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# Thickness-dependent structural properties of chemically deposited $Bi_2S_3$ thin films

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## ABSTRACT

*Thin films of $Bi_2S_3$ have been prepared by chemical bath deposition method using Bismuth nitrate and Sodium thiosulphate. Films were deposited onto well cleaned glass substrates with different bath temperatures. The effect of bath temperature on thickness was studied. The thickness goes on increasing with bath temperature reaches to maximum at $60^0C$ and decreases further increases in temperature after $60^0C$. The good quality of film is obtained at $60^0C$. The X-ray diffraction pattern revealed that bismuth sulphide thin films exhibit orthorhombic structure with polycrystalline in nature. The structural parameters (grain size 25-358Å, dislocation density $0.7789\text{-}159.57X10^{15}$ $l/m^2$ and strain (ε) $14.61\text{-}1.027X10^{-3}$) have been calculated. Grain size increases with film thickness but the strain and dislocation density decreases. The films are oriented in (330) direction.*

**Keywords:** Bismuth sulphide, Chemical bath deposition, Structural properties, Thin films

## INTRODUCTION

Presently nanocrystalline materials have opened a new chapter in the field of electronic applications, since material properties could be changed by changing the grain size and thickness of the film [1]. Bismuth trisulphide in thin film form is a particularly challenging material because of its midway band gap ($E_g$=1.7eV), absorption coefficient of the order of $10^4$ to $10^5$ $cm^{-1}$, reasonable conversion efficiency and stability together with low cost [2, 3]. Several methods such as cathodic electrodeposition, anoidic electrodeposition, vacuum evaporation, the hot wall method, solution gas interface, spray pyrolysis and chemical deposition have been used for $Bi_2S_3$ film preparation[4-7]. As compared to other methods, chemical deposition is simple, economic and suited for a large area of any configuration [8].

The present work describes a chemical method for deposition of $Bi_2S_3$ thin film using thiosulfate as a sulphide ion source. The thickness of the films was varied by changing the bath temperature its effect on the structural parameters (grain size, dislocation density and strain) was studied and results are reported.

## MATERIALS AND METHODS

### 2 Experimental details

Bismuth nitrate ($Bi(No_3)_3$), sodium thiosulfate ($Na_2S_2O_3$) and ethylene di amine tetra acetic acid (EDTA) were used to prepare the $Bi_2S_3$ films. Glass was used as the substrate. Before the deposition of the films, the glass substrate was firstly ultrasonically cleaned by acetone and the ultrasonically cleaned by distilled water.

For the deposition of the $Bi_2S_3$ films, $Bi(No_3)_3$ solution was added into EDTA solution, finally $Na_2S_2O_3$ solution was added to the mixed solution. The concentration of $Bi(No_3)_3$, EDTA and $Na_2S_2O_3$ in the deposition solution was 0.2M, 0.1M and 0.2M respectively. After the preparation of the deposition solution, glass substrates were immersed into the solution. The temperature of the solution was increased slowly up to $60^0$C, and then it was kept at room temperature for 12 hrs deposition time period. Likewise, the films were prepared at different bath temperatures ($40^0$C, $50^0$C and $70^0$C), rinsed in distilled water and dried.

## RESULTS AND DISCUSSION

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 films occurs when the ionic product $Bi^{3+}$ 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 EDTA, which forms a complex $Bi[(EDTA)n]^{3+}$ with $Bi^{3+}$. The chemical reaction responsible for $Bi_2S_3$ film from an acidic bath using $Na_2S_2O_3$ as the sulphide ion source [5] could be:

$$Na_2S_2O_3 \rightarrow 2Na^+ + S_2O_3^{-2} \quad (1)$$

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

$$6S_2O_3^{-2} \rightarrow 3S_4O_6^{-2} + 6e^{-'} \quad (2)$$

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

$$3S_2O_3^{-2} + 3H^+ \rightarrow 3HSO_3^- + 3S \quad (3)$$

The released electrons react with sulphur as:

$$3S + 6e^- \rightarrow 3S^{-2} \quad (4)$$

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

$$2Bi^{3+} + 3S^{-2} \rightarrow Bi_2S_3 \quad (5)$$

### 3.1 Structural Characterisation

The X-ray diffraction patterns of chemically deposited $Bi_2S_3$ thin films of four different bath temperatures ($40^0$C, $50^0$C, $60^0$C and $70^0$C) for 12 hrs deposition time period are shown in Figure 1-4. The presence of the peaks in diffractogram suggests the polycrystalline nature with orthorhombic structure of the film [9, 10, 11]. The observed 'd' spacing and hkl planes (Table 1) are good in agreement with the JCPDS data file(65-2435). From XRD profiles, the grain size, dislocation density, strain and orientation factor were calculated in Table 2 and Table 3. The degree of structural order of $Bi_2S_3$ films improves with an increase in film thickness.

There is an increase in grain size and decrease in strain as well as dislocation density with the increase in the film thickness [12-14]. Temperature effect on $Bi_2S_3$ films indicates that the thickness goes on increasing with bath temperature, reaches to maximum at $60^0$C and decreases with further increase in temperature after $60^0$C. This may be due to etching process involved at temperature higher than optimum [15]. The Full width at Half maximum (FWHM) was found to decreases remarkably with film thickness. Such a decrease reflects the decrease in the concentration of lattice imperfection due to a decrease in the internal micro strain with in the films and increase in grain size [16]. Table 3 shows that $f(330)$ is greater compared to other orientations in all films, it can be concluded that $Bi_2S_3$ films have the preferential orientation along (330) plane.

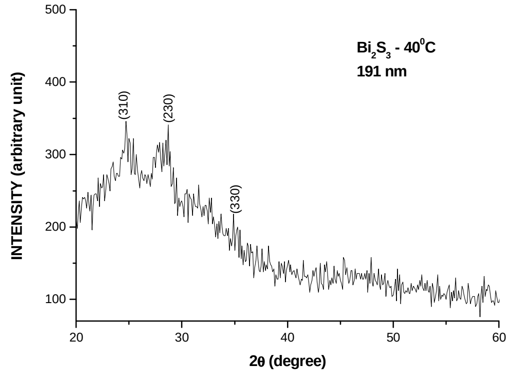


**Fig.1. X-ray diffraction pattern of $Bi_2S_3$ thin films of thickness 191 nm (bath temperature $40^0$C)**

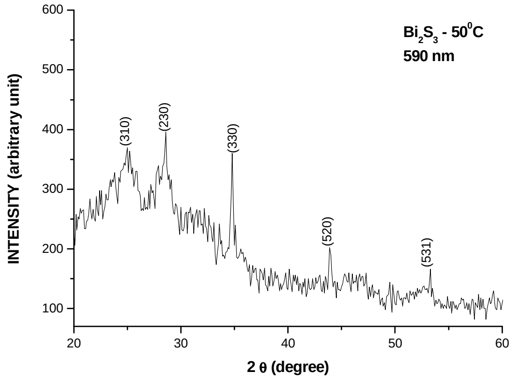


**Fig.2. X-ray diffraction pattern of $Bi_2S_3$ thin films of thickness 590 nm (bath temperature $50^0$C)**

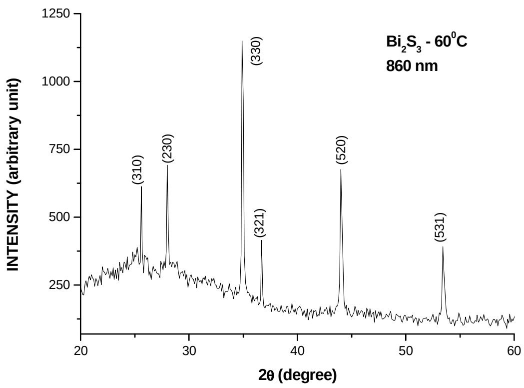


**Fig.3. X-ray diffraction pattern of $Bi_2S_3$ thin films of thickness 860 nm (bath temperature $60^0$C)**

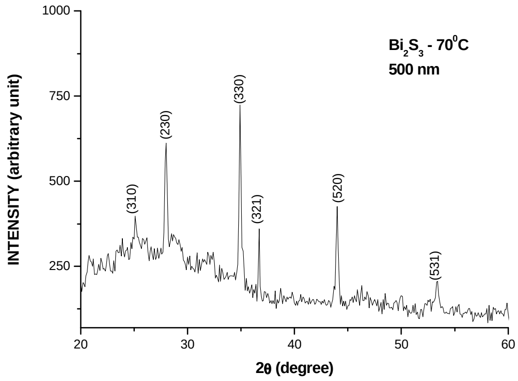


**Fig.4. X-ray diffraction pattern of $Bi_2S_3$ thin films of thickness 500 nm (bath temperature $70^0$C)**

**Table 1 Comparison of XRD data for $Bi_2S_3$ thin films with the JCPDS card (65-2435)**

| Temperature ($^0$C) | Thickness (nm) | Planes (hkl) | 2θ values (degree) | | d-spacing values d (Å) | | FWHM (β) (degree) |
|---|---|---|---|---|---|---|---|
| | | | JCPDS | Experiment | JCPDS | Experiment | |
| 40 | 191 | 310 | 25.288 | 25.26 | 3.5190 | 3.5036 | 3.4172 |
| | | 230 | 28.729 | 28.79 | 3.1049 | 3.1645 | 0.8696 |
| | | 330 | 34.017 | 34.06 | 2.6334 | 2.6342 | 0.6496 |
| 50 | 590 | 310 | 25.288 | 25.26 | 3.5190 | 3.5867 | 0.6926 |
| | | 230 | 28.729 | 28.76 | 3.1049 | 3.1985 | 0.6269 |
| | | 330 | 34.017 | 34.09 | 2.6334 | 2.6743 | 0.6016 |
| | | 520 | 43.751 | 43.79 | 2.4404 | 2.4786 | 0.8456 |
| | | 531 | 53.118 | 53.16 | 2.0674 | 2.0626 | 0.9145 |
| 60 | 860 | 310 | 25.288 | 25.26 | 1.7228 | 1.7469 | 0.4864 |
| | | 230 | 28.729 | 28.79 | 3.1049 | 3.1475 | 0.4334 |
| | | 330 | 34.017 | 34.06 | 2.6334 | 2.6899 | 0.2448 |
| | | 321 | 36.799 | 36.70 | 2.4404 | 2.4450 | 0.6864 |
| | | 520 | 43.751 | 43.76 | 2.0674 | 2.0776 | 0.4416 |
| | | 531 | 53.118 | 53.12 | 1.7228 | 1.7958 | 0.6811 |
| 70 | 500 | 310 | 25.288 | 25.26 | 3.5190 | 3.5678 | 0.6806 |
| | | 230 | 28.729 | 28.79 | 3.1049 | 3.1957 | 0.4679 |
| | | 330 | 34.017 | 34.06 | 2.6334 | 2.6976 | 0.3916 |
| | | 321 | 36.799 | 36.76 | 2.4404 | 2.4796 | 0.6969 |
| | | 520 | 43.751 | 43.79 | 2.0674 | 2.0956 | 0.6796 |
| | | 531 | 53.118 | 53.16 | 1.7228 | 1.9826 | 0.9446 |

**Table 2 The Structural parameters of the deposited $Bi_2S_3$ films**

| Temperature ($^0$C) | Thickness (nm) | Planes (hkl) | Grain size d (Å) | Dislocation Density X$10^{15}$ lines/m$^2$ | Strain ε X$10^{-3}$ |
|---|---|---|---|---|---|
| 40 | 191 | 310 | 25.033 | 159.57 | 14.610 |
| | | 230 | 98.965 | 10.210 | 3.6950 |
| | | 330 | 133.88 | 5.5790 | 2.7317 |
| 50 | 590 | 310 | 98.184 | 10.373 | 2.9612 |
| | | 230 | 137.28 | 5.3062 | 2.6642 |
| | | 330 | 135.75 | 5.3238 | 1.9085 |
| | | 520 | 105.35 | 9.0101 | 3.4717 |
| | | 531 | 100.33 | 9.9343 | 3.6452 |
| 60 | 860 | 310 | 176.70 | 3.2027 | 2.0698 |
| | | 230 | 199.77 | 2.5057 | 1.8308 |
| | | 330 | 358.30 | 0.7789 | 1.0207 |
| | | 321 | 128.73 | 6.0344 | 2.8410 |
| | | 520 | 204.66 | 2.3874 | 1.7871 |
| | | 531 | 137.66 | 5.2769 | 2.6567 |
| 70 | 500 | 310 | 125.69 | 6.3299 | 2.9097 |
| | | 230 | 183.92 | 2.9795 | 1.9886 |
| | | 330 | 222.06 | 2.0279 | 1.6471 |
| | | 321 | 125.53 | 6.3460 | 2.9134 |
| | | 520 | 126.04 | 6.2948 | 2.9017 |
| | | 531 | 97.13 | 10.599 | 3.7655 |

**Table 3 Preferential orientation factor of $Bi_2S_3$ thin films**

| Temperature ($^0C$) | Thickness (nm) | Plane (hkl) | Orientation factor (f) |
|---|---|---|---|
| 40 | 191 | 310 | 0.0766 |
| | | 230 | 0.7700 |
| | | **330** | **0.9912** |
| 50 | 590 | 310 | 0.3291 |
| | | 230 | 0.3174 |
| | | 330 | **0.3606** |
| | | 520 | 0.1563 |
| | | 531 | 0.1250 |
| 60 | 860 | 310 | 0.1847 |
| | | 230 | 0.2131 |
| | | **330** | **0.4122** |
| | | 321 | 0.1177 |
| | | 520 | 0.2071 |
| | | 531 | 0.1105 |
| 70 | 500 | 310 | 0.1711 |
| | | 230 | 0.2892 |
| | | **330** | **0.3621** |
| | | 321 | 0.1525 |
| | | 520 | 0.1854 |
| | | 531 | 0.0836 |

The significant improvement in crystallite size is due to controlled slow release of bismuth ions form its complex $[Bi(EDTA)]^+$ in the solutions which give probability of growth of larger particles [15]. But after $60^0C$, grain size decreases with film thickness[17]. This may be reason due to etching process involved at temperature higher than optimum (above $60^0C$).

## CONCLUSION

The films are found to be polycrystalline in nature with orthorhombic structure. The films are oriented in (330) direction. The grain size of $Bi_2S_3$ thin films are found to increase with increase of film thickness. The good quality of films are obtained at $60^0C$ (optimum temperature).

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