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Investigation of Atomic Layer Futuristic Memory Devices of Binary Chalcogenides WX_2 (X = S and Se): First-Principles Study

Narender Kumar[1,4], Na'il Saleh,[1,4]*, Arun Kumar[2], Mohan Lal Verma[3], Pranay Ranjan[5]*
[1]Chemistry Department, College of Science, UAE University, P.O. Box 15551, Al-Ain, United Arab Emirates.
[2]Department of Physics, Swami Vivekanand Government College Ghumarwin, Himachal Pradesh 174021, India.
[3]Department of Applied Physics, FET- SSGI, Shri Shankaracharya Technical Campus, Junwani, Bhilai, Chhattisgarh, India
[4]National Water and Energy Centre, UAE University, P.O. Box 15551, Al-Ain, United Arab Emirates.
[5]Department of Metallurgical and Materials Engineering, Indian Institute of Technology Jodhpur, Karwar-342037, India.
*Corresponding Authors: n.saleh@uaeu.ac.ae, pranay.ranjan@iitj.ac.in

***Abstract*—We have investigated the spin-dependent structural, electronic and localized-induced magnetic moment in an atomic layer of binary chalcogenide semiconductors, Tungsten sulphide/selenide (WX_2, where X= S, Se) using first-principle calculations. It was observed that the addition of fluorine to the WX_2 monolayer lattice reduces the bandgap of the material and induced a magnetic moment of ~1 Bohr magneton. Moreover, the reasons behind this magnetic transition from non-magnetic semiconductors to magnetic semiconductors were investigated and discussed. The calculated binding energy reveals that the pristine monolayer is more stable than the fluorine doped WX_2 sheet. Also, intermittent energy levels were created due to the fluorine atoms and resulted in p-type acceptor semiconductor behaviour in spin up and n-type donor behaviour in spin-down of WX_2 monolayer. It was observed that the unparalleled behaviour of spin can be tuned to suitable applications such as memory devices and spintronics.**

Keywords— Transition Metal Dichalcogenides, Tungsten Sulfide, Spintronics

I. INTRODUCTION

Graphene the wonder material fails to deliver the promise it holds for the upcoming electronic industries due to zero bandgap. After the inception of graphene in 2004 by Novoselov and co-workers [1-2], different 2D materials and their polymorphs have been exfoliated from their bulk counterpart and have various promising properties such as superconductor [4], [5], insulator [6], [7], semiconductor [8], [9], [10], metallicity [11], [12] and half-metallicity [13], [4-14]. These unprecedented properties of the 2D materials compared to their bulk counterpart have fuelled the research on layered materials. However, layered materials such as transition metal dichalcogenides (TMDs) have found to have the bandgap suitable to replace the trivial silicon-based devices. In addition, TMDs [15-19] have a very unique polymorphic structural, electronic and optical properties, and holds the promises to electronic and magnetic devices as the upcoming next generation materials. For example, sulphur atom having a symmetry such that one sulphur atom is just above the other sulphur atom, it results in a trigonal

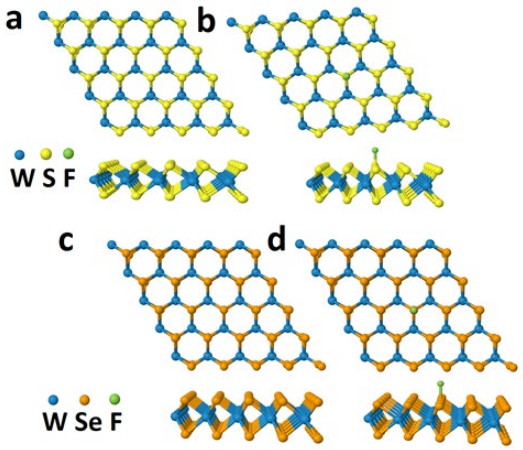

Fig. 1. Geometrical structure of a) pristine WS2, b) F@WS2, c) pristine WSe2, d) F@WSe2.

prismatic symmetry also known as the 2H-semiconducting phase, whereas a displaced sulphur atom will lead to a new phase and symmetry called as 1T-metallic phase and octahedral symmetry [20]. Moreover, these TMDs possessing intrinsic p-type nature is easy to tune through change in thickness and introduction of defects. However, any change or absence in the atomic position of the metal (W or Mo) or sulphur or selenium atoms develops a strain in the system resulting to change in the structural, electronic, and magnetic properties. In addition, TMDs such as MoS2 is well established for its potential hydrogen storage [21, 22] and of its catalytic behaviour. However, WS2 has always been deprived [23] for multiple application due to its cumbersome synthesis process. Interestingly, it has high thermal-stability and has enhanced mechanical strength compared to MoS2. These unmatched properties of WS2 have driven us to explore its fluorination properties as it will pave the way for various semiconducting applications. Herein, we

envisaged this layered electronic material for memory devices through functionalization of WS2 sheets.

In this work, using first-principles calculations, we found an effective and efficient way to tune the bandgap, structure and inject magnetic moments in tungsten sulphide/selenide monolayers by induction of fluoride atom in a more real time approach, such that it can be replicated experimentally.

II. STRUCTURAL AND COMPUTATIONAL DETAILS

In this paper, first principle density functional theory (DFT) calculations were implied using SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) for the investigation [24-25] of the structural, electronic and magnetic properties of WS_2ML (ML is the multi-layer). Fully relativistic Troullier Martin, norm conserving, pseudopotentials [26-27] is employed. The exchange and corelation energy were described by the GGA-PBE [28] functional under the double zeta polarization (DZP) basis set with confinement energy as 20 meV and 350 Ry mesh cut-off energy in all the calculations. 15 × 15 × 1 Monkhorst pack [29] were used for Brillouin zone integration. We have used 15 Å vacuum along z direction to avoid the interaction of periodic images. Structures were relaxed until each atom had forces less than 0.01/Å.

III. STRUCTURAL PROPERTIES

The optimized structure of WX_2 (where X = S, Se) and Fluorine doped WX_2 (F@WX_2) is presented in figure 1. The WX_2 monolayer is 5 × 5 supercell of unit cell which have one W atom two X atoms. The detailed optimized lattice parameters are represented in table.1. The optimized lattice constant (LC) for WX_2 (X = S, Se) are found a=b= 3.18 Å [30] and 3.35 Å [8] respectively. The calculated average bond length for W-S and W-Se is 2.44 Å [30-31] and 2.57 Å [31] respectively. The atomic distance increases as we increase atomic number of Chalcogen atoms. This difference is more pronounced for X-F (X = S, Se) which is 1.96 Å and 2.07 Å respectively due to the large difference between the atomic radii or scalar relativistic effects.

We calculate the stability of F@WX_2 using the binding energy (E_b) defined as:

$$E_b = \frac{E_{total} - (nE_w + mE_X + lE_F)}{n+m+l}$$

Where, E_{total} is the total energy of the F@WX_2, E_W, E_X and E_F represents the energy of the single atoms in the system and n, m and l are the total number of W, X (X = S, Se) and F atoms of the respective system studied. It is found that the binding energies for WX_2ML (X = S, Se) are -5.230 eV and -4.950 eV respectively while binding energies for F@WX_2ML (X = S, Se) are -5.344 eV and -4.819 eV respectively. Negative values suggest that the F@WSe_2 monolayer exhibiting higher stability than WSe_2 monolayer while F@WS_2ML is less stable than WS_2 monolayer. Therefore, the stability order can be found F@WSe_2ML > WSe_2ML > WS_2ML > F@WS_2ML.

IV. ELECTRONIC AND MAGNETIC PROPERTIES

The spin resolved electronic bandgap are calculated along the GAMMA-M-K-GAMMA high symmetry direction, results are plotted in and represented in fig. 2 and fig.3 respectively. It was found that WX_2ML (X = S, Se) are direct band gap semiconductors and non-magnetic in nature.

In addition, on further investigation, it was realized that the WS_2ML and WSe_2ML are direct bandgap semiconductor having energy gap is 1.83 eV [30] and 1.53 eV [32] respectively as valence band minima (VBM) at -0.76 eV for WS_2 and -0.77 eV for WSe_2 and conduction band minima (CBM) at 1.07 eV and 1.79 eV respectively. Moreover, it should be noted that when we have introduced the fluorine in WX_2ML for opening of the band gap.

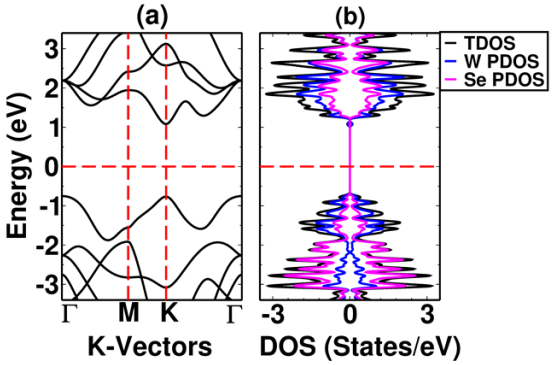

Fig. 2. a) The electronic band structure of WS2ML, b) spin polarized TDOS and PDOS of WS2ML. The red dotted horizontal line is the Fermi level set 0 eV.

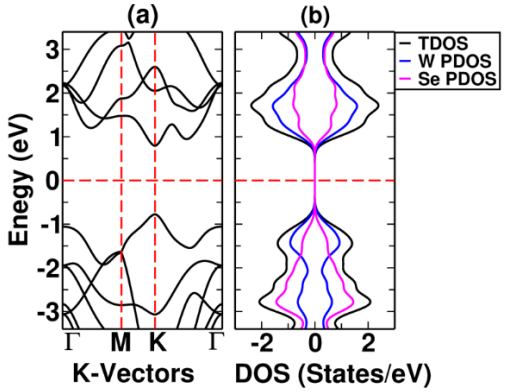

Fig. 3. a) The electronic band structure of WSe_2ML, b) spin polarized TDOS and PDOS of WSe_2ML. The red dotted horizontal line is Fermi level at 0 eV.

Interestingly, the presence of F in WS_2ML the VBM is shifted to -0.53 eV for spin up (↑) and -0.52 eV for spin down (↓) and CBM shifted to 1.29 eV for ↑ and 1.30 eV for ↓. Moreover, the presence of F generates extra two extra band (acceptor and donor) one below the fermi level (-0.27 eV) and one above the fermi level at (+0.27) which reduced the bandgap as shown in fig 5 and 6 respectively. This shift of CBM and VBM is more pronounced in F@WSe_2ML.

Further, both CBM and VBM is shifted 0.51 eV as compared to pristine WSe_2ML. However, the same extra band generates between the conduction and valence band. One in spin up region while another in spin down region which is mainly due to the symmetric position of the fluorine [He] $2s^2$, $2p^5$ over the chalcogenides ($3/4p^4$).

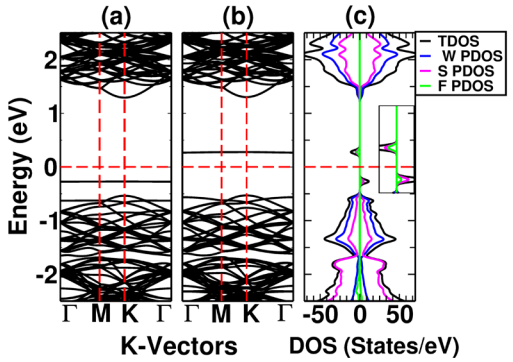

Fig. 4. The spin polarized EBS of fluorine doped WS2ML, a) for spin up, b) Spin down, c) spin polarized TDOS and PDOS. The red dotted horizontal line is Fermi level set 0 eV.

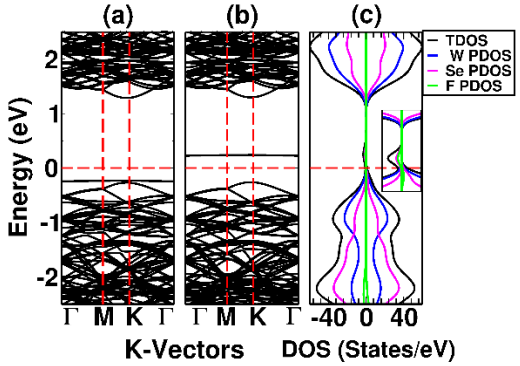

Fig. 5. The spin polarized EBS of fluorine doped WSe2ML, for a) spin-up, b) spin-down, c) spin polarized TDOS and PDOS. The red dotted horizontal line represents Fermi level at 0 eV.

To check the individual contribution of atoms, we have plotted projected density of states (PDOS). It is found that in pristine monolayer mainly W atom is contributed more as compared to S or Se. The TDOS and PDOS for spin up and spin down are symmetric for both monolayers which indicate that the systems are non- magnetic in nature. When we doped F in these monolayers the number of valence electron increasing, and non-bonding impurity states start to become occupied. Hence, enhanced atomic signature and localization of state leads to origination of spin moment [33]. The magnetic moment associated to fluorine doped both monolayers are 1.00 μB. After analysing PDOS it is clearly observed (fig. 4 and 5) that the extra electronic states between the CBM and VBM is mainly generated from the hybridization with fluorine Pxy/2Pz orbital state. So, it can be concluded that the F has the ability to induced magnetisation in transition metal dichalcogenides monolayers.

V. CONCLUSION

The structural, electronic, and magnetic induced properties of two-dimensional material WX_2 monolayer (where X = S, Se) have been investigated. Magnetisation was observed that by doping the fluorine (F) in WX_2ML. Slightly weaker bond are found in F@WX_2ML as compared to pristine monolayer. However, F is strongly bonded with Se chalcogenides as compared to S due to higher electronegativity of Se. Binding energy indicates that F@WSe_2ML is more stable than pristine WSe_2ML. The density of states of F@WX_2ML exhibit two acceptor and donor type extra band between CBM and VBM, due to enhanced number of valence electron, and non-bonding impurity states start to become occupied, which is the indication of faster response to the electronic properties. The pristine monolayers bandgap is reduced, and antiferromagnetic behaviour is observed in F doped WX_2ML with magnetic moment 1.00 μB. The development of spin states is useful to design chips, storage devices, sensing and considerable interest in the context of next-generation data storage and communication device.

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