OPEN ACCESS INTERNATIONAL JOURNAL OF SCIENCE & ENGINEERING

EFFECT OF ANNEALING ON CHEMICALLY DEPOSITED Bi_2S_3 THIN FILM BY DIP TECHNIQUE

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Abstract: **In the present paper, we have reported the room temperature growth of bismuth sulphide (Bi_2S_3) thin films by dip method and detailed characterization of these films. The films were deposited from a reaction bath containing bismuth nitrate, glycine and sodium thiosulphate. We have analyzed the structure, morphology, composition, X- ray diffraction pattern, showed that the film were polycrystalline. The scanning electron micrograph of Bi_2S_3 thin film on glass substrate showed that sample contains many rods, they are formed in thin rope shape, the rods show no alignment and dispersedly distributed, but their diameter and lengths are rather uniform, elemental composition was performed by EDAX, the atom ratios of Bi and S are 2:3 according to EDAX.**

Keywords: Bi_2S_3, thin films, Annealing effect**, X**-ray, EDAX

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I INTRODUCTION

Thin Films have number of applications in various Fields. Few of them are A.R. coating, interference Filters, polarizer's, narrow band falters, solar cells, photoconductors, IR detectors, Waveguide coatings, temperature control of satellites, photothermal solar coatings such as black chrome, nickel, cobalt etc., magnetic Films, superconducting Films, anticorrosive Films, microelectronics devices, diamond Films, reduction of fabrication through coating or surface modifications i.e. epitaxy and heterostructure Films, high temperature wear resistance Films, hard coatings etc. Rapid progress in Film devices has helped for ICs of monolithic and hybrid microelectronics. Thin chalcogenide Films are of particular interest for the fabrication of large area photodiode arrays, solar selective coatings, solar cells, photoconductors, sensors etc. Deposition of these films by vacuum evaporation, sputtering and chemical methods such as chemical vapor deposition, spray pyrolysis, electrodeposition, anodization, electro conversion, electroless, dip growth, successive ionic adsorption and reaction, chemical bath deposition and solution-gas interface techniques are well known [1-7].

Among the V–VI compound semiconductor, Bi_2S_3 has attracted significant interest because of its superior properties such as high absorption co-efficient, direct band gap energy of 1.2–1.7 eV, high figure of merit, and good chemical stability. These intriguing properties make Bi_2S_3 as a techno-logically important material with widespread applications including photovoltaics, photodiode arrays, thermoelectric, switching devices and IR spectroscopy [8–15].

It is also used in pigments, luminescence devices, solar cells [16–19]. Bi_2S_3 thin-films have advocated considerable interest in thermoelectric cooling technologies such as biothermoelectric chip, thermochemistry on a chip, and cooling system for microelectronic components, owing to its high thermoelectric capacity through Peltier effect [20,21]. Up to now, diverse morphologies of Bi_2S_3 nanostructures including one-dimensional (1D) nanowires, nanoribbons, nanorods, nano-tubes as well as their complex assemblies such as nanofabrics, necklace architectures, disc-like networks, sheaf-like arrays, snowflake-like patterns and flower-like or urchin-like micro- spheres have been produced [22–32]. Several ligands have been utilizing in the deposition of Bi_2S_3, such as ethylene diamine tetra acetic acid [33, 34], tartaric acid [35] and triethanolamine [36]. Similarly,

different sources of sulphide ion, such as thioacetamide [37], thiourea [38, 39] and sodium thiosulphate [40] were used. Biswas et al. [41] prepared Bi_2S_3 thin films in an alkaline bath using TEA and thioacetamide as complexing agent and sulphide ion source, respectively. The films were amorphous with resistivity of 105–107 ohm-cm.

We report synthesis of Bi_2S_3 thin film by dip method. The deposited film samples were characterized by various techniques such as X-ray diffraction, scanning electron micrograph,

EDAX.

II EXPERIMENTAL DETAILS

The substrates used for depositing the films were nonconducting glass slides of the size 75 X 25 X 2 mm (Blue Star Co., Mumbai). All the chemicals used for the deposition were of AR grade. All the solutions were prepared in double distilled water.

To prepare the bath, 10 mL (0.2 M) $Bi(NO_3)_3$ was poured in 100 mL beaker; other chemicals were used in the following sequence: 4 mL (1 M) glycine, 15 mL (0.2 M) sodium thiosulphate. The pH of the reactive mixture is 4.53. The total volume was made 50 mL with double distilled water. The temperature of the bath was maintained at 278 K using ice bath. The solution was stirred vigorously before dipping non-conducting glass substrates. The substrates kept vertically slightly tilted in a reactive bath. The temperature of the bath was then allowed to increases up to 298 K very slowly. The film was deposited on both sides of slides. After 4 h, the slides were removed washed several times with double distilled water. The film was dried naturally and preserved in dark desiccators over anhydrous $CaCl_2$.

The film thickness was measured by weight difference method by using relation

$$t = m/\rho A$$

where, m is the mass of the film deposited on the substrate, A is the area of the deposited films and ρ is the density of deposited material (Bi_2S_3 = 6.78 g/cm^3). The terminal

thickness was found to be 0.32 μm.

III RESULT AND DISCUSSIONS

3.1 Growth mechanism

The deposition process of Bi_2S_3 is based on the slow release of Bi^{+3} and S^{-2} ions in the solution which then condenses ion by ion basis on the substrates. Deposition of Bi_2S_3 thin film occurs when the ionic product of Bi^{+3} and S^{-2} ions exceeds the solubility product of Bi_2S_3. The

Concentration of Bi^{+3} and S^{-2} ions in the solution controls the rate of Bi_2S_3 formation. The rate of Bi^{+3} ions is controlled by glycine, which forms a complex $Bi[(Gly)n]^{+3}$ with Bi^{+3}. The reaction for the formation of Bi_2S_3 thin films can be written as follows.

$$Bi\,[(Gly)_n] \rightarrow Bi^{+3} + n(Gly)$$

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

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

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

$$3S_2O_2^{-2} + H^+ \rightarrow 3HSO_3^- + 3S$$

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

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

When the amount of chalcogenide ion is more sufficient to permit nucleation to begin, then the deposition process will start. The growth is afterward the nucleation. As the maximum reactant is consume, the rate growth will decay and ultimately end because of exhaustion of the reactant [42-43]

3.2 X-ray diffraction

The X-ray diffractogram of annealed Bi_2S_3 thin samples synthesized on non-conducting templates such as glass are shown in Figure 1. The crystalline structure of the materials became decided from numerous peaks in diffraction pattern. The investigation of spectrum suggests that the annealed thin films have been belonging to orthorhombic nature for entire temperature limit under investigations. The diffused background is due to amorphous template as well as some amorphous nature present in Bi_2S_3 samples. The utmost strong reflection indicates that for annealed Bi_2S_3 thin films were originating from (211) peaks.

Annealing of thin samples at 348K enhance the intensity of the all peaks. (101) (021) (311) (002) peaks were not observed in the annealed sample. No new peaks were observed. The plane intensity enhance with go up in temperature suggesting rising crystallinity of thin samples. The diffractrogram of annealed sample indicates the slight alteration in the peak position towards smaller two theta value. All films show the most preferred plane (211) in addition to other (230) (130) (211) (221) (410) (240) (430) (431) (132) prominent reflections. The absence of other peak indicates the annealed sample remains in the single phase orthorhombic nature. The slight variation in the interplanar

magnitude of prominent planes suggests that because of annealing, the sample is slightly expanding. Consequently the cell symmetry is not altered by heating.

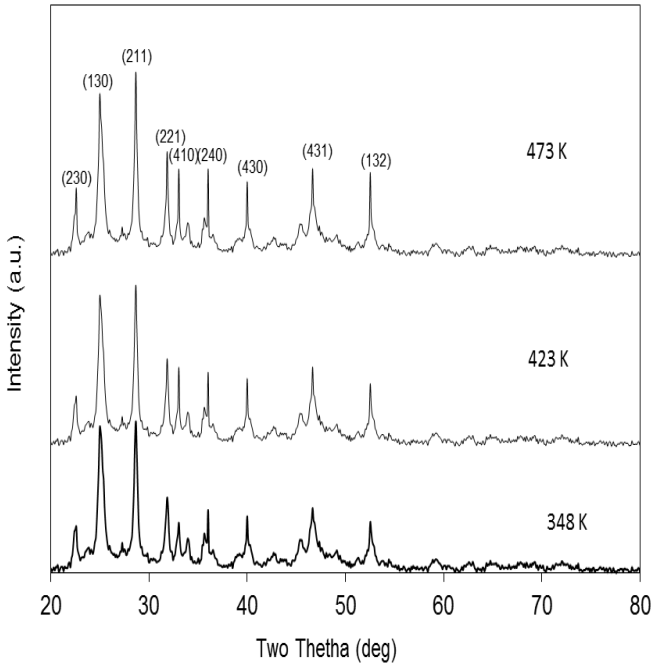

Figure 1: X-ray diffraction pattern of annealed Bi_2S_3 sample

Modify in lattice factors has too been observed for entire annealed samples. The lattice factors have been measured by applying relation

$$(1/d^2) = (h^2/a^2+k^2/b^2+l^2/c^2)$$ ------[1]

It is found out that as annealing temperature of the sample go up, the lattice factor 'a' differ gradually from 11.414 (Annealing temperature = 348 K) to 11.470 Å (Annealing temperature = 473 K). The lattice parameter 'b and c' enhance correspondingly from 11.154 to 11.229 Å and 3.823 to 3.842 Å as the annealing temperature enhance. Alter in lattice constant for chemically prepared thin samples against bulk obviously indicate that the grains are strained. This is because of nature and amount of the native defect changing.

The expansion of the cell is indicated by measuring the volume of the lattice. The volume is estimated by applying relation[44]

$$V= abc$$----------[2]

for the entire the samples. As the annealing temperature go up the volume too increases. For temperature 348 K having least volume whilst temperature 473 K having utmost volume. The significance of volume change from 486.71 to 494.83 $(Å)^3$. The average particle dimension became determined by using Scherrer's method (expression).[45]

$$D = 0.9\lambda /\beta\cos\theta$$----------[-3]

The average particle dimension was estimated via assuming the utmost intensity peak. The average particle dimension for the annealed samples was found in the order of 854 to 920Å. The derivation in the strain is associated to lattice misfit who depends upon the synthesis parameter. The microstrain generate in annealed samples the films were estimated (equation)[46]

$$\varepsilon = \beta\cos\theta/4$$---------[4]

It is observed that the microstrain reduce with enhance in annealing temperature. The for microstrain is 4.057×10^{-4} for annealing temperature 348 K and 3.764×10^{-4} for sample annealed at 473 K. Dislocation density is estimated applying the relation[47]

$$\delta = n/D^2$$ --------[5]

The magnitude of dislocation density was determined to be 1.37×10^{14} m^{-2} for sample annealed at 348 K and 1.179×10^{14} m^{-2} for sample annealed at 473 K. The dislocation density decreases as the annealed temperature and crystallite dimensions go up.

3.3 Scanning electron microscopy

The scanning electron image of the annealed Bi_2S_3 samples prepared on the non-conducting material was studied Figure 2 (a-c). Image shows a lot of rods. The size of the rods increases as the annealing temperature increases. These rods were produced in tiny rope structure. The rods are randomly spread, however their size and shape are rather consistent. These rods fused with each other. They well covered the glass substrate. No spherical grains were observed. The rods are no grouping.

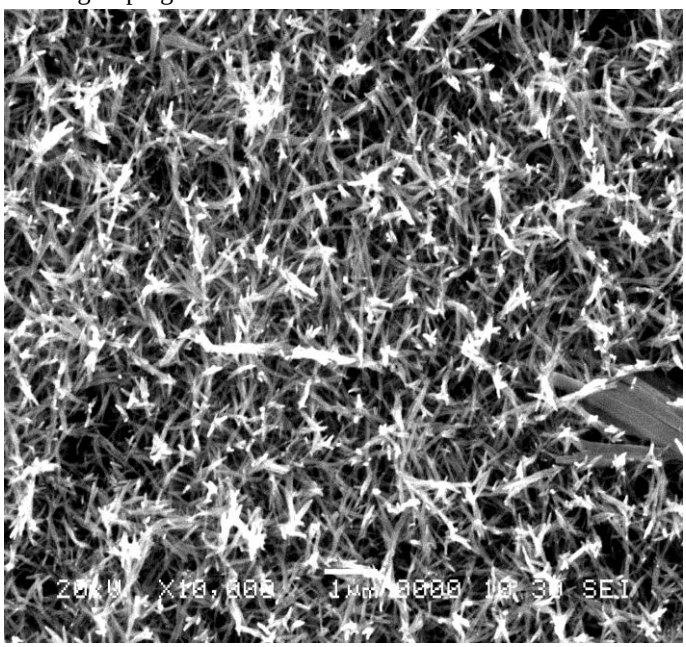

Figure 2 (a): Scanning electron image of annealed Bi2S3 sample at 348K.

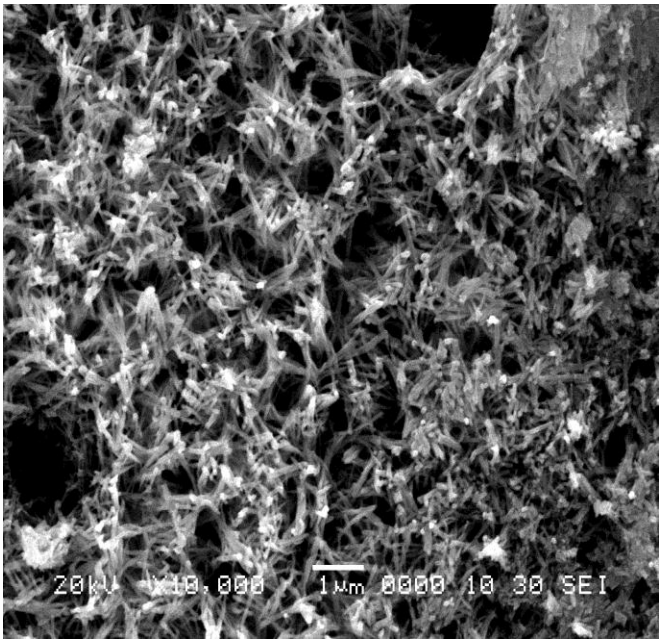

Figure 2 (b): Scanning electron image of annealed Bi2S3 sample at 423K.

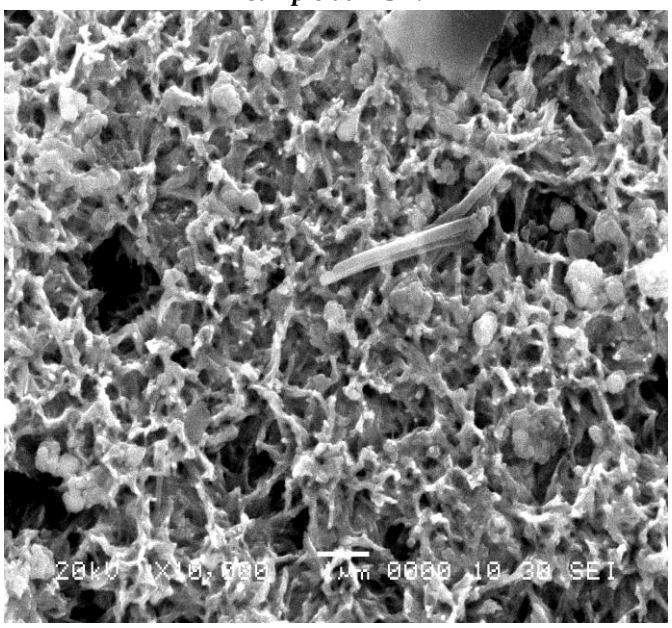

Figure 2 (c): Scanning electron image of annealed Bi2S3 sample at 473K.

3.4 Compositional analysis

Compositional analysis is too significant for estimating stoichiometry of grow thin film. Consequently compositional analysis makes available valuable information regarding the material property. Elemental properties of the sample was carried out using the energy dispersive method for Bi_2S_3 to find out the components in the sample. Figure 3. Shows EDAX pattern of Bi_2S_3 thin film samples.., the amount of Bismuth entered in the lattice of sulphar was determined. There is no other impurity in the film. The composition of the films are 47.16:52.84.

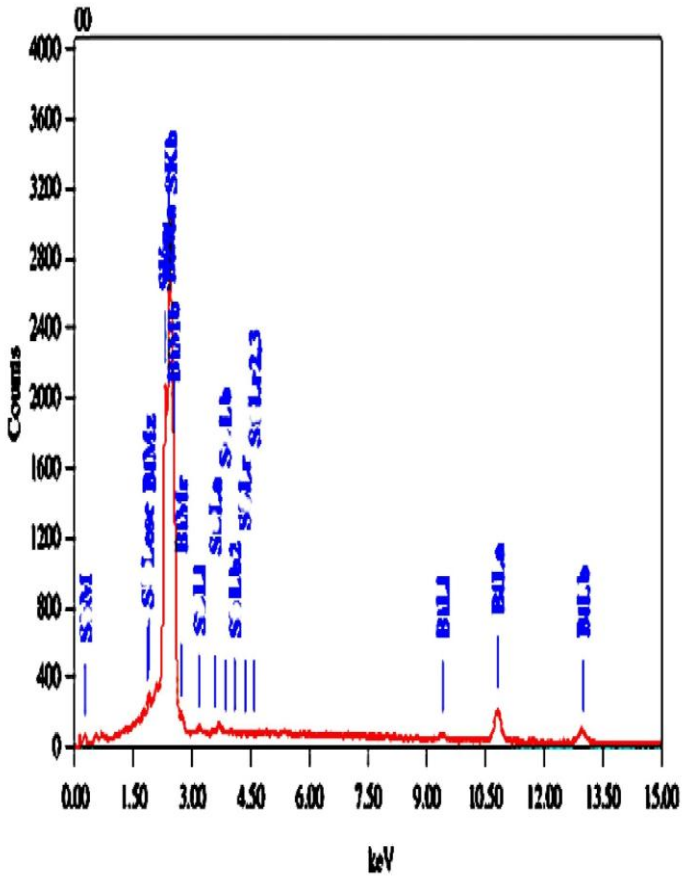

Figure: 3 EDAX pattern of Bi_2S_3 sample

III CONCLUSIONS

The deposition of crystalline Bi_2S_3 thin films by an easy and cheap technique represents a challenge to the chemistry and electronic material science researchers. This paper has succeeded in presentation a new low cost dip technique. Development of Bi_2S_3 thin films from acidic media using precursor's bismuth nitrate and sodium thiosulphate in the ratio of 2:3 (Thickness = 0.32 μm). The scanning electron image of the annealed Bi_2S_3 samples prepared on the non-conducting material shows a lot of rods. The size of the rods increases as the annealing temperature increases. These rods were produced in tiny rope structure. The rods are randomly spread, however their size and shape are rather consistent. These rods fused with each other.

The composition of the films are 47.16:52.84. As deposited Bi_2S_3 films are amorphous in nature in nature and have small grain size.

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