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Properties Study of SILAR Deposited Cobalt Selenide Thin Films

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ABSTRACT

Thin films are attractive materials to be used in laser, solar cells, sensors, phosphors, light emitting diodes, IR windows and flat panel displays. Several deposition methods have been employed to deposit thin films as reported by many researchers. In this report, the cobalt selenide thin films have been deposited onto microscope glass slide via successive ionic layer adsorption and reaction method. This deposition method is a simple method owing to the inexpensive technique and can produce films at a low bath temperature. All the samples were investigated by using XRD, FESEM and UV-visible spectrophotometer. The XRD pattern confirmed that cubic phase cobalt selenide thin films. The FESEM image exhibited that the obtained sample is dense, uniform, and smooth surface.

Key Words: XRD, FESEM, Thin films, Cobalt selenide, SILAR technique, Semiconductor, Band gap

INTRODUCTION

Researcher highlighted that thin film deposition is the process of depositing thin film coatings onto various types of substrates [1-3]. It is considered as very important step in the synthesis of several opto-electronic [4-6], solid state and medical devices. The obtained films showed some unique properties such as high dielectric constant, excellent absorption coefficient [7-9], good refractive index, and wide band gap [10-12]. Several deposition techniques were used to produce thin films including SILAR method, Solvo thermal technique [13], pulsed laser deposition [14], vacuum evaporation [15], electron beam evaporation, molecular beam epitaxy, radio frequency sputtering [16], atomic layer deposition [17], chemical vapour deposition, chemical bath deposition [18-20], electro deposition [21-23] and spray pyrolysis. Physical properties of the deposited films have been characterized by X-ray diffractometry, Fourier transform infrared spectroscopy [24], reflection high-energy electron diffraction [25], Field emission scanning electron microscopy [26], Atomic force microscopy A(FM), Raman spectroscopy [27], Transmission electron microscopy [TEM], Scanning probe microscopy [28], X-ray photoelectron spectroscopy [29], Energy Dispersive X-Ray Analysis and spectroscopic ellipsometry [30].

One of the chemical deposition methods, is called successive ionic layer adsorption and reaction (SILAR) technique, was employed for making large area thin film onto substrate [31]. During the deposition process, the cleaned substrate will be immersed into cationic precursor solution [32] and anionic precursor solution, respectively. In between the cation and anion immersions, the substrate is rinsed with distilled water also in order to remove undesired materials onto the surface of substrate [33]. This deposition technique offers several advantages to researcher including convenient for large area deposition at low temperature [34], starting materials used are commonly available [35], can control the film thickness, simple and low cost deposition method [36].

Cobalt was observed in some minerals such as erythrite, cobaltite and skutterudite. It is one of the transition elements, with atomic number "27" and chemical symbol "Co". The production of cobalt was 79900 metric tons in 2008 (Table 1). The cobalt can be used to produce drying agents for paints, lithium ion battery, high strength alloys, catalyst for the petroleum, airbags in automobile industry. The global production reached 140000 in metric tons in 2020. Selenium was found in the soil, water and some foods. Selenium is a non-metal with the chemical symbol "Se", and atomic number of "34". The table 2 showed the refinery production global of selenium from 2009 until 2017. The obtained data indicated a minor increase in production from 2009 (2.16 million kg) to 2017 (2.71 million kg).

Table 1: Worldwide mine production of cobalt from 2008 to 2020 [37]

Year	Production (in metric tons)
2008	79900
2009	79900
2010	107000
2011	110000
2012	103000
2013	110000
2014	123000
2015	126000
2016	123000
2017	120000
2018	148000
2019	144000
2020	140000

Table 2: Refinery production global of selenium from 2009 until 2017 [38]

Year	Production
2009	2160000 kg
2010	2150000 kg
2011	2180000 kg
2012	2260000 kg
2013	2280000 kg
2014	2470000 kg
2015	2660000 kg
2016	2800000 kg
2017	2710000 kg

The objective of this work is to report the properties of cobalt selenide thin films deposited onto glass substrate under specific experimental conditions. The properties of films were investigated by using XRD (x-ray diffraction), FESEM and UV-visible spectrophotometer.

MATERIALS AND METHODS

Chemical such as cobalt (II) chloride hexahydrate ($CoCl_2.6H_2O$) and sodium selenite (Na2O3Se) were used without further purification in this work. The substrate (microscope glass slide) was chosen, washed by acetone, and de-ionized water before use. During the experiment, the cleaned substrate was immersed in the cationic solution (0.2M of Co^{2+} ion) for 30 seconds. Then, rinsing with de-ionized water for 10 seconds. Following that, the substrate was immersed in anionic solution (0.2M of Se^{2-} ions) for 30 seconds. Finally, rinsing with de-ionized water for another 10 seconds. The deposition process was carried out at room temperature, by using 15 cycles.

The X-ray diffraction was used to study the structure of the film. The Malvern Panalytical diffractometer (EMPYREAN) equipped with a Cu Kα (λ = 0.15418 nm) radiation source was used. The data were analyzed by step scanning from 10° to 80° with a step size of 0.02° (2θ). The field emission scanning electron microscope (FEI, Nova Nanosem 230) was employed for the characterization of the morphology of films. The Perkin Elmer UV/Vis Lambda 35 Spectrophotometer was utilized in order to study the optical properties and band gap energy value of obtained films.

RESULTS AND DISCUSSION

The field emission scanning electron microscope (FESEM) gives topographical and elemental information at various magnifications [39]. Many researchers highlighted that FESEM can provide clearer and less electrostatically distorted images [40] if compared to scanning electron microscopy. The FESEM image of SILAR deposited thin films at 15 cycles as shown in figure 1. The FESEM image confirmed that the obtained films were dense, smooth surface, full coverage to the surface of substrate with the grain size varies from 1-2.5 µm.

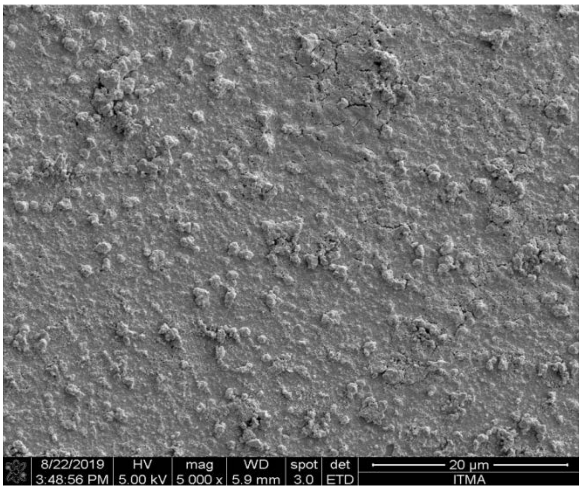

Figure 1: Field emission scanning electron microscope for the cobalt selenide thin films

The x-ray diffraction is a very fast analytical method [41] employed for phase identification of crystalline materials in different fields such as material science [42], environmental science, geology, biology and engineering. Figure 2 exhibited the X-ray diffraction pattern for the cobalt selenide thin films prepared under specific conditions. Based on the results, diffraction peak was attributed to (111) plane, and matched the standard Joint Committee on Powder Diffraction Standards (Reference code: 98-004-4857). The lattice parameter values are a=b=c=10.431 Å.

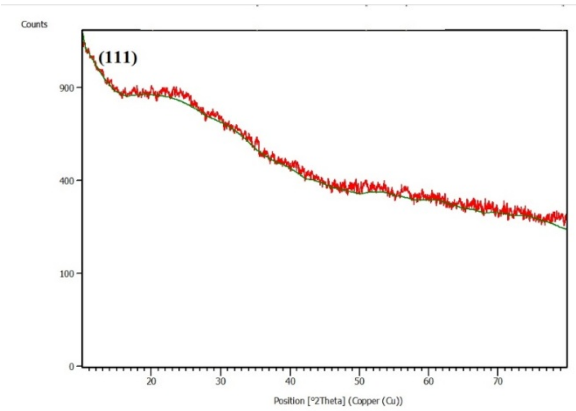

Figure 2: X-ray diffraction pattern for the cobalt selenide thin films

The UV-visible spectroscopy is employed to study how much substance absorbs light during the experiment [43]. This process will be carried out by measuring the intensity of light [44] that passes through thin film with respect to the intensity of light via reference sample (glass slide). Figure 3 indicated the UV-visible absorption spectrum in the wavelength regions of 300 to 1000 nm. The obtained films exhibited high absorbance value because of these films showed the smooth and homogeneous surface topography. The band gap was calculated based on the Stern equation.

$$\boldsymbol{A = \frac{[k(hv - E_g)^{n/2}}{hv}}\textbf{[Equation 1]}$$

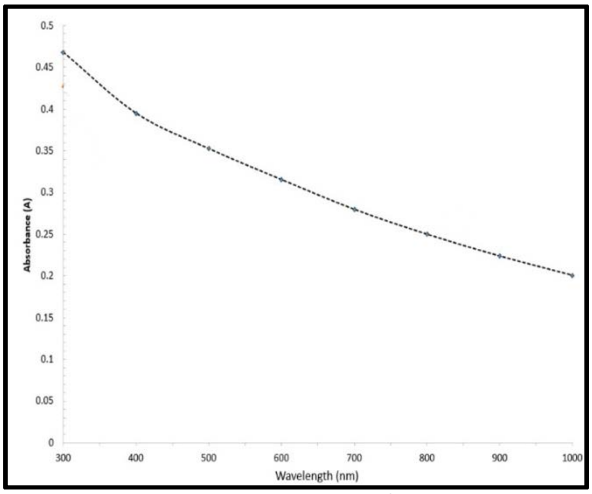

Figure 3: Optical absorbance spectrum of cobalt selenide thin films

where v is the frequency, h is the Planck's constant, k equals 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 figure 4 exhibited the plot of $(Ahv)^2$ against hv. The extrapolation of this straight line will intercept the hv-axis to produce the band gap value. The band gap value to be 2.1 eV.

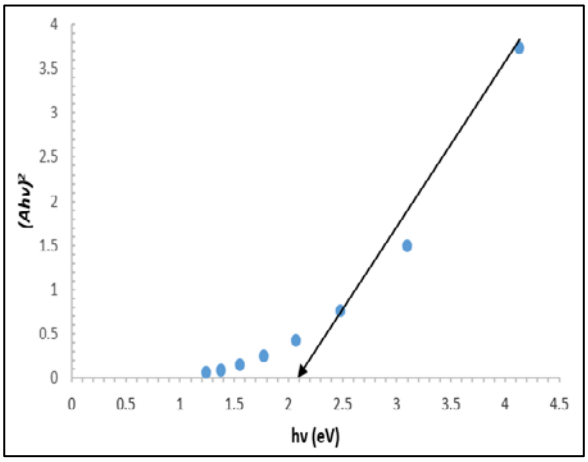

Figure 4: Curve (Ahv)2 against (hv) for the cobalt selenide thin films

Based on the literature review, many researchers [45-51] have been used SILAR deposition method to produce various types of thin films. The obtained experimental results confirmed that the unique properties of thin films strongly depended on the experimental conditions including pH, deposition times, deposition temperature, the number of immersion cycles, the presence of complexing agent and the nature of substrate.

CONCLUSION

The nanostructured cobalt selenide thin films have been deposited onto microscope glass slide successfully via SILAR deposition technique. The XRD results confirmed the existence of cobalt selenide films. The FESEM images indicated dense and smooth surface morphology of the obtained films. The band gap value was about 2.1 eV.

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