CHAPTER-VI

6 Summary and future work

6.1 Summary

Crystal growth from solution is an important method to obtain various functional materials. Generally, it is difficult to control crystal growth kinetics during crystallization using volatile solvents. Demand for seeking new materials for non-linear applications forces the researchers to grow crystals using volatile solvents. This often results experimental limitation on size and quality of the crystal. Under these circumstances an attempt was made to introduce a thermal gradient cell in Sankaranarayanan-Ramasamy method of crystal growth since it offers unidirectional crystals of required size, quality and also having cylindrical shape. Further, the crystalline quality of the growing crystal can be influenced by the thermal gradient imposed on the progressing solid–liquid interface.

The introduction of a thermal gradient cell in Sankaranarayanan-Ramasamy method of crystal growth offers a way to eliminate the difficulty in growing unidirectional crystals using organic solvent having high vapour pressure since there is no any solvent evaporation involves in this method. Hence, attainment of supersaturation and controllability over the supersaturation was enhanced in the case of solvent having vapour pressure. By using this method, single crystalline KAP crystals were grown in the present study and thin substrates were fabricated for the application. The HRXRD analysis on the grown crystals resulted a diffraction curve having FWHM of 22 arc s which is very close to that expected from the plane wave theory of dynamical X-ray diffraction. On comparing the FWHM of 33 arc s of the diffracted curve recorded on the unidirectional KAP crystal grown from the
Sankaranarayanan-Ramasamy method, the present introduction of temperature gradient cell is more beneficial to influence the crystalline quality. The CdS/KAP structure prepared during this work can be effectively applied as an optical filter in the wavelength range of 318 - 500 nm. The optical band gap of the grown KAP substrate is much bigger than the CdS film hence KAP can be used as a substrate to deposit important wide-band gap thin films in future work too.

An experimental set-up was developed in our laboratory to deposit the chalcogenide family semiconducting materials such as CdS, CdZnS, CuCdS thin films on various substrates by chemical bath method. Basically the instrument consists of a glass bath of volume 250 ml and attached with a plate-heater at the bottom. The bath temperature was maintained at the desired temperature by a constant voltage regulator. The substrate can be suspended vertically inside the chemical bath using teflon-disc substrate holder and can be rotated at 20 rpm. Rotating the substrate facilitates to make the solution more homogenized and to expose the substrate surface in phase with the growth units available in the growth solution thereby more uniform films can be expected.

The prepared materials were subjected for various characterization studies such as X-ray diffraction, HRXRD, SEM, AFM, EDX, UV-Vis-NIR, PL emission spectroscopy and XPS in order to investigate the physical and chemical properties. Results from these characterization studies implies the effectiveness of the fabricated equipment for preparing semiconductor thin films with high repeatability in terms of their chemical and physical characteristics.

Preparation and characterization of the chemical bath deposited cadmium sulfide (CdS) thin films on glass, ITO coated glass, chemically polished p-Si <111> and p-Si
<100> substrates were investigated. The crystal shapes of the chemical bath deposited nanocrystalline CdS film on different substrates were computed using the reported crystal shape algorithm. With the use of the $2\theta$ value and the peak width at half-maximum (i.e., $\beta$ value) for the recorded XRD peaks, the crystallite thicknesses, $t_{hkl}$, along the recorded directions are computed using the Scherrer’s formula. The set of crystal planes defined by the set of computed $t_{hkl}$ is used to determine the mathematical envelope for the crystal shape. These mathematical envelopes give the three-dimensional crystal shapes. The shape of the CdS nano crystals have been built with the help of an algorithm and that exhibits the crystal shape / habit changes due to the selection of substrates. The CdS film on glass, ITO coated glass and polished p-Si substrates show a disordered cubic crystal shape with well defined faces, a nearly cubic crystal shape and a nearly hexagonal crystal shape with well defined faces respectively. The resulted influence on crystal shapes may be attributed to the self influence of the chosen substrates and their preparation conditions. When compared with CdS deposited on glass and ITO coated glass substrates, the degree of organization, crystallinity, crystal habit, stoichiometry and the PL intensity was better in the case of CdS film on p-Si <100> substrate.

One of the well studied chelating agent viz., ethylenediamine tetraacetic acid was added in the chemical bath solution to investigate the effect of its concentration during the chemical bath deposition of CdS thin films. Chemical bath deposited CdS thin films were deposited on glass substrates from pure and EDTA - added bath solutions having different concentrations of 0.003, 0.004, 0.005 and 0.006 M. In the case of CdS deposited from pure solution reflects hexagonal structure whereas the CdS film deposited from EDTA – added solution possess crystals belongs to
hexagonal and cubic crystal structures. On comparison with the CdS film deposited from pure solution, the increasing concentration of EDTA in the solution reduces the amorphousity and enhances the crystallinity of the film. The EDTA concentration of 0.006 M has resulted better crystalline quality than all other studied samples. The film deposited from the bath solution containing the EDTA concentration of 0.006 M attains 80% of transmittance over other films. A close observation on these pictures revealed a fact that the addition of EDTA in the bath solution greatly reduces the grain size and macroscopic defects such as voids and pinholes in the thin film. Also, a noticeable shift towards green emission was observed while increasing the concentration of the EDTA in the bath solution. In the case of film deposited from 0.006 M EDTA added solution, there was no blue emission and only green emission around 504 and 550 nm.

The fabricated p-Si / CdS heterojunctions have been characterized for their I-V measurements which show good rectification characteristics with an ideality factor of ~1.3.

CdZnS thin films were deposited on to glass substrates by chemical bath deposition technique. The composition of the chemical bath was maintained with 5 ml of 0.25 M : CdCl2, 5 ml of 0.25 M : ZnCl2, 10 ml of 0.2 M : NH4Cl, 5 ml of 0.3 M : CS(NH2)2, 30 ml of 2M : NH4OH and 50 ml of de-mineralized H2O. The bath temperature was maintained at 90 °C by a constant voltage regulator. The substrate was suspended vertically inside the chemical bath using teflon-disc substrate holder and was rotated at 20 rpm. X-ray diffraction measurements were carried out to investigate the crystal structure and crystalline quality of as-deposited CdZnS thin film. The major peak located at 28.49° is attributed to (111) diffractive peak of cubic
CdZnS. All other diffracted peaks are attributed to the scattering from the hexagonal phase of CdZnS.

The surface texture characteristic of CdZnS thin films was determined by AFM in contact mode. The surface roughness parameters such as root mean square surface roughness, average height, and maximum height were estimated using the reported AFM software. The room temperature optical absorption spectrum of the prepared CdZnS thin film was presented in the wavelength range of 300-1200 nm by UV-Vis-NIR spectrometer. The absorption studies revealed that the fabricated films are having low absorption in the studied wavelength range.

Effect of annealing on the structural, surface and optical properties on the conventional chemical bath deposited CdZnS thin films were elaborated. The conventionally deposited CdZnS sample shows the hexagonal / cubic mixed structure. The annealing of films at 400 °C enhances the (002)-H phase against the dominant (111)-C phase as in the as-deposited films. Further, (101)-H peak was newly detected when the films are annealed at 200 and 400 °C. The samples fabricated by microwave assisted chemical bath deposition technique and conventionally deposited Cd$_{0.8}$Zn$_{0.2}$S films exist only in the hexagonal structure. Investigation on the optical transmittance characteristics shows very low absorption. The observed SEM images of microwave assisted chemical bath deposition of CdZnS films show that synthesized material has the flake like surface morphology. All other studied samples exhibit a well packed, pinhole free smooth surface morphology having spherical grains. The surface roughness of the film was influenced through thermal annealing of the deposited film and varying the Zn concentration in the chemical bath during deposition. Band gap energies of the CdZnS samples obtained using optical absorption spectra vary between
2.27 and 2.62 eV. The fabricated n-Cd$_{0.8}$Zn$_{0.2}$S/p-Si $<$100$>$ heterostructure shows good rectification characteristics when compared to n-CdS/p-Si $<$100$>$ heterostructure and the calculated ideality factor was $\sim$ 1.2.

Chemical bath deposition of Cu$_x$Cd$_{1-x}$S$_y$ thin films fabricated on silicon substrate exhibits intense blue emission than the film fabricated on glass and ITO coated glass substrates. The observed intense blue luminescence in the prepared CuCdS thin film with pre-determined composition justifies its possible optical application as UV sensor.

6.2 Future work

The feasibility of growing large size unidirectional KAP crystal by Sankaranarayanan-Ramamsamy method will find the opportunity for the fabrication of optical filters. Hence, efforts will be made to grow large size and cylindrical shaped KAP crystal. Improvement in the characteristics of the microwave assisted chemical bath deposition of II–VI compounds such as CdS, CdZnS and CuCdS will be investigated in order to reduce the experimental time and yield while keeping the desired physical and chemical properties. The newly synthesized, CuCdS material will be thoroughly investigated in order to understand its physical, chemical and optical properties for the possible application as UV sensors. The fabrication of solar cell structure based on the chemical bath deposited II–VI thin films will be undertaken for practical applications.