

Article

Bandgap Engineering in InAs/GaSb II Superlattices: Modulation and Vacancy Defects Analysis

Yan Jiang, Yulin Zhou, Zongyao Zhang, Zhengdao Li, Liyuan Jiang, Xinxin Zhao and Jianbao Wu * 

School of Mathematics, Physics and Statistics, Shanghai University of Engineering Science, 333 Longteng Road, Shanghai 201620, China; m440223126@sues.edu.cn (Y.J.); m440223108@sues.edu.cn (Y.Z.); m440223103@sues.edu.cn (Z.Z.); m440223104@sues.edu.cn (Z.L.); m440222114@sues.edu.cn (L.J.); bighunter@sues.edu.cn (X.Z.)

* Correspondence: wujianbao@sues.edu.cn

Abstract: The computational analysis of InAs/GaSb type-II superlattices utilizing density functional theory (DFT) with pseudopotentials has been performed. The PBE+U method was employed to correct for the strong correlation effects of the P orbitals of In, As, Ga, and Sb, thereby improving the accuracy of the bandgap calculations. The study investigated the impact of the number of layers in the InAs and GaSb bulk materials on the superlattice bandgap. The results revealed that as the number of InAs layers increased while keeping the number of GaSb layers constant, the bandgap decreased. Conversely, when the number of GaSb layers increased with a constant number of InAs layers, the bandgap increased. In conjunction with the interface issues and vacancy defects frequently encountered in InAs/GaSb type-II superlattices, electronic structure analyses indicate that InAs, as the primary electron aggregator, significantly influences the modulation of the superlattice bandgap.

Keywords: first principles; InAs/GaSb type-II superlattices; PBE+U; vacancy defects

1. Introductory

InAs/GaSb type-II superlattices are periodic structures composed of two types of narrow-gap semiconductor materials, InAs and GaSb, whose bandgaps and detection wavelengths can be precisely controlled by adjusting the cycle thickness. Their low dark current, high electron-effective mass, excellent material homogeneity, and low thermal conductivity render them highly effective in the field of infrared detection, particularly long-wave infrared detection [1,2]. The current criterion for classifying superlattices is to categorize them according to their respective constrained energy schemes, with class II superlattices periodically repeating in three dimensions and exhibiting planar structural characteristics. This configuration confines the electrons and holes in the InAs and GaSb layers, respectively, resulting in spatial separation of electrons and holes [3–5]. When the thickness of the GaSb layer is less than a few nanometers, the electrons between neighboring InAs layers interact under the quantum effect, and the electron wavefunctions overlap to form electron microbands. The bandgap of the InAs/GaSb type-II superlattices is determined by the energy difference between the electron microbands and the first heavy-hole band. The energy gap of the superlattice depends on the thickness of the period, which can be varied continuously in the range of 0–400 meV by adjusting the thicknesses of the InAs and GaSb layers [6,7]. Utilizing the theoretical energy arrangement of the InAs/GaSb type-II superlattices enables the realization of any LWIR bandgap required for IR detection by tuning the effective bandgap.



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2. Calculation Method

All DFT calculations in this study were performed using the Device Studio and the Projection Augmented Wave (PAW) method [8]. For the $(\text{InAs})_m(\text{GaSb})_n$ and gap calculations, we employed the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) with the Hubbard U correction determined by Bayesian optimization. The Brillouin zone of the interface was sampled using an $8 \times 8 \times 1$ k-point grid with a plane-wave truncation energy of 400 eV [9–11]. The effective Hubbard U is defined as $U_{\text{eff}} = U - J$ [12], where U denotes the strength of the Coulomb repulsion and J denotes the strength of the exchange interaction. The DFT + U (BO) method yields negative U_{eff} values. When the exchange term J exceeds the on-site Coulomb repulsion U, a negative U_{eff} value is theoretically permissible [13,14]. The calculations demonstrated that negative values are necessary for narrow-gap semiconductors (e.g., InAs and GaSb) to produce a bandgap. Take $U_{\text{eff}}^{\text{In,p}} = -0.5$ eV, $U_{\text{eff}}^{\text{As,p}} = -7.5$ eV, $U_{\text{eff}}^{\text{Ga,p}} = 0.8$ eV, $U_{\text{eff}}^{\text{Sb,p}} = -6.9$ eV. The comparison revealed an overall good agreement between PBE + U (BO) and HSE03 [15]. Conventionally, $U_{\text{eff}} > 0$ is employed to enhance the correlation effects (e.g., in transition metals); however, negative values may be necessary in certain specific scenarios. For instance, in the case of InAs/GaSb superlattices, where both InAs and GaSb are narrow-band semiconductors, the electronic association strength is significantly lower than that of transition metals, and the exchange energy is underestimated by the PBE (resulting in a small bandgap). This error can be counteracted by a negative U-value, which brings the calculated results closer to the experimental ones. For the defect calculations, a $3 \times 3 \times 4$ supercell was constructed, and the total energy of the system and the forces acting on each atom were characterized by first-principles calculations within the density functional theory (DFT) framework. These calculations cannot be performed using hybridization generalizations because of the typical presence of hundreds of atoms in the defect systems [16]. A cutoff energy of $2 \times 2 \times 1$ k points centered on Γ and 50 Ryd was selected. The criterion for relaxation of the electronic degrees of freedom required a total energy change in less than 10^{-5} eV. Geometric optimization of the structure was achieved by minimizing the Hermann–Feynman force acting on each atom until the maximum force acting on the ions was less than 0.01 eV/Å.

In general, the formation energy of a charged defect in a semiconductor or insulator has both ionic and electronic effects. In a superlattice, its formation energy is related to the Fermi energy level as follows.

$$E(X) = E_{\text{total}}(X) - E_{\text{bulk}} + \sum_i n_i \mu_i + q(E_{\text{VBM}} + E_f) + E_{\text{corr}}$$

$E_{\text{total}}(X)$ represents the total energy of the supercell containing the charge state q defects, E_{bulk} denotes the total energy of the neutral intact supercell without any defects, and n_i signifies the number of atoms removed from the formation supercell owing to defects with a positive or negative value, where μ_i is the chemical potential of atom i . When an atom is added to the system, the associated electrons are incorporated and contribute to the formation of energy. This contribution is described in terms of the chemical potential of the electron, referred to as the Fermi energy level E_f at zero temperature, where the E_f of the semiconductor is considered an independent variable that can assume any value within the bandgap. E_{VBM} represents the value of the valence band top (VBM) of an intact supercell without defects. As the precise value of the formation energy cannot be determined with respect to the chemical potential in the Fermi energy level n_i , it is utilized as a parameter for the calculation of the formation energy [17–20]. All defect formation energies are presented under the limiting conditions associated with a specific type of atomic growth. The correction term E_{corr} was employed to eliminate errors caused by finite-size effects, periodic boundary conditions, and Coulombic interactions between image

charges in the case of charged defects [21–23]. There is no definitive conclusion regarding the performance and applicability of correction terms, such as the Makov and Payne (MP) scheme [24], the Freysoldt, Neugebauer and Van de Walle (FNV) scheme [25], and the Lany and Zunger (LZ) scheme [26]. The interrelationships between the various schemes and the conditions defining their application were discussed by Komsa et al. [27], which referred to mirror charge correction for the specifics of the correction method utilized in this study [28].

3. Results and Discussion

A class II superlattice is a semiconductor material formed by alternating the growth of two distinct semiconductor materials. In a class II superlattice, the energy band structures of the two semiconductor materials interact to form a specific distribution of electronic states. For InAs/GaSb type-II superlattices, the modulation of the energy band structure can be achieved through the precise control of the alternating growth parameters and thicknesses of the two materials, InAs and GaSb, to meet various device performance requirements. For concise representation, $(\text{InAs})_m/(\text{GaSb})_n$ is denoted as InAs/GaSb (m, n).

3.1. Electronic Structure of Homocyclic InAs/GaSb (n, n)

Cycle thickness is a critical parameter in the design of InAs/GaSb type-II superlattice detector devices and exerts a substantial influence on the response range, absorption coefficient, and quantum efficiency of the devices. The effect of identical period thickness of InAs/GaSb (n, n) ($n \in \{2, 3, 4, 5, \dots, 20\}$) on the electronic structure of the superlattices was initially investigated. InAs and GaSb were cleaved along the (001) direction to construct InAs/GaSb type-II superlattices. The calculated results are presented in Figure 1, and the bandgap exhibits a trend of initial increase followed by a decrease as the number of layers n increases.

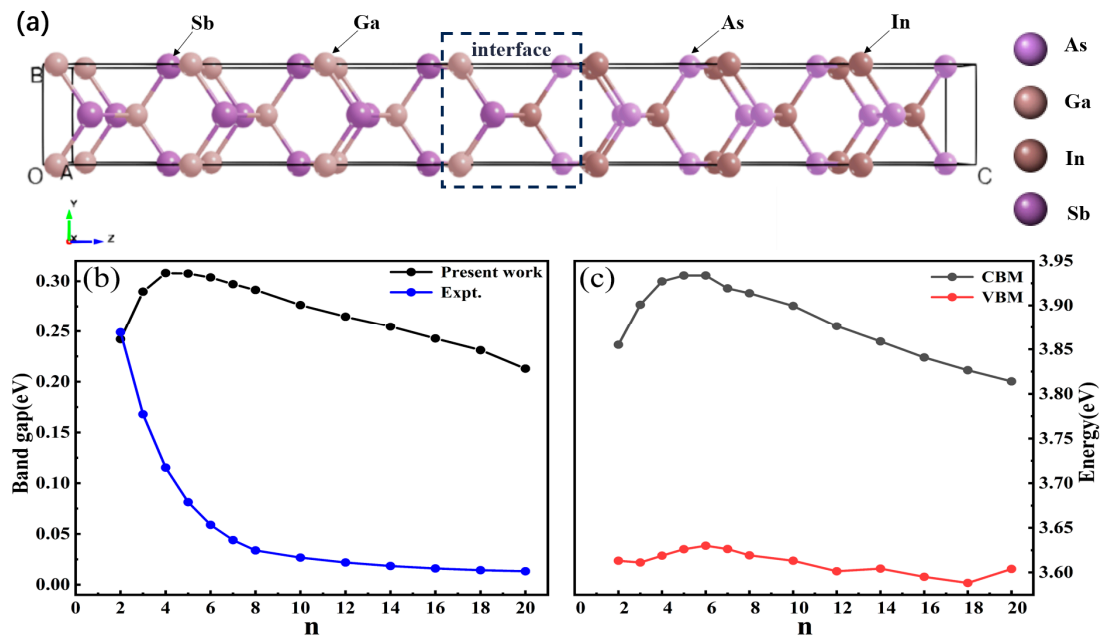


Figure 1. Electronic structure of homocyclic InAs/GaSb (n, n) superlattice ($n \in \{2, 3, 4, 5, \dots, 20\}$): (a) structural schematic-(7, 7), (b) band gap, and (c) band-edge energy.

As illustrated in Figure 1a, the energy band structure of the InAs/GaSb (7, 7) superlattice exhibits the AO direction defined as the x-axis (lattice basis vector direction), the OB direction as the y-axis, and the AC direction as the z-axis (perpendicular to the superlattice plane). The experimental data shown in Figure 1b demonstrate that when the thicknesses

of the InAs and GaSb monolayers are equivalent, the bandgap value of the system exhibits a significant decreasing trend with an increase in the thickness of the superlattice period. This observation aligns with the energy-band engineering regulation mechanism of class II superlattices. In this paper, using first-principles calculations as observed in Figure 1b, the band gap exhibits a sharp increase with an increase in periodic thickness when $n < 4$. This observation contradicts experimental findings; however, this effect is rapidly counterbalanced by the increase in the periodic thickness. The variation in the distribution of the valence band maximum (VBM) and conduction band minimum (CBM) with cycle thickness corroborates this assertion. When $n > 4$, the InAs/GaSb type-II superlattices demonstrates characteristics typical of a type II superlattice with significant electron–hole separation. Conversely, when $n < 4$, the electron density at the In-Sb interface increases, as does the hole density at the Ga-As interface. This suggests that these superlattices with ultra-short periods do not exhibit typical type II superlattice behavior, but rather resemble polarization-controlled systems [29].

Figure 1c illustrates that as the cycle thickness increases, the CBM demonstrates a distinct trend of initial increase followed by decrease, while the VBM exhibits a more gradual trend. During electron excitation, the conduction band minimum (CBM) is occupied by excited electrons, while the valence band maximum (VBM) is characterized by the vacancies left by the excited electrons, referred to as holes. In type II heterojunctions, the electrons and holes are spatially separated due to the arrangement of their energy bands and are localized in different material layers. In the InAs/GaSb type-II superlattice, electrons are predominantly concentrated in the InAs layer, while holes are primarily concentrated in the GaSb layer.

Information regarding the role of strain in bandgap modulation, the impact of interfacial mixing on the potential formation of InAsSb, leading to alterations in the material's bandgap, for further details, please refer to Tables S1 and S2 in the Supporting Information. From an electronic structure perspective, the electron localization function (ELF) [30] can be utilized to visualize the degree of electron localization in space.

Electron localization is a phenomenon in which electrons are relatively concentrated and localized within a specific region in space. As illustrated in Figure 2a–c, the degree of electron localization does not substantially change with increasing superlattice cycle thickness. This indicates the high structural stability of the InAs/GaSb type-II superlattices as the number of layers increases. It also reflects the constraining influence of the superlattice's periodicity and symmetry on electronic behavior, which keeps the electron distribution relatively constant within a certain range. Additionally, the periodicity of the superlattice allows the interfacial properties between the InAs and GaSb layers to remain largely unchanged as the thickness increases.

3.2. Electronic Structure of InAs/GaSb (m, n) with Different Cycles

The thickness ratio of the InAs/GaSb type-II superlattices, specifically the asymmetric thicknesses of the InAs and GaSb layers, is a critical parameter in detector design. Various combinations of thicknesses influence the energy band structure of the superlattice, enabling precise adjustment of the detector response range through modification of the InAs/GaSb type-II superlattices thickness ratio. To investigate the effect of thickness variations in the InAs and GaSb layers on the electronic structure of the superlattice, the cycle thickness of one semiconductor material remained constant, while the thickness of the other semiconductor material incrementally increased. Specifically, this study considers InAs/GaSb ($m, 7$) containing $m, n \in \{3, 5, 7, 9, 11, 13, 15\}$ layer thicknesses and ($7, n$) two structures. The calculated bandgaps for these structures are presented in Figure 3a, and the conduction band minimum and valence band maximum energy levels are shown in Figure 3b.

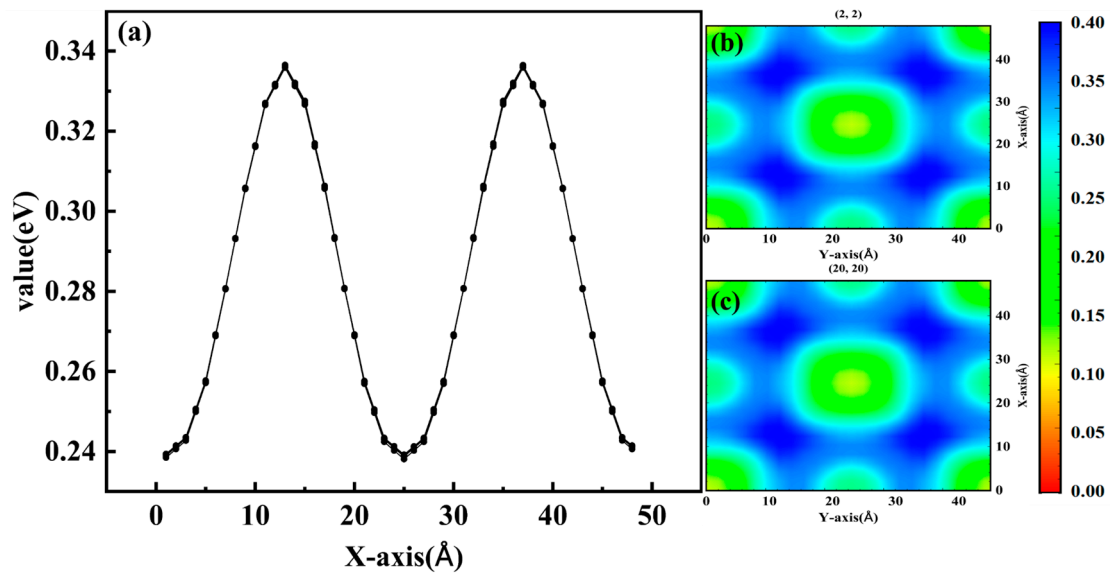


Figure 2. ELF of InAs/GaSb (n, n) with same cycles ($n \in \{2, 3, 4, 5, \dots, 20\}$): (a) mean value of 1D YZ in-plane; (b,c) mean value of 2D Z-axis averages.

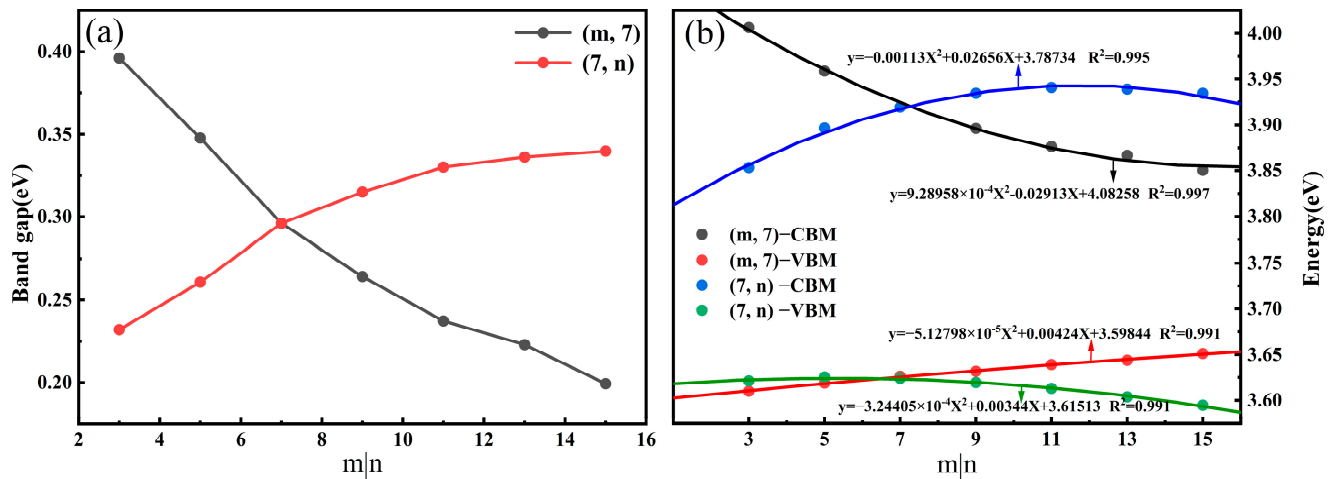


Figure 3. Electronic structure of InAs/GaSb ($m, 7$) and ($7, n$) superlattices ($m, n \in \{3, 5, 7, 9, 11, 13, 15\}$): (a) bandgap; (b) band-edge energy.

Electrons and holes were partially confined within the InAs and GaSb layers, respectively. Figure 3a illustrates the trend of the bandgap: the bandgap of InAs/GaSb ($m, 7$) decreases with an increase in the number of InAs layers m , whereas the bandgap of InAs/GaSb ($7, n$) increases with an increase in the number of GaSb layers n . The two lines intersect at $m = n = 7$, and the two lines intersect at $m = n = 7$. increases, and the two lines intersect at $m = n = 7$. The bandgap of ($m, 7$) was significantly larger than that of ($7, n$) when $m = n < 7$, and the bandgap of ($m, 7$) was smaller than that of ($7, n$) when $m = n > 7$. This phenomenon occurs because the change in the number of InAs layers m alters the binding energy of electrons, and the change in the number of GaSb layers n modifies the binding energy of the holes. In InAs/GaSb type-II superlattices, electrons predominantly occupy the conduction band, and holes occupy the valence band. When the number of GaSb layers was fixed at seven, the bandgap decreased as the number of InAs layers, m , increased, and the electrons experienced greater quantum confinement. Conversely, when the number of InAs layers is fixed at seven, the bandgap increases gradually with an increase in the number of GaSb layers, as the holes experience stronger quantum confinement. A comparison of the two cases reveals that the rate of the ($m, 7$) bandgap increase and

decrease is greater than the rate of the (7, n) bandgap increase, indicating that the binding force of electrons is stronger than that of holes in the InAs/GaSb type-II superlattices. This phenomenon results in a gradual decrease in the bandgap of the class II superlattice as the number of layers increases when the period thickness of both the InAs and GaSb bulk materials is fixed and increases. Figure 3b illustrates the variation in the conduction band minimum (CBM) versus the valence band maximum (VBM), reflecting the effect of the change in the number of layers on the energy band structure. Upon fitting the CBM and VBM functions for (m, 7) and (7, n), it was observed that the change in the slope of the conduction band minimum was significantly larger than the change in the slope of the valence band maximum for (m, 7), suggesting that the CBM is more sensitive to changes in the thickness of the cycle. In (7, n), the slope of the valence band maximum is slightly larger than that of the conduction band minimum, indicating that the VBM is marginally more sensitive than the CBM to changes in thickness; however, the magnitude of the change is not as pronounced as that in (m, 7). Consequently, the bandgap of (7, n) increases more slowly and to a lesser extent, whereas that of (m, 7) decreases more significantly. These trends can be quantitatively understood through changes in the quantum confinement of electrons and holes.

InAs/GaSb type-II superlattices are structures composed of alternating layers of two materials, InAs and GaSb, containing four distinct types of atoms. The variation in the density of electronic states per unit energy interval for each type of atom in InAs/GaSb (m, 7) and (7, n) with the growth of different layers was analyzed [31]. As illustrated in Figure 4, with an increase in the number of InAs layers (m), the distribution densities of both In and As atoms across different energy intervals gradually increase, whereas the distribution densities of Ga and Sb atoms across different energy intervals gradually decrease. The rate of increase in the density of states (PDOS) of the In and As atoms was significantly greater than the rate of decrease observed for the Ga and Sb atoms.

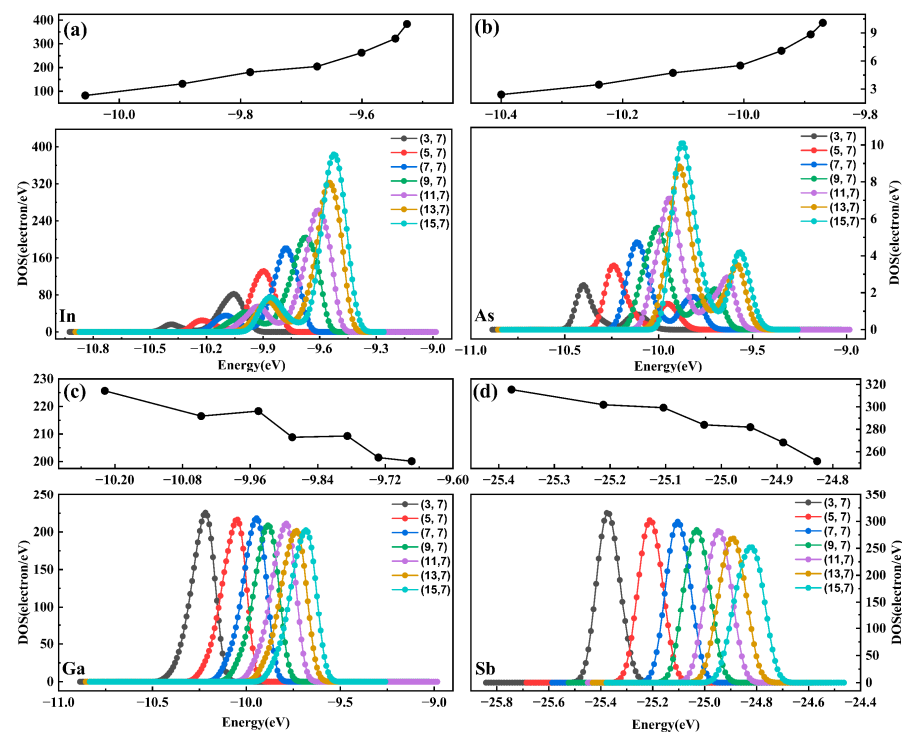


Figure 4. InAs/GaSb (m, 7) superlattices: (a) PDOS of In atoms; (b) PDOS of As atoms; (c) PDOS of Ga atoms; (d) PDOS of Sb atoms.

In contrast, as can be observed in Figure 5, InAs/GaSb (7, n) exhibits an inverse trend, where the increase in n results in a gradual increase in the density of Ga and Sb atoms distributed across the In and As energy intervals, accompanied by a gradual decrease in the density of In and As atoms distributed across different energy intervals. Concurrently, the rate of increase in the density of states of Ga and Sb atoms was substantially higher than that of the density of states of In and As atoms.

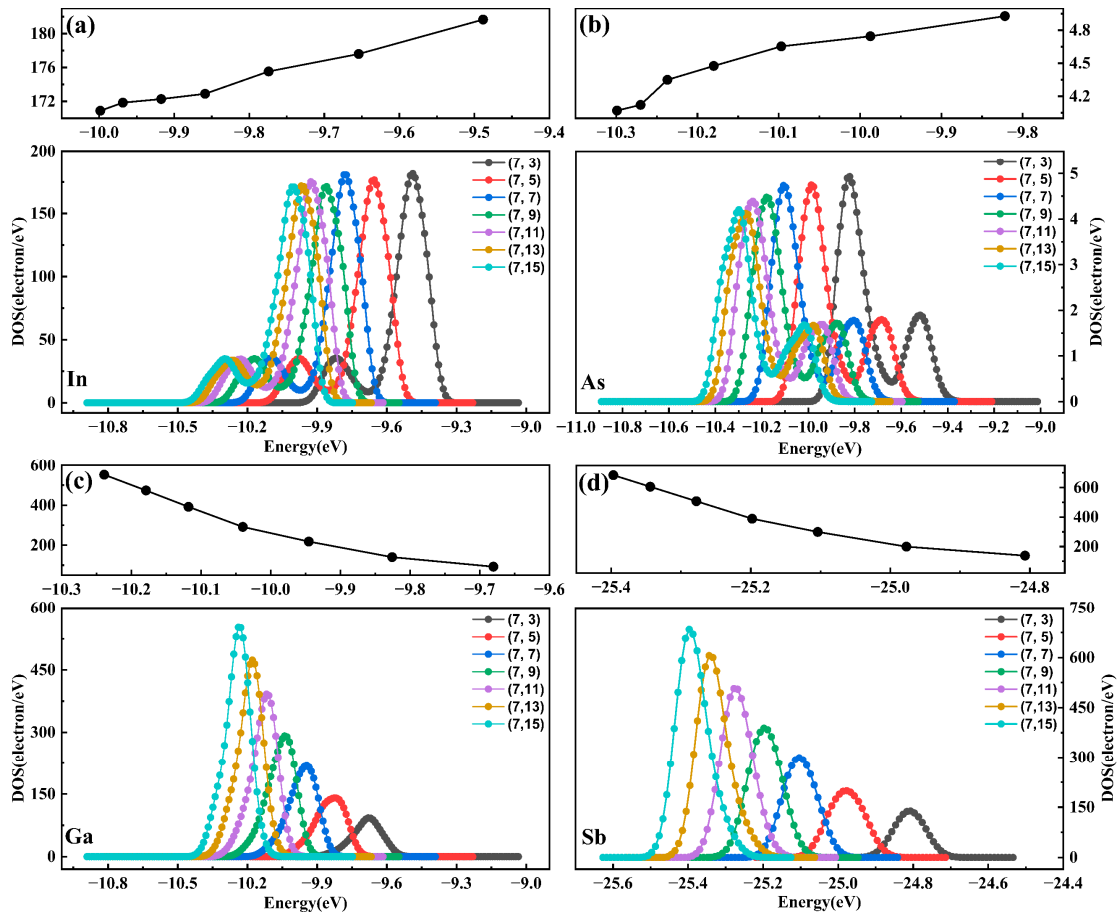


Figure 5. InAs/GaSb (7, n) superlattices: (a) PDOS of In atoms; (b) PDOS of As atoms; (c) PDOS of Ga atoms; (d) PDOS of Sb atoms.

This phenomenon can be more effectively elucidated through the ELF. ELF facilitates the visualization of electron distribution properties in space, thereby providing a more comprehensive physical explanation for the variations in the density of states.

From the perspective of electronic structure, when $n = 7$ layers, as the number of InAs layers m increases, the number of electrons correspondingly increases. This phenomenon is evident in Figure 6, which depicts the InAs/GaSb ($m, 7$) electron-localized function. The blue region gradually expands and intensifies in color, indicating an increase in the frequency of electron transitions. This observation corroborates the patterns observed in Figure 7a,b, demonstrating that at a fixed number of GaSb layers n of 7, the degree of electron delocalization decreases as the number of InAs layers m increases. Conversely, when $m = 7$ layers and the number of GaSb layers n increases, the number of electrons remains constant, whereas the number of holes increases. In Figure 7, for InAs/GaSb (7, n), the blue region gradually diminishes and becomes concentrated within the quadrangle region. This trend further validates the pattern illustrated in Figure 7c,d, wherein, with the number of InAs layers n fixed at 7, the degree of electron delocalization gradually increases as the number of GaSb layers increases.

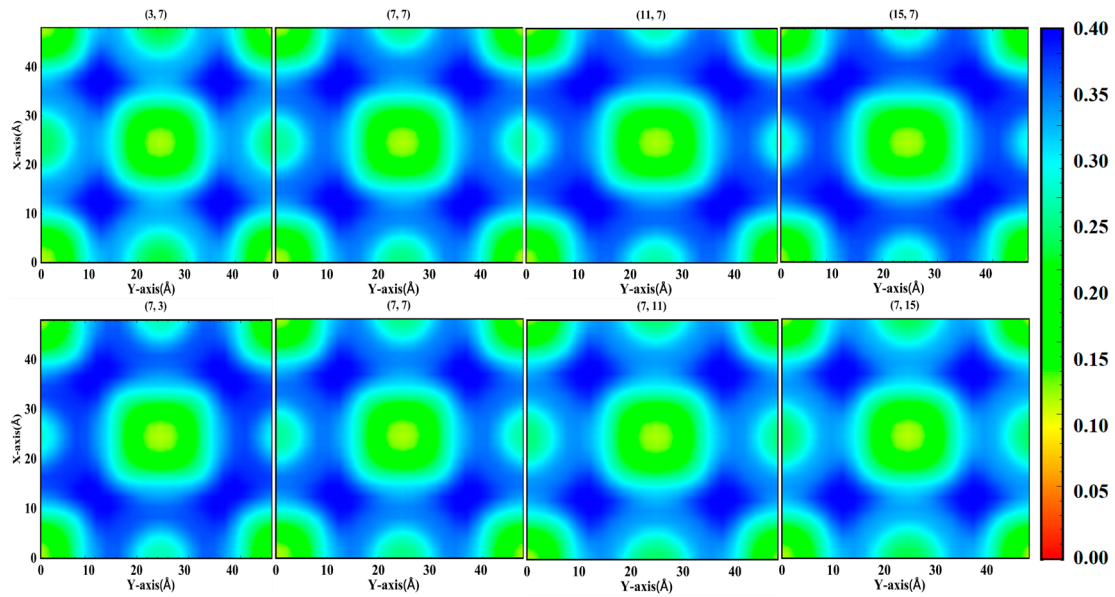


Figure 6. ELF of InAs/GaSb with different cycles ($m, n \in \{3, 5, 7, 9, 11, 13, 15\}$): (1) mean value of ($m, 7$) in 2D Z-axis; (2) mean value of ($7, n$) in 2D Z-axis.

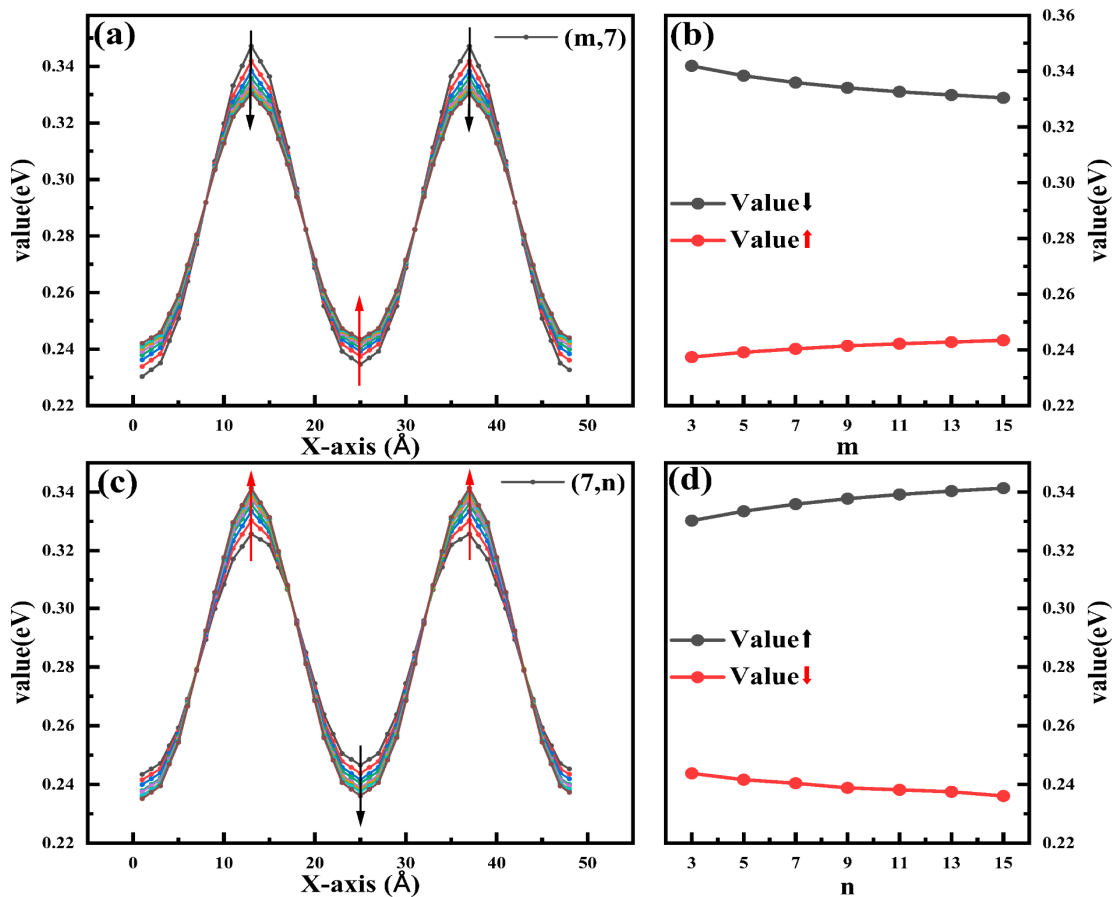


Figure 7. ELF of periodically different InAs/GaSb ($m, n \in \{3, 5, 7, 9, 11, 13, 15\}$). (a) Mean value in 1D YZ-plane and (b) degree of electron delocalization vs. localization of InAs/GaSb ($m, 7$); (c) mean value in 1D YZ-plane and (d) degree of electron delocalization vs. localization of InAs/GaSb ($7, n$).

The 3D ELF image (Figure 8) reveals that electrons at higher degrees of localization contours are predominantly localized on the bonds between Ga-Sb and In-As, with a minor distribution of electrons at the bond junction. This observation suggests that these electrons

are shared among the Ga, Sb, In, and As atoms. Furthermore, the localized electrons exhibit a hemispherical configuration, with the hemisphere's base positioned closer to the Sb and As atoms. This arrangement indicates that while the electrons are shared between Ga and As, they demonstrate a greater affinity towards Sb and As, which possess higher electronegativity and exert a stronger attraction on bonded electron pairs.

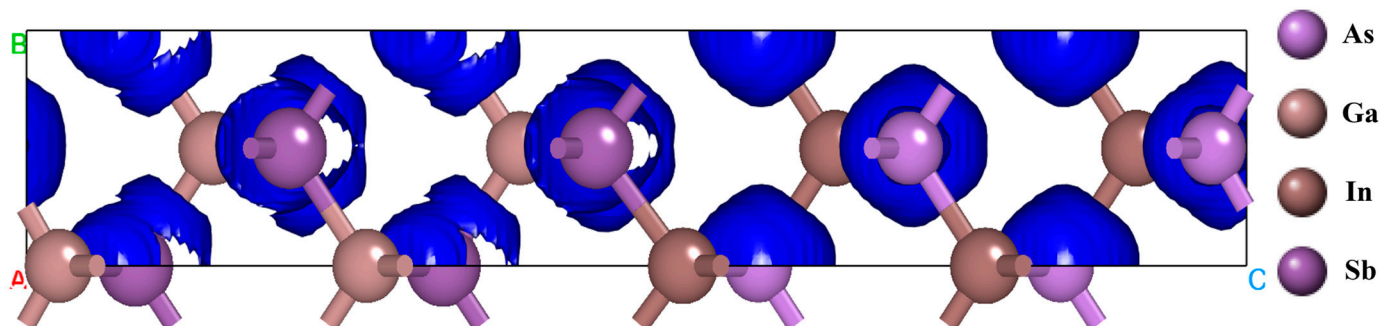


Figure 8. Three-dimensional ELF of InAs/GaSb (4, 4). In: dark brown, As: light purple, Ga: light brown, Sb: dark purple.

The presence of interfaces is inevitable in the construction of InAs/GaSb type-II superlattices, and they significantly influence the fundamental properties of the superlattices, such as the energy band structure and carrier behavior. From an interfacial perspective, the definition of InAs/GaSb (7, 7) inherently implies the coexistence of a GaSb interface monolayer and an InSb interface monolayer at the interface of a superlattice cycle, which is commonly referred to as a “neutral” structure. One variation entails the removal of the GaAs monolayer by growing $(\text{GaSb})_7/(\text{InSb})_1/(\text{InAs})_6$, which is designated as a “heavy” interface structure. Another variation involves the removal of the InSb monolayer by growing a $(\text{GaSb})_6/(\text{GaAs})_1/(\text{InAs})_7$ structure, which is termed a “light” interface structure. There are discernible differences in the band gaps of these three structures: the $(\text{GaSb})_7/(\text{InSb})_1/(\text{InAs})_6$ band gap is 0.225 eV, the $(\text{GaSb})_7/(\text{InAs})_7$ band gap is 0.292 eV, and the $(\text{GaSb})_6/(\text{GaAs})_1/(\text{InAs})_7$ has a band gap of 0.355 eV. Combining the analysis with the YZ plane of the one-dimensional image of ELF provides a more intuitive understanding of the influence of the interface structure on the electronic behavior, which offers theoretical support for the further elucidation of the role of interfacial modulation on the properties of superlattices. For an assessment of the structural stability of the interface, refer to Table S3 in the Supporting Information for comprehensive details.

As shown in Figure 9, the bandgap increased in the following order: $(\text{GaSb})_7/(\text{InSb})_1/(\text{InAs})_6$, $(\text{GaSb})_7/(\text{InAs})_7$, and $(\text{GaSb})_6/(\text{GaAs})_1/(\text{InAs})_7$. The results demonstrate that the interface structure significantly influences the bandgap of the superlattice. Figure 9c,d further indicates that the removal of the InSb monolayer from $(\text{GaSb})_7/(\text{InAs})_7$ to $(\text{GaSb})_6/(\text{GaAs})_1/(\text{InAs})_7$ affects the degree of its electronic localization. Conversely, the removal of the GaAs monolayer from $(\text{GaSb})_7/(\text{InAs})_7$ to $(\text{GaSb})_7/(\text{InSb})_1/(\text{InAs})_6$ substantially affects the degree of electron delocalization. Examining Figure 9b–d collectively reveals that a higher degree of electron delocalization corresponds to a larger bandgap, whereas a higher degree of electron localization corresponds to a smaller bandgap. This observation suggests that the spatial distribution characteristics of electrons directly influence the bandgap magnitude.

To conduct a more comprehensive analysis of the electronic structure of InAs/GaSb type-II superlattices, processes such as interatomic interactions and electron transitions can be examined using partial wave density of states (PDOS). This approach facilitates the elucidation of the intrinsic mechanisms governing the electronic behavior and enhances the understanding of superlattice characteristics.

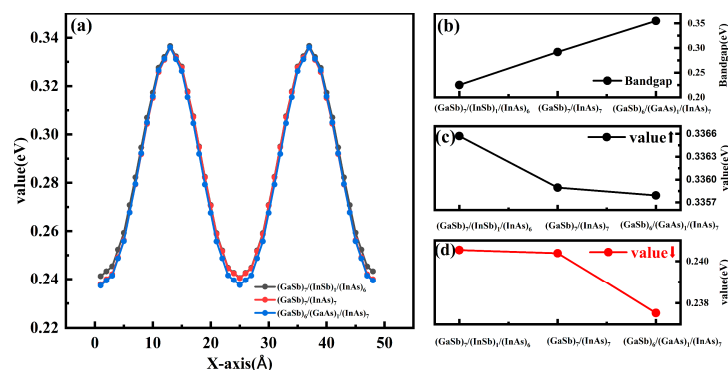


Figure 9. (a) ELF in the 2D YZ plane for three interfaces; (b) band gap, (c) electron localized state distribution, (d) electron off-domain state distribution.

As shown in Figure 10, the analysis of the four atoms in the three interfaces reveals that the contribution of their fractional-wave state densities to the total state densities is primarily concentrated in the 3d orbital of Ga, 4d orbital of Sb, 4d orbital of In, and 4s orbital of As. The position and intensity of the density of states peaks for these orbitals differ for various interfacial structures, indicating that the interfacial structure significantly influences the contribution of atomic orbitals to the total electronic density of states. The magnitude of the contribution of each orbital to the total density of states is $(\text{GaSb})_6/(\text{GaAs})_1/(\text{InAs})_7 > (\text{GaSb})_7/(\text{InAs})_7 > (\text{GaSb})_6/(\text{InSb})_1/(\text{InAs})_6$, which is consistent with the trend in the degree of electron localization. Furthermore, the orbitals of Ga and Sb exhibit higher PDOS peaks at deeper energy levels, suggesting that the electrons of these atoms are predominantly localized, whereas the orbital density of state distributions of As and In are closer to the Fermi energy level in the energy scale, indicating that their contribution to the off-domain states is more pronounced. From the perspective of the atomic orbital contribution, it is demonstrated that the higher density of states in certain energy intervals corresponds to a high degree of electron localization, indicating that this orbital plays a crucial role in the modified energy and spatial region, thus demonstrating that the interface structure has a significant influence on regulating the distribution of localized electronic states.

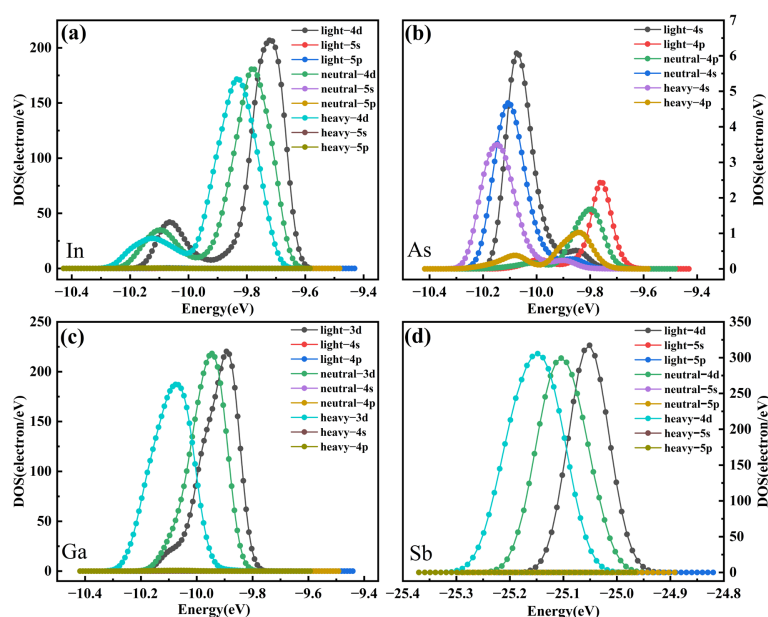


Figure 10. PDOS of three interfaces: (a) PDOS of In atoms; (b) PDOS of As atoms; (c) PDOS of Ga element; (d) PDOS of Sb atoms.

3.3. Vacancy Defects in InAs/GaSb Type-II Superlattices

However, during the preparation of superlattice semiconductors, unavoidable defects frequently arise owing to thermodynamic, kinetic, or external factors. These defects can be further categorized into point, line, surface, and body defects. Subsequently, the influence of defect formation energy on the Fermi energy level was investigated using common vacancy defects as an example. Four types of vacancy defects were selected: V_{In} , V_{As} , V_{Ga} , and V_{Sb} . In the selection of defect positions, identical atomic species at the In-Sb and Ga-As interfaces in the (InAs)₇/(GaSb)₇ superlattice cycle and distant from the interfacial junction were chosen to analyze the effect of the defect positions on the modulation of the Fermi energy level, thereby facilitating a more comprehensive understanding of the role of interfaces and defects on the electronic structure of the superlattice.

As illustrated in Figure 11, there are four types of intrinsic vacancy defects (V_{In} , V_{As} , V_{Ga} , and V_{Sb}), with their respective Fermi energy levels plotted against the formation energies. It is evident that V_{Sb} exhibits the lowest formation energy among the four types of defects, suggesting that Sb atoms as anionic vacancies have the highest propensity to form defects in InAs/GaSb type-II superlattices. Similarly, four classes, V_{In} , V_{As} , V_{Ga} , and V_{Sb} , are present at the interface as well as in the superlattice body away from the interfacial connection. The energy required for the formation of vacancy defects by atoms located at the interface is lower than that required for vacancy defects within the superlattice, particularly for V_{In} and V_{Sb} . This observation indicates that the atoms at the interface are more susceptible to external influences, which can lead to defect formation. Further analysis reveals that as the Fermi energy level changes, V_{In} and V_{Ga} demonstrate a greater tendency to exhibit the charge state $q = -3$ and are more prone to form donor defects. Their formation energies decrease when the Fermi energy level is elevated (closer to the conduction band), resulting in InAs/GaSb type-II superlattices that favor n-type conducting properties. For V_{As} and V_{Sb} , the formation energy gradually increases with the Fermi energy level, and when the Fermi energy level exceeds 1 eV, it tends to stabilize and form a dominant defect state, causing the InAs/GaSb type-II superlattices to exhibit p-type conducting properties. Consequently, the susceptibility to defect formation at the interface indicates that interface quality exerts a significant influence on the transport properties of the superlattice device.

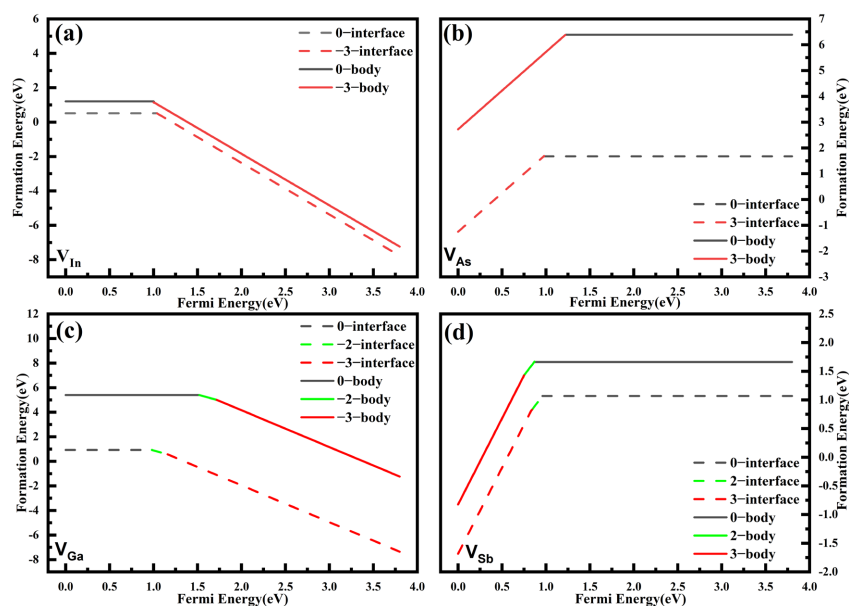


Figure 11. Fermi energy levels versus formation energies for four different types of atomic vacancies: (a) V_{In} , (b) V_{As} versus, (c) V_{Ga} , and (d) V_{Sb} , dashed lines are vacancy defects at the interface, solid lines are in vivo defects.

4. Conclusions

InAs/GaSb type-II superlattices are narrow-bandgap semiconductors that can independently adjust the positions of the conduction and valence band edges, thus providing a broad operating space for the energy-band engineering of antimonide superlattices. By manipulating the material composition and individual film layer thickness, the energy gap can be tuned to the infrared range, which is a crucial characteristic for infrared detection applications. It was observed that the bandgap of the superlattice decreased gradually when the period thicknesses of both the InAs and GaSb bulk materials were simultaneously fixed and gradually increased. When the thickness of one of the InAs or GaSb is further fixed, and the number of layers of the other material is gradually increased, the bandgap of InAs/GaSb ($m, 7$) decreases with an increase in the period thickness, whereas the bandgap of InAs/GaSb ($7, n$) increases with increasing cycle thickness. Quantitative analysis demonstrated that the binding effect of electrons was stronger than that of the holes. This suggests that in the InAs/GaSb type-II superlattice, the InAs bulk material, which serves as the electron aggregation region, plays a dominant role in the modulation of the superlattice bandgap. Furthermore, there are three distinct types of interfaces in the InAs/GaSb type-II superlattice whose partial wave density of states (PDOS) is proportional to the bandgap. In studies of InSb and GaAs interfaces, it was determined that vacancy defects are more likely to form at the interfaces than at locations away from the interfaces within the superlattice body. The charge states of the defects are closely associated with the Fermi energy level: as the Fermi energy level changes, V_{In} and V_{Ga} exhibit a greater tendency to form donor defects, which display n-type conducting properties; V_{As} and V_{Sb} exhibit a greater tendency to form acceptor defects and display p-type conducting properties. This shift in the conductive properties is closely related to the change in the Fermi energy level and also indicates that defects at the interface are more likely to form than defects within the superlattice body.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/photonics12030249/s1>, Table S1. Modulation of Lattice Mismatch Rate by the Number of InAs/GaSb Type II Superlattice Layers; Table S2. Effect of InAsSb Formed by Intermixing on the Band Gap of InAs/GaSb Type-II Superlattices ($m = n$); Table S3. Evaluation of the stability of different interface types.

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References

1. Sun, W.-F.; Li, M.-C.; Zhao, L.-C. First-principles study of interface relaxation effect on interface and electronic structures of InAs/GaSb superlattices with different interface types. *Superlattices Microstruct.* **2011**, *49*, 81–90. [\[CrossRef\]](#)
2. Asadi, Y.; Nourbakhsh, Z. First principle characterization of structural, electronic, mechanical, thermodynamic, linear and nonlinear optical properties of zinc blende InAs, InSb and their InAs_xSb_{1-x} ternary alloys. *J. Phys. Chem. Solids* **2019**, *132*, 213–221. [\[CrossRef\]](#)
3. Kim, Y.S.; Marsman, M.; Kresse, G.; Tran, F.; Blaha, P. Towards efficient band structure and effective mass calculations for III-V direct band-gap semiconductors. *Phys. Rev. B* **2010**, *82*, 205212. [\[CrossRef\]](#)
4. Fang, S.L.; Hao, R.T.; Zhang, L.G.; Guo, J.; Liu, W.M. Simulation of the Band Structure of InAs/GaSb Type II Superlattices Utilizing Multiple Energy Band Theories. *Front. Phys.* **2022**, *10*, 822800. [\[CrossRef\]](#)
5. Efimov, O.; Yoon, Y.G. First-Principles Study of InAs/GaSb Semiconductor Superlattice Structures. *J. Comput. Theor. Nanosci.* **2013**, *10*, 1684–1687. [\[CrossRef\]](#)
6. Chai, X.; Zhou, Y.; Xu, Z.; Chen, J.; He, L. Mid-wavelength interband cascade infrared photodetectors with two and three stages. *Infrared Phys. Technol.* **2020**, *107*, 103292. [\[CrossRef\]](#)
7. Patra, A.; Chatterjee, S.; Roy, A. Strain distribution in (InAs)/(InSb)multilayer: A first principles calculations. *Solid State Commun.* **2019**, *291*, 24–27. [\[CrossRef\]](#)
8. Blöchl, P.E. Projector augmented-wave method. *Phys. Rev. B Condens. Matter* **1994**, *50*, 17953–17979. [\[CrossRef\]](#)
9. Sun, W.-F.; Zheng, X.-X. First-principles study of interface relaxation effects on interface structure, band structure and optical property of InAs/GaSb superlattices. *Acta Phys. Sin.* **2012**, *61*, 117301. [\[CrossRef\]](#)
10. Wang, J.W.; Zhang, Y. Band-gap corrected density functional theory calculations for InAs/GaSb type II superlattices. *J. Appl. Phys.* **2014**, *116*, 214301. [\[CrossRef\]](#)
11. Nakamura, H.; Hayashi, N.; Nakai, N.; Okumura, M.; Machida, M. First-principle electronic structure calculations for magnetic moment in iron-based superconductors: An LSDA+negative U study. *Phys. C Supercond.* **2009**, *469*, 908–911. [\[CrossRef\]](#)
12. Himmetoglu, B.; Floris, A.; De Gironcoli, S.; Cococcioni, M. Hubbard-Corrected DFT Energy Functionals: The LDA + U Description of Correlated Systems. *Int. J. Quantum Chem.* **2014**, *114*, 14–49. [\[CrossRef\]](#)
13. Micnas, R.; Ranninger, J.; Robaszkiewicz, S. Superconductivity in narrow-band systems with local nonretarded attractive interactions. *Rev. Mod. Phys.* **1990**, *62*, 113–171. [\[CrossRef\]](#)
14. Hase, I.; Yanagisawa, T. Madelung energy of the valence-skipping compound BaBiO₃. *Phys. Rev. B* **2007**, *76*, 174103. [\[CrossRef\]](#)
15. Yang, S.; Dardzinski, D.; Hwang, A.; Pikulin, D.I.; Winkler, G.W.; Marom, N. First-principles feasibility assessment of a topological insulator at the InAs/GaSb interface. *Phys. Rev. Mater.* **2021**, *5*, 084204. [\[CrossRef\]](#)
16. Peng, Q.; Chen, N.J.; Huang, D.H.; Heller, E.R.; Cardimona, D.A.; Gao, F. First-Principles Assessment of the Structure and Stability of 15 Intrinsic Point Defects in Zinc-Blende Indium Arsenide. *Crystals* **2019**, *9*, 48. [\[CrossRef\]](#)
17. Wang, J.; Lukose, B.; Thompson, M.O.; Clancy, P. Ab initio modeling of vacancies, antisites, and Si dopants in ordered InGaAs. *J. Appl. Phys.* **2017**, *121*, 045106. [\[CrossRef\]](#)
18. Northrup, J.E.; Zhang, S.B. Dopant and defect energetics: Si in GaAs. *Phys. Rev. B* **1993**, *47*, 6791–6794. [\[CrossRef\]](#)
19. Lee, C.-W.; Lukose, B.; Thompson, M.O.; Clancy, P. Energetics of neutral Si dopants in InGaAs: An ab initio and semiempirical Tersoff model study. *Phys. Rev. B* **2015**, *91*, 094108. [\[CrossRef\]](#)
20. Lee, S.-G.; Chang, K.J. Energetics and hydrogen passivation of carbon-related defects in InAs and GaAs. *Phys. Rev. B* **1996**, *53*, 9784–9790. [\[CrossRef\]](#)
21. Freysoldt, C.; Grabowski, B.; Hickel, T.; Neugebauer, J.; Kresse, G.; Janotti, A.; Van de Walle, C.G. First-principles calculations for point defects in solids. *Rev. Mod. Phys.* **2014**, *86*, 253–305. [\[CrossRef\]](#)
22. Leslie, M.; Gillan, N.J. The energy and elastic dipole tensor of defects in ionic crystals calculated by the supercell method. *J. Phys. C Solid State Phys.* **1985**, *18*, 973. [\[CrossRef\]](#)
23. Schultz, P.A. Charged Local Defects in Extended Systems. *Phys. Rev. Lett.* **2000**, *84*, 1942–1945. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Makov, G.; Payne, M.C. Periodic boundary conditions in ab initio calculations. *Phys. Rev. B* **1995**, *51*, 4014–4022. [\[CrossRef\]](#)
25. Freysoldt, C.; Neugebauer, J.; Van de Walle, C.G. Fully Ab Initio Finite-Size Corrections for Charged-Defect Supercell Calculations. *Phys. Rev. Lett.* **2009**, *102*, 016402. [\[CrossRef\]](#) [\[PubMed\]](#)
26. Lany, S.; Zunger, A. Assessment of correction methods for the band-gap problem and for finite-size effects in supercell defect calculations: Case studies for ZnO and GaAs. *Phys. Rev. B* **2008**, *78*, 235104. [\[CrossRef\]](#)
27. Komsa, H.-P.; Rantala, T.T.; Pasquarello, A. Finite-size supercell correction schemes for charged defect calculations. *Phys. Rev. B* **2012**, *86*, 045112. [\[CrossRef\]](#)
28. Suo, Z.-J.; Luo, J.-W.; Li, S.-S.; Wang, L.-W. Image charge interaction correction in charged-defect calculations. *Phys. Rev. B* **2020**, *102*, 174110. [\[CrossRef\]](#)
29. Yao, L.C.; Zhou, X.H.; Chen, X.S. Hybrid functional calculation of electronic structure of InAs/GaSb superlattice in (111) orientation. *J. Infrared Millim. Waves* **2016**, *35*, 646–651. [\[CrossRef\]](#)

30. Lu, T.; Chen, Q.X. Revealing Molecular Electronic Structure Analysis of Valence Electron Density. *Acta Phys.-Chim. Sin.* **2018**, *34*, 503–513. [[CrossRef](#)]
31. He, Y.; Sun, J.; Yao, W.; Lu, K.; Liu, D.; Xie, H.; Huang, C.; Jia, N. A self-powered photoelectrochemical molecular imprinted sensor for chloroquine phosphate with enhanced cathodic photocurrent via stepped energy band alignment engineering. *Chem. Eng. J.* **2023**, *451*, 138748. [[CrossRef](#)]

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