SYNTHESIS AND STRUCTURAL STUDY OF PtSe² THIN FILM

DISSERTATION

SUBMITTED TO SCHOOL OF PHYSICAL SCIENCES DOON UNIVERSITY, DEHRADUN IN PARTIAL FULFILLMENT OF THE REQUIREMENTS OF THE DEGREE OF

> **Masters in PHYSICS** BY

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Declaration

I declare that the work presented in the Dissertation entitled **'Synthesis and structural study of PtSe² thin film'** being submitted to the Department of Physics, School of Physical Sciences, Doon University, Dehradun for the award of Masters in Physics is my original research work.

The Dissertation embodies the results of investigations, observations, and experiments carried out by me. I have neither plagiarized any part of the dissertation nor have submitted the same work for the award of any other degree/diploma anywhere.

Date: Ankita Bisht

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Certificate

This is to certify that the Dissertation entitled **'Synthesis and structural study of PtSe² thin film'** submitted by **Ankita Bisht** has been done under my supervision. It is also certified that the work in this Dissertation embodies original research and hard work of the candidate.

The assistance and support received during the course of investigation and all the sources of literature have been fully acknowledged.

Supervisor/Guide Head of Department

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(Ankita Bisht)

ABSTRACT

Platinum Diselenide (PtSe₂) is the 2-dimensional metal which belongs to the Transition Metal Dichalcogenide family (TMDCs). It varies from semimetal to semiconductor as its thickness varies from bulk to monolayer. The monolayer of PtSe₂ is an indirect semiconductor which has band gap in the range $1.2 - 1.8$ eV.

In this study we are going to report the synthesis and structural study of Platinum Diselenide (PtSe2) thin film using pulsed laser deposition technique. During pulsed laser deposition technique most of the experimental parameters can be altered, which creates a strong influence on film properties. The laser parameters such as wavelength, pulse duration etc. can be altered. The preparation conditions, including target-to-substrate distance, substrate temperature, background gas and pressure, may be varied, which impacts the growth of thin film.

X-ray diffraction (XRD) is used for the characterization of thin films. Field emission scanning electron microscopy (FESEM) and atomic field microscopy (AFM) images are also being investigated in order to study morphology and roughness of the thin film.

PtSe₂ is a 2D material which has tunable band gap and high carrier mobility which makes it a promising candidate for high performance in gas-sensing, high-speed electronics and optoelectronics.

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Chapter 1

INTRODUCTION

Transition-metal dichalcogenides (TMDCs) are thin [semiconductors](https://en.wikipedia.org/wiki/Semiconductor) of the type MX² consisting of a transition-metal M (Ti, Hf, Zr, V, Nb, Ta, Mo, W, Tc, Re, Pd, Pt) and chalcogen atoms X (S, Se, Te). There are approximately 60 compounds in the transition metal chalcogenide family. Layered transition metal dichalcogenides (TMDCs) are materials that have long been of interest, and with the advent of modern synthetic methods and exfoliation techniques. Transition-metal dichalcogenides (TMDCs) have unique features that are increasingly being exploited to solve key scientific and technological problems.

1.1 Thin film

Thin film is a layer of 2-dimension having thickness range from fraction of nanometres to several micrometres. Thin film coating is used to change the physical and chemical properties of material as well as their morphology without changing composition of the bulk material. Different chemical reaction takes place during the deposition process which give rise to variety of microstructures and these resulting microstructures can either be amorphous or polycrystalline.

- **Amorphous thin film:** these are essentially short-range order structures and their growth takes place at low substrate temperature where the mobility of the adatoms at the surface of the substrate is limited this is because at low temperature the atoms undergo to the thermal equilibrium with the substrate and do not have that much energy to diffuse through the surface of the substrate.
- **Polycrystalline thin films:** these are large number of nano/micro crystallites with different orientations separated by grain boundaries. Their growth takes place at high

substrate temperature where the mobility of adatoms at the surface of the substrate is not limited this is because at high temperature the atoms do not undergo thermal equilibrium with the substrate and they have that much energy to diffuse through the surface of the substrate.

We can use different deposition technique for the deposition of thin film but here, we are using pulsed laser deposition technique (PLD) for coating of thin film pulsed laser deposition technique comes under physical vapor deposition (PVD). This whole process takes place in vacuum a chamber, a pulsed laser is used to irradiate the bulk material which leads to the production thin film using PLD.

Thin films play an essential role in development and study of new and unique properties of materials and it also has allowed vast range development in areas like electronic semiconductor devices, LEDs, optical coating etc.

Figure1.1 Thin films

1.2 Material used for Deposition

In this study we are using pulsed deposition technique to deposit platinum diselenide (PtSe₂). PtSe₂ is a 2-dimensional TMDC material having unique optical properties. PtSe₂ has got lot of attention because of its captivating physical features and practical use potential.

2-dimemsional PtSe² has exhibited potential in many areas such as photocatalytic, hydrogen evolution reaction, electronic, and optoelectronic devices. PtSe₂ has strong layer dependent band structure. Bulk PtSe₂ is semi metallic in nature while monolayer of PtSe₂ are semiconductors. Moreover, PtSe₂ exhibits anisotropic carrier mobility along different directions. Its carrier mobility is greater than any other TMDC. It is a semiconductor with band gap of 1.2 eV and 0.21 eV in monolayer and bilayer form respectively and losses its band gap when thickness reaches trilayer or even more. A semimetal has non-zero conductivity, whereas a semiconductor has zero conductivity at zero temperature. PtSe₂ monolayers can be used in visible and mid-infrared photodetectors.

1.2.1 Crystal Structure

Generally, there are two common structural phases for monolayer TMDCs, which are characterized by either octahedral or trigonal prismatic (2H or D_{3h}) or (1T or D_{3d}). Unlike group-6 TMDCs, group-10 TMDCs tend to form d2sp3 hybridization due to group-10 metal atoms holding rich d-electrons and less d orbitals are involved. As a result, group-10 TMDCs lead to the generation of the thermodynamically favoured 1T-phase. PtSe2 has a thermodynamically favoured 1T-phase structure and the atoms stack in the AA arrangement. PtSe₂ crystal belongs to the p3ml space group of the trigonal system. Many techniques have been employed to characterize the atomic structure of monolayer PtSe₂, such as high-resolution scanning transmission electron microscope (HR-STEM), scanning tunnelling microscope (STM), low energy electron diffraction (LEED), and density functional theory (DFT) calculation which clearly shows that each Pt atom is in a tilted octahedral site and surrounded by six Se atoms, which is consistent with the octahedral structure of 1T phase TMDCs.

Figure 1.2 Crystal structure of Ptse²

1.2.2 Properties of Ptse2

This section highlights unique properties of 2-dimensional PtSe₂ such as band gap tunability, phase transition, vibration spectroscopic and optical properties.

Band gap tunability

Band structure of 2-dimensional TMDCs can be tuned by doping, defect engineering, strain and external electric field. Besides the inherent thickness-dependent band gap, Band gap of PtSe₂ can also be tuned by applying external parameters, Band gap of few-layer PtSe₂ can be tuned by applying strain. Monolayer PtSe₂ exhibits properties of direct band as its compressive strain reaches-8%.

Phase Transition

The structure of the 2-dimensional material strongly depends on varying external effects (pressure, strain, irradiation, annealing) due to the strong covalent bond strength and weak interlayer interaction. Phase transition can be introduced by intercalation, high pressure, strain, thermal treatment and external electrical and magnetic field. Since $1T-PtSe₂$ is a very stable structure, it's difficult to expect a continuous phase transition unless inducing additional electron beam irradiation and annealing treatment. Phase transformation from $1T$ PtSe₂ into nonlayered PtSe² induced due to loss of Se during additional heating at high temperature $(550^{\circ}C)$. Phase transition occurred only in bilayer region. Besides the annealing and heating process, plasma treatment process has also been proved as an efficient method to induce phase transition in 2-dimensional PtSe2. Phase transition drive by thermal heating makes it possible for fabricating lateral heterojunctions composed of $1T-PtSe_2$, $1H-PtSe_2$ and $PtSe_2$.

1.3 Deposition Technique

Thin-films are generally developed to provide special properties such as electrical, optical, mechanical, chemical according to the need for specific applications. Desired properties of resulting thin film structure strongly depends on the selected deposition technique. Deposition technique is the very important aspect in deposition of thin film. Various number of deposition techniques have been developed to optimize the properties of a thin film out of which there are two techniques which are generally used to deposit a thin film. One is chemical vapor deposition (CVD) and the another one is physical vapor deposition (PVD). In CVD thin film is formed when atoms and molecules undergo a chemical reaction with the substrate and on the other hand in PVD the thin film is formed when atoms and molecules simply condense on the substrate.

1.3.1 Chemical vapor deposition (CVD)

CVD is the deposition technique in which a volatile compound of a substance is introduced into a reactor with an inert gas to induce a chemical reaction which produces thin film onto the substrate at elevated temperature. Due to its versatility to work with a broad range of reactant and precursors this technique is able to deposit variety of structures including metal alloys and compound semiconductor. It is important to note that the mechanism behind CVD and PVD is very different. In PVD, condensation of atoms or molecules on the surface of the substrate is done by evaporation, ion bombardment, or sputtering. On the other hand, CVD is a thermodynamically complex process that involves chemical reactions under specified parameters such as temperature, pressure, reaction rates, and the transmission of momentum, mass, and energy.

The most established CVD methods are

- **Thermally activated CVD:** This is the method in which the thermal energy produced inside the reactor triggers the chemical reaction. In this type of CVD two variants are noticeable in relation to the pressure range namely Atmospheric pressure CVD and Low-pressure CVD. Both reactions are same consisting of creation of vapor from the reactants after that these vapor species are directed into the reactor. Depending on the deposition parameter homogeneous reaction takes place in gas phase while heterogenous reaction takes place near substrate and finally the crystallization of a film occurs near the substrate.
- **Plasma enhanced CVD:** This is the type of CVD in which deposition is done at lower temperature using organic, inorganic and inert precursors. In this plasma energy is induced in addition to the thermal energy to improve the dissociation of the reactive gases. The plasma is created when electric field is introduced into the reactor then

complex chemical reaction takes place in plasma under reduced pressure which produce the energetic ions that travel towards the substrate that give rise to a film.

Metal organic CVD: This is the type of CVD in which metalorganic compounds are used as precursors instead of organic ones. The metalorganic compounds are decomposed through pyrolysis reaction at low temperature which allow film deposition to carry out at low temperature than in CVD. This technique is attractive because of the gas flow rate and the partial pressure of the precursor can be controlled allowing the fabrication of the film with right stoichiometry at high deposition rate.

1.3.2 Physical Vapour Deposition

PVD is the deposition technique in which atoms or molecules are physically removed by evaporation then this vapor is transported towards substrate and then condensed onto the substrate in a vacuum, low-pressure gaseous, or plasma environment. The evaporation is generally carried out under the reduced pressure chamber to avoid impurities in the film formation which are produced due to collision between vapor particles and residual gas particles during their movement from target to substrate. PVD offers number of advantages including deposition of almost any material, high reproducibility of the film, possibilities of tailoring the film properties through modification of deposition parameters and obtaining films with high purity.

The most common PVD techniques are:

• **Vacuum evaporation:** This PVD technique is very popular due to its simplicity in operation and high deposition rate. In this technique heat source is used to evaporate the deposition material within the vacuum chamber. This technique is suitable for deposition of elements or compounds at temperature below 2000 K. This technique is further divided into resistance-heated evaporation and electron beam evaporation

In *Resistance-heated evaporation* the target material is deposited in one of the multiple configurations of the evaporation. Due to high temperature requirement, they are generally fabricated from metals with high melting point. The evaporation of the of the target is done by passing high electric current. Once the appropriate evaporation source is selected vacuum chamber should reach pressure lower than 10^{-5} mbar for optimising the deposition coverage and purity of the thin film.

In *Electron-beam evaporation* the electron beam from a charged tungsten filament is bombarded on the target material which is then evaporated and gets deposited onto the substrate. As this process takes place in a high vacuum chamber, these atoms or molecules in a vapor phase precipitate and form a thin film coating onto the substrate. To avoid target contamination the chamber should not be prone to erosion at high temperature.

• **Sputtering:** this type of PVD technique consists of bombardment of energetic particles with the target material to dislodge atoms from its surface which travels through plasma and gets condensed onto the substrate. This process takes place at low temperature because this process does not include evaporation. This process is very good for compounds or combinations of various compounds which has different evaporation rate. Sputtering technique for the growth of the thin film is further divided in DC diode sputtering, RF-diode sputtering and magnetron sputtering.

In *DC diode sputtering* the topmost electrode contains the substrate and the bottom electrode contains the target material. An inert gas is incorporated into the chamber at a reduced pressure. Plasma is formed by applying voltage between cathode and anode in the presence of inert gas. Electrons emitted from the cathode accelerate towards the anode and in their way, they ionize the gas molecule which will lead to the production positively charged ions now these positively charged ions will accelerate towards the cathode and a continuous

bombardment of positive ions against cathode will lead to surface sputtering and subsequent condensation of the thin film onto the substrate.

In *Radio-frequency sputtering* deposition of insulating material is done by preventing the accumulation of the positive ions in the front side of the insulator. In this process an alternating signal is applied to the cathode for continuous sputtering process of the target. Apart from the insulator this technique is also used for depositing metals and semiconductors.

Magnetron sputtering is used to improve sputtering rate with respect to the previous one by optimising the ionization of the sputtering gas molecules. In this process magnetic field is also applied with electric field between cathode and anode which makes electrons to get diverted from their path due to which electron takes longer time to travel from target to substrate and thus increasing the ionization. This increase in the ionization allows the sputtering gas to reduce its pressure which significantly reduces the collision of sputtered atoms within the plasma which increase the deposition rate.

• **Pulsed laser deposition:** this process is carried out in a vacuum chamber in which a target is placed parallel to the substrate and high-power pulsed laser is placed outside the chamber. A pulsed laser beam is focused inside the vacuum chamber which induces the energy to the target material. When this energy is absorbed by the target it produces the plume which condense onto the substrate. This technique is used for deposition of alloys, compounds, polymers, semiconductors due to its stoichiometry transfer of thin film.

Chapter 2

PULSED LASER DEPOSITION

This chapter will present the technical attributes of the pulsed laser deposition (PLD) system and will give a general guide for type of equipment used in PLD. The PLD technique is versatile in the fabrication of various types of thin film. There is a brief background on the principle of operation and some advantages and disadvantages related to the PLD technique. Thickness properties and how thin film is being deposited and how different parameters are used in PLD are also described here.

2.1 Background and Theory

Pulsed laser deposition has been used for depositing thin film since 1960's. The first PLD experiment was carried out more than 30 years ago, shortly after the invention of the pulsed ruby laser. In 1965, Smith and Turner were first to use pulsed laser deposition with a ruby laser onto multiple substrates as a semiconductor and dielectrics.

Pulsed laser deposition (PLD) is a simple technology for depositing thin films. Interaction between laser and target governs this process. A high energy pulse is set to interact with the target material and the material from the target is removed by vaporisation. The target ablated material generates a plasma (or plume) perpendicular to the surface of the target that gets condense onto the surface of the substrate to produce a thin film. The substrate is generally kept 5-10 cm away from the target on which the film growth occurs. Amorphous, polycrystalline can be grown depending on the nature and the temperature of the substrate.

PLD has several characteristics that distinguish it from other film growth techniques as PLD can ablate a wide range of materials and it can convert various types of condensed matter into thin films. Multi-layered structure with different chemical compositions can be synthesize in a single continuous structure via different targets being exchanged during film synthesis. One advantage of PLD over sputtering is that consumption of the material can be kept to a minimum. Target area of 1 cm² is required for PLD as compared to target area of 5 cm² for sputtering. Although this method has numerous advantages it also has several limitations in terms of both experimental and commercial application. Thin film growth can be disrupted by large particles adhering to the substrate, resulting in rough films. Another limitation of PLD is the lack of film thickness uniformity due to varying plume density.

2.2 PLD EQUIPMENTS

The PLD technique is versatile in the fabrication of numerous types of thin films just like a versatile PLD system. One advantage of PLD is that users can build and assemble a system according to their specifications. Firstly, an appropriate laser must be selected for the desired application. The second aspect is the vacuum system which includes a processing chamber, vacuum pumps and pressure sensors. Finally, target and substrate are kept at a proper distance for the growth of thin film.

2.2.1 Laser

There are many reasons for the use of a pulsed laser though the main reason is that a pulsed laser can easily achieve the energies required for a material to transform into plasma. Of equal importance is the laser's operating wavelength; thin film growth can be done at various wavelengths but when considering a laser for PLD most thin film growth is done between 200 nm and 400 nm laser wavelengths. The primary purpose for using these wavelengths is because the majority of the materials used for PLD have strong absorption in these ranges. Till now the most important work has been done with the help of pulsed laser system that operates in ultraviolet region, specifically excimer laser and neodymium-doped yttrium aluminium garnet (Nd: YAG) pulsed lasers are used. Excimer laser are the type of gas laser in which energy is pumped into a gaseous lasing medium that give rise to excimer molecule. These molecules undergo spontaneous emission and give rise to stimulated emission of photons in the UV wavelength. The Nd: YAG is a solid-state laser system. Flash lamps in the laser excite the Nd in the YAG crystal, a Q-switch allows gain medium to reach the condition of population inversion to begin the lasing process.

2.2.2 PLD Optics

The optical setup of the PLD system is shown in the figure 2.1 which shows focusing lens mirrors and beam splitters and a deposition chamber window. It is the simplest configuration and assures the least amount of the laser energy loss between target and laser. Another way to assure least amount of laser energy loss is to keep optics clean. This will also protect optical components from damage.

This section will discuss the purpose of each component

- **Lenses:** Any system which contains optics laser play an important role in the design of the system. In PLD the lenses are used to focus and control the laser fluence. Spherical lens is used in PLD because it magnifies in two planes and the projected laser energy is oriented as a point. Cylindrical lenses can also be used to magnify in one plane and hence projected image will be a line. A fused silica plano-convex lens with a focal length of 772mm is the main lens used in the system.
- **Mirrors and beam Splitters:** These mirrors and beam splitters allow a PLD system to contain multiple deposition chambers. These components allow redirection of laser beam in multiple chambers for different PLD experiments. These components also make it possible to perform dual beam PLD in single chamber.
- **Deposition chamber windows:** The deposition chamber windows are the simplest optical component of the PLD system. Multiple window ports can be located on a deposition chamber. A chamber used for dual beam PLD have two laser windows. View windows are used to observe the plasma plume and helps in target alignment with laser beam.

2.2.3 Deposition system

When referring to the deposition system it includes the deposition chamber and all components attached to it. Deposition chamber is the central hub when combined with the vacuum pumps, gauges and target and substrate holder. With the laser and optics, the user should choose the right deposition system. Deposition system are easiest when assembling the PLD system.

• **Deposition chamber:** Deposition chamber is the important part of the PLD system.

The chamber should have vacuum capabilities, additional inlets for new components,

and is large enough to vary the target and substrate distance. The vacuum subsystem includes a multi-port vacuum chamber, two vacuum pumps and pressure sensors. The main chamber has six ports for the target and substrate stages, power supply, laser beam delivery, connecting sensors, and evacuating of the chamber.

• **Vacuum pump:** High vacuum can be achieved using a turbo-molecular pump and rotary vane pump. The two pumps work as one unit, vane pump is used as a backing pump to bring the chamber below 10^{-2} Torr and then turbo-molecular pump is used to achieve high vacuum. Turbo-molecular pump are high speed pumps which are unable to operate above 10^{-2} Torr as exceeding this condition TMP blades will become slow and pump will become inefficient.

2.2.4 Target and substrate holder

Most of the target holders are made such a way that this design has multiple holder stages that can rotate in and out of the laser path. This design enables deposition of multilayer film without opening the deposition chamber in between the deposition process. A copper water cooled shield prevents other targets from cross contamination, substrate and heater radiation when they are not in use.

Substrate holder is placed in such a way that plume is on same plane as that of the substrate. The distance between substrate and target is adjustable and heater can maintain the temperature of the substrate up to 1000° C.

Chapter 3

MECHANISM OF THIN FILM DEPOSITION

3.1 Process of pulsed laser deposition

Pulsed laser deposition is a process which is carried out in a vacuum chamber in which a target is placed parallel to the substrate and high-power pulsed laser is placed outside the chamber. A pulsed laser beam is focused inside the vacuum chamber which induces the energy to the target material. When this energy is absorbed by the target it produces the plume which condense onto the substrate. Process of pulsed laser deposition is generally divided into four processes which includes laser interaction with the target, dynamics of the ablated material, deposition of ablated material on the substrate and nucleation and growth of thin film.

3.1.1 Laser interaction with the target

In this stage laser beam is focused onto the surface of the target at high energy at short pulse duration and the incident laser pulse penetrates into the surface of the material within the penetration depth. This dimension is dependent on the laser wavelength and the index of refraction of the target material at the applied laser wavelength The strong electrical field generated by the laser light is sufficiently strong to remove the electrons from the bulk material of the penetrated volume. The free electrons oscillate within the electromagnetic field of the laser light and collide with the atoms of the bulk material thus transferring some of their energy to the lattice of the target material within the surface region. The surface of the target is then heated up and the material is vaporized. Beam was irradiated onto the target at an incident angle of 45 degree to avoid overlapping between the laser beam and the plume.

3.1.2 Dynamics of the ablated material

In the second stage the material expands in a plasma parallel to the normal vector of the target surface towards the substrate due to Coulomb repulsion and recoil from the target surface this spatial distribution of the plume is dependent on the background pressure inside the PLD chamber. The dependency of the plume shape on the pressure can be described in three stages:

- The vacuum stage, where the plume is very narrow and forward directed; almost no scattering occurs with the background gases.
- The intermediate region where a splitting of the high energetic ions from the less energetic species can be observed. The time-of-flight (TOF) data can be fitted to a shock wave model; however, other models could also be possible.
- High pressure region where we find a more diffusion-like expansion of the ablated material. Naturally this scattering is also dependent on the mass of the background gas and can influence the stoichiometry of the deposited film.

3.1.3 Deposition of the ablated material on the substrate

This third stage is very important to determine the quality of the deposited films. The high energetic species ablated from the target bombards onto the surface of the substrate and can cause damage to the surface by sputtering off atoms from the surface of the substrate. These sputtered species from the substrate and the particles emitted from the target form a collision region which serves as a source for condensation of particles. When the condensation rate is high enough, a thermal equilibrium can be reached and the film grows on the substrate surface.

3.1.4 Nucleation and growth of the thin film

Nucleation and growth of the thins film depends on several growth parameters including:

- Laser parameters several factors such as the laser fluence [Joule/cm²], laser energy, and ionization degree of the ablated material affects the thin film quality, [stoichiometry](https://en.wikipedia.org/wiki/Stoichiometry) and the deposition flux. Generally, the nucleation density increases when the deposition flux is increased.
- *Surface temperature* The surface temperature has a large effect on the nucleation density. Generally, the nucleation density decreases as the temperature is increased.
- *Substrate surface* The nucleation and growth can be affected by the surface preparation such as chemical etching, the miscut of the substrate, as well as the roughness of the substrate.
- *Background pressure* Common in oxide deposition, an oxygen background is needed to ensure stoichiometric transfer of the thin film from the target to the substrate. If the oxygen background is too low, the film will grow off [stoichiometry](https://en.wikipedia.org/wiki/Stoichiometry) which will affect the nucleation density and film quality.

In PLD, three growth modes are possible which depends on the deposition parameters explained above:

• **Van der Merwe or island growth mechanism:** In this mechanism atoms accumulate on the surface and grow in three dimensions to form an island this is because the adherence between the atom to atom is greater than the bonding between the substrate and the atoms.

- **Volmer Weber or layer mechanism:** In this mechanism thin film grows layer by layer on the surface of the substrate and can be used for dense coating. This occurs when the adhesion between the atom and the surface is greater than the bonding between atom and atom.
- **Stranski-Krastanov (S-K) mechanism:** In this mechanism in which the atoms begin to accumulate and form islands after an initial layer has grown.

Figure 3.1 Growth modes of a thin film

3.4 Advantages and Disadvantages of PLD

When we compared PLD with other techniques like arc discharge, molecular beam epitaxy, ion beam sputtering it was seen that PLD has several advantages. By changing the background gas and by modifying the laser parameters, deposition duration, and substrate to target distance we can regulate the rate of film growth in PLD. Transfer of the stoichiometry of the target material onto the substrate, deposition at high temperature, and high deposition rate are some of the key benefits of PLD over other PVD techniques.

3.4.1 Advantages of PLD

- Pulsed laser deposition is a versatile technique as many materials can be deposited in a wide variety of gases over a broad range of gas pressures.
- Pulsed laser deposition is a very cost-effective technique as one laser can serve many vacuum systems.
- Pulsed laser deposition is a fast process, high quality samples can be grown reliably in 10 to 15 minutes.
- In pulsed laser deposition is a process in which it is easy to obtained multicomponent film of desired stoichiometric ratio.
- Pulsed laser deposition uses UV pulsed laser of high photon capability and high energy density as the energy source for generation of plasma so it is non-polluting and easy to control.
- The laser is not the part of the vacuum system. Therefore, there is a considerable degree of freedom in the geometry of the ablation.

3.4.2 Disadvantages of PLD

- In pulsed laser deposition sometime, there are small molten particles or fragments of target in the deposited film which are sputtered during the laser induced explosion and presence of these particles reduces the quality of the thin film.
- Feasibility of laser method for large area deposition is not yet proved.
- Pulsed laser deposition has slow average deposition rate

CHAPTER 4

OPTIMISATION PARAMETERS OF A THIN FILM

This chapter has details about the parameters and optimisation parameters used by us during the deposition of the thin film.

4.1 Substrate used

Substrate used for this research was Silicon (Si) which is a N-type semiconductor with orientation as (110) with thickness of 0.7 mm. A silicon substrate also known as a silicon wafer is a thin slice of crystalline silicon. Silicon wafer are the most extensively utilised wafers in the industry because of its outstanding mechanical and electrical qualities. It allows you to customise the surface attributes. Polished silicon is an ideal substrate for imaging studies, nanotechnology, and micro fabrication applications. Silicon is a good sample substrate in imaging applications for microscopic particles due to the minimal background signal of the highly polished surface. SEM, FIB, and STM applications benefit from the good conductivity of these wafers. The characteristics of $PtSe₂$ thin films were investigated using silicon as the substrate in this experiment. Silicon is a highly stable semiconductor that is a suitable base substrate due to its potential scalability, coefficient of thermal expansion, and cost.

4.2 Experimental procedure

Pulsed laser deposition technique was used to fabricate PtSe₂ films on Silicon substrate (Si) which is a N-type semiconductor of thickness 0.7 mm. The PLD chamber comprises of a target station which rotate and position the target with the laser beam. A Krypton fluoride (KrF) excimer laser was used which produces laser pulse of 10 ns at wavelength of 248 nm

and at energy of 0.2 J per pulse. The laser beam is incident on the target at an angle of 45°C with a spot area around 0.01 mm^2 creating a plasma plume emitted from the target. The evaporated target particles start moving towards the substrate and get condensed onto substrate which is positioned opposite to the target. The target holder rotates such that laser pulse hit the target at different position, preventing crater formation resulting from severe local heating and melting of the target material. The distance between the target and substrate was kept around 4 cm. The chamber is evacuated by a combination of a rotary pump and turbomolecular pump to a base pressure less than 10-6 Torr these rotary vanes and turbomolecular pump allow the deposition chamber to achieve high vacuum. The two pumps work as one unit, the rotary pump is used as a backing pump to bring the chamber pressure below 10^{-3} Torr and then the turbomolecular pump is switched on to achieve high vacuum conditions. Turbomolecular pump are high speed pump and need a backing pump to operate because most of the turbomolecular pump are unable to operate at pressures higher than 10^{-3} Torr by design. If the pressures exceed 10^{-3} Torr the turbomolecular pump blades will be subjected to high strains and due to this the blades can get slow, the pump will become inefficient, and damage could occur. The laser ablation was carried out at a laser fluence of 1.025 J/cm² . Argon gas was the background gas in the chamber. The films were deposited in the substrate with varying temperature range of 100-550°C. The substrate was shielded and the pulse was allowed to strike the substrate surface. This is done to remove a thin layer off the target surface which would otherwise contain impurities. This is necessary to ensure that the depositing material is devoid of impurities. At first, we took an idealistic case, thus we made a bulk deposition whose parameters were similar to that of the target. Later on, the temperature was varied with the number of laser shots and XRD curve was studied. An X-ray diffractometer was used to investigate the crystallographic structure of the thin film samples. It was seen that till 300° C we didn't get any peak in XRD, after that we start getting the

phase but along with the impurities. At 500° C peak was obtained. But when temperature is increased above 550°C, there was a chance that Selenium can get evaporated. So, we optimised our temperature at 500° C.

4.3 Optimisation parameters used for deposition of PtSe2 thin film

Table 3.1 Optimisation Parameters used for PtSe² Thin Film

4.4 Annealing of the sample

Annealing is very important process used for the fabrication of the thin film. After annealing the microstructure and phases of the material can be altered. As a result of this modification the characteristics of the thin films are improved. In this study, the sample was annealed in vacuum for 2 min at 500°C inside the Chamber. After that, the sample was investigated using various characterization technique.

The thermal annealing procedure involves heating a material above the temperature at which it recrystallizes. After that, the temperature must be maintained for a particular amount of time. After thermal annealing, the material is gently cooled to room temperature. Thermal energy is transmitted to the material during the annealing process, causing redistributions within it to generate a crystalline structure. Laser annealing is a similar process that creates crystalline material by locally heating material.

CHAPTER 5

TECHNIQUES USED FOR CHARACTERISATION

All samples, once grown in the PLD system, are removed and stored in a dry air cabinet and characteristic measurements were later carried out. These main techniques of structural, morphological, and optical measurements are discussed below. This chapter is focused on the principles and design of the X-Ray Diffraction (XRD), Scanning electron microscopy (SEM) and Atomic force microscopy (AFM).

5.1 X-Ray diffraction (XRD)

X-ray diffraction (XRD) is used on all samples throughout this work to structurally analyse the crystallography of the grown thin film.

XRD is a non-destructive technique used to identify crystalline phases and orientation. It is also used to determine structural properties like Lattice parameters, strain, Grain size, Epitaxy, Phase composition, preferred orientation. XRD is used to measure the thickness of thin film and multilayer and to determine atomic arrangement

Von Laue attempted his first X-ray diffraction experiment on copper sulphate crystal and a diffraction pattern on a photographic plate was evidence of the regular arrangement of atoms in the crystal. Therefore, this idea of diffraction of x-rays in a regular pattern became a pioneering idea for crystallographers to study and understand the atomic arrangement in the crystal. Later in 1912, Von Laue's idea of x-ray diffraction gathered interest from W.H. Bragg and his son W.L.Bragg and they further simplified Von Laue mathematical expressions to study the structure of NaCl, KCl, KBr, KI. Furthermore, the simplified

mathematical form, now known as Bragg's law, can be used to estimate several crystal parameters.

Bragg's law

W.H. Bragg and W.L. Bragg derived an expression for x-ray diffraction of crystals, based on the wavelength of the x-rays and atoms in the crystal plane. X-ray are scattered When they pass through a crystal plane where the position of atoms is periodically arranged. X-rays scattered from many atoms can constructively interfere to get a diffracted beam in a particular orientation. In all other directions, there will be destructive interference, meaning there is no diffraction beam in that direction. The shape of the diffraction pattern can give information about the crystal structure of the material under study. To understand the link between an observed diffraction pattern and the crystal structure, we consider the Figure 4.1. Here, n crystal planes parallel to the surface are considered, with a distance d (interplanar spacing) between them.

Figure 5.1 Bragg's diffraction on the crystal

When X-ray falls on a crystal the electrons start vibrating with the frequency of incident xray these accelerated electrons re-emit radiations of frequency which is same as the frequency of the incident x-ray these emitted radiations interfere constructively determined by the brag's law and gives valuable information about the structure properties and orientation of the crystal.

$2d \sin \theta = n \lambda$

This Bragg's law equation is the necessary criteria for diffraction to occur. By changing the angle θ , it is possible to determine d for an unknown crystal (as long as λ of the x-rays is known), d is an Interplanar distance and it is different for different crystal system.

Figure 5.2 Schematic diagram of an X-ray Diffractometer

We use Bragg's law in XRD to determine an unknown crystal structure that is by measuring angle θ from 2 θ value for which there is a maximum diffraction and d can be determined by using Bragg's law. X-Ray detector gives the value of the ray at 2θ angle and we obtained the diffraction direction of the lattice. This helps in the formation of the graphs and with the help of peaks we can determine the structure and the properties of the given material.

5.2 Field emission scanning electron microscopy (FESEM)

FESEM is used to produce real-space magnified images of a surface showing what it looks like. In general, it give information about surface [crystallography](https://en.wikipedia.org/wiki/Crystallography) means how the atoms are arranged at the surface, surface morphology means the shape and size of topographic features making the surface, and surface composition means the elements and compounds the surface is composed of. It produces image of a sample by scanning it with focused beam of electrons Within the high vacuum column these primary electrons are focussed and deflected by electronic lenses to produce a narrow scan beam that bombards the object. As a result, secondary electrons are emitted from each spot and detector catches these secondary electrons and produces an electronic signal that contains the information about the surface morphology and composition.

The electron gun of FESEM typically accelerates electrons through 1-30 kV accelerating voltage. 15-30 KeV electrons are typically used for routine imaging. A 1-5 KeV low voltage FESEM operating mode can be used to reduce electron penetration and achieve higher resolution image. The pressure inside the FESEM chamber is usually low vacuum 0.1-10-4 Pa. Electromagnetic lenses are used to focus the electrons into a beam, adjust beam, to move the beam across the specimen, and to scan the beam to generate images. In modern machines, a range of different scan patterns are pre-programmed for the user, including adjustable scan dimensions, scan speed/spot dwell time, and pattern repetition. These parameters gives a high degree of control of the imaging process to users and an expert user can achieve images with resolution of a few nm.

FESEM is the tool used in many industries due to its ability to image materials and structures with submicron resolution. Here we used FESEM to analyse morphology, chemistry, and

crystallography of the thin film. However, there are many more methodologies available to advanced users.

Figure 5.3 Schematic diagram of FESEM

While SEM has many advantages, it does have a major disadvantage over some other methods in that it requires the surface of the sample to be conductive. Since the imaging is based upon utilizing high energy electrons impinging upon the surface, the surface will quickly become locally charged if it is an insulator. The local charging, in turn, drastically reduces the resolution and clarity of the images created.

5.3 Atomic force microscopy (AFM)

The atomic force [microscope](https://microbenotes.com/types-of-microscopes/) (AFM) is a type of scanning probe microscope whose primary role is to measure properties such as magnetism, height, friction. The resolution is measured in nanometre, which is much more accurate and effective than the optical diffraction limit

The Atomic Force Microscope works on the principle measuring intermolecular forces and sees atoms by using probed surfaces of the specimen in nanoscale. Its functioning is enabled by three of its major working principles that include Surface sensing, Detection, and Imaging The Atomic Force Microscope (AFM) takes the image of the surface topography of the sample by force by scanning the cantilever over a section of interest. Depending on how raised or how low the surface of the sample is, it determines the deflection of the beam, which is monitored by the Positive-sensitive photo-diode (PSDP). The microscope has a feedback loop that controls the length of the cantilever tip just above the sample surface, therefore, it will maintain the laser position thus generating an accurate imaging map of the surface of the image.

AFM consists of a sharp tip that is approximately 10 to 20 nm in diameter, which is attached to a cantilever. The tip moves in response to tip– surface interactions, and this movement is measured by focusing a laser beam with a photodiode.

An AFM is operated in two basic modes, such as contact and tapping modes. In the contact mode, the AFM tip is in continuous contact with the surface. In contrast, in the tapping mode, the AFM cantilever is vibrated above the sample surface such that the tip is only in intermittent contact with the surface. This process helps to reduce shear forces associated with the tip movement. The tapping mode is the recommended mode that is commonly used for AFM imaging. The contact mode is only used for specific applications, such as force

curve measurements. The AFM is used to image and manipulate atoms and structures on a variety of surfaces. The atom at the apex of the tip 'senses' individual atoms on the underlying surface when it forms incipient chemical bonds with each atom. Because these chemical interactions delicately alter the tip's vibration frequency, they can be detected and mapped.

Figure 5.4 Schematic diagram of AFM

CHAPTER 6

RESULTS AND DISCUSSION

The deposition of Ptse₂ thin films on silicon substrate was carried out under different temperatures between 100°-550°C in the chamber. Table 1 shows optimisation parameters used for deposition of the thin film. The crystal structure, morphology and phase purity of the samples prepared under different laser shots and temperatures were characterized using XRD, SEM and AFM. But it can be seen from the graphs below that the XRD pattern of the samples synthesized till 400°C were not showing proper diffraction peaks there were impurities present on them. As we further increased the temperature up to 550°C, diffraction peaks were obtained but there was chance that selenium can get evaporated at this temperature. Therefore, for the rest of the samples the temperature was kept at 500°C and the number of shots were varied.

At first bulk deposition was done by giving 10,000 laser shots at different temperature. Figure (5.1) shows the XRD graph of samples with bulk deposition at different temperature. After getting sharp peaks the temperature was kept 500°C for other samples and laser shots were varied to obtain a thin uniform film. Figure (5.2) shows the XRD graph of samples with thin film deposition at 500°C with varying laser shots. XRD was used to figure out the crystalline structure of Ptse₂ thin film for all samples at 500°C. It was observed that with the decrease in the number of laser shots the impurity peaks disappears and a uniform thin film was obtained over a substrate.

Sample	Pressure	Temperature	Distance	Laser Shots
	5 _m T	200° C	4 cm	10,000
2	5 _m T	300° C	4 cm	10,000
3	5 _m T	400° C	4 cm	10,000
4	5 _m T	500° C	4 cm	10,000

Table 6.1 samples at varying temperatures

Figure 6.1 Graph shows the XRD peak of the Sample 1 at 200° C, Sample 2 at 300° C, Sample 3 at 400° C, Sample 4 at 500° C.

This can be seen from the XRD pattern that the depositions of Ptse2 thin films on silicon substrate was carried out under different Temperatures between 200°-550°C in the chamber. But the XRD pattern of the samples synthesized till 400°C were not showing proper diffraction peaks there were impurities present on them. With the increase in temperature up to 500°C diffraction peaks were obtained.

The XRD spectra shows the changes in the film deposition when the temperature is varied while fixing the number of Laser shots.

The graph shows that at 500°C a uniform thin film gets deposited on the substrate while at lower temperature some impurity peaks can be seen.

The main characteristic peak of PtSe₂ with orientation at (001) is detected approximately at 17.6 \degree peak with orientation at (011) is at 33.29 \degree peak with orientation at (111) is at 40.11 \degree and peak with orientation at (102) is at 54.10° and the peak of silicon with orientation at (400) is at 69.35°.

COMPARISON OF XRD GRAPH AT 500 ^OC and 550 ^OC

Figure 6.2 Graph at temperature 500 ^OC and 550 ^OC

As we further increased the temperature up to 550°C, diffraction peaks were obtained but selenium can get evaporated at this temperature. Therefore, for the rest of the samples the temperature was kept at 500°C. The no. of laser shots was varied. It was observed that as we decreased the number of laser shots the impurity peaks got disappeared and a uniform thin film was obtained over a substrate.

Field emission scanning electron microscopy (FESEM)

FESEM is used to produce real-space magnified images of a surface showing what it looks like. In general, it give information about surface [crystallography](https://en.wikipedia.org/wiki/Crystallography) means how the atoms are arranged at the surface, surface morphology means the shape and size of topographic features making the surface, and surface composition means the elements and compounds the surface is composed of.

FESEM images of a thin film formed at a temperature of 500° C at $10,000$ laser shots and at 5mt pressure was obtained at two different magnifications shown below

Figure 6.3 FESEM image of the sample at 50.00 K X

Figure 6.4 FESEM image of the sample at 100.00 K X

FESEM image of both samples was investigated and the grain size of the thin film was

observed approximately 91nm.

Atomic force microscopy

AFM images were used to find the roughness of the thin film. AFM image of the sample at temperature of 500° C at 10,000 laser shots and at 5mt pressure was obtained at two different magnifications shown below

Figure 6.5 2-D AFM image of the sample

Figure 6.6 3-D AFM image of the sample

AFM image show uniform peaks except for some region concluding that the film is deposited uniformly.

CONCLUSION

The aim and objective of this project work was to examine the deposition of thin film PtSe₂ on a silicon substrate at various temperatures and laser shots and to determine the crystallographic structure of the material using XRD also to determine morphology of the thin film using FESEM and to determine the roughness of the produced thin film using AFM.

We used a pulse laser deposition technique to successfully synthesize a high quality, wellcrystallized PtSe₂ thin film at different temperatures and with different numbers of laser shots. All of the samples were characterized using XRD for the fabrication of a thin film of PtSe₂ on silicon. FESEM images were observed by changing the position of the samples, both samples resulted in uniform thin film deposition on the substrate. The AFM images were examined to determine the roughness of the sample. From XRD we concluded that when temperature was increased to 500°C, a fine uniform thin film was obtained with no impurities. Further the temperature was increased to 550°C but there was chance that the selenium in PtSe₂ can get evaporated at 550° C, then we optimised temperature at 500° C. Thus, our research contributes to the development of a new approach and strategy for increasing the family of transition-metal dichalcogenides (TMDs).

PtSe₂ a layered 2-dimensional material, was successfully synthesized. The composition and crystalline quality of the resulting PtSe₂ are confirmed by structural analysis. The observed results open up new avenues for improving the preparation technique (particularly the deposition time) in order to make the nanostructure synthesis approach for $2D$ PtSe₂ applications more convenient. We divulge a comprehensive review based on experimental and theoretical research evolution on 2D layered PtSe2, covering the progress, challenges, and future prospects.

FUTURE SCOPE

In recent years, emerging 2-dimensional platinum diselenide (PtSe₂) has quickly attracted the attention of the research community due to its unique physical and chemical properties. Increasing research breakthroughs on 2D PtSe₂ have been reported in the fundamental science and numerous possible applications during the last several years. Among 2D group-10 noble TMDCs materials, platinum diselenide (PtSe₂) has emerged as promising materials for investigating quasiparticle interactions and for the development of the photoelectric devices. PtSe2 has recently gained popularity in 2D materials research due to its unique properties like tunable band gap, high carrier mobility, and great air stability. 2D PtSe2 has exhibited potential in many areas such as photocatalytic, hydrogen evolution reaction, electronic, and optoelectronic devices. Some of the applications are Photodetectors which can directly convert optical signals to electrical signals. It has been widely applied in many fields such as optical communication, industrial automatic control, and military. 2D materials PtSe₂ have been widely utilized as saturable absorber in the laser cavity for ultrafast pulse generation. One of the important applications of 2D PtSe₂ materials is in the field effect transistors (FETs). It has been widely used as a high performance photocatalyst due to its large specific area and excellent electronic properties. The unique structural and electronic properties of 2D PtSe₂ also make it a promising material for pressure sensors. The development of 2D PtSe₂ based flexible film or nanostructure thermoelectric materials may provide great opportunities for fabricating highly efficient thermoelectric devices. 2D $PtSe₂$ has been theoretically predicted to be a promising candidate to fabricate high speed electronic and optoelectronic devices due to is high carrier mobility.

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