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(54) **COMPOUND SEMICONDUCTOR DEVICE  
EPITAXIAL GROWTH SUBSTRATE,  
SEMICONDUCTOR DEVICE, AND  
MANUFACTURING METHOD THEREOF**

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(75) **Inventors: Tatsuya Takamoto, Ikoma-gun (JP);  
Takaaki Agui, Yamatokoriyama-shi (JP)**

(57) **ABSTRACT**

**Correspondence Address:**  
**NIXON & VANDERHYE, PC**  
**901 NORTH GLEBE ROAD, 11TH FLOOR**  
**ARLINGTON, VA 22203 (US)**

A compound semiconductor device epitaxial growth substrate, wherein a semiconductor substrate, a substrate protective layer made of a material that is different from the material of the substrate, a middle layer for making separation of the semiconductor substrate and a compound semiconductor device layer possible, and a compound semiconductor device layer that is formed through epitaxial growth are layered in this order; and a semiconductor device which uses the compound semiconductor device layer that is gained by separating the semiconductor substrate, the substrate protective layer and the middle layer from this compound semiconductor device epitaxial growth substrate; as well as manufacturing methods for these.

(73) **Assignee: Sharp Kabushiki Kaisha, Osaka (JP)**

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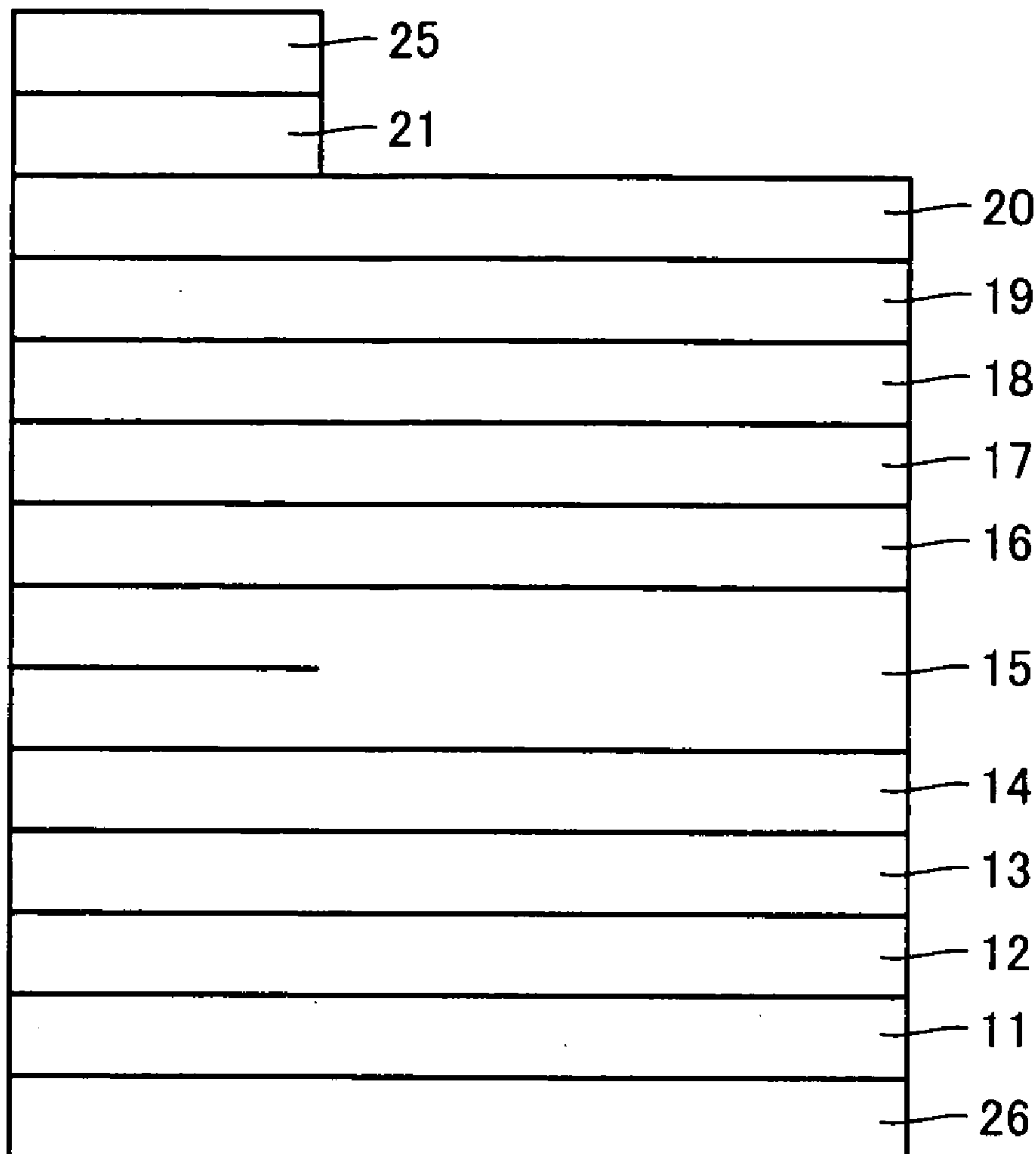


FIG.1

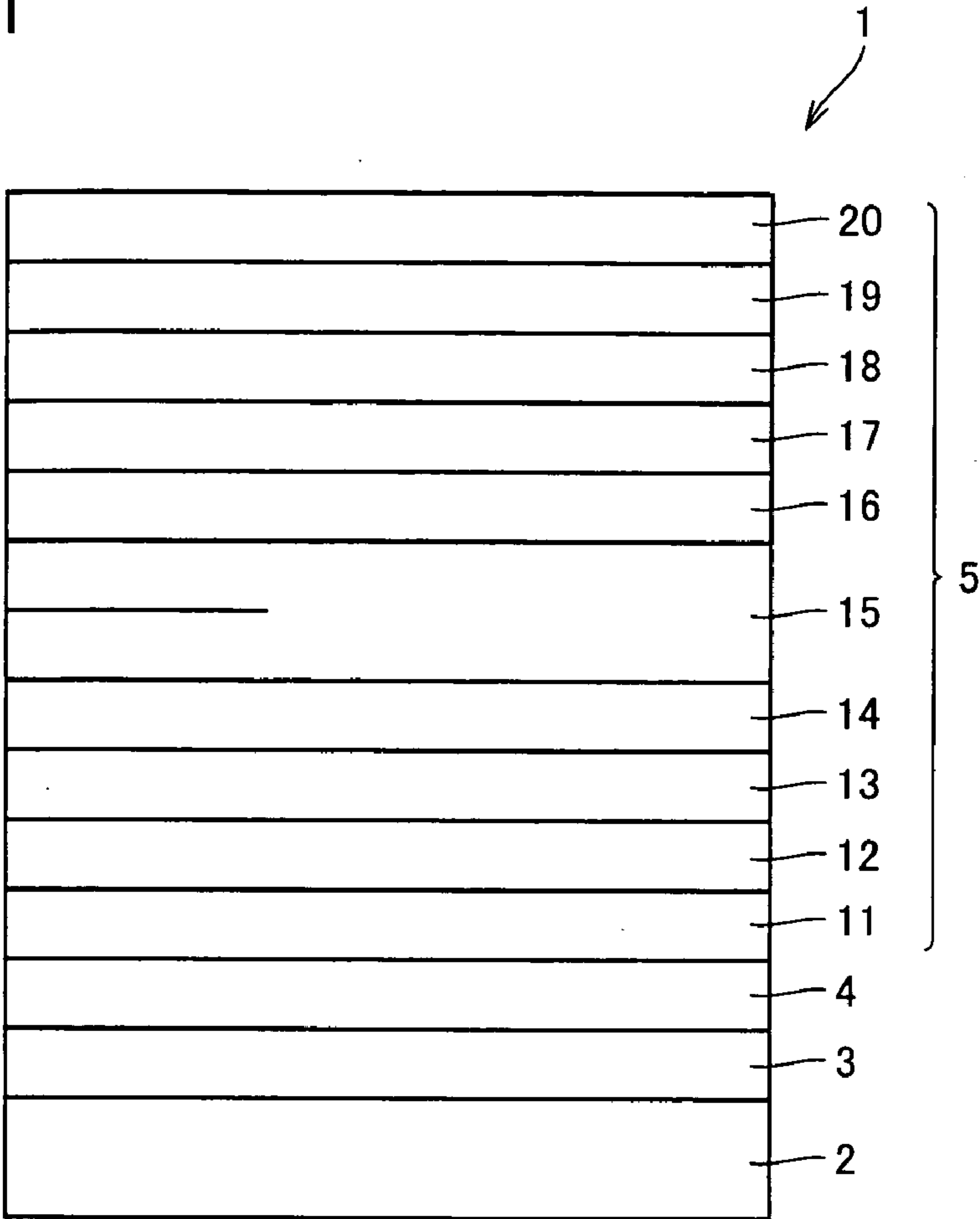


FIG.2

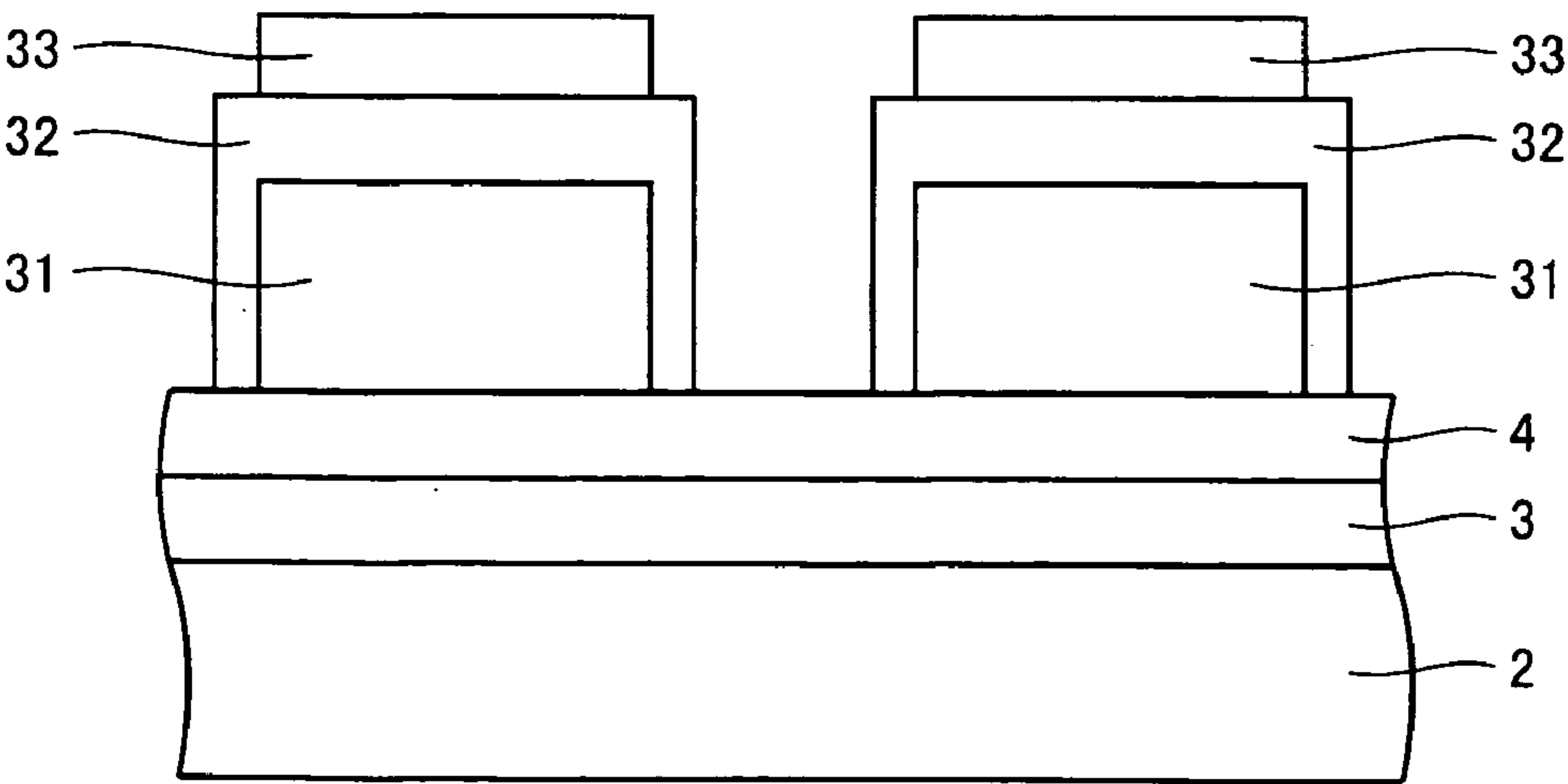
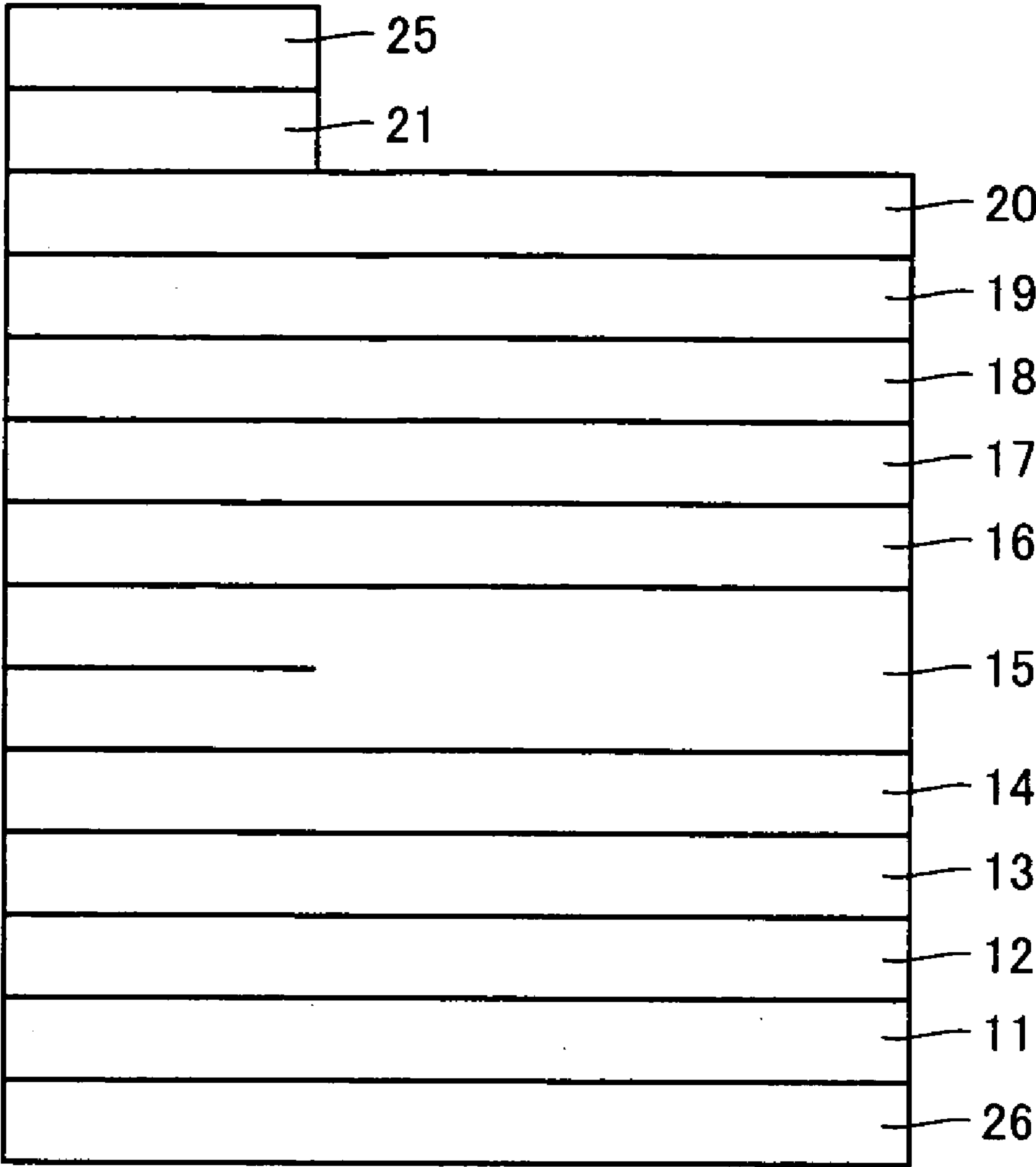


FIG.3





**COMPOUND SEMICONDUCTOR DEVICE  
EPITAXIAL GROWTH SUBSTRATE,  
SEMICONDUCTOR DEVICE, AND  
MANUFACTURING METHOD THEREOF**

[0001] This nonprovisional application is based on Japanese Patent Application No. 2004-262854 filed with the Japan Patent Office on Sep. 9, 2004, the entire contents of which are hereby incorporated by reference.

**BACKGROUND OF THE INVENTION**

[0002] 1. Field of the Invention

[0003] The present invention relates to reduction in cost of a compound semiconductor device epitaxial growth substrate which is manufactured through epitaxial growth, and in particular, to reduction in cost of a semiconductor device such as a high efficiency multijunction-type compound solar cell. In addition, the present invention relates to reduction in cost of a semiconductor substrate that is used for epitaxial growth by reusing the substrate.

[0004] 2. Description of the Background Art

[0005] In the case of a semiconductor device that needs a large amount of epitaxial films having a large area, such as a solar cell, it is required that the material cost is as low as possible. Concerning the material cost, the ratio of the cost of the substrate is large, and therefore, ideas for reducing the material cost by means of techniques such as reusing the substrate after peeling the substrate from the element have been put forth for a long time.

[0006] As for a technology where a semiconductor substrate for epitaxial growth is reused after the substrate is separated from a compound semiconductor device that has been epitaxially grown, a conventional method is known, where pores are formed in, for example, the surface of a substrate, and after that, an element layer is epitaxially grown, and a great number of voids which exist in the portion where the pores have been formed (middle layer) are cut through so as to mechanically separate the substrate from the element layer. According to this method, however, the pores remain on the surface of the substrate, and therefore, flattening or cleaning through surface processing becomes necessary.

[0007] In addition, a conventional method is also known, where an atom displaced layer is formed in a portion that is extremely shallow from the surface of the substrate, by means of ion implantation, and after that, an element layer is epitaxially grown and the atom displaced layer (middle layer) is cut through so as to mechanically separate the substrate from the element layer, and thereby, the substrate is reused. According to this method, however, the surface of the substrate is damaged, and therefore, flattening or cleaning through surface processing becomes necessary.

[0008] Furthermore, a method where an element layer is epitaxially grown after a middle layer that can be selectively etched has been formed on the surface of the substrate and the middle layer is etched and removed, and thereby, the substrate and the element layer are separated from each other through chemical treatment is also known as a conventional technology for reusing a substrate. According to this method, however, a layer that has deteriorated due to a

chemical change remains on the surface of the substrate, and therefore, flattening or cleaning through surface processing, again, becomes necessary.

[0009] As described above, any method which is known as a conventional technology for reusing a substrate has a problem where the surface of the substrate becomes coarse or polluted after the separation, and requires processing for flattening or cleaning, such as polishing on the surface of the substrate, lapping or the like. Therefore, cost becomes high, due to surface processing, and in addition, a problem arises, where the number of times that use is possible is reduced due to reduction in the thickness of the substrate, and the yield is reduced due to cracking of the substrate.

[0010] Here, Electron Lett. 35, p. 1024, by B. Asper et al. (1999), Appl. Phys. Lett. 76, p. 2131, by J. Schermer et al. (2000) and 19<sup>th</sup> European Photovoltaic Solar Energy Conference, 7-11, Jun. 2004, Paris, France, pp. 169-172 by M. M. A. J. Voncken et al. (2004), for example, can be cited as documents that disclose conventional technologies concerning the present technology.

[0011] The present invention is provided in order to solve the aforementioned problems, and an object thereof is to provide a compound semiconductor device epitaxial semiconductor growth substrate where an element layer can be formed through epitaxial growth again after the substrate and the element layer that has been epitaxially grown have been separated from each other without causing an increase in the cost due to surface processing of the substrate, such as polishing or lapping, a reduction in the number of times that use is possible due to reduction in the thickness of the substrate, or a problem of reduction in the yield due to cracking of the substrate, as well as a semiconductor device that uses such a substrate, and a manufacturing method of the same.

**SUMMARY OF THE INVENTION**

[0012] The present invention provides a compound semiconductor device epitaxial growth substrate characterized in that a semiconductor substrate, a substrate protective layer made of a material that is different from the material of the substrate, a middle layer for making-separation of the semiconductor substrate and a compound semiconductor device layer possible, and a compound semiconductor device layer that is formed through epitaxial growth are layered in this order.

[0013] In accordance with this compound semiconductor device epitaxial growth substrate of the present invention, the element layer and the semiconductor substrate can be separated at the middle layer, and thereby, a semiconductor substrate where a flat and clean surface is maintained can be gained, by removing the substrate protective layer on the semiconductor substrate after the separation.

[0014] According to the present invention, it is preferable for the aforementioned substrate protective layer to be removable through etching with an etching selection ratio of no less than 80% against the semiconductor substrate.

[0015] In addition, it is preferable for the aforementioned substrate protective layer according to the present invention to lattice match with the semiconductor substrate.

[0016] In addition, it is preferable for the aforementioned middle layer according to the present invention to be made



of a material that can be etched with a liquid or a gas which does not etch the substrate or the element layer.

[0017] It is preferable for the aforementioned semiconductor substrate to be GaAs and for the substrate protective layer to be  $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ ,  $(\text{AlGa})_{0.5}\text{In}_{0.5}\text{P}$  or  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  ( $x>0.3$ ) in the compound semiconductor device epitaxial growth substrate of the present invention.

[0018] The present invention also provides a semiconductor device which uses a compound semiconductor device layer that is gained by separating the semiconductor substrate, the substrate protective layer and the middle layer from the aforementioned compound semiconductor device epitaxial growth substrate.

[0019] The present invention also provides a manufacturing method of a compound semiconductor device epitaxial growth substrate that includes the steps of: removing a middle layer from a compound semiconductor device epitaxial growth substrate where a semiconductor substrate, a substrate protective layer made of a material that is different from the material of the substrate, a middle layer for making the separation of the semiconductor substrate and a compound semiconductor device layer possible, and a compound semiconductor device layer that is formed through epitaxial etching are layered in this order so as to separate the semiconductor substrate and the compound semiconductor device layer; removing the substrate protective layer through etching so as to expose the surface of the semiconductor substrate; and sequentially growing a substrate protective layer, a middle layer and a compound semiconductor device layer on the exposed semiconductor substrate.

[0020] In addition, the present invention provides a manufacturing method of a semiconductor device, characterized in that a semiconductor device is manufactured using a compound semiconductor device layer that is gained in accordance with the aforementioned manufacturing method of a compound semiconductor device epitaxial growth substrate.

[0021] The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0022] FIG. 1 is a diagram schematically showing a compound semiconductor device epitaxial growth substrate 1 according to one preferable example of the present invention;

[0023] FIG. 2 is a diagram illustrating a manufacturing method of a compound semiconductor device epitaxial growth substrate according to the present invention; and

[0024] FIG. 3 is a diagram schematically showing a solar cell that is gained in accordance with a manufacturing method according to the present invention.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0025] FIG. 1 is a diagram schematically showing a compound semiconductor device epitaxial growth substrate 1 according to one preferable example of the present inven-

tion. Compound semiconductor device epitaxial growth substrate 1 of the present invention has a basic structure where a substrate protective layer 3, a middle layer 4 and a compound semiconductor device layer (element layer) 5 are sequentially layered on a semiconductor substrate 2. Here, "upward direction" of the substrate indicates the direction upward, as opposed to downward, along the thickness of the substrate. Here, "semiconductor device" in the present specification includes a compound semiconductor device, and concretely, a solar cell (a multijunction solar cell where a single or a number of solar batteries from among a GaAs solar cell, an InGaAs solar cell, an InGaP solar cell, an AlInGaP solar cell and an InGaNaAs solar cell are connected to each other through tunnel junctions) and the like can be cited.

[0026] As for semiconductor substrate 2 according to the present invention, conventional materials that have been widely used in the present field can be used without particular limitation as the material for forming the semiconductor substrate. GaAs, Ge, InP, sapphire, Si and the like can be cited as examples of the material for forming this semiconductor substrate 2. In particular, GaAs is preferable, because this allows high quality layers with a low crystal defect density to lattice match and grow for the formation of a high efficiency solar cell element.

[0027] Though the thickness of semiconductor substrate 2 is not particularly limited, it is preferable for it to be  $100\text{ }\mu\text{m}$  to  $10000\text{ }\mu\text{m}$ , and it is more preferable for it to be  $300\text{ }\mu\text{m}$  to  $1000\text{ }\mu\text{m}$ . In the case where the thickness of semiconductor substrate 2 is less than  $100\text{ }\mu\text{m}$ , the substrate tends to easily warp during growth and easily break during handling, whereas in the case where the thickness exceeds  $10\text{ }000\text{ }\mu\text{m}$ , support of the substrate within the device for growth tends to become complicated or heavy, making it difficult to handle.

[0028] Substrate protective layer 3 is formed of a material that is different from that of the aforementioned semiconductor substrate 2, and it is preferable for the material to be removable through etching with an etching selection ratio of no less than 80% (more preferably, no less than 98%) against semiconductor substrate 2. Such an etching selection ratio makes it possible for only substrate protective layer 3 on semiconductor substrate 2 to be efficiently removed through etching after the separation of substrate protective layer 3 and compound semiconductor device epitaxial element layer 5 in accordance with the below described manufacturing method of a compound semiconductor device epitaxial growth substrate of the present invention, and thereby, semiconductor substrate 2 where a flat and clean surface is maintained can easily be collected, so that it can be reused for the manufacture of a compound semiconductor device epitaxial growth substrate.

[0029] In addition, it is preferable for substrate protective layer 3 according to the present invention to lattice match semiconductor substrate 2. This is because, in the case where substrate protective layer 3 lattice matches semiconductor substrate 2, no atomic layers from the surface of the substrate to the vicinity of the protective layer warp, and thus, little damage is caused to the surface of the substrate, and therefore, the number of times of reuse of the substrate can be increased.

[0030] The material that forms substrate protective layer 3 according to the present invention is not particularly limited,



as long as it is different from that of the aforementioned semiconductor substrate **2**, and InGaP, AlGaInP, AlGaAs, GaAsP and the like can be cited as examples when a GaAs substrate is used. In particular,  $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ ,  $(\text{AlGa})_{0.5}\text{In}_{0.5}\text{P}$  or  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  ( $x>0.3$ ) are preferable, because they lattice match the substrate and have an etching selection ratio of no less than 80%.

[0031] It is preferable for the thickness of substrate protective layer **3** to be  $0.01\ \mu\text{m}$  to  $2\ \mu\text{m}$ , and it is more preferable for it to be  $0.05\ \mu\text{m}$  to  $0.5\ \mu\text{m}$ . This is because in the case where the thickness of substrate protective layer is less than  $0.01\ \mu\text{m}$ , the layer is too thin and tends to partially peel during etching, whereas in the case where the thickness exceeds  $2\ \mu\text{m}$ , the cost of epitaxial growth tends to increase.

[0032] Middle layer **4** is formed between substrate protective layer **3** and element layer **5** in order to make the separation of semiconductor substrate **2** and element layer **5** possible, in accordance with the below described manufacturing method of a compound semiconductor device epitaxial growth substrate of the present invention, and it is preferable to form the middle layer of a material which can be etched with a liquid or a gas that does not etch the substrate, the protective layer or the element layer. AlAs,  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  ( $x>0.5$ ), InGaP, AlInGaP and the like can be cited as examples of this material, in the case where the substrate is formed of an appropriate material selected from the above, and the element layer is formed of an appropriate material that is selected from below. In particular, AlAs,  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  ( $x>0.5$ ),  $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$  and  $(\text{AlGa})_{0.5}\text{In}_{0.5}\text{P}$  are preferable. As for the liquid or gas for etching, a hydrofluoric acid based solution, a hydrochloric acid based solution, a sulfuric acid based solution, an ammonium based solution, a potassium hydroxide based solution, a chlorine based gas, a fluorine based gas and the like can be cited as examples.

[0033] It is preferable for the thickness of middle layer **4** to be  $0.003\ \mu\text{m}$  to  $2\ \mu\text{m}$ , and it is more preferable for it to be  $0.005\ \mu\text{m}$  to  $0.1\ \mu\text{m}$ . This is because in the case where the thickness of middle layer **4** is less than  $0.003\ \mu\text{m}$ , a region where the middle layer is not formed tends to form within the surface of the substrate, whereas in the case where the thickness exceeds  $2\ \mu\text{m}$ , the amount of etching increases and the etching rate tends to lower.

[0034] The material of element layer **5** is not particularly limited, as long as it is made up of one or more layers which are formed on the aforementioned middle layer **4** through epitaxial growth and can be formed of a conventionally known appropriate material in accordance with the application. It is preferable for element layer **5** to have a two-layer structure where the two layers are connected via a tunnel junction in the structures of the rear surface electrical field layer, the base layer, the emitter layer and the window layer, in order to gain a highly efficient solar cell. In element layer **5** of the example shown in FIG. 1, a p-InGaP layer, which is a rear surface electrical field layer **11**, a p-GaAs layer, which is a base layer **12**, an n-GaAs layer, which is an emitter layer **13**, and an AlInP layer, which is a window layer **14**, are formed as the first layer structure. In addition, a p-AlInP layer, which is a rear surface electrical field layer **16**, a p-InGaP layer, which is a base layer **17**, an n-InGaP layer, which is an emitter layer **18**, and an AlInP layer, which is a window layer **19**, are formed as the second layer structure on top of the first layer structure with an InGaP

layer and an AlGaAs layer, which make up a tunnel junction layer **15**, in between. Furthermore, an n-GaAs layer, which is a contact layer **20**, is formed as the topmost surface layer. An appropriate thickness of each layer can be selected within a preferable range, in accordance with the function thereof. The layered structure of element layer **5** shown in FIG. 5 is, of course, illustrative, and element layer **5** according to the present invention is not limited to this.

[0035] Compound semiconductor device epitaxial growth substrate **1** of the present invention is provided with substrate protective layer **3** made of a material that is different from the material of the substrate, and formed on semiconductor substrate **2** and middle layer **4** for making the separation of substrate **2** and element layer **5** possible, which are sequentially layered between semiconductor substrate **2** and compound semiconductor device layer **5**, as described above. This compound semiconductor device epitaxial growth substrate **1** of the present invention allows element layer **5** and semiconductor substrate **2** to be separated at middle layer **4**, and thereby, semiconductor substrate where a flat and clean surface is maintained can be gained, by removing substrate protective layer **3** on semiconductor substrate **2** after the separation.

[0036] Compound semiconductor device epitaxial growth substrate **1** of the present invention that is provided with the aforementioned structure can be manufactured in accordance with, for example, the following procedure.

[0037] First, a vertical type MOCVD device is used to sequentially grow and layer substrate protective layer **3** and middle layer **4** on semiconductor substrate **2**. In the case where, for example, a GaAs substrate is used as semiconductor substrate **2**, an InGaP layer is formed as substrate protective layer **3**, and an AlAs layer is formed as middle layer **4**. TMI (trimethyl indium), TMG and  $\text{PH}_3$  (phosphine) can be used as the materials for the growth of the InGaP layer, and in addition, TMA (trimethyl aluminum) and  $\text{AsH}_3$  (arsine) can be used as the materials for the growth of the AlAs layer.

[0038] Furthermore, element layer **5** is epitaxially grown on top of this. In the case where element layer **5** which has a layered structure as in the example shown in FIG. 1 is formed, a p-InGaP layer, which is rear surface electrical field layer **11**, a p-GaAs layer, which is base layer **12**, an n-GaAs layer, which is emitter layer **13**, and an AlInP layer, which is window layer **14**, are formed as the first layer structure. In addition, a p-AlInP layer, which is rear surface electrical field layer **16**, a p-InGaP layer, which is base layer **17**, an n-InGaP layer, which is emitter layer **18**, an AlInP layer, which is window layer **19**, and an n-GaAs layer, which is contact layer **20**, are sequentially formed and layered on top of the first layer structure as the second layer structure, with an InGaP layer and an AlGaAs layer, which make up tunnel junction layer **15**, in between. TMI (trimethyl indium), TMG (trimethyl gallium) and  $\text{PH}_3$  (phosphine) can be used as the materials for the growth of the InGaP layers, and TMG and  $\text{AsH}_3$  (arsine) can be used as the materials for the growth of the GaAs layers, in the same manner as in the above. In addition, TMA (trimethyl aluminum), TMI and  $\text{PH}_3$  can be used as the materials for the growth of the AlInP layers.  $\text{SiH}_4$  (mono-silane) can be used as an impurity for the formation of n-type layers, and DEZn can be used as an impurity for the formation of p-type layers during the growth of all of the



GaAs layers, InGaP layers and AlInP layers. In addition, TMI, TMG and AsH<sub>3</sub> can be used as the materials, and CBr<sub>4</sub> (carbon tetrabromide) can be used as a p-type impurity for the growth of the AlGaAs layer that forms the tunnel junction. In this manner, the compound semiconductor device epitaxial growth substrate **1** having a structure as in the example shown in **FIG. 1** can be manufactured.

[0039] It is preferable for the temperature for growing layers other than the tunnel junction layer to be within a range from 600° C. to 700° C., in order to increase the lifetime of minor carriers, while it is preferable for the temperature for growing the tunnel junction layer to be within a range from 500° C. to 600° C., in order to prevent re-vaporization of the impurity, so that the impurity can be doped at a high concentration.

[0040] **FIG. 2** is a diagram illustrating a manufacturing method of a compound semiconductor device epitaxial growth substrate according to the present invention, and **FIG. 3** is a diagram schematically showing a solar cell as one example of a semiconductor device that is gained in accordance with the manufacturing method of the present invention. The present invention also provides a manufacturing method of a compound semiconductor device epitaxial growth substrate that includes the steps of: removing middle layer **4** from compound semiconductor device epitaxial growth substrate **1** which is provided with semiconductor substrate **2**, substrate protective layer **3** made of a material that is different from the material of the substrate and formed on semiconductor substrate **2**, and compound semiconductor device layer **5** that is formed on substrate protective layer **3** through epitaxial growth, and which further has middle layer **4** for making the separation of substrate **2** and element layer **5** possible between substrate protective layer **3** and compound semiconductor device layer **5**, so that the semiconductor substrate and the compound semiconductor device layer are separated; removing the substrate protective layer through etching so that the surface of semiconductor substrate **2** is exposed; and sequentially growing substrate protective layer **3**, middle layer **4** and compound semiconductor device layer **5** on the exposed semiconductor substrate **2**.

[0041] Prior to implementing the manufacturing method of a compound semiconductor device epitaxial growth substrate of the present invention, a process is carried out on element layer **5** of compound semiconductor device epitaxial growth substrate **1** having, for example, a structure as shown in **FIG. 1**, that has been prepared as described above so that a cell precursor (precursor of a solar cell) is formed. First, a GaAs layer **21** is formed on contact layer **20** of compound semiconductor device epitaxial growth substrate **1** shown in **FIG. 1**, and after that, a surface electrode **25** having a desired pattern is formed. In the formation of surface electrode **25**, first, a resist where windows are created in a desired electrode pattern form in accordance with a photolithographic method, for example, is applied, and the substrate is placed in a vacuum vapor deposition device so as to form a resist, and after that, a layer (for example, 100 nm) made of Au that includes 12% of Ge, for example, is formed in accordance with a resistance heating method, and then, an Ni layer (for example, 20 nm) and an Au layer (for example, 5000 nm) are sequentially formed in accordance with an EB vapor deposition method, and thus,

the electrode is formed with a desired pattern in accordance with, for example, a lift-off method.

[0042] Next, surface electrode **25** is used as a mask, and the portion of GaAs layer **21** where surface electrode **25** is not formed is etched using, for example, an alkaline solution. Subsequently, a resist with windows opened in a mesa-etching pattern is formed in accordance with a photolithographic method, and the epitaxial layer in the portions where windows are open is etched with an alkaline solution and an acid solution, so that middle layer **4** is exposed (element layer **5** that remains after etching and where surface electrode **25** is formed is referred to as “cell precursor **31**”).

[0043] Next, support substrates **33** made of plastic are made to adhere to cell precursors **31** after wax **32** has been applied to the surface of cell precursors **31**, so as to form the structure shown in **FIG. 2**. Apiezon wax, for example, is appropriate for use as wax **32**. In addition, plates formed of glass, ceramics or Si having high chemical proof properties, for example, can be used as support substrates **33**. Support substrates **33** can be made adherent using, for example, a removable wax or resist.

[0044] The structure of **FIG. 2** is formed in this manner, and after that, the aforementioned manufacturing method of a compound semiconductor device epitaxial growth substrate is implemented according to the present invention. Namely, in the initial step, middle layer **4** is first removed so that semiconductor substrate **2** and compound semiconductor device layer **5** (cell precursor **31** in the example shown in **FIG. 2**) are separated. The structure shown in **FIG. 2** is immersed in a hydrofluoride solution, and thereby, removal of middle layer **4** can be carried out, by etching middle layer **4**. Each cell precursor **31** after the separation can be formed into a structure (solar cell) as shown in **FIG. 3**, by forming electrode (rear surface electrode) **26** in accordance with a method such as vapor deposition, sputtering, electrolytic plating, non-electrolytic plating, ion plating, spraying, adhesion or printing, and after that, melting wax at a high temperature so as to separate the precursor from the support substrate, and then, immersing the precursor in an organic solvent so as to remove wax **32**.

[0045] In the next step, substrate protecting layer **3** is removed from semiconductor substrate **2** through etching, so that the surface of semiconductor substrate **2** is exposed. Semiconductor substrate **2** that is gained in this manner has a flat and clean substrate surface, unlike conventional substrates. As described above, substrate protective layer **3** is preferably selected so as to be removable through etching at an etching selection ratio of no less than 80% against the semiconductor substrate, and thereby, a flat and clean substrate surface can be easily gained without causing damage to the surface of the substrate. Etching of substrate protective layer **3** can be carried out with an appropriate etching solution under appropriate conditions, in accordance with the material that forms the substrate protective layer. In the case where, for example, an InGaP layer is used as substrate protective layer **3**, as shown in **FIG. 1**, substrate protective layer **3** can be removed through etching, by immersing the substrate in an HCl solution.

[0046] After that, substrate protective layer **3**, middle layer **4** and compound semiconductor device layer **5** are sequentially grown on the exposed semiconductor substrate **2**. At



this time, it is preferable to provide several nm or more of the same material as the substrate as a buffer layer between the substrate and the substrate protective layer in a conventional process through epitaxial growth. Before carrying out this step, it is preferable to rinse semiconductor substrate **2** with ultra pure water, and after that, dry it by means of  $N_2$  blowing. In addition, in a conventional process, before the epitaxial growth, it is preferable to etch the substrate by approximately several nm from the surface of the substrate with the solution with which the substrate is etched. The formation of substrate protective layer **3**, middle layer **4** and compound semiconductor device layer **5** may be carried out in the same manner as described above. Compound semiconductor device epitaxial growth substrate **1** having a structure as shown in **FIG. 1** is manufactured again using semiconductor substrate **2** that has been collected as described above. According to the manufacturing method of a compound semiconductor device epitaxial growth substrate of the present invention, this cycle is repeated, so that semiconductor substrate **2** is reused many times, and thereby, solar cells as shown in **FIG. 3** can be manufactured.

[0047] Here, as described above, the present invention also provides a semiconductor device (for example, a solar cell as that shown in **FIG. 3**) which uses a compound semiconductor device layer that is gained by separating the semiconductor substrate, the substrate protective layer and the middle layer from the compound semiconductor device epitaxial growth substrate of the present invention.

[0048] In addition, the scope of the present invention also includes a manufacturing method of a semiconductor device, characterized in that a semiconductor device is manufactured using a compound semiconductor device using that is gained in accordance with the aforementioned manufacturing method of a compound semiconductor device epitaxial growth substrate of the present invention.

#### EXAMPLES

[0049] In the following, the present invention is more concretely described, but the present invention is not limited to these examples.

##### Example 1

[0050] First, the layer structure shown in **FIG. 1** was fabricated on an n-type GaAs substrate, which is semiconductor substrate **2**, by means of an MOCVD method. That is to say, a GaAs substrate ( $1E18\text{ cm}^{-3}$ , Si doped) having a diameter of 50 mm was placed in a vertical type MOCVD device, and first,  $0.1\text{ }\mu\text{m}$  of a  $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$  layer was formed as substrate protective layer **3**. Subsequently,  $0.02\text{ }\mu\text{m}$  of an AlAs layer was formed as middle layer **4** for the separation through etching,  $0.1\text{ }\mu\text{m}$  of an InGaP layer was grown, for stopping etching, and layers were sequentially grown for a solar cell layer structure, and thus, element layer **5** was formed.

[0051] The temperature for growth was  $700^\circ\text{C}$ ., and TMG (trimethyl gallium) and  $\text{AsH}_3$  (arsine) were used as the materials for the growth of the GaAs layers. TMI (trimethyl indium), TMG and  $\text{PH}_3$  (phosphine) were used as the materials for the growth of the InGaP layers.  $\text{SiH}_4$  (mono-silane) was used as an impurity for the formation of an n-type layer, and DEZn was used as an impurity for the formation of a p-type layer during the growth of all of GaAs, InGaP and

AlInP layers. TMI, TMG and  $\text{AsH}_3$  were used as the materials for the growth of the AlGaAs layer that forms the tunnel junction, where  $\text{CBr}_4$  (carbon tetrabromide) was used as a p-type impurity.

[0052] A resist where windows were open for an electrode pattern was formed on the contact layer (n-type GaAs layer) on the surface of the epitaxial layer in accordance with a photolithographic method, the substrate was placed in a vacuum vapor deposition device, so that a layer (100 nm) made of Au that contains 12% of Ge was formed on the formed resist in accordance with a resistance heating method, and after that, an Ni layer (20 nm) and an Au layer (5000 nm) were sequentially formed in accordance with an EB vapor deposition method. After that, a surface electrode in a desired pattern was formed in accordance with a lift-off method. Next, the surface electrode was used as a mask, and the portion of the GaAs contact layer where the electrode was not formed was etched with an alkaline solution.

[0053] Subsequently, a resist with windows opened in a mesa etching pattern was formed in accordance with a photolithographic method, and the portions of the epitaxial layer where the windows were open were etched with an alkaline solution and an acid solution, so that the AlAs layer, which is middle layer **4**, was exposed.

[0054] Next, wax was applied and a plastic plate was made to adhere to the light receiving surface of the cell, excluding the mesa etching portion, so that a cross sectional structure as that shown in **FIG. 2** was fabricated. After that, the wafer was immersed in an Hf solution, and the AlAs middle layer beneath the cell layer was etched and removed from the mesa etching portion, and thereby, the cell layer and the substrate were separated. After that, an electrode was formed on the rear surface of each cell, and then, the wax was removed, so that a solar cell was completed in the first process, so as to have a structure as that shown in **FIG. 3**. The size of the cell was  $10\text{ mm}\times 10\text{ mm}$ , and 12 cells were fabricated from a substrate having a diameter of 50 mm.

[0055] After that, the InGaP layer, which is substrate protective layer **3**, formed on the substrate side, was removed through etching with HCl, so that the surface of the GaAs substrate was exposed. The substrate was rinsed with ultra pure water, and after that, dried through  $N_2$  blowing, placed into the MOCVD device again, and the structure of **FIG. 1** was again epitaxially grown. The above described process was carried out again, and a solar cell was completed in the second process, so as to have the same structure as that shown in **FIG. 2**.

[0056] Evaluation of cell characteristics was carried out with a solar simulator which radiates AM 1.5G standard solar beams, so as to measure the current voltage characteristics at the time of radiation of the beams, and the short circuit current, the open voltage and the conversion efficiency were measured. Table 1 shows a comparison of various characteristics between the cells that were fabricated in the first and second processes.

TABLE 1

	Voc(V)	Isc(mA)	F.F.	Eff(%)
FIRST PROCESS	2.41	13.7	0.85	28.2
SECOND PROCESS	2.42	13.6	0.85	28.2

[0057] Characteristics which were essentially the same as those of the cells of the first process were gained in the cells



of the second process, which were fabricated on the reused substrate, and thus, it was confirmed that substrates can be reused effectively according to the present invention.

[0058] Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

What is claimed is:

1. A compound semiconductor device epitaxial growth substrate, wherein

a semiconductor substrate,

a substrate protective layer made of a material that is different from the material of the substrate,

a middle layer for making separation of the semiconductor substrate and a compound semiconductor device layer possible, and

a compound semiconductor device layer that is formed through epitaxial growth are layered in this order.

2. The compound semiconductor device epitaxial growth substrate according to claim 1, wherein

said substrate protective layer can be removed through etching at an etching selection ratio of no less than 80% against the semiconductor substrate.

3. The compound semiconductor device epitaxial growth substrate according to claim 1, wherein

said substrate protective layer lattice matches the semiconductor substrate.

4. The compound semiconductor device epitaxial growth substrate according to claim 1, wherein

said middle layer is made of a material which can be etched with a liquid or a gas that does not etch the substrate or the element layer.

5. The compound semiconductor device epitaxial growth substrate according to claim 1, wherein

said semiconductor substrate is GaAs, and the substrate protective layer is  $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ ,  $(\text{AlGa})_{0.5}\text{In}_{0.5}\text{P}$  or  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  ( $x>0.3$ ).

6. A semiconductor device which uses the compound semiconductor device layer that is gained by separating the semiconductor substrate, the substrate protective layer and the middle layer from the compound semiconductor device epitaxial growth substrate according to claim 1.

7. A manufacturing method of a compound semiconductor device epitaxial growth substrate, comprising the steps of:

removing a middle layer for making possible separation of a semiconductor substrate and a compound semiconductor device layer that is formed through epitaxial growth from a compound semiconductor device epitaxial growth substrate, wherein the semiconductor substrate, a substrate protective layer made of a material that is different from the material of the substrate, the middle layer, and the compound semiconductor device layer are layered in this order, so that the semiconductor substrate and the compound semiconductor device layer are separated;

removing the substrate protective layer through etching so as to expose the surface of the semiconductor substrate; and

sequentially growing a substrate protective layer, a middle layer and a compound semiconductor device layer on the exposed semiconductor substrate.

8. A manufacturing method of a semiconductor device, wherein

a semiconductor device is manufactured using the compound semiconductor device layer that is gained in accordance with the manufacturing method of a compound semiconductor device epitaxial growth substrate according to claim 7.

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