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Annealing Effects and Film Thickness Dependence of Cobalt Selenide Thin Films Grown By the Chemical Bath Deposition Method

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Abstract : *Thin films of CoSe (cobalt selenide) were prepared using the chemical bath deposition technique. The deposition variables such as the pH, bath temperature, and source to substrate distance were kept constant and the film thickness was varied by varying the concentrations. The films were then annealed at annealing temperatures $\leq$ 250 ^oC. The films were characterised using scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDAX), and X-ray Diffractometry (XRD) to investigate the morphological, compositional and structural properties of the as-deposited and annealed layers. The results show that the post-deposition annealing improved the properties of the layers. In particular, an increase in the grain size was recorded for annealing temperatures $\leq$ 200 ^oC.*

Keywords: *– Annealing, Chemical bath deposition, Film thickness, Grain size, Thin films*

I. Introduction

The use of different selenides in thin film form for applications in different electronic, optoelectronics and in nanotechnology industry has been widely reported in the literature. In recent times, interest in the chalcogenides of semiconductors, metals and transition metals have increased tremendously because of their tunable properties which makes them useful candidates in various electronics and optoelectronic devices including solar cells, sensor, laser materials, photoconductors, diodes and transistors [1-15]. It is generally understood that chemical techniques for the preparation of semiconducting chalcogenides thin films offer the advantages of economy, convenience and the capability of large-area deposition. Thin film deposition of chalcogenides of nickel, bismuth, antimony, cadmium, copper, zinc tin, and indium selenides have been reported by various research groups [16-25]. Most recently, cobalt selenides is reported to be used as high performance counter electrodes in dye sensitized solar cells [26-27], as catalysts [28], waste water treatments [29], photoelectrodes [30-32], and magnetic devices [33].

It has been established in the literature by different research groups that thin films of cobalt selenides can be grown using different low cost deposition techniques. These deposition methods include chemical bath deposition technique [34-35], electro-deposition [30-32, 36-38], solvothermal synthesis [29], and chemical synthesis [39-41]. Chemical bath deposition is a cost effective technique that yield high quality thin films and the basic principles is mostly by the controlled precipitation of the desired compound from a solution of its constituents. In the present investigation, the deposition of cobalt selenides thin films grown by chemical bath deposition at room temperature is reported, with emphasis on the influence of the different annealing temperatures on the morphological compositional and structural properties of the films. The effect of the deposition conditions and post deposition annealing on the film thickness is also presented. This report is a fundamental step in determining the optimised conditions needed for increased efficiency of cobalt selenides thin films especially when utilised in electronic devices such as solar cells, diodes, and transistors.

II. Materials And Method

The glass microslides used as substrates were initially soaked in dilute hydrochloric acid for 2 hours, removed and dipped into acetone for 1 hour after which they were removed, washed with foam- sponge in ethanol and finally rinsed in distilled water. They were then dried in oven at 30^oC above room temperature for 30 minutes. Before deposition of films on them, the substrates were brought out of the oven and their temperature allowed to drop to room temperature. Pre-cleaned glass substrates were then inserted vertically into the growth mixtures using synthetic foam. The loaded substrates were labelled for easy identification. The deposition time was fixed for 4 h at a constant temperature of 60 ^oC. The films were removed and rinsed with distilled water and then dried in air. The films were then annealed in an oven with the annealing temperatures kept between the range of 100 ^oC to 250 ^oC with the annealing time fixed for 1 hour.

The films were characterised using scanning electron microscopy to investigate the morphological properties, using the Hitachi 5-4200 analytical scanning electron Microscope at Sheda Science and Technology complex, Abuja, Nigeria. The compositional analysis was done with the energy dispersive X-ray spectroscpy. The photomicrographs of the thin films were taken with Olymus B.H.3 photomicroscope at 200 magnification at Engineering and Material Development Institute, Akure, Nigeria. The structural characterisation was done with the X-ray diffractometry with the MD -10 mini diffractometer at Engineering and Material Development Institute, Akure, Nigeria.

III. Results And Discussion

Fig. 1 show the scanning electron micrograph for a typical as-deposited CoSe thin film for a thickness of 550 nm. As indicated in Fig. 1, the grains are relatively scattered with dense leaf-like structures. This scattering of grains can be due to the mode of the film formation. Film formation for chemical bath deposited films is mostly by nucleation. The major modes of film formation has been widely discussed in the literature [42]. In the literature, variation of grain morphology have been reported for other chalcogenides thin films independent of the deposition techniques [1, 13, 21] while Guar et al [39] reported on poly-crystalline leaf-like cobalt selenide thin films.

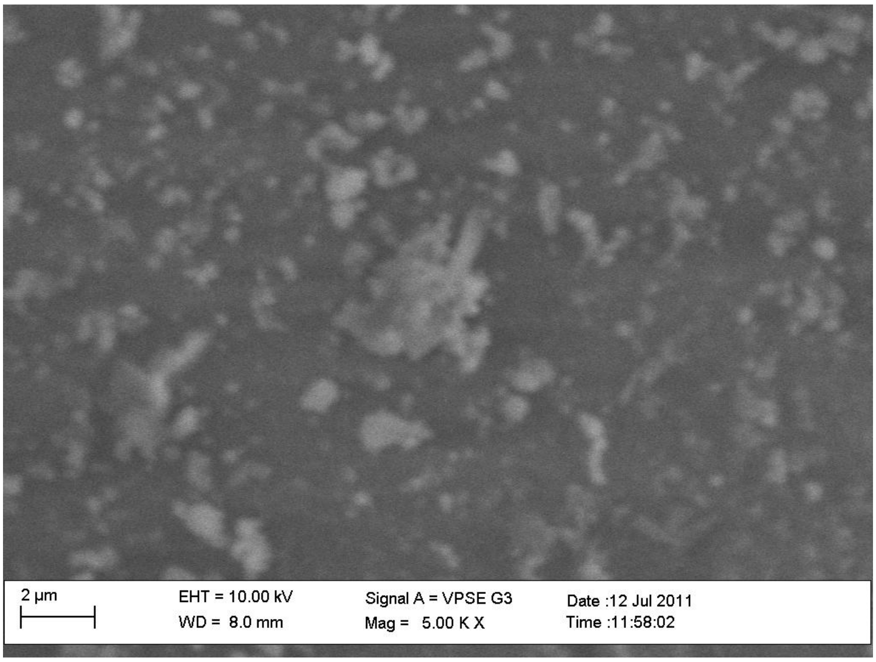

Fig. 1. Scanning electron micrograph of CoSe thin film with film thickness of 550 nm

Fig. 2 gives the scanning electron micrograph of an annealed CoSe thin film. As shown in Fig. 2, there was a clear evidence of the densification of the grains after the post-deposition heat treatments. The grains were enlarged such that the islands that were slightly observed physically in Fig. 1, were almost filled up, implying a decrease in the grain boundary. Post-deposition annealing is amongst the established process of improving grain size in thin film deposition. An increase in the grain size due to post-deposition annealing has been reported by other authors independent of the deposition techniques [43-44].

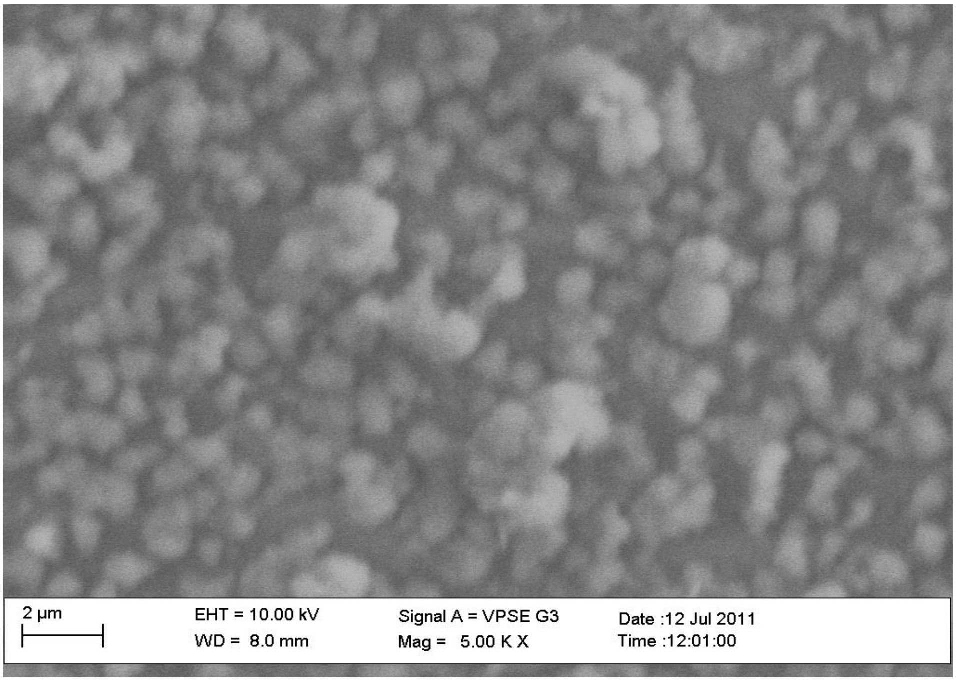

Fig. 2. Scanning electron micrograph of annealed CoSe thin film with film thickness of 545 nm

From the X-ray diffraction (XRD) profiles of the CoSe thin films deposited using different film thicknesses, the spectra (not shown) indicated that all the grown films were polycrystalline in nature. The films had the hexagonal crystal structure with observed peaks that are consistent with the Powder Diffraction File: 25-0125. The observed prominent peaks included the <121>, <112>, <222>, <212>, and <032> diffraction peaks that correspond to CoSe, in line with the Joint Committee on Powder Diffraction Standard (JCPDS) : 25-0125. Wang et al [38] reported on electrodeposited Se-rich CoSe thin films and observed similar hexagonal crystal structure and compact morphology, while Lai et al [30] also observed hexagonal crystal structure for electrodeposited CoSe thin films. The data extracted from the X-ray diffractometry analysis was used to deduce the crystallite size using the Scherrer's formula. The Scherrer's formula is given in the literature as [21-23, 42-43];

$$D = \frac{0.94\,\lambda}{\beta\ Cos\ \theta} \qquad (1)$$

In equation (1), D is the crystallite size, β is the full width at half maximum (FWHM) of the diffraction peak, θ is the Bragg angle, and λ is the wavelength of CuKα radiation source given as (λ = 0.15406 nm). The results show that the best layers had an average crystallite size of 30.61 nm. This is indicated in Table 1.

Table 1: Variation of crystallite size of annealed CoSe Thin Films (film thickness = 545 nm)

2θ	<h k l>	d	FWHM	Crystallite Size (nm)
28.71	1 2 1	3.109	0.276	53.85
30.19	1 1 2	2.960	1.329	11.28
39.49	2 2 2	2.261	0.812	18.82
40.90	2 1 2	2.206	0.226	68.34
41.17	0 3 2	2.192	0.208	7.73

Fig. 3 indicates the variation of film thickness with concentration. As shown on Fig. 3, the film thickness was maximum at the concentration of 0.25 M, and then decreased thereafter. The decrease in film thicknes for concentrations > 0.25 M was attributed to the effect of dissociation in the growth media. Other research groups have reported similar findings in the literature [45].

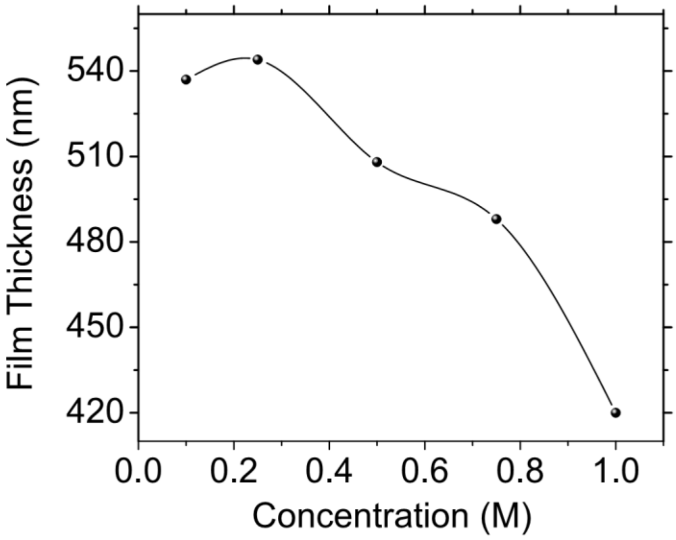

Fig. 3. Variation of film thickness at different concentrations.

Fig. 4 show the effect of the post-deposition annealing on the film thickness of the cobalt selenides thin films at the different annealing temperatures. As shown on Fig. 4, there is an increase in the film thickness for annealing temperatures ≤ 200 ^{o}C. The observed increase in the film thickness is

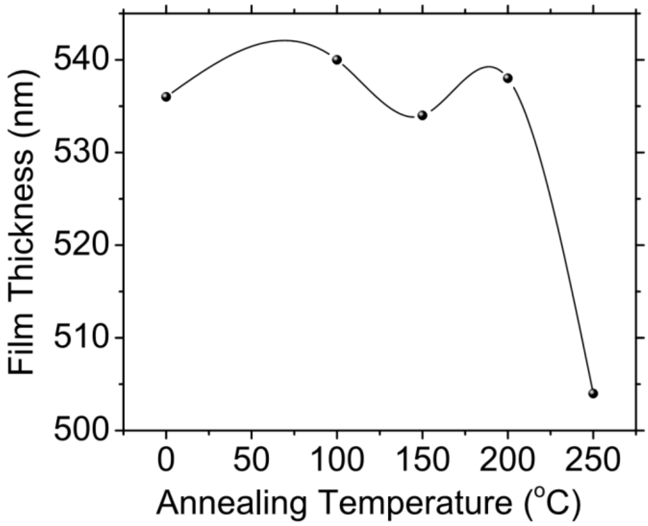

Fig. 4. Variation of film thickness at different annealing temperatures.

In line with the earlier observation indicated in Fig. 2. The increase in the film thickness was due to the increase in the grain sizes induced by the post- deposition heat treatments. Increase in film thickness caused by the change of deposition variables/post deposition annealing has been widely reported in the literature [46-47]. Cifuentes et al [48], observed an increase of film thickness for thermally evaporated SnS thin films and noted that this was caused by the changes in the band structure and the superposition degree of electron clouds of neighboring atoms in the films.

IV. Conclusion

In the present investigation, the morphological, compositional and structural properties of cobalt selenides thin films grown using the chemical bath deposition method, and the effect of post-deposition annealing on the as-grown layers is reported. The results show that the influence of annealing on the layers resulted on the increase in the crystallite size with better and uniform film thicknesses. The average crystallite size that was obtained for the best layers was 30.61 nm.

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