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Structural Morphological and Optical Characterization of Cobalt Sulfide Thin Films Synthesized by Chemical Bath Deposition

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Abstract:

Uniformly distributed thin film of cobalt sulphide (CoS) is synthesized by using inexpensive chemical bath deposition method. The as-grown samples were characterized by using X-ray diffraction (XRD), Scanning electron microscopy (SEM) and UV-VIS spectroscopy. The as-grown sample shows amorphous nature of the thin film of CoS by means of X-ray diffraction pattern. SEM shows that the grains of CoS are completely covered over the substrate. The UV-VIS absorption spectrum of CoS thin films shows high absorption in the visible region around at 670 nm.

Keywords **—Chemical Bath Deposition, CoS thin film, XRD, SEM, UV-vis spectroscopy.**

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I. Introduction

Solar power is by far the leading renewable energy source and arguably the only reliable alternative to fossil fuels for the production of electrical energy without the production of carbon dioxide. For this reason, scientists have been working on the development of various kinds of cells that which convert solar energy into electrical energy, and the cells that have been developed include silicon-based p-n junction solar cells, photoelectrochemical solar cells, organic solar cells, quantum dot solar cells, dye-sensitized solar cells (DSSCs) etc.[1]. Among these photovoltaic cells, Dye-sensitized solar cells (DSSCs) have attracted much interest in recent years due to better energy conversion efficiency, ease of fabrication, low manufacturing cost and environmental friendliness [2]. In general, a DSSC device consists of dye molecules coated metal-oxide semiconductor as working electrode, electrolyte, spacer, and counter electrode (CE). Recent studies have focused on various technologies in the fabrication of DSSCs, including (1) synthesis of new dye molecules to absorb all types of solar light wavelengths (2) new graded semiconductor materials for the working electrode (3) growth of solid-state DSSCs using hybrid perovskite $CH_3NH_3PbI_3$ dye and (4) substitution of platinum (Pt) counter electrode.

Although the use of platinum in DSSC has an excellent catalytic property, platinum is a rare and noble metal and therefore extremely expensive. It makes the cost of DSSC expensive. In order to reduce production costs DSSCs, it is necessary to use cheaper materials with similar performance to replace platinum. So far, a variety of alternatives such as polymeric carbon and transition metal-containing conducting materials have been proposed in the literature to replace the Pt counter electrode [3,4]. For use as a counter electrode in place of Pt, it is essential to have the following properties, such as better conductivity, stability and electrocatalytic capability for reduction of the electrolyte. Considering these requirements, cobalt sulfide (CoS_2) has been considered as one of the most promising candidates. Cobalt sulfide is a metal sulfide group from inorganic material with formula Co_xS_y..In 2009, CoS_2 was used as counter electrode in dye sensitized solar cell (DSSC) for the first time to replace platinum as counter electrode and shows the good catalytic activity for tri-iodide reduction then achieved 6.5% of efficiency [5]. Thin films of Cobalt sulfide are produced via different techniques electrodeposition, chemical bath deposition, spray pyrolysis and surfactant-assisted preparation of a metal organic framework.

In this study, thin film of CoS is prepared onto glass substrate using an inexpensive chemical bath deposition (CBD) method at room temperature, resulting CoS_2 thin film. The technique of CBD is based on the controlled precipitation of a compound from a solution on a suitable substrate. This technique offers many advantages over the more established gas phase routes, such as CVD, MBE and spray pyrolysis. In the technique it is possible to control the film thickness and composition by varying the solution pH, temperature and reagent concentration.

II. EXPERIMENTAL DETAILS:

Cleaning of substrate plays an important role in the deposition of thin films. Microscope glass slides were used as substrates for thin films deposition. The cleaning of the glass slide was done by first washing with soap solution and running water. Then they are dried by wiping with cotton and immersed in concentrated hydrochloric acid and kept overnight. The acid dipped slides were thoroughly washed with double distilled water and ultrasonically cleaned in methanol for 15 minutes. Finally, the glass slides were dried in oven for 2h at 60°C.

All the reagents are AR grade and used without any further purification. A brief description of Synthesis method of the thin film of CoS is summarized as follows [6]. First of all, 10 ml of 1 M $CoSO_4$ (cobalt sulfate) solution was freshly prepared in double distilled water. To this solution, 2 ml of triethanolamine (TEA) was mixed under continuous stirring which makes Co^{2+}–TEA complex. It was seen that in starting, the mixture does milk and turbid solution. After addition of 16 ml, 25% aqueous ammonia under stirring condition it became transparent clear solution. To this mixture, 10 ml of 1 M thiourea and around 115 ml double distilled water was finally added under constant vigorous stirring. Total volume of the resulting mixture was then made up to around 200 ml. Resulting pH (≈11±0.3) of the bath containing above reaction mixture was measured with the help of digital pH meter. The pre cleaned glass slides were mounted on a specially designed substrate holder attached to a constant speed motor and kept rotating with at 70±2 rpm in the reaction mixture for an hour. During thin film growth the temperature of water bath was held constant at 80 ± 2 ^{0}C.

A: Characterization of thin film of CoS

The thickness of CoS film was measured with the help of weight difference method employing sensitive electronic microbalance (Citizen CX-265). The structural characterization of CoS thin film was performed by an X-ray diffractometer (Rigaku rotating anode H-3R) using Cu-Kα radiation taken from 10^0 to 60^0.The surface morphology of the films was characterized by scanning electron microscopy (SEM).The optical absorbance of the sample was measured in 600 –1100 nm wavelength rangewith Shimadzu (1800) spectrophotometer.

III. RESULTS AND DISCUSSION:

A: Thickness measurement

Film thickness is important parameter in the study of film properties. The thickness of CoS film was measured with the help of weight difference (gravimetric) method employing sensitive electronic microbalance. In this method, area and weight of the film are measured. The thickness (t) was obtained using the formula [7]

$$t = \frac{M}{\rho \times A} \qquad (1)$$

Where, M = $m_1 - m_2$, is mass of the film material (in gm), m_1 is mass of the substrate with film, m_2 is mass of the substrate without film, ρ is density of the film material (gm/cm^3) and A is area of the film (in cm^2).The thickness of the film is estimated to be 320 nm.

B: Structural Characterization

Figure 1 shows the XRD pattern of the CoS thin film. It shows broad humps which could be due to the amorphous nature of the sample and glass substrate. From the XRD diffractogram it can be seen that two peaks are clearly located at 2θ value of 14.86^0 and 21.1^0.

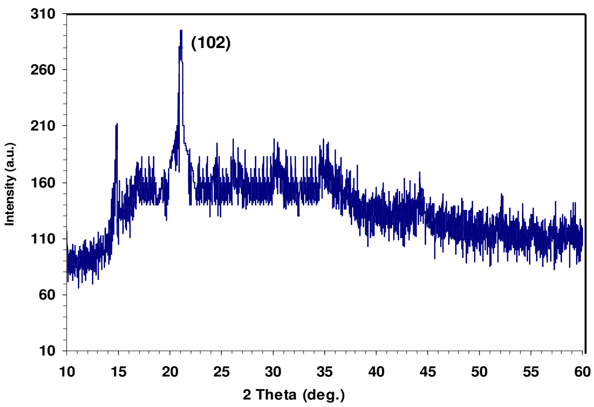

Figure-:1 X-ray diffraction pattern of CoS thin films

The highly oriented peak located at 21.1^0 is assigned (102) plane of the hexagonal CoS structure (JCPDF file 011-279). It is also observed that no other intense peaks are observed in the XRD patterns. This suggested that pure CoS films is deposited onto the glass substrate.

The average crystallite size D, is calculated from the full width at half maximum (β) of the dominant (102) peak using Scherrer's equation [8]-

$$D = \frac{0.9\lambda}{\beta cos\theta} \qquad (2)$$

where, λ and θ are the, wavelength of the X-raysource and Bragg's angle respectively. The size ofthe crystallite is found to be 20 nm.

3.3 Surface morphology

Figure 2 shows the SEM image of as prepared thin film of cobalt sulfide onto glass substrate. The SEMimage clearly depicts that the as synthesized materials is well covered the whole substrate. The micrographalso reveals the morphology of the CoS have texture structure and pit shaped structures. Such types of structure of materials are very useful in dye sensitized solar cells as a counter electrode.

3.4Optical properties

The UV–Visible absorption spectra of the thin film of cobalt sulphide is shown in Fig. (3). From the figure it is clear that a strong absorption in the visible region was observed between 600 and 700 nm wavelength region. The absorption spectra also depict fundamental absorption edge around at 670 nm.

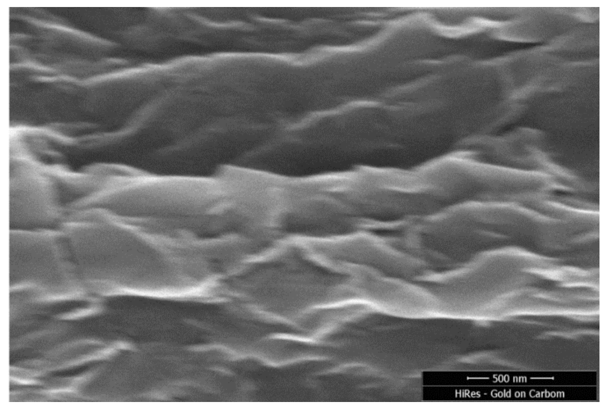

Figure-:2 SEM image of cobalt sulfide onto glass substrate

The band gap value has been calculated by the Tauc's formula [9]

$$(\alpha h\nu)^{\frac{1}{n}} = A(h\nu - E_g)(3)$$

The value of band gap of cobalt sulphide has beencalculated by extrapolating the linear region of the plots$(\alpha h\nu)^2$ vs $h\nu$on the energy axis, as shown in Fig.4 The band gap values are calculated to be 1.85 eV which is blue shifted from the bulk counterpart.

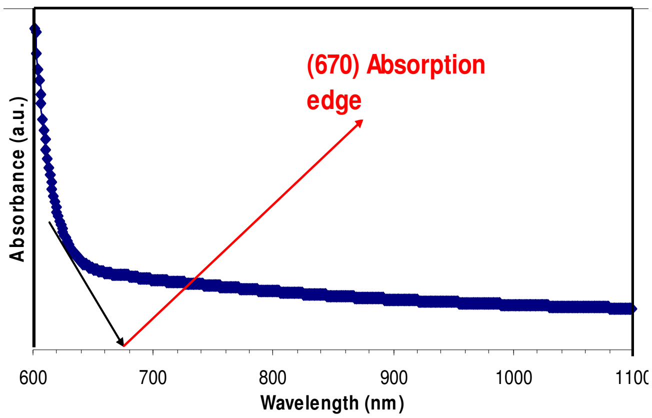

Figure-:3 UV-vis spectra of CoS thin films onto glass substrates

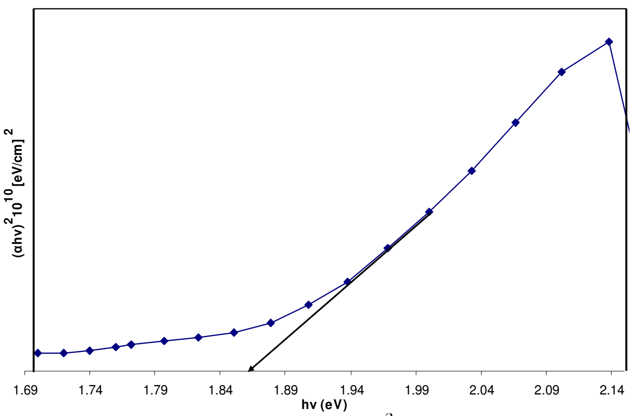

Figure-: 4 Plots of $(\alpha h\nu)^2$versus $h\nu$

4. Conclusion

In conclusion, good quality thin film of CoS_2 was synthesized successfully by the inexpensive and simple chemical bath deposition on glass substrate. The structural, morphological and optical properties of the films of CoS_2 is reported. XRD of the thin film revealed hexagonal CoS structure. SEM image exhibits that the as-grown thin films are texture and pit shaped structures without pinholes and cracks. The optical studies result shows the high visible light absorption of the films and a blue shift in the band gap 1.85 eV. It is suggesting that the CoS_2 will be inexpensive, abundant and best alternative to platinum when used as counter electrode in DSSCs.

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