Chapter 1

Introduction
1.1 EXISTING INFORMATION ON LAYERED SEMICONDUCTORS:

Being most studied class of materials, since long, layered semiconductors of IV-VI and VIA-VIB group have great importance in technical applications due to their unique and extraordinary characteristics. These compound semiconductors have been exclusively studied in different forms and dimensions. These materials can be found in crystalline as well as amorphous form. Apart from these, their property is strongly influenced by dimensions and hence, huge research has been reported for different forms namely, in nano-thinfilm form, nanoparticles, nanocrystallite, nanotubes, etc. The single crystals have proven the great importance in technical application due to exotic behaviour and ordered structure. Owing to huge demand of artificial crystalline materials, several crystal growth techniques such as vapour transport technique, slow evaporation, Bridgeman, Czochralski, flame fusion, solution growth, etc. has been invented. Among these, vapour transport technique have drawn huge attention due to its simplicity, high purity, controlled growth process and high productivity. The compound semiconductors of IV-VI, II-VI and VIA-VIB group have been found to be grown by vapour transport technique. In vapour transport technique, the catalyst like I$_2$, Br$_2$ and NH$_4$Cl are used to obtain large size crystals and it can also be possible to enhance the rate of growth process using catalyst.

Since last decade, the quasi two-dimensional transition metal dichalcogenides (TMDCs) raised considerable interest because of their unique properties. The versatility in electronic and optical properties of layered materials of TMDC family has captivated huge attention of researchers in academic and technical world. The electronic transport can be tuned from metallic to semiconductors through compositional variations or doping processes. The exotic band structure and distinctive physical properties of TMDC materials have opened up new prospects and hence applications in the field such as spintronic, electronics, photonics, and optoelectronics [1-3]. The TMDC
compounds, whose generalised formula is MX$_2$ (where, M is transition metal atom and X is a chalcogen atom) are composed of two dimensional tri-layer X-M-X sandwich structures. The M atom plane is in the middle of two hexagonal X atom planes. These MX$_2$ sheets are weakly bonded together by van der Waal bonding to form crystals [4]. Generally, VIA-VIB group semiconducting materials crystallize in hexagonal (2H-polypye) structure with P$_{63}$/mmc or in rhombohedral (3R-polytype) structure with R$_{3m}$ space group [5]. In particular, research interest in chalcogenides of tungsten and molybdenum has increased dramatically due to their thickness dependent physical properties, for example there is a transition from indirect band gap in bulk form to direct band gap in monolayer form [6-13]. The excitonic resonances are another relevant ingredient which determines the optical properties of these layered semiconductors [14] and are also expected to play a defining role in the optoelectronic processes, such as photoconduction and photocurrent generation. Other members of this TMDC family namely VS$_2$ and VSe$_2$, structurally similar to MoS$_2$, have drawn tremendous attention because of their charge density wave (CDW), versatility in electronic structures and intercalation properties [15-21].

1.2 SYNTHESIS TECHNIQUES AND PROPERTIES OF ULTRATHIN LAYERS OF 2D-TMDCs:

Recently, due to success of graphene, huge interest in two dimensional materials has been induced in academic and technical research. Unlike semi-metallic graphene, layered semiconductors of 2D-TMDCs have tunable band gap with important ingredient excitonic resonances and hence, they have shown tremendous potential in solar cell technologies. The transition metal dichalcogenides, quasi two-dimensional materials, are formed through strong covalent bonding in individual crystallographic a-b atomic layers and the adjacent layers are bonded together by weak van der Waals interaction along crystallographic c-axis. Most intensively exploited member of TMDC family, WSe$_2$ has been comprised through stacking of Se-W-Se layer in
which W-atom plane is sandwiched in the middle of two hexagonal Se-atom planes [22-25]. The two-dimensional WSe$_2$ layers are bonded weakly by Van der Waals bonds to form bulk crystal. The inter-layer bonding allows the separation of single layer by simple exfoliation technique. The 2D-TMDCs have captivated attention of researchers due to unique transformation of indirect band gap in bulk form to direct band gap into single/bi-layer form. The single layer of WSe$_2$ has direct band gap of 1.76 eV and in addition to this, excitonic resonances make it more appropriate for technical applications. For synthesis of single to few layer nanosheets both top-down such as electrochemical, mechanical or sonication-assisted exfoliation technique and bottom-up method such as chemical vapour deposition been employed effectively. The synthesis of WSe$_2$ nanosheets by micro-mechanical exfoliation or chemical vapour deposition has been successfully demonstrated. However, these techniques are non-scalable process which suffer from relatively low efficiency and small layer in size with relatively less control on the process. The most convenient and high yield technique is liquid medium assisted sono-chemical exfoliation technique that relies on liquids like acetone, methanol, ethanol, NMP, DMF, etc. [26-28].
Table 1.1 Elemental information of tungsten (W), vanadium (V) and selenium (Se):

<table>
<thead>
<tr>
<th>Properties</th>
<th>Tungsten (W)</th>
<th>Vanadium (V)</th>
<th>Selenium (Se)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Number</td>
<td>74</td>
<td>23</td>
<td>34</td>
</tr>
<tr>
<td>Atomic Weight</td>
<td>183.84 gm/mol</td>
<td>50.94 gm/mol</td>
<td>78.96 gm/mol</td>
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<tr>
<td>Electron configuration</td>
<td>[Xe] 4f⁴ 5d⁴ 6s²</td>
<td>[Ar] 3d³ 4s²</td>
<td>[Ar] 3d¹⁰ 4s² 4p⁴</td>
</tr>
<tr>
<td>Phase</td>
<td>Solid</td>
<td>Solid</td>
<td>Solid</td>
</tr>
<tr>
<td>Density</td>
<td>19.3 gm/cm³</td>
<td>6.0 gm/cm³</td>
<td>4.81 gm/cm³</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>3695</td>
<td>2183</td>
<td>494</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>6203</td>
<td>3680</td>
<td>958</td>
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<tr>
<td>Heat of fusion</td>
<td>52.31 kJ/mol</td>
<td>21.5 kJ/mol</td>
<td>6.69 kJ/mol</td>
</tr>
<tr>
<td>Heat of vaporization</td>
<td>774 kJ/mol</td>
<td>444 kJ/mol</td>
<td>95.48 kJ/mol</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>24.27 J/mol K</td>
<td>24.89 J/mol K</td>
<td>25.36 J/mol K</td>
</tr>
<tr>
<td>Oxidation states</td>
<td>+4</td>
<td>+3</td>
<td>-4</td>
</tr>
<tr>
<td>Electron negativity</td>
<td>2.36</td>
<td>1.63</td>
<td>2.55</td>
</tr>
<tr>
<td>Atomic radius</td>
<td>139 pm</td>
<td>134 pm</td>
<td>120 pm</td>
</tr>
</tbody>
</table>

1.3 DOPING AND ALLOY ENGINEERING IN TMDC MATERIALS:

1.3.1 Electrical and optical properties:

The most versatile technique to engineering the material properties is the atomic doping or substitution of dopant species during synthesis process. It can significantly alter the structure and/or properties of materials depending on dopant type and its concentration. In order to produce high performance electronic
devices, the alloy engineering in transition metal dichalcogenides is exclusively demonstrated, since long. The most important amongst the characteristics of TMDC semiconductors, the band gap can be tuned up to several meV using doping or alloying different semiconductors. The pronounced tailoring of electrical transport has been most intensively studied in IV-VI and VIA-VIB compounds due to substitutional doping. The direct substitution of dopant atoms can be possible if size, valancy and coordination are well matched with atoms of host materials. The dopant atom can settle in interstitial site in lattice, however it can cause the structural defects or can generate strain in lattice structure of host material. In the family of TMDCs with layered structure, the intercalation of dopants between the layers is also possible. The p-type and n-type semiconducting behaviour can be controlled by doping, useful aspect in fabrication of optoelectronic devices. This is also the effective technique to modulate Fermi level. The group IV elements such as Ti and Zr can be used to enhance the tribological applications of TMDCs. The group IV elements have maximum oxidation state of IV and hence, they can be isovalently substituted for W(IV) and Mo(IV) in their respective sulphides. The intercalation of V in MoS₂ has been demonstrated, recently. The 2H-MoS₂ with intralayer vanadium ions preserves 2H polymorph and inclusion of vanadium enhances the electrical conductivity and carrier concentration. The enhanced hydrogen evolution is demonstrated due to vanadium incorporation. Another member of group III, niobium (Nb), exhibiting oxidation state III, can alter the semiconducting behaviour from n-type to p-type in MoS₂. The synthesis of Nb-doped MoS₂ with degenerate hole density of $3 \times 10^{19}$ cm$^{-3}$ is reported. Appropriate dopant can also yield magnetism in TMDC semiconductors and which is useful in fields of spintronics. Zhao et al has demonstrated the generation of anti-ferro-magnetism in Mn-doped MoS₂ [29]. The n-type semiconducting behaviour of MoS₂ can be further be improved by Fe-doping, which increases the carrier concentration. Besides these, the substitutional doping of doping of Sb
can transform native p-type semiconducting behaviour of WSe$_2$ into n-type semiconductors and in addition, carrier mobility can be enhanced significantly [30].

1.3.2 Structural Properties:

As shown in Figure 1.1, multilayer crystals of WSe$_2$ binary alloy has layered structure and is formed by stacking of Se-W-Se layers through weak van der Waals interaction. In tri-layer, W-atom layer is coordinated with two Se-atom layers through covalent bond. The alloy engineering or doping relies on atomic size of host elements and the dopant-foreign element. The dopant atom can substitute the host element when atomic size and oxidation states are similar to those of the host element. In case of larger variation in there parameters, dopant elements may take interstitial sites and may perturb effectively the host crystal structure [31].

![Schematic diagram of crystal structure of 2H-WSe$_2$ binary compound.](image)

**Figure 1.1** Schematic diagram of crystal structure of 2H-WSe$_2$ binary compound.
In case of TMDCs of layered structure, intercalation of tiny elements like Li is also possible in between stacked layers. In present research, $V_xW_{1-x}Se_2$ ($X = 0, 0.25, 0.5, 0.75, 1$) ternary alloys are grown in the form of multilayer single crystals by direct vapour transport technique. Here, vanadium is incorporated in host $WSe_2$ crystal structure because of similar ionic size of $W^{+4}$ (2.05 Å) and $V^{+3}$ (1.94 Å). Due to similar size, vanadium atoms are predicted to well substitute on tungsten lattice sites. As shown in Figure 1.2, change in structure due to incorporation of vanadium is schematically shown. The structure of ternary alloys or doped compounds is strongly influenced by type and/or concentration of dopants. Sometime, the excess of dopant concentration and larger size mismatch between dopant and host elements leads to the excess strain in lattice and generates the structural defects. The improper growth parameters in ternary alloys cause the secondary phase generation. The dendrites can also be produced due to rapid growth process [31, 32].

1.4 APPLICATIONS OF TMDCS:

1.4.1 Optoelectronic devices based on TMDCs:

In the field of optoelectronics, TMDCs with desired bandgap at around 1-2 eV with high on/off current ratio are suitable for FETs.
rather than graphene. Moreover, the unique features such as high mobility, lack of dangling bond and structural stability make them more attractive for nano-electronics. The electronic devices such as hetero- and homo-junction devices, field effect transistors, photodiodes, photo-transistors, LDR (Light dependent resistance) based on layered TMDCs have been demonstrated effectively. For optical communication systems, photodetectors are of great importance because they readily convert optical signal into electrical signal. The layered TMDCs are the centre of attraction for fabrication of high performance photodetectors. Apart from excellent optical properties, TMDCs have desired electronic properties such as high carrier mobility, high carrier concentration and tunable semiconducting behaviour. However, theoretical and experimental results show that TMDCs are suffering from poor response because of their higher synthesis temperature. The binary alloys such as MoX2 and WX2 are found to be grown in single crystalline form at temperature of 1000-1100 °C which is significantly higher and causes the higher concentration of defects. The structural defects such as dislocations, stacking faults, dendrites, chalcogen vacancies are introduced during synthesis of TMDCs. One of the most affecting defects, chalcogen vacancies generates the localised “deep-level-defect states” (DDLS) and these DDLS acts as scattering centres and opposes the flow of carriers. Besides these, DDLS acts as recombination centres for photo-generated charge carriers (electron-hole pairs) and hence, carriers lifetime is greatly shorten. In addition, rate of defect assisted recombination is of several orders higher than that of recombination of free electrons and holes. Therefore, the photodetectors fabricated from binary TMDCs are suffering from low photo-responsivity and long response time for switching action. The alloy engineering is the potential solution to reduce the problem of DDLS. The ternary alloys based on TMDCs such as MoSSe, WSSe, MoWSe, CrWSe2, etc. has been widely explored due to tuning of properties through compositional variations. According to literature
survey, the ternary alloys are thermodynamically more stable than the binary counterparts. In addition, the binary alloys have low work function which leads to longer response time due to dominance of processes of defect state-filling and release. On the other hand, the ternary alloys having low defect states exhibit large work function and only small fraction of carriers recombines into defect states. Hence, the amount of photocurrent is more in case of ternary alloys and response time is also of the order of μs to ms [33-65].

1.4.2 Human interactive sensors:

Recently, human-friendly interactive electronics including humidity sensors, photo sensors, gas sensors, skin-mountable and wearable devices and so forth have raised curiosity in technical and academic world. In particular, humidity sensors have captivated the attention of researchers because of their vast applications in fields of textile industry, environmental monitoring, defence aircrafts, agriculture and biomedical processing [66-70]. Although, traditional humidity sensors based on metal oxide, carbon-based materials have shown good stability and response to high humidity atmosphere, difficult preparation techniques for highly sensitive functional form of the material has ruined out their application [71-74]. Recently, humidity sensors based on various transduction techniques such as capacitance, resistance, optical fiber, field effect transistors (FET) have been developed [70, 75-77]. Despite all techniques, resistive sensing is most favourable owing to its low cost and easy implementation of simpler structure [78]. To develop high performance sensor having fast response and recovery times and high sensitivity for biomedical applications and breath analysers, many researchers have proposed use of organic-inorganic hybrid materials in which sensing properties can be controlled by the structure and content of organic units [79, 80]. Besides these, nano semiconducting materials have shown great potential because of their high surface to volume ratio and high quantum confinement [81].
In recent years, two-dimensional (2D) layered materials including graphene, graphene oxide, phosphorene and transition metal dichalcogenides (TMDCs) have become potential candidates for sensor applications considering their wide range of compositions, unique thickness dependent properties etc. [82-86]. Owing to high surface to volume ratio, they can significantly adsorb gas molecules or water molecules which results into excellent sensing performance [87-90]. Apart from high surface to volume ratio, better crystalline quality, environmental stability, remarkable carrier mobility and high density of electronic states make these materials most favourable for sensors.

1.5 SELECTION OF MATERIAL FOR RESEARCH WORK:

According to literature survey, TMDCs have been extensively studied in field of electronics and opto-electronics. In order to produce high performance devices, alloy engineering is the key path to improve the material characteristics. The incorporation of vanadium in WSe\textsubscript{2} compound was completely unexploited and hence, to introduce new member in TMDC family, V\textsubscript{X}W\textsubscript{1-X}Se\textsubscript{2} (X = 0, 0.25, 0.5, 0.75, 1) ternary alloys are grown in single crystalline form. The incorporation of vanadium was carried out to tune some properties of WSe\textsubscript{2} such as band gap, conductivity, etc. and also to check the possibilities of high temperature superconductivity.
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