Wide band gap polycrystalline CdS ($E_g = 2.42 \text{eV}$) thin films are extensively used as a window material in heterojunction solar cells together with several narrow band gap semiconductors (Cu$_2$S, CdTe, CuInSe$_2$ etc.). Recently very thin CdS films, prepared by chemical technique are found to be extremely useful as the window material in thin film solar cells with efficiency $>12\%$. In the present work the analysis of chemically prepared single layer CdS as well as CdS based bilayer films are done using different techniques. The major tool used for this work is a home made Variable Angle Spectroscopic Ellipsometer (VASE).

Ellipsometry is a non destructive optical technique for the surface analysis of thin films and crystals. It belongs to a class of optical instruments in which polarization represents the fundamental property of the light. Ellipsometry is the optical characterization technique in which the change in polarization state of light that occurs due to reflection from the surface of a sample is measured and interpreted to determine the physical properties of the sample. In spectroscopic ellipsometry the measurement and analysis are done as a function of wavelength. Since ellipsometry is highly sensitive to the surface imperfections, inter diffusion, interlayer formation in multilayer thin film system, etc.; this technique gives the information about the surface roughness, structural changes and layer structure of the thin films under investigation. Here Bruggeman's effective medium theory is used for the volume fraction analysis of mixed layers with the help of ellipsometry. Photometric ellipsometer calculate the parameters $\psi$ and $\Delta$ using the measured values of intensity of reflected light from the sample surface. The values of these two parameters are used for the calculation of optical parameters of thin film system.
In the VASE system fabricated for the present work the azimuth of analyser and polariser can be measured with an accuracy of 1 minute while the angle of incidence can be measured at an accuracy of 20 sec. The accuracy of intensity measurement is ±0.5% of full scale reading of 4½ DMM. The possible wavelength range is 400-750 nm. The angle of incidence can vary from 20 to 80°.

In this thesis we describe the details of the construction of VASE (photometric type) and the methods and application of this sensitive equipment to study surface, interlayer structure and material properties of thin films. We have also used the other characterization techniques like X-ray Photoelectron Spectroscopy (XPS), X-ray Diffractometer (XRD), Scanning Electron Microscope (SEM), Spectro Photometer and in some cases electrical conductivity measurement for corroborating the results. The materials selected for these studies are CdS, SnO₂ and CuInSe₂ which find large application in thin film solar cells. The single and bilayer thin film systems used for the study are CdS, CdS/Cu, CdS/SnO₂ and CdS/CuInSe₂. These films are prepared by different techniques like spray pyrolysis, vacuum evaporation and chemical bath deposition (CBD).

The chapter 1 gives an introduction to the works presented in this thesis with emphasis on thin films. A brief description of different preparation techniques of thin films and methods of thickness measurements are given. The bilayer structure of thin films is also discussed in this section which has applications in thin film solar cells. A detailed account of optical reflection and transmission by an ambient-film-substrate system is given along with a brief introduction to ellipsometer. Towards the end of this chapter, a brief description of the techniques used for the optical studies of thin films is added. The other experimental techniques used in the present study for the characterization
of the samples like XRD, XPS, SEM are also described in this chapter after dealing with the optical techniques.

The chapter 2 contains the detailed description of theory of ellipsometry and the variation of polarization due to different optical components used in ellipsometry. Jones matrix is used for this analysis. It also contains an account of photometric ellipsometer and a brief description of other ellipsometric systems. Next part of this chapter describes the VASE set up (Polarizer-System-Analyzer) fabricated as a part of this work and different components used for this such as light source, polarizing elements, monochromator, light detection and signal processing etc. It also describes the measurement of $\psi$ and $\Delta$ spectra of glass surface.

The chapter 3 contains the calculation techniques of photometric ellipsometer. This chapter also includes the computer programming techniques used in the forward and reverse problems. Ellipsometer measures only the parameters $\psi$ and $\Delta$ and not the material parameter. These material parameters (like thickness, refractive indices surface/interface roughness etc) have to be inferred from the ellipsometric parameters by selecting the correct optical model. The parameter values of the best fit model is attributed to the film system. This section describes the techniques for selecting the best model by minimizing the error values. In order to get the best results using VASE, the angle of incidence and wavelength should be in the most sensitive region of the system. Here the sensitive regions of $\psi$ and $\Delta$ of the CdS single layer film, and two CdS based bilayer films (viz. CdS/SnO$_2$, CdS/CuInSe$_2$) which are studied in the present work are given. The analysis of rough surface/interface using the Bruggeman's effective medium theory (EMT) is also included in this chapter. This chapter comes to an end with the flow chart of the FORTRAN computer programme used for the analysis of various parameters of the
multilayer thin film systems analysed in the present work.

Chapter 4 describes the details of spray pyrolysis technique and the setup of spray coating. The CdS thin films are widely used as a window material in several thin film solar cells. The ellipsometric analysis of CdS film prepared at different temperatures are given. The results of ellipsometric analysis of variation of surface and structural properties of these films with preparation temperature are given along with the supporting results using SEM and XRD spectrum. The variation of surface roughness of the film is explained using the growth rate at different substrate temperature. The refractive index spectra (in the visible region) of CdS film (both real and imaginary) is calculated taking into account of surface roughness. The effect of annealing on surface roughness of the CdS films prepared by spray pyrolysis technique is also included in this chapter.

Chapter 5 describes the variation taking place on the CdS/Cu bilayer thin film systems due to annealing. The CdS film is prepared by spray pyrolysis and Cu is coated over this CdS film by vacuum evaporation. The ellipsometer is used for the studies of diffusion of Cu into CdS due to annealing. Bruggeman’s EMT is used for the analysis of mixture layers (CdS:Cu). It is observed that the doping of Cu into CdS changes CdS at first into intrinsic, and on increasing the percentage of Cu in CdS, the latter is converted into p-type. It has wide application in thin film solar cells because these films can form CdS homojunctions. The results of the analysis of CdS:Cu film using XRD, XPS and optical absorption studies are also given in this chapter along with the electrical properties of the films.

SnO₂ and CuInSe₂ are widely used in thin film solar cells. SnO₂ film is often used as transparent conducting electrode material for thin film solar cell. SnO₂ films with very low resistivity and high percentage transmission are
prepared by spray pyrolysis technique as a part of the present work. CuInSe₂ is p-type material and it is widely used with CdS film to form p-n junctions. In the present study we have prepared SnO₂/CdS bilayer thin film by spray coating technique and the interface of SnO₂ and CdS is analyzed using ellipsometry and the results are given in chapter 6. CuInSe₂ film are prepared by CBD technique. The main attraction of CBD is that it can reduce cost of preparation of thin film and is very much important in developing low cost photovoltaic devices. Optical constants of CuInSe₂ film are also calculated in wavelength range 470 to 650 nm and this result is much useful for solar cell fabrication work. CdS/CuInSe₂ films are prepared by CBD technique. The interface of these layers are also studied using ellipsometer after annealing at different temperatures.

The last chapter contains the conclusion of all the results given in the previous sections and also the scope of this type of work for the single and multilayer semiconductor analysis.

The following papers have been published/communicated for publication in different journals during the course of the work.

**List of publications.**


5. Ellipsometric studies of structural properties of CdS thin films.

Sunny Mathew and K.P. Vijayakumar. (Communicated to J. Phys. Soc. Japan.)


Sunny Mathew and K.P. Vijayakumar. (Accepted for publication in Bull. Mater. Sci.)

Sunny Mathew, P.S. Mukerjee and K.P. Vijayakumar. (Accepted for publication in Thin Solid Films)

Sunny Mathew and K.P. Vijayakumar (XXI Nat. symp on Optics, IIT, Madras Feb. 10-12, (1994))

Sunny Mathew, P.S. Mukerjee and K.P. Vijayakumar. (Accepted for publication in Jpn. J. Appl. Phys).
12. Interdiffusion studies of CdS/\text{SnO}_2 thin films prepared by spray pyrolysis technique.
   Sunny Mathew and K.P. Vijayakumar. (Communicated Solid State Commun.)

13. Interdiffusion studies of CdS/CuInSe$_2$ thin films system prepared by chemical bath technique.
   Sunny Mathew, P.K. Vidyadharan Pillai and K.P. Vijayakumar.
   (Communicated to Thin solid Films)