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**BATH PARAMETER DEPENDENCE OF CHEMICALLY-  
DEPOSITED COPPER SELENIDE THIN FILM**

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In this article, a low cost chemical bath deposition (CBD) technique has been used for the preparation of  $\text{Cu}_{2-x}\text{Se}$  thin films on to glass substrate. Different thin films (0.2-0.6 $\mu\text{m}$ ) were prepared by adjusting the bath parameter like concentration of ammonia, deposition time, temperature of the solution, and the ratios of the mixing composition between copper and selenium in the reaction bath. From these studies, it reveals that at low concentration of ammonia or TEA, the terminal thicknesses of the films are less, which gradually increases with the increase of concentrations and then drop down at still higher concentrations. It has been found that complexing the  $\text{Cu}^{2+}$  ions with TEA first, and then addition of ammonia yields better results than the reverse process. The film thickness increases with the decrease of value x of  $\text{Cu}_{2-x}\text{Se}$ .

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## 1. Introduction

Copper selenide is a semiconducting material, which has electrical and optical properties suitable for photovoltaic application. The techniques adopted for deposition of this metal chalcogenide vary from reaction of metallic copper with selenium dissolved in a benzene medium [1] or an aqueous medium [2], flash evaporation [3], vacuum evaporation [4-7], melting of Cu and Se [8,9], and electrodeposition [10], to the simplest method of chemical bath deposition (CBD) [11-22]. Copper selenide exists in widely differing crystallographic structures depending on the method of preparation even at room temperature. Okimura and Matsumae deposited  $\text{Cu}_{2-x}\text{Se}$  thin films on to glass substrates by vacuum evaporation method and reported the dc electrical properties. They found p-type conduction with low resistivity. They fabricated  $\text{Cu}_{2-x}\text{Se}$  thin film solar cells, which showed conversion efficiency of about 8.8% and good stability [5]. Chen *et al.* used copper selenide as an absorbing layer and reported a  $\text{Cu}_{2-x}\text{Se}/\text{CdS}$  heterojunction solar cell with an efficiency of 5.38% [7]. Lakshmi *et al.* reported the depth profiling of as-deposited  $\text{Cu}_3\text{Se}_2$  film [21, 22].

During the last two decades, less expensive methods, like chemical and electrochemical conversion, precipitation, ion displacement, electrodeposition and low temperature dip type for the preparation of copper selenide and their characterization have been reported by several authors [1, 2, 8-23]. CBD is a method of growing thin film of certain materials on a substrate immersed in an aqueous bath containing appropriate reagents at temperatures ranging from room temperature to 373K. It has been identified as one of the techniques for growing  $\text{Cu}_{2-x}\text{Se}$  films at low cost.

Lakshmi *et al.* observed different phases of copper selenide thin films with N, N-dimethylselenourea by controlling bath parameters [21]. In this experiment copper selenide thin films with various ratios of copper and selenium, using sodium selenosulfate as sources of  $\text{Se}^{2-}$  ions, were deposited onto a glass substrate using low cost CBD method. Recently, we have reported the brief result on the characterization of copper selenide thin films deposited by CBD technique [24]. This paper describes the results observed using different bath parameters on the  $\text{Cu}_{2-x}\text{Se}$  film prepared by CBD.

## 2. Experimental details

The chemicals used for the preparation of thin films were LR grade (Merck) cupric chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ), selenium powder of 99.99% purity, sodium sulfite ( $\text{Na}_2\text{SO}_3$ ), tri-ethanol amine (TEA) and ammonium hydroxide ( $\text{NH}_4\text{OH}$ ). First, sodium selenosulfate was made by refluxing fine selenium powder with sodium sulfite solutions for about 30 minutes at 393K by stirring in a beaker. A constant stirring machine with a constant temperature bath was used during the reaction. Secondly,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  solution was mixed with  $\text{NaSeSO}_3$  at constant stirring. 10 ml TEA (0.1 M) was added to this solution.  $\text{NH}_4\text{OH}$  was used to adjust the pH of the reaction bath. Microscope glass slides of  $76 \times 26 \times 1 \text{ mm}^3$  were used as substrates. The substrates were cleaned with detergent and distilled water, and were kept in  $\text{H}_2\text{SO}_4$  for about 1h. Then the substrates were rinsed with distilled water and were dried in air prior to film deposition. The substrates were then immersed vertically into the deposition bath against the wall of the beaker containing the reaction mixture. The deposition was allowed to proceed at room temperature for different time durations from 15 to 180 minutes. After deposition, the glass slides were taken out from the

bath, washed with distilled water and were dried in blowing air. All the samples were annealed in air at higher temperatures up to 523K to observe annealing effects.

A laboratory dc power supply (GPR-3020, GW, Taiwan), an electrometer Keithley 614 (Keithley Instrument Inc. USA) and a digital multimeter (GDM-354A, GW, Taiwan) were used for the measurements. Two points (1.5mm width and 13.6 mm length) on the surface of the film 45 mm apart were made with silver paste for electrical contact. The thickness of the films was determined by using data pack in a UV-121V spectrophotometer (Shimadzu Corp., Japan). Using data pack for the determination of the thickness of the sample is a completely automatic process.

### 3. Results and discussion

The thickness of the film as a function of duration of deposition for different ammonia concentrations at room temperature is shown in Fig. 1. It is seen that at low concentration of ammonia or TEA, the terminal thicknesses of the films are less, which gradually increase with the increase of concentrations and then drop down at still higher concentrations. The same behavior was found for CBD CdSe thin films [25, 26]. Both ammonia and TEA are bases and liberate OH<sup>-</sup> ions in solution, i.e., they increase the pH of the solution. Again, they form complexes with Cu<sup>2+</sup> ions. Hence, on addition of TEA or ammonia to the reaction solution, two processes starts simultaneously. Firstly Cu<sup>2+</sup> ions form the complexes thereby retards the rate of formation of thin films and secondly, the increased pH of the solution enhances the rate of formation of copper selenide thin films. Results show that optimum amounts of both the reagents present in the reaction solution lead to a controlled reaction yielding the maximum terminal thickness of the film. Moreover, it has been found that complexing the Cu<sup>2+</sup> ions with TEA first, and then addition of ammonia yields better results than the reverse process. Hence in all the experiments TEA has been added before ammonia.

Variation of film with the duration of deposition for various concentration of the selenosulfate solution at room temperature is shown in Fig. 2. An optimum amount of the selenosulfate solution is required to deposit the thickest film. The deposition process may be explained as follows: at low selenosulfate concentration, the number of Se<sup>2-</sup> ions being insufficient to combine with all the available Cu<sup>2+</sup> ions, the terminal thickness is observed to be less. As selenosulfate concentration increases, more Se<sup>2-</sup> ions become available to form copper selenide thin films, leading to greater film thickness (curve *b*). Above a certain concentration, when rate of reaction becomes very fast, precipitation dominates over film formation, leading again to lower terminal thickness (curve *c*).

The temperature dependence of film formation as a function of duration of deposition is shown in Fig. 3. With the increase of temperature, the rate of deposition of thin films increases due to increase in the kinetic energy of the reacting ions, i.e., an increase in frequency of collision among the ions. This is reflected in the curve *b* obtained at 338 K, which has a higher deposition rate than that obtained at 303 K. Deposition at further higher temperature, i.e., at 358 K, however, again lead to lower deposition rate on the substrate surface. Here the rate of precipitation becomes much faster than the rate of deposition at the surface. However, deposition at 358 K yields greater terminal thickness than that at 338 K. This is because a total loss of complexation of the Cu<sup>2+</sup> ions occurs at 358 K yielding a colorless solution. While up to 338 K, the solution remains dip-blue even after the experiments were over. This extra release of Cu<sup>2+</sup> ions at 358 K helps to attain greater terminal thickness. One disadvantage that crops up with increase on the

deposition temperature is that the adherence property of the film decreases gradually. The films start peeling off the substrates at higher temperatures of deposition. Moreover, at higher temperatures, the deposition is not uniform. Hence, room-temperature deposition is always preferred at any circumstances.

The variation of film thickness as a function of  $x$  of  $\text{Cu}_{2-x}\text{Se}$  thin film is shown in Fig. 4. It is seen in the figure that the thickness decreases gradually with the increase of  $x$ . This may be due to the increase of concentration of  $\text{Cu}^{2+}$  that react with more available selenium ion in the reaction bath, that increase the nucleation rate and consequently the deposition rate decreases.

Film deposition was also carried out under stirring condition at room temperature. As expected, the rate of deposition in this case was greater than that obtained for the unstirred solution. This is due to the faster arrival of the ions on the substrate surface. However, in case of the stirred solution, an adherent deposit of the precipitate was found to develop gradually at particular positions over the film after the deposition for about 3 to 4 hr. This gives rise to non-uniform film deposition.

In all the experiments, it has been found that an initial induction period of about 5-10 minutes was required after which film deposition starts. This may be due to the fact that the complexing of  $\text{Cu}^{2+}$  ions with TEA and ammonia being quite strong, the release of  $\text{Cu}^{2+}$  ions from the complexes after the addition of selenosulfate solution is a time-consuming process leading to a longer time for the ionic product of copper selenide to exceed its solubility product. Powdery deposits and lack of specular reflection usually accompany higher deposition rate and higher film thickness.

## 4. Conclusions

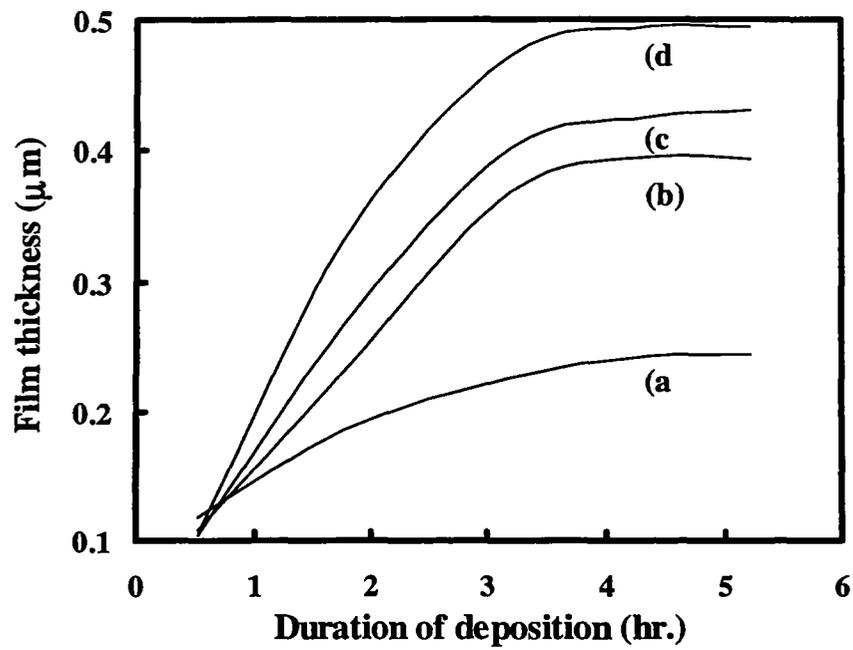
From this study, it reveals that at low concentration of ammonia or TEA, the terminal thicknesses of the films are less, which increases gradually with the increase of concentrations and then drop down at still higher concentrations. It has been observed that by adding TEA first, and then addition of ammonia yields better results than the reverse process. Good quality thin films of smooth surface of copper selenide thin films of compositions  $\text{Cu}_{2-x}\text{Se}$  ( $x=0.1-0.5$ ) was deposited using sodium selenosulfate as a source of selenide ions. Copper selenide thin films of various thicknesses can be found by varying deposition time. For better film TEA has been added before ammonia and without stirring at room temperature deposition with pH value  $\sim 9$  is always preferred at any circumstances.

## Acknowledgments

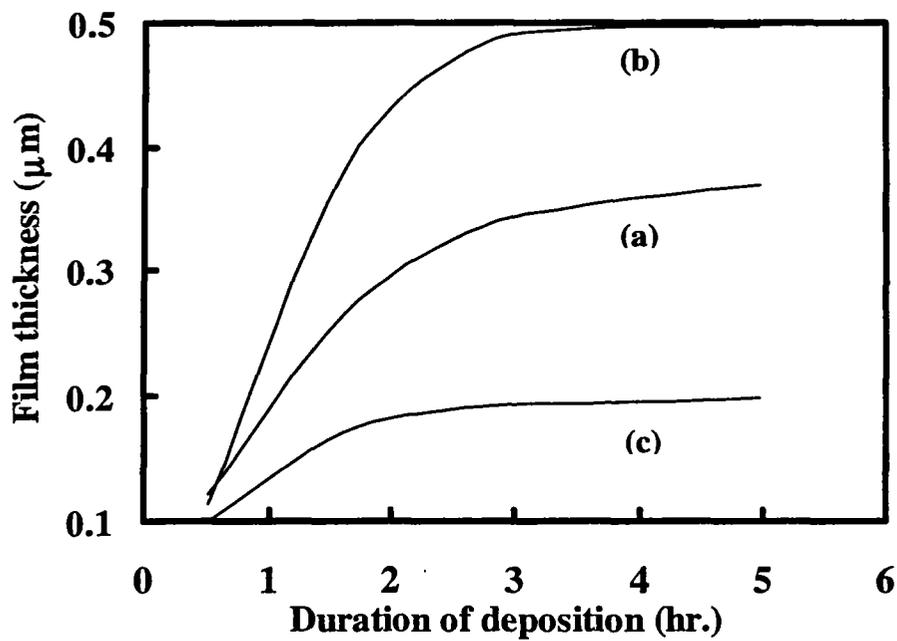
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**Fig. 1.** Variation of  $\text{Cu}_{2-x}\text{Se}$  film thickness with duration of deposition for different ammonia concentrations: curve (a) without  $\text{NH}_3$ , (b) 2 ml of 0.5%  $\text{NH}_3$  (c) 4 ml of 0.5%  $\text{NH}_3$  (d) 6 ml of 0.5%  $\text{NH}_3$ .



**Fig. 2.** Variation of  $\text{Cu}_{2-x}\text{Se}$  film thickness with duration of deposition for different selenosulfate concentrations: curve (a) 100 ml 0.1 M  $\text{Na}_2\text{SeSO}_3$ , (b) 150 ml 0.1 M  $\text{Na}_2\text{SeSO}_3$ , (c) 200 ml 0.1 M  $\text{Na}_2\text{SeSO}_3$ .

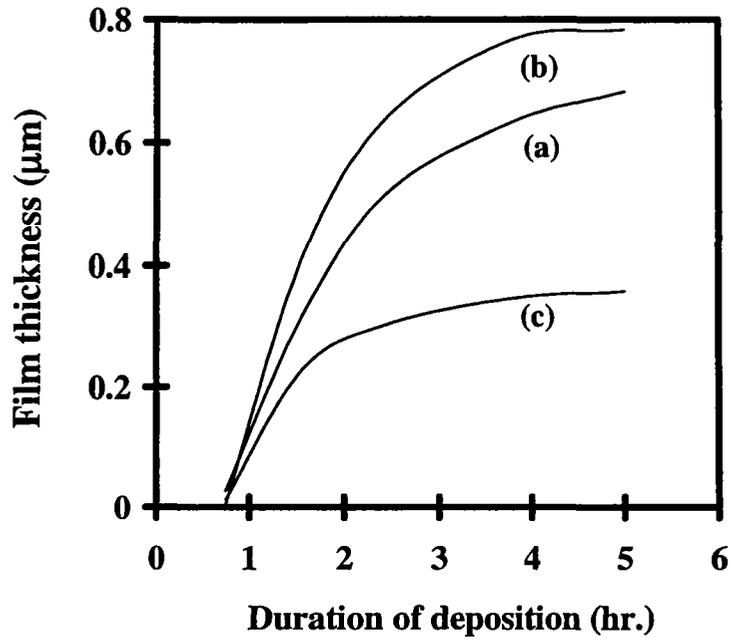


Fig. 3. Variation of  $\text{Cu}_{2-x}\text{Se}$  film thickness with duration of deposition time at different temperatures: curve (a) deposition at room temperature (303 K), (b) deposition at 338 K, (c) deposition at 358 K.

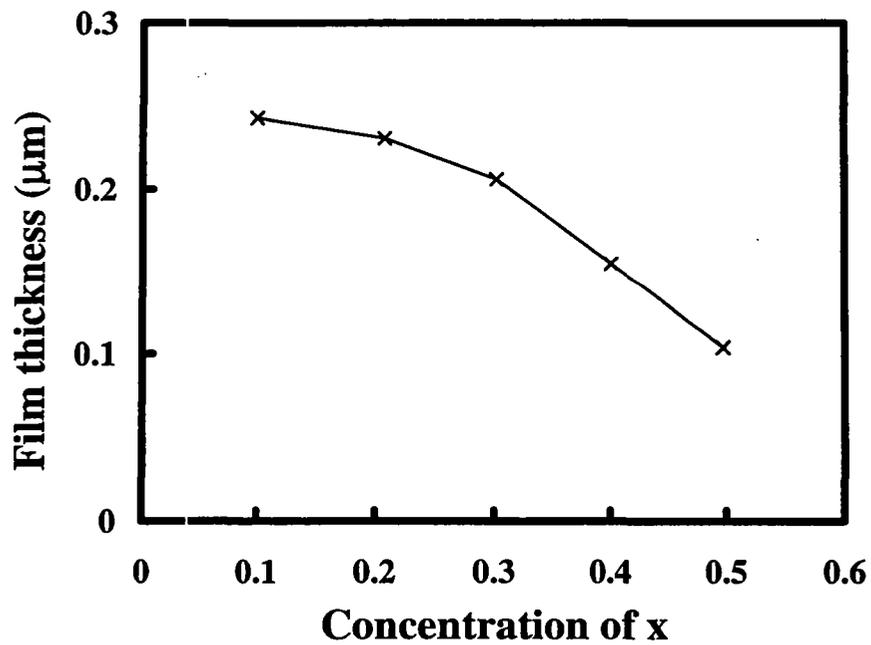


Fig. 4. Variation of film thickness with the value of  $x$  of  $\text{Cu}_{2-x}\text{Se}$  for deposition time 1hr.