C H A P T E R -VI

SUMMARY AND CONCLUSIONS

The range of thin film applications is so vast that it extends from micrometer dots in microelectronics to coatings of several square meters on window glasses. Polycrysalline thin films of metals, metal oxides and metal chalcogenides find wide spread applications in industrial sector. The rapid progress in thin film micro and nano materials has given birth to a whole new technology of junction devices and integrated circuits of monolithic and hybrid types.

In the field of materials research a relatively simple method to prepare the materials so as to reduce the cost and access quickly the various physico-chemical properties of materials is preferred. Preparation of materials in thin film form is relatively simple and less expensive as compared to that of growing the single crystals. There are many methods of film preparation such as (i) chemical deposition (2) spray pyrolysis (3) electrodeposition (4) painting (5) dipping (6) co-evaporation (7) sputtering etc. Amongst these electrodeposition has many advantages that it is a simple, inexpensive and short duration method.

The present investigation deals with the electrodeposition of Bi_2S_3, Sb_2S_3 and As_2S_3 thin films at room temperature from acidic medium using sodium thiosulphate as a S^{2-} ion source. The effect of various preparative parameters such as bath composition, complexing agent, pH of bath, current density and deposition time on the film microstructure, crystal structure and optical and photoelectrochemical (PEC) properties is studied. The present work is divided into six phases.

First chapter is introductory in nature. A brief survey of literature is given which is followed by the scope of the present work.

The theoretical background of electrodeposition is outlined in chatper II. The effect of various preparative parameters such as bath composition, concentration of EDTA , pH of bath, nature of substrate, current density and deposition time on deposition is also explained. The theory of semiconductor – electrolyte interface, Helmholtz and Gouy-Chapman layer along with conversion of light energy into electricity via photoelectrochemical route has also been discussed.

Chapter III deals with the electrodeposition of Bi_2S_3 from aqueous acidic bath and its characterisation. The films have been deposited from various baths containing 0.1 M $Bi(NO_3)_3$ and 0.1 M $Na_2S_2O_3$ in different volumetric proportions. The deposition potentials were recorded from the polarization curves. The effect of concentration of complexing agent, pH of bath, nature of substrate, current density and deposition time on deposition is studied. Following are the optimized preparative parameters of Bi_2S_3 thin films.

1) Bath composition- 0.1 M $Bi(NO_3)_3$- 0.1 M $Na_2S_2O_3$ in 2:8 volumetric proportion
2) EDTA concentration - 0.1 M
3) pH of bath - 2
4) Nature of substrate- Stainless steel
5) Current density- $3mA/cm^2$
6) Deposition time - 10 minutes
7) Terminal thickness - 0.63 μm

The good quality films are obtained from acidic medium and the films deposited on stainless steel are found to be unifrom, smooth and adhesive as compared to those deposited on copper, brass, titanium and FTO coated glass substrates.

The X-ray diffraction studies of the films show that the films are polycrystalline in nature and increase in crystallinity is observed after annealing the films to 250^{0}C temperature in nitrogen atmosphere for an hour. Microstructural study is carried out using scanning electron microscopy. The cracks are observed in the films and there is increase in grain size due to annealing of the films. The grain size for the annealed films is found to be 2 μm ,optical absorption is recorded at room temperature with the films deposited on FTO coated glass substrate. The coefficent of optical absorption 'α' is of the order of $10^5 cm^{-1}$ and bandgap energy 'Eg' of the Bi_2S_3 films is estimated to be 1.58 eV.

Photoelectrochemical characterisation of n-Bi_2S_3 films is carried out by forming the PEC cell of the configuration n-Bi_2S_3/1M NaOH -1 M Na_2S - 1 M S/c. I-V characteristics both in dark and under illumination in forward and reverse bias condition of the PEC cell show that Bi_2S_3 exhibits n-type conductivity. From the measurement of depletion region capacitance (c) with applied reverse bias voltage (v) at 1 KHz frequency, Mott-Shottky plot (c^{-2}Vs v) is plotted, which gives the value of flat band potential v_{fb} to be 0.7 v (SCE).

Fourth chapter opens up with the preparation and characterisation of Sb_2S_3 films. The films have been deposited from the bath containing different volumetric proportions of 0.05 M $SbCl_3$ and 0.05 M $Na_2S_2O_3$ and the volumetric proportion 7:3 is found to be suitable for deposition of Sb_2S_3 thin films. The effect of conc. of EDTA on the deposition potential and on the quality of deposits is studied. Due to addition of EDTA, the deposition potential is found to be increased negatively from -0.44 to -0.51 V(SCE). The 0.05 M EDTA is found sufficient for complex formation. The effect of preparative conditions such as pH of bath nature of substrate, current density and deposition time on the deposition of Sb_2S_3 is studied. Following are the optimised preparative parameters of Sb_2S_3 thin film.

1) Bath composition-0.05 M - $SbCl_3$ -0.05M $Na_2S_2O_3$ in 7:3 volumetric proportion
2) EDTA concentration -0.05 M
3) pH of bath -2.5
4) Nature of substrate-stainless steel
5) current density - 3 mA/cm^2
6) Deposition time-10 minutes
7) Terminal thickness -0.75 μm

The films prepared under these optimised conditions of parameters were further characterised by different techniques.

The XRD patterns were recorded by using X-ray diffractometer Philips PW 1710 system employing CuK_α radiation (Ni filtered , λ = 1.5406 A^o). The XRD patterns of Sb_2S_3 films deposited from uncomplexed and complexed bath show that films are polycrystalline. The difference in the XRD patterns of films from uncomplexed and complexed bath is due to different mechanism of film formation, lattice mismatch between substrate and material etc. The increase in crystallinity is observed when the films obtained from uncomplexed and complexed bath are annealed at 175^{o}C temperature in nitrogen atmosphere for an hour. The films are further analysed by SEM. The scanning electron micrographs of Sb_2S_3 films obtained from uncomplexed and complexed bath and annealed at 175^{o}C temperature in nitrogen atmosphere for an hour show that films are rough and the grain growth of material is favourably affected by use of complexing agent.

The absorption spectrum has been studied by UV-VIS-NIR spectrophotometer (Hitachi Model 330) in 400 to 700 nm wavelength range. The optical absorption coefficient 'α' is of the order of 10^4 cm^{-1} .The material is found to be direct bandgap type with bandgap energy 'Eg' to be 1.66 eV .The photoelectrochemical properties have been studied by constructing a PEC cell of the configuration Sb_2S_3 /polyiodide/c. The counter electrode used was graphite. The C-V measurements show that the flat band potentioal V_{fb} is 0.3 v(SCE).

The details of electrodeposition and characterisation of As_2S_3 thin films from acidic bath have been dealt with in the fifth chapter. The As_2S_3 films deposition is carried out from the bath containing 0.1 M As_2O_3 and 0.1 M $Na_2S_2O_3$. The bath composition of As_2O_3 and $Na_2S_2O_3$ is optimized to get good quality films. The deposition potential for As_2S_3 varies between -0.4 to -0.6 v(SCE) due to variation in sulphur composition. An increase in sulphur composition in the bath shifts the deposition potential of As_2S_3 towards sulphur deposition potential. The effect of concentration of complexing agent EDTA on the deposition potentrial of As_2S_3 is studied. The increase in conc. of EDTA, negatively increases the deposition potential of As_2S_3 . This can be attributed to the slow release of ions due to complex formation. The EDTA with conventration 0.15 M in the bath produces thin, uniform and adherent films of As_2S_3. The effect of pH of bath on the film formation is studied. The various substrates for As_2S_3 film deposition are tested and it is found that the deposition potential also depends on the nature of the substrates. The optimized preparative parameters for the As_2S_3 thin film deposition are :

1) Bath composition-0.1 M As_2O_3-0.1 M $Na_2S_2O_3$ in 2:8 volumetric proportion
2) EDTA concentration -0.15 M
3) pH of bath -2
4) Nature of substrate-stainless steel
5) current density - $3mA/cm^2$
6) Deposition time -10 minutes
7) Terminal thickness -0.65 μm

Crystallographic studies show that the films are polycrystalline in nature. Effect of annealing at 175^oC temperature on the film in nitrogen atmosphere for an hour shows enhancement in the preferred orientations. The SEM of the As_2S_3 films obtained from uncomplexed and complexed bath are rough and non uniform. Some line traces are also observed. This may be due to roughness of the substrate. The different microstructural features exhibited by films from different baths could be due to different rates of nucleation causing different reaction mechanisms for a film formation. The photoelectrochemical studies of As_2S_3 photoelectrode has been carried out using a PEC cell of configuration As_2S_3 /Electrolyte/C. The counterelectrode used is graphite and the electrolytes used are polysulphide, polyiodide and ferriferrocyanide. The C-V measurements are carried out using As_2S_3 as a photoelectrode. The plot of C^{-2} Vs V(SCE) is linear and intercept at $C^{-2}=0$ gives the value of flat band potential v_{fb} to be 0.42 v(SCE).

B I O-D A T A

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