A comparative study of low energy radiation response of AlAs, GaAs and GaAs/AlAs superlattice and the damage effects on their electronic structures

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In this study, the low energy radiation responses of AlAs, GaAs and GaAs/AlAs superlattice are simulated and the radiation damage effects on their electronic structures are investigated. It is found that the threshold displacement energies for AlAs are generally larger than those for GaAs, i.e., the atoms in AlAs are more difficult to be displaced than those in GaAs under radiation environment. As for GaAs/AlAs superlattice, the Ga and Al atoms are more susceptible to the radiation than those in the bulk AlAs and GaAs, whereas the As atoms need comparable or much larger energies to be displaced than those in the bulk states. The created defects are generally Frenkel pairs, and a few antisite defects are also created in the superlattice structure. The created defects are found to have profound effects on the electronic properties of GaAs/AlAs superlattice, in which charge transfer, redistribution and even accumulation take place, and band gap narrowing and even metallicity are induced in some cases. This study shows that it is necessary to enhance the radiation tolerance of GaAs/AlAs superlattice to improve their performance under irradiation.

In the past decades, the development in micro-fabrication such as molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD) opens a new stage in science where artificial materials are designed for specific studies and applications1. It is noted that gallium arsenide (GaAs) and aluminum arsenide (AlAs) are perfectly lattice matched, and few difficulties are expected in the growth of (GaAs)m/(AlAs)n semiconductor superlattice (SL), which consists of m monolayers of GaAs alternating with n monolayers of AlAs. The artificial SL has been widely used in different applications like the optoelectronic devices with quantum cascade laser, high-frequency oscillators and thermoelectric devices2-9, due to the new physical phenomena such as quantum confinement, Brillouin-zone folding and the obtaining of a direct-gap superlattice from their indirect-gap constituents10. In the application field of military and aerospace, the semiconductor materials are exposed to different radiation environments, which may result in defect generation, migration and aggregation, and ultimately may deteriorate their optical and electronic properties and influence their performance which may lead to permanent failure10-15. For example, Tanaka et al. reported that the photoluminescence intensity and the two-dimensional electron gas mobility of GaAs/AlGaAs heterostructures decreased obviously under electron irradiation14. Therefore, it is of great importance to study their phase stability and the radiation damage effects on the electronic properties of the semiconductor materials.

The radiation damage effects of GaAs and AlAs have been extensively studied16-21. Wesch et al. compared the radiation responses of GaAs and AlAs, and they found the AlAs behaves more robustly under Au+ ion irradiation18. Sayed et al. investigated the low energy displacement events of GaAs and AlAs employing the molecular dynamics (MD) method, who found that the threshold displacement energies (Eₜₛ) for Al atoms are significantly higher than those for Ga atoms along certain directions19. Nordlund et al. predicted that interstitials are dominant...
isolated defects in GaAs under He\(^+\) ion irradiation\(^{21}\). By contrast, the radiation responses of \((\text{GaAs})_m/(\text{AlAs})_n\) SL have received relatively scant attentions\(^{22–24}\). Cullis\textit{et al}. irradiated the AlAs/GaAs heterostructures with Si\(^{+}\) ions, and they suggested that the AlAs resisted ion damage accumulation far more strongly than the GaAs\(^{22}\). Jenčič\textit{et al}. have studied the radiation responses of Al\(_x\)Ga\(_{1-x}\)As/GaAs (\(x = 0.2\) and 0.85) samples to Kr\(^+\) and Xe\(^+\) irradiation and reported that the AlGaAs is more resistant to amorphization than GaAs and the resistance increases with the increasing Al content\(^{24}\). In spite of these experimental investigations, no theoretical simulation of dynamic process of radiation damage of GaAs/AlAs SL has been reported in the literature thus far. There still lacks an atomic-level understanding of the micro-structural evolution and the underlying mechanism for defect generation in the semiconductor superlattices.

In recent years, the \textit{ab initio} MD (AIMD) method has made it possible to simulate radiation damage of materials with the inclusion of motion of electrons, and has been extensively applied to simulate the displacement events in ceramic and semiconductors materials\(^{25–33}\). As compared with the classical MD method, the interatomic potentials are obtained from electronic structure calculations rather than empirical fitting of experimental results. Consequently, a lot of physical parameters like \(E_{\text{dss}}\) can be determined with \textit{ab initio} accuracy. Lucas and Pizzagalli have demonstrated that the average \(E_{\text{dss}}\) for both C and Si sublattices in SiC determined from AIMD are in very close agreement to the experimental consensus and such an agreement has never been obtained with semi-empirical potentials or tight-binding methods\(^{30}\). Gao\textit{et al}. carried out AIMD simulation of ion-solid interactions in SiC and revealed that during the dynamic process of displacement events a significant charge transfer occurs between atoms, and the charge transfer to and from recoiling atoms can alter the energy barriers and dynamics for stable defect formation\(^{34}\). Wang\textit{et al}. investigated the radiation responses of pyrochlores to electron irradiation using the AIMD method and predicted a number of new mechanisms for defect generation and new defective states that are different from classical MD simulations\(^{33}\). These simulations have demonstrated that the AIMD method is a powerful tool in describing the ion-solid interactions in materials. In this study, the AIMD methods are employed to investigate the response behaviors of AlAs, GaAs and GaAs/AlAs SL under low energy irradiation. The geometrical configurations of AlAs, GaAs and GaAs/AlAs SL are illustrated in Fig. 1. The computational details are described in the Methods section. The threshold displacement energies have been determined, and the defect distribution and the pathway for defect generation have been provided. Meanwhile, the radiation damage effects on the electronic structures of these materials have also been investigated. The presented results provide a fundamental insight into the microscopic mechanism of displacement events in AlAs, GaAs and GaAs/AlAs SL, and advance the understanding of the electronic properties of these materials under radiation environment.

**Results and Discussion**

**Lattice constants and cohesive energies for bulk AlAs and GaAs.** The original point group of AlAs and GaAs crystal is the \(T_d\) group of zinc blende\(^{35}\), as shown in Fig. 1(a). The lattice constants and cohesive energies for AlAs and GaAs are calculated and compared with the available results in Table 1. Our calculated lattice
constant of 5.66 Å for AlAs is slightly smaller than the value of 5.71 Å for GaAs, which is in good agreement with the experimental results\(^3\) reported by Wyckoff and other theoretical results\(^7,37,38\). In this study, the lattice constant of GaAs/AlAs SL is set to be the intermediate value of 5.685 Å due to the small lattice mismatch between GaAs and AlAs.

The cohesive energy is the condensed-matter analog of molecular atomization energy and a measure of the inter-atomic bond strength, which is calculated by

\[
E_{\text{coh}} = \frac{E_{\text{total}}(AB) - nE_{\text{iso}}(A) - mE_{\text{iso}}(B)}{n + m}
\]

Here, \(n\) and \(m\) denote the total number of A and B atoms in the unit cell, respectively, \(E_{\text{total}}(AB)\) represents the energies of GaAs and AlAs, and \(E_{\text{iso}}(A)\) and \(E_{\text{iso}}(B)\) are the total energies of isolated A and B atoms, respectively.

The cohesive energies of AlAs and GaAs are determined to be 3.74 and 3.21 eV/atom, respectively, which are in good agreement with the experimental results reported by Cohen et al.\(^39\) and the theoretical results reported by Ahmed et al.\(^40\). It is shown that our results are smaller than the calculated results of Ihm et al.\(^41\), which is resulted from the different computational details. In the study of Ihm et al., the nonlocal (angular-momentum-dependent) pseudopotentials were employed, and the exchange-correlation potential was described by the local-density approximation (LDA) within Winger parameterization\(^41\), while in our study norm-conserving Troullier-Martins pseudopotentials are employed, and the LDA method within Ceperly-Alder parameterization is used to describe the exchange-correlation potential. We also find that the cohesive energy of AlAs is larger than that of GaAs, i.e., the <Al-As> bond is stronger than the <Ga-As> bond, which may be partially responsible for their different radiation tolerance.

### Threshold displacement energies in AlAs, GaAs and GaAs/AlAs superlattice.

The threshold displacement energy \((E_d)\), which is defined as the minimum transferred kinetic energy for the primary knock-on atom (PKA) to be permanently displaced from its lattice site, is one of the critical physical parameters for estimating damage production rates and predicting the defect profile under electron, neutron and ion irradiation. In this study, the threshold displacement energies in AlAs, GaAs, and GaAs/AlAs superlattice are calculated for PKAs of Al, Ga and As in the [001], [110], [111], [221], and [110] directions. The calculated threshold displacement energies \((E_d)\) for Al, Ga and As recoils in bulk AlAs and GaAs are shown in Table 2. The minimum values for PKAs are indicated in bold.

### Table 1. The calculated and experimental structural and energetic properties for bulk GaAs and AlAs. The \(E_{\text{coh}}\) and \(a_0\) refer to the cohesive energy and the lattice constant, respectively. \(^*\)Ref.\(^7\), \(^*\)Ref.\(^37\), \(^*\)Ref.\(^38\), \(^*\)Ref.\(^41\), \(^*\)Ref.\(^40\), \(^*\)Ref.\(^40\), \(^*\)Ref.\(^40\), \(^*\)Ref.\(^40\)

|        | \(a_0\) (Å) | \(E_{\text{coh}}\) (eV/atom) | \(a_0\) (Å) | \(E_{\text{coh}}\) (eV/atom) |
|--------|-------------|-----------------|-------------|-----------------|
| Our Cal. | 5.66 | 3.74 | 5.71 | 3.21 |
| Other Cal. | 5.64\(^*\) 5.63\(^*\) | 4.14\(^*\) 3.74\(^*\) | 5.66\(^*\) 5.65\(^*\) | 3.74\(^*\) 3.18\(^*\) |
| Exp. | 5.66\(^*\) 5.62\(^*\) | 3.85\(^*\) | 5.65\(^*\) 5.66\(^*\) | 3.35\(^*\) |

### Table 2. Calculated threshold displacement energy \((E_d)\) for Al, Ga and As recoils in bulk AlAs and GaAs. The minimum values for PKAs are indicated in bold. \(^*\)Ref.\(^1\)

| Direction | \(E_d\) (eV) | \(E_d\) (eV) |
|-----------|--------------|--------------|
| Al PKA | As PKA | Ga PKA | As PKA |
| [001] | 20.14\(^*\) | 13.5,16\(^*\) | 14.5,14\(^*\) | 10,16\(^*\) |
| [110] | 13.20\(^*\) | 21.5,18\(^*\) | 12,16\(^*\) | 10,20\(^*\) |
| [111] | 23.22\(^*\) | 13.18\(^*\) | 12,16\(^*\) | 8.5,16\(^*\) |
| [111] | 39 | 32.5 | 8 | 20 |
| [013] | 29 | 22.5 | 17.5 | 12 |
| [112] | 17.5 | 17 | 22.5 | 10 |
| [123] | 37 | 13 | 30 | 10 |

### Table 3. Calculated threshold displacement energy \((E_d)\) for Al, Ga and As recoils in GaAs/AlAs superlattice.

| Direction | \(E_d\) (eV) | \(E_d\) (eV) | \(E_d\) (eV) |
|-----------|--------------|--------------|--------------|
| As PKA | Al PKA | Ga PKA |
| [001] | 15 | 33 | 18 |
| [110] | 17.5 | 15 | 14 |
| [111] | 30 | 10 | 9.5 |
| [111] | 12 | 22.5 | 17.5 |
| [013] | 17.5 | 20 | 22.5 |
| [112] | 24 | 17 | 11 |
| [123] | 15 | 17 | 12 |
GaAs/AlAs superlattice. The average threshold displacement energy ($E_d$) for Al, Ga and As atoms in bulk AlAs, bulk GaAs and GaAs/AlAs superlattice are studied. The average $E_d$ values for Al PKAs are generally less than those for Ga PKAs, except for the [111] direction. For GaAs, the minimum $E_d$ for Ga PKA is 8 eV along the [111] direction, which is comparable to the minimum value of 8.5 eV for As PKA along the [111] direction. Similar to AlAs, the As atoms are generally more difficult to be displaced than Al atoms, except for the case of [110] where the energy of 21.5 eV for As atom is 8.5 eV larger than that for Al atom. These results show that the As displacement may be dominant in the recoil events of AlAs.

For GaAs, the minimum $E_d$ for Ga PKA is 8 eV along the [111] direction, which is comparable to the minimum value of 8.5 eV for As PKA along the [111] direction. Similar to AlAs, the As atoms are generally more easily to be displaced than Ga atoms, except for the case of [110] where the energy of 21.5 eV for As atom is 8.5 eV larger than that for Al atom. These results indicate that the As displacement may be dominant in the recoil events of AlAs.

For GaAs, the minimum $E_d$ for Ga PKA is 8 eV along the [111] direction, which is comparable to the minimum value of 8.5 eV for As PKA along the [111] direction. Similar to AlAs, the As atoms are generally more easily to be displaced than Ga atoms, except for the case of [110] where the energy of 21.5 eV for As atom is 8.5 eV larger than that for Al atom. These results indicate that the As displacement may be dominant in the recoil events of AlAs.

As shown in Fig. 1(b), the GaAs/AlAs SL is terminated by the As layer and the Ga, Al and As atoms on the boundary of the As interface are selected as the PKA. As can be seen from Table 3, the maximum and minimum $E_d$ values for the As PKAs are along the [111] and [112] directions, respectively, and the respective $E_d$ values are 30 and 12 eV. In these two cases, the radiation damage end states show different character. For As[111], the As PKA moves away from its lattice site to eject its neighboring Al atom and occupies an interstitial site ($As_{int}$). The collided Al atom moves along the [111] direction and occupies another nearby As lattice site to form an antisite defect ($Al_{As}$). Then, the third ejected As atom occupies its neighboring Ga lattice site ($As_{Ga}$), and the Ga atom forms an interstitial defect ($Ga_{int}$). In the end, one pair of As FP, one Al vacancy ($V_{Al}$), one $As_{int}$ antisite defect, one $As_{Ga}$ antisite defect and one $Ga_{int}$ defects are created. The associated defects in the case of As[112] are relatively simple, which consist of only one As vacancy ($V_{As}$) and one $As_{int}$. For Al PKAs, the maximum and minimum $E_d$ values are determined to be 33 eV along the [001] direction and 10 eV along the [111] direction, respectively, and the pathway for defect generation are very different from each other. In the case of Al[001], besides the Al PKA, a number of neighboring Al and Ga atoms are also involved in the displacement events, which results in the formation of one pair of Al FP, one pair of Ga FP and two $Ga_{Al}$ and $Al_{Ga}$ antisite defects after recoil events. The displacement event in the case of Al[111] is much simpler, and only one pair of Al FP is created. Similarly, the Ga PKA is easy to be displaced along the [111] direction, as indicated by the minimum value of 9.5 eV. It is noted that the $E_d$ values of Ga PKAs are generally smaller than those of the Al atoms, except the [013] direction, indicating that the Ga atoms are more easily to be displaced than Al atoms.

The average threshold displacement energies for PKAs in bulk GaAs and AlAs as well as GaAs/AlAs SL are plotted in Fig. 2. The average $E_d$ in the case of Al[111] is 25.8 eV, the average $E_d$ in the case of Ga[111] is 20.3 eV, and the average $E_d$ in the case of As[111] is 18.2 eV.

**Figure 2.** The average threshold displacement energy ($E_d$) for Al, Ga and As atoms in bulk AlAs, bulk GaAs and GaAs/AlAs superlattice.
(n₁ + n₂ + n₃ + n₄ + n₅ + n₆ + n₇) where n₁, n₂, n₃, n₄, n₅, n₆, and n₇ are the number of equivalent directions for a specific direction. In bulk GaAs and AlAs, the average Ed values for cation recoils are obviously larger than that for As atoms, indicating that As displacement may be the dominant. We also find that the average value of 25.8 eV for Al PKAs is larger than the value of 20.3 eV for Ga PKAs. Although the Ga atom has larger atomic radius and mass than the As atom, the <Ga-As> bond is weaker than the <Al-As> bond, as indicated by the lower cohesive energy of GaAs in Table 1. On the other hand, the screening of the Coulomb force between the Ga PKA and its neighbors is more effective and the interaction between them is relatively smaller, which decreases the energy barrier for defect generation. Consequently, the Ga atoms are relatively more easily to be displaced than the Al atoms. Moreover, we find that higher energies are needed for the As atoms in AlAs to be displaced than those for As atoms in GaAs. These results indicate that the AlAs may behave more robustly than the GaAs under radiation environment, agreeing well with theoretical and experimental findings. As for GaAs/AlAs SL, the average Ed values for cation recoils in AlAs and GaAs are from 20.3 to 18.4 eV in bulk AlAs and SL, respectively. It is shown that the cations in bulk state behave more robustly than those in the SL under electron irradiation. Bryant and Cox have irradiated the samples of CdS and CdTe employing the electron irradiation, and found that the CdS is more resistant to electron irradiation than the CdTe, due to the larger Ed value of ~9.6 eV for S atoms than the value of ~7.9 eV for Te atoms. As for the As atoms in the SL structure, the Ed values for Ga recoil in bulk GaAs and SL correspond to 898 and 815 keV electron irradiation, respectively. As for Al recoil, the Ed values in bulk AlAs and SL correspond to 715 and 651 keV electron irradiation, respectively. The created defects after each recoil event in bulk AlAs and GaAs are summarized in Tables 4 and 5, respectively.

### Table 4

| Al PKA | As PKA |
|--------|--------|
| Defect type | d_{pak} (Å) | Defect type | d_{pak} (Å) |
| [001] V_{Al} + Al_{Al} | 5.20 | V_{As} + As_{int} | 5.22 |
| [110] V_{Al} + Al_{As} | 4.68 | As_{Ga} + Al_{Al} | 3.68 |
| [111] V_{Al} + Al_{Al} | 5.02 | V_{As} + As_{Al} | 4.57 |
| [111] V_{Al} + Al_{Al} | 1.82 | V_{As} + As_{Ga} + Al_{Al} + V_{As} + Al_{Al} | 3.33 |
| [013] V_{Ga} + Al_{Al} | 2.32 | V_{As} + As_{Al} | 5.14 |
| [012] V_{Ga} + Al_{Al} | 4.18 | V_{As} + As_{Ga} | 4.32 |
| [123] Al_{Ga} + As_{Al} | 4.24 | V_{As} + As_{Ga} + V_{Al} + Al_{Al} | 1.89 |

### Table 5

| Ga PKA | As PKA |
|--------|--------|
| Defect type | d_{pak} (Å) | Defect type | d_{pak} (Å) |
| [001] V_{Ga} + Ga_{Al} | 5.51 | V_{As} + As_{int} + V_{Ga} + Ga_{Al} | 2.63 |
| [110] Ga_{Al} + As_{Ga} | 4.19 | V_{As} + As_{Al} | 4.09 |
| [111] Ga_{Al} + As_{Ga} + V_{Ga} | 2.08 | V_{As} + As_{Al} | 3.94 |
| [111] V_{Ga} + Ga_{Ga} | 4.87 | V_{As} + As_{Ga} + Ga_{Al} | 1.97 |
| [013] V_{Ga} + Ga_{Ga} | 1.85 | Ga_{Al} + As_{Ga} + V_{Ga} | 2.83 |
| [012] V_{Ga} + Ga_{Ga} | 1.84 | V_{As} + As_{Al} | 4.18 |
| [123] 2V_{Ga} + 2Ga_{Al} + V_{As} + As_{int} | 4.17 | V_{As} + As_{Al} | 4.24 |

**Defect distribution in AlAs, GaAs and GaAs/AlAs superlattice after recoil events.** The created defects after each recoil event in bulk AlAs and GaAs are summarized in Tables 4 and 5, respectively. For Al...
Defect configuration and the displacement for As, Al and Ga PKAs ($d_{PKA}$) in GaAs/AlAs superlattice. V$_X$: X vacancy (X = Al, Ga and As); X$_{int}$: X interstitial (X = Al, Ga and As); X$_Y$: X occupying the Y lattice site (X, Y = Al, Ga and As).

| Al       | Ga       | As       |
|----------|----------|----------|
| [001]    | V$_{Ga}$ + Al$_{int}$ + Ga$_{As}$ + Ga$_{Al}$ + Al$_{Al}$ | 2.57     | V$_{Ga}$ + As$_{As}$ + Al$_{int}$ | 5.20 |
| [110]    | V$_{Al}$ + Al$_{int}$  | 4.96     | As$_{As}$ + Ga$_{As}$           | 4.38 |
| [111]    | V$_{Al}$ + Al$_{int}$  | 4.68     | V$_{Ga}$ + Ga$_{As}$           | 4.30 |
| [111]    | V$_{Al}$ + Al$_{int}$  | 4.68     | V$_{Ga}$ + Ga$_{As}$           | 4.30 |
| [111]    | V$_{Al}$ + Al$_{int}$  | 4.87     | V$_{Ga}$ + Ga$_{As}$ + As$_{int}$ | 1.73 |
| [112]    | V$_{As}$ + Al$_{int}$  | 2.32     | As$_{As}$ + V$_{Ga}$ + As$_{int}$ | 4.63 |
| [112]    | V$_{As}$ + Al$_{int}$  | 6.08     | V$_{Ga}$ + Ga$_{As}$           | 4.91 |
| [112]    | V$_{As}$ + Al$_{int}$  | 4.56     | V$_{Ga}$ + Ga$_{As}$           | 5.07 |

Table 6. Defect configuration and the displacement for As, Al and Ga PKAs ($d_{PKA}$) in GaAs/AlAs superlattice. V$_X$: X vacancy (X = Al, Ga and As); X$_{int}$: X interstitial (X = Al, Ga and As); X$_Y$: X occupying the Y lattice site (X, Y = Al, Ga and As).
Figure 3. Illustration of schematic view of defects created by PKA recoils in bulk AlAs and GaAs. (a) Al[110]; (b) Al[123]; (c) As[001] in bulk AlAs; (d) Ga[001]; (e) Ga[110] and (f) As[110] in bulk GaAs. The blue, red and green spheres represent the Ga, Al and As atoms, respectively. $V_X$: X vacancy ($X = \text{Al, Ga or As}$); $X_{\text{int}}$: X interstitial ($X = \text{Al, Ga or As}$); $X_{Y}$: $X$ occupying the Y lattice site ($X, Y = \text{Al, Ga or As}$). The yellow and pink spheres represent the vacancy and interstitial defects, respectively.
displacements of 2.49 and 4.17 Å, respectively, indicative of different defect mechanisms. The associated defects for three other cases are more complex, especially for As[111] recoil, where one pair of As FP, one V Al defect, one Al As defect, one As Ga defect and one As int defect are created. Comparing the defect distributions in AlAs, GaAs and GaAs/AlAs SL, we find that a number of antisite defects are created in GaAs/AlAs SL, whereas very few antisite defects are generated in bulk AlAs and GaAs. However, Frenkel pairs are dominant defects under low energy irradiation in both the bulk and SL structures, which is in good agreement with the results reported by Nordlund et al. and Pronko et al.

The radiation damage effects on the electronic properties of AlAs, GaAs and GaAs/AlAs superlattice. The (GaAs)_m/(AlAs)_n SLs with (m + n) ranging from 2 to 10 have been widely applied in luminescence and optical absorption, two-phonon absorption and Raman as well as infrared spectra due to their unusual properties. Under radiation environment the defect creation, clustering and accumulation may have profound effects on their structural stability and electronic properties, and deteriorate their performance, which may lead to permanent failure. In order to further explore how the radiation damage influences the electronic properties of GaAs/AlAs SL, first-principles calculations based on density functional theory are carried out to investigate the electronic structures of some representative damaged states. The computations are based on a 2×2×2 supercell consisting of 64 atoms, with a 6×6×6 k-point sampling in reciprocal space and a cutoff energy of 500 eV.

Figure 4. Band structures for ideal and defective AlAs. (a) Ideal state; (b) Al[110]; (c) Al[123] and (d) As[001]. Al[110]: Al int and VAl defective state; Al[123]: AsAl and AlAs antisite defective state; As[001]: As int and VAs defective state.

For AlAs and GaAs, the considered defective states are illustrated in Fig. 3(a–c) and (d–f), respectively. The band structures for ideal and defective AlAs are shown in Fig. 4. In Figure 4(a), AlAs has an indirect gap at X point, and the energy gap is determined to be 1.31 eV, whereas it is smaller than the experimental value of 2.16 eV, due to the well-known discontinuity of exchange-correlation energy of the LDA. As one V Al and one Al int defects with separating distance of 4.68 Å are introduced in AlAs, defect levels are observed in the forbidden band region and the energy gap decreases to 0.34 eV, as shown in Fig. 4(b). In the case of Al[123], the Al PKA replaces the As lattice site (AlAs) and the ejected As atom occupies the PKA lattice site (AsAl). Figure 4(c) shows that the band gap of antisite-defect state for Al[123] decreases to 0.17 eV. As for As[001], one V As and one As int defects are created, which are separated by 5.22 Å from each other. Similarly, the band gap As-FP-defect state for As[001] is narrowed to 0.15 eV, as illustrated in Fig. 4(d).

Figure 5 describes the band structures for ideal and defective GaAs. Different from AlAs, the energy gap for GaAs is direct with the value of 0.5 eV. This value is comparable with other LDA value of 0.41 eV, while much
smaller than the experimental value of 1.52 eV. As shown in Fig. 5(b), the defect levels are observed near the valence band maximum (VBM), and cross the Fermi level, indicative of metallic character of defective GaAs with one pair of Ga FP defect. For Ga[110], one pair of GaAs and AsGa antisite defects separated by 4.19 Å are created, and a number of electrons are distributed on the Fermi level, indicative of the metallic character (see Fig. 5(c)). In the case of As[110], the As PKA occupies the interstitial site, which is 4.09 Å away from the lattice site, and one pair of As Frenkel pair defects are created in the end. It is noted that the As[110] defective state also behaves metallic character.

For GaAs/AlAs SL, the damage end states are mainly Frenkel pair and antisite defects. The considered defective states are presented in Fig. 6. The density of state distribution and band structure for ideal and defective SL are illustrated in Figs 7 and 8, respectively. As shown in Fig. 7(a), the energy gap for ideal GaAs/AlAs SL is determined to be 1.14 eV, which is smaller than the experimental value of 2.09 eV, whereas it is in agreement with the theoretical value of 1.16 eV. What is more, the band structure for the ideal SL shows a direct gap at the Γ point, as illustrated in Fig. 8(a). Botti et al. have investigated the band structures of (GaAs)m/(AlAs)n SL using density functional theory and a semi-empirical method. They suggested that the energy gap for SL is direct at the Γ point when the number of monolayer is no less than 2, which is consistent with our results.

In the case of Al[110], the band gap of GaAs/AlAs SL with one pair of Al FP is decreased by about 0.86 eV, as compared with the ideal SL. In Fig. 8(b), the defect levels are observed near the VBM and in the forbidden band region. The charge density difference contour of the SL containing the VAl and Al int defects is illustrated in Fig. 9(a). The Al interstitial forms new bonds with the nearest As atoms, as shown by the charge accumulation in the bonding regions. Figure 9(a) also clearly shows that VAl does not pair with its neighboring atoms, and the Al vacancy is negatively charged. For Al[112], the introduced defects are also Al FP, whereas defective SL behaves metallic character, as confirmed by the density of state distribution (see Fig. 7(c)) and the band structure (see Fig. 8(c)). As shown in Fig. 9(b), significant charge redistribution occurs and electrons are shared by the Al interstitial and its neighboring As atoms. In the case of Ga[111], the introduction of the VGa and Ga int defects induces the metallicity of GaAs/AlAs SL, as shown in the Figs 7(d) and 8(d). The Ga interstitial donates electrons to its neighboring As atoms and forms new bonds with them, resulting in electron localization. In the case of As[110], the defect levels appear near the VBM and cross the Fermi level, as shown in Figs 7(e) and 8(e). Figure 9(d) clearly shows that the GaAs and AsGa antisite defects interact with each other and charge delocalization is induced. For the case of As[123], the defect configuration is unstable and the As interstitial recombines with the As vacancy upon structural relaxation. These results suggest that under irradiation the electronic structures of GaAs/AlAs SL are affected significantly, in

Figure 5. Band structures for ideal and defective GaAs. (a) Ideal state; (b) Ga[001]; (c) Ga[110] and (d) As[110]. Ga[001]: Ga int and VGa defective state; Ga[110]: AsGa and GaAs antisite defective state; As[110]: As int and VAs defective state.
which charge transfer, redistribution and even accumulation may occur, and band gap narrowing and even metallicity are induced. Consequently, the carrier concentration and mobility, as well as the electrical properties will be influenced. Therefore, it is necessary to enhance the radiation tolerance of GaAs/AlAs SL to improve its electrical performance under radiation environment.

Figure 6. Illustration of schematic view of defects created by PKA recoils in GaAs/AlAs superlattice. (a) Al[110]; (b) Al[112]; (c) Ga[111]; (d) As[110] and (e) As[123]. The blue, red and green spheres represent the Ga, Al and As atoms, respectively. $V_X$: X vacancy ($X = \text{Al, Ga or As}$); $X_{\text{int}}$: X interstitial ($X = \text{Al, Ga or As}$); $X_{\text{Y}}$: X occupying the Y lattice site ($X, Y = \text{Al, Ga or As}$). The yellow and pink spheres represent the vacancy and interstitial defects, respectively.
Conclusions
In summary, low energy recoil events in AlAs, GaAs and GaAs/AlAs superlattice (SL) have been investigated by an \textit{ab initio} molecular dynamics method. The radiation damage effects on the electronic structures of these materials are also studied. In bulk AlAs and GaAs, the threshold displacements energies ($E_d$) for As atoms are generally smaller than those for cations, indicating that the As displacements are dominant in the recoil events of bulk states. Besides, the $E_d$ values for AlAs are generally larger than those for GaAs, suggesting that AlAs behaves more robustly under radiation environment. As compared with their bulk states, the cations in GaAs/AlAs SL structure are more susceptible to the radiation, whereas the As atoms are more difficult to be displaced, i.e., the GaAs/AlAs SL exhibits different radiation tolerance from their bulk states. The radiation damage states in bulk AlAs and GaAs are vacancy and interstitial defects. As for GaAs/AlAs SL, the created defects are generally Frenkel pairs (FP) and antisite defects. The band structures of defective GaAs/AlAs SL show that the introduction of FP
and antisite defects generally induce metallicity except for the Al FP in the case of Al[110], in which the band-gap of SL decreases by about 0.86 eV, suggesting that the created defects have profound effects on the electronic structures. It is thus necessary to enhance the radiation tolerance of GaAs/AlAs SL to improve its electrical performance under radiation environment.

**Methods**

The low-energy displacement events of AlAs, GaAs and (GaAs)$_m$/(AlAs)$_n$ SL are simulated by the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) code. The norm-conserving Troullier-Matrices pseudopotentials are employed to determine the interaction between ions and electrons, and the exchange-correlation potential is described by the local-density approximation (LDA) in Ceperly-Alder parameterization. The valence wave functions are expanded by a basis set of localized atomic orbitals, and double-$\zeta$ basis sets plus polarization orbital (DZP) are employed, with a K-point sampling of $1 \times 1 \times 1$ in the Brillouin zone and a cut-off energy of 60 Ry. The AIMD calculation is computationally expensive and is limited by the system size. However, if the system size is too small, the irradiated atoms will be knocked out of the box. In these cases, a (GaAs)$_2$/(AlAs)$_2$ superlattice, which consists of two monolayers of GaAs alternating with two monolayers of AlAs (see Fig. 1(b)) and totally 128 atoms, is considered in this work. A specific atom is selected as the primary knock-on atom (PKA), and it is given a kinetic energy to initiate a recoil event. If the PKA returns to

**Figure 8.** Band structures for ideal and defective GaAs/AlAs superlattice. (a) Ideal state; (b) Al[110]; (c) Al[112]; (d) Ga[111]; (e) As[110] and (f) As[123]. Al[110]: Al$_{\mathrm{int}}$ and V$_{\text{Al}}$ defective state; Al[112]: Al$_{\mathrm{int}}$ and V$_{\text{Al}}$ defective state; Ga[111]: Ga$_{\mathrm{int}}$ and V$_{\text{Ga}}$ defective state; As[110]: As$_{\mathrm{int}}$ and Ga$_{\text{As}}$ antisite defective state; As[123]: As$_{\mathrm{int}}$ and V$_{\text{As}}$ defective state.
its original position at the end of the recoil event, the simulation is restarted at higher recoil energy with an energy increment of 5 eV. Once the PKA is permanently displaced from its lattice site, additional runs are performed to improve the precision to 0.5 eV. For each atom type, seven principal incidence directions are taken into account in the present study, as shown in Fig. 1(a). The simulations are conducted with an NVE ensemble and the maximum duration of each run is 1.2 ps to avoid the instability of the system.

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Author Contributions
H.X. and X.Z. designed the calculations. M.J. conducted the calculations and wrote the manuscript. S.P., G.Y. and Z.L. contributed the discussion and interpretation of the results. All authors discussed the results and reviewed the manuscript.

Additional Information
Competing Interests: The authors declare that they have no competing interests.
