The Influence of Bath Temperature on the Properties of SILAR Deposited Cobalt Selenide Thin Films

Abstract—In this paper, cobalt selenide thin films have been deposited onto glass slides with the SILAR method under various bath temperatures. The structure, optical properties, and morphology of thin films were investigated. The X-ray diffraction patterns confirmed that the number of peak intensities increased with increasing bath temperature. From the AFM images, bigger sizes and thicker films were observed for the films prepared at 80°C. The average grain size was estimated to be 0.2μm, 0.15μm, and 0.25μm when the bath temperature was 40°C, 50°C, and 80°C respectively. The highest absorbance value was observed for films prepared at 80°C. The band gap values range from 2eV to 2.4eV.

Keywords—thin films; cobalt selenide; semiconductor; band gap; solar cells; SILAR technique

I. INTRODUCTION

Growing fuel prices and the fast depleting of conventional energy sources lead to the necessity of the investigation on sustainable and efficient energy sources. Renewable energy has been suggested as a viable approach. Presently, many research groups have focused on solar energy as the most promising renewable energy to cater the future energy demand due to its abundance and inexhaustibility [1, 2]. Due to the effort of finding new materials, Transition Metal Chalcogenides (TMCs) are proposed as the most satisfactory semiconductor materials for Photo Electro Chemical (PEC) application. TMCs are a combination of transition metals and chalcogenides (group 16), MX₂ (M: Cd, Mo, Co, Zn, Cu, Ni, Fe, Sn, etc., X: S, Se, and Te). TMCs possess excellent optical, electrical, and semiconductor properties, especially in the thin film form [3]. This advancement has motivated many researchers to investigate TMC materials namely, CdS [4], CdSe [5], ZnS [6], SnS [7], ZnSe [8], CuInTe₂ [9], CuInS₂ [10], ZnTe [11], Ni₃Pb₂S₄ [12], CuTe [13], and Cu₂SnS₄ [14]. Chalcogenide thin films can be fabricated by electrodeposition, spray pyrolysis, electrochemical deposition [15], and sputtering [16]. One attractive method for producing cobalt chalcogenide thin films, due to the possibility of large area deposition at low cost, is the Successive Ionic Layer Adsorption and Reaction (SILAR) deposition method. It is a cost-effective method that can be controlled easily [17, 18]. It is the process of enlarging the thin film by separating the weakly bound elements in the pure water from the surface after immersing the substrate material at certain times and immersing it in cationic and anionic solutions [19, 20]. The SILAR method consists of four steps [21]: dipping into cationic solution, rinsing in de-ionized water, dipping in anionic solution and rinsing again in de-ionized water. It is shown that cobalt chalcogenides have higher electronegativity, so it is proposed to study the synthesis, growth mechanism, optical and semiconducting properties of these thin films in a more systematic way. Selenium and sulphur (X=S, Se), are non-metal while tellurium (Te) is a metalloid. Hence, the chemical behavior and reaction of sulphur and selenium are similar to telluride. In the present research work, focus is given only to cobalt selenide. The aim of this work is to investigate the influence of bath temperature on the formation of cobalt selenide thin films. The SILAR deposition technique was used to synthesize films for the first time. Characterization of films was carried out by using XRD (X-Ray Diffraction), AFM (Atomic Force Microscopy), and an UV-visible spectrophotometer.

Thin films can be used in various fields including solar cells, optical devices, energy storage devices, environmental applications, laser devices, and telecommunications devices. These materials have a great impact on the modern era of technology. Thin films (binary, ternary, quaternary, and penternary compounds) can be produced by physical and chemical deposition techniques [22-24]. The selection of deposition method depends on the production cost, the specific application, the properties of films and available resources. Cobalt sulphide [25-30], cobalt telluride [31-34], and cobalt selenide [35-40] thin films have been synthesized via various deposition techniques. In this work, the SILAR method was selected to produce cobalt selenide films. Staring materials such as cobalt (II) chloride hexahydrate and sodium selenite were used to deposit thin films onto glass substrate for the first time.

II. EXPERIMENTAL PART

Cobalt (II) chloride hexahydrate (CoCl₂·6H₂O) and sodium selenite (Na₂SeO₃·Se) were used without further purification. Microscope glass slide was used as substrate during the deposition process. This substrate was cleaned by acetone and de-ionized water before use. During the deposition process, the glass substrate was immersed in a 0.25M cationic solution (Co²⁺ ion) with pH=3 for 30s. After rinsing with de-ionized...
water for 10s, it was immersed in 0.25M anionic solution (Se$^{2-}$ ions) with pH=3 for 30s. Then, it was rinsed with de-ionized water for 10s again in order to remove the loose material. The reaction solutions were put in a beaker into the water bath under various temperatures (40, 50, and 80°C). After the deposition process (after 10 cycles), the films were collected, rinsed by de-ionized water, and finally, put in the oven for 24h. The structure of the film was investigated by XRD with a Malvern Panalytical diffractometer (EMPYREAN) equipped with a Cu Kα ($\lambda$=0.15418nm) radiation source. Data were collected by step scanning from 10° to 80° with a step size of 0.02° ($2\theta$). Surface morphology, thickness, and roughness were examined by recording the AFM images with Bruker. The mode was Scanasy peak force tapping. The cantilever was scanasy-air (material: silicon tip on nitride lever) with spring constants of 0.4N/m and resonance frequencies of 70kHz. The optical properties of the films were studied with the Perkin Elmer UV/Vis Lambda 35 Spectrophotometer. The band gap energy values were calculated based on the absorption data.

III. RESULTS AND DISCUSSION

AFM measurements were carried out in order to investigate surface roughness and surface topology. The surface roughness was studied on the $R_q$ value which is defined as the root mean square average of height deviation taken from the mean image data plane. Figure 1 shows the AFM images of SILAR deposited cobalt selenide thin films under different bath temperatures. These images were measured over 1$\mu$m×1$\mu$m scanning range. The films deposited at lower temperatures (40°C and 50°C) indicated uneven morphology in comparison with the ones deposited at higher temperature. Uniformly grained and compact morphological surface was observed at 80°C. These results are consistent with several other studies, indicating that grain grows more compactness and regularity in morphology with increase in temperature [41, 42]. The average grain size (0.2, 0.15, and 0.25$\mu$m) and surface roughness (0.0191, 0.0102, 0.0192$\mu$m) were reduced from 40 to 50°C and increased at 80°C. On the other hand, we found that film thickness (1.4 to 1.7$\mu$m) increased with increasing temperature. The temperature effect on the film thickness has been reported by many researchers [43, 44].

Figure 2 indicates the XRD patterns for the cobalt selenide thin films prepared under various bath temperatures. It can be seen that the XRD patterns exhibited diffraction peaks at $2\theta$=13°, which can be indexed as reflection from the (111) plane of the cubic structure Co$_9$Se$_8$ compound (films prepared at 40°C and 50°C). Other researchers have reported similar findings (cubic cobalt selenide structure) [45, 46]. An additional peak attributed to the (113) plane became more visible for the films synthesized at 80°C. A sharp diffraction peak can be observed in Figure 2(c) reflecting the better crystallinity of the sample. The obtained XRD patterns were well matched with the standard Joint Committee on Powder Diffraction Standards (JCPDS) (Reference code: 98-004-4857) as indicated in Table I. Based on the JCPDS data, the lattice parameter values are a=b=c=10.431Å. The crystal system, space group and space group number were cubic, Fm-3m and 225 respectively.

### Table I. Comparison of Observed d-Spacing Values with Standard d-Spacing Values of Cobalt Selenide Thin Films

| Temperature (°C) | Reflection Plane (hkl) | Observed d-Spacing Values (Å) | Standard d-Spacing Values (Å) |
|-----------------|------------------------|------------------------------|-------------------------------|
| 40              | 111                    | 6.8                          | 6.0                          |
| 50              | 111                    | 6.8                          | 6.0                          |
| 80              | 113                    | 3.2                          | 3.1                          |

![Fig. 1. AFM images for films prepared at (a) 40°C, (b) 50°C, (c) 80°C.](image-url)
The band gap was calculated by the Stern equation which is a very useful and commonly used method [51-57].

\[
A = \frac{k(h\nu-E_g)^{n/2}}{h\nu}
\]  

(1)

In (1) \(v\) is the frequency, \(h\) is the Planck’s constant, \(k\) is a constant, while \(n\) carries the value of either 1 or 4. The \(n\) value is 1 for a direct gap material and 4 for indirect gap material. The plot of \((Ah\nu)^2\) against \(h\nu\) is shown in Figure 4. Extrapolation of the linear portion of the curve to \((Ah\nu)^2=0\) produces the band gap energy. The band gap increased from 2.1eV (40°C) to 2.4eV (50°C), and dropped to 2eV (80°C) as shown in Figure 4. Other research groups have highlighted similar band gap values (Table II). These cobalt selenide films have been prepared by using different methods including chemical bath deposition, electro deposition, magnetron sputtering method and mechano chemical method. The obtained thin films could be used in solar cell applications because of direct band gap between 1 to 2eV [58, 59].

| Remarks | Band gap value (eV) | Reference |
|---------|---------------------|-----------|
| Thin films were produced onto glass substrate by using chemical bath deposition method in the presence of ammonia, cobalt (II) acetate and sodium selenosulphate. | 1.8 to 3.6 | [35] |
| Thin films were synthesized onto tin oxide glass substrate via electro deposition technique in the presence of \(H_2SO_4\) and \(Co(CH_3COO)_2\) solutions. | 1.53 | [36] |
| Thin films were prepared onto non-conducting micro glass slide through chemical bath deposition method, in the presence of cobalt nitrate, ammonia and sodium selenosulphate. | 1.7 | [37] |
| Thin films were produced using magnetron sputtering method | 1.53 | [38] |
| Thin films were synthesized onto tin oxide coated glass by using electrodeposition method. | 1.53 | [39] |
| Thin films were grown using the mechanochemical method. | 1.7 | [40] |
The influence of bath temperature on the formation of SILAR deposited cobalt selenide thin films was studied in this paper. The XRD data supported the existence of cubic phase cobalt selenide films. The XRD patterns confirmed that the number of peaks increased with increasing bath temperature. The films prepared at 80°C have higher absorption, crystallinity, and the most homogeneity. Band gap values were observed in the range of 2eV to 2.4eV.

IV. CONCLUSIONS

The influence of bath temperature on the formation of SILAR deposited cobalt selenide thin films was studied in this paper. The XRD data supported the existence of cubic phase cobalt selenide films. The XRD patterns confirmed that the number of peaks increased with increasing bath temperature. The films prepared at 80°C have higher absorption, crystallinity, and the most homogeneity. Band gap values were observed in the range of 2eV to 2.4eV.

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