

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
15 May 2003 (15.05.2003)

PCT

(10) International Publication Number  
WO 03/041137 A1

(51) International Patent Classification<sup>7</sup>: H01L 21/20

(21) International Application Number: PCT/KR02/01799

(22) International Filing Date:  
24 September 2002 (24.09.2002)

(25) Filing Language: Korean

(26) Publication Language: English

(30) Priority Data:  
2001-0068427 5 November 2001 (05.11.2001) KR

(71) Applicant (for all designated States except US): VICHSEL INC. [KR/KR]; 3Fl. JANG Bldg. 92-6, Yangjae1-dong, Seocho-gu, 137-890 Seoul (KR).

(72) Inventor; and

(75) Inventor/Applicant (for US only): KANG, Sang-kyu [KR/KR]; 208-302 Moklyun apt., 1052, Hogae-dong, Dongan-ku, Anyang-City, 431-080 Gyeonggi-do (KR).

(74) Agents: KIM, Dong-jin et al.; 9th Fl. Star Tower. 737, Yeoksam1-dong, Gangnam-gu, 135-984 Seoul (KR).

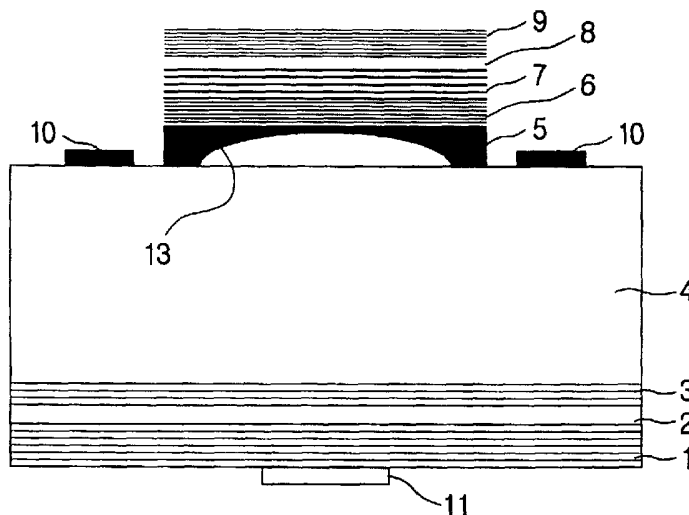
(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:  
— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD OF MANUFACTURING AN InGaNaS COMPOUND SEMICONDUCTOR THIN FILM AND THE THIN FILM MANUFACTURED BY THE SAME



(57) Abstract: Disclosed is a method of manufacturing an InGaNaS compound semiconductor thin film and the thin film manufactured by the same. The method of manufacturing the InGaNaS compound semiconductor thin film used as a structural element of a compound semiconductor device, wherein a plurality of precursors are deposited using a deposition apparatus comprises the steps of preparing at least one metal organic compound containing molecular Ga-N as the precursors, and providing nitrogen atoms from such metal organic compound to a reactor in the deposition apparatus during a deposition process for growth of the InGaNaS film so as to distribute the nitrogen atoms in a predetermined concentration within the InGaNaS thin film. Hence, detachment of nitrogen atoms can be prevented by means of strong bonding strength of Ga(Al,In)-N molecules, whereby the content of nitrogen atoms within the InGaNaS can be effectively regulated under control of inflow of the precursors used for providing the nitrogen atoms.



WO 03/041137 A1

METHOD OF MANUFACTURING AN InGaNAs COMPOUND  
SEMICONDUCTOR THIN FILM AND THE THIN FILM MANUFACTURED BY  
THE SAME

TECHNICAL FIELD

5           The present invention relates, in general, to a method of manufacturing an  
InGaNAs compound semiconductor thin film and the thin film manufactured by the  
same, and more specifically, to a method of manufacturing an InGaNAs compound  
semiconductor thin film of a compound semiconductor capable of introducing ing  
effectively the nitrogen component in a desired concentration to the InGaNAs thin  
10 film from a metal organic compound containing a Ga(Al,In)-N molecule and the  
thin film manufactured by the same.

BACKGROUND ART

15           In recent years, nitride-based semiconductors, which are the Group III-V  
compound semiconductors containing a nitrogen component, have received a great  
deal of attention as new materials for use in an optical communication and electrical  
and electronic fields. Such nitride-based semiconductors are expected to cope with  
technical limitations experienced in the optical and electronics industries due to  
properties of conventional silicon and compound semiconductors, and also to  
improve conventional industries, with development of new industries realizing high  
20 added value.

          Particularly, an InGaNAs/GaAs material system of four novel elements is  
suitable for use as a direct band gap material to emit light within wavelength of  
about 1.3-1.55  $\mu\text{m}$  on a substrate such as GaAs. So, research on application of  
such material to a long-wavelength laser diode (LD) or a long-wavelength surface  
25 emitting semiconductor laser (VCSEL) for an optical light source of an optical  
communication has been vigorously carried out.

          Consequently, according to an embodiment of an InGaNAs thin film  
formation method used at present, the InGaNAs thin film can be fabricated by use of

precursors containing Ga, In, Al, N and As, for instance, four organic reactants of TMIn (trimethyl indium), TMGa (trimethyl gallium),  $\text{NH}_3$  and  $\text{AsH}_3$  through MOCVD (metalorganic chemical vapor deposition) process.

As such, the used MOCVD process is a technique for preparing a thin film by means of a thermal chemical vapor deposition using metal organic compounds. This technique, similar to MBE (molecular beam epitaxy) process, has been under study to achieve growth of very thin crystalline film, manufacture of multilayered structures, control of variously mixed compositions, and mass production of compound semiconductors.

In addition, the MOCVD process has the following advantages: first, a semiconductor device with one heating place comprises a simplified structure and thus can be easily designed as a mass production device; second, a growth rate of the film can be determined by gas inflow, so easily regulating such rate; third, growth of crystals can be performed under control of on-off state of a valve and inflow of each gas; fourth, epitaxial growth can be carried out on an  $\text{Al}_2\text{O}_3$  insulation layer, and selective epitaxial growth can be conducted; fifth, a substrate or a device is not etched because of no introduction of halogenides, such as HCl, during growth reaction.

However, the MOCVD process has the disadvantages of generating large quantities of residual impurities, uncontrollable thickness of crystals, flammable and toxic reaction gases, and expensive raw materials.

Meanwhile, in order to use the InGaNaNs materials as a long-wavelength laser diode (LD) for an optical light source of an optical communication, the concentration of nitrogen atoms (N) inside the InGaNaNs film should be suitably controlled so that the thin film can function with respect to a specific wavelength.

But in the case of fabricating the InGaNaNs compound semiconductor thin film by use of such conventional method and device, when nitrogen atoms are added to the grown InGaNaNs film from  $\text{NH}_3$ , the nitrogen atoms are easily detached from the grown surface due to low solubility of nitrogen to the InGaNaNs film and high equilibrium vapor pressure at 600 °C or higher, whereby it is difficult to provide sufficient nitrogen atoms to the film. Thus, excellent optical properties cannot be conferred on long-wavelength optical devices, such as long-wavelength laser diode

(LD) and long-wavelength VCSEL.

Additionally, since metal organic reactants are present on the grown surface during film growth, the nitrogen component is not located to an original position and the concentration of nitrogen atoms within the film is not increased.

5 Further, nitrogen atoms independently move on the thin film grown surface and are thus misplaced to the Group III position, or form undesirable nitrides, thereby lowering the properties of the device.

Therefore, it is an object of the present invention to alleviate the problems in the prior art and to provide a method of manufacturing an InGaNA<sub>s</sub> compound semiconductor thin film, capable of preventing detachment of nitrogen atoms at  
10 growth temperatures of 600 °C or higher and easily controlling the content of nitrogen atoms by adjustment of the amount of organic reactants containing Ga-N used as a precursor; and the film manufactured by the same.

#### DISCLOSURE OF THE INVENTION

15 In order to accomplish the above object, a method of manufacturing the InGaNA<sub>s</sub> compound semiconductor thin film of the present invention is characterized in that the method of manufacturing the InGaNA<sub>s</sub> compound semiconductor thin film from a plurality of precursors using the deposition apparatus comprises the steps of preparing at least one metal organic compound  
20 containing Ga-N of molecular form as the precursors, and providing nitrogen atoms from such metal organic compound containing Ga-N of molecular form to a reactor of the deposition apparatus during a deposition process for growth of the InGaNA<sub>s</sub> thin film so as to distribute the nitrogen atoms in a predetermined concentration within the InGaNA<sub>s</sub> thin film.

25 As the plurality of precursors used in the present invention, a member selected from the group consisting of TMIn, TEIn, DMIn and DEIn, a member selected from the group consisting of TMGa, TEGa, DMGa and DEGa, and AsH<sub>3</sub> are used, along with the Ga-N molecule-containing metal organic compound which is preferably selected from group of consisting of H<sub>2</sub>GaN<sub>3</sub>, Cl<sub>2</sub>GaN<sub>3</sub>, Ga<sub>2</sub>(NH<sub>3</sub>)<sub>3/2</sub>  
30 and Ga<sub>2</sub>(N(CH<sub>3</sub>)<sub>2</sub>)<sub>6</sub>.

In addition, it is preferred that MOCVD (metalorganic chemical vapor deposition) or MBE (molecular beam epitaxy) apparatus is used as the deposition apparatus.

5 In addition, an InGaNA<sub>s</sub> compound semiconductor thin film formed by the above-mentioned methods is disclosed in the present invention.

Further, a compound semiconductor device provided with the above InGaNA<sub>s</sub> compound semiconductor thin film is disclosed in the present invention.

10 The inventive method is characterized in that the nitrogen atoms are effectively introduced to the film by use of gallium (Ga) and nitrogen (N) in molecular form charged into the reactor. That is to say, the metal organic compound comprising Ga-N in the molecular form is added to the reactor, together with other three organic reactants of TMI<sub>n</sub>, TMGa and AsH<sub>3</sub>, and then subjected to general MOCVD process, yielding the InGaNA<sub>s</sub> thin film. As such, the Ga-N molecules remain in bonded state because of strong bonding strength between  
15 gallium and nitrogen atoms, even though other radicals are decomposed at general reactor temperature (about 700 °C). When such Ga-N molecules reach the growth surface, the gallium component is automatically placed to the Group III position and the nitrogen component is also automatically placed to the Group V position. In other words, since detachment of the nitrogen component is  
20 prevented due to a strong bonding with gallium, quantities of nitrogen atoms can be introduced to the desired position. Further, such Ga-N molecular form is low in mobility to the growth surface and thus formation of nitrides, by-products of the reactions can be prevented.

25 Therefore, the content of nitrogen atoms can be simply, easily and precisely adjusted under the control of inflow of the metal organic compound, in the InGaNA<sub>s</sub> thin film functioning as an important element emitting wavelengths of 1,200-1,600 nm, preferably, 1,310-1,550 nm, from a long-wavelength laser diode for an optical light source of an optical communication system. The optical device having more excellent optical properties can be provided at a low price,  
30 compared to conventional optical devices.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows schematically a structure of gaseous  $H_2GaN_3$  trimer ( $N_2$  portions in  $N_3$  groups are omitted).

FIG. 2 shows schematically a structure of gaseous  $Cl_2GaN_3$  trimer.

FIG. 3 is a cross sectional view showing an illustration of a surface emitting semiconductor device containing an InGaNaNs compound semiconductor thin film of the present invention.

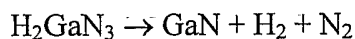
### BEST MODES FOR CARRYING OUT THE INVENTION

In the examples as stated below, deposition of the InGaNaNs thin film is illustrated using some organic reactants containing Ga-N molecules as precursors.

#### EXAMPLE 1

In the present example  $H_2GaN_3$  was used as a precursor providing Ga-N molecules. Such  $H_2GaN_3$  is sensitive to air at room temperature and is a volatile liquid, which is capable of producing vapor at about 40 °C (0.200 Torr) and exists as a trimer form in gas state. The structure of gaseous  $H_2GaN_3$  trimer is shown in FIG. 1, in which  $N_2$  portions of  $N_3$  groups are omitted for clearer understanding the drawing.

Reaction 1

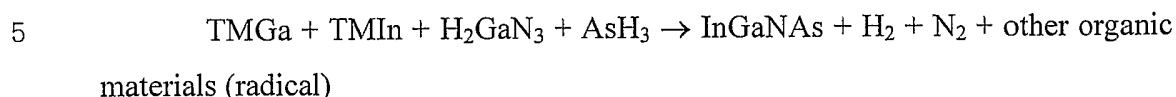


The above reaction 1 shows the decomposition process of  $H_2GaN_3$  to a Ga-N molecule, a hydrogen molecule and a nitrogen molecule. Such reaction was easily performed at relatively low temperature of about 150 °C, and did not produce impurities including carbon, oxygen molecules, etc., upon formation of the Ga-N molecule. Thus, since other materials, exclusive of gallium and nitrogen atoms, were not introduced to the reaction, the content of the nitrogen atom could be precisely controlled.

In the present example, three organic materials including TMGa, TMIIn

and AsH<sub>3</sub>, and a metal organic compound, H<sub>2</sub>GaN<sub>3</sub>, were charged into a reactor and then subjected to MOCVD process, to deposit an InGaNA<sub>s</sub> thin film as represented in the following reaction 2.

Reaction 2



## EXAMPLE 2

In the present example, Cl<sub>2</sub>GaN<sub>3</sub> was used as the precursor for provision of the Ga-N molecule. Such Cl<sub>2</sub>GaN<sub>3</sub> reacts in a trimer form in the temperature  
10            range of 500 to 700 °C. FIG. 2 shows a schematic structure of the expectant Cl<sub>2</sub>GaN<sub>3</sub> trimer.

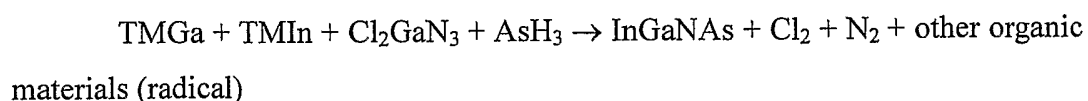
Reaction 3



The above reaction shows the decomposition process of Cl<sub>2</sub>GaN<sub>3</sub> to a Ga-  
15            N molecule, a gallium chloride and a nitrogen molecule. In such reaction, impurities including carbon, oxygen molecules, etc., were not produced upon formation of the Ga-N molecule, similarly to the above example 1. Accordingly, the content of the nitrogen atom could be effectively and precisely controlled through control of inflow of Cl<sub>2</sub>GaN<sub>3</sub> due to no addition of impurities other than  
20            gallium and nitrogen atoms.

In the present example, similar to the example 1, into the reactor, three organic materials of TMGa, TMI<sub>n</sub> and AsH<sub>3</sub>, and a metal organic compound, Cl<sub>2</sub>GaN<sub>3</sub>, were charged and then subjected to MOCVD process, to deposit the InGaNA<sub>s</sub> thin film as represented in the following reaction 4.

25            Reaction 4



In the present InGaNA<sub>s</sub> film formation method, the metal organic

compound including Ga-N of molecular form was utilized, instead of conventionally used  $\text{NH}_3$ , whereby problems related to conventional deposition process were solved and the compound semiconductor device having excellent optical properties could be fabricated, with the use of a conventional device and method.

### EXAMPLE 3

In the present example a compound semiconductor device having the thin film prepared by the inventive method is described with reference to the appended drawing. Such compound semiconductor device is illustrated as an embodiment applied with the InGaNA's compound semiconductor thin film. Thus the present invention is not defined to the present example.

FIG. 3, which is disclosed in Korean Patent Application No. 2001-64829, filed by the present inventors, shows a cross sectional view of vertically integrated surface emitting semiconductor laser device having high output (hereinafter, referred to as "compound semiconductor device").

Referring to FIG. 3, there is shown the compound semiconductor device comprising a first light-emitting structure, a second light-emitting structure, a substrate, an optical lens and at least one pair of electrodes. More specifically, the first light-emitting structure consists of a lower DBR (distributed Bragg reflector) 1 with regard to a first wavelength, an active layer 2 (cavity), a first upper DBR 3 with regard to the first wavelength and a second upper DBR 6 with regard to the first wavelength. The lower DBR 1 and the first upper DBR 3 with regard to the first wavelength are doped to p-type and n-type, respectively, thus having electrical conductivity. An n-type GaAs substrate 4 is located between the first upper DBR 3 and the second upper DBR 6 with regard to the first wavelength. In addition, an optical lens 13 formed by wet-oxidizing an AlGaAs layer 5 is further disposed between the first upper DBR 3 and the second upper DBR 6 with regard to the first wavelength. The second light-emitting structure is composed of a lower DBR 7 with regard to a second wavelength, an active layer 8 (cavity) and an upper DBR 9 with regard to the second wavelength. The second light-



emitting structure is placed on the second upper DBR 6 with regard to the first wavelength. On a circumferential periphery of the n-type GaAs substrate 4 facing the second light-emitting structure, n-type electrodes 10 are positioned, and on the back face of the substrate 4 is positioned a p-type electrode 11, adjacent to the lower DBR 1 of the first wavelength.

The InGaNAs compound semiconductor thin film manufactured by the method of the present invention is formed as the active layer 8 in the compound semiconductor device.

As described in the above examples 1 and 2, the InGaNAs thin film of the compound semiconductor device is fabricated using the metal organic compound including Ga-N of molecular form as the precursor, whereby optical devices, such as LD, VCSEL, etc., having excellent optical properties over the wavelength range of from 1,200 to 1,600 nm can be provided.

In addition, as the precursors, one member selected from among TMIIn (trimethyl indium azide), TEIn (triethyl indium azide), DMIIn (dimethyl indium azide) and DEIn (diethyl indium azide) and the other member selected from among TMGa, TEGa, DMGa and DEGa, can be used, along with AsH<sub>3</sub> and the metal organic compound containing Ga-N of molecular form.

Further, as the precursor of supplying Ga-N molecule, suitable other metal organic compounds, such as Ga<sub>2</sub>(NH<sub>3</sub>)<sub>3/2</sub>, Ga<sub>2</sub>(N(CH<sub>3</sub>)<sub>2</sub>)<sub>6</sub>, etc., may be used, other than the metal organic compound of H<sub>2</sub>GaN<sub>3</sub> and Cl<sub>2</sub>GaN<sub>3</sub> used in the above examples.

The present invention is not defined to the examples using the metal organic compound containing Ga-N of molecular form, and Al-N or In-N metal organic compound which has similar physical and chemical properties to Ga-N molecule may be used to form the InGaNAs film.

Though the InGaNAs thin film was deposited by means of MOCVD method in the above examples, the other appropriate deposition methods, such as MBE (molecular beam epitaxy), can be used to deposit the InGaNAs thin film, within the technical scope of the present invention.

#### INDUSTRIAL APPLICABILITY

As described above, the detachment of nitrogen atoms can be prevented due to strong bonding strength of a Ga-N molecule at high temperatures of up to 700 °C.

5           Thereby, there is the advantage of efficient control of the content of nitrogen atoms within the InGaNAs thin film due to control of inflow of precursors used for providing the nitrogen atoms. This means that the optical devices, such as VCSEL, of the wavelength ranging from 1,200 to 1,600 nm, can be easily fabricated.

10           Additionally, the nitrogen atoms can be provided in the Ga-N molecular form and thus defects caused by nitrogen atom misplacement to the Group III position or formation of undesired nitrides can be prevented. Therefore, the optical devices having very excellent optical properties of the InGaNAs thin film can be provided.

15

CLAIMS

1. A method of manufacturing an InGaNA<sub>s</sub> compound semiconductor thin film from several precursors using a deposition apparatus, comprising the steps of:

5 preparing at least one metal organic compound containing Ga-N of molecular form as the precursors; and

providing nitrogen atoms from said metal organic compound containing Ga-N of molecular form to a reactor of the deposition apparatus during a deposition process for growth of the InGaNA<sub>s</sub> thin film so as to distribute the nitrogen atoms in a predetermined concentration within the InGaNA<sub>s</sub> thin film.

10 2. The method as defined in claim 1, wherein said several precursors further comprise a member selected from the group consisting of TMI<sub>n</sub>, TEI<sub>n</sub>, DMI<sub>n</sub> and DEI<sub>n</sub>, a member selected from the group consisting of TMGa, TEGa, DMGa and DEGa, and AsH<sub>3</sub>, and said metal organic compound containing Ga-N of molecular form is a member selected from the group consisting of H<sub>2</sub>GaN<sub>3</sub>,  
15 Cl<sub>2</sub>GaN<sub>3</sub>, Ga<sub>2</sub>(NH<sub>3</sub>)<sub>3/2</sub> and Ga<sub>2</sub>(N(CH<sub>3</sub>)<sub>2</sub>)<sub>6</sub>.

3. The method as defined in claim 1, wherein said deposition apparatus is a metalorganic chemical vapor deposition apparatus or a molecular beam epitaxy apparatus.

20 4. An InGaNA<sub>s</sub> compound semiconductor thin film manufactured by method of any one of claims 1 to 3.

5. A compound semiconductor device comprising the InGaNA<sub>s</sub> compound semiconductor thin film of claim 4.

1/2

FIG. 1

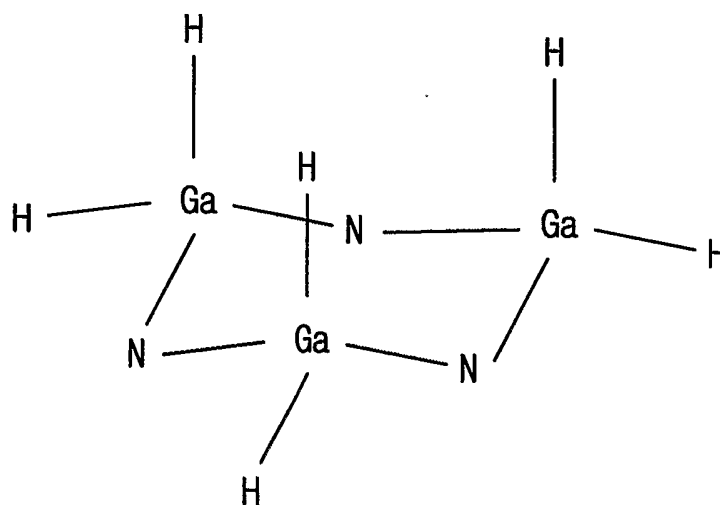


FIG. 2

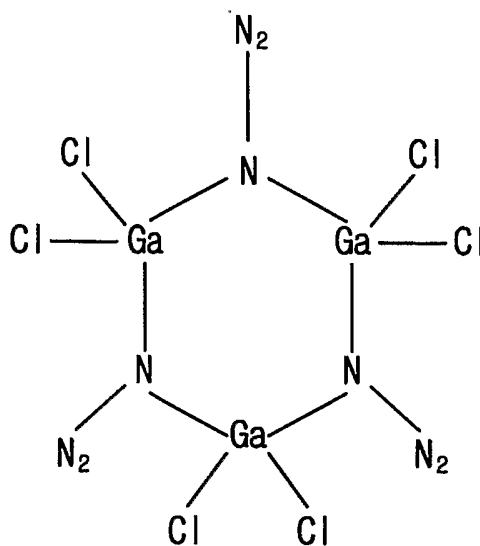
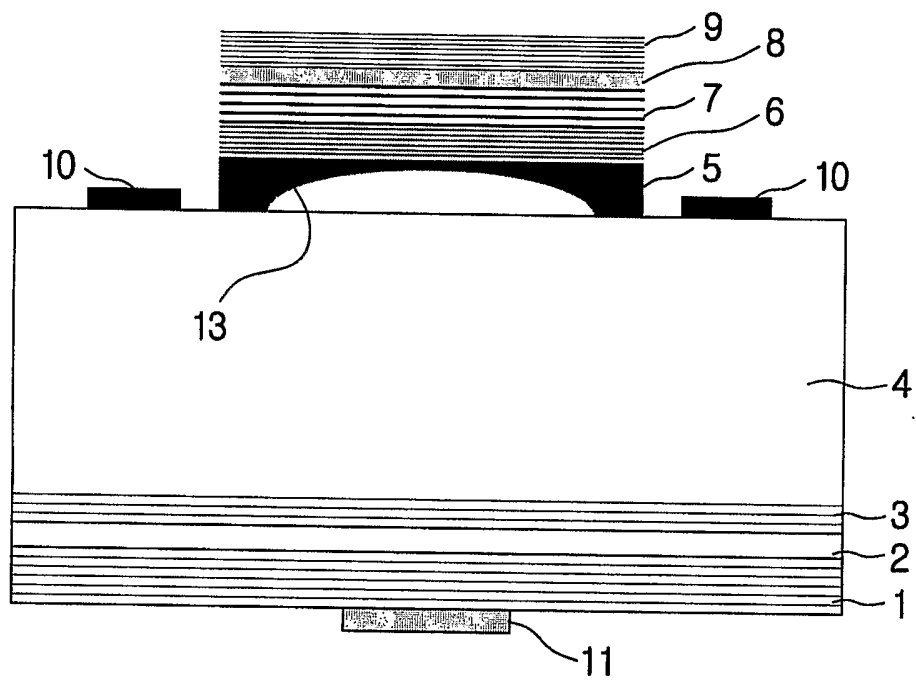


FIG. 3



**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/KR02/01799

**A. CLASSIFICATION OF SUBJECT MATTER**  
**IPC7 H01L 21/20**  
 According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**  
 Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 H)1L 33/00, H01L 5/343, H01S 3/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 USPAT, PAJ, FPD

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, A 10233557 (RICOH CO LTD) 2 September 1997 see abstract, paragraph 12 - 15	1
Y	JP, A 2001094151 (SHARP CORP) 6 April 2001 see abstract, paragraph 88 - 91	1
A	JP, A 10075017 (RICOH CO LTD) 17 March 1998 see the whole document	1


Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents:  
 "A" document defining the general state of the art which is not considered to be of particular relevance  
 "E" earlier application or patent but published on or after the international filing date  
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)  
 "O" document referring to an oral disclosure, use, exhibition or other means  
 "P" document published prior to the international filing date but later than the priority date claimed  
 "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art  
 "&" document member of the same patent family

Date of the actual completion of the international search  
 20 DECEMBER 2002 (20.12.2002)

Date of mailing of the international search report  
 23 DECEMBER 2002 (23.12.2002)

Name and mailing address of the ISA/KR  

 Korean Intellectual Property Office  
 920 Dunsan-dong, Seo-gu, Daejeon 302-701,  
 Republic of Korea  
 Facsimile No. 82-42-472-7140

Authorized officer  
 SUH, Tae Jun  
 Telephone No. 82-42-481-5732  
