

Nathan Hugh Barr

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Abstract

Abstract here

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Chapter 1

Introduction

In December 2017 and May 2018, I was asked to partake in Grazing-incidence small-angle scattering (GISAXS) experiments investigating the structure of thin films at The Cornell High Energy Synchrotron Source (CHESS). A thin film is a thin layer of polymer deposited onto a wafer, in this case a silicon wafer. The experiments were conducted with the aim of understanding the reorganisation of star-block polymers on a silicon wafer when exposed to vapour annealing. GISAXS maps were used to study how the star-block polymers arranged themselves when the volume of the polymer increased. GISAXS maps gives the researcher a snapshot of the polymers structure at that point in time. The GISAXS maps can be used to calculate the thickness of the polymer, this is not a trivial since it involves fitting a model[explain a bit more], it is also done post experiment and is time consuming.

This leads to the experimental method called Spectroscopic Reflectometry, and the meaning of these two words gives insight into the nature of the method. Spectroscopic is a study of the interaction between electromagnetic radiation and matter [1] and reflectometry is the study of an object using reflected light. This experimental technique can be used to measure the thickness of a thin film. The idea of running the two experimental technique parallel at CHESS was to monitor the thin films in-situ giving us the ability to explore different vapour annealing protocols and see how the structure changed during these. The thickness measurements done at CHESS using Spectroscopic Reflectometry were not successful since the software's thin film model and the reflectance data did not fit well. Since beam time is precious, this problem was not investigated during the GISAXS.

Spectroscopic Reflectometry is not the only experimental technique available that can measure thin film thickness, there is Atomic force microscopy, Ellipsometry and X-ray reflectometry. Spectroscopic reflectometry has been chosen to complement GISAXS because it can be used in-situ and used in harsh conditions. The size of

the apparatus plays a huge role as the free space in a synchrotron hutch is limited. It is a primitive technique compared to the other techniques that use electromagnetic radiation, and it is important investigate how far this technique can be pushed.

This thesis has two purposes, it is a study of the third party apparatus called NanoCalc XR spectrometer and software made by the company Ocean Optics[Insert link] and an investigation into how the reflectance changes during swelling of [Insert which polymers].

The first purpose provides a experimental fundament since the NanoCalc XR spectrometer and software will be used to investigate the thin films and this thesis will serve as an introduction to the apparatus and how light reflects and transmits through the thin film since the user manual for the spectrometer and software is lacking in an explanation of the theory behind the thin film modelling and fitting.

The second purpose is the investigate how the reflectance curves change during swelling. From the reflectance curves thickness can be calculated. This will be usefully for experiments conducted at synchrotron sources as the promising swelling protocols can be used.

1.1 Research Question

1.2 Structure of this thesis

The structure of this thesis is as follows. Chapter 2 will introduce the basic theory of light propagation through a vacuum and through a transparent medium. It will touch on the complex refractive index and the Fresnel equations used to model light reflecting and transmitting in the thin films. Chapter 3 will introduce the Nanocalc spectrometer and software, the protocol for the thin film creations. The polymers used will be described and experimental protocol for measuring the thin films.

Chapter 2

Theory

2.1 Electromagnetic Radiation

Electromagnetic radiation can be expressed as a one dimensional sinusoidal wave using either cos or sin:

$$\varphi = A \sin(\omega t - Kx + \delta), \quad (2.1)$$

where A is the wave amplitude, $K = \frac{2\pi}{\lambda}$ is the propagations number and λ is the wave length, angular frequency $\omega = 2\pi\nu$ where ν is the frequency, time t and initial phase δ . From electromagnetic theory, the radiation is composed of an electric field and magnetic field that are both perpendicular to the direction of propagation. Both fields can be expressed as one-dimension complex sinusoidal wave. A complex number can be expressed as $C = a + ib = Re(C) + iIm(C) = r \cos(\theta) + ir \sin(\theta)$. Using Eulers formula $\exp(i\theta) = \cos(\theta) + i \sin(\theta)$, the one dimension sinusoidal wave can be expressed as:

$$\varphi = A \cos(\omega t - Kx + \delta) = Re\{A \exp[i(\omega t - Kx + \delta)]\} = A \exp[i(\omega t - Kx + \delta)]. \quad (2.2)$$

The wave travels to the right if the phase is $(\omega t - Kx)$ and to the left if the phase is $(\omega t + Kx)$. Changing the order of the first two terms in the phase does not change the propagation of the wave, only the initial phase δ . The wave equation in equation 2.1 uses sin in the expression but the complex wave in equation 2.2 uses cos, it is the same representation of the wave just moved 2π in the positive direction. The electric field and magnetic field can be expressed as:

Find
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$$E = E_0 \exp[i(\omega t - Kx + \delta)] \quad (2.3)$$

$$B = B_0 \exp[i(\omega t - Kx + \delta)]. \quad (2.4)$$

The relationship between the electric field and magnetic field is given by $E = cB$, and can be derived using the Maxwell-Faraday equation and one dimension wave equations for the electric and magnetic field:

$$\frac{\partial E}{\partial x} = -\frac{\partial B}{\partial t} \quad (2.5)$$

$$E = E_0 \cos(Kx - \omega t) \quad (2.6)$$

$$B = B_0 \cos(Kx - \omega t). \quad (2.7)$$

Using the Maxwell-Faraday equation the following equation can be formed:

$$\frac{\partial E}{\partial x} = -\frac{\partial B}{\partial t} \quad (2.8)$$

$$-KE_0 \sin(Kx - \omega t) = -\omega B_0 \sin(Kx - \omega t) \quad (2.9)$$

$$E_0 = \frac{\omega}{K} B_0 \quad (2.10)$$

$$E_0 = sB_0. \quad (2.11)$$

The constant $\frac{\omega}{K}$ is expressed as the speed s of the light through a medium. In vacuum the speed is equal to the speed of light $s = c$, through a transparent medium the speed is equal to the speed of light divided by the refractive index of the medium $s = \frac{c}{n}$.

2.2 Refractive index

Light travelling from one medium to another will undergo change. The speed of the light and the wavelength will change, but not the frequency. The refractive index is a material constant which describes the change and is greater than or equal to one. The refractive index is defined as:

$$n \equiv \frac{c}{s}, \quad (2.12)$$

where c is the speed of light and s is the speed of light in the medium. The amplitude of the wave will decrease in the medium because the propagation number $K = \frac{2\pi n}{\lambda}$ increases:

$$E = E_0 \exp \left[i \left(\omega t - \frac{2\pi n}{\lambda} x + \delta \right) \right]. \quad (2.13)$$

The change in wavelength is $\lambda = \frac{\lambda_0}{n}$, where λ_0 is the wavelength before entering the medium. The medium can also absorb light, a term is added to the refractive index to correct this, and is called the extinction coefficient k . The complex refractive index is given:

$$N = n - ik. \quad (2.14)$$

Placing the complex refractive index into equation 2.13, it can be seen that the wave amplitude will decrease exponentially.

$$E = E_0 \exp \left[i \left(\omega t - \frac{2\pi N}{\lambda} x + \delta \right) \right] = E_0 \exp \left(-\frac{2\pi k}{\lambda} x \right) \exp \left[i \left(\omega t - \frac{2\pi n}{\lambda} x + \delta \right) \right] \quad (2.15)$$

It needs to be stated that if the phase of the wave is expressed as $(Kx - \omega t)$ and the complex refractive index is given by $N = n - ik$, the exponential factor will be positive which is incorrect. If the phase of the wave is expressed as $(Kx - \omega t)$ the complex refractive index must be defined as $N = n + ik$.

2.3 Reflectance and Transmittance

When light is reflected upon a surface at an oblique angle, light is reflected and transmitted. The electric field of light is grouped into two oscillation directions which can be defined by two planes, the parallel plane p and the perpendicular plane s . The same applies for the magnetic field of light. The parallel plane is defined by the incident and reflected light and the perpendicular plane is perpendicular to the parallel plane. Theory of light regards the two oscillation directions as the p -polarisation and s -polarisation. The reflectance of both p -polarisation and s -polarisation are defined by the ratio of reflected light intensity by the incident light intensity.

$$R_p \equiv \frac{I_{r,p}}{I_{i,p}} = \frac{|E_{r,p}|^2}{|E_{i,p}|^2} = |r_p|^2 \quad R_s \equiv \frac{I_{r,s}}{I_{i,s}} = \frac{|E_{r,s}|^2}{|E_{i,s}|^2} = |r_s|^2 \quad (2.16)$$

The transmittance can also be expressed using the intensity ratio, $I = N |E|^2$ and the ratio cross-sectional area for the transmitted and incident ray.

$$T_p \equiv \frac{I_{r,p} \cos(\theta_t)}{I_{i,p} \cos(\theta_i)} = \frac{N_t \cos(\theta_t) |E_{tp}|^2}{N_i \cos(\theta_i) |E_{ip}|^2} = \frac{N_t \cos(\theta_t)}{N_i \cos(\theta_i)} |t_p|^2 \quad (2.17)$$

$$T_s \equiv \frac{I_{r,s} \cos(\theta_t)}{I_{i,s} \cos(\theta_i)} = \frac{N_t \cos(\theta_t) |E_{ts}|^2}{N_i \cos(\theta_i) |E_{is}|^2} = \frac{N_t \cos(\theta_t)}{N_i \cos(\theta_i)} |t_s|^2 \quad (2.18)$$

$$(2.19)$$

When the extinction coefficient in the refractive index is zero, $k = 0$, the sum of the reflectance and transmittance is equal to one, $R + T = 1$. If the extinction coefficient is greater than zero, $k > 0$, then the sum becomes less than one $R + T < 1$.

2.4 Fresnel equations for the ambient-substrate model

Light is reflected and transmitted at the interface of the ambient and substrate. The boundary conditions at the interface for the electric and magnetic field in the p-polarisation can be written as:

$$E_{i,p} \cos(\theta_i) = E_{t,p} \cos(\theta_t) + E_{r,p} \cos(\theta_r) \quad (2.20)$$

$$\implies E_{t,p} \cos(\theta_t) = E_{i,p} \cos(\theta_i) - E_{r,p} \cos(\theta_r) \quad (2.21)$$

$$B_{i,p} + B_{r,p} = B_{t,p}. \quad (2.22)$$

The subscripts of the electric and magnetic field denote the incident ray i , reflected ray r and transmitted ray t in the p-polarisation p plane. The same boundary conditions for the s-polarisation can be expressed. This introduction to the Fresnel equations will use the p-polarisation light. The boundary conditions of the magnetic field need to be reformulated to express the electric field, this is done using the relation $E = sB$. The magnetic field boundary conditions equation 2.22 can be expressed as:

$$\frac{E_{i,p}}{s_i} + \frac{E_{r,p}}{s_i} = \frac{E_{t,p}}{s_t} \quad (2.23)$$

$$\frac{N_i}{c}(E_{i,p} + E_{r,p}) = \frac{N_t}{c}E_{t,p} \quad (2.24)$$

$$N_i(E_{i,p} + E_{r,p}) = N_t E_{t,p}. \quad (2.25)$$

Though the law of reflection the angle of incident is also the angle of reflection $\theta_i = \theta_r$, placing this into the electric field boundary conditions equation 2.21, the electric field and magnetic field can be expressed as:

$$(E_{i,p} - E_{r,p}) \cos(\theta_i) = E_{t,p} \cos(\theta_t) \quad (2.26)$$

$$\frac{N_i}{N_t}(E_{i,p} + E_{r,p}) = E_{t,p}. \quad (2.27)$$

Placing equation 2.27 into equation 2.26, the amplitude reflectance coefficient and the reflectance can be calculated for the ambient-substrate system:

$$E_{i,p} \cos(\theta_i) - E_{r,p} \cos(\theta_i) = \frac{N_i}{N_t}(E_{i,p} + E_{r,p}) \cos(\theta_t) \quad (2.28)$$

$$E_{i,p} \cos(\theta_i) - \frac{N_i}{N_t}E_{i,p} \cos(\theta_t) = \frac{N_i}{N_t}E_{r,p} \cos(\theta_t) + E_{r,p} \cos(\theta_i) \quad (2.29)$$

$$E_{i,p}(N_t \cos(\theta_i) - N_i \cos(\theta_t)) = E_{r,p}(N_i \cos(\theta_t) + N_t \cos(\theta_i)) \quad (2.30)$$

$$r_p = \frac{E_{r,p}}{E_{i,p}} = \frac{N_t \cos(\theta_i) - N_i \cos(\theta_t)}{N_i \cos(\theta_t) + N_t \cos(\theta_i)} \quad (2.31)$$

$$R_p = |r_p|^2. \quad (2.32)$$

The amplitude transmission coefficient and transmission can be equivalently formulated.

2.5 Fresnel equations for the ambient-thin film-substrate model

The light reflecting and transmitting in this system will interfere both constructive and destructively. To model the optical interference, the Fresnel equation for reflection will be used:

$$r_{jk,p} = \frac{N_k \cos(\theta_j) - N_j \cos(\theta_k)}{N_k \cos(\theta_j) + N_j \cos(\theta_k)} \quad r_{jk,s} = \frac{N_j \cos(\theta_j) - N_k \cos(\theta_k)}{N_j \cos(\theta_j) + N_k \cos(\theta_k)}. \quad (2.33)$$

The subscripts denote the reflection and transmission at definite interface. For example $r_{jk,p} = r_{01,p}$, denotes the reflection at the ambient-thin film interface. In the ambient-thin film-substrate model, light at the ambient-thin film interface will be both reflected and transmitted into the layer. The transmitted ray will then be reflected and transmitted at the thin film-substrate interface. The reflected and transmitted phenomenon will proceed through out the thin film. The change in phase at the interface is given by $\exp(-i\beta)$. Figure 2.1 represents the ambient-thin film-substrate model, this figure will be used to define the phase variation β .

The phase of the reflected ray will vary at the the ambient-thin film interface. This variation can be expressed as $K_0 \bar{AD}$, where $K_0 = \frac{2\pi N_0}{\lambda}$, is the propagation number in air. The phase variation of the transmitted ray is expressed as $K_1(\bar{AB} + \bar{BC})$, where $K_1 = \frac{2\pi N_1}{\lambda}$, is the propagation number in the thin film. The length difference can be denoted as $\bar{AB} + \bar{BC} - \bar{AD}$, thus the phase variation of this length difference is:

$$\alpha = \frac{2\pi N_1}{\lambda}(\bar{AB} + \bar{BC}) - \frac{2\pi N_0}{\lambda} \bar{AD}. \quad (2.34)$$

Using snells law, $\bar{AD} = \bar{AC} \sin(\theta_0)$ and $\bar{AC} = 2d \tan(\theta_1)$ as seen from figure 2.1, this reduces \bar{AD} to:

$$\sin(\theta_0) = \frac{N_1}{N_0} \sin(\theta_1) \quad (2.35)$$

$$\bar{AD} = 2d \frac{\sin(\theta_1)}{\cos(\theta_1)} \sin(\theta_0) \quad (2.36)$$

$$\implies \bar{AD} = 2d \frac{\sin(\theta_1)^2}{\cos(\theta_1)} \frac{N_1}{N_0}. \quad (2.37)$$

Inserting this into equation 2.34, and $\bar{AB} = \bar{BC} = \frac{d}{\cos(\theta_1)}$, as seen from figure 2.1, the equation is reduced to:

$$\alpha = \frac{2\pi N_1}{\lambda} \frac{2d}{\cos(\theta_1)} - \frac{2\pi N_0}{\lambda} \frac{2d \sin(\theta_1)^2 N_1}{\cos(\theta_0) N_0} \quad (2.38)$$

$$= \frac{4d\pi N_1}{\lambda} \left(\frac{1 - \sin(\theta_1)^2}{\cos(\theta_1)} \right) \quad (2.39)$$

$$= \frac{4d\pi N_1}{\lambda} \cos(\theta_1). \quad (2.40)$$

α is the total phase difference of the transmitted beam thus the expression $\alpha = 2\beta$ must hold. β is called the film phase thickness and given as:

$$\beta = \frac{2\pi d_1}{\lambda} N_1 \cos(\theta_1). \quad (2.41)$$

Using figure 2.2 as a reference the amplitude reflection coefficient can be expressed as the sum of the reflected waves. The first time the ray meets the ambient-thin film interface, the ray will reflect and transmit. The reflected ray r_{01} can be calculated using equation 2.31. The transmitted ray will proceed to the next interface reflect back to the ambient-thin film interface and transmit, giving the second reflected wave in the sum expressed as $t_{01} r_{12} t_{10} \exp(-i2\beta)$. The factor $\exp(-i2\beta)$ comes from the phase difference due to the two interactions at the thin film-substrate

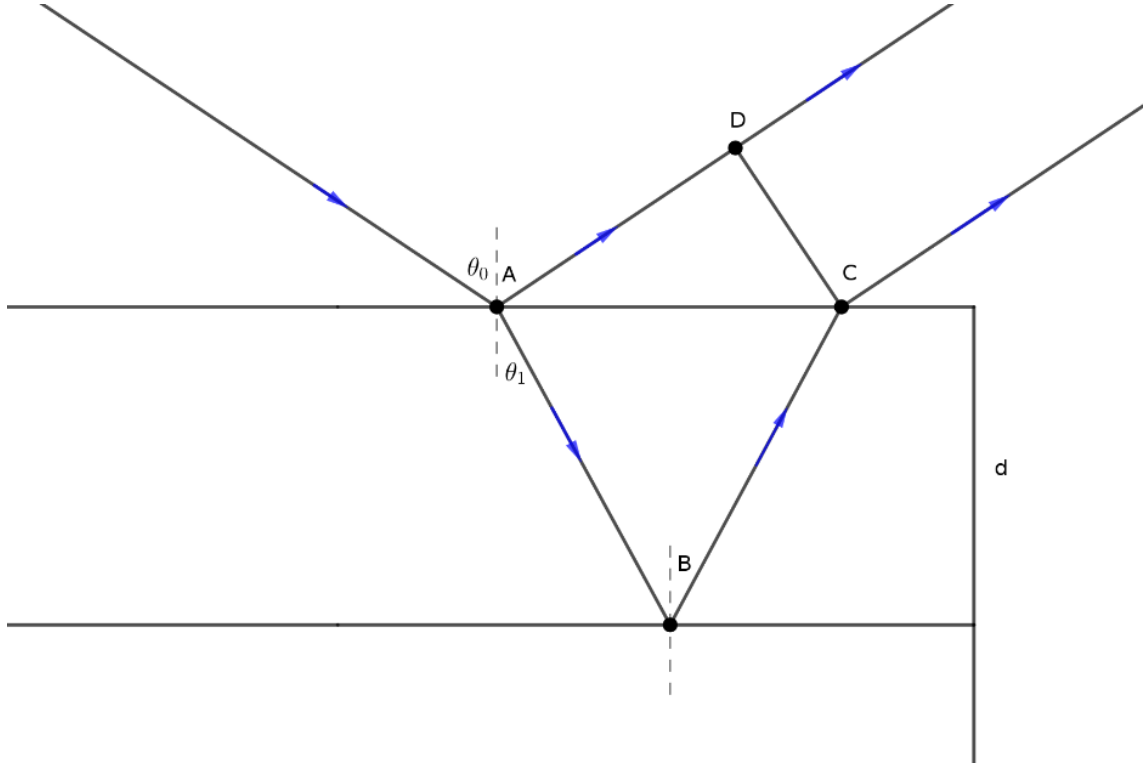


Figure 2.1: Light rays from the left will be reflected and transmitted at point A. The reflected light will experience at phase change at point A. The transmitted light will proceed to point B, where it will reflect undergoing a phase change then transmitting at point C. The phase difference between the primary and secondary ray can be calculated by $\alpha = K_1(\bar{AB} + \bar{BC}) - K_0(\bar{AD})$

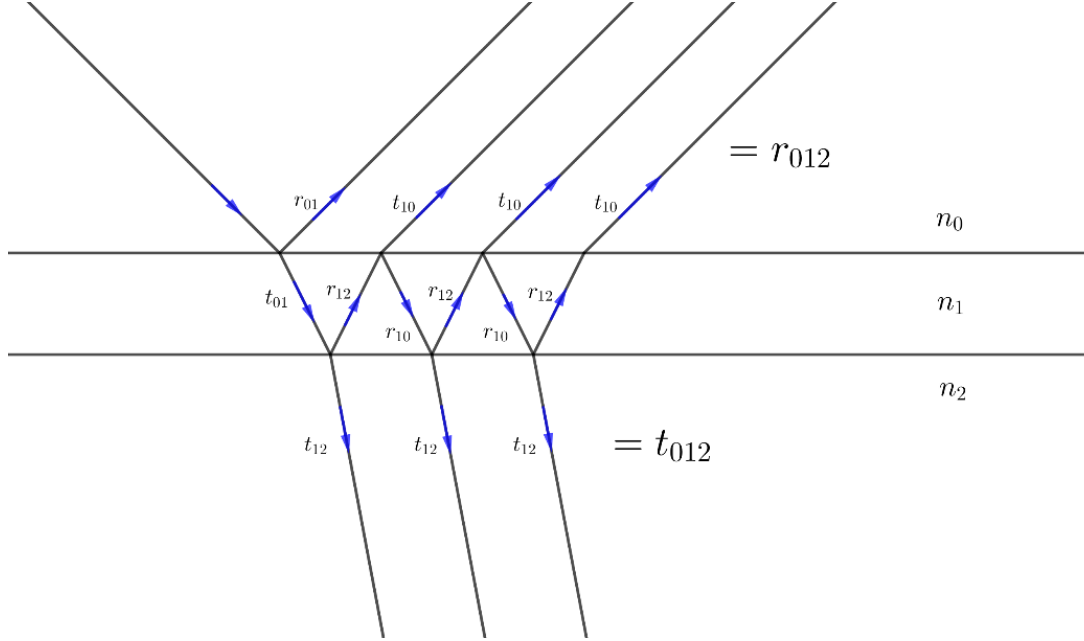


Figure 2.2: When light meets an interface, it reflects or transmits. Each light ray is name either reflection r or transmission t . Each reflected and transmitted ray is also indexed with two numbers, these denote at which interface the light was reflected or transmitted. A variation of phase happens to each reflected and transmitted rays at every interface. The phase variation at an interface can be expressed by the factor $\exp(-i\beta)$. The primary reflected beam is denoted as r_{01} , the second primary reflected beam is denoted $t_{01}r_{12}t_{10} \exp(-i2\beta)$. The reflection amplitude coefficient is the sum of reflected rays that exit the model. The transmission amplitude coefficient is the sum of the transmitted rays that continue into the substrate.

interface and thin film-ambient interface. The phase difference factor can be collected and multiplied onto the expression since $\varphi = A \exp(i(\omega t - (Kx + 2\beta) + \delta)) = A \exp(i(\omega t - (Kx) + \delta)) \exp(-i2\beta)$. The total amplitude reflection coefficient can be expressed:

$$r_{012} = r_{01} + t_{01}t_{10}r_{12} \exp(-i2\beta) + t_{01}t_{10}r_{10}r_{12}^2 \exp(-i4\beta) + t_{01}t_{10}r_{10}^2r_{12}^3 \exp(-i6\beta) + \dots \quad (2.42)$$

The amplitude reflection coefficient becomes an infinite geometric series which can be reduced using $y = \frac{a}{(1-r)}$, leading to the coefficient being rewritten to:

$$r_{012} = r_{01} + \frac{t_{01}t_{10}r_{12} \exp(-i2\beta)}{1 - r_{10}r_{12} \exp(-i2\beta)}. \quad (2.43)$$

The equation 2.43 can be reduced to a more simple equation using $r_{10} = -r_{01}$ and $t_{01}t_{10} = 1 - r_{01}^2$:

$$r_{012} = \frac{r_{01} + r_{12} \exp(-i2\beta)}{1 + r_{01}r_{12} \exp(-i2\beta)}. \quad (2.44)$$

The following Fresnel equation, reflectance and Snell's law for this model are expressed as:

$$r_{012,p} = \frac{r_{01,p} + r_{12,p} \exp(-i2\beta)}{1 + r_{01,p}r_{12,p} \exp(-i2\beta)} \quad r_{012,s} = \frac{r_{01,s} + r_{12,s} \exp(-i2\beta)}{1 + r_{01,s}r_{12,s} \exp(-i2\beta)} \quad (2.45)$$

$$R_p = |r_{012,p}|^2 \quad R_s = |r_{012,s}|^2 \quad (2.46)$$

$$N_0 \sin(\theta_0) = N_1 \sin(\theta_1) = N_2 \sin(\theta_2). \quad (2.47)$$

2.6 Fresnel equations for a multilayer model

In the previous sections, the Fresnel equations for two different models were evaluated. The Fresnel equations for a multilayer model is an amalgamation of the previous models. The reflection amplitude coefficient r_{123} for the multilayer model seen in the figure 2.3 with an ambient, two layers and a substrate can be calculated using equation 2.44. These equations produce the following expressions:

$$r_{123} = \frac{r_{12} + r_{23} \exp(-i2\beta_2)}{1 + r_{12}r_{23} \exp(-i2\beta_2)}. \quad (2.48)$$

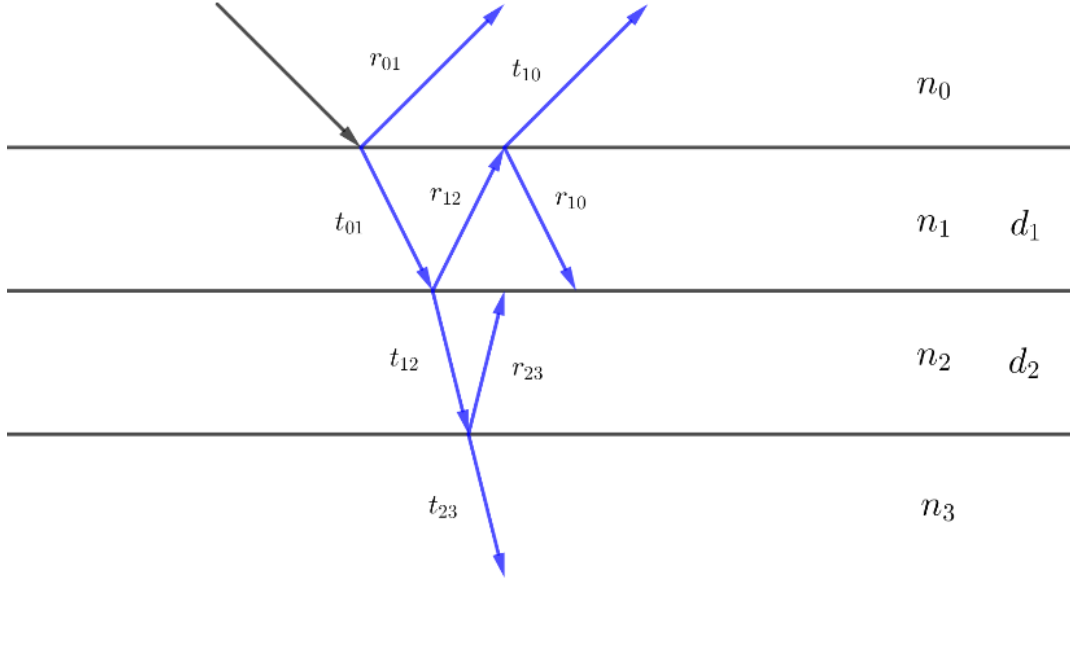


Figure 2.3: The model consists of the ambient, first thin film layer, second thin film layer and substrate. Each layer has a refractive index associated to it and both thin films have a thickness d_1 and d_2 respectively.

β_2 is the phase variation in the second thin film layer with thickness d_2 . This is given as $\beta_2 = \frac{2\pi d_2 N_2 \cos(\theta_2)}{\lambda}$. The substrate and the layer on top of the substrate can be considered as one layer as seen in figure 2.4, thus the reflection amplitude coefficient and transmission amplitude coefficient is expressed as:

$$r_{0123} = \frac{r_{01} + r_{123} \exp(-i2\beta_1)}{1 + r_{01}r_{123} \exp(-i2\beta_1)}. \quad (2.49)$$

Inserting r_{123} into equations 2.49 gives the expanded Fresnel equation for this multilayer model:

$$r_{0123} = \frac{r_{01} + r_{12} \exp(-i2\beta_1) + [r_{01}r_{12} + \exp(-i2\beta_1)]r_{23} \exp(-i2\beta_2)}{1 + r_{01}r_{12} \exp(-i2\beta_1) + [r_{12} + r_{01} \exp(-i2\beta_1)]r_{23} \exp(-i2\beta_2)}. \quad (2.50)$$

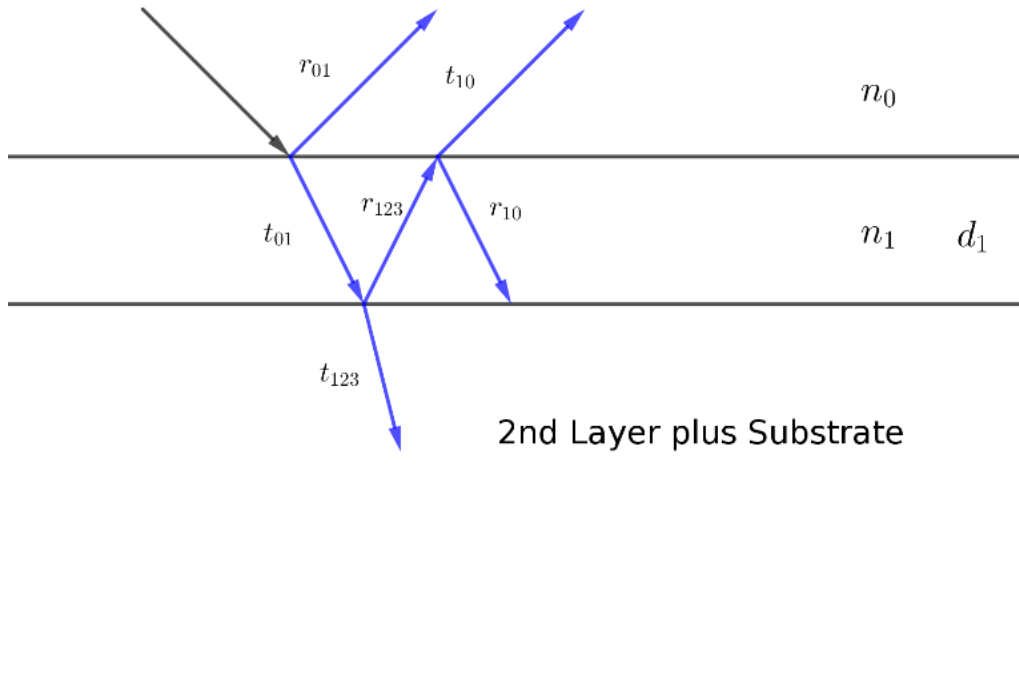


Figure 2.4: The model consists of the ambient, first thin film layer and second thin film layer plus substrate. The second thin film layer and substrate layer has been grouped together because r_{123} and t_{123} has been calculated the model seen in figure 2.3 and r_{0123} and t_{0123} can easily be calculated from this model. The ambient and first thin film layer have a refractive index and the first thin film layer has a thickness d_1 .

Chapter 3

Experimental method

3.1 Polymers

3.2 The Experimental Setup

The experimental setup is comprised of a NanoCalc XR and a Halogen light source(HL-2000-FHSA) which can produce wavelengths of 360 nm to 2400 nm. When the samples are being measured they are either placed on the ocean optics single point stage(ADD PICTURE) or in the test chamber(ADD PICTURE) made by the RUC workshop/machinists for x-ray scattering experiments. The NanoCalc is comprised of a spectrometer and an internal light source as seen in the figure 3.1, which can produce wavelengths of 250 nm to 1050 nm and measure thicknesses of 10 nm to 100 μ m. The NanoCalc XR is connected to a computer where the NanoCalc software is installed and operated. For the experiments the halogen light source is used since it has a larger output power then the internal light source of the NanoCalc XR. The larger intensity output is need when performing experiments in the test chamber. To reiterate, white light is produced in the light source(HL-2000-FHSA), which travels through optical fiber and strikes that sample. The reflected light travels back through the optical fiber and the intensity across every wavelength of the white light is collected in the spectrometer and is sent to the NanoCalc software.

3.3 Reflectance measurements in the NanoCalc spectrometer

The NanoCalc spectrometer measures three light intensities which will be called a measurement onwards. The three measurements are the dark measurement (dark),

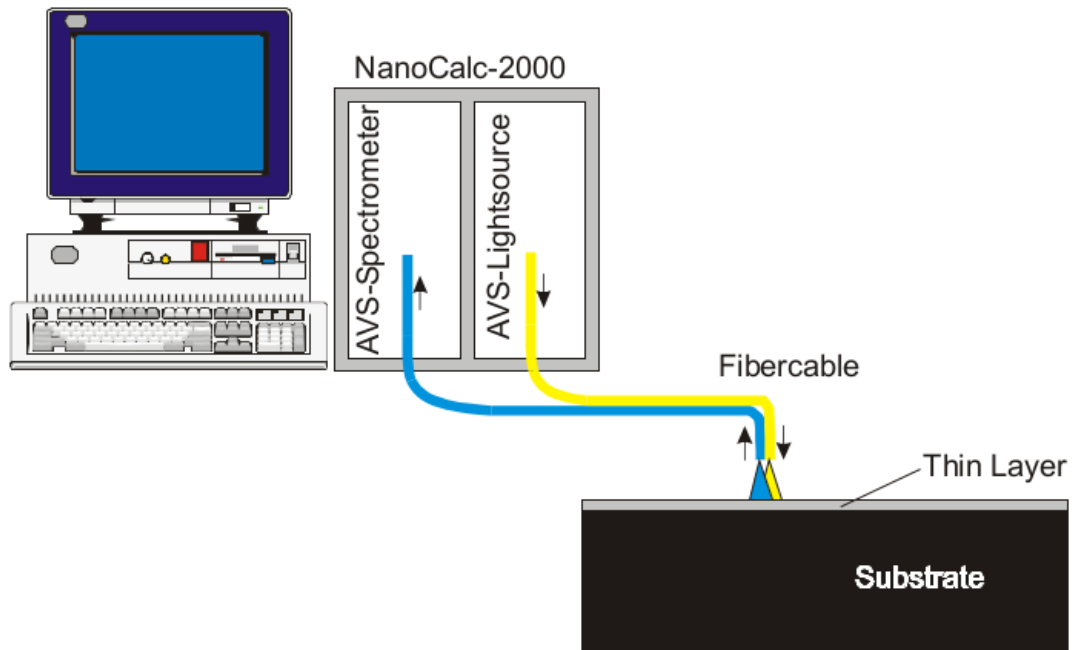


Figure 3.1: This figure describes the NanoCalc set-up and has been taken from [2]. Light from a light source travels down the optical fiber illuminating the sample. The reflected light is collected by the optical fiber and analysed in the spectrometer. The spectrometer is connected to the computer by USB and the data is stored, modelled and manipulated through the NanoCalc software.

the reference measurement (ref) and the thin-film measurement (meas). The dark measurement is the amount of light received by the optical fiber from external sources. The reference measurement is the amount of light reflected from a blank silicon wafer and the thin film measurement is the amount of light reflected from the sample. From chapter 2.3, the reflectance of a sample can be expressed as :

$$R_{sample} = \frac{I_{sample}}{I_{incident}} \quad (3.1)$$

The spectrometer does not measure the intensity of the incident light, therefore the reflectance of the substrate is used to isolate the incident light intensity and inserted into equation 3.1. The reflectance of the substrate is used because it is easily calculated using the Fresnel equations as described in chapter 2.4.

$$R_{ref} = \frac{I_{ref}}{I_{incident}} \quad (3.2)$$

$$\implies I_{incident} = \frac{I_{ref}}{R_{ref}} \quad (3.3)$$

Inserting equation 3.3 in equation 3.1, the reflectance for the sample is expressed without the incident light intensity as:

$$R_{sample} = \frac{I_{sample}}{I_{ref}} \cdot R_{ref} \quad (3.4)$$

The reflectance of the sample is given as:

$$Reflectance = \frac{Meas - Dark}{Ref - Dark} \cdot R_{sub}, \quad (3.5)$$

This is the same expression given in the NanoCalc spectrometer manual [2]. Through reproduction of the data and curves given by the NanoCalc spectrometer, i can deduce that the reference measurement has already had the dark measurement subtracted, giving the following reflectance expression:

$$Reflectance = \frac{Meas - Dark}{Ref} \cdot R_{sub}, \quad (3.6)$$

Placing equation 3.6 equal to the reflectance equations using the Fresnel equations from chapters 2.4, 2.5 and 2.6, the NanoCalc spectrometer software can fit a thickness of the sample.

3.4 Experimental Protocol

In this section the experimental protocol for both taking measurements without the optics and with the optics are given. The protocol will be formulated in steps.

3.4.1 Without Optics

1. Take a continuous reference measurement and adjust the light intensity, such that the reference measurements maximum is 50% of the y-axis.
2. Clear the reference measurement.
3. Take the optic fiber and point it away from anything that can reflect light. Take a dark measurement.
4. Place the optic fiber into ocean optics single point stage. The optic fiber is positioned 4mm above the single point stage.
5. Place a blank silicon wafer under the optic fiber and take a reference measurement.
6. Save the dark and reference measurement.
7. Place a thin film under the optical fiber and take a measurement.

3.4.2 With Optics

1. Take a continuous dark measurement with the optic fiber in the optics and adjust the light intensity, such that the dark measurements maximum is at 100% of the y-axis.
2. Clear the dark measurement.
3. Take the optics as a whole and point it away from anything that can reflect. Take a dark measurement.
4. Place a blank silicon wafer into the test chamber and place the optics into the test chamber. Take a reference measurement.
5. Save the dark and reference measurement.
6. Take the optics off the test chamber, remove the blank silicon wafer and place in a thin film sample. Place the optics onto the test chamber. Take a measurement.

Chapter 4

Analysis

Chapter 5

Bibliography

- [1] I. Levine. *Physical Chemistry*. McGraw-Hill, 1995.
- [2] Ocean Optics. *NanoCalc Software Manual*, version 4 edition, 2014.