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EFFECT OF SUBSTRATE TEMPERATURE ON OPTICAL PROPERTIES OF Bi_2S_3 CHALCOGENIDE THIN FILMS

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Polycrystalline Bi_2S_3 thin films were prepared by a spray pyrolysis technique on glass substrate. The influence of substrate temperature on the structural and optical properties has been studied. The crystal structure and orientation of the prepared films were investigated by x-ray diffraction and observed that bismuth sulfide corresponds to orthorhombic crystal structure. The surface morphology was studied using field emission scanning electron microscopy. We have studied the variation in crystallite size and grain size with substrate temperature and observed a linear increase in crystallite size with substrate temperature along with increase in the size of grains. The size increment of the particles with substrate temperature was explained in terms of Ostwald ripening. The absorption spectra have been taken in the wavelength range 500 nm to 800 nm. The direct band gap of thin films was calculated from absorption spectra, which reveals that band gap decreases as the substrate temperature increases.

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1. Introduction

Recently, the synthesis of metal chalcogenides group $A_2^V B_3^{VI}$ (A = As, Sb and Bi; B = S, Se and Te) has been the focus of attention because of their important physical and chemical properties [1], wide applications in semiconductors [2], pigments [3], luminescence devices [4], solar cells [5], IR detectors [6], and thermoelectric devices [7]. Especially, Bi_2S_3, which is one family member of metal chalcogenides group, have drawn much attention by a large number of researchers [8, 9]. Many Bi_2S_3 nanostructures, such as nanowires, nanotubes, nanoflowers and nanorods, have been synthesized [10, 11]. Particularly, extensive investigations on the synthesis of Bi_2S_3 thin films have been carried out [12, 13]. There are many techniques including reactive vacuum diffusion [14], the hot wall chemical deposition technique [15], electrodeposition [16] and spray deposition [17], by which the Bi_2S_3 films may be deposited on glass substrates. Films prepared by these techniques are generally polycrystalline in structure, and their properties are critically influenced by the deposition process. In addition, the spray pyrolysis technique is particularly attractive because of its simplicity. It is widely used for large scale production of films owing to low production cost. It is also fast, inexpensive, vacuum-less and suitable for mass production [18].

2. Experimental details

The thin films of Bi_2S_3 were deposited by spray pyrolysis technique on glass substrates with different substrate temperature. The glass substrates were cleaned by diluted chlorhydric acid (HCl), washed by double distilled water and dried. The spraying solutions were obtained by

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dissolving the bismuth chloride ($BiCl_3$) and thiourea ($CS(NH_2)_2$) in doubly distilled water with a concentration of 0.2 M. The prepared solutions of bismuth chloride and thiourea were appropriately mixed to obtain a Bi: S proportion of 2: 3. One also notes that the prepared solutions were immediately sprayed to avoid any possible chemical changes with time. The orientation and crystallinity of these films were studied using x-ray diffractometer (Bruker AXS D-8 advanced) using CuK_α radiation (λ=1.54 Å) in θ–2θ geometry at scan speed of 0.5°/min. The microstructure was studied using a field emission scanning electron microscope (FEI Quanta 200 M). To prevent the charge buildup during FESEM observations, samples were coated with gold. Absorption and transmission spectra were taken using UV-vis-NIR spectrophotometer (Varian Cary 500) in the wavelength range 300-800 nm.

3. Result and discussion

3.1 Structural characterization

Fig. 1 shows the XRD pattern of Bi_2S_3 thin films deposited by spray pyrolysis technique on glass substrates at different substrate temperature, which revealed that the Bi_2S_3 corresponds to orthorhombic crystal structure. The intensity of diffraction peaks for the thin film phase increases and shift towards higher value as the substrate temperature increases from 350 °C to 550 °C. Fig. 2 shows the FE-SEM images of Bi_2S_3 samples at different substrate temperature.

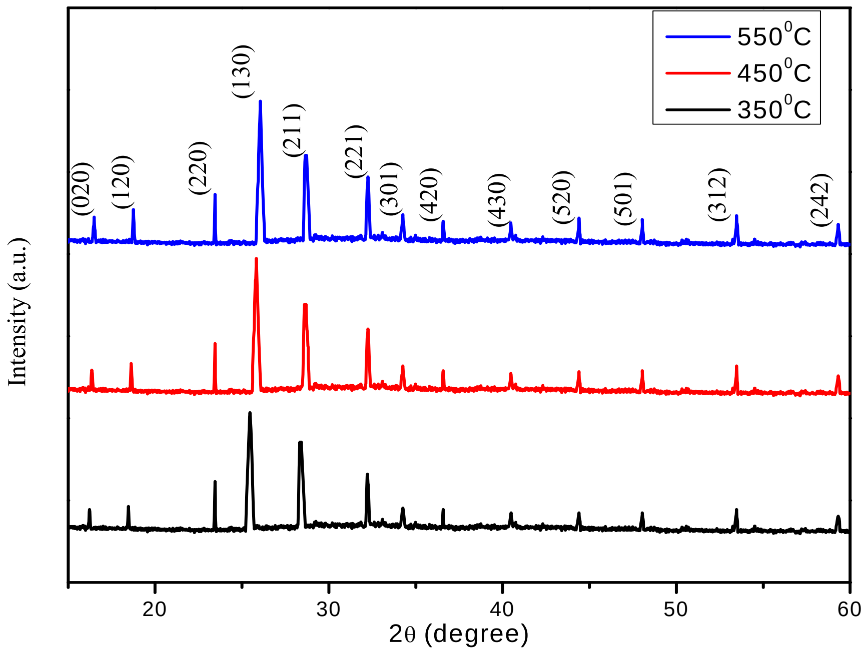

Fig. 1: X-ray diffraction patterns of Bi_2S_3 thin films prepared by spray pyrolysis method

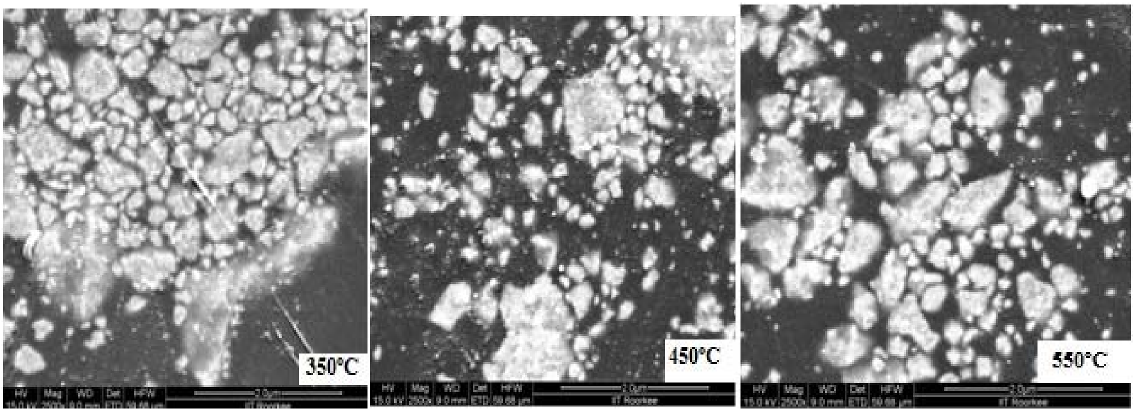

Fig. 2: SEM Micrograph of Bi_2S_3 thin films at different substrate temperature

For the orthorhombic lattice parameters evaluation, we have used the quadratic relation:

$$d_{h,k,l} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}} \tag{1}$$

where (h, k, l) are the Miller indices of reflecting planes appearing on the diffraction spectrum and $d_{h,k,l}$ is the spacing between adjacent planes. The calculated lattice parameters (orthorhombic unit cell parameters a, b, c) and unit cell volume (V = abc) are shown in Table 1. It is observed that the unit cell volume decreases as the substrate temperature increases.
The crystallite size of the samples is determined from x-ray data using Scherer's formula [19]

$$t = \frac{k\lambda}{\beta \cos\theta} \tag{2}$$

where k = 0.89 is the shape factor, λ is the wavelength of the x-rays, β is the full width half maximum (FWHM) and θ is the Bragg's angle. The calculated crystallite size is shown in **Table 1**. It is found that the crystallite size increases and full width half maximum (FWHM) decreases with substrate temperature. According to Ostwald ripening [20], the increase in the particle size is due to the merging of the smaller particles into larger ones and is a result of potential energy difference between small and large particles and can occur through solid state diffusion.

Table 1. Calculated values of various parameters for different substrate temperature.

Substrate Temperature (^oC)	lattice parameters			unit cell volume V(nm^3)	crystallite size (nm)
	a (nm)	b (nm)	c (nm)		
350	1.1192	1.1246	0.3993	0.5026	65
450	1.1032	1.1180	0.3912	0.4824	73
550	1.0987	1.1010	0.3897	0.4714	89

3.2 Optical properties

The optical absorption spectra of thin film at different substrate temperature are shown in Fig. 3.

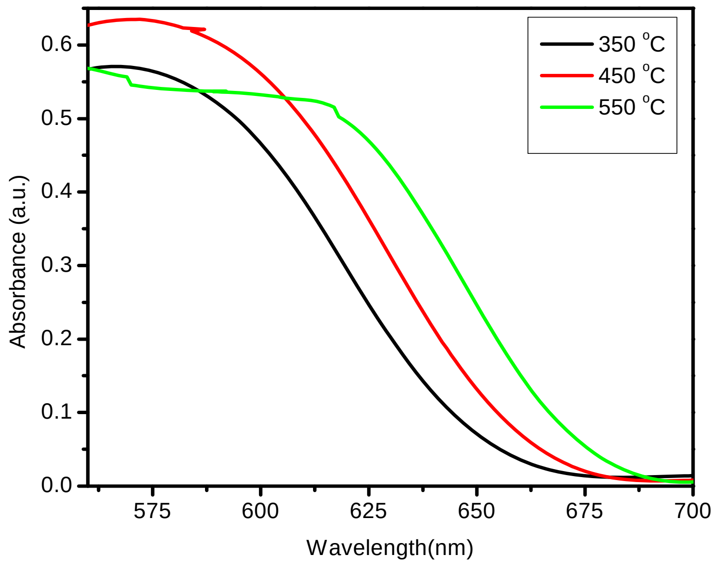

Fig. 3. Absorption spectra of Bi_2S_3 thin films with different substrate temperature

For the direct band-gap semiconductor, the relation between the absorption edge and photon energy (*hν*) can be written as follows [21]:

$$\alpha h\nu = A\,(h\nu - E_g)^{\frac{1}{2}} \tag{3}$$

where α is the absorption coefficient, A is a constant, h is Planck's constant, ν is the photon frequency and E_g is the optical band gap. The plot of $(\alpha h\nu)^2$ versus hν at different substrate temperature is shown in Figure 4. An extrapolation of the linear region of a plot of $(\alpha h\nu)^2$ on the y-axis versus photon energy (hν) on the x-axis gives the value of the optical band gap E_g. The variation of band gap with substrate temperature is given in Table 2. Typically band gap decreases from 1.96 to 1.89 eV because the particle size increases.

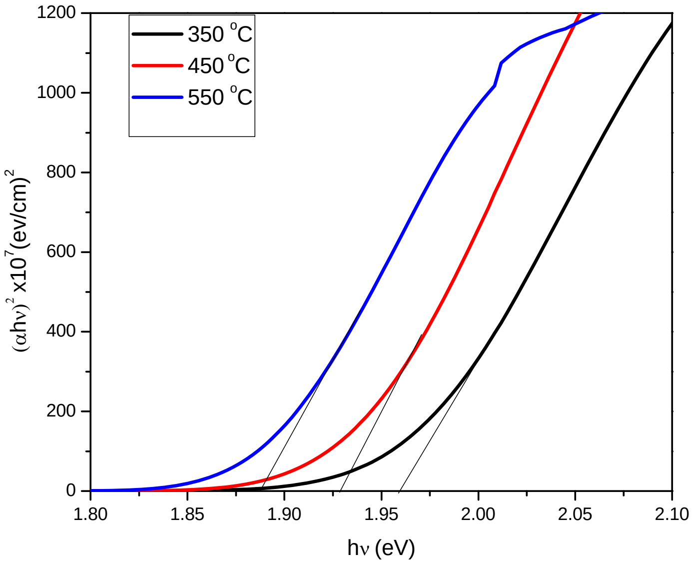

Fig. 4: Plot of $(\alpha h\upsilon)^2$ versus hυ for Bi_2S_3 thin films with different substrate temperature

Table 2. Variation of band gap with substrate temperature.

Sr. No.	Substrate Temperature (°C)	Band gap (eV)
1	350	1.96
2	450	1.92
3	550	1.89

4. Conclusion

Polycrystalline Bi_2S_3 thin films of orthorhombic phase were prepared by spray pyrolysis technique on glass substrates with different substrate temperature. The films were found to be uniform and adherent to the substrate. With the increase in substrate temperature, the diffraction intensity increases with a (1 3 0) preferred orientation. The particle size of Bi_2S_3 was changed from 65 nm to 89 nm as the temperature was changed from 350 to 550 °C. The band gap decreases from 1.96 to 1.89 eV as the substrate temperature increases from 350 to 550 °C.

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