

Chapter 4

Measurement and Calculation Techniques

4.1 Introduction

This chapter discusses the various measurement and calculation techniques used in characterizing the a-Si:H thin film sample in this work. Section 4.2 discusses the Fourier-Transform Infra-red spectroscopy technique which is used to study the structural property of the a-Si:H thin film sample. This technique identifies the spectral signatures for sites containing one H atom, SiH₂, or more than one H atom, SiH₂ and/or SiH₃ thus simultaneously allows the H content of the film to be determined. Section 4.3 is concerned with the electrical measurements carried out in this work. Direct-current conductivity measurements which is carried out from the liquid nitrogen temperature to 350K enables the conductivity and the activation energy of the sample to be determined. The field-effect technique which is used to determine the density of states of the a-Si:H thin film material is also presented in this section. This measurement technique is still in a premature stage and needs further works to be done on it. Section 4.4 presents the optical characterization

techniques which consists of the Tolansky technique, the Brewster's Technique, the ellipsometry technique and the Optical Transmission Spectroscopy Technique. All these four techniques are used to determine the thickness and the refractive index of the film which are critical parameters in characterizing the film. The Optical Transmission Spectroscopy technique is a very useful technique since it can also be used to determine the density of valence electrons, the hydrogen content of the film and the energy gap of the material.

4.2 Chemical Bonding Analysis

In this work, Fourier-Transform Infra-red (FTIR) Spectroscopy technique is utilized to analyse the chemical bonding structure in a-Si:H films produced by our dc plasma glow discharge system. It provides useful information which identifies the spectrum signatures for sites containing one H atom, SiH, one or more than one H atom, SiH₂ and/or SiH₃. The SiH environment usually are characterized by a bond-stretching mode at 2000cm⁻¹ and a bond-bending mode at 630cm⁻¹, whereas sites with more than one H atom exhibit additional features in bond-bending frequency regime , 800-900cm⁻¹, as well as new bond-stretching modes between 2050 and 2150cm⁻¹. In this work, this technique is further utilized to determine the concentration of bonded hydrogen in silicon atoms which will be presented in chapter 6. The Perkin-Elmer model 1600 FT-IR spectrophotometer is used in this work to scan thin film a-Si:H deposited on crystal silicon substrate. A schematic diagram of the optical system is shown in figure 4.1. Crystal silicon is used as a substrate because of its symmetry , infrared photons are not absorbed¹. The background is first scanned over the range 4000 to 2000cm⁻¹

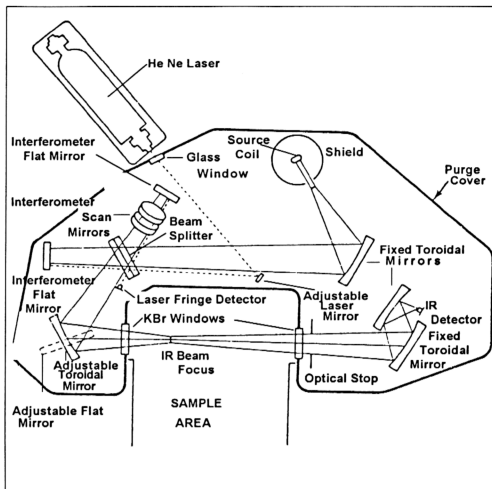


Figure 4.1 : Schematic diagram of the Optical System of the model 1600 Perkin-Elmer FTIR.²

followed by the crystal silicon substrate. The a-Si:H film on crystal silicon is then scanned over the same range. The latter spectrum minus the two earlier spectrums results in the infra-red spectrum for the film a-Si:H.

4.3 Electrical Characterization

The main electrical characterization carried out in this work are direct-current conductivity measurements. Direct-current current-voltage measurements are carried out at liquid nitrogen temperature, room temperature and 350K to determine the conductivities and the ohmic region at these temperatures. The activation energies in the extended , ($E_c - E_f$) and tail states region , ($E_t - E_f$) and the density of states at the Fermi level are then determined using the $\ln(\text{current})$ versus $(1/\text{Temperature})$ curve at a fixed voltage in the ohmic region.

4.3.1 Direct-Current Conductivity Measurements

Current-voltage measurement done on thin film a-Si:H samples is an important tool used to determine the conductivity of the material. If this is done at different temperatures ranging from as low as 4K to 350K more information can be obtained on the electrical properties of the material. For this work, current-voltage measurement is done at 77K(liquid nitrogen temperature), at 300K(room temperature) and at 350K. The conductivity of the sample is then determined at these temperatures. The current-voltage measurements also provide valuable information regarding the different regions on the current-voltage curve namely the ohmic region, the space charge limited current region, the trap-filled limit region and the trap-free region. However, for this work ,usually only the ohmic region is observed since measurements

are done for the voltage range of 0 to 100 volts only on co-planar electrode configuration used for the sample. Using a fixed voltage in the ohmic region, the variation of current with temperature measurement is done in the range of 77K to 350K. The $\ln(\text{current})$ versus inverse temperature curve is then used to determine the activation energy (E_c-E_f), the tail state region (E_c-E_a) and the density of states at the fermi level, $N(E_f)$. These parameters provide valuable information on the electrical properties of the material.

The experimental set-up for the conductivity measurement is illustrated in figure 4.2. The set-up consists of an Oxford Instrument Liquid Nitrogen Cryostat model DN1704 , an Oxford Instrument temperature controller model 3120 and a Keithley 617 programmable electrometer and Edwards EM2 rotary pump. The a-Si:H thin film sample which is deposited on soda glass substrate has two rectangular aluminium electrodes evaporated on it in a co-planar configuration (refer to insert in figure 4.2). For electrical contacts electrical conductive paste is used to connect the electrodes to connecting copper wires on the sample holder. The sample holder is then top loaded into the liquid nitrogen cryostat. An electrical lead-through on top of the cryostat leads the connecting wires from the sample to the Keithley 617 electrometer. The sample is cooled by a static column of exchange gas which thermally links the sample to a heat exchanger. The heat exchanger is positioned at the lower end of the tube and is connected to a liquid nitrogen reservoir (see figure 4.3). A platinum temperature sensor and a heater are fixed to the heat exchanger. Electrical connections to the heater and temperature sensor (the temperature controller) are made via a 10-pin feed-through on the top plate of the cryostat.

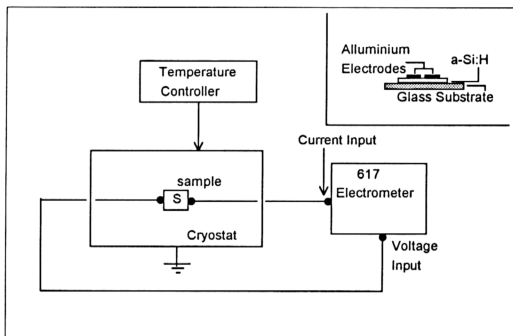


Figure 4.2 : Experimental Set-up for Direct-Current Conductivity measurement. Insert shows the sample configuration.

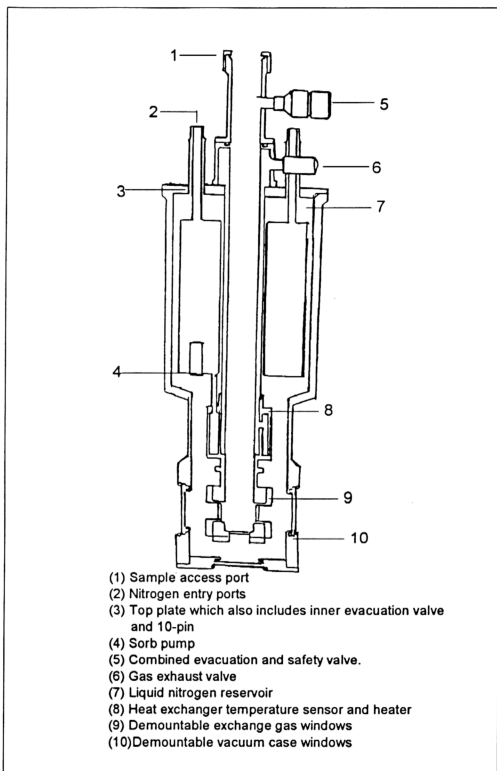


Figure 4.3 : Variable Temperature Liquid Nitrogen Cryostat
(Oxford Instrument model DN1704)

The Keithley 617 programmable electrometer is a package of instruments consisting of a variable power supply, a current meter and a volt meter designed to do current measurement through a sample with very high resistivity. This instrument is ideal for current-voltage measurement on a-Si:H thin film samples. The circuit diagram for current-voltage measurement using the Keithley 617 programmable electrometer is as shown in figure 4.4(a) and the equivalent circuit diagram is shown in figure 4.4(b). The Keithley 617 electrometer is turned on for two hours for warming up prior to any measurement. The sample space is evacuated and trap-emptying process is carried out. This process is carried out by putting a voltage of 50 volts across the sample for half an hour at room temperature. This particular voltage and duration of time is selected after doing several trap-emptying experiments at different voltages over various time durations. This process is carried out prior to all current-voltage and activation energy measurements. The current-voltage measurement is done over a voltage range of 0 to 100 volts. For current-voltage measurement at liquid nitrogen temperature, the temperature of the sample space is lowered to this temperature before starting the measurements. The operational procedure of the cryostat will be discussed in the following paragraphs.

The sample holder is first loaded into the sample space and the access port is sealed with a metal plug provided. The sample space is then evacuated and the space is filled with nitrogen which is used as an exchange gas. The temperature controller is set to 77K for measurements at liquid nitrogen

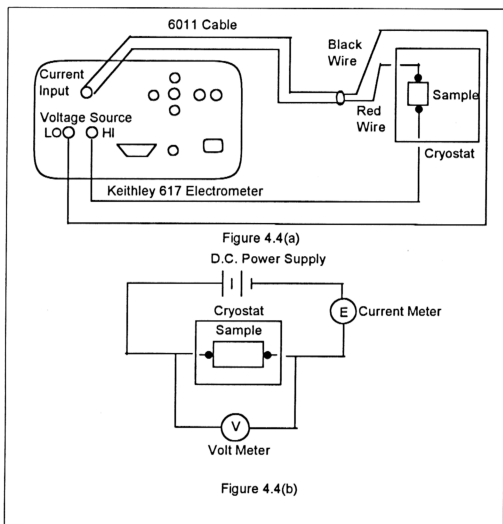


Figure 4.4: (a) Experimental Set-Up of Current-Voltage Measurement using the Keithley 617 Programmable Electrometer.
 (b) The equivalent Circuit Diagram for Current-Voltage Measurement.

temperature. The gas exhaust valve on the cryostat top plate is then opened. The reservoir is then filled by slowly pouring in liquid nitrogen until it is full, indicated by bubbles of nitrogen coming out from the free vent tubes. When the temperature is just below the required value, the gas exhaust valve is throttled back to achieve a stable temperature. For activation energy measurement the voltage is elevated to a fixed voltage in the ohmic region of the sample and then the temperature controller is set to 350K. The variation of current with temperature is recorded as the temperature rises to 350K.

4.4 Optical Characterization

Optical techniques are used in this work to determine various critical parameters of a-Si:H thin film material. Film thickness and the refractive index are important parameters in thin film characterization studies. The deposition rate of the film is dependent on the film thickness often determines the quality of the film. Also, film thickness and refractive indices are important parameters in optical and electrical characterization studies of a material. Since the films are very thin (less than $1\mu\text{m}$ thick) optical techniques are the most accurate technique for determining the thickness and of course the refractive indices are obtained using optical techniques. In this work, the optical transmission spectroscopy is used to provide valuable information on the properties of thin film a-Si:H. The interference fringes of this spectrum is used to determine the thickness and the refractive index of the film at various wavelength. This spectrum is further used to determine the valence electron and hydrogen concentration in the film and also to determine the optical band gap of the film material.

4.4.1 The Tolansky Technique

The Tolansky technique which is also known as multiple-beam interferometry utilizes the resulting interference effects when a wedge of a small angle is formed between unsilvered glass plate which are illuminated by a monochromatic light. Interference between the light beams reflected from the glass result in broad fringes on the two sides of the wedge. When the edge of the film is positioned underneath the wedge, discontinuity of fringes occur at the film edge. The thickness of the film, d is determined by the relationship

$$d = \frac{\lambda b}{2a} \dots\dots\dots (4.1)$$

where λ is the wavelength of the monochromatic light, a is the fringe separation and b is the fringe displacement.

The optical setup of the Tolansky technique is as illustrated in figure 4.5. Since the colour of a-Si:H thin films are usually reddish yellow, the best fringes seem to be produced by sodium light. The monochromatic sodium light is reflected on to a reflecting plate which then reflects the light on to the film. The edge of the film is covered by a thin microscope slide to enhance the fringes produced. A top plate which is a glass slide is tilted relative to the film edge by this microscope slide. This produces equal path length fringes at right angles to the film edge, where a distinct displacement is observed. These fringes are observed with the aid of a travelling microscope.

4.4.2 Brewster Reflection Technique

When unpolarized light or partially polarized light is incident at an angle ϕ on a dielectric like glass, a reflected and refracted ray are produced. Brewster discovered that at an angle ϕ when the reflected and the refracted rays are just 90° apart, the reflected ray is totally plane-polarized. This shows that the angle

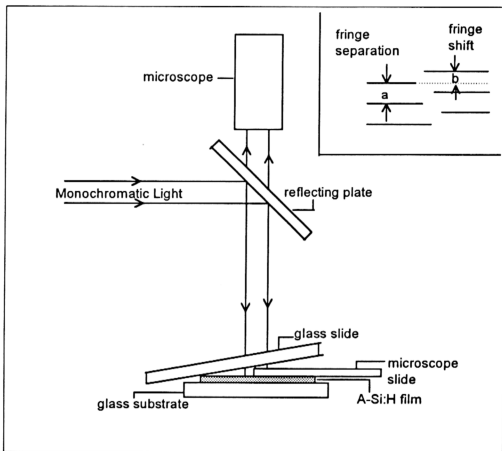


Figure 4.5 : The Tolansky Technique Set-up. Insert shows the fringe displacement observed in Tolansky measurement.

of incidence for maximum polarization depends only on the refractive index and the angle of incidence for maximum polarization which is easily derived is called Brewster's Law

$$n = \tan \phi \dots\dots\dots (4.2)$$

Using this law the set-up for determining the refractive index of thin film samples is built in the laboratory. The set-up as shown in figure 4.6 consists of a He-Ne laser, a polarizer for polarizing the incoming light parallel to the plane of incidence, a rotating platform onto which the sample is mounted, a photodiode enclosed in a collimator with a pinhole to admit the reflected light and a voltmeter to record the variations in the reflected intensity as a function of the incident angle ϕ . Proper alignment is critical in this set-up for accurate value of the refractive index. The tangent of the angle at which the intensity is minimum is the refractive index of the thin film sample. Usually two minima are observed, one of the minima corresponds to the refractive index of the substrate material since a second reflection occurs at the surface of the substrate. Thus, this technique is most suitable for thin film on substrate material which has a refractive index value distinguishable from the thin film material.

4.4.3 Ellipsometry

Ellipsometry is a technique that applies the fact that the state of polarization is altered upon reflection from both plain and coated surface. The analysis of the elliptically polarized reflection can be used to determine the refractive index (n) and extinction coefficient (k) of a clean, film-free surface

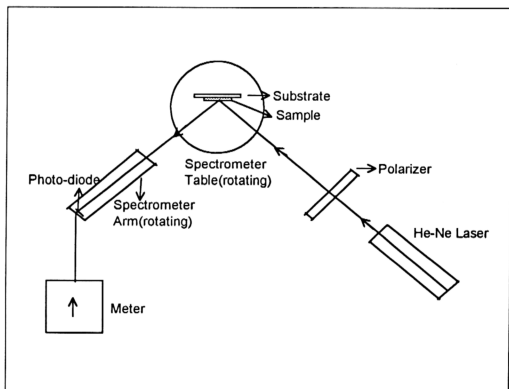


Figure 4.6 : Experimental set-up for determining the refractive index of thin film material by The Brewster's Angle Technique.

and for a coated surface the refractive index and the thickness of the coating layer can be determined. In commercialized ellipsometer, this technique is quoted to be sensitive enough to measure changes in film growth down to less than one angstrom. Elliptically polarized light reflected from solid surfaces are characterized by two parameters ψ (PSI), the amplitude ratio and Δ (DELTA), the phase difference. Professor Paul Drude, a German professor who introduced the two parameters also developed the fundamental equation of ellipsometry

$$\tan \psi e^{i\Delta} = \frac{[r_{p01} + r_{p12}e^{-2ix}][1 + r_{s01}r_{s12}e^{-2ix}]}{[1 + r_{p01}r_{p12}e^{-2ix}][r_{s01} + r_{s12}e^{-2ix}]} \dots\dots (4.3)$$

$$x = \frac{2\pi}{\lambda d(n_1^2 - n_0^2 \sin^2 \phi)^{1/2}} \dots\dots\dots (4.4)$$

where r_{p01} and r_{s01} are the Fresnel reflection coefficients for the ambient medium-film, r_{p12} and r_{s12} are the Fresnel reflection coefficients of the thin film-substrate interfaces [refer to figure 4.7], n_0 is the refractive index of the ambient medium, λ is the wavelength of the incident light and ϕ is the angle of incidence.

The ellipsometer built in this laboratory for measuring the refractive index and thickness of thin film semiconducting material consists of a He-Ne laser as the monochromatic light source, a rotatable polarizer, a rotatable quarter wave-plate as a compensator, a sample holder, a rotatable analyser and a photodiode enclosed in a cylindrical tubing with a pinhole to admit the reflected light. The amount of light reaching the photodiode is indicated by a voltmeter which acts as an extinction meter for the ellipsometer. An EM2

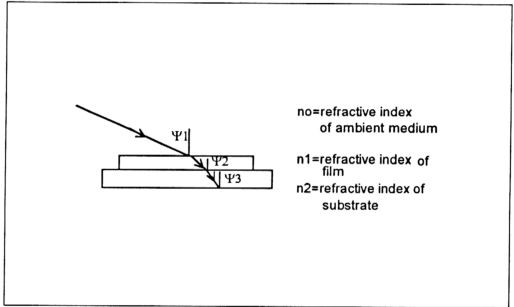


Figure 4.7 : Film-substrate interface to define Fresnel reflection coefficients for ambient-medium-film, r_{p01} and r_{s01} and Fresnel reflection coefficients of film-substrate interface r_{p12} and r_{s12} .

$$r_{p01} = \frac{n_1 \cos \Psi_1 - n_0 \cos \Psi_2}{n_1 \cos \Psi_1 + n_0 \cos \Psi_2}$$

$$r_{s01} = \frac{n_1 \cos \Psi_1 - n_1 \cos \Psi_2}{n_0 \cos \Psi_1 - n_1 \cos \Psi_2}$$

$$r_{p12} = \frac{n_2 \cos \Psi_2 - n_1 \cos \Psi_3}{n_2 \cos \Psi_2 + n_1 \cos \Psi_3}$$

$$r_{s12} = \frac{n_1 \cos \Psi_2 - n_2 \cos \Psi_3}{n_1 \cos \Psi_2 + n_2 \cos \Psi_3}$$

Edward vacuum pump is connected to an air duct on the reverse side of the sample holder to keep the sample in position. A schematic diagram of the ellipsometer set-up is shown in figure 4.8. The angle of incidence ϕ can be set at 70° , 50° or 30° depending on the requirement of the film material to be measured. The measurement procedure starts off with the setting the polarizer to 85° and the analyzer drum to 45° . The compensator is then adjusted until the voltmeter gives a maximum reading. Then the analyzer drum is rotated slowly within the range of 0° and 90° until a minimum reading is achieved on the voltmeter. Next the polarizer drum is rotated within 315° to 135° until a new minimum which is lower than the reading yielded on the voltmeter prior to this is obtained. The analyzer and the polarizer is rotated alternately until a very low reading is obtained on the voltmeter. The first analyzer drum reading and the first polarizer drum reading are recorded as A_1 and P_1 respectively. After recording the values of A_1 and P_1 , 90° is added to P_1 and A_1 is subtracted from 180° and the polarizer drum and analyzer drum is then rotated and set to these new values. The polarizer drum is then slowly rotated until it yields a minimum value. The analyzer and polarizer are again rotated alternately to obtain the final lowest reading on the voltmeter. The final analyzer and polarizer drum reading are recorded as A_2 and P_2 respectively. Using the relationships below

$$\psi = \frac{180^\circ - (A_2 - A_1)}{2} \dots\dots\dots (4.5)$$

$$\Delta = 360^\circ - (P_1 + P_2) \dots\dots\dots (4.6)$$

ψ , the amplitude ratio and Δ , the phase difference are obtained. If $(P_1 + P_2)$ is

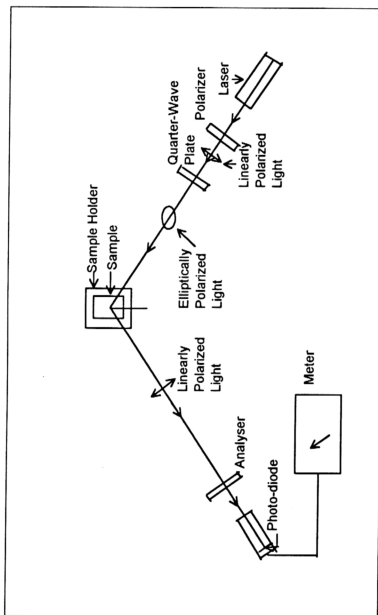


Figure 4.8 : A schematic diagram of an ellipsometer set-up.

greater than or equal to 360° , 360° is subtracted from it before using the above relationships. The refractive index and the thickness of the film is then calculated using an ellipsometer program obtained from the Thin Film Laboratory, University of Cambridge England programmed by Dr. Paul Barden. In order to iterate the final value of the refractive index and the thickness of the film, estimates of the refractive index and thickness are needed for these parameters. The values of these estimates are obtained by the interference fringes technique if the transmission spectrum produces observable fringes otherwise the Tolansky and the Brewster's techniques are used to determine the estimated thickness and refractive index of the film respectively.

4.4.4 Optical Transmission Spectroscopy

The Optical Transmission Spectroscopy is indeed a very useful technique in thin film characterization. The transmission spectrum produced provides valuable information about the film. In this work, the transmission spectrum is obtained using a Shimadzu UV-VIS-NIR Scanning Spectrophotometer model UV-3101PC. A schematic block diagram of the apparatus is as shown in figure 4.9. The set-up consists of a light source, a monochromator, a sample compartment which holds a reference and a sample holder, a photomultiplier tube which is used as a detector and a computer to automate the measurement. The light source can be automatically changed depending on the scanning range. For this measurement, the scanning range is set to 2000nm. A-diagnostic program appears on the computer monitor when it is turned on to ensure that the system is functioning. The baseline is first obtained by scanning with two glass slides which is used as substrates for the

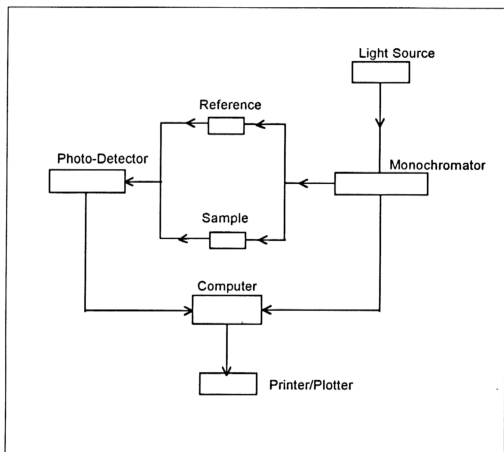


Figure 4.9 : Block Diagram of the Optical Transmission Set-up.

film in both the reference and sample holders. One of the glass slides is used as a reference and the other is removed and is replaced by the thin film a-Si:H sample. The transmission spectrum for the sample is then obtained. Figure 4.10 shows a typical transmission spectrum for a-Si:H thin film sample. However, not all the thin film samples produce transmission spectrum with interference fringes since the appearance of these fringes are strongly dependent on the refractive index and the thickness of the film. In cases where interference fringes are obtained the film thickness and the refractive index for various wavelength are determined using the technique proposed by J.C. Manifacier et al.³

The refractive index and the film thickness is determined by considering a continuous function of interference maxima, T_{\max} and interference minima, T_{\min} as shown in figure 4.10. The refractive index at a particular wavelength of the thin film is determined using the following equations

$$n(\lambda) = \left[N + \left(N^2 - n_0 n_1 \right)^{1/2} \right]^{1/2} \dots\dots\dots (4.7)$$

where

$$N(\lambda) = \frac{n_0^2 - n_1^2}{2} + 2n_0 n_1 \frac{T_{\max}(\lambda) - T_{\min}(\lambda)}{T_{\max}(\lambda) T_{\min}(\lambda)} \dots\dots\dots (4.8)$$

where n_0 and n_1 are the refractive indices of air and the substrate respectively.

The thickness of the thin film, t is then determined using the interference fringes and the variation of the refractive index with wavelength derived above.

$$t = \frac{[M\lambda_1\lambda_2]}{2[n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1]} \dots\dots\dots (4.9)$$

where M is the number of oscillations between two extremas occurring at λ_1

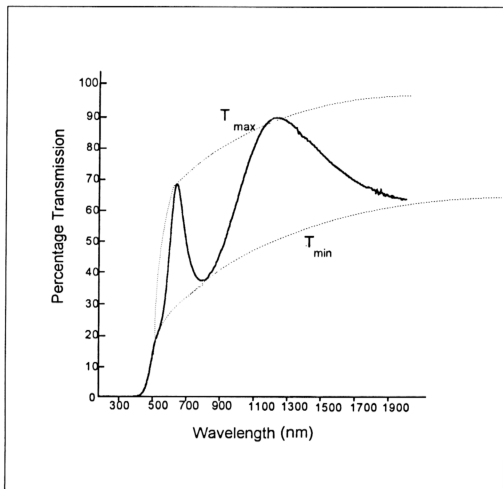


Figure 4.10 : Typical Transmission Spectrum of a-Si:H thin film on glass.

and λ_2 and $n(\lambda_1)$ and $n(\lambda_2)$ are the refractive indices at λ_1 and λ_2 respectively. In chapter 6, the dispersion curve of refractive index versus energy obtained using the above technique will be used to determine the hydrogen content of the a-Si:H thin film.

The transmission spectrum of the a-Si:H film is also used to determine the optical band gap of the film material. The absorption coefficient, α is calculated from the transmission curve by the relationship

$$\alpha = \frac{1}{d} \ln \left\{ \frac{1}{X} \right\} \dots\dots\dots (4.10)$$

where d is the film thickness. X is derived from the expression for transmission, T through air-film-substrate interface as given by Brodsky⁴

$$T = \frac{(1 - R_1)(1 - R_2)(1 - R_3)e^{-\alpha d}}{(1 - R_2 R_3) \left[1 - (R_1 R_2 + R_1 R_3 (1 - R_2)^2) e^{-2\alpha d} \right]} \dots\dots\dots (4.11)$$

where R_1 , R_2 and R_3 are the reflectivities at the air-film, film-glass and glass-air surfaces respectively. Bahl's relations⁵ are used to determine the reflectivities

$$R_1 = \frac{(n_f - 1)^2}{(n_f + 1)^2} \dots\dots\dots (4.12)$$

$$R_2 = \frac{(n_f - n_s)^2}{(n_f + n_s)^2} \dots\dots\dots (4.13)$$

$$R_3 = \frac{(n_s - 1)^2}{(n_s + 1)^2} \dots\dots\dots (4.14)$$

where n_s is the refractive index of the substrate and n_f is the refractive index of

the film. The refractive index of air is 1.0. The following constants are substituted into the equation 4.11.

$$A = (1 - R_1)(1 - R_2)(1 - R_3) \dots \dots \dots (4.15)$$

$$B = R_1 R_3 \dots \dots \dots (4.16)$$

$$C = R_1 R_2 + R_1 R_3 (1 - R_2)^2 \dots \dots \dots (4.17)$$

Thus equation 4.11 can be written in a more simplified form

$$T = \frac{Ax}{(1 - B)(1 - Cx^2)} \dots \dots \dots (4.18)$$

which can be written in the quadratic form

$$(TC - TBC)x^2 + Ax - (T - TB) = 0 \dots \dots (4.19)$$

which gives a solution of

$$X = \frac{-A \pm \sqrt{A^2 + 4T^2 C(1 - B)^2}}{2TC(1 - B)} \dots \dots \dots (4.20)$$

The software LOTUS 1-2-3 version 4 is then used to calculate the absorption coefficient at different wavelength. The optical gap is deduced from the Tauc's plot ie from the extrapolation of $(\alpha h\nu)^{1/2}$ versus $h\nu$ in the high energy range and also from the energy value at which the absorption coefficient reaches a value of 10^4 cm^{-1} .

4.5 Conclusion

The characterization techniques described above are indeed very useful in determining the quality of the a-Si:H films produced. The chemical bonding analysis enables the various bonds present in the film to be identified and their significance to the structural properties of the film. This technique also enables the hydrogen content in the film to be determined. The electrical and optical characterizations of the film lead to the determination of various parameters critical in determining the film quality. These properties can then be related to each other to provide better understanding of the material.

4.5 References

1. J. Tauc, "Infrared and Raman Spectroscopy of Amorphous Semiconductors", "Physics of Structurally disordered Solids" ed. S.S. Mitra, Plenum Press, p526(1976).
2. Perkin-Elmer Model 1600 FT-IR Vol.1 , User Manual Spectrophotometer.
3. J.C. Manifacier, J. Gasiot and J.P. Fillard, J.Phys. E9,1002(1978)
4. M.H. Brodsky, R.S.Title, K. Weiser, G.D. Pettit, Phys. Rev. B, 1 No.6, 2633(1970).
5. S.K. Bahl, S.M. Bhagat, J. of Non-Cryst. Solids 17, 418(1975).