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The magic of III-Vs

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Abstract: III-V compound semiconductors have abundant features for various electronic, optoelectronic and photonic applications, all arise from variform magic combination of group III and group V elements formed binaries, resulting in ever-changing characteristics. In this paper, diversified ternaries, quaternaries and quinaries are presented geometrically based on the binaries of arsenide, phosphide and antimonide, mainly concerned of their bandgap, lattice constant and the lattice match domain on different substrates. The features of nitride and dilute nitride, bismide and dilute bismuth, as well as boride, are also discussed briefly. An overall observation of whole III-Vs may contribute to the comprehensive understanding of their latent capacity and sustainable development, along with a lot of challenges.

Key words: III-V compound semiconductors, binary, ternary, quaternary, quinary

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摘要：三五族化合物半导体具有丰富的特性，使其在电子学、光电子学以及光子学领域获得了各种应用，这些都源自于三族元素和五族元素构成之二元系的各种魔幻组合形成的多变特性。本文基于二元系砷化物、磷化物及锑化物，对其构成的各种三元系、四元系和五元系的特征进行了几何图示阐述，主要涉及其带隙、晶格常数及其与不同衬底的晶格匹配区域。对氮化物和稀氮、铋化物和稀铋以及硼化物的一些特性也进行了简要讨论。通过对整个三五族化合物半导体的全面了解将有助于深入了解其潜力和可持续发展态势，包括存在的诸多挑战。

关 键 词：三五族化合物半导体；二元系；三元系；四元系；五元系

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Introduction

75 years have passed since the invention of Ge point contact transistor [1-3]. Closely after that Si entered the stage [4-5], and became the dynast of semiconductors finally. Even before the spring up of those two group IV elemental semiconductors, compound semiconductors had been on the stages [6], including II-VIs, IV-VIs, IV-IVs and III-Vs. Among the big compound family, III-Vs show unique features. The III-Vs are from group III elements of B, Al, Ga, In, Tl and group V elements of N, P, As, Sb, Bi, among them metallic Al, Ga, In and nonmetallic N, P, As, Sb have been well manipulated,

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whereas Bi and B are still under developing. To gain a complete image of the III-Vs, diversified ternaries, quaternaries and quinaries of the III-Vs are presented geometrically based on the binaries of arsenide, phosphide and antimonide, mainly concerned of their bandgap, lattice constant and the lattice match domain on different substrates. With regard to lattice match condition in epitaxy, as common scenes for bulky materials the lattice mismatch should below about 0.1%, whereas for thinner film the mismatch could be much higher depending on the thickness and structure, extending from the match domain. Moreover, with the adopting of strain compensation, as well as introducing of two dimensional, one dimensional or even zero dimensional structures, the restriction of lattice match could be released further. The parameters concerned in this paper are at room temperature if not specifically pointed out. The features of nitrides and dilute nitride, bismides and dilute bismuth, as well as boride, are also introduced simply.

The abundant features of III-V compound semiconductors are aroused from variform magic combination of group III and group V elements, resulting in ever-changing characteristics. Based on those magic characters great success have been gained in electronic, optoelectronic and photonic fields, some important applications will be mentioned in brief. The sustainable development of the semiconductors will be discussed curtly, including their latent capacity and challenges.

1 Arsenide and phosphide

Arsenide and phosphide are relatively mature among III-Vs. The basic binary arsenide and phosphide are AlAs, GaAs, InAs and AlP, GaP, InP with zinc blende (cubic) crystal structure. From those binaries, 9 ternaries, 5 quaternaries and 1 quinary could be constructed. Geometrically, two types of quaternary could be presented using two dimensional regular triangle or square, each binary occupied a corner and each ternary became an edge of those regular triangle or square, as shown in Fig. 1, the bandgaps and lattice constants of the binaries are all marked. The constituent and geometrical presentations expressed in this paper are summarized in Table. 1. The regular triangle type of quaternaries is composed of four elements of three group III and one group V, or three group V and one group III. Analogous to conventional metal alloys, it could be known as the alloy of three binaries, so those types of quaternaries are also called quasi-ternary. As shown in Fig. 1, quaternary AlGaInAs is the quasi-ternary alloy of AlAs, GaAs and InAs, quaternary AlGaInP is the quasi-ternary alloy of AlP, GaP and InP. The square type of quaternaries is also composed of four elements, but two group III and two group V. Analogous to conventional metal alloys, it could be known as the alloy of four binaries, so those types of quaternaries are also called quasi-quaternary. As shown in Fig. 1, quaternary InGaAsP is quasi-quaternary alloy of InAs, GaAs and InP, GaP, analogously the AlGaAsP and AlInAsP. Among binary AlAs, GaAs, InAs arsenide and AlP, GaP, InP phosphide, InAs, GaAs and InP are direct bandgap, AlAs, AlP and GaP are indirect bandgap. When constructing ternaries and quaternaries, their bandgap types are extended from those binary points or corners, with a cross point or cross line at certain compositions as shown in Fig. 1. The shadow area represents indirect zone. In Fig. 1, the direct and indirect bandgap zone is separated by straight lines for simplification, but in fact they should be curved lines or both in most cases.

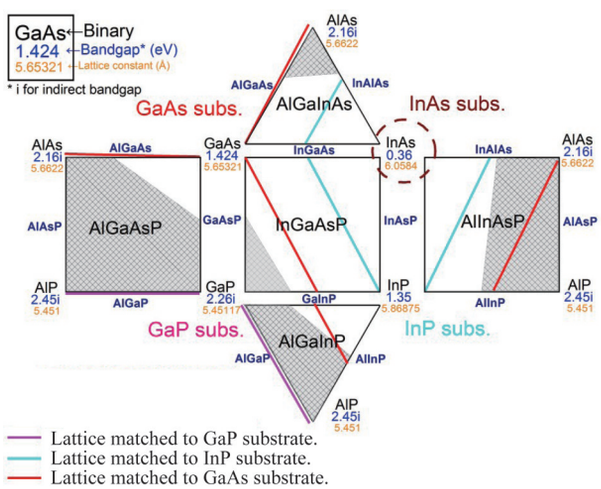

Fig. 1 Geometrical schematic of the ternary and quaternary combinations composed of binary arsenide AlAs, GaAs and InAs, as well as phosphide AlP, GaP and InP, the lattice matched domain to different substrate was also shown. The bandgap and lattice constant of the binaries was marked, shadow area represents indirect bandgap zone

图1 由二元系砷化物AlAs、GaAs及InAs和磷化物AlP、GaP及InP构成的三元系及四元系组合的几何示意图,其与不同衬底的晶格匹配区域已绘于图中。各二元系材料的带隙及晶格常数也在图中标示,阴影表示间接带隙区域

The syntheses of ternaries and quaternaries, especially towards device applications adopting fine structure and favorable material quality, are normally using epitax-

Table 1 Summary of constituent and geometrical presentations of the III-V compound semiconductors
表1 III-V族化合物半导体的构成及几何表达方式汇总

Compounds	Element numbers	Constituent	Geometrical presentations
Binary	2 elements	1 binary	Corner point (0D)
Ternary	3 elements	2 binaries	Edge line (1D)
Quaternary	4 elements	3 binaries/quasi-ternary	Regula triangle (2D)
		4 binaries/quasi-quaternary	Square (2D)
Quinary	5 elements	6 binaries/quasi-hexahydric	Regular triangle prism (3D)

ial growth, in which the important basis is a suitable substrate and the limiting factor is lattice match. In this arsenide and phosphide system, mature GaAs, GaP, InP and InAs binary substrates are available. The substrate restrict compositions of the system were also shown in Fig. 1. From Fig. 1 it could be seen that, the lattice match composition for a quaternary is along straight lines, with ternary or binary points at two ends. In the system, InP substrate inhabit in quaternaries of AlGaInAs, InGaAsP and AlInAsP along three composition lines, in conjunction with two ternary points of InAlAs and InGaAs. All compositions are with direct bandgap in the range between 0.74 eV and 1.5 eV; leaves a great room for applications. GaAs substrate inhabit in quaternaries of AlGaInP, InGaAsP and AlInAsP along three composition lines, in conjunction with two ternary points of GaInP and AlInP. The compositions pass through both direct and indirect bandgap zone, with direct bandgap in the range between 1.43 eV and 2.18 eV. Besides, because of the quite similar lattice constant of GaAs and AlAs, conventional AlGaAs ternary could be grown on GaAs substrate in full composition range, so GaAs/AlGaAs system has been well developed. Also, the GaP and AlP have ever similar lattice constant, the AlGaP ternary could be grown on GaP substrate in full composition range, but with indirect bandgap.

As two typical quaternary examples, quasi-ternary $Al_zGa_xIn_yAs$ and quasi-quaternary $In_{1-x}Ga_xAs_yP_{1-y}$ alloy systems are shown in Fig. 2 [6-7], their bandgap and lattice constant contour are plotted in detail. Normally, the bandgap contour is not straight but bending lines, and the curving degree depends on the alloy bowing parameters of different ternaries [8], whereas the lattice constant contour are always straight lines. In the quasi-ternary $Al_zGa_xIn_yAs$, there are three axes for dependent composition parameters x, y and z of $x+y+z=1$, to keeping the atomic ratio of group III to group V constant as 1. In the quasi-quaternary $In_{1-x}Ga_xAs_yP_{1-y}$, there are two axes for independent composition parameters x and y, keeping the atomic ratio of group III to group V constant as 1 independent of x and y. Quasi-ternary $Al_zGa_xIn_yAs$ system contains the lattice match line to InP substrate, which is almost parallel to x axis and results in a constant In composition of $y=0.52+0.02x\approx0.53$ ($0\leqslant x\leqslant0.47$) and $z=0.48-1.02x$ ($0\leqslant x\leqslant0.47$). At two ends of $x=0.47$ and $x=0$, the direct bandgap ternaries $In_{0.53}Ga_{0.47}As$ and $In_{0.52}Al_{0.48}As$ play a very important role in various applications, especially HEMT (high electron mobility transistor), MIR (mid-infrared) QWIP (quantum well infrared photodetector) and QCL (quantum cascade laser), the high mobility of $In_{0.53}Ga_{0.47}As$ and large conduction band offset of $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$ heterojunction provides a favorite freedom for device design. Another familiar ternary AlGaAs of full composition range on GaAs substrate, had been the building block of many types of devices as laser and photodetectors for a long time, the variable conduction band offset of the AlGaAs/GaAs hetero system makes it distinct for the QWIP and QCL extending to FIR (far-infrared) or THz band. It should be mentioned that, from engineering point of view the manipulating of only one group V element of As brings to superiority in epitaxial growth, other three metallic elements of Al, Ga and In with contiguous features are advisable. Besides, conventional quasi-quaternary $In_{1-x}Ga_xAs_yP_{1-y}$ system contains lattice match lines for both InP and GaAs substrates, with $x=0.47y$ ($0\leqslant y\leqslant1$) for InP substrate and $x=0.51y+0.49$ ($0\leqslant y\leqslant1$) for GaAs substrate. Broad wavelength tuning range, as well as $In_{0.49}Ga_{0.51}P$/GaAs wider bandgap hetero system, supported the important applications of this quaternary including laser diode (LD) and photo detector (PD) of longer wavelength for fiber communication and shorter wavelength for optical disc, as well as heterojunction bipolar transistor (HBT).

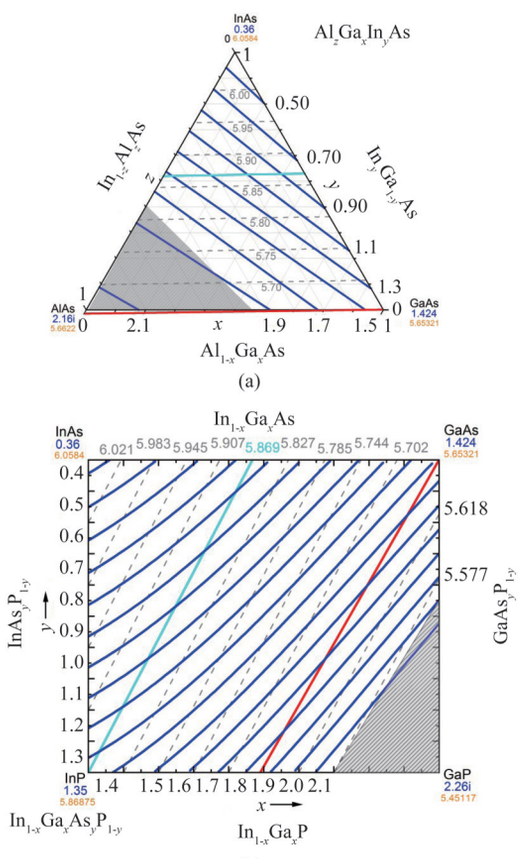

Fig. 2　Schematic of two typical quaternary alloys (a) quasi-ternary $Al_zGa_xIn_yAs$, (b) quasi-quaternary $In_{1-x}Ga_xAs_yP_{1-y}$. The solid (blue) and dashed (gray) line show their direct bandgap and lattice constant contour respectively, shadow area is indirect bandgap. The composition lines lattice matched to InP or GaAs substrates are also shown

图 2　两个典型的四元系示意图 (a)赝三元 $Al_zGa_xIn_yAs$, (b) 赝四元 $In_{1-x}Ga_xAs_yP_{1-y}$。图中实线(蓝色)和虚线(灰色)分别为其直接带隙和晶格常数等高线,阴影区为间接带隙。其与 InP 或 GaAs 衬底晶格匹配的组分线也已示出

Based on the binaries above in conjunction with related ternaries and quaternaries, a III-V compound containing five elements of Al, Ga, In and As, P could be constructed, but in fact it is the alloy of six binaries, or known as quasi-hexahydric inherit and develop their

characteristics. This quinary could be considered as the paper folding of Fig. 1, presented by a regular triangle prism as shown in Fig. 3. It could be seen that, in this quinary the lattice matched composition planes exist for both InP and GaAs substrates, with the shape of triangle or quadrangle respectively. On those planes the characteristics of the quinary compound could be deduced from the features of the quaternary and/or ternary edges almost completely, the bandgap of each concerned composition points could be calculated by using binary, ternary and quaternary data, the direct or indirect bandgap could also be decided. From an overall point of view, the parameters of the quinary are limited by related binary, ternary and quaternary without breakthrough, but could be tuning to a precise desired value. However, adding more elements in the compound also increase the difficulties for material syntheses, so adopting quinary AlGaInAsP in the device is still rare excepting for some research purpose, which also leaves a room for further development.

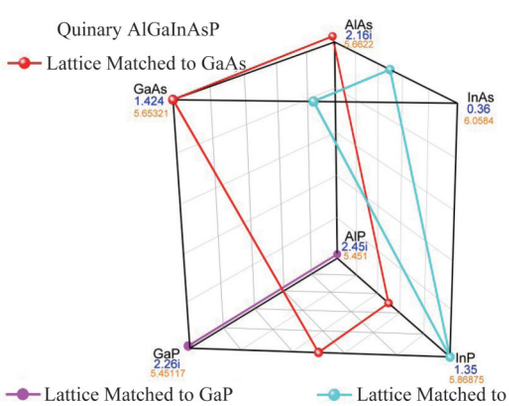

Fig. 3 Geometrical schematic of the quinary AlGaInAsP. The lattice matched domain to different substrate was shown, the bandgap and lattice constant of the binaries was also marked
图3 五元系AlGaInAsP的几何示意图。其与不同衬底的晶格匹配区域已示于图中,各二元系材料的带隙及晶格常数也已在图中标示

2 Antimonide

With the participating of antimony, the pictures of III-Vs become more colorful. In cases of three group V elements P, As and Sb, the antimonide could be classified into three categories: arsenic containing antimonide, phosphor containing antimonide, as well as arsenic and phosphor containing antimonide, still with zinc blende crystal structure, and their features will be discussed below.

2.1 Arsenic containing antimonide

Arsenic containing antimonide are especially important compared with the other two categories, which had been developed for many type devices continuously. The binaries for this category are AlAs, GaAs, InAs and AlSb, GaSb, InSb, from which 9 ternaries, 5 quaternaries and 1 quinary could also be constructed as before, and the geometrical schematic is shown in Fig. 4. Similar to Fig. 1, quaternaries AlGaInAs and AlGaInSb are quasi-ternary alloys; quaternary InGaAsSb, AlGaAsSb and AlInAsSb are quasi-quaternary alloys. Among those binaries, InAs, GaAs, GaSb and InSb are direct bandgap; AlAs and AlSb are indirect bandgap. As shown in Fig. 4, quaternary InGaAsSb is direct bandgap in full composition range, the others are partially.

Although on InP substrate some ternary or quaternary antimonides could be developed, their bandgap coverages are substitutable, so InP substrate is seldom used for antimonides, the GaSb and InAs substrates become dominant. GaSb and InAs have quite similar lattice constants around 6.1 Å, this means from lattice match point of view those two substrates are interchangeable, from this arose the 6.1 Å III-V antimonides. Among them the quaternaries InGaAsSb, AlGaAsSb and AlInAsSb forms a most popular group. From those quaternaries type-I lasers around about 2~3 μm has been developed well, along with photodetectors. From lattice match point of view, type-I device of this category mainly adopts the bandgap of 0.36~0.73 eV of InAs to GaSb, in the wavelength range around 2~3 μm.

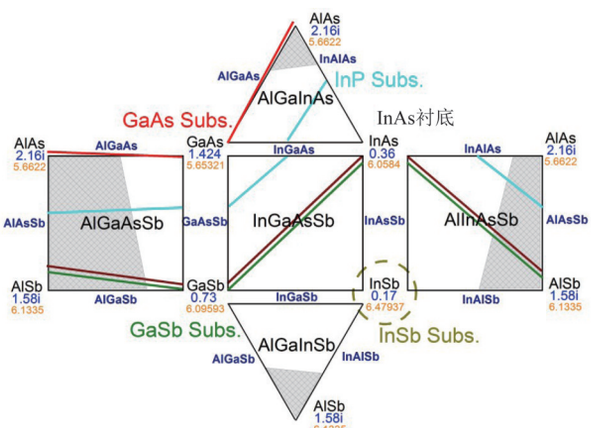

Fig. 4 Geometric schematic of the ternary and quaternary combinations composed of binary antimonide AlSb, GaSb and InSb, as well as arsenide AlAs, GaAs and InAs, the lattice matched domain to different substrate was also shown. The bandgap and lattice constant of the binaries was marked, shadow area represents indirect bandgap zone
图4 由二元系锑化物AlSb、GaSb及InSb和砷化物AlAs、GaAs及InAs构成的三元系及四元系组合的几何示意图,其与不同衬底的晶格匹配区域已绘于图中。各二元系材料的带隙及晶格常数也在图中标示,阴影表示间接带隙区

More amazingly, the GaSb and InAs hetero system forms type-II misaligned (or so called type-III) band alignment that means the valence band of GaSb is higher than the conduction band of InAs. Furthermore, slightly extending from the binary corner increases the design freedom dramatically, the bandgap and band alignment could be adjusted finely. As could be seen from Fig. 4 that, from InAs corner ternaries InAsSb, InGaAs, InAlAs and quaternaries InGaAsSb, AlInAsSb exist, from GaSb corner ternaries InGaSb, AlGaAs, AlAsSb and quaternaries InGaAsSb, AlGaAsSb exist. As examples, in InGaAs/GaAsSb system type-II staggered band alignment could

be formed, in GaInSb/InAs or AlSb/GaInSb system type-II misaligned band alignment could be formed, letting alone a variety of type-I systems. Rich features of the antimonides promoting the birth of colorful category of type-II devices, such as interband cascade laser (ICL) and type II superlattice (T2SL) photodetector. In conjunction with the quantum confinement formed sub-band and mini-band, the wavelength of type-II category devices covers a much wider range than type-I, extending deep into mid-infrared.

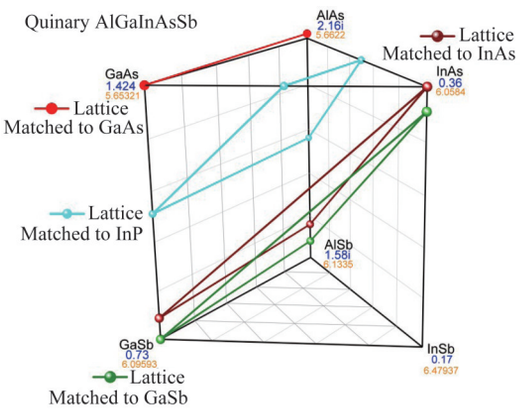

Fig. 5　Geometric schematic of the quinary AlGaInAsSb. The lattice matched domain to different substrate was shown, the bandgap and lattice constant of the binaries was also marked
图5　五元系 AlGaInAsSb 的几何示意图。其与不同衬底的晶格匹配区域已绘于图中,各二元系材料的带隙及晶格常数也已在图中标示

Based on the binaries, ternaries and quaternaries above, an antimonide containing five elements of Al, Ga, In and As, Sb could be constructed, but in fact it is still the alloy of six binaries inherit and develop their characteristics. This quinary could be considered as the paper folding of Fig. 4, presented by a regular triangle prism as shown in Fig. 5. It could be seen that, in this quinary the lattice matched composition planes exist for InP, InAs and GaSb substrates, with the shape of triangle or quadrangle respectively. On those planes the characteristics of the quinary compound could be deduced from the features of the quaternary and/or ternary edges almost completely, the bandgap of each concerned composition points could be calculated by using binary, ternary and quaternary data, the direct or indirect bandgap could also be decided. From Fig. 5 it could be deduced that, the band coverage and alignment of this quinary are overlapped by related binary, ternary and quaternary without further breakthrough, so adopting this quinary in the device are still rare. However, in arsenic containing antimonide two group V elements As and Sb have existed already, manipulating one more group III element is not critical, so this AlGaInAsSb quinary leaves an opportunity for further excavating.

2.2　Phosphor containing antimonide

Phosphor containing antimonide is not as important as arsenic containing antimonide mainly because of its band coverage and band alignment diversification. The binaries for this category are AlP, GaP, InP and AlSb, GaSb, InSb, from which also 9 ternaries, 5 quaternaries and 1 quinary could be constructed as before, Fig. 6 shown the schematic, which is quite similar to those of Fig. 4 geometrically. In this system, quaternaries AlGaInP and AlGaInSb are the same as before of quasi-ternary alloys, quaternary InGaPSb, AlGaPSb and AlInPSb are quasi-quaternary alloys. Quaternary InGaPSb lattice matched to GaSb or InAs substrates is with direct bandgap in full composition range, the band coverage is from GaSb of 0.73 eV to InPSb of above 0.46 eV [9], which is quite useful but replaceable, as of InGaAsSb system. The hetero InP/GaSb system, expanding to InPSb/GaSb, has type-II staggered band alignment, which is also promising for design. The phosphor containing antimonide could also be applied to GaAs or InP substrate as shown in Fig. 6. On GaAs substrate the antimonides are mainly in indirect bandgap zone, whereas on InP substrate all in direct bandgap zone, the bandgap extending from above 0.8 eV of GaPSb to 1.34 eV of InP, the GaPSb/InP hetero system also has type-II staggered band alignment [10]. Notice that for material growth using solid source molecular beam epitaxy (SSMBE), manipulating of As is easier than P, but for gas source molecular beam epitaxy (GSMBE) or metalorganic vapor phase epitaxy (MOVPE) the situation are different. In a word, the phosphor containing antimonide is still not well developed, some challenges remain.

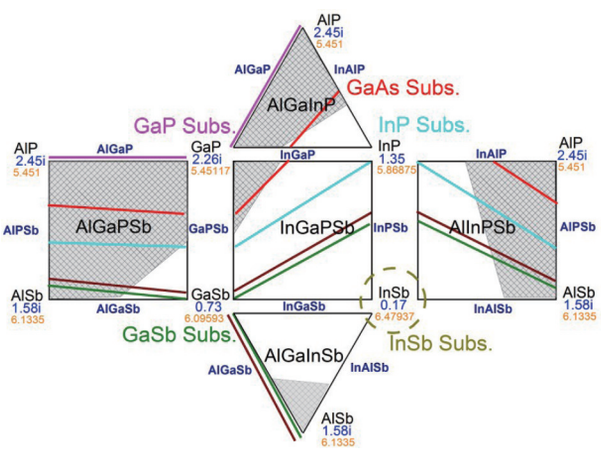

Fig. 6　Geometric schematic of the ternary and quaternary combinations composed of binary antimonide AlSb, GaSb and InSb, as well as phosphide AlP, GaP and InP, the lattice matched domain to different substrate was also shown. The bandgap and lattice constant of the binaries was marked, shadow area represents indirect bandgap zone
图6　由二元系锑化物 AlSb、GaSb 及 InSb 和磷化物 AlP、GaP 及 InP 构成的三元系及四元系组合的几何示意图,其与不同衬底的晶格匹配区域已绘于图中。各二元系材料的带隙及晶格常数也在图中标示,阴影表示间接带隙区

Doing a paper folding of Fig. 6 as before results in a quinary antimonide containing five elements of Al, Ga, In and P, Sb as shown in Fig. 7. From Fig. 7 it could be seen that, in this quinary the lattice matched composition planes exist for multiple substrates of GaAs, InP,

InAs and GaSb, with the shape of quadrangle or triangle respectively. On those planes the characteristics of the quinary compound could also be deduced from the features of their binary corners, ternary edges and quaternary lines. From Fig. 7 it could be deduced that, the band coverage and alignment of this quinary have been overlapped by related binary, ternary and quaternary without unexpected surprise, adopting of this quinary in real device are still rare. In this quinary system manipulating of two group V elements P and Sb simultaneously is critical, leaves opportunities for further excavating.

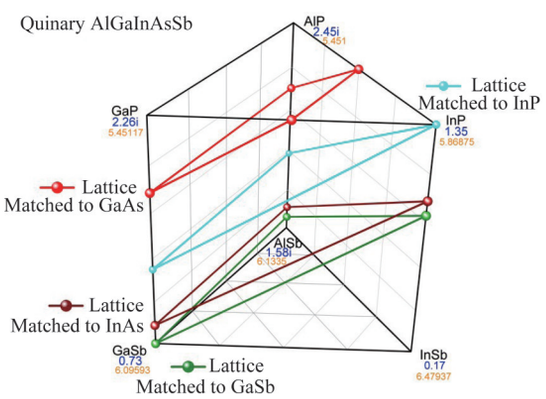

Fig. 7 Geometric schematic of the quinary AlGaInPSb. The lattice matched domain to different substrate was shown, the bandgap and lattice constant of the binaries was also marked
图7 五元系AlGaInPSb的几何示意图。其与不同衬底的晶格匹配区域已绘于图中,各二元系材料的带隙及晶格常数也已在图中标示

2.3 Arsenic and phosphor containing antimonide

With the join of both arsenic and phosphor, the antimonide become more colorful. For arsenic and phosphor containing antimonide, the starting points are from three quaternaries, with partaking of etch group III elements Al, Ga or In, Fig. 8 shows the schematic. In those three quaternaries, the Al or Ga containing antimonides could be lattice matched to GaAs or InP substrates, but for InAs or GaSb substrates only touches the AlSb or GaSb corners. The Al containing AlAsPSb is indirect bandgap in full composition range because of the indirect bandgap of Al containing binaries AlAs, AlP and AlSb, whereas the Ga containing GaAsPSb is partially direct bandgap excepting the indirect GaP corner. The bandgaps of those quaternaries are relatively large and their coverages seems not unusual so could be substituted by other arsenide or phosphide mentioned above. Therefore, considering the difficulties in manipulating three group V elements simultaneously, those two quaternaries are rarely introduced. However, for the In containing InAsPSb quaternary situations become different.

As shown in Fig. 8, the InAsPSb quaternary is direct bandgap in full composition range and with relatively small bandgap until into mid-infrared wavelength band. The In containing InAsPSb quaternary could be lattice matched to GaSb or InAs substrates, the compositions begin from InAs corner extending to InPSb ternary side,

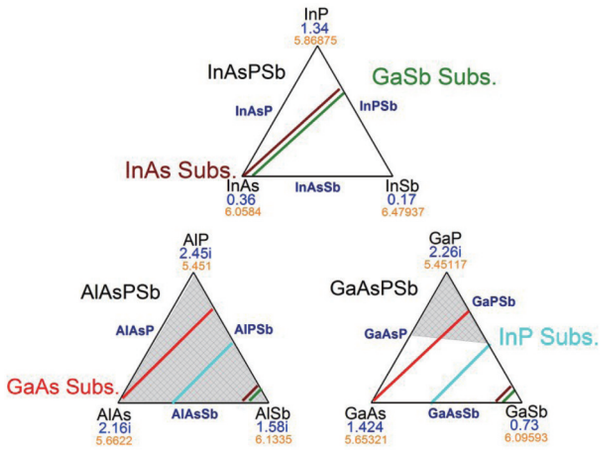

Fig. 8 Geometric schematic of some ternary and quaternary combinations composed of binary antimonide AlSb, GaSb and InSb with both arsenide and phosphide, the lattice matched domain to different substrate was also shown. The bandgap and lattice constant of the binaries was marked, shadow area represents indirect bandgap zone
图8 由二元系锑化物AlSb、GaSb及InSb和砷化物及磷化物构成的一些三元系及四元系组合的几何示意图,其与不同衬底的晶格匹配区域已绘于图中。各二元系材料的带隙及晶格常数也在图中标示,阴影表示间接带隙区

forms another one in the 6.1 Å antimonide category. To see more clearly, the lattice constant, bandgap, and lattice matching lines of InAsPSb quaternary are calculated as shown in Fig. 9. The band bowing parameters used for the InAsP, InAsSb and InPSb ternaries are 0.1, 0.67 and 1.9 eV respectively [8]. Notice that for the InAsSb and InPSb ternaries their band bowing parameters are even large than the bandgap of composed binaries, so the band energy bowing of this system around InSb corner is very significant. Form Fig. 9 it could be seen that, the bandgap could be down to below 0.1 eV, much lower than the smallest binary one of InSb of 0.17 eV, give rise to an interesting feature. When lattice matched to GaSb or InAs substrates, the bandgaps of quaternary InAsPSb cover 0.290~0.456 eV and 0.360~0.569 eV respectively, this located in a promising band at the short wavelength side of mid-infrared. The quaternary InAsPSb had been used to develop LDs and PDs of wavelength large than 2 μm since more than four decades ago, mainly adopting liquid phase epitaxy (LPE) on InAs substrate. Those devices still go on type-I mechanism of interband transition, pioneer to the devices of type-II mechanism or intraband transition as QCL, ICL and QWIP. The performance of the devices seems moderate and promising. With the development of MOVPE or MBE, this quaternary still could be further explored. As shown in Fig. 9, the quaternary InAsPSb involves all important space remote sensing band of short-wave infrared (SWIR), mid-wave infrared (MWIR), vapor infrared (VIR) and long-wave infrared (LWIR) bands. Similar situations exist in other antimonide systems, leaves a lot of potential.

From Fig. 8 it could be deduced that, from those arsenic and phosphor containing antimonides, three qui-

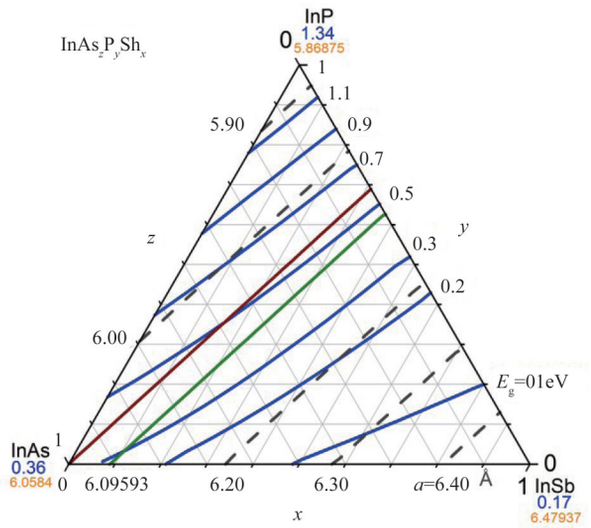

Fig. 9 Schematic of quaternary alloys of quasi-ternary InAs$_z$P$_y$Sb$_x$. The solid (blue) and dashed (gray) line show bandgap and lattice constant contour respectively. The composition lines lattice matched to InAs or GaSb substrates are also shown

图9　赝三元InAs$_z$P$_y$Sb$_x$四元系合金的带隙、晶格常数和组分示意图。图中实线(蓝色)和虚线(灰色)分别为其带隙和晶格常数等高线。其与InAs或GaSb衬底晶格匹配的组分线也已示出

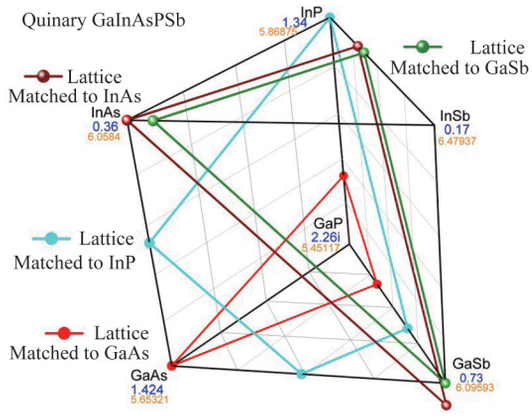

Fig. 10　Geometric schematic of the quinary GaInAsPSb. The lattice matched domain to different substrate was shown, the bandgap and lattice constant of the binaries was also marked

图10　五元系GaInAsPSb的几何示意图。其与不同衬底的晶格匹配区域已绘于图中,各二元系材料的带隙及晶格常数也已在图中标示

naries of AlInAsPSb, AlGaAsPSb and GaInAsPSb could be developed. Among those quinaries, all composed quasi quaternaries had appeared before, in conjunction with three quasi ternaries, their features could be estimated in detail like before. Here as an example, the geometrical structure of quinary GaInAsPSb system is plotted as shown in Fig. 10 based on related binaries, ternaries and quaternaries. With five elements of As, P, Sb and Ga, In, this quinary is the alloy of six binaries inherits and develops their characteristics. From Fig. 10 it could be seen that, in this quinary the lattice matched composition planes exist for four substrates of InP, GaAs, GaSb and InAs, with the shape of quadrangle or triangle respectively. On those planes the characteristics of the quinary compound could be deduced from the features of the quaternaries and/or ternary edges without exception, the bandgap of each concerned composition points still could be calculated by using binary, ternary and quaternary data, the direct or indirect bandgap could also be decided. From Fig. 10 it could be deduced that, on this quinary system, the interesting bandgap coverage and band alignment compositions may still locate around some binary corners as well as ternary edges, especially the 6.1 antimonide category. The worries for the epitaxy of this quinary are still manipulating three group V elements As, P and Sb simultaneously, but leave an opportunity for further excavating.

3　Nitride and dilute nitride

Nitride forms a unique category in III-Vs, which "appears" much later than arsenide or phosphide, and even antimonide, but has become popular much fast. Different from the arsenide, phosphide and antimonide mentioned before with zinc blende (belong to cubic crystal system) structure mostly, nitride could also have wurtzite (belong to hexagonal crystal system) structure. The discussion of nitrides will only on wurtzite structure below with two hexagonal lattice constant a and c, because it is the main trend now. Three nitride binaries AlN, GaN and InN are all with direct bandgap, they could form three ternaries of AlGaN, AlInN and InGaN, as well as one quaternary AlGaInN, all of them are also with direct bandgap therefore, as shown schematically in Fig. 11. Nitride forms a large bandgap system with bandgap of 3.4 eV for GaN and even 6.2 eV for AlN, their lattice constants are quite similar, so AlGaN ternary becomes the most popular wide bandgap nitride material, and AlGaN/GaN forms most useful hetero structure in the system. As for nitride, no perfect substrate exists for epitaxy expecting GaN itself, but the crystal growth of GaN is still difficult, so different type of substrates have been explored, including sapphire, 6H-SiC, 4H-SiC of hexagonal, and 3C-SiC or even Si of cubic, as marked in Fig. 11. Besides, different types of template with thin GaN film or hydride vapor phase epitaxy (HVPE) grown and stripped thick GaN film are also used as substrates for nitride, and reached better effects. Nitrides GaN or AlGaN are mainly used for LED in blue or UV bands, as well as LD, and reached great success. Furthermore, the wide bandgap, high breakdown electric field, high electron saturation velocity of GaN, and high electron mobility of the GaN/AlGaN 2D electron gas, makes them play an important role in high temperature, high voltage, high power and high frequency electron devices. The AlN, GaN and InN system has type-I band alignment, the higher band offset of the system makes them interesting for optoelectronic devices of intraband transition, leaves a room to be explored, but from application point of view their wavelength coverage is not irreplaceable.

Because of the big difference of nitrogen atoms with other group V elements As, P and Sb, the combination of N into III-Vs to form other N containing ternary, quaternary or even quinary is extremely difficult. However,

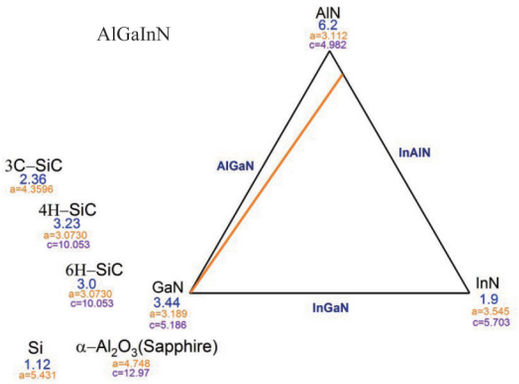

Fig. 11 Geometric schematic of quaternary AlGaInN and ternaries AlGaN, InGaN, InAlN composed of binary nitride AlN, GaN and InN of wurtzite structure (hexagonal crystal system). The bandgap and lattice constant of the binaries was marked, some substrates for this nitride system were also noted

图11 由纤维锌矿(六方晶系)结构二元系氮化物AlN、GaN及InN构成的四元系AlGaInN及三元系AlGaN、InGaN、InAlN的几何示意图。各二元系材料的带隙及晶格常数如图中标示,对此氮化物系统的一些衬底也在图中注出

adding slight amount of N into existing III-Vs, forming so called dilute nitride, has been attempted, where GaAs based dilute nitride could be a typical example. Of all the III-Vs, GaAs/AlGaAs system should be the best one of high quality GaAs substrate available, full composition matching, mature growth technique, and so on. Vertical cavity surface emitting lasers (VCSELs) have been developed successfully on GaAs/AlGaAs system profit from relatively higher contrast of their refractive index essentially for the distributed Bragg reflector (DBR) structure, whereas the wavelength could be only on short side around 850 nm. For longer wavelength of optical fiber band, lasers work well by using InP based InGaAsP system as shown before, but lack of high contrast material pair for the DBR, makes VCSEL difficult. About dilute nitride, as adding a litter N (about 1% ~ 2%) into InGaAs, could decrease the lattice constant and increase the bandgap wavelength to make it matching to GaAs substrate and fall into optical fiber band [11-12]. In the epitaxy Sb could be used as a surfactant to improve the material quality [12]. As a trial, adding more cell to the multi-junction solar cell on GaAs or Ge substrate by using InGaAsN(Sb) also reported [13]. Considering numerous III-Vs introduced above, there are still massive dilute nitrides could be explored, the motivation is mainly applications, and the difficulty still be the mixing of N into lattice.

4 Bismide and dilute bismide

Known as metal or semimetal, bismuth is the heaviest non-radioactive element at the bottom of periodic table. The characteristics of bismuth are quite different from other group V elements previously mentioned. For III-Vs, binary bismide may be semimetals rather than semiconductors; some detailed features are still unclear, single crystal growth or epitaxy is seldom seen. Although some other bismuth compounds as Bi_2Te_3, which is the best thermoelectric material and a semiconductor, have made great successes for device applications as thermoelectric cooler (TEC) or energy convertor, the bismuth III-V binaries are still rarely used for practical semiconductor devices because the lack of both theoretical expects and technical supports, which leaves an imaginary room. As an example of bismuth ternary, only considering the nearest neighbor InSb with InBi; the InSb is with quite narrow a bandgap of 0.17 eV and belong to cubic (zinc blende) crystal structure, while InBi is known as semimetal with zero or even negative bandgap and belong to tetragonal crystal structure [14]. It could be deduced that, the bandgap of ternary InSbBi could cover the wavelength band from MIR to FIR, which should be interested for applications. However, different types of crystal structure and lack of suitable substrate make things complex inevitably. Extrapolated from InSbBi or InAsBi with lower Bi content, the lattice constant of InBi is large than 6.62 Å regardless of its crystal structure [15-16], which is out of the 6.1 Å antimonide category.

Noteworthily, dilute bismides has attracted much attention recent years based on the feasibility of adding a small amount of Bi into existing III-Vs mentioned before[17], similar to the dilute nitrides. Many types of dilute bismides have been explored including ternaries as GaAsBi, AlAsBi, GaPBi, InNBi, GaNBi, InPBi, GaSbBi, InAsBi, InSbBi, and quaternaries as InGaAsBi, InGaPBi, InAlPBi, GaAsNBi, GaNSbBi, etc. The adopted substrates including GaAs, InP and GaSb. The adding of a small amount of Bi into existing III-Vs normally did not change their crystal structures, but was accompanied by increasing the lattice constant, and more importantly decreasing the bandgap. The bandgap decreasing effect of Bi is more notable than other elements. For example, in quaternary InGaAsBi system the bandgap narrowing effect of Bi is stronger than that of In. Fig. 12 showed the bandgap contour of the quaternary InGaAsBi at its dilute bismide area with Bi content less than 10%, in which the lattice matching line and ~1.3% mismatching line to the InP substrate were also plotted. The ternary InGaAs is lattice matched to InP at In composition of 0.53, suitable for photodetectors with cutoff wavelength of 1.7 μm. To extending the cutoff wavelength, as to about 2.2 μm, the In composition should increase to about 0.72, and therefore introduce ~1.3% lattice mismatch, those mismatch degrading the device performance obviously. Seeing from Fig. 12 that, by adding about 5% of Bi and decreasing about 3% of In, the cutoff wavelength could also be extending to about 2.2 μm but still keeping the InGaAsBi lattice matched to InP substrate, therefore eliminating the lattice mismatch effects. Besides, the temperature sensitivity of the bandgap of bismides is lower. Based on this consideration, gas source molecular beam epitaxy of quaternary InGaAsBi system was explored [18], wavelength extending InGaAsBi photodetectors have been demonstrated[19-20], and temperature coefficient of the cutout wavelength is decreased from 1.29 nm/K of InGaAs device to 0.96 nm/K [20]. Besides, Bi could also be used as a surfactant in the epitaxy to improve material quality, as in the lasers with pseudomor-

phic structures [21]. For dilute bismides, the introducing of Bi gives a valuable room for the tailoring of various parameters including lattice constant, bandgap, band alignment and so on, the principle of choice lies in that the benefits should compensate the difficulties in the epitaxy growth and therefore originated material degradation.

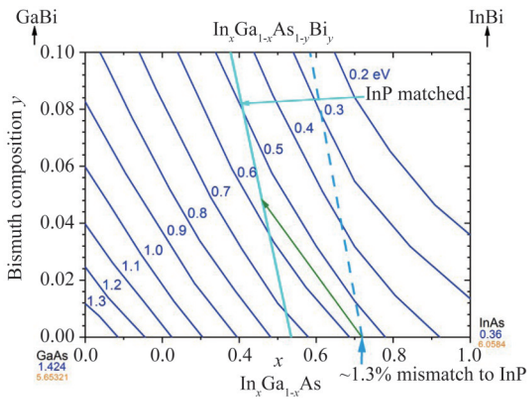

Fig. 12　Bandgap contour of the quaternary InGaAsBi at dilute bismide area with Bi content less than 10%, in which the lattice matching line and ~1.3% positive mismatching line to the InP substrate were also plotted

图 12　四元系 InGaAsBi 中铋含量小于 10% 稀铋区域的带隙等高线图,其中也绘出了与 InP 衬底的晶格匹配线及~1.3% 正失配线

5　Boride

Among III-Vs boride should be the last and interested one, although had been investigated for so long a time till now. For example, cubic boron nitride (cBN) had been artificially synthesized in 1950's, whereas the natural mineral (Qingsongite) formed in earth mantle was only founded from southern Tibet, China until 2009 [22]. III-V borides may have different crystal structure as cubic, hexagonal or rhombohedral; the lattice constant of cBN is 3.615 Å close to that of diamond. Known as a semiconductor, cBN is with a very wide bandgap (indirect) exceeding of 6 eV similar to that of AlN, whereas its ceramic alike features of very high melting point, hardness and thermal conductivity, as well as very low density, are more famous for other types of applications. The wide bandgap and high thermal conductivity are the figure of merits of semiconductors for high temperature and high power devices, but the utilization of cBN still has a long way ahead. Similarly, cubic boron phosphide (cBP) had been artificially synthesized since 1960's. An indirect bandgap of about 6 eV was reported at the time [23], than amended to be about 2 eV [24]. The lattice constant of cBP is 4.536 Å. The difficulties in the growth especially epitaxy of thin films limited their device applications.

Very recently, the cubic boron arsenide (cBAs), which is another III-V boride with cubic crystal structure, has attracted public attention. The predicted and measured carrier mobility of cBAs are quite high for both electrons and holes, forms a high ambipolar mobility semiconductor material exceeding those of Si, and the thermal conductivity remains a very high value as cBN [25-26]. The bandgap of cBAs is reported to be a moderate value around 2 eV suitable for doping, the lattice constant is around 4.8 Å not far away from those of Si or GaAs, makes it a compatible material for future integrated circuit or power devices potentially.

6　Applications, sustainable development and summary

Main applications, including but not limited to, of the III-V compound semiconductors mainly in three categories of electronics, optoelectronics and photonics, which are listed briefly in Table 2. As for electronics, their applications extending from power and RF devices to millimeter wave or even THz amplifiers and oscillators. Refer to optoelectronics, mainly the lasers and photodetectors, the wavelength range extending from deep ultraviolet (DUV) to far infrared (FIR) also including THz band. With regard to photonics, the integration of optoelectronic device especially the lasers with different type of optical components makes so called photon processing possible. Among those applications adopting III-Vs, somewhat may be substituted by using other materials, but most of them are irreplaceable, that is why the III-Vs had been developed so many years, and have to be in progress continuously.

Table 2　Main applications of III-V compound semiconductors in three categories of electronics, optoelectronics and photonics

表 2　三五族化合物半导体在电子学、光电子学和光子学三个方面的主要应用

Electronics	Optoelectronics	Photonics
Transferred electron microwave sources (Gunn, IMPATT, BARRITT, …)	Photodetector and FPA (PIN, APD, QWIP, T2SL, …)	Waveguide, Coupler, Divider, Isolator, …
Mixer, Hall, …	Photocathode	Filter
High power, high temperature devices	Solar cell, thermal cell	Modulator (Amplitude, Phase)
Heterojunction bipolar transistor (HBT)	Light emitting diode	Multiplexer
High electron mobility transistor (HEMT), Pseudomorphic HEMT, …	Lasers (FP, DFB, VCSEL, QCL, ICL, …)	Semiconductor optical amplifier (SOA), Wavelength convertor, …
Monolithic microwave integrated circuit (MMIC)	Optoelectronic integrated circuit (OEIC)	Photonic integrated circuit (PIC)
……	……	…,,,

Sustainable developments of a material system are not only depending on the application aspects, but also on many other effects include resources, capitals, geopolitics, etc. Table 3 listed the earth's crust abundance of some elements related to group IV, III-V and II-VI semiconductors, including their density and melting

Table 3 The earth´s crust abundance, density and melting points of some elements related to group IV, III-V and II-VI semiconductors, the noble metal silver and gold were also listed for comparison

表3 一些四族、三五族和二六族半导体元素的地壳丰度及密度和熔点,贵金属金和银也列于表中作为比较

element	Si	Ge	Al	Ga	In	P	As	Sb	Bi	Te	Cd	Hg	Se	Ag	Au
abundance/ppm	270k	1.5	82k	18	0.16	1k	2.1	0.2	0.025	0.005	0.11	0.05	0.05	0.08	0.003
density/(g/cm^3)	2.33	5.35	2.70	5.91	7.30	1.82	5.73	6.68	9.8	6.25	8.65	13.5	4.81	10.5	19.3
melting point/°C	1410	938	660	29.8	157	Sub.	817	631	271	449	321	−39	221	962	1064

points. The noble metal silver and gold were also included for comparison. The dependence of resources for different types of applications is certainly different. As an example, the material consumed for bulky solar cells should be very high, but for thin film solar cells could be much lower. Among the elements for III-Vs, the abundances are below 1 ppm for In, Sb and Bi, whereas Al and P should be sufficient. Certainly, earth′s crust abundance is not the only factor, the mineralization, mine grade, mining and smelt, as well as the extraordinary purification of the elements for semiconductors, all play very important role, say nothing of capitals and geopolitics. Fortunately, the resources of some elements as In, Sb and Bi are quite rich in China; others are not poor relatively, sufficient to support the sustainable developments of III-Vs.

In summary, through systematical depiction of III-Vs, including their binaries, ternaries, quaternaries and quinaries combined with schematic diagrams briefly, a complete image of those compound semiconductor category was established. Based on analysis, the magic of the III-Vs could be realized, the uniqueness of this material category could be apperceived, and the potentiality of the compounds for further development could be comprehended.

References

[1] Bardeen J, Brattain W H. The transistor, a semi-conductor triode [J]. *Physical Review*. 1948, **74**:230-231.

[2] Brattain W H, Bardeen J. Nature of the forward current in Germanium point contacts [J]. *Physical Review*. 1948, **74**:231-232.

[3] Bardeen J, Brattain W H. Physical principles involved in transistor action [J]. *Physical Review*. 1949, **75**:1208-1225.

[4] Shockley W, Pearson G L. Modulation of conductance of thin films of semi-conductors by surface charges [J]. *Phys. Rev.* 1948, **74**: 232-233.

[5] Shockley W, The theory of p-n junctions in semiconductors and p-n junction transistors [J]. *Bell System Technical Journal*. 1949, **28**:435-489.

[6] Gong H M, Li X, Zhang Y G. InGaAs photodetectors and focal plane arrays [M] Science express, Beijing.(龚海梅,李雪,张永刚。铟镓砷光电探测器及其焦平面阵列[M]. 北京:科学出版社) 2022. **ISBN: 978**)-7-03-072094-8.

[7] Zhang Y G, Gu Y, Shao X M, *et al*. Short-wave infrared InGaAs photodetectors and focal plane arrays [J]. *Chin. Phys.* B. 2018, **27** (12):128102.

[8] Vurgaftman I, Meyer J R, Ram-Mohan L R. Band parameters for III-V compound semiconductors and their alloys [J]. *J. Appl. Phys.*, 2001, **89**(11):5815-5875.

[9] Biefeld R M, Baucom K C, Kurtz S R, *et al*. The growth of $InP_{1-x}Sb_x$ by metalorganic chemical vapor deposition [J]. *J. Cryst. Growth 1*. 1993, **33**:38-46.

[10] Loualiche S, Corre A Le, Salaun S, *et al*. GaPSb: A new ternary material for Schottky diode fabrication on InP [J]. *Appl. Phys. Lett*. 1991, **59**:423-424.

[11] Riechert H, Ramakrishnan A, Steinle G. Development of InGaAsN-based 1.3 μm VCSELs [J]. *Semicon. Sci. Technol*. 2002, **17**: 892-897

[12] Yang X, Jurkovic M J, Heroux J B, *et al*. Molecular beam epitaxial growth of InGaAsN: Sb/GaAs quantum wells for long-wavelength semiconductor lasers [J]. *Appl. Phys. Lett*. 1999, **75**(2):178-180.

[13] Cheriton R, Wilkins M M, Sharma P, *et al*. Design optimizations of InGaAsN(Sb) subcells for concentrator photovoltaic systems [J]. *J. Vac. Sci. Technol. B*. 2016, **34**(2):02M103.

[14] Degtyareva V F, Winzenick M, Holzapfel W B. Crystal structure of InBi under pressure up to 75 GPa [J]. *Physical Review B*. 1998, **57** (9):4975-4978.

[15] Rajpalke M K, Linhart W M, Yu K M, *et al*. Bi-induced band gap reduction in epitaxial InSbBi alloys [J]. *Appl. Phys. Lett*. 2014, **105**: 212101.

[16] Shalindar A J, Webster P T, Wilkens B J, *et al*. Measurement of InAsBi mole fraction and InBi lattice constant using Rutherford backscattering spectrometry and X-ray diffraction [J]. *J. Appl. Phys*. 2016, **120**: 145704

[17] Wang S M, Lu P F Eds). Bismuth-containing alloys and nanostructures [M]. Springer Nature Singapore Pte Ltd, Singapore. 2019. ISBN 978-981-13-8077-8

[18] Chen X Y, Gu Y, Zhang Y G, *et al*. Characteristics of InGaAsBi with various lattice mismatches on InP substrate [J]. *AIP advances*. 2016, **6**:075215.

[19] Gu Y, Zhang Y G, Chen X Y, *et al*. Nearly lattice-matched short-wave infrared InGaAsBi detectors on InP [J]. *Appl. Phys. Lett*. 2016, **108**:032102

[20] Du B, Gu Y, Zhang Y G, *et al*. Wavelength extended InGaAsBi detectors with temperature-insensitive cutoff wavelength [J]. *Chin. Phys. Lett*. 2018, **35**(7):078501.

[21] Ji W Y, Gu Y, Zhang Y G, *et al*. InP-based pseudomorphic InAs/InGaAs triangular quantum well lasers with bismuth surfactant [J]. *Appl. Opt*. 2017, **56**(31):H10-H14.

[22] Dobrzhinetskaya L F, Wirth R, Yang J, *et al*. E.S. (2013) Qingsongite, IMA 2013-030. CNMNC newsletter no. 16, August 2013, page 2708 [J]. *Mineralogical Magazine*, 2013, **77**(16):2695-2709.

[23] Stone B, Hill D. Semiconducting properties of cubic boron phosphide [J]. *Phys. Rev. Lett.*, 1960, **4**(6): 282-284.

[24] Archer R J, Koyama R Y, Loebner E E, *et al*. Optical absorption, electroluminescence, and the band gap of BP [J]. *Phys. Rev. Lett.*, 1964, **12**(19):538-540.

[25] Yue S, Tian F, Sui X Y, *et al*. High ambipolar mobility in cubic boron arsenide revealed by transient reflectivity microscopy [J]. *Science*. 2022, **377**:433-436.

[26] Shin J W, Gamage G A, Ding Z W, *et al*. High ambipolar mobility in cubic boron arsenide [J]. *Science*. 2022, **377**:437-440.