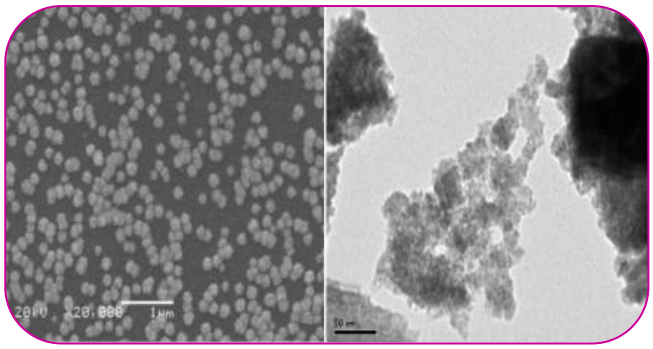
REVIEW OF RESEARCH

ISSN: 2249-894X
IMPACT FACTOR : 5.2331(UIF)
VOLUME - 7 | ISSUE - 1 | OCTOBER – 2017



NANOSTRUCTURE STUDIES ON BI_2S_3 THIN FILM

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ABSTRACT:

In this work, thin film of Bi_2S_3 have been deposited by chemical bath deposition technique, using thisulphate ($Na_2S_2O_3$) as sulphate ion source where as Ethylene diamine tetracetic acid (EDTA) used as complexing agent to get adisive quality films. The effect of morphological, structural and optical properties of Bi_2S_3 film were investigated. The SEM showed that the morphological surface of the Bi_2S_3 film. The X-Ray Diffraction (XRD) pattern shows films structure. The optical properties measurement of U- Visible Spectrometer and the band gap value of energy were varying from 1.9 to 3.8 eV and determined. The stoichiometric and nonstiochiometric Bi_2S_3 film were observed to n-

KEY WORDS: *Nanothin film, C.B.D., Bi_2S_3, Structral, Optical Properties, XRD.*

1. INTRODUCTION:

In various field of science and technology, semiconducting chalcogenide film of different metal have found world-wide application in various field of science and technology. The member of the V-VI group of compound semiconductors are technically important materials, which gives important application as photoconductivity, photosensitivity , and thermoelectric power [1,2] Bismuth sulfide is one of the important member of V-VI group of compound semiconductor. The easy availability and low cost material. The more recent values of several researchers have reported its band gap values in the range of 1.1 to 1.7 eV [10-17].

Thin film formation of these compounds can be carried out by various sophisticated deposition techniques. such as spray pyrolysis, vacuum evaporation, chemical vapour deposition,Sputtering,Chemical bath deposition One of the technique , chemical bath deposition is presently attracting considerable attention because it is relatively inexpensive, simple and convenient for large area deposition and doping capability. It is a slow process in which the film growth can take place by ion-by-ion condensation of the material on the substrate or by adsorption of the colloidal particles from the solution on to a substrate. Various semiconducting materials have been prepared by the solution growth technique [1-9, 21-23].

type nature.

In present work, chemical bath deposition technique, the deposition of Bi_2S_3 thin film using thiosulfate as sulphide ion source .when increase in at% of bismuth in the composition of the film the band gap energy of Bi_2S_3 film was increasing .

2. EXPERIMENTAL DETAIL :

Synthesis of Bi_2S_3 thin films:

To prepare Bi_2S_3 thin film . the(Bi $(NO_3)_3$), sodium thiosulfate, Ethylene dia amine tetra acidic acid (EDTA) are used. Before the deposition of the film , the glass substrate cleaning process is carried out , First glass substrate were clean by ethanol ultrasonically then etched by HF solution were decreased by chromic acid and well rinsed with double distilled water and lastly washed with methanol . Put 10-15 minute distilled water, remove dust and dry. The glass substrate were kept vertically in the beaker contained resultant solution 0.2 M solution of disodium salt of EDTA was added into 0.2M bismuth nitrate solution in a beaker. The solution was stirred continuously by using magnetic stirrer for few minutes. The solution of sodium thiosulphate (0.2M) was then added into a beaker. The resultant solution was stirred for few minutes whose pH was found to be between 0.6 to 1.7. Initially the solution was faint yellow, gradually turned into brown colour and finally turned into brown black. The films were kept in solution for 3-4 hrs at 60^0C. After deposition, the substrates were taken out of the beaker, washed with double distilled water and dried in air. The dried films are kept in desiccators for further characterization.

The chemical reactions responsible for the formation of Bi_2S_3 film in an acidic bath using $Na_2S_2O_3$ as the sulphide ions source [23,24,25] could be presented as follows:

$$Na_2S_2O_3 \longrightarrow 2Na^+ + S_2O_3^{-2}$$

$Na_2S_2O_3$ is a reducing agent by a virtue of the half-cell reaction as :

$$6S_2O_3^{-2} \longrightarrow 3S_4O_6^{-2} + 6e^-$$

In acidic medium, dissociation of $S_2O_3^{-2}$ would take place as:

$$3S_2O_3^{-2} + 3H^+ \longrightarrow 3HSO_3^- + 3S$$

The released electrons would react with sulphur as:

$$3S + 6e^- \longrightarrow 3S^{-2}$$

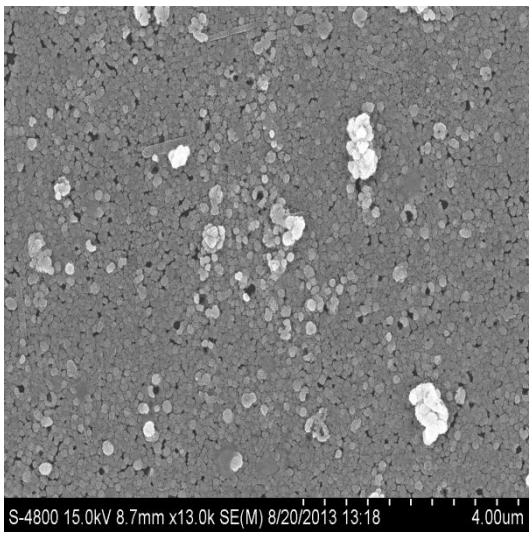
Bi^{3+} from Bi $(NO_3)_3$ solution or a complex of Bi^{+3} formed by EDTA would react to give

$$2Bi^{3+} + 3S^{-2} \longrightarrow Bi_2S_3$$

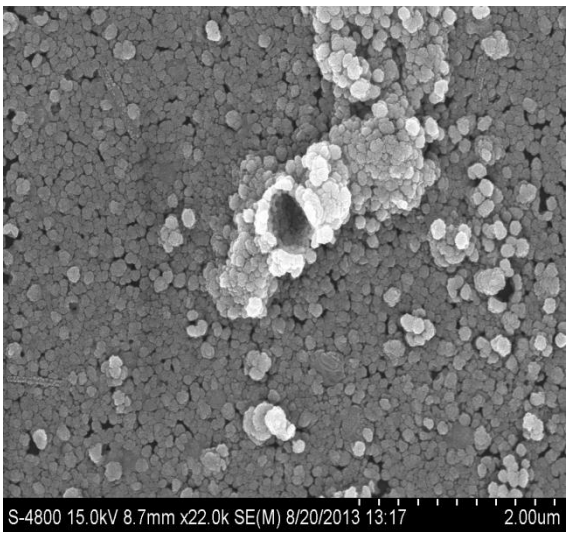
The Na^+ would form the nitrate and remain in solution as soluble product. This product could then be separated out easily.

3. MORPHOLOGICAL ANALYSIS

In order to know the texture of the films, SEM images of the as prepared films were taken. SEM micrographs (with same magnifications) of films from series are represented with the variation of the ratio of Bi to S (at%) in figure 6. Figures 6(a-c) represent SEM images of stoichiometric and non-stoichiometric Bi_2S_3 thin films. The surface morphology of the films was found to be very sensitive to the Bi/S ratio. SEM micrographs (with same magnifications) of films were represented with the variation of the ratio of Bi to S (at%) in figure 6. The sample consists spherical particles with larger sizes having larger average particle size (~120 nm). The SEM image of sample film with relatively larger amount of sulphur and smaller amount of bismuth as compared to the sample The sample consists spherical particles with average particle sizes of 200 nm.



Sample 1



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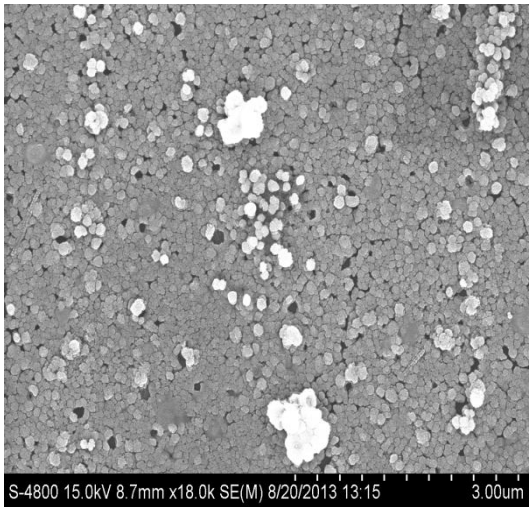

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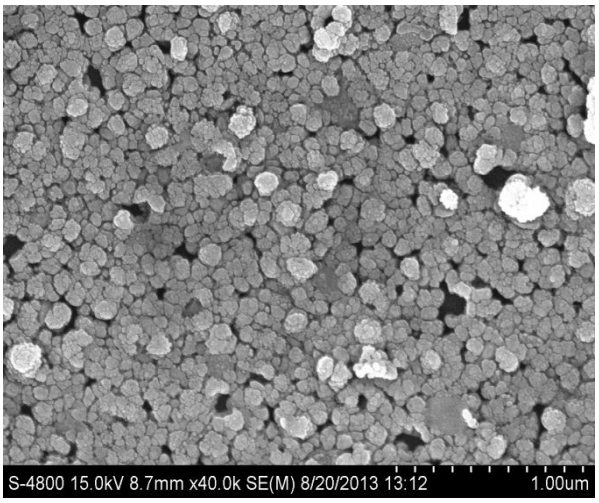

Sample 3

4.STRUCTURAL PROPERTIES :

X-ray diffraction is a powerful non-destructive method for material characterization, by which the crystal structure,grain size and orientation factor can be determined. Structural identification of Bi2S3 films was carried out with X-ray diffraction

Figure 8 represent the XRD patterns of stoichiometric Bi_2S_3 residual precipitate corresponding to the film. The XRD pattern, of the collected residue corresponding to film consists of peaks matching with standard ASTM data of stoichiometric Bi_2S_3. Table 2 represents the observed and reported XRD data. This confirmed the formation of Bi_2S_3. The precipitate settled down, during the preparation of film, was collected, washed several times and dried. XRD of this powder was taken. The crystalline nature of the films and the corresponding residue was observed to be increased by annealing them in an inert atmosphere.

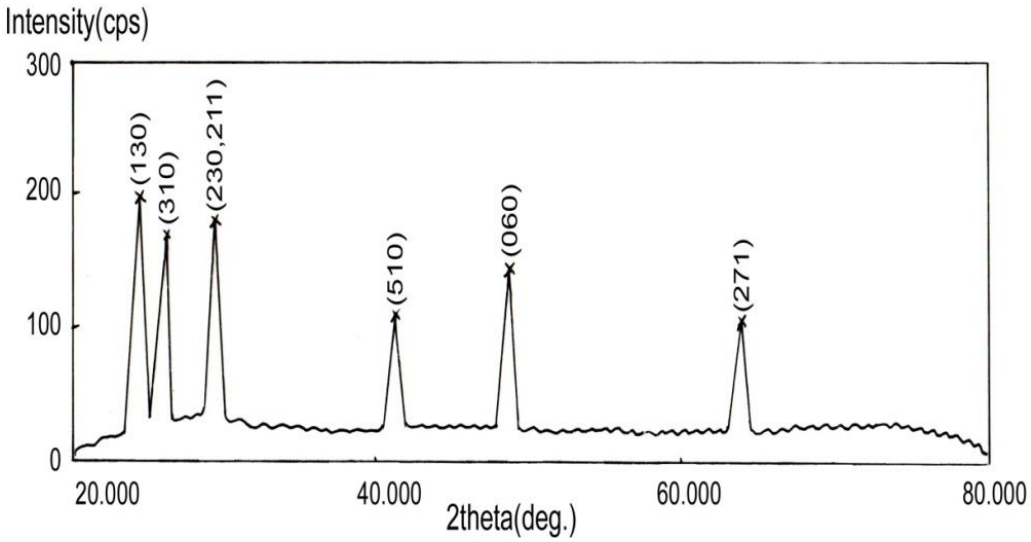

Table 2 : XRD data of crystalline Bi_2S_3

2θ Observed	d-Values (Å)		I / I_{max}	
	Observed	Reported	Observed	Reported
24.690	3.603	3.569	100	100
25.230	3.527	3.530	75	60
28.600	3.1185	3.118	50	80
41.200	2.1892	2.188	25	6
48.200	1.8864	1.884	6	25
64.400	1.4455	1.4451	9	6

5. OPTICAL PROPERTIES:

The optical absorption study of the as prepared films was carried out in the wavelength range 300-1100 nm. The variations of absorbance with wavelength of the thin film samples are shown in figure (3

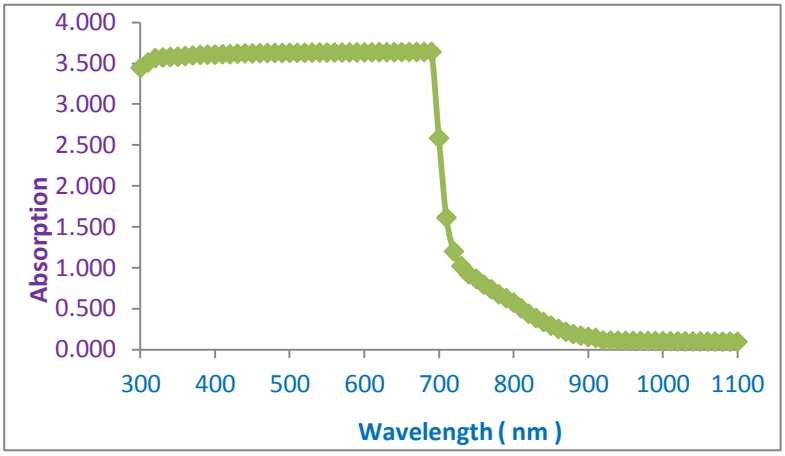

Fig . (3): Absorption spectra of Bi_2S_3 thin films

RESULT AND DISCUSSION :

The stoichiometric and nonstoichiometric Bi_2S_3 films were synthesized to understand the effect of change in composition on the crystalline and on their optical properties. Bismuth sulfide films of any composition could be prepared. The Bi to S ratio (at%) was varied from 0.86 to 0.59. All the films except one the film with Bi/S ratio (at%) were observed to be stoichiometric in nature. It is clear from SEM images that the number of particles associated in the film are largest, while the number of particles are smallest in case of film with lowest Bi/S (at%) ratio . This could be attributed films are associated with spherical particles with largest bismuth to sulphur ratio to the atomic radii of constituent elements of Bi_2S_3. The atomic radii of Bi and S are 0.74 Å and 1.84 Å respectively. The stoichiometric and nonstoichiometric Bi_2S_3 films were observed to be n-type in nature. The band gap energy values of Bi_2S_3 were varying from 1.6 to 3.7 eV. The band gap energy value corresponding to stoichiometric Bi_2S_3 was observed to be 1.72 eV

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