Master Thesis

Titanium dichalcogenides: from synthesis to 2D Device Fabrication

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Certificate

This is to certify that this dissertation entitled "**Titanium dichalcogenides: from synthesis to 2D Device Fabrication**" towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents study/work carried out by **Sagar Gupta** at **IMPMC,UPMC Paris** under the supervision of Prof. Abhay Shukla during the academic year **2018-2019.**

Supervisor

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Professor, IMPMC

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Date : 19/03/2019

Declaration

I hereby declare that the matter embodied in the report entitled "**Titanium dichalcogenides: from synthesis to 2D Device Fabrication** are the results of the work carried out by me at the **IMPMC, UPMC Paris** under the supervision of **Prof. Abhay Shukla** & **Department of Physics,IISER Pune** under the cosupervision of **Prof. Surjeet Singh** and the same has not been submitted elsewhere for any other degree.

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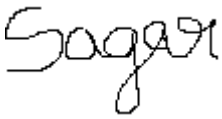
Date: 19/03/2019



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Acknowledgements

I express my high gratitude to my parents who always supported and motivated me to make my career bright and guiding me to be a better person. I am highly thankful to my elder brother who always guide me during my study and advising me for a good career.

I am highly thankful and grateful to my supervisor Prof. Abhay Shukla (Professor,IMPMC,UPMC Paris) for giving me the opportunity to do the research work in his lab and to guide me for my master project. I am highly thankful for his support and motivation during entire project. He always guided me to understand the scientific problem and motivated me to tackle the problem in the schematic way. I am thankful to Dr. John Biscaras (Asst. Professor,IMPMC,UPMC Paris) who also guided me to learn and use the instrument during project and for his suggestions during my project

I am thankful to my cosupervisor Prof. Surjeet Singh(Assoc. Prof., Dept. of Physics,IISER Pune) and Dr. Luminita Harnagea(Postdoc,IISER Pune) for cosupervising me in my project in my meanwhile stay in IISER Pune. I am thankful for guiding me to learn about crystal synthesis and characterization in the lab. I am grateful to Luminita Mam for guiding me to understand the basic concept ad other aspects in the project.

I am thankful to my TAC advisor Prof. Nirmalya Ballav(Assoc. Prof., Department of Chemistry,IISER Pune) for advising and assisting for my master project.

I am thankful to my colleague Ali Fakh(PhD Student), Weinyl Wu (PhD Student), Fang Wang(PhD Student) and Onkar Shinde (Postdoc) in IMPMC for helping me in my project. I specially thankful to Weinyl for helping me to learn about device fabrication.

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Abstract:

Titanium based dichalcogenides attract interest due to interesting electronic properties. TiTe2 material is semi metallic in nature with overlap of valence and conduction bands and TiSe2 is a low band gap semiconductor. The appearance of electronic phase transitions like (CDW, Superconductivity) in recent researches[1-2] also attracts lot attention and interests to the research community towards this material.

This project presents fabrication methods like Chemical Vapour Transport (CVT) and the determination of the necessary parameters for the synthesis of the high-quality single crystals of TiTe2 and TiSe2. These crystals are characterized by different techniques like XRD, SEM and EDXA to ensure the quality of the crystals.

These Crystals are further exfoliated using exfoliation technique as anodic bonding technique and chemical exfoliation technique to get monolayer or very thin layer of these materials. Anodic bonding technique emerges as an efficient and easy technique alternative to scotch tape exfolaition. Few layers samples with large area and high quality such as graphene and other 2D semiconductors like MoS2, GaS NbSe2 has been successfully reported by the lab using this method.[3-5]

The samples are characterized with Raman spectrocopy and thickness is measured with AFM. A detailed Raman study is further done to test the integrity of few layer sample of TiSe2.

These thin layer samples further will be used to study the electronic properties of the sample by applying the efficient space charge doping technique used by our lab to change their electronic properties and to induce electronic phase transitions.

I. Introduction:

Ultrathin films single or few layers have wide applications in electronics, optoelectronics, sensors and other material research[6-9] because of intriguing changes in physical properties due to extreme quantum confinement and dimensional reduction[10].Graphene has already opened a whole new research area because of its extensive applications in electronics biomedical, sensing, energy generation, energy storage devices due to its excellent electronic, chemical, thermal and sensing properties[11]. Materials alternative to graphene with non zero band gap are sought. Transition metal chalcogenides (TMDs) can be exfoliated easily[12] and have very interesting electronic and optical properties. The band structure of some semiconductor TMDs changes dramatically from indirect band gap to direct band gap due to dimensional reduction from bulk to single layer[13].

1.1 Transition Metal Chalcogenides: Transition metal chalcogenides have chemical formulae MX2 where M is a transition (e.g. Ti, Mo ,Ta) metal and X is a chalcogen atom (eg S,Se,Te) and the X-M-X sandwichstructure which is attracted by the van der Wall Forces between the layers

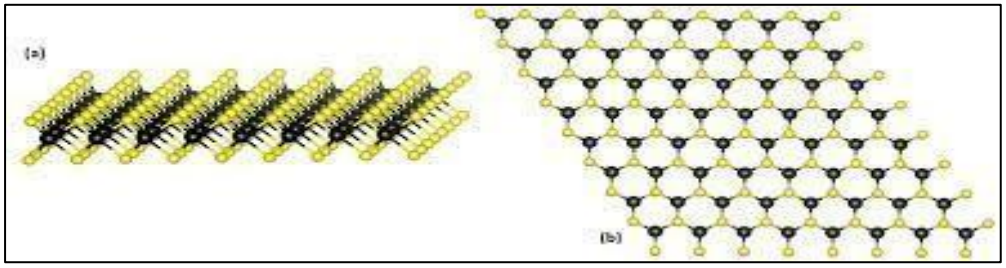


Fig.1(a) **Fig. 1(b)**

Fig.1 (a) represents the sandwich structure (X-M-X) of TMDs **Fig.1(b)** represents monolayer of TMDs from top view

TMDs mainly have local coordination of metal species in two forms in bulk trigonal Prismatic and octahedral as shown below

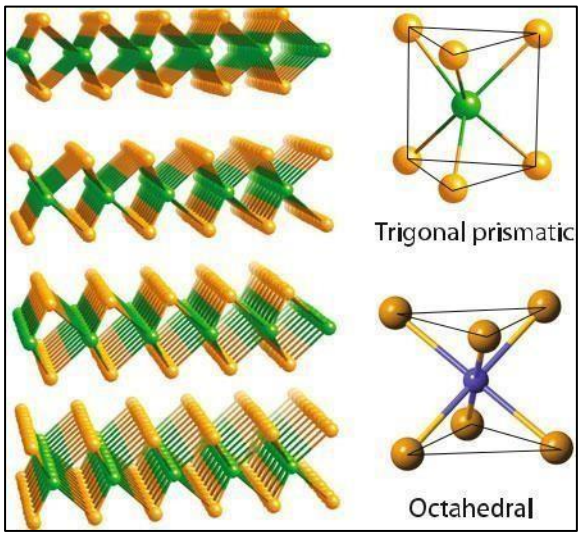


Fig.2 represents the local coordination of metal species in a layer in bulk (from Alexander V.Two Dimensional Transition-metal Dichalcogenides, p.30.Springer (2006))

1.2Titanium- based chalcogenides specifically TiTe2 and TiSe2 are layered materials which exhibit typical quasi 2D behaviour in bulk and are readily exfoliated in the few or single layer form. Though structurally these materials are very similar, changing the chalcogenide induces interesting changes in electronic properties. The possibility of isolating single or few layers is potentially important because intriguing changes in electronic structure have been predicted or even observed in the 2D limit such as changes in phase transition parameters and appearance of new phenomena like superconductivity.

The presence of a semiconducting electronic gap in TiSe2 is a plus for possible applications. The enhancement in the CDW transition temperature is observed in 2D limit which makes this material very interesting towards research community[1]. TiTe2 on the other hand does not exhibit a charge density wave in the bulk but only in the single layer form indicating enhanced electron phonon coupling. An intriguing pseudo gap also appears in this 2D limit[10]

There are reports claiming the superconductivity present in these materials by applying the external pressure.[14-15]Pressure is an important parameter and can tune the lattice structure applying uniaxially and corresponding band structure can also be affected. Uniaxial Pressure can introduce superconductivity in the TMDs and study can be done for the relationship between the superconductivity and other physical phenomena for instance the CDW transitions and its relationship with superconductivity in these systems.

1.3 Charge Density Wave: Charge density wave is the phenomena known as formation of a wave by the interaction of atoms and electrons organized in a wave-like structure, and this transition occurs at certain characteristics temperature. Researchers are studying the CDWs transitions and its relationship with superconductivity in many systems.[16]

The diagram explains the basic of charge density wave at critical temperature

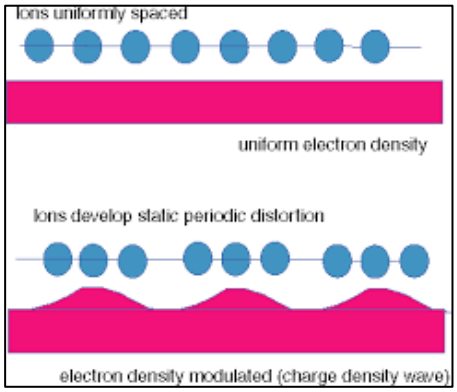


Fig. 3

Fig.3 represents the diagram showing the formation of charge density wave (from ong lab charge density wave)

Crystal growth technique mainly depends on the factors such as melting point of the constituent, vapour pressure and solubility in aqueous solution and there are many different crystal growth techniques based on these factors such as Czocharlski method, Verneuil method, Bridgman method, Chemical Vapour Transport (CVT) etc.

Chemical Vapour Transport technique is one of the major technique for the synthesis of single crystals. TMDs single crystals are mainly grow by this technique. Single crystals are of particular interest because of their intrinsic properties. Single crystal are widely used in electronics, device fabrication and optics due to these properties.[17] TMDs are majorly insoluble in aqueous solution and CVT technique is suitable for high melting compound or for those which decompose before melting such as TMDs. A brief introduction of CVT Crystal growth technique given below which is used to grow the TiTe2 and TiSe2 Crystals in the project

1.4 Chemical Vapour Transport (CVT) Crystal Growth Technique: This technique is popularized by Shafer in which a condensed Phase typically a solid (source zone) is volatilized in presence of a gaseous reactant (transport agent) and deposited in the form of crystal in other zone called as Sink Zone. There is a temperature gradient maintained between source zone and sink zone and reaction occurs in the source zone. The reaction product is volatile and transported by transporting agents to deposit in the form of crystal in the sink zone. Typical transport agent includes halogens and halogen compounds.

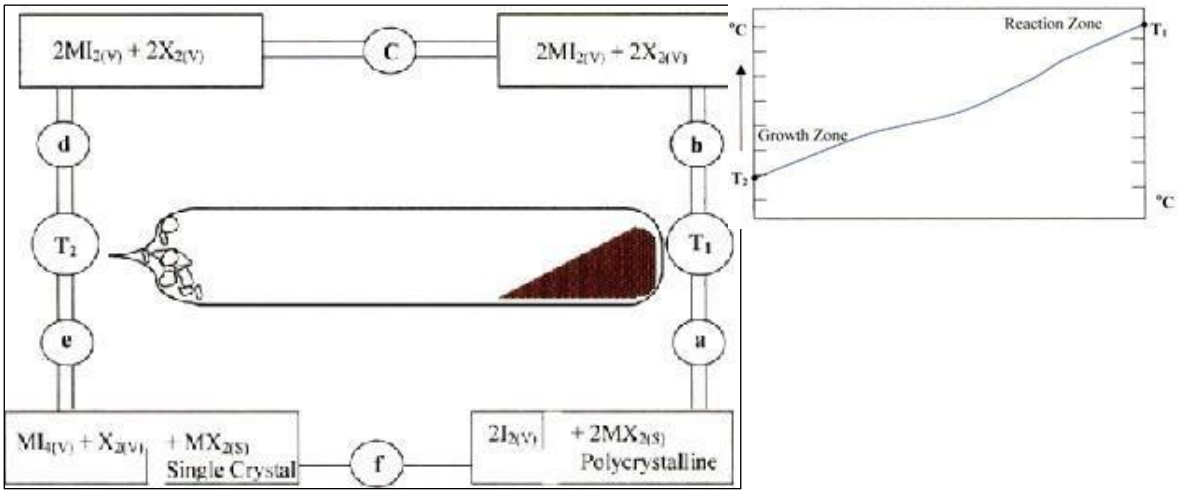


Fig.4 represents the overall reaction map in ampoule with temperature gradient (from T.H. Patel. Crystal growth by Direct Vapour Transport Technique.Ch.3, p.106, (2002))

Various parameters must be optimized for a successful CVT[18]

The suitable transport agent: The transport agent should be able enough to turn all the components of solid into gaseous phase and should not have side reactions with the solid phase.

The Basic Condition of equilibrium: The equilibrium condition of the transport reaction should not be much favourable to any particular direction so that evaporation to gasphase from solid phase in source zone and re-condensation from gas phase to solid phase in sink zone is possible under variable experimental condition.

The optimum Temperature: The Most suitable temperature for the transport reaction is when the equilibrium constant Kp=1 and the Gibbs free energy $\Delta_r G^0=0$ for the reaction We know that $\Delta_r G^0 = \Delta_r H^0 - T\Delta_r S^0$ -Gibbs Free Equation

$\ln Kp = -\Delta_r H^0 / RT + \Delta_r S^0 / R$ – Vont Hoff Equation

For the balanced equilibrium $\Delta G^0=0$ or Kp=1 results $T_{opt} = \Delta H^0 / \Delta S^0$

The Transport Direction: The transport direction is based on Le Chatelier's Principle therefore the reaction should not be extreme exothermic or endothermic due to the reversibility of transport reaction.

The rate of Mass Transport: Chemical Vapour Transport reaction mainly occurred in three steps reaction between the source material in the source zone, the gas motion and back reaction that forms crystal in sink zone from recondensation of gas phase to solid phase. The slowest rate determining step is the diffusion of gas to the solid phase so the pressure condition inside the ampoule is also crucial and pressure condition is also appropriately maintained for formation of high-quality crystals.

II. Experimental:

The materials and the method for the fabrication of the crystal is given below-

Materials: Ti(Titanium,99.99%) metal basis powder, dehydrated was purchased from Alpha Alsar ; Te(Tellurium,99.99%) metal basis Se(Selenium,99.99%) metal basis were purchased from Alpha H. All the compounds were employed as received.

Methods: The reaction in the ampoule most probably takes place for $TiTe_2$ crystal as follow. The below discussion and methods are similar for TiSe2 crystal growth.$Ti+2Te/Se \rightarrow TiTe_2/TiSe_2$ reaction happened at sink zone. $2TiTe_2/TiSe_2+2I_2 \rightarrow 2TiI_2+2Te_2/2Se_2$ gas phase reaction takes place where I_2 is the transporting agent for the reaction in the ampoule.

$2TiI_2+2Te_2/2Se_2 \rightarrow TiI_4+TiTe_2/TiSe_2$ (Crystal) $+Te_2$ $/Se_2$re condensation in sink zone

The Pressure in the ampoule should be maintained below 2 atm and I_2 quantity accordingly maintained

PV=nRT ideal gas equation used for calculation

Pressure in the Ampoule (P)≤ 2atm ,Volume of the ampoule (V)≈36cm^3,Gas Constant(R)=82.05745cm3-atm-K^{-1}-mol^{-1} T=1173K. I_2 gas should be between 3-6 cm^3 according to the calculation used above.

The total weight for the Ti, Te mixture and Ti, Se mixture was taken 2g according to the reaction. The mixture was sealed under vacuum (10^{-4} Torr) in a quartz ampoule with an internal diameter of 8mm and length of 120 mm. The sealed quartz reactor was placed in a horizontal tubular furnace as shown below in the presence of a thermal gradient and results show good crystal growth with T_1 source Zone Temperature=900°C with

ΔT=100 °C sink zone temperature at 800 °C for $TiTe_2$ Crystal growth and similar results for $TiSe_2$ Crystals.

At the end of the crystal growth process whose duration was ten days the furnace was switched off and the temperature decreased to room temperature. Many $TiTe_2$ and $TiSe_2$ crystals nucleate and grow in the sink zone of ampoule and collected.

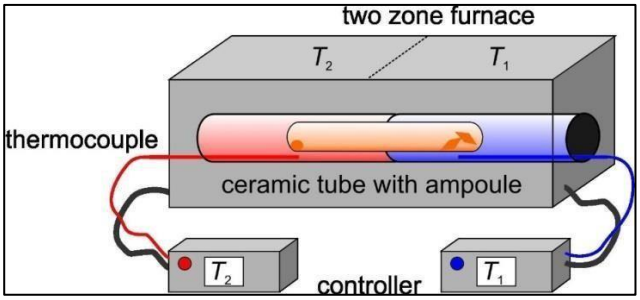


Fig.5 (a) **Fig.5 (b)**

Fig.5 (a) shows a typical ampoule used to prepare the crystals the dark area is source zone where reaction take place and the narrower is sink zone. **Fig.5(b)** represents the two zone furnace used for chemical vapour transport method (P.Schmidt, M. Binnewies, Advanced Topic on Crystal Growth.,ch.9,p.297,(2013))

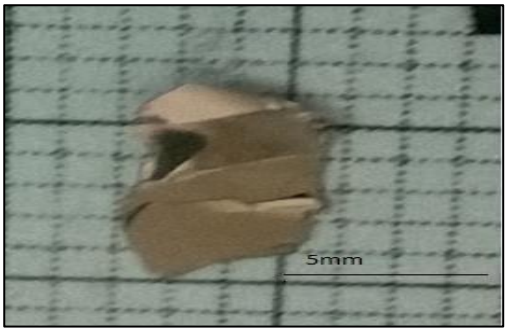
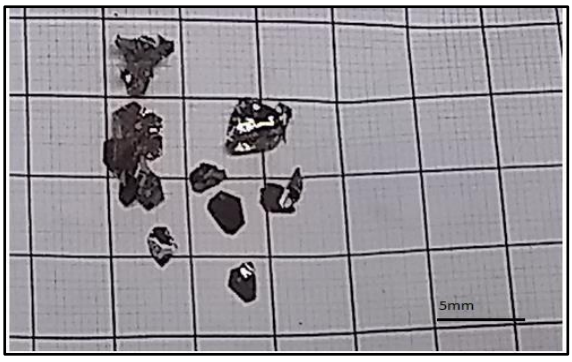


Fig. 6(a) **Fig. 6(b)**



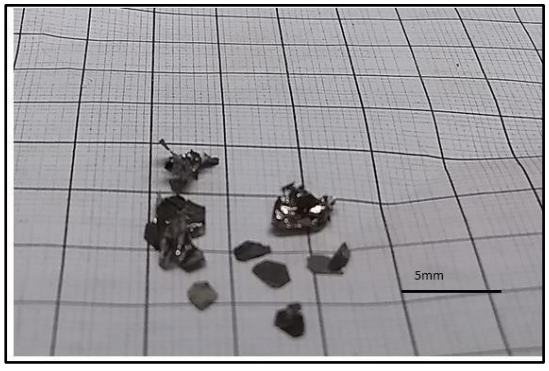


Fig.6(c) **Fig.6(d)**

Fig 6(a) and Fig 6 (b) show the images of the $TiSe_2$ Single crystal. These $TiSe_2$ Crystal were grown in two zones horizontal tube furnace as explained above with T_1 source zone temperature =900°C and ΔT=100°C with T_2 sink zone temperature=800°C.The image clearly shows a high-quality crystal growth of $TiSe_2$.Fig. 6(a) shows various single crystals with some 2-3mm in size and 4-5mm size. Fig.6 (b) shows a single crystal of $TiSe_2$ of 4-5mm size.Fig6(c) and Fig.6(d) show the images of the $TiTe_2$ Single crystal. These $TiTe_2$ Crystal were also grown similarly in two zones horizontal tube furnace as explained above with T_1 source zone temperature =900°C and ΔT=100°C with T_2 sink zone temperature=800°C.Fig 6(a) and 6(b) show various single crystal of $TiTe_2$ with some 1-2mm in size and some of them are 2-3mm in size. The edges in these crystals are sharp and some of them appear shiny indicating minimal defects in growth. Titanium chalcogenides materials are layered materials and can easily be exfoliated and images also clearly show the layered crystals suitable for further exfoliation to make thin layer samples.

III Results and Discussion:

3.1 XRD Characterization: X-ray diffraction technique is one of the major technique to identify and characterize the crystal based on their diffraction pattern. A crystalline structure contains different planes of atoms and causes a beam of incident X rays to diffract into many specific directions. A diffraction pattern is formed by measuring the angles and intensities of these diffracted beams. Crystal contains array of atoms, ions or molecules with interatomic spacing in the order of 1Å The wavelength of the Xray is in the order of spacing of atoms in crystal. A monochromatic beam of Xray (Kα) line is scattered by atom's electrons and this phenomena is elastic scattering. An array of spherical waves is produced by the atoms and there is constructive interference occur in specific direction given by Bragg's equation as shown in Fig. 7

$2dSin\theta=n\lambda$

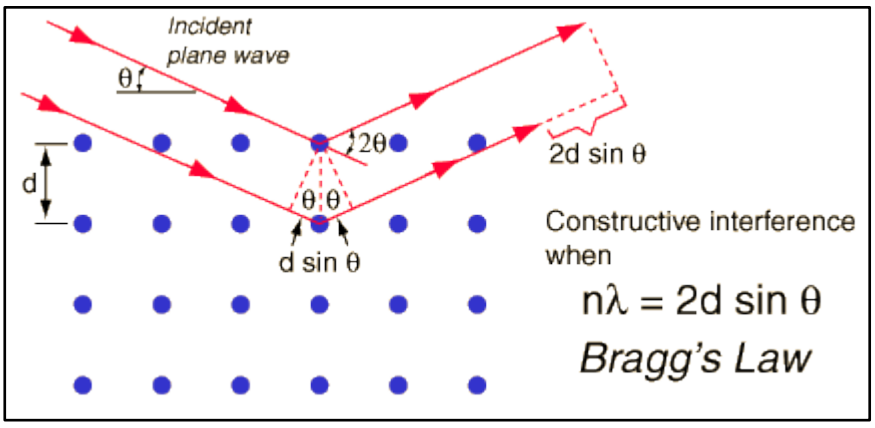


Fig.7(http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/bragg.html)

Where θ is the angle of the incident wave with interface and d is the interplanar distance between the diffraction planes causing constructive interference of wave. A crystal contains number of planes of periodic arranged atoms and h,k and l miller indices define these planes. d_{hkl} is the shortest distance between {hkl} planes. The lattice constant is determined by the these {hkl} planes arising peak in XRD graph of Intensity vs 2theta and d_{hkl} adjacent distance between these planes. The lattice constant or dimension of the unit cell can be determined by using these information. This relation depends on the type of crystal system for instance in our case the TiTe2 and TiSe2 are hexagonal crystal system.

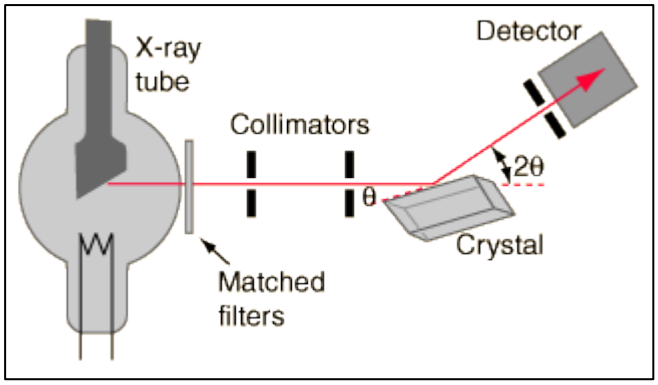


Fig.8(http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/bragg.html)

Fig. 8 shows the basic instrumentation of a XRD diffractometer where K_α and K_β characteristic Xrays are generated. The beam is filtered to remove the continuum radiation and K_β radiation is absorbed. Collimators align and focus the Xray towards the crystal and detector detects diffracted Xrays from crystals satisfying bragg's condition.

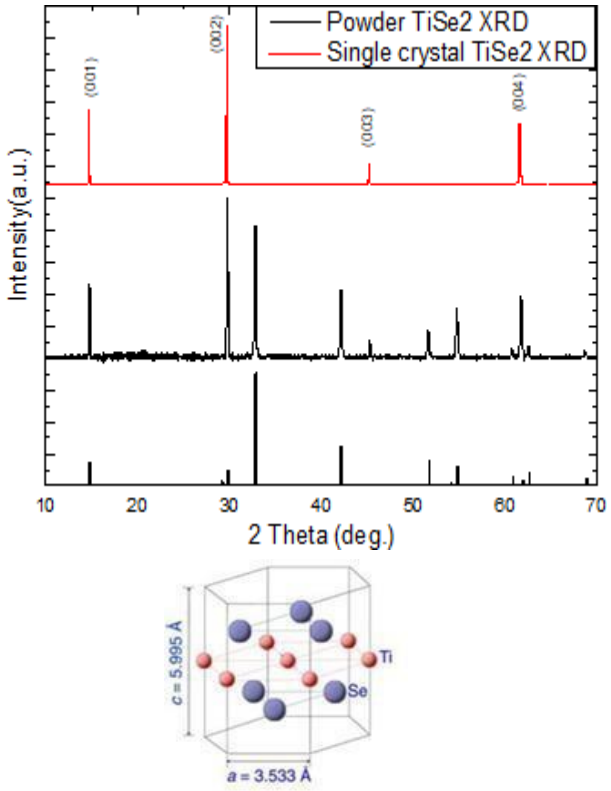


Fig. 9(a)

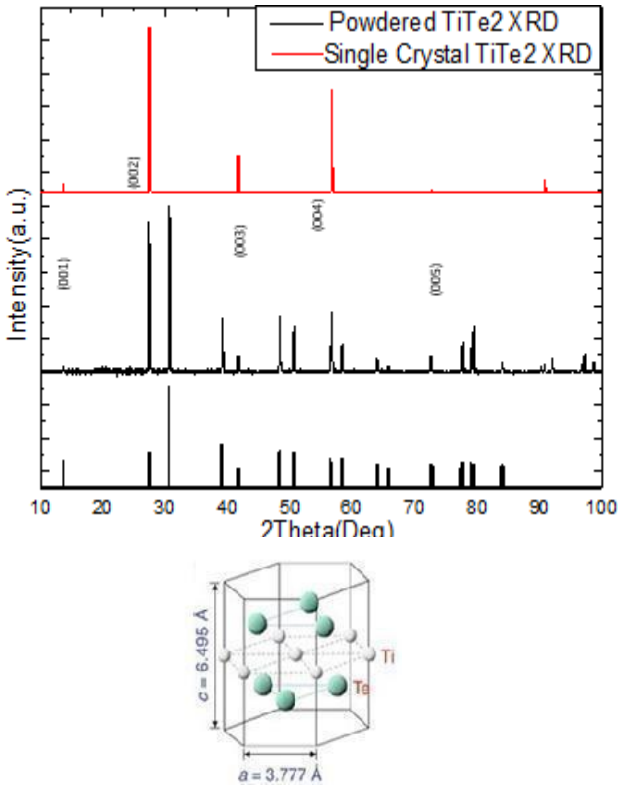


Fig. 9(b)

Fig9 (a) and Fig9 (b) show the X-ray diffraction pattern of single crystal and powdered TiSe2 and TiTe2 crystal respectively. A standard powdere pattern of TiSe2 and TiTe2 is also shown in the bottom of each figure to compare the diffraction pattern of synthesized crystal. Powder diffraction pattern (black) peaks of each crystal match with the standard one as shown in figure. Single Crystal XRD pattern(red) of both crystals are also consistent as the diffraction pattern arise due to planes perpendicular to the c direction and in the figure we can see the peaks of planes(hkl) perpendicular to the c direction. The lattice parameter are also calculated by the XRD data and for TiSe2 the lattice parameters a=3.540 A^O and c=6.008A^O and for TiTe2 crystal a=3.766 and c=6.491A were found (Appendix 1 and Appendix 2) which are consistent with the dimensions of the unit cells reported as shown in above figure 9(a) and 9(b)

Calculation:

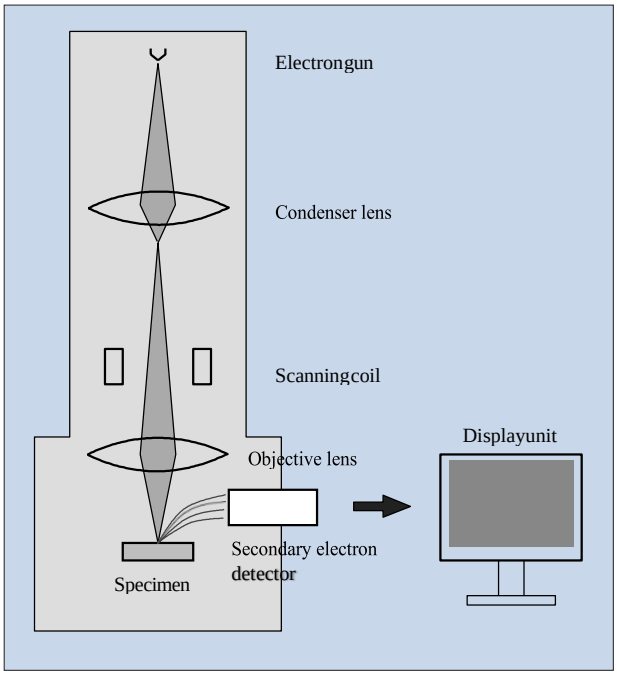
For Hexagonal Lattice

$$\frac{1}{d^2}=\frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right)+\frac{l^2}{c^2}$$

Where h,k and l are the miller indices of the plane and a and c are the the lattice parameters of the hexagonal system and d is the shortest distance between {hkl} planes. We take the Single Crystal XRD data along c axis only so we consider the data only from {00l} family plane. So by putting the h=k=0 in the equation we get the calculate c parameter according to the 2 theta and {00l} plane by the XRD data. The d value the shortest distance between the plane is simply calculated by Braggs equation as discussed above. The powder XRD data is also used to calculate the a parameters by software.

3.2 SEM characterization:

Scanning Electron Microscopy is a technique to take high resolution images of the sample. A focused electron beam scans the surface of the samples and produce images of the surface topography of sample. The instrumentation of scanning electron microscope is shown below in Fig. 9(a). An electron beam is generated by an electron gun which is focused by condenser and objective lens to the specimen in the specimen stage. The electron beam enters the specimen and various types of electrons and signals are generated as backscattered electrons, secondary electrons, transmitted electrons and absorbed electrons. The secondary electrons detector generates a topography of specimen based on these signals.[19]



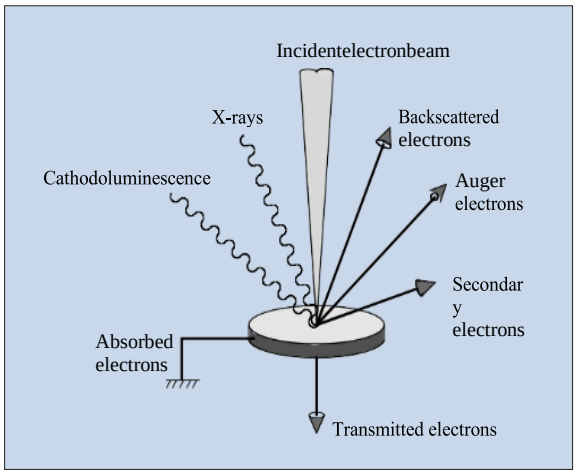


Fig.9 (a) **Fig.9(b)**

(from https://www.jeol.co.jp/en/applications/pdf/sm/sem_atoz_all.pdf)

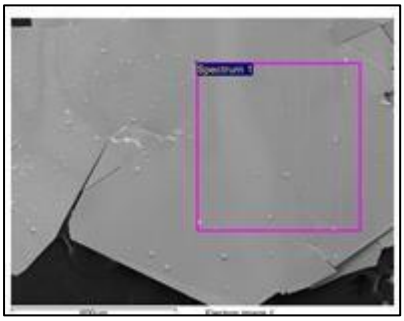


Fig. 10(a)

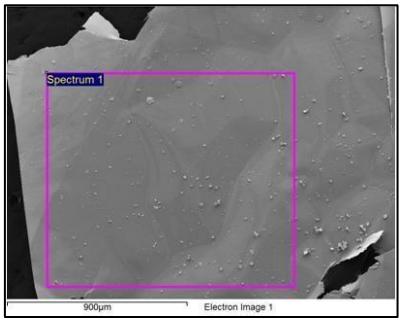


Fig.10(b)

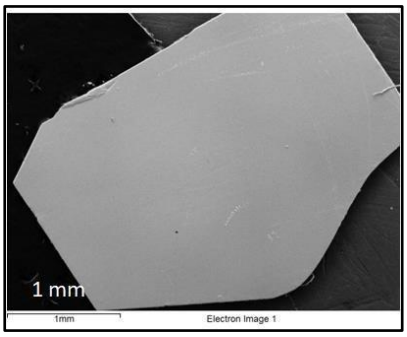


Fig.10(c)

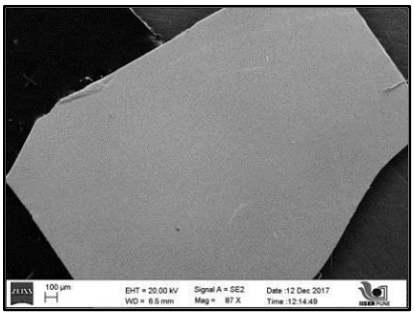


Fig.10(d)

Fig 10(a) and Fig10 (b) are the SEM images of the TiSe2 crystals and Fig10(c) and Fig10 (d) are the SEM images of the TiTe2 crystals.

The Surface appears very clean and no defects are observed as shown in SEM images. Clean and sharp edges are visible in the images and there are no grain boundaries and growth defects appear in the images indicating the high quality of Single Crystals.

3.3 EDXA Characterization

Energy Dispersive X-ray analysis is a technique for chemical characterization of the sample. This technique is based on the interaction of X ray with sample. Each atom has its own signature in the emission spectrum and show its unique peak in the emission spectrum based on the Xray interaction. Electron beam irradiate the sample and electron and inner shell electrons are emitted due to this irradiation. The vacant orbital is filled by outer shell electrons and X ray is generated corresponding to energy difference between orbitals. This X ray is the characteristic feature of that individual element and therefore called as Characteristics X ray as shown in below figure.[19]

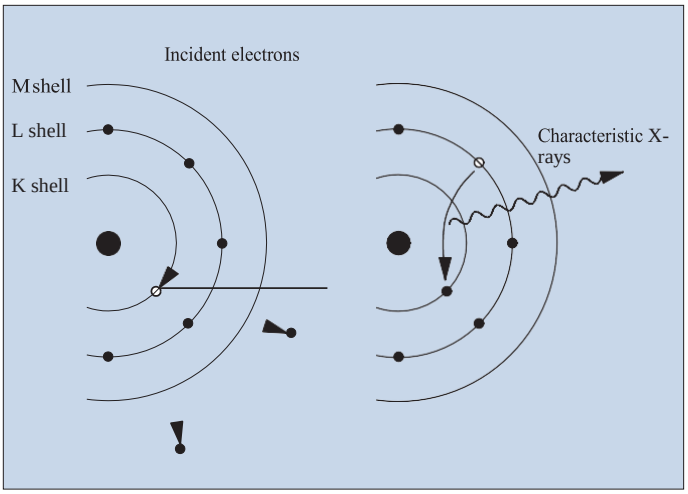


Fig.11(https://www.jeol.co.jp/en/applications/pdf/sm/sem_atoz_all.pdf)

Fig. 11 shows the K shell of the atom which is ionized by incident electron and inner K shell electron is emitted. When the K shell is filled by an L shell electron a characteristic X ray of the atom is emitted.

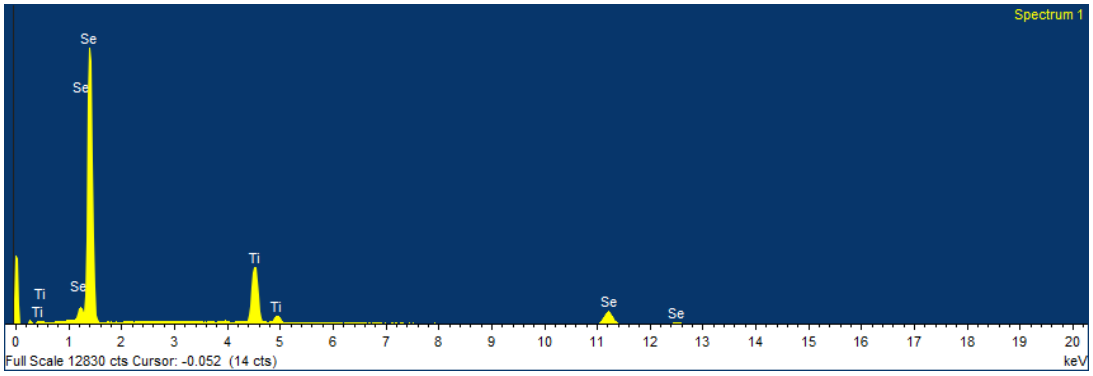


Fig.12(a)

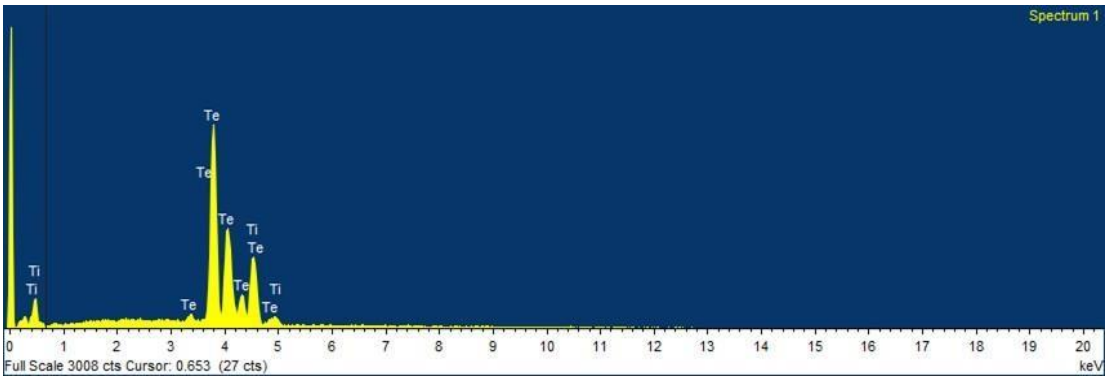


Fig.12(b)

Figure 12(a) and 12(b) are the one of the EDXA spectrum of $TiSe_2$ and $TiTe_2$ crystal taken on some surfaces respectively. The spectrum clearly indicates the abundances of only Ti,Se and Te without any other impurities of atoms. The chemical analysis result by EDXA for TiSe2 a

For $TiSe_2$

for $TiTe_2$

Atom	Atomic%
Ti	33.52±.0376
Se	66.68±0.407

Atom	Atomic%
Ti	33.52±0.141
Te	66.48±0.142

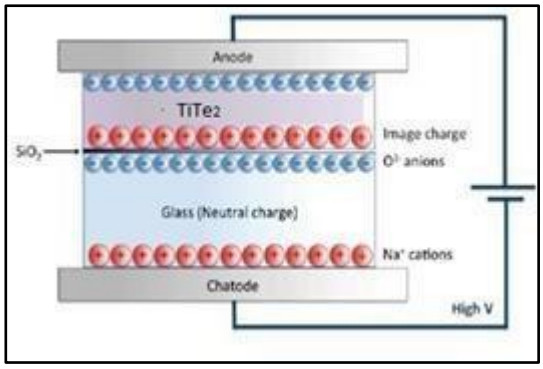
The EDXA data is consistent with the ideal Atomic% Ti=33.33% and Se/Te=66.67% in $TiTe_2$/$TiSe_2$ and clearly indicates the high quality of $TiTe_2$ and $TiSe_2$ without any other impurities or defect

3.4 Exfoliation

3.4.1 Anodic Bonding Technique: Anodic bonding technique is based on the electrostatic interaction between the precursor and a glass substrate to stick a 2D thin film on glass substrate. The Sample TiTe2 and TiSe2 Crystal is exfoliated using a scotch tape to get a very thin precursor and this precursor is put on the Borosilicate glass with 1 cm surface area and 0.5 mm thickness. This glass is put on the anodic bonding setup where the base is heated with certain temperature and glass is placed over this base. There is small tip in this setup which touches the precursor top on the glass and voltage is applied throughthis tip between Precursor and glass for certain time. After this the Precursor is again exfoliated or peeled off from glass by scotch tape to get the very thin layer of desirable material on the glass substrate.

The substrate glass contains Na2O and at high temperature dissociates to Na^{+} and O^{-2}ions. Due to high mobility of Na+ ions the Na^{+} ion move in glass and accumulates to the bottom of glass as voltage is negative there.

O^{-2} ions in form of negative charge remain at the top interface of the glass. As a consequence this negative charge induces a positive charge in the few bottom layers of precursors and there is strong electrostatic interaction occurs between precursors and glass and it stick on the glass. As the glass is removed from the anodic bonding setup as shown below the temperature decreases to room temperature which further reduce ionic mobility and the electrostatic field does not diminish.



$TiTe_2$ Anodic Bonding: TiTe2 material has not been exfoliated before by the anodic bonding technique. A series of voltage and temperature is used to find out the optimum condition for the formation of thin layer or monolayer of this material on glass substrate after exfoliation. 450 Volt to 700 Volt and 170°C to 185°C temperature is used for preparing the material. There is no anodic bonding of this material is observed below 450 V and 170°C and above the 700 V and 185℃ the material stick to the glass substrate tightly so that only bulk material is observed. The optimum condition found out to be 550V-700V and 175℃ -180℃ for 5 minutes to get good results. TiTe2 material is very sensitive towards oxidation so the material should be prepared very carefully. The environmental factors are so crucial during sample preparation.

Voltage	Temperature	Observation
Below 450 Volt	Below 170℃	There is no anodic bonding observed
450 Volt	170℃	Anodic Bonding started observing (Environmental Factors are crucial
450 -550 Volt	170℃-180℃	Anodic Bonding is observed Samples should be kept in vacuum soon due to sensitivity of TiTe2 towards oxidation and exfoliation should be done carefully
550-700 Volt	170℃-180℃	Anodic Bonding is observed but exfoliation have to be done very carefully
Above 700 Volt	Above 180℃	Precursor Stuck up tightly only bulk is observed after exfoliation.

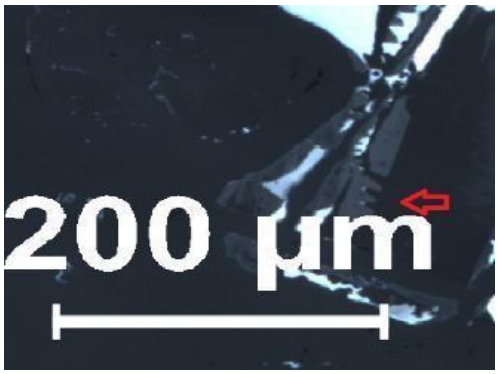


Fig.13(a)

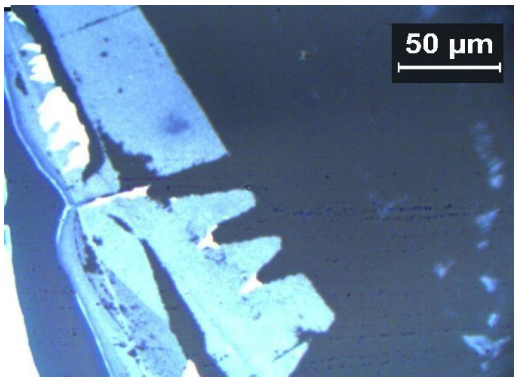


Fig. 13(b)

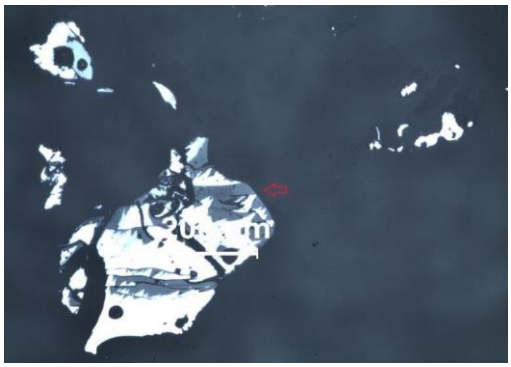


Fig. 13(c)

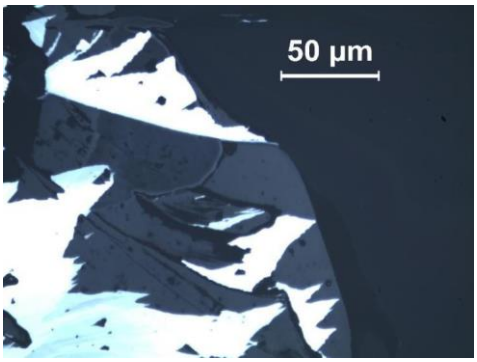


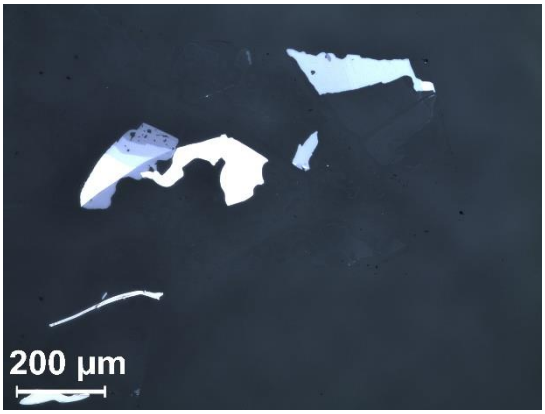
Fig 13(d)

13(a) and 13(b) are the images of the sample of $TiTe_2$ (T1) sample.13 (a) is 10x image of the sample and it is cropped from the original image to clearly show the area of focus. The red arrow indicates that area.[The original image can be seen in the appendix 3 section].13(b) is the 50x image to clearly show that area where 7-8 nm layer of the $TiTe_2$ was found on AFM characterization (16(a)) given below in AFM characterization section.13(c) and 13(d) are the images of the Sample of TiTe2(T17). A 2nm thick layer and 8-10nm thick large area found for this sample by AFM characterization(16(b)) given below.The red arrow indicates the area where characterization is focused. As we can see there are lots of bright area in the image which are the thick parts and less bright parts which are the area of focus because these parts may contain the very thin layers.

$TiSe_2$ Anodic Bonding: TiSe2 material shows different behaviour towards anodic boning as compared to the TiTe2. The temperature higher than 140-150 °C induce the selenium migration in thin layer which is discussed in detail in Raman study of the TiSe2 material. The oxidation and high temperature both factors are responsible for selenium migration in TiSe2. The high temperature between precursor material and base further can support more oxidation in this material during sample preparation. A very high voltage between the tip and precursor material 950V -1100V is used to keep the temperature less to avoid the selenium migration and oxidation. There are some good sample obtained by applying a voltage higher than 950V between tip and precursor and the temperature between 120 -125°C between the base of anodic bonding apparatus and material. A table below shows some of the observation during sample preparation of the TiSe2.

Voltage	Temperature	Observation
550V -700V	Above 140 °C	Anodic bonding is observed between precursor and glass but selenium migration is observed in thin layer due to high temperature and oxidation
950V-1100V	Below 110 °C	No Anodic bonding is observed as temperature is not enough to stick the precursor to the glass
950V –1100V	110 °C - 1200°C	Anodic bonding start observing without selenium migration in the thin part of the sample
950V -1100V	130°C	There were some good sample obtained.

As mentioned above the environmental factor is crucial during sample preparation and the glass substrate should be very clean for anodic bonding between precursor and the material.



Fig, 14(a)

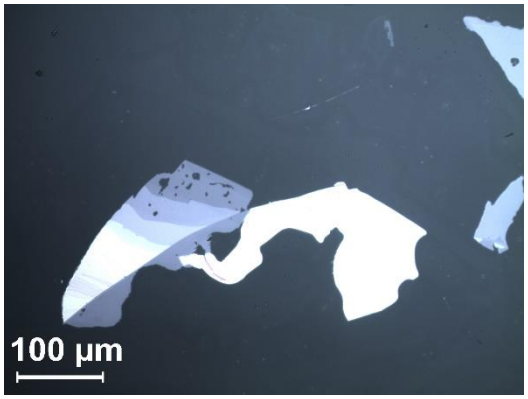


Fig.14(b)

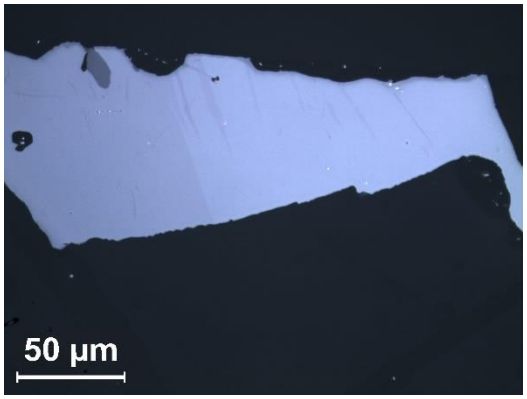


Fig.14(c)

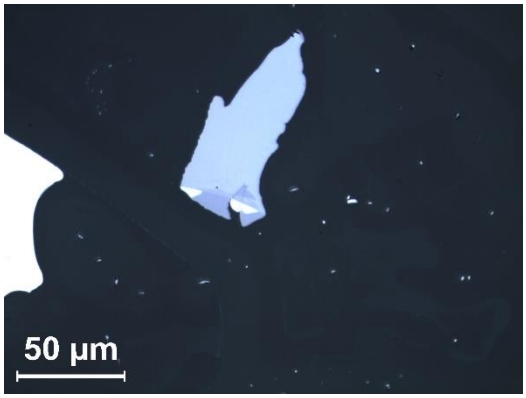


Fig. 14(d)

Fig. 14(a) is the 10x image of the sample obtained using 1000V and 130 °C temperature anodic bonding parameter. The three region is indicated as shown in Fig.14(b) shows the 20x image of the region 1 Similarly Fig. 14(c) and Fig. 14(d) are the 50x image of the region 2 and region 3 named respectively. AFM and Raman characterization is done in all three section The region 1 Fig. 14(b) is around 20nm thick as shown in the AFM characterization data. Region2 Fig. 14(c) is around 40 nm thick and region 3 is around 28-30nm thick. Raman data is taken for all three region and all three region shows the characteristics peak of TiSe2 material at 200 cm^{-1}without showing the peak at 250 cm-1 associated with amorphous selenium. The region 2(Fig. 14(c)) is used for the device fabrication.

3.4.2 AFM Characterization

Atomic Force Microscopy is a technique which can measure the thinnest part in the sam- ple in the nanoscale level. There is a sharp tip in AFM setup and in the proximity of the sample surface the deflection in the tip reproduces the topography of the surface. The instrumentation of AFM consists of a probe made of semiconductor material attached to a flexible cantilever. When this probe come very close to the surface; Attractive and repulsive forces between probe and sample surface causes deflection in cantilever and this deflection in the cantilever is detected by a Laser beam. The amount of force between the probe and sample is dependent on the stiffness of the cantilever and the short distance between sample and probe. This Force can be described by Hookes Law F=Kx Where K is the measure of the stiffness of the cantilever and x is the distance between the probe and sample surface. As the tip move over the surface it move up and down according to surface characteristics and the different type of interaction (electrostatic, Van der Wall , magnetic, Capillary)between the surface and probe creates fluctuation in Cantilever. The sample is placed on a piezoelectric material and this piezoelectric material is responsible for motion of the sample in the x,y,z direction. These piezoelectric materials is very sensitive towards applied voltage and shirk or enlarge according to voltage. These piezoelectric materials monitored the very precise motion of the sample in x,y,z direction. A laser beam reflects the deflection of the cantilever to the photodiode detector and detector measure these deflection. A topographical image of the surface is created.

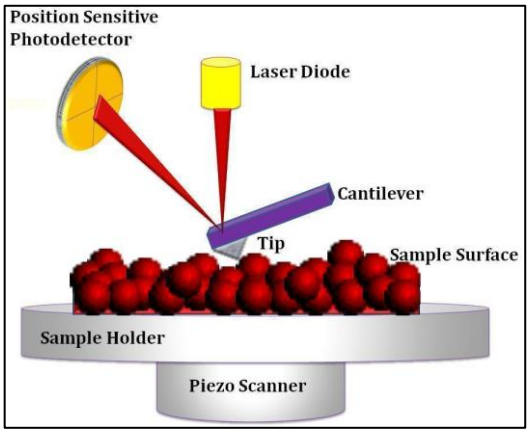
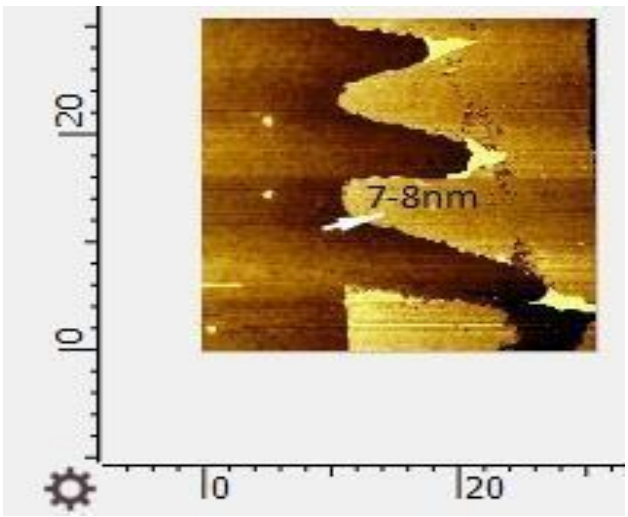
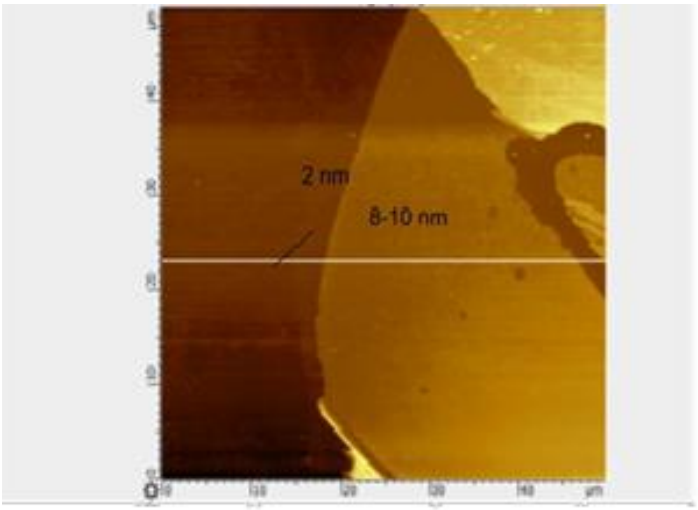
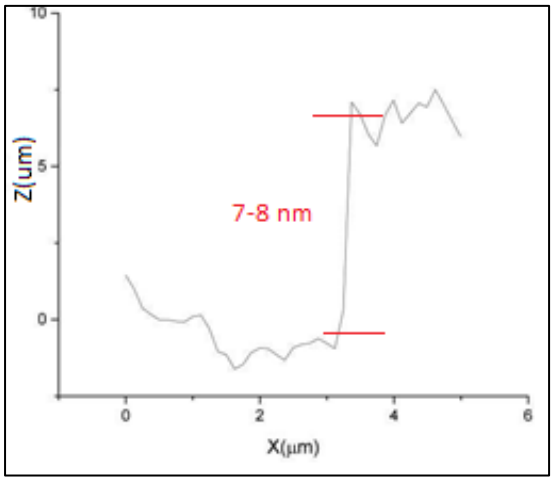


Fig.15 shows the basic instrumentation of a AFM
(http://users.metu.edu.tr/chem355/assets/11-355-AFM.pdf)







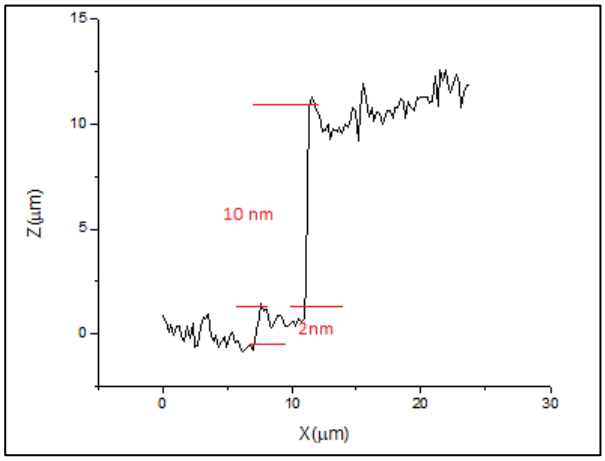
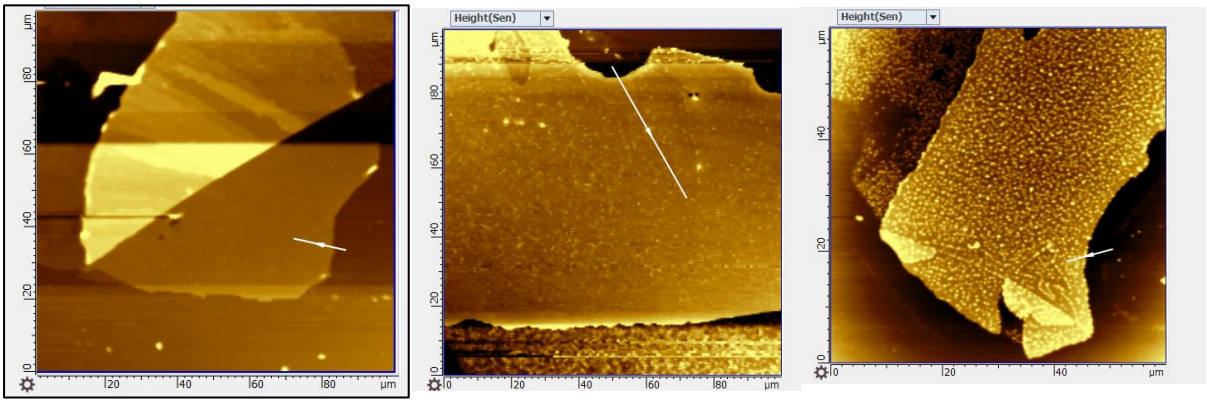


Fig. 16 (a) **Fig. 16(b)**

16(a) is the AFM characterization of the area as discussed above in 13(a) and 13(b) the graph clearly indicate the step of 7-8 nm and 7-8 nm layer thickness of this part.16(b) AFM characterization of the area as discussed above in 13(c) and 10(d).There are two steps in the graph the first step is of 2nm and another step is 8-10 nm shown. This indicates a 2nm layer and 8-10 nm layer in this area.



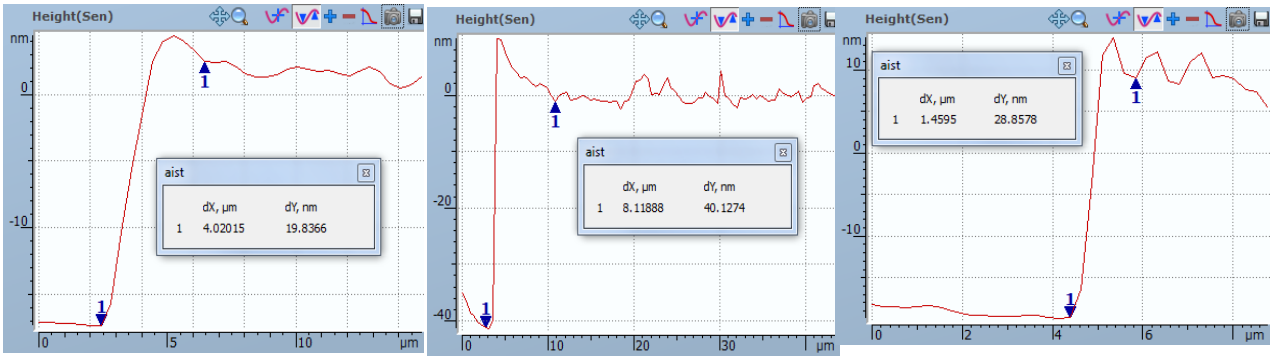
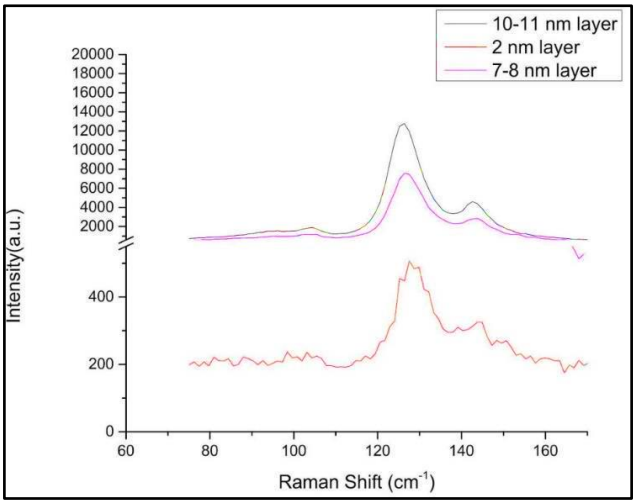


Fig.17(a) **Fig.17(b)** **Fig.17(c)**

Fig. 17(a) is the AFM characterization of the Region 1(Fig.14(b) .This layer is around 20nm thick found during AFM characterization. Similarly the region 2(Fig. 14(c) is 40 nm around 40nm thick and Region3 is 28-30nm thick as shown by Fig.17(b) and Fig.17(c)

3.4.3 Raman Characterization

Raman Spectroscopy is a spectroscopic technique used to provide a structural fingerprint by which characteristic atomic or molecular vibrations can be identified, leading to identification and characterization of materials. This technique is based on the inelastic scattering of monochromatic light from a laser which interacts with vibrations of phonons or molecules in the sample. The energy of photons is accordingly shifted up and down which causes shift in wavelength and gives information about vibrational modes. When electromagnetic wave interacts with the molecular vibration or the with the phonons in the crystal it can scatter with the same frequency as the source frequency (Rayleigh scattering) or it can scatter with a different frequency known as Raman scattering. The material is characterized by its Raman Spectrum giving particular peaks in the spectrum.



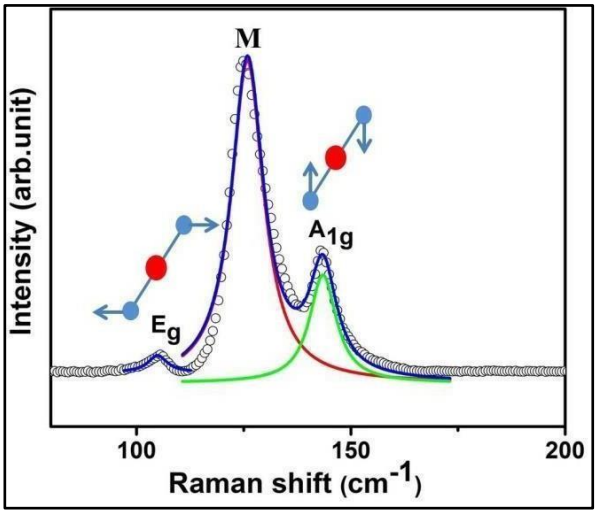


Fig. 18(a) **Fig.18(b)**

The Raman Characterization is also done to see the characteristics of these layers as discussed above. As we can see the intensity of the Raman spectrum is increasing with the layer thickness. There is peak around 130cm^{-1}and 145cm^{-1} which is consistent with the standard Raman spectrum of TiTe2 single Crystal[20] 13(b).There is small shift in 145cm^{-1} peak varying the thickness of the layer and this peak is not sharp in 2nm layer due to very small intensity.

Raman Characterization: TiSe2 a detailed study

A detailed Raman Study of TiSe2 was done during this project. The typical Raman Spectra of TiSe2 shows a peak at 200 cm-1 (A1g mode) and 136 cm-1 (E1 g mode) as reported. Fig. 19 shows the Raman spectra of the freshly cleaved crystals which were synthesized previously in the project. This crystal is freshly cleaved and the Raman spectrum is taken from four different cleaved surfaces to ensure repeatability. The Raman spectra clearly show the strong peak at 200 cm^{-1}(A1g) and a weaker broad peak around 135 cm^{-1} which is consistent with the reported data[21].

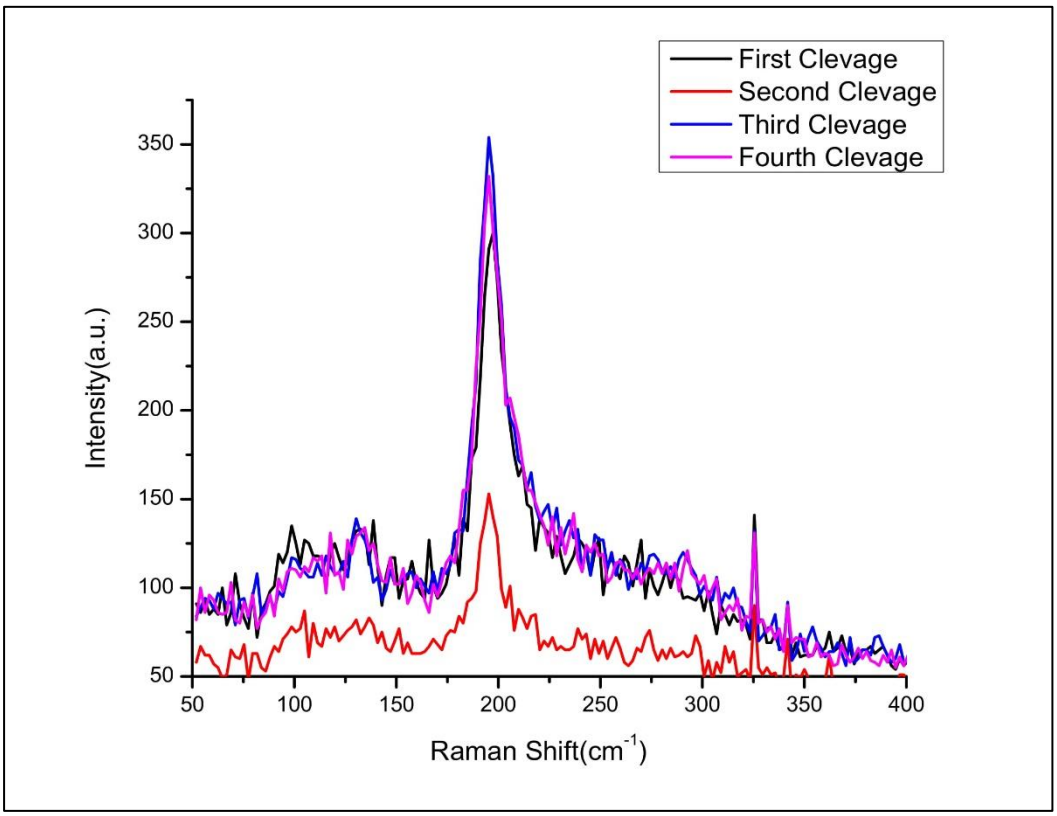
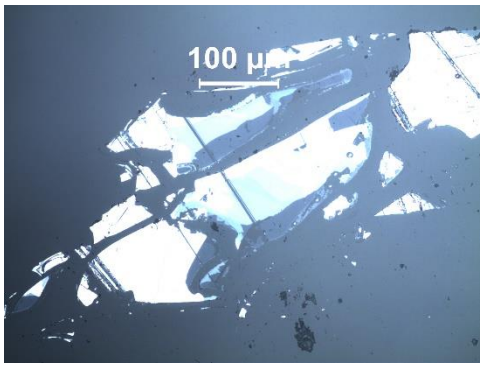


Fig.19

The Raman spectra of the samples prepared by anodic bonding method using high temperature shows a large shift at 250 cm-1 for the thin layer (<30 nm) during sample preparation after exfoliation compared to the standard Raman spectra of the TiSe2 fresh crystal and bulk part of the sample. This large shift further led to the detailed Raman study of the TiSe2 sample. The figure 20(a) and Fig. 20(b) below shows the sample prepared by the anodic bonding method and its two different regions where the Raman study is done. This sample is prepared with the 180°C and 650V anodic bonding parameter.



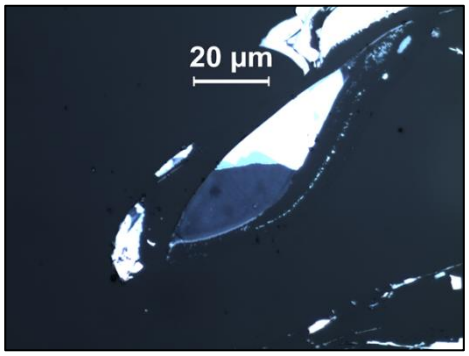
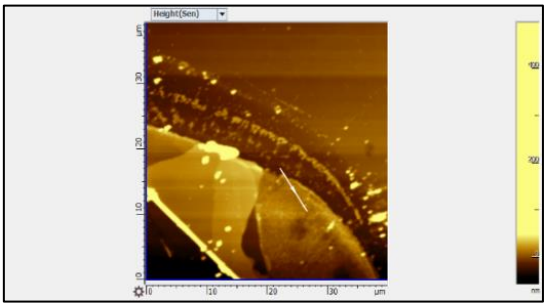
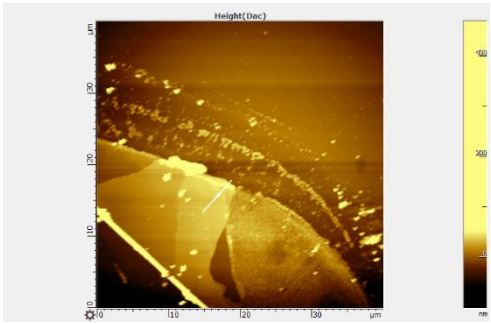
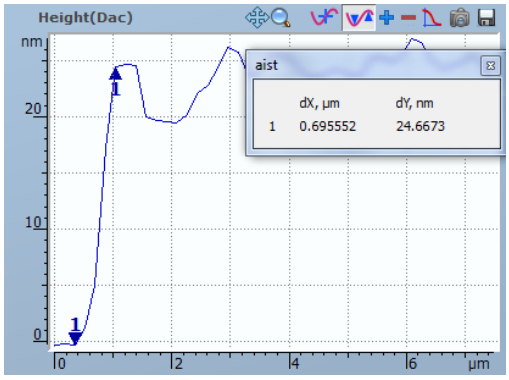


Fig.20(a) **Fig. 20(b)**

Fig.20(a) is the 20x image of the sample prepared using 180°C and 650V anodic bonding parameter. The two regions are indicated in the image with red box. Fig.20(a) and Fig. 20(b) are the 100x image of the region 1 and region 2 respectively.







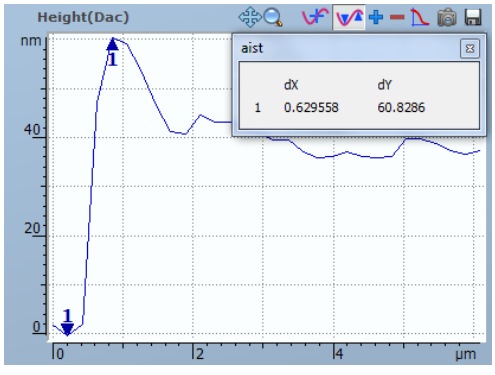


Fig. 21(a) **Fig. 21 (b)**

Fig. 21(a) is the AFM image of the thinner layer of the region 1(Fig. 15a) and its thickness is around 20-26nm as shown in the step and 21(b) is the thickness of the bulk part of the region 1 and the thickness of the bulk part is around 60 nm as shown in figure

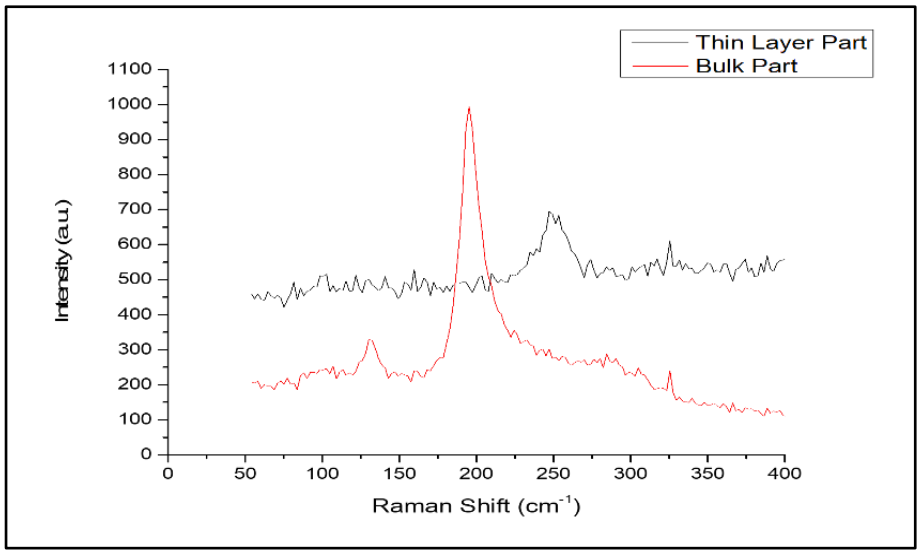


Fig. 22

Fig. 22 shows the Raman spectrum of the region 1. The Bulk part represents the brighter area in the image whose thickness is around 40 nm measured by AFM above. The thinner layer is the darker area of the region1 whose thickness is 20-25 nm as discussed above. The Raman spectrum of the thin layer shows peak at 250 cm^{-1} which is a big shift as compared to the Raman spectrum of the bulk part which shows peak at 135$cm^{-1}$and 200cm-1 as usually reported peak for the TiSe2 crystal. This huge shift cannot be due to varying thickness of the layer.

The origin of the peak at 250 cm-1 of $TiSe_2$ samples was found by reviewing literature. Some works report selenium migration to the surface due to atmospheric oxidation of the $TiSe_2$ sample[22]. $TiSe_2$ samples are very sensitive towards atmospheric oxidation under ambient conditions and the peak emerging around 253 cm^{-1} is due to amorphous selenium as reported in this work. The other oxidation product is TiO_2 which is Raman inactive. In the above cited work Auger electron spectroscopy confirms TiO_2 presence in the oxidized flakes of $TiSe_2$ and also showing the Ti-O-Se as intermediate structure. There is another report claiming the photon and temperature combined induced effect of the diffusion of selenium in the TiSe2 crystal [23]. This report could also explain our observation as our samples are prepared at 140°C and high temperature provides migration energy for selenium in the TiSe2 Crystal.

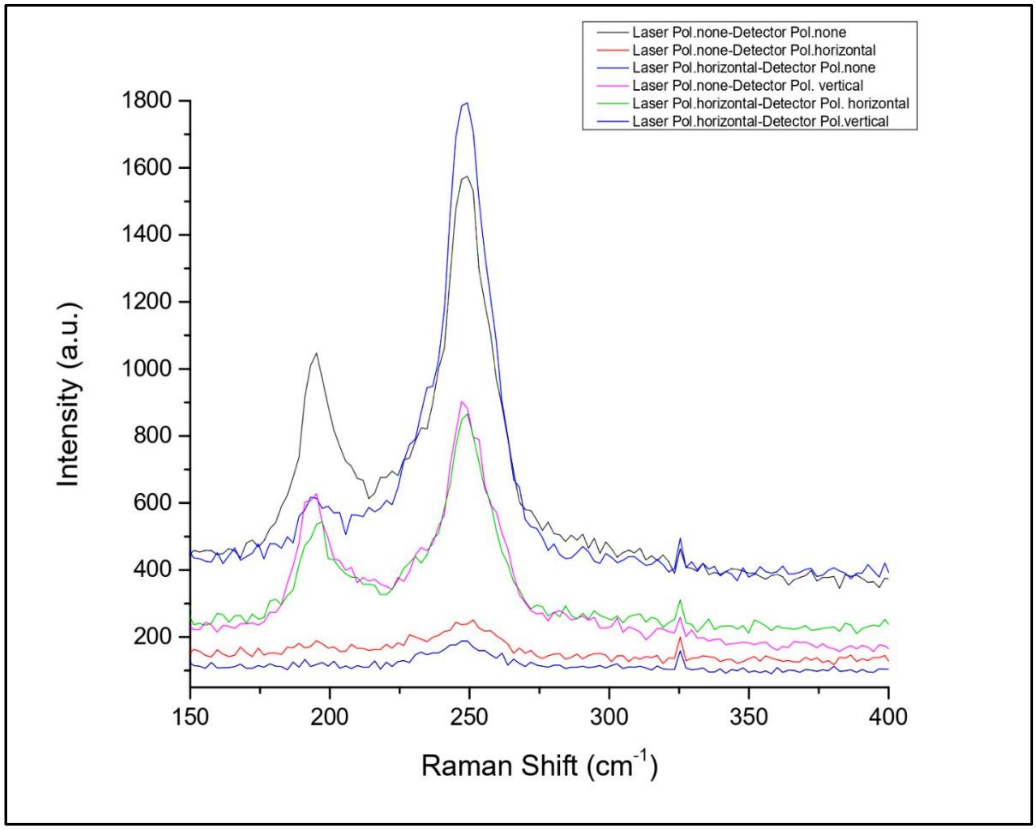
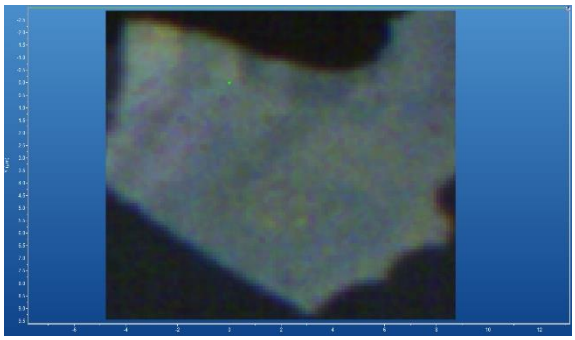


Fig. 23

Fig. 23 shows the Raman polarization experiment of a sample in which peak around 200 cm^{-1} and 250 cm-1 appears without using any polarizer. Raman polarization experiment can give the information about the symmetry and orientation present in the crystal and the bond vibrations present in the materials. The polarizer linearly polarized the monochromatic light either coming from source or the light going back to detector. As we know that the peak around 200 $cm^{-1}$is due to A1g mode of vibration and this vibration disappears at the cross polarization condition(horizontal-none or none-horizontal).The data is compatible with the peak around 250cm-1 due to amorphous Selenium as reported in some research journals[24-25]as we can see the 250cm^{-1}peak is always present in any polarization condition.



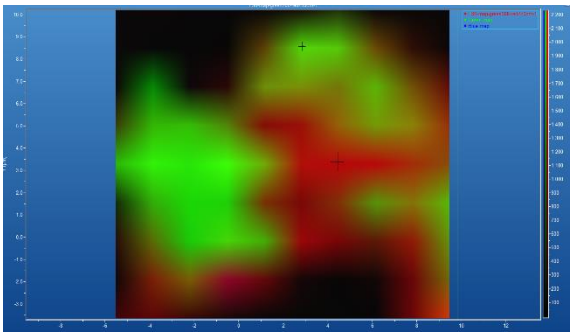


Fig. 24 (a) **Fig. 24(b)**

Fig. 24(a) shows the image of the region of an exfoliated $TiSe_2$ sample in which the Raman mapping is done. Fig. 24(b) is the Raman map of the sample. As we can see the two regions in the sample with green and red area. Fig. 24(c) shows the Raman spectrum from these two regions. Red regions shows the area where selenium migration is occurred due to which there is only one peak around 250 $cm^{-1}$is present in the spectrum. The green region is the area in which both peak at 200cm-1 and 250 cm-1 is present which shows that this is the area where TiSe2 sample is start oxidizing and selenium migration is occurring.

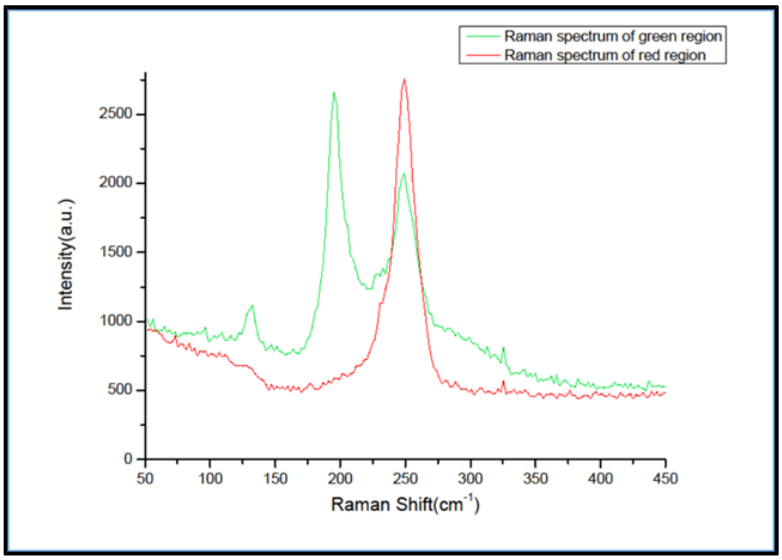


Fig. 24(c)

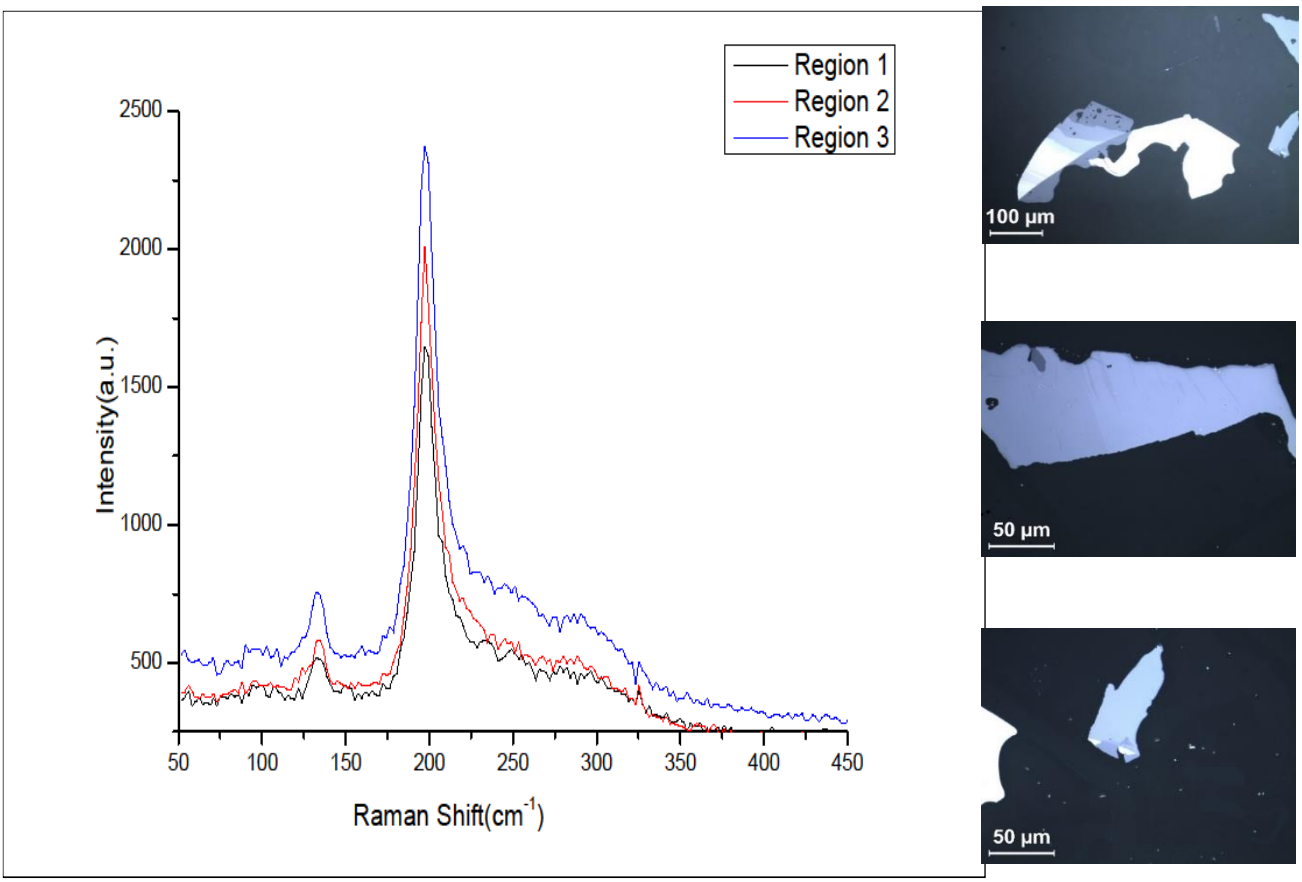


Fig. 25

Fig. 25 shows the Raman spectrum immediately after sample preparation of the three different region of a sample as discussed in the TiSe2 anodic bonding observation section. All of the three region show the 200cm^{-1}peak intrinsic to TiSe2. This sample is made with high voltage and lower temperature (xxx indicate voltage and temeprature) hence avoiding selenium migration.

3.5 Chemical Exfoliation

A different method was also tried to to chemically exfoliate the crystal.

Liquid exfoliation: in this technique we take the crystal in a solvent and keep it for some course of time and then sonicate and drop-cast it into substrate. The solvent molecules are expected to intercalate the layered material. The choice of solvent, time

period to intercalate the single crystal and sonication period all these factors affect the results. TiSe2 crystal are dipped in the 5ml butanol for 48-72hours and sonicated for 15 minutes and then dropcasted on glass substrate

Li intercalation exfoliation method: This method is similar to liquid exfoliation. In this method one dissolve the Li salts in solvent system and put the crystal in this solvents system for some time to intercalate the layered materials

LiOH salt is dissolved in ethylene glycol solution and stirred for 24 hours at 65° and TiTe2 crystal was put in this solution for 72 hours to intercalate the layer

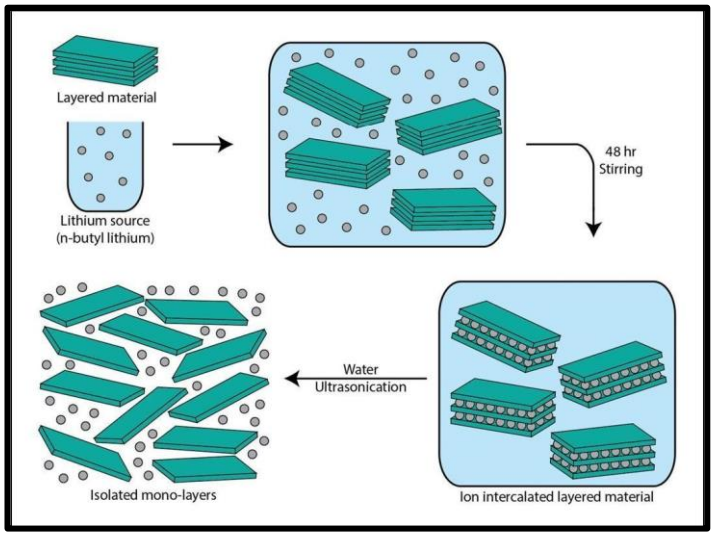


Fig.25

Fig.25 (from E.Nguyen et al. Liquid Exfoliation of Layered Transition Metal Dichalcogenides for Biological Applications. Current Protocls in Chem Bio,97-108,(2016))

Fig 25 show an overall scheme of chemical exfoliation where Li ion intercalate between the layers and after sonication layers are further apart due to intercalation and this sonicated solution further dropcasted on the substrate.

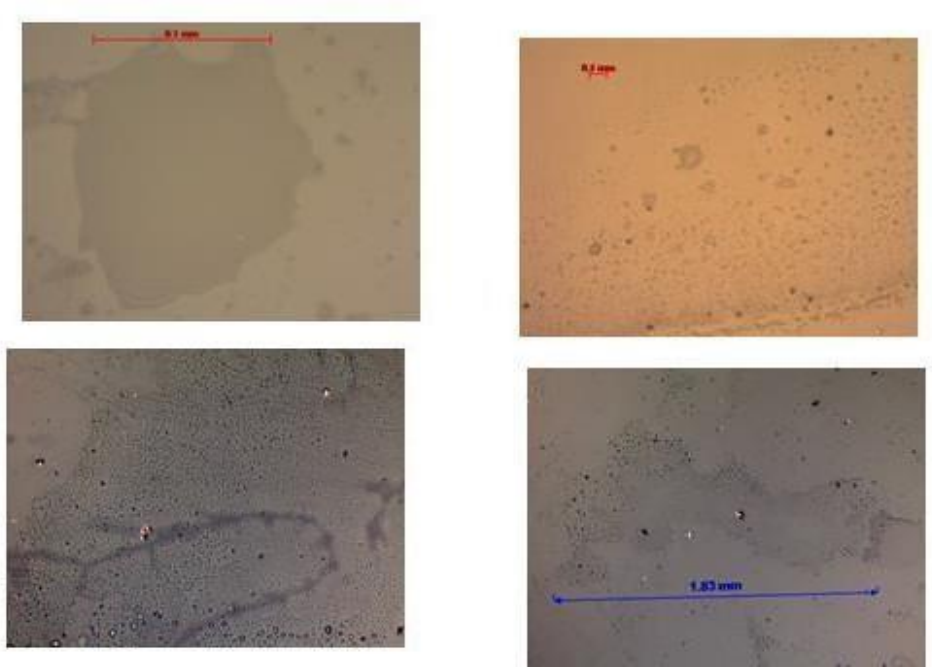


Fig. 26(a) Fig.26(b)

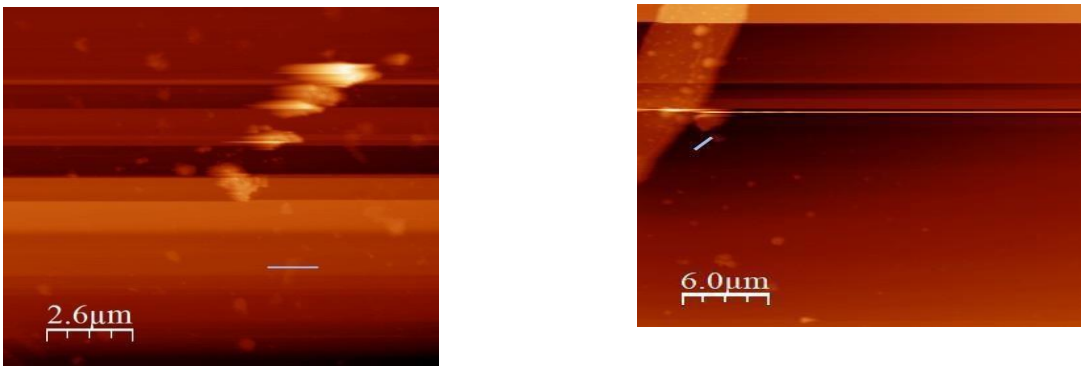


Fig.26(a) and Fig.26(b) are some of the images of the sample chemically exfoliated

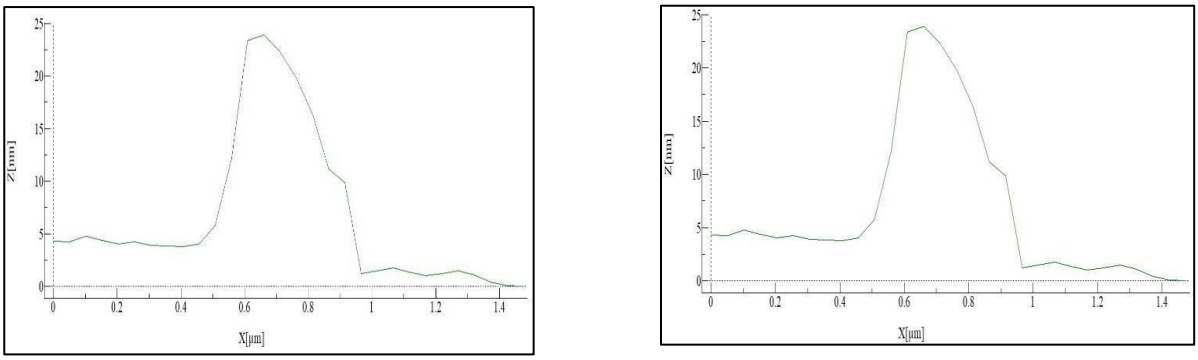


Fig.27 (a) Fig.27b)

Fig. 27(a) and Fig. 27(b) shows the AFM characterization of the sample show the layers of 18-20 nm layer indicating the layer is not intercalated properly. The results for the chemical exfoliation were not very good

3.6Device Fabrication:

3.6.1 Gold Contact Deposition: Gold contact deposition was made on substrate using Edward high Vaccum evaporator. Gold is heated in a tungeston crucible by providing a high current. The high temperature and high vaccum condition led gold to go in gas phase and deposit on the mask and on the substrate. Th gold deposition is started when a vaccum level of 5 X 10^{-6} is achieved. The Mask we use to make gold contact is shown below

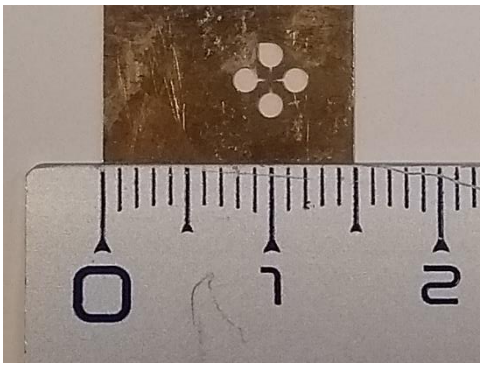


Fig. 28

Fig. 17 shows the mask used for gold deposition. This mask is made of steel and the distance between two contacts of mask is 50µm. So the dimension of the mask should be higher than 50µm X 50 µm to get all contacts in the sample and these mask should be very flat to have better results

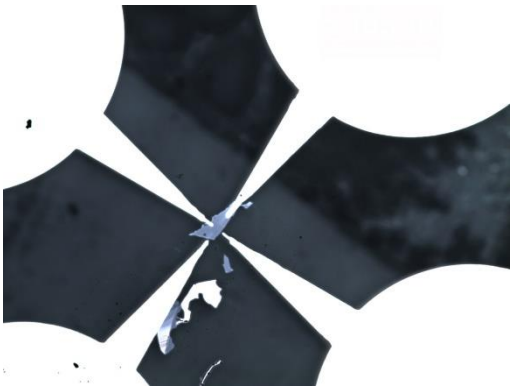


Fig. 29

Fig. 29 shows the samples in which gold contacts were made. It can be noted that only two contacts were made in sample . Fig. 29 is the region 2(Fig.14(c) as discussed in TiSe2 anodic bonding method

,

3.6.2 Measurement and observation

A very basic two wire resistance measurement is done in this sample at room temperature. Sample 18(a) has the Resistance value across its contacts is 20MΩ measured at room temperature. The next step is to take that sample to a cryostat sample holder where a wire bonding is done between gate of the sample holder and gold contacts in the sample.

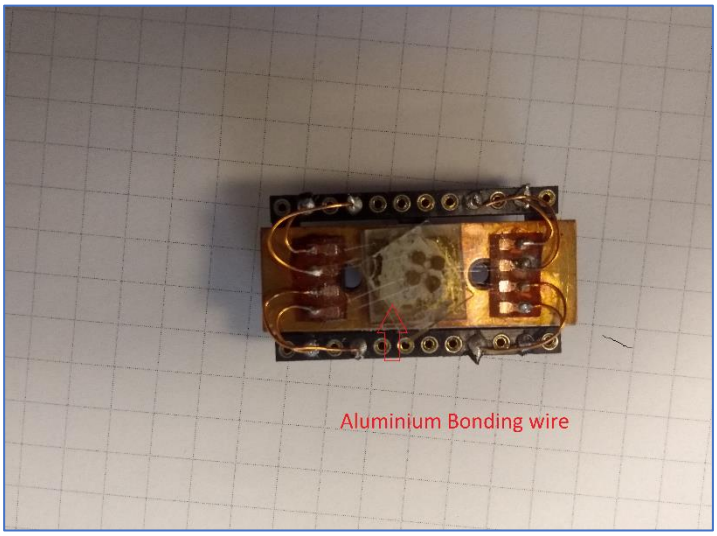


Fig. 30

Fig. 19 shows a cryostat sample holder and aluminium bonding wire which is attached between gold contacts and gate of the sample.

There is silver paste between the glass and the base of the sample holder. The wire is made of aluminium as shown in figure and attach the gate of the holder.

IV Conclusion

4.1Single crystal Fabrication and Crystallization- The above result and discussion concludes the synthesis of very high quality of the $TiTe_2$ and $TiSe_2$ single crystals.The fabrication stragies are successful and Chemical Vapour transport found as the optimum parameter. The Parameter used for TITe2 crystal Tsource =900°C with temperature gradient =100°C and found best for crystal synthesis. Similarly for the TiSe2 crystal the Tsource=900°C and the gradient temparature=100°C found out most suitable for crystal synthesis. The crystal is characterized by various technique such as XRD,SEM and EDX technique. The XRD characterization is consistent with the standard one and lattice parameters calculated by XRD data also indicate the high quality of crystals. SEM characterization shows sharp edges and single crystal characteristics' characterization shows the layered structure and crystal character shows the synthesis layer by layer. The EDX characterization is done for both crystal and the atomic composition for TiTe2 and TiSe2 is found consistent with the ideal composition for these crystals and there is no impurity was detected during characterization. The characterization of the crystals shows the fabrication strategies successful and the optimum parameters found out for these crystals by chemical vapour transport (CVT).

4.2 2D Samaples: These high-quality crystals further can be used for exfoliation and to make good quality of devices. The anodic bonding method is also an efficient method to get the thin layer and the parameters in this method are crucial to get the better results. The results for the chemical exfoliation of the crystals are not much satisfying. There are some thin layers samples 8- 10nm and 7-8nm got by this method but these TiTe2 sample is not compatible to make the devices because of the limitation of the separation between contact of mask used. As the dimension of these region is less than 50μm x 50 μm. We got some TiSe2 sample which is 20 -30 nm thick without affecting the quality of sample as shown by the standard Raman characteristics of TiSe2.

3.Raman Characterization and detailed Raman study: The detailed Raman study is done for the TiSe2 sample and we can conclude that 250 cm-1 peak in the sample is due to the migration of amorphous selenium in TiSe2 crystal. The Raman polarization data is compatible with the raman charecterstics of the Amorphous

Selenium reported in journals. There are some good sample obtained using the temperature less than 130 C and a high voltage greater than 950 V which shows no peak at 250 cm-1 immediately after Raman characterization. The study also conclude that this migration is assisted by high temperature and oxidation.

4.3Device Fabrication: A detailed procedure and fundamentals are learnt to fabricate 2D TiSe2 samples for making devices including aligning mask with the region of the sample with good accuracy by Microscope to have contacts in region then gold contact deposition in these samples in the clean room. The sample resistance is measured by a two-wire contact measurement at room temperature as we have the two contacts in the sample. The sample resistance was found 20MΩ at room temperature which was quite high. As we have discussed earlier the 2D TiSe2 samples is very ambient to oxidation and sensitive to temperature. The devices made by these materials is not suitable at ambient condition and the samples must be kept in high vacuum to have good quality of samples. These gold contact TiSe2 sample is further used for the wire bonding between cryostat holder gate and gold contacts in the sample. These cryostat sample holders will further put on high vacuum cryostat and the electronic properties will further be studied at very low temperature and High pressure.

V Prospective

The TiSe2 sample is wire bonded between cryostat holder gate and gold contacts. These are fundamental devices which will be further studied by the lab to study the electronic properties of the sample with low temperature and high pressure. The TiSe2 sample electronic properties will be induced by space charge doping. The space charge doping is a modern technique used by our lab to dope the sample which is based on the ionic mobilities of the glass sample and use these ions to create a charge imbalance between glass and sample interface to induce charges in the sample. The soda lime glasses used for making sample contains mobile Na+ ions and when we apply a positive voltage at the gate it will repel Na+ ions in the bottom and the top of the glass become positively charged and it will further induce a negative charge in the sample or n dope the sample. Similarly, when we apply a negative voltage it will induce the positive charges in the sample or p dope the sample as shown in below figure(Fig.31)

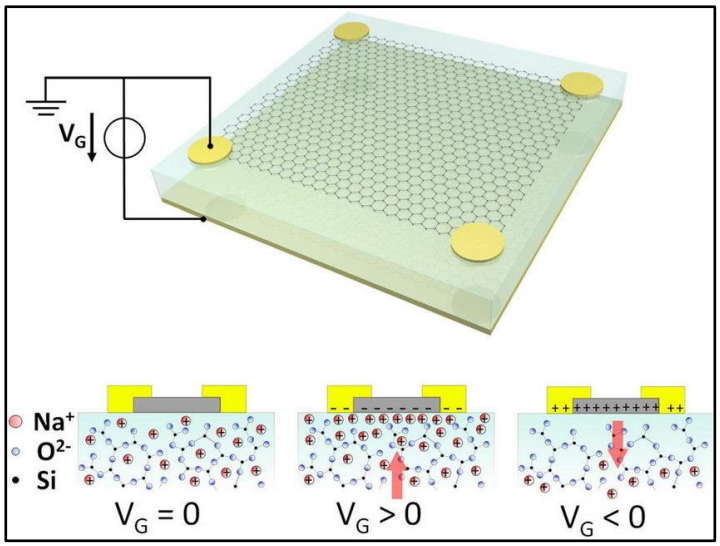


Fig. 31(A. Shukla et al. Space charge induced electrostatic doping of two-dimensional materials: Graphene as a case study, Appl.Phys. Lett.107,143103(2015)

Fig. 31 shows the schematic representation of the space charge doping. The tyepe of the doping depends on the nature of the gate voltage.

APPENDIX 1

Pattern : 01-089-2759 **Radiation =** 1.540600 **Quality :** Calculated

$TiTe_2$

Titanium Telluride

Lattice : Hexagonal
S.G. : P-3m1 (164)

a = 3.76600
c = 6.49100

Z = 1

Mol. weight = 303.10
Volume [CD] = 79.73
Dx = 6.313
I/Icor = 9.85

ICSD collection code: 043413
Remarks from ICSD/CSD: REM M PDF 32-1388, 48-1386.
Remarks from ICSD/CSD: REM M Cell for Ti.4 Te.6: 3.884, 6.348, with additional Ti i
Test from ICSD: No R value given.
Test from ICSD: At least one TF missing.
Data collection flag: Ambient.

Gronvold, F., Kjekshus, A., Haraldsen, H., Z. Anorg. Allg. Chem., volume 317, page 91 (1962)
Calculated from ICSD using POWD-12++

Radiation : CuKa1
Lambda : 1.54060
SS/FOM : F22=277(0.0033,24)

Filter : Not specified
d-sp : Calculated spacings

2th	i	h	k	l
13.631	83	0	0	1
27.323	93	1	0	0
27.460	200	0	0	2
30.653	999	0	1	1
39.125	289	0	1	2
41.711	3	0	0	3
48.294	209	1	1	0
50.584	200	1	0	3
56.452	117	2	0	0
*56.452	117	1	1	2
56.678	71	0	0	4
58.293	118	2	0	1
63.827	50	2	0	2
64.038	34	0	1	4
65.681	3	1	1	3
72.528	52	0	2	3
72.792	27	0	0	5
77.347	8	2	1	0
77.605	73	1	1	4
78.996	76	1	2	1
79.381	41	0	1	5
83.893	36	1	2	2
84.083	20	2	0	4

APPENDIX 2

Pattern : 00-030-1383 **Radiation =** 1.540600 **Quality :** Calculated

$TiSe_2$
$/(Se_2Ti)$

Titanium Selenide

Lattice : Hexagonal
S.G. : P-3m1 (164)

a = 3.54000
c = 6.00800

Z = 1

Mol. weight = 205.82
Volume [CD] = 65.20
Dx = 5.242
I/Icor = 7.46

Additional pattern: To replace 5-645.
Data collection flag: Ambient.

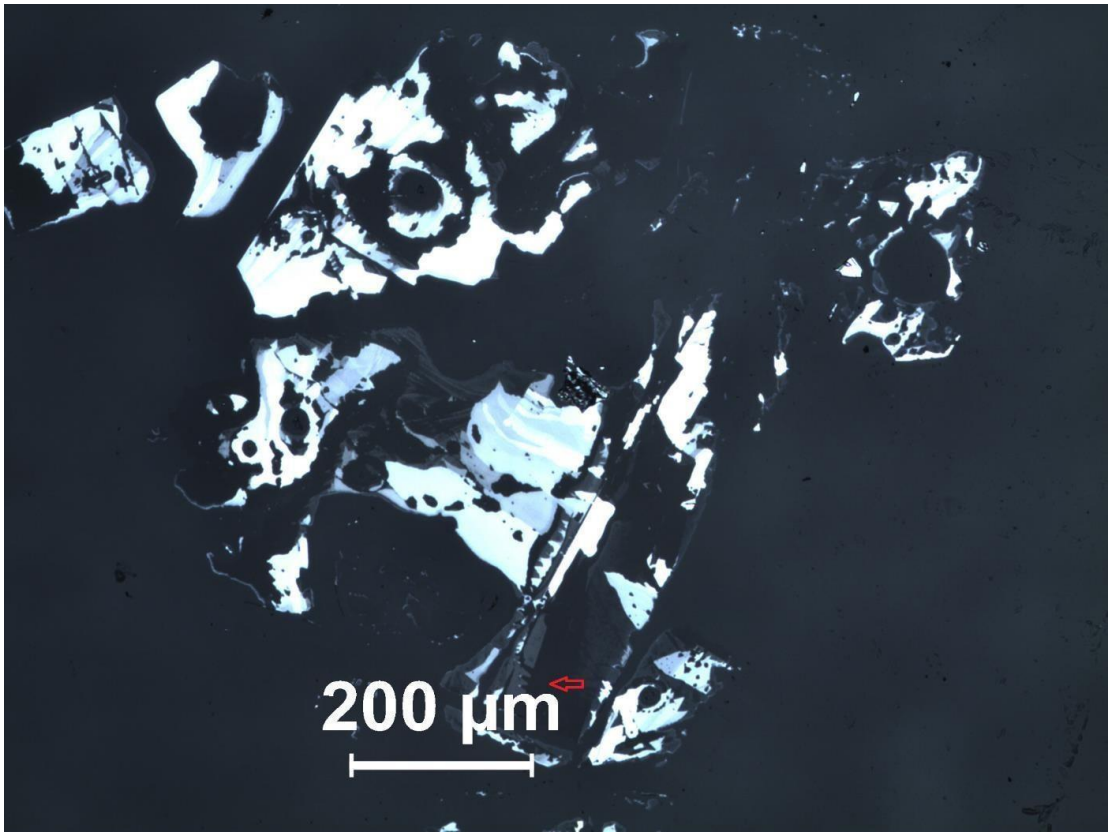
Calvert, L., National Research Council of Canada, Ottawa, Canada., ICDD Grant-in-Aid (1978)

Radiation : CuKa
Lambda : 1.54188
SS/FOM : F30=150(0.0049,41)

Filter : Not specified
d-sp : Calculated spacings

d (Å)	i	h	k	l
6.00500	15	0	0	1
3.06400	3	1	0	0
3.00400	12	0	0	2
2.72990	100	1	0	1
2.14560	35	1	0	2
2.00280	1	0	0	3
1.76990	23	1	1	0
1.69790	2	1	1	1
1.67670	18	1	0	3
1.53270	1	2	0	0
1.52500	8	1	1	2
1.50220	4	0	0	4
1.48530	12	2	0	1
1.36550	6	2	0	2
1.34870	1	1	0	4
1.32620	1	1	1	3
1.21720	5	2	0	3
1.14520	8	1	1	4
1.13780	8	2	1	1
1.11860	4	1	0	5
1.08110	5	2	1	2
1.02190	3	3	0	0
1.00290	6	2	1	3
0.96750	2	3	0	2
0.95190	2	1	0	6
0.94570	3	2	0	5
0.88500	2	2	2	0
0.87150	1	1	1	6
0.84890	1	2	2	2
0.84490	4	3	0	4
0.84190	4	3	1	1
0.83830	2	2	0	6
0.83400	4	2	1	5
0.82640	2	1	0	7
0.81810	3	3	1	2
0.78270	5	3	1	3

APPENDIX 3



APPENDIX 3 show the origin image for the 10(a) where the focus area is shown by red arrow and 10(a) is part of the APPENDIX 3 image

APPENDIX 4 Points to be mentioned : There are some necessary actions and problem to be men- tioned during the project –

1. TiTe2 material is very sensitive to oxidation and the samples must be kept in Vacu- um and during sample preparation there should be proper arrangement to keep bulk material in vacuum and also the environmental factors are so crucial for TiTe2 sample preparation.

2. There are lots of rough surfaces found during AFM Characterization and exfolia- tion should be done very carefully. The precursor should be flat and fresh.

3 .The Raman Characterization should be done at the same time taking AFM character- ization because TiTe2 material is sensitive enough to oxidative environment and it can affect the Raman profile.

4.Only Bulk and glass observed in many samples because in many samples precursors is not bonding properly to the glass. So the anodic bonding parameters are so crucial during sample preparation and also exfoliation should be done very carefully with proper scotch tape.

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