THE INFLUENCE OF IMMERSION TIME ON THE STRUCTURE AND MORPHOLOGY OF SILAR DEPOSITED COBALT SELENIDE FILMS

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ABSTRACT: *The successive ionic layer adsorption and reaction deposition technique was employed to synthesis cobalt selenide thin films onto the soda-lime glass. The influence of immersion time on the structure and morphology of the sample was reported for the first time. Characterization of obtained films was studied by using X-ray diffraction and atomic force microscopy. The X-ray diffraction analysis revealed the presence of different phases in all samples under different conditions. The morphology of films strongly depends on the immersion time based on the atomic force microscopy images.*

Keywords: thin films, SILAR method, cobalt selenide, semiconductor, solar cell

INTRODUCTION:

The metal sulfide [1, 2], metal selenide [3, 4], and metal telluride films [5, 6] showed unique physical properties. Therefore, these films have attracted great attention, could be used in solar cells [7-9], light-emitting diode [10], capacitor, photodetector [11], holographic [12], laser device [13], sensor devices [14], solar control device, ultraviolet optoelectronics [15], photonic integrated circuit. Several deposition methods have been used to produce thin films as reported by many researchers [16-20]. The successive ionic layer adsorption and reaction (SILAR) method has many advantages such as simple equipment [21], inexpensive [22], large-area deposition at low temperature [23]. In the SILAR deposition method, the substrate is immersed in turn into the cation and the anion precursor solutions [24]. In between the cation and anion immersions, the substrate is rinsed with distilled water [25]. The thin film growth takes place through the adsorption and reaction of these ions [26]. By repeating these cycles, the thin films are grown layer by layer [27].

The objective of this work is to investigate the influence of immersion time on the properties of SILAR deposited cobalt selenide thin films prepared onto a soda-lime glass substrate. This is the first time, the structure and morphology of films were studied by using X-ray diffraction and atomic force microscopy, respectively.

EXPERIMENTAL:

Preparation of thin films

Cobalt (II) chloride hexahydrate ($CoCl_2.6H_2O$) and sodium selenite (Na_2O_3Se) were used without further purification. The soda-lime glass was employed as a substrate during the deposition process. This substrate was cleaned with acetone and de-ionized water before use. During the deposition process, the glass substrate was immersed in the 0.2 M cationic solution (Co^{2+} ion) for a specific immersion time [20, 40, 60 seconds]. After rinsing with de-ionized water for 5 seconds, it was immersed in 0.2 M anionic solution (Se^{2-} ions) for a specific immersion time [20, 40, 60 seconds]. Then, rinsing with de-ionized water for 5 seconds again in order to remove the loose material on it. The reaction solutions were put in a beaker at pH 3.5. The desired pH value was adjusted by adding sodium hydroxide (NaOH) and hydrochloric acid (HCl) solution. After the deposition process (after 15 cycles), the films were collected, rinsed by de-ionized water, and finally, put in the oven for 24 hours.

Characterization of thin films

The structural properties of the films were investigated by X-ray diffraction (XRD) with a Malvern Panalytical diffractometer (EMPYREAN) equipped with a Cu Kα (λ = 0.15418 nm) radiation source. Data were collected by step scanning from 10° to 80° with a step size of 0.02° (2θ). The surface morphology, thickness, and roughness were examined by recording atomic force microscope (AFM) images with Bruker. The mode is Scanasyst peak force tapping. The cantilever is scanasyst-air (material: silicon tip on nitride lever with spring constants 0.4 N/m and resonance frequencies 70 kHz.

RESULTS AND DISCUSSION

Generally, the deposition technique could be divided into physical technique [28, 29] and chemical method [30, 31]. The SILAR deposition method has been used to prepare binary [32, 33], ternary [34, 35], and quaternary thin films [36, 37]. The atomic force microscopy (AFM) analysis was conducted to investigate the surface topology of the prepared sample. The AFM image was recorded as a three-dimensional view, over 1 µm X 1 µm scanning range. The surface roughness was studied by the R_q value. R_q is defined as the root mean square average of height deviation taken from the mean image data plane. The cobalt selenide films produced at immersion time (20 seconds) indicated the surface consisting of grains of various sizes as shown in figure 1. It has dense morphology, compact structure and covers the entire surface area of the substrate. The grains (average diameter is 0.05 to 0.1 µm) are nearly spherical in shape and quite small. Film thickness and surface roughnesses were 1.3 µm and 0.008 µm, respectively. Several researchers have highlighted that the nature of grains has less porous and consisting of small spherical grains [38-40]. Spherical or grain-shaped semiconductor materials are considered as unique properties in thin films. These materials could be used in solar cell applications [41]. The figure 2 showed the AFM image of films prepared at immersion time (40 seconds). The image revealed that longer immersion time leads to bigger grains (average diameter is 0.3 µm to 0.5 µm). The surface roughness and thickness values were 0.022 µm and 1.6 µm, respectively. The cobalt selenide films synthesized at immersion time (60 seconds) consisted of closely packed uniform crystal (average diameter about 0.2 µm to 0.3 µm) as shown in figure 3. The surface roughness was 0.028 µm for the cobalt selenide layer thickness of 1.8 µm.

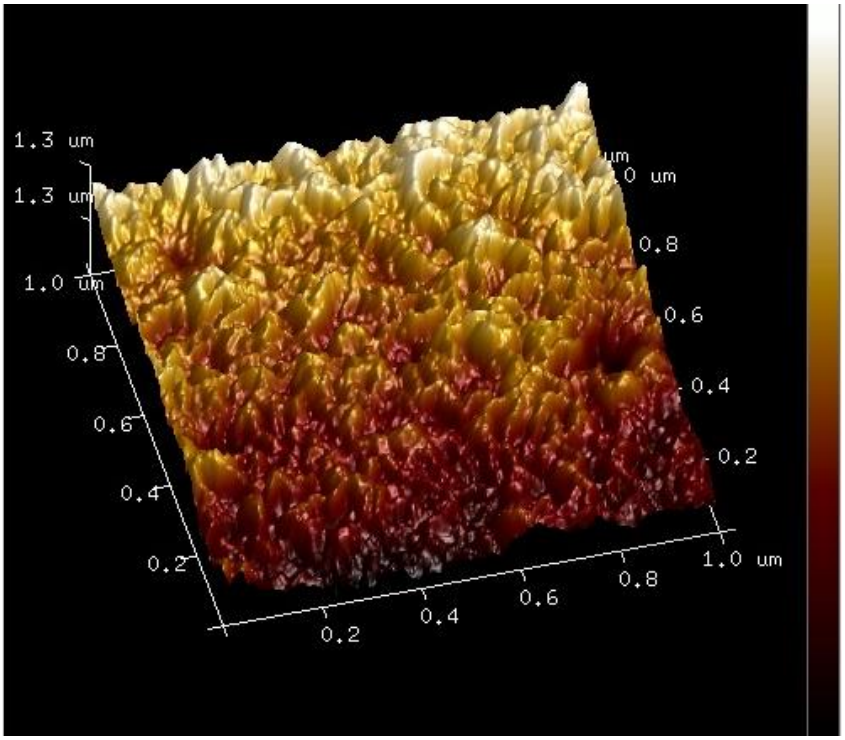

Figure 1: AFM images of cobalt selenide thin films deposited on soda-lime glass substrate when the immersion time was 20 seconds

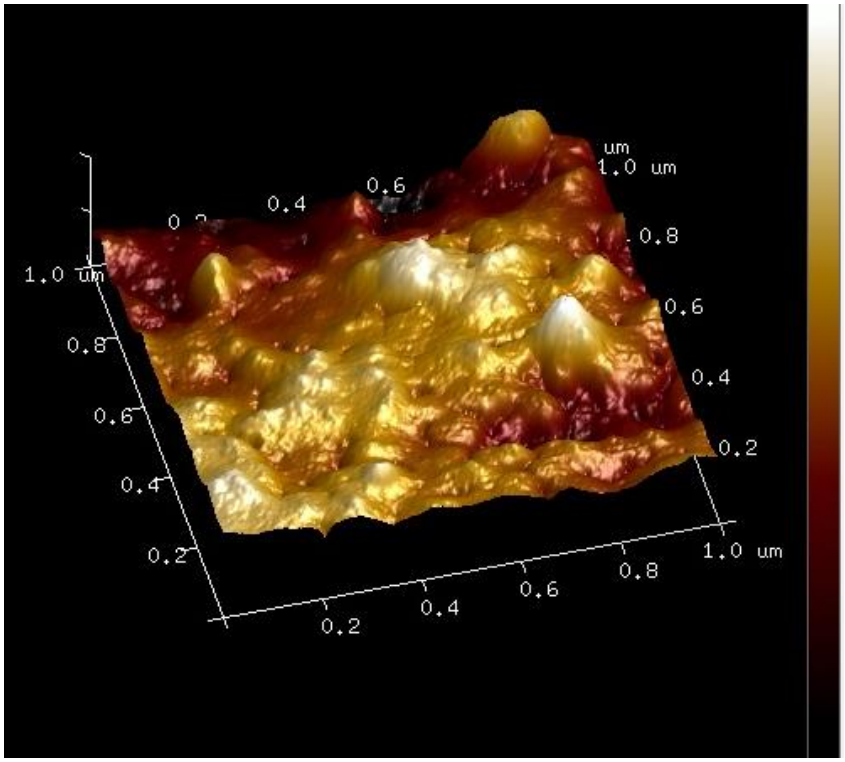

Figure 2: AFM images of cobalt selenide thin films deposited on soda-lime glass substrate when the immersion time was 40 seconds

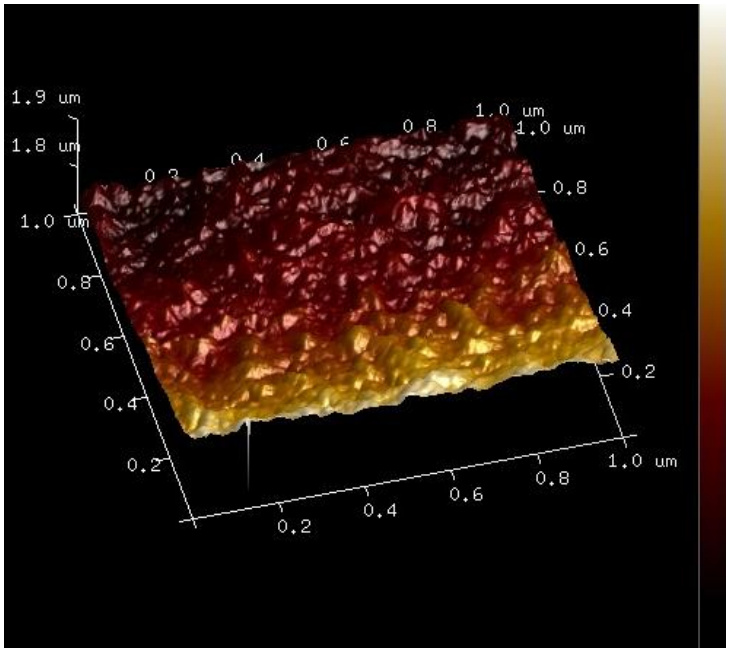

Figure 3: AFM images of cobalt selenide thin films deposited on soda-lime glass substrate when the immersion time was 60 seconds

X-ray diffraction (XRD) was used to investigate the structure of obtained samples. XRD analysis confirmed the different phases of the obtained samples. The films prepared at immersion time (20 seconds) showed two diffraction peaks (figure 4), corresponded to 2θ=30.2° and 34.4°. The films indicated tetragonal structure (CoSe), and d-spacing values matched well with JCPDS (98-016-2902) as highlighted in Table 1. The films produced at immersion time (40 seconds) exhibited four diffraction peaks (figure 5) at 2θ= 12.9°, 24.9°, 31.6° and 72.1° which can be indexed as a reflection from the (001), (020), (201) and (242) plane of the monoclinic structure $Co_{6.8}Se_8$ compound [JCPDS 98-009-9992]. A comparison of observed d-spacing values with standard d-spacing values as indicated in Table 2. The films synthesized at immersion time (60 seconds) displayed two peaks (figure 6), attributed to 2θ=13.1° and 27.2°, indexed as a reflection from the (111) and (113), respectively. The experimental d-spacing values matched with JCPDS data (98-004-4857) as listed in Table 3. Other researchers have reported similar findings (cubic cobalt selenide structure) in the literature [42, 43]. According to the Joint Committee on Powder Diffraction Standards (JCPDS) data, lattice parameter values are a=b=c=10.431 Å. The crystal system, space group and space group number were cubic, Fm-3m and 225, respectively.

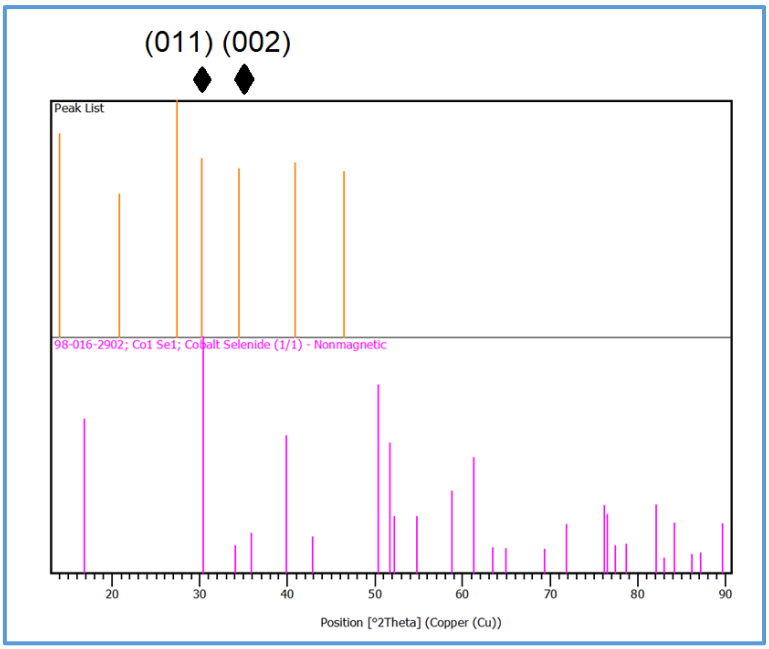

Figure 4: XRD pattern of cobalt selenide thin films deposited on soda lime glass substrate when immersion time was 20 seconds

Table 1: Comparison of observed d-spacing values with standard d-spacing values of cobalt selenide thin films deposited on soda-lime glass substrate when immersion time was 20 seconds.

2θ (°)	*hkl*	Observed d-spacing values (Å)	Standard d-spacing values (Å)
30. 2	011	2.9	2.9
34.4	002	2.6	2.6

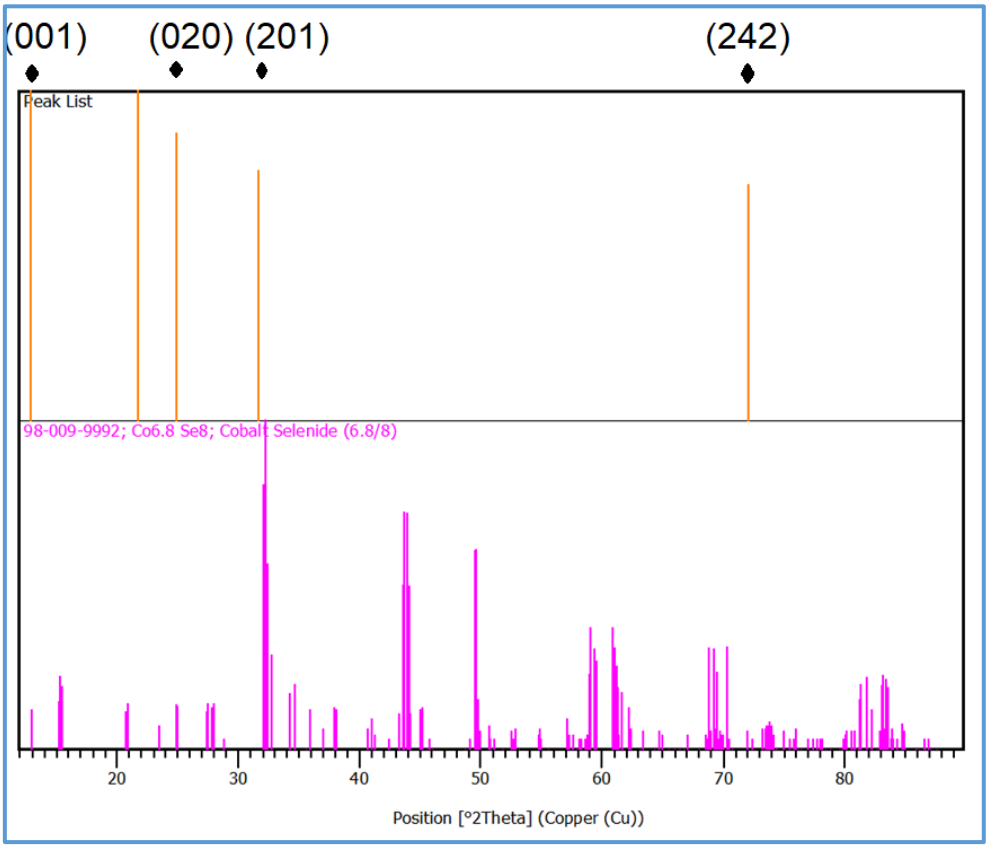

Figure 5: XRD pattern of cobalt selenide thin films deposited on soda-lime glass substrate when immersion time was 40 seconds

Table 2: Comparison of observed d-spacing values with standard d-spacing values of cobalt selenide thin films deposited on soda-lime glass substrate when immersion time was 40 seconds.

2θ (°)	*hkl*	Observed d-spacing values (Å)	Standard d-spacing values (Å)
12.9	001	6.8	6.2
24.9	020	3.6	3.6
31.6	201	2.8	2.7
72.1	242	1.3	1.3

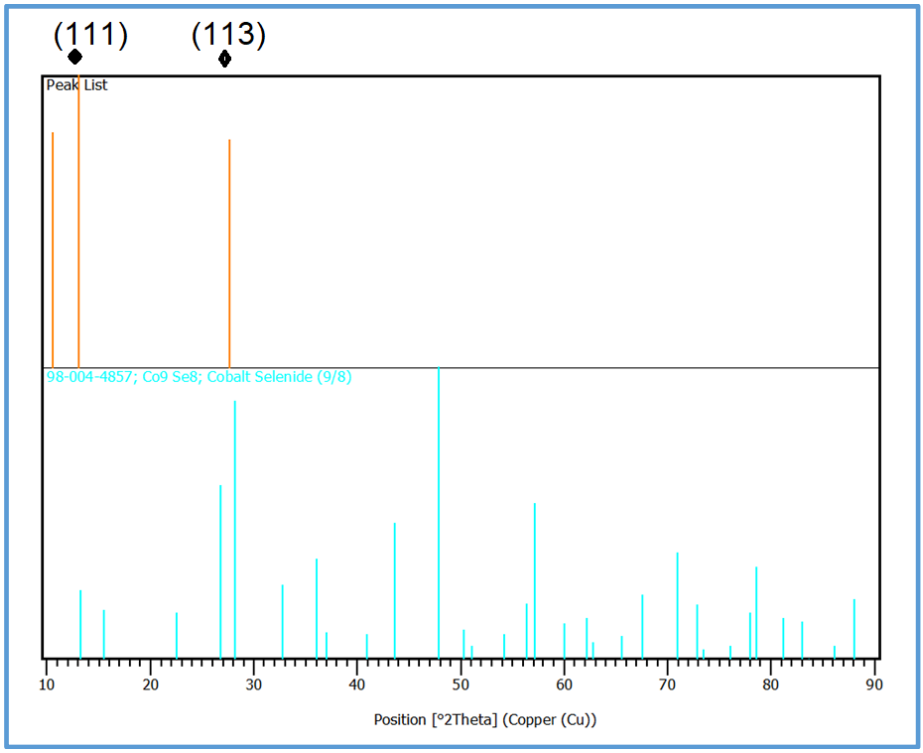

Figure 6: XRD pattern of cobalt selenide thin films deposited on soda-lime glass substrate when immersion time was 60 seconds

Table 3: Comparison of observed d-spacing values with standard d-spacing values of cobalt selenide thin films deposited on soda-lime glass substrate when immersion time was 60 seconds.

2θ (°)	*hkl*	Observed d-spacing values (Å)	Standard d-spacing values (Å)
13.1	111	6.8	6.0
27.7	113	3.2	3.1

CONCLUSIONS

The influence of immersion time on the formation of SILAR deposited cobalt selenide thin films was investigated. These films were deposited onto soda-lime glass at room temperature. XRD pattern confirmed the existence of cobalt selenide films. The immersion time was observed to affect the morphology of the films based on the AFM images.

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