Defects and dopants in zinc-blende aluminum arsenide: a first-principles study

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Abstract
AlAs is a semiconductor that can form heterostructure, superlattice, and ternary alloy with GaAs. We systematically investigate the formation energies, transition energy levels, as well as defect and carrier densities of intrinsic defects and extrinsic impurities in AlAs using first-principles simulations. Most of the intrinsic defects, including vacancies, antisites and interstitials, show similar features as those of GaAs. Intrinsic defects are found not to be the origin of the n-type or p-type conductivity due to their high formation energies. For extrinsic dopants (Si, C, Mg and Cu), Mg can be an effective p-type dopant under both As-rich and As-poor conditions. Si-doping can introduce either n-type or p-type, depending on the specific growth condition. C serves as a p-type dopant under As-poor and As-moderate conditions, and Cu-doping has little effect on the conductivity.

1. Introduction
Zinc-blende AlAs is a III–V semiconductor that has not only the same crystal structure and nearly same lattice constant with GaAs, but also a wider band gap (2.16 eV vs 1.42 eV), making AlAs and GaAs an excellent semiconductor pair to grow alloys [1], heterostructures [2, 3] and superlattices [4]. Due to the superb miscibility and high carrier mobility of GaAs and AlAs, these structures can be applied in high-speed digital, high-frequency microwave, electronic and electro-optic devices [1, 4], such as high electron mobility transistors [1, 3, 4] and quantum well infrared photodetectors [5].

As defects and impurities inevitably exist in the semiconductors, their effects on the electronic and optical properties are essential for the performance. First-principles simulations can provide rich theoretical insights for understanding the defects and impurities [6–12]. The defect properties of AlAs/GaAs alloy and heterostructure, as well as GaAs have been extensively studied [13–19], however, a systematic study of defects in AlAs has not been reported yet. Jiang et al [16] investigated six types of intrinsic defects of AlAs in their neutral states, including interstitials (Al and As), antisites (AlAs and AsAl), and vacancies (VAl and VAs). It was found that the neutral AsAl antisite has the lowest formation energy among these defects, but the defects in charged states, which normally have significant impact, were not considered. Chroneos et al [20–23] studied more intrinsic defects with more charge states using Perdew–Burke–Ernzerhof (PBE) and local-density approximation functionals, but the underestimated band gap may introduce inaccuracy into the defect calculations. Besides the intrinsic defects, extrinsic dopants/impurities may have a significant effect on the properties. Spectrographic analysis reveals that AlAs can be mostly contaminated by Si, as well as Mg, and Cu impurities [24]. Their properties such as formation energies and transition energy levels...
have not been investigated theoretically. Moreover, both n-type and p-type conductivity have been observed in AlAs samples with these extrinsic dopants [24–30], however, the origins of such conductivities have not been well understood from a theoretical perspective. Overall, a systematic study of the intrinsic and extrinsic defects in AlAs is in need for better understanding of the electronic and optical performance of AlAs and related semiconductors.

In this work, we systematically study the intrinsic defects and dopants (Si, C, Mg and Cu) in AlAs using first-principles calculations. Three chemical conditions including As-rich (Al-poor), As-moderate and As-poor (Al-rich) are considered. Our results show that most of the intrinsic defects, including vacancies, antisites and interstitials, exhibit similar properties as GaAs. All intrinsic defects are determined to have low concentrations. Neither n-type nor p-type conductivity is predicted to exist in AlAs with merely intrinsic defects considered, however, doping of extrinsic element Si makes the materials n-type or p-type, and C and Mg doping makes it p-type. Doping of Cu leads to weak n-type conductivity. Our finding explains the origin of the measured n-type and p-type conductivity in AlAs samples containing Si [24–26], as well as the strong p-type conductivity induced by C- and Mg-doping in other experiments [27–30]. We also predict that Cu-doping is not the source of p-type or n-type conductivity in previous experiments [24].

2. Computational details

Our first-principles simulations based on density functional theory (DFT) [31, 32] are performed using the Vienna _ab initio_ simulation package [33–35]. The PBE [36] and Heyd–Scuseria–Ernzerhof (HSE06) [37] exchange–correlation functionals are adopted for structural optimization and electronic structure calculation, respectively. Based on PBE functional, HSE06 functional replaces 25% short-range exchange with Hartree–Fock exact exchange, and the range-separation parameter is selected as 0.11 bohr\(^{-1}\). The projector augmented waves method is utilized to treat the atomic core regions [38]. The cutoff energy is chosen as 400 eV, and a 216-atom supercell is used to simulate the defects. The first Brillouin zones of the primitive cell and the supercell are sampled by \(2 \times 2 \times 2\) and \(1 \times 1 \times 1\) Monkhorst–Pack [39] \(k\)-point mesh, respectively. Spin polarization is considered for charge states with unpaired spins. The energy convergence of electronic steps is set as \(10^{-5}\) eV.

In terms of defects, the formation energy \(\Delta H_f(\alpha, q)\) of a point defect \(\alpha\) with charge state \(q\) is determined by

\[
\Delta H_f(\alpha, q) = \Delta E(\alpha, q) + \sum n_i \mu_i + qE_F, \tag{1}
\]

where \(\Delta E(\alpha, q) = E(\alpha, q) - E(\text{host}) + \sum n_i E_i + q\varepsilon_{\text{VBM}}(\text{host})\). \(E(\text{host})\) and \(E(\alpha, q)\) are the total energies of the supercells without and with defect \(\alpha\), respectively. \(n_i\) is the number of type-\(i\) defect atoms, and \(\mu_i\) and \(E_i\) are the chemical potential and energy per \(i\) element in its pure phase. For charged defects, \(\Delta H_f(\alpha, q)\) depends on not only the Fermi level \(E_F\), which is referenced to the valence band maximum (VBM), or \(\varepsilon_{\text{VBM}}(\text{host})\), but also the chemical potentials of component elements. The potential alignment and image charge correction are used in the calculation of the energies of charged defects [40, 41].

There exist several thermal dynamic conditions of the chemical potentials for the growth of the material under equilibrium. To avoid Al, As and other involved elements \(X\) forming their elemental phases, it is required that

\[
\mu_{\text{Al}} \leq 0, \mu_{\text{As}} \leq 0, \mu_X \leq 0. \tag{2}
\]

In addition, AlAs should be stable under equilibrium, meaning

\[
\mu_{\text{Al}} + \mu_{\text{As}} = \Delta H_f(\text{AlAs}) \tag{3}
\]

In equation (3), \(\Delta H_f(\text{AlAs})\) is the formation energy of the compound AlAs. \(\Delta H_f(\text{AlAs})\) is calculated as \(-1.2787\) eV, which is consistent with the experimental values around \(-1.26\) eV [42–44]. Furthermore, the formation of other possible secondary compounds involving the host and dopant elements, or \(\text{Al}_mX_n\) and \(X_n\text{As}_m\), should also be avoided, which requires

\[
m\mu_X + m\mu_{\text{Al}} \leq \Delta H_f(\text{Al}_mX_n), \tag{4}
\]

and

\[
m\mu_X + m\mu_{\text{As}} \leq \Delta H_f(X_n\text{As}_m). \tag{5}
\]

For instance, the formation energy of \(\text{SiAs}_2\) is \(-1.24\) eV, so the highest possible \(\mu_{\text{Si}}\) is \(-1.24\) eV under As-rich condition (\(\mu_{\text{As}} = 0, \mu_{\text{Al}} = -1.28\) eV) and 0 eV under Al-rich condition (\(\mu_{\text{As}} = -1.28\) eV, \(\mu_{\text{Al}} = 0\)). The sample will have no residue of the secondary compounds for instance \(\text{SiAs}_2\) in the Si-doped AlAs only when these chemical potential conditions are met.
The carrier concentrations are investigated using the approach as described in reference [45]. The hole and electron concentrations are given by

\[ p_0 = N_v e^{\frac{E_g}{k_B T}}, \quad \text{and} \quad n_0 = N_c e^{\frac{E_g}{k_B T}}, \] (6)

where \( E_g \) is the band gap of AlAs (2.16 eV), \( k_B \) is Boltzmann constant, and \( T \) is temperature. \( N_v \) and \( N_c \) are the effective densities of states of the valance bands and conduction bands, respectively. \( N_v \) and \( N_c \) are given by

\[ N_v = \frac{2(2\pi m^*_v k_B T)^{3/2}}{\hbar^3} \quad \text{and} \quad N_c = \frac{2(2\pi m^*_c k_B T)^{3/2}}{\hbar^3}. \] (7)

The effective mass of hole \( (m^*_p) \) and electron \( (m^*_e) \) are 0.195 \( m_0 \) and 0.517 \( m_0 \), respectively. The charge neutrality condition without dopants satisfies

\[ n_0 = p_0. \] (8)

In case of doping, with the concentrations of acceptors \( N_A^- \) and donors \( N_D^+ \), the charge neutrality condition gives

\[ n_0 + N_A^- = p_0 + N_D^+. \] (9)

By solving this equation, we can obtain the Fermi energy and hole/electron concentrations at equilibrium as a function of temperature and dopant concentrations.

Finally, defect concentration for defect \( \alpha \) in charge state \( q \) is given by

\[ c(\alpha, q) = N_{\text{sites}} g_q e^{\frac{\Delta U(\alpha, q)}{k_B T}}, \] (10)

where \( N_{\text{sites}} \) is the density of possible atomic sites of defects, \( g_q \) is degeneracy factor [45].

3. Results and discussion

3.1. Electronic structure

For zinc-blende lattice of AlAs, the lattice parameter is calculated as 5.67 Å using HSE06, agreeing with the experimental value of 5.66 Å [46]. The calculated Al–As bond length is 2.48 Å. Based on the optimized structure, we further calculate the electronic band structure as well as the density of state (shown in figure 1). AlAs exhibits an indirect bandgap of 2.16 eV, with VBM located at \( \Gamma \) point, and the conduction band minimum (CBM) located at \( X \) point (0.5, 0.5, 0). Our calculated band gap size is highly consistent with the experimental values 2.23–2.25 eV [47–49].

The orbital-projected density of state is displayed in figure 1. The valence band is mostly composed of Al–3p and As–4p orbitals, whereas the conduction band is mainly contributed by Al–3s, Al–3p and As–4p electrons.
3.2. Intrinsic defects

The calculated formation energies as functions of the Fermi level under As-rich conditions are shown in figure 2(a). Among all the defects, \( \text{As}_2^{2+} \text{Al} \) is found to have the lowest formation energy when the Fermi level is close to VBM. Its positive charge state indicates that it is a donor defect. As Fermi level increases to 0.53 eV and 1.02 eV, its charge state transits to \( 1^+ \) and neutral states, respectively. The \( (-0/0) \) transition energy level is found to be comparatively close to CBM. With Al substituted by As, the Al–As bonds are broken, and the As 4p states in the conduction band (figure 1) move down, leading to the deep \( (0^+/2^+) \) and \( (2^-/0^-) \) defect levels in the middle of the gap. For Fermi level higher than 1.87 eV above VBM, \( \text{V}_{\text{As}}^3 \text{Al} \) is determined to have the lowest formation energy, while the \( \text{As}_{\text{Al}} \) becomes the second favorable defect. In this regime, \( \text{V}_{\text{As}}^3 \text{Al} \) serves as an acceptor and a significant donor-passivating defect. Its \( (2^-/0^-) \) and \( (3^-/2^-) \) transition energy levels lie at 1.40 eV and 1.01 eV below the CBM, respectively. The transition energy levels of the main defects are also summarized in figure 3.

Under the As-poor condition, as shown in figure 2(b), \( \text{Al}_i \) is the defect that has the lowest formation energy for Fermi energy between VBM and 0.98 eV above. \( \text{Al}_i \) bonds with the neighboring As (Al – As bond length is 2.48 Å), as well as a nearby Al (Al–Al bond length is also 2.48 Å). The \( (2^-/3^+) \) transition energy level of \( \text{Al}_i \) is approximately 0.73 eV above the VBM, as shown in figure 3. The formation energy of \( \text{Al}_i^0 \) is lower than that of \( \text{As}_i^0 \) under As-poor condition, which is similar to the formation of \( \text{Ga}_i^0 \) being lower than \( \text{As}_i^0 \) in GaAs under the same condition [16]. \( \text{Al}_{\text{As}} \) becomes the defect with lowest formation energy for Fermi energy between 0.98 eV and CBM. Other defects and defect clusters (\( \text{V}_{\text{As}}-\text{V}_\text{Al}, \text{Al}_{\text{As}}-\text{As}_{\text{Al}} \) and \( \text{As}_i \)) have much higher formation energies in both As-rich or As-poor cases, and thus their concentration is very low.

Following equations (6) – (10), we calculate the Fermi energy, concentrations of defects and carriers at 300 K as a function of the chemical potentials \( \mu_{\text{As}} \). As shown in figure 2(c), although the maximum
Figure 3. Summary of the transition energy levels of the intrinsic point defects in the band gap of AlAs.

Figure 4. Formation energies of Si-doped AlAs as a function of Fermi level under (a) As-rich and (b) As-poor conditions. (c) Fermi energy, concentrations of defects and carriers at room temperature for Si-doped AlAs as a function of $\mu_{\text{As}}$ from As-rich to As-poor.

Concentrations of $\text{As}_{\text{Al}}^{0}$ and $\text{V}_{\text{As}}^{0}$ are $10^{16}$ cm$^{-3}$ and $10^{14}$ cm$^{-3}$ respectively, neutral defects have no effect on carrier concentration and conductivity. The Fermi level and carrier density show nonmonotonic behavior.
between As-moderate and As-poor condition, which is caused by the rising of the $\text{Al}_{\text{As}}^\text{−}$. The electron concentration at any chemical potential $\mu_{\text{As}}$ is determined to be relatively low ($10^7–10^8 \text{ cm}^{-3}$), which is not only caused by Fermi level being pinned moderately above the middle of the band gap, but also the high formation energies of the intrinsic defects under both As-rich and As-poor conditions (figure 2). Such low carrier density indicates the non-conductivity in AlAs with only intrinsic defects considered. It also indicates that the experimentally observed conductivity comes from impurities [24–26] rather than intrinsic defects.

3.3. Extrinsic dopants/impurities
We also study the common impurity defects, such as Si, C, Mg and Cu. These impurities are found in the sample during growth and postprocessing [24–26]. Our discussion below will reveal that Mg can be an effective p-type dopant, only Si doping under the As-rich or As-moderate conditions can introduce high n-type conductivity, while other dopants, e.g. C leads to p-type conductivity. In addition, Cu doping has relatively weak effect on conductivity.

3.3.1. Si and C doping
The formation energies of Si-doping, as well as some important intrinsic defects are summarized in figure 4. Under As-rich condition, as plotted in figure 4(a), $\text{Si}_{\text{Al}}^{1+}$ is determined to have the lowest formation energy between 0.36 and 1.20 eV above VBM, taking over the place from $\text{As}_{\text{Al}}$ in this Fermi level range. Formation energy of $\text{Si}_{\text{Al}}$ is generally lower than those of $\text{Si}_{\text{As}}$ and $\text{Si}_i$, indicating that the Si impurities mostly exists in the form of $\text{Si}_{\text{Al}}$ under As-rich condition. As presented in figure 4(a), the $(-/+/)$ transition

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Figure 5. Formation energies of C-doped AlAs as a function of Fermi level under (a) As-rich and (b) As-poor conditions. (c) Fermi energy, concentrations of defects and carriers at room temperature for C-doped AlAs as $\mu_{\text{As}}$ changes from As-rich to As-poor.
Figure 6. Formation energies of Mg-doped AlAs as a function of Fermi level under (a) As-rich and (b) As-poor conditions. (c) Fermi energy, concentrations of defects and carriers at room temperature for Mg-doped AlAs as μ\textsubscript{As} changes from As-rich to As-poor.

energy level is of Si\textsubscript{Al} is 0.12 eV below the CBM. Si\textsubscript{Al} is an acceptor above this level while a donor below this level.

Under As-poor condition, as shown in figure 4(b), Si\textsuperscript{1+}\textsubscript{Al} is a donor defect that has the lowest formation energy defects for Fermi energy between VBM and 0.80 eV above. In the rest energy range, Si\textsuperscript{−}\textsubscript{As} is the most energetically favorable. Si\textsubscript{As} is a donor when the Fermi level is near VBM, and serves as an acceptor in a larger Fermi level range above the (−/0) transition energy level.

Figure 4(c) shows the defect and carriers concentrations as functions of μ\textsubscript{As} for Si-doping. Si-doped AlAs exhibits n-type conductivity under As-rich and As-moderate condition. The densities of electron carrier is calculated to be around 2 × 10\textsuperscript{16} cm\textsuperscript{−3} under As-rich and As-moderate condition, one order of magnitude lower than the measured values in experiments (6 × 10\textsuperscript{17}–8.5 × 10\textsuperscript{17} cm\textsuperscript{−3}) [24, 25]. The Si\textsuperscript{1+}\textsubscript{Al} concentration is around 10\textsuperscript{17} cm\textsuperscript{−3} under aforesaid condition, also slightly less than the measured values in experimental values (10\textsuperscript{18} cm\textsuperscript{−3}) [24]. High electron carrier density in Si-doped AlAs indicates its strong n-type conductivity. Si-doping pushes the Fermi level close to the CBM under the As-rich and As-moderate condition [figure 4(c)]. Under As-poor condition, the Si\textsuperscript{1−}\textsubscript{As} acceptor and the Si\textsuperscript{1+}\textsubscript{Al} donor correspond to their lowest formation energies. Fermi level is relatively close to VBM level, leading to the relatively weak p-type conductivity. Therefore, the conductivity transits from strong n-type to weak p-type as μ\textsubscript{As} decreases to As-poor condition.

For C doping, intrinsic defects have lower formation energies than most of C-induced defects, such as C\textsubscript{i} and C\textsubscript{Al} under As-rich condition [figure 5(a)]. The C-induced defect with the lowest formation energy is C\textsubscript{As}. C\textsubscript{As} has a (0/+) transition energy level at 0.02 eV and a (−/0) level at 0.19 eV in figure 8. Defects C\textsubscript{Al} and C\textsubscript{i} have much higher formation energies in both As-rich or As-poor conditions, so they have low impact on the carrier densities. Under As-poor condition [figure 5(b)], intrinsic defect Al\textsuperscript{1+}\textsubscript{i} has the lowest...
Figure 7. Formation energies of Cu-doped AlAs as a function of Fermi level under (a) As-rich and (b) As-poor conditions. (c) Fermi energy, concentrations of defects and carriers at room temperature for Cu-doped AlAs as $\mu_{\text{As}}$ changes from As-rich to As-poor.

formation energy between VBM and 0.50 eV above, and $\text{C}_{\text{As}}^{-}$ take over for Fermi levels higher than 0.50 eV above VBM. The defects concentration as a function of $\mu_{\text{As}}$ are plotted for C-doping in figure 5(c). The highest concentration of $\text{C}_{\text{As}}^{-}$ defect is in the order of $10^{16}$ cm$^{-3}$ for most of the $\mu_{\text{As}}$ values. Under As-poor and As-moderate conditions, the Fermi level is pinned at around 0.18 eV above VBM, indicating that the conductivity is p-type under this condition. The hole density of $2 \times 10^{16}$ cm$^{-3}$ [see figure 5(c)] in As-poor condition is smaller than the values ($10^{19}$ cm$^{-3}$) measured in Raman, photoluminescence spectroscopy and other experiments [28–30].

3.3.2. Mg and Cu doping
Figure 6 shows the formation energies of defects related to Mg doping, as well as the intrinsic defects. Mg-doping mainly introduces two types of defects, Mg$_2^{2+}$ and Mg$_{\text{Al}}^{-}$, with lower formation energies than intrinsic defects. Under both conditions, the defect with lowest formation energy is Mg$_2^{2+}$ for Fermi energies on the VBM side, while it transits to Mg$_{\text{Al}}^{-}$ on CBM side. The energies for this transition are 0.26 eV and 0.67 eV above VBM for As-rich and As-poor conditions, respectively.

Mg$_{\text{Al}}$ is an acceptor in most part of the Fermi level range. Its (0/+ and −/0) transition energy levels lie at 0.02 eV and 0.19 eV above the VBM, respectively, as shown in figure 8. The Mg$_2^{2+}$ concentration is $10^{19} \sim 10^{22}$ cm$^{-3}$, higher than the experimental value ($2 \times 10^{17}$ cm$^{-3}$) [24]. Mg$_{\text{Al}}^{-}$ concentration is also high, but neutral state does not contribute to electrical conductivity. The concentration of Mg$_2^{2+}$ is calculated to be significantly high ($9 \times 10^{21}$ cm$^{-3}$) under As-rich condition, due to its low formation energies [figure 6(c)]. Meanwhile, it should be noticed that the carrier (hole) density ($6 \times 10^{15}$ cm$^{-3}$) of Mg-doping, and its Fermi level is pinned 0.27 eV above VBM. Thus, Mg-doping is a suitable way to improve the p-type conductivity, which is similar to Mg-doped GaAs in experiments [50, 51].
Figure 8. Charge transition energy levels of four dopants (Si, C, Mg and Cu) in AlAs.

For Cu-doping, the formation energies of Cu-doping as a function of Fermi level are shown in figures 7(a) and (b), as well as charge transition energy levels of Cu-doping in AlAs as presented in figure 8. Under As-rich condition [figure 7(a)], Cu$_{Al}^{2-}$ emerges with the lowest formation energy between 1.01 eV above VBM and CBM, whereas Cu$_{Al}^{1+}$ has slightly lower formation energy than the lowest intrinsic As$_{Al}$ for a small energy range in the middle of the band gap. Under As-poor condition in figure 7(b), Cu$_{Al}^{1+}$ and Cu$_{Al}^{2-}$ exhibit lower formation energies than all intrinsic defects for Fermi energy higher than 0.16 eV above VBM. As shown in figure 7(c), the densities of Cu$_{Al}^{1-}$ and Cu$_{Al}^{1+}$ both decreases monotonically from 10$^{17}$ cm$^{-3}$, as $\mu_{As}$ varies from the As-rich to As-poor condition. The calculated Cu concentration (10$^{17}$ cm$^{-3}$) agree with the detected values in experiments (8.4 $\times$ 10$^{17}$ cm$^{-3}$) [24]. Cu$_{Al}^{2-}$ and Cu$_{Al}^{1+}$ pin the Fermi level at 0.70 eV below the CBM under As-poor condition, while it makes the Fermi level not close to CBM under As-rich condition. The carrier (electron) density of Cu-doping is 6 $\times$ 10$^{12}$ cm$^{-3}$ under As-poor condition, while it is close to 0 under As-rich condition. As a result, the conductivity is barely affected by Cu-doping under As-rich condition, while weakly n-type conductivity is introduced by Cu-doping under As-poor condition.

4. Conclusion

In summary, we have investigated the formation energies, transition energy levels, and the defect and carrier concentrations of the intrinsic defects and several common extrinsic dopants in AlAs. For intrinsic defects, As$_{Al}$ and V$_{Al}$ are determined to have the lowest formation energies under As-rich condition, whereas Al$_{i}$ and Al$_{AS}$ have the lowest formation energies with different Fermi energy range under As-poor condition. Though their formation energies are calculated to be lower than other intrinsic defects, they are still generally high, causing low defect concentrations. As a result, the intrinsic defects cannot be the source of n-type or p-type conductivity. For extrinsic doping, doping of Si, C, Mg, and Cu all shows lower formation energies for related defects depending on the growth chemical conditions, leading to higher defect and carrier concentrations. Si-doping introduces high electron concentration and n-type conductivity under As-rich condition, and high hole concentration and p-type conductivity under As-poor condition. C-doping can make AlAs p-type conductive under As-poor and As-moderate conditions, while Mg is an efficient p-type dopant under any growth condition. In addition, Cu is not an effective n-/p-type dopant according to our calculations. Our results provide insights for optimizing the performance of the AlAs-related semiconductors.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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