Tailoring electronic, mechanical and dynamical properties of two dimensional materials using density functional theory

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Introduction

In recent years, two-dimensional (2D) materials are well known for their variety of properties such as optical, electronic and mechanical properties, and have been investigated extensively to overcome limitations of graphene, that is zero band gap, oxidative nature and many more [1-3]. To overcome these drawbacks, many 2D materials such as mono-elements that exhibit planar or bulked like structures have been predicted and synthesised experimentally. The mono-element 2D materials include silicene, germanene and stanene that exhibit same electronic nature as graphene [3, 4]. However, these materials do not resolve the problem of semi-metallic nature of graphene, which is one of the hindrances for electronic applications. Further, group III-V binary compounds (h-BN, h-AlN) [5–8] and transition-metal dichalcogenides (TMD) [9–13] were predicted theoretically and synthesized successfully. The hexagonal boron nitride (h-BN) and h-AlN are known for their wide band gap nature, which is also not suitable candidate for electronic application. Finally, the transition-metal dichalcogenides (TMD) exhibit semiconductor nature which makes them suitable for electronics applications. Moreover, some of the TMD materials exhibit indirect band gap, which is not suitable for optoelectronic applications. Despite of above limitations these materials have been used in various fields such as hydrogen storage, water splitting, ionic batteries and many more [14-21]. Till date many 2D materials are predicted and shown to exhibit variety of properties and their potential applications. Still graphene is considered as thinnest and strongest materials among these classes of 2D materials, so there is no chance of replacements of certain materials. Previously, it is shown that the properties of 2D materials can be tuned by various means of tool such as strain, electric field, doping, creating defect etc. [22-25]. Most of the 2D materials such as silicene, germanene, stanene etc. do not occur naturally and they need to be synthesized on some substrates. Therefore, the choice of suitable substrate is also one of the important factors for the growth of 2D materials as they can alter the properties of these classes of 2D materials. Besides, the selection of substrate is quite crucial as sometimes they offer

mechanical support while sometimes they provide disorder [26]. The properties of 2D materials depend on structural configuration, lattice mismatch and interaction between substrates and 2D materials. If the interaction between two sheets is weak van der Waals interaction then that allows the layer to cleave easily, otherwise if interaction is too strong, then it leads to the formation of hetero-structure. Best example of this is free standing graphene that exhibit semi-metal nature whereas graphene on h-BN substrate shows opening of band with varying interlayer distance [27]. Graphene/h-BN heterostructures had been a topic of interest for both theoretical and experimental point of view to know the role of the graphene/h-BN interface in their hetero-structure. Furthermore, it is shown that the growth of silicene on TMD such as MoS_2, WS_2 and $PtSe_2$ tunes the electronic properties of silicene [28-30]. The electronic properties of 2D materials basically depend on the lattice mismatch between substrate and material itself that leads to strain within material during growth process. Besides, it is found that applying uniaxial or bi-axial strain on two dimensional materials not only tunes its electronics properties but also its dynamical and mechanical properties [31-33]. Moreover, many graphene allotropes such as graphyne, graphdiyne, penta-graphene and many more are predicted using density functional theory and synthesized which show semiconductor nature as compared to graphene counterpart and various applications in field of nanotechnology as nano-fillers, transistors, sensors, anisotropic conductors, and desalinators [34-35]. Recently, these allotropes attracted a lot of interest and motivated to find allotropes of TMD such as penta-CdS_2 which is dynamically stable and show their versatility in various fields [36]. There are many possibilities of predicting allotropes of TMD such penta-$CdSe_2$ and penta-$CdTe_2$ that will show potential applications in various fields as compared to penta-CdS_2.

In this work, we have studied class of 2D materials such as arsenene, silicene, TMD using density-functional theory based on first-principles calculations and also tuning of their properties for better applications in different fields such as optoelectronics, hydrogen production and solar cell applications.

Objectives

The present work aims to investigate some of the noble 2D materials such as arsenene, bismuthene (Bi), bismuth arsenide (BiAs), bismuth antimonide (BiSb), silicene and some transition metal di-chalcogenides using density-functional theory based on first-principle calculations, to understand the structural, electronic and dynamical properties. In addition, we aim to tune the electronic properties of materials by means of applying strain and doping with different dopants. The specific objectives of the present work are following:

1. To optimize the structure and calculate the electronic band structure and density of states.

2. To analyse the results of band structure calculation in terms of conducting behaviour useful for possible potential applications.

3. Using optimized parameter calculate the phonon dispersion curve and phonon density of states to understand the dynamical stability of the considered materials and their phonon properties.
4. To investigate the structure-dynamics-properties and mechanical properties by calculating elastic constants.
5. To investigate Raman spectra using first-principles calculations.
6. To understand the effect of strain, layer, doping and dimensionality

Summary of Research Work

The present thesis is organized in the following manner.

Chapter 1 is about the progress and development of two-dimensional (2D) materials for their unique properties and their applications in the novel fields such as electronics, optical, hydrogen storage, nanocatalysis for hydrogen evolution reaction (HER) and solar cells applications. Further, the prediction of new 2D materials provides an emerging way to have better technology and applications to society. Today's world not only demands better technology for their comfort but also required energy for electronic appliances. Therefore, there is a need of eco-friendly production of renewable sources. One of the cleanest forms of energy is hydrogen which is produced by the process called water splitting. Moreover, many 2D materials such as TMD, borophene, graphene have attracted a lot attention as a catalyst for hydrogen evolution reaction to have cost effective catalyst as compared to platinum [33, 37-38]. Further, studies shows that the catalytic activity of these classes of 2D materials can be enhanced with doping, creating defect, applying field and strain and including substrate [40-42]. Newly predicted 2D materials are also equally potential as compared to existing 2D materials as their bands nature varies from semiconductor to metallic. The structure of arsenene, antimonene and bismuthene shares buckled honeycomb structure similar to those of buckled silicene which helps to stabilize the structures. Besides, it overcomes the drawback of silicene which is semi-metal in nature whereas arsenene, antimonene and bismuthene exhibit semiconducting nature that makes more suitable for opto-electronic devices, catalyst and photo detector. Further, their properties can be tuned by above mention methods. These show the importance of studying and the need of tuning properties of these materials for potential applications.

Theoretical description of computational methodology used throughout the work is presented in **Chapter 2**. In this chapter, theoretical concepts which are the basis of density

functional theory (DFT) are presented and discussed. In particular, all quantities which help to calculate the electronic, dynamical and mechanical properties of 2D materials on the basis of DFT are discussed. We present all basic ideas of many body problems, Born-Oppenheimer, Hartree and Hartree-Fock approximations followed by density based method and Kohn-Sham equation [43] in chapter 2. Moreover, the use of plane wave to represent electron wave functions and density needed to deal with valance and core electrons implemented in Quantum Espresso simulation code [44] are discussed. We also discuss the Grimme's dispersion correction which is important not only to predict correct cohesive and adsorption energies but also important to consider van der Waals interaction which is important for layered systems.

In **Chapter 3,** we reported the results of our systematically investigated, stability and electronic properties of two dimensional honeycomb structure of arsenic known as arsenene and studied its catalytic activity for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) using density-functional theory (DFT) based first-principles calculations. We have included dispersion correction (DFT-D2) to get accurate adsorption energy to have better understanding of hydrogen and oxygen adsorption on arsenene for HER and OER. From our calculations, we found that the arsenene has indirect band gap of 1.62 eV and shows potential for HER as photocatalyst. Furthermore, we sieved the dopant for better catalytic activity through ban gap modulation as band gap is one of the important parameters for catalytic activity. The fundamental band gap of arsenene can be altered with functionalization of arsenene by dopant B, N, O, Ga, Ge and Se dopant. We found that B, N and Ga-doped arsenene show a p-type semiconductor nature as Fermi level is close to valence band maximum (VBM) with band gap of 0.74, 0.65 and 0.57 eV respectively, while Ge-doped arsenene shows n-type semiconducting nature as minimum of conduction band is near to Fermi level.

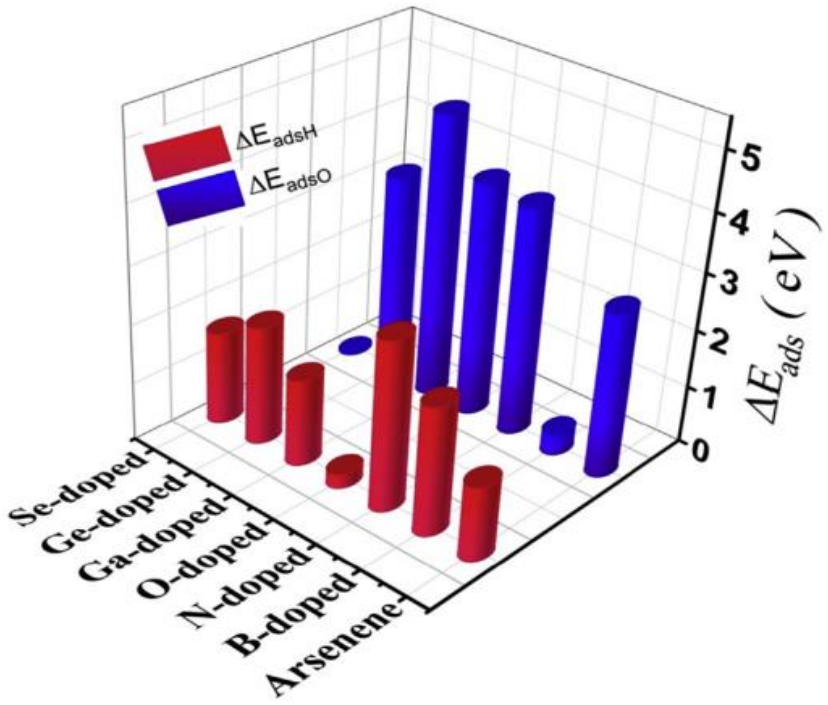

Fig. 1 - Adsorption energy of hydrogen and oxygen on pristine and B, N, O, Ga, Ge and Se doped arsenene.

However, O and Se functionalized arsenene shows the metallic nature. Fig 1. depicts that the O doped arsenene is the most promising candidate for HER, as its adsorption energy is 0.24 eV, whereas B doped arsenene is most promising candidate for OER among all other dopants as its adsorption energy is 0.37 eV being very close to 0.33 eV. Moreover, HER activity increases by 82% for O-doped arsenene and OER activity by 87% for B-doped arsenene as compared to pristine arsenene.

Chapter 4 presents the strain dependent electronic and lattice dynamic studies for 2D monolayers of Bi, BiAs and BiSb and $CdSe_2$ using density functional theory based on first principles calculation. Our calculations show that the bandgap of these materials can survive for strains up to large tensile strain and direct-indirect-metal transition occurs for compressive strain in all these materials. Absence of negative frequencies of the calculated phonon dispersion indicates the dynamical stability of monolayer Bi, BiAs and BiSb. We predict that monolayer structure of Bi, BiAs and BiSb to be stable and compressive strain induces direct-

indirect metallic transition whereas tensile strain reduces the direct band gap. Under strain, the phonon dispersion curves of Bi, BiAs and BiSb show remarkable changes, whereas the out of plane ZA mode turns quadratic in nature from its linear relationship with **k**. Two of the acoustic modes LA and TA preserve linear behavior as expected. Owing to greater stability at large strain BiAs and BiSb can be a potential candidate in many electronic devices.

In **Chapter 5,** we investigate the structural and electronic properties of silicene, $SnSe_2$, and hetero-structure Si/$SnSe_2$ using first-principles calculations based on dispersion corrected density-functional theory. To know the energetically favorable configuration of hetero-structure and possibility of growth of silicene over $SnSe_2$, we have calculated the formation energy and cohesive energies of these systems. Moreover, we have used lattice match model [27] as lattice mismatch between $SnSe_2$ and silicene is about 0.48 %. After optimization of individual structure, we found that the buckling height of free standing silicene monolayer is 0.47 Å which increases by 5.4 % in hetero-structure due to strong interaction between both Si and $SnSe_2$ monolayers. The silicene exhibits semi-metallic nature while $SnSe_2$ shows semiconducting nature with band gap of 0.84 eV. Moreover, their hetero-structure shows metallic nature. The calculated formation energy of hetero-structure is -0.54 eV which attributes that the formation of hetero-structure is exothermic process and is energetically favorable as compared to the values of the semiconducting substrates investigated previously i.e. −0.12 eV over MoS_2, −0.13 eV over GaS and −0.28 eV over $PtSe_2$ [28-30]. Further, our results show that the hetero-structure is energetically stable and growth of silicene on $SnSe_2$ is possible.

In **Chapter 6**, we have analysed the effect of quantum confinement; biaxial and uniaxial strains on electronic properties of 2D, one dimensional (1D) and layered system of methylammonium lead iodide (MAPI) in cubic phase using density-functional theory based on first-principle calculations for its implications to solar cell. Moreover, the solar performance parameters can be tuned varying electronic band gap of materials. With this motivation, we tuned the electronic

properties of MAPI by applying biaxial and uniaxial strain respectively to 2D and 1D MAPI. We have imposed strain in the present calculations from −6% to 6% for uniaxial strain for 1D MAPI and biaxial strain for 2D MAPI respectively. From our calculations, we found that the band gap of 2D MAPI increases on increasing tensile strain (positive strain) and reduces under compressive strain (negative strain). Moreover, there is a direct to indirect band gap transition beyond 4% of compressive strain. However, in case of 1D MAPI, the band gap increases in both tensile and compressive strains and shows parabolic behaviour with strain. Our studies show that the solar cell parameters of MAPI are highly influenced by confinement; strain and number of layers in the case of 2D MAPI. 2D MAPI is better for solar cell applications due to lower effective mass of electron and hole arising from the strong s-p anti-bonding coupling. The calculated solar cell parameters suggest that the 2D MAPI is best suited for solar cell applications. We get the highest theoretical efficiency of 23.6% for 2D MAPI with mesoporous (mp)-TiO_2 electrode.

The detailed systematic investigation of our results on electronic, dynamical and mechanical properties of 2D materials using DFT has been summarized in **Chapter 7**. The unique properties of 2D materials and tuning of their properties have been conclude with their potential applications such as optoelectronic, hydrogen production and solar cell. Finally, we have concluded our thesis with a brief discussion on possible future work.

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List of Publications related to Thesis

1. **N. N. Som**, V. Mankad, P. K. Jha, *Int. J. of Hydrogen Energy* **43**, 21634 (2018).
2. **N. N. Som**, P.M.W.P. Sampath, S. D. Dabhi,V. Mankad, S. Shindee,M. L. C. Attygalle and P. K.Jha, *Solar Energy* **173**, 1315 (2018).
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4. S. B. Pillai , S. D. Dabhi**, N. N. Som**, and P. K. Jha, *AIP Conference Proceedings* **1942**, 090022 (2018).

List of Publications non-related to Thesis

1. A. Patel, H. K.Machhi, P. Chauhan, **N. N. Som**, V. Dixit, S. Soni, P. K. Jha and V. Pathak, *ACS applied materials & interfaces* (in press 2019).
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Signature of Candidate **Signature of Supervisor**