Study of electronic structure and transport coefficients of GaN-MoS$_2$ heterostructure

Gurpal Singh Khosa$^{1,*}$, Ranjan Kumar$^{1,2,}$ and Shuchi Gupta$^3,$

$^1$Department of Physics, Panjab University, Chandigarh 160014, India,
$^2$Department of Physics, King Abdulaziz University, Jeddah 21589, Kingdom of Saudi Arabia,
$^3$University Institute of Engineering and Technology, Panjab University, Chandigarh 160014, India

$^*$khosagurp@gmail.com
$^*$ranjan@pu.ac.in
$^*$sgupta@pu.ac.in

Abstract. The electronic structure and transport properties of GaN-MoS$_2$ heterostructure have been theoretically investigated using first principles calculations. Among the various possibilities of stacking MoS$_2$ over GaN monolayers to form heterostructure, we studied the case in which the S atom is directly placed over the Ga atom. This type of stacking is energetically favourable. The GaN-MoS$_2$ heterostructure preserves the direct band gap nature of MoS$_2$ monolayer i.e. it has direct band gap of 0.97 eV. The valence bands and conduction bands adjoining the fermi level are mostly contributed by N and Mo atoms. To study the performance of both n-type and p-type GaN-MoS$_2$ heterostructure in thermoelectric applications, we investigate the transport coefficients on which the ZT parameter depends. We found that p-type heterostructure has high electrical conductivity as compared to n-type heterostructure. Due to which it has a high magnitude of power factor which is one of the deciding factors in the evaluation of ZT parameter.

1. Introduction

After the experimental synthesis of graphene in 2004 [1,2], numerous layered materials have been explored [3,4,5,6,7,8]. The existence of band gap in these layered materials make them potential candidates to be used in the fabrication of electronic devices such as field effect transistors, thermoelectric devices, solar cells, photovoltaic devices etc. [9,10,11]. The several studies proposed that the electronic properties of materials can be modified by alloying [12], by doping [13] and by super lattice formation [14]. In parallel with these investigations of layered materials, the experimental synthesis and theoretical investigation of vanderwaal (vdw) heterostructures by vertically stacking these layered materials has offered additional possibilities to use these materials in electronic applications. Recently the transition metal dichalcogenide(TMD)/graphene heterostructures have been used in the fabrication of electronic devices such as memory cells, vertical field effect transistors etc. [15,16,17,18]. The existence of vdw heterostructures has attracted much attention because of novel properties as compared to their parent layers. Long et al. [19] investigated that the recombination time
of photoexcited holes and electrons of bilayer Janus MoSSe heterostructure is large as compared to the single layer. Tong et al. [20] studied the electronic properties of MoS$_2$-WSe$_2$ heterostructure and found that heterostructure has band gap of 1.48 eV which was smaller as compared to the individuals band gaps of single layer MoS$_2$ (1.5 eV) and WSe$_2$ (1.60 eV). Khan et al. [21] studied the electronic structure and thermoelectric properties of bilayered MX$_2$ (M= Zr, Hf and X= S, Se) and found that Seebeck coefficient (electrical conductivity) have enhanced values in n(p)-type doping as compared to monolayers. This enhancement in transport coefficients further boost the performance of layered materials in thermoelectric applications. Zhang et al. investigated that MoS$_2$/GaN heterostructure is energetically stable having enhanced capability in the application of photocatalytic hydrogen generation [22,23]. The GaN-MoS$_2$ heterostructure is experimentally synthesised using various methods such as enhanced plasma molecular beam technique [24], chemical vapour deposition (CVD) technique [25, 26] and by transferring MoS$_2$ layer on GaN [27].

Motivated by the above investigations of vanderwaal heterostructures, we study the structural and electronic properties of GaN monolayer, MoS$_2$ monolayer and GaN-MoS$_2$ heterostructure. The electronic transport coefficients of GaN-MoS$_2$ heterostructure have also been explored. The study of electronic transport coefficients such as electrical conductivity, Seebeck coefficients, power factor etc. are very valuable because these coefficients are the deciding factors in the performance of materials in thermoelectric applications.

Figure 1. GaN-MoS$_2$ layered heterostructure viewed from top and side. The green, pink, gold and red balls indicate Ga, N, Mo and S atoms, respectively.

2. Computational Methods

The Density Functional Theory (DFT) based first principles calculations have been done using Quantum Espresso simulation package [28]. The ultrasoft pseudopotential (USPP) of functional type Perdew-Burke-Ernzerhof (PBE) is used for calculations [29]. The kinetic energy cutoff of magnitude 80 Ry and k-mesh of $12 \times 12 \times 1$ is used after performing the convergence test of total energy w.r.t to the kinetic energy cutoff and k-mesh. For Density of states (DOS) and projected density of states (PDOS) calculations, a highly densed k-mesh of $28 \times 28 \times 1$ is used to achieve smooth curves. The vacuum gap of more than 15 Å is used in the formation of bilayer to avoid interaction effect of adjoining layers. The BoltzTrap code has been used for the determination of electronic transport coefficients [30].

3. Results and Discussion

The GaN-MoS$_2$ heterostructure is vertically stacked arrangement of two layers i.e. GaN monolayer and MoS$_2$ monolayer. We calculate the structural parameters and electronic bandstructure of GaN and MoS$_2$ monolayers. The optimised lattice constants of these monolayers are 3.21 Å and 3.18 Å
respectively. The small lattice mismatch between lattice constants depicts that formation of freestanding heterostructure of these monolayers is possible. Figure 1 shows that GaN-MoS$_2$ heterostructure has a hexagonal lattice geometry similar to their parent monolayers. After optimisation the lattice constant of heterostructure is found to be 3.20 Å. These obtained structural parameters agree with the previous predictions [32,33,23]. Figure 2(a) and (b) show the band structure, density of states (DOS) and projected density of states (PDOS) of GaN monolayer. The GaN monolayer is a semiconductor in which conduction band minima (CBM) and valence band maxima (VBM) reside at $\Gamma$ and K points respectively. It has indirect energy band gap of 2.17 eV. The PDOS shows that the ‘p’ orbital of N and Ga atoms mainly contributed in the formation of valence bands and conduction bands respectively. Figure 3(a) and (b) show electronic band structure, DOS and PDOS calculations for MoS$_2$ monolayer. The CBM and VBM reside at a highly symmetric K point (direct band gap) having a gap of 1.17 eV. The valence bands and conduction bands near the fermi level are mainly contributed by the ‘d’ and ‘p’ orbitals of Mo and S atoms, respectively. These results of both monolayers are in good agreement with the previous calculations [8, 34, 35]. Out of different stacking arrangements of GaN-MoS$_2$ heterostructure, we choose the most stable arrangement as investigated by several groups [31,36,37] in which N, Ga atoms are placed directly below the Mo and S atoms respectively.

![Figure 2](image1.png)

**Figure 2.** Electronic band structure, total DOS and projected DOS of GaN monolayer.

![Figure 3](image2.png)

**Figure 3.** Electronic band structure, total DOS and projected DOS of MoS$_2$ monolayer.
Figure 4. Electronic band structure, total DOS and projected DOS of GaN-MoS$_2$ heterostructure.

Table 1. The lattice constant ($a_0$), atomic distance ($d_{X-Y}$), and energy band gap ($E_g$) for GaN monolayer, MoS$_2$ monolayer and GaN-MoS$_2$ heterostructure. I stand for indirect band and D stands for direct gap. The values in bracket are the results obtained by the work of Wen-Jin and co-authors [31].

|          | $a_0$ (Å) | $d_{Ga-N}$ (Å) | $d_{Mo-S}$ (Å) | $d_{S-S}$ (Å) | $d_{Ga-S}$ (Å) | $E_g$ (eV)  |
|----------|-----------|----------------|---------------|--------------|---------------|------------|
| GaN      | 3.21 (3.25) | 1.85 (1.87)     |               |              |               | 2.17 I (1.98 I) |
| MoS2     | 3.18 (3.15) | 2.41 (2.40)     | 3.12          |              |               | 1.71 D (1.78 D) |
| GaN-MoS2 | 3.20 (3.21) | 1.84            | 2.41          | 3.11         | 3.37 (2.96)   | 0.94 D (0.77 D) |

Figure 4 shows the band structure, DOS and PDOS calculations for GaN-MoS$_2$ heterostructure. We found that GaN-MoS$_2$ heterostructure has a direct band of magnitude 0.97 eV at a highly symmetric K point. The band gap of heterostructure is smaller as compared to that of their parent monolayers. It shows that formation of heterostructure leads to the reduction in the band gap. Similar behaviour in the variation of band gap observed in the MoS$_2$-WS$_2$ heterostructure [38]. The nature of band gap in heterostructure is similar to that of MoS$_2$ monolayer which shows that the direct band gap character of MoS$_2$ monolayer is preserved. From the PDOS profile of GaN-MoS$_2$ heterostructure, we found that the main contribution in the formation of valence band is of N atom’s ‘p’ orbital whereas conduction bands are formed by the ‘d’ orbital of Mo atom. So the GaN (MoS$_2$) monolayer contributes in the formation of valence (conduction) bands of GaN-MoS$_2$ heterostructure. The structural parameters and energy band gap values for both monolayers and heterostructure are shown in Table 1. After that the electronic transport coefficients of heterostructure has been investigated. Figure 5 shows the behaviour of Seebeck coefficient at three different temperatures under n-type and p-type doping for GaN-MoS$_2$ heterostructure. The magnitude of Seebeck coefficient varies directly (inversely) w.r.t the temperature (carrier concentration) which strictly follows the equation 1, where $T$ is the temperature and ‘n’ is the carrier concentration.

$$ S = \frac{8\pi^2 K_B^2}{3e\hbar^2} m^* T \left( \frac{\pi}{3n} \right)^{2/3} $$

(1)
The Seebeck coefficient as a function of carrier concentration for (a) n-type and (b) p-type GaN-MoS\(_2\) heterostructure at different temperatures.

Figure 5. The Seebeck coefficient as a function of carrier concentration for (a) n-type and (b) p-type GaN-MoS\(_2\) heterostructure at different temperatures.

Figure 6 (a) and (b) show the electrical conductivity (\(\sigma\)) behaviour of GaN-MoS\(_2\) heterostructure under different temperatures w.r.t the carrier concentration. The electrical conductivity obtained from BoltzTrap code depends on the carrier relaxation time. To know the exact behaviour of \(\sigma\), we calculated the relaxation time (\(\tau\)) for electrons and holes by solving the equation (2) below

\[
\tau = \frac{\mu m^*}{e} \tag{2}
\]

For relaxation time calculations, we required carrier effective mass and carrier mobility. We use carrier mobility of electrons and holes reported by Neo and co-authors [31]. The carrier effective mass is calculated by solving equation 3 where the second order derivative of energy w.r.t the k path is obtained by solving the polynomial equation 4.

\[
\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} \tag{3}
\]

where the second order derivative of E(k) w.r.t. k is solved by fitting the E(k) to the cubic polynomial

\[
E(k) = ak^3 + bk^2 + ck + d \tag{4}
\]

Table 2. Carrier effective mass, mobility and relaxation time of GaN-MoS\(_2\) heterostructure. The values in bracket are the results obtained by the work of Wen-Jin and co-authors [31].

|        | \(m^*_e\) [\(m_0\)] | \(m^*_h\) [\(m_0\)] | \(\mu_e\) (cm\(^2\) V\(^{-1}\) s\(^{-1}\)) | \(\mu_h\) (cm\(^2\) V\(^{-1}\) s\(^{-1}\)) | \(\tau_e\) (fs) | \(\tau_h\) (fs) |
|--------|---------------------|---------------------|--------------------------------|--------------------------------|----------------|----------------|
| GaN-MoS\(_2\) | 0.45(0.44) | 1.21(1.27) | (266) | (3050.91) | 66 | 2575 |

The obtained values of carrier's effective mass and relaxation time are shown in table 2. Using the calculated value of relaxation time, we evaluate the behaviour of electrical conductivity (\(\sigma\)) w.r.t increasing carrier concentration under different temperatures as shown in Figure 6. The p-type GaN-MoS\(_2\) heterostructure has high electrical conductivity in contrast to n-type heterostructure because of the high carrier mobility as shown in equation 5 that \(\sigma\) varies directly with the carrier mobility (\(\mu\)).
\[ \sigma = ne\mu = \frac{ne^2\tau}{m^*} \]  

(5)

Figure 6. Electrical conductivity as a function of carrier concentration for (a) n-type and (b) p-type GaN-MoS₂ heterostructure at different temperatures.

To investigate the performance of this heterostructure in thermoelectric applications, we calculated the power factor (P.F. = \(S^2\sigma\)) of this heterostructure. The behaviour of power factor for both n and p-type doped heterostructures are shown in Figure 7. The p-type heterostructure has enhanced power factor in contrast to n-type because of the high values of Seebeck coefficients and electrical conductivity at higher concentration.

Figure 7. Power factor as a function of carrier concentration for (a) n-type and (b) p-type GaN-MoS₂ heterostructure at different temperatures.

As we know the dimensionless figure of merit parameter ZT is calculated by solving equation 6,

\[ ZT = \frac{S^2\sigma T}{K} \]  

(6)
where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity and $K$ is the total thermal conductivity of the material. As we see that the ZT parameter strongly depends on P.F., from this we conclude that the GaN-MoS$_2$ heterostructure could be used in the fabrication of thermoelectric devices. The calculations of thermal conductivity of this heterostructure are under investigation, once the calculations complete, we will figure out the ZT parameter of GaN-MoS$_2$ heterostructure.

4. Conclusion

We systematically examine the structural parameters, electronic band structure and transport coefficients of GaN-MoS$_2$ heterostructure using the density functional theory based first principles calculations. The GaN-MoS$_2$ heterostructure is energetically stable, having a direct band gap of magnitude 0.94 eV, which is lower than the band gaps of their parent monolayers. The direct band gap character of MoS$_2$ monolayer is preserved in the GaN-MoS$_2$ heterostructure. The valence (conduction) bands of heterostructure are formed by the contribution of N(Mo) atoms. The evaluated values of electronic transport coefficients state that GaN-MoS$_2$ heterostructure is highly favourable material in the thermoelectric applications. From our evaluated results, we conclude that p-type GaN-MoS$_2$ heterostructure has a high magnitude of power factor as compared to n-type heterostructure and it could be used in the fabrication of thermoelectric devices.

Acknowledgments

This work was funded by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah, under grant No. (KEP-00-130-42). The authors, therefore, acknowledge with thanks DSR technical and financial support. G.S.K gratefully acknowledges UGC, India for financial support under grant number MANF-2018-19-PUN-98540. We also thank the Department of Physics and University Institute of Engineering and Technology, Panjab University, Chandigarh for providing technical facilities required in this work.

References

[1] Novoselov KS, Geim AK, Morozov SV, Jiang DE, Zhang Y, Dubonos SV, Grigorieva, IV and Firsov AA 2004 Electric field effect in atomically thin carbon films Sci. 306 666-69
[2] Geim AK and Novoselov KS 2010 The rise of graphene. In Nanoscience and technology: a collection of reviews from nature journals 11-19
[3] Cahangirov S, Topsakal M, Aktürk E, Şahin H and Ciraci S 2009 Two-and one-dimensional honeycomb structures of silicon and germanium Phys. Rev. Lett. 102 236804.
[4] Bandurin DA, Tyurnina AV, Geliang LY, Mishchenko A, Zólyomi V, Morozov SV, Kumar RK, Gorbachev RV, Kudrynskyi ZR, Pezzini S and Kovalyuk ZD 2017 High electron mobility, quantum Hall effect and anomalous optical response in atomically thin InSe Nat. Nanotechnol. 12 223-27
[5] Wang QH, Kalantar-Zadeh K, Kis A, Coleman JN and Strano MS 2012. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides Nat. Nanotechnol. 7 699-12
[6] Jeong S, Yoo D, Jang JT, Kim M and Cheon J 2012 Well-defined colloidal 2-D layered transition-metal chalcogenide nanocrystals via generalized synthetic protocols J. Am. Chem. Soc. 134 18233-36
[7] Coleman JN, Lotya M, O’Neill A, Bergin SD, King PJ, Khan U, Young K, Gaucher A, De S, Smith R J and Shvets I V 2011 Two-dimensional nanosheets produced by liquid exfoliation of layered materials Sci. 331 568-71
[8] Mak KF, Lee C, Hone J, Shan J and Heinz TF 2010 Atomically thin MoS 2: a new direct-gap
semiconductor Phys. Rev. Lett. 105 136805.

[9] Rehman G, Khan S A, Amin B, Ahmad I, Gan LY and Maqbool M 2018 Intriguing electronic structures and optical properties of two-dimensional van der Waals heterostructures of Zr 2 CT 2 (T= O, F) with MoSe 2 and WSe 2 J. Mater. Chem. C 6 2830-39

[10] Rao C N R, Ramakrishna Matte HSS and Maitra U 2013 Graphene analogues of inorganic layered materials Angew. Chem. Int. Ed. 52 13162-85

[11] Tang Q and Zhou Z 2013 Graphene-analogous low-dimensional materials Prog. Mater. Sci. 58 1244-1315.

[12] Komsa HP and Krasheninnikov AV 2013 Electronic structures and optical properties of realistic transition metal dichalcogenide heterostructures from first principles Phys. Rev. B 88 085318

[13] Komsa HP, Kotakoski J, Kurasch S, Lehtinen O, Kaiser U and Krasheninnikov AV 2012 Two-dimensional transition metal dichalcogenides under electron irradiation: defect production and doping Phys. Rev. Lett. 109 035503

[14] Lu N, Guo H, Wang L, Wu X and Zeng XC 2014. van der Waals trilayers and superlattices: modification of electronic structures of MoS 2 by intercalation Nanosc. 6 4566-71.

[15] Bertolazzi S, Krasnozhon D and Kis A 2013 Nonvolatile memory cells based on MoS 2/graphene heterostructures ACS nano 7 3246-52.

[16] Britnell L, Gorbachev RV, Jalil R, Belle BD, Schedin F, Mishchenko A, Georgiou T, Katsnelson M I, Eaves L, Morozov SV and Peres NMR 2012 Field-effect tunneling transistor based on vertical graphene heterostructures Sci. 335 947-950

[17] Georgiou T, Jalil R, Belle BD, Britnell L, Gorbachev RV, Morozov SV, Kim YJ, Gholinia A, Haigh SJ, Makarovskiy O and Eaves L 2013 Vertical field-effect transistor based on graphene–WS 2 heterostructures for flexible and transparent electronics Nat. Nanotechnol. 8 100-03

[18] Yu W J, Li Z, Zhou H, Chen Y, Wang Y, Huang Y and Duan X 2013 Vertically stacked multi-heterostructures of layered materials for logic transistors and complementary inverters Nat. Mater. 12 246-52

[19] Long C, Dai Y, Gong ZR and Jin H 2019. Robust type-II band alignment in Janus-MoSSe bilayer with extremely long carrier lifetime induced by the intrinsic electric field Phys. Rev. B 99 115316

[20] Tong L, Liu T, Liang R, Wang S, Chen J, Dai J and Ye L 2017. Growth of Transition Metal Dichalcogenides and Directly Modulating Their Properties by Chemical Vapor Deposition Gen. Chem. 3

[21] Khan F, Din H U, Khan SA, Rehman G, Bilal M, Nguyen CV, Ahmad I, Gan LY and Amin B 2019 Theoretical investigation of electronic structure and thermoelectric properties of MX2 (M= Zr, Hf; X= S, Se) van der Waals heterostructures J. Phys. Chem. Solids 126 304-09

[22] Zhang Z, Qian Q, Li B and Chen KJ 2018. Interface engineering of monolayer MoS2/GaN hybrid heterostructure: modified band alignment for photocatalytic water splitting application by nitridation treatment ACS Appl. Mater. Interfaces. 10 17419-26.

[23] Liao J, Sa B, Zhou J, AHuja R and Sun Z 2014 Design of high-efficiency visible-light photocatalysts for water splitting: MoS2/AlN (GaN) heterostructures J. Phys. Chem. C. 118 17594-99.

[24] Yamada A, Ho KP, Maruyama T and Akimoto K 1999 Molecular beam epitaxy of GaN on a substrate of MoS2 layered compound Appl. Phys. A 69 89-92.

[25] Gupta P, Rahman AA, Subramanian S, Gupta S, Thamizhavel A, Orlova T, Rouvimov S, Vishwanath S, Protasenko V, Laskar MR and Xing HG 2016 Layered transition metal dichalcogenides: promising near-lattice-matched substrates for GaN growth Sci. Rep. 6 1-8

[26] Mishra P, Tangi M, Ng TK, Hedhili MN, Anjum DH, Alias MS, Tseng CC, Li LJ and Ooi BS 2017 Impact of N-plasma and Ga-irradiation on MoS2 layer in molecular beam epitaxy Appl. Phys. Lett. 110 012101

[27] Lee EW, Lee CH, Paul PK, Ma L, McCulloch WD, Krishnamoorthy S, Wu Y, Arehart AR and Rajan S 2015 Layer-transferred MoS2/GaN PN diodes Appl. Phys. Lett. 107 103505
[28] Giannozzi P, Baroni S, Bonini N, Calandra M, Car R, Cavazzoni C, Ceresoli D, Chiarotti G L, Cococcioni M, Dabo I and Dal Corso A 2009 QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials J. Condens. Matter Phys. 21 395502.
[29] Perdew JP, Burke K and Ernzerhof M 1996. Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865
[30] Madsen GK and Singh DJ 2006 BoltzTraP. A code for calculating band-structure dependent quantities Comput. Phys. Commun. 175 67-71.
[31] Yin WJ, Zeng XL, Wen B, Ge, Q X, Xu Y, Teobaldi G and Liu LM 2021. The unique carrier mobility of Janus MoSSe/GaN heterostructures Front. Phys. 16 1-9
[32] Zhuang HL, Singh AK and Hennig RG 2013. Computational discovery of single-layer III-V materials Phys. Rev. B 87 165415.
[33] Komsa HP and Krasheninnikov AV 2012 Effects of confinement and environment on the electronic structure and exciton binding energy of MoS 2 from first principles Phys. Rev. B 86 241201.
[34] Splendiani A, Sun L, Zhang Y, Li T, Kim J, Chim CY, Galli G and Wang F 2010 Emerging photoluminescence in monolayer MoS2 Nano. Lett. 10 1271-75.
[35] Khosa GS, Kumar R and Gupta S 2020 Effect of biaxial strain on electronic transport coefficients of monolayer MoS2. In AIP Conference Proceedings 2265
[36] Ren D, Tan X, Zhang T and Zhang Y 2019. Electronic and optical properties of GaN–MoS2 heterostructure from first-principles calculations Chinese Physics B 28 086104.
[37] Yelgel C 2017 First-principles modeling of GaN/MoSe S $ _ { _ 2 } $ van der Waals heterobilayer Turk. J. Phys. 41 463-68.
[38] Kośmider K and Fernández-Rossier J 2013. Electronic properties of the MoS 2-WS 2 heterojunction Phys. Rev. B 87 075451.