

# Origin of the anomalous trends in band alignment of GaX/ZnGeX<sub>2</sub> (X = N, P, As, Sb) heterojunctions

Ruyue Cao<sup>1,2</sup>, Hui-Xiong Deng<sup>1,2,†</sup>, Jun-Wei Luo<sup>1,2,3,†</sup>, and Su-Huai Wei<sup>4,†</sup>

<sup>1</sup>State Key Laboratory of Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

<sup>2</sup>University of Chinese Academy of Sciences, Beijing 100049, China

<sup>3</sup>Synergetic Innovation Center of Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei 230026, China

<sup>4</sup>Beijing Computational Science Research Center, Beijing 100193, China

**Abstract:** Utilizing first-principles band structure method, we studied the trends of electronic structures and band offsets of the common-anion heterojunctions GaX/ZnGeX<sub>2</sub> (X = N, P, As, Sb). Here, ZnGeX<sub>2</sub> can be derived by atomic transmutation of two Ga atoms in GaX into one Zn atom and one Ge atom. The calculated results show that the valence band maximums (VBMs) of GaX are always lower in energy than that of ZnGeX<sub>2</sub>, and the band offset decreases when the anion atomic number increases. The conduction band minimums (CBMs) of ZnGeX<sub>2</sub> are lower than that of GaX for X = P, As, and Sb, as expected. However, surprisingly, for ZnGeN<sub>2</sub>, its CBM is higher than GaN. We found that the coupling between anion *p* and cation *d* states plays a decisive role in determining the position of the valence band maximum, and the increased electronegativity of Ge relative to Ga explains the lower CBMs of ZnGeX<sub>2</sub> for X = P, As, and Sb. Meanwhile, due to the high ionicity, the strong coulomb interaction is the origin of the anomalous behavior for nitrides.

**Key words:** GaX/ZnGeX<sub>2</sub> heterojunctions; band offsets; atomic orbital coupling

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## 1. Introduction

Band offsets between two semiconductors AX and BY play a vital role in electronic devices, because they can lead to different electron quantum confinements and determine the spatial distribution of carriers. III–V compound semiconductor materials such as GaX (X = N, P, As, Sb) are important materials for electronic and optoelectronic applications<sup>[1–3]</sup>. However, the number of the III–V semiconductors and their available material properties are limited. One of the approaches to extend their range of applications is through atomic transmutation, in which, two group III elements (e.g., Ga) are replaced by one group-II element (e.g., Zn), and one group-IV element (e.g., Ge) to systematically obtain new heterovalent II–VI–X<sub>2</sub> compounds (e.g., ZnGeX<sub>2</sub>)<sup>[4–8]</sup>. These new compounds have the same number of valence electrons as the original III–V compounds, so they are expected to obey the octet rule with the same semiconductor characters. However, although some ternary compounds such as ZnGeN<sub>2</sub> and ZnGeP<sub>2</sub> have been synthesized and are predicted to have interesting properties for novel applications such as nonlinear optical devices<sup>[9,10]</sup>, the electronic band structures of these compounds are poorly understood. For example, it is not clear what the relative positions of the conduction band minimums (CBMs) and valence band maximums (VBMs) are between GaX and ZnGeX<sub>2</sub> after Ga is replaced

by its neighboring Zn and Ge elements and how the band offsets change as the anion atomic number increases from N to P to As to Sb.

In this paper, we systematically calculate the band offsets of heterojunctions GaX/ZnGeX<sub>2</sub> (X = N, P, As, Sb) using the first-principles method. We show that the band alignment is type-I for X = P, As, and Sb, that is the VBM of ZnGeX<sub>2</sub> is higher than that of GaX and the CBM of ZnGeX<sub>2</sub> is lower than that of GaX. Surprisingly, it is type-II for the nitrides because the CBM of ZnGeX<sub>2</sub> is higher than GaX. By analyzing the VBM and CBM wavefunction characters, we found that the coupling between anion *p* and cation *d* states play a decisive role in determining the position of the valence band maximum, and the increased electronegativity of Ge relative to Ga can explain the lower CBM of ZnGeX<sub>2</sub> for X = P, As, and Sb. The anomalous behavior for nitrides can, however, be explained by the strong coulomb interaction between Ge and N ions, which shortens the Ge–N bond length and raises the antibonding CBM energy in ZnGeN<sub>2</sub>.

## 2. Method

X-ray photoemission spectroscopy (XPS) is widely used experimentally to determine the energy difference between the core-level and VBM, and hence to deduce the valence band alignment of two systems<sup>[11]</sup>. Following the same procedure, the valence band offset (VBO) of heterojunction AX/BY are calculated using the following equations:

$$\Delta E_v(AX/BY) = \Delta E_{v,C'}^{BY} - \Delta E_{v,C'}^{AX} + \Delta E_{C,C'}^{AX/BY}, \quad (1)$$

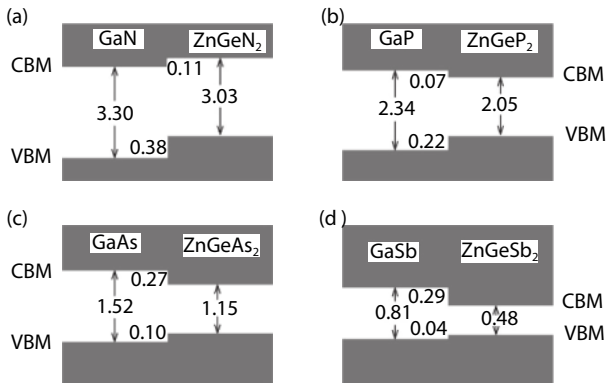
Correspondence to: H X Deng, [hxdeng@semi.ac.cn](mailto:hxdeng@semi.ac.cn); J W Luo, [jwluo@semi.ac.cn](mailto:jwluo@semi.ac.cn); S H Wei, [suhuaiwei@csrc.ac.cn](mailto:suhuaiwei@csrc.ac.cn)

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Table 1. Calculated lattice constants, bond lengths and band gaps of GaX and ZnGeX<sub>2</sub> (X = N, P, As, Sb) compounds using HSE functional compared with experimental values.

Crystal	Lattice constant (Å) HSE (Exp.)	Bond length (Å) HSE (Exp.)	Band gap (eV) HSE (Exp.)
GaN	$a = b = c = 4.512$ (4.50)	1.954 (1.949)	3.12 (3.30 <sup>[20]</sup> )
GaP	$a = b = c = 5.483$ (5.45)	2.374 (2.360)	2.32 (2.34 <sup>[21]</sup> )
GaAs	$a = b = c = 5.695$ (5.65)	2.466 (2.448)	1.35 (1.52 <sup>[20]</sup> )
GaSb	$a = b = c = 6.154$ (6.10)	2.665 (2.640)	0.79 (0.81 <sup>[20]</sup> )
ZnGeN <sub>2</sub>	$a = b = 4.572$ , $c = 8.776$	(Ge-N) 1.871, (Zn-N) 2.043	3.03
ZnGeP <sub>2</sub>	$a = b = 5.473$ (5.46), $c = 10.749$ (10.76)	(Ge-P) 2.334 (2.309), (Zn-P) 2.378 (2.398)	2.02 (2.05 <sup>[22]</sup> )
ZnGeAs <sub>2</sub>	$a = b = 5.711$ (5.67), $c = 11.226$ (11.15)	(Ge-As) 2.446 (2.396), (Zn-As) 2.472 (2.488)	1.07 (1.15 <sup>[23]</sup> )
ZnGeSb <sub>2</sub>	$a = b = 6.156$ , $c = 12.193$	(Ge-Sb) 2.664, (Zn-Sb) 2.650	0.48

Fig. 1. (Color online) The crystal structure of superlattice GaX/ZnGeX<sub>2</sub> (X = N, P, As, Sb). The Ga, Zn, Ge and X atoms are in light green, purple, gray and blue, respectively.Fig. 2. Band alignments of (a) GaN/ZnGeN<sub>2</sub>, (b) GaP/ZnGeP<sub>2</sub>, (c) GaAs/ZnGeAs<sub>2</sub>, (d) GaSb/ZnGeSb<sub>2</sub> heterojunctions.

where,

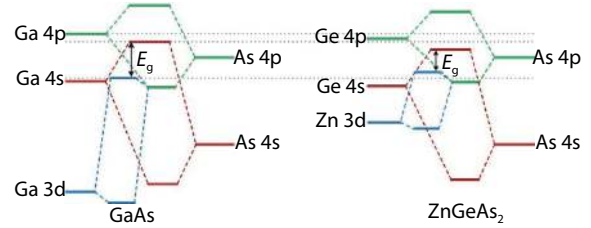
$$\Delta E_{v,C}^{AX} = E_v^{AX} - E_C^{AX}, \quad (2)$$

$$\Delta E_{v,C}^{BY} = E_v^{BY} - E_C^{BY}, \quad (3)$$

$$\Delta E_{C,C'}^{AX/BY} = E_{C'}^{BY} - E_C^{AX}, \quad (4)$$

where  $\Delta E_{v,C}^{AX}$  and  $\Delta E_{v,C}^{BY}$  are the energy difference between core level and valence band for pure AX and BY, respectively.  $\Delta E_{C,C'}^{AX/BY}$  is the core level difference of AX and BY at the AX/BY heterojunction, which can be obtained from (AX)<sub>n</sub>/(BY)<sub>n</sub> superlattice<sup>[12]</sup>. After we obtain the valence band offsets, the conduction band offsets (CBO) can be obtained from the measured band gaps.

The electronic band structure calculations are performed at the experimental lattice constants based on the density functional theory (DFT)<sup>[13, 14]</sup>. The hybrid functional parametrized by Heyd-Scuseria-Ernzerhof (HSE06)<sup>[15]</sup>, as implemented in the plane-wave basis code VASP<sup>[16, 17]</sup>, is used to calculate the band offsets<sup>[18]</sup>. The pseudopotential is described by the projector-augmented-wave (PAW) method<sup>[19]</sup>. The cutoff energy for the wave-function expansion is 500 eV. A  $\Gamma$  centered  $6 \times 6 \times 6$   $k$ -point for GaX bulks and  $6 \times 6 \times 3$  for ZnGeX<sub>2</sub> ternary com-

Fig. 3. (Color online) Band edge atomic orbital wavefunctions cubic GaAs and ZnGeAs<sub>2</sub>.

pounds were used in the calculations. For the structure relaxation the force on each atom was converged to 0.02 eV/Å. Table 1 summarizes both the experimental and HSE calculated lattice constants, bond lengths and band gaps of GaX and ZnGeX<sub>2</sub> (X = N, P, As, Sb) crystals.

To obtain the core level difference  $\Delta E_{C,C'}^{AX/BY}$ , we build the (GaX)<sub>2n</sub>/(ZnGeX<sub>2</sub>)<sub>n</sub> superlattice along (001) direction. The anion 1s core levels are chosen as reference. We find that  $n = 5$  is enough to give converged results. Because Zn and Ge are adjacent to Ga in the Periodic Table, (GaX)<sub>2</sub> and ZnGeX<sub>2</sub> have similar lattice constants, so the strain at the GaX/ZnGeX<sub>2</sub> interface is small. Fig. 1 shows the crystal structure of GaX/ZnGeX<sub>2</sub> and each superlattice contains 160 atoms. To reduce the computation complexity, a  $3 \times 3 \times 1$   $k$ -point sampling was used in atomic relaxation.

### 3. Results and discussion

Using these procedures discussed, we calculated the band offsets of the GaX/ZnGeX<sub>2</sub> heterojunction. The results are shown in Fig. 2.

Fig. 2 shows that: (i) for all the heterojunctions, the VBM of ZnGeX<sub>2</sub> is higher than that of GaX, and the VBO decreases as the atomic number of the anion increases; and (ii) for each heterojunction except GaN/ZnGeN<sub>2</sub>, the CBM of ZnGeX<sub>2</sub> is lower than that of GaX. Thus, there is an anomalous trend in CBM for ZnGeN<sub>2</sub> because its CBM is higher than that of GaN.

To understand the calculated results, we first analyze the atomic wavefunction characters of the VBM and CBM states. Take GaAs and ZnGeAs<sub>2</sub> as an example. The valence electrons of Ga and As atoms are respectively  $3d^{10}4s^24p^1$  and  $4s^24p^3$ . The couplings between different states are drawn schematically according to the chemical trends of atomic energy levels of the elements in Fig. 3. To further distinguish the localization of charge densities, we plot in Fig. 4 the electron charge densities of CBM and VBM in the (1 $\bar{1}$ 0) plane for both GaX and ZnGeX<sub>2</sub> compounds.

As the Ga and As atoms approach each other, their

Table 2. Atomic energy levels (eV) of valence states of elements studied in this paper.

Orbit	N	P	As	Sb	Zn	Ga	Ge
$ns$	-18.49	-14.09	-14.77	-13.16	-6.31	-9.25	-12.03
$np$	-7.32	-5.68	-5.42	-5.08	-1.31	-2.82	-4.13
$(n-1)d$	-	-	-40.60	-33.32	-10.49	-19.18	-29.57

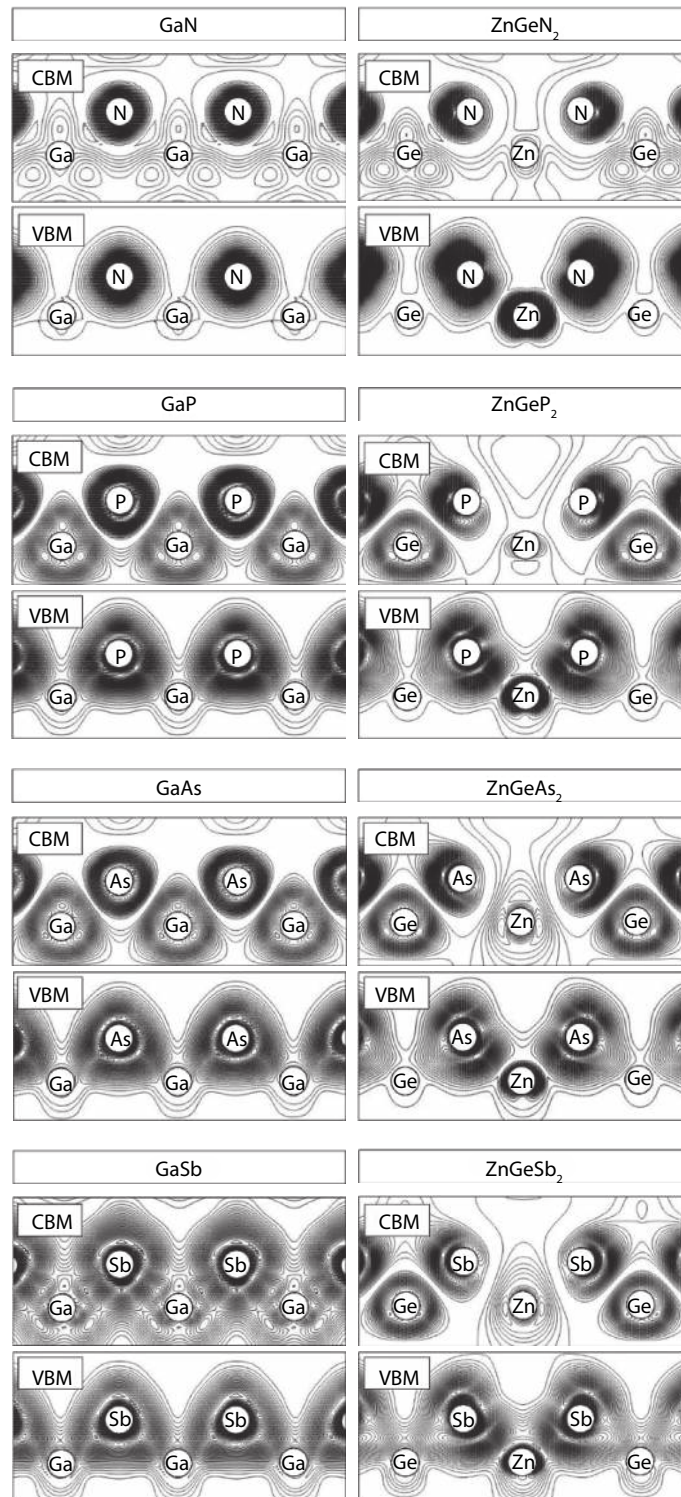


Fig. 4. Contour plot of electron charge density of VBM and CBM states in  $(1\bar{1}0)$  plane for  $\text{GaX}$  and corresponding plane in  $\text{ZnGeX}_2$  ( $X = \text{N, P, As, Sb}$ ).

valence orbitals overlap and hybridize, leading to the formation of bonding and anti-bonding states. As shown in Figs. 3 and 4, CBM is an antibonding state with mostly cationic  $s$  charac-

ter, while VBM is a bonding state with mostly anion  $p$  orbital which also couples with cation  $d$  orbitals<sup>[24]</sup>. For VBM of  $\text{GaX}$  and  $\text{ZnGeX}_2$ , because the Zn  $3d$  has higher orbital energy than



Ga 3d (see Table 2), its coupling to the anion p orbital is stronger (see Fig. 4). The stronger p–d coupling<sup>[25, 26]</sup> in ZnGeX<sub>2</sub> pushes upwards the VBM of ZnGeX<sub>2</sub>, making it higher than that of GaX. This explains why the VBM of ZnGeX<sub>2</sub> is higher than that of GaX. Moreover, as the anion atomic number increases, the p–d repulsion decreases due to the increased bond length and p–d energy separation, so the VBO becomes smaller when anion atomic number increases. Meanwhile, the CBM of GaX is more localized on Ga site, whereas it is more on the Ge site in ZnGeX<sub>2</sub> (see Fig. 4). Because Ge 4s orbital energy is much lower than the Ga 4s orbital energy, the CBM of ZnGeX<sub>2</sub> is expected to be lower in energy than that of the CBM of GaX, as observed in our calculation for X = P, As, Sb. However, CBM is an antibonding state and, therefore, its energy position also depends on the coupling strength of the anion s and cation s orbitals, which increases as the bond length decreases. For more covalent ZnGeSb<sub>2</sub>, the bond lengths are large. Moreover, the covalent Ge–Sb bond is larger than that of the Zn–Sb bond, suggesting the s–s level repulsion between Ge 4s and Sb 5s orbitals is weak, so the potential effects dominant, thus the CBM of ZnGeSb<sub>2</sub> is lower than that of GaSb. As the atomic number of X decreases, the bond length d decreases, thus the CBO decreases.

It is interesting to see that the CBM of ZnGeN<sub>2</sub> is higher than that of GaN (Fig. 2), which is in contrast to the common expectation. This anomalous trend can be understood as follows: N is much more electronegative than other group V anions so the coulomb interaction between the nominal Ge<sup>4+</sup> and N<sup>3-</sup> ions is extremely strong. This leads to a much smaller ionic Ge<sup>4+</sup>–N<sup>3-</sup> bond length compared to that of Ga<sup>3+</sup>–N<sup>3-</sup> and even smaller than that of Zn<sup>2+</sup>–N<sup>3-</sup> (see Table 1). The very short Ge–N bond length enhances the coupling between the Ge 4s and N 2s states, pushing the anti-bonding CBM state up in energy, which explains why ZnGeN<sub>2</sub> can have an anomalous higher CBM energy than GaN.

#### 4. Conclusion

In summary, the unusual chemical trends in band offsets of the heterojunctions GaX/ZnGeX<sub>2</sub> (X = N, P, As, Sb) are calculated and explained by first-principles theory. The calculated results suggest that for common-anion systems, the VBM of ZnGeX<sub>2</sub> is higher than that of GaX; and the VBO decreases when the anion atomic number increases. The CBM of ZnGeX<sub>2</sub> is found to be lower than that of GaX for X = P, As, and Sb, and the CBO decreases when the anion atomic number decreases. However, the CBM of ZnGeN<sub>2</sub> is higher than that of GaN. Using the orbital hybridization theory, we explained the chemical trend of the band alignments of the four heterojunctions and demonstrated that p–d coupling determines the position of the VBMs. The change of the CBO can be understood by noticing the increased electronegativity of Ge relative to Ga and the variation of anion–cation bond lengths. The anomalous behavior for the nitrides can be explained by the strong coulomb interaction between Ge and N ions, which shortens the ionic Ge–N bond length significantly, thus raised the antibonding CBM energy in ZnGeN<sub>2</sub>.

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#### References

- [1] Yoon J, Jo S, Chun I S, et al. GaAs photovoltaics and optoelectronics using releasable multilayer epitaxial assemblies. *Nature*, 2010, 465, 329
- [2] Kent P R C, Hart Gus L W, Zunger A. Biaxial strain-modified valence and conduction band offsets of zinc-blende GaN, GaP, GaAs, InN, InP, and InAs, and optical bowing of strained epitaxial InGaN alloys. *Appl Phys Lett*, 2002, 81, 4377
- [3] Monroy E, Munoz E, Sanchez F J, et al. High-performance GaN p–n junction photodetectors for solar ultraviolet applications. *Semicond Sci Technol*, 1998, 13, 1042
- [4] Paudel T R, Lambrecht W R L. First-principles calculations of elasticity, polarization-related properties, and nonlinear optical coefficients in Zn–IV–N<sub>2</sub> compounds. *Phys Rev B*, 2009, 79, 245205
- [5] Punya A, Lambrecht W R L, Schilfgaarde M. Quasiparticle band structure of Zn–IV–N<sub>2</sub> compounds. *Phys Rev B*, 2011, 84, 165204
- [6] Ma J, Deng H X, Luo J W, et al. Origin of the failed ensemble average rule for the band gaps of disordered nonisovalent semiconductor alloys. *Phys Rev B*, 2014, 90, 115201
- [7] Du K, Bekele C, Hayman C C, et al. Synthesis and characterization of ZnGeN<sub>2</sub> grown from elemental Zn and Ge sources. *J Cryst Growth*, 2008, 310, 1057
- [8] Clément Q, Melkonian J, Barrientos-Barria J, et al. Tunable optical parametric amplification of a single-frequency quantum cascade laser around 8 $\mu$ m in ZnGeP<sub>2</sub>. *Opt Lett*, 2013, 38, 4046
- [9] Narang P, Chen S, Coronel N C, et al. Bandgap tunability in Zn(Sn, Ge)N<sub>2</sub> semiconductor alloys. *Adv Mater*, 2014, 26, 1235
- [10] Zhang S R, Xie L H, Ouyang S D, et al. Electronic structure, chemical bonding and optical properties of the nonlinear optical crystal ZnGeP<sub>2</sub> by first-principles calculations. *Phys Scri*, 2016, 91, 015801
- [11] Kowalczyk S P, Cheung J T, Kraut E A, et al. CdTe–HgTe (–1, –1, –1) heterojunction valence-band discontinuity: A common-anion-rule contradiction. *Phys Rev Lett*, 1986, 56, 1605
- [12] Deng H X, Luo J W, Wei S H. Chemical trends of stability and band alignment of lattice-matched II–VI/III–V semiconductor interfaces. *Phys Rev B*, 2015, 91, 075315
- [13] Hohenberg P, Kohn W. Inhomogeneous electron gas. *Phys Rev*, 1964, 136, 864
- [14] Kohn W, Sham L J. Self-consistent equations including exchange and correlation effects. *Phys Rev*, 1965, 140, 1133
- [15] Heyd J, Scuseria G E, Ernzerhof M. Hybrid functionals based on a screened Coulomb potential. *J Chem Phys*, 2003, 118, 8207
- [16] Kresse G, Furthmüller J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Compute Mater Sci*, 1996, 6, 15
- [17] Kresse G, Furthmüller J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys Rev B*, 1996, 54, 11169
- [18] Wadehra A, Nicklas J W, Wilkins J W. Band offsets of semiconductor heterostructures: A hybrid density functional study. *Appl Phys Lett*, 2010, 97, 092119
- [19] Blöchl P E. Projector augmented wave method. *Phys Rev B*, 1994, 50, 17953
- [20] Vurgaftman I, Meyer J, Ram-Mohan L. Band parameters for III–V

- compound semiconductors and their alloys. *J Appl Phys*, 2001, 89, 5815
- [21] Lorenz M R, Pettit G D, Taylor R C. Band gap of gallium phosphide from 0 to 900 °K and light emission from diodes at high temperatures. *Phys Rev*, 1986, 171, 876
- [22] Ullah S, Murtaza G, Khenata R, et al. Towards from indirect to direct band gap and optical properties of  $XYP_2$  ( $X = \text{Zn, Cd}$ ;  $Y = \text{Si, Ge, Sn}$ ). *Physica B*, 2014, 441, 94
- [23] Solomon G S, Timmons M L, Posthill J B. Organometallic vapor-phase-epitaxial growth and characterization of  $\text{ZnGeAs}_2$  on GaAs. *J Appl Phys*, 1989, 65, 1952
- [24] Wei S H, Zunger A. Calculated natural band offsets of all II–VI and III–V semiconductors: Chemical trends and the role of cation d orbitals. *Appl Phys Lett*, 1998, 72, 2011
- [25] Wei S H, Zunger A. Role of d orbitals in valence-band offsets of common-anion semiconductors. *Phys Rev Lett*, 1987, 59, 144
- [26] Wei S H, Zunger A. Role of metal d states in II–VI semiconductors. *Phys Rev B*, 1988, 37, 8958