

Comparative analysis of the structural and optical properties of some selected Selenides for applications in optoelectronic devices

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ABSTRACT

The study reports on the comparative investigations of some selected selenides (cadmium selenide CdSe, lead selenide PbSe and copper selenide CuSe) grown using the chemical bath deposition technique, with emphasis on the influence of concentration and annealing temperatures on the structural and optical properties of the layers. The as-grown layers were deposited at a temperature of 50 °C and annealed at annealing temperatures ≤ 400°C. The layers were characterised using X-ray diffractometry (XRD) and optical spectroscopy analysis. The results show that the film thickness increased with an increase in the concentration and annealing temperatures for PbSe films. For CdSe layers, the film thickness increased up to a concentration of 0.4 M and then exhibited a marginal decrease thereafter while for CuSe a sharp increase was observed for concentrations > 0.6 M. At concentrations > 0.6 M, the crystallite size increased with an increase in concentration for CuSe layers and decreased for PbSe thin films while a marginal increase was observed for CdSe layers. The energy bandgap of the trio were found to be in the range 1.15 eV to 2.4 eV for the as-deposited layers. However, annealing the layers resulted in the decrease of the energy band gap for the PbSe layers. The range of the energy bandgap obtained in the study, suggest possible use of the layers in various optoelectronic devices.

Keywords: Selenides, Optoelectronic devices, Concentration, Annealing.

INTRODUCTION

Binary selenides has been widely investigated for applications in various industries. These selenides mostly find applications in the optoelectronic industry as; solar cells, infrared detectors, photo-detectors, and in microwave devices. For instance, CdSe thin films has been utilised in solar cell devices as window layers owing its wide energy bandgap and n-conductivity type [1-2] while PbSe-based solar cell devices are also reported [3]. Copper selenide is amongst the semiconductor that is mostly used as absorber layers in solar cell fabrication because of it has been shown to exhibit p-type conductivity. Successful use of these selenides in transistors [4-6], switching devices [7-12], and detectors [13-18], has been reported in the literature. These selenides (cadmium selenide CdSe, lead selenide PbSe and copper selenide CuSe) can easily be deposited using low cost deposition technique which include chemical bath deposition [19-33], SILAR (successive ionic layer and reaction) [34-36], electrodeposition [37-45], and spray pyrolysis [46-51].

In this study, the structural and optical properties of these selenides were investigated to determine their possible use in different optoelectronic applications such as solar cells and in other photonic devices. Although there are some reports in the literature on the study of these selenides, reports on their comparative studies is rare, hence this

investigation will fill a fundamental and important gap in the literature of binary selenides and thus serve as useful tool for further investigations by the research community.

MATERIALS AND METHODS

Substrate preparation : The substrates used were sodalime glass. The substrates were thoroughly cleaned with detergent and degreased with acetone. The sodalime glasses were further cleaned ultrasonically for 15 min and then dried.

CdSe preparation: For the CdSe films, the first step was the preparation of a 1M CdCl₂ (cadmium chloride), 2M TEA (*Tetraethylammonium*), 3M NH₄OH (ammonium hydroxide), and 1M Na₂SeSO₃ (sodium selenide trioxosulphate (vi)), with each of these solution put in a separate beaker. This was followed by the formation of a reaction bath made by preparing the respective concentrations (0.2 M, 0.4 M, 0.6 M, 0.8 M and 1.0 M) of CdSe in different graduated beaker. The sodalime glass slides were carefully labeled and then dipped into the solution. The deposition time was fixed for 5 h and the deposition temperature was 50 °C in all cases. After 5 h, the films were removed and then washed thoroughly with distilled water and then dried.

PbSe preparation: The lead selenides films were grown by preparing varying solutions of the appropriate salts (lead nitrate, sodium citrate, sodium hydroxide, and sodium selenosulphate). The substrates were held vertically through a synthetic foam and then immersed into the solution, with the deposition temperature and time maintained at 50 °C and 5 h as in the case of the cadmium selenide film.

CuSe preparation: The thin films of copper selenide were grown on glass substrate using the chemical bath deposition technique and the starting materials used were cupric chloride and sodium selenosulphate. The pH of the reaction mixture was adjusted with the presence of sodium hydroxide and ammonia solution. The substrates were held vertically through a synthetic foam and then immersed into the solution, with the deposition temperature and time kept constant at 50 °C and 5 h respectively.

Film deposition: Film deposition using chemical bath deposition occurs through different process. It has been established that film deposition on a substrate occurs in two steps of nucleation and particle growth [52]. Nucleation and film growth can be due to an inter-play of other processes such as: simple-ion cluster mechanism, simple hydroxide cluster mechanism, complex ion-by-ion decomposition mechanism, and the complex-cluster decomposition mechanism. The simple ion process could diffuse to the substrate to initiate nucleation and the nucleated layers then grow by adsorption of ions in the solution and or nucleation of new crystals. It is believed that film deposition in this study is by simple-ion cluster mechanism.

Post-deposition heat treatments: The films were annealed using an annealing furnace with a constant annealing time of 60 min and the annealing temperature was varied between 100 °C to 400 °C.

Characterisation of the films: The structural characterisation of the as-deposited and annealed layers was investigated using a Philips PW 1500 XRD equipment while the optical spectroscopy (absorbance and transmittance measurements) was done using a Unico –UV-2102PC spectrophotometer at normal incident of light in the wavelength range of 400 nm to 1100 nm.

RESULTS AND DISCUSSION

Structural Analysis: Fig. 1 gives the variation of the film thickness with different concentrations. The film thickness increased with an increase in the concentration for the PbSe layers. The variation of the concentration with film thickness for CdSe and CuSe could be approximated to a decreasing trend except for concentration > 0.8 M for copper selenides layers. Increase in the concentration of thin films with film thickness is commonly observed despite the deposition method as reported by other authors [24, 28, 35, 53]. However a decrease in film thickness with increase in concentration is also observed [36, 54] and could attributed to the mode of film formation and nature of the source or substrate materials. The data extracted from the XRD measurement was used to deduce the crystallites size. The crystallite size was calculated using the Scherrer's formula given as [55-57]:

$$C = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

In equation (1), C is the crystallite size, k is a constant (0.89-0.94), λ is the wavelength of the wavelength of the $\text{CuK}\alpha$ radiation source given as ($\lambda = 0.15406 \text{ nm}$), β is the full width at half maximum of the most prominent peak and θ is the Bragg angle.

The crystallite size was observed to increase sharply with an increase in concentration at certain range, for PbSe and CuSe layers, with a marginal increase for CdSe layers. Fig. 2 gives the variation of the crystallites size with concentration. The most striking feature was observed for concentration $> 0.6 \text{ M}$ in that the crystallites size decreased for lead selenide films and exhibited a rapid increase for the copper selenides films. The decrease in the crystallite size of the lead selenides can be caused by the fragmentation of crystallites arising from the increased concentration or other effects. Fragmentation of the crystallites in thin films have been reported in the literature for the chalcogenides (tin sulphide) grown by the thermal evaporation technique [58-60].

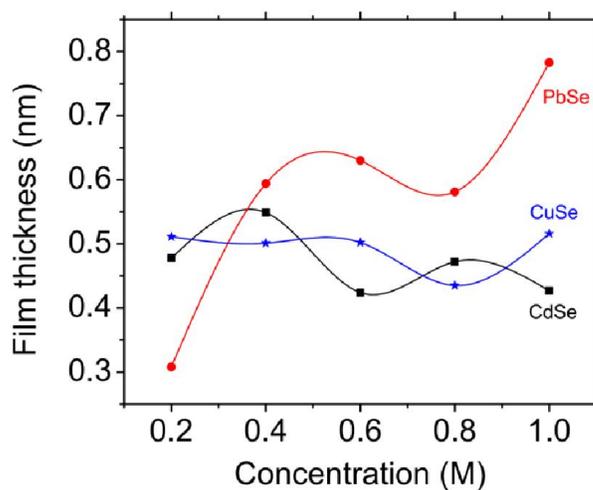


Fig. 1: Variation of film thickness with concentration

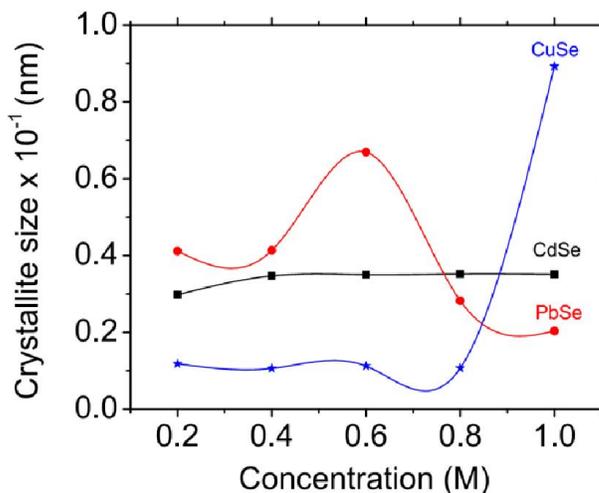


Fig. 2: Variation of crystallite size with concentration

Optical Analysis: Fig. 3 gives the change of the energy bandgap with concentration. The absorption coefficient (α) and the energy bandgap E_g was calculated using the relation given as [61-64];

$$\alpha = \frac{\left[\ln\left(\frac{1}{T}\right) \right]}{t} \text{ for } \lambda_c > \lambda \quad (2)$$

In equation (2), T is the transmittance, t is the film thickness, where λ and λ_c are the incident and critical wavelengths at the regions where absorption takes place. According to Kawano et al. [65], the absorption in the regions near the fundamental absorption edge, behaves as;

$$\alpha E = A(E - E_g - E_p)^x \quad (3)$$

In equation (3), E is the photon energy, E_g is the optical band gap, and E_p is the phonon energy. Usually for processes involving direct transitions, the exponent x is equal to 1/2 for allowed transition and 3/2 for forbidden transition. The exponent x is equal to 2 for allowed transition and 3 for forbidden transitions for process involving indirect transition. As shown in Fig. 3, the energy bandgap decreased with an increase in concentration for the lead selenides layer and increased otherwise for copper selenides thin films. This behavior is in line with that observed for the variation of the crystallites size with the film thickness. The energy bandgap were obtained as direct and the values are within the range reported by other authors [26-27, 35, 44, 46, 66].

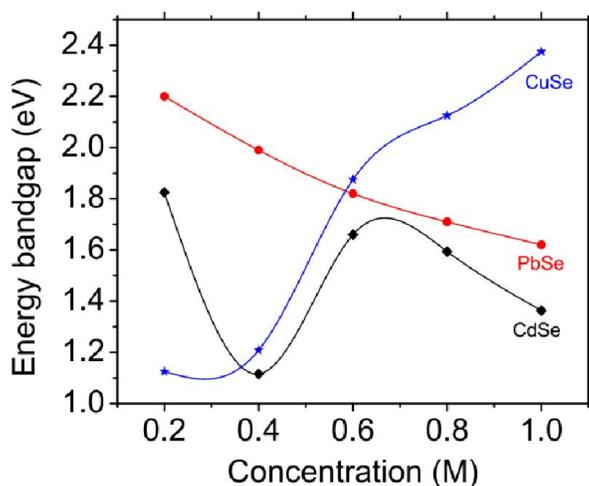


Fig. 3: Variation of energy bandgap with concentration

Influence of Heat Treatments: The film thickness increased with the annealing temperatures at the onset and then decreased as indicated in Fig. 4. For annealing temperatures < 200 °C, the effect of the annealing on the reduction of the film thickness is very much pronounced for the PbSe and CdSe layers. There is an increase in the film thickness at annealing temperatures ≥ 200 °C for PbSe and CdSe layers, and decreased compared to the as-deposited case thereafter. For the higher annealing temperatures, there is a decrease in film thickness for lead selenides and an increase for cadmium selenides. This behavior is explained on the basis of the difference in the vapour pressure of the respective selenides (PbSe and CdSe). For the CuSe layers, the film thickness was relatively constant. The relative change in film thickness with increasing annealing temperature is due to the re-evaporation of copper particles during the annealing process. Post-deposition heat treatments of copper selenide thin films has been reported in the literature [20, 44].

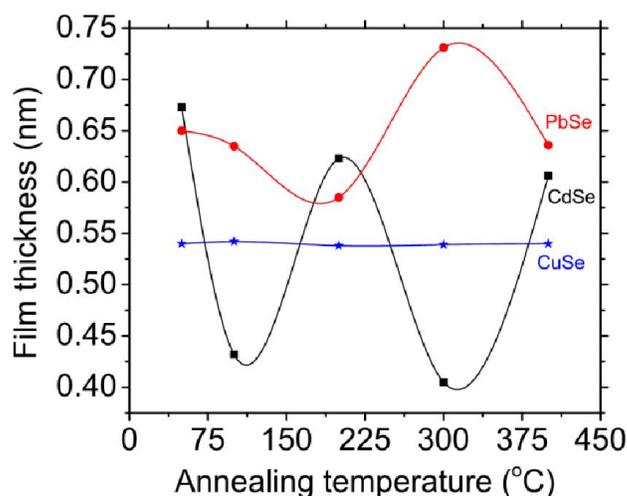


Fig. 4: Variation of film thickness with annealing temperature

The effect of annealing on the energy bandgap is indicated on Fig. 5. The results show an increase in the energy bandgap with increasing annealing temperatures for the copper selenides and cadmium selenides layers for annealing temperatures > 225 °C. This is possibly due to an increase in the crystallite size/grain size caused by the post deposition annealing treatments. The decrease in the energy bandgap for the copper selenides for annealing temperatures < 225 °C was attributed to the low thermal energy at the lower annealing temperatures such that grain enlargement was not possible due to low surface mobility. The decrease in the energy bandgap observed for the lead selenides layers was more steep at the onset, and then becomes more gradual and marginal at the higher annealing temperatures. Variation in the energy bandgap in

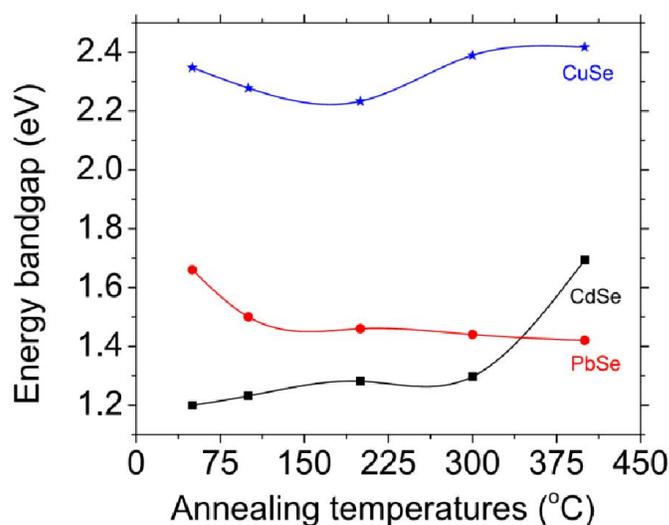


Fig. 5: Variation of energy bandgap with annealing temperature

thin films, induced by a post-deposition heat treatments has been reported by other authors in the literature for other selenides and sulphides of similar/different materials and these authors attribute it to the change in the deposition variables or due to a quantum size effect [66-70].

CONCLUSION

Selected selenides were deposited using the chemical bath deposition method and investigated using structural and optical characterisation techniques to establish the suitability of the layers in various optoelectronic applications. The effect of concentration on the properties of the layers and the influence of post deposition annealing was also investigated and reported. The results show that the film thickness increased with an increase in the concentration for the lead selenide layers and decreased for the copper and cadmium selenides thin films. The energy bandgap obtained for the three different selenides suggest the possible use of the layers solar cell devices and in other optoelectronic and photonic devices.

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