anspruch 1, wobei die SiC-Oberfläche einen Versatzwinkel von 0 bis 15° bezüglich der (0001)_{Si}- oder (0001)_C-Ebene aufweist.

3. Verfahren zum Züchten eines Kristalls nach Anspruch 1 oder 2, wobei der Schritt des Züchtens des AlN unter einem Unterdruck von 10⁻² bis 10⁻⁴ Pa durchgeführt wird.

Revendications

1. Procédé de croissance de cristal, comportant les étapes consistant à :

former une surface en SiC plane et propre ;
faire croître de l'AlN sous vide poussé par un apport d'atomes d'Al et N, un apport de Ga ou In comme élément de détermination de surface pour commander le mode de croissance de cristal dudit AlN commençant avant le début de ladite croissance ; et **caractérisé en ce qu'il** est mis fin audit apport de Ga ou In pour commander le mode de croissance de cristal dudit AlN après que ladite croissance a commencé.

2. Procédé de croissance de cristal selon la revendication 1, dans lequel ladite surface en SiC a un angle de décalage de 0 à 15° par rapport au plan (0001)_{Si} ou (000-1)_C.

3. Procédé de croissance de cristal selon la revendication 1 ou la revendication 2, dans lequel l'étape de croissance dudit AlN est exécutée sous un vide de 10⁻² à 10⁻⁴ Pa.

Fig. 1(A)

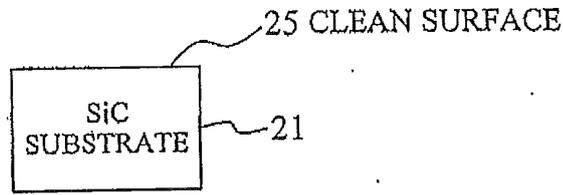


Fig. 1(B)

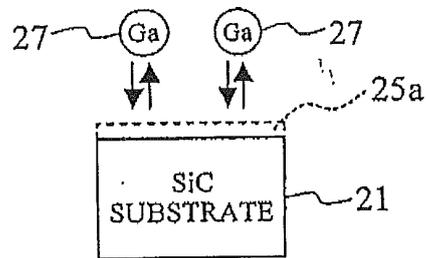


Fig. 1(C)

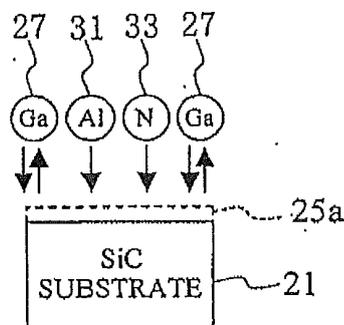


Fig. 1(D)

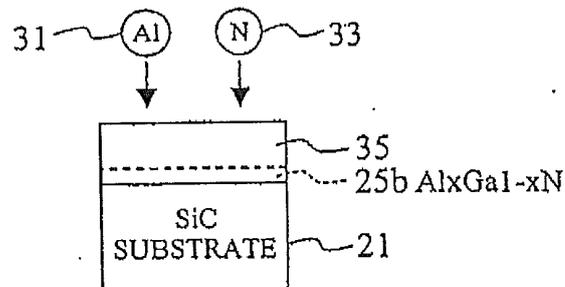


Fig. 2

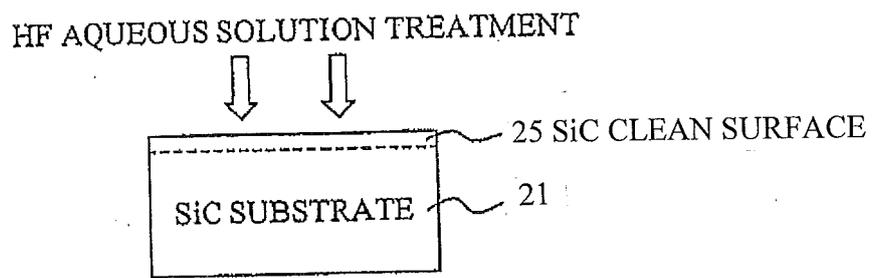


Fig. 3

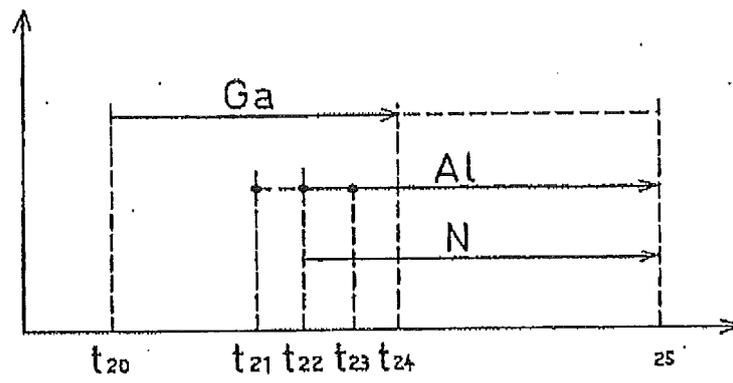


Fig. 4(A)



Fig. 4(B)

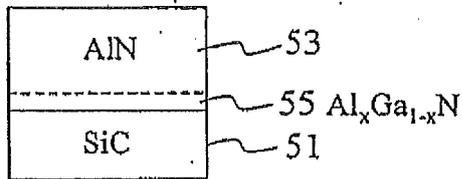


Fig. 4(C)

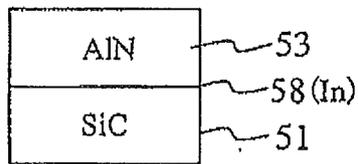


Fig. 4(D)

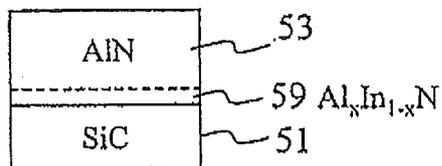


Fig. 5(A)

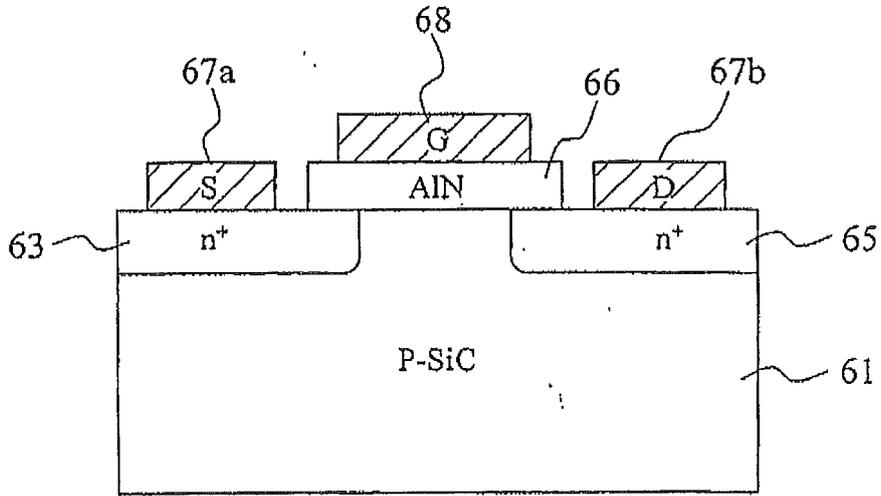


Fig. 5(B)

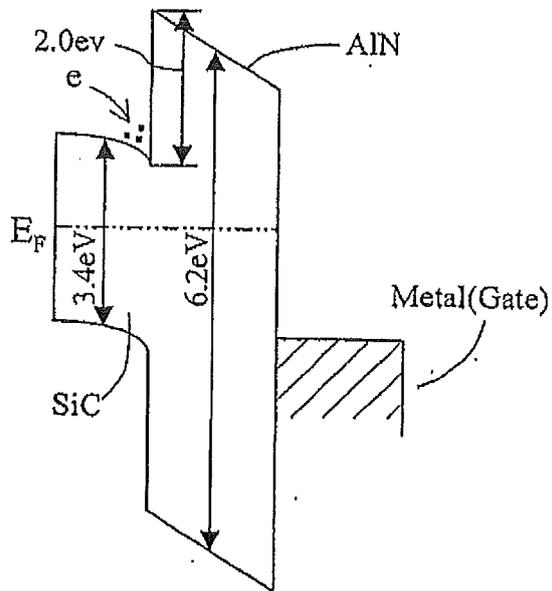


Fig. 6

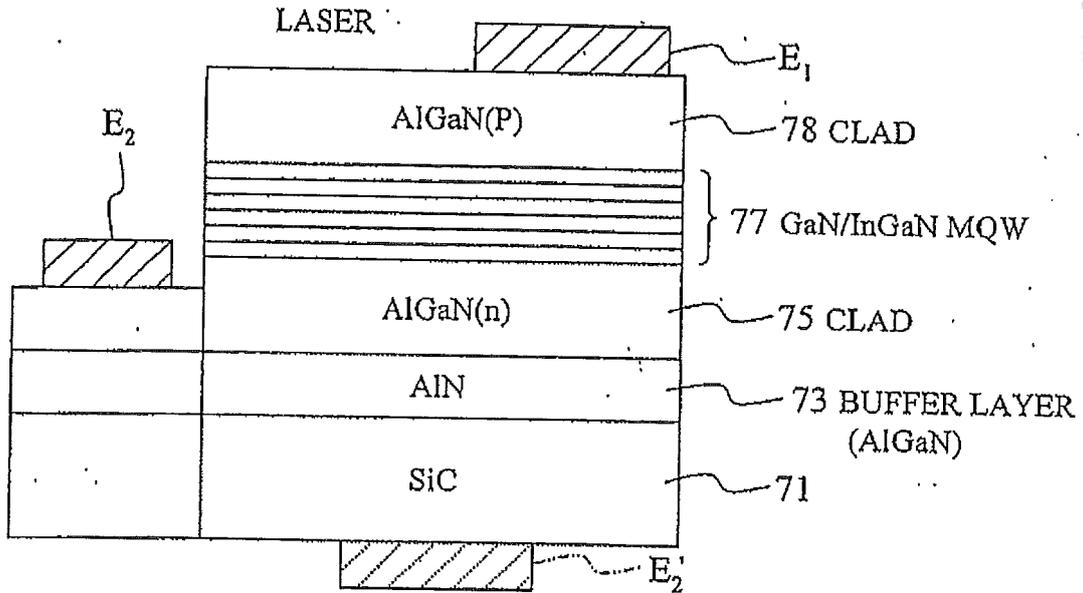
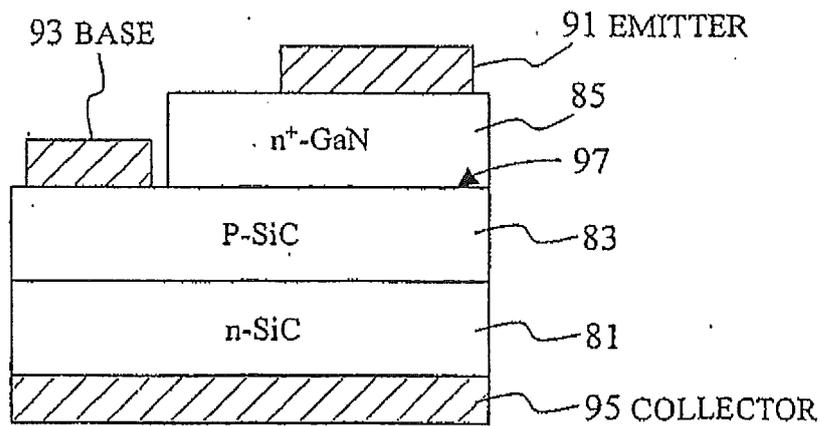


Fig. 7



REFERENCES CITED IN THE DESCRIPTION

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