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(54) **METHOD FOR GROWING NON-POLAR M-PLANE EPITAXIAL LAYER OF WURTZITE SEMICONDUCTORS ON SINGLE CRYSTAL OXIDE SUBSTRATES**

(75) Inventors: **Li Chang**, Yonghe City (TW); **Yen-Teng Ho**, Tainan City (TW)

(73) Assignee: **National Chiao Tung University**, Hsinchu (TW)

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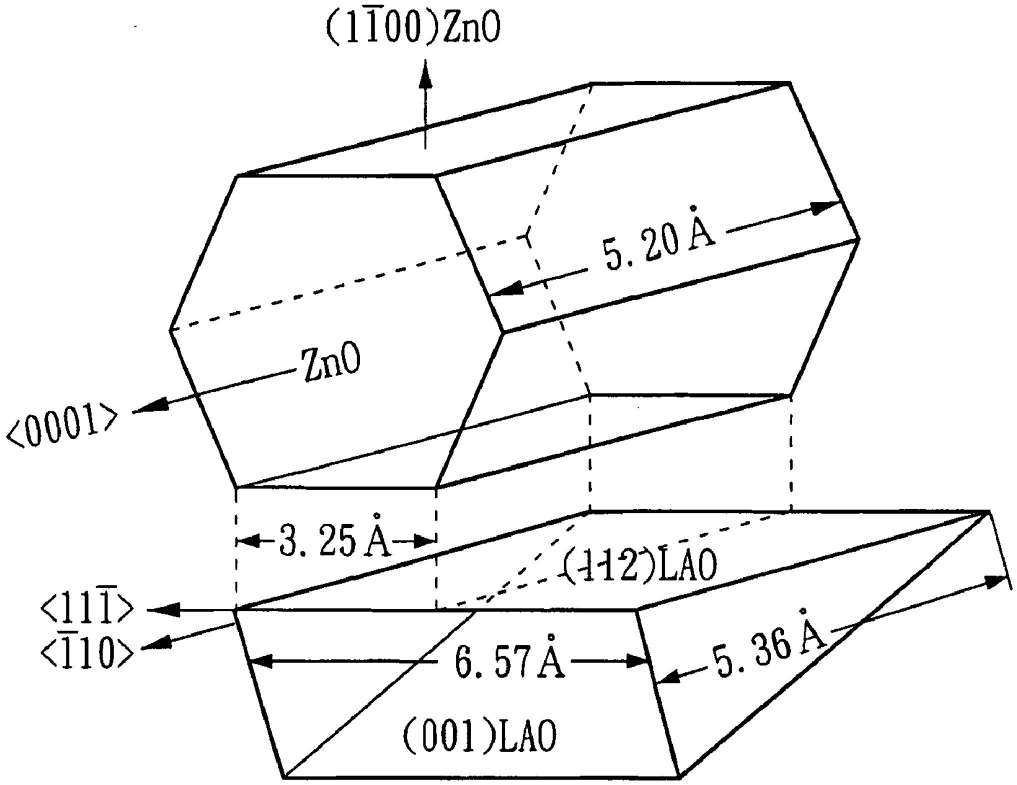
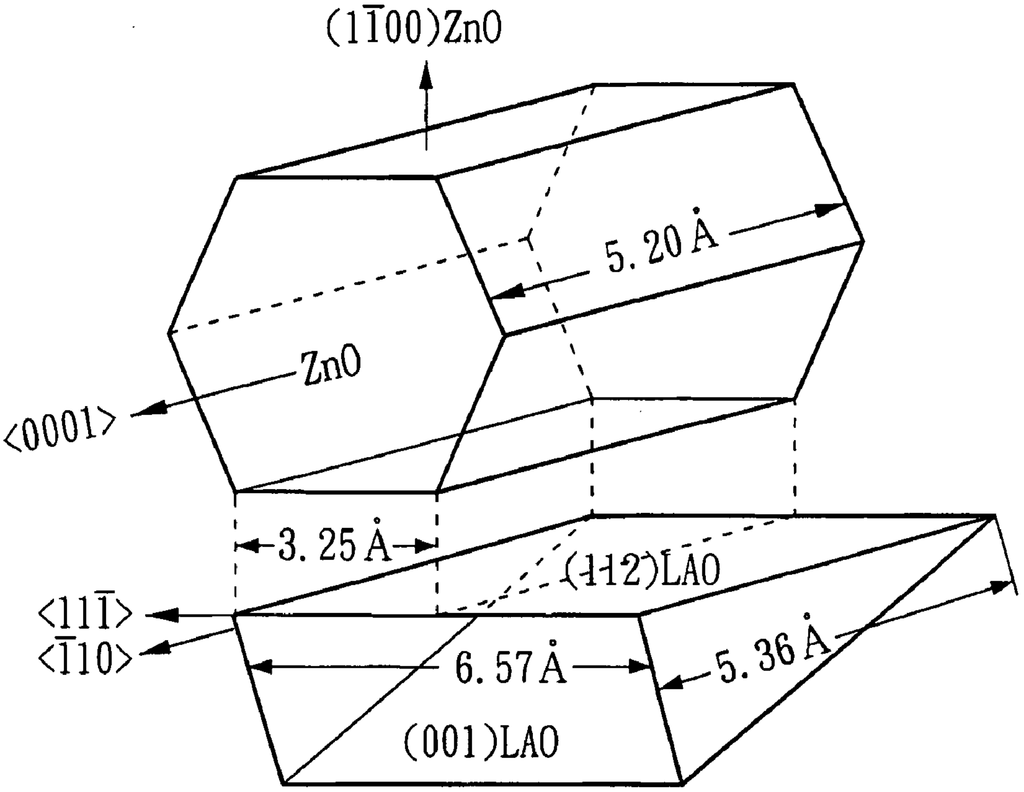
(57) **ABSTRACT**

The present invention relates to a method for growing a non-polar m-plane epitaxial layer on a single crystal oxide substrate, which comprises the following steps: providing a single crystal oxide with a perovskite structure; using a plane of the single crystal oxide as a substrate; and forming an m-plane epitaxial layer of wurtzite semiconductors on the plane of the single crystal oxide by a vapor deposition process. The present invention also provides an epitaxial layer having an m-plane obtained according to the aforementioned method.

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ZnO
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(-1-12)LAO
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6.57 Å
5.36 Å
(001)LAO

FIG. 1

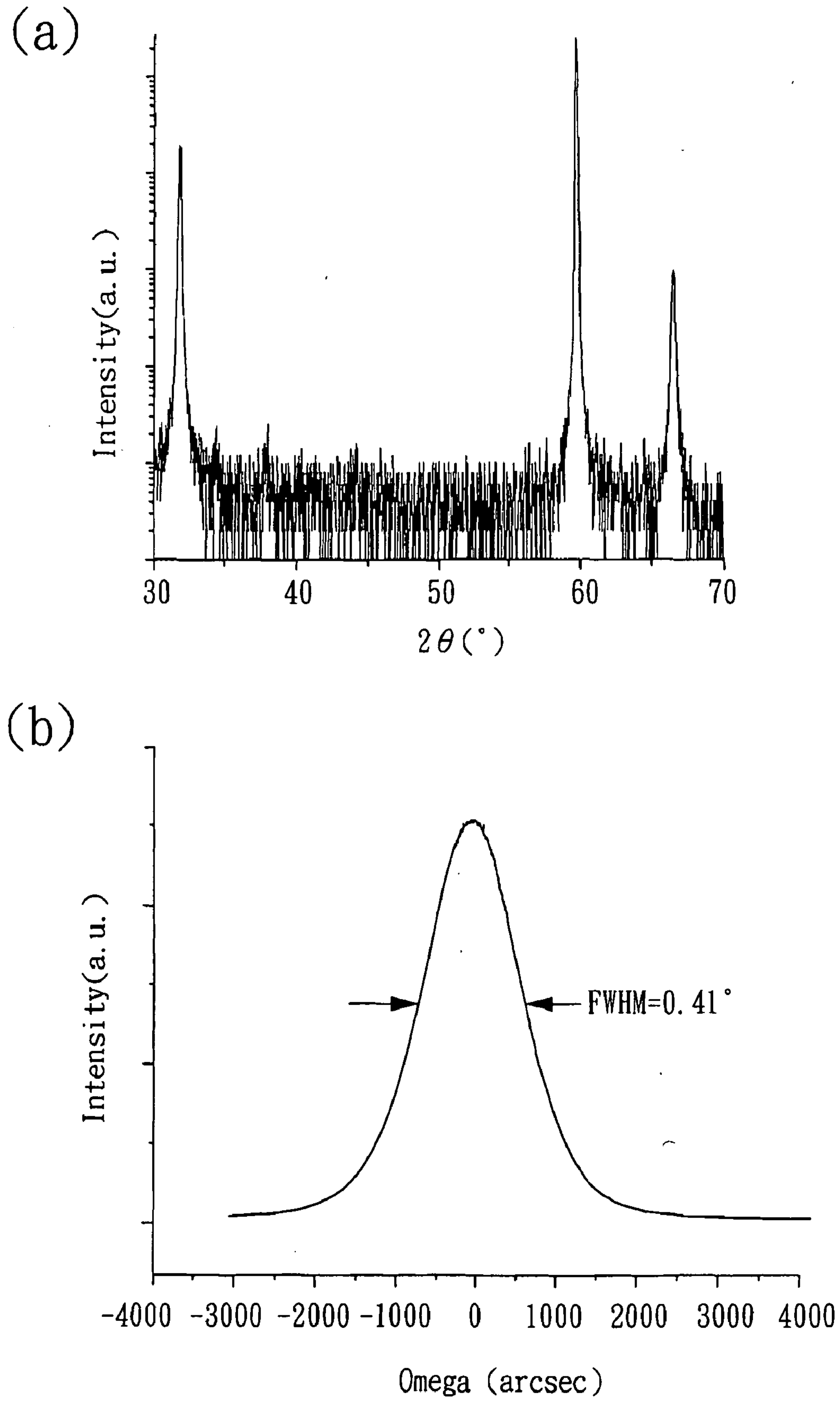
(a)
Intensity(a. u.)
30
40
50
60
70
2θ(°)
(b)
Intensity(a. u.)
FWHM=0. 41°
-4000
-3000
-2000
-1000
0
1000
2000
3000
4000
Omega (arcsec)

FIG. 2

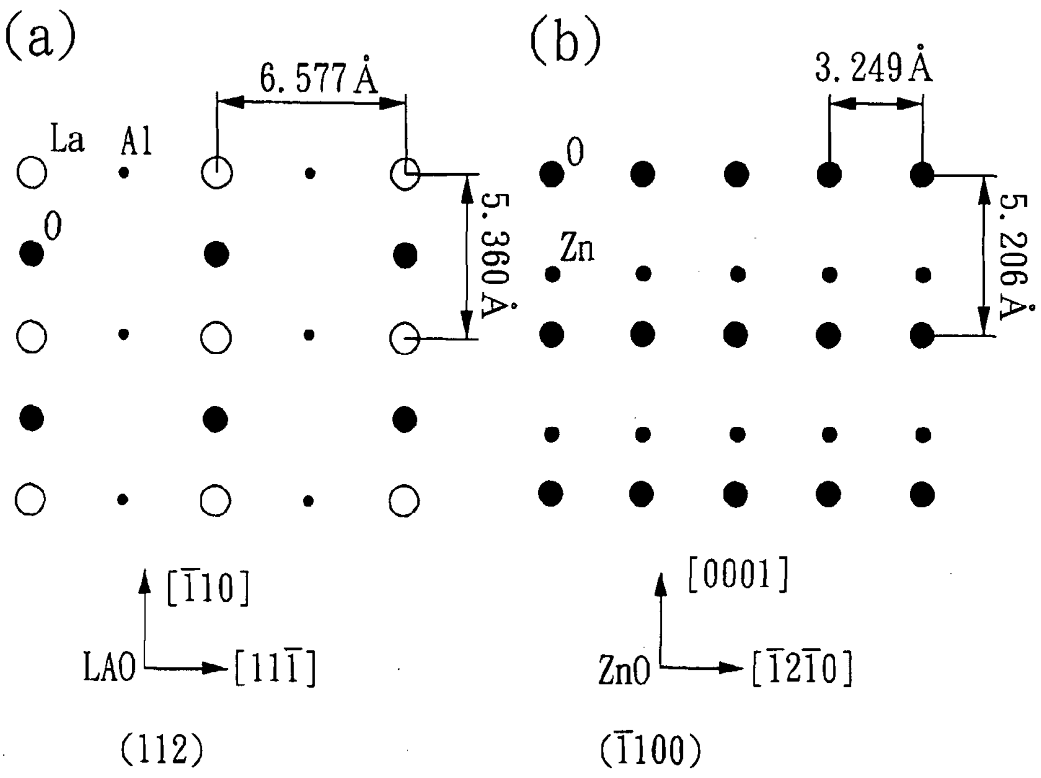
(a)
6. 577 Å
La
Al
0
5. 360 Å
$[\bar{1}10]$
LAO
$[11\bar{1}]$
(112)
(b)
3. 249 Å
0
Zn
5. 206 Å
[0001]
Zn0
$[\bar{1}2\bar{1}0]$
$(\bar{1}100)$

FIG. 3

METHOD FOR GROWING NON-POLAR M-PLANE EPITAXIAL LAYER OF WURTZITE SEMICONDUCTORS ON SINGLE CRYSTAL OXIDE SUBSTRATES

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to a method for growing a non-polar m-plane epitaxial layer of wurtzite semiconductors on a single crystal oxide substrate and, more particularly, to a method for growing a non-polar m-plane epitaxial layer of ZnO or III-nitrides with the nature of both low lattice mismatch and good thermal stability. The present invention also provides an epitaxial layer having a non-polar m-plane obtained according to the aforementioned method.

[0003] 2. Description of Related Art

[0004] Currently, GaN and other III-nitrides have attracted considerable interest for its successful applications on blue-to-UV light solid-state electronic devices and laser diodes. The crystal structures of these nitrides belong to a hexagonal wurtzite structure, so the crystals of these nitrides are grown along a c-axis direction [0001]. However, some studies found that a polarization effect along the c-axis may occur in c-axis GaN, due to the internal electric fields induced by the orientation of Ga and N atoms. The internal fields not only result in the shift of the valence bands and the conduction bands, but also reduce the internal quantum efficiencies of the emitting devices.

[0005] To overcome the polarization effect to increase the internal quantum efficiencies, growth of GaN or other III-nitrides in non-polar plane, such as (1-100) m-plane and (11-20) a-plane, is highly desirable. In addition, ZnO-based UV lasers with exciton binding energy of 60 meV are expected to possess a highly efficient laser action to compete with GaN-based ones or III-nitrides-based ones. Hence, it is also desirable to investigate non-polar ZnO materials, in order to overcome the low internal quantum efficiencies of ZnO.

[0006] Conventional non-polar m-plane epitaxial layers of GaN or ZnO are heteroepitaxially grown on m-plane SiC substrate, m-plane sapphire substrate, or (100) γ-$LiAlO_2$ substrate. However, large lattice mismatch may occur between the desired epitaxial layers of GaN or ZnO and m-plane SiC substrate and m-plane sapphire substrate, so the grown epitaxial layers may have higher defect density, which may cause the reduction of device performance. In addition, the thermal stability of γ-$LiAlO_2$ substrate is poor when the growth temperature is high. Also, the small size of γ-$LiAlO_2$ substrate (~1 inch) may limit its application.

[0007] Therefore, it is desirable to provide a suitable substrate for m-plane epitaxial layers of ZnO or III-nitrides growth with the nature of both low lattice mismatch and good thermal stability, and a method for growing the m-plane epitaxial layer thereon.

SUMMARY OF THE INVENTION

[0008] The object of the present invention is to provide a method for growing a non-polar m-plane epitaxial layer on a single crystal oxide substrate, to reduce the lattice mismatch between the substrate and the epitaxial layer. Also, the single crystal oxide substrate used in the method of the present invention has good thermal stability at high growth temperature, so it is suitable for the growth of the m-plane epitaxial layer of ZnO or III-nitrides thereon.

[0009] Another object of the present invention is to provide a non-polar m-plane epitaxial layer, which can inhibit the shift of the valence bands and the conduction bands due to the orientation of atoms in the epitaxial layer. Hence, the problem of the decrease in internal quantum efficiencies can be solved.

[0010] To achieve the aforementioned objects, the present invention provides a method for growing a non-polar m-plane epitaxial layer on a single crystal oxide substrate, which comprises the following steps: providing a single crystal oxide with a perovskite structure; using a plane of the single crystal oxide as a substrate; and forming a non-polar m-plane epitaxial layer of wurtzite semiconductors on the substrate by a vapor deposition process.

[0011] In addition, the present invention further provides an epitaxial layer having a non-polar m-plane, which is obtained by the following steps: providing a single crystal oxide with a perovskite structure; using a plane of the single crystal oxide as a substrate; and forming a non-polar m-plane epitaxial layer on the substrate by a vapor deposition process.

[0012] In the method and the epitaxial layer of the present invention, the substrate means a growth face for forming the non-polar m-plane epitaxial layer thereon.

[0013] According to the method of the present invention, the lattice mismatch between the substrate and the non-polar m-plane epitaxial layer is smaller than that prepared in the prior art. Hence, the method of the present invention is particularly suitable for growth of the non-polar m-plane layer in epitaxy. When the non-polar m-plane epitaxial layer is grown on the substrate by use of the method of the present invention, the lattice mismatch between the substrate and the non-polar m-plane epitaxial layer can be reduced to 10% or less. Furthermore, the plane of the single crystal oxide is a crystal plane or a cross section plane, and the crystal plane or the cross section plane is used as a substrate for growing the non-polar m-plane epitaxial layer. Preferably, the plane is a plane with Miller index of {112}.

[0014] According to the method and the epitaxial layer of the present invention, an oxide layer may optionally be formed on the single crystal oxide, a plane of the oxide layer is used as a substrate, and then a non-polar m-plane epitaxial layer of wurtzite semiconductors is formed on the substrate by a vapor deposition process. Herein, the compositions of the oxide layer and the single crystal oxide may be the same or different. It means the oxide layer and the single crystal oxide may be composed of the same or different compounds.

[0015] According to the method and the epitaxial layer of the present invention, the material of the single crystal oxide with the perovskite structure or the oxide layer is not particularly limited, and as long as it is a material which has good thermal stability and can inhibit the growth of other plane layers. Preferably, the single crystal oxide or the oxide layer is $LaAlO_3$, $SrTiO_3$, $(La,Sr)(Al,Ta)O_3$, or an $LaAlO_3$ alloy with a lattice constant difference of 10% or less compared to $LaAlO_3$. The single crystal oxide of $LaAlO_3$ has good thermal stability due to its high melting point of 2450K, and can also inhibit the growth of other plane layers. In addition, two inches (~50 mm) or more of crystal faces of the single crystal oxide or the oxide layer of $LaAlO_3$ can be used as a substrate for the growth of the non-polar m-plane epitaxial layer, and the cost of the substrate using the single crystal oxide or the oxide layer of $LaAlO_3$ is lower than the conventional substrate. Hence, the substrate using the single crystal oxide or the oxide layer of $LaAlO_3$ can be applied in various fields.

[0016] The non-polar m-plane epitaxial layer formed according to the method of the present invention may be ZnO, or III-nitrides, wherein the ZnO may further comprise an alloy doped with Mg, Ca, Sr, Ba, Cd, Al, Ga, In, or a combination thereof if it is necessary, and the III-nitride may be gallium nitride, indium nitride, aluminum nitride, indium gallium nitride, aluminum gallium nitride, aluminum indium nitride, aluminum indium gallium nitride, or a combination thereof.

[0017] The method for forming the non-polar m-plane epitaxial layer on the substrate used in the present invention is not particularly limited, and can be on the substrate. Preferably, the method for growing the non-polar m-plane epitaxial layer used in the present invention is pulsed laser deposition (PLD), sputtering process, electron beam evaporation (EBE), molecular beam epitaxy (MBE), or metal-organic chemical vapor deposition (MOCVD).

[0018] The method for growing the non-polar m-plane epitaxial layer on the single crystal oxide substrate of the present invention may further comprise a step of washing the substrate with an organic solvent, before the non-polar m-plane epitaxial layer is formed on the substrate by a vapor deposition process. Herein, the type of the organic solvent is not particularly limited. Preferably, the substrate is washed with hot acetone and isopropanol.

[0019] Hence, according to the method for growing a non-polar m-plane epitaxial layer on a single crystal oxide substrate of the present invention, a substrate, which has good thermal stability at high temperature and low lattice mismatch between the substrate and the epitaxial layer, is selected for the growth of a m-plane epitaxial layer of ZnO or III-nitrides. In addition, the non-polar m-plane epitaxial layer obtained by the aforementioned method can inhibit the polarization effect resulting from the orientation of atoms in the epitaxial layer. Hence, the shift of the valence bands and the conduction bands can be reduced, and the internal quantum efficiencies of emitting devices can be improved when the epitaxial layer obtained by the method of the present invention is used.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] FIG. **1** is a perspective view showing the growth of a non-polar m-plane epitaxial layer of ZnO in a preferred embodiment of the present invention;

[0021] FIGS. **2**(*a*) and **2**(*b*) are X-ray diffraction patterns of non-polar m-plane epitaxial layer of ZnO in a preferred embodiment of the present invention;

[0022] FIG. **3**(*a*) is an atomic configuration of a (112) plane of $LaAlO_3$ single crystal oxide in a preferred embodiment of the present invention; and

[0023] FIG. **3**(*b*) is an atomic configuration of an epitaxial m-plane $(1\bar{1}00)$ ZnO in a preferred embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0024] The present provides a method for growing a non-polar m-plane epitaxial layer on a single crystal oxide substrate and a non-polar m-plane epitaxial layer obtained by the same. The method comprises the following steps: providing a single crystal oxide with a perovskite structure; using a plane of the single crystal oxide as a substrate; and forming a non-polar m-plane epitaxial layer of wurtzite semiconductors on the substrate by a vapor deposition process.

[0025] Hereafter, the method for growing a non-polar m-plane epitaxial layer on a single crystal oxide substrate of the present invention is described in detail.

Embodiment 1

[0026] First, a single crystal oxide with a perovskite structure is provided, wherein the material of the single crystal oxide with the perovskite structure is not particularly limited, and as long as it is a material which has good thermal stability and can inhibit the growth of other interface layers.

[0027] Preferably, the single crystal oxide or the oxide layer is $LaAlO_3$, $SrTiO_3$, $(LaSr)(AlTa)O_3$, or an $LaAlO_3$ alloy with a lattice constant difference of 10% or less compared to $LaAlO_3$. In the present embodiment, a 2-inch (~50 mm) sized $LaAlO_3$ single crystal oxide was used.

[0028] Then, a crystal plane or a cross section plane of the $LaAlO_3$ single crystal oxide is used as a substrate, as shown in FIG. **1**, which is a perspective view showing the growth of a non-polar m-plane epitaxial layer in the present embodiment. In the present embodiment, the plane with Miller index of $\{112\}$ was used as a substrate. Then, the substrate was loaded into a chamber, washed with hot acetone and isopropanol, heated at 850° C. in high vacuum for 1 hour to remove impurities on the substrate.

[0029] Then, a hot-pressed ZnO cake was used as an ablation target. Herein, the ZnO cake can be an alloy doped with Mg, Ca, Sr, Ba, Cd, Al, Ga, In, or a combination thereof if it is necessary.

[0030] An epitaxial m-plane $(1\bar{1}00)$ ZnO layer was grown on the substrate in a DCA PLD-500 pulsed laser deposition system. A KrF excimer laser of 248 nm wavelength with 3 Hz repetition frequency was adopted as ablation source, the oxygen partial pressure in the chamber was kept less than 20 mtorr, and the temperature of the chamber was kept 800° C. during deposition. Then, an epitaxial m-plane $(1\bar{1}00)$ ZnO layer was deposited on the substrate, as shown in FIG. **1**.

[0031] FIGS. **2**(*a*) and **2**(*b*) are x-ray diffraction patterns of non-polar m-plane epitaxial layer of ZnO in the present embodiment. According to the data shown in FIG. **2**(*a*), only an m-plane ZnO epitaxial layer was grown on the (112) $LaAlO_3$ single crystal oxide in the present embodiment. In addition, according to the data of x-ray rocking curve shown in FIG. **2**(*b*), the full-width half maximum (FWHM) value was 0.41°, which suggested that m-plane ZnO epitaxial layer with good crystallinity was obtained in the present embodiment.

Embodiment 2

[0032] The materials and method used in the present embodiment are the same as those in Embodiment 1, except that the ablation target is a III-nitride, such as GaN which has similar lattice parameters (a=0.3189 nm, c=0.5185 nm) as ZnO. In the present embodiment, an epitaxial layer of III nitride, i.e. a GaN epitaxial layer, was obtained. The functions and the applications of the non-polar m-plane epitaxial layer of III nitride (GaN) grown in the present embodiment are the same as those of the epitaxial layer of ZnO grown in Embodiment 1.

[0033] Though only GaN was used as an ablation target in the present embodiment, other III-nitrides, such as indium nitride, aluminum nitride, indium gallium nitride, aluminum gallium nitride, aluminum indium nitride, aluminum indium gallium nitride, or a combination thereof, can also be used as an ablation target for growth of an epitaxial layer through the same method described in Embodiment 1. Also, the epitaxial layer formed by other III-nitrides has the same functions and applications as those of the epitaxial layer of ZnO grown in Embodiment 1.

Embodiment 3

[0034] The materials and method used in the present embodiment are the same as those in Embodiment 1 or 2, except that an oxide layer (not shown in the figure) was formed on the single crystal oxide, and a plane of the oxide layer was used as a substrate.

[0035] In the present embodiment, an $SrTiO_3$ single crystal oxide with a perovskite structure was provided, and then an $LaAlO_3$ oxide layer was formed on the $SrTiO_3$ single crystal oxide. A plane of the $LaAlO_3$ oxide layer with Miller Index of {112} was used as a substrate, and a non-polar m-plane epitaxial layer of wurtzite semiconductors was formed on the substrate through a vapor deposition process with the same deposition conditions as described in Embodiment 1. Though the $SrTiO_3$ single crystal oxide and the $LaAlO_3$ oxide layer were exemplified in the present embodiment, the compositions of the oxide layer and the single crystal oxide can be the same or different if it is needed. Also, the functions and applications of the epitaxial layer obtained in the present embodiment are the same as those of the epitaxial layer grown in Embodiment 1 or 2.

Experimental Example 1

[0036] In the present experimental example, the lattice mismatch between the non-polar m-plane ZnO epitaxial layer obtained in Embodiment 1 and the plane of the (112) $LaAlO_3$ single crystal oxide used as a substrate is described in detail.

[0037] FIG. **3**(*a*) is an atomic configuration of a plane of (112) $LaAlO_3$ single crystal oxide, and FIG. **3**(*b*) is an atomic configuration of a non-polar m-plane $(1\bar{1}00)$ ZnO layer which can be in epitaxy. According to FIG. **3**(*a*), the distance between oxygen atoms in the plane of (112) $LaAlO_3$ single crystal oxide is 5.360 Å and 6.566 Å respectively. According to FIG. **3**(*b*), the distance between oxygen atoms in the non-polar m-plane $(1\bar{1}00)$ ZnO epitaxial layer is 5.206 Å and 3.249 Å respectively. After calculation, the lattice mismatch between the non-polar m-plane $(1\bar{1}00)$ ZnO epitaxial layer and the plane of (112) $LaAlO_3$ single crystal oxide is estimated to be −2.9% along the direction parallel to the c-axis of ZnO ((5.206−5.360)/5.360=−2.9%), and −1.0% perpendicular to the c-axis ((3.249×2−6.566)/6.566=−1.0%). Compared to the conventional substrate, the lattice mismatch between the substrate and the epitaxial layer of the present invention is low. In addition, the substrate used in the present invention has good thermal stability at high temperature, and is suitable for the growth of m-plane epitaxial layers of ZnO or III-nitrides.

[0038] In conclusion, according to the method for growing a non-polar m-plane epitaxial layer on a single crystal oxide substrate of the present invention, a substrate, which has good thermal stability at high temperature and low lattice mismatch between the substrate and the epitaxial layer, is selected for the growth of an m-plane epitaxial layer of ZnO or III-nitrides. In addition, the non-polar m-plane epitaxial layer obtained by the aforementioned method can inhibit the polarization effect resulting from the orientation of atoms in the epitaxial layer. Hence, the shift of the valence bands and the conduction bands can be reduced, and the internal quantum efficiencies of emitting devices can be improved.

[0039] Therefore, when the epitaxial layer obtained by the method of the present invention is applied to blue-to-UV light solid-state electronic devices and laser diodes, the polarization effect can be eliminated and the internal quantum efficiencies can be increased, so that the light-emitting efficiencies of the emitting devices can be improved greatly.

[0040] Although the present invention has been explained in relation to its preferred embodiment, it is to be understood that many other possible modifications and variations can be made without departing from the scope of the invention as hereinafter claimed.

What is claimed is:

1. A method for growing a non-polar m-plane epitaxial layer on a single crystal oxide substrate, comprising the following steps:
providing a single crystal oxide with a perovskite structure;
using a plane of the single crystal oxide as a substrate; and
forming a non-polar m-plane epitaxial layer of wurtzite semiconductors on the substrate by a vapor deposition process.

2. The method as claimed in claim **1**, further comprising the following steps:
forming an oxide layer on the single crystal oxide;
using a plane of the oxide layer as a substrate; and
forming a non-polar m-plane epitaxial layer of wurtzite semiconductors on the substrate by a vapor deposition process,
wherein, the compositions of the oxide layer and the single crystal oxide are the same or different.

3. The method as claimed in claim **1** or **2**, wherein the lattice mismatch between the substrate and the non-polar m-plane epitaxial layer is 10% or less.

4. The method as claimed in claim **1** or **2**, wherein the single crystal oxide is $LaAlO_3$, $SrTiO_3$, $(La,Sr)(Al,Ta)O_3$, or an $LaAlO_3$ alloy with a lattice constant difference of 10% or less compared to $LaAlO_3$.

5. The method as claimed in claim **1** or **2**, wherein the non-polar m-plane epitaxial layer is ZnO, or III-nitrides.

6. The method as claimed in claim **5**, wherein the ZnO further comprises: an alloy doped with Mg, Ca, Sr, Ba, Cd, Al, Ga, In, or a combination thereof.

7. The method as claimed in claim **5**, wherein the III nitride is gallium nitride, indium nitride, aluminum nitride, indium gallium nitride, aluminum gallium nitride, aluminum indium nitride, aluminum indium gallium nitride, or a combination thereof.

8. The method as claimed in claim **1**, wherein the plane is a crystal plane, or a cross section plane.

9. The method as claimed in claim **1** or **2**, wherein the plane is a plane with Miller index of **{112}**.

10. The method as claimed in claim **1** or **2**, wherein the vapor deposition process is physical vapor deposition (PVD) or chemical vapor deposition (CVD), which comprises pulsed laser deposition (PLD), sputtering process, electron beam evaporation (EBE), molecular beam epitaxy, or metal-organic chemical vapor deposition (MOCVD).

11. The method as claimed in claim **1** or **2**, further comprising a step of washing the substrate with hot acetone and isopropanol, before the non-polar m-plane epitaxial layer is formed on the substrate by a vapor deposition process.

12. An epitaxial layer having a non-polar m-plane, which is obtained by the following steps comprising:

providing a single crystal oxide with a perovskite structure;

using a plane of the single crystal oxide as a substrate; and

forming a non-polar m-plane epitaxial layer of wurtzite semiconductors on the substrate by a vapor deposition process.

13. The epitaxial layer having a non-polar m-plane as claimed in claim **12**, further comprising the following steps:

forming an oxide layer on the single crystal oxide;

using a plane of the oxide layer as a substrate; and

forming a non-polar m-plane epitaxial layer of wurtzite semiconductors on the substrate by a vapor deposition process,

wherein, the compositions of the oxide layer and the single crystal oxide are the same or different.

14. The epitaxial layer having a non-polar m-plane as claimed in claim **12** or **13**, wherein the lattice mismatch between the substrate and the non-polar m-plane epitaxial layer is 10% or less.

15. The epitaxial layer having a non-polar m-plane as claimed in claim **12** or **13**, wherein the single crystal oxide is $LaAlO_3$, $SrTiO_3$, $(La,Sr)(Al,Ta)O_3$, or an $LaAlO_3$ alloy with a lattice constant difference of 10% or less compared to $LaAlO_3$.

16. The epitaxial layer having a non-polar m-plane as claimed in claim **12** or **13**, wherein the non-polar m-plane epitaxial layer is ZnO, or III-nitrides.

17. The epitaxial layer having a non-polar m-plane as claimed in claim **15**, wherein the ZnO further comprises: an alloy doped with Mg, Ca, Sr, Ba, Cd, Al, Ga, In, or a combination thereof.

18. The epitaxial layer having a non-polar m-plane as claimed in claim **15**, wherein the III nitride is gallium nitride, indium nitride, aluminum nitride, indium gallium nitride, aluminum gallium nitride, aluminum indium nitride, aluminum indium gallium nitride, or a combination thereof.

19. The epitaxial layer having a non-polar m-plane as claimed in claim **12**, wherein the plane is a crystal plane, or a cross section plane.

20. The epitaxial layer having a non-polar m-plane as claimed in claim **12** or **13**, wherein the plane is a plane with Miller index of $\{112\}$.

21. The epitaxial layer having a non-polar m-plane as claimed in claim **12** or **13**, wherein the vapor deposition process is physical vapor deposition (PVD) or chemical vapor deposition (CVD), which comprises pulsed laser deposition (PLD), sputtering process, electron beam evaporation (EBE), molecular beam epitaxy, or metal-organic chemical vapor deposition (MOCVD).

22. The epitaxial layer having a non-polar m-plane as claimed in claim **12** or **13**, further comprising a step of washing the substrate with hot acetone and isopropanol, before the non-polar m-plane epitaxial layer is formed on the substrate by a vapor deposition process.

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