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Structural and Morphological Investigation of Chalcogenide Thin Film Prepared by Physical Vapour Deposition Technique using Antimony Trisulphide

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Abstract: The intention of this study is to review the status of deposition of a thin layer of chalcogenide film over a glass substrate by employing physical vapour deposition technique and its morphological characters at different annealed temperature. The character of a thin-film is depending on the nature of the substrate and the thickness. The morphological aspects of the thin films prepared using Antimony trisulphide have examined by various characterization techniques.

XRD examination shows, as-deposited and annealed at 378K, 453K Sb_2S_3 thin films were amorphous in nature but annealed at 528K and 603K were polycrystalline in nature. SEM images revealed that the sample annealed at 603K shows the clear orthorhombic phase of Sb_2S_3thin film. Among various deposition methods, thermal evaporation is a well-established technique and is preferred for its simplicity. Therefore, in the present work prime importance has given to the formation of Sb_2S_3 and its characterization. The film was annealed above 600 K and concluded as orthorhombic phase and polycrystalline in nature.

Keywords: Annealed, Chalcogenide, Morphology, Physical vapour deposition, Thin film

I. INTRODUCTION

In recent years, antimony trisulphide is having significance in the field of optoelectronics and corrosion-resistant coating [1]. The thin films synthesized by various techniques has already been used in different fields including semiconductor devices, wireless communications, IC chips, solar cell and particularly in medical and environmental research[1][3]. A thorough literature survey reveals that many investigations has been carried out on Sb2S3 thin films by different techniques such as sol-gel method, chemical deposition method, physical vapour deposition, and sputtering techniques etc. Among these techniques, vacuum evaporation is a well-established technique and is preferred for its simplicity and cost effective [2]. Therefore, this research's prime concern is in the formation of Sb_2S_3 thin film and its characterization at different annealed temperature.

Deposition technics are widely using for thin film production, either chemical or physical methods. The usefulness of the optical and structural properties of the metal film and scientific interest about the behaviour of two-dimensional solid has been liable for immense curiosity in the investigation of science and technology of the thin film. The study in the remarkable, unique character of a thin films such as geometry, thickness and structure has directly or indirectly paved the way for various novel areas of research in material science[2][3].

Now days much more importance has been given to the field of chalcogenide compounds, since it exhibits strong size and surface dependent properties [4]. The surface morphology of a thin film, both amorphous and crystalline has immense relevance in the age of high technology. Since the thickness constrain play a vital role, as thickness is exceptionally microscopic compared to its lateral dimension and its enormous surface to volume ratio as contrasted with the same ratio in the bulk solid-state[5][6]. Chalcogenide compounds such as As_2S_3, CuIn2, CdS, are the crucial material for today's typical thin-film photovoltaic technologies [7]. Although these materials have already been used in commercial products, their growth and thin film productions remains a subject of versatile research. The present method explains the preparation of chalcogenide thin films using physical vapour deposition technique. The crystallographic nature of the film was examined using XRD technique for as-deposited film and annealed at 378 K, 453 K, 528 K, and 603 K and the morphology of films subjected to investigation using SEM (scanning Electron microscope)[8].

Majority of the films are associated with some growth imperfection such as lattice discrepancy, stacking error, twinning default in atomic arrangement, dislocation, foreign atom inclusion, etc. irrespective of whether it is prepared by evaporation technique or by any other method [9]. Surface morphology of a film also plays a dominant role in modifying electrical and other properties besides, due to high surface to volume proportion in a film. A newly created film surface becomes highly sensitive further because of the distortion in balancing force near the surface region, new phenomena such as thermionic emission, adsorption of gases, catalysis, solid-state reaction, etc. The typical character of a surface is most often detected in the thin film rather than in bulk [10].

II. MATERIALS AND METHOD

A. *Selection of the Substrate:*

The substrates show great influence on the growth and the orientation of the film. The property of the film deposited is externally influenced by the nature and surface morphology of the substrate. Therefore, glass substrates were used, since they are very economical can be easily cleaned, and due to their stability in surface studies, glass substrates of dimension 75mm×25mm with a thickness of 1mm were taken.

B. *Cleaning of the Substrates:*

The glass substrates used were washed thoroughly before employing deposition. The high standard of thin film with durable, adherence and reproducible properties depends mostly on the cleanliness of the substrates. The condition of the substrate surface influences the film growth (Nucleation of the films) largely, a pre-requisite for the formation of thin films. The usual contaminants limit residues, fingerprints, oil and greasy materials. The selection of cleaning techniques depends on the property of the substrates, the type of impurity and the degree of cleanliness required. The cleaning process results in the breaching of bonds between the contaminant molecules .

Initially, the substrates have cleaned with a soap solution. Then the substrates were dipped in the hot water at 80^0c for 30 minutes and washed in such a way that no trace of soap would be formed. After that, a series of dipping in hot chromic acid (Potassium Chromate and conc.H2SO4) for 20 minutes and washing with distilled water for 3 times were carried out, which results in the removal of Oxides and greasy materials.

Then the substrates positioned in an ultrasonic agitator where they are vigorously agitated for 30 minutes in distilled water and a solution of soap. The substrates were dried in a hot oven followed by a second agitation in distilled water. Isopropyl alcohol was used for the final cleaning of the substrate and then heated at 100^0c for about one hour in an oven. Thus, the cleaned substrates were obtained.

C. *Preparation of Sb_2S_3 Thin Films*

In order to obtain thin film, fine powder of Sb_2S_3 alloy has thermally evaporated in a high vacuum system (HIND HIVAC 12AD4M) at a pressure of about 2×10-5Torr to prepare the stibnite. A thin film of antimony trisulphide of thickness $2000A^0$ deposited on the well-polished glass substrates held at ambient temperature. The deposition rate was maintained at 2 to 6 A^0/s. At four different temperatures 378 K, 453 K, 528 K, and 603 K the films were annealed in a controlled atmosphere for one hour.

III. RESULTS AND DISCUSSION

A. *Characterization of Structure*

The x-ray diffraction study of the crystallographic structure of stibnite annealed at four different temperatures and as-deposited was employed using Cu-Kα radiation (1.54 A0) in the θ range $10^0 – 90^0$. It is shown in figure (1).The thin film of stibnite annealed at 378K and 453K and of as-deposited shows amorphous nature from the pattern of XRD. The thermal annealing of the film increases the crystallinity of the structure. The surface mobility of the atom increases at an elevated annealing temperature during the course of deposition. Under these circumstances, the growth of the film is favoured. The prepared samples annealed at 378 K, 453 K, 528 K, and 603 K.

A characteristic peak of stibnite in orthorhombic phase has obtained at 29.58^0, when the film annealed at 603 k. The peaks at $2\theta=25.33^0$, 27.96^0 and 32.4^0, which also corresponds to the peaks due to orthorhombic phase through the preferred orientation along (1 0 3), (2 1 0) and (2 1 2) respectively.

There are some other peaks, due to oxidization. Most of the report discloses that the XRD figure of Sb_2S_3 thin films onto glass substrates are either amorphous or poor crystalline. The crystal texture of the film can be changed by growing the thickness of the sample or by tuning stoichiometry of Sb_2S_3 thin films.

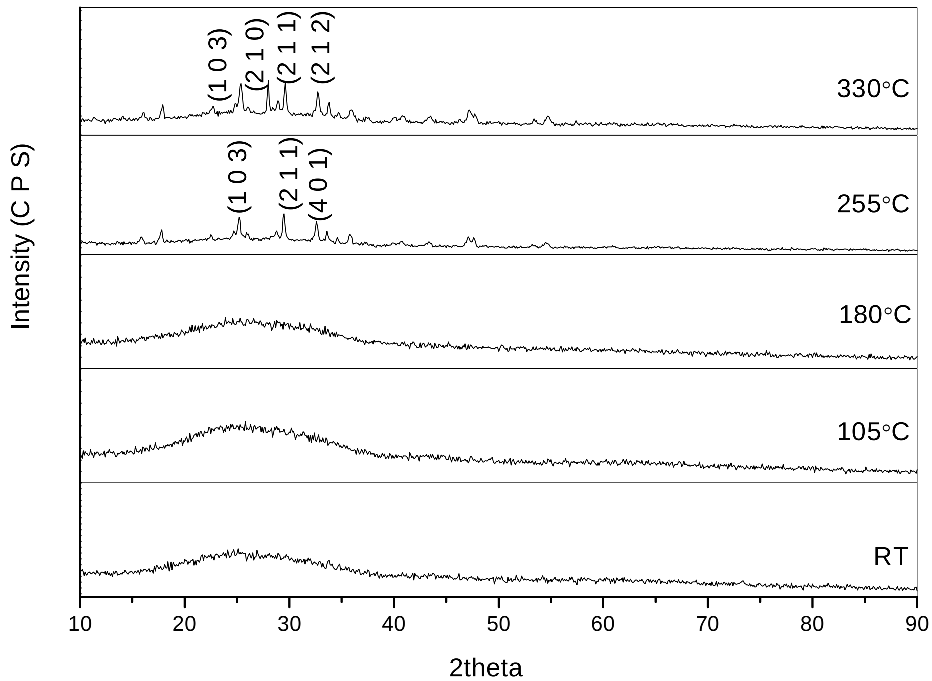

Fig.1. XRD pattern of annealed Sb2S3 and as-deposited thin films

The lattice constants at 603K, a, b and c are found, which are in covenant with the JCPDS data having the values 11.182 A^{o}, 11.376 A^{o} and 3.892 A^{o} respectively for orthorhombic phase. The average dislocation density, grain dimension, and strain were tabulated.

TABLE I
Microstructural Parameters Of As-Deposited And Annealed Sb_2S_3 Thin Films

SL NO	ANNEALED TEMP(K)	LATTICE			FWHM((β)	$d_{hkl}(A^0)$		hkl	Grain size(D)nm	Dislocation density $\times 10^{15}$ lines/m^2	Strain $\times 10^{-3}$ m	Crystalline nature
		a	b	c		observed	calculated					
1	As Deposited	-	-	-	-	-	-	-	-	-	-	Amorphous
2	378	-	-	-	-	-	-	-	-	-	-	Amorphous
3	453	-	-	-	-	-	-	-	-	-	-	Amorphous
4	528	-	-	-	0.29	3.03	3.05	211	28	1.32	1.26	Polycrystal
5	603	11.1	11.4	3.9	0.31	3.06	3.05	211	26	1.5	1.33	Polycrystal

The temperature dependence of the grain size of the sample is evident from most of the characterization report. According to the report, the grain size of the film annealed at 528 K has a small grain size as compared to the grain size of the sample at 603K. However, here the sample annealed at 528K has the maximum grain size. This is due to the oxidation of the sample. i.e. the sample annealed at 528K is more oxidized than other films. It has been confirmed by the EDAX analysis. When the film is oxidized automatically, the crystallite size would be increased. So that the film annealed at 528K has the larger grain size than the sample annealed at 603K.Due to the smaller grain size of the film annealed at 603 K, it exhibits more strain and dislocation density as compared to the film annealed at 528 K.

B. Morphological Characterization

Scanning Electron Microscope has used to evaluate the morphology and microstructure of as-deposited and annealed Sb2S3thin film. The amorphous nature of as-deposited thin film has disclosed in the SEM image. The sample annealed at 528K shows the formation of Sb2S3particles. The film annealed at 603K shows a clear picture of film surface. From the image of SEM, we concluded that the particles are in the orthorhombic phase, as we expected. As the film annealed at 528 K was more oxidized, the structure of the film could not be produced.

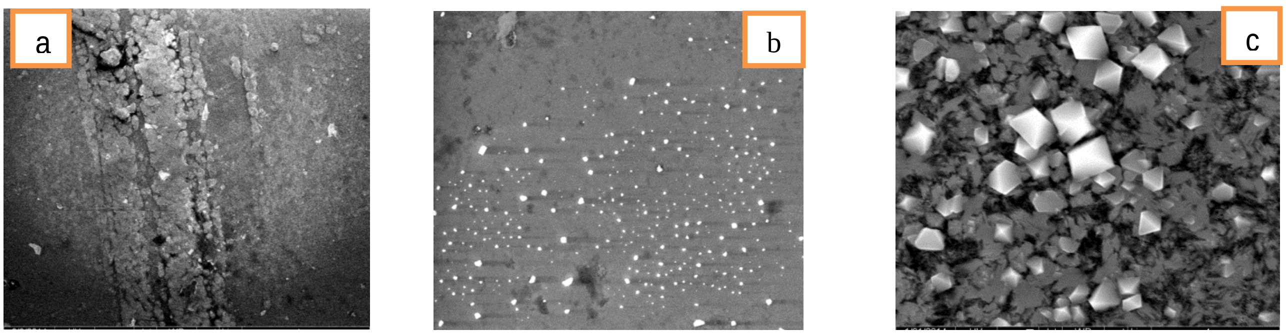

Fig.2.SEM image of Sb2S3 thin film at different temperature (a) as deposited (b) 528K (c) 603K

C. Energy dispersive analysis of x-rays

The figure (3) exhibits the chemical composition of annealed and as-deposited stibnite thin film. From the analysis of EDAX, the presence of Sulphur and Antimony were confirmed. There was the presence of silica because of the glass substrate. Presence of O_2 indicates that the films were oxidized, because the films were not kept in a perfectly controlled atmosphere.

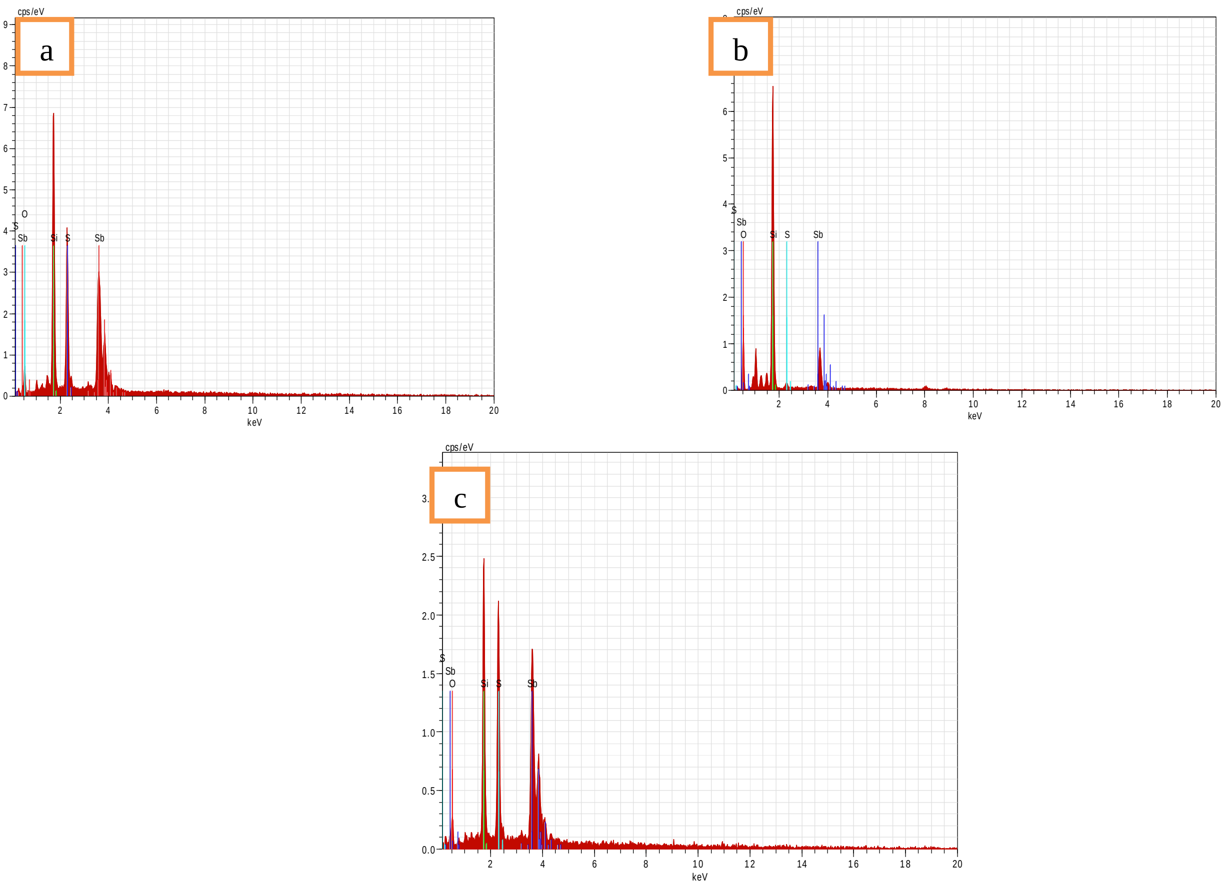

Fig.3. Chemical composition of Sb2S3 thin films (a) as-deposited (b) 528K(c) 603K

When the temperature increases to 603K, the Sb and S content increases largely. The result is following the XRD result, in which the sample annealed at 603K shows, mainly the characteristics of Sb2S3. The oxidization percentage is decreased, in the film annealed at 603K than as-deposited film. Hence, the SEM image of this film gives clear characteristic details. The film annealed at 528K is somehow more oxidized than the other films. When a film gets more oxidized the grain size will be increased. This finding is in covenant with the XRD data. The reason for this excess oxidization is may be due to the exposure of the film to the atmosphere

IV. CONCLUSION

The Sb2S3 thin films were produced through PVD technique by thermal evaporation. From the X-Ray diffraction analysis, it has been ascertained that the as-deposited and annealed at 378K and 453K Sb2S3 thin films were amorphous in nature, while annealed at 528K and 603K are polycrystalline in nature. As the film annealed at 528 K was oxidized more than other films, it has a higher grain size than the film annealed at 603K. From the Scanning Electron Microscopic image, the film annealed at 603K exhibit the clear orthorhombic phase of Sb2S3thin film. From the EDAX Analysis, when the temperature increases to 603K, the Sb and S content increases largely. The report is in accordance with the XRD result, in which the sample annealed at 603K shows, mainly the characteristics of Sb2S3.

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