EPITAXIAL GROWTH OF CUBIC CRystalline SEMICONDUCTOR ALLOYS ON BASAL PLANE OF TRIGONAL OR HEXAGONAL CRYSTAL

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Abstract

Hetero-epitaxial semiconductor materials comprising cubic crystalline semiconductor alloys grown on the basal plane of trigonal and hexagonal substrates, in which misfit dislocations are reduced by approximate lattice matching of the cubic crystal structure to underlying trigonal or hexagonal substrate structure, enabling the development of alloyed semiconductor layers of greater thickness, resulting in a new class of semiconductor materials and corresponding devices, including improved hetero-bipolar and high-electron mobility transistors, and high-mobility thermoelectric devices.

5 Claims, 10 Drawing Sheets
Sapphire (Al₂O₃) Trigonal or hexagonal structure (0001) plane

Si, Ge diamond structure (111)

\[ a' = \frac{\sqrt{3}}{2} a \]
Coordinates are rotated by 30°, but the angle between reciprocal basis vectors, $\vec{a}$ and $\vec{b}$, is only 60°.
Atomic alignment which was interpreted from XRD data shows 30 degree rotation: Type [B]

Cubic symmetry includes trigonal symmetry along <111> orientation

SiGe view on [111]

Sapphire view on [0001]
Two types of possible crystal structure alignment on trigonal crystal substrate Type [A] and Type [B]

Lattice constant relationship in Type [B]
Fractional (2/3) of Type [A]

\[ \frac{2}{3} \text{ of Type } [A] \]

Fig. 8
Fig. 10

- Sn: 6.48 Å
- Ge: 5.66 Å
- Si: 5.43 Å
- C: 3.57 Å

Energy Gap:
- Si: 1.12 eV
- SiSn: 0.3 eV
- Ge: 0.7 eV

Gradient:
- SiₐₓSnₜₓ
- Siₗ₋ₓGeₓ

Faster electron mobility.
1. Field of the Invention

The present invention is in the fields of solid-state physics, semiconductor material and heteroepitaxy, and more particularly concerns lattice-matching methods for rhombohedral growth of crystals comprised of semiconductor alloys of group IV and other cubic crystalline materials on the basal plane of trigonal or hexagonal crystal substrates, and the resulting semiconductor compositions.

2. Description of the Related Art

The alloys of group IV elements, including carbon (C), silicon (Si), germanium (Ge), and tin (Sn) are important semiconductor materials. For example, SiGe alloy is widely used in Hetero Bipolar Transistors (HBT) and High Electron Mobility Transistors (HEMT) for high speed computing and high-mobility thermoelectric devices, and high-mobility thermoelectric devices.

To achieve these results, the present invention generally uses a new lattice matching technique to calculate alloy compositions in order to approximately match substrate lattices, and thereby allow the growth of group IV alloy and other cubic crystal layers that are much more free of dislocation defects than those that could be obtained under prior approaches. The present approach relates to any alloys of silicon (Si), germanium (Ge), carbon (C) and tin (Sn) (generally referred to in this specification as “SiGeCSn”) on any trigonal/hexagonal substrate, such as sapphire (i.e. single crystalline Al₂O₃) (or hexagonal substrates, such as quartz), as well as to other cubic crystalline materials, including group III-V and II-VI materials in trigonal or hexagonal substrates, such as sapphire.

In one embodiment, lattice matching equations, when satisfied by a particular alloy composition, will result in good crystal growth of the alloy on rhombohedral, trigonal, or hexagonal substrates. Further, techniques for calculating Bragg angles and inter-planar angles for twin detection for all group IV alloys as well as group III-V and II-VI materials in trigonal or hexagonal substrates, may be applied to a new X-ray diffraction method for twin detection developed in accompanying patent application Ser. No. 12/254,150, entitled "METHOD OF GENERATING X-RAY DIFFRACTION DATA FOR INTEGRAL DETECTION OF TWIN DEFECTS IN SUPER-HETERO-EPITAXIAL MATERIALS."
field for faster SiGeCSn HBT and HEMT devices and more efficient SiGeCSn TE devices than previously possible. Other aspects and advantages of the present invention will be apparent from the accompanying drawings, and the detailed description that follows.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more complete understanding of the present invention and the advantages thereof, reference is now made to the following description taken in conjunction with the accompanying drawings, wherein like reference numerals represent like parts, in which:

FIG. 1 graphically depicts in FIG. 1 (a) the primitive unit cell of trigonal crystal structure of sapphire (Al₂O₃) and FIG. 1 (b) the diamond structure of Si, Ge, C and Sn.

FIG. 2 shows the crystal lattice constant relationship between rhombohedral transformation of diamond cubic structure and simplified crystal structure of sapphire. The actual crystal structure of sapphire is very complex and not shown here.

FIG. 3 shows plots of two kinds of X-ray diffraction data which were obtained at different Euler angles (the two sets of data were obtained at Phi angles which were apart by 60°).

FIG. 4 shows the direction of SiGe [220] in FIG. 4 (a) real-lattice and sapphire [1-104], in FIG. 4 (b) reciprocal lattice and in FIG. 4 (c) real-space lattice. All arrows are projected on the basal plane.

FIG. 5 shows atomic alignment of SiGe on sapphire, in a Type [B] alignment.

FIG. 6 shows 30° rotated atomic alignment of GaN on sapphire, in a Type [B] alignment.

FIG. 7 shows a comparison between Type [A] and Type [B] atomic alignment, with different lattice matching conditions.

FIG. 8 shows fractional 1/2 of Type [A] alignment."

FIG. 9 shows fractional 1/2 of Type [B] alignment."

FIG. 10 illustrates (Top) lattice constants of group IV semiconductor elements, (Lower Left) fast electron mobility in SiGeCSn HBT, and (Lower Right) even faster electron mobility in SiGeCSn HBT.

DETAILED DESCRIPTION

The following is a detailed description of certain embodiments of the invention chosen to provide illustrative examples of how it may preferably be implemented. The scope of the invention is not limited to the specific embodiments described, nor is it limited by any specific implementation, composition, embodiment or characterization depicted in the accompanying tables or drawings or stated or described in the invention summary or the abstract. In addition, it should be noted that this disclosure describes a number of methods that each comprise a plurality of steps. Nothing contained in this written description should be understood to imply any necessary order of steps in such methods, other than as specified by express claim language.

In the ensuing description, the well-known Miller indices notation of lattice planes is used. That is, crystal planes are designated by numbers within "< >", groups of similar planes are designated by numbers within "[ ]", direction or length is designated by numbers within "< >", and groups of similar directions are designated by numbers within "< >".

Sapphire has a trigonal crystal structure as shown in FIG. 1 (a). The group IV elements, Si, Ge, C, and Sn, have cubic diamond structures as shown in FIG. 1 (b) (and group III-V and II-VI crystalline materials in zinc-blende configuration have a similar crystal structure). Therefore, the direct comparison of lattice constants does not have a meaning since the cubic basal plane, i.e. {001} planes according to Miller index classification, cannot be aligned on the trigonal basal plane, i.e. the [001] or "C" plane. However, if we consider a rhombohedral transformation of cubic crystals along the <111> direction, we can see that trigonal [111] planes of cubic crystals can match the trigonal [001] planes easily, as shown in FIG. 2. In this case, a new lattice parameter of cubic crystal, shown as a' in FIG. 2, can match the corresponding lattice parameter, a, of the underlying trigonal or hexagonal crystalline substrate. Here, the [220] atomic distance a' is given by the rhombohedral transformation relation:

\[ a' = \frac{\sqrt{3}}{2} a_{cubic} \]  

"Type [A]" alignment is used for the above atomic arrangement at the interface of epitaxial material and substrate material.

XRD methods are used to confirm the present crystal growth methodology and the resulting materials. FIG. 3 shows two sets of X-ray diffraction data (angle-dependent single crystalline XRD) of one SiGe layer on sapphire substrate which was grown at a certain growth condition. Two sets of data were obtained at the same 2-Theta (detector), Omega (goniometer), Chi (tilt) angles, but at different Phi angles, which were apart by 60°. In this tilted XRD data, (111), (113), (220), and (224) peaks were obtained in 0-20 scan, which means that poly-crystalline SiGe films were formed on sapphire under a certain growth condition. It is important to notice that the first and the second order peaks of sapphire (1-104) were obtained in the second set of data, but there is no sapphire (1-104) peak in the first set of data. The lack of (1-104) peak in the first set of data shows the trigonal symmetry of sapphire substrate such that 60° rotational symmetry is broken and only 120° rotational symmetry is valid in sapphire. The (220) peak in the first set of data shows one domain and another (220) peak in the second set of data shows the other domain, which was aligned with sapphire’s (1-104). The coexistence of SiGe’s (220) peak and sapphire’s (1-104) peak in one single 0-20 scan shows a different new atomic alignment scheme, as shown in FIG. 4 and FIG. 5.

In a non-cubic crystal system, the reciprocal lattice orientation can be different from the real space lattice orientation. In a trigonal/hexagonal system, the reciprocal basis vectors (shown as α and β in FIG. 4 (b)) have 30° rotation from real-space lattice vectors (shown as x and y in FIG. 4 (c)). But the angle between the reciprocal basis vectors, α and β is not 120°, but only 60° according to the definition equation below. On the other hand, the cubic system’s reciprocal basis vectors are the same as real space basis vectors. Therefore, extra-care must be paid to the crystal plane orientation between the cubic system and the trigonal/hexagonal system because of the transformation of the basis vectors. The vector transformation relation is given in the following equation (See N. W. Ashcroft, N. D. Mermin, Solid State Physics, in Chapter 5 “The Reciprocal Lattice”, Harcourt College Publishers, New York, ISBN:0-06-083993-9 (1976)):
where \( \mathbf{a}_1, \mathbf{a}_2, \) and \( \mathbf{a}_3 \) are the basis vectors of real-space and \( b_1, b_2, \) and \( b_3 \) are the basis vectors of reciprocal space.

In FIG. 4, \( a_1, a_2, \) and \( a_3 \) are shown as \( x \) and \( y, b_1 \) and \( b_2 \) are shown as \( \alpha \) and \( \beta. \) The comparison of crystal orientations between cubic and cubic, or between trigonal/hexagonal and trigonal/hexagonal systems do not have this problem. By contrast, the comparison of crystal orientations between cubic and trigonal/hexagonal systems must consider the rotation and inter-vector-angle change of lattice vectors in reciprocal space of the trigonal/hexagonal crystal. Because the line 401 in FIG. 4 (a) and line 403 in FIG. 4 (c) have to be aligned in the same direction for two peaks to appear in the same 0-20 XRD scan, the SiGe crystal is atomically aligned to sapphire's hexagonal basal plane as shown in FIG. 5, which shows 30° rotation.

In FIG. 5, sapphire substrate is shown as hexagon 501 with three dots that represent trigonal symmetry, and SiGe epitaxial layer is shown as superimposed hexagon 503 with three tiny parallelograms that is aligned with 30° rotation with respect to hexagon 501. Six angle-dependent single crystal XRD data sets are shown in the corresponding azimuthal orientation. Therefore, all the drawings and data in FIG. 5 show that the grown epitaxial layer is atomically aligned according to a new atomic alignment lattice-matching scheme, which is characterized by 30° rotation between the projected lattice axis of epitaxial layer and substrate layer. This additional atomic alignment will be referred to as "Type [B]" alignment.


Both atomic alignment configurations, Type [A] and Type [B], have to be considered in order to expand the lattice matching methods for various group IV alloys and group III-V and group II-VI crystalline materials in zinc-blende structure on many different trigonal or hexagonal substrates. FIG. 7 shows the lattice matching conditions in Type [A] alignment and Type [B] alignment (See also FIG. 2 with regard to Type [A]). The lattice matching conditions are different for Type [A] and Type [B]. See equations (13)-(16) below.)

In addition, comparable alignments are possible with similar orientations, where the rhombohedral structures are smaller in relation to the underlying trigonal/hexagonal structure than in the cases of the Type [A] and [B] alignments discussed above. This is shown in FIGS. 8 and 9. The additional lattice-matching conditions for these possible arrangements must be considered as well.

In this reduced form of Type [A] alignment, if the rhombohedral dimensions are reduced relative to the underlying trigonal/hexagonal dimensions, there is a third lattice-match-
other hand, ternary alloys have two variables (x and y) and quaternary alloys have three variables (x, y, and z). Therefore, lattice matching can occur at or about different compositions while varying multiple variables. This additional degree of freedom can control additional physical properties, such as band-gap energy and thermal expansion while the alloy is still in the lattice-matching condition. The following equations show the method to fix the composition to match multiple physical properties, such as index of refraction, band-gap energy, lattice constant, absorption coefficient, work-function, and so on.

Three properties will now be considered. L is a lattice constant, E is band-gap energy, and a is a linear thermal expansion coefficient. The derivation of these equations will now be shown.

(1) For Binary Alloy (AB):

\[ xL_A + (1-x)L_B = L_{\text{target}} \]

Matching the lattice constant

(2) For Ternary Alloy (AB₃):

\[ xL_A + yL_B + (1-x-y)L_C = L_{\text{target}} \]

Matching the lattice constant

\[ xE_A + yE_B + (1-x-y)E_C = E_{\text{target}} \]

Matching the band-gap energy

Two equations with two variables give one answer with unique x and unique y. Only the answer with x and y between 0 and 1 is meaningful. This answer matches two physical parameters at the same time.

(3) For Quaternary Alloy AB₃C₄:

\[ xL_A + yL_B + (1-x-y)\frac{1}{2}L_C + (1-x-y-z)\frac{1}{2}L_D = L_{\text{target}} \]

Matching the lattice constant

\[ xE_A + yE_B + (1-x-y)\frac{1}{2}E_C + (1-x-y-z)\frac{1}{2}E_D = E_{\text{target}} \]

Matching the band-gap energy

Three equations with three variables give one answer with unique x, unique y, and unique z. Only the answer with x, y, and z between 0 and 1 is meaningful. This answer matches three physical parameters at the same time.

Lattice Matching Technique

As noted above, previous attempts were made to match the lattice constant of cubic structures directly by an approach wherein \( L_{\text{target}} = L_{\text{substrate}} \) (the lattice constant of cubic substrate). In the present approach, \( L_{\text{target}} \) should aim to match a corresponding atomic distance of a trigonal/hexagonal substrate, not the direct lattice constant of a cubic substrate. To do this, equation (14) below for type [A] alignment and equation (16) below for type [B] alignment are used. The following is the derivation of these equations.

For example, in the type [A] alignment, the following equation holds as shown in FIG. 2.

\[ \frac{1}{2}a_{\text{trig/hex}}^\parallel = \frac{\sqrt{3}}{2}L_{\text{target}} = a_{\text{trig/hex}}^\parallel \]

where \( a' \) is the atomic distance of [2-20] direction in FIG. 2, and \( a_{\text{trig/hex}}^\parallel \) is the lattice constant of basal plane of the trigonal or hexagonal crystalline substrate.

Therefore, \( L_{\text{target}} \) should equal the transformed atomic distance, such as:

\[ L_{\text{target}} = \frac{2}{\sqrt{3}}a_{\text{trig/hex}}^\parallel \]

As another example, in the type [B] alignment, the following equation holds as shown in FIG. 4.

\[ \frac{1}{2}a_{\text{trig/hex}}^\parallel = \frac{\sqrt{3}}{2}L_{\text{target}} = \frac{2}{\sqrt{3}}a_{\text{trig/hex}}^\parallel \]

where \( a' \) is the atomic distance of [2-20] direction in FIG. 2, and \( a_{\text{trig/hex}}^\parallel \) is the lattice constant of basal plane of the trigonal or hexagonal crystalline substrate.

Therefore, \( L_{\text{target}} \) should equal the transformed atomic distance, such as:

\[ L_{\text{target}} = \frac{4}{3}a_{\text{trig/hex}}^\parallel \]

As noted above, two other fractional coincidence atomic alignments are possible as shown in FIGS. 8 and 9, i.e., “Two Thirds (2/3) of Type-A” and “Half (1/2) of Type-B”.

For 2/3 of Type [A] alignment as shown in FIG. 8, the following equation holds:

\[ \frac{1}{2}a_{\text{trig/hex}}^\parallel = \frac{2}{\sqrt{3}}L_{\text{target}} = \frac{2}{3}a_{\text{trig/hex}}^\parallel \]

where \( a' \) is the atomic distance of [2-20] direction in FIG. 2, and \( a_{\text{trig/hex}}^\parallel \) is the lattice constant of basal plane of the trigonal or hexagonal crystalline substrate.

Therefore, \( L_{\text{target}} \) should equal the transformed atomic distance, such as:

\[ L_{\text{target}} = \frac{4}{3\sqrt{3}}a_{\text{trig/hex}}^\parallel \]
Therefore, \( L_{\text{target}} \) should equal the transformed atomic distance, such as:

\[
L_{\text{target}} = \frac{2}{3} \theta_{\text{target}} \cos \theta \quad \text{(20)}
\]

There are many crystal wafers that have a trigonal crystal structure. The following list shows a few selected materials with their lattice constants, \( a_{x,z} \) and \( a_{x,y} \), as the lattice constants of basal plane and \( c \) as vertical lattice constant.

Trigonal Crystals (by Point Group Symmetry):
- Sapphire (\( Al_2O_3 \)), \( a_{x,z} = 4.738 \, \text{Å}, c = 12.99 \, \text{Å} \)
- Gallium Nitride (GaN), \( a_{x,z} = 3.189 \, \text{Å}, c = 5.185 \, \text{Å} \)
- Aluminum Nitride (AIN), \( a_{x,z} = 3.111 \, \text{Å}, c = 4.98 \, \text{Å} \)
- Indium Nitride (InN), \( a_{x,z} = 3.54 \, \text{Å}, c = 8.70 \, \text{Å} \)
- Zinc Oxide (ZnO), \( a_{x,z} = 3.25 \, \text{Å}, c = 5.21 \, \text{Å} \)
- Lithium Niobate (LiNbO\(_3\)), \( a_{x,z} = 5.148 \, \text{Å}, c = 13.863 \, \text{Å} \)
- Lithium Copper Tantalate (LiCuTaO\(_3\)), \( a_{x,z} = 5.983 \, \text{Å}, c = 13.788 \, \text{Å} \)
- Lithium Tantalum Nitride Oxide(LTNO) (Lt16N8O11Ta2), \( a_{x,z} = 5.2004 \, \text{Å}, c = 9.168 \, \text{Å} \)
- (In this list, trigonal lattice was described in the hexagonal frame instead of the rhombohedral frame.)

Hexagonal Crystals (by Point Group Symmetry):
- Quartz, \( a_{x,z} = 4.91 \, \text{Å}, c = 5.40 \, \text{Å} \)
- Boron Nitride (BN) in Hexagonal form, (Space group D\(_{6h}\), P6\(_{3}\)mc), \( a_{x,z} = 2.50 \, \text{Å}, c = 6.66 \, \text{Å} \)

Therefore, the equations (14), (16), (18) and (20) can be applied to all trigonal crystal and hexagonal crystal wafers made with the materials, including but not limited to the above list. The use of these equations is not limited to group IV alloys in diamond structure. They may also be applied to group III-V and II-VI materials in zinc-blende structure. The above lattice matching equations can be applied for all of these materials. The trigonal and hexagonal crystals can both be described in hexagonal frame, but the main difference between the two structures is that the hexagonal crystal allows 60° rotational symmetry, whereas the trigonal crystal has only 120° rotational symmetry without 60° rotational symmetry.

With this general expansion of technology, we formulate a group IV alloy made with any of Si, Ge, C, and Sn, or group II-V and II-VI in zinc-blende structure, on any of the trigonal or hexagonal substrates, whose alloy composition is designed to hold the equation (14) in Type [A] alignment, equation (16) in Type [B] alignment, (18) in \( \frac{1}{2} \) of Type [A] alignment, or equation (20) in half of Type [B] alignment within \( \pm 10\% \) error of alloy composition. We also note that the same analysis should be applicable to other materials in Body Centered Cubic (BCC) and Face Centered Cubic (FCC) structures as well.

For example, Sb\(_{1-x}\)Sn\(_x\)\(_{0.86}\) can match lattice constant of sapphire in Type [B] alignment. Therefore the alloy of Si,Sn on sapphire in the range of \( y = 0.86\pm0.086(10\%) = 0.774-0.946 \) and \( x = 1-y = 0.226-0.054 \) is within this formulation.

General XRD Method for Cubic Crystal Material on any Trigonal/Hexagonal Substrate:

(1) Bragg Angle of X-Ray Diffraction Peak:

Generally, X-ray diffraction occurs whenever the Bragg condition is satisfied:

\[
2d \sin \theta = n \lambda \quad \text{(b 21)}
\]

where \( d \) is the atomic spacing distance of plane \( (h,k,l) \), \( \theta \) is the X-ray diffraction angle, \( \lambda \) is the wavelength of the X-ray, and \( n \) is an integer. Here \( d(h,k,l) \) is determined by the crystal structure and the lattice constant, \( L \).

In cubic diamond structure,

\[
d_{h,k,l} = \frac{L}{\sqrt{h^2+k^2+l^2}}.
\]

Therefore, the XRD peak occurs at the angle \( \theta_{h,k,l}(x,y,z) \), such that:

\[
\sin^2 \theta_{h,k,l}(x,y,z) = \frac{n^2 - L^2(x,y,z)}{2 L^2(x,y,z)}.
\]

(2) Inter-Planar Angle:

For a cubic diamond structure, the inter-planar angle cubic, \( \Phi_{\text{cubic}} \), between two planes, \((h_1, k_1, l_1)\) and \((h_2, k_2, l_2)\), is given by:

\[
\cos \Phi_{\text{cubic}} = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\sqrt{(h_1^2 + k_1^2 + l_1^2)(h_2^2 + k_2^2 + l_2^2)}}.
\]

(For general X-ray diffraction analysis, refer to "Elements of X-ray Diffraction" by B. D. Cullity, Addison-Wesley Publishing Co., 2\textsuperscript{nd} or higher edition.)

Similarly, for a trigonal crystal in hexagonal frame and a hexagonal crystal, the inter-planar angle, \( \Phi_{\text{Hex}} \), between two planes, \((h_1, k_1, l_1)\) and \((h_2, k_2, l_2)\), is given by:

\[
\cos \Phi_{\text{Hex}} = \frac{h_1 h_2 + k_1 k_2 + \frac{1}{2}(h_1 h_2 + k_1 k_2 + l_1 l_2)}{\sqrt{(h_1^2 + k_1^2 + l_1^2)(h_2^2 + k_2^2 + l_2^2)}} - \frac{3\lambda^2}{4\pi^2 l_2^2}.
\]

(3) Twin Detection XRD for Cubic Crystalline Alloys on Trigonal/Hexagonal Substrate:

Using the above equations (24), (25), and (26), the twin detection XRD method can be completed for all general cubic crystalline alloys on any trigonal or hexagonal substrate.

As an example, calculated XRD peak positions for selected cubic crystalline alloy compositions on selected substrates are shown in the following tables. The actual compositions are not limited to these tables, but can be extended according to the equations from (3) to (20).
### Table 1

<table>
<thead>
<tr>
<th>Epitaxial Layer</th>
<th>Si Ge C Sn</th>
<th>Lattice C of Substrate</th>
<th>Lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeC/Sapphire-A</td>
<td>0.05</td>
<td>0.95</td>
<td>3.66</td>
</tr>
<tr>
<td>SiC/LiNbO3-B</td>
<td>0.225</td>
<td>0.775</td>
<td>4.60</td>
</tr>
</tbody>
</table>

### Table 1-continued

<table>
<thead>
<tr>
<th>Epitaxial Layer</th>
<th>Si Ge C Sn</th>
<th>Lattice C of Substrate</th>
<th>Lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeC/LiNbO3-B</td>
<td>0.185</td>
<td>0.815</td>
<td>3.99</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Epitaxial Layer</th>
<th>Si Ge C Sn</th>
<th>Lattice C of Substrate</th>
<th>Lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeC/LiNbO3</td>
<td>0.185</td>
<td>0.815</td>
<td>3.99</td>
</tr>
</tbody>
</table>

### Table 2-continued

<table>
<thead>
<tr>
<th>Epitaxial Layer</th>
<th>Si Ge C Sn</th>
<th>Lattice C of Substrate</th>
<th>Lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeC/LiNbO3-B</td>
<td>0.185</td>
<td>0.815</td>
<td>3.99</td>
</tr>
</tbody>
</table>
## TABLE 2-continued

<table>
<thead>
<tr>
<th>Epitaxial Laver</th>
<th>Si</th>
<th>Ge</th>
<th>C</th>
<th>Sn</th>
<th>Lattice Composition</th>
<th>Substrate Name</th>
<th>Lattice C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoC/LTHO - 1/2 of B</td>
<td>0.2</td>
<td>0.8</td>
<td>3.99</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiGeC/LTNO - 1/2 of B</td>
<td>0.1</td>
<td>0.1</td>
<td>3.99</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Bragg angles of X-ray diffraction were calculated and are listed in the following tables for select lattice matching conditions on various substrates. Table 3 and Table 5 were calculated with copper Cu Kα, X-ray source and Table 4 and Table 6 were calculated with X-ray from cobalt, with weighted average of Co Kα and Kα2.

### TABLE 3

<table>
<thead>
<tr>
<th>L.C. of alloy</th>
<th>CuKα X-ray Wavelength: 1.54056 Ångstrom</th>
<th>1st order Bragg angle, Theta, for various peaks (in degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L.C._alloy</td>
<td>111</td>
<td>220</td>
</tr>
<tr>
<td>Sapphire Type A</td>
<td>5.49</td>
<td>14.065</td>
</tr>
<tr>
<td>Sapphire Type B</td>
<td>6.34</td>
<td>12.148</td>
</tr>
<tr>
<td>GaN Type A</td>
<td>3.68</td>
<td>21.257</td>
</tr>
<tr>
<td>GaN Type B</td>
<td>4.25</td>
<td>18.296</td>
</tr>
<tr>
<td>AIN Type A</td>
<td>3.45</td>
<td>21.816</td>
</tr>
<tr>
<td>AIN Type B</td>
<td>4.15</td>
<td>17.753</td>
</tr>
<tr>
<td>InN Type A</td>
<td>4.09</td>
<td>19.038</td>
</tr>
<tr>
<td>InN Type B</td>
<td>4.72</td>
<td>16.419</td>
</tr>
<tr>
<td>ZnO Type A</td>
<td>3.75</td>
<td>20.841</td>
</tr>
<tr>
<td>ZnO Type B</td>
<td>4.33</td>
<td>17.046</td>
</tr>
<tr>
<td>Quartz Type A</td>
<td>5.67</td>
<td>13.609</td>
</tr>
<tr>
<td>Quartz Type B</td>
<td>6.01</td>
<td>14.155</td>
</tr>
</tbody>
</table>

### TABLE 4-continued

<table>
<thead>
<tr>
<th>X-ray Wavelength: 1.79026 Ångstrom</th>
<th>1st order Bragg angle, Theta, for various peaks (in degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L.C._alloy</td>
<td>111</td>
</tr>
<tr>
<td>InN Type B</td>
<td>4.72</td>
</tr>
<tr>
<td>ZnO Type A</td>
<td>3.75</td>
</tr>
<tr>
<td>ZnO Type B</td>
<td>4.33</td>
</tr>
<tr>
<td>Quartz Type A</td>
<td>5.67</td>
</tr>
</tbody>
</table>

### TABLE 5

<table>
<thead>
<tr>
<th>X-ray Wavelength: 1.79026 Ångstrom</th>
<th>1st order Bragg angle, Theta, for various peaks (in degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L.C._alloy</td>
<td>111</td>
</tr>
<tr>
<td>Sapphire Type A</td>
<td>3.66</td>
</tr>
<tr>
<td>Sapphire Type B</td>
<td>3.17</td>
</tr>
<tr>
<td>GaN Type A</td>
<td>3.96</td>
</tr>
<tr>
<td>GaN Type B</td>
<td>4.34</td>
</tr>
<tr>
<td>InN Type A</td>
<td>4.6</td>
</tr>
<tr>
<td>InN Type B</td>
<td>3.99</td>
</tr>
<tr>
<td>LiNO - 1/2 of Type A</td>
<td>4.00</td>
</tr>
<tr>
<td>LiNO - 1/2 of Type B</td>
<td>3.47</td>
</tr>
</tbody>
</table>
The inter-planar angle between \{111\} plane and a few other planes are listed in the following Table 7.

**Table 7**

<table>
<thead>
<tr>
<th>Inter-planar Angle between {111} plane and various other planes.</th>
<th>Inter-planar Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>{111}/{224}</td>
<td>19.471</td>
</tr>
<tr>
<td>{111}/{220}</td>
<td>38.409</td>
</tr>
<tr>
<td>{111}/{113}</td>
<td>57.264</td>
</tr>
<tr>
<td>{111}/{004}</td>
<td>64.736</td>
</tr>
</tbody>
</table>

The inter-planar angle between \{111\} plane and a few other planes are listed in the following Table 7.

**Table 6**

| Bragg angles (°) for selected XRD peaks of alloys of fractional lattice matching condition on various substrates (X-ray source: Co Kα (weighted average)). |
|---|---|---|---|---|
| Type A alloy | \{111\} | \{220\} | \{113\} | \{224\} | \{004\} |
| Sapphire - Type A | 53.004 | 69.477 | N/A | N/A |
| Type B LiNbO3 - Type A | 3.47 | 26.539 | 58.822 | N/A | N/A |
| LTNO - Type A | 4.6 | 19.697 | 33.394 | 40.195 | 72.423 |
| LTNO - Type B | 3.99 | 22.866 | 39.386 | 48.079 | 63.815 |
| LiCuTaO3 - Type A | 4 | 22.805 | 39.268 | 47.919 | 63.525 |
| LiCuTaO3 - Type B | 3.47 | 26.539 | 46.855 | 58.822 | N/A | N/A |

These calculated numbers can be applied to the technology of copending application Ser. No. 12/254,150, entitled “METHOD OF GENERATING X-RAY DIFFRACTION DATA FOR INTEGRAL DETECTION OF TWIN DEFECTS IN SUPER-HETERO-EPITAXIAL MATERIALS,” and Ser. No. 12/288,380, entitled “X-RAY DIFFRACTION WAFER MAPPING METHOD FOR RHOMBOHEDRAL SUPER-HETERO-EPITAXY,” which are both incorporated herein by reference in their entirety, for XRD twin detection to all group IV semiconductor alloys made from any of Si, Ge, C, and Sn elements, and group III-V and group II-VI crystalline materials in zinc-blende structure, on any trigonal/hexagonal substrate.

### ADVANTAGES OF THE TECHNOLOGY

The rhombohedral-trigonal (hexagonal) lattice matching technology described herein enables the development of new cubic crystalline semiconductor alloys substantially relieved from misfit dislocation defects on various substrates. One example is shown in FIG. 10 for today’s fastest transistor, Hetero Bipolar Transistor (HET), which is made with SiGe alloy with small Ge content. The electron mobility of the thin base region of HBT is much faster than that of conventional Si transistors because the conduction band of the gradient SiGe alloy layer in the Base region has a built-in electric field due to the band-gap energy difference between the Si layer and the SiGe layer, which is shown as “Slope” in FIG. 10. In spite of these advantages, it has been extremely difficult to make a defect-free SiGe alloy with high Ge content because the lattice constant of Ge is larger than that of Si, as shown at the top of FIG. 10. This difference resulted in a critical thickness, which is a theoretical limit that epitaxial layer can be grown without dislocation defects.

The present invention makes it possible to incorporate high content of Ge and Tin (Sn) atoms into Si free from the prior critical thickness limit because it is lattice-matched, in order to increase the built-in electric field for even faster SiGeSn HBT devices and more efficient SiGeSn TE devices. Note the greater slope in the graph for SiGeSn on the lower right-hand side of FIG. 10. Because faster mobility of electrons and holes are very important to increase ZT factor of TE materials, this technology will be of great use in developing faster semiconductors.

Thus, it is apparent that the methods and materials described in the present disclosure satisfy the objects of the invention set forth above.


Although the present invention has been described in detail, it should be understood that various changes, substitutions, and alterations may be readily ascertainable by those skilled in the art and may be made herein without departing from the spirit and scope of the present invention as defined by the following claims.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A method of forming a hetero-epitaxial crystal structure of a group IV, group III-V or group II-VI alloy on the basal (0001) plane of a trigonal crystal or hexagonal crystal substrate so as to minimize crystalline dislocation defects between the hetero-epitaxial crystal structure of the group IV, group III-V or group II-VI alloy and the trigonal crystal or hexagonal crystal substrate, said method comprising:
   a) if said alloy is a type in which the trigonal arrangement of atomic sites of the \{111\} plane of said alloy crystal directly meets the hexagonal or trigonal coincidence lattice of atomic sites in the basal plane of said substrate
without any rotation, calculating a target lattice constant
($L_{\text{target}}$) as $2/\sqrt{3}$ basal plane lattice constant of the
substrate ($a_{\text{sub}}$);
(b) if said alloy is of a type in which the trigonal arrange-
m ent of atomic sites of the {111} plane of said alloy
is of a type in which the trigonal arrangement of atomic sites of the {111} plane of said alloy
crystal meets the hexagonal or trigonal coincidence lattice of atomic sites in the basal plane of said substrate
without any rotation, calculating $L_{\text{target}}$ as $4/3$ basal plane
lattice constant of the substrate ($a_{\text{sub}}$);
(c) if said alloy is of a type in which the trigonal arrangement of atomic sites of the {111} plane of said alloy
crystal directly meets the inner vertices of the hexagonal or trigonal coincidence lattice of atomic sites in the basal
plane of said substrate without any rotation, calculating
a target lattice constant ($L_{\text{target}}$) as $4/(3 \sqrt{3})$ basal plane
lattice constant of the substrate ($a_{\text{sub}}$);
(d) if said alloy to be of a type in which the trigonal arrangement of atomic sites of the {111} plane of said alloy
crystal meets the inner vertices of the hexagonal or
trigonal coincidence lattice of atomic sites in the basal
plane of said substrate with a 30° rotation, calculating
$L_{\text{target}}$ as $4/(3 \sqrt{3})$ basal plane lattice constant of the substrate ($a_{\text{sub}}$);
(e) determining the respective proportions of the group IV, group III-V or group II-VI elements in said alloy by
approximating $L_{\text{target}}$ as a linear function of the individual lattice constants for the constituent group IV,
group III-V or group II-VI elements weighted in accordance
with said proportions and a Bowing Parameter, and solving for said proportions; and
(f) growing the group IV, group III-V or group II-VI alloy
on the basal (0001) plane of the trigonal crystal or hexagonal crystal
substrate so as to minimize crystalline dislocation defects between the hetero-epitaxial crystal structure of the
group IV, group III-V or group II-VI alloy and the
trigonal crystal or hexagonal crystal substrate.
2. The method of claim 1, wherein the Bowing Parameter is
treated as zero, thereby reducing step c to the step of solving
a system of linear equations.
3. The method of claim 2, wherein said alloy is a binary
alloy in which the two group IV, group III-V or group II-VI
components have relative proportions of x and 1–x and lattice
constant $L_A$ and $L_B$, and, after $L_{\text{target}}$ has been determined in accordance with steps (a) or (b) in claim 1, x is determined by
solving the equation $x^2L_A + (1-x)^2L_B - L_{\text{target}}$.
4. The method of claim 2, wherein said alloy is a ternary
alloy in which the three group IV, group III-V or group II-VI
components have relative proportions of x, y and 1–x–y, lattice constants $L_A$, $L_B$ and $L_C$, and band-gap energies $E_A$, $E_B$ and $E_C$, and, after $L_{\text{target}}$ has been determined in accordance with steps (a) or (b) in claim 1, x and y are determined by
solving the equations $x^2L_A + y^2L_B + (1-x-y)^2L_C - L_{\text{target}}$ and
$x^2E_A + y^2E_B + (1-x-y)^2E_C - E_{\text{target}}$, and the solution is chosen
for which x and y are each between 0 and 1.
5. The method of claim 2, wherein said alloy is a quaternary
alloy in which the four group IV, group III-V or group II-VI
components have relative proportions of x, y, z and 1–x–y–z,
lattice constants $L_A$, $L_B$, $L_C$ and $L_D$, and band-gap energies $E_A$, $E_B$, $E_C$ and $E_D$, and linear thermal expansion coefficients $\alpha_A$, $\alpha_B$, $\alpha_C$ and $\alpha_D$, and, after $L_{\text{target}}$ has been determined in accordance with steps (a) or (b) in claim 1, x, y and z are determined by
solving the equations $x^2L_A + y^2L_B + z^2L_C + (1-x-y-z)^2L_D - L_{\text{target}}$, $x^2E_A + y^2E_B + z^2E_C + (1-x-y-z)^2E_D - E_{\text{target}}$ and
$x^2\alpha_A + y^2\alpha_B + z^2\alpha_C + (1-x-y-z)^2\alpha_D - \alpha_{\text{target}}$, and the solution is chosen for which x, y and z are each between 0 and 1.

* * * * *