CHAPTER-III

CHAPTER III

STUDIES ON STRUCTURAL, ELECTRICAL, AND OPTICAL PROPERTIES OF Sb_2S_3 THIN FILMS

3.1 Introduction 38

3.2 Theoretical Considerations 38

3.2.1 Techniques of thin film deposition : Inbrief 38

3.2.2 Mechanism of Sb_2S_3 film formation 46

3.3 Experimental Details 48

3.3.1 Deposition of Sb_2S_3 thin films 48

3.3.2 Structural properties 49

3.3.3 Electrical properties 49

3.3.4 Optical properties 50

3.4 Discussion of Results 50

3.4.1 Structural studies 52

3.4.2 Electrical studies 55

3.4.3 Optical studies 59

3.5 Conclusions 62

3.1 Introduction

The experimental details necessary for the deposition and characterisation of antimony trisulphide thin films are presented in chapter II. As we are intending to prepare antimony trisulphide thin films with properties suitable for photoelectrochemical conversion, it is essential to characterise the Sb_2S_3 thin films (photoelectrode) for their electrical, optical, and structural properties. Sections 2.4 and 3.3 respectively embodies the techniques of thin film characterisation and experimental details involved while studying the above properties.

The survey of various thin film deposition processes and mechanism of Sb_2S_3 film formation are outlined in section 3.2. The experimental observations on various film properties are discussed in section 3.4.

3.2 Theoretical Considerations

3.2.1 Techniques of thin film depositions : Inbrief

The modern day technology requires various types of thin film materials for a variety of applications |40|. The thin films can be single or multicomponent, alloy/compound or multilayered, coatings on substrates of different shapes and sizes |41-43|. The different properties of the thin films which are needed, can be depending on the applications, high optical reflection/transmission, hardness, wear resistances, single or polycrystal nature etc. Such a versatility in thin films can be brought about by the techniques of thin film deposition |42-45|. The structure of thin films is complex (in view of their

applications) which demand taylor-made properties and therefore, sophisticated characterisation techniques have emerged out for better understanding of the multifarious properties of thin films. Depending on the property of interest, a host of characterisation techniques are available for giving some times similar and more often additional and complementary informations. No one technique is sufficient to characterise a thin film completely even in any one domain such as crystal structure, chemical, and physical nature etc. The properties relevant for thin film studies and corresponding characterisation methods are so many that it is impossible to cover all the aspects in any one of the reviews. Further thin film properties are extremely sensitive to a method of formation and it is quiet obvious that no one technique can deposit the film covering all the beneficial aspects and selective properties of the thin films.

The basic steps involved in a thin film formation process are :

1] Creation of material(s) to be deposited in an atomic, molecular or particulate forms prior to the deposition.

2] Transport of material(s) thus, created to the substrate in the form of a vapour stream or solid or spray etc.

3] Deposition of the material(s) on the substrate and film growth by a nucleation and growth process.

All the deposition techniques can be distinguished by the way the three basic steps above are effected. One can in principle, get the films of desired properties by properly modifying these three steps.

Thin film depostion techniques have been broadly classified as : a] Physical Vapour Depositions (PVD) b] Chemical Vapour Depositions (CVD) c] Electroless or Solution Growth Depositions d] Electrochemical Depositions (ECD).

a] Physical vapour depositions (PVD)

The physical vapour deposition techniques are those in which the material to be deposited is made availabel in an atomic, molecular or particulate form before being put for deposition. The PVD's can further be subdivided into:

i] Termal Evaporation (TE) ii] Electon Beam Evaporation iii] Molecular Beam Epitaxy (MBE), iv] Activated Reactive Evaporation (ARE) and v] Ion Plating.

The first three techniques are different in the way the vapour beam is created (step 1). In ARE, step 2 is modified in that the vapour beam is transported through a reactive plasma. In ion plating, conditions at the substrates (step-3) are modified by an ion beam. The major advantage of using PVD techniques is that all the three depostion steps (steps 1,2,3) can be independently controlled. However this spells out a warning that the deposition parameters should be carefully monitored in order to achieve reproducible films. The details of all the PVD techniques is beyond the scope of this dissertation.

b] Chemical deposition techniques

Chemical deposition techniques are the most powerful tools for the growth of thin films owing to their versatility for depositing a very large number of elements and compounds at relatively low temperature |46,47|.

BARR. BALASAHEB KHARDEKAR LIBRARY
SHIVAJI UNIVERSITY KOLHAPUR

These films can be deposited with required stoichiometry in both vitreous and crystalline layers with high degree of perfection and purity. Large or small and even or uneven surfaces of all types can be coated with relative ease and the processes are very economical and have been industrially used on large scale. The various chemical deposition processes are as follows : i] Chemical vapour deposition (CVD), ii] Spray pyrolysis, iii] Electrodeposition. (~~MBE~~) iv] Anodization, v] Screen Printing, vi] Solution growth etc.

A detailed history of each of the above technique is not possible to mention here however, a short account is presented for the sake of understanding.

i] Chemical vapour deposition (CVD)

A CVD is a process in which condensation of compound(s) from the gas phase onto a substrate where reaction occurs to produce a solid deposit. A liquid or solid compound to be deposited is made gaseous by volatilization and is caused to flow either by a pressure difference or by the carrier gas to the substrate. The chemical reaction is initiated at or near the substrate surface to produce the desired deposit on the substrate. In some processes the chemical reaction may be activated through an external agency such as heat, R.F.field, light, X-rays, electric field or glow discharge, electron bombardment etc. The morphology microstructure, and adhesion of the deposit is dependent on the nature of the reaction and the activation process. The possible reactions involved in CVD are : thermal decomposition, hydrogen reduction, nitridation, carbidization or

12255
A
SHIVAJI UNIVERSITY LIBRARY

oxidation, disproportionation, chemical transport and combined reactions.

The deposition may be either heterogeneous or homogeneous. The homogeneous deposition produces powdery or flaky deposits. The feasibility of CVD process can be predicted by studying the thermodynamics of the reactions. The reaction kinetics and mechanism of film formation are so different in individual processes, that a generalised account is not possible. However, some of the important features common to all these methods are 1] CVD set-ups are simple and fast recycle times are possible, 2] high deposition rates are achieved, 3] deposition of the compounds and multicomponent alloys and control of their stoichiometry is possible, 4] epitaxial layer of high perfection and low impurity content can be grown, 5] objects of complex shapes and geometries can be coated, and 6] in-situ chemical vapour etching of the substarates prior to deposition is possible. The factors which are uncommon and affect the deposition, uniformity, composition, and properties of film are :

1] thermodynamics and reaction kinetics are very complex and are poorly understood.

2] the working temperatures are higher compared to PVD processes.

3] highly toxic sometimes explosive and corrosive gases and volatile products are involved in the reactions. These may attack the substrate deposit and the chamber walls.

4] high temperature lead to diffusion, alloying or to a limited choice of the substrate materials.

5] uniformity of the deposit and masking of the substrates is

usually difficult.

ii] Spray pyrolysis

This is essentially a thermally stimulated reaction between clusters or liquid/vapour atoms of different spraying solution of the desired compound onto a substrate maintained at elevated temperatures. The sprayed droplets on reaching the hot substrate undergo pyrolytic decomposition and form a single crystal or clusters of a crystallite of the product. The other volatile byproducts and excess solvents escape in the vapour phase. The thermal energy for decomposition, subsequent recombination of the species, sintering, and recrystallisation of crystallite are provided by hot substrates.

The chemicals used for this method should be such that the desired thin film materials must be obtained as a result of thermally activated reaction between the different species and remainder of the chemical constituents. The carrier liquid/gas, should be volatile at the deposition temperature. Growth of the film by spray pyrolysis is determined by the nature of substrate, chemical nature, and concentration of the spray solution and spray parameters. The films are in general strong and adherent, mechanically hard, pinhole free and stable with time and temperature. The topography of the films is generally rough and dependent on spray conditions.

As the deposition temperature is usually high, the choice is limited to glass, quartz, ceramics or oxide, nitride or carbide coated substrates. Metallic substrates found unsuitable for this process. Stoichiometry for oxides is difficult to maintain with

this process.

iii] Electrodeposition

It is a process of depositing a substance upon an electrode by electrolysis, the chemical changes being brought about by the passage of a current through an electrolyte. When a metal electrode is dipped in a solution containing ions of that metal, a dynamic equilibrium $M \rightleftharpoons M^{+x} + X_e$ (metal atom) is set up. The electrode gains a certain charge on it which attracts oppositely charged ions and molecules, holding them at the electrode/electrolyte interface. A double layer consisting of an inner layer of water molecules and outer layer of the charge opposite to that on the electrode is formed. During deposition ions reach the electrode surface, stabilise on it, release their ligands, release their charges, and undergo electrochemical reaction. The rapid depletion of the depositing ions from the double layer is compensated by a continuous supply of fresh ions from the bulk of the electrolyte. The transport of ions to depletion region occur due to the diffusion, owing to concentration gradient and migration owing to the applied electric field and convection currents. The factors influencing electrodeposition process are : 1] pH of the electrolyte, 2] current density, 3] temperature of the bath, 4] bath composition, 5] electrode shape and 6] agitation.

iv] Anodization

It is an electrolytic process wherein the metal is made the anode in a suitable electrolyte. When an electric current is passed, the surface of the metal is converted into its oxide

having decorative, protective or other properties. The cathode is metal or graphite where H_2 evolves. The pH of the electrolyte plays an important part in obtaining the coeherent films. Thickness of the oxide layer depends on the metal, voltage applied, temperature of the bath, and time of deposition.

v] Screen printing

Screen printing is essentially a thick film process in which pastes containing the desired material are screen printed by a conventional method onto a suitable substrate to define conductor, resistor or a device pattern. Subsequently, the substrate is kept under appropriate conditions of time and temperature to yield rugged components bonded to the substrate. The substrates which have smooth surface, capability of withstanding for higher temperature, mechanical strength, high thermal conductivity and good electrical properties and are compatible with film material pastes are used (alumina, beryllia, magnesia, thoria and zirconia). The paste to be used normally consists of : 1] a metallic/resistive/dielectric/ semiconducting component in finely divided powder form, 2] bonding agent, 3] an organic suspension medium and 4] an organic diluent. Semiconductors like CdTe, CdS, CdSe etc can be deposited by this technique.

vi] Solution growth

Films can be grown on either metallic or nonmetallic substrates by dipping them in appropriate solutions of metal salts without the application of any electric field. Deposition may occur by homogeneous chemical reactions usually by reduction

of metal ions in solution by a reducing agent. If this occurs on a catalytic surface, it is called an electroless deposition. Silvering is the most widely used of this techniques. Metallic as well as compound films (sulphides, selenides) and their alloys can be deposited. For non-metallic surfaces a sensitizer has to be used. The rate of growth and degree of crystallinity depends upon the temperature of the solution. One of the chief advantages of such a method is to deposit the films on nonaccessible surfaces i.e. inside of glass tubes etc.

3.2.2 Mechanism of Sb_2S_3 film formation

A modified chemical deposition process for the deposition of thin films of II-VI and III-V compounds is relatively inexpensive, simple, and convenient technique. The thin films of antimony trisulphide have been deposited using this technique onto the glass substrates by allowing them to remain in an aqueous solution of the reactants for a pre-determined deposition time. The preparation of Sb_2S_3 thin films is carried out in an alkaline medium in the presence of complexing agent and therefore, the formation of Sb_2S_3 films is made possible on the basis of the slow release of Sb^{3+} and S^{2-} ions and their subsequent condensation on the substrate support |31,34,38,46,48|. In a chemical deposition process, the film forms slowly which provides better orientation of crystallites of antimony trisulphide with improved grain structure |31,34,38,46|. Depending on the deposition conditions such as temperature of the mixture, stirring rate, pH of the solution, solution concentration and its purity and quality of the substrates, the

film growth can take place either by ion-by-ion condensation of the material on the substrate or by adsorption of the colloidal particles from the solution on the substrate |31,34,38,46,48|. The process of precipitation of Sb_2S_3 from the solution onto a substrate depends mainly on the formation of nucleus and subsequent growth of the thin film. The concept of nucleation in a solution is that the clusters of molecules formed undergo rapid decomposition and the decomposed particles combine to grow upto a certain thickness of the film beyond which no further building up of thickness occurs |31,34,38,46|. The nucleation starts at some local inhomogenity when ionic product exceeds the solubility product. Growth of these nuclei by the addition of more and more ions from the solution results in the formation of stable nucleoid of the size greater than the critical size and further growth results in the formation of colloidal dispersion. The primary colloids adsorb and start nucleating forming thin adherent and reflecting films indicating the cluster by cluster growth of the film.

The film deposition was carried out by the reduction of antimony, complexed with triethanolamine using thioacetamide as the reducing agent. For a typical film, bath composition was 0.1 M potassium antimony tartrate, 7.4 M triethanolamine and appropriate amount of 17 M ammonia in a beaker 250 ml in capacity. The resulting mixture was raised to a 93 ± 0.5°C temperature. The substrates were kept rotating in the reaction mixture at a constant speed of 80 ± 2 rpm for 30 minutes. The series of chemical reactions proposed for the film formation are

|31,34,48| :

$$SbO^{+} + n(TEA) \longrightarrow SbO^{+}\ (TEA)_n \qquad ...(3.1)$$

$$CH_3 - \overset{\overset{S}{\|}}{C} - NH_2 \rightleftharpoons CH_3 - \overset{\overset{SH}{|}}{C} = NH \qquad ...(3.2)$$

$$CH_3 - \overset{\overset{SH}{|}}{C} = NH + OH^{-} \longrightarrow CH_3 - \overset{\overset{OH}{|}}{C} = NH + SH^{-} \qquad ...(3.3)$$

$$2SbO^{+}\ (TEA)n + 3SH^{-} \longrightarrow Sb_2S_3 + n\ TEA + OH^{-} + H_2O \qquad ...(3.4)$$

The tautomeric reactions (3.2) should proceed from left to right for the next step of reaction (3.3). It is also clear from the above chemical reactions (3.1), (3.3), and (3.4) that the growth rate is controlled by the concentrations of potassium antimony tartrate, thioacetamide, and aqueous ammonia. Therefore, the concentrations were varied to optimise the deposition conditions for the preparation of Sb_2S_3 films.

It also appears from the above equations that the rate of deposition would increase with increasing concentrations of Sb^{3+} SH^{-}, and OH^{-}. This is in agreement with the experimental results performed by us |31,34| and with that of the results of Savadogo and Mandal |48|. Ammonia added in the reaction mixture slows down the formation of Sb_2S_3 and helps to the adherence of Sb^{3+} and S^{2-} ions on the substrates. This is quiet analogous to our previous observations on Bi_2S_3 thin films prepared in the same way using this technique |38|.

3.3 Experimental Details

3.3.1 Deposition of Sb_2S_3 thin films

Details of the preparation procedure and mechanism of film formation for antimony trisulphide thin layers are given in

sections 2.3 and 3.2.2, respectively. The method involves : a reaction container, consisting of 100 ml 0.1M antimony potassium tartrate, 100 ml 0.1M thioacetamide, and solutions of triethanolamine and aqueous ammonia in appropriate amounts, is raised to a deposition temperature of 93 ± 0.5°C. The substrates (properly cleaned) were attached to a specially designed substrate holder and were kept rotating at a speed of 80 ± 2 rpm in a reaction mixture for half an hour. The samples were detached from the substrate holder and kept in a dark desiccator for further processings.

3.3.2 Structural properties

a] XRD studies

The crystal structure and hence the lattice parameters have been determined from the XRD analysis of thin film samples. The analysis was carried out using CuKα radiation in the span of diffraction angles between 10° to 80°.

b] SEM studies

The samples have been analysed by a Scanning Electron Microscopy (SEM) technique with a magnification of 11,000.

3.3.3 Electrical properties

a] Electrical conductivity

The dc electrical conductivity of the sample was measured in dark both for heating and cooling cycles in the 300K to 575K temperature range. Air drying silver paint was used as a contact material |31,32,34|. A regulated dc power supply was used to pass the current through sample. The current was noted with a HIL-2665, 4½ digit currentmeter.

b] Thermoelectric power (TEP)

Measurements on thermo e.m.f generated by a sample were carried out in the range of temperature from 300K to 450K. The sample of the size 2.5 cm x 0.5 cm on plain amorphous glass was utilised for this purpose. Silver paint was applied to the sample |31,32,34| and copper press contacts were drawn from the sample. A chromel-alumel thermocouple was used to record the temperature difference. The thermovoltage and thermal gradients were measured with the sensitive HIL-2665 and Agronic-113 microvoltmeters. The details of the measurements and necessary care those were taken are summarised in section 2.4.4.

3.3.4 Optical properties

The observations on optical absorbance of the samples were noted. Optical density was measured for various scanning wavelengths. The range of wavelengths utilised was 3500 A° to 8400 A°. The studies have also been confirmed with a spectronic -20D, Milton & Roy spectrophotometer in the 3500 A° to 9000 A° wavelength range. An optical absorption coefficient, mode of transition, and optical band gap were determined from these observations.

3.4 Discussion of Results

A relatively new method has been developed for obtaining the thin layers of antimony trisulphide on ordinary glass substrates. We believe in the newness of the process by which it has several superiorities over the other conventional methods described elsewhere |31,34,38,46|. Thin films of various chalcogenides, mixed and/or doped and multifarious thin film structures can be

obtained |31,34,38,46|. The preparation of Sb_2S_3 thin films is carried out in an alkaline medium in the presence of complexing agent and therefore, the film formation is made possible on the basis of the slow release of Sb^{3+} and S^{2-} ions and subsequent condensation on the substrate support |46,48|. It appeared from the growth mechanism that the rate of film growth would increase with increasing concentrations of Sb^{3+}, SH^-, and OH^- and therefore, chemical compositions were varied randomly to obtain good quality films and to optimise the preparation conditions. It is only the appearance and physical properties of the samples from which we have, for the present case, decided the quality of the samples. No thorough analysis and studies have been made in respect of the above parameters. The deposition time and temperature required to produce the minimum terminal thickness of the layer are also examined. The duration for the film growth so far reported is in terms of few days and several hours and it is highly difficult to control all the experimental conditions for such a long period |48|. We have succeeded in optimising the deposition period equal to 30 minutes for our experimental conditions at a optimised working temperature equal to 93 ± 0.5°C |34,49|. The films are highly uniform, crackfree, strongly adherent to the substrates, smooth, and diffusely reflecting with a terminal thickness around 0.4 to 0.5 μm. The as-deposited layers are orange-red in color and baking around 180°C results into dark grey color of the samples. For intermediate temperatures the sample color appeared to be a mixture of both orange-red and dark grey colors.

3.4.1 Structural studies

a] X-ray diffraction studies

The structure and crystallinity of the Sb_2S_3 samples were tested by XRD studies in the span of angles from 10° to 80°. The X-ray diffractograms of the as deposited and heat treated (200°C, 250°C) samples are shown in Fig.3.1. The patterns suggest that the as deposited material is amorphous (microcrystalline) and crystallinity improves after heating. The peak intensities corresponding to different planes are stronger for dark grey samples indicating that it is more crystalline and coarse than orange red variety. The `d' values for the peaks are calculated and compared with the standard `d' values from ASTM data |50|. The `d' values are in excellent agreement with the standard `d' values of the material. This confirms that the material is purely Sb_2S_3 |31,34,48,49|. The comparison of `d' values for the heat treated sample is shown in table I.

The calculation of lattice constants show orthorhombic type of lattice with, a=11.220 A°, b=11.283 A°, and C=3.837 A°. These are in consonance with the ASTM values (ASTM, a=11.229 A°, b=11.310 A°, and C=3.839 A°) and our reported results |31,34,48,49|.

(b) SEM studies.

The crystalline nature of the as deposited and heat treated (250°C) Sb_2S_3 samples was further examined by SEM micrographs. The SEM micrographs show well defined grains, and grain size improves with baking temperature. Both varieties are finely divided where as the dark-grey variety is more coarse and

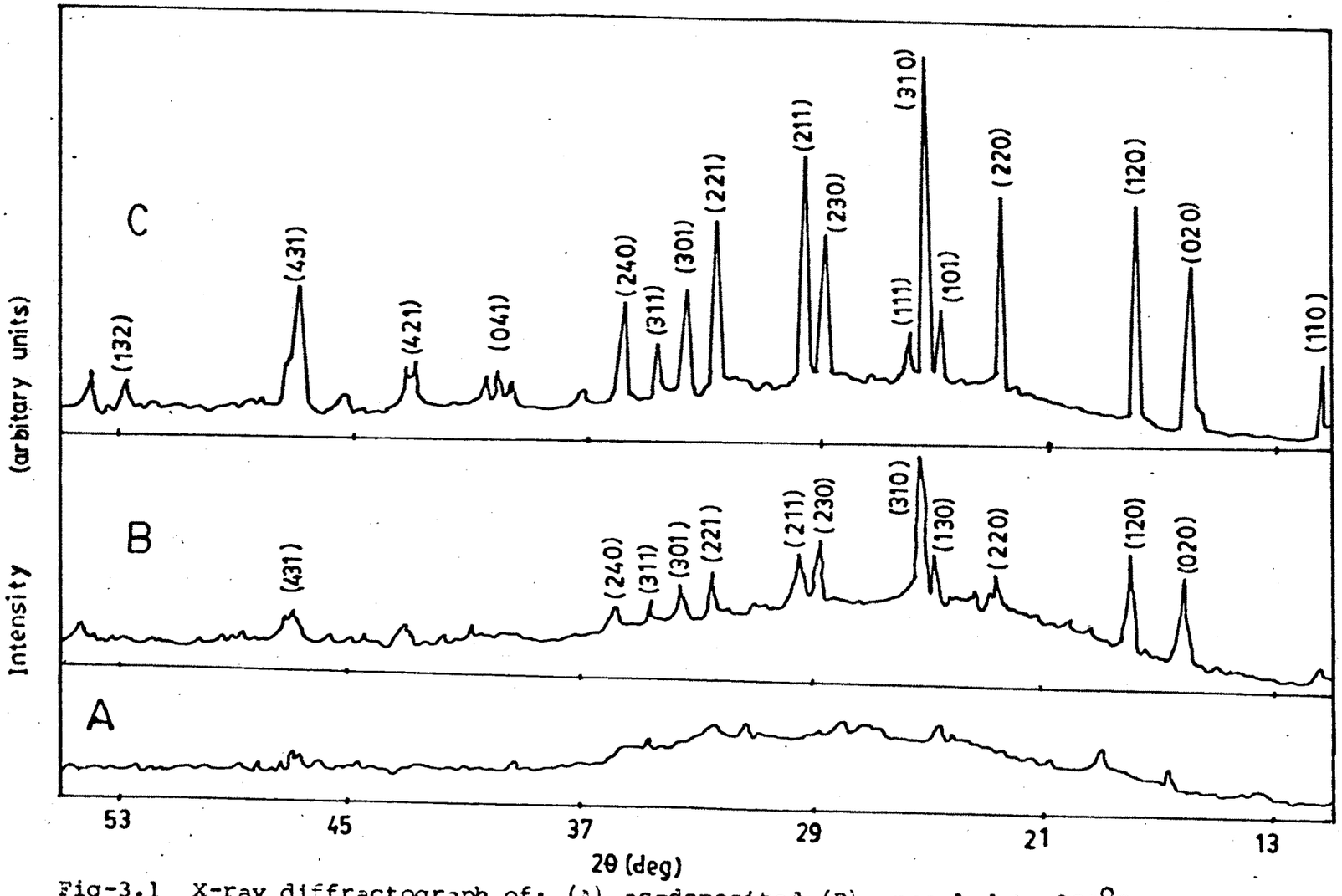


Fig-3.1 X-ray diffractograph of: (A) as-deposited (B) annealed to 200°C (C) annealed to 250°C, Sb_2S_3 films.

TABLE I

Comparison of lattice distances for the thin Sb_2S_3 samples

Sr No	d (A°) ASTM	Temperature 200°C		Temperature 250°C	
		d (A°) observed	hkl	d (A°) observed	hkl
1	7.990	-	-	7.805	110
2	5.654	5.582	020	5.574	020
3	5.052	4.996	120	4.994	120
4	3.987	3.950	220	3.956	220
5	3.632	-	---	3.607	101
6	3.573	3.595	130	-	-
7	3.556	3.530	310	3.524	310
8	3.458	-	-	3.435	111
9	3.121	3.110	230	3.104	230
10	3.053	3.025	211	3.034	211
11	2.764	2.753	221	2.751	221
12	2.680	2.663	301	2.669	301
13	2.609	2.597	311	2.597	311
14	2.525	2.513	240	2.516	240
15	2.277	-	-	2.268	041
16	2.101	-	-	2.102	421
17	1.940	1.943	431	1.936	431
18	1.691	-	-	1.697	132

crystalline than orange-red The SEM micrographs for both type of samples are shown in Fig. 3.2. The grain sizes are of the order of 0.2 to 0.5 μm however, it is larger for dark grey samples.

3.4.2 Electrical studies

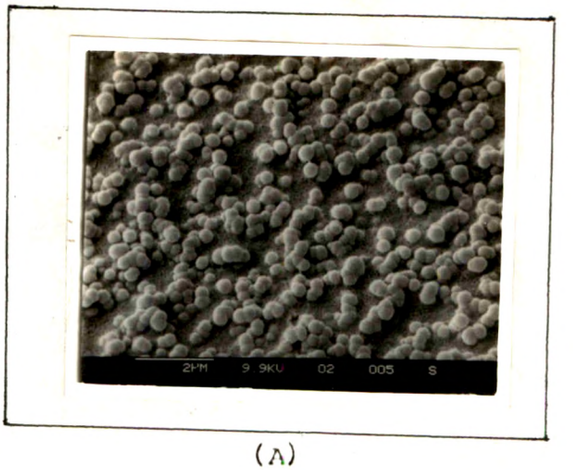
[a] Electrical conductivity

The dark resistance measurements were carried out in the temperature interval 300-575K for both heating and cooling cycles. The resistance decreases with increasing temperature indicating the semiconducting nature of the samples. It is found that the plot of logR vs 1/T is linear and gives thermal energy band gap (E_{gth}) in the intrinsic region of the semiconductor. The thermal energy gap estimated is 1.60 eV and seems to be in fair agreement or little bit lower than Alzwel et al |30|, Bhosale et al |32| and George and Radhakrishnan |23|. The conductivity was calculated from these observations and at room temperature Sb_2S_3 has an electrical conductivity of $10^{-9}\ \Omega^{-1}\ cm^{-1}$.

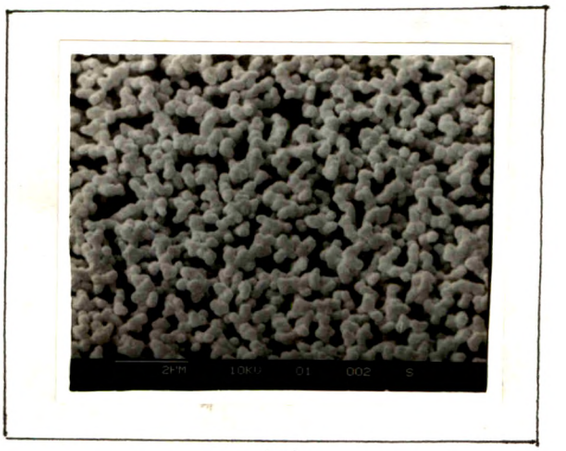
It is seen that both for heating and cooling cycles, the variation of $\log\sigma$ vs 1/T follows almost the same track which partly confirms the uniformity of the samples those are deposited using our modified chemical deposition process |31,34,49|. The temperature dependence of an electrical conductivity is shown in Fig.3.3. The thermally activated electrical conductivity is :

$$\sigma = \sigma_o \exp(-E_a/KT) \qquad \ldots (3.1)$$

Where, E_a is the activation energy and other terms have their usual significance. An activation energy of an electrical conduction has been determined from the slope of the log σ vs 1/T variation and is found to be 0.80 eV. The magnitude of E_a is



(A)



(B)

Fig. 3.2 SEM micrographs of:

A) as-deposited

B) annealed to 250°C, Sb_2S_3 films.

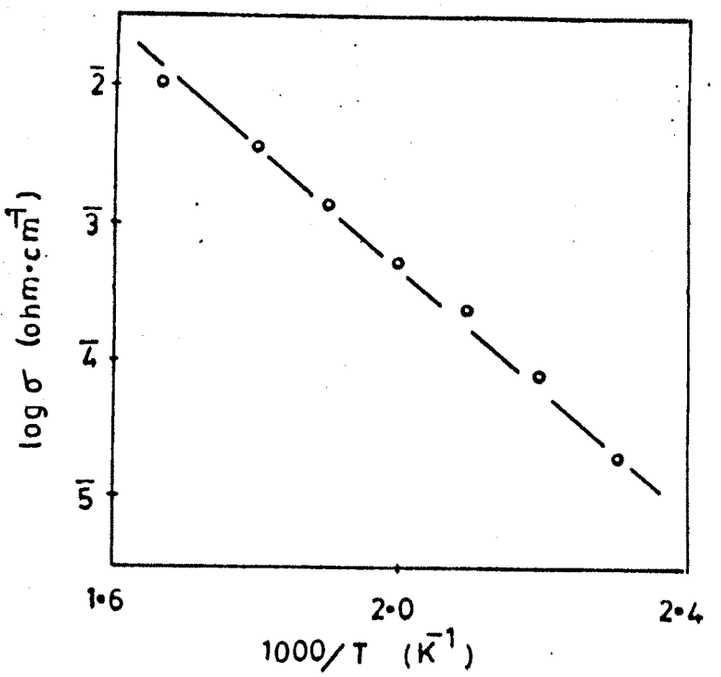


Fig-3.3 Temperature dependence of conductivity for Sb_2S_3 thin films.

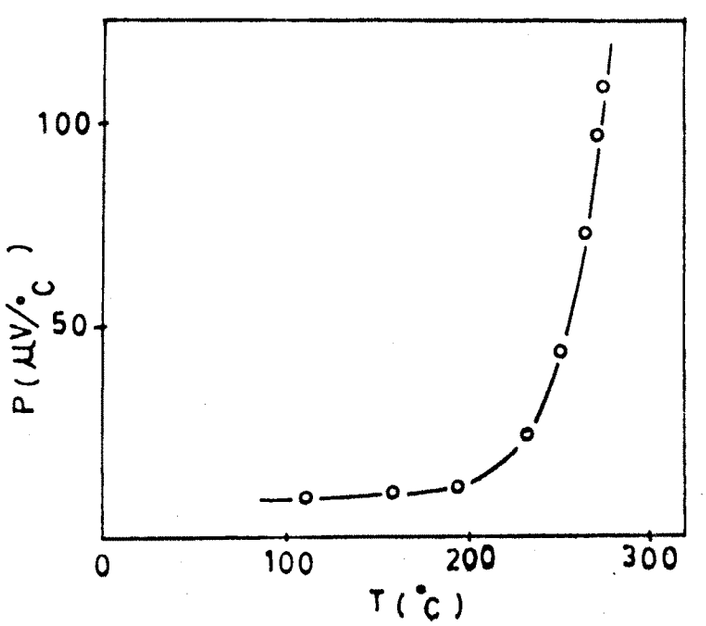


Fig-3.4 Temperature dependence of thermoelectric power(P) for Sb_2S_3 thin films.

found to be smaller than that reported by others. This can be attributed to the comparatively lower resistivity of our samples |31,34,38,49| than the samples prepared by other conventional techniques viz solution gas interface, dip and dry, spray pyrolysis, vacuum evaporation, sintering, and sulfurization. The lower resistivity observed in our case can be due to the improved degree of crystallinity provided by the preferred orientation while depositing the layer on the substrates. We now believe that this flexibility can thus be accounted for in the use of substrate holder geometry |31,34,38,49|. We have observed similar results in case of bismuth trisulphide with this improved technique |38|.

At high temperature (>450K) fast increase in conductivity is observed which can be attributed to the fact that at high temperature, jumping of electrons from one antimony site to other take place. It is reported that when bands are narrow with the presence of localised states, the conduction occurs due to hopping mechanism |28|. The activation energy can then be considered to be the energy required for hopping.

b] Thermoelectric power (TEP)

Another technique to characterise the thin film electrically is the measurement of the thermoelectric power (TEP) as a function of temperature. The technique helps to detect the type of material under investigation. Thermoelectric power (P) generated by Sb_2S_3 sample was measured in the temperature range 300K to 450K, and the polarity of the thermally generated voltage is positive towards the hot end of the sample. The order of

thermoelectric voltage is in terms of a few μV. The temperature variation of thermoelectric power is depicted in Fig 3.4. It is found that the material is of n-type conduction. The thermoelectric power (P) varies according to the relation |32,51,52| :

$$P = -\frac{K}{q}\left[A + \ln \frac{2(2m_e^*.KT)^{3/2}}{nh^3} \right] \qquad \ldots (3.2)$$

where, q = an eletronic charge, h = plank's constant,

A = thermoelectric factor introduced by the kinetic energy of electrons and hence depends on the scattering process.

n = carrier concentration, m_e^* = effective mass of an electron,

k = Boltzmann's constant, T = absolute temperature. P for Sb_2S_3 material is of the order of μV/°C, and is observed to increase with increase in temperature. The results are in close agreement with those of the reported |31,32,49|.

3.4.3 Optical studies

Studies on optical and structural aspects of III-V chalcogenides have been chiefly restricted to sputtered and vacuum evaporated films |53-55|. However, flash evaporation, chemical transport, chemical deposition, dip-dry, and solution gas interface technique could be used to obtain homogeneous films |35,55-57|. The literature survey points out that the conventional solution growth techniques are being widely employed for the growth of binary and ternary compounds. If the experimental results on optical studies are to be interpreted properly, it is important to know what type of transitions are taking place in the material under investigation. It is also

possible to differentiate direct and indirect transitions by the examination of energy ($h\nu$) dependence of absorption coefficient (α). Therefore, the Sb_2S_3 thin films are further characterised by means of an optical band gap technique. The absorption spectra has been studied at 300K in the wavelength range from 3500 A° To 8400 A°.

The absorption coefficient is high and is of the order of 10^{+4} - 10^{+5} cm^{-1}. The energy absorbance spectrum is shown in Fig 3.5. Following the usual theoretical analysis, the energy dependent absorption coefficient can be expressed by the relation for both allowed direct and indirect transitions as :

$$\alpha_{(d,i)} = \beta(h\nu - E_{(d,i)})^n \qquad \ldots (3.3)$$

Where, β is a constant, E_d and E_i refer to the direct or indirect band edges. For direct transition `n' assumes a value of ½ and 2 for indirect transition. Fig 3.5 shows that the absorption coefficient (α) is falling eventually near the band gap value which is in agreement with the reports of Bohac and Kaufmann |58| for single crystal Sb_2S_3. The steep rise of an absorption coefficient (α) from 1.8 to 2.5 eV appears to locate the band gap of Sb_2S_3 due to direct transition |28,32,49|. The appearance of an exponential tail within the same energy range is a characteristic of chalcogenide microcrystalline materials |32|. Mode of transition was also examined by the variation of α^2 vs $h\nu$ as suggested by Shanthi et al |59|. The variation of α^2 vs $h\nu$ is found to be a straight line indicating the dominant direct type of transition. The linearity of the plot extends from an energy gap of about 1.8 eV to 2.5 eV. These observations are in good agreement with those reported by Bhosale |32| and

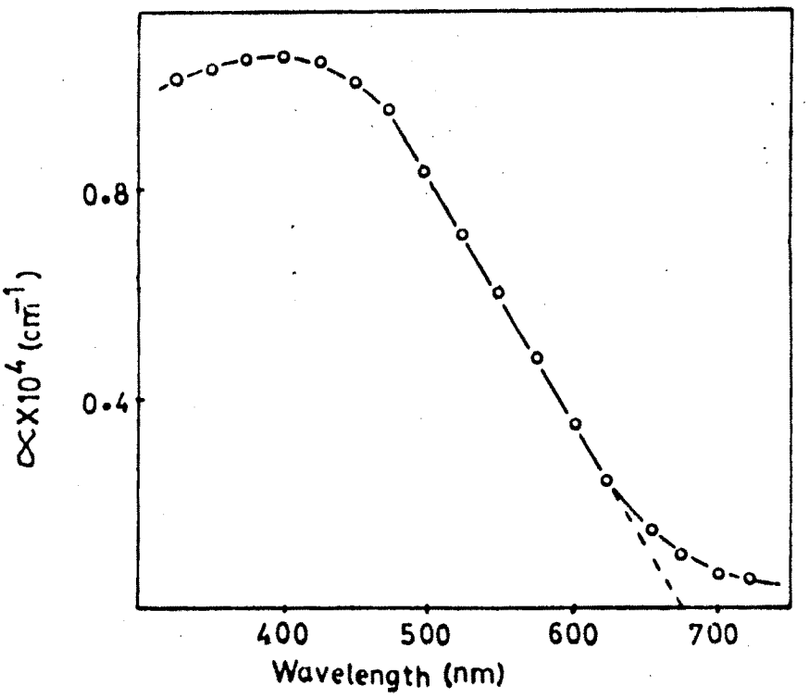


Fig-3.5 Energy absorption spectrum for or ange-red Sb_2S_3 sample.

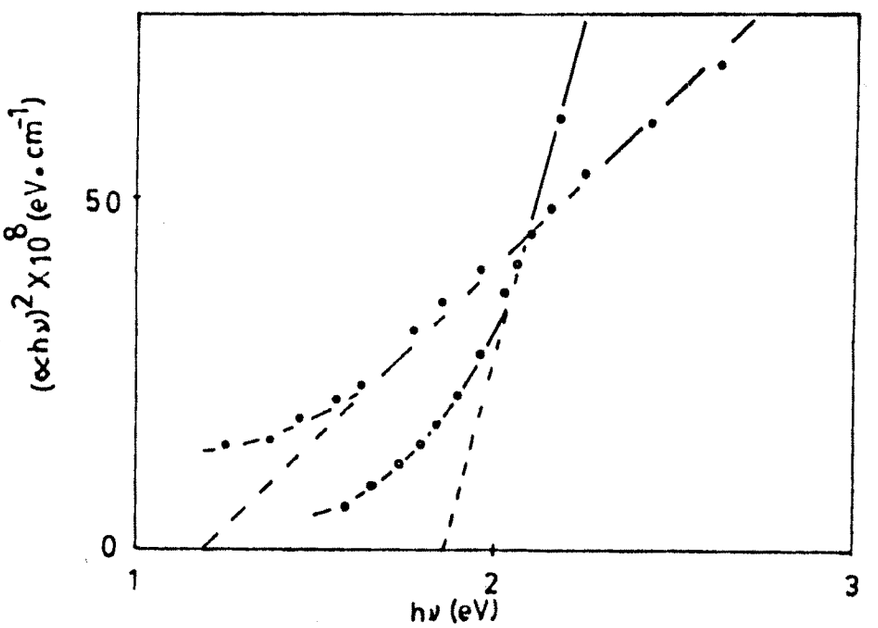


Fig-3.6 Determination of optical bandgap from variation of $(\alpha h\nu)^2$ vs $h\nu$.

Deshmukh et al |31,34|.

An optical gap is computed from the variation of $(\alpha h\nu)^2$ vs $h\nu$ as shown in Fig 3.6. The extrapolation of the plot to energy axis gives a value equal to 1.83 eV. This resembles closely with the already reported results.

The optical absorbance spectrum was also examined for dark grey samples as shown in Fig.3.7. The samples show maximum absorption in the range of energy gap from 1.62 eV to 3.1 eV |31|. The reason for such change is not clearly understood. The energy gap of dark-grey samples is found to be 1.17 eV. The absorption edge becomes still sharp compared to an orange red Sb_2S_3. These reports are similar to the reports of Ristov et al |60| and our previous observations on Sb_2S_3 thin films |31,34,49|. The variations of $(\alpha h\nu)^2$ vs $h\nu$ for dark grey samples are shown in Fig 3.6.

3.5 Conclusions

A novel way of obtaining Sb_2S_3 thin films using a modified chemical deposition process is presented. The deposition is carried out in an alkaline medium and the growth of thin films is by the slow release of Sb^{3+} and S^{2-} ions in a complex solution and subsequent condensation on the substrate support. Good quality deposition of Sb_2S_3 thin films with less consumption of both an electrical power and the active materials is possible. The as-deposited samples are orange red in color and color changes to dark-grey when heated to 180°C. Both varieties are crystalline in nature as revealed by X-ray diffraction and SEM analysis. The crystal structure is of orthorhombic type with

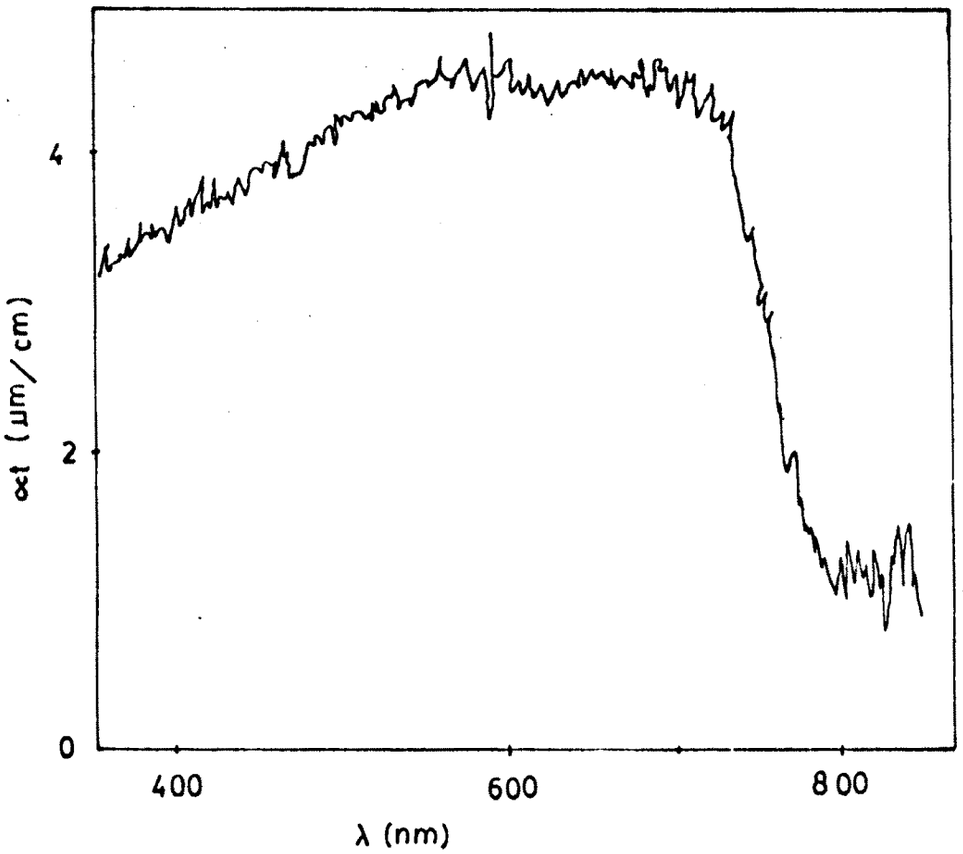


Fig-3.7 Optical absorption spectrum for dark-grey Sb_2S_3 sample.

grain dimension around 0.2 to 0.5 μm. The samples are highly resistive with n- type conduction. An activation energy of electrical conduction is 0.80 eV and the thermally generated voltage is of the order of μV. The data on optical studies show high absorption coefficient (10^{+4} - 10^{+5} cm^{-1}), direct mode of transition, and forbidden energy gap of 1.83 eV. The grey samples are more crystalline and more coarse. The optical band gap of the grey variety is 1.17 eV. The absorption coefficient of the grey variety is still higher and shows maximum absorption over a wide range of photon energies (1.62 eV to 3.10 eV).