Effect of Local field and Polarization on Optical Properties of $Mo_{1-x}W_xS_2$ Alloy Structure: A first-principle study

Akhilesh Dhar Dwivedi, Bramha P.Pandey

Abstract— Optical properties of $Mo_{1-x}W_xS_2$ alloy structure have been studied in this paper. The optical properties calculation is evaluated using DFT (density functional theory) simulations considering polarization in parallel and perpendicular to the plane of alloy structure. We observed that the optical properties like EELS (electron energy loss function), refractive index, and absorption spectrum are highly relying on light polarization directions. The effect of local field is found to be negligible which is the case with the semiconductors with uniform charge density. High intensity of peaks and wider range of absorption spectra makes this alloy structure useful in the field of optoelectronic system.

Index Terms— Alloy structure, DFT calculation, Local field effect, Optical properties, Polarization.

1 Introduction

SINCE the discovery of graphene, 2D materials have become more popular among researchers because of its excellent properties. But, zero energy band gap is the biggest drawback of graphene hence it is quite difficult to use graphene in optoelectronic devices. Along with resolving these shortcomings of graphene, researchers have also searched alternate 2D materials like TMDs (transition metal di-chalcogenides), SiC (silicon carbide), hBN (hexagonal boron nitride), etc [1], [2], [3], [4], [5], [6]. Unlike graphene, monolayer of TMDs are defined as semiconductors having natural bandgap [7]. One more advantage of TMDs over graphene is that bulk TMDs layers are interlinked by weak van der Waals forces, hence it's easier to get monolayers by simple methods.

Heterostructures of TMDs are quite attractive for generating semiconducting properties of corresponding materials, which thereby leads to fulfillment of novel optoelectronic and electronic devices. Similarly, for realization of probable prospects of these materials, we have to convey TMDs bandgap engineering whereas alloying of materials can be modified by changing bandgaps. Various techniques have been implied for the representation of TMDs derived alloys. Using chemical vapor transport, Chen et al. developed monolayers of $Mo_{1-x}W_xS_2$ along with mechanical exfoliation of single-crystal $Mo_{1-x}W_xS_2$ [4], on the other hand, Gong et al. showed the direct growth of mono layer and bilayers of $MoS_{2(1-x)}Se_{2x}$ using single step by CVD [5]. Lately, comparable alloys have been predicted in the zone of heterojunction inter-layers between TMDs heterostructure [1],[2],[8].

The scope of 2D materials can be improved by forming alloy structures instead of their elemental form. This way we can get better results along with keeping the performance of the primitive 2D materials. Due to the flexibility of tuning the bandgap of such alloy structures, these structures could found several applications in optoelectronic devices. Higher values of absorption in alloy structures as compared to the pure single crystal materials is also an added advantage for applications like solar cells and photodetectors [9],[10],[11],12].

In many research works it has been found that $WS_2/MoSe_2$ heterostructure can be used in applications like solar cells and photodetectors [8]. Heterostructures like WS_2/MoS_2 or $WS_2/MoSe_2$ have been investigated thoroughly in recent times [13], [14]. In my area of interest, certain optical properties of MoS_2/WS_2 alloy structure are investigated in the presence of local field effect and different plane of polarization using DFT calculations. Our main focus was to analyze the different optical properties of this alloy structure like refractive index, dielectric function, extinction coefficient, EELS and absorption coefficient in the presence of local field.

2 Computional Method

The optical properties of $Mo_{1-x}W_xS_2$ alloy structure have been investigated in this work using YAMBO code for the accurate calculation of properties. Since this code depends on the previous DFT level calculations, it is interfaced with QUANTUM ESPRESSO simulation package. Also, PBE (Perdew-Burke-Ernzerhof) functional dependent on GGA (Generalized gradient approximation) and RPA (random phase approximation) has been used in this work. In this calculation, we have taken a k-point mesh of 10x10x1 Monkhorst-pack for the sampling of the first Brillouin Zone (BZ) for optical properties. This MoS_2/WS_2 alloy heterostructure has total energy of -51328.496849 (eV) in its relaxed state. An addition of 10 Å vacuum was implied in the perpendicular direction (z-axis) of the 2D periodic plane of alloy structure to counter the interaction between the two neighboring periodic slabs.

In this work, we have focused mainly on the basic optical properties of the MoS_2/WS_2 alloy structure. The general form of dielectric function is complex in nature and given by the expression $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, where $\varepsilon_1(\omega)$, $\varepsilon_2(\omega)$ represents the real and imaginary part respec-

- *Akhilesh Dhar Dwivedi is currently pursuing M.Tech form MMM University of technology Gorakhpur ,Uttar Pradesh. E-mail: akhildwivedi96@gmail.com*
- *Bramha P.Pandey is currently Assistant Professor at MMM University of technology Gorakhpur ,Uttar Pradesh*

tively. The real component of the complex dielectric function can be obtained by using Kramers-Kronig relation. The imaginary part $\varepsilon_2(\omega)$ is given by

$$\varepsilon_2^{ij}(\omega) = \frac{4\pi^2 e^2}{Vm^2\omega^2} \sum_{knn'\sigma} \langle kn\sigma | p_i | kn'\sigma\rangle\langle kn'\sigma | p_j | kn\sigma\rangle \times f_{kn}(1 - f_{kn'})\delta(E_{kn'} - E_{kn} - h\omega) \quad (1)$$

Where V depicts unit cell volume, ω is the incident photon frequency, charge and mass of electron is represented by e and m respectively, $\langle | kn\sigma\rangle$ as wave function with the eigen value E_{kn} and f_{kn} as fermi energy distribution function.

Similarly, the coefficient of absorption α(ω) and EELS L(ω) can be obtained from the real and imaginary components of ε(ω) as shown below.

$$\alpha(\omega) = \frac{\sqrt{2}\omega}{c}\sqrt{\left\{\sqrt{\left(\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)\right)}\right\} - \varepsilon_1(\omega)} \quad (2)$$

$$L(\omega) = -Im(\varepsilon^{-1}) = \frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega)+\varepsilon_2^2(\omega)} \quad (3)$$

The real and imaginary part of complex dielectric function ε(ω) can also be expressed in terms of refractive index and extinction coefficient.

$$\tilde{n}(\omega) = n(\omega) + ik(\omega) \quad (4)$$

Where, $\tilde{n}(\omega)$ = complex refractive index
$n(\omega)$ = real refractive index
$k(\omega)$ = extinction coefficient

$$n(\omega) = \frac{1}{\sqrt{2}}\sqrt{\left\{\sqrt{\left(\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)\right)}\right\} + \varepsilon_1(\omega)} \quad (5)$$

$$k(\omega) = \frac{1}{\sqrt{2}}\sqrt{\left\{\sqrt{\left(\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)\right)}\right\} - \varepsilon_1(\omega)} \quad (6)$$

The relation between absorption coefficient α(ω) and extinction coefficient $k(\omega)$ is expressed as

$$\alpha(\omega) = \frac{2\omega\, k(\omega)}{c} \quad (7)$$

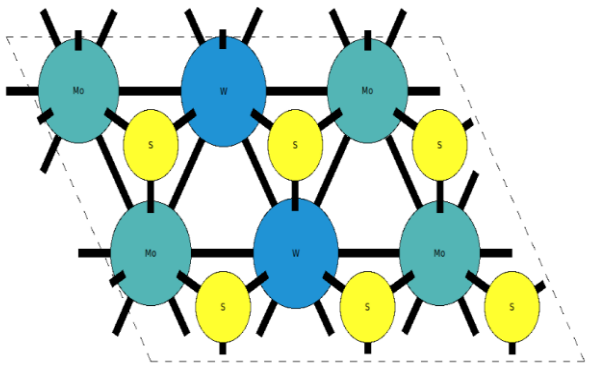

Fig. 1. Top view of Atomic structure of $Mo_{1-x}W_xS_2$ in XY-plane with 50 percent substitution of Tungsten (W).

3 Results and Discussion

In this work, the effect of local field and different polarization have been studied on the optical properties of MoS_2/WS_2 alloy structure. First of all, we have calculated the dielectric function ε(ω) of the structure which is complex in nature. The complex dielectric function ε(ω), have been plotted in Fig. 2 with polarization in periodic x and y directions. It is evident from the plot that in both the cases the first peak occurs around 1.9 eV but the intensity of the peaks varies differently in the range of 2.5-6 eV.

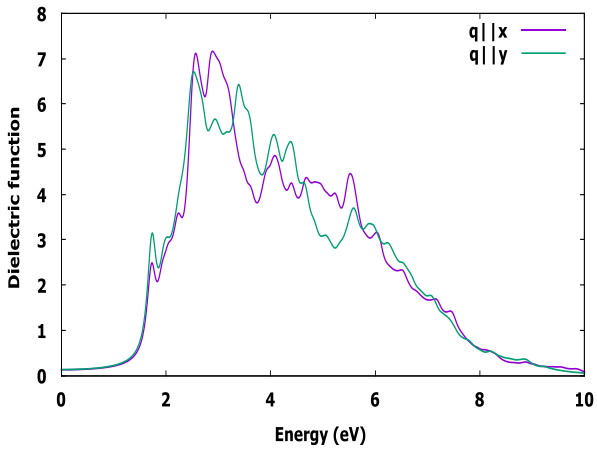

Fig. 2. Dielectric function verses energy of incident photon in different periodic direction.

Fig. 3 shows the real and imaginary part of the complex dielectric function with and without the effect of local field. From the graph it is visible that there is negligible effect of local field which is the case with the semiconductors with uniform charge density. The first peak of the imaginary part is obtained around 1.9 eV and the second peak is around 2.5 eV. The intensity of these peaks have been increased as compared to the monolayer of MoS_2. Higher intensity of peaks has been observed in the energy range of 2-6 eV which shows a better absorption in the visible range.

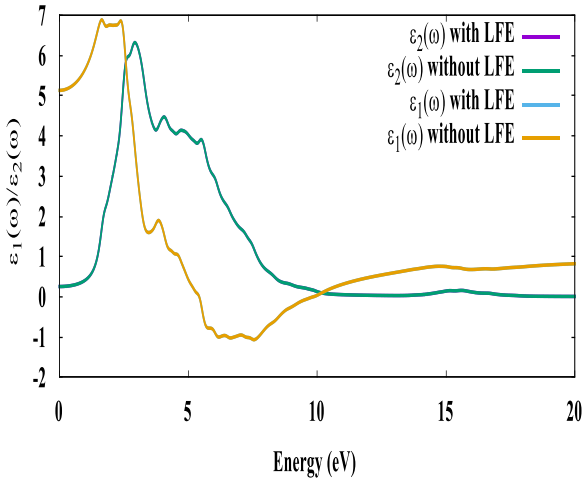

Fig. 3. Real and imaginary part of dielectric function with and without local field effect.

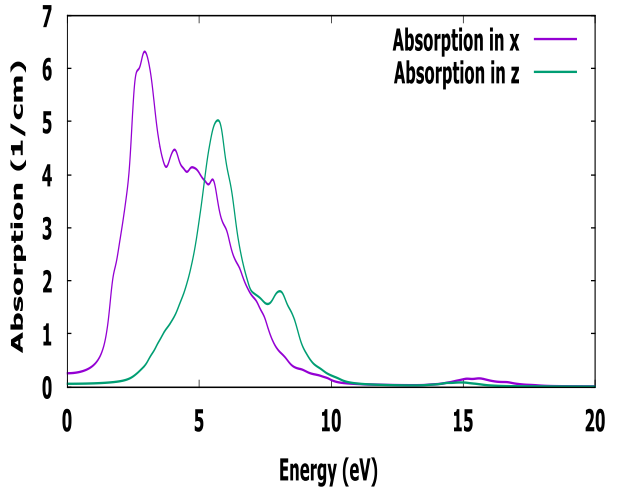

Fig. 4. Absorption coefficient w.r.t photon energy with different polarization.

Fig. 4 shows the variation in the absorption spectrum with in-plane and out-of-plane polarization. A blueshift is observed in the spectrum with reduced intensity of peaks. In case of in-plane polarization the first peak is observed at 1.9 eV and second peak is around 2.5 eV whereas in case of out-of-plane polarization the first peak is observed around 6 eV. The value of absorption is found to be good in the periodic x and y-direction. From the above plot it can be observed that the value of absorption coefficient has been increased excellently in the visible spectrum range which ensures the use of this alloy structure in the optoelectronic devices, solar cells etc.

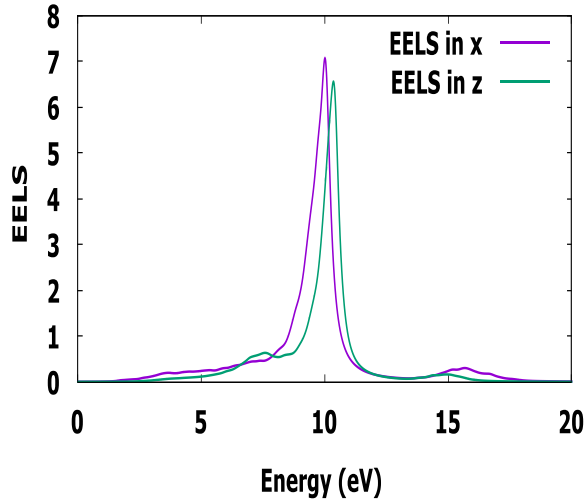

Fig. 5. Electron energy loss spectrum w.r.t photon energy when

From Fig. 5 it can be observed that the intensity of the peak has been reduced slightly for the electron energy loss spectrum when it is measured in the non-periodic z-direction. Also there is a shift in the spectrum.

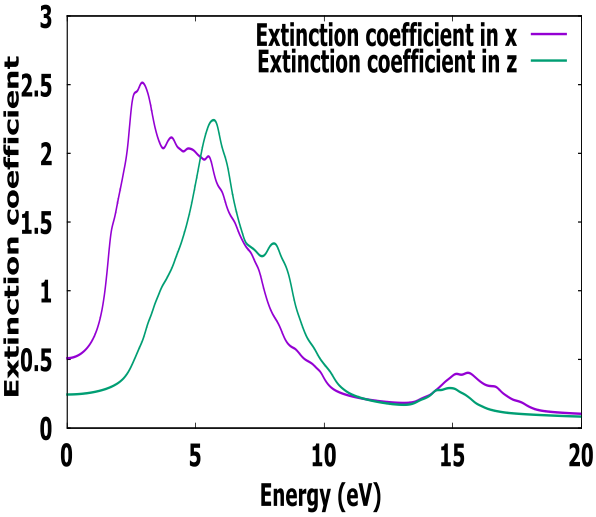

Fig. 6. Extinction coefficient w.r.t photon energy with different polarization.

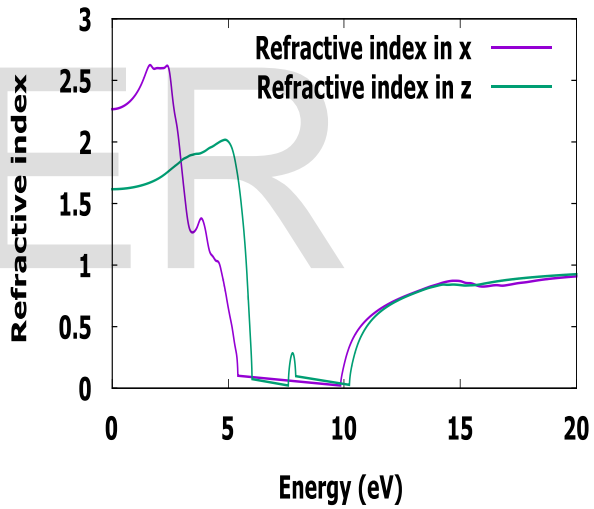

Fig. 7. Refractive index w.r.t photon energy with different polarization.

In Fig.6 the plot of extinction coefficient $k(\omega)$ is shown which is the imaginary part of complex refractive index. A blueshift is observed when the polarization of incident wave is out-of-plane. The relation between $k(\omega)$ and absorption coefficient $\alpha(\omega)$ is shown in (7). Similarly, Fig.7 shows the variation of refractive index for $Mo_{1-x}W_xS_2$ alloy structure which is an important parameter for the prediction of optical properties of materials. Again there is a shift in the plot and the intensity of the peak is reduced. A spike is observed around 8 eV and for the higher energy ranges there is an overlap between both the plots.

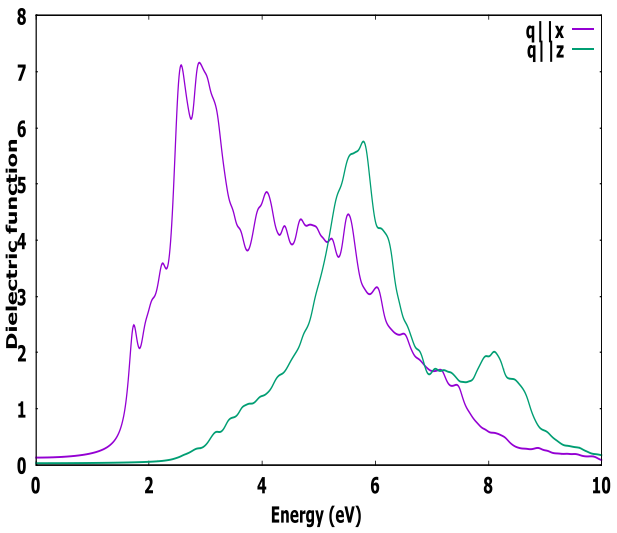

Fig. 8. Dielectric function w.r.t photon energy with in-plane and out-of-plane polarization.

Fig.8 shows the blueshift in the dielectric function as the polarization changes from in-plane to out-of-plane. In case of in-plane polarization intensity of peaks is high in the visible range as compared to the out-of-plane case. First peak is at 1.9 eV for in-plane polarization whereas for out-of-plane polarization first peak occurs around 6 eV.

4 Conclusion

We have examined the effect of local field and different polarization on the optical properties of $Mo_{1-x}W_xS_2$ alloy structure. It is evident from our calculation that absorption of this alloy structure has been improved significantly in the visible spectrum range. The effect of local field is found to be negligible on the optical properties of this alloy structure. A blueshift is observed in the dielectric function when polarization is changed from in-plane to out-of-plane. High intensity of peaks and wider range of absorption spectrum ensures the use of this alloy structure in many optoelectronic applications.

References

[1] M. Bernardi, M. Palummo, and J. C. Grossman, "Extraordinary Sunlight Absorption and One Nanometer Thick Photovoltaics Using Two-Dimensional Monolayer Materials," Nano Lett., vol. 13, no. 8, pp. 3664–3670, Aug. 2013.

[2] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, "Single-layer MoS2 transistors," Nat. Nanotechnol., vol. 6, no. 3, pp. 147–150, 2011.

[3] J. Pu, Y. Yomogida, K.-K. Liu, L.-J. Li, Y. Iwasa, and T. Takenobu, "Highly Flexible MoS 2 Thin-Film Transistors with Ion Gel Dielectrics," Nano Lett., vol. 12, no. 8, pp. 4013–4017, Aug. 2012.

[4] O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic, and A. Kis, "Ultrasensitive photodetectors based on monolayer MoS2," Nat. Nanotechnol., vol. 8, no. 7, pp. 497–501, 2013.

[5] Y. Gong et al., "Vertical and in-plane heterostructures from WS2/MoS2 monolayers," Nat. Mater., vol. 13, pp. 1135–1142, December 2014.

[6] J. Mei et al., "Molybdenum disulfide field-effect transistor biosensor for ultrasensitive detection of DNA by employing morpholino as probe," Biosens. Bioelectron., vol. 110, pp. 71–77, 2018.

[7] S. Susarla et al., "Deformation Mechanisms of Vertically Stacked WS2 /MoS2 Heterostructures: The Role of Interfaces," ACS Nano, vol. 12, pp. 4036–4044, April 2018.

[8] M. Farkous et al., "Strain effects on the electronic and optical properties of Van der Waals heterostructure MoS2/WS2: A first-principles study," Phys. E Low-dimensional Syst. Nanostructures, vol. 116, pp. 113799, February 2020.

[9] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, "Electronics and optoelectronics of two-dimensional transition metal dichalcogenides," Nat. Nanotechnol., vol. 7, no. 11, pp. 699–712, 2012.

[10] L. Kou et al., "Graphene-Based Topological Insulator with an Intrinsic Bulk Band Gap above Room Temperature," Nano Lett., vol. 13, no. 12, pp. 6251–6255, Dec. 2013.

[11] L. Kou, S.-C. Wu, C. Felser, T. Frauenheim, C. Chen, and B. Yan, "Robust 2D Topological Insulators in van der Waals Heterostructures," ACS Nano, vol. 8, no. 10, pp. 10448–10454, Oct. 2014.

[12] H.-L. Liu, C.-C. Shen, S.-H. Su, C.-L. Hsu, M.-Y. Li, and L.-J. Li, "Optical properties of monolayer transition metal dichalcogenides probed by spectroscopic ellipsometry," Appl. Phys. Lett., vol. 105, no. 20, p. 201905, Nov. 2014.

[13] J. N. Coleman et al., "Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials," Science (80-.)., vol. 331, no. 6017, pp. 568–571, Feb. 2011.

[14] K. S. Novoselov et al., "Two-dimensional atomic crystals," Proc. Natl. Acad. Sci., vol. 102, no. 30, pp. 10451–10453, Jul. 20