CHAPTER V

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SUMMARY AND CONCLUSIONS

5.1 General

The applications of thin films range from micrometer dots in microelectronics to coatings of several square meter on window glasses. Their methods of synthesis and commercial applications are so enormous and common that we are hardly aware of the extent to which they have become part of our way of life. Thin films of metals, metal oxides and metal chalcogenides are of immense importance and found wide spread utility in this respect (electronics, optical devices, solar cells etc). Moreover, the rapid development in thin film micro and nanomaterials has given birth to a whole new technology of junction devices and integrated circuits of monolithic and hybrid types. Dictated by the considerations of processing simplicity, economicability and input feed, large area thin film materials necessarily have to be obtained by a solution growth processes. Among the various chemical methods, chemical bath deposition process is presently an attractive tool and is considered to be an universal method for the preparation of large area II-VI, IV-VI, I-III-VI etc compound thin films. A variety of substrates (metals, insulators, semiconductors etc) can be used since the working temperature of the process is low. The preparative parameters can be easily controlled and better orientation of the crystallites resulting into the improved grain structure can be achieved. The ternary $CuBiSe_2$, a member of I-III-VI group compounds, is a technically important class of materials. It has n-type electrical conduction, high optical absorbance and direct mode of transitions with a considerable scope for band gap engineering. A relatively new method has been adopted to prepare these $CuBiSe_2$ thin films with a varying Cu-concentration at relatively low temperature. Initially many fold research work was planned and the actual work that has been carried out is divided into five chapters. Chapter-I is a short survey of the thin film technology. It describes the

ternary compounds and a short survey of $CuBiSe_2$ thin film materials and also outlines the different thin film deposition methods. Chapter II describes the chemical deposition method and the detailed procedure for preparation of the $CuBiSe_2$ thin film deposits. The mechanism of film formation and growth kinetics have also been studied. In Chapter III compositional, structural and microscopic studies on these films are described. Chapter IV gives the necessary fabrications and experimental techniques for the electrical and optical properties. The various milestones of the studies undertaken are as follows:

5.2 Synthesis of The Bi_2Se_3 and $CuBiSe_2$ Samples

The bismuth triselenide thin films were deposited onto the glass substrates by employing a chemical deposition process. The triethanolamine complex of bismuth was allowed to react with the selenium ions, which were released by the decomposition of sodium selenosulphite. The preparative parameters and deposition conditions, which were optimised are:

i) deposition temperature = 55°C,

ii) speed of the substrate rotation = 50 rpm,

iii) deposition time = 1 hr and

iv) pH of the reaction mixture = 10 ± 0.2.

Sodium hydroxide and aqueous ammonia solutions were used to adjust the pH of the reaction mixture and to increase the adhesiveness of the film on the substrate support. For deposition of the $CuBiSe_2$ films, the same procedure was adopted and only the Cu-concentration was varied from 0.005 mol % to 0.3 mol % so as to obtain a series of $CuBiSe_2$ thin films. The source of Cu^{2+} ions employed was $CuSO_4$ (AR grade).

5.3 Reaction Mechanism and Growth kinetics of The Bi_2Se_3 and $CuBiSe_2$ Films

5.3.1 Reaction mechanism

The Bi_2Se_3 thin films were obtained from an aqueous alkaline bath consisting of Bi salt in complex form and selenide ions. The deposition process was based on the slow release of the Bi^{3+} and Se^{2-} ions in the solution state which then condensed on an ion-by-ion basis on the substrate surface. A series of the reactions proposed are:

$$Na_2SeSO_3 + OH^- \longrightarrow Na_2SO_4 + HSe^- \quad ---(5.1)$$

$$HSe^- + OH^- \longrightarrow H_2O + Se^{2-} \quad ---(5.2)$$

The source of bismuth ions was made available from the dissociation of the triethanolamine complex of bismuth.

$$[Bi\ N(CH_2CH_2OH)_3]^{3+} \longrightarrow Bi^{3+} + N(CH_2CH_2OH)_3 \quad --- (5.3)$$

The reactions (5.2) and (5.3) show that the Se^{2-} and Bi^{3+} ions will condense on the glass substrate as;

$$2\ [Bi\ N(CH_2CH_2OH)_3]^{3+} + 3\ Na_2SeSO_3 \xrightarrow{\text{aq. alk.}} Bi_2Se_3 + 3\ Na_2SO_4 + 2[N(CH_2CH_2OH)_3] \quad ---(5.4)$$

The $CuBiSe_2$ films were obtained from the reaction mixture containing Bi^{3+} ions in a complex form, copper ions and refluxed selenium ions. The reaction mechanism is as follows.

$$Bi(NO_3)_3 + 2N(CH_2CH_2OH)_3 + 3OH^- \xrightarrow{\text{aq. alk.}} Bi[N(CH_2CH_2O)_3]_2^{3-} + 3\ HNO_3 + 3\ H_2O \quad --- (5.5)$$

$$Bi[N(CH_2CH_2O)_3]_2^{3-} + CuSO_4 + 2\ Na_2SeSO_3 + 6\ H_2O \xrightarrow{\text{aq. alk.}} CuBiSe_2 + 2Na_2SO_4 + 2N(CH_2CH_2OH)_3 + H_2SO_4 + 4OH^- \quad --- (5.6)$$

5.3.2 Growth kinetics

The growth of Bi_2Se_3 and $CuBiSe_2$ thin films initiates by an ion-by-ion condensation and cluster-by-cluster deposition of molecules under different

deposition conditions. It depends on the concentration of the ions, their velocities, nucleation efficiency and various growth processes. The various deposition parameters such as deposition temperature, deposition time and pH decides the rate of deposition and terminal layer thickness. At about 55 °C good quality $CuBiSe_2$ samples with maximum terminal layer thickness were obtained. Below and above 55°C the terminal layer thickness is decreased. It has been seen that variation of growth rate with time is initially almost linear and then it becomes quasilinear. For a deposition time of 60 minutes, the maximum terminal layer thickness was obtained and for higher deposition time it saturated. The effect of pH (7 to 12) was studied on the deposition of the films. The better deposits were obtained around a pH value equal to 10 ± 0.2.

5.4 Physical Observations

The as grown samples are thin, uniform, densely packed, smooth and physically adherent to the substrate support. The colour of the deposits changed from dark chocolate brown to greenish chocolate brown as the Cu-concentration was varied from 0 to 0.3 mol %. The change in colour with increasing Cu-concentration indicated substitution of Bi^{3+} ions by Cu^{2+} ions. The terminal layer thickness was measured by the weight difference-density and an interference fringes techniques to ensure more accuracy. It is found that the layer thickness increased initially with the mol % Cu-concentration upto 0.05 and then decreased further for higher copper concentrations in Bi_2Se_3. The variation in layer thickness with Cu-concentration has been explained on the basis of Cu^{2+} as a nucleation and charge scattering centres, respectively.

5.5 The Structural and Microscopic Studies on Bi_2Se_3 and $CuBiSe_2$ Films

The structural and microscopic investigations on these films were made to understand the various crystallographic aspects and surface features. The informations pertaining to the crystal structure (involving interplaner distances, (hkl) planes, intensities of reflections, lattice parameters, crystallite sizes etc) and surface topography (involving actual growth, size of the crystallites, intercrystallite distances etc) are obtained from these studies. The structure and crystallinity of both Bi_2Se_3 and $CuBiSe_2$ films were therefore examined by the XRD and SEM techniques. The observations indicated that the materials are polycrystalline in nature. Bi_2Se_3 is grown as a hexagonal phase whereas $CuBiSe_2$ as a mixture of $BiSe_3$ and hexagonal CuS phases. A little amount of tetragonal Cu_3Se_2 phase has also been detected in some cases. The grain size was determined by using the Scherrer's relation

$$\bar{D} = k\lambda / B\cos\theta$$

where, symbols have their usual significance. The average crystal size increased with increase in Cu-concentration.

5.6 The Optical and Transport Studies on Bi_2Se_3 and $CuBiSe_2$ Films

The optical sensitivity of these samples was tested in the wavelength range from 300 nm to 980 nm and the absorption spectra were analysed to determine the absorption coefficient (α), optical energy gap (E_g) and the nature of the optical transitions. The absorption coefficient is high (10^4 to 10^5 cm^{-1}) for all the samples. The absorption edge is found to be shifted from 825 nm to 650 nm as Cu-content was increased from 0 to 0.3 mol %. The optical gaps were determined from these studies. It is found that the variation in E_g is continuous and non-linear and typically, E_g increased

from 1.50 eV to 1.88 eV as Cu-concentration was increased from 0 to 0.3 mol %. The transitions are of the direct type.

The composition and temperature dependent conductivity was studied for all the samples. The temperature variation of an electrical conductivity showed two distinct conduction mechanisms; a variable range hopping (low temperature) and a grain boundary scattering limited (high temperature). The electrical conductivity is found to be increased initially with Cu-concentration up to 0.05 mol % and then decreased up to 0.1 mol % and again increased with increase in Cu-content and saturates. Thermoelectric power measurements showed n-type conduction. The temperature dependence of thermo power is approximately linear in the low temperature region whereas it deviates from the linear behaviour at higher temperatures and obeys the power law dependence of the temperature. The carrier concentration (n) and mobility (μ) were then calculated from these studies. The order of carrier concentration is 10^{19} cm^{-3}. The dependence of n and μ on temperature was also studied. It is seen that carrier density is enhanced by approximately an order with the temperature and more or less the same with the increased Cu-concentration whereas the mobility is much influenced by both temperature and Cu-concentration. The intercrystallite barrier heights were determined from the temperature dependence of mobility. It is seen that the barrier potential decreased with increase in the Cu-concentration in Bi_2Se_3.

5.7 Future Directions

Although bismuth triselenide has a high coefficient of an optical absorption and an energy gap matching closely with the maxima of the electromagnetic spectrum, its photoelectrochemical activity is very poor, may be because of its higher resistivity (10^8 to 10^9 Ω cm) and extremely poor photosensitivity. Copper was, therefore, intentionally incorporated in

to Bi_2Se_3 to decrease its electrical resistivity and enhance the photosensitivity. In view to attempt this, copper concentration in mol % was incorporated in to Bi_2Se_3. The salient features of our studies are that the electrical resistivity of Bi_2Se_3 has been decreased considerably, however, the optical absorption coefficient decreased a little. Because of our experimental limitations and time bound programme (Teacher Research Fellow, TRF) we were unable to test the photoelectrochemical activity of these materials. It is now under progress.