Symmetry Breaking-induced Band-splitting in GaAs Thin Film by First-principles Calculations

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We investigated the band-splitting of GaAs thin film by invoking broken inversion symmetry within the bulk region and the lost of 2D symmetry on the surface due to strain in first-principles calculations using density functional theory with spin-orbit interaction. The system is modeled by unreconstructed GaAs(001)–(1×1) slab, and by its strained counterpart arising from As dimerization. For the unstrained system, we found that the valence bands split while the conduction bands remain degenerate. This degeneracy is attributed to the sole contribution of p-state of As atoms found on the surface to this band, where 2D symmetry is preserved. When strain is imposed on this surface, the symmetry is broken and the conduction bands are split. These findings identify the changes in the band structure due to broken symmetry, suggesting their incorporation in the conventional degenerate theoretical description of the GaAs thin films done to date.

1. Introduction

Theoretical studies on GaAs thin films are gaining importance due to the need for deeper understanding of mechanisms associated with their applications in optoelectronics1,2. For instance, the low-temperature molecular beam epitaxy (MBE)-grown GaAs (LT-GaAs), crucial to the development of terahertz electronic, and optical properties recently investigated theoretically9–12. In general, the GaAs(001) facet is considered due to the (2×4) or (4×4) reconstructions observed in the reflection high energy electron diffraction (RHEED) and scanning tunneling microscopy (STM)13–15. Such reconstructions are characteristic of LT-GaAs and are formed by As dimerization on the surface9,13–15. Other LT-GaAs systems are grown on (001) facets of Si or GaAs substrates, hence the prevalence of (001) facet16–18. The main outcome of the above theoretical works is the bandstructure of GaAs and the lack of experimental direct observation of the electronic structure of such systems, making benchmarking of theoretical results with SO-effects difficult. However, recently, the bulk electronic structure of GaAs has been probed experimentally using hard X-ray angle-resolved photoemission (HARPES)21,22, providing the experimental precise maps of the band structure of GaAs along the Γ-X dispersion. Noticeable in the HARPES-obtained21 band structure is the splitting of the valence band maximum into doubly and singly degenerate states at Γ and is determined to be Δv = 0.341 ± 0.002 eV23,24. Since the HARPES above has provided a bandstructure for the bulk restricted to occupied bands, the investigation of both occupied and unoccupied bands, and both bulk and surface structures, is worthwhile. Thus, this work will provide the theoretical confirmation of the HARPES findings on bulk GaAs and will present the changes in the bandstructure of strained and unstrained GaAs(0001) slab, which model GaAs thin films, due to symmetry-breaking using spin density functional theory within PAW potential and hybrid exchange-correlation functional with spin-orbit interaction. Further mechanisms associated with the retention of degeneracy of some bands and how the degeneracy can be lifted are also presented.

2. Computational Methods

The first principles method used is based on spin density functional theory (SDFT)25,26, which is implemented in Vienna Ab-initio Simulation Package (VASP)27,28. The ion-electron interaction is treated using Projector Augmented Wave (PAW)29 method and the exchange-correlation is described by the hybrid functional, HSE06 by Heyd-Scuseria-Ernzerhof30. This hybrid functional uses: (1) Perdew-Burke-Ernzerhof (PBE) functional for the correlation and the long-range exchange interaction...
parts; and (2) a combination of Hartree-Fock and PBE for the short range interaction part via the mixing parameter, $\alpha$ and $\omega$. For these parameters, we used $\alpha = 1/4$ and $\omega = 0.20^{(9)}$. A supercell approach is used to model the systems with plane waves basis set of 300 eV cut-off energy. The Brillouin zone (BZ) is sampled using $\Gamma$-centered $6 \times 6 \times 6$ k points for the bulk and $6 \times 6 \times 1$ k points for the slabs using Monkhorst-Pack k-mesh generation$^{11}$ to obtain the geometry, while relevant high-symmetry k-points are explicitly used to obtain the bandstructures. Other details of the method for each of the systems are discussed in the succeeding section. So far, the methods and functionals used above yielded a lattice parameter of 5.665Å in excellent agreement with experiment (5.653 Å$^{19}$).

Next, the SO interaction is incorporated using the PAW method as described below. In this method, a linear transformation, $\hat{T}$, transforms a pseudo-wavefunction (PS), $|\psi_n\rangle$ to an all-electron wavefunction (AE), $|\phi_n\rangle$, which is the Kohn-Sham single-electron wavefunction in the DFT framework:

$$|\psi_n\rangle = \hat{T} |\phi_n\rangle$$

where,

$$\hat{T} = 1 + \sum_R \hat{T}_R$$

The second term in equation (2) is non-zero within the spherical augmentation region enclosing an atom, $\Omega_R$ or the PAW sphere and beyond this region the two wavefunctions are the same as indicated by the first term. The PS $|\psi_n\rangle$ can be expanded to PS partial waves, $|\phi_n\rangle$ as shown below:

$$|\psi_n\rangle = \sum c_i |\phi_i\rangle$$

and the corresponding AE $|\psi_n\rangle$ can be expanded to AE partial waves $|\phi_i\rangle$,

$$|\psi_n\rangle = \sum c_i |\phi_i\rangle$$

Since $\hat{T}$ is a linear transformation operator, the coefficient, $c_i$ is the inner product, $c_i = \langle p_i | \hat{T} | \phi_i \rangle$, where $|p_i\rangle$ is a projector function that should obey, $\sum |\phi_i\rangle \langle p_i | = 1$, so that the expansion, $\sum_i |\phi_i\rangle \langle p_i | \psi_n\rangle$ of the PS wavefunction, $|\psi_n\rangle$ is identical to itself. This implies that $\langle p_i | \hat{T} | \phi_i \rangle = \delta_{ij}$. The $|\phi_i\rangle$ and $|\phi_i\rangle$ are local basis functions. Thus, $\hat{T}$ becomes:

$$\hat{T} = 1 + \sum_R (|\phi_i\rangle \langle \phi_i | - |\phi_i\rangle \langle p_i |$$

and the AE wavefunction is now:

$$|\psi_n\rangle = |\psi_n\rangle + \sum_i (|\phi_i\rangle - |\phi_i\rangle \langle p_i | \psi_n\rangle$$

Thus, within the PAW method, any (semi)-local operator, $D$, acting on $|\psi_n\rangle$ can be written as pseudo-operator, $\tilde{D}$ acting on the PS wavefunction $|\phi_i\rangle$.

$$\tilde{D} = D + \sum |p_i\rangle \langle \phi_i | D | \phi_i\rangle - \langle \phi_i | D | \phi_i\rangle$$

The SO interaction acts predominantly in the immediate vicinity of the nuclei and since the partial waves $\tilde{\phi}_i$ form a complete basis set within this region, the first and third term of equation (7) cancel, and the SO coupling reduces to AE one-center contribution:

$$\tilde{H}_{SO} = \sum_{ij} |p_i\rangle \langle \phi_j | H_{SO} | \phi_j \rangle \langle p_j |$$

(8).

The Dirac equation from which the $H_{SO}$ can be derived is actually a four-component Hamiltonian. However, by potential-dependent transformations, the four-component Dirac Hamiltonian can be transformed into effective two-component$^{32}$. The zeroth-order is given as:

$$H_{SO} = -\frac{\hbar^2}{(2m_e)^2} \frac{1}{dr} \hat{\sigma} \cdot \hat{L}$$

(9),

where $\hat{L}$ is the angular momentum operator, the $\hat{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ are the $(2 \times 2)$ Pauli spin matrices and the $V(r)$ is the spherical part of the AE potential within the PAW sphere. Therefore, equation (8) can be written as:

$$\tilde{H}_{SO} = \sum_{ij} |\phi_j\rangle \langle \phi_j | \frac{dV_{sphere}}{dr} | \phi_j \rangle \langle p_j | \hat{\sigma} \cdot \hat{L} | p_j \rangle$$

(10),

where spherical harmonics is used for the basis for $\hat{L}$. The $\alpha$ and $\beta$ are the spin-up and spin-down components of the spinor wavefunctions necessary to describe non-collinear magnetism, where PS wavefunctions are defined to consist of 2N eigenspinors ($N$ is the number of eigenvalues)$^{33}$. Thus, the $\tilde{H}_{SO}$ operator's action on the PS wavefunctions is:

$$|\phi_n\rangle = \sum |\tilde{H}_{SO}| \phi_n\rangle$$

(11).

In bulk GaAs and strained GaAs slab, the inversion symmetry and the 2D symmetry are broken and thus SO interaction can arise by the coupling of the spin directions to the crystal structure. The method of incorporation of SO described above is tested for bulk GaAs, compared with experiment and is discussed in the following section.

3. Results and Discussions

3.1 GaAs bulk

We used a two-atom primitive unit cell to model the bulk structure as shown in Fig. 1(a). Figure 1(a) gives the corresponding band structure without the spin-orbit effects. Since, the HARPES$^{21}$ shows energy dispersion from $\Gamma$ to $X$ and so in this work, we use the same direction of the dispersion. First, we note that the valence bands, labeled as VB1 and VB2 in Fig. 1(a) are degenerate at $\Gamma$. A 1.580 eV direct band gap at $\Gamma$ is obtained, in good agreement with experiment (i.e. 1.519 eV) at low temperature$^{34,35}$. Same features of the VBs are also observed in HARPES$^{21}$ except for the splitting at $\Gamma$, which is $\Delta_0 = 0.341 \pm 0.002$ eV$^{23,24}$. Upon inclusion of SO effects in this work, the splitting is confirmed, as shown in Fig. 1(b). In particular, the VB1 and VB2 are now split at $\Gamma$ with $\Delta_S = 0.337$ eV, in excellent agreement with experiment above. VB1 is further split at $\Gamma$ to $X$ direction, while the conduction band (CB) remains degenerate. The splitting of the VB1 is minimal, hence, it is not decipherable in HARPES, which relies on contrast
of the images (i.e. bright bands and dark background), and so the bands, which are well dispersed and appear brighter, can be smeared out producing a single image in the HARPES. Here, we obtained 0.201 eV splitting at X. Also, the band gap obtained now is 1.472 eV and considering the typical range of phonon energies of the system, which is 0.01–0.03 eV, this value is then in excellent agreement with room temperature band gap of 1.43 eV for bulk GaAs36). This finding suggests that the inclusion of SO due to broken inversion symmetry is as important as the search for suitable exchange-correlation functional in obtaining the correct bandstructure. Furthermore, the methods employed above have well-reproduced key features of the band structure observed experimentally.

Next, because the CB remains degenerate, we decomposed the bands into various contributions from the As and Ga orbitals using partial charge density described by the equation (12) below:

$$\rho_{i,k} = \sum_i \sum_j \phi_{i,j}(\mathbf{r}) \phi_{j,k}(\mathbf{r})^*$$

(12),

where $i$ and $k$ are indices for bands and k-points, $\phi_{i,k}(\mathbf{r})$ is a Bloch state, and the double summation runs over all sampled k-points and bands. Hence, equation (12) is the charge density corresponding to the “sampled” Bloch state, in analogy to using molecular orbitals in describing bonding. Here, we use the spatial and symmetric characteristics of the sampled Bloch states to determine the orbitals involved. In Fig. 1(c), we note that the CB is contributed from As-s orbital, having zero orbital angular momentum, renders this band still degenerate. To confirm this line of reasoning, we checked the contribution of As orbital in the split VB1 (Fig. 1(d)) and we found that it is contributed by As-p, which has a non-zero orbital angular momentum.

3.2 GaAs(001)

We used a (1 × 1) unit cell with a 12 Å of vacuum and 8-layer atoms, as depicted in Fig. 2(a) to model the unstrained GaAs(001) slab, referred to as GaAs(001)–(1 × 1). The surface is As-terminated and a dipole correction in the direction perpendicular to the surface is included. The atoms are fixed at their bulk positions such that the As-Ga interlayer distance is 1.415 Å and the As-As interlayer distance is 4.002 Å. The number of layers is sufficient to model a thin film, where the prevalence of the bulk nature of the atoms is important and is well-described in the fixed slab. Figure 2(b) shows the top view of the atomic structure. In this figure, we confirm the equivalent As-As distance in a and b directions, verifying the GaAs(001)–(1 × 1) structure. The corresponding bandstructure without SO is given in Fig. 3(a). For direct comparison with the bulk structure, the same symmetry k-points are used for this slab. Since, similar features of the bands as compared to that of the bulk are noted, the same labeling mechanism is used, namely: (1) the bands between the apparent gap are labeled as CB and VB1; and (2) the lower-energy valence bands are indicated as VB$n$, where $n$ is an integer greater than 1. $n$ increases as the bands go deeper in energy. In Fig. 3(a), we note that the CB and VBs are all degenerate. Then, upon inclusion of SO interaction, VB1 and VB2 and the rest of valence bands, except VB3, are split as depicted in Fig. 3(b). The CB remains degenerate as in the bulk, while the VB1 is largely split at $\Delta$. In the following, we derive the origin of such differences in the splitting of the bands. Fig. 3(c)–(e) show the partial charge density corresponding to the bands identified above. First, we note that the CB is contributed from the p-state of As atoms (not As-s state)
Fig. 3 (Color online) Band structure of unreconstructed GaAs(001)-(1×1) (a) without spin-orbit effects; (b) with spin-orbit effects; and the partial charge density corresponding to (c) conduction band (CB); (d) highest energy valence band (VB1) and third valence band (VB3). Ga and As atoms are shown. Partial charge densities are depicted in 0.02e-/Å³ isosurface value.

(Fig. 3(c)). However, this partial charge density is localized only to As atoms on the surface, where 2D symmetry is preserved, therefore, CB remains degenerate. Next, VB3 also remains degenerate as depicted in Fig. 3(e) because this band is contributed by the p-state of As located on the surface (2D symmetry is preserved) and s-states of As located in the bulk region (where inversion symmetry is broken). Finally, to confirm the effect of broken symmetry in the splitting of VB1, the partial charge density for As is also obtained and is shown in Fig. 3(d). This band is mainly from p-states of As within the bulk region, where inversion symmetry is broken, hence, split.

3.3 Strained GaAs(001)

Owing to the characteristics of the CB, which is degenerate whether in bulk GaAs or GaAs(001)-(1×1), as shown by the bandstructure in Fig. 1(b) and Fig. 3(b), the splitting of this band in the slab structure, which models a thin film, can be studied by breaking the 2D symmetry. We imposed a lateral strain along b direction on the surface of GaAs as shown in Fig. 4(a). As-As lateral distance is now compressed to 2.520 Å, forming series of As-dimers. This strain is typical in (2×4) and (4×4) reconstructions of GaAs(001) and hence mimics the reconstructions found in LT-GaAs because of As dimerization, as discussed previously. Also, the As-As distance reproduced the As dimers’ bond length on such reconstructions37,38. A (2×2) surface unit cell is deemed appropriate to accommodate such changes in the surface structure. Distances along a direction remained the same. The bandstructure after breaking the 2D symmetry on the surface is shown in Fig. 4(b). CBs are now split via just one compressive strain, further confirming that the preservation of the 2D symmetry as the origin of the degenerate CBs in the GaAs(001)-(1×1). This result also suggests, that reconstructions brought about by As dimerization, common to LT-GaAs, can contribute to modification of conduction bands by virtue of broken 2D symmetry. It is thus suggested to incorporate SO effects in investigating reconstructed surfaces of GaAs thin film.

4. Conclusion

We have investigated the spin-orbit effects on the band structure of GaAs bulk, GaAs(001)-(1×1) arising from broken inversion symmetry and the strained GaAs(001) slabs due to broken 2D symmetry, using first-principles calculations based on density functional theory with spin-orbit interaction. We have confirmed the experimentally observed splitting of the valence band maximum at Γ and obtained the band gap of bulk, also in agreement with experiment. The valence band maximum (or VB1) is split while the conduction band minimum (CB) remains degenerate. We explain this degeneracy despite the broken symmetry via the contribution of s-state of As atoms to this band. For the unreconstructed GaAs(001) slab, the valence bands are also split and the CB remained degenerate. The CB, although found to
consist of p-state of As, these As atoms are located on the surface, where 2D symmetry is preserved, thus degenerate. Finally, this 2D symmetry is broken by imposing a lateral strain on the As atoms forming As dimers, typical in the (2×4) and (4×4) reconstructions of GaAs(001) leading to LT-GaAs and the band structure of this strained system shows a split CB, suggesting the importance of spin-orbit effects in modeling GaAs thin films such as LT-GaAs.

Acknowledgments

M.C.S. Escaño extends gratitude to Japan Society for Promotion of Science (JSPS) Grants-in-aid for Young Scientist B Grant Number 15K21028, and “Kenkyu Doujou” Program of Research Center for Development of Far-Infrared Region, University of Fukui for research funds. The calculations are done using the ACCMS supercomputer of Kyoto University as supported by CII, University of Fukui and the High-Performance Computing Cluster Fukui (HPCCF).

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