Design and Development of Setup for Measurements of Optical Constants at Low Temperature

M.Tech. Thesis

By

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Discipline of Metallurgy Engineering and Materials Science

INDIAN INSTITUTE OF TECHNOLOGY INDORE

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Design and Development of Setup for Measurements of Optical Constants at Low Temperature

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of

Master of Technology

By

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Discipline of Metallurgy Engineering and Materials Science
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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "**Design and Development of Setup for measurements of optical constants at low temperature"** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF TECHNOLOGY** and submitted in the **Discipline of Metallurgy Engineering and Materials Science, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July 2015 to June 2017 under the supervision of **Dr. Pankaj R. Sagdeo , Associate Professor**, Discipline of Physics, IIT Indore

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Signature of the student with date
Sandeep Jain

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

Signature of the Supervisor with date

Dr. Pankaj R. Sagdeo

Sandeep Jain has successfully given his M.Tech. Oral Examination held on…………………….

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Dedicated To

My Family

&

My Teachers

Acknowledgement

A successful completion of my M.Tech Project work is the result of dedicated efforts put by many others and this report would be incomplete without giving credit to them. To bear a fruit one has to reap a seed and that is not all that has to be done. It takes a lot of effort and time, and it is not a layman's job. The support and guidance of experienced people yields a better fruit. This project is the outcome of the efforts I had put in under the guidance of my supervisors and with the help of well-wishers. I would like to take this opportunity to thank all those who have directly or indirectly contributed to this project.

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Abstract

In this work, we report the fabrication of an experimental setup for low temperature optical properties measurement. Our design is appropriate for the characterization of thin films samples with different geometries like square shape, circular shape etc. UV Visible spectroscopy technique was used to measure the optical properties. Simple design and a small sample holder are developed with limited components. The sample holder is placed in vacuum chamber with all accessories related to the setup to fulfil its all requirement. The setup is fabricated using the materials which are easily available in market so that any part can be replaced in case of damage. The working and preciseness of presently developed setup has been validated by recording the data for a standard $SrTiO_3$ single crystal substrate. The obtained data was found to be closely consistent with the data reported in the literature. Some important physical quantities /parameters (like transmission, band gap, disorderness), for $SrTiO_3$, have also been studied (87K to 300K) through presently fabricated setup.

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Abbreviations

Ultra Violet	UV
Visible	Vis
Infra-Red	IR
Nanometer	nm
Electron Volts	eV
Highest Occupied Molecular Orbital	HOMO
Lowest Unoccupied Molecular Orbital	LUMO
Strontium	Sr
Titanium	Ti
Automated Computer Aided Design	AutoCAD

Chapter 1: Introduction

1. Introduction

From the beginnings of the development of the modern scientific method, its emphasis on testable hypotheses required the ability to make quantitative and ever more accurate measurements—for example, of temperature with the thermometer in 1593, of cellular structure with the microscope in 1595 and of the universe with the telescope in 1609. Instruments have been an integral part of our nation's growth since explorers first set out to map the continent. A large fraction of the differences between 19th century, 20th century, and 21st century science stems directly from the instruments available to explore the world. Instrumentation has often been cited as the pacing factor of research; the productivity of researchers is only as great as the tools they have available to observe, measure, and make sense of nature [1]**.** Research instrumentation work requires some concepts and specifications and turn them into finished precision instruments. First of all, the idea is refined, evaluate this according to engineering principles and then develop elegant design and manufacturing solutions. The design and fabrication work should be done in most efficient and cost effective manners and maintain high quality and integrity in the design.

This thesis describes the design, development, fabrication [2] and testing of an instrumentation and measurement to identify the optical constants through transmission, reflection, absorption measurements of different materials as a function of temperature [3,4]. By measuring the effect of temperature on properties of many optical materials, we can analyze the working and effectiveness of the devices. As we know that various devices like satellites, cameras, telescope, etc. (fig. 1.1) in which optical components are widely used. The optical components used in above mentioned devices, these may face extreme temperature conditions and hence it is important to study the temperature dependent of optical properties for some of the essential optical components used in the space applications in order to ensure the applicability and working of these devices.

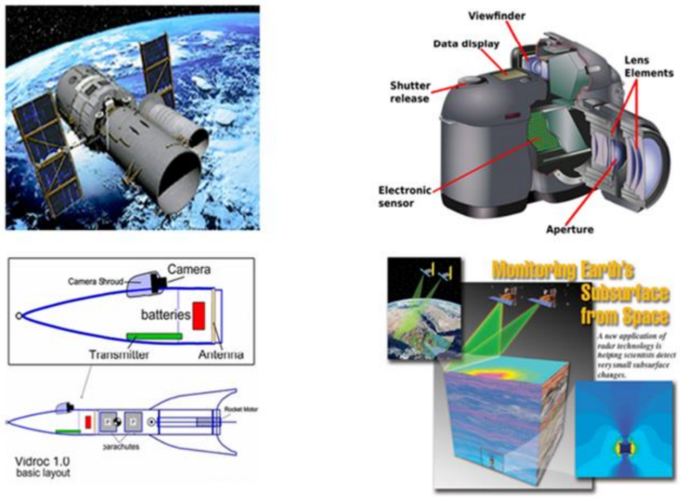

Figure 1.1 *Devices in which optical components are used*

Optical transmission experiments provide a good way of examining the properties of optical materials like absorption coefficient, energy band gap etc. The absorption coefficient "α" of a material at a given wavelength determines the spatial region in which most of the light is absorbed. For high absorptivity, most of the light is absorbed close to the energy band gap region. Thus measuring the absorption coefficient for various energies gives information about the band gaps of the material which decides the working spectral range of the given optical device.

This report describes experiments of this kind. Using the techniques of transmission spectroscopy to measure absorption coefficients we studied the properties of thin optical films. Ultraviolet-Visible near-Infra red (UV-Vis-NIR) spectroscopy is used to characterize the absorption, transmission of a variety of technologically important materials [5]. The wavelength range of the UV-Visible region is 200-800 nm. This more qualitative application usually requires recording at least a portion of the spectrum for characterization of the optical or electronic properties of materials. Optical spectroscopy particularly in the visible and UV region of the electromagnetic spectrum, is one of the most versatile and widely used techniques.

In the present scenario, analysis of optical properties variation with temperature [6] is very important to find out the correct materials for space applications [7]**.** Low temperature optical properties measurement is using UV-Visible spectroscopy is one of the leading characterization techniques.

In the case of thin film base optical components such as optical filters etc. interference method is used to measure the properties of optical thin film samples [8]**.** In everyday life, the interference of light most commonly gives rise to easily observable effects when light impinges on a thin film of some transparent material. For instance, the brilliant colors seen in soap bubbles and oil films floating on puddles of water are due to the interference effects.

In most of the optical devices the optical material is generally deposited on a substrate and hence it is important to first extract the optical constant of substrate. This is generally done as described by R. Swanepoel [9]. The transmission spectrum from substrate is shown in (Fig. 1.2)

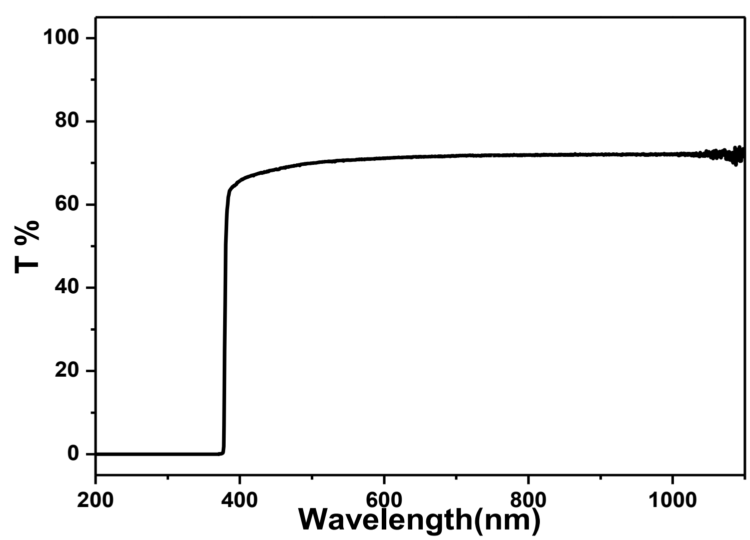

Figure 1.2 *Transmission spectra shows the transmission variation with wavelength*

Using transmission spectra, refractive index and reflectance are easily calculated from the formula which is reported by R. Swanepoel [9].

Refractive index is calculated by using the equation which is given below:

$$n = \frac{1}{T_s} + \left(\frac{1}{T_s^2} - 1 \right)^{1/2}$$

After calculating the refractive index by above equation, we can calculate reflectance by the equation which is given below:

$$R = \left(\frac{n-1}{n+1} \right)^2$$

This is well known that the sum of transmission, reflectance and absorbance is equal to input power (normalized to unity for simplicity) .So using this rule absorbance is calculated easily using transmission and reflectance values and the same can be used to calculate absorbance, band gap, urbach energy etc. either at constant temperature or as a function of temperature.

The band gap variation with the temperature is the fundamental characteristics of an optical semiconductor [10]. The temperature dependence of band gap, determined from the absorption edge, can be described by empirical relation named as Varshni's equation is given below [11].

$$E_g(T) = E_g(0) - \frac{\gamma T^2}{T + \beta}$$

Where ϒ and β are fitting parameters characteristic of a given material. E_g (0) is the band gap of semiconductor at 0K.

In the optical absorption spectrum, the tail arising as a result of optical transitions involving the tail states [12]. Experimentally, it is reported that this absorption tail broadens with increasing the level of thermal and structural disorder. In the case of the Urbach behavior of the absorption edge, the temperature and spectral dependence of absorption coefficient [13] is given as below

$$\alpha = \alpha_0 \exp\left(\frac{h\nu - E_0}{E_U}\right)$$

Where α_o is a constant, E_0 is the optical band gap and E_U is the urbach energy which is equal to the energy width of the absorption edge.

Taking the logarithm of the two sides of the equation, a straight line is equation is obtained which is given by:

$$\ln\alpha = \ln\alpha_0 + \left(\frac{h\nu - E_0}{E_U}\right)$$

Therefore, the band tail energy or Urbach energy (E_U) can be obtained from the slope of the straight line of plotting *ln α* against the incident photon energy *(hν)*. Straight line between *ln α* & *incident photon energy* is shown in (fig.1.3).

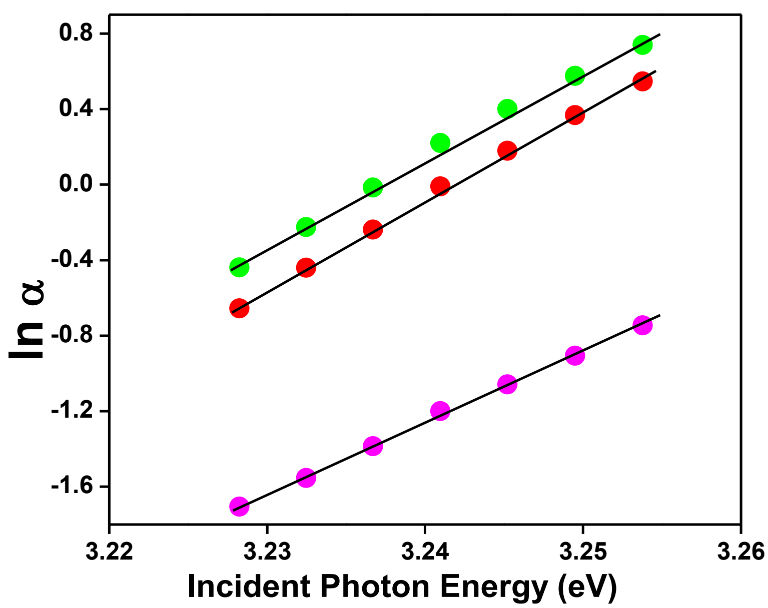

Figure 1.3 *ln α Vs. Energy (eV) straight line*

After plotting the figure we can calculate the slope of the straight line. From this slope, Urbach Energy behavior can be analyzed. From the values of Urbach energy the amount one can quantify the total disorder present in the sample.

In the present project work we have studied the effect of temperature on the optical properties as a function of temperature and using temperature dependent optical transmission; we have estimated the temperature dependent optical properties such as band gap and Urbach energy.

Chapter 2: Literature Review

2.1 Instrumentation and Measurement

"*A very common feeling about measurement activity is that it does not involve anything else than connecting a suitable instrument to a measured system, reading the instrument's display and, if needed, making a few calculations on the value provided by the instrument*."[14]

- John R. Kearney

It is this understanding of principals that enables us to design instrumentation and measurement systems that perform measurements on our target system and to determine how close the measurement is to the actual performance of the item measured. The closer we can come to bringing these two issues into equality, the better the description we will have of the measured system, which is, after all, what we are trying to achieve.

Before we present our actual work we would like to discuss few measurements principles related to the present topic.

2.2 Thin-film interference

Thin-film interference is a natural phenomenon in which light waves reflected by the upper and lower boundaries of a thin film interfere with one another, either enhancing or reducing the reflected light**.**

A thin film is a layer of material with the thickness of the order of wavelength of light. As light strikes the surface of a film it is partly transmitted and partly reflected. The light that is transmitted reaches the bottom surface once again partly transmitted and partly reflected. The Fresnel equations provide a quantitative description of how much of the light will be transmitted or reflected at an interface. The light reflected from the upper and lower surfaces will interfere. The degree of constructive or destructive interference between the two light waves depends on the difference in their phase/path difference. This difference in turn depends on the thickness of the film layer, the refractive index of the film, and the angle of incidence of the original wave on the film as shown in (fig. 2.1). Additionally, a phase shift of 180° may be introduced upon reflection at a boundary depending on the refractive indices of the materials on either side of the boundary. This phase shift occurs if the refractive index of the medium the light is traveling through is less than the refractive index of the material it is striking. In other words, if the light is traveling from material 1 to material 2, then a phase shift occurs upon reflection. The pattern of light that results from this interference can appear either as light and dark bands or as colourful bands depending upon the source of the incident light [10].

Optical path difference is given by the equation

$$OPD = 2n_2 d\cos(\theta_2)$$

Interference will be constructive if the optical path difference is equal to an integer multiple of the wavelength of light, λ

$$2n_2 d\cos(\theta_2) = m\lambda$$

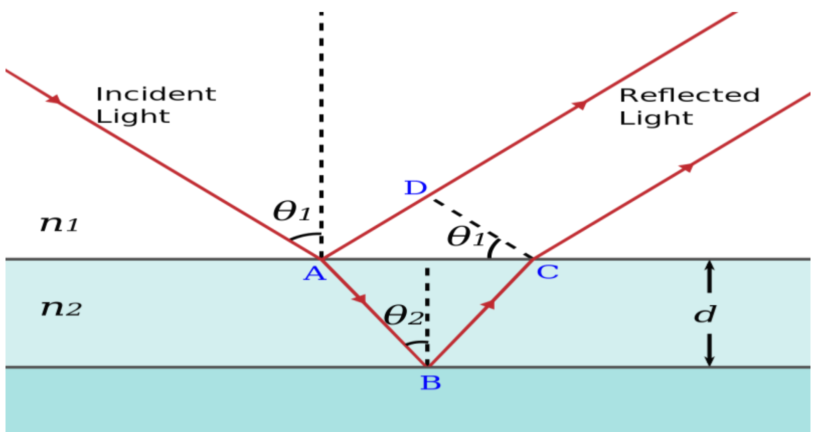

Figure 2.1 *Demonstration of the optical path length difference for light reflected from the upper and lower boundaries of a thin film.*

2.3 Ultraviolet–visible spectroscopy

UV-Vis spectroscopy refers to absorption or reflectance spectroscopy in the UV-Vis spectral region (generally from 190 nm to 800 nm). This means it uses light in the visible and adjacent ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, the atoms and molecules undergo electronic transitions. Absorption spectroscopy is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state [15]**.** UV-Vis spectrometer is used for the measurement of transmission spectra which is shown below:

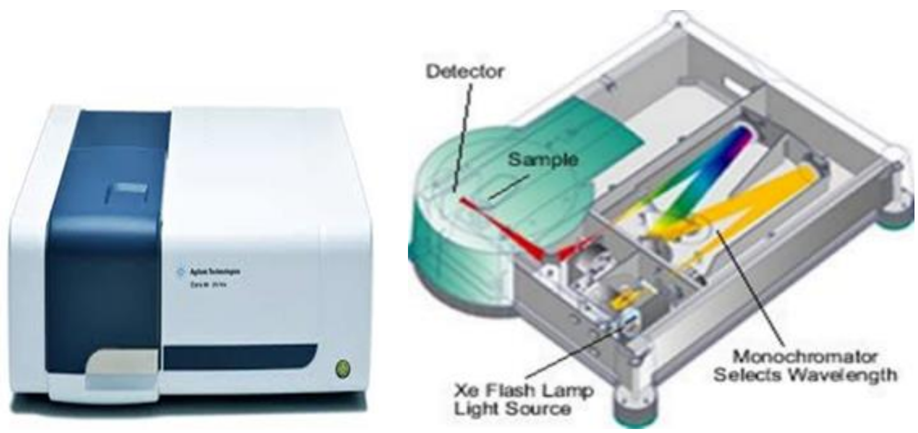

Figure 2.2 *Working of UV-Vis spectrometer*

The principle of UV–Vis spectrometer can be explained by the schematic diagram which is shown in (fig. 2.3).

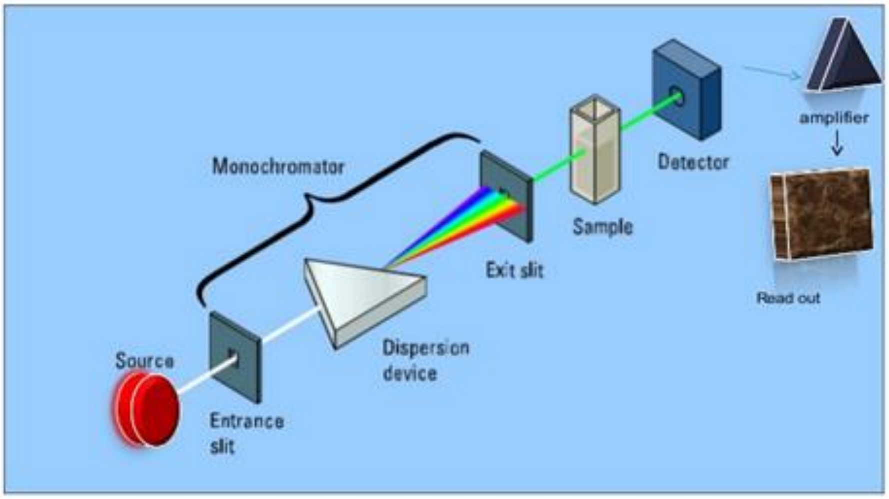

Figure 2.3 *schematic diagram which shows the working of UV-Vis spectrometer*

2.4 Transmission and Reflection Measurement

Using the techniques of transmission and reflection spectroscopy to measure absorption coefficients we studied the properties of thin semiconductor films.

For transmission and reflection spectroscopy we used a commercial spectrophotometer that is capable of recording spectra in the visible range as well as in the near infrared and UV range. To compensate for the complicated intensity distribution of the light source the spectrometer did not measure absolute values but compared the signal from the sample to a reference beam. Additionally, a baseline was recorded prior to the actual measurements to calibrate the instrument [16].

However, the transmission and reflection measurements are limited to wavelengths at which the sample has an average absorption coefficient. For high absorption, there is virtually no transmission. As both reflection and transmission spectra are required to calculate the absorption coefficient this method is no more applicable then. If α is too low however thin film interference effects will appear because light waves that are reflected on the two sides of the sample film will undergo interference. Therefore, spectrophotometry has to be used in combination with other techniques in order to obtain a complete absorption spectrum for a sample.

2.4.1 Transmission

Transmission is the ratio of transmitted light intensity to incident light intensity through the sample as shown in (Fig. 2.4)

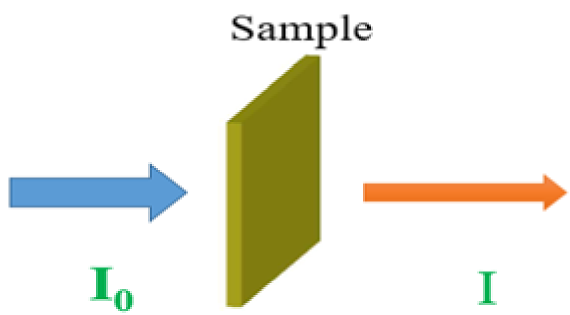

Figure 2.4 *Transmission phenomena*

Transmission is given by

$$T = \frac{I}{I_0}$$

The samples consisted of a thin semiconductor film that was imposed on a quartz substrate that did not absorb much light itself in the visible, near IR and UV ranges. For high energies there is no transmission because all the light is absorbed. For low energies, however, there are no appropriate electronic transitions possible so transmission is very high in this range. It is not 100% however, because of reflection. There is a relatively sharp delimitation between the areas of high and low absorption. The energy at which absorption starts seems to be characteristic of each material. Example for GaN it corresponds to the direct band gap of 3.4 eV. As crystalline silicon is an indirect semiconductor which cannot absorb a photon without simultaneously creating a phonon, absorption does not start at the band gap (1.1 eV) but at an energy that is high enough for exciting an electron and creating a phonon with the appropriate impulse. For our sample of amorphous silicon there exist many possible transitions around 2 eV. However, this cannot be generalized because the properties of a-Si: H depend on many parameters and will, therefore, be different for different samples. For low energies, we observe thin film interference effects that result from the overlaying of light that is reflected on both sides of the thin film. If this interference is constructive or destructive depends on the wavelength. For c-Si, this effect is not visible because the thickness of this sample (20 μm) was too great to allow coherent overlaying of the two reflected beams.

2.4.2 Refractive index

In optics, the refractive index or index of refraction *n* of a material is a dimensionless number and it is define as a

$$n = \frac{c}{V}$$

Where *c* is the speed of light in vacuum and *V* is the phase velocity of light in the medium. For example, the refractive index of water is 1.33, meaning that light travels 1.33 times faster in a vacuum than it does in water. It should be noted that the refractive index of a material is a function of energy of photon thus the correct expression may be written as

$$n(E) = \frac{c}{V(E)}$$

The refractive index determines how much light is bent, or refracted when entering a material.

Using the transmission value, which is obtained from the transmission spectra, refractive index is calculated using the well-known formula which is reported by R. Swanepoel as given below[9].

$$n = \frac{1}{T_s} + \left(\frac{1}{T_s^2} - 1 \right)^{1/2} \qquad \text{………….(1)}$$

Using the equation 1, the refractive index is obtained with the variation of wavelength.

2.4.3 Reflection

Reflection is the change in direction of a wavefront at an interface between two different media so that the wavefront returns into the medium from which it originated. Common examples include the reflection of light, sound and water waves. The law of reflection says that for specular reflection the angle at which the wave is incident on the surface equals the angle at which it is reflected. Mirrors exhibit specular reflection as shown in (fig. 2.5).

Reflection of light is either specular (angle of incidence is equal to angle of reflection) or diffuse depending on the nature of the interface. A mirror provides the most common model for specular light reflection and typically consists of a glass sheet with a metallic coating where the reflection actually occurs. Reflection is enhanced in metals by suppression of wave propagation beyond their skin depths. Reflection also occurs at the surface of transparent media, such as water or glass.

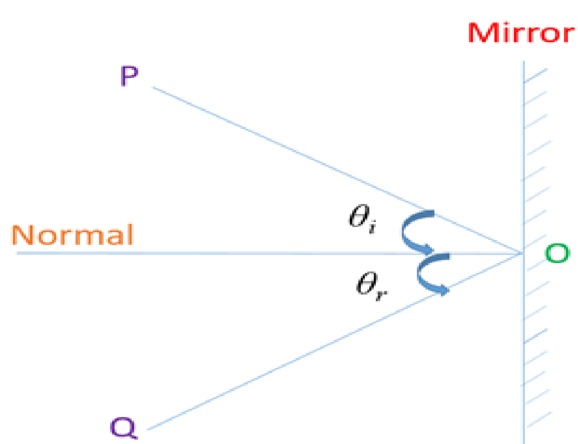

Figure 2.5 *Mirrors exhibit specular reflection*

After calculating the refractive index, as mentioned in 2.4.2, the reflectance is also calculated using the well known formula [9] which is as given below:

$$R = \left(\frac{n-1}{n+1}\right)^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Using the equation 2, the reflectance is obtained with the variation of wavelangth.

2.4.4 Absorption

Absorption of electromagnetic radiation is the way in which the energy of a photon is taken up by matter, typically the electrons of an atom or by the molecules vibrating at some specified in case of solid samples. Thus, the electromagnetic energy is transformed into internal energy of the absorber. The reduction in intensity of a light wave propagating through a medium by absorption of a part of its photons is often called attenuation. The absorbance of an object quantifies how much of the incident light is absorbed by it (instead of being reflected or refracted).

2.5 Band gap and Urbach energy Measurement

2.5.1 Band gap

In solid-state physics, a band gap also called an energy gap or forbidden energy state is an energy range in a solid where no electron states can exist. In graphs of the electronic band structure of solids, the band gap generally refers to the energy difference (in eV or meV) between the top of the valence band and the bottom of the conduction band in insulators and semiconductors or glassy systems. It is the energy required to promote a valence electron bound to an atom to become a conduction electron, which is nearly free to move within the crystal lattice and serve as a charge carrier to conduct electric current. It is related to the HOMO/LUMO gap a term generally used in chemistry. If the valence band is completely full and the conduction band is completely empty, then electrons cannot move in the solid; however, if some electrons transfer from the valence to the conduction band, then current can flow (see carrier generation and recombination) as shown in (fig. 2.6). The photocurrent in silicon is an example of the above said phenomenon. Therefore, the band gap is a major factor determining the electrical conductivity of a solid. Substances with large band gaps are generally insulators, those with smaller band gaps are semiconductors, while conductors have valence and conduction bands overlap.[17]

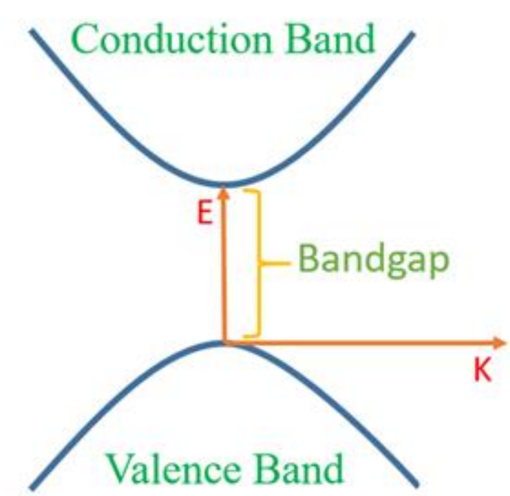

Figure 2.6 *Bandgap with E and K directions*

A semiconductor is a material with a small but non-zero band gap that behaves as an insulator at absolute zero but allows thermal excitation of electrons into its conduction band at temperatures that are below its melting point. In contrast, a material with a large bandgap is an insulator. In conductors, the valence and conduction bands may overlap, so they may not have a bandgap.

The band gap variation with the temperature is the fundamental characteristics of a semiconductor. The present report on the temperature dependence of the recently revealed band gap of $SrTiO_3$ was based on measurement of transmission spectra at different temperature. Thus here we show the variation of band gap of $SrTiO_3$ as a function of temperature using UV-Vis spectroscopy.

The temperature dependence of band gap, determined from the absorption edge, and the temperature dependence of bandgap can be described by empirical relation named as Varshni's equation is given below [10,18,19]

$$E_g(T) = E_g(0) - \frac{\gamma T^2}{T + \beta}$$

Where ϒ and β are fitting parameters characteristic of a given material. E_g (0 K) is the band gap of semiconductor at 0K.

This equation represents a combination of a linear high temperature dependence with a quadratic low temperature dependency. This equation suggests that band gap shifts in semiconductor as a function of temperature is mainly due to electron-phonon interaction and thermal expansion-contraction also play an important role.

2.5.2 Urbach energy

Along the absorption coefficient curve and near the optical band edge there is an exponential part called Urbach tail [20,21]. This tail varies exponentially (not as a Gaussian) into the band gap. Due to temperature variation or incorporation of impurities spatial arrangement of atoms gets disturbed and electron feels slightly different potential. Due to this variation of potential edges of valance band and conduction band gets blur i.e. localized states are formed in the form of tail in between the valance band and conduction band. Due to these band tails, optical absorption edge is did not fall sharp and has tail at lower energies. This exponential variation in absorption coefficient along the absorption band edge is a well-known universal feature in optical properties as shown in (fig. 2.7 & 2.8).

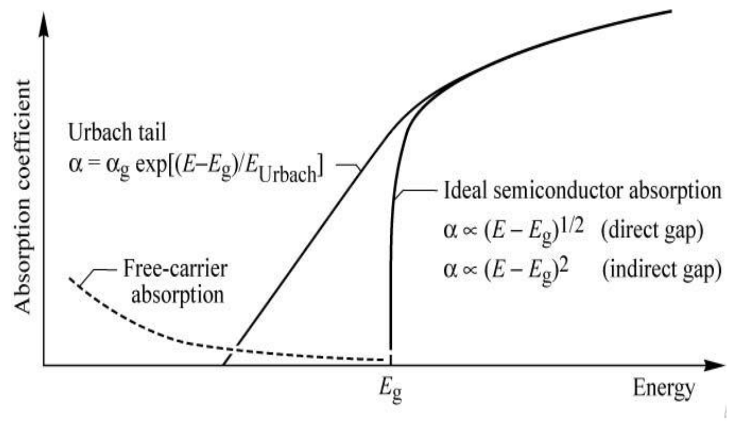

Figure 2.7 *Exponential variation of Urbach tail*

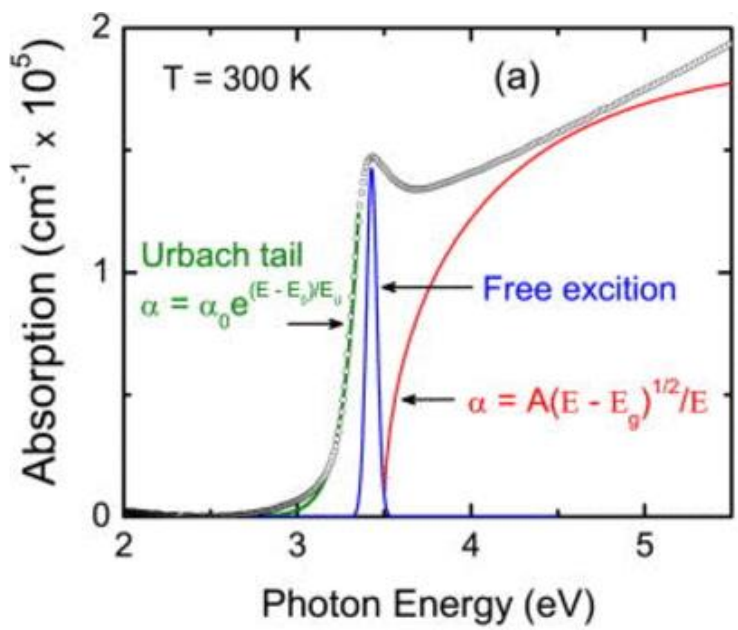

Figure 2.8 *Absorption variation with the photon energy*

This tail also arises because of various kinds of defects, local structural incoherency (strain, defects etc.), chemical in-homogeneity etc. Due to presence of these disorders the valence band and conduction band do not have sharp cut off but have localized tails states nearby. The universal phenomena have been observed in all imperfect crystalline solids and amorphous solids as shown in (fig. 2.9).

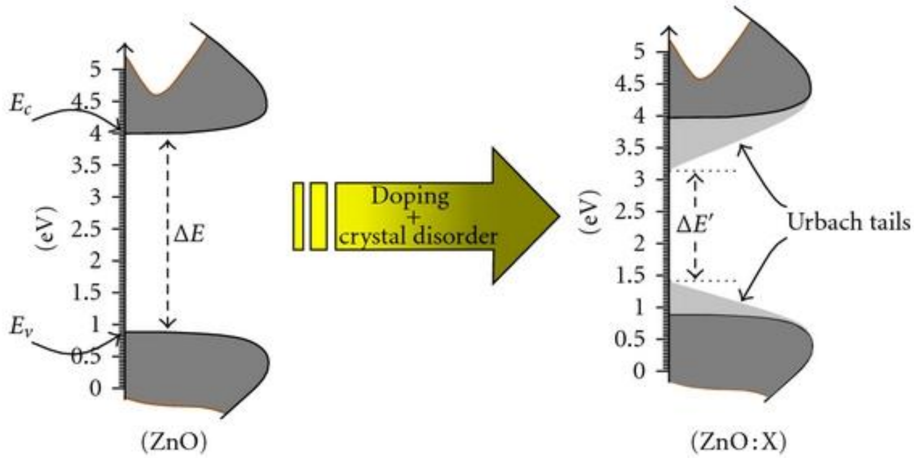

Figure 2.9 *Urbach tail due to doping and disorder*

The above said disorder in the materials creates the states which extended in the band gap [22]. In the low photon energy range, the spectral dependence of the absorption coefficient (α) and photon energy (hν) is known as Urbach empirical rule [13], which is given by the following equation:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu - E_0}{E_U}\right)$$

Where α_o is a constant, E_0 is the optical band gap and E_U is the Urbach energy, which is also dependent upon temperature and is often interpreted as the width of the band tail due to disorder in the sample.

Chapter 3: Low Temperature Transmission Experimental Setup Design

The low temperature setup is composed of five main elements: base plate, vacuum chamber, sample holder, cover plate, liquid Nitrogen tank as shown in (Fig. 3.1, 3.2, 3.3). The heater is winded on a copper sample holder & a wire connector is embedded with the cover plate of vacuum chamber as shown in (Fig. 3.4).

In this chapter, the fabrication processes, all design parameters, guidelines for selection of the material, shape and size are presented [23]

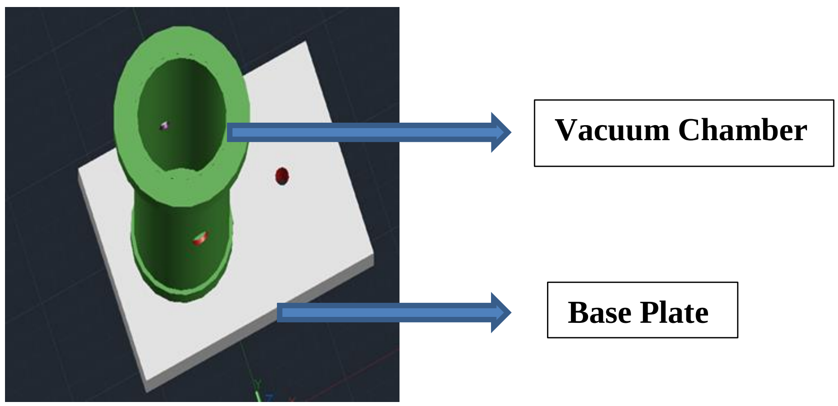

Figure 3.1 *The prototype of base plate and vacuum chamber*

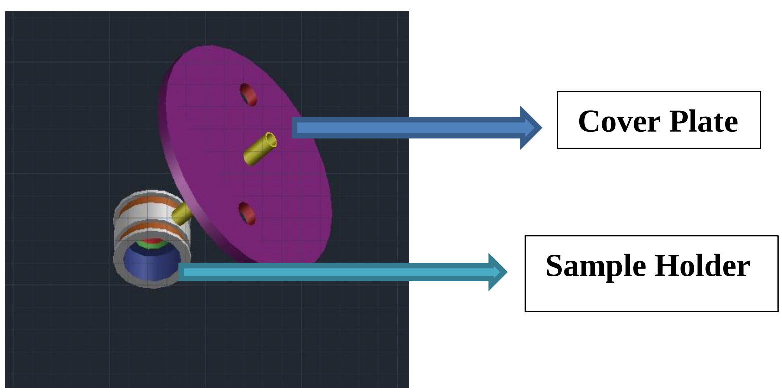

Figure 3.2 *The prototype of cover plate and sample hold*

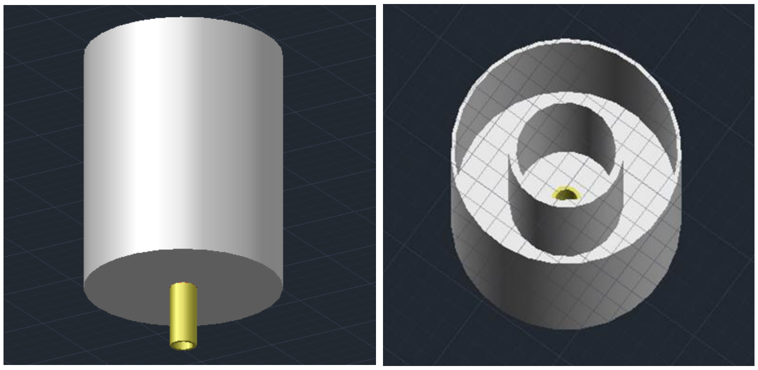

Figure 3.3 The prototype of liquid nitrogen tank

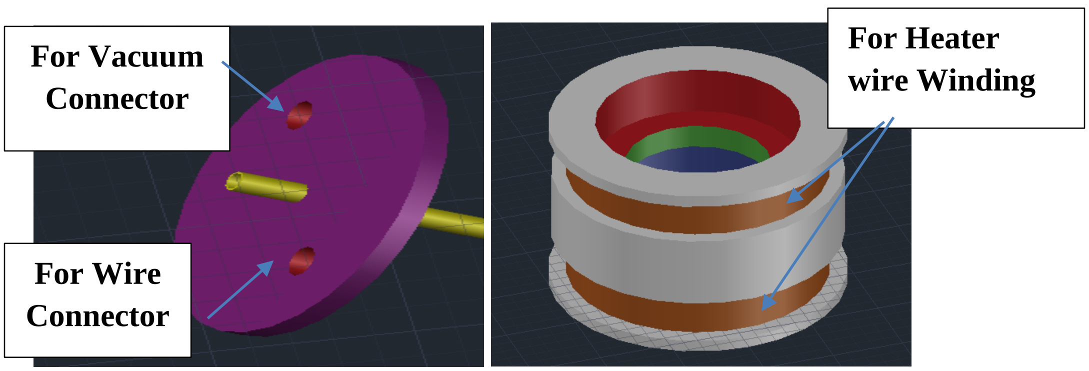

Figure 3.4 *The prototype of cover plate and heater winded on sample holder*

3.1 Prototype Design

The whole prototype is designed using AutoCAD software. This design is completed in following steps:

Step 1:

First of all, we have studied the mechanical layout of UV-Vis setup where we wish to put our setup and accordingly the base plate and height of the optical windows were decided. The base plate is made using rectangle and extrusion command as shown in (Fig. 3.5).

The base plate is designed to fix the setup with the UV-Visible spectroscopy. There are 3 screw holes [1 hole (in red color) is throughout of plate and two holes are given from bottom side] are given according to the availability of space in UV-Vis spectrometer.

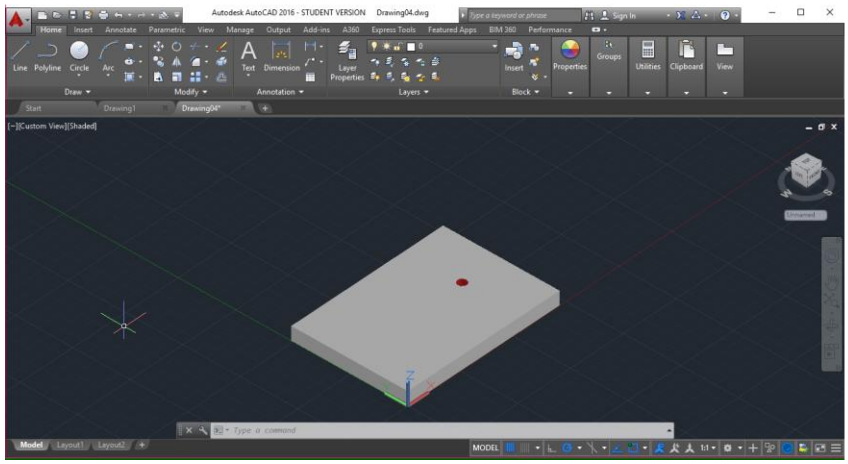

Figure 3.5 *Design of base plate on AutoCAD*

Step 2:

Vacuum chamber is mounted over the base plate using circle and extrusion command as shown in (Fig. 3.6).The vacuum chamber (in green color) is designed to create the vacuum in the setup using vacuum compatible SS304L material. Our sample with its assembly is kept within the vacuum chamber. In the chamber two optical windows are given which named as *source side window and detector side window.* These windows are used with quartz to pass the light from source to detector with a sample in between.

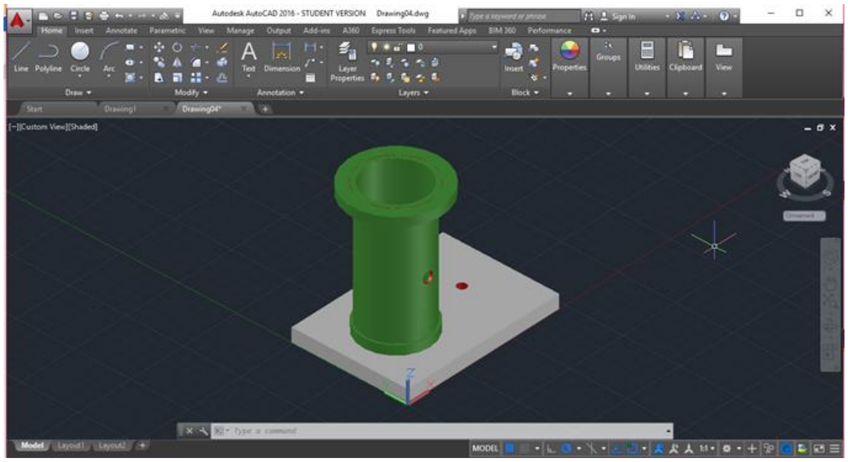

__Figure 3.6__ Design of mounting of vacuum chamber on AutoCAD

Step 3:

Cover plate is designed for vacuum chamber using circle and extrusion command as shown in (Fig. 3.7). It is used to cover the vacuum chamber that’s why it is called cover plate. Two hole (in red color) are given in the plate in which one is for vacuum and other is for wires which are coming outside from the chamber. One pipe (in yellow color in the fig.) is also connected from the cover plate to liquid nitrogen tank.

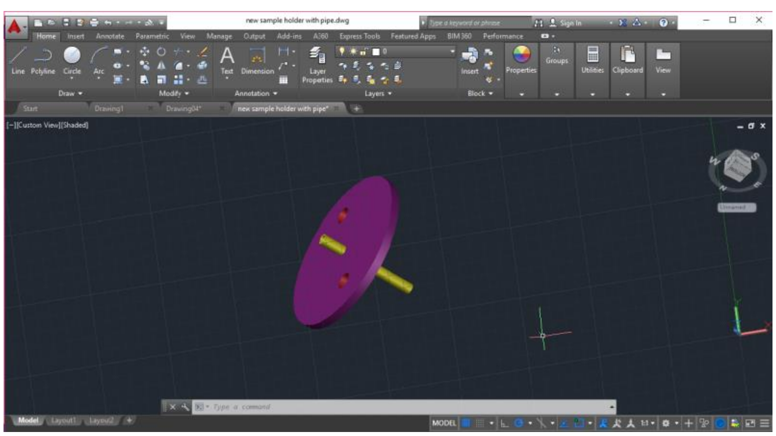

__Figure 3.7__ Design of cover plate for vacuum chamber on AutoCAD

Step 4:

A sample holder is designed for holding the sample and heater winding as shown in (Fig. 3.8). Sample holder is used to holding the sample. The sample should be fixed tightly in the sample holder and due to this reason, a perfect shape is given to the sample holder. Heating wire is also winded on the sample holder so some space is given for winding the wire.

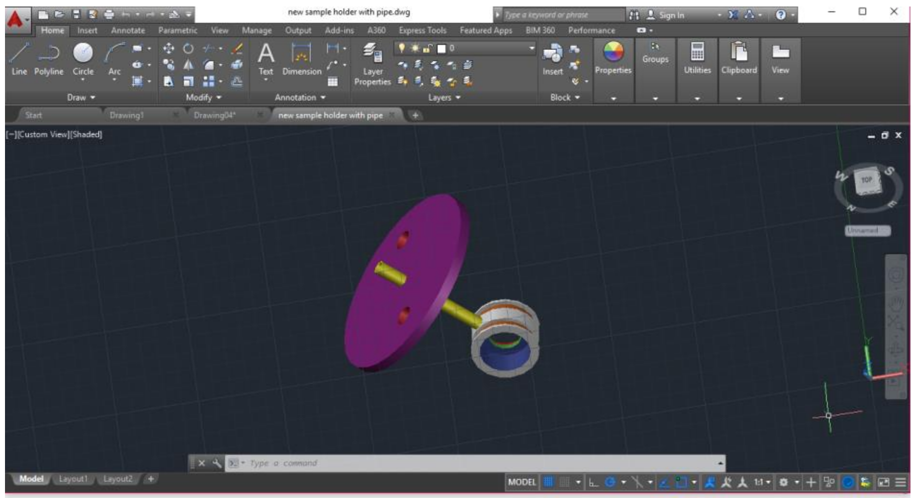

Figure 3.8 *Design of sample holder with cover plate on AutoCAD*

Step 5:

A liquid nitrogen tank is designed as shown in (Fig. 3.9). Liquid nitrogen tank is designed to store the liquid nitrogen for a long time. Two concentric circle shape is designed to provide the space for heat insulation material.

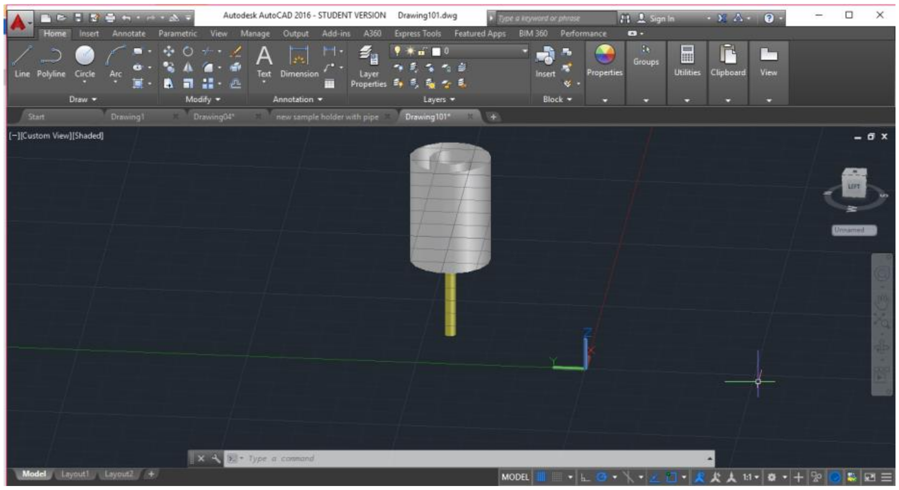

Figure 3.9 Design of liquid nitrogen tank on AutoCAD

With these 5 main elements, there are other elements are also designed by me as shown below:

1. **Sample holding plate:** Sample holding plate is designed for supporting/holding the sample in sample holder. As the sample can vary according to size so we designed these plates of various size as shown in (Fig. 3.10)

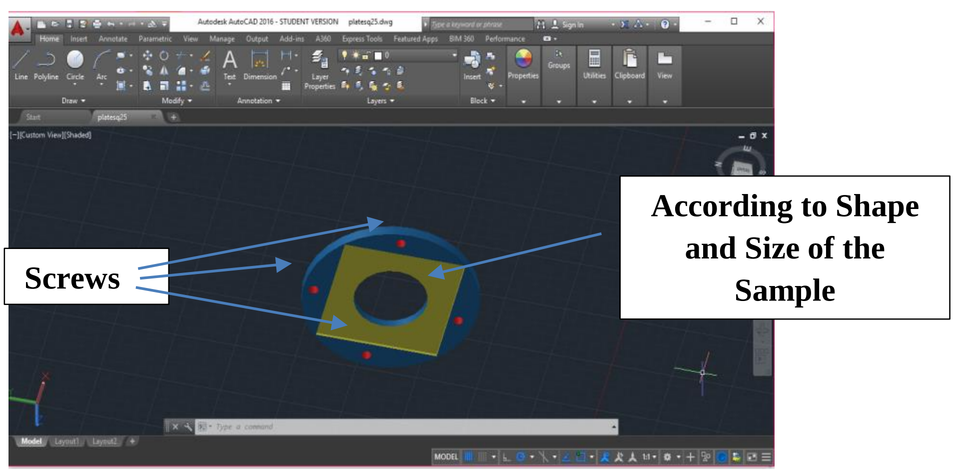

Figure 3.10 *Design of sample holding plate on AutoCAD*

The square shape is given according to the sample shape. This shape can be designed circular if there are possibility of circular shape sample.

Four Screws are given for clamping this plate with sample holder and if there are any inclination then we can arrange this inclination by using these screws.

Other plates of different size are shown below in (Fig. 3.11)

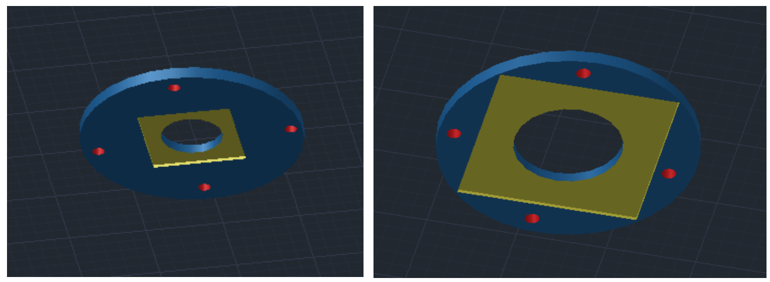

Figure 3.11 *Design of different size of sample holding plate*

2. Thermal insulation material: Insulation is necessary to reduce heat loss/transfer from liquid nitrogen to atmosphere. To reduce the heat transfer there should be some insulation material. To fulfil this condition space is given in the design of liquid Nitrogen tank as shown below in (Fig. 3.12).

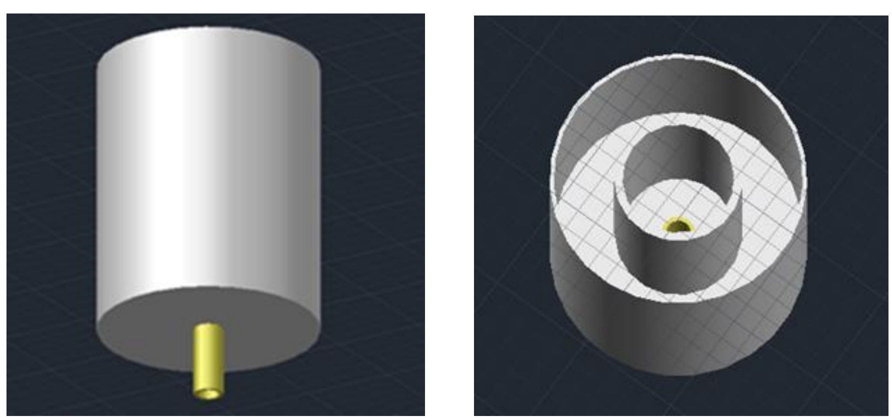

Figure 3.12 *Design of liquid nitrogen tank with space for insulation material*

Now, the design is completed and it is ready for fabrication.

3.2 Fabricated setup

The fabricated setup and it's all parts are shown below in (fig. 3.13).

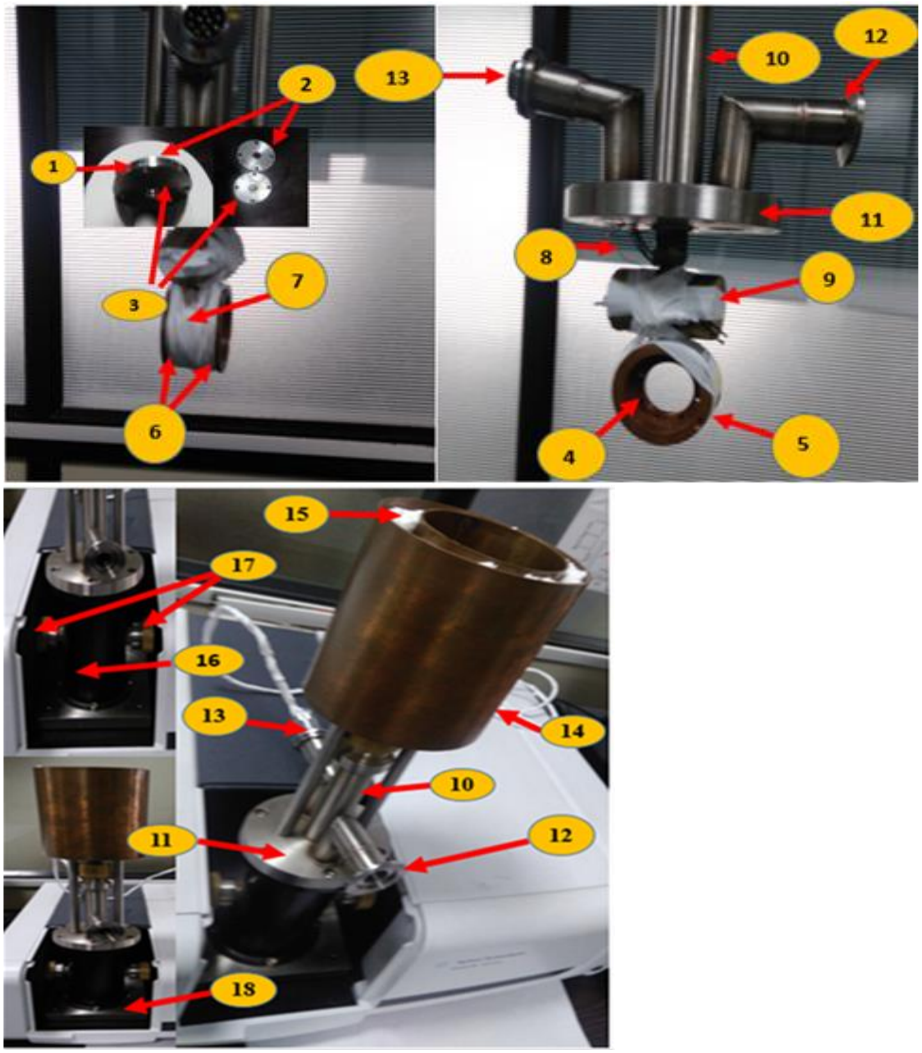

Figure 3.13 Fabricated setup with its all parts

(1). Sample, (2 & 3). Two blocks, (4). Place for sample with blocks, (5).Sample holder, (6). End of winding wire, (7). End of wires of sensor (8). Four wires connected through KF25 port, (9). Small liquid nitrogen tank, (10). A pipe to connect main liquid nitrogen tank with the system (11). Cover plate, (12). KF25 port for vacuum, (13). KF25 port for wires, (14). A main liquid nitrogen tank, (15). Heat insulation material, (16). Vacuum chamber, (17). Two optical windows, (18). Base plate

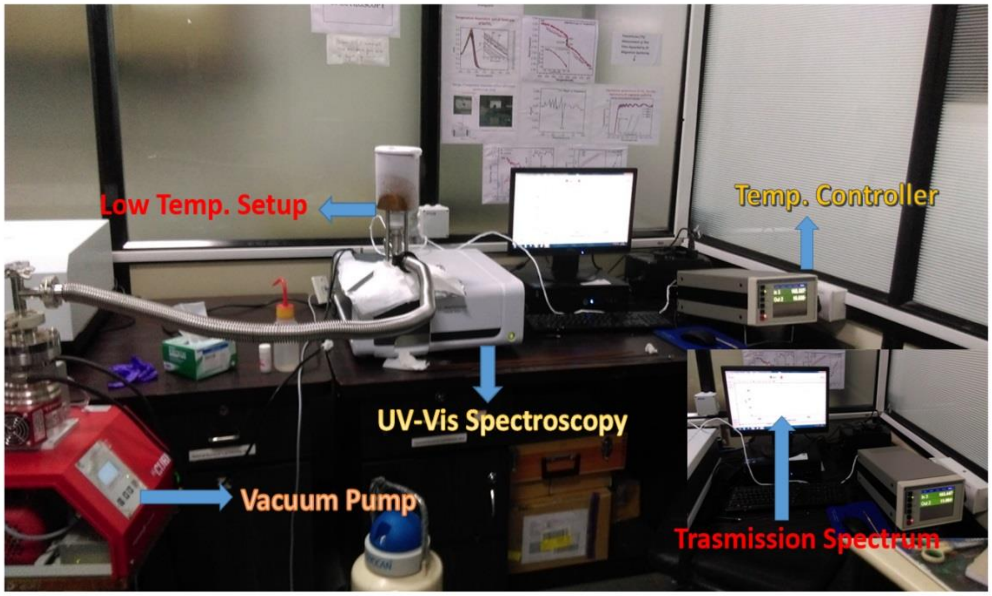

Figure 3.14 *Complete setup with its all accessories*

3.3 Complete description of measurement setup

The real photograph of the measurement setup is shown in (Fig. 3.13) and complete setup with its all accessories is shown in (Fig. 3.14), where different components of the equipment are represented by numbers.

The sample (**1**) is kept between stainless steel 304 blocks (**2** & **3**) of ϕ=37 mm cross-section and 2 mm thickness. After placing the sample between blocks (**2** & **3**) like sandwich of sample between both blocks, this arrangement is kept at place (**4)** in the sample holder (**5)**.For temperature variation, a Nichrome wire is wrapped around the sample holder (**5)** in such a way that there is an equal temperature gradient at the sample (**1)** from both sides to heat the sample [24]. A temperature sensor (**7)** is mounted at the center part of the sample holder (**5)**. Two wires are coming out from winded wire (**6)** and two wires are coming out from sensor (**7)**. These four wires (**8)** are coming out through KF25 port using a connector (**13)**. Here these wires are covered by Teflon tape.

This instrument is used to measure optical properties as a function of temperature from low temperature to room temperature. For fulfil this purpose, the temperature of sample (**1**) should be maintained at liquid Nitrogen temperature. For this purpose, a small liquid Nitrogen tank (**9)** is attached in which liquid nitrogen are come through pipe (**10)** from a main liquid Nitrogen tank (**14)**.

The sample holder (**5)** assembly is placed inside the vacuum chamber (**16).** The vacuum chamber is made up of SS304L pipe of 70 mm diameter and 140 mm height. As SS 304 is a vacuum compatible, low carbon content with a 0.03% maximum carbon ,with a higher chromium content that eliminates the chances of corrosion [25]. A KF25 port (**12)** is provided to the vacuum chamber at the top. Using this port we connect this vacuum chamber with the vacuum pump. Turbo molecular vacuum pump is used to create vacuum inside the vacuum chamber up to a level of 10^{-8} mbar.

A temperature controller is used to supply power to the heater to measure the present value of temperature and to control the temperature of the sample under investigation. Temperature controller is a high performance instrument that can monitor and control temperatures with high resolution ~0.01K. The system consists of four sensor inputs, two powered and four analog voltage outputs, and up to six feedback control loops. We can vary the power supply according to condition and requirement.

A big liquid Nitrogen tank (**14)** have two concentric cylinders with some gap in which heat insulator material (**15)** are filled to reduce the heat transfer from liquid Nitrogen to atmosphere.

There are two optical windows (**17)** are also provided at source and detector side to provide proper path for light without any losses and to maintain vacuum in the chamber.

One base plate **(18)** is also used. This plate is used to fix the setup with the UV-Visible spectroscopy so that there is no movement of setup during experiment and to do this we can maintain a straight light path because straight light path is necessary for taking transmission spectra in good condition.

3.4 Need of the vacuum

When the temperature of the sample is lowered the condensation of gases on the surface of the samples becomes the big problem during the experiment. Hence it is necessary to take out most of the gas molecules from the chamber. This can be understood as shown in the figure (Fig.3.15) which represents the condensation of water on the surface of a can.

Figure 3.15 *Surface condensation phenomena*

3.4.1 Accessories to maintain the vacuum in the system

For creating vacuum of the order of 10^{-8} mbar in the chamber, we used a turbo molecular pump which is shown here in (Fig. 3.16)

Figure 3.16 *Turbo molecular pump used to create vacuum*

- . A vacuum feed through for electrical connection is used in the setup is shown in (Fig. 3.17)

Figure 3.17 *Feed Through for maintaining the vacuum in the chamber*

The setup is now ready for taking the data to study the effect of temperature on optical constants of different materials.

The data obtained from the setup will be discussed in chapter 4 and the conclusion from these data will be discussed in chapter 5.

Chapter 4: Results and Discussion

We have calibrated our instrument by using standard $SrTiO_3$ substrate as $SrTiO_3$ is well known wide band gap semiconductor material.

First of all the setup is connected to the vacuum pump and after achieving the vacuum of 10^{-8} mbar the setup was heated at high temperature in order to produce moisture free space. After hating/baking the heater was switched off and we have slowly poured the liquid Nitrogen in to the tank. As the bottom of the tank is directly connected to the sample holder through a copper connecter, we observed that the temperature of the sample starts decreasing and reaches to 87K approximately after 1 hour. When the temperature of the sample is reached at 87 K, we started our transmission measurement experiment using the setup. The temperature of the sample is increased in control manner using temperature controller and the transmission data is recorded at fix interval of one by one by increasing the temperature of the sample and when the temperature of the sample is reached at room temperature then we stop the experiment.

The results which are obtained from the experiment are discussed one by one as given below:

4.1 Transmission measurements

Transmission data of $SrTiO_3$ substrate as a function of temperature is shown in (fig. 5.2).The magnified view of the data near the absorption edge is shown in the inset.

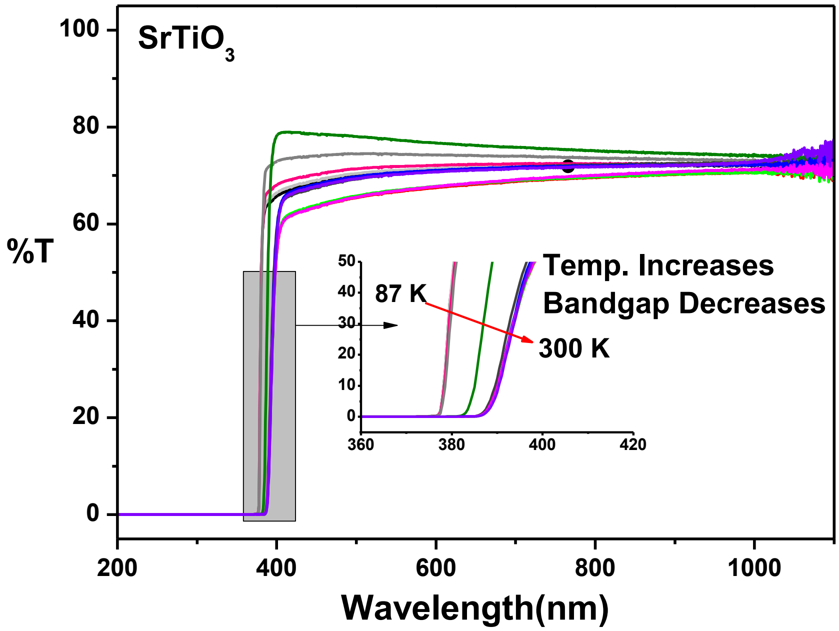

Figure 4.1 *Transmission spectrum shows bandgap variation*

4.2 Band gap measurements

The band gap variation with the temperature is the fundamental characteristics of a semiconductor. The present report on the temperature dependence of the recently revealed band gap of $SrTiO_3$ is based on measurement of transmission spectra at different temperature [27]. The temperature dependence of band gap, determined from the absorption edge, can be described by empirical relation named as Varshni's equation is given below:[11]

$$E_g(T) = E_g(0) - \frac{\gamma T^2}{T + \beta}$$

Where ϒ and β are fitting parameters characteristic of a given material. E_g (0) is the band gap of semiconductor at 0K.

From the absorption edge of the transmission spectra the variation of the band gap as a function of temperature is extracted and the same is shown in (Fig. 5.3)

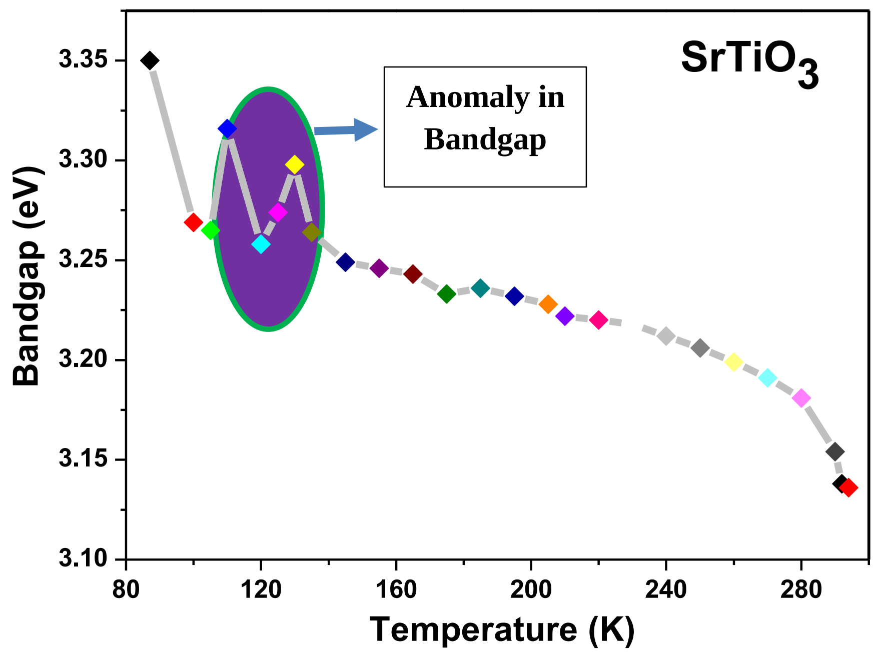

Figure 4.2 *Bandgap variation with the temperature*

This (Fig. 5.3) shows that bandgap is decrease continuously with the increase in the temperature. That's match with the standard data and validate the Varshni's equation. With these results some anomaly is also occurred near the temperature 105 K. In this region, bandgap variation is deviates from regular variation. This is possibly due to the structural phase transition [28,29].

4.3 Urbach energy measurements

Useful information like effect of disorder on the electronic properties of various kind of semiconductors can be obtained from the measurements of the optical absorption spectrum [30]**.** When a defect-free crystalline semiconductor associated with the absorption spectrum, It terminates sharply at the energy gap, in an disorder semiconductor a tail intrudes into the gap region [12].

In the optical absorption spectrum, this tail arising as a result of optical transitions involving the tail states [31]**.** Experimentally, it is reported that this absorption tail broadens with increase the level of thermal and structural disorder. It is often found that there is a shift in the optical gap towards lower energies with the greater disorder.

In the case of the urbach behavior of the absorption edge, the temperature and spectral dependence of absorption coefficient [13] is given below :

$$\alpha = \alpha_0 \exp\left(\frac{h\nu - E_0}{E_U}\right)$$

Where α_o is a constant, E_0 is the optical band gap and E_U is the urbach energy which is equal to the energy width of the absorption edge.

Taking the logarithm of the two sides of the equation, a straight line is equation is obtained which is given by:

$$\ln\alpha = \ln\alpha_0 + \left(\frac{h\nu - E_0}{E_U}\right)$$

Therefore, the band tail energy or urbach energy (E_U) can be obtained from the slope of the straight line of plotting *ln α* against the incident photon energy (*hv*).

Graph between *ln α* vs. incident photon energy (*hv*) is shown in (fig. 5.4 & 5.5).

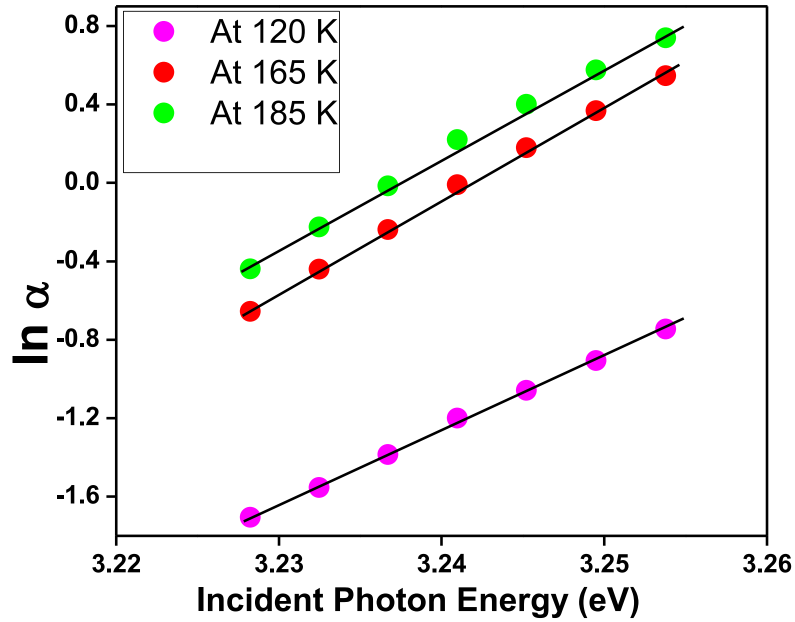

Figure 4.3 *Plot between ln α Vs. hν*

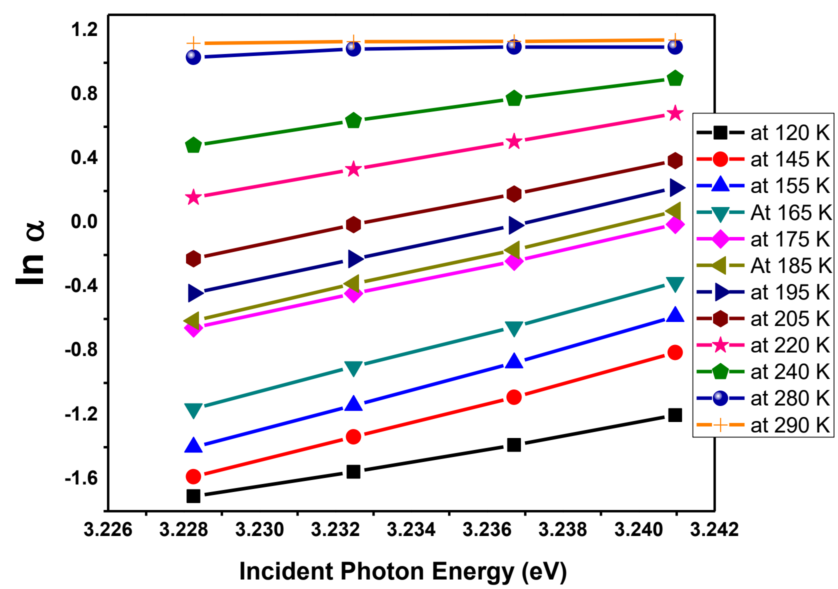

Figure 4.4 *Slope variation with the temperature*

Fig. 5.4 & 5.5 shows that with the increase in the temperature, Slope of the straight line are decreases continuously.

Now by following these steps we got the values of urbach Energy with the variation of temperatures.

A graph showing the relationship between Urbach energy and temperature

shown in (fig. 5.6)

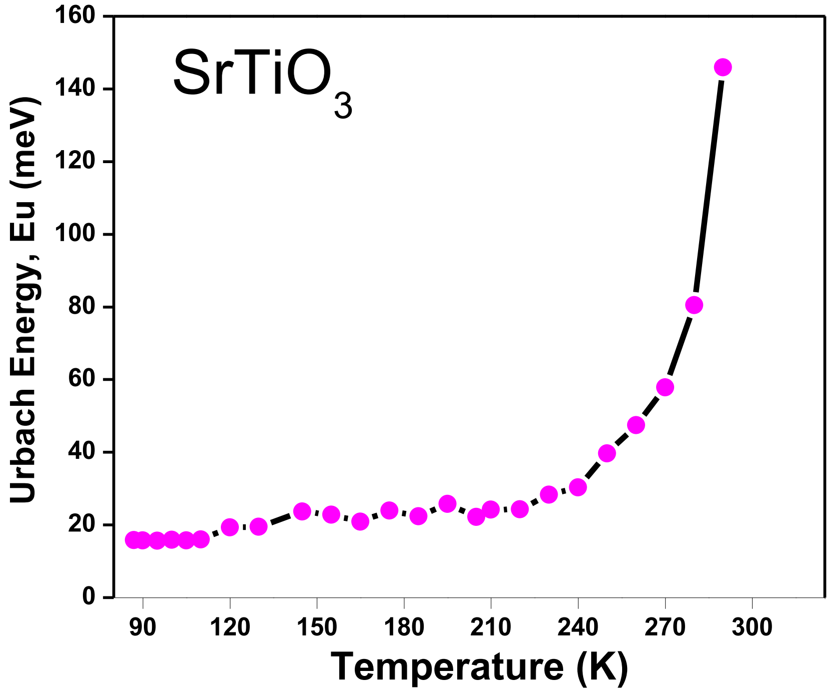

Figure 4.5 *Urbach energy variation with the temperature*

Figure 5.6 shows that Urbach energy is increased with the temperature and disorders are also increased which is matched with the reported data [12].

Chapter 5: Conclusion and Future Scope

5.1 Conclusions

The major conclusions of the research work reported in this thesis being summarized below:

- We successfully have designed and fabricated low temperature experimental transmission measurement setup.
- We have tested the setup using single crystal $SrTiO_3$ sample.
- The results obtained from the setup matched well with the standard results which validates the working and accuracy of the setup.

5.2 Future Scope

- Design and fabrication of setup for samples which are optically opaque: such as powder. For this purpose diffuse reflectance spectroscopy setup will be useful.

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