Graphene, 2014, 3, 52-59
Published Online October 2014 in SciRes. http://www.scirp.org/journal/graphene
http://dx.doi.org/10.4236/graphene.2014.34008

Scientific Research

A Comparative Study of Electronic Properties of Bulk MoS_2 and Its Monolayer Using DFT Technique: Application of Mechanical Strain on MoS_2 Monolayer

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Received 17 August 2014; revised 13 September 2014; accepted 12 October 2014

Abstract

Electronic structure calculation of bulk and monolayer MoS_2 has been performed using plane wave pseudopotential method based on density functional theory. The indirect band gap in the bulk MoS_2 was found to be 0.9 eV, whereas in the monolayer-MoS_2 the band gap of 1.57 eV was found to be direct one. The calculated physical parameters of monolayer MoS_2 are found to be very close to the bulk MoS_2 and compare well with available experimental and other theoretical results. The calculated density of states (DOS) may help explain this change in the nature of band gap in bulk and in monolayer MoS_2. A further variation in band gap has been observed in MoS_2 monolayer on applying biaxial strain.

Keywords

MoS_2, DFT, Electronic Properties, Mono Layer, Strain

1. Introduction

Layered transition-metal di-chalcogenides (LTMDCs) have been extensively reviewed in the recent past [1]. MoS_2 is a typical example of LTMDC family of materials which attracts investigation because of its distinctive industrial applications, ranging from use as a lubricant [2] and a catalyst [3] as well as in photo-voltaics [4] and energy storage [5]. In its bulk form MoS_2 is a semiconductor with an indirect band gap of about 1.23 eV while

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How to cite this paper: Ahmad, S. and Mukherjee, S. (2014) A Comparative Study of Electronic Properties of Bulk MoS_2 and Its Monolayer Using DFT Technique: Application of Mechanical Strain on MoS_2 Monolayer. *Graphene*, **3**, 52-59.
http://dx.doi.org/10.4236/graphene.2014.34008

its monolayer has a direct energy gap of 1.8 eV [6]. A special attention has been paid on single layer MoS_2 in the recent years. Upon thinning from the bulk [7]-[9] the electronic structure of MoS_2 undergoes an interesting transition. Recently, a monolayer MoS_2-based field effect transistor (FET) with HfO_2 as gate insulator has been successfully implemented [10]. These ideal properties make monolayer MoS_2 a very promising candidate for next generation FET and as optoelectronic devices [11]. This has raised enormous interest in exploring the extraordinary properties of mono layers of MoS_2.

Theoretically, there are various possibilities of energy gap manipulation in MoS_2. By reducing the layer thickness from bulk to monolayer, the indirect band gap energies in the bulk are shifted relative to the direct band gap in the monolayer limit [12]. It undergoes a transition from an indirect to direct gap exhibiting strong photoluminescence when confined in a 2D monolayer [13]. It has been suggested a way to engineer 3D semiconducting MoS_2 nanoparticles with direct band gaps as well as metallic di-chalcogenides nanowires with promising catalytic and thermoelectric properties [14]. Eellis *et al*. carried out a study using HSE screened hybrid functional and offered improvement over semi local density functional [13]. All electron calculations including spin orbit coupling were performed [15] and confirmed indirect to direct band gap transition. Electronic structure of transition metal di-chalcogenides has been studied using *ab initio* theory using Troullier-Martin norm conserving, relativistic pseudopotentials in fully separable Kleinman and Bylander form [16]. They used exchange and correlation energies within LDA.

The properties of transition metal di-chalcogenides (TMDs) not only can be tuned by varying number of layers, but also can be modified by application of external field or strain engineering. Studies [17] [18] have confirmed that applying strain is one of the best possible strategies to tune the band gap, since it neither attenuates the properties nor is inefficacious for single layers. It has been predicted that straining MoS_2 modifies the band gap energy and the carrier effective mass. Moreover, at strains larger than 1% the lowest lying band gap changes from direct to indirect [19]-[22]. It has been suggested that strain engineering of the band structure of MoS_2 could be used to increase carrier mobility of MoS_2, to create tunable photonic devices and solar cells [23] and even to control the magnetic properties of MoS_2 [19] [20]. While strain perturbs the band structure of all materials, two-dimensional materials such as MoS_2 can sustain strains greater than 11% [24] allowing exceptional control of material properties by strain engineering. In a recent study [25] the conduction band valley structure of a few layer MX_2 by close examination of temperature dependent indirect excitation emission peaks has been explored. A study on elastic constants and electronic structures of two-dimensional monolayer MoS_2 under elastic strain using first principle calculations has been made [26]. It is shown that the band gap of monolayer MoS_2 undergoes a descent trend with the increase in strain. They observed a direct to indirect transition at strain of 0.01 and semiconductor to metal transition at strain of 0.10.

With the goal of understanding the electronic properties of bulk and monolayer MoS_2 and strain engineering, we carried out *ab initio* calculations of bulk and monolayer MoS_2 using gradient corrected exchange-correlation functional in DFT framework and observed a transition from indirect to direct band gap. However if this band gap can be tuned such that a semiconductor with a lower band gap or a semiconductor to metal transition can be achieved with the application of strain, then a wide range of tunable nano device can be fabricated. In the present work, therefore we study the effects of mechanical strains on the electronic properties of monolayer of MoS_2. Our results suggest a way of band gap engineering in MoS_2.

2. Computational Details

The calculations were performed using self consistent plane wave pseudopotential total energy method based on density functional technique as implemented in Quantum Espresso code [27]. This method has been previously used to study the electronic properties of undoped and doped graphene [28] [29]. The exchange correlation potential was approximated by generalized gradient approximation using Perdew-Wang 91 functional (GGA-PW91) [30]. The atomic positions and cell parameters were fully relaxed until an energy convergence of 10^{-9} eV reached. We used wave function- and charge-density cut-offs of 70 Ryd and 300 Ryd, respectively. First, we obtained lattice constants a and c by the process of total energy minimization. Optimized structure (coordinates) was used to perform self consistent calculations with a Monkhorst-Pack [31] $8\times8\times8$ k-mesh followed by the non-self consistent calculations for band structures, density of states and partial density of states of bulk MoS_2. We used $80\times80\times80$ k-points mesh along the path Γ-K-M-Γ in the irreducible Brillouin zone to obtain the band structure with a very fine mesh points. However, for monolayer we used $8\times8\times1$ and $80\times80\times1$ Monkhorst-Pack of *k*-points respectively for sampling Brillouin zone for calculations of structural properties and electronic structure. In case of monolayer MoS_2, we created 15 Å vacuum along *Z* axis to isolate it and to prevent any interaction between the layers. The cohesive energy per atom of bulk MoS_2 was calculated as $E_{coh} = E(MoS_2) - E(Mo) - 2E(S)$, where $E(MoS_2)$ is the total energy of the unit cell of Molybdenum disulphide, $E(Mo)$ is the energy of Mo atom and $E(S)$ is the energy of S atom. The cohesive energies per atom of monolayer MoS_2 was also calculated accordingly. A uniform tensile strain ranging from 0 to 10% were applied on monolayer MoS_2 to study the change in behavior of its band gap.

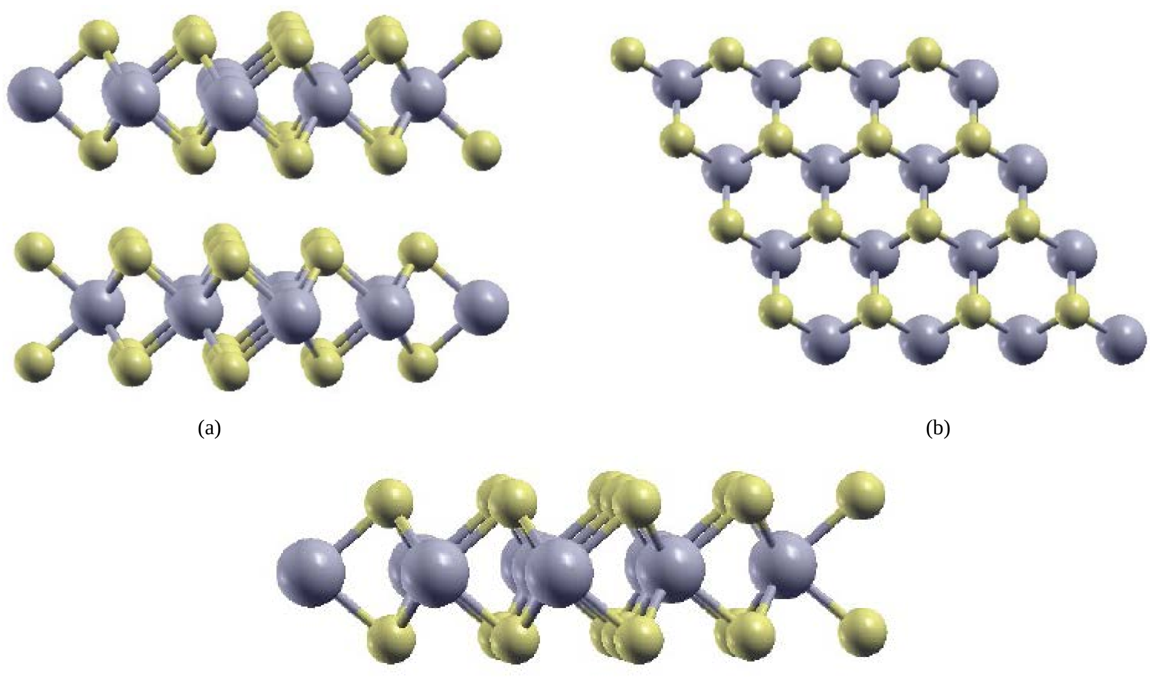
3. Results and Discussion

3.1. Structural Parameters

Molybdenum disulphide has a hexagonal structure consisting of S-Mo-S layers as shown in **Figure 1**. Bulk MoS_2 has two such layers and Mo atoms of one layer are directly above the sulphur atoms of the other layer and vice versa while monolayer MoS_2 has a single S-Mo-S layer. We have calculated the structural parameters of bulk and monolayer MoS_2 using GGA as shown in **Table 1**. The results of bulk MoS_2 have been compared with experimental data while the results of monolayer are compared with some other theoretical results. We find excellent agreements as can be seen in **Table 1**. Our calculated lattice parameters overestimate the experimental values which is an inherent feature of standard GGA functional. It is concluded that all the structural parameters calculated for monolayer MoS_2 are nearly identical to the structural parameters calculated for bulk MoS_2.

3.2. Electronic Band Structure and Density of States

The electronic band structure of bulk MoS_2 and corresponding density of states are shown in **Figure 2**. The electronic band structure and density of states can be divided into three sets of bands and states respectively, separated by gaps. In the first set, bands in electronic band structure and states in density of states around −14 eV are mainly due to 3*s* orbital of S atom separated by large gap from second set below Fermi energy in which 3*p* orbital of S and 4*d* orbital of Mo are mainly contributing and show strong hybridization. Third set above the Fermi energy in which main contribution is due to 4*d* orbital of Mo is separated by band gap from second group



(a) (b) (c)

Figure 1. (a) Side view of bulk MoS_2; (b) Top view of bulk and monolayer MoS_2; and (c) Side view of mono layer MoS_2. The Mo-atoms are denoted by gray and S-atoms by pale yellow balls.

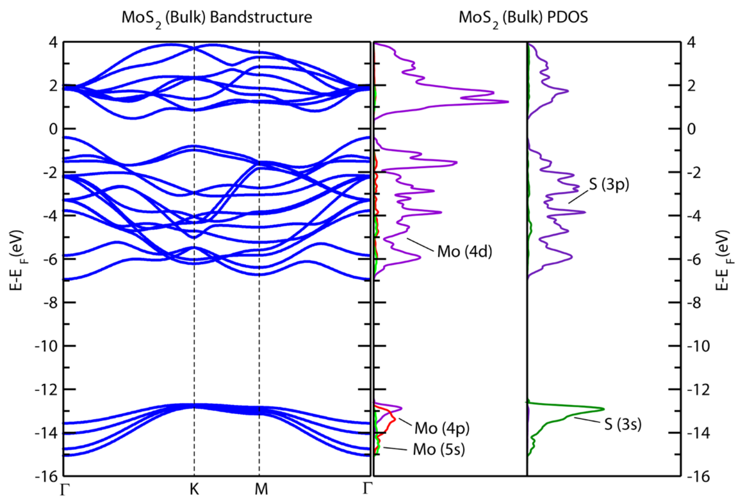


Figure 2. Calculated band structure (left panel) and orbital-projected density of states (PDOS) on Mo (middle panel) and S atoms (right panel) in bulk MoS_2.

Table 1. Calculated structural parameters of bulk MoS_2 and mono layer MoS_2 using GGA. The available results have also been given for the purpose of comparison.

Properties	Bulk-MoS_2	Monolayer MoS_2
Lattice constant (*a*) [angstrom]	3.19 (present calculation) 3.16 (Ref [1])	3.195 3.20 (Ref [32]) 3.23 (Ref [16])
c/*a* ratio	3.86 (present calculation) 3.89 (Ref [1])	
Cohesive energy (eV/atom)	4.960	4.979

below Fermi energy. A comparative band structure of MoS_2 bulk and its monolayer and bilayer are shown in **Figure 3**. The bands on each side of the band gap are derived mainly from the 4*d* states of Mo and 3*p* states of S in bulk, bilayer and monolayer MoS_2. The bands around the band gap are relatively flat, as expected from the *d*-character of electron states at these energies.

For bulk MoS_2 the valence band maximum is at high-symmetric Γ-point and conduction band minima is in between Γ- and K-points, revealing indirect band semiconductor as can be seen in **Figure 3**. If we compare the band structure of bulk and monolayer MoS_2, we observe that the band edge near Γ point has been shifted up by around 0.7 eV. In case of monolayer, at Λ and Σ point the band edge shifted up in such a way that the conduction band minima occurs at K-point. For monolayer the valence band maxima and conduction band minima are both at high-symmetric K-point revealing direct band gap semiconductor as can be seen in **Figure 3**. Thus there is a transition from indirect band gap to direct band gap as we go from bulk MoS_2 to its monolayer. A PDOS comparison of bulk and mono layer MoS_2 (as shown in the **Figure 4**) reflects that the states are essentially due to d_{z2} and degenerate states d_{xy} and $d_{x2\text{-}y2}$. The states $d_{x2\text{-}y2}$ and d_{xy} are degenerate in case of bulk while little bit separating in monolayer. The calculated and measured band gap for mono layer MoS_2 and bulk are shown in **Table 2**. Our calculated band gaps are in good agreements with other theoretical values.

3.3. Tuning Electronic Properties by Biaxial Strain

To study the effect of strain on the electronic properties of monolayer MoS_2, we first relaxed the atomic position and obtained the optimized geometry. We apply the uniform strain (ε) to the monolayer MoS_2 in the range 0.0 - 0.10. The strained atomic structure is achieved by enlarging the hexagonal lattice a_0 with an increment of εa_o. Similarly the atomic structure is fully optimized and the band structure is calculated. As for strained structure of MoS_2, the band gap versus strain is shown in the **Figure 5**. The band gap is monotonic as the strain increases.

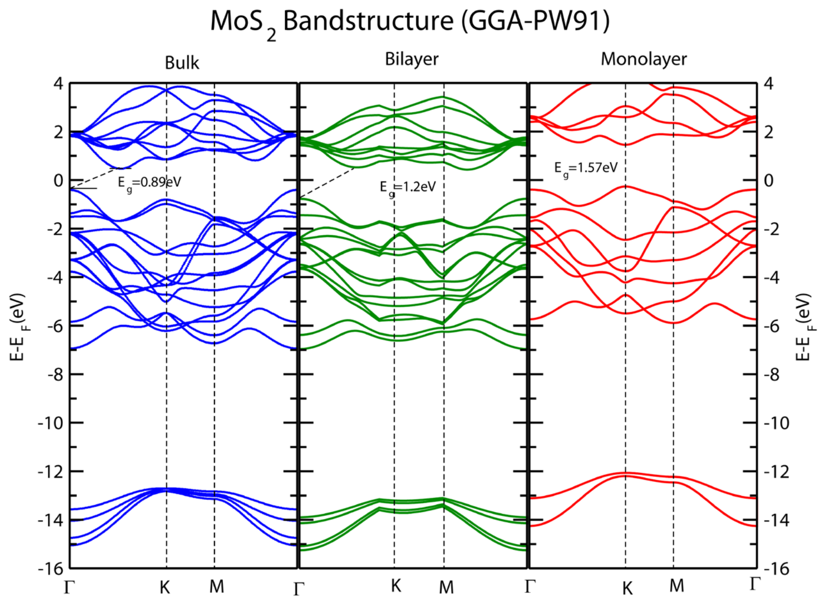


Figure 3. Calculated band structure of bulk (left), bilayer (middle) and monolayer (right) of MoS_2 at high-symmetric points in the irreducible Brillouin zone. The position of valence band maxima, conduction band minima and the band gap (E_g) are indicated. For monolayer MoS_2 the direct band gap occurs at K-point, unlike in other cases.

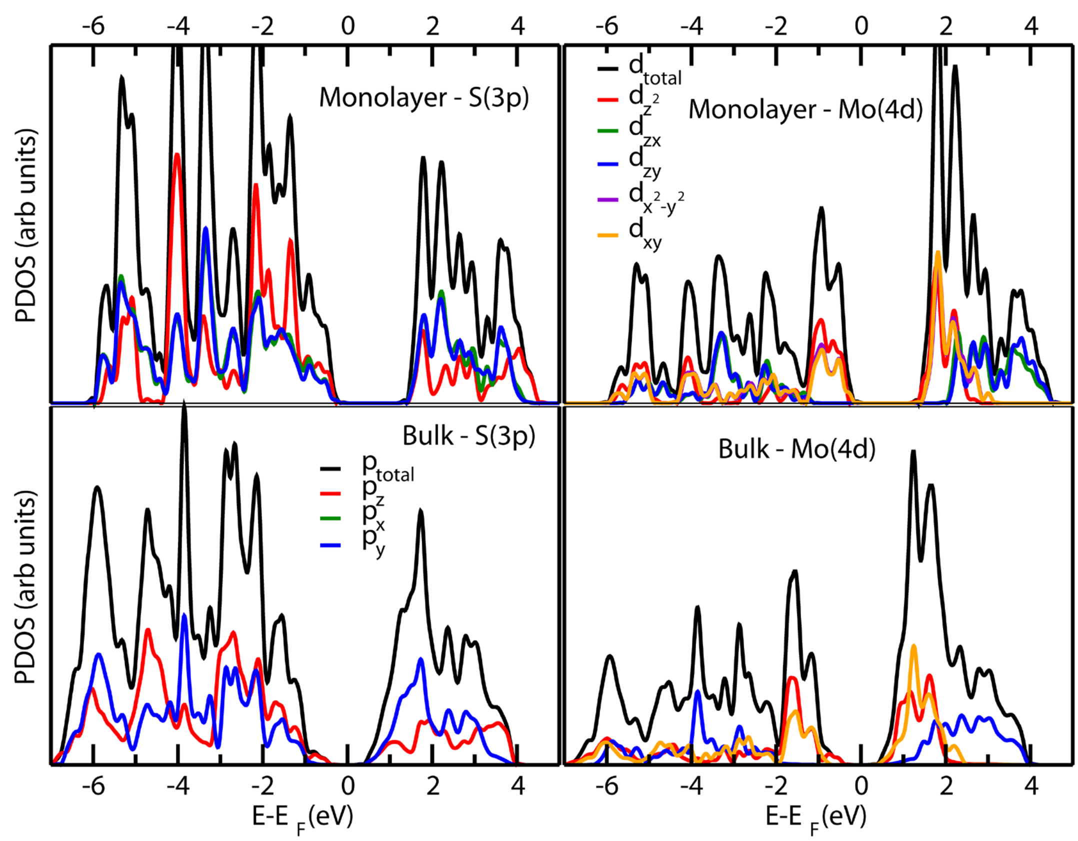


Figure 4. Calculated projected density of states (PDOS) of bulk and monolayer of MoS_2 are shown for Mo(4*d*) and S(3*p*) states. The legends for the *p*- and *d*-orbitals are similar for the monolayer and bulk.

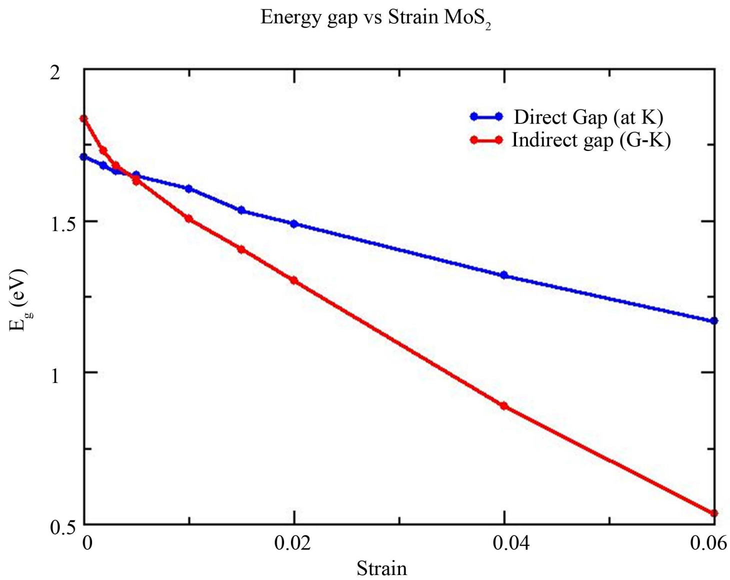


Figure 5. The variation of band gap energy with strain of monolayer MoS_2.

Table 2. Energy gaps (eV) for bulk MoS_2 and monolayer MoS_2.

	Bulk MoS_2	Monolayer MoS_2
Present calculation	0.89	1.57
Experimental value	1.23 (Ref [6]) 1.29 (Ref [35])	1.80 (Ref [6])
Theoretical results	0.7 (Ref [36]) 1.05 (Ref [16]) 1.15 (Ref [37])	1.55 (Ref [16]) 1.70 (Ref [33]) 1.78 (Ref [34]) 1.9 (Ref [38])

While the strain reaches 0.06, the indirect band gap vanishes. We observe a cross over in the figure. Upon ε = 0.0, the monolayer MoS_2 shows a behavior of semiconductor with direct gap, at $\varepsilon = 0.005$ it has direct (at K) and indirect (Γ-K) band gap of almost equal amount. These results are interesting. Not only the band gap of monolayer MoS_2 can be tuned by uniform strain, but also direct to indirect and semiconductor to metal transitions are controlled.

Very recently, in a paper by Das *et al.* [39] the strain driven direct to indirect transition in the band gap of MoS_2 and ZnO has been theoretically studied. They have found such transition in MoS_2 to occur at strain 0.83%, close to our calculated value of 0.5%.

4. Conclusion

In summary, we studied the structural and electronic properties of MoS_2 using plane wave pseudopotential method under GGA scheme based DFT calculations. Electronic band structure and density of states calculation show many similarities between monolayer-MoS_2 and bulk-MoS_2 except the nature of the band gap which is found direct for monolayer-MoS_2 as compared to indirect for bulk-MoS_2. This observation is consistent with the theoretical prediction of indirect to direct band gap transition in going from bulk to monolayer. Such behavior, arising from *d*-orbital related interaction in MoS_2, may also arise in other layered transition metal di-chalcogenides. A further variation in band gap has been observed in MoS_2 monolayer on applying strain. It points out a new direction of band engineering, hence such capability can lead to engineering novel behaviors and holds promise for new applications.

Acknowledgements

Part of the calculations was performed on High-Performance cluster computer of SNBNCBS, Kolkata for which authors are thankful. SA acknowledges valuable discussion with T.P. Kaloni. This work was initiated at S.N. Bose National Centre, when one of us (SA) was a visiting scientist under the Extended Visitors Linkage Programme (EVLP), which is gratefully acknowledged.

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