JOURNAL OF SOLID STATE CHEMISTRY 55, 116–119 (1984)

Effect of Bath Parameters on Chemically Deposited Thin Films of CuSe

A. MONDAL AND P. PRAMANIK

Department of Chemistry, Indian Institute of Technology, Kharagpur-721302, India

Received April 11, 1983; in revised form May 14, 1984

Introduction

Compound semiconductors and their alloys are of considerable technical interest in the field of electronics and electrooptical devices. These materials can be obtained in thin film form by evaporation, sputtering, pyrolysis, and chemical deposition techniques (*1*). Among all these techniques, chemical solution growth is relatively inexpensive, simple, and convenient for large area deposition. Depositions of thin films of CdS, CdSe, PbS, PbSe, and ZnSe by this method are well known (*2–6*). Various chalcogenide thin films, e.g., Bi_2Se_3, Bi_2S_3, Sb_2Se_3, TlSe, and $Cu_{1.8}S$ (*7–10*) have been developed in our laboratory by this method. We have recently reported the deposition of CuSe (*11*) thin film on glass substrate by this technique. In this paper we present a detailed study on the growth of CuSe thin film on glass substrate depending on various bath parameters.

Experimental Techniques

Copper selenide films have been prepared by using the following overall reactions

$$[Cu(TEA)_n]^{2+} + SeSO_3^{2-} + 2OH^- \rightarrow CuSe + n\text{TEA} + SO_4^{2-} + H_2O \quad (n = 1, 2, 3, \ldots) \qquad (1)$$

$$[Cu(NH_3)_4]^{2+} + SeSO_3^{2-} + 2OH^- \rightarrow CuSe + 4NH_3 + SO_4^{2-} + H_2O \qquad (2)$$

where TEA stands for triethanolamine.

The standard deposition technique has been discussed elsewhere (*11*). The following experiments have been performed to study the growth of the CuSe thin films on glass substrate:

Variation of thicknesses: (i) with change in the concentrations of TEA, ammonia, and sodium selenosulfate solutions, (ii) with different bath temperatures, and (iii) with stirred solutions.

The solution was stirred with a magnetic stirrer.

Results and Discussion

It has been observed that film deposition as a function of dip time versus ammonia and TEA concentrations behave similarly. In Fig. 1 film deposition has been shown as a function of dip time versus ammonia concentration. At low concentrations of ammo-

0022-4596/84 $3.00

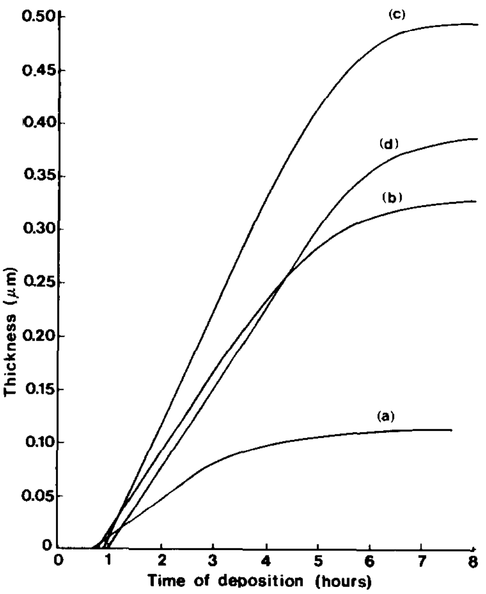

FIG. 1. Variation of CuSe film thickness with deposition time for different ammonia concentrations, curve (a) without NH_3, (b) 3 ml of 0.25% NH_3, (c) 6 ml of 0.25% NH_3, (d) 10 ml of 0.25% NH_3. [Mixture composition: 5 ml of 0.5 *M* $CuSO_4$, 10 ml of 9.8% TEA, varying concentrations of NH_3, 5 ml of 0.45 *M* Na_2SeSO_3, distilled water. Total volume = 50 ml.]

nia or TEA, the terminal thicknesses of the films are less, which gradually increase with increase in their concentrations and then drop down at still higher concentrations. Both of these are bases and liberate OH^- ions in solution, i.e., they increase the pH of the solution. Again, both form complexes with Cu^{2+} ions. Hence, with the addition of TEA or ammonia to the reaction solution, two processes start simultaneously, one the complexation of Cu^{2+} ions, which retards the rate of formation of CuSe and secondly, the increase in the pH of the solution which enhances the rate of formation of CuSe. 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^{2+} ions with TEA first, and then adding ammonia yields better results than the reverse process. Hence in all the reported experiments TEA has been added before ammonia.

In Fig. 2 the effect of various concentrations of the selenosulfate solution on the film thickness of CuSe has been plotted. Here also an optimum amount of the selenosulfate solution is required to deposit the thickest film. The deposition may be explained as follows. At low selenosulfate concentration, the number of Se^{2-} ions being insufficient to combine with all the available Cu^{2+} ions, the terminal thickness obtained is less. As selenosulfate concentration increases, more Se^{2-} ions become available to form CuSe, leading to greater film thickness. Above a certain concentration, when rate of reaction becomes very

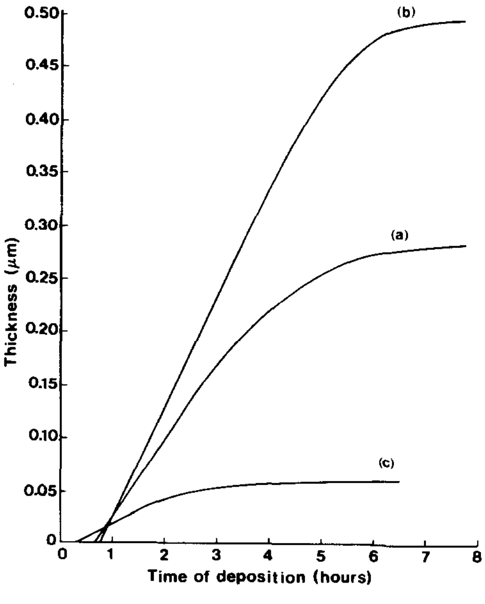

FIG. 2. Variation of CuSe film thickness with deposition time for different selenosulfate concentrations, curve (a) 3 ml of 0.45 *M* Na_2SeSO_3, (b) 5 ml of 0.45 *M* Na_2SeSO_3, (c) 8 ml of 0.45 *M* Na_2SeSO_3. [Mixture composition: 5 ml of 0.5 *M* $CuSO_4$, 10 ml of 9.8% TEA, 6 ml of 0.25% NH_3, varying amount of Na_2SeSO_3 solution, distilled water. Total volume = 50 ml.]

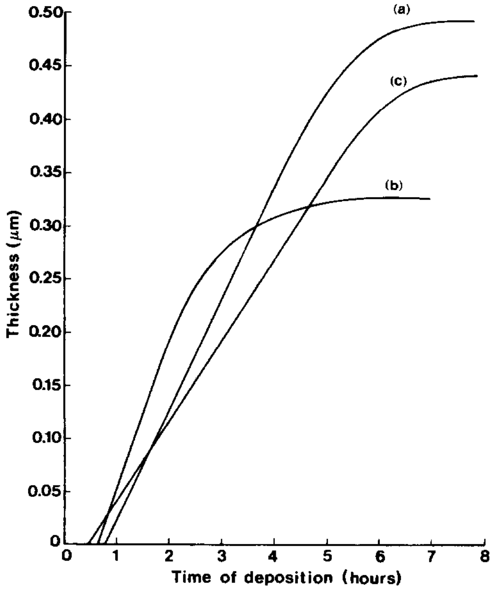

FIG. 3. Variation of CuSe film thickness with deposition time at different temperatures: curve (a) deposition at room temperature (32°C), (b) deposition at 41°C, (c) deposition at 60°C. [Mixture composition: 5 ml of 0.5 *M* $CuSO_4$, 10 ml of 9.8% TEA, 6 ml of 0.25% NH_3, 5 ml of 0.45 *M* Na_2SeSO_3, distilled water. Total volume = 50 ml.]

fast, precipitation dominates over film formation, leading again to lower terminal thickness.

The temperature dependence of film formation has been shown in Fig. 3. With increase in temperature, the rate of deposition of CuSe 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 obtained at 41°C, which has a higher deposition rate than that obtained at 32°C. Depositions at still higher temperature, i.e., at 60°C, 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 60°C yields greater terminal thickness than at 41°C. This is because a total loss of complexation of the Cu^{2+} ions occurs at 60°C yielding a colorless solution. While up to 41°C, the solutions remain deep-blue colored even after the experiments were over. This extra release of Cu^{2+} ions at 60°C helps to attain greater terminal thickness. One disadvantage that crops up with increase in the deposition temperature is that the adherence property of the film is gradually lost. 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.

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 about 3 to 4 hr of deposition. This gives rise to nonuniform films creating an inaccuracy in thickness measurement.

In all the experiments it has been found that an initial induction period of about half an hour to one hour is required after which film deposition starts. This may be due to the fact that the complexing of Cu^{2+} ions with TEA and ammonia being quite strong, the release of Cu^{2+} ions from the complexes after the addition of selenosulfate solution is a time-consuming process leading to a greater time for the ionic product of CuSe to exceed its solubility product.

Acknowledgment

One of the authors (A. M.) is indebted to the Council of Scientific and Industrial Research, India, for financial aid in carrying out this project.

References

1. K. L. Chopra, "Thin Film Phenomena," McGraw–Hill, New York (1969).
2. N. R. Pavaskar, C. A. Menezes, and A. P. B. Sinha, *J. Electrochem. Soc.* **124,** 743 (1977).
3. G. A. Kitaev and T. S. Terekhova, *Russ. J. Inorg. Chem.* **15,** 25 (1970).
4. F. Kicinski, *Chem. Ind.* **17,** 54 (1948).
5. J. Bloem, *Appl. Sci. Res. Sect. B* **6,** 92 (1956).
6. G. A. Kitaev and T. P. Sokolova, *Russ. J. Inorg. Chem.* **15,** 167 (1970).
7. P. Pramanik, R. N. Bhattacharya, and A. Mondal, *J. Electrochem. Soc.* **127,** 1857 (1980).
8. P. Pramanik and R. N. Bhattacharya, *J. Electrochem. Soc.* **127,** 2087 (1980).
9. R. N. Bhattacharya and P. Pramanik, *Sol. Energy Mater.* **6,** 317 (1982).
10. R. N. Bhattacharya and P. Pramanik, *Bull. Mater. Sci.* **3,** 403 (1981).
11. A. Mondal and P. Pramanik, *J. Solid State Chem.* **47,** 81 (1983).