Engineering of electronic and optical properties of monolayer gallium sulfide/selenide in presence of intrinsic atomic defects

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Abstract

In this paper, the electronic and optical properties of various point defects in gallium sulfide (GaS) and gallium selenide (GaSe) are studied. Various vacancy defects in each monolayer GaX (X = S, Se) include V_X, V_Ga, 2V_X, 2V_Ga, 1V_Ga1V_X, 1V_Ga2V_X, 2V_Ga1V_X, 2V_Ga2V_X. We compute the band structure, zero-bias transmission spectrum, and dielectric function for all considered structures. The calculations are carried out by the first-principles method. The calculation results indicate that the absence of S/Se atom in these semiconductors leads to the transition from an indirect band gap for the pristine materials to a direct band gap in their defective systems and the band gap energies change from 2.3 eV/2.11 eV to 1.33 eV/0.98 eV, respectively. Also, 2V_X causes that the semiconductor band gap changes from indirect to direct. Furthermore, GaX monolayer is converted to a p-type semiconductor in the presence of V_Ga. Moreover, these findings represent that some of the point defects in this system lead to magnetic states which can be employed in spintronic devices. In addition, for the defective GaX monolayers with the direct band gap, the first peak of imaginary part of the dielectric function occurs around their band gap energy. The study of intrinsic structural defects in monolayer GaX provides new opportunities for optimizing the electronic and optical properties of these materials via defect engineering.

1. Introduction

The great interest in two dimensional (2D) materials has been led to extensive studies of their physical, chemical and mechanical properties. In recent years, 2D materials beyond graphene, transition metal chalcogenides (TMCs) have attracted much attention due to their sizable band gap, high on/off current, and large area to volume ratio [1–6]. Among the TMCs family, many scientific works have been done on the electronic, optical and mechanical properties of the transition metal dichalcogenides (TMDCs), especially MoS2 [7–9]. In contrast, little attention has been concentrated on the other new class of TMCs, namely transition metal monochalcogenides (TMMCs). TMMCs are III-VI semiconductors and unlike TMDCs include the light elements of the periodic table. GaX (X = S or Se) is a kind of layered TMMCs in which two sublayers of gallium atoms are sandwiched between two sublayers of X atoms in the form of X–Ga–Ga–X [10–12]. They synthesized successfully by using micromechanical cleavage in recent experiments [13–15]. In addition, they have thermal stability [16]. Gallium sulfide (GaS) and gallium selenide (GaSe) monolayers are indirect semiconductors with a wide band gap and they show nonmagnetic behavior [12]. These materials can be perfect candidates for using in the field effect transistors (FETs), photodiodes, and photodetectors and open a fascinating new gate in nanoelectronics. Ma et al [17] studied the electronic and dielectric behavior of single layer and few-layer of GaX by using the first principle calculation. They showed GaSe has a direct to indirect band gap transition from bulk to monolayer whereas the nature of indirect band gap is maintained for GaS in bulk and monolayer phases. Moreover, they found the band gap of these materials can be set by employing mechanical deformation. The mechanical properties of GaX monolayer were reported by Yagmurcukardes et al [18]. They indicated that the...
GaS monolayer is more rigid than the GaSe monolayer. In addition, they found that the single layer GaX have higher fracture strain value compared with graphene and MoS$_2$. Also, they demonstrated that by applying strain up to 14% (17%) to the single layer GaS (GaSe), a transition from semiconductor to metal occurs. Chen et al.\cite{19} investigated the electrical and magnetic properties of single layer GaS by substituting Ga and S with non-metal and transition metal doping by using the first principles calculations. They found that the substitution of Ga and S with these atoms changes the electronic and magnetic properties of single layer GaS. They showed among the nonmetallic atoms, the doping with N atom at the S site is an appropriate candidate to make holes in GaS and lead to p-type doping. Wenbin Li and Ju Li\cite{20} studied piezoelectricity in 2D group-III monochalcogenides. They displayed these materials have good piezoelectric properties as well as superior photosensitivity.

Processes such as the mechanical exfoliation and ion or electron irradiations can create defects in 2D materials which can dramatically change their mechanical, electronic, and optical properties. In the present work, we consider various vacancies in each monolayer GaX include: one X vacancy ($V_X$), one Ga vacancy ($V_{Ga}$), two X vacancies ($2V_X$), two Ga vacancies ($2V_{Ga}$), one Ga and one X vacancies ($1V_{Ga}1V_X$), one Ga and two X vacancies ($1V_{Ga}2V_X$), two Ga and one X vacancies ($2V_{Ga}1V_X$), and two Ga with two X vacancies ($2V_{Ga}2V_X$).

We investigate the electronic properties (band structure, zero-bias transmission spectrum) and optical properties (imaginary and real parts of the dielectric function) of single layer GaX in the presence of point defects by using the first principles calculations based on density functional theory (DFT). Our results demonstrate that varying electronic and optical properties of the GaX in presence of different vacancies can provide new opportunities for achieving photonic and nano electronic devices.

This paper is given the following structure: In section 2, the detail of computational method is represented. The electronic and optical properties of pristine GaX, the effect of the point defects on their properties, and the formation energy for the defective systems are explained in section 3. Finally, the conclusions are drawn in section 4.

### 2. Computational methods

Our calculations are implemented in the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) package\cite{21} within the DFT framework. The local density approximation (LDA) with the Perdew-Zunger (PZ) functional is considered as the exchange-correlation function\cite{22}. The cut-off energy is set to 150 Ry. We construct a $4 \times 4$ supercell containing 64 atoms to study the single layer GaX. Ga, S, and Se atoms contribute their valence electrons $3d^{10}4s^24p^1$, $3s^23p^4$, and $4s^24p^4$, respectively. For all calculations, a $3 \times 3 \times 1$ k-point mesh is employed. All calculations are spin-polarized. A 10 Å vacuum region is adopted to avoid the interaction of images under the periodic boundary condition. The energy and forces are converged until $10^{-5}$ eV and 0.01 eV/Å, respectively. The structures are optimized geometrically and all DFT calculations are done at absolute zero temperature (0 K). Figure 1 indicates the atomic structure of single layer GaX from the top and side views. The thickness of GaS and GaSe monolayers are equal to 4.66 Å and 4.86 Å, respectively. To obtain the dielectric function ($\varepsilon(\omega)$) of pristine and defective GaX monolayer at the photon energy ($h\omega$), we employ the dipole approximation using Fermi’s golden rule. This function includes two parts: the real part ($\text{Re} \varepsilon(\omega)$) and the imaginary part ($\text{Im} \varepsilon(\omega)$) and it is defined as: $\varepsilon(\omega) = \text{Re} \varepsilon(\omega) + i \text{Im} \varepsilon(\omega)$, where the imaginary and real parts are derived from the Kramers-Kronig relation\cite{23}.

We consider eight different configurations ($V_X$, $V_{Ga}$, $2V_X$, $2V_{Ga}$, $1V_{Ga}1V_X$, $1V_{Ga}2V_X$, $2V_{Ga}1V_X$, $2V_{Ga}2V_X$) of point defects for single layer GaX. The defect concentration, $C_d$ is defined as $C_d = n_d/N_{total}$.

Where $n_d$ is the number of vacancy defects in the lattice and $N_{total}$ is the total number of atoms in the pristine structure.

In the present study, vacancy concentrations are 1.56%, 3.12%, 4.68%, 6.25% for $V_X$ ($V_{Ga}$), $2V_X$ ($2V_{Ga}$ and $1V_{Ga}1V_X$, $1V_{Ga}2V_X$, $2V_{Ga}1V_X$, $2V_{Ga}2V_X$, respectively)

The formation energy of the defective systems ($E_{form}$) can be defined as:

$$E_{form} = E_{\text{defective GaX}} - E_{\text{pure GaX}} + n_1E_{Ga} + n_2E_X$$

Where $E_{\text{defective GaX}}$ and $E_{\text{pure GaX}}$ are total energies of the defective and pristine GaX monolayer, respectively. $n_1$ and $n_2$ represent the number of Ga and X atoms which are removed from the cell, respectively. $E_{Ga}$ and $E_X$ correspond to the total energy of the isolated Ga and X atoms.
3. Results and discussion

3.1. Electronic and optical properties of pristine GaX monolayer

Firstly, we obtain the structural parameters of the bare GaX monolayer. The results are given in table 1. The lattice constants \( a_0 \) of GaS and GaSe monolayers are 3.584 Å and 3.742 Å, respectively. These results are consistent with those of other studies [12, 17, 18].

Next, we compute the spin-polarized band structure, zero-bias transmission spectrum, and dielectric function of the pristine GaX monolayer as shown in figure 2.

The spin-polarized band structure of pristine GaS and GaSe monolayers are presented in figures 2(a)–(c). In all structures, the Fermi level is set at 0 eV. It is obvious from these figures, both pristine structures have an indirect band gap because their valence band maximum (VBM) locates in the middle of X and \( \Gamma \) and their conduction band minimum (CBM) lies in the \( \Gamma \) point. The band gap energies for the pristine GaS and GaSe monolayers are 2.3 eV and 2.11 eV, respectively. These results are in agreement with obtained results from [18]. Moreover, the pristine structures of GaX show symmetrical spin-up and spin-down bands and these structures are nonmagnetic semiconductors. Figures 2(b) and (d) illustrate the zero-bias transmission spectra of spin-up and spin-down electrons for pristine GaS and GaSe. In addition, the imaginary and real parts of the dielectric function of GaS and GaSe monolayer are shown in figures 2(e) and (f), respectively. The former indicates absorption whereas the latter refers to the impacts of optical dispersion. As shown in figures 2(e) and (d), the first peak of the imaginary part occurs in 5.3 eV and 2.8 eV, respectively. These results are close to the obtained results in [24].

![Figure 1. Top and side views of the atomic structure of the single layer (a) GaS, and (b) GaSe.](image.png)

### Table 1. The structural parameters of bare GaX monolayer. \( a_0 \) is the lattice constant of GaX monolayer. \( d_1 \) and \( d_2 \) are the bond length of Ga-Ga and X-X, respectively.

| GaX  | \( a_0 \) (Å) | \( d_1 \) (Å) | \( d_2 \) (Å) |
|------|--------------|--------------|--------------|
| GaS  | 3.584       | 2.47         | 2.36         |
| GaSe | 3.742       | 2.46         | 2.50         |

Figure 1. Top and side views of the atomic structure of the single layer (a) GaS, and (b) GaSe.
3.2. Electronic and optical properties of defective GaS monolayer

To understand the influence of point defects on the electronic and optical properties of the GaS monolayer, we concentrate on eight various types of defective systems. Figures 3(a)–(h) displays the relaxed geometry structures of defective GaS.

The calculated formation energies for GaS monolayer with various vacancies are listed in table 2.

It is evident from table 2 that the S vacancy formation energy is lower than those of another type of defective GaS monolayer. This suggests that the defect is more likely to form in single layer GaS.

Figure 2. The band structure, zero-bias transmission spectrum, and dielectric function of the pristine GaS and GaSe monolayers are shown in (a)–(f), respectively. The Fermi level is marked by a dotted line.
Figures 4(a)–(h) presents the spin-polarized band structure and zero-bias transmission spectrum of considered defective GaS monolayer. As can be seen in these figures, the point defects modify the electronic band structures of GaS monolayer and semiconducting or metallic features for both spins are observed. Moreover, the values of transmission coefficients in the zero-bias transmission spectra of these systems relate to the contribution of states in their corresponding band structures.

Structural defects create extra states near the edge of conduction and valence bands and lead to a change in the two-dimensional material band gap. The states near the Fermi level can act as scattering centers in GaX monolayer.

As shown in figure 4(b), the absence of one Ga atom in GaS monolayer causes to reduce the band gap energy to 1.65 eV in comparison with that of pristine GaS monolayer and its band gap changes from indirect to direct, with CBM and VBM located at the Γ point. Moreover, the zero-bias transmission spectrum of VGa system shifts to positive energies. Therefore, the nature of this material is converted to the p-type semiconductor. Its reason is the increase of occupied states below the Fermi level in the presence of this kind of defect.

For the case of 2VGa in GaS structure (figure 4(d)), the spin-up and spin-down states behave as a semiconductor and metal, respectively. Furthermore, the asymmetry of the zero-bias transmission spectrum deduces its magnetic property.

Figures 4(a) and (c) display the impact of removing one and two S atoms on the electronic properties of this monolayer, respectively. As shown in these figures, both structures are direct semiconductors with the band gap energies of 1.33 eV and 0.79 eV.
In figures 4(e) and (h) (1V$_{Ga}$1V$_{S}$ and 2V$_{Ga}$2V$_{S}$), the defective GaS monolayers are magnetic and for each case, the spin-up and spin-down states exhibit the semiconducting behavior. As shown in figures 4(f) and (g), in the cases of 1V$_{Ga}$2V$_{S}$ and 2V$_{Ga}$1V$_{S}$, the structures are magnetic. In the case of 1V$_{Ga}$2V$_{S}$, the spin-up state is gapless and the spin-down state displays a direct semiconductor, whereas in the case of 2V$_{Ga}$1V$_{S}$, the spin-up state is a direct band gap and spin-down state is gapless. The detailed characteristics of all assumed defective GaS are listed in table 3.

In order to the investigation of the optical properties of defective GaS monolayer systems, the real and imaginary parts of their dielectric function are represented in figure 5.

As seen in figure 5, the systems with V$_{S}$, V$_{Ga}$, and 2V$_{S}$ did not display any spin polarization due to the symmetry of spin-up and spin-down. In addition, for the direct semiconductors such as V$_{S}$ and V$_{Ga}$ structures, the first peak of imaginary part occurs around their band gap energies. Our results can influence in selecting these materials as a suitable candidate for optoelectronic applications.

### 3.3. Electronic and optical properties of defective GaSe monolayer

In order to determine the comparative stability of GaSe monolayer in the presence of intrinsic atomic defects, their formation energies are obtained as shown in table 4.

As shown in table 4, the formation energies of V$_{Se}$, V$_{Ga}$, 2V$_{Se}$, and 2V$_{Ga}$ in single layer GaSe are 5.58 eV, 5.94 eV, 11.16 eV, and 13.18 eV, respectively. These values are consistent with the results obtained in [25].

Comparing with the $E_{form}$ of 2.18 eV, 6.28 eV, 4.25 eV, and 15.18 eV for the V$_{S}$, V$_{Ga}$, 2V$_{S}$, and 2V$_{Ga}$ in the GaS monolayer, it is found that V$_{X}$ and V$_{Ca}$ in the single layer GaS and GaSe can occur easier, respectively.

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**Figure 4.** The band structure, and zero-bias transmission spectrum of the defective GaS monolayer. (a) V$_{S}$, (b) V$_{Ca}$, (c) 2V$_{S}$, (d) 2V$_{Ga}$, (e) 1V$_{Ga}$1V$_{S}$, (f) 1V$_{Ga}$2V$_{S}$, (g) 2V$_{Ca}$1V$_{S}$, and (h) 2V$_{Ca}$2V$_{S}$. Inset in figures 4(d), (f), and (g): zooming in a small portion of the band structure.
In addition, we investigate the band structure and zero-bias transmission spectrum for eight different configurations of defective GaSe monolayer in figure 6.

As shown in this figure, similar to the GaS monolayer, the removal of atoms from this material leads to the change of its electronic properties. To understand this behavior, we present the details of this study in table 5.

The real and imaginary parts of dielectric function for defective GaSe semiconductors are plotted in figure 7. As shown in figure 7, similar to the defective GaS monolayer with the direct band gap, the first peak of imaginary part corresponds to the band gap energy of the material. These results can provide an effective and efficient approach to engineering the band gap, magnetic, and optical properties of single layer GaX for application in opto/nanoelectronic devices.
4. Conclusion

In order to realize the electronic and optical properties of defective GaX, we investigated various structures of GaX monolayer in the absence of one or more atoms using DFT. Our calculated results showed that depending on the type of point defects in GaX monolayer, these systems are direct band gap semiconductor, semi-metallic, metallic. Furthermore, they can be magnetic due to the asymmetry of spin-up and spin-down states. For instance, 1VGa1VSe in GaX monolayer leads to semiconductor with magnetic states which the spin-up and spin-down states have a direct and an indirect band gap, respectively. In addition, the presence of 1VGa1VSe and 2VSe in GaSe monolayer, lead to the metallic nature of this material. Calculation of the formation energies of defective

| No. | Type of vacancy in GaSe | $E_{\text{form}}$(eV) |
|-----|-------------------------|-----------------------|
| I.  | $V_{\text{Se}}$         | 5.58                  |
| II. | $V_{\text{Ga}}$         | 5.94                  |
| III. | 2$V_{\text{Se}}$       | 11.16                 |
| IV. | 2$V_{\text{Ga}}$        | 13.18                 |
| V.  | 1$V_{\text{Ga}}$1$V_{\text{Se}}$ | 10.87                |
| VI. | 1$V_{\text{Ga}}$2$V_{\text{Se}}$ | 15.58                |
| VII. | 2$V_{\text{Ga}}$1$V_{\text{Se}}$ | 17.71                |
| VIII. | 2$V_{\text{Ga}}$2$V_{\text{Se}}$ | 22.69                |

Figure 6. The band structure and zero-bias transmission spectrum of defective GaSe monolayers. (a) $V_{\text{Se}}$, (b) $V_{\text{Ga}}$, (c) 2$V_{\text{Se}}$, (d) 2$V_{\text{Ga}}$, (e) 1$V_{\text{Ga}}$1$V_{\text{Se}}$, (f) 1$V_{\text{Ga}}$2$V_{\text{Se}}$, (g) 2$V_{\text{Ga}}$1$V_{\text{Se}}$, and (h) 2$V_{\text{Ga}}$2$V_{\text{Se}}$. 

Table 4. The formation energy ($E_{\text{form}}$) of the defective GaSe monolayer.
GaX monolayers show that sulfur and gallium defects occur earlier than the other defects in the single layer GaS and GaSe, respectively. Moreover, investigation of the optical properties of defective GaX monolayer reveals that the systems with direct band gap have the first peak of imaginary part of the dielectric function in near their band gap energy. The study of point defects in single layer GaX can provide useful information to design nanoelectronic and photoelectron devices based on GaX monolayer in the future.

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**Table 5.** The band gap energy, electronic and magnetic properties, and applications of defective GaSe monolayer.

| Vacancy      | Band gap energy (eV) | CBM-VBM       | Properties       | Applications       |
|--------------|----------------------|---------------|------------------|--------------------|
| VSe          | 0.98                 | Direct (Z to Z) | Semiconductor     | Optoelectronics     |
| VGa          | 1.36                 | Indirect (Γ to Γ′-X) | p-Semiconductor | Electronics         |
| 2VSe         | 0.73                 | Direct (Z to Z) | n-Semiconductor  | Electronics         |
| 2VGa         | Gapless              |                | metallic          | Spintronics         |
| VGaVGa       | 0.9                  |                | metallic          | Spintronics         |
| 1VGa1VSe     | 0.63 Spin-up         | Direct (Γ to Z) | p-Semiconductor  | Electronics         |
| 2VGa1VSe     | 0.097 Spin-down      | Indirect (Z to Γ) | Semiconductors    | Spintronics         |
| 1VGa2VSe     | 0.02                 | Indirect (Z to Γ) | Semiconductor     | Electronics         |

**Figure 7.** The imaginary and real parts of the dielectric function for defective GaSe monolayer. (a) VSe, (b) VGa, (c) 2VSe, (d) 1VGa2VSe, (e) 2VGa1VSe, and (f) 2VGa2VSe.
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