

CHAPTER I
GENERAL INTRODUCTION

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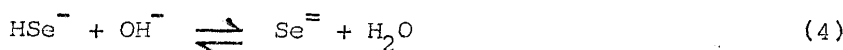
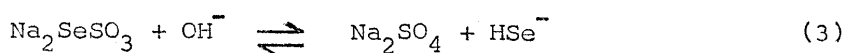
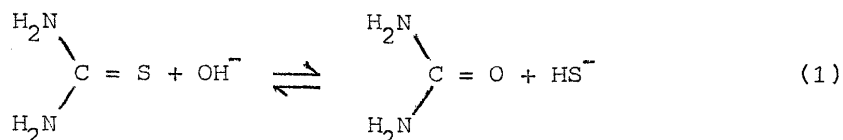


Recent trends in using polycrystalline thin film semi-conductors in various electronic and electrooptical devices in place of single crystals have led to a drastic cut in the cost of production of these devices. Polycrystalline thin films can be prepared by both physical and chemical methods (1.01), the commonly used are the vacuum evaporation, sputtering and spray pyrolysis. Complicated instrumentations, wastage of materials, high cost per surface area of deposition, instability of some compounds at the deposition temperature are a few of the many disadvantages of the physical methods. A relatively less common but inexpensive and convenient method for large area preparation of thin films at low temperatures is a chemical solution growth technique, which has been known for some time for thin film deposition of semiconductors. In general, the process involves the application of a controllable chemical reaction which proceeds at a low rate in an aqueous solution. The substrates are immersed in this solution. The reaction rate can be controlled by adjustment of pH, temperature and the relative concentrations of the various reactants in the solution. Since the solution growth technique is a low temperature (less than 90°C) deposition method, a variety of substrates (insulators, semiconductors and metals) can be used for film deposition. By contrast, in spray pyrolysis only a

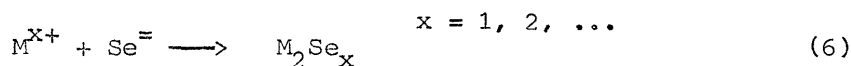
limited number of substrate materials which can withstand high temperature and chemical corrosion during pyrolysis can be used. Further, in a solution growth technique, since the deposition is from ions in aqueous solution, which are slowly being generated, the solubility product helps to maintain the stoichiometry constant for any ratio of cations and anions. As a result of these processes homogenous phases of compounds are obtained. It must be emphasized that formation of homogeneous and stoichiometric compound films by vacuum evaporation requires a critical adjustment of the substrate and various source temperatures, as well as the adjustment of the concentrations of the various components.

Thin films which are of considerable interest for various devices are those of the metal chalcogenides (sulfides, selenides and tellurides). Chemical method for the preparation of telluride thin films from solution has not yet been reported. Thin films of sulfides or selenides are prepared by decomposition of thiourea or selenourea in alkaline solutions of the salts of the corresponding cations. They furnish sulfur and selenium ions respectively on hydrolysis in alkaline solution (1.02-1.05). Selenourea is very unstable and has to be stabilized using antioxidants like sodium sulfite. In addition, the compound cannot be synthesized easily. Another compound which can generate selenium ions is sodium selenosulfate. It can be synthesized easily by dissolving selenium in a sodium sulfite solution, the resulting solution is fairly stable.

The dissociations of thiourea and sodium selenosulfate in alkaline solutions follow respectively :



In the presence of metal ions ($\text{M}^{\text{x}+}$) in the solution, metal sulfide (M_2S_x) or metal selenide (M_2Se_x) will be formed if the ionic product of $\text{M}^{\text{x}+}$ and $\text{S}^{=2-}$ or $\text{M}^{\text{x}+}$ and $\text{Se}^{=2-}$ exceed the solubility product of M_2S_x or M_2Se_x respectively.



To control the number of ions and hence rate of reaction, the metal ions are taken in the form of a fairly stable complex $\text{M}(\text{A})_n^{\text{x}+}$, where A denotes the complexing agent $n = 1, 2, \dots$. The complex dissociates to give controlled number of $\text{M}^{\text{x}+}$ ions which then combine with $\text{S}^{=2-}$ or $\text{Se}^{=2-}$ ions to form M_2S_x or M_2Se_x respectively.

Similar to formation of precipitate in the solution, formation of film on the substrate takes place by nucleation and growth processes. It is well known that nucleation of a precipitate in the solution starts at some local inhomogeneities present in the solution (e.g. due to some solid impurities), where the ionic product exceeds the solubility product. Growth of these nuclei by addition of more ions from the solution results in formation of stable nuclei of size greater than the critical size. Further growth, up to a particle size of 10 μm , results in formation of a colloidal dispersion. Nucleation on the substrate, according to Kitaev et al (1.03) takes place by adsorption of these primary colloids. Growth takes place as a result of surface coagulation of these particles. With time, the growth increases giving rise to a continuous thin and adherent film. This is generally known as the cluster-by-cluster growth model. Another type of film formation occurs by the atomistic (ion-by-ion) nature of nucleation and growth. In this method the metal chalcogenide nuclei are formed by the combination of ions on the substrate surface. This requires preferential adsorption of at least one type of the reacting ions on the substrate. If preferential adsorption of either the cation or anion on the substrate is not possible then some catalytic solid phase on the substrate is required which can preferentially adsorb either the cation or the anion.



Thin film deposition by the solution growth technique started with the deposition of PbS thin films. The chemical deposition of PbS films was described by Hauser (1.06) in 1910. This method involves the reaction of dilute solutions of thiourea with lead acetate. Almost all subsequent investigations dealing with the chemical deposition of PbS essentially have employed modifications of Hauser's method (1.07 - 1.10). An exception to the lead acetate - thiourea reaction is the method described by Wilman (1.11). In this case H_2S is passed over an acidic solution of lead acetate and a floating film of PbS is formed. Pick (1.12) has discussed the factors which influence film formation in homogenous precipitation reactions. These include the rate of diffusion of colloidal particles to the glass surface and the influence of crystallization nuclei which can be formed by the addition of metal ions whose sulfides are extremely insoluble such as silver, mercury, platinum and gold. The mechanism of precipitation of PbS out of alkaline lead-thiourea solutions in terms of a thiourea-lead hydroxide complex has been discussed by Kicinski (1.13).

Following the chemical deposition of PbS thin films, came the methods for depositing thin films of PbSe. Wilman (1.11) has described the formation of a thin mirror of PbSe on the surface of lead acetate solutions acidified with acetic acid over which H_2Se was passed. A method described by Milner and Watts (1.14) involves the reaction of lead acetate with

selenourea in aqueous solution. Prior to carrying out this reaction, a very thin film of PbS is deposited on the surface to be coated. This fine deposit furnishes the nuclei which act as a seeding layer for the growth of microcrystalline PbSe. However, the investigators give no information regarding the conditions of the reaction, the stability of the selenourea solution, or the concentration of reagents used. Roberts and Baines (1.15) and Arnquist (1.16) have also deposited PbSe thin films using selenourea solution. A modification was made by Zingaro and Skovlin (1.02). They used dimethylselenourea as the precipitant and utilized citrate ion to control the lead ion concentration.

The use of sodium selenosulfate solution started in the late sixties. Fofanov and Kitaev (1.17) and Suryanarayana et al (1.18) have used this solution for depositing thin films of PbSe.

Gradually, thin film deposition of various other metal chalcogenides by the solution growth technique was started. In our laboratory thin films of bismuth sulfide (1.19), bismuth selenide (1.20), copper sulfide and thallium selenide (1.21), antimony selenide (1.22), lead oxide and thallium oxide (1.23) were achieved by different workers by the solution growth technique.

A thorough literature survey has yielded no reported chemical methods for the deposition of thin films of copper selenide and thallium sulfide. Chemical methods for the deposition of copper selenide (1.24) and thallium sulfide (1.25) films have been developed by the author. The author also improves conditions for film deposition of the cadmium chalcogenides (1.26).

The thesis embodies the preparations and characterizations of the metal chalcogenide thin films prepared by solution growth technique in our laboratory. It also includes studies on photoelectrochemical solar cells with cadmium chalcogenide thin films.

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