Chapter: 9

Conclusions and scope for future work
9.1 CONCLUSIONS:

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$_2$ compound was completely unexploited and hence, to introduce new member in TMDC family, $V_xW_{1-x}Se_2$ ($X = 0, 0.25, 0.5, 0.75, 1$) ternary alloys are grown in single crystalline form. The incorporation of vanadium was carried out to tune some properties of WSe$_2$ such as band gap, conductivity, etc.

The $V_xW_{1-x}Se_2$ ($x = 0, 0.25, 0.50, 0.75, 1$) single crystals were successfully grown by direct vapour transport technique. During growth process, heating was carried out in two steps with different heating rates which make this technique more suitable for the growth of these crystals. The dimensions of grown single crystals were measured. The stoichiometry of grown compositions was investigated by EDAX analysis. The results confirm the purity and stoichiometry grown single crystals.

The XRD patterns of $V_xW_{1-x}Se_2$ ($x = 0, 0.25, 0.50, 0.75$) are well indexed to hexagonal structure with WSe$_2$ type 2H-poly-type and P63/mmc space group. The XRD pattern of VSe$_2$ was well indexed to 1T-polytype with $P\overline{3}m$ space group. The results of powder XRD depicts substitution of V-atoms on W-lattice sites. The atomic size mismatch between W-atom and V-atom is the cause of strain production in lattice structure of grown ternary compounds. The strain energy increases as the content of vanadium increases. As a result shifting of diffraction peaks is revealed from XRD data. Lattice parameters, Unit cell volume and $c/a$ ratio falls on increasing vanadium content. The crystallite size also reduces on incorporation of vanadium. The morphological studies present usual features such as helical spirals, Frank-Read dislocations, terminated layers, clean
surface, impurity centres and hexagonal cavity on flat surface of grown crystals. The morphological investigation has also been carried out using scanning electron microscope. Transmission electron microscopy reveals the presence of nano-strips like structures in colloidal solutions of sono-chemically exfoliated samples. The selected area electron diffraction reveals the single crystalline nature of $V_xW_{1-x}Se_2$ ($x = 0, 0.25, 0.50, 0.75, 1$) ternary alloys.

The $V_xW_{1-x}Se_2$ ($x = 0, 0.25, 0.5, 0.75, 1$) single crystals grown by direct vapour transport technique have been investigated by several characterizing techniques. The preliminary results of temperature dependent resistivity measurements suggest the semiconducting nature with absorption of structural and phase transitions. The electrical resistivity is found to be higher parallel to c-axis than perpendicular to c-axis, attributing the electrical anisotropy. Anisotropy decreases on increasing the temperature. The activation energy is also determined using Arrhenius relation. The lower value of activation energy confirms extrinsic semiconducting behaviour of electrical transport properties. The Hall-effect measurements are performed for 1kG magnetic field at room temperature and typical parameters such as mobility, carrier concentration and Hall co-efficient are calculated. The results of Hall-effect is attributing the p-type semiconducting behaviour of $V_xW_{1-x}Se_2$ ($x = 0, 0.25, 0.5, 0.75, 1$) single crystals. The study of electrical transport properties is found to be improved due to incorporation of vanadium in grown alloys. The variation of resistance with pressure is measured up to 5GPa pressure. The high pressure study illustrates the squeezing of layered samples on increasing the pressure and hence resistance decreases as pressure increases on layered crystals of $V_xW_{1-x}Se_2$ ($x = 0, 0.25, 0.5, 0.75, 1$) alloys. The magnetic moment of grown compound was also measured in magnetic field from 0 to 10 kG and it is enhanced on increasing vanadium concentration in grown compounds.
The single crystal of $V_xW_{1-x}Se_2$ ($X = 0, 0.25, 0.5, 0.75, 1$) ternary alloys are studied by Raman Spectroscopy for phase confirmation and identification of vibrational mode. The peaks are observed at 785 and 581 nm due to inter-band transition at K and M-point in Brillouin zone. Besides these, additional peaks are observed on lower spectral side 530 nm and 464 nm which are attributing splitted A’ and B’ transitions. Furthermore, strong peak due to allowed indirect transition between valance band and conduction band is illustrated at 840 nm. The indirect band gap was also calculated which is changing between 1.3-1.43 eV for alloy engineering in $V_xW_{1-x}Se_2$ ($X = 0, 0.25, 0.5, 0.75, 1$) ternary alloy. The concept of Urbach’s rule for band tailing is applied to absorption edge observed at 840 nm. The Urbach’s energy and steepness constant are evaluated for $V_xW_{1-x}Se_2$ ($X = 0, 0.25, 0.5, 0.75, 1$) ternary alloys. The smaller values of Urbach’s energy and the phonon energy lead to the conclusion that the absorption tail is the result of two effects: interaction of electrons/excitons with phonons as well as the static structural disorder. The Raman spectra of $V_xW_{1-x}Se_2$ ($X = 0, 0.25, 0.5, 0.75, 1$) ternary alloys reveal the presence of $A_{1g}$, $E_{2g}$, $2LA$ and $3LA$ vibrational modes. The obtained results of Raman spectroscopy show the substitution of $V^{+3}$ on $W^{+4}$ lattice site due to almost similar ionic size.

Apart from this, two stage synthesis of ultrathin $V_xW_{1-x}Se_2$ ($X = 0, 0.25, 0.5, 0.75$) ultrathin layers and its application in photodetection is studied in detail. The preservation of 2H-polymorph is confirmed from results of Raman spectroscopy. The ultrathin nanosheets contain 2-4 layers. The absorption spectra show resonances at approximately 670 nm and 600 nm, attributing the excitonic inter-band transitions at K point of Brillouin zone. The direct bandgap of about 1.61 eV is determined for $V_xW_{1-x}Se_2$ ($X = 0, 0.25, 0.5, 0.75$) ultrathin layers. The TEM image presents few layer nano-sheets with lateral dimensions 2 to 50 nm. The time-resolved photoresponse is measured in air under 670nm illumination. The highest photo-
responsivity of 206 mAW⁻¹, specific detectivity of 38.19 × 10¹⁰ Jones and EQE of 38.19% are achieved for photodetector. It can be inferred from the observation that the alloy engineering in VₓW₁₋ₓSe₂ (X = 0, 0.25, 0.5, 0.75) ternary alloy can be of great importance in field of optoelectronics.

The WS₂/VₓW₁₋ₓSe₂ (x = 0, 0.25, 0.5, 0.75) hetero junction was fabricated from the multilayer flakes of WS₂ and VₓW₁₋ₓSe₂ crystals. The fabricated junction was examined by current-voltage technique and photoresponse is investigated under polychromatic illumination of different power intensity ranging from 10 to 100mW/cm². The ideality factor of the junction is found to be higher than 2 due to inhomogeneity of junction. The photoconduction is realised at higher intensity of illumination and the typical photodiode parameters such as photocurrent and responsivity are calculated at different bias and intensity of illumination. The substantial change in photo responsivity is found increase on rising in bias voltage and intensity of illumination. The SnSe₂/VₓW₁₋ₓSe₂ (X = 0, 0.25, 0.5, 0.75) hetero junction was also fabricated and investigated under polychromatic illumination. The excellent photoresponse of fabricated heterojunction is attributing the future application of these devices in field of optoelectronics.

The grown crystals of VₓW₁₋ₓSe₂ (X = 0, 0.25, 0.5, 0.75, 1) ternary alloys were extracted for their application in photodetection. The photodetectors are analysed under 670 nm illumination. The enhanced performance with maximum responsivity of 253.09 mA/W and moderately fast response with rise and decay time of 0.8 sec is achieved by alloy engineering in VₓW₁₋ₓSe₂ (X = 0, 0.25, 0.5, 0.75, 1) ternary alloys. The results indicate that the defect concentration decreases due to alloy engineering. Under white light of 50 mW/cm² power intensity, the excellent switching action depicts the efficient absorption of light by grown ternary alloys. Surprisingly, due to indium layer on grown crystals, the photodetection is exceptionally
improved, e.g. the photocurrent and responsivity are enhanced 20 times than that for crystals without In-layer. This is the novel path for tuning of performance of photodetector. The present finding on tuning of photodetection by alloy engineering can open up efficient ways to produce high performance optoelectronic devices. In the present research tuning of photodetection is accomplished by using different illumination and structural geometry along with alloy engineering.

9.2 SCOPES FOR FUTURE WORK:

As it is identified the emerging field of research in TMDCs particularly in ultrathin form, there can be future scope for research from two distinct points of views:

(1) **Material engineering aspect:**

In present study vanadium incorporated WSe$_2$ crystals are investigated to evaluate material parameters to identify this material for its suitability in certain applications e.g. solar cells, photodetector, temperature and humidity sensors, etc. Thus the present material may be used in nanoparticle or thin film form to future tuning of its properties. Furthermore, its 2D-form may be studied to address problems related to basic physics phenomena taking place at low dimensions.

(2) **Device physics aspect:**

The present work involves study of various simple devices based on V$_x$W$_{1-x}$Se$_2$ (X = 0, 0.25, 0.5, 0.75, 2) crystals. However, to tap full potential of this material it is required to prepare devices at very small scale that involves lithographic techniques. There are reports showing drastic change in electronic properties of TMDCs while transforming then from bulk to single layer form. To observe this sudden change, conventional materials like Si and GaAs needs to be doped to their degeneracy limits. This would lead to ionized impurity scattering and carrier frees out
effect when used in applications like MESFETs etc. at cryogenic temperatures.

Considering both of the views, following future study may be planned in order to prepare this material to exploit its properties in fascinating modern day devices.

1) Nanoparticles and quantum dots may be prepared to study tuning of optical response.
2) Thin films may be prepared by conventional e-beam as well as by CVD methods to have desired dimension of devices.
3) Single layer to few layer structure are successfully identified by Raman spectroscopy. However, further confirmation may be made by AFM.
4) Field effect transistors based on this mono-layer to few layers structure may be formed to study FET response. It is now established that in single layer form mobility of charge carriers is increased by many folds. Due to this there is a good ON to OFF state current ratio identified at a very faster rate. So, this fast transition may be applied to memory devices operating at higher speed than existing devices, today.