Journal of Electron Devices, Vol. 20, 2014, pp. 1746-1754

© JED [ISSN: 1682 -3427]

Journal of Electron Devices
www.jeldev.org

EFFECT OF NANORIBBON WIDTH AND STRAIN ON THE ELECTRONIC PROPERTIES OF THE WS2 NANORIBBON

Bahniman Ghosh [1,2] and Aayush Gupta [2]

[1]Microelectronics Research Center, 10100, Burnet Road, Bldg. 160, University of Texas at Austin, TX, 78758
[2]Department of Electrical Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India
bghosh@utexas.edu)

Received 2-07-2014, online 2-09-2014

ABSTRACT
Materials of the general form MX2 (transition metal dichalcogenides) have generated a lot of interest recently. They can form nanoribbons like graphene and such nanoribbons have versatile electronic structures and can be metallic or semiconducting by changing the edges of the ribbon. The electronic properties of such materials are not fully understood till now. In this paper we investigate one such material, Tungstenite (WS2). We investigate the band-structure of the zigzag and the armchair nanoribbon. We observe the direct bandgap in the nanoribbons as opposed to indirect bandgap in the bulk material. Also by changing the edge orientation of the nanoribbon from armchair to zigzag, the properties change considerably with zigzag as metallic and armchair as semiconducting. Further we investigate the effect of increasing the ribbon width and the effect of uniaxial and biaxial strain on the nanoribbon.

I. INTRODUCTION

In 2004, the discovery of graphene [1] triggered the possibility of the existence of the layered structures of other inorganic materials. Transition Metal Dichalcogenides (TMD) have layered structures and they have a general form of MX2.They have received significant attention recently because of their unique characteristics [2]. The layered structure consist of the X-M-X stacks which are held together by van der Waal forces. They have rhombohedral or hexagonal symmetry depending upon the composition of the material [3]. Because of the weak interlayer forces these structures can exist in monolayer, bilayer, trilayer and other structures. WS2 and Mos2 nanosheets have been synthesized through various processes like exfoliation, molybdenum sheets sulfurization and sulfurization of WO_3 films [4-11].

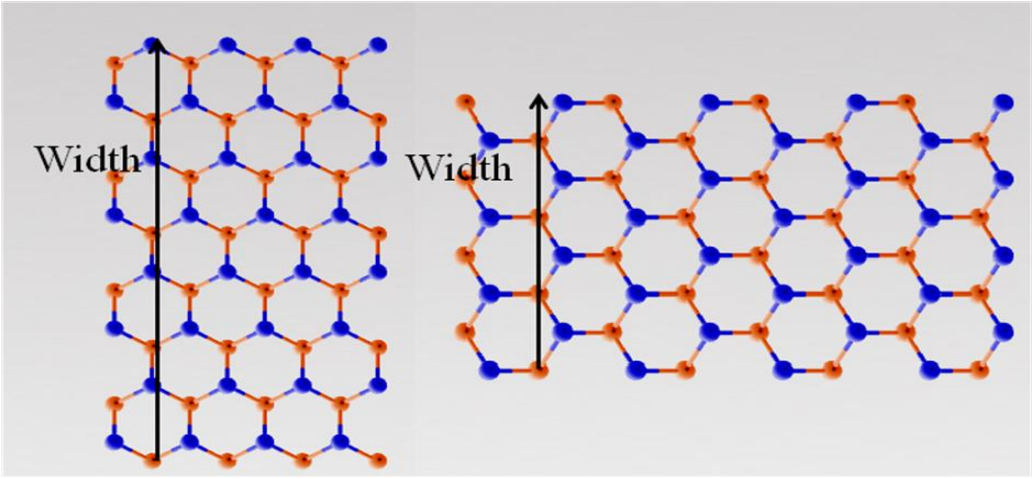
In WS2, each W atom is bonded to six S atom and each S atom is bonded to 3 W atom. The monolayer structure of WS2 is reported to have a bandgap of 1.8 eV [12-14] while some other report the bandgap of about 2.1 eV [15]. WS2 nanoribbons have some peculiar properties for e.g. when they are doped with Nb or Ta atoms they show metallic behaviour as compared to semiconducting behaviour [12]. Graphene heterostructure using WS2 as a vertical transport barrier shows an ON/OFF ratio of 10^6 at room temperature [16]. A strong photoluminescence is observed in the WS2 monolayer at the room temperature and this arises because of the transition of WS2 from Indirect band-gap material in bulk to direct band-gap material in the monolayer [11].

Low dimensional material can exhibit very different properties than their bulk counterpart and a lot of studies have been done on the bulk. Therefore there is a need of studying the low dimensional

structures like nanoribbon in great detail. For making the nano devices from WS2 it is critical that we have to understand the properties of 1D WS2 nanoribbon.

We have studied the properties of the WS2 nanoribbon in this work. WS2 nanoribbon can exist in two states depending upon the edge orientation i.e. zigzag and armchair. We have studied both the types of nanoribbon. Apart from that, for the semiconducting armchair nanoribbon, we have studied the dependence of bandgap on the width of the nanoribbon. and also the dependence of the bandgap on the uniaxial and biaxial strain on the ribbon.

Figure 1 shows the basic structure of the zigzag and armchair nanoribbon. The width of the nanoribbon which can also be depicted in terms of N_a(no of atoms in the width direction) is shown in the figure1.



a) b)

Figure 1: a) Zigzag nanoribbon with the vertical line marking the direction of width b) Armchair nanoribbon with vertical line marking the direction of width

II. METHODOLOGY

In this work we have utilized the Atomistix Toolkit (ATK) to carry out the bandstructure calculation for the different types of nanoribbon [17-19]. Self consistent calculations with Density functional theory [DFT] were used to calculate the bandstructures for the above type of nanoribbon. To remove the interaction between neighbouring periodic ribbon a vacuum spacing of 10 Å has been used. Sampling of the Brillouin zone (BZ) was done with the Monkhorst-Pack scheme [20] and for the zigzag nanoribbon 1X1X27 k points were used and for armchair nanoribbon 1X1X15 K points were used. For approximating exchange correlation energy generalized gradient approximation (GGA) [21,22] has been used.

III. RESULTS AND DISCUSSIONS

Bulk form of WS2 exists as a semiconductor with a bandgap of 1.35 eV which is in close approximation to the other works in literature [15]. The bandstructure of bulk WS2 is shown in figure 2 and we can clearly see that the bandgap is indirect in bulk WS2.

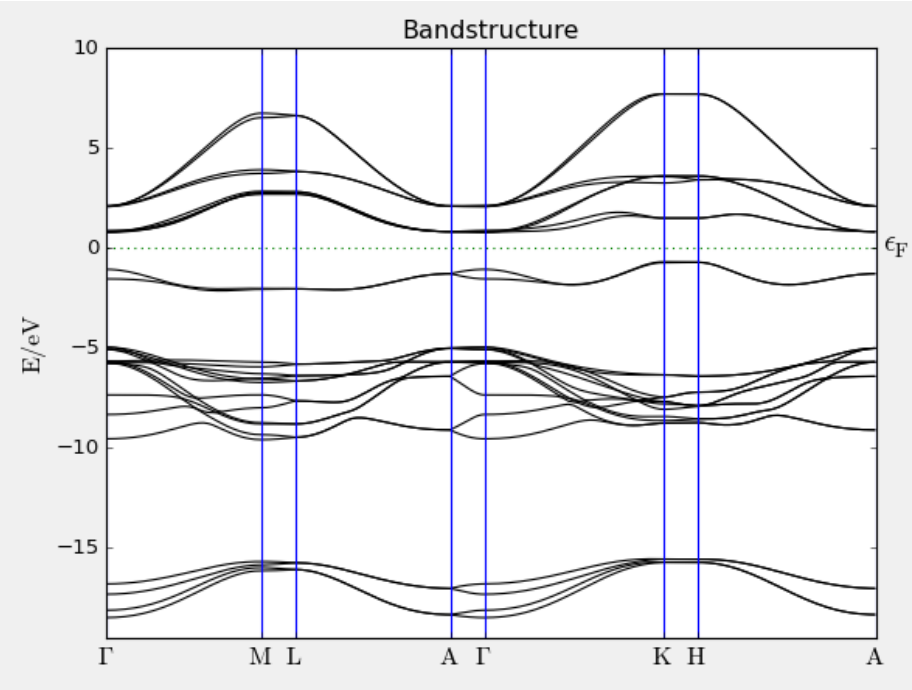


Figure 2: Calculated bandstructure of the Bulk WS2

When the bulk structure is confined to the smaller dimensions such as monolayer structure, we observe a change from indirect bandgap in bulk to the direct bandgap in the monolayer structure. Figure 3 shows the bandstructure of the WS2 monolayer. We can clearly see that there is a direct bandgap in the monolayer structure and the direct bandgap is 1.86 eV which is in close approximation to the other works done in literature [23,24].The valence band maximum and conduction band minimum lies at the k point symmetry.

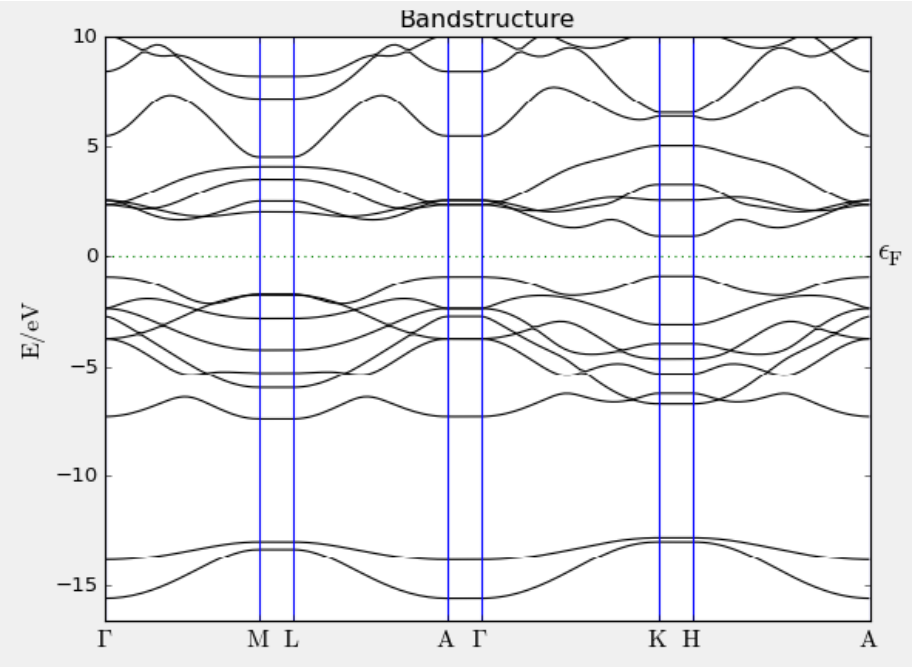


Figure 3: Calculated bandstructure for the Monolayer WS2

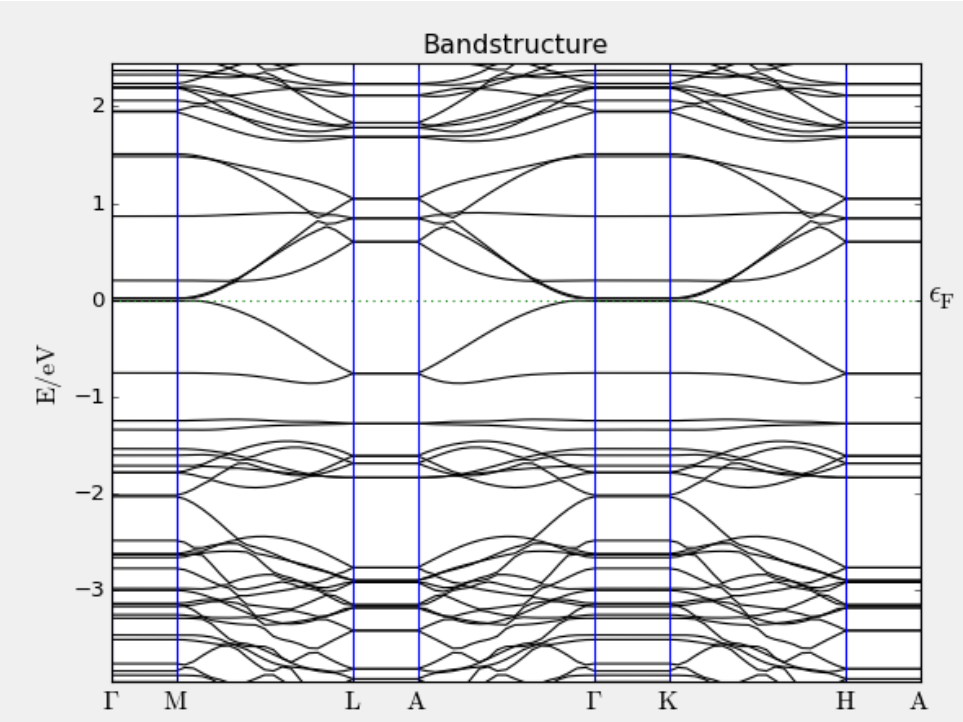


Figure 4: Calculated bandstructure for the Zigzag Nanoribbon of WS2

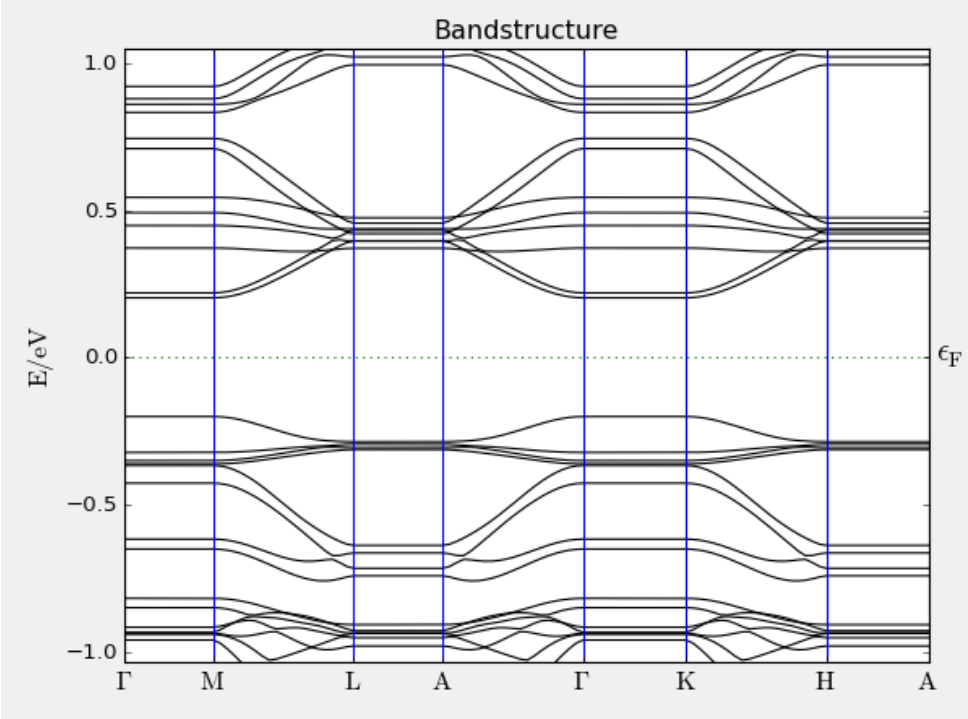


Figure 5: Calculated bandstructure for the Armchair Nanoribbon of WS2

Nanoribbons of WS2 exist in two states depending upon the edge orientation. Figure 4 shows the bandstructure of the zigzag nanoribbon. We have taken the width of the nanoribbon of N_a=8 and 1x1x27 k points are used for the calculation. We can see from the bandstructure that the valence band and the conduction band meet at the Fermi level and hence the bandgap is quite low and we can consider the nanoribbon as showing the metallic behaviour.

The second state in which WS2 nanoribbon can exist according to the edge state is armchair nanoribbon. Figure 5 shows the bandstructure of the armchair nanoribbon for WS2. Number of atoms along the width of the ribbon is 10 (N_a). The figure shows that armchair nanoribbon has a bandgap as opposed to the zigzag state and the bandgap is direct. Thus by changing the state of the ribbon from zigzag to armchair we can get different electronic properties in WS2 nanoribbon.

Next we studied the effect of ribbon width on the bandgap of WS2. The width of the ribbon is shown in terms of number of atoms in the width direction as shown in Figure 1. We changed the width of the ribbon from 8 atoms to 30 atoms in the width direction. The effect of width is shown in figure 6 with bandgap on the y axis and number of atoms in width direction on x axis.

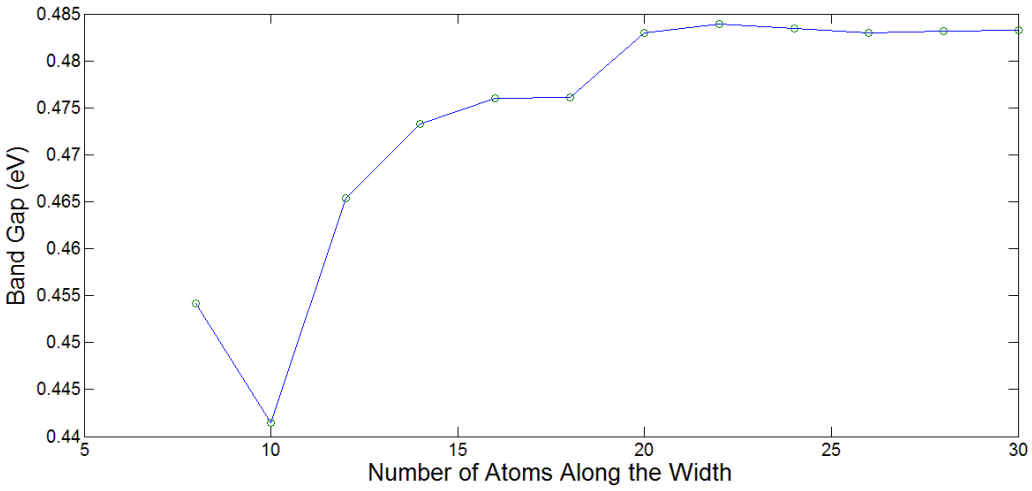


Figure 6: Variation of bandgap with nanoribbon width (number of atoms in width direction)

From the graph we can see that on increasing the width the bandgap rises with occasional fluctuations and finally converges to a value of 0.483 eV.

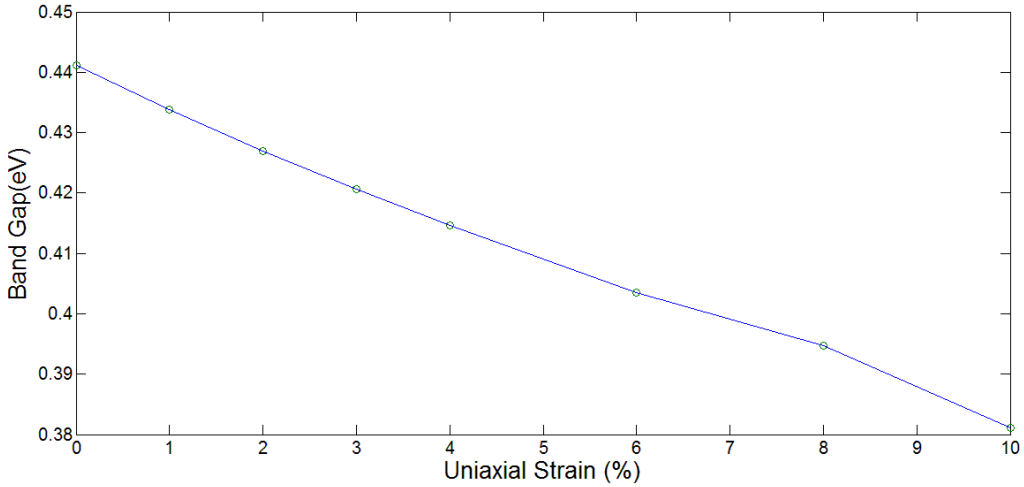


Figure 7: Variation of Bandgap with Uniaxial strain in the direction of nanoribbon

Due to the widespread usage of the electronic properties, materials width tunable electronic properties find much more usability. Therefore it is very necessary to understand if we can change the properties of a material by some external means. One of such external means is the mechanical stress that can be

applied to the material. Hence we also studied the effect of external strain on the bandgap of WS2. We applied the unidirectional strain in the direction of nanoribbon and also bidirectional strain in the plane of nanoribbon. In the case of uniaxial strain the lattice constants are changed only in the direction of nanoribbon while in biaxial strain lattice constants are changed in the plane of nanoribbon. We have applied tensile strength in both the cases.

For calculations we have taken WS2 armchair nanoribbon with N_a=10 and varied the strain from 0 % to 10 %. In figure 7 the strain is marked on the x axis and bandgap on the y axis. As we can see from the graph that by increasing tensile strength on nanoribbon, the bandgap decreases. Also the decrease is almost linear with the applied strain on the ribbon.

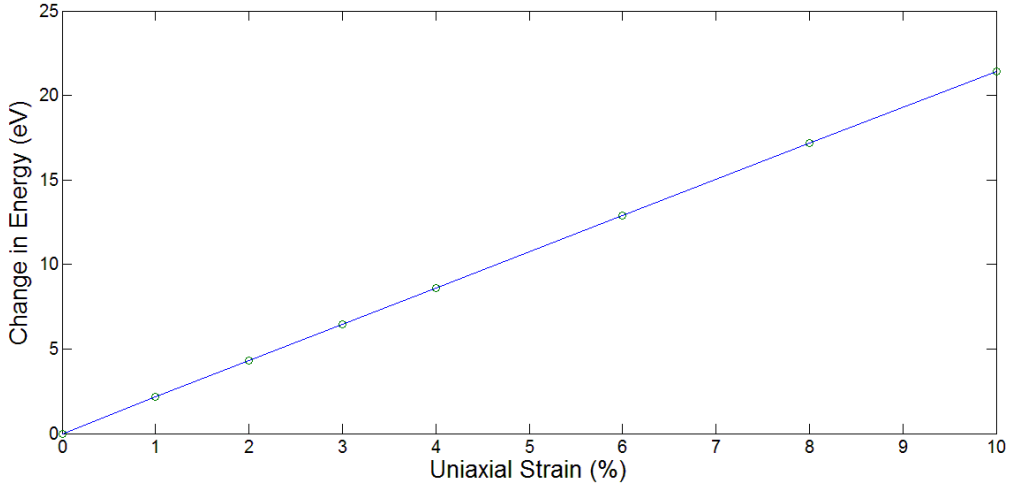


Figure 8: Variation of change in energy with the uniaxial strain.

Figure 8 shows the variation of change in energy with the uniaxial strain in the direction of ribbon. We have taken the base energy of N_a=10 WS2 armchair nanoribbon which is under no strain. From the graph we can see that the energy change increases linearly with the applied strain.

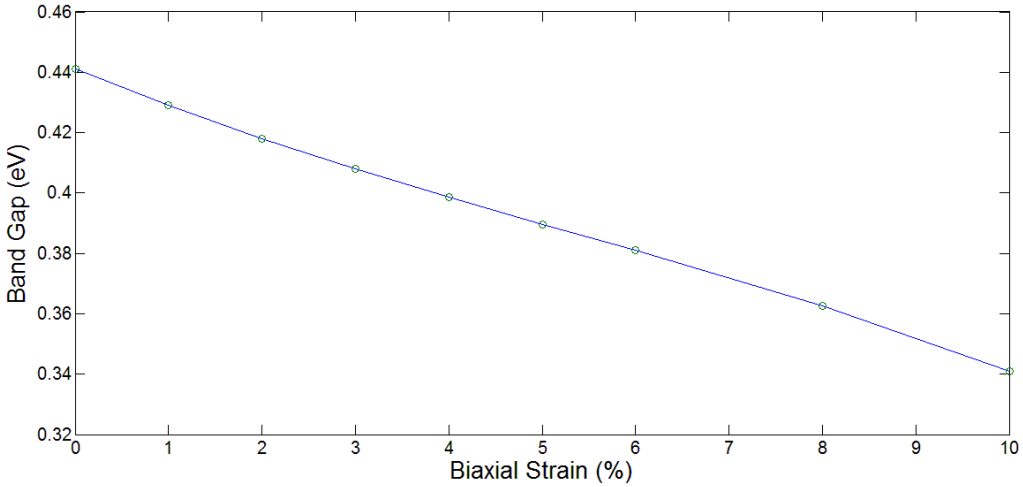


Figure 9: Variation of Bandgap with Biaxial strain in the direction of nanoribbon

Next we investigate the change in electronic property of material with biaxial strain. We have varied the strain from 0% to 10 % (x% biaxial strain means both the directions undergo same amount of

strain i.e. x%). Figure 9 shows the result. As in the case of uniaxial strain here also the band gap decreases with uniaxial strain. Here also the nature of decrease is linear. Figure 10 shows the change in energy with applied biaxial strain. As in the case of uniaxial strain, the base energy is taken of the N_a=10 WS2 armchair nanoribbon. The energy change increases linearly with the biaxial strain. All the bandgap in case of increasing width and applied strain are direct in nature.

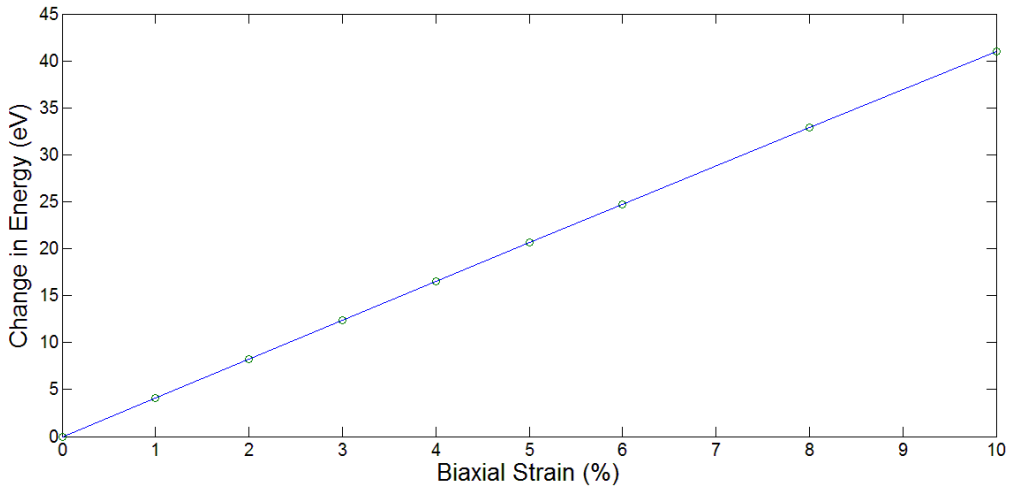


Figure 10: Variation of change in energy with the biaxial strain.

IV. CONCLUSION

In this work we studied the electronic property of the layered material WS2. As confirmed by previous literature, the bulk WS2 shows a bandgap of 1.3 eV which is indirect in nature. As we confine the bulk WS2 monolayer the bandgap changes its nature from indirect to direct and increases to 1.8 eV. After that we further confined it to the nanoribbon structure. The nanoribbon of WS2 exist in two states depending upon the edge orientation i.e. Zigzag and Armchair. The zigzag nanoribbon is essentially metallic in nature whereas armchair nanoribbon has intrinsic bandgap which is less than the monolayer bandgap. We studied the effect of nanoribbon width on the nature of material and found out that by increasing the width the bandgap increases with some fluctuations and finally converges at a value of 0.483 eV for N_a>25. The zigzag nanoribbon remains metallic independent of the nanoribbon width. Next we studied the effect of uniaxial and biaxial strain on the armchair nanoribbon. In both the cases of strain, the bandgap decreases with the increase in strain and nature of decrease is essentially linear. The energy of the ribbon also increases linearly in both the cases of strain. All these properties can be used to tune the bandgap of WS2 nanoribbon which can find a variety of applications in the electronic devices.

References

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, "Electric Field Effect in Atomically Thin Carbon Films", Science **306**, 666 (2004).

[2] S. Z. Butler, S. M. Hollen, L. Cao, Y. Cui, J. A. Gupta, H. R. Gutierrez, T.F. Heinz, S. S. Hong, J. Huang, A. F. Ismach, E. Johnston-Halperin, M.Kuno, V. V. Plashnitsa, R. D. Robinson, R. S. Ruoff, S. Salahuddin, J.Shan, L. Shi, M. G. Spencer, M. Terrones, W. Windl, and J. E. Goldberger," Progress, Challenges, and Opportunities in Two-Dimensional Materials Beyond Graphene", ACS Nano **7**, 2898 (2013).

[3] Qing Tang, Zhen Zhou, Graphene-analogous low-dimensional materials, "Graphene-analogous low-dimensional materials", Progress in Materials Science **58**, 1244-1315 (2013).

[4] J. N. Coleman, M. Lotya, A. O'Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, I. V. Shvets, S. K. Arora, G. Stanton, H. Y. Kim, K. Lee, G. T. Kim, G. S. Duesberg, T. Hallam, J. J. Boland, J. J. Wang, J. F. Donegan, J. C. Grunlan, G. Moriarty, A. Shmeliov, R. J. Nicholls, J. M. Perkins, E. M. Grieveson, K. Theuwissen, D. W. McComb, P. D. Nellist, and V. Nicolosi, "Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered", Materials,Science **331**, 568 (2011).

[5] G. Cunningham, M. Lotya, C. S. Cucinotta, S. Sanvito, S. D. Bergin, R. Menzel, M. S. P. Shaffer, and J. N. Coleman, "Solvent exfoliation of transition metal dichalcogenides: dispersibility of exfoliated nanosheets varies only weakly between compounds", ACS Nano **6**, 3468 (2012).

[6] S. F. Wu, C. M. Huang, G. Aivazian, J. S. Ross, D. H. Cobden, and X. D. Xu, "Vapor–Solid Growth of High Optical Quality MoS_2 Monolayers with Near-Unity Valley Polarization", ,ACS Nano **7**, 2768 (2013).

[7] H. Li, G. Lu, Y. L. Wang, Z. Y. Yin, C. X. Cong, Q. Y. He, L. Wang, F. Ding, T. Yu, and H. Zhang, "Mechanical Exfoliation and Characterization of Single- and Few-Layer Nanosheets of WSe_2, TaS_2, and $TaSe_2$, "Smal **9**, 1974 (2013).

[8] Matte H. S. S. R., Gomathi A., Manna A. K., Late D. J., Datta R., Pati S. K., Rao C. N. R., "MoS2 and WS2 analogues of grapheme", Angewandte Chemie-International Edition **49**, 4059-4062 (2010).

[9] Eda G., Yamaguchi H., Voiry D., Fujita T., Chen M. W., Chhowalla, M., "Photoluminescence from Chemically Exfoliated MoS_2", Nano Letters **11** ,5111-5116 (2011).

[10] Zhan, Y.; Liu, Z.; Najmaei, S.; Ajayan, P. M.; J., L., "Large-Area Vapor-Phase Growth and Characterization of MoS_2 Atomic Layers on a SiO_2 Substrate", Small **8**, 966–971 (2012).

[11]Humberto R. Gutiérrez, Nestor Perea-López, Ana Laura Elías, Ayse Berkdemir, Bei Wang, Ruitao Lv, Florentino López- Urías, Vincent H. Crespi, Humberto Terrones, and Mauricio Terrones, éLarge-Area Vapor-Phase Growth and Characterization of MoS_2 Atomic Layers on a SiO_2 Substrate", Nano Letters **13**, 3447-3454 (2013).

[12] Y. Ding, Y. L. Wang, J. Ni, L. Shi, S. Q. Shi, and W. H. Tang, "First principles study of structural, vibrational and electronic properties of graphene-like MX_2 (M=Mo, Nb, W, Ta; X=S, Se, Te) monolayers", Physica B **406**, 2254 (2011).

[13] Y. D. Ma, Y. Dai, M. Guo, C. W. Niu, J. B. Lu, and B. B. Huang, "Electronic and magnetic properties of perfect, vacancy-doped, and nonmetal adsorbed $MoSe_2$, $MoTe_2$ and WS_2 monolayers", Phys. Chem. Chem. Phys. **13**, 15546 (2011).

[14] L. T. Liu, S. B. Kumar, Y. Ouyang, and J. Guo, "Performance Limits of Monolayer Transition Metal Dichalcogenide Transistors", IEEE Trans. Electron Devices **58**, 3042 (2011).

[15] A. Kuc, N. Zibouche, and T. Heine, "Influence of quantum confinement on the electronic structure of the transition metal sulfide TS_2", The Phys. Rev. **B 83**, 245213 (2011).

[16] T. Georgiou, R. Jalil, B. D. Belle, L. Britnell, R. V. Gorbachev, S. V. Morozov, Y. J. Kim, A. Gholinia, S. J. Haigh, O. Makarovsky, L. Eaves, L. A. Ponomarenko, A. K. Geim, K. S. Novoselov, and A. Mishchenko, "Vertical field-effect transistor based on graphene–WS_2 heterostructures for flexible and transparent electronics", Nat. Nanotechnol. **8**, 100 (2013).

[17] Atomistix ToolKit **version 13.8**, QuantumWise A/S, Denmark.

[18] M. Brandbyge, J.-L. Mozos, P. Ordejón, J. Taylor, and K. Stokbro, Density-functional method for nonequilibrium electron transport", The Phys. Rev. **B 65**, 165401 (2002).

[19] M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, "The SIESTA method for *ab initio* order-*N* materials simulation", J. Phys. Condens. Matter 14, 2745 (2002).

[20] H. J. Monkhorst and J. D. Pack, "Special points for Brillouin-zone integrations", ThePhys. Rev. **B 13**, 5188 (1976).

[21] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, and C. Fiolhais., Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation", The Phys. Rev. **B 46**, 6671 (1992).

[22] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, and C. Fiolhais., "Erratum: Donor transition energy in GaAs superlattices in a magnetic field along the growth axis", The Phys. **Rev. B 48**, 4978 (1993).

[23] Hui Zhang, Xi-Bo Li, and Li-Min Liu, "Tunable electronic and magnetic properties of WS2 nanoribbons", Journal of Applied Physics "114, 093710 (2013).

[24] Yandong Ma, Ying Dai,Meng Guo, Chengwang Niu, Jibao Lu and Baibiao Huang, "Electronic and magnetic properties of perfect, vacancy-doped, and non-metal adsorbed $MoSe_2$, $MoTe_2$ and WS_2 monolayers", Phys. Chem. Chem. Phys. **13**, 15546-15553 (2011).