Characterization of Cobalt Sulfide Thin Films Synthesized from Acidic Chemical Baths

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Cobalt sulfide thin films were synthesized from acidic chemical baths by varying the deposition time. The powder X-ray diffraction studies indicated that there are hexagonal CoS, face-centered cubic $Co_3S_4$, and cubic $Co_9S_8$ phases of cobalt sulfide. The crystallite size of the hexagonal CoS phase decreased from 52.8 nm to 22.5 nm and that of the cubic $Co_3S_4$ phase increased from 11 nm to 60 nm as the deposition time increased from 2 hrs to 3.5 hrs. The scanning electron microscopic images revealed crack and pinhole free thin films with uniform and smooth background and few large polygonal grains on the surface. The band gap of the cobalt sulfide thin films decreased from 1.75 eV to 1.3 eV as the deposition time increased from 2 hrs to 3.5 hrs. The photoluminescence (PL) spectra of the films confirmed the emission of ultraviolet, violet, and blue lights. The intense PL emission of violet light at 384 nm had red shifted with increasing deposition time that could be resulted from the increase in the average crystallite size. The FTIR spectra of the films indicated the presence of OH, C-O-H, C-O, double sulfide, and Co-S groups. As the deposition time increased, the electrical resistivity of the cobalt sulfide thin films decreased due to the increase in both the crystallite size and the films’ thickness.

1. Introduction

Metal chalcogenide thin films are getting increasing attention in a variety of electrical, optical, and optoelectronic devices due to their physical and optoelectronic properties [1, 2]. Cobalt sulfide is one of the magnetic transition metal chalcogenides that exists in a number of phases such as $Co_3S_3$, $Co_{1.5}S$, $Co_S$, $CoS_2$, $CoS_3$, and $CoS_8$. These multiphase structures are resulted from the existence of cobalt in the oxidation state of +2, +3, or +4 [3, 4]. Therefore, cobalt sulfide has a complicated chemical composition. These different phases of cobalt sulfide are of particular interest due to their unique applications as supercapacitors [5–7], water splitter to produce hydrogen [8, 9], catalysts [10–12], diluted magnetic materials [13, 14], counter-electrodes for dye synthesized solar cells [15, 16], anode materials for advanced sodium and lithium ion batteries [17–19], optical waveguides, thermal sensors, solar selective coatings, and optical filters [20].

Currently, various deposition technologies, including chemical bath deposition, are used to deposit metal chalcogenide thin films [1]. Chemical bath deposition (CBD) has been employed as a thin film deposition technique for metal sulfides, selenides, oxides, and others for a period of nearly a century and half [21]. Despite an edged technique, CBD still has a big unexploited potential to deposit different chalcogenides with intended properties by controlling the deposition parameters [22]. The first formal deposition of cobalt sulfide thin films by the CBD method is credited to Basu and Pramanik, almost 120 years after the CBD technique had been used as a thin film deposition technique [23]. Review of literatures indicates that there are very few reports on chemical bath-deposited cobalt sulfide thin films [3, 20, 24–26]. Lokhande reported chemical bath-deposited...
cub sulfide thin films using sodium thiosulfate as a sulfur source, cobalt sulfate as cobalt source, and disodium EDTA as complexing agents in an acidic solution [27]. As far as the authors are aware, there is no report on cobalt sulfide thin films deposited under acidic baths except Lokhande’s report. Therefore, characterization of cobalt sulfide thin films synthesized by changing various deposition conditions under acidic medium could have paramount importance for technologies that use cobalt sulfide thin films. In this work, we report the synthesis and characterization of cobalt sulfide thin films from acidic baths using thioacetamide, cobalt acetate, and EDTA as starting materials.

2. Experiment Procedure

Before the actual deposition of the cobalt sulfide thin films, the preparation conditions were optimized. Aqueous solutions of analytical grade cobalt acetate (Loba Chemie), thioacetamide (Titan), and disodium EDTA (Fine Chemicals) were used as starting reagents. In a typical experiment, 9 ml (1 M) of cobalt acetate was mixed with 3 ml (0.2 M) of disodium EDTA in a 150 ml beaker under continuous stirring. Then, 63 ml of deionized water was added to make up the volume to 75 ml. The pH of the solution was adjusted to 4.6 before the addition of thioacetamide. After the addition, the volumeto75ml. The pH of the solution was adjusted to 4.6 before the addition of thioacetamide. After the addition, the solution color at this instant was pink. The stock solution was transferred to the water bath of temperature adjusted to 85°C. The pre-cleaned soda lime glass substrates were suspended vertically in the stock solution. Four samples were prepared by taking out a deposit in 30 minutes interval starting from 2 hrs after the deposition began. The color of the films changed from brown to black as the deposition time increased. The films were partially reflecting like a mirror. The reflectivity of the films increased with increasing the deposition time, and films deposited at 3 hrs and 3.5 hrs reflect as a plane mirror. The gravimetry film thickness measurement method was used to estimate the thickness of the cobalt sulfide thin films. The obtained film thickness for cobalt sulfide thin films deposited at 2 hrs, 2.5 hrs, 3 hrs, and 3.5 hrs were 356 nm, 361 nm, 385 nm, and 434 nm, respectively. As the deposition time increases, the films get sufficient time for deposition on the substrate surface, thus increasing the layer thickness [20].

Crystallographic study of the thin films was carried out by a Shimadzu X-ray diffractometer with Cu Kα monochromatic radiation (λ = 0.15406 nm) operating at 40 kV and 30 mA. The optical absorption of the samples was investigated by a Shimadzu UV-3600 Plus UV-VIS-NIR spectrophotometer, and the FTIR spectrum was recorded using a Perkin Elmer Frontier MIR/FIR infrared spectrometer. The surface morphology and elemental composition of the thin films were investigated using a field emission scanning electron microscope (FESEM, Zeiss, Sigma) integrated with an energy dispersive X-ray analyzer (EDX). The fluorescence measurement was carried out by using a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer using a xenon lamp for the electron excitation. The electrical resistance of the films was measured by the two-probe method.

3. Results and Discussion

3.1. Structural Analysis. Figure 1 shows the XRD patterns of cobalt sulfide thin films deposited at different deposition time. The XRD patterns of the films deposited at 2 hrs and 2.5 hrs exhibited two clearly visible peaks at 2θ values of 14.8° and 21.2° with preferred orientation along 21.2° due to (102) plane of the hexagonal CoS structure (Pdf# 01-1279). Five additional faint peaks were also observed for the film deposited at 2 hrs as shown in Figure 1 and Table 1. The peak at 16.4° is the reflection from the (111) plane of the face-centered cubic Co9S8, and the peak at 24.4° is the reflection from the (220) plane of the cubic Co3S4. The peak at 45.6° could not be assigned for a particular phase as both the cubic Co3S4(Pdf#19-0364) and the face-centered cubic Co3S4(Pdf#02-1338) structures have a common (400) plane about this 2θ value. The peak at 50.4° is also common for Co3S4, Co9S8, and Co4S3 as can be observed from the listed Pdf card numbers on the same table. The peaks at 45.6° and 50.4° disappeared and six new peaks appeared at 17.26°, 18.36°, 22.32°, 23.52°, 29.54°, and 30.76° for the cobalt sulfide thin film deposited at 2.5 hrs. The new obtained peaks are related to the hexagonal CoS and cubic Co9S8 with no new peaks related Co3S4 and Co4S3 phases. A new peak related to the hexagonal CoS structure was observed at 20 value of 20.4° when the deposition period increased to 3 hrs. As the deposition period increased to 3 and 3.5 hrs, the intensity of the prominent peaks decreased and the faint peaks vanished gradually. However, the intensity of the peaks at 18.36° and 22.32° which started to appear from 2.5 hrs deposition time increased gradually. For the deposition period of 2 hrs, 2.5 hrs, and 3 hrs, the preferred orientation was along the (102) plane of the hexagonal CoS structure. The preferred orientation changed to the (200) plane of the cubic Co9S8 structure for 3.5 hrs deposition period. In addition, the preferred orientation of the hexagonal CoS structure changed from about 21.26° to 20.34° at 3.5 hrs deposition time. The peak at 12.4° observed in the cobalt sulfide thin films deposited at 2 hrs, 2.5 hrs, and 3 hrs does not match to any of the observed cobalt sulfide phases. The structural analysis showed that as the deposition period increased, the presence of the face-centered Co9S8 [28] and the hexagonal CoS structures decreased and the Co9S8 phase increased [12].

The average crystallite size of the films was calculated using Scherer’s equation as follows [29]:

$$D = \frac{k \lambda}{\beta \cos \theta}$$

where $D$ is the average crystallite size, $k = 0.9$ is the particle shape factor, $\lambda = 0.15406$ nm is the wavelength of the X-ray used, $\beta$ is the full-width half maximum of the diffraction peaks, and $\theta$ is the Bragg diffraction angle. The obtained crystallites sizes along the (102) plane of CoS were 52.8 nm, 51.7 nm, 47.1 nm, and 22.5 nm for films deposited at 2 hrs, 2.5 hrs, 3 hrs, and 3.5 hrs, respectively. For the Co9S8 phase, the obtained crystallite sizes for the cobalt sulfide thin films deposited at similar deposition periods were 10.95 nm,
24.26 nm, 56.32 nm, and 60.02 nm, respectively. These results show that the dominant hexagonal CoS phase observed at 2 hrs deposition time was gradually decreased, and at 3.5 hrs of deposition time, it was dominated by the cubic Co₉S₈ phase [29]. The Co₃S₄ phase did not show consistent crystallite size variation with deposition time.

Table 1: Some structural parameters of cobalt sulfide thin films and their reference Pdf file numbers.

| Deposition time (hrs) | Measured 2θ (deg) | Phase               | Index                | Standard       |
|-----------------------|-------------------|---------------------|----------------------|----------------|
| 2                     | 12.4              | —                   | —                    | —              |
|                       | 14.8              | Co₃S₄               | Pdf# 01-1279         | (111)          |
|                       | 16.4              | Co₉S₈               | Pdf# 75-1561         | (102)          |
|                       | 21.18             | CoS                 | Pdf# 01-1279         | (220)          |
|                       | 24.64             | Co₉S₈               | Pdf# 75-2023         | (220)          |
|                       | 50.5              | Co₃S₄/Co₉S₈/Co₄S₃ | Pdf# 190364/Pdf#021338 | (511)/(331)/(331) |
| 2.5                   | 12.24             | —                   | —                    | —              |
|                       | 14.8              | CoS                 | Pdf# 01-1279         | —              |
|                       | 16.4              | Co₃S₄               | Pdf# 75-1561         | (111)          |
|                       | 18.36             | Co₉S₈               | Pdf# 75-2023         | (200)          |
|                       | 21.14             | CoS                 | Pdf# 01-1279         | (102)          |
|                       | 22.32             | Co₃S₄/Co₉S₈         | Pdf# 01-1279/Pdf#190364 | (200)          |
|                       | 23.52             | CoS                 | Pdf# 01-1279         | —              |
|                       | 24.64             | Co₉S₈               | Pdf# 75-2023         | —              |
|                       | 29.54             | Co₉S₈               | Pdf# 75-2023         | (331)          |
|                       | 30.76             | CoS                 | Pdf# 01-1279         | —              |
|                       | 3                 | 12.26               | —                    | —              |
|                       | 14.82             | CoS                 | Pdf# 01-1279         | —              |
|                       | 16.32             | Co₃S₄               | Pdf# 75-1561         | (111)          |
|                       | 18.24             | Co₉S₈               | Pdf# 75-2023         | (200)          |
|                       | 20.24             | CoS                 | Pdf# 01-1279         | —              |
|                       | 21.46             | CoS                 | Pdf# 01-1279         | —              |
|                       | 22.02             | Co₃S₄/Co₉S₈         | Pdf# 01-1279/Pdf#190364 | (200)          |
|                       | 23.52             | CoS                 | Pdf# 01-1279         | —              |
|                       | 24.58             | Co₉S₈               | Pdf# 75-2023         | —              |
|                       | 49.8s₄            | Co₉S₈               | Pdf# 190364          | (331)          |
|                       | 14.92             | CoS                 | Pdf# 01-1279         | —              |
|                       | 15.28             | Co₃S₄/Co₉S₈         | Pdf# 01-1279/Pdf#75-2023 | (111)          |
|                       | 18.44             | Co₉S₈               | Pdf# 75-2023         | (200)          |
| 3.5                   | 20.34             | CoS                 | Pdf# 01-1279         | —              |
|                       | 21.36             | CoS                 | Pdf# 01-1279         | —              |
|                       | 22.12             | Co₃S₄/Co₉S₈         | Pdf# 01-1279/Pdf#190364 | (200)          |
|                       | 50.48             | Co₃S₄/Co₉S₈/Co₄S₃ | Pdf# 190364/Pdf#021338 | (511)/(331)/(331) |

Figure 1: XRD pattern of cobalt sulfide thin films deposited at different deposition time.
3.2. Morphology and Composition Analysis. Figures 2(a) and 2(b) show typical SEM images of cobalt sulfide thin films deposited at 2 hrs and 3 hrs, respectively. The films covered the substrate uniformly with cottony spherical grains at the background. No pinholes and cracks were observed for both films. The SEM images also show isolated spherical-shaped and polygonal-shaped grains on the surface of the films deposited at 2 and 3 hrs, respectively. The size of the polygonal-shaped grains varied from 0.9 μm to 2.28 μm. Many authors reported complex multifaceted SEM images of cobalt sulfide thin films formed by a network of elongated grains [3, 20, 30, 31]. However, few authors reported SEM images similar to the current result [24, 25, 32], particularly, when they used Na2S as an anion source. Na2S is expected to generate free S2− easily to assist ion-by-ion deposition mechanism for the film growth. The observed morphology in the current work could be resulted from the ion-by-ion film growth mechanism, which is common in most of the acidic bath-deposited chalcogenide thin films [22, 33]. However, the larger top grains indicate the adsorption of cluster of grains on the surface of the substrate at the final growth stage of the films, which were initially grown in the solution.

Typical EDX spectra of the cobalt sulfide thin films are presented in Figures 3(a) and 3(b). The EDX analysis of the thin films deposited at 2 hrs and 3 hrs revealed the presence of cobalt (Co) and sulfur (S) with no Co to S ratio variation with deposition time. The ratio of Co : S in the cobalt sulfide thin films deposited at 2 hrs and 3 hrs is 23:77. The significant dominance of sulfur could be resulted from the existence of free sulfur in the interstitial site as well as the cobalt vacancy in the crystal structure. However, many reports show Co-dominated cobalt sulfide thin films [20, 30]. The presence of carbon, oxygen, sodium, aluminum, and other elements could be related to the glass substrate and the carbon coating of the films before SEM/EDX measurements [34].

3.3. Optical Properties

3.3.1. UV-Vis Spectroscopic Study. The UV-Vis optical properties of the cobalt sulfide thin films deposited at different deposition periods were investigated by measuring the absorbance of the films in the wavelength range of 500–1500 nm. All the films have broad absorption edge and high absorption in the visible region. Energy band gaps and transition type of the thin films were obtained using Stern relationship (Equation (2)) at the near-fundamental absorption edge [35].

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

(2)

where A is the absorbance, $k$ is the constant, $\nu$ is the frequency of the radiation, $h$ is Planck’s constant, and $n$ is 1 for the direct transition and 4 for the indirect transition. In the case of direct transition $(A\nu)^2$, the photon energy $(h\nu)$ (Equation (2)) has linear relation in the region next to the onset of fundamental absorption [36]. Such a linear relation is observed in all the current samples as shown in Figure 4, implying a direct transition; thus, $n = 1$. The band gap energy $(E_g)$ was obtained by extrapolating the linear portion of the $(A\nu)^2$ vs $(h\nu)$ curve towards the $h\nu$ axis. The band gaps of the thin films deposited at 2 hrs, 2.5 hrs, 3 hrs, and 3.5 hrs were 1.75 eV, 1.65 eV, 1.55 eV, and 1.3 eV, respectively (Figure 4). The decrease in the band gap could be due to the increase in the thickness and the crystallite size with deposition time as the terminal thickness and crystallite size have a significant influence on the band gap of the films [20]. The relatively higher band gap values of the films compared to the commonly reported value could be related to the existence of excess sulfur in the thin films. The high absorbance in the visible light region and the band gaps of the films within the range from 1.3 eV to 1.75 eV make the films an appropriate material as an absorber layer in thin film solar cells [37, 38] as well as efficient visible light photocatalyst [39].

3.3.2. FTIR Analysis. FTIR spectroscopy can provide fundamental information on the molecular structure of organic and inorganic components. Figure 5 shows the FTIR spectra of cobalt sulfide thin films deposited at 2 hrs and 3.5 hrs. Both spectra consist of five absorption peaks. The film deposited at 2 hrs has absorption peaks at 3209 cm−1, 1638 cm−1, 1428 cm−1, 1067 cm−1, and 607 cm−1. The peak at 3209 cm−1 and 1638 cm−1 are characteristic peaks to the stretching vibration and bending vibration of OH groups due to H2O molecules, indicating the absorption of water by the samples [40]. The absorption peaks at 1428 cm−1 and 1067 cm−1 were assigned to C–O–H and C–O stretching vibrations, respectively. The carbon containing compounds could be either from the starting reagents as all of them are carbon containing reagents or from atmospheric CO2. In addition, the intense peaks at 1067 cm−1 and 1068 cm−1 correspond to the bending vibration of sulfonated groups in the CoS, Co3S4, and Co9S8 phases. The peak observed at 607 cm−1 is a characteristic peak of Co-S stretching vibration modes and the polysulfide bond group [41, 42]. The presence of the 608 cm−1 frequency polysulfide band is consistent with excess of sulfur in the thin films, as confirmed by the EDX analysis. The observed bands of the OH bending vibration and C–OH deformation vibration significantly shifted to lower frequency position with increasing deposition time signifying the weakening of different modes of vibrations of different functional groups, particularly the OH and C–OH, groups. However, no significant shift on the position of the bands for the sulfonated group bending vibration and the double sulfide group is observed with deposition time. The increase in the absorption intensity of the polysulfide group could be related to the increase in the particle size and thickness of the films with deposition time. The band broadening observed in the sulfur containing group indicates the nonuniform distribution of particle size and shape with deposition time. The two most intense absorption bands due to the sulfur
containing compound at the frequency of 607 cm\(^{-1}\) and 1068 cm\(^{-1}\) implies the existence of minimum impurities due to other nonsulfide groups [5].

3.4. Photoluminescence Analysis. The photoluminescence (PL) property of the cobalt sulfide thin films was studied by using xenon lamp for electron excitation at room temperature. The emission spectra were observed in the range of 340–500 nm. Broad intense peaks corresponding to violet light were observed at 381 nm, 384 nm, 386 nm, and 391 nm for cobalt sulfide thin films deposited at 2 hrs, 2.5 hrs, 3 hrs, and 3.5 hrs, respectively (Figure 6). The violet emission peaks could appear at 366 nm as the size of CoS nanoparticles reduces [43]. The peak broadening could be resulted from the nonuniform distribution of grains due to
the presence of different phases of cobalt sulfide. The red shift in the violet light PL emission could be due to the conduction and valence bands broadening as a result of increase in crystallite size with deposition time. The fluorescence spectra of all the thin films have shown blue emission peaks at the same wavelength of 467 nm. Blue PL emission peak of wavelength 460 nm was reported by Emadi et al. [44] for cobalt sulfide nanoparticles. Films deposited for a period of 3 hrs and 3.5 hrs have shown additional ultraviolet emission peaks of 349 nm. As the PL properties of semiconductors are extremely sensitive to the local environment and to the presence of structural defects, the violet and blue emissions are expected to be originated from Co vacancy and S interstitial-related defects [24, 45].

3.5. Electrical Resistivity Measurement. The electrical resistivity of the films was measured by the two-probe method at room temperature. The measured values for films deposited at 2 hrs, 2.5 hrs, 3 hrs, and 3.5 hrs were $1.7 \times 10^6$, $5 \times 10^4$, $5 \times 10^3$, and $1.3 \times 10^4 \Omega \cdot \text{cm}$, respectively. The room temperature resistivity of the films is in the range of semiconductors’ resistivity except the film deposited at 2 hrs. The resistivity values agreed with other researchers’ report [46, 47]. The decrease in resistivity could be attributed to the increase in film thickness and crystallite size as the deposition period increases [48, 49]. This results in the valence and conduction band broadening, which in turn results in band gap narrowing. The narrow band gap films become more conductive as electrons can easily be raised from the
valence band to conduction band by room temperature thermal energy.

4. Conclusion

Cobalt sulfide thin films were synthesized from acidic chemical baths containing cobalt acetate, thioacetamide, and disodium EDTA by varying the deposition time. The effects of deposition time on the structural, morphological, optical, photoluminescence, and electrical properties of the films were investigated. The films consisted of mixed phases of hexagonal CoS, face-centered cubic Co$_3$S$_4$, and cubic Co$_9$S$_8$ phases. The films deposited at 2 hrs and 2.5 hrs are dominated by the hexagonal CoS phase and that deposited at 3.5 hrs are dominated by the cubic Co$_9$S$_8$ phase. The films’ surface morphologies were dominantly formed from compacted cottony spherical grains without pinholes and cracks. The EDX and the FTIR spectra confirmed the presence of Co and S in the films. PL investigation confirmed emission of ultraviolet, violet, and blue lights upon excitation by xenon lamp. The violet light gets red shifted as the deposition period increased from 2 hrs to 3.5 hrs. The optical analysis result revealed high visible light absorption of the films and a red shift in the band gap with increasing deposition time. The two-probe electrical measurement showed decrease in the resistivity of the films with increase in the crystallite size.

Data Availability

The XRD, UV-VIS, FTIR, and photoluminescence data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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