Strain and Electric Field Modulated Indirect to Direct Band Transition of Monolayer GaInS₂

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Research Article

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Abstract

Strain and electric field dependent electronic and optical properties have been calculated using density functional theory (DFT) and time-dependent DFT (TD-DFT) for GaInS₂ monolayer. GaInS₂ monolayer shows an indirect band gap of 1.79 eV where valance band maxima (VBM) and conduction band maxima (CBM) rest between K and Γ point and at Γ point, respectively. Under a particular tensile strain (8%), a phase change from semiconductor to semimetal has been noticed. While at 4% compressive strain, the material changes from indirect to direct band gap of 2.22 eV having VBM and CBM at Γ point. With further increase in compressive strain, CBM shifted from Γ to M point, which leads to an indirect band gap again. The electric field also affects the band structure of monolayer GaInS₂ and shows the transition between indirect to direct band gap at positive electric field of 4 V/nm, which acts normal to the surface. The strain-dependent optical properties are also calculated, which suggests that the absorption coefficient increases with compressive strain.

1. Introduction

The discovery of graphene^{1,2}, a two-dimensional (2D) material, has made researchers curious about further research on new low-dimensional materials due to their magnificent physical, electronic, and optical properties. Owing to their excellent electronic, optical, mechanical, thermoelectric properties 2D materials can be used as nanoelectronic and optical devices³⁻⁷. Enormous research has been gone on developing the properties, for that 2D materials such as arsenic sulfide^{8,9} silicene^{10,11} black phosphorus are being studied. Along with these materials, other novel 2D materials like transition metal dichalcogenides (TMDC)^{12,13}, metal diiodides¹⁴, metal chalcogenides^{15,16} are now at the peak of interest for the researchers. Low dimensional TMDCs were used for various applications such as transistors, gas sensors, photodetectors, solar cells, and light-emitting diode¹⁷⁻²². Metal diiodides monolayers with hexagonal honeycomb structures can be used as thermoelectric devices due to their ultra-low lattice thermal conductivity^{23,24}. Metal monochalcogenides are being studied for their recent application in nanoelectronic devices. However, band modulation is required for various device applications, which can be done by applying strain or external electric field on 2D materials. By strain engineering, enhancement of materials properties has been reported²⁵.

Two-dimensional group-III monochalcogenides are being studied because of their exceptional optoelectronic properties, and these properties can be modified by applying strain and external electric fields. Gallium and indium chalcogenides are the well known 2D materials with indirect band gap and are layered hexagonal structures²⁶. Among them, gallium chalcogenides are being focused on due to their possibilities to be utilized in experiments. Experimental synthesis of the monolayers has been done to study their properties^{27,28}. Along with these materials, different types of designed materials are required for the development of nanoscale devices. Because of that, different types of material structures have been designed, Janus structure is one of them. It is well known that optical and electronic properties depend on the structure and symmetry of the materials. Janus structure gives different and improved

results because of its symmetry breaking to meet the requirement of applications. Bui et al. designed Janus Ga₂SSe, Ga₂STe, Ga₂SeTe monolayer and shows its optical and electronic properties²⁹. In this study, they showed that Ga₂SSe has indirect band gap while Ga₂STe and Ga₂SeTe show direct band gap. The optical absorptions peaks are observed in the UV region.

In this work, we have designed Janus GaInS₂ monolayer by replacing one Ga atom with In atom from the Ga₂S₂ monolayer structure. After atomic relaxation, its electronic and optical properties have been studied. Unstrained structure exhibits an indirect band gap of 1.79 eV. Application of biaxial tensile strain results a semiconductor to semimetal phase change while compressive strain causes indirect to direct band gap for the material. The external electric field also causes indirect to direct band gap transition for the material. It shows a high absorption coefficient starting at the visible range and has a peak at the UV region. This work indicates that the material can be used in optoelectronic device as a photovoltaic absorber layer, UV photodetection and many more applications.

2. Computational Details

First principle calculations of monolayer GaInS₂ were performed using DFT. Structural optimization, electronic properties were calculated using ultrasoft pseudopotential³⁰ with nonlinear core correction and Perdew-Burke-Ernzerhof (PBE) functional³¹ as implemented in QUANTUM ESPRESSO (QE) package³². The calculations were performed with 15×15×1 k-mesh sampling for monolayer with Methfessel-Paxton first order spreading. Atoms were relaxed until force convergence minimum of 10⁻³ Ry/bohr has been attained. 45 Ry cut-off energy of plane wave was considered to perform the calculations. The biaxial strain was applied on the unit cell, can be calculated using the equation $\epsilon = \frac{(a-a_0)}{a_0} \times 100\%$. Where, a , a_0 are lattice constant with and without strain. The positive and negative value of applied strain are known as tensile and compressive strain, respectively. The optical properties were calculated by using the Time Dependent Density Functional Perturbation Theory (TD-DFPT) with SIESTA package³³. Imaginary and real parts of dielectric function were optimized from momentum space formulation and Kramers-Kronig transformation³⁴ respectively. From dielectric function other optical properties like absorption coefficient (α), refractive index (η), extinction coefficient (K) can be obtained from the following equations.

$$\eta = \left[\frac{(\epsilon_1^2 + \epsilon_2^2)^{1/2} + \epsilon_1}{2} \right]^{1/2} \quad (1)$$

$$K = \left[\frac{(\epsilon_1^2 + \epsilon_2^2)^{1/2} - \epsilon_1}{2} \right]^{1/2} \quad (2)$$

$$\alpha = \frac{2K\omega}{c} \quad (3)$$

Where, ε_1 , ε_2 , ω , C are the real and imaginary functions of dielectric, frequency of incident light, and speed of light respectively.

3. Results And Discussions:

3.1. Structural details:

GaInS₂ monolayer has a hexagonal structure with four atomic layers stacked in the order of S-In-Ga-S. The geometric design is the same as Ga₂S₂, which is a layered structure having broken inversion and mirror symmetry. The GaInS₂ structure is modeled from the structure Ga₂S₂ by replacing one Ga atom with In atom. This Janus structure belongs to P3m1 (C_{3v}) with space group number 156. The side view and top view of a 4×4×1 supercell have been shown in Fig. 1. It shows that the Ga atom and S atom are exactly vertically above the In and S atom, respectively. The lattice constant of the hexagonal unit cell was optimized by relaxing the structure, gives a value $a = b = 3.78 \text{ \AA}$, which matched well as reported previously³⁵. The distance between Ga-In, Ga-S, In-S, and S-S atoms are 2.66 Å, 2.41 Å, 2.52 Å, and 4.95 Å, respectively. The atoms make the following angles between them: $\angle \text{Ga-In-S}$, $\angle \text{In-Ga-S}$, $\angle \text{In-S-S}$, and $\angle \text{Ga-S-S}$ and their corresponding values are 119.98°, 115.29°, 60.01°, and 64.7°, respectively.

3.2. Electronic properties:

The electronic band structure and density of states (DOS) of the relaxed system have been calculated as shown in Figs. 2 (a) and (b). Band structure of monolayer has been studied along the high symmetric k-path K- Γ -M-K of hexagonal Brillouin zone. The GaInS₂ monolayer shows indirect band gap of 1.79 eV. The conduction band minima (CBM) rests at Γ point, while the valance band maxima (VBM) rests between K and Γ point and Fermi level rests between VBM and CBM. The valance band has two nearly degenerate states, rest between K- Γ and Γ -M point, which is because two S atoms contributed to the valance band.

To know the contribution of atoms in the VBM and CBM, total DOS and partial DOS have been studied. Figure 2 (b) indicates that VBM is contributed mainly by the p orbital of the S atoms. CBM is contributed by P orbitals of Ga and In atom. Further insight revealed that the VBM is contributed primarily by P_x orbital and some of P_y and P_z orbitals of S atom and minor contribution of P_x orbitals of Ga and In atom. The CBM contributed by P_y , P_z orbital of Ga and In atom and P_x orbital of S atom. Two dimensional charge density of the monolayer has been plotted to know about charge distribution. The different color shows the amount of charge accumulation as shown in the scale bar. It can be easily concluded that the maximum charge is accumulated on S atoms and less amount of charge is on Ga and In atoms. The more accumulation of charge on S atom can be understood by its electronegativity property. Sulfur is more electronegative than Ga and In atom and that causes more charge accumulation on it.

3.3. Effect of biaxial strain:

The effect of biaxial strain on the band structure of GaInS₂ monolayer was studied. We have applied up to 10% tensile and compressive strain with an increment of 2% to the studied band structure. The band

structure and projected density of states (PDOS) with 4% and 8% tensile strain and compressive strain (-4% and -8%) are shown in Figs. 3 (a)-(d). At 4% tensile strain, the band remained indirect, as shown by the red arrow. The band gap was found to be decreasing to 0.98 eV. At 8% strain as shown in Fig. 3(b), the band gap decreases to 0.47 eV, which means phase transition from semiconductor to semimetal has occurred at 8% tensile strain. Compressive strain results indirect to direct type semiconducting properties and little increase in the band gap. At -4% strain, monolayer changes its semiconducting state from indirect to direct type. The VBM and CBM rest at Γ point, and the bandgap for the monolayer at that particular strain is 2.22 eV. The position of VBM remains at Γ point for further increase in compressive strain, but CBM shifted from high symmetric Γ to M point at -6% strain, and again CBM shifted from M to K point at -8% strain. The bandgap at -6% and -8% strain is 2.08 eV and 1.73 eV, respectively.

3.4. Effect of the electric field:

A finite electric field is applied to the monolayer along the perpendicular direction of the surface (Z-direction) using the modern theory of polarization as implemented in QE. The effect of finite electric field on electronic band structure has been studied. Upon application of a finite electric field, the structural change is negligible. An external electric field is applied up to 4 V/nm and -4 V/nm with an increment of 2 V/nm, which can be considered as a perturbation on a stable system or application of gate voltage on field effect transistor (FET) device. The field dependent modification of band structures is shown in Figs. 4 (a)-(d). For the 2 V/nm applied field, the band type remains the same, although the bandgap reduced to 1.54 eV. With 4 V/nm, the material becomes a direct band gap semiconductor with a gap of 1.03 eV. The negative electric field does not affect the band structure much, and the band gap also does not change significantly. At the -2 V/nm field, the band gap decreases slightly to 1.77 eV, while at -4 V/nm, the gap increases to 1.82 eV. Band structure remains indirect for both negative electric fields.

The variation of VBM and CBM with applied strain and finite electric field along the transverse direction is shown in Fig. 5 (a) and (b). At the positive strain region, the band gap decreases linearly with applied strain. Along the negative region non-linear variation of band gap has been occurred. The band gap increases linearly up to -4% compressive strain and then decreases linearly. We have divided the variation of VBM and CBM energy into four regions, namely A, B, C, and D. The VBM energy varies linearly with applied positive strain and at -2% strain, as shown in region A. As the negative strain increases, a jump in VBM energy has been observed, and again a linear variation with a different slope has been occurred (region B). In CBM, linear variation of energy was observed from -4-10% strain (region C). A non-linear region (region D) was observed from -6% to -10% applied strain. In the whole A region, the VBM rests between Γ and K, but at -4% strain, VBM shifts to Γ point. This is why a certain jump in VBM energy has occurred. In the whole B region, VBM rests at Γ point. Similarly, CBM rests at Γ point throughout the C region, which causes linear variation there. At -6%, CBM shifted to M point, and at -8% of strain again shifted to K point, resulting in a non-linear region. To understand the linear trend of the states, PDOS has been studied as shown in Fig. 3 (a)-(d). The region A is dominated by the P_x orbital of the S atom, while the P_z orbital of the S atom dominates region B. Region C is dominated by as expected P_y and P_z orbital of Ga atom as CBM rests at same Γ point. In the region D, a change of high symmetric point from M to K

has been occurred and caused non-linear characteristics. At -6% strain, CBM energy moves to the M point, and for - 8% and - 10% strain, it remains at K point.

External electric field-dependent variation of VBM and CBM has three different regions E-F. The slope of linearly variant F and G are almost the same, which is responsible for not changing the bandgap. At 4 V/nm electric field, VBM changes to Γ point and causes a band gap reduction.

3.5. Optical properties:

The optical properties of the GaInS_2 monolayer have been calculated along the transverse direction of the material. The real part of the dielectric function (ϵ_1), the imaginary part of the dielectric function (ϵ_2), and absorption coefficient (α) varying with photon energy is shown in Figs. 6 (a)-(c). The zero-point value of ϵ_1 for the unstrained structure is 3.16. Although with 4% tensile and compressive strain, the value does not change remarkably but at 8% strain, the value increases to 3.39. The highest value peak arises at 3.49 eV with a value of 5.28 for the unstrained layer. The peak value increases slightly at -4% strain but again decreases for - 8% applied strain. The lowest peak has been observed at 8% tensile strain with a value of 4.37 at 3.59 eV. Some negative value for ϵ_1 has been observed with the highest value of -0.81 for - 4% strain. All the ϵ_1 values were found almost stable on a high photon energy range. The value of ϵ_2 has started to increase at the visible energy region at 1.25 eV for all strained and relaxed layers. Only for 8% applied strain, it starts increasing at 0.3 eV. The peak value for the unstrained layer is 4.6 at 4.25 eV. The peak value is highest for 4% applied strain and decreases for compressive strain. The monolayer has been seen to be a very good absorber of light with high absorption coefficient. Although the strain does not have much effect on peak position, it changes the absorption value. The absorption starts in the visible region at 1.3 eV for unstrained monolayer, which starts decreasing for all strains except - 4% compressive strain. The absorption started at 0.65 eV for 8% strain. The first peak arises at 4.84 eV for the relaxed system, and the highest peak arises at 7.09 eV with a value of $8.54 \times 10^5 \text{ cm}^{-1}$. The absorption decreases with tensile strain, but the first peak is getting prominent with tensile strain, while it started vanishing with applied compressive strain. The material shows absorption near visible and ultraviolet region.

4. Conclusion

We have studied the electronic and optical properties of the GaInS_2 monolayer. GaInS_2 monolayer has an indirect band gap which changes to direct band gap with applied 4% compressive strain. 8% tensile strain causes a change of the state of the material from semiconducting to semi-metallic state. An external electric field with a value of 4 V/nm, applied normal to the plane, also changes the semiconducting property from indirect to direct band gap type. However, the band gap does not change effectively with the electric field. The Janus monolayer also possesses exciting optical properties with a high value of absorption coefficient and dielectric function.

Declarations

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Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Novoselov, K. S. *et al.* Two-dimensional gas of massless Dirac fermions in graphene. *Nature* **438**, 197–200 (2005).
2. Geim, A. K. & Novoselov, K. S. The rise of graphene. in *Nanoscience and technology: a collection of reviews from nature journals* 11–19 (World Scientific, 2010).
3. Yin, Z. *et al.* Single-layer MoS₂ phototransistors. *ACS Nano* **6**, 74–80 (2012).
4. Bera, J., Betal, A. & Sahu, S. Spin Orbit Coupling Induced Enhancement of Thermoelectric Performance of HfX₂ (X= S, Se) and Its Janus Monolayer. *J. Alloys Compd.* 159704 (2021).
5. Pu, J. *et al.* Highly flexible MoS₂ thin-film transistors with ion gel dielectrics. *Nano Lett.* **12**, 4013–4017 (2012).
6. Lee, H. S. *et al.* MoS₂ nanosheet phototransistors with thickness-modulated optical energy gap. *Nano Lett.* **12**, 3695–3700 (2012).
7. Choi, W. *et al.* High-detectivity multilayer MoS₂ phototransistors with spectral response from ultraviolet to infrared. *Adv. Mater.* **24**, 5832–5836 (2012).
8. Mochalov, L. *et al.* Structural and optical properties of arsenic sulfide films synthesized by a novel PECVD-based approach. *Superlattices Microstruct.* **111**, 1104–1112 (2017).
9. Mochalov, L. *et al.* Optical emission of two-dimensional arsenic sulfide prepared by plasma. *Superlattices Microstruct.* **114**, 305–313 (2018).
10. Li, X. *et al.* Intrinsic electrical transport properties of monolayer silicene and MoS₂ from first principles. *Phys. Rev. B* **87**, 115418 (2013).
11. Tao, L. *et al.* Silicene field-effect transistors operating at room temperature. *Nat. Nanotechnol.* **10**, 227–231 (2015).
12. Meckbach, L., Stroucken, T. & Koch, S. W. Giant excitation induced bandgap renormalization in TMDC monolayers. *Appl. Phys. Lett.* **112**, 61104 (2018).
13. Gao, Y.-P. *et al.* Two-dimensional transition metal diseleniums for energy storage application: a review of recent developments. *CrystEngComm* **19**, 404–418 (2017).
14. Sinha, S. *et al.* Atomic structure and defect dynamics of monolayer lead iodide nanodisks with epitaxial alignment on graphene. *Nat. Commun.* **11**, 1–13 (2020).
15. Li, P. & Appelbaum, I. Symmetry, distorted band structure, and spin-orbit coupling of group-III metal-monochalcogenide monolayers. *Phys. Rev. B* **92**, 195129 (2015).

16. Sun, H., Wang, Z. & Wang, Y. Band alignment of two-dimensional metal monochalcogenides MXs (M= Ga, In; X= S, Se, Te). *AIP Adv.* **7**, 95120 (2017).
17. Fuhrer, M. S. & Hone, J. Measurement of mobility in dual-gated MoS₂ transistors. *Nat. Nanotechnol.* **8**, 146 (2013).
18. Radisavljevic, B. & Kis, A. Reply to 'Measurement of mobility in dual-gated MoS₂ transistors'. *Nat. Nanotechnol.* **8**, 147–148 (2013).
19. Radisavljevic, B. & Kis, A. Mobility engineering and a metal–insulator transition in monolayer MoS₂. *Nat. Mater.* **12**, 815–820 (2013).
20. Li, H. *et al.* Fabrication of single-and multilayer MoS₂ film-based field-effect transistors for sensing NO at room temperature. *small* **8**, 63–67 (2012).
21. Perea-López, N. *et al.* Photosensor device based on few-layered WS₂ films. *Adv. Funct. Mater.* **23**, 5511–5517 (2013).
22. Feng, J., Qian, X., Huang, C.-W. & Li, J. Strain-engineered artificial atom as a broad-spectrum solar energy funnel. *Nat. Photonics* **6**, 866 (2012).
23. Peng, B. *et al.* High thermoelectric efficiency in monolayer PbI₂ from 300 K to 900 K. *Inorg. Chem. Front.* **6**, 920–928 (2019).
24. Betal, A., Bera, J. & Sahu, S. Low-temperature thermoelectric behavior and impressive optoelectronic properties of two-dimensional XI₂ (X = Sn, Si): A first principle study. *Comput. Mater. Sci.* **186**, 109977 (2021).
25. Bera, J. & Sahu, S. Strain induced valley degeneracy: A route to the enhancement of thermoelectric properties of monolayer WS₂. *RSC Adv.* **9**, 25216–25224 (2019).
26. Zolyomi, V., Drummond, N. D. & Fal'ko, V. I. Band structure and optical transitions in atomic layers of hexagonal gallium chalcogenides. *Phys. Rev. B* **87**, 195403 (2013).
27. Jin, H. *et al.* Ohmic contact in monolayer InSe-metal interface. *2D Mater.* **4**, 25116 (2017).
28. Late, D. J. *et al.* GaS and GaSe ultrathin layer transistors. *Adv. Mater.* **24**, 3549–3554 (2012).
29. Bui, H. D., Jappor, H. R. & Hieu, N. N. Tunable optical and electronic properties of Janus monolayers Ga₂SSe, Ga₂STe, and Ga₂SeTe as promising candidates for ultraviolet photodetectors applications. *Superlattices Microstruct.* **125**, 1–7 (2019).
30. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758 (1999).
31. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865 (1996).
32. Giannozzi, P. *et al.* QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. **395502**, (2009).
33. Soler, J. M. *et al.* The SIESTA method for ab initio order-N materials simulation. *J. Phys. Condens. Matter* **14**, 2745 (2002).

34. Boukamp, B. A. A linear Kronig-Kramers transform test for immittance data validation. *J. Electrochem. Soc.* **142**, 1885–1894 (1995).
35. Wang, H. *et al.* First-principles study of electronic, optical and thermal transport properties of group III–VI monolayer MX (M= Ga, In; X= S, Se). *J. Appl. Phys.* **125**, 245104 (2019).

Figures

Figure 1

The side view and top view of GaInS₂ monolayer 4×4×1 supercell. It forms a hexagonal honeycomb structure.

Figure 2

(a) The electronic band structure of Janus GaInS2 monolayer, calculated without strain. (b) Total DOS and local DOS of Ga, In, S atoms plotted with energy to check the atomic contribution near the band edge. (c) Two dimensional charge density plot of monolayer GaInS2.

Figure 3

Electronic band structure of GaInS2 monolayer with (a) 4%, (b) 8% tensile strain and (c) 4%, (d) 8% compressive strain and their corresponding PDOS is plotted. Red arrow showing the VBM to CBM position.

Figure 4

Electric field dependent band structure of monolayer with (a) 2 V/nm, (b) 4 V/nm, (c) -2 V/nm, and (d) -4 V/nm applied electric field.

Figure 5

(a) Variation of VBM and CBM with applied biaxial strain. (b) Variation of VBM and CBM with applied finite electric field along the transverse direction.

Figure 6

(a) Real part of dielectric function (b) imaginary part of dielectric function (c) absorption coefficient for different applied strain, plotted with photonic energy.