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Cobalt sulfide thin films: Chemical growth, reaction kinetics and microstructural analysis

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ABSTRACT

CoS thin films were successfully deposited from an aqueous alkaline bath containing ammonia and TEA as the complexing agents. Under the pre-optimized conditions (temperature = 80 ± 0.5 °C, speed of the substrate rotation = 65 ± 2 rpm and deposition period = 90 min), ammonia and TEA quantities in the reaction bath were found to play a decisive role in the final product yield. Highly uniform, dark sea-green colored and tightly adherent deposits were obtained at our experimental conditions. As-obtained CoS thin films were polycrystalline in nature with hexagonal class of crystal system as derived from the X-ray diffraction analysis. Complex multifaceted webbed network of as-grown CoS crystals elongated and threaded into each other were observed through a scanning electron microscope. Atomic force micrographs revealed collapsing of the hillocks and filling of the valleys triggering decrease in the RMS roughness for increased TEA and NH₃ quantities. Magnetic force microscopy (MFM) was employed to study surface topography in terms of magnetic mapping. MFM images highlighted the existence of the magnetic clusters imitating topography. Broad absorption edge with high absorption coefficient ($\alpha \approx 10^4$ cm⁻¹) was observed for as-grown CoS thin films. Determined values of the optical bandgaps revealed influence of complexing environment on the final product.

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1. Introduction

II–VI and IV–VI group chalcogenides are classified as direct band gap semiconductors with a sharp optical absorption edge and large absorption coefficients [1,2]. Especially, assent to alter physical and material properties craft them as a requisite optoelectronic class of materials. They are relatively easy to synthesize and are generally prepared as the particles or in thin film forms [1,2]. Consequently, semiconductor thin films of II–VI and IV–VI groups, are of great interest due to their unique physical and electro-optic properties and their potential applications in a variety of optoelectronic devices such as in photoconductors, radiation detectors, DMS materials, light emitting diodes, lasers, thin film transistors and photoelectric cells including photoconductive and photovoltaic solar cells. Cobalt sulfide is one of the members of this family that exists in a number of metal chalcogenide phases (such as CoS, CoS₂, Co₃S₄ and Co₉S₈) and is complicated in view of its chemical composition [3–8]. They are of particular interest due to their unique catalytic, electrical, optical, and magnetic properties and

exhibit strong intrinsic absorption in the visible and near infrared regimes of the electromagnetic spectrum. In view to gain insight into these inherent properties, several efforts have been dedicated to the synthesis of cobalt sulfides with various morphologies such as nanoparticles, nanowires, thin films, octahedrons and recently sea urchin-like phases [3–8].

Considering thin films as a reliable and cost-competitive means for industrial escalation, we have adopted a novel chemical route as a synthesizing tool. The technique is indigenously developed and automated to provide highly adherent and uniform deposits of controlled composition [1–3,9–12]. Moreover, the method allows for the production of large area films for industrial purpose. Till today, the technique has been successfully used to deposit a variety of semiconductor thin films and it has earned a core place in the flexible electronics [1,2,9–14]. Instead, the mechanism of thin film formation by this method have not been understood sufficiently well [9,13]. For instance, particle size control with this technique is difficult so far. Present studies were undertaken to ascertain and control the growth mechanism of CoS thin films through the alterations in growth parameters, in particular concentrations of ammonia and triethanolamine were varied. The as-observed changes in the materials characteristics such as film

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thickness, surface morphology, RMS roughness and energy band-gap were noted and have been correlated adequately.

2. Experimental details

2.1. Cobalt sulfide thin film deposition

The thoroughly cleaned amorphous spectroscopic grade glass substrates were used for deposition of the CoS films. Chemical deposition is the occurrence of a moderately slow chemical reaction in the solution bath that results into a solid product on the immersed substrate. All the solution precursors used for the preparation of CoS films were prepared in fresh double distilled water using AR Grade chemicals. In actual, the CoS films were prepared by; first, 10 ml, 1 M cobalt sulfate solution was mixed with triethanolamine (TEA) in a 250 ml beaker under continuous stirring to form a Co^{2+} -TEA complex. Initially, the mixture was milky and turbid which became clear with addition of 25% aqueous ammonia and the mixture was stirred for 5 min. To this mixture, 10 ml, 1 M thiourea was finally added under constant vigorous stirring. Total volume of the resulting mixture was then made up to 200 ml by adding distilled water. Resulting pH of the bath containing above reaction mixture was measured with the help of digital pH meter. Then beaker containing reacting solution was transferred to temperature oil bath which was held constant at 80 ± 0.5 °C. To study the effect of ammonia and TEA concentrations on CoS thin films growth, the deposition trend was adopted such that, sample series were prepared by varying the ammonia concentration or TEA concentration separately while keeping the other conditions and reagent concentrations constant. In case of ammonia variation arbitrary value of TEA = 4 ml was selected and for TEA variation 15 ml of NH_3 concentration was selected based on the terminal layer thickness measurement outcomes.

Pre-cleaned glass substrates were mounted on a specially designed substrate holder and then set in rotation (65 ± 2 rpm). After deposition duration of 90 min, substrates were taken off the beaker, rinsed with double distilled water to remove loosely adherent CoS particles from the surfaces before they were dried in air and preserved carefully. The CoS samples deposited optimistically as above were uniform, strongly adherent to the substrate support, and dark sea-green colored.

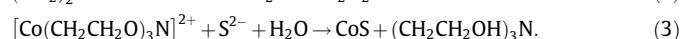
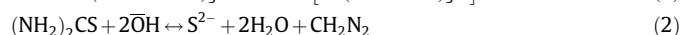
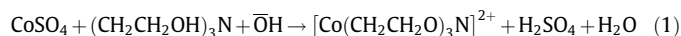
2.2. Sample characterization

The as-grown thin films were analyzed using different techniques. An interference technique was employed to measure the terminal layer thickness of the films. X-ray diffraction was used to identify the structure of the CoS thin films using Cu α radiation ($\lambda = 1.5406$ Å, 40 kV, 30 mA, in the 2θ range from 10° to 80°). Surface morphologies were observed through the scanning electron microscope (A JEOL 6360-2300 SEM) and an atomic force microscope (AFM-Innova: Bruker). Magnetic force microscopy was performed on the samples in order to obtain further magnetic morphological insights of deposited films. The optical transmission measurements were recorded using UV-Vis spectrophotometer (BIO-AGE UV = VIS 2800 PC), in the 200–1600 nm wavelength range.

3. Results and discussion

3.1. Reaction kinetics and growth mechanism

In general, deposition of the metal chalcogenide initiates only when the concentration of anions and cations exceeds the solubility product (K_{sp} CoS = 10^{-21}) [9,14]. Excess concentration in the reaction bath leads to supersaturation, providing the driving force and therefore favoring nucleation due to unstable thermodynamic condition [9]. Thus, supersaturation forms necessary constraint for nucleation to occur, which can be attained by adding the necessary reactants. The ionic product exceeds the solubility product and precipitation occurs via heterogeneous growth reaction on the substrate. Co^{2+} and S^{2-} ions react with each other and form nuclei which either precipitates spontaneously or very slowly in highly alkaline medium. When the ionic product starts to exceed the solubility product, cobalt sulfide nuclei are produced both on the substrate and in the solution. Thus, they serve as an ideal building blocks and tend to assemble into the form of primary structures. This activates the nucleation of the CoS layer in an aqueous alkaline environment and consequently initiates the development of a thin solid deposit onto the substrate surface [9,10]. A possible growth process for the formation of CoS thin film layer can be proposed as follows:



Initially, TEA forms a complex with Co^{2+} , which controls and decreases the release rate of free Co^{2+} ion concentration and in turn reduces the rate of film growth. Formation of the Co^{2+} -TEA complex avoids homogeneous nucleation in the solution due to the binding of Co^{2+} ions and provides priority to the heterogeneous nucleation on the substrate. On the other hand, $(\text{NH}_2)_2\text{CS}$ is considered to decompose at a particular temperature to produce S^{2-} ions slowly for the final formation of CoS. The reaction between Co^{2+} -TEA complex and S^{2-} anions originating from the hydrolysis of $(\text{NH}_2)_2\text{CS}$ results in the formation of a single CoS nuclei.

Dynamics of thin film formation ensues nucleation and recurrent growth from the seed to spreaded structure/layer. Because an individual nucleus exhibits high surface energy, such nuclei aggregate perpendicularly to the substrate surface to decrease the surface energy. Vivacious role of cohesive forces (viz. van der Waals forces or chemical attractive forces) embrace adsorption of the nuclei onto the surface of a growing seed to form primary structure and spread outward in the form of layers, with more layers forming and growing on top [9,10]. Both the mechanical churning and growth time enhances the arrangement of aggregate to form CoS layers as the reaction proceeds.

3.2. Role of complexing agents

As a general rule in chemical bath deposition, thin film deposition proceeds at some moderate ion release rate [1,2,9,13]. This route is based on the controlled precipitation of the desired compound from the reaction bath. A complexing agent is usually employed to control the reaction at a suitable rate to obtain the desired thin film growth [1,9,10]. Habitually metal ions are manageable to form chalcogenides/oxides or other un-expected compounds in the reaction bath. Complexing agent conceal metal ions to be deposited owing to its chelating behavior, consequently, forming complex with the metal ions and catalyzing nucleation by adsorbing metal ions at the substrate surface. In our case, it is observed that the rate of reaction is governed by the presence of complexing agent, which controls release rate of Co^{2+} ions and arrange them to deposit as a final desired product. Both ammonia and TEA liberate $\bar{\text{O}}\text{H}$ ions in the solution bulk and form complex with Co^{2+} ions. Hence, with the addition of ammonia and TEA, two processes start simultaneously; (i) the complexation of Co^{2+} ions, and (ii) the control of the pH of the resulting solution which enhances the rate of thin film layer formation. The addition of $\bar{\text{O}}\text{H}$ ions (increase in ammonia quantity) makes the Co^{2+} -TEA complex more stable and metal ions are well arrested by the complexing agent which controls the rate of release of metal ion species and consequently the layer thickness [9,10]. Therefore, quantities of NH_3 and TEA in the reaction bulk were varied one by one and the terminal layer thickness was measured. Fig. 1(a) shows variation in layer thickness with ammonia concentration, varied from 10 ml to 25 ml with arbitrary concentration of TEA (4 ml). It has been observed that the terminal layer thickness increased almost linearly with increase in NH_3 concentration up to 15 ml and then decreased for further increase in NH_3 in the bath. Similar trend is observed when TEA concentration in the bath was varied from 2 ml to 6 ml and NH_3 concentration was kept at its optimized value (15 ml). The variation in layer thickness with TEA concentration is shown in Fig. 1(b).

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