EFFECT OF DEPOSITION TIME ON CHEMICAL BATH DEPOSITION PROCESS AND THICKNESS OF BaSe THIN FILMS.

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BaSe thin films were prepared through chemical bath deposition technique. The effect of deposition time was studied to determine the optimum condition for deposition process. The structure and morphology of thin films were investigated by X-ray diffraction and optical microscopy, respectively. The optical properties were measured to determine transition type and band gap value. The thin films produced were found to be polycrystalline with cubic structure. The x-ray diffraction peak at $2\theta = 25.8°$ shows the preferential orientation along the (021) plane. As the deposition period was increased up to 24hours, the film gradually grew thicker as shown by the photomicrograph. Also, the photomicrograph of the film revealed that the grains were distributed evenly over the substrate surface. The band gap value was found to vary from 2.6 – 2.9eV with direct transition.

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1. Introduction

The thin films technology has attracted much attention because of its unique size-dependent properties and applications in the optoelectronic devices, solar cells, sensors, and laser materials. In the past few decades, several techniques such as chemical bath deposition, vacuum evaporation, electro deposition, molecular beam epitaxy, thermal evaporation, spray pyrolysis, sputter deposition, metal organic chemical vapour deposition, and plasma-enhanced chemical vapour deposition have been used in the deposition of thin films. The preparation of thin films by chemical bath deposition technique is currently attracting a great deal of attention as the technique is relatively cost effective, has minimum material wastage, does not need sophisticated instrument and can be applied in large area deposition at low temperature. The chemical bath deposition method uses a controlled chemical reaction to deposit a thin film. In the typical experimental approach, the substrates are immersed in solution containing the chalcogenide source, metal ion, and complexing agent. The preparation and characterization of thin films by chemical bath deposition have been reported by many researchers. For example, CdSe (1), PbSe (2), CdS (3), CdSe (4), SnSe (5), ZnS (6), $CuInSe_2$ (7), Ag_2Se (8), $PbSnS_3$ (9) and ZnSe (10).

In this paper, we focus on the deposition of BaSe thin films using $Na_2S_2O_3$ as a complexing agent by chemical bath deposition method. In order to get good quality of thin films, the preparation parameter such as deposition period was optimized. The thin films have been characterized by x-ray diffraction for structure determination, optical microscope analysis for surface morphology study, and UV-Visible spectrophotometer for optical properties studies.

2. Materials and methods

The chemical bath contained 10 ml of 0.5 M of barium chloride ($BaCl_2$) mixed with 5ml of 0.1M K_2SeO_4. Then, 5 ml of 0.1 M of sodium thiosulphate ($Na_2S_2O_3$) used as complexing agent was added into this mixture and stirred well. The films are grown using a complexing agent in order to obtain good quality thin films. NH_3 was used to provide an alkaline medium for the growth of the films. The previously cleaned glass substrate was immersed vertically into chemical bath. The film growth was carried out at room temperature. The films were deposited in various

deposition periods (20-24 hrs) and pH 11 in order to determine the optimum condition for the deposition of barium selenide thin films. During deposition process, the chemical bath was kept undisturbed. The deposited films were tested for adhesion by subjecting it to a steady stream of distilled water. X-ray diffraction (XRD) analysis was carried out using a diffractometer for the 2θ ranging from 20˚- 70° with CuK_{α} (λ=1.5418 Å) radiation.

3. Results and discussion

Figure -1 shows the XRD patterns of thin films chemically deposited for a different deposition periods at pH 11. The chemical bath deposited thin films are found to be polycrystalline in nature.

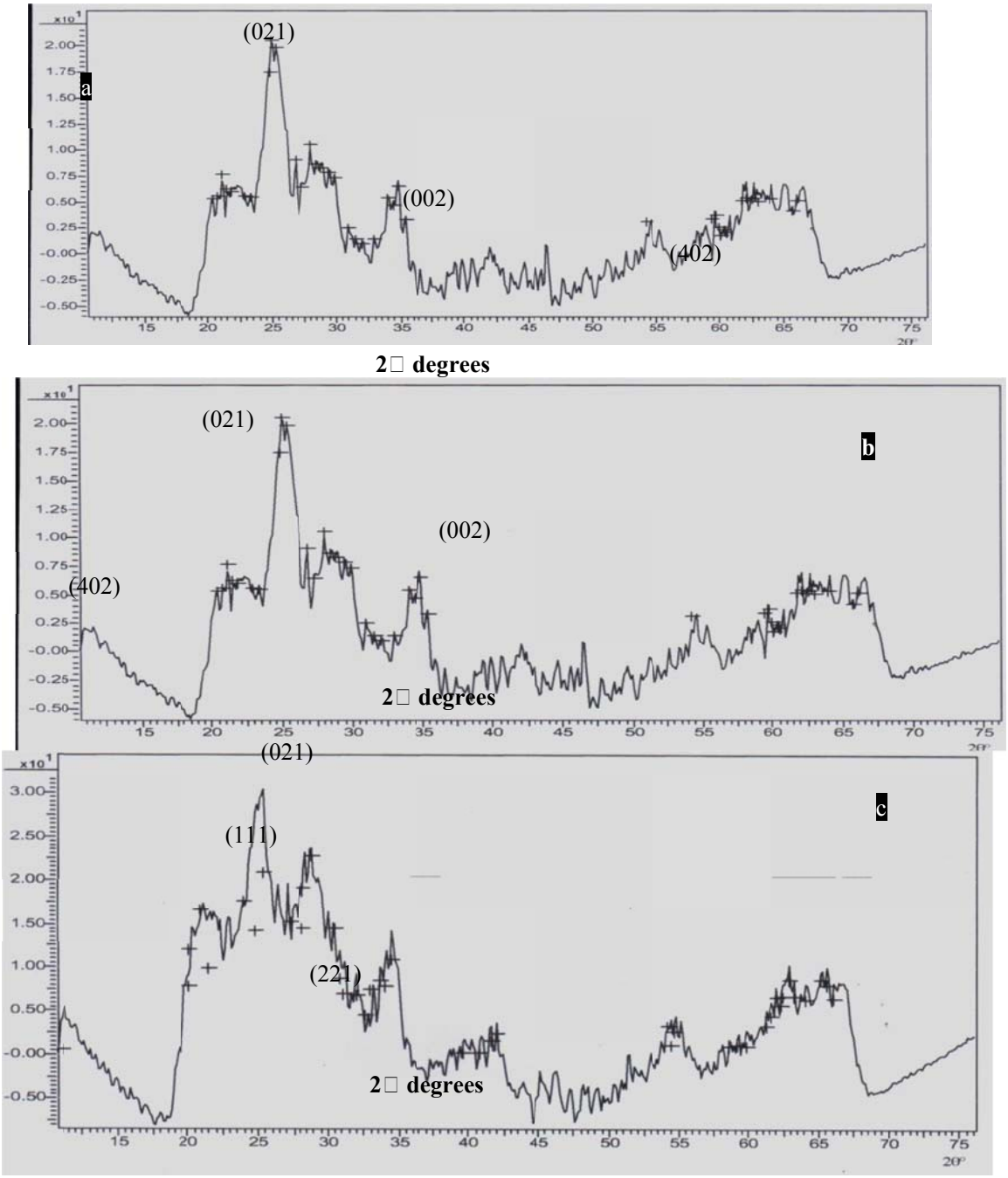

Fig. 1. X-ray diffraction patterns of BaSe thin films chemically deposited for a different deposition time at pH 11. (a) 20 hours (b) 22 hours and (c) 24 hours.

All the samples show at least three diffraction peaks at 25.8°, 35.4°, and 54.2° for L_9 & L_{10} which are associated with the (021), (002) and (402) reflections of cubic BaSe structure (figure- 1a & 1b) while L_{11} has diffraction peaks at 23.9˚, 25 8˚ and 54.2˚ which are associated with the (111), (021) and (221) reflections of cubic structure of BaSe (figure-1c). The x-ray diffraction peak at 2θ = 25.8° shows the preferential orientation along the (021) plane (11). The lattice parameter value for the dominant cubic structure is **a** = 6.6 Å. The grain sizes, D of the films which was calculated using Scherer formula were found to be 3.87Å, 3.90 Å and 4.03Å. It was revealed that the grain size increases with increase in film thickness. As the deposition time was increased from 20 to 22 hours, the grain size was increased from 3.87Å to 3.90Å. When the deposition time was further extended to 24 hours the grain size was 4.03Å and this was confirmed from the photomicrograph of the film which revealed that there were more materials deposited onto the substrate and thicker film was formed (fig.2c).

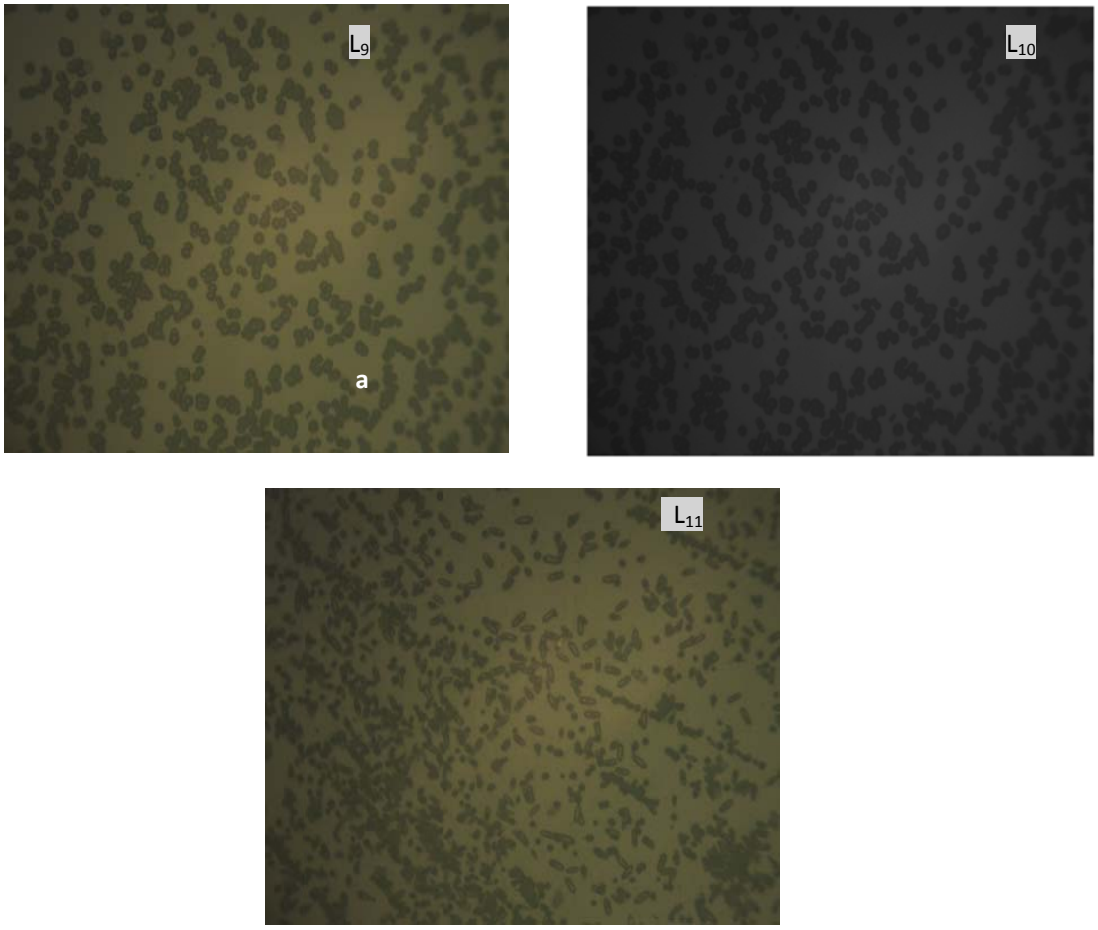

Fig. 2. Optical microscopy images of BaSe thin films chemically deposited for a different deposition times at pH 11. (a) 20 hours (b) 22 hours (c) 24 hours.

The optical properties of the films deposited on glass substrates were investigated from the absorption measurements in the range of 0.36-1.10µm. Figure -3 shows the UV-Visible absorption spectra of the films grown from a chemical bath at pH 11 under different deposition periods. The results show that the films deposited for 24hours produced higher absorption characteristics compared with other deposition periods. The spectra also showed a gradually increasing absorbance throughout the visible region, which makes it possible for this material to be used in photo electrochemical cells. The optical absorbance decreases as the film thickness increases.

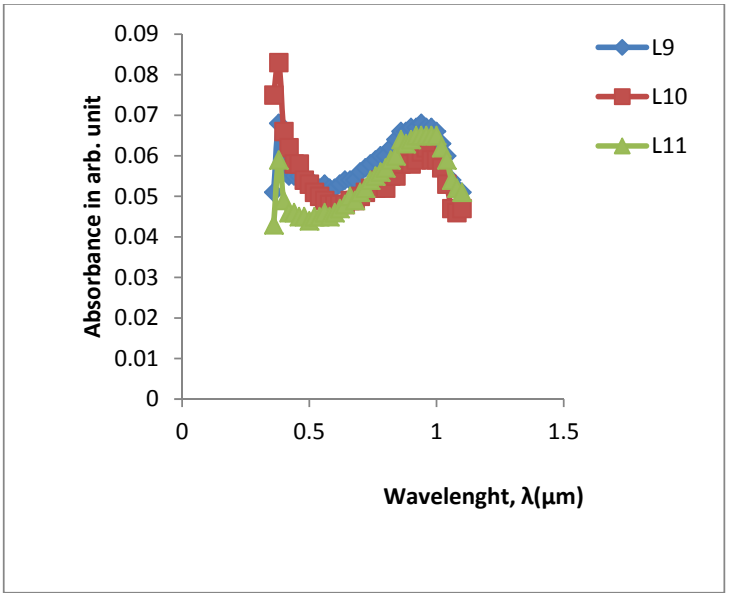

Fig. 3: Optical absorbance versus wavelength of the BaSe thin films chemically deposited in different deposition time at pH 11.

Band gap energy and transition type can be derived from mathematical treatment of data obtained from optical absorbance versus wavelength with relationship of near-edge absorption: $\alpha = (h\upsilon - \varepsilon_g)^{n/2}$ where α is the frequency, h is the Planck's constant, while n carries the value of either 1 or 4. The value of n is 1 and 4 for the direct transition and indirect transition, respectively. The band gap (E_g) can be obtained from a straight line plot of α^2 as a function of hν. Extrapolation of the line to the base line, where the value of α^2 is zero, will give the band gap. The α^2 versus hν plot is a straight lin (Fig. 4) indicating that the energy band gap of BaSe is direct, and intercept on the hν axis yields a band gap of 2.9 eV for the film deposited at pH 11 for 24 hours.

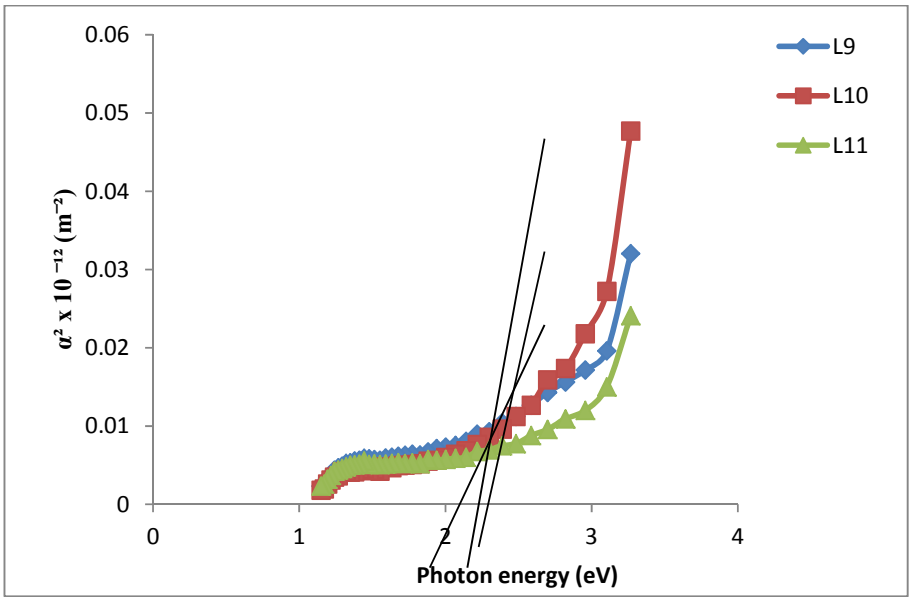

Fig. 4. Absorption coefficient square versus photon energy of the BaSe thin films chemically deposited in different deposition time at pH 11.

Fig. 4 shows that the band gap decreases as the film thickness increases. The variation of film thickness with energy band gap of BaSe film is shown in table-1

Table-1: Variation of band gap with film thickness.

Reaction Bath	Film Thickness (μm)	Time of Deposition (hr)	Band gap (eV)
L_9	1.64	20	2.90
L_{10}	1.65	22	2.80
L_{11}	1.66	24	2.60

It is found that the band gap of barium selenide is thickness dependent. The increase in film thickness results in decrease in energy band gap of BaSe films. This is true because with increase in film thickness the individual levels of the free atoms will broaden the energy bands and create overlapping levels .This occurs when atoms are brought closer to each other. Hence with high film thickness there are several energy levels resulting in several overlapping energy bands in the band gap of these films. The overlapping energy bands therefore tend to reduce the energy band gap, (12-13) resulting in lower band gaps for thicker films.

4. Conclusions

BaSe thin films have been chemically deposited on glass substrates from aqueous solutions containing $BaCl_2$, K_2SeO_4, $Na_2S_2O_3$, and NH_3. The thin films produced are found to be polycrystalline with cubic structure. The x-ray diffraction patterns showed that the most intense peak at $2\theta = 25.8°$ belonged to (021) plane of BaSe. As the deposition period was increased up to 24 hours, the film starts to grow thicker as could be seen in the photomicrograph. The optical microscopy image showed that this film has uniform, smaller crystal size and covered the entire substrate surface completely. Therefore, deposition at deposition period for 24 hours and growth at room temperature was found to be the optimum condition to prepare good quality thin films under the current condition. The band gap value was found to vary from 2.6eV - 2.9 eV with direct transition.

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