Chapter 5

THIN FILMS OF $Bi_{2-x}Sb_xTe_3$(x=0, 0.05 and 0.1)

A bulk solid material is easily distinguished by its three dimensions, i.e. by its length, breadth and thickness. As one works on decreasing the thickness eventually it reduces to a nearly two dimensional material which can be called as a “FILM” .

These solid films can be classified on the basis of their thickness as,

a) Thick films:

They are the films with thicknesses several microns or more.

b) Thin films:

They are the films with thicknesses several thousand angstroms.

c) Ultrathin films:

They are the films with thicknesses less than a thousand angstrom.

A given material tends to behave quite differently in its bulk form from its thin film form. The main reasons attributed to this behavior are:

1. Much large (100 times or more) surface to volume ratio accompanied by larger imbalance between atomic forces at the surfaces as compared to the normal one in the bulk polycrystalline and single crystalline sample. This is why the films exhibit some interesting specific surface and size dependent features in

conductivity, catalysis, adsorption, surface tension, thermionic emission, etc. Metals such as Na, K and Rubidium which behave as metallic conductors in bulk state exhibit semiconducting properties in thin film form[1].

2. Much larger variations in the structure and concentration of defects as compared to those normally found in bulk polycrystalline and single crystalline samples. That is why various properties of thin films are also found dependent on the techniques, conditions and parameters used and adopted in the film preparation.

HISTORY AND DEVELOPMENT

While non-solid films and the associated phenomenon of interference colours have been studied for over three centuries, thin solid films were probably first obtained by electrolysis in 1838. In the recorded literature, however, Bunsen and Grove obtained metal films in 1852 by means of a chemical reaction and by glow-discharge sputtering, respectively. Faraday obtained metal films in 1857 by thermal evaporation on explosion of a current carrying wire. The free evaporation and condensation of thin films in vacuum were probably first observed by Edison and then by Fleming in 1883 who reported a metal film formed on inside of a carbon filament lamp envelope. The possibility of depositing thin films of metals by Joule heating of platinum wire was discovered in 1887 by Nahrwold and was adapted by Kundt in 1888 for the purpose of measuring refractive indices of the metal films.

The rapid growth of thin film technology started during the time of Second World War when vacuum evaporated metal and dielectric films were used in optics for mirrors and antireflection coatings, respectively.

The technology and understanding of films less than 1 micron thick have made tremendous advances in the last decade, primarily because of the industrial demand for reliable thin film microelectronic devices to fulfill the urgent needs of sputnik era. In addition to major contributions to a variety of new and future scientifically based technologies, thin film studies have directly or indirectly advanced many new areas of research in solid-state physics and chemistry which are based on phenomena uniquely characteristic of the thickness, geometry and structure of films.

THIN FILM TECHNOLOGY

The demand for ultra high vacuum conditions for vacuum evaporation has been largely responsible for the growth of a highly specialized and precision based vacuum industry. In addition to the conventional oil pumps, variety of high speed and of oil free, getter ion, sublimation and cryogenic pumps have emerged.

A multitude of techniques have been developed to prepare developed to prepare polycrystalline and nearly single-crystalline films of all types of materials. Deposition rates may range from a fraction of an angstrom to thousands of angstrom per second. The thermal evaporation may be carried out at different rates of evaporation from one or more source, with a high uniformity of film thickness over a large surface (such as that of artificial satellite.)

Examples of successful industrial processes are the use of thermal evaporation of Al for aluminization of foils, inert and reactive spattering of Ta-for thin-film microminiaturized resistors and capacitors and chemical deposition of Nb_3Sn on foils for the winding of superconducting magnets.

Several micro analytical techniques have been improved and others invented to determine the composition and microstructure of thin films. Electron diffraction and electron microscopy which owe their present high level of sophistication to the availability of thin films, are now responsible for much of the understanding of the structure of thin films themselves. Among various by products in terms of new analytical techniques, that of the Mover fringes is significant since it is capable of revealing images of lattice and lattice defects down to a dimension of few angstroms.

IMPORTANCE OF THIN FILMS

Properties of thin films differ greatly from those of the same bulk material chiefly because of their extremely small thickness, large surface to volume ratio and unique physical structure which is a direct consequence of the growth process. Some of the phenomena resulting due to the small thickness are optical interference, high resistivitylow temperature coefficient of resistance, the planar magnetization,electronic tunneling through an insulating layer,etc. The high surface to volume ration of a thin film is known to influence gas adsorption, diffusion and catalytic activity to a significant extent. Due to metastable disordered structure in thin films of certain materials,it is found possible to enhance superconducting transition temperature, hardness, corrosion resistance, thermo power and optical absorption.

Thus, because of the properties of thin films different from those of bulk materials and also due to the possibility of their preparation to obtain desired properties thin films find their applications in many fields.

VAPOUR GROWTH AND EPITAXY

The vapour deposition and epitaxial methods of preparing thin films provide a general platform easily susceptible to development of theory of thin film growth. When an atom impinges on a surface it selects for itself a position which is compatible (in terms of potential energy) with the surrounding conditions. The position of the deposited atoms are governed by the positions of the atoms in the very beginning on the initial surface and by positions of the atoms of the successive layers of the crystals as the growth proceeds. As soon as the growing deposit reaches a thickness of about four to five atom layers, the substrate surface, in general, will have no influence on further growth of the deposit. As it is quite often the growth takes place simultaneously on two or more layers and hence the atom at the junction will not be in a maximum stable condition, thereby giving rise to crystal defects such as dislocations, stacking faults, twins etc.

Pashley[2], Hirth & Pound[3], Rhodin and Walton[4] Baner[5] and Van der Merwe[6] and Pashley et al[7] have suggested that the vapour phase deposits grow in the form of grains on individual sites on a surface and as growth proceeds, the grains grow until they touch one another. Some of them coalesce with one another like liquid drops. When coalescence nearly completes there still remain what are known as channels which will be filled only during further growth of deposit to give rise to a smooth and continuous film. In certain materials the “island structure” persists up to a large thickness. During the initial stages of film growth i.e., when island are quite small, they are observed to be perfect single crystals. But when island become large enough so that they touch at grain boundaries, lattice defects will be incorporated in the film unless island coalesce to form a single grain.

The term epitaxy (arrangement on) was first introduced by Royer[8.9] to denote the phenomenon of oriented overgrowth of one crystal on to the other. The nature of the substrate bears a great influence on the epitaxial growth of films, their orientations and hence their properties however. Other parameters like substrate temperature, impurities, deposition rate, thickness electric field, etc .also affect epitaxial growth.

Structure of Thin Film

Solids, including thin films can be classified in to forms, namely, crystalline and amorphous phases. crystalline solids can be sub –divided as single crystalline and polycrystalline. With or without any preferred orienatiton. Amorphous materials do not have any such ordered arrangement of atoms or ions. The thin films of most of the materials assume the same crystal structure as that of the bulk materials. However, the structural order, as for example, size and orientation of the crystallites, departs considerably from that of the bulk.

Characterization of thin films

Thin films have been assuming increasingly complex structures in view of their applications which demand tailor- made properties; as a result sophisticated characterization techniques have emerged for the understanding of the multifaceted properties of thin films and no single technique is sufficient for characterizing a film completely even in any one domain.For example, crystal structure, chemical nature, etc .Table 1 below shows a few aspects of thin film characterization, namely, surface topography, surface and structure and chemical analysis with their corresponding techniques.

TABLE-I

Property of Thin Film	Characterization Technique
Topography	1. Stylus 2. SEM (Scanning Electron Microscopy) 3. TEM (Transmission Electron Microscopy) in the replica mode.
Crystal Structure	1. XRD (X-ray Diffraction) 2. TEM
Surface Structure	1. LEED (Low Energy Electron Diffraction) 2. RHEED (Reflection High Energy Electron Diffraction) 3. FEM/FIM/APFIM (Field Emission Microscopy/Field Ion Microscopy/Atom Probe Field Ion Microscopy)
Chemical Analysis	1. EPM (Electron Probe Micro Analysis) 2. AES (Auger Electron Spectroscopy) 3. SAM (Scanning Electron Microprobe) 4. ESCA (Electron Spectroscopy for Chemical Analysis) 5. ISS (Ion Scattering Spectroscopy) 6. SIMS (Secondary Ion Mass Spectrometry) 7. RBS (Rutherford Back Scattering)

THIN FILM PREPARATION TECHNIQUES

There are many deposition techniques for thin film formation. These techniques have been broadly classified into four main groups.

1) Physical vapor deposition (PVD)

2) Chemical vapor deposition (CVD)

3) Electroless or solution deposition

4) Electrochemical deposition

By combining PVD and CVD, hybrid techniques such as reactive evaporation/sputtering and plasma deposition have been established [10]. We will discuss some important techniques involved in the PVD since this technique has been used in this investigation.

Physical Vapour Deposition

This includes vacuum deposition techniques such as evaporation and sputtering. The main feature of these techniques is that that the coating material passes through vapor phase by any one of the physical mechanism such as evaporation, sublimation or ion bombardment.

Thermal Evaporation:

In this PVD process, thermal evaporation is used to change the material to the vapour state. The material to be deposited, the evaporator and the substrate on which it is to be deposited are sealed in a chamber which is evacuated to the order of 10^{-5} Pa. The material to be evaporated is generally melted in a refractory filament or boat heated electrically under high vacuum. Evaporation from the melt of the material takes place and develops thin film on any obstruction placed in the path of substrate. The quality of thin film produced depends on

(a) Purity and form of vaporising material

(b) cleaning and pretreatment of substrate material

(c) residual gas pressure and condensation rate.

The actual vacuum coating unit[11] used for the preparation of $Bi_{2-x}Sb_xTe_3$(x=0, 0.05 and 0.1) film is shown in Chapter 2. The assembly in the vacuum chamber is as required for thin film deposition by resistive heating method.

A substrate stand is provided to hold the substrate. The quartz crystal film thickness monitor is kept near the substrate to know the rate of deposition and thickness of the film being deposited To fix the evaporation source, two metal electrodes are provided across which voltage is applied during deposition. The evaporation source and the substrate are kept in a straight line and the distance between them is normally about 20 cm.

A penning ionization gauge is connected to the chamber to measure vacuum and a pirani gauge in the backing line to sense the roughing pressure The diffusion pump is connected directly below the chamber by a baffle valve. Rotary pump is placed away from the chamber via the roughing valve. The diffusion and the rotary pumps are connected by a backing valve. There is an air inlet valve to rotary pump is closed and air is let in.

An air inlet valve is provided at the bottom of the chamber to break vacuum in the chamber. The dome of the chamber is made of stainless steel and gasket fitted to the base.

Vacuum Chamber

The chamber gadgetry comprises of work holder ring which has a useful diameter of 8”. The work holder ring is supported by three pillars fitted to the base plate. A standard filament holder is fitted to the L.T. Live electrode and an earth electrode. The filament is normally positioned vertically below the centerof the work holder to give uniform distribution of vapours. A stainless steel wire mesh is fitted over the base plate to prevent foreign bodies falling into the baffle valve.

Vacuum Generation and Measurement

For the preparation thin films, maintaining the vacuum in the chamber becomes an essential parameter. Vacuum affects the film growth in two ways:

(a) It avoids oxidation and contamination of the film.

(b) With decrease in pressure, sublimation time also decrease.

The oil sealed rotary pump gives vacuum upto 10^{-3} torr. The diffusion pump backed by the rotary pump gives vacuum of the order of 10^{-3} to 10^{-6} torr..

To measure vacuum attained in the vacuum chamber, the total gas pressure is the quantity most often used to characterize the degree of vacuum attained in a system. For this purpose various gauges are available. There are two basic principles based on which such measuring of vacuum is done.

a) The direct measurement of pressure, i.e., force exerted per unit area.

b) The measurement of some physical property like thermal conductivity, resistance, degree of ionization of the gas as a function of gas density.

The vacuum gauges used in the present system were Thermocouple gauge/Pirani gauge and Penning gauge which work on second principle to measure the vacuum upto 10^{-3} - 10^{-6} torr respectively.

Thickness Measurement Techniques

While the various techniques commonly used for thickness measurement has been outlined below, the quartz crystal monitor has been used in the actual experiment.

a) Quartz Crystal Monitor/Digital Thickness Monitor:

The digital thickness monitor which is used by the author allows direct display of film thickness and rate of deposition during the evaporation. An oscillator quartz crystal with frequency of 6 MHz is positioned in the vacuum chamber so that vapour is deposited both on the substrate and defined area of the crystal. A second crystal (reference) having frequency of 6.4 MHz is positioned inside the monitor. The difference of 400 Hz initially is mixed with the output from a variable frequency oscillator to produce zero reading before each deposition. When deposition takes place on the crystal, a difference in the crystal frequency oscillator to produce zero reading before each deposition. When deposition takes place on the crystal, a difference in the crystal frequency is created which is amplified and fed into a circuit where it is converted to a D.C. Signal and the thickness of film is displayed on the monitor.

Source of Evaporation

Temperature of a material for evaporation may be raised by direct or indirect heating. The simplest and the most common method is to support the material in a filament or a boat which is heated electrically.

A variety of sources are used to evaporate materials depending on whether they are available in wire, foil, ingot or compacted powder form and whether they react with the material or not. Many shapes and sizes of filaments and boats of a number of materials are available to suit a wide range of evaporation materials and applications. The most commonly used sources are W, Mo, Ta and other refractory materials. The sources used in this work were molybdenum boats.

Substrate for Deposition

Various types of substrates are used for deposition of thin films. Commonly used materials are glass, mica, alumina etc. Stolzer et al. [12] have found polyimide (Kapton) foil to be a cheap substrate material that is of low thermal conductivity, chemically and thermally stable and has nearly the same thermal expansion coefficient as the $Bi_{0.5}Sb_{1.5}Te_3$ semiconductor. Gol'tsman et al. [13] have investigated the influence of mechanical stresses in films $(BiSb)_2Te_3$ prepared by thermal evaporation on to muscovite (mica) substrates. X-ray diffraction analysis showed that the films had single crystalline structure with the three-fold axis oriented normally to the substrate. The type of substrate to be used depends on the type of application. In the present work the $Bi_{1.95}Sb_{0.05}Te_{3,}$ $Bi_{1.9}Sb_{0.1}Te_{3,}$ and Bi_2Te_3 films were deposited on NaC1 crystal for optical band-gap measurements.

a) **Preparation of substrate for deposition**

Glass substrates have to be cleaned to remove grease, dirt etc. present on them the substrates used are usually optically flat slides. For cleaned. The glass substrates are then held under running water to remove the dirt, grease and the detergent solution. It is then dried with tissue paper and cleaned with cotton. The dry glass substrates are further cleaned with acetone and dried in an oven. While the glass substrate has been used for characterization and electrical study of BiSbTe3 films, freshly cleaved NaCl crystals have been used for optical study since NaC1 is transparent to infrared radiation. The NaC1 crystals have been used for optical study since NaC1 is transparent to infrared radiation. The NaC1 crystal itself was affixed to a glass plate.

CHARACTERIZATION

In order to understand the film growth phenomena, two modes can be visualized. One, in which the film thickness increases as more and more material is deposited on it and second, in which grain growth and structural transformations takes place due to post deposition treatments. Transport properties of films of almost all materials are determined by the micro-and nano-structure evolved during condensation, nucleation and growth processes of impinging ad atoms on a given surface. Hence structural characterization of the films is essential whenever any studies on them are to be carried out, irrespective of the nature of the properties. This is because of the fact that all the properties of thin film as are controlled to a large extent-more so than in the case of bulk materials-by the structure of the films. The structure in general includes their crystal structure, micro-structure, defect structure and chemical composition. These would change with the changes in the film deposition parameters and also from method to method. As the structure itself changes, it is expected that the properties of different films should also be different. Hence the structural investigation of the films whose properties are being studied is mandatory so that the data collected for the measurement of the properties are useful and reproducible.

Films of the solid solutions based on Bi_2Te_3 and Sb_2te_3 are of interest as the starting point for the production of high-efficiency thin-film thermoelectric elements, radiationdetectors, etc. Rajagopalan and Ghosh[14] reported electrical and thermoelectric properties of Sb_2Te_3 films deposited by a direct evaporation method. Patel and Patel [15] have reported optimization of growth conditions for Sb_2Te_3films. Recently, Patel and Patel [16] have reported the variation of electrical and optical properties with the thickness of Sb_2Te_3 films. Patel and Patel [17] reported that Sb_2Te_3 films grown at 423 K by flash evaporation method are found to be single-phase polycrystalline, stoichiometric and to exhibit a minimum electrical resistivity. The thermoelectric properties of single-crystal and polycrystalline $Bi_{0.5}Sb_{1.5}Te_3$ films were investigated earlier and data were obtained on the influence of the grain-boundary scattering of charge and heat carrier on the transport properties of this films. Gol'tsman and komissarchik[13], Boikov et al.[19] and Lidorenko et al.[20] have studied the transport properties of thin films of solid solutions of antimony telluride and bismuth telluride. While there are a few reports on $Bi_xSb_{2-x}Te_3$(x=0.5) thin films [18-22], there is no report found, to the best of authors' knowledge, on the thin films of $Bi_{1.95}Sb_{0.05}Te_{3,}$ $Bi_{1.9}Sb_{0.1}Te_.$

In the present case, thin films of $Bi_{1.95}Sb_{0.05}Te_{3,}$ $Bi_{1.9}Sb_{0.1}Te_{3,}$ and Bi_2Te_3 films were thermally evaporated (as discussed above). Keeping other deposition conditions constant, films of different thicknesses were prepared, all at the rate of 0.2-0.5 nm/s. All the material placed in the source boat was evaporated to avoid chances of preferential evaporation which would impair film composition. The films were then characterized by measuring the optical properties'. Dheepa et al. [23] The Bi_2Te_3 thin films grown by flash evaporation have been found to exhibit an amorphous nature. The possible optical transitions in these films are found to be direct and allowed. The optical band gap decreases with an increase in wavelength.

OPTICAL BAND GAP OF $Bi_{1.95}Sb_{0.05}Te_3$, $Bi_{1.90}Sb_{0.1}Te_3$, and Bi_2Te3 THIN FILMS

For the optical band gap study, films of different thickness were deposited on NaCl crystals and the IR absorbance spectra were obtained using F.T.I.R-4100, JASCO. The details of spectrophotometer used are given in chapter.2. The optical absorption was measured in the wave number range 400-4000 cm^{-1}. The absorption coefficient was calculated from the absorbance spectra at various incident photon energies.

The plots of $(\alpha h\nu)^2 \rightarrow h\nu$ obtained for Bi_2Te_3 films of different thicknesses are given in Fig 1-5. Similar plots for the films of other concentration were plotted and band gaps obtained (Fig. 6-15). The band gap is found to vary as the inverse square of the film thickness as shown in Figures 16,17 and 18 for $Bi_{1.9}Sb_{0.1}Te_3$, $Bi_{1.95}Sb_{0.05}Te_3$ and Bi_2Te_3 respectively. It is seen that with increasing film thickness the band gap decreases. Such thickness dependence of band gap can be explained in terms of quantum size effect [24]. In semiconductors, the quantum size appears when their film thickness is comparable with or less than the mean free path or effective de Broglie wavelength of carriers. Because of the small thickness of the films, the transverse component of quasi momentum of carriers is quantized and it assumes discrete values along the thickness dimension. The energy spectrum represents a system of the discrete levels with the separation between them given by the uncertainty principle. Due to this quantization, the bottom of the conduction band and the top of the valence band are separated by an additional amount of E_z [24]. In the thin film specimens, provided smearing of energy levels by temperature and diffuse scattering of the carriers at the film surfaces are not significant, this shift will increase the band gap and affect the optical behavior of semiconducting films.

The band gap variation with film thickness follows the relation [24];

$E_z = \frac{\hbar^2\pi^2}{2m^*}\frac{1}{t^2}$ Where m^* is the effective mass of the charge carrier, t the thickness of the film and E_z is the kinetic energy contribution due to motion normal to the film plane. Accordingly, the plots of E_g vs $1/t^2$ is found to be linear. Such variation can be explained in terms of quantum size effect. This is generally define as the dependence of certain physical properties of a solid on its characteristic geometric dimensions when these dimensions become comparable to the de Broglie wavelength charge carriers [24-28]. Because of the finite thickness of the film, the transerverse component of quasi-momentum is quantized. Therefore the electron-hole states assume quasi-discrete energy values in a thin film. As a consequence, the separation of valence and conduction bands increases by an amount ΔE given by the above the relation. The effective mass of holes calculated from the slope of the E_g versus $1/T^2$ plot (assuming electrons to be heavy) is found to be 5.01×10^{-4} $m_{0,}$ 0.704×10^{-4} m_0 and 0.1193×10^{-4} m_0 in Bi_2Te_3, $Bi_{1.95}Sb_{0.05}Te_3$ and $Bi_{1.9}Sb_{0.1}Te_3$ respectively, where m_0 is the electron rest mass. The estimates of de Broglie wavelength of the holes estimated by talking the Fermi energy to be half of the average band gap, turns out to be

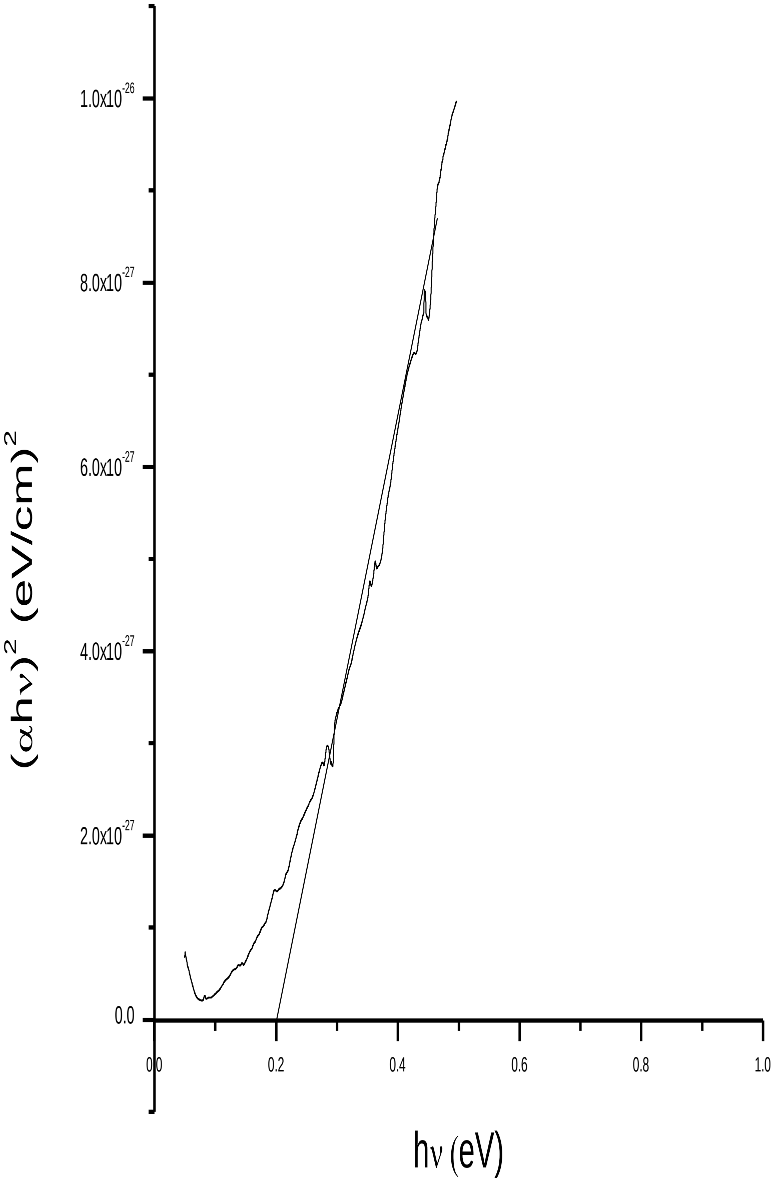

Fig.1 Plot of αhν^2→hν (356 Å, Bi_2Te_3)

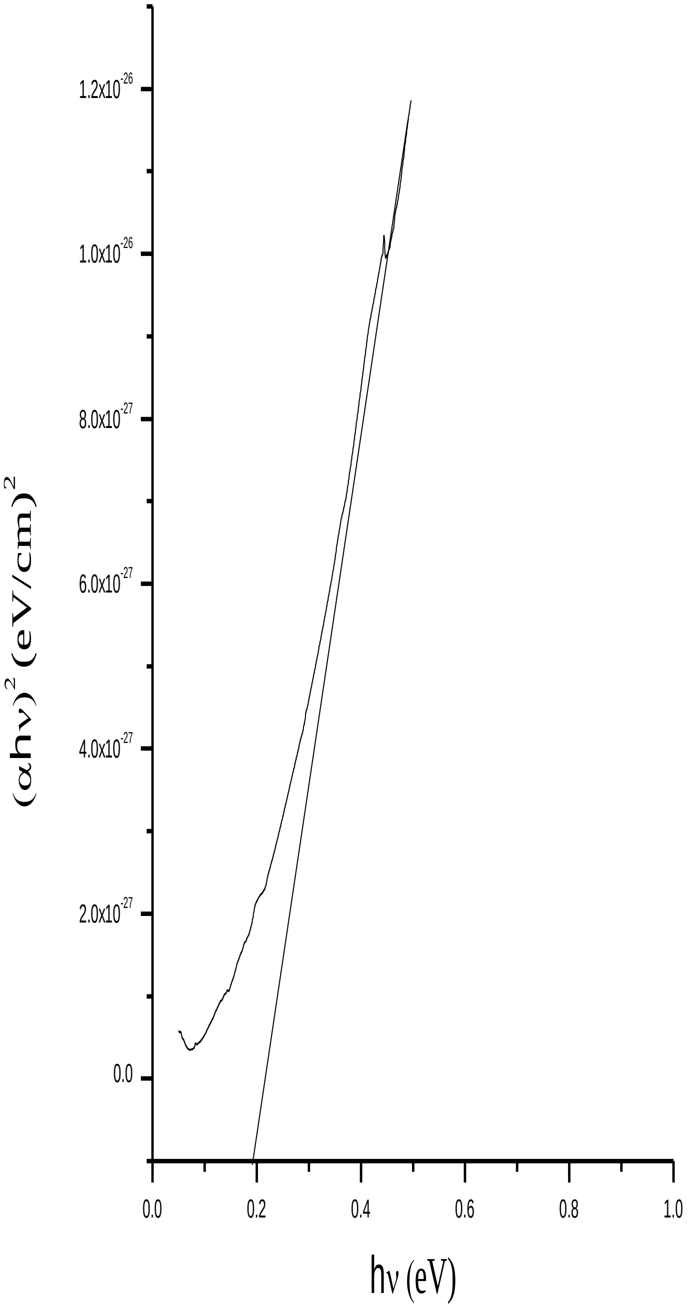

Fig.2 Plot of $\alpha h\nu^2 \rightarrow h\nu$ (564 Å, Bi_2Te_3).

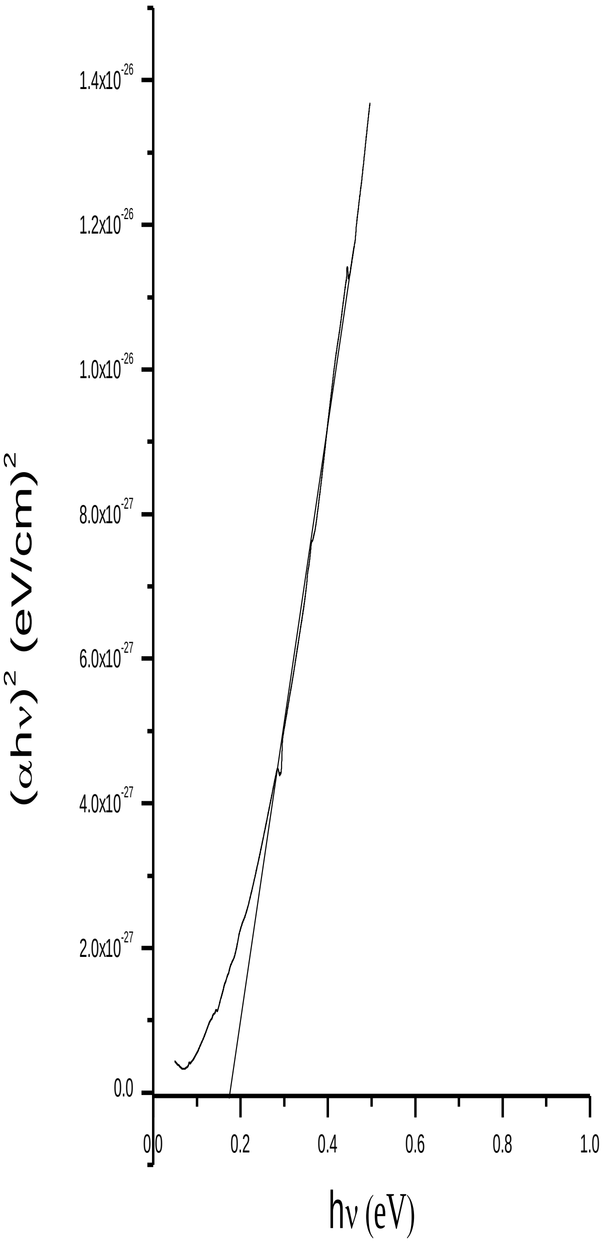

Fig.3 Plot of $\alpha h\nu^2 \rightarrow h\nu$ (731 Å, Bi_2Te_3)

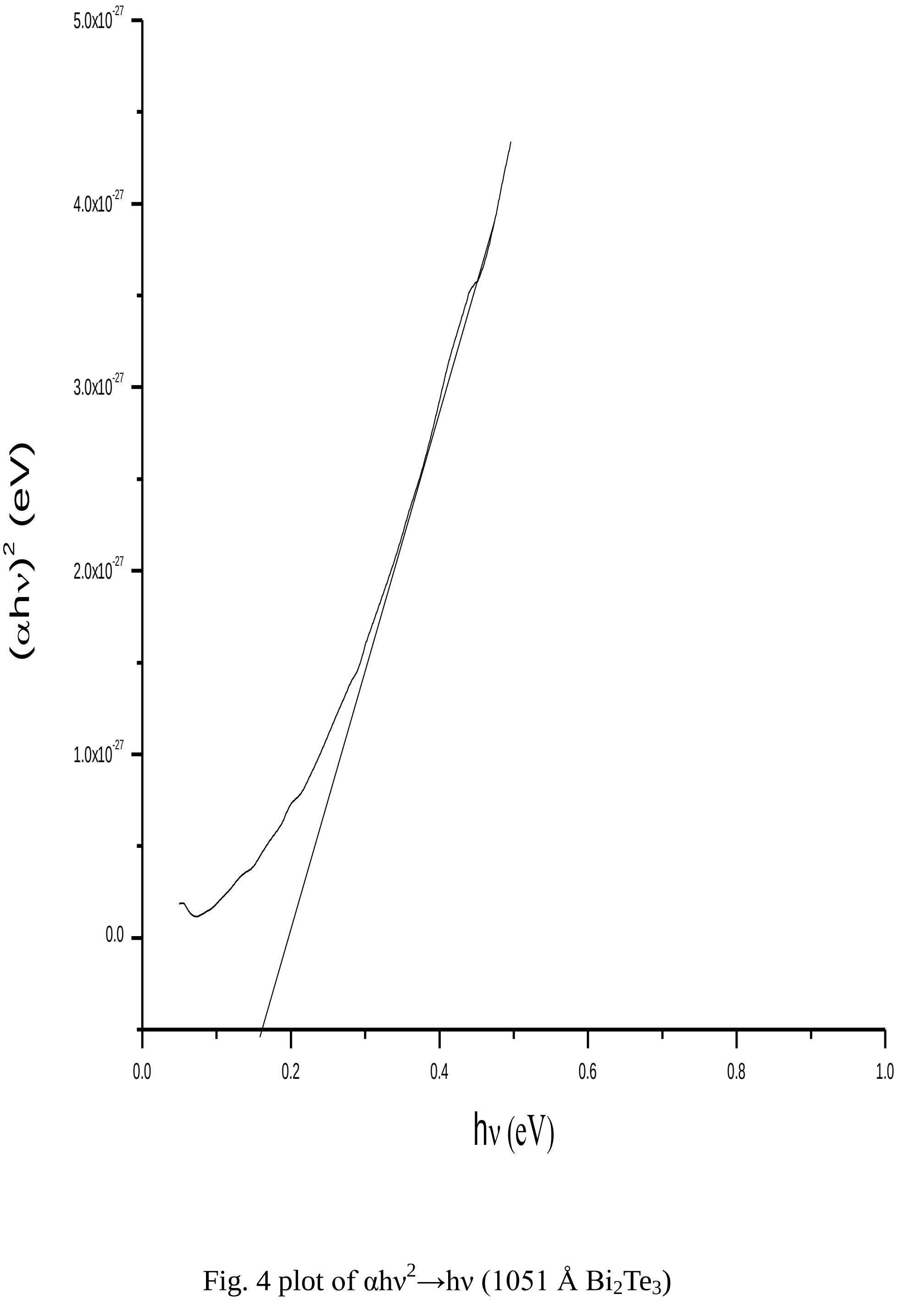

Fig. 4 plot of αhν^2→hν (1051 Å Bi_2Te_3)

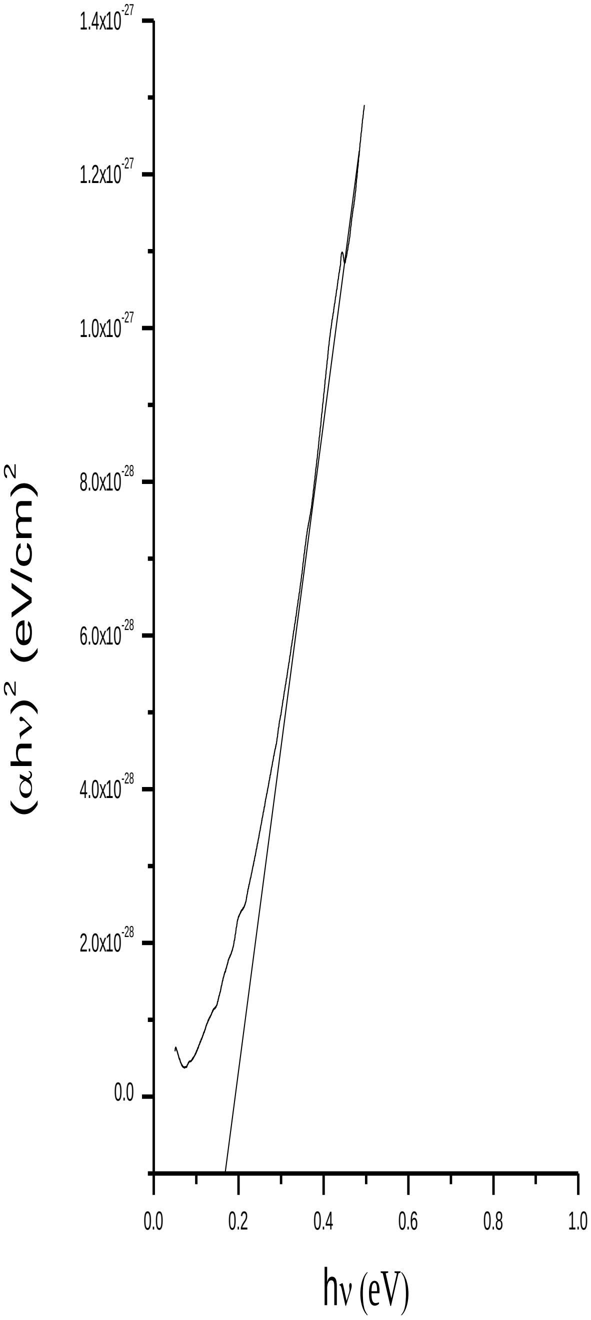

Fig.5 Plot of $\alpha h\nu^2 \rightarrow h\nu$ (1710 Å, Bi_2Te_3)

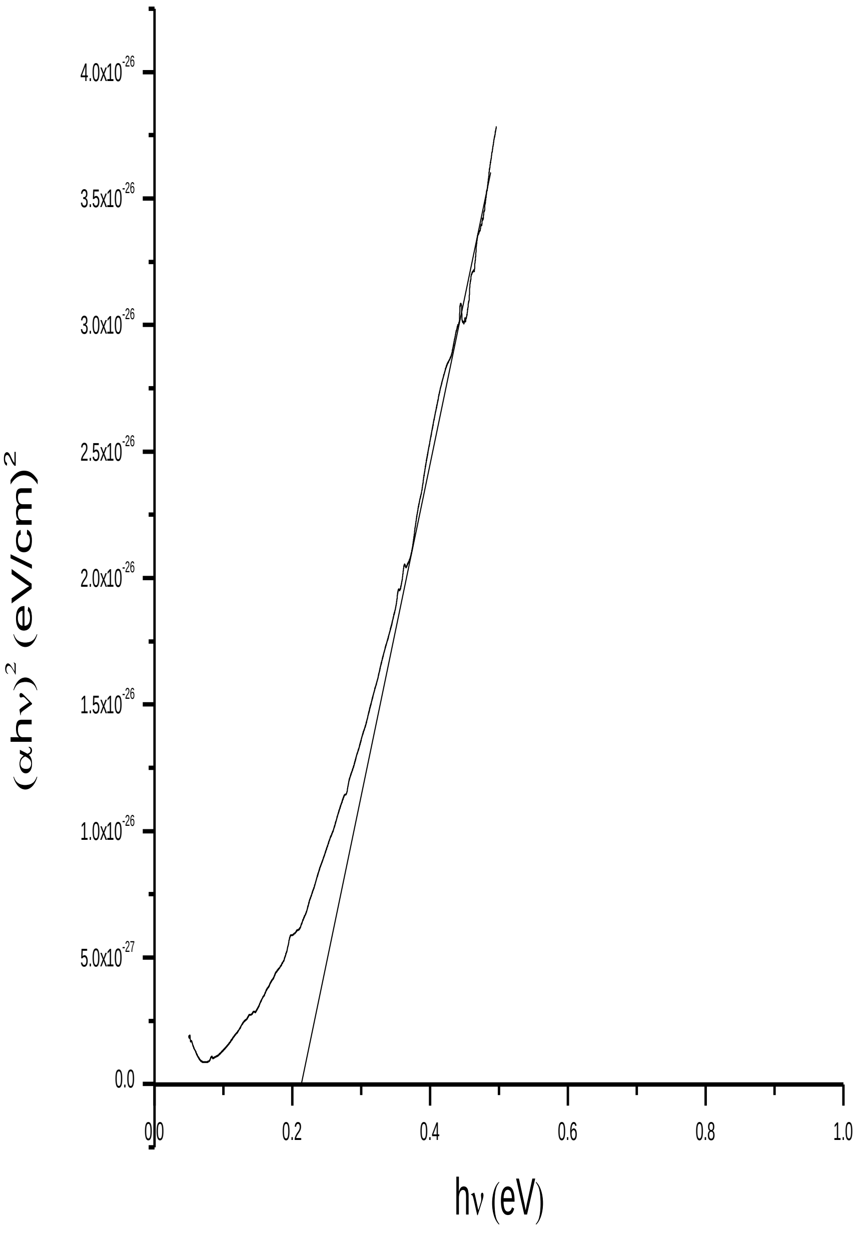

Fig.6 Plot of $\alpha h\nu^2 \rightarrow h\nu$ (358Å, $Bi_{1.95}Sb_{0.05}Te_3$)

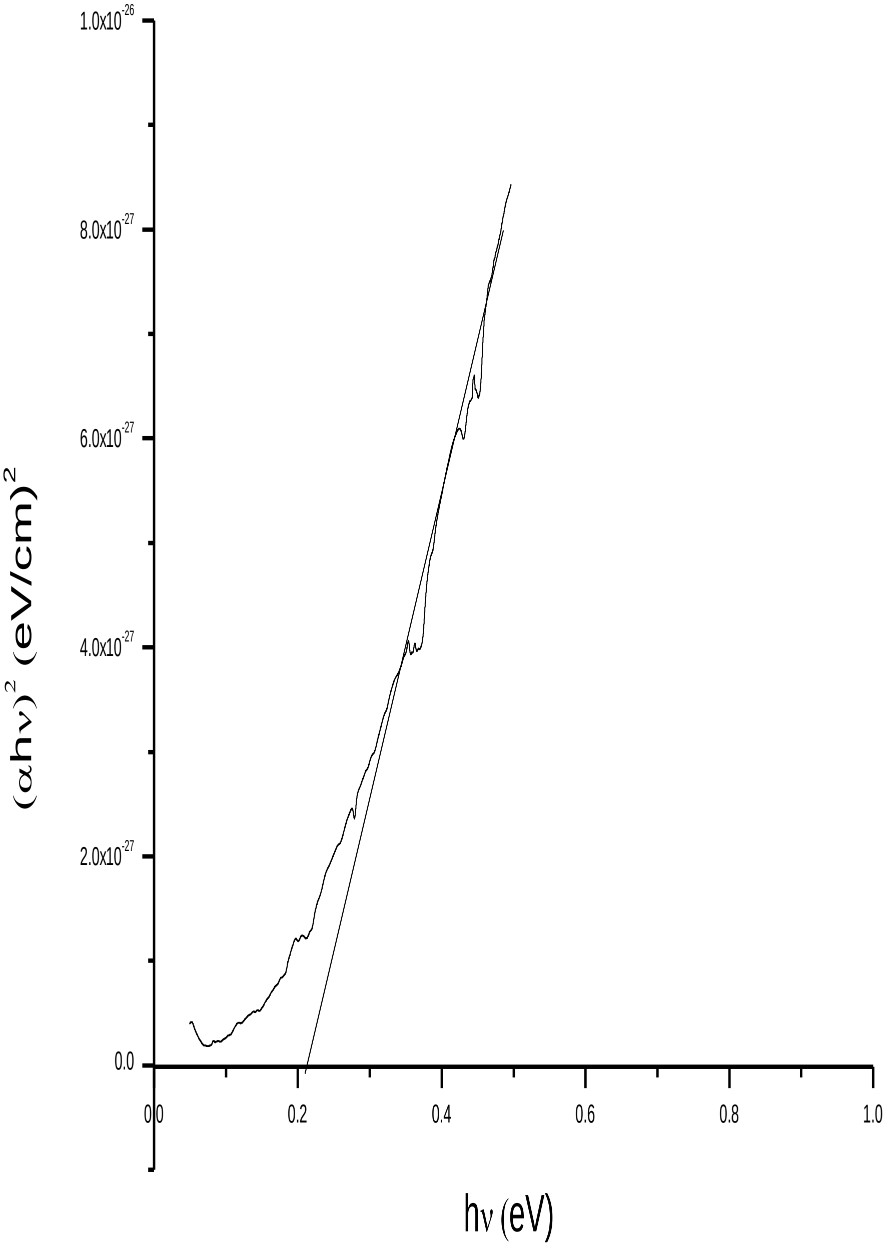

Fig.7 Plot of $\alpha h\nu^2 \rightarrow h\nu$ (562 Å, $Bi_{1.95}Sb_{0.05}Te_3$)

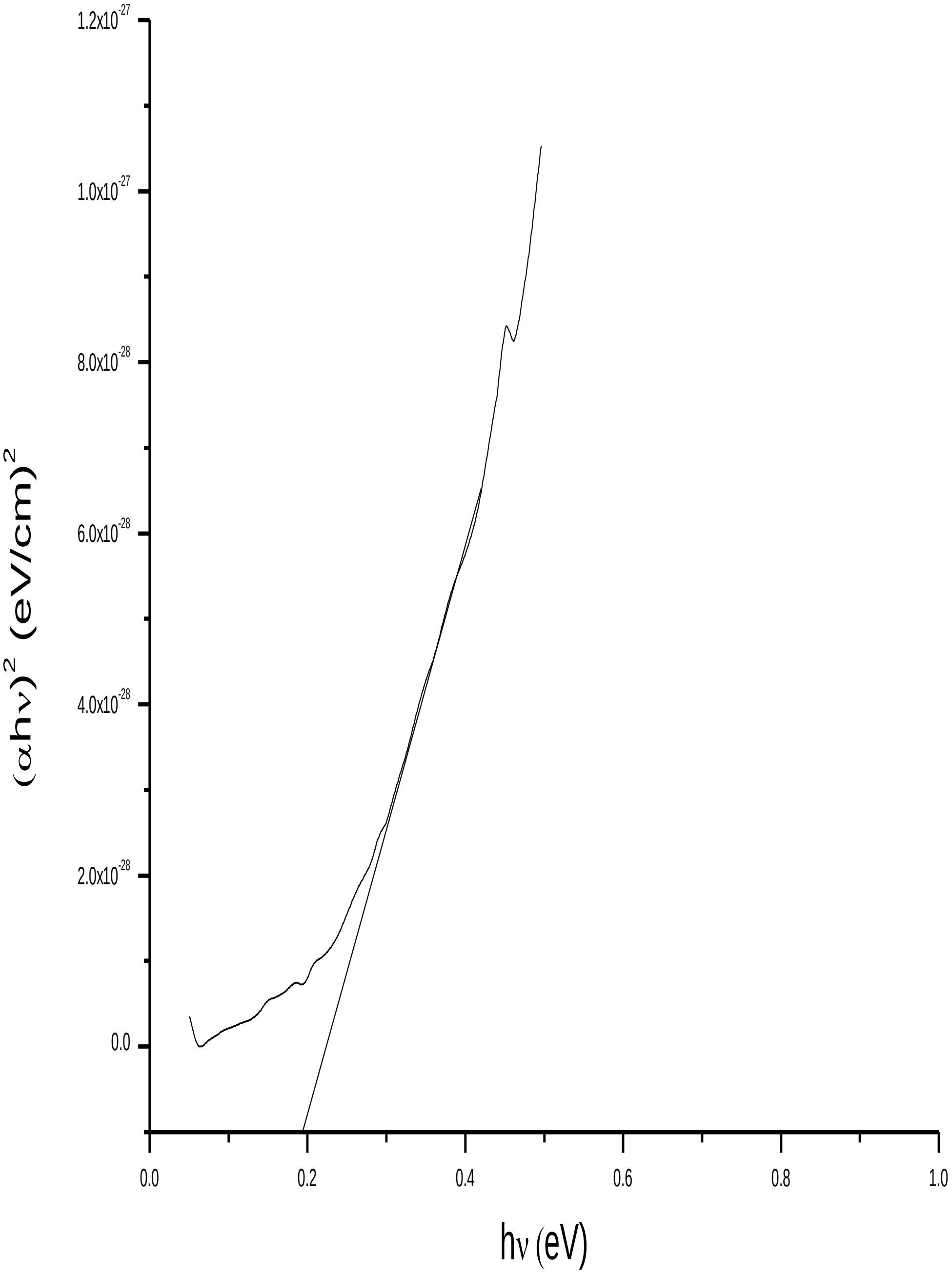

Fig.8 Plot of αhν^2→hν (809 Å, $Bi_{1.95}Sb_{0.05}Te_3$)

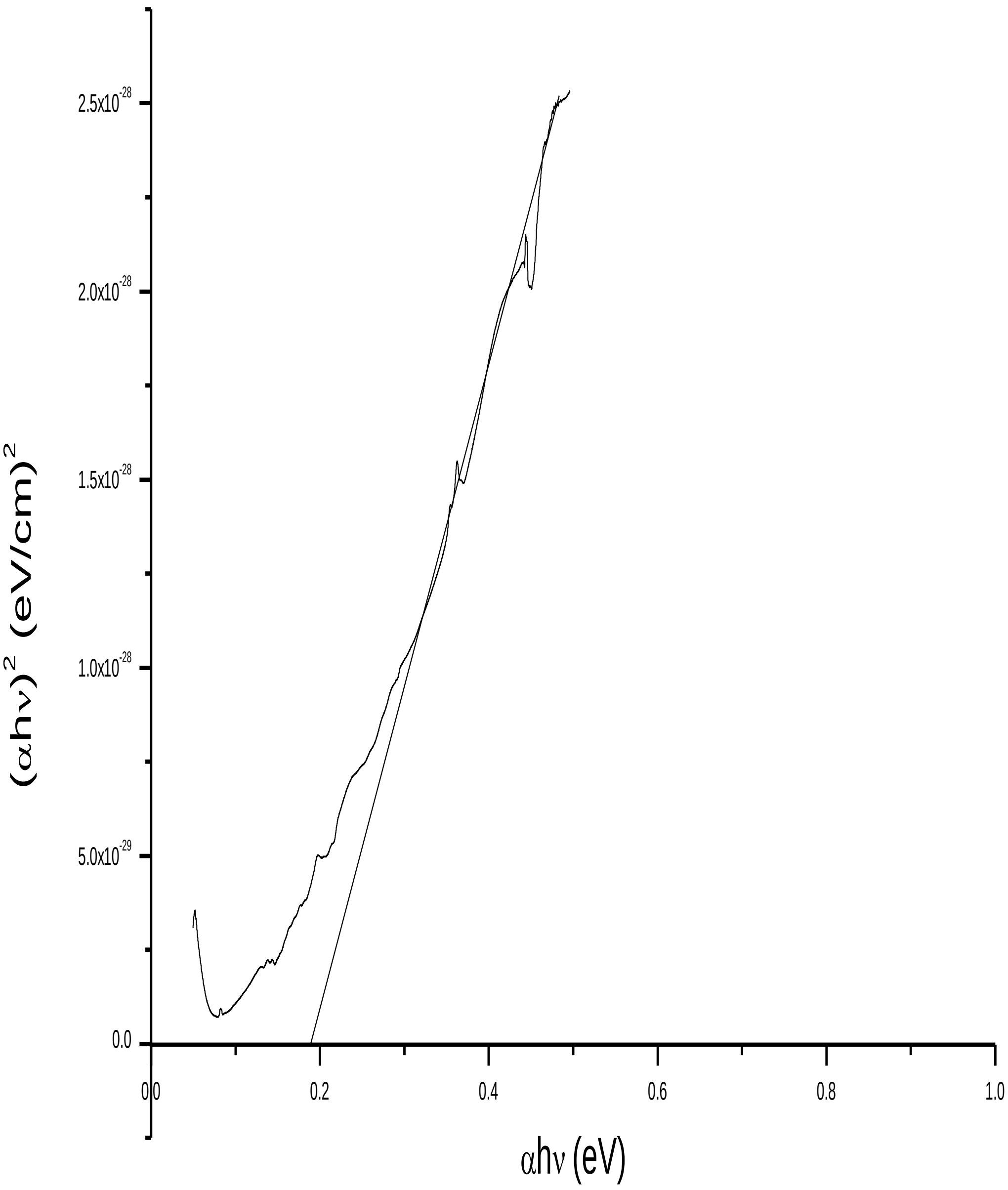

Fig.9 Plot of $\alpha h\nu^2 \rightarrow h\nu$ (1518Å, $Bi_{1.95}Sb_{0.05}Te_3$)

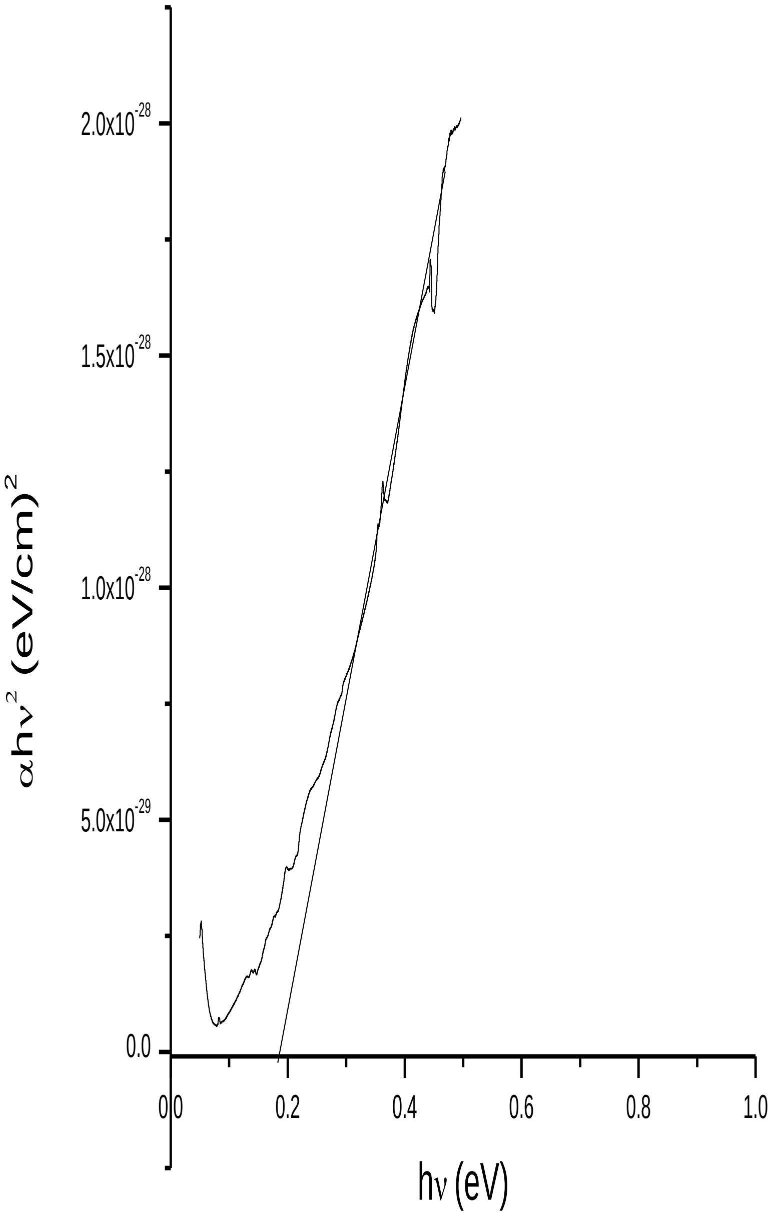

Fig.10 Plots of $\alpha h\nu^2$→hν (1704 Å, $Bi_{1.95}Sb_{0.05}Te_3$)

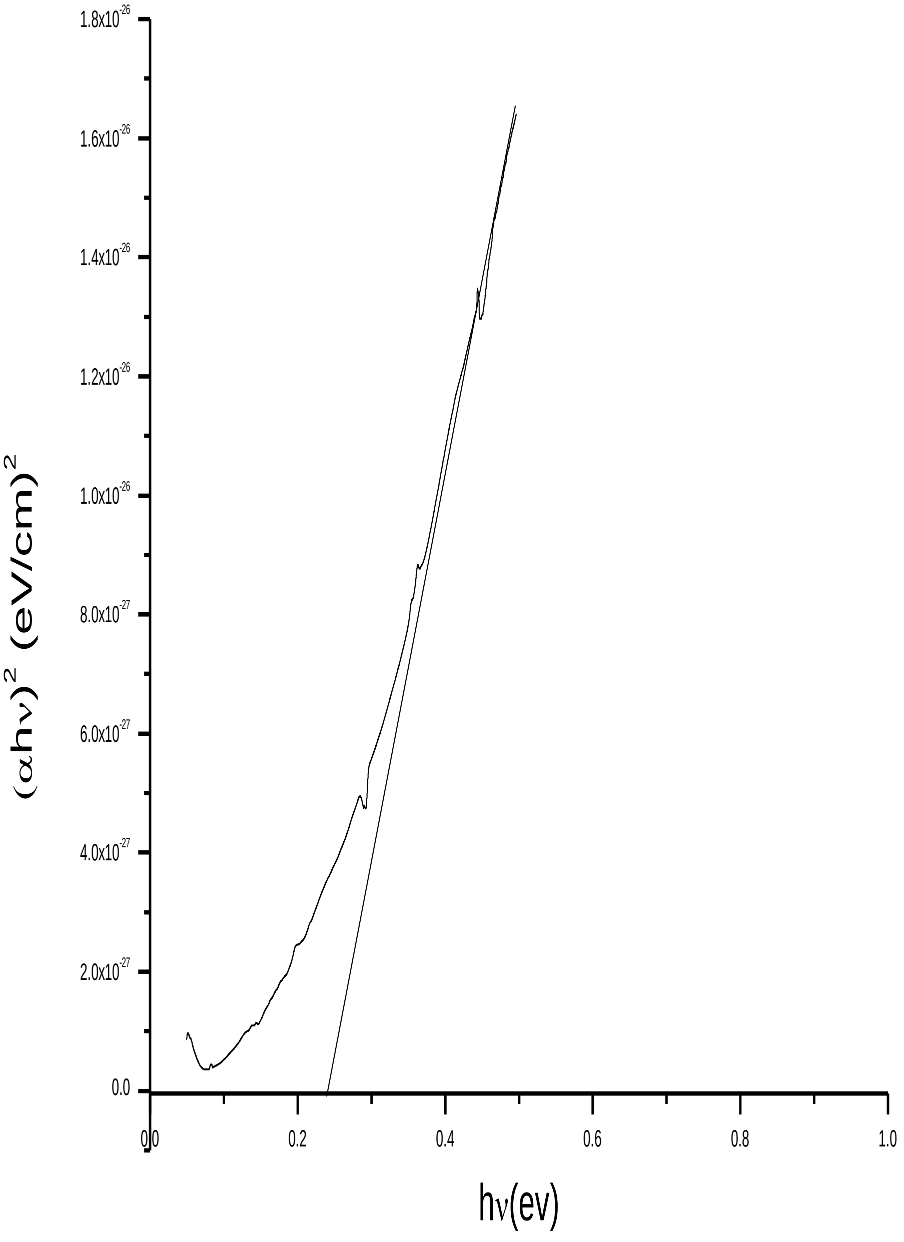

Fig.11 Plot of αhν^2→hν (326 Å, $Bi_{1.9}Sb_{0.1}Te_3$)

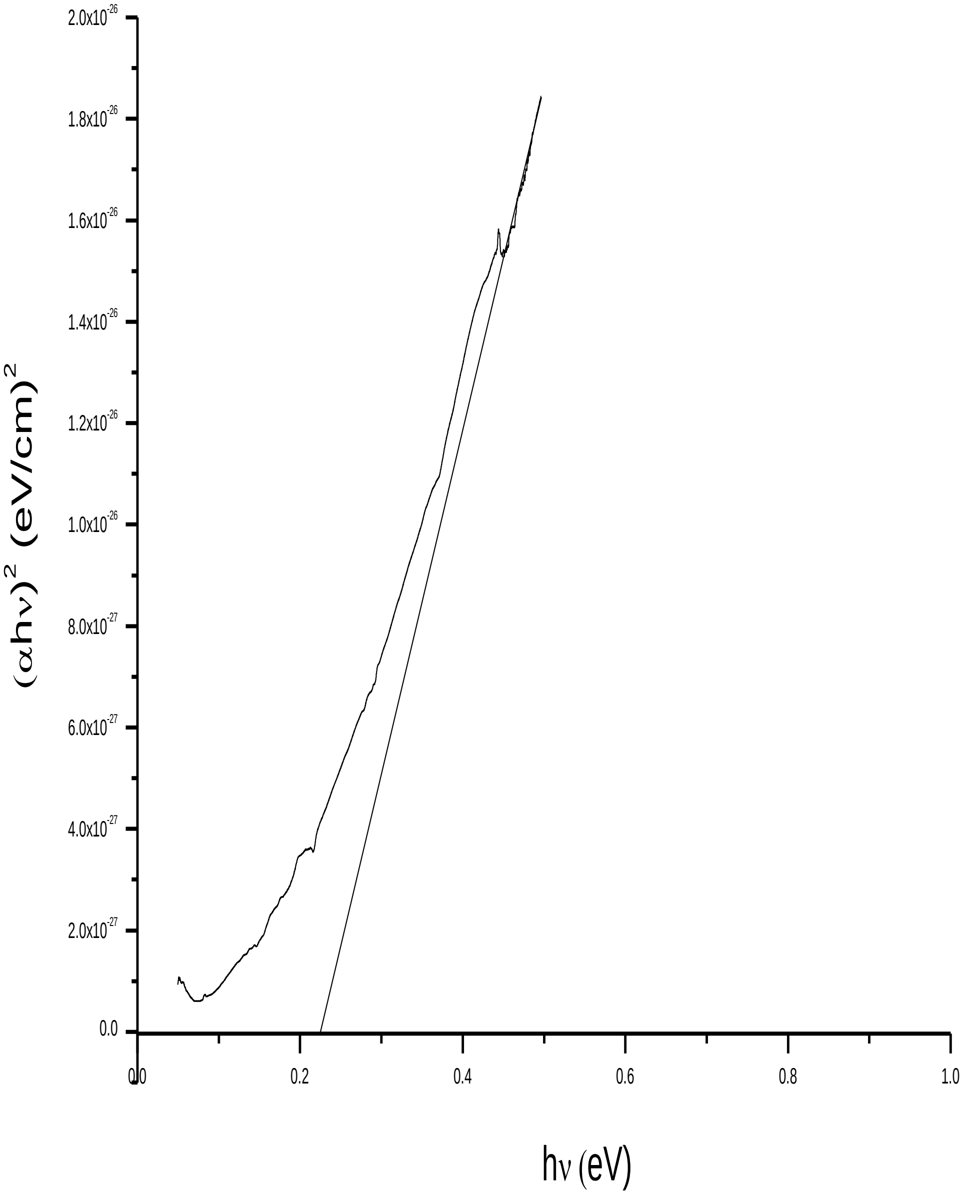

Fig.12 Plot of $\alpha h\nu^2 \rightarrow h\nu$ (405 Å, $Bi_{1.9}Sb_{0.1}Te_3$)

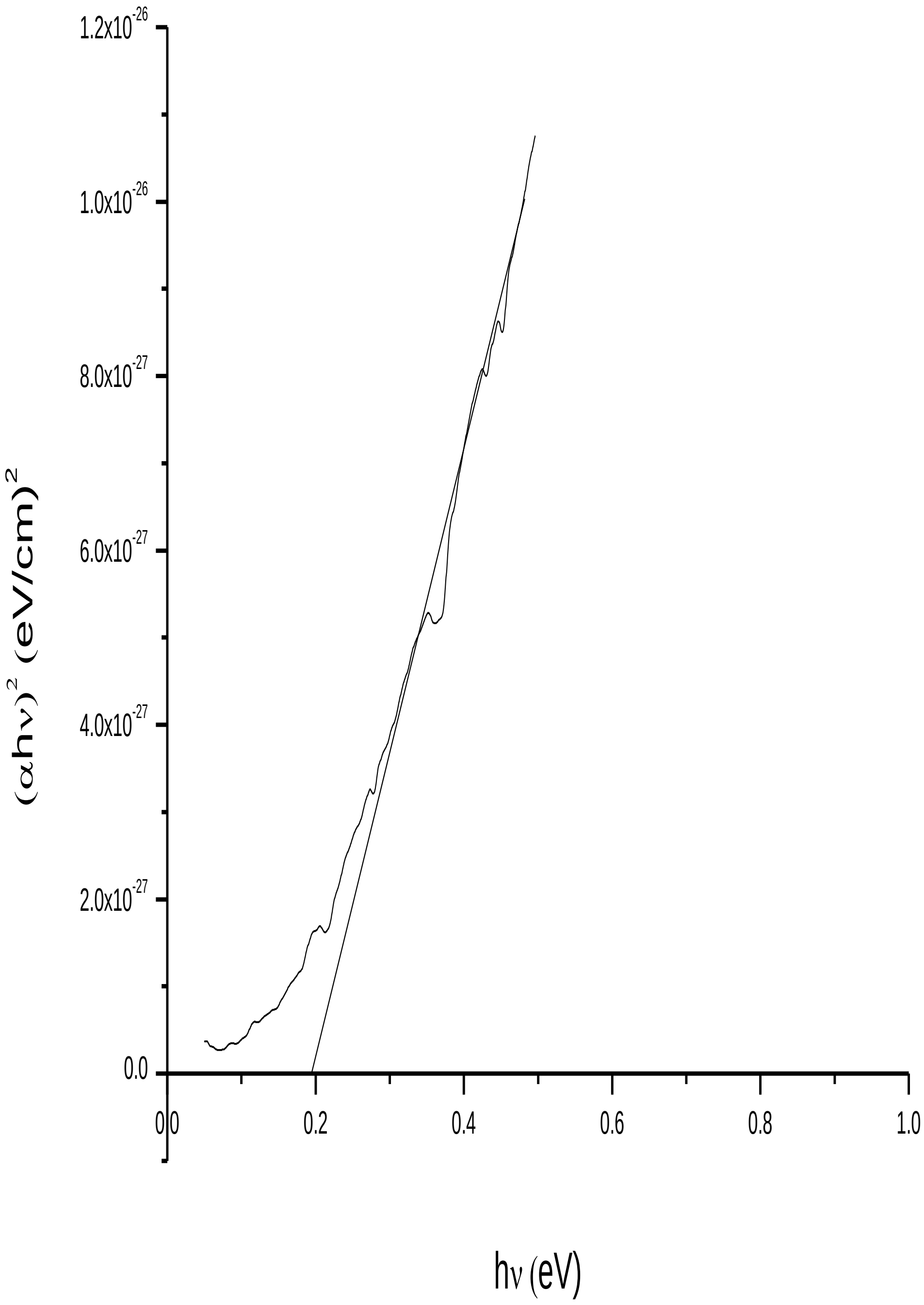

Fig.13 Plot of $\alpha h\nu^2$→hν (811 Å, $Bi_{1.9}Sb_{0.1}Te_3$)

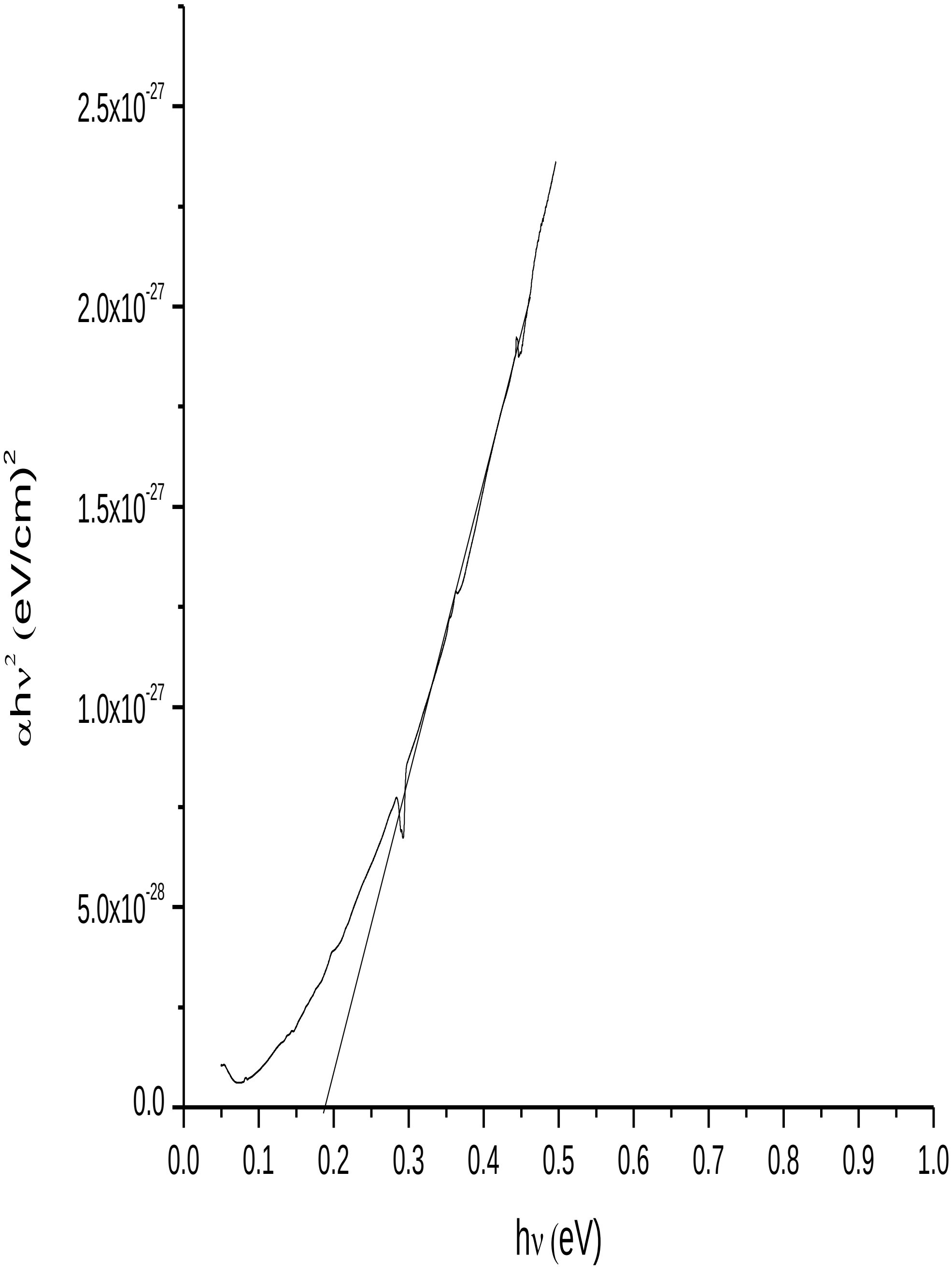

Fig.14 Plot of $\alpha h\nu^2 \rightarrow h\nu$ (1214 Å, $Bi_{1.9}Sb_{0.1}Te_3$)

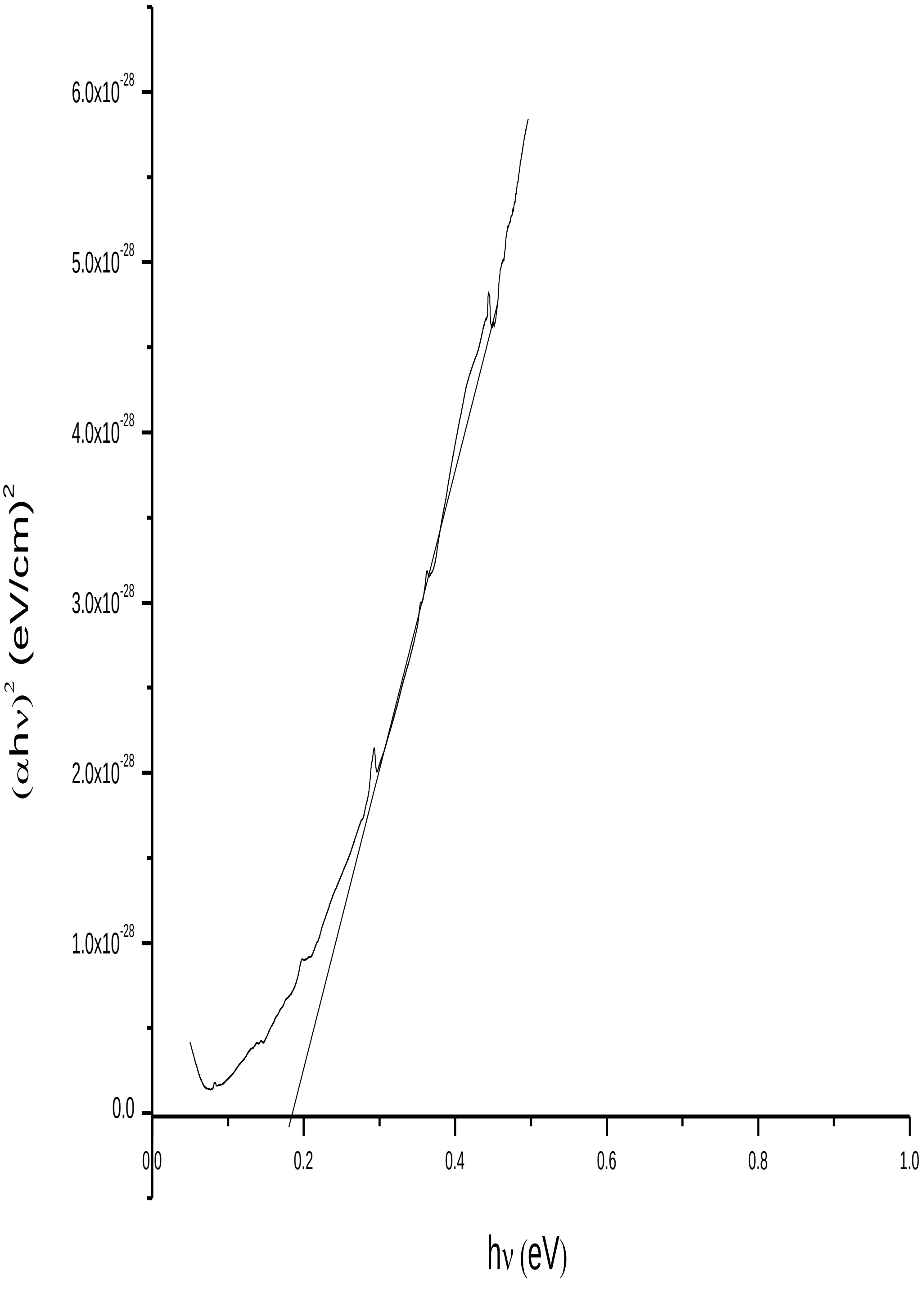

Fig.15 Plot of αhν^2→hν (1718 Å, $Bi_{1.9}Sb_{0.1}Te_3$)

about 100 nm, 113 nm, 118 nm. Thus, quantum size effect is expected to be exhibited by the films. It is also known that a fairly large number of dislocations are created during the formation of the thin films and their density increases as the thickness increases up to a particular thickness beyond which the density is practically constant. However, the dependence of dislocation density on thickness has not been quantified and in any case the dependence is complex. There are considerable lattice disturbances due to dislocations, viz., the local stress fields around a dislocation, disrupted or dangling bond with its specific charge and the space charge domain that forms immediately in semiconductors. The compression and dilation in strain patterns brought about by edge dislocations have an effect in changing the forbidden gap of the semiconductor. This is because of resulting local compression increment in the deformation potential relation. Another influence is due to dangling bond resulting in an energy level within the forbidden gap.

With the increase in film thickness, the effect of the initial granular structure on the optical properties decreases but is not eliminated completely. Therefore, thickness dependence is still observed although the general behavior of the optical parameter, i.e. band gap , follows that of the bulk, at least qualitatively. For a very thick crystal, (i.e., ideally infinite thickness) the electron energy is a multi valued continuous function of the quasimomentum. The variation of band gap with the crystallite size has been explained by the modified form of Steller's formula[29]. According to him the increased barrier height is given by

$$E = E_0 + C (X - f D)^2$$

where, C = term depending on density of charge carriers,

and dielectric constant of the material,

E_0 = original barrier height,

X = barrier width,

D = grain dimension,

f = factor depending on the charge accumulation and carrier concentration.

From literature, it is known that the grain size is approximately proportional to the thickness. Hence grain size increases due to the increase in thickness of the film[30]. So, if we replace D, the grain size in the above equation, by the film thickness t, E should be proportional to $(X - f\,t)^2$.

In the present observations we find that the band gap varies inversely as the square of the film thickness. Hence it can be concluded that the observed band gap variation with thickness cannot be attributed to the above effect. Thus in these $Bi_{1.9}Sb_{0.1}Te_3$, $Bi_{1.95}Sb_{0.05}Te_3$ and Bi_2Te_3 films the quantum size effect is dominant, rather than the effect produced by the dislocation density variation. [31].

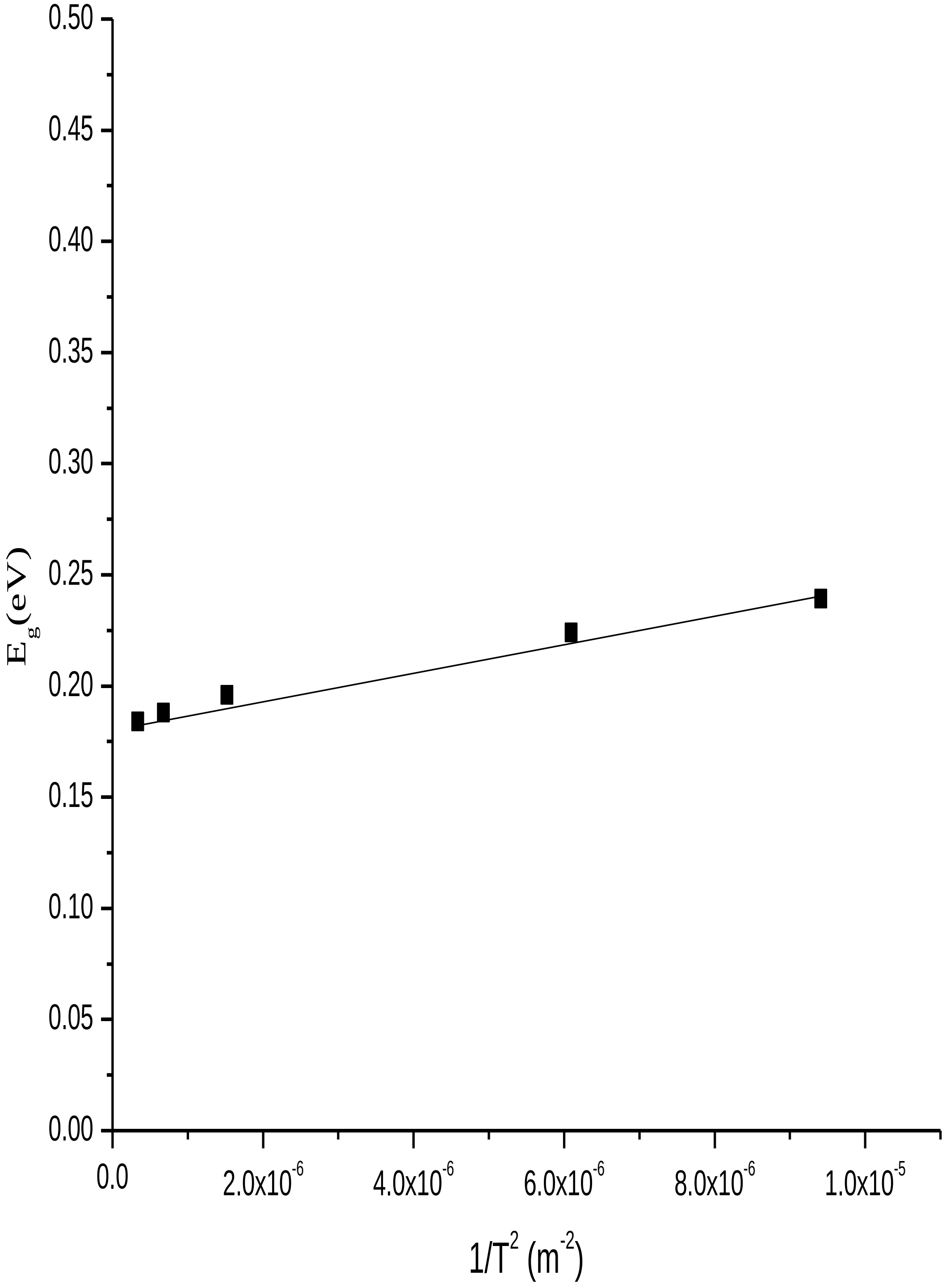

Fig.16 Plot of E_g vs $1/t^2$ ($Bi_{1.9}Sb_{0.1}Te_3$ Thin Films)

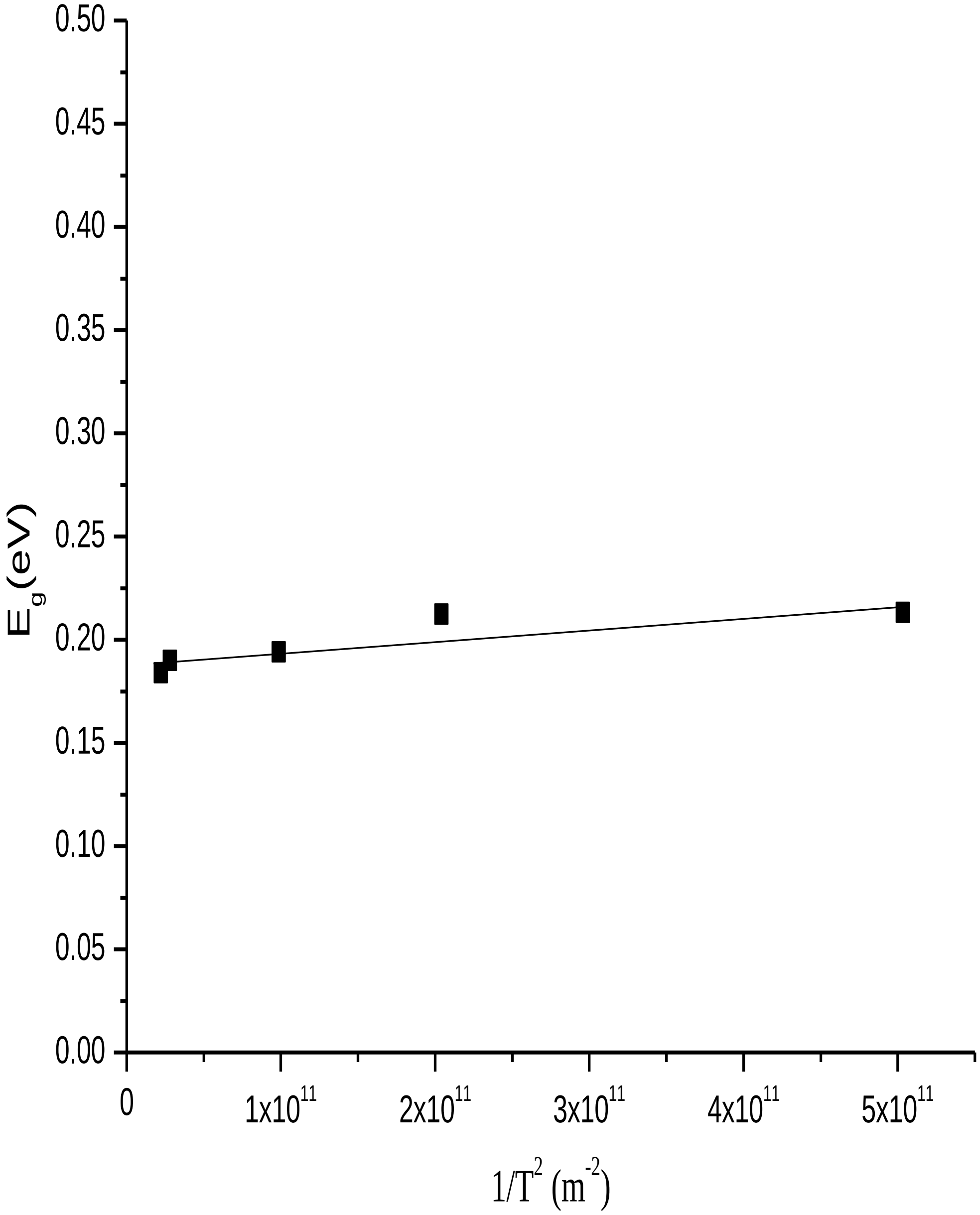

Fig.17 Plot of E_g vs $1/t^2$ ($Bi_{1.95}Sb_{0.05}Te_3$ Thin Films)

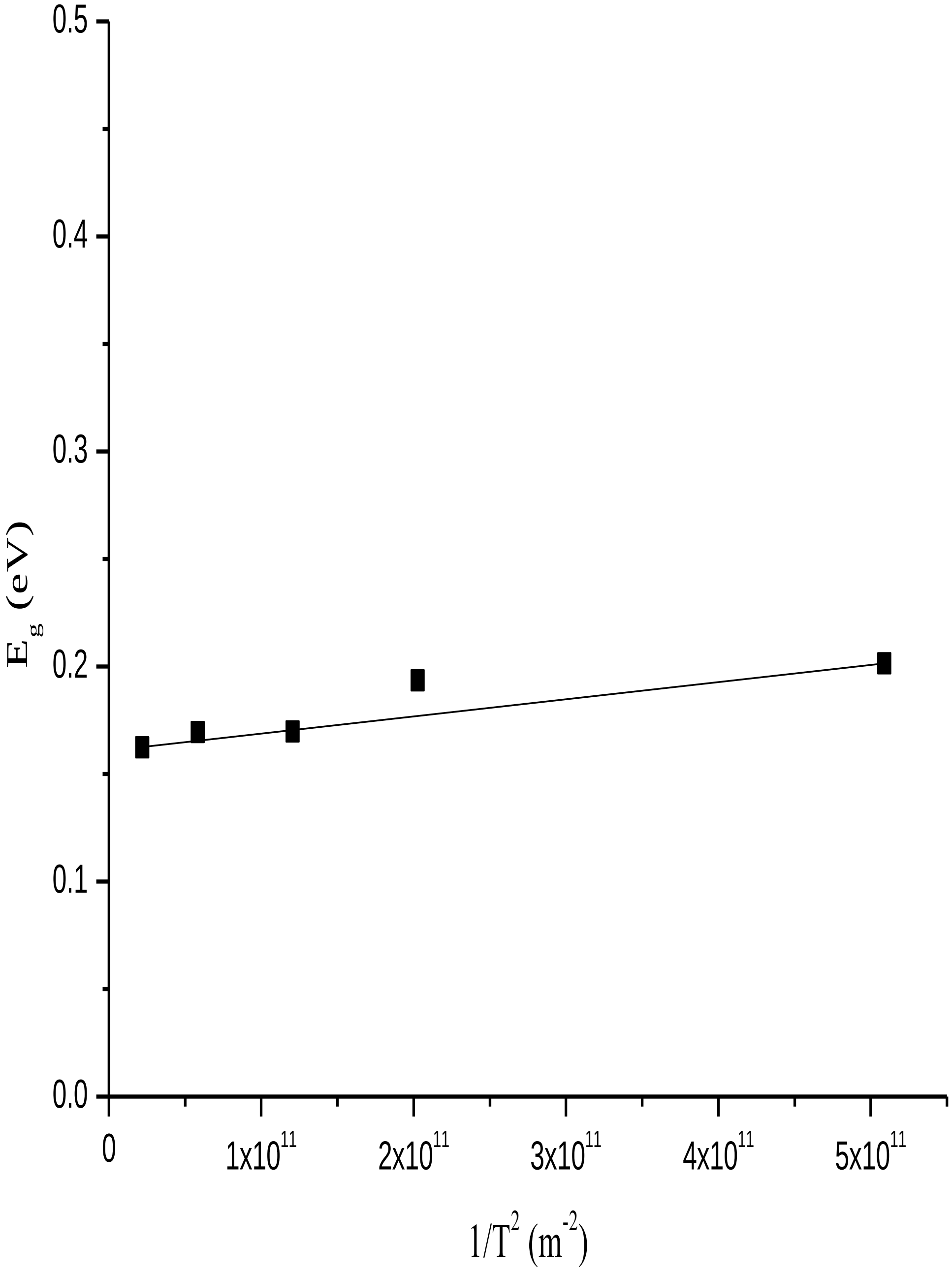

Fig.18 Plot of E_g vs $1/t^2$ (Bi_2Te_3 Thin Films)

CONCLUSIONS:

1. The band gap of Bi_2Te_3, $Bi_{1.95}Sb_{0.05}Te_3$ and $Bi_{1.9}Sb_{0.1}Te_3$ thin films are on an average 0.17 eV, 0.19 eV, 0.20 eV (direct), respectively, for film thickness around 1800 Å. At smaller thickness the band gaps are larger than the bulk values.
2. The film thickness dependence of the band gap of Bi_2Te_3, $Bi_{1.95}Sb_{0.05}Te_3$ and $Bi_{1.9}Sb_{0.1}Te_3$ indicate the optical transition to be governed by quantum size effect within the thickness range studied.

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Future Scope of work

Bismuth telluride and its alloys are unique materials. They are an excellent thermoelectric material, and they are as important to the thermoelectric industry – for cooling and energy generation applications – as silicon is important to the electronic industry. Bismuth Telluride may increase significantly the speed of microchips and be the basis for the next generation technology known as "Spintronics". Spintronics is a new, very promising (although still in its infancy) technology in which the intrinsic spin of electrons, rather than the value of a voltage like in today's electronics, is used to store and transport information to be interpreted as either a "1" or a "0". The materials most apt to use in the field of Spintronics are what experts call topological insulators, something that scientists have been searching for years and have now finally found in bismuth telluride. Topological insulators, something that scientists have been searching for years and have now finally found in bismuth telluride. Topological insulators have the property of opposing no resistance at all to an electrical flow next to their surface, thus allowing for minimal heat dissipation. Integration of efficient solid state thermoelectric micro devices with microelectronics is desirable for both local cooling and thermoelectric micro generation. Tellurium alloys (p-type Bi_2Te_3 and n-type Sb_2Te_3) are well-established room-temperature thermoelectric materials that are widely used in the thermoelectric industry due to their high Seebeck coefficient, low electrical resistivity and relatively low thermal conductivity.

Thin-film planar technology can scale down conventional bulk thermoelectric devices to the micron size range or even to nanothick film. Thin-film technology allows for an enlarged choice of the type of substrate, for the possibility of patterning the devices to micro or sub-micro dimensions and for easy integration with standard Si technology.

Application of radiation in semiconductor technology is of great importance in achieving some desired improvement in crystal properties. Ion beam treatment provides a unique way to modify the chemical, structural, optical, mechanical and electrical properties of crystal by causing irreversible changes in their macromolecular structure. It can be used to change, in a controlled way, the physical properties of thin films or to modify the near-surface characteristics of a bulk crystal. The ion beam irradiation affects the crystal structure by cross-linking as well as by degradation. So ion beam treatment can be used for these crystals to modify their properties.

Further, photoconductivity and electrical properties of thin film, chemical etching, , creep and quench micro hardness of crystal can be studied.