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SILAR deposition of cobalt selenide thin films by using tartaric acid as complexing agent

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Abstract
The nanostructured cobalt selenide films have been prepared onto substrate by using successive ionic layer adsorption and reaction method. The deposition of the thin films was carried out in the presence of tartaric acid (complexing agent) for the first time. The structure and morphology of obtained films have been analyzed by using X-ray diffraction, and atomic force microscopy. The XRD pattern confirmed that the formation of cobalt selenide in cubic phase. The atomic force microscopy image showed the uniformly grained and compact morphological surface. The average grain size, film thickness and surface roughness values were 0.05 µm, 96.5 nm and 0.001 µm, respectively.

Keywords: *thin films, cobalt selenide, semiconductor, roughness, SILAR technique*

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I. INTRODUCTION

The metal chalcogenide thin films are semiconducting materials with appropriate band gap of at room temperature [1,2]. These films could be used in solar cell [3-5], laser screens, near infrared detector, light emitting diodes [6], thin film transistor, photo detectors [7], holographic recording media [8], and photo electrochemical cells. Thin films have been synthesized by various deposition methods including chemical bath deposition [9-12], electro deposition [13-15], thermal evaporation [16], rf sputtering [17], vacuum evaporation [18], spray pyrolysis [19], chemical vapor deposition [20], hydrothermal method [21] and SILAR deposition method. Researcher highlighted that production of thin films under various deposition methods is of great importance for gaining variation in bandgap and absorption coefficient values [22-25]. SILAR deposition method is one of the simplest chemical techniques [26] which synthesizes binary, ternary, quaternary compounds of good quality for device applications. This deposition method is a low cost [27], low materials wastages [28], large scale production [29] and, it does not require vacuum at any stage [30], easily deposition method [31]. Researchers explain that the SILAR deposition method is based on the immersion of substrate into separately placed cation solution and anion solution [32]. Then, rinsed with water to avoid homogeneous precipitation in solution [33].The film thickness and deposition rate are strongly depended on the deposition cycles.

In the present work, the cobalt selenide films were prepared using the SILAR method in the presence of complexing agent (tartaric acid) for the first time. The structure and morphology of films have been studied by using XRD and AFM, respectively.

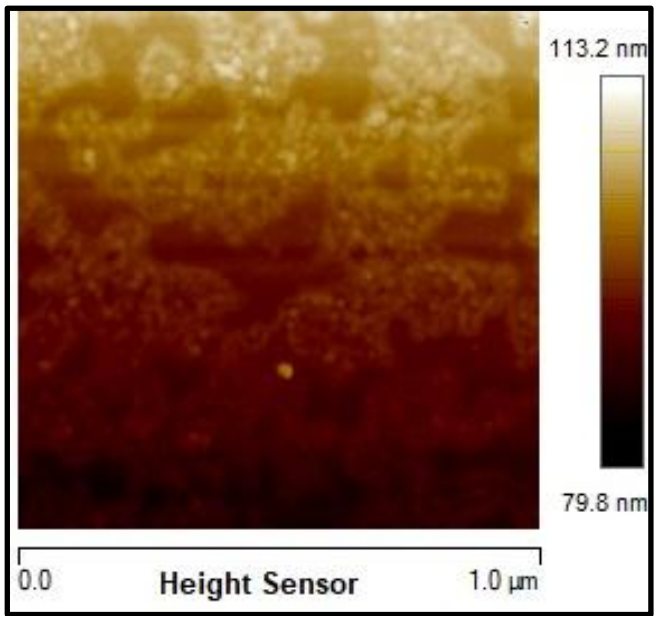
II. EEPERIMENTAL

In this work, the cobalt (II) chloride hexahydrate ($CoCl_2.6H_2O$) and sodium selenite (Na_2O_3Se) were used without further purification, acted as a source of Co_2^+ and Se^{2+} ions, respectively. During the formation of thin films, the (0.2M) tartaric acid was employed as complexing agent while the substrate was microscope glass slide. Before deposition, this substrate was cleaned by acetone, and de-ionized water. In the deposition process, the glass substrate was immersed in the cationic solution (0.2M of Co^{2+} ion) complexed with complexing agent for 30 seconds. Then, rinsing with de-ionized water for 10 seconds. Following that, it was immersed in anionic solution (0.2M of Se^{2-} ions) complexed with complexing agent for 30 seconds. Lastly, rinsing with de-ionized water for 10 seconds again (to remove the loose material on it). The synthesis of thin films was carried out at room temperature, and the deposition cycle was 18 cycles. The films were collected, and rinsed by de-ionized water, and finally, put in the oven for 24 hours. The X-ray diffraction data were obtained by means of Malvern Panalytical diffractometer using CuKα ($\lambda = 0.15418$ nm) radiation. The XRD pattern was recorded by step scanning from 10° to 80° with a step size of 0.02° (2θ). On the other hand, the atomic force microscopy was used to study the film thickness, surface morphology and roughness of the sample. The mode in this technique

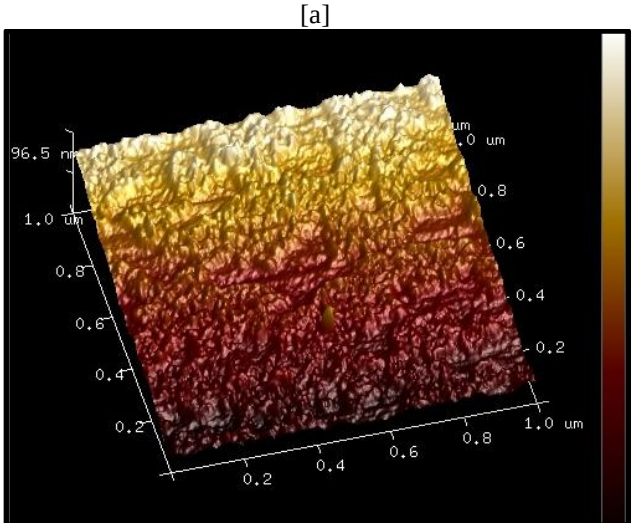
was Scanasyst peak force tapping. The cantilever was scanasyst-air (material: silicon tip on nitride lever) with spring constants of 0.4 N/m and resonance frequencies of 70k Hz.

III. RESULT AND DISCUSSION

Cobalt is the transition element. The chemical symbol and atomic number are "Co" and "27", respectively. Generally, it was found inerythrite, cobaltite and skutterudite. The cobalt could be employed in various areas such as the lithium ion battery, high strength alloys, catalyst for the petroleum, airbags in automobile industry, paint. Selenium is non-metal element. The atomic number and chemical symbol are "34" and "Se", respectively. It could be observed in the soil, food and water. Abundant literature is available on the synthesis of binary, ternary and quaternary compounds via SILAR method [34-38]. In this work, SILAR method was used to prepare cobalt selenide films because of it has many advantages if compared to other deposition techniques. There are many researchers investigate the surface roughness and surface morphology by using atomic force microscopy (AFM). During the experiment, the surface roughness was investigated on the Rq value which is defined as the root mean square average of height deviation taken from the mean image data plane. Figure 1 shows the 2-dimensional (Figure 1a) and 3-dimensional AFM images (figure 1b) of SILAR deposited cobalt selenide thin films. These images were studied over specific scanning range (1μm×1μm). The obtained films indicated uniformly grained and compact morphological surface. The average grain size, film thickness and surface roughness values were 0.05 μm, 96.5 nm and 0.001 μm, respectively.



[a]



[b]

Figure 1: The 2-dimensional (Figure 1a) and 3-dimensional AFM images (figure 1b) of SILAR deposited cobalt selenide thin films.

Figure 2 shows the XRD pattern for the SILAR deposited cobalt selenide thin films. There are two diffraction peaks at 2θ=13.04° and 28.05° could be observed, corresponding to d-spacing value of 6.78 Å and 3.18 Å, respectively (Table 1). The XRD results confirm the cubic structure, and all these data were well matched with the standard Joint Committee on Powder Diffraction Standards (Reference code: 98-004-4857). The lattice parameter values are a=b=c=10.431Å. On the other hand, the crystal system, space group and space group number were found to be cubic, Fm-3m and 225, respectively.

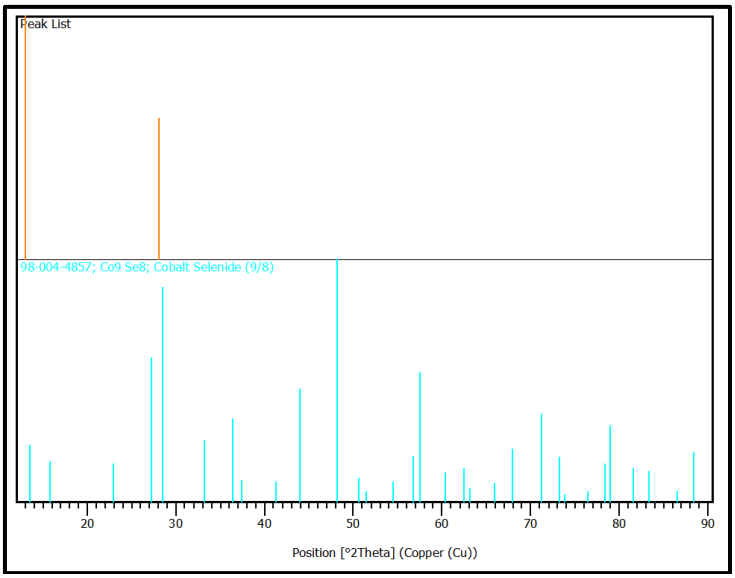


Figure 2: The XRD analysis of SILAR deposited cobalt selenide thin films.

Table 1: XRD diffraction peak position and d-spacing values in cobalt selenide thin films.

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Tip Width	Matched by
13.0403	124.64	0.3936	6.78923	100.00	0.4723	98-004-4857
28.0533	42.12	0.9446	3.18079	33.80	1.1336	98-004-4857

SILAR deposition method is considered as one of the popular deposition methods. Many researchers produced various types of thin films by using this method [Table 2]. Several complexing agents such as ethylene diamine tetraacetate, hexamethylenetetramine, Ethylenediaminetetra acetic acid, 2-methoxyethanol $C_3H_8O_2$ and triethanolamine were used during the formation of thin films. The properties of obtained SILAR-deposited thin films were studied via XRD, SEM (scanning electron micrograph), UV-visible spectrophotometer, energy dispersive x-ray analysis (EDX) and atomic force microscopy.

Table 2: SILAR-deposited thin films prepared by using various types of complexing agents.

Thin films	Complexing agent	Experimental results
FeCuS films	ethylene diamine tetraacetate [EDTA] and triethanolamine	• Average reflectance was observed less than 30% for all films • The band gap values are in the range of 3.42 eV to 3.76 eV [39]
Bi_2S_3 films	2-methoxyethanol $C_3H_8O_2$	• XRD studies revealed the amorphous structure and orthorhombic phase in as-deposited film and annealed films, respectively [40]. • The films indicated high absorption co-efficient (more than 10^4 cm^{-1}), and the band gap values (1.5 eV to 1.8 eV)
CdS films	hexamethylenetetramine	• XRD patterns confirmed cubic structure and the crystallite size about 2.43 nm. • SEM showed uniform morphology and well-crystallized grains [41].
ZnCuS films	EDTA, TEA	• Electrical results such as sheet resistance

		(7.47×10^6 to $1.94 \times 10^7 \Omega/m^2$), resistivity ($1.49 \times 10^6$ to $3.86 \times 10^6 \Omega m$) and conductivity values (2.57×10^{-7} Sm^{-1}) of the obtained thin films were discussed [42].
SnS films	Ethylenediaminetetra acetic acid	• The direct band gap could be detected in the range of 200 to 900 nm, based on UV-visible spectral. • Also, the band gap reduces when the particle size was increased [43].
Cu_3SnS_4 films	triethanolamine	• XRD studies showed tetragonal structure with polycrystalline nature. • SEM revealed homogeneous morphology and majority consisted of spherical grains (some large sparse clusters) in sample [44].
ZnS films	triethanolamine	• The band gap and refractive index were found to be 3.7 eV to 3.9 eV, and 1.9 to 2.4, respectively [45].
CdS films	triethanolamine	• XRD analysis showed the strongest diffraction peak assigned to the (111) peak, and grow with Face Centered Cubic (FCC) structure. • EDX analysis highlighted the S/Cd ratio was about 0.8 for the thin films [46].
CuSnS films	triethanolamine	• Atomic force microscopy images showed the surface roughness, grain size and height reduced with increasing the concentration. • XRD patterns pointed out the amorphous nature of films [47].
FeS films	triethanolamine	• Experimental results confirmed that surface roughness and grain size reduced when the concentration of precursors was increased [48].
$CuInSe_2$ films	triethanolamine	• Experimental results indicated well-crystallized and smoothly morphology in annealed films under argon at 400 °C for 60 minutes [49].

IV. CONCLUSION

It was observed that the SILAR deposition method could be used to produce cobalt selenide thin films. The tartaric acid was employed to synthesis thin films onto substrate for the first time. XRD analysis showed the cubic phase in the obtained films. Based on the AFM studies, the uniformly grained and compact morphological surface could be observed.

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