Determining Thickness of Zinc Sulfide Thin Films Through Optical Spectroscopy

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Abstract

A method has been developed to measure the thickness of ZnS thin films on Si using optical interference. Thin film optical interference fringes are dependent upon the thickness of the film, and for this reason the thickness can be determined by measuring reflectance spectrum of a thin film. A grating spectrometer was used to measure the reflectance of the thin films. The thickness of the films was then determined by matching the measured reflectance with a theoretical model. This is a non-destructive method, and has worked for films as thin as 17 nm, but could potentially work for even thinner films. Due to lack of rigorous statistical analysis, the accuracy can only be estimated to be within 1 to 2 nm depending on the quality of the data and the film. It was thought that ZnS on Si could convert the UV portion of the solar spectrum into electrical energy, but in order to test this, the ZnS film had to be of an appropriate thickness.

Acknowledgements

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1. Introduction

1.1 Zinc Sulfide

ZnS is a direct bandgap semiconductor with the ability to emit light in the visible spectrum upon interaction with electrical energy. For this reason, ZnS is often used to coat the inside of fluorescent light bulbs [1]. ZnS has two forms: the cubic, sphalerite, and the hexagonal, wurtzite. The ZnS films used for this research were of the sphalerite form, so that will be the focus of this section.

A ZnS thin film on a Si substrate is an optical filter, a material used to change the spectral intensity distribution of incident radiation [2]. The hope for the ZnS on Si system was that it would allow a solar cell to convert the UV portion of the solar spectrum into usable electrical energy through a process called impact ionization [3]. The lattice parameter for sphalerite ZnS is 0.541 nm [1], and the lattice parameter for Si is 0.543 nm [4]. Closely matched lattice parameters allow the epitaxial deposition of ZnS onto Si with a clean interface [5]. A clean interface allows the avoidance carrier recombination, the process in which electrons and holes exterminate each other [6].

The purpose of my research is to determine the thickness of ZnS films on Si substrates by characterizing their optical properties. Reflectance measurements were taken for light in the 250 nm to 800 nm wavelength range using a grating spectrometer. The reflectance spectra were then plotted and compared to a model generated using known optical constants in Mathematica. Highly uniform films of tens of nanometers exhibit optical interference known as thin film interference, which determines the intensity of the reflected light. Light is reflected at each surface interface. In the case of ZnS on Si, light is reflected where air meets the ZnS surface and where the ZnS meets the Si. The degree to which the interference is either constructive or destructive depends on the phase difference between the light waves which is directly dependent on the thickness of the film [6]. If the complex indices of refraction for ZnS and Si are known, a model can be constructed to define the reflectance spectrum based on film thickness.

The ZnS thin films were created by Christopher Reidy, using pulsed laser deposition (PLD). A pulsed laser beam strikes dense targets of the material to be deposited, in this case ZnS, causing it to vaporize and be deposited on the heated Si substrate [7]. This process takes place in a vacuum chamber at a pressure of $<10^{-8}$ mTorr for most of the samples. Transmission electron microscopy was used to confirm that the samples are oriented sphalerite ZnS [3]. Figure 1 is a photograph of ZnS on Si made in this manner.
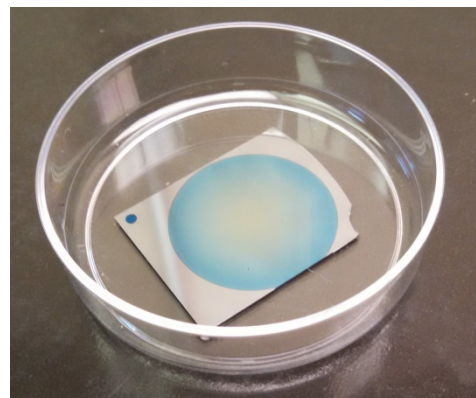

Figure 1: The silver region is the Si substrate and the blue region is the ZnS film.

1.2 Thin Film Optics and the Mathematica Model

When light is incident on a surface it is reflected, transmitted or absorbed. To determine the thickness of the ZnS thin films, the reflectance of the sample was measured using optical spectroscopy. Reflectance is the ratio of reflected power to incident power:

$$R(\lambda) = \frac{I_R(\lambda)}{I_o(\lambda)} = r^2. \tag{1}$$

Absorption can be accounted for by a complex index of refraction, n_i, where n is the real part of the index of refraction and k is the absorption coefficient.

$$n_i[\lambda] = n[\lambda] - ik[\lambda] \tag{2}$$

The samples consisted of two layers, so light was reflected, transmitted and absorbed at each interface a seemingly infinite number of times as in Figure 2.
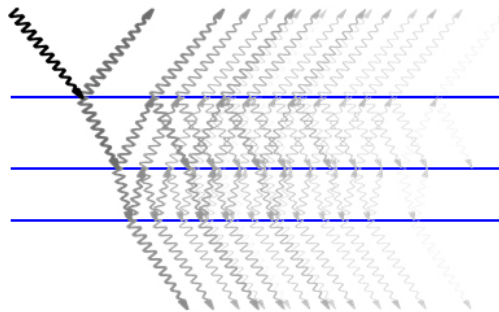

Figure 2: Arrows pointing up and to the right represent reflected light [8].

A Mathematica program created by Dr. David McIntyre, with some changes and additions done by myself, uses matrix theory for multilayer optics as described in Fundamentals of Photonics by Saleh and Teich to determine a model reflectance spectrum that can be varied according to the thickness of the ZnS film [9]. For the complex index of refraction, the program uses n and k values that have been published by SOPRA, a French thin film metrology company [10]. Because the SOPRA values are not continuous as a function of wavelength, they are first plotted in the Mathematica program and continuous values are interpolated. For plots of the SOPRA values and the interpolated values see Appendices B and C.

The matrix theory for multilayered films relies on two main matrices, the transfer matrix, M, and the scattering matrix, S. The scattering matrix is useful because it can be defined in terms of the transmittance coefficients, t_{12} and t_{21}, and reflection coefficients, r_{12} and r_{21}, where the subscript 12 refers to light traveling from left to right, and the subscript 21 refers to light traveling from right to left. The transmission coefficient is defined as the ratio of the amplitude of the transmitted wave to the incident wave and the reflection coefficient is the ratio of the reflected wave to the incident wave [11]. Reflectance and transmittance are the squares of these ratios, so reflectance can be determined directly from the scattering matrix.

Figure 3 shows a slab of dielectric material with waves Ψ_1^+ and Ψ_2^- entering the slab, and Ψ_1^- and Ψ_2^+ exiting, on either side. The scattering matrix relates the waves entering the dielectric to the waves exiting it [12].
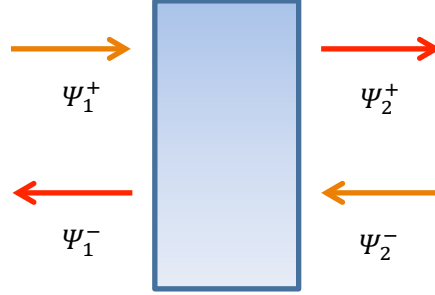
Figure 3: The arrows in orange are light entering the dielectric and the arrows in red are light exiting the dielectric.

$$\begin{bmatrix} \Psi_2^+ \\ \Psi_1^- \end{bmatrix} = \begin{bmatrix} S_1 & S_2 \\ S_3 & S_4 \end{bmatrix} \begin{bmatrix} \Psi_1^+ \\ \Psi_2^- \end{bmatrix} \tag{3}$$

$$\Psi_2^+ = S_1 \Psi_1^+ + S_2 \Psi_2^- \tag{4}$$

$$\Psi_1^- = S_3 \Psi_1^+ + S_4 \Psi_2^- \tag{5}$$

$$\therefore S_1 = t_{12}, \qquad S_2 = r_{21}, \qquad S_3 = r_{12}, \qquad S_4 = t_{21} \tag{6}$$

$$S = \begin{bmatrix} t_{12} & r_{21} \\ r_{12} & t_{21} \end{bmatrix} \tag{7}$$

The wave transfer matrix relates the waves on one side of the dielectric to the waves on the other side [12].

$$M = \begin{bmatrix} A & B \\ C & D \end{bmatrix} \tag{8}$$

$$\begin{bmatrix} \Psi_2^+ \\ \Psi_2^- \end{bmatrix} = \begin{bmatrix} A & B \\ C & D \end{bmatrix} \begin{bmatrix} \Psi_1^+ \\ \Psi_1^- \end{bmatrix} \tag{9}$$

$$\Psi_2^+ = A\Psi_1^+ + B\Psi_1^- \tag{10}$$

$$\Psi_2^- = C\Psi_1^+ + D\Psi_1^- \tag{11}$$

The matrix elements A, B, C, and D can be determined using equations (4) and (5).

$$M = \begin{bmatrix} A & B \\ C & D \end{bmatrix} = \frac{1}{t_{21}} \begin{bmatrix} t_{21}t_{12} - r_{12}r_{21} & r_{21} \\ r_{12} & 1 \end{bmatrix} \tag{12}$$

In a multilayer system such as ZnS on Si, determining the scattering matrix can be very difficult, but the transfer matrix can be determined by taking the product of individual transfer matrices for each slab and shared boundary. The transfer matrix can then be converted to the scattering matrix to find R. To determine the total transfer matrix three matrices are needed: one for the boundary between air and ZnS, one for the solid slab of ZnS, and one for the boundary of ZnS and Si. The boundary matrices can be derived by using the equations for r and t. Figure 4 shows the ZnS/Si system and the regions that require a transfer matrix.
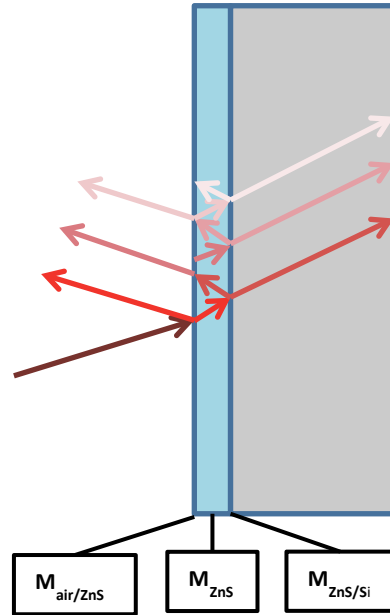
Figure 4: The product of the three matrices is the total transfer matrix.

$$M_{Air/ZnS} = \frac{1}{2n_{ZnS}}\begin{bmatrix} n_{ZnS} + n_{air} & n_{ZnS} - n_{air} \\ n_{ZnS} - n_{air} & n_{ZnS} + n_{air} \end{bmatrix} \tag{13}$$

$$\tag{14}$$

$$M_{ZnS/Si} = \frac{1}{2n_{Si}}\begin{bmatrix} n_{Si} + n_{ZnS} & n_{Si} - n_{ZnS} \\ n_{Si} - n_{ZnS} & n_{Si} + n_{ZnS} \end{bmatrix}$$

The transfer matrix for the slab of ZnS must take thickness and absorption into account, and because there is no boundary with a different index of refraction within the slab, there is no reflection.

$$M_{ZnS}[\lambda] = \begin{bmatrix} e^{-\frac{i2\pi nd}{\lambda}} & 0 \\ 0 & e^{\frac{i2\pi nd}{\lambda}} \end{bmatrix} \tag{15}$$

$$M_T = M_{ZnS/Si} \cdot M_{ZnS} \cdot M_{air/ZnS} \tag{16}$$

By taking the product of the three matrices and converting them into a scattering matrix, we get the reflection coefficient, r_{21}, and the reflectance, $R[\lambda]$.

$$R[\lambda] = |r_{21}|^2 \tag{17}$$

To determine the thickness of the thin film, the model and the experimental reflectance spectra are plotted together on a single graph as a function of wavelength to be compared. The thickness of the model ZnS film, d, can be changed in the program to find a model reflectance spectrum that most closely matches the experimental spectrum. To do this as accurately as possible, the program can calculate the coefficient of determination (R^2) and plot it as a function of film thickness. This is first done as a plot with thicknesses ranging from 0 nm to 1000 nm in 20 nm steps. The plot is then changed to focus on the range with the R^2 value closest to 1 until a single thickness with the best coefficient of determination is found. Figure 5 is a plot of R^2 for thicknesses from 0 to 1000 nm for the sample 0312ZnS204. Figure 6 is a close-up plot of R^2 values corresponding with the best value in Figure 5. It is used to determine the best thickness within 1 nm.
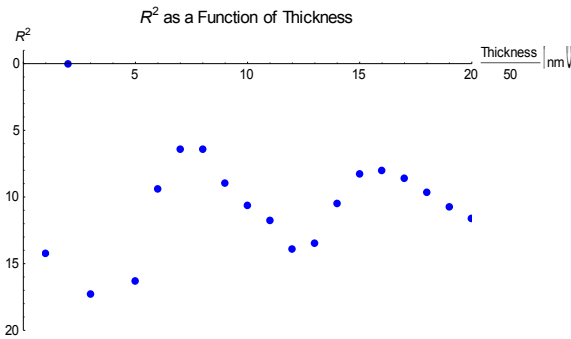
Figure 5: The second data point, which corresponds to 20 nm is the point with the best R^2 value .
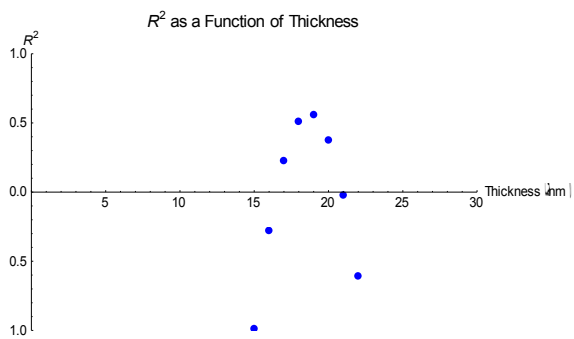
Figure 6: This plot is zoomed in on the points with the best R^2 values to determine the best thickness.

The coefficient of determination proved to be an effective method for approximating thickness; but without more statistical analysis, the exact accuracy is unknown. It can be estimated that the thicknesses are accurate within 1 or 2 nm depending on the data and film.

Another feature of the Mathematica program is that it can approximate the color of the film at different thicknesses. This is done using a system created by the International Commission on Illumination [13]. While modeling color was not a primary concern, this feature offered another helpful point of comparison. All of the colors predicted by the model were in close agreement with the observed colors of the samples.

2. Methods

2.1 The Grating Spectrometer

A grating spectrometer is an optical device that uses a diffraction grating to separate light into individual wavelengths in order to measure the reflectance and transmittance spectra of a material or object. Figure 7 is a schematic of the grating spectrometer arranged to measure reflectance.
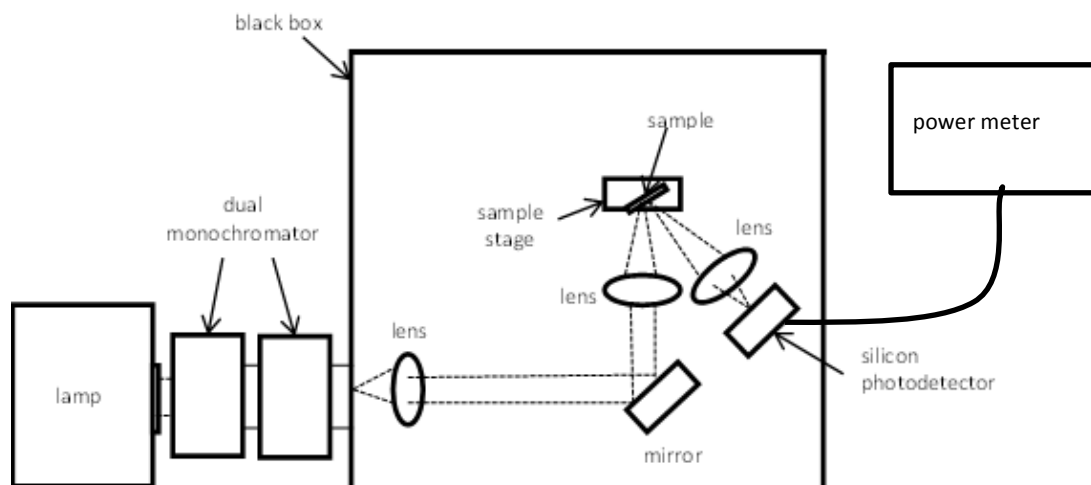
Figure 7: A schematic of the grating spectrometer arranged for reflectance measurement. Not to scale.

The lamp encloses two different light sources: a xenon arc lamp and a tungsten halogen lamp. The xenon arc lamp is a 150 watt lamp with a spectrum that ranges from 200 nm to beyond 2400 nm [14]. The tungsten halogen lamp is a 50 W lamp with a spectrum from approximately 300 nm to beyond 2400 nm [15]. A knob on top of the lamp adjusts the positions of the sources so that light from only one of the two sources may exit the lamp and enter the first of two Oriel Corporation model 77250 monochromators.

Light from the lamp enters the first monochromator via the entrance slit where it reaches a blazed diffraction grating. A blazed diffraction grating is an apparatus etched with a series of grooves that separates light into individual wavelengths. An example of a blazed diffraction grating is in figure 8. The angles of the grooves direct the majority of the light into the first diffraction order [16]. The monochromator mechanically alters the angles of the diffraction grating so that ideally only a specific wavelength of light exits the monochromator through another slit. Because ideal is not the norm, this particular grating spectrometer uses a double monochromator system. The wavelength(s) of light that leave the first monochromator enter a second monochromator where the process is repeated to further narrow the span of wavelengths of light that exits the second monochromator. The

Figure 8: A blazed diffraction grating [18].

light then exits the second monochromator and enters the black box.

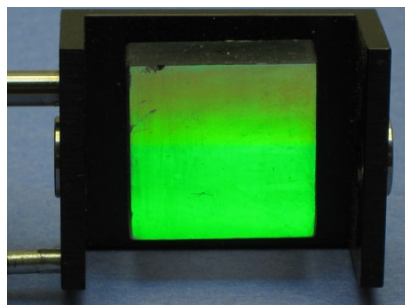The black box contains the bulk of the spectrometer's parts and keeps external light sources from interfering with the measurements. Once inside the box, the light interacts with a series of fused silica lenses and mirrors before reaching the sample [17]. The sample is placed in the sample stage and angled to reflect or transmit light onto a silicon photodetector. The detector is connected to a model 835 Newport optical power meter which measures the intensity of the reflected light. The power meter is interfaced with a computer running LabView, a program which records the intensity of the light at the given wavelength, which is typically of the order of nanowatts or microwatts.

The positions of the gratings are then changed to allow the next wavelength of light to reach the exit slit. This process is repeated until the reflection intensity of the desired range of 250 to 800nm wavelengths has been measured. Once the measurements are complete, the data from Lab View is imported into a Microsoft Excel spreadsheet.

2.2 Procedure

Measurements were taken in 1 nm wavelength increments. Different diffraction gratings are best suited for different wavelength ranges, depending on the spacing of the etched grooves. The experiments spanned from 250 to 800 nm and used gratings with a blaze wavelength of 0.5 μm, which are best suited for taking measurements over the 300 to 1000 nm wavelength range [17]. The blaze wavelength is the wavelength of maximum diffraction efficiency.

All measurements were made using the xenon arc lamp. To ensure that the intensity of emitted light did not change with time, the source was always given a minimum of 30 minutes to warm up before any measurements were taken. Each component of the spectrometer interacts with the light and has its own spectrum -- meaning that in addition to detecting reflected light from the sample, the detector is detecting reflected light from every object in the spectrometer. To isolate the reflectance of the sample from the reflectance of its surroundings, two preliminary measurements had to be taken, a raw spectrum and a dark spectrum.

After the warm-up period, the detector was positioned to measure transmission, and the selected gratings were placed in the dual monochromator. First the transmittance of the raw lamp was measured and recorded. No objects were placed between the detector and the final lens, and transmittance measurements were taken over the desired range of wavelengths. This was the raw spectrum that set the baseline for the intensity of the lamp and detected light from surrounding objects. Then the dark spectrum was measured. A piece of black foam core was placed in the sample stage to block all source light. The detected light from the objects within the spectrometer was measured without the source light directly interacting with the detector.

Finally, the detector was moved to the reflection position and the sample was secured in the sample stage angled so that the light reflecting from its surface reached the detector. The reflectance of the sample and its surroundings was measured over the desired wavelength range. LabView software then extracted the sample's reflectance data which was imported into an

Excel spreadsheet. The spreadsheet would be converted to a comma separated value file to be imported into the Mathematica program.

3. Results.

To ensure an accurate measurement, the resolution of the spectrometer was measured using a HeNe laser. This laser was chosen because its spectrum has a narrow line at 632.8 nm with an intrinsic bandwidth of 0.01 nm [19], which is much smaller than the grating resolution. After measuring the power of the laser via the spectrometer, a plot was created. The peak and its two neighboring points were used to calculate the width of a triangle from the peak to the zero point, and the width at half of the maximum of the triangle was calculated. The resolution of the spectrometer was found to be 1.2 nm. Because the resolution was much smaller than the typical interference fringe this resolution was acceptable for measurement. Figure 9 is the plot of the HeNe laser spectrum used to determine the resolution of the spectrometer. The plot also shows that the spectrometer was miscalibrated, as the peak of the HeNe laser occurred at 637 nm rather than 633 nm. All results have been shifted to the left by 4 nm to compensate for the miscalibration. Figure 10 is a plot of the original data and the shifted data for sample ZnS111Series_HP. While the shift is not extreme, it made a difference of several nanometers for many of the thickness approximations.
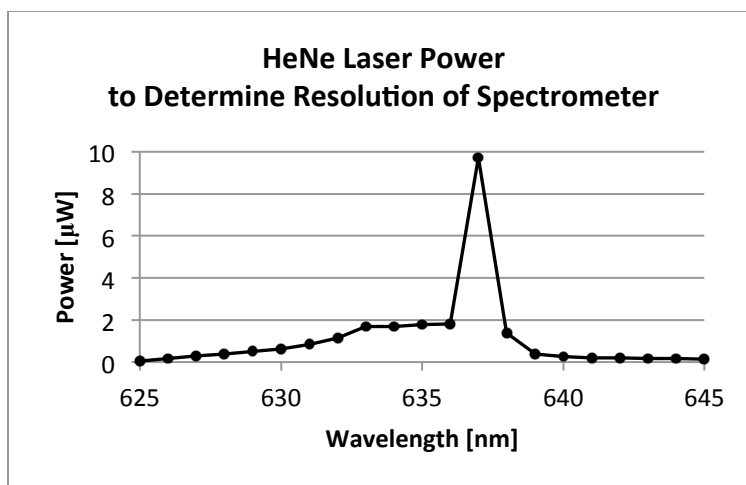
Figure 9: The narrow peak of the HeNe laser spectrum was used to determine the resolution of the spectrometer.
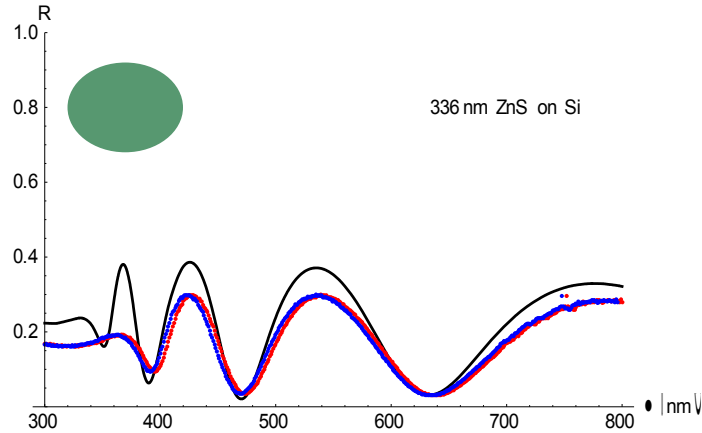
Figure 10: The original data is in red, the adjusted data is in blue and the model in is black.

Another factor in determining the accuracy of the reflectance measurements is ensuring that the reflectance spectrum has been properly extracted from the lamp spectrum and dark spectrum. Figures 10 and 11 are plots of the raw lamp spectrum and the raw dark spectrum respectively. By comparing these spectra with the ZnS reflectance spectra, it is clear that the lamp and dark spectra did not influence the ZnS reflectance measurements.
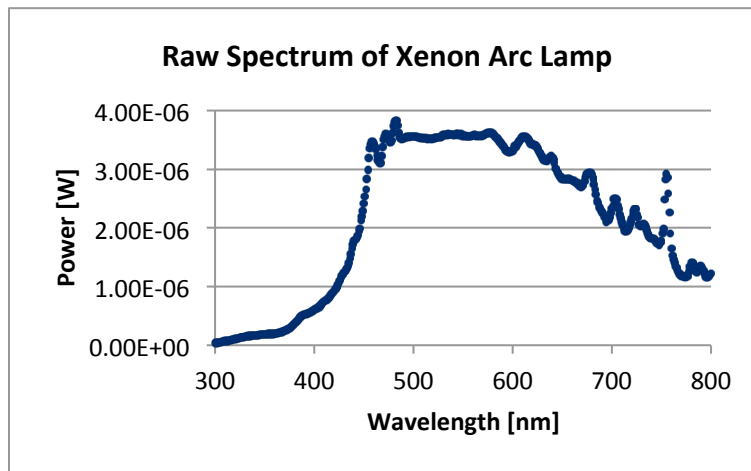
Figure 11: The raw lamp spectrum does not resemble the ZnS reflectance spectra.
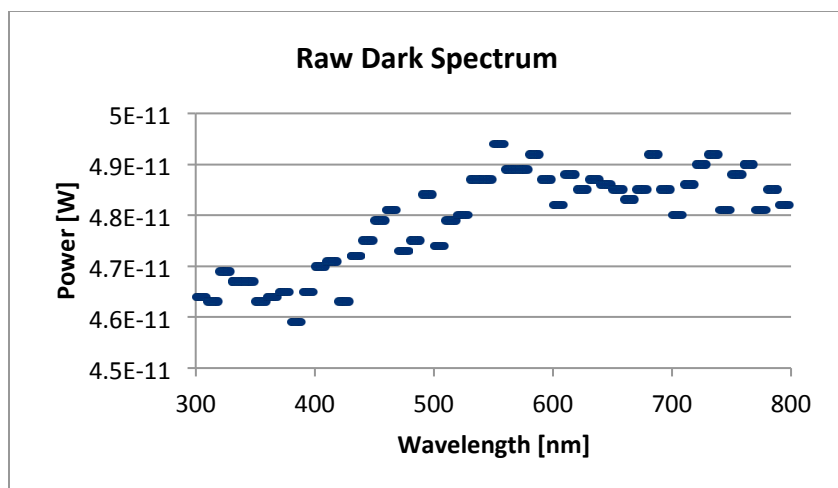
Figure 12: The raw dark spectrum does not resemble the ZnS reflectance spectra.

To determine how well the Mathematica program modeled the silicon substrate, the reflectance of a substrate was measured then compared to the model with 0nm of ZnS. Figure 12 shows a strong correlation between the data and the model.
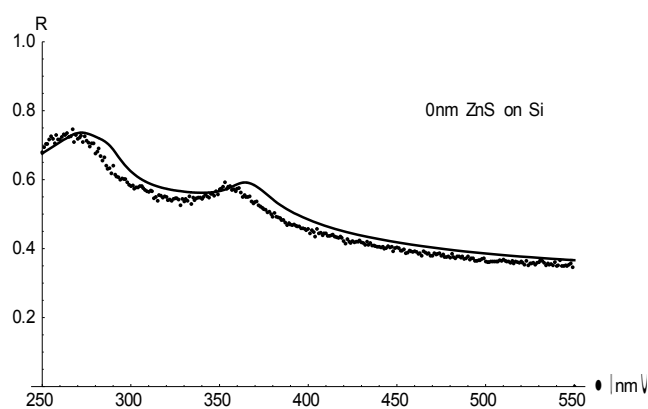
Figure 13: The experimental data are dots and the model is the smooth line.

As previously stated, the experimentally determined reflectance spectrum of the sample was plotted against a model reflectance spectrum. Thickness was determined by finding the model reflectance spectrum that best fit the data, which was based on R^2 calculations. Figure 13 is the comparison plot for the sample 0301ZnS203. The approximate thickness of the ZnS film is on the upper right side. The film color approximation is the disk in the upper left corner. Thickness approximation plots for all samples are located in Appendix D.
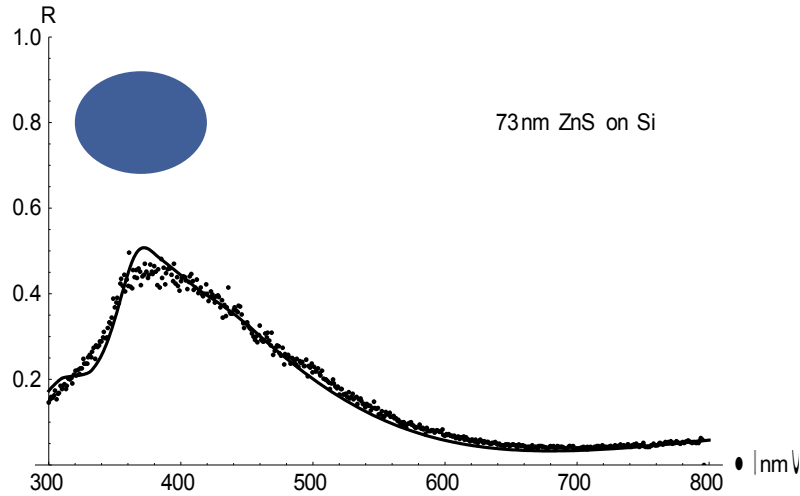
Figure 14: The experimental data is in dots and the model is a line.

Samples were made over a two year period and are listed in the order they were created and measured in Table 1.

**Reflectance Measurement From 300 to 800 nm wavelengths
with 0.5 μm Diffraction Grating**

Samples and Thickness Approximations		
Sample	**Thickness [nm]**	**Coefficient of Determination**
ZnS101b_green	225	0.54
ZnS101b_Ar10	394	0.08
ZnS111series_LP	257	0.49
ZnS111series_UHV	241	0.18
ZnS111series_HP	336	0.52
ZnS132_blue	73	0.98
0301ZnS203	91	0.97
0312ZnS204	18	0.56
0402ZnS205	17	-0.86

Table 1: Results for all samples measured using the 0.5 μm diffraction grating.

4. Discussion

None of the measurements has a perfect R^2 value; although some are very close to 1 others are very small or even negative. There are a few reasons for this. First, this model assumes that the film is composed entirely of ZnS, however getting the exact stoichiometry was not always

possible. In some cases oxygen may have been present in the vacuum chamber of the PLD system, meaning that some portion of the film may be ZnO, this is particularly true for the earliest samples. In addition, there was not always a 50:50 ratio of Zn to S which resulted in films that were not pure ZnS. Chemical differences in the surface resulted in variation from the ideal model as each chemical has unique indices of refraction.

Sample 0402ZnS205 has a negative R^2 value, which is possible when doing a non-linear fit.

$$R^2 = 1 - \frac{SS_{res}}{SS_{tot}} \tag{18}$$

Where SS_{res} is the variance of the residuals, and SS_{tot} is the variance of the data [20], [21]. When the variation that is not described by the model is much greater than the variation of the data from the mean, the R^2 value can be negative. Figure 14 is the thickness approximation for 0402ZnS205. The reflectance has little variation from wavelengths of 400nm to 800nm, so there is a small variation from the mean. However, the model and the experimental data only overlap at a few wavelengths, meaning the variation not described by the model is large. For this reason, a negative R^2 value can be expected. In cases where the R^2 value was either negative or very small, it was still best to select the thickness corresponding to the R^2 value closest to 1, as this thickness still had the least variation from the model.
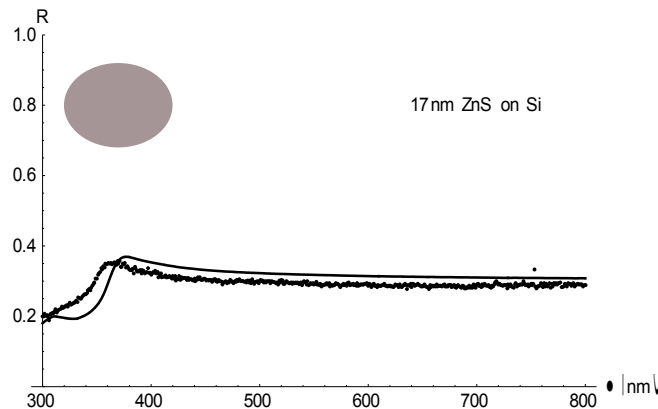
Figure 15: The experimental data is in dots and the model is a line.

There are some measurement methods that can give an exact thickness of a film including profilometry and ellipsometry. Profilometry is a process where the thickness of a sample is measured by a flexible cantilever as it is drawn across the surface. Ellipsometry is also a spectroscopic method similar to reflection spectroscopy, but information about the polarization of the light source is known. Both methods are advantageous in the sense that they can give more exact measurements, but they have some disadvantages when compared to spectroscopy. First, profilometry can damage the surface of a thin film, which can affect the results of other measurements preformed on the sample. Ellipsometry can pinpoint the thickness of a film, but getting an accurate measurement involves knowledge of many variables; and without this knowledge, any answer can be wrongly obtained. Reflection spectroscopy does not damage the surface of a film and does not require expert manipulation of variables. For an application where

an approximate film thickness is sufficient, optical spectroscopy is a simple and efficient way to obtain a film thickness.

5. Conclusion

Thin film interference makes reflectance spectroscopy a useful means of determining the thickness of thin films. The grating spectrometer took measurements without damaging the films and without the guesswork involved in ellipsometry. Using a model that was created to determine the reflectance spectrum of the film/substrate system, the thickness of the ZnS film was determined within one or two nanometers, depending on the quality of the data. In the future, to obtain more accurate readings I would check the calibration of the spectrometer regularly, and make sure that it is calibrated properly. This would be much easier and more accurate than shifting all of the data after measurement. The results from stoichiometry testing could also be useful, as the Mathematica program could potentially be adapted to accommodate less than perfect films. I would also include more rigorous statistical analysis. The coefficient of determination is useful in this instance, but is not ideal for non-linear fitting.

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Appendix A: Mathematica Program

Zn Film on Si Substrate with Color

David McIntyre
22 June 2012
adapted from may 2011 file on SiO2 on SiN
Edited by Kathleen Prudell
May 2014

Initialization

In[14]:=
```
SetOptions[Plot, BaseStyle -> {FontFamily → "Arial", FontSize → 14},
          PlotStyle → {{Black, AbsoluteThickness[1.5]}},
          AxesStyle -> {{Black, AbsoluteThickness[0.5]},
          {Black, AbsoluteThickness[0.5]}}, TicksStyle ->
{{Black, AbsoluteThickness[0.5]}, {Black, AbsoluteThickness[0.5]}}];
```

In[15]:=
```
SetOptions[ListPlot, BaseStyle -> {FontFamily → "Arial", FontSize → 14},
          PlotStyle → {{Black, AbsoluteThickness[1.5]}},
          AxesStyle -> {{Black, AbsoluteThickness[0.5]},
          {Black, AbsoluteThickness[0.5]}}, TicksStyle ->
{{Black, AbsoluteThickness[0.5]}, {Black, AbsoluteThickness[0.5]}}];
```

Notes

Matrix analysis of thin film reflection and transmission. See Saleh and Teich Chap 7 of 2nd edition.

Define matrices

Propagation through slab eqn. 7.1-4 Saleh

In[16]:=
```
Mspace[n_, d_, λ_] :=
{{Exp[-I * n * d * 2 * π / λ], 0}, {0, Exp[I * n * d * 2 * π / λ]}}
```

Dielectric Interface eqn 7.1-19 Saleh na->nb

In[17]:=
```
Md[na_, nb_] := {{nb + na, nb - na}, {nb - na, nb + na}} / (2 * nb)
```

ZnS data

SOPRA DATA USE THIS

In[18]:=   `SetDirectory[]`

Out[18]= `C:\Users\Kat`

In[19]:=   `ZnSSopraN =`
`Import["C:\\Users\\Kat\\Desktop\\Thesis\\SOPRA\\ZNSCUB_n.csv"];`

In[20]:=   `ZnSSopraK =`
`Import["C:\\Users\\Kat\\Desktop\\Thesis\\SOPRA\\ZNSCUB_k.csv"];`

In[21]:=   `nexp = ListPlot[ZnSSopraN, PlotRange → {2, 3.3},`
`AxesLabel → {"λ (nm)", "n"}, ImageSize → 500]`

In[22]:=   `ZnSN = Interpolation[ZnSSopraN]`

Out[22]= `InterpolatingFunction[{{206.642, 1239.85}}, <>]`

In[25]:=   `ZnSN[560]`

Out[25]= `2.38343`

In[24]:=

$$\text{Plot}[\text{ZnSN}[x], \{x, 210, 850\}, \text{PlotRange} \to \{2, 3.3\},$$
$$\text{AxesLabel} \to \{"\lambda \ (nm)", "n"\}, \text{AxesOrigin} \to \{200, 2\}, \text{ImageSize} \to 500]$$

Out[24]=
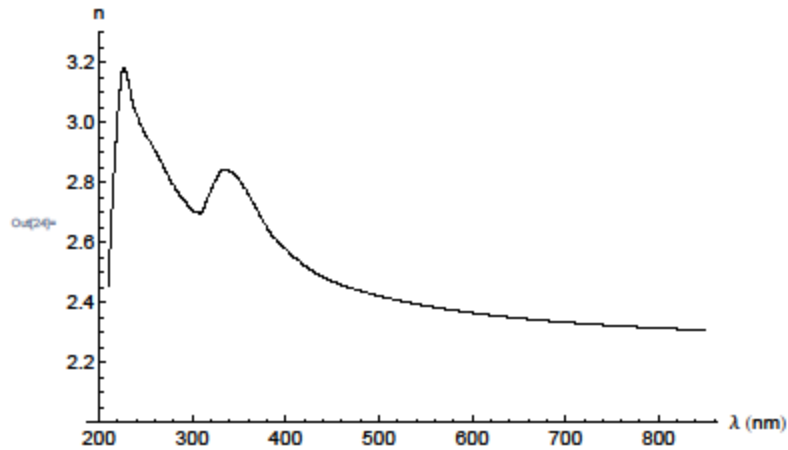
In[25]:=

$$\text{ListPlot}[\text{ZnSSopraK}, \text{PlotRange} \to \{0, 2\},$$
$$\text{AxesLabel} \to \{"\lambda \ (nm)", "k"\}, \text{ImageSize} \to 500]$$

Out[25]=
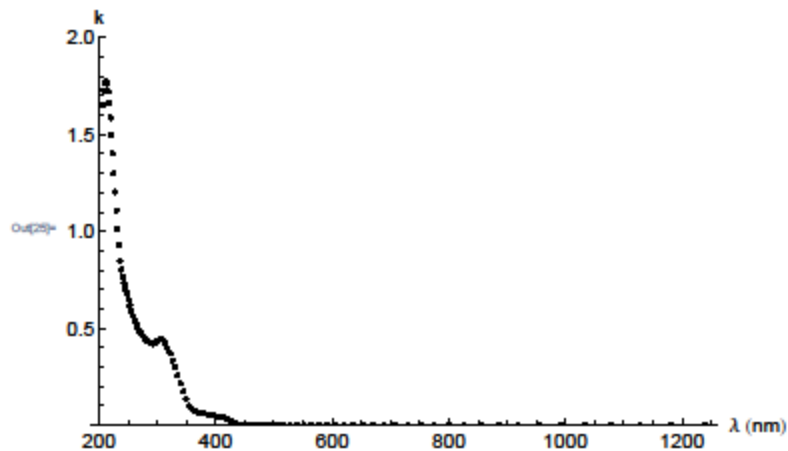
In[26]:=   ZnSK = Interpolation[ZnSSopraK]

Out[26]= InterpolatingFunction[{{206.642, 1239.85}}, <>]

A-3

In[27]:=
```
                    Plot[ZnSK[x], {x, 210, 850}, PlotRange → {0, 2},
            AxesLabel → {"λ (nm)", "k"}, AxesOrigin → {200, 0}, ImageSize → 500]
```

Out[27]=
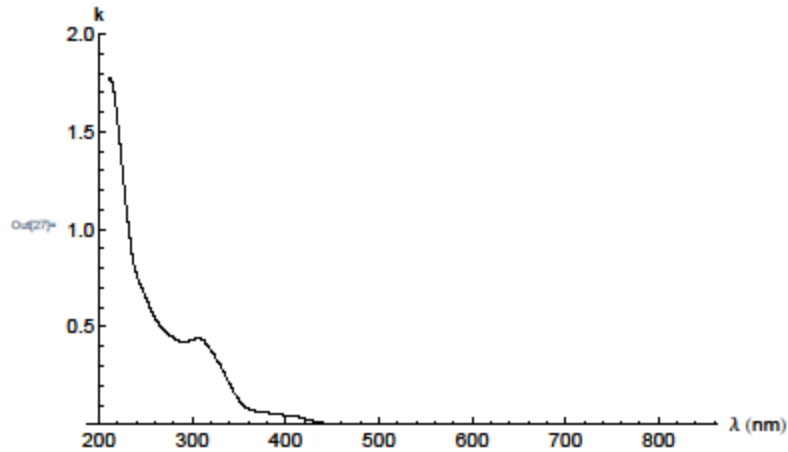
Si data

Si Data for 100 surface. Goes from 230 to 840 nm
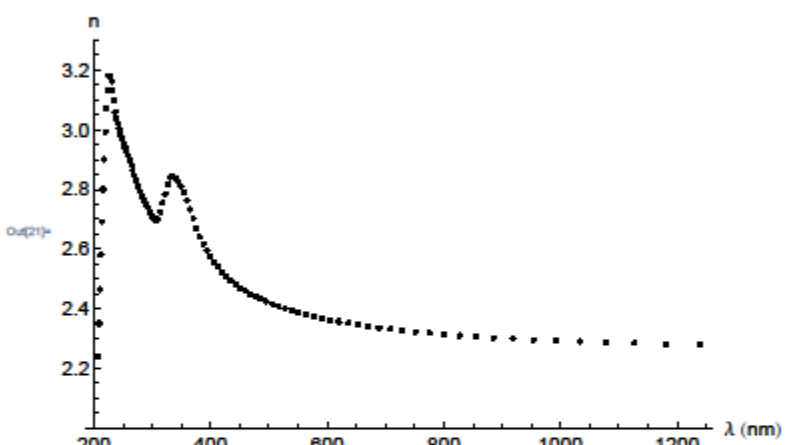
In[28]:=   **SetDirectory[]**

Out[28]= C:\Users\Kat

In[29]:= **SiSopraN = Import["C:\\Users\\Kat\\Desktop\\Thesis\\SOPRA\\SI111_n.csv"];**

In[30]:= **SiSopraK = Import["C:\\Users\\Kat\\Desktop\\Thesis\\SOPRA\\SI111_k.csv"];**

In[31]:=   `ListPlot[SiSopraN, PlotRange → {1, 7.3},`
`AxesLabel → {"λ (nm)", "n"}, AxesOrigin → {200, 1}, ImageSize → 500]`

Out[31]=
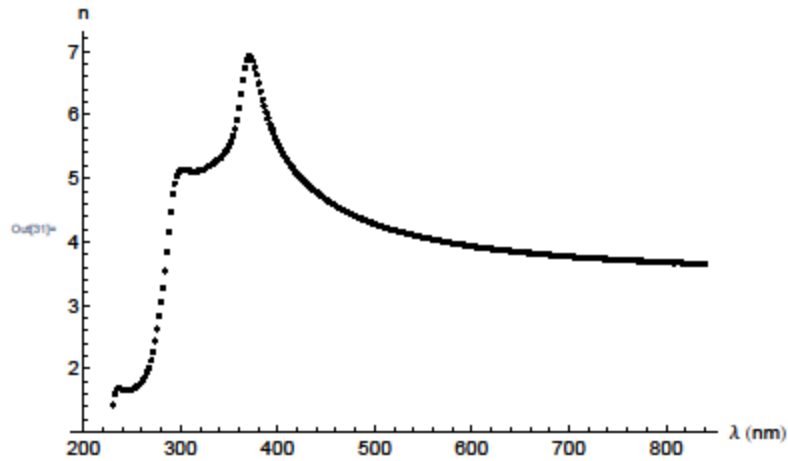
In[32]:=   `ListPlot[SiSopraK, PlotRange → {0, 6},`
`AxesLabel → {"λ (nm)", "k"}, AxesOrigin → {200, 0}, ImageSize → 500]`

Out[32]=
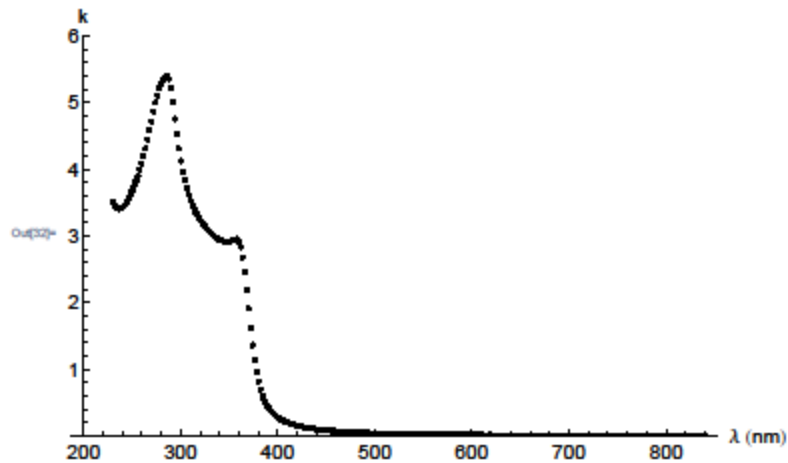
In[33]:=   `Sinnn = Interpolation[SiSopraN]`

Out[33]=   `InterpolatingFunction[{{230., 840.}}, <>]`

In[34]:=
```
Plot[Sinnn[x], {x, 230, 840}, PlotRange → {1, 7.3},
  AxesLabel → {"λ (nm)", "n"}, AxesOrigin → {200, 1}, ImageSize → 500]
```

Out[34]=
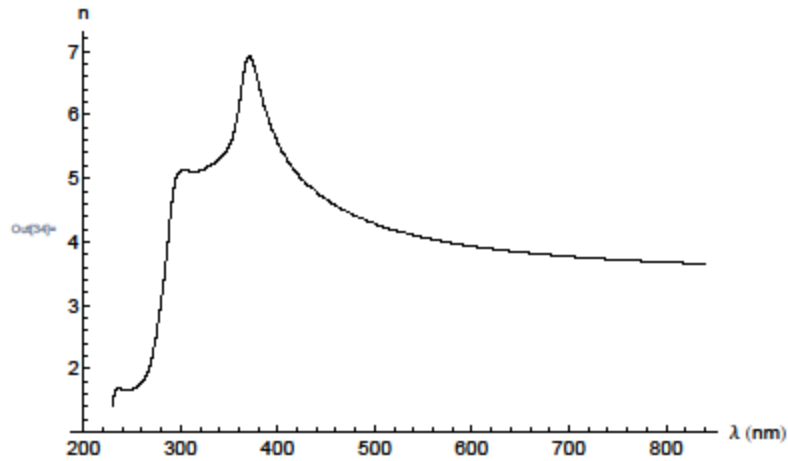
In[35]:=
```
Sikkk = Interpolation[SiSopraK]
```

Out[35]= InterpolatingFunction[{{230., 840.}}, <>]

In[36]:=
```
Plot[Sikkk[x], {x, 230, 840}, PlotRange → {0, 6},
  AxesLabel → {"λ (nm)", "k"}, AxesOrigin → {200, 0}, ImageSize → 500]
```

Out[36]=
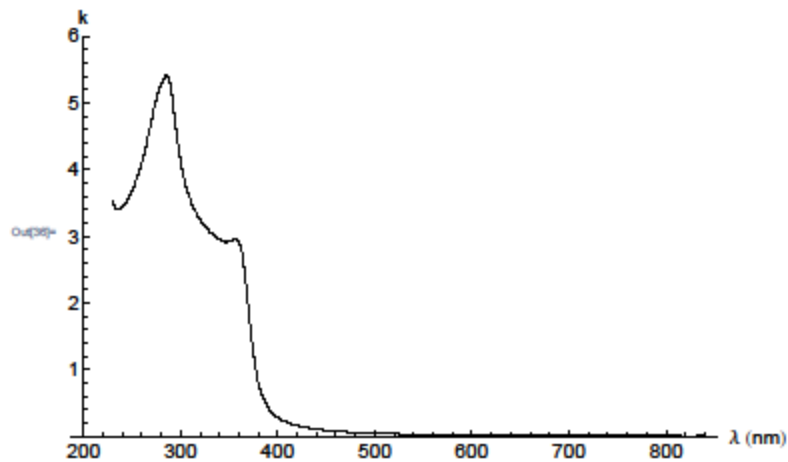
ZnS film on Si substrate

Air (na) -> ZnS -> Si Substrate (Sinnn)
No absorption yet

In[37]:=   **Clear[R]**

In[38]:=   **ZnSN[380]**

Out[38]= 2.64744

In[39]:=   **Sinnn[400]**

Out[39]= 5.56147

In[40]:=   **na = 1.0;**
                                                            nfilm[λ_] := ZnSN[λ]
                                                            nsub[λ_] := Sinnn[λ]
                                                                            d = 100;

In[44]:=   **MT[λ_] := Md[nfilm[λ], nsub[λ]].Mspace[nfilm[λ], d, λ].Md[na, nfilm[λ]]**

In[45]:=   **MT[400][[1, 1]]**

Out[45]= - 0.365018 + 0.334402 i

In[46]:= $$ST[\lambda\_] := \frac{1}{MT[\lambda][[2, 2]]}$$
                       {{MT[λ][[1, 1]] MT[λ][[2, 2]] - MT[λ][[1, 2]] MT[λ][[2, 1]], MT[λ][[1, 2]]},
                                                             {-MT[λ][[2, 1]], 1}}

In[47]:=   **ST[400]**

Out[47]= {{- 0.267822 + 0.245359 i, 0.337907 - 0.389994 i},
         {- 0.418028 + 0.302538 i, - 1.48949 + 1.36456 i}}

In[48]:=   **ST[500][[2, 1]]**

Out[48]= - 0.61842 - 0.0362551 i

In[49]:=   **R[λ_] := Chop[ST[λ][[2, 1]] * Conjugate[ST[λ][[2, 1]]]]**

In[50]:=   **R[500]**

Out[50]= 0.383757

In[51]:=

                                     Plot[R[λ], {λ, 230, 840}, PlotRange → {0, 1},
                                       PlotStyle → {Black, AbsoluteThickness[2]},
                          AxesLabel → {"λ (nm)", "R"}, AxesOrigin → {200, 0}, ImageSize → 500,
                               Epilog → Text[ToString[d] <> "nm ZnS on Si", {700, 0.8}]];

In[52]:=   **R[250]**

Out[52]= 0.419165

In[53]:=   **Plot[ZnSN[λ] * d / λ, {λ, 230, 840},**
                          Epilog → Table[Line[{{230, 0.25 + i / 2}, {840, 0.25 + i / 2}}], {i, 4}]];

In[54]:=
$$\text{NSolve}[\text{ZnSN}[x] = 2.6, x]$$

NSolve::ifun : Inverse functions are being used by NSolve, so
some solutions may not be found; use Reduce for complete solution information. ≫

Out[54]= {{x → InverseFunction[InterpolatingFunction[{{206.642, 1239.85}}, <>], 1, 1][2.6]}}

In[55]:=
ZnSSopraN;

COLOR

In[56]:=
```
                                              (*
                          The 1931 CIE colour matching
                  functions and standard illuminant data in the
        format: {wavelength(nm),x-bar,y-bar,z-bar, D65 standard illuminant}*)
                    ciedata = {{380, 0.00137, 0.00004, 0.00645, 49.97550},
                               {385, 0.00224, 0.00006, 0.01055, 52.31180},
                               {390, 0.00424, 0.00012, 0.02005, 54.64820},
                               {395, 0.00765, 0.00022, 0.03621, 68.70150},
                               {400, 0.01431, 0.00040, 0.06785, 82.75490},
                               {405, 0.02319, 0.00064, 0.11020, 87.12040},
                               {410, 0.04351, 0.00121, 0.20740, 91.48600},
                               {415, 0.07763, 0.00218, 0.37130, 92.45890},
                               {420, 0.13438, 0.00400, 0.64560, 93.43180},
                               {425, 0.21477, 0.00730, 1.03905, 90.05700},
                               {430, 0.28390, 0.01160, 1.38560, 86.68230},
                               {435, 0.32850, 0.01684, 1.62296, 95.77360},
                               {440, 0.34828, 0.02300, 1.74706, 104.86500},
                               {445, 0.34806, 0.02980, 1.78260, 110.93600},
                               {450, 0.33620, 0.03800, 1.77211, 117.00800},
                               {455, 0.31870, 0.04800, 1.74410, 117.41000},
                               {460, 0.29080, 0.06000, 1.66920, 117.81200},
                               {465, 0.25110, 0.07390, 1.52810, 116.33600},
                               {470, 0.19536, 0.09098, 1.28764, 114.86100},
                               {475, 0.14210, 0.11260, 1.04190, 115.39200},
                               {480, 0.09564, 0.13902, 0.81295, 115.92300},
                               {485, 0.05795, 0.16930, 0.61620, 112.36700},
                               {490, 0.03201, 0.20802, 0.46518, 108.81100},
                               {495, 0.01470, 0.25860, 0.35330, 109.08200},
                               {500, 0.00490, 0.32300, 0.27200, 109.35400},
                               {505, 0.00240, 0.40730, 0.21230, 108.57800},
                               {510, 0.00930, 0.50300, 0.15820, 107.80200},
                               {515, 0.02910, 0.60820, 0.11170, 106.29600},
                               {520, 0.06327, 0.71000, 0.07825, 104.79000},
                               {525, 0.10960, 0.79320, 0.05725, 106.23900},
```

```
{530, 0.16550, 0.86200, 0.04216, 107.68900},
{535, 0.22575, 0.91485, 0.02984, 106.04700},
{540, 0.29040, 0.95400, 0.02030, 104.40500},
{545, 0.35970, 0.98030, 0.01340, 104.22500},
{550, 0.43345, 0.99495, 0.00875, 104.04600},
{555, 0.51205, 1.00000, 0.00575, 102.02300},
{560, 0.59450, 0.99500, 0.00390, 100.00000},
{565, 0.67840, 0.97860, 0.00275, 98.16710},
{570, 0.76210, 0.95200, 0.00210, 96.33420},
{575, 0.84250, 0.91540, 0.00180, 96.06110},
{580, 0.91630, 0.87000, 0.00165, 95.78800},
{585, 0.97860, 0.81630, 0.00140, 92.23680},
{590, 1.02630, 0.75700, 0.00110, 88.68560},
{595, 1.05670, 0.69490, 0.00100, 89.34590},
{600, 1.06220, 0.63100, 0.00080, 90.00620},
{605, 1.04560, 0.56680, 0.00060, 89.80260},
{610, 1.00260, 0.50300, 0.00034, 89.59910},
{615, 0.93840, 0.44120, 0.00024, 88.64890},
{620, 0.85445, 0.38100, 0.00019, 87.69870},
{625, 0.75140, 0.32100, 0.00010, 85.49360},
{630, 0.64240, 0.26500, 0.00005, 83.28860},
{635, 0.54190, 0.21700, 0.00003, 83.49390},
{640, 0.44790, 0.17500, 0.00002, 83.69920},
{645, 0.36080, 0.13820, 0.00001, 81.86300},
{650, 0.28350, 0.10700, 0.00000, 80.02680},
{655, 0.21870, 0.08160, 0.00000, 80.12070},
{660, 0.16490, 0.06100, 0.00000, 80.21460},
{665, 0.12120, 0.04458, 0.00000, 81.24620},
{670, 0.08740, 0.03200, 0.00000, 82.27780},
{675, 0.06360, 0.02320, 0.00000, 80.28100},
{680, 0.04677, 0.01700, 0.00000, 78.28420},
{685, 0.03290, 0.01192, 0.00000, 74.00270},
{690, 0.02270, 0.00821, 0.00000, 69.72130},
{695, 0.01584, 0.00572, 0.00000, 70.66520},
{700, 0.01136, 0.00410, 0.00000, 71.60910},
{705, 0.00811, 0.00293, 0.00000, 72.97900},
{710, 0.00579, 0.00209, 0.00000, 74.34900},
{715, 0.00411, 0.00148, 0.00000, 67.97650},
{720, 0.00290, 0.00105, 0.00000, 61.60400},
{725, 0.00205, 0.00074, 0.00000, 65.74480},
{730, 0.00144, 0.00052, 0.00000, 69.88560},
{735, 0.00100, 0.00036, 0.00000, 72.48630},
{740, 0.00069, 0.00025, 0.00000, 75.08700},
{745, 0.00048, 0.00017, 0.00000, 69.33980},
```

```
                          {750, 0.00033, 0.00012, 0.00000, 63.59270},
                          {755, 0.00023, 0.00008, 0.00000, 55.00540},
                          {760, 0.00017, 0.00006, 0.00000, 46.41820},
                          {765, 0.00012, 0.00004, 0.00000, 56.61180},
                          {770, 0.00008, 0.00003, 0.00000, 66.80540},
                          {775, 0.00006, 0.00002, 0.00000, 65.09410},
                          {780, 0.00004, 0.00001, 0.00000, 63.38280}};
            (* Use thin film reflection function describing
                                  interference phenomena *)
                                                        R[380]
                      (* nonlinear rotation matrix to
                  convert CIE XYZ cooords to RGB(linear) *)
                              M = {{3.2406, -1.5372, -0.4986},
                  {-0.9689, 1.8758, .0415}, {.0557, -.204, 1.057}};
                  cal = {Total[ciedata[[All, 2]] * ciedata[[All, 5]]],
                          Total[ciedata[[All, 3]] * ciedata[[All, 5]]],
                          Total[ciedata[[All, 4]] * ciedata[[All, 5]]]};
            (* Gamma correction set at γ = 2.2 (standard computer monitor) *)
                                                        gc[x_] :=
              Clip[If[x ≤ 0.0031308, 12.92 * x, -.055 + 1.055 * (x^(1/2.4))], {0, 1}];
                      (* definition for the value of a colour channel =
                  ∫ I(λ)×channel_bar(λ)×Illuminant(λ) dλ *)
                          chan[n_] := Total[Map[R, ciedata[[All, 1]]] *
                  ciedata[[All, n]] * ciedata[[All, 5]]] / cal[[n-1]];
                              XYZ = {chan[2], chan[3], chan[4]}
                          Graphics[{RGBColor[Map[gc, M.XYZ]], Disk[]}]
```
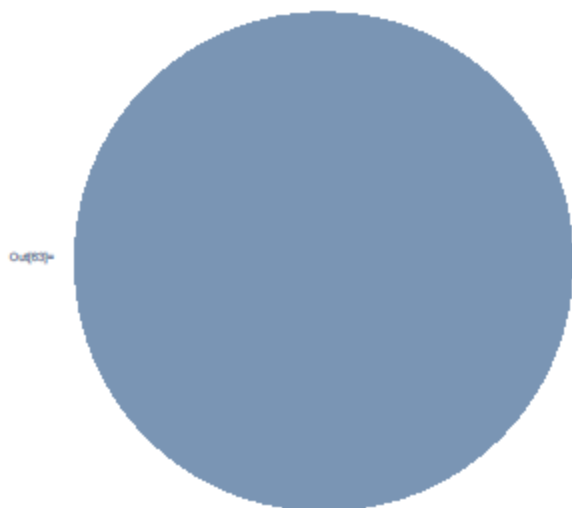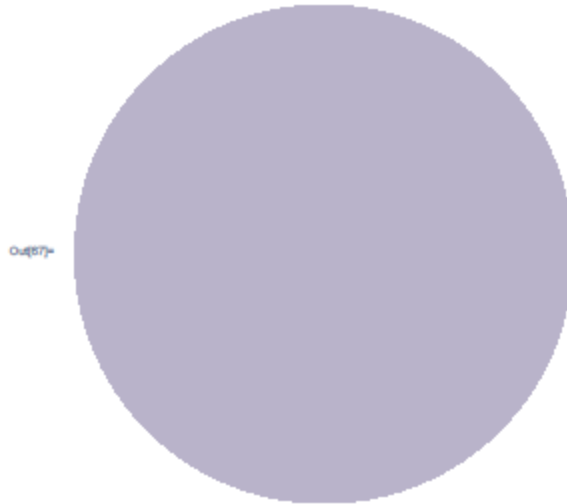
Out[57]= 0.112651

Out[62]= {0.290018, 0.315536, 0.386963}

Out[63]=

```
In[84]:=                                                         f[x_] := 0.5;
                                                        chan[n_] :=
           Total[Map[f, ciedata[[All, 1]]] * ciedata[[All, n]] * ciedata[[All, 5]]] /
                                                        cal[[n - 1]];
                                     XYZ = {chan[2], chan[3], chan[4]}
                          Graphics[{RGBColor[Map[gc, M.XYZ]], Disk[]}]

Out[86]= {0.5, 0.5, 0.5}
```

Out[87]=

ZnS film on Si substrate with absorption added

Air (na) -> ZnS -> Si Substrate (Sinnn)
Add absorption effect by making index complex
d is thickness of the filmand

```
In[88]:=                                                                    na = 1.0;
                                                    nfilm[λ_] := ZnSN[λ] - I * ZnSK[λ]
                                                    nsub[λ_] := Sinnn[λ] - I * Sikkk[λ]
                                               (*d should be changed to find plot of
                              best fit based on R^2 value*)                  d = 94;
         MT[λ_] := Md[nfilm[λ], nsub[λ]].Mspace[nfilm[λ], d, λ].Md[na, nfilm[λ]];
                                                                      1
                                                   ST[λ_] := ─────────────
                                                               MT[λ][[2, 2]]
        {{MT[λ][[1, 1]] MT[λ][[2, 2]] - MT[λ][[1, 2]] MT[λ][[2, 1]], MT[λ][[1, 2]]},
                                                             {-MT[λ][[2, 1]], 1}}
                          R[λ_] := Chop[ST[λ][[2, 1]] * Conjugate[ST[λ][[2, 1]]]];
                                                                      chan[n_] :=
        Total[Map[R, ciedata[[All, 1]]] * ciedata[[All, n]] * ciedata[[All, 5]] /
                                                                    cal[[n - 1]];
                                            XYZ = {chan[2], chan[3], chan[4]};
                                            Plot1 = Plot[R[λ], {λ, 300, 800},
        PlotRange → {0, 1}, PlotStyle → {Black, AbsoluteThickness[2]},
    AxesLabel → {"λ (nm)", "R"}, AxesOrigin → {300, 0}, ImageSize → 500,
            Epilog → {Text[ToString[d] <> "nm ZnS on Si", {700, 0.9}],
            RGBColor[Map[gc, M.XYZ]], Disk[{370, 0.9}, {50, 0.12}]}];


                                                          ZnSdata = Import[
    "C:\\Users\\Kat\\Desktop\\Thesis\\reflection csv\\0301ZnS203.csv"];
                                               Plot2 = ListPlot[ZnSdata];


                                               Show[Plot1, Plot2]
```

94nm ZnS on Si
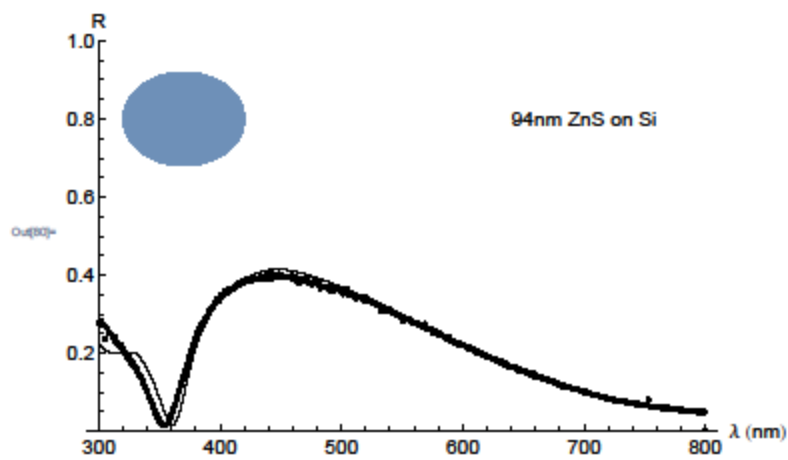
R^2 Value for a Specific Thickness

Thickness is the same value as d in previous section.

```
In[81]:=                                                      ZnSdata[[2, 1]];
In[82]:=                                                    R[ZnSdata[[2, 1]]];
In[83]:=              ModelR = Table[R[ZnSdata[[i, 1]]], {i, 1, Length[ZnSdata]}];
                                      DataAvg = Mean[ZnSdata[[All, 2]]];
                           SSres = Total[(ZnSdata[[All, 2]] - ModelR)^2];
                           SStot = Total[(ZnSdata[[All, 2]] - DataAvg)^2];
                                      rSquared = 1 - (SSres / SStot)
```

Out[87]= 0.973289

R^2 Value Plotted for Many Thicknesses

Note that x-axis is not thickness, but the step number. The x-axis label should be changed according to thickness range and steps taken in "AxesLabel."

```
Marker = Graphics[{Blue, Disk[]}];
ListPlot[
Table[ModelR = Table[R[ZnSdata[[i, 1]]], {i, 1, Length[ZnSdata]}];
DataAvg = Mean[ZnSdata[[All, 2]]];
SSres = Total[(ZnSdata[[All, 2]] - ModelR)^2];
SStot = Total[(ZnSdata[[All, 2]] - DataAvg)^2];
rSquared = 1 - (SSres / SStot), {d, 1, 1000, 50}],
PlotRange → {{0, 20}, {-3, 1}}, AxesLabel → {(Thickness / 50) [nm], R^2},
PlotStyle → Blue, PlotMarkers → {Marker, 0.03},
PlotLabel → "R² as a Function of Thickness", ImageSize → 600]
```


R^2 as a Function of Thickness
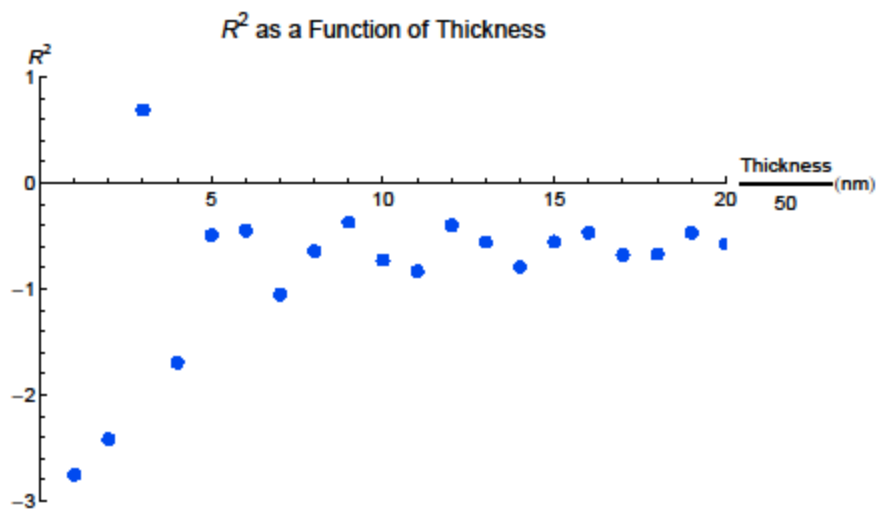
Appendix B: *n* and *k* Plots for ZnS
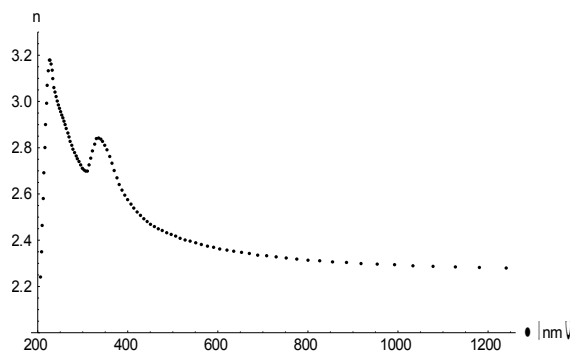
Figure C.1: SOPRA values for *n[λ]*.
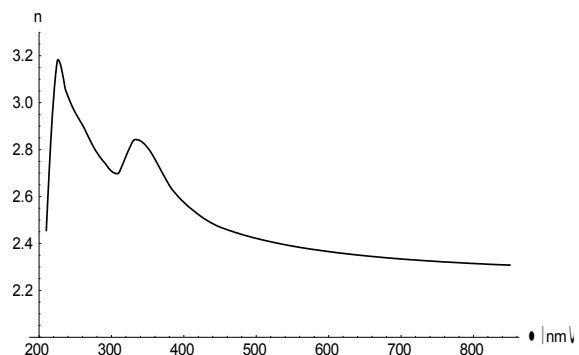
Figure C.2: Interpolated values for *n[λ]*.
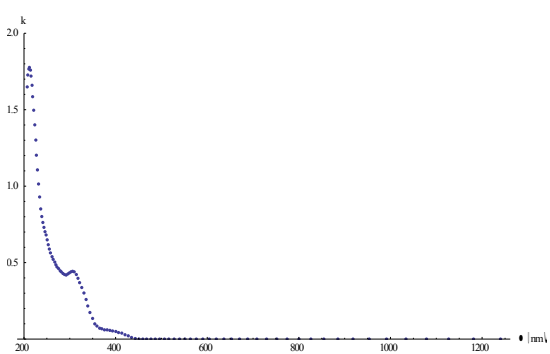
Figure C.3: SOPRA values for k[λ].
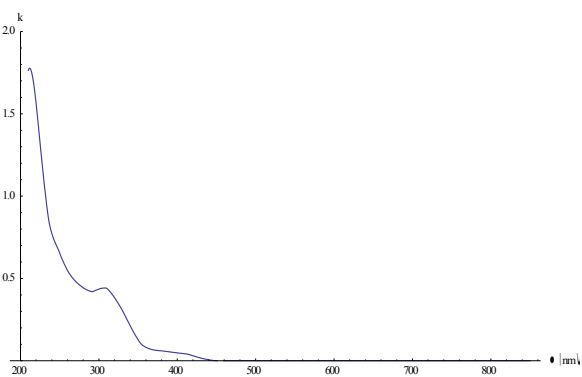
Figure C.4: Interpolated values for k[λ].

Appendix C: *n* and *k* Plots for Si
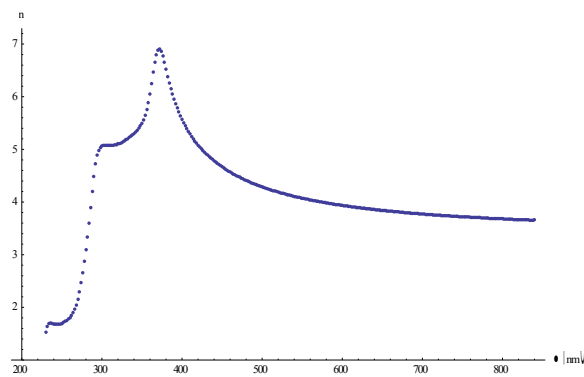
Figure D.1: SOPRA values for *n[λ]*.
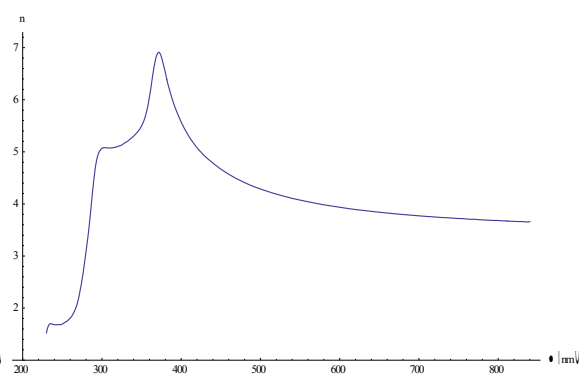
Figure D.2: interpolated values for *n[λ]*.
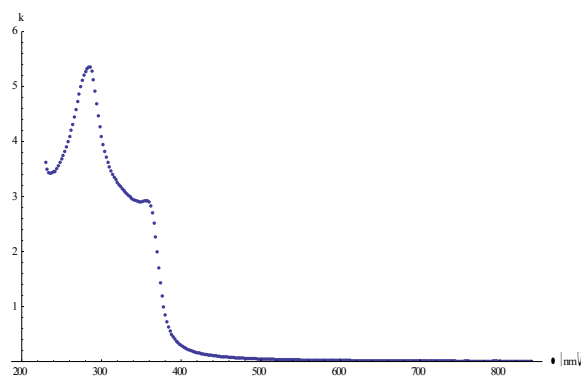
Figure D.3: SOPRA values for *k[λ]*.
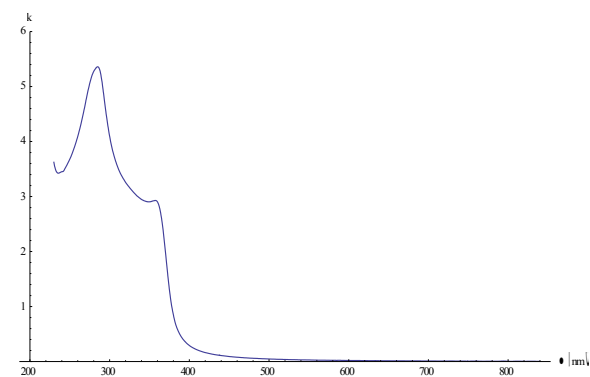
Figure D.4: Interpolated values for *k[λ]*.

Appendix E: Thickness Approximations

Sample: ZnS101b_green
Coefficient of Determination: 0.54

223 nm ZnS on Si
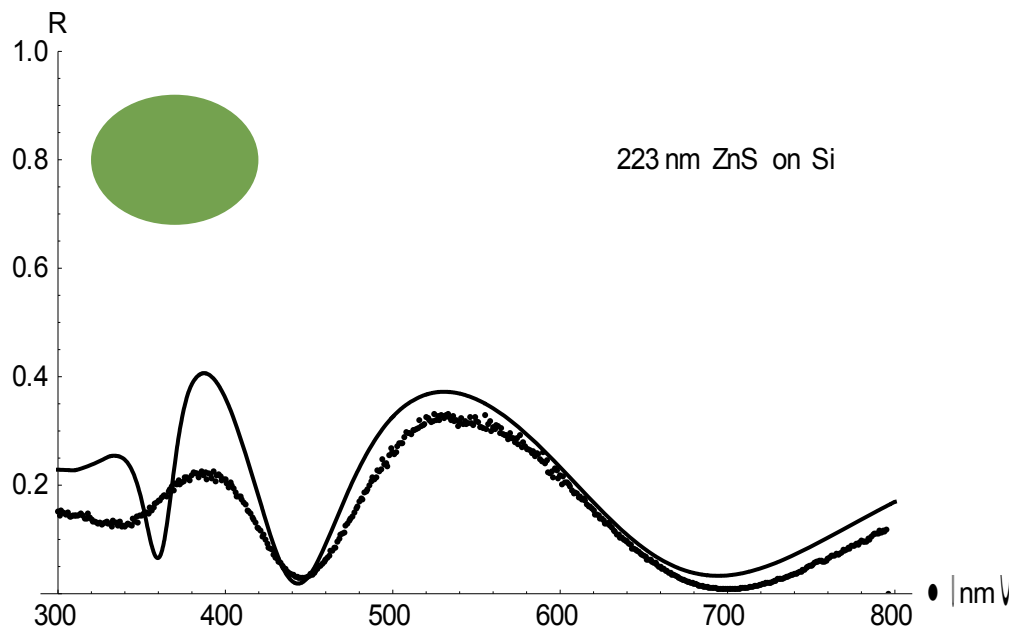
Sample: ZnS101b_x225Ar10
Coefficient of Determination: 0.08

394 nm ZnS on Si
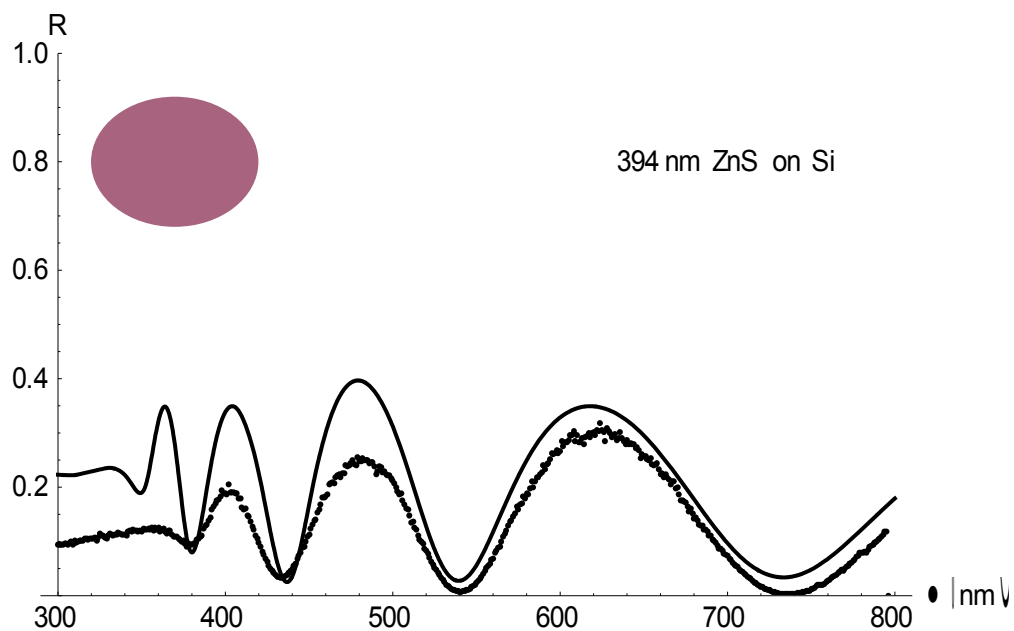
Sample: ZnS111series_LP
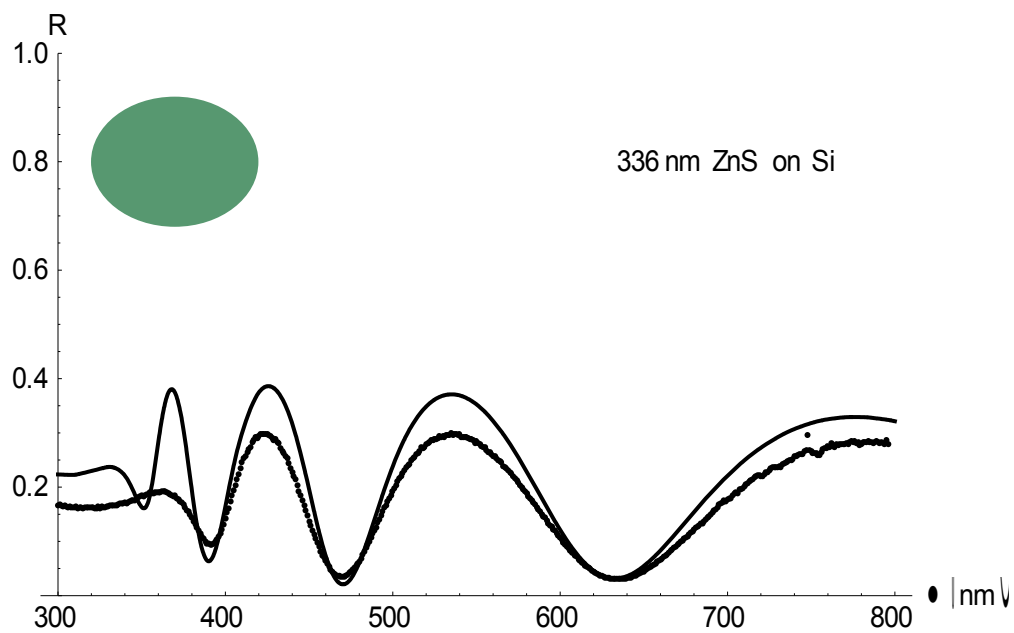Coefficient of Determination: 0.49

254 nm ZnS on Si
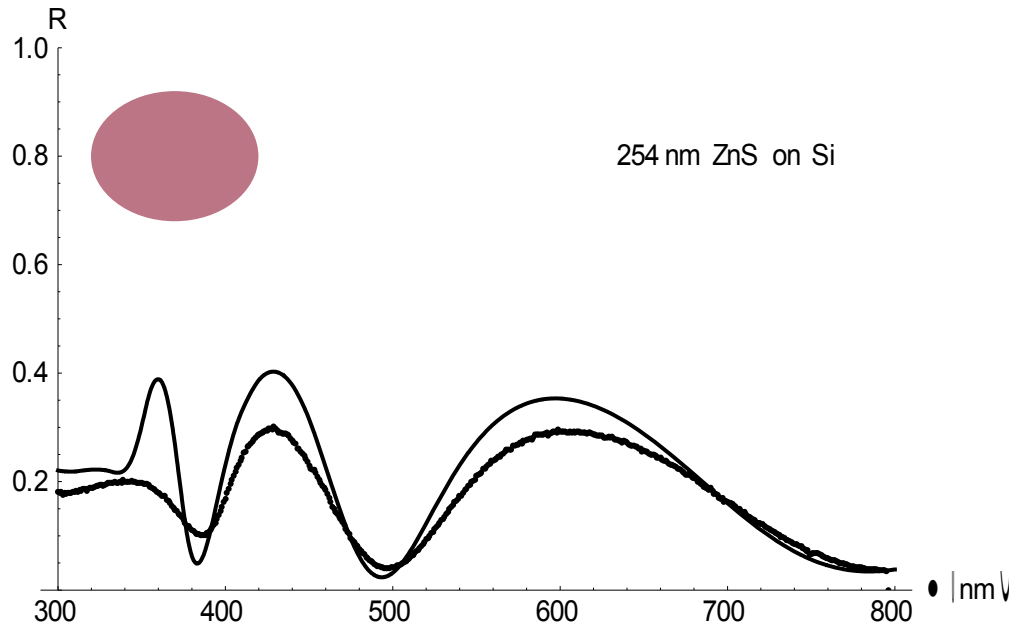
Sample: ZnS111Series_UHV
Coefficient of Determination: 0.18

242 nm ZnS on Si
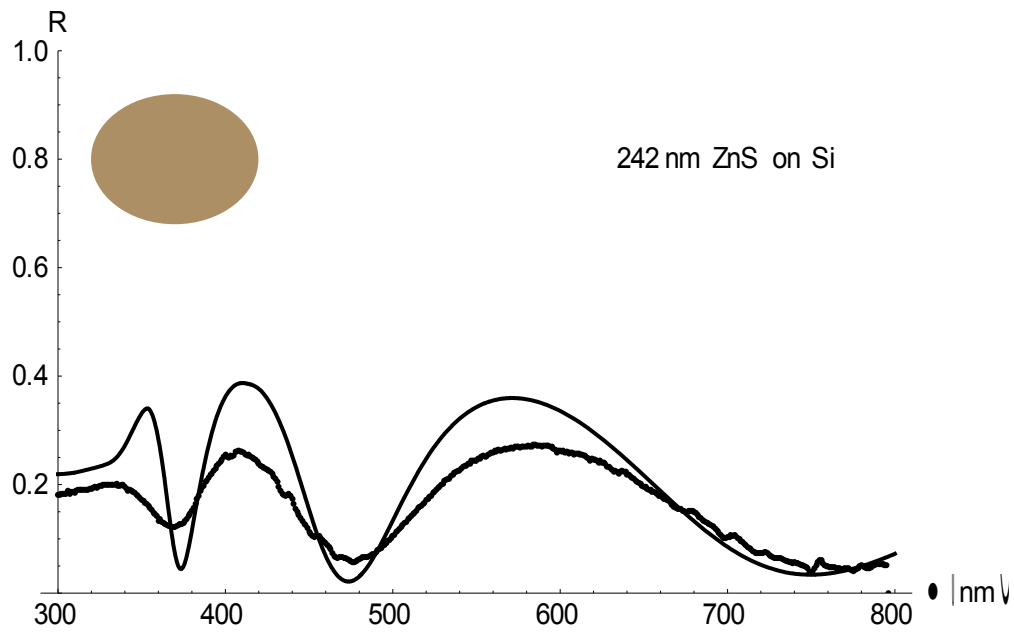
Sample: ZnS111series_HP
Coefficient of Determination: 0.52

336 nm ZnS on Si

Sample: ZnS132_blue
Coefficient of Determination: 0.98

73 nm ZnS on Si
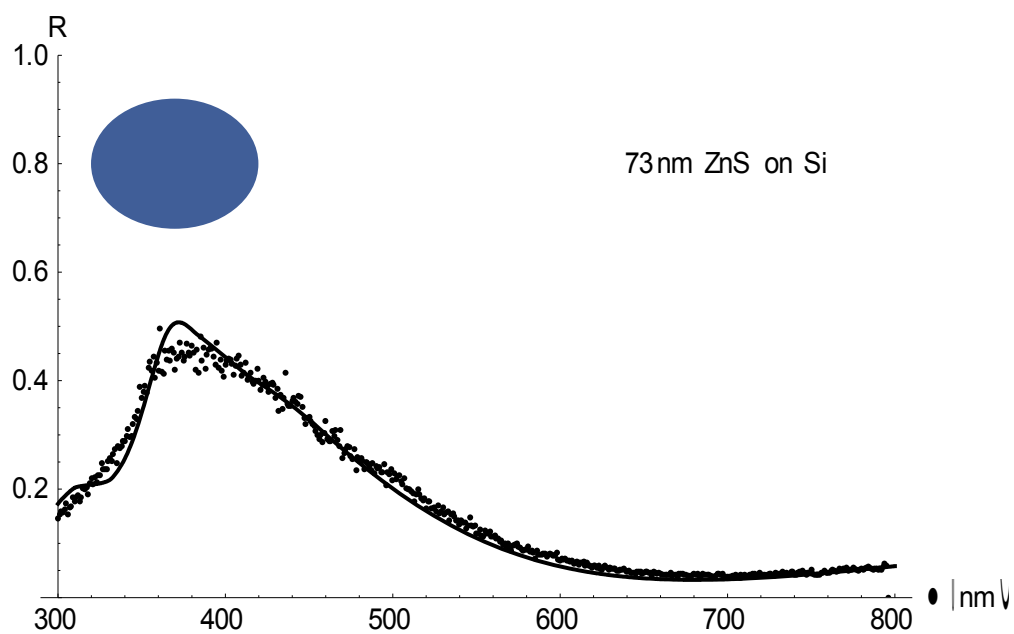
Sample: 0301ZnS203
Coefficient of Determination: 0.97

92 nm ZnS on Si
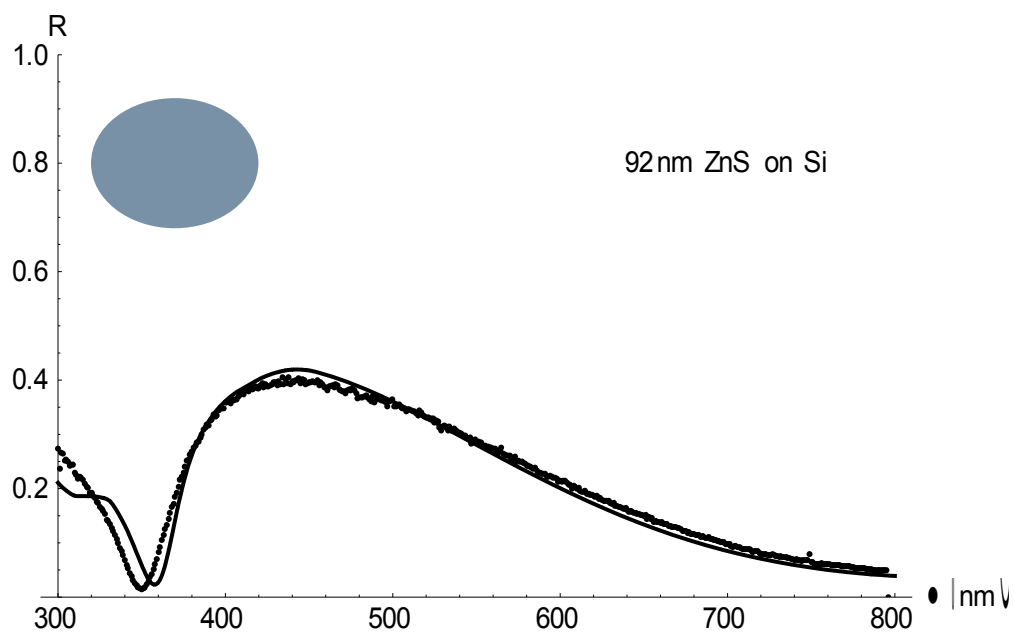
Sample 0312ZnS204
Coefficient of Determination: 0.56

18 nm ZnS on Si
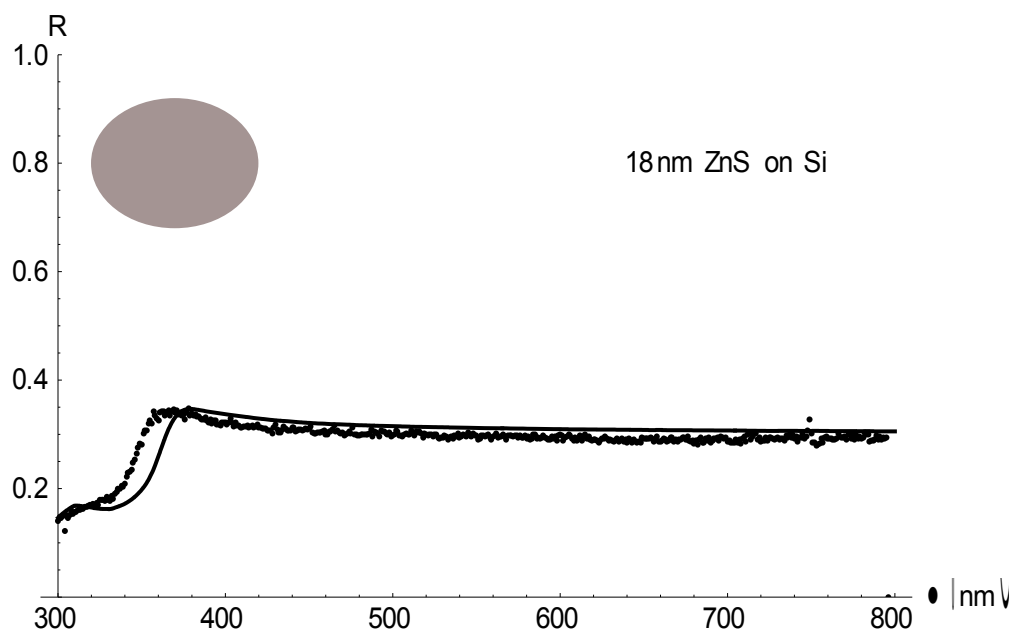
Sample 0402ZnS205
Coefficient of determination: -0.86

17 nm ZnS on Si