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AFIT/GEP/ENP/92D 03

PROCESSABILITY OF POLYTHIOPHENE THIN FILMS
BY
ULTRAVIOLET PHOTO BLEACHING

THESIS

Derek D. Fletcher, Second Lieutenant, USAF

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THESIS

Presented to the Faculty of the School of Engineering
of the Air Force Institute of Technology
Air University
In Partial Fulfillment of the
Requirements for the Degree of
Master of Science in Engineering Physics

Derek D. Fletcher, B.S.
Second Lieutenant, USAF

December 1992

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Preface

The goal of this research was to investigate the possibility of laying down a wave guiding pattern in polythiophene thin films with the ultimate hope of eventually seeing this material used for optical switches. Using a material possessing a refractive index that changes linearly with light intensity one could produce optical switches that are analogous to electrical diodes. In an electrical diode, reversing the voltage bias can either turn the switch on or off. In an optical switch the same switching would be achieved by varying the light intensity to high or low. Optical signals traveling down a wave guide travel faster than electrical signals. As long as polythiophene's refractive index changes rapidly with the onset of intensity variation, in other words the switch is "fast", optical logic elements made out of this material could potentially operate several orders of magnitude faster than electrical logic circuits.

This research investigates photo bleaching as a method for production of such wave guiding patterns. Photo bleaching involves exposing the material to Ultra Violet radiation with the hope of permanently changing the optical properties such as refractive index and dispersion index. This thesis is divided into two parts. Part I deals with photo bleaching of a sample followed spectroscopic ellipsometry to obtain measurements for refractive index, dispersion coefficient, and film thickness. A single silicon wafer coated with polythiophene was exposed to UV radiation at 20 minute increments up to a total of 60 minutes. The refractive, dispersive and thickness parameters are actually obtained by fitting a set of theoretical curves to the raw ellipsometer data using a piece of software titled SIDISP, developed by Dr. James Targove of AFIT. This software is based on a theoretical model of an isotropic thin film deposited on a completely absorbing substrate, where the index of refraction is assumed to vary quadratically with wavelength. With this software, theoretical ellipsometry curves are compared to the raw ellipsometry data given an initial set of values for the refractive index, dispersion coefficient, and film thickness. I, thus, obtained values for each of those parameters in an iterative manner. As such, this software was crucial to my thesis because the parameters I was looking for could not be read directly from the raw ellipsometer data.

In the process of investigating index changes, I discovered that the polythiophene film was getting thinner exponentially in time. This unanticipated result prompted the research presented in Part II. Ellipsometric measurements were made on thick (1.6 µm) and thin (87 nm) polythiophene samples after incremental exposures to UV radiation. In Part II, emphasis was given to finding the thickness parameter only from the raw ellipsometer data. With the thin sample the exponential thinning was confirmed, giving me strong evidence that the film is getting denser either by out-gassing of trapped material and/or by cross-linking of polymer chains.

Over the duration of this ten week effort I have taken note of my developing proficiency in the performance of research. I'm sure that like the rest of my colleges who have gone through this trial, my first few weeks were ones of panic and daily supervision. But, as the weeks progressed my intellectual skills were honed by this thing called "experimental research", and I spent the last few weeks working mostly on my own, touching base with my advisor every few days or so.

I owe a great deal of my intellectual development to my advisor, Captain Peter Haaland, a man, from my perspective, of seemingly infinite intelligence and infinite patience. I would like to give my sincerest thanks to Carl Kutsche for giving me all the inside information about what Pete Haaland expects out of thesis work, having been a student under him also. Thanks have to go out to Hao Jiang of Wright Labs for selflessly taking time from his own research to grow my polythiophene samples and to show me how to do the ellipsometry. I want to thank Joe Williams also of Wright Labs for his help on the SEM.

My love goes out to Mom and Dad, as always, for the home cooked meals on Sunday and use of their laundry facilities thanks to the convenient proximity of this assignment. And, finally, to Christopher Gardner, Jeffrey Williams, and the people at ECLC for preserving my sanity.

Derek D. Fletcher

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Abstract

Processability of Polythiophene Thin Films by Ultraviolet Photo Bleaching. D. Fletcher, Air Force Inst. of Tech.--- Materials possessing strong $\chi^{(3)}$ optical properties, such as Polythiophene, are sought for the production of optical switches. Polythiophene thin films produced by plasma enhanced CVD[1] show a surface rms roughness of 10-15 angstroms over 1 μm^2 areas[1] which is acceptable for wave guiding in the near IR. This research investigates permanently changing the optical properties of such a thin film by exposure to UV radiation (254 nm, 35 mW/cm^2), known as photo bleaching, in the hope of creating a refractive index boundary for use in total internal reflection of optical signals. After 60 minutes exposure, the refractive index shows no change at 400 nm, a 0.3% increase at 600 nm, and a 0.9% increase at 800 nm. The extinction coefficient shows no change at 300 nm and a 218% increase at 500 nm. There is a corresponding increase in absorbance of 160% at 500 nm, but this increase is seen to drop off at 700 nm. The thin films are observed to lose thickness exponentially over time, suggesting that they are getting denser possibly as a result of escaping gases trapped within the film and/or cross-linking between polymer chains. It is not known if the $\chi^{(3)}$ property is affected after the 60 minute UV exposure as a result of possible cross-linking.

[1] P. Haaland and J. Targove. Appl. Phys. Lett. 61 (1), 6 July 1992

Introduction

Transparent materials possessing a non-linear optical response (known as $\chi^{(3)}$ materials) are being sought to produce very fast switches that could be used for optical logic elements, offering a significant decrease in switching time over electrical logic elements (7:1). Switching of optical signals transmitted via wave guides would be accomplished in principle similar to electrical switches. These optical switches would be turned on and off by varying the optical intensity, analogous to changing the voltage bias in an electrical diode. A candidate material known to possess $\chi^{(3)}$ properties is polythiophene (7:1) (see Figure 1 for molecular structure). Unfortunately, the usual method for producing polythiophene thin films, 'wet chemical deposition,' produces a morphology similar to spaghetti on a micron scale (9:310). These micron size features scatter light out of the wave guide rather than transmit it (7:1).

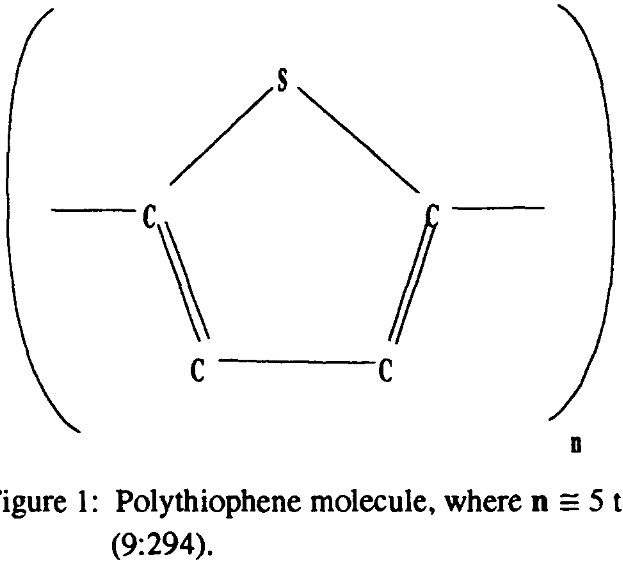


Figure 1: Polythiophene molecule, where **n** ≅ 5 to 10 (9:294).

The problem of micron size features has been solved by a new polythiophene growth synthesis based on plasma enhanced chemical vapor deposition (Plasma Enhanced CVD) (4). Polythiophene thin films have been reported with a root mean square roughness of 10-15 angstroms over 1 μm^2 areas (4:2). this roughness is much less than that required for waveguides, typically 0.1λ (10:77). These thin films have in fact been confirmed to wave guide at 620 nm (visible) and 830 nm (near IR) by Steve Clarson from the University of Cincinnati, Ohio (5).

To produce optical devices from polythiophene one would 1) grow a thin film of polythiophene via Plasma Enhanced CVD, 2) produce a pattern of wave guides (analogous to the production of circuit patterns for microelectronics), and 3) couple an IR source into the appropriate optical channels. Parts 1) and 3) for the production of optical switches out of polythiophene have been proved. This thesis concerns itself with part 2), the production of wave guide patterns. In particular, it investigates the question "How can one write acceptable wave guiding patterns on polythiophene thin films?"

One approach to creating these wave guide patterns involves physically removing material from the film in order to form channels. Photo lithographic techniques using chemical washes common to ordinary micro circuit fabrication have been demonstrated, and the polythiophene films were found to be "chemically robust enough to withstand many conventional semiconductor processing conditions (7:3)." Reactive ion etching might also be used to remove material from the film, as well as ablation of material using a laser.

If the optical properties of polythiophene could be permanently altered by exposure to UV radiation, a process known as photo bleaching, one could more simply write patterns on the thin film by laying down a non-UV-transmitting mask and exposing the material to a UV light source. This would create channels of varying refractive index which could act as wave guides on the principle of total internal reflection at a boundary. This single step method is potentially simpler than the previously mentioned approaches to laying down patterns.

Investigation of photo bleaching is the main thrust of this research, and constitutes Part I of this thesis. A polythiophene thin film grown on a 2 inch silicon wafer is exposed to a controlled UV source (35 mW/cm^2, 254 nm) in increasing time intervals and investigated for changes in refractive index and extinction coefficient using spectroscopic ellipsometry. A thin film grown on a 1 inch quartz disk is also exposed alongside the silicon wafer. After exposure, the absorbance spectrum for the quartz grown sample is found using a Perkin Elmer Spectrometer and compared to its unexposed spectrum. Any changes in the extinction coefficient found by ellipsometry should correspond to changes in the absorbance spectrum. Finally, the 2 inch silicon wafer is cracked and its edge is examined under a scanning electron microscope (SEM). This is done to compare the film thickness with that found by ellipsometry, as well as to look for evidence of a surface layer on the thin film that may affect the ellipsometric measurements.

In the process of making ellipsometric measurements, the polythiophene films are found to lose thickness. Investigation of a possible mechanism for this "thinning" becomes the object of Part II of this thesis. In Part II, a thick (1.6 µm) and thin (87 nm) polythiophene film are again exposed to a UV source (35 mW/cm^2, 254 nm), but this time with a greater number of time increments in order to distinguish a possible mechanism for the observed "thinning".

Part I

Photo Bleaching of Polythiophene

Background and Theory

Photo bleaching

As explained in the introduction, one way of writing wave guide patterns on polythiophene would be to "bleach" a pattern (permanently change the refractive index) using a non-UV-transmissive mask and UV light source. The result is similar to putting a cladding of different refractive index around an optical fiber. Because of the index boundary at the cladding, the optical signal will be transmitted down the channel via total internal reflection. In the case of polythiophene, the photo bleached channel would act as either the "fiber" or the "cladding" depending on which has the higher and lower refractive index. Of course, this is dependent on the actual photo beaching of polythiophene, which is the aim of Part I of this thesis.

Ellipsometry

The occurrence of photo bleaching could manifest itself as a change in refractive index, and/or absorption coefficient. Measurement of these properties in a 0.1 μm thin film is not a trivial task. The method of spectroscopic ellipsometry is used to accomplish this. The following is a basic description of ellipsometry taken from Azzam's book Ellipsometry and Polarized Light, (1:chap.3).

Light from a well defined (wavelength controlled) light source 'L' passes through a linear polarizer 'P' and a linear retarder 'C,' resulting in a known elliptical polarization (Figure 2). This known polarization is reflected off the sample 'S,' which changes the polarization. The unknown polarization is then passed through a variable polarization analyzer 'A' and finally hits the photo detector 'D.' Since the polarization is known at both points 'C' and 'A', the change in polarization phase and magnitude caused by reflection off sample 'S' is now known.

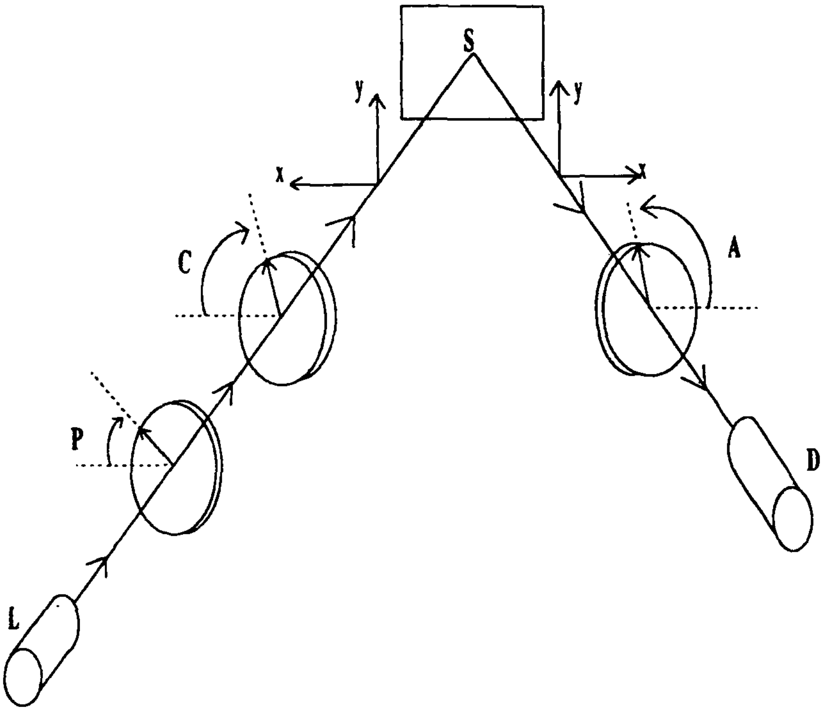


Figure 2: Basic ellipsometer schematic.

Assuming the sample is isotropic and non-gyrotropic, the polarizations parallel (p) and perpendicular (s) to the plane of incidence are reflected with their polarization direction unchanged. The (p) and (s) polarizations are known as eigenpolarizations. The eigenvalues, V_{ex} and V_{ey}, associated with these polarizations are the complex reflection coefficients R_{pp} and R_{ss}, respectively.

$$\begin{aligned} V_{ex} &= R_{pp} = |R_{pp}|e^{i\delta_{pp}} \\ V_{ey} &= R_{ss} = |R_{ss}|e^{i\delta_{ss}} \end{aligned} \tag{1}$$

δ_{pp} and δ_{ss} are phase constants of the parallel and perpendicular polarizations respectively. The ellipsometer actually measures the ratio between these reflection coefficients,

$$\rho_s = \frac{R_{pp}}{R_{ss}} = \frac{|R_{pp}|}{|R_{ss}|} e^{i(\delta_{pp}-\delta_{ss})} \tag{2}$$

more often written as,

$$\rho_s = \tan\psi e^{i\Delta} \tag{3}$$

where,

$$\tan\psi = \frac{|R_{pp}|}{|R_{ss}|} \tag{4}$$

$$\Delta = \delta_{pp} - \delta_{ss} \tag{5}$$

The values for $\cos\Delta$ and $\tan\psi$ are plotted against wavelength to yield characteristic curves for a given material. (See Figure 4, p.14 for example of $\cos\Delta$ and $\tan\psi$ curves)

Deriving the six material parameters from ellipsometry

Obtaining refractive indices, absorption coefficients and thickness from the characteristic curves just mentioned involves fitting a series of theoretical curves to the raw $\cos\Delta$ and $\tan\psi$ data using software developed by Dr. James Targove of AFIT (see Appendix A for SIDISP program). This software incorporates a simple quadratic dispersion formula to compute $\cos\Delta$ and $\tan\psi$ in terms of six parameters: the refractive indices at three wavelengths, the absorption coefficient (Im[refractive index]) at two wavelengths, and the film thickness. Using a set of initial values for the six parameters, the theoretical $\cos\Delta$ and $\tan\psi$ curves can be compared to the raw $\cos\Delta$ and $\tan\psi$ data (see Appendix B for examples of curve fits). The six parameters are then adjusted iteratively in order to improve the computed data fit.

A least squared error method is used to optimize the computed fit to the raw cos Δ and tan ψ data. This method involves first, squaring the difference between calculated and observed (cos Δ, tan ψ) values, then adding these squared differences at each point to get a numerical value for the total squared error. Next, small variations are made around one of the six parameters to yield the derivative in the squared error with respect to that single parameter. Once the derivative in the squared error is known with respect to a given parameter, that parameter can be adjusted accordingly to minimize the total squared error. After the total squared error with respect to one parameter is minimized, the derivative with respect to another parameter is taken, and that parameter can now be optimized. Because the mapping from (n(800),n(600),n(400),k(500),k(300),d) to (cos Δ, tan ψ) is extremely nonlinear, this process is repeated iteratively until the computed data falls within the 2% instrument measurement error of the raw cos Δ and tan ψ data at all points on the spectrum.

At this point, the refractive, extinction, and thickness parameters can be reported with some measure of error. These parameter errors were obtained by small, linear variations about a single parameter, holding the other parameters constant. Thus the reported error represents the variation which produces a 2% error at any wavelength between computed and raw data for these small, linear variations.

Film thinning mechanisms

Several factors may contribute to thinning of polythiophene films over timed UV exposure. Of these factors, the most probable are thought to be: severing of molecular bonds resulting in ablation or evaporation of material; out-gassing in which case various gases or solvents escape from within the material ;and cross-linking between polymer chains resulting in closer molecular bonding, thus forming a denser material (5). Whichever factor or combination of factors is actually occurring, the net result is an observed time dependence in sample thickness. The simplest model to describe this time dependence in any general observable "A", is given by:

$$\frac{dA}{dt} = c \tag{6}$$

where "c" is a time independent constant. This model predicts a linear time dependence in "A" and would be used to describe constant processes such as ablation or evaporation, where the rate of material loss is independent of the amount of remaining material (5).

The next simplest model describing the time dependence of "A" is given by:

$$\frac{dA}{dt} = cA \tag{7}$$

This model predicts an exponential time dependence in "A". It would be used to describe a process, for example out-gassing or polymer cross-linking, in which the rate of change of observable "A" is dependent upon the remaining gases or the remaining non-cross-linked chains in the film. As more gases evolve or as more polymers are cross-linked, the rate of thinning would not remain constant, but would decrease.

Absorbance spectra

Absorbance spectra of a polythiophene film are taken along with ellipsometric data in order to look for a correspondence between absorption and extinction. Care must be taken with terminology describing absorption. "Absorption" is given as $\frac{I_0}{I}$, where I_0 and I are the incident and transmitted radiation intensities respectively (2:68). "Absorbance" is defined by the Beer-Lambert law, expressed in the common form:

$$A = \log_{10} \frac{I_0}{I} \qquad (8)$$

where "A" is the absorbance (2:68). Thus, a reported "absorbance" value will be used to compute the "absorption" of the film by solving for the ratio $\frac{I_0}{I}$.

Experimental Setup and Procedure

Sample preparation

First, polythiophene thin films are grown on a 1 inch diameter quartz disk and a 2 inch diameter silicon wafer using Plasma Enhanced CVD (4:1-3). The samples are grown to approximately 150 nm in thickness and are stored in a room temperature, dry nitrogen chamber to minimize contamination by water vapor in the atmosphere.

Measurement and exposure

Ellipsometric measurements are then taken at five points across the coated silicon wafer (Figure 3) using a Rudolph Research Spectroscopic Ellipsometer, type 43603-200E. The 5-point pattern shown in Figure 3 was chosen to provide both a statistical sampling of the thin film as well as to confirm a suspected gradient in thickness across the wafer as seen by interference rings on its surface. This sampling pattern would later show that the film decreases in thickness uniformly over the wafer with exposure to UV radiation. The absorbance spectrum of the coated quartz disk is also taken at this time using a Perkin Elmer UV/VIS Spectrometer model Lambda 19.

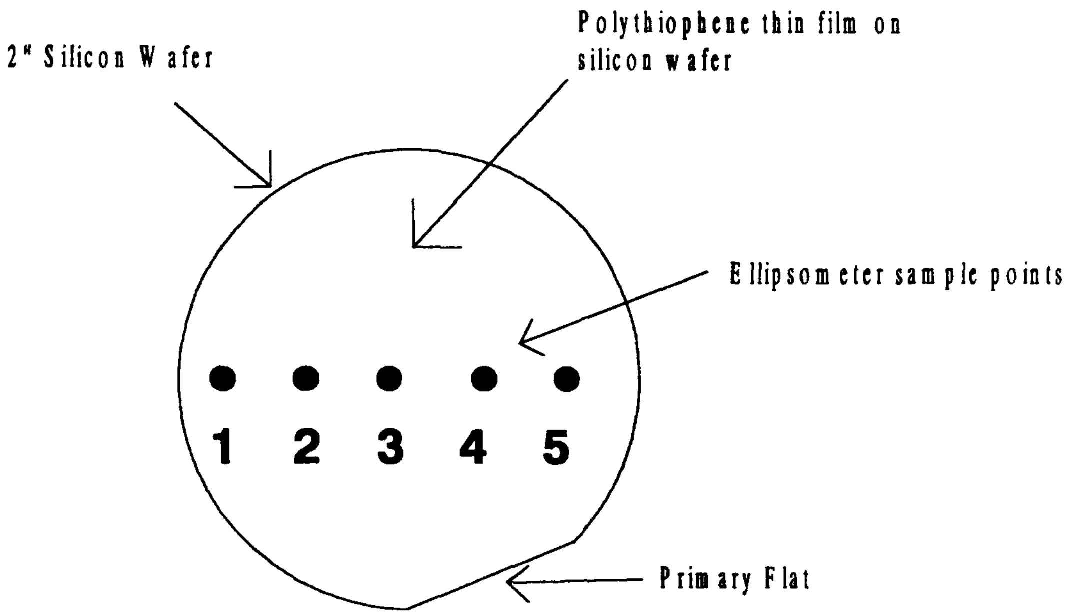


Figure 3: Sampling pattern on silicon wafer.

The next step is to expose both the silicon wafer and quartz disk to a controlled source of UV radiation. A JBA model 55 deep UV flood exposure tool was used to accomplish this with a 20 minute exposure at 254 nm, 35 mW/cm^2. Ideally, one would want to perform this exposure in a vacuum to avoid chemical reactions between the thin film surface and the atmosphere. This was not possible using this particular system. An attempt was made, however, to de-oxygenate the atmosphere by flooding the exposure chamber with N_2 gas using a hand-held nitrogen gun. This did not completely de-oxygenate the atmosphere nor did it preclude nitrogen interactions, if any, with the polythiophene surface. Ar or He gas would be better choices for future research, assuming of course that a vacuum is not available.

The ellipsometric and absorbance measurement procedures are then repeated on the coated silicon and quartz samples respectively, followed by subsequent 20 minute UV exposures. Data is thus taken for 0, 20, 40, and 60 minute total UV exposure times.

Analysis of data

At this point, the raw $\tan\psi$ and $\cos\Delta$ curves obtained from ellipsometry can be analyzed using the SIDISP program (Appendix A). The process of fitting those curves yields refractive indices, extinction coefficients, and film thickness for each sampled point per time exposure.

Finally, the coated silicon sample is cracked and its edge is examined under the SEM for film thickness as well as visible signs of a surface layer on the thin film.

Results

Typical $\tan\psi$ and $\cos\Delta$ data and calculated fits are shown in Figure 4 where the solid lines represent raw data, and the dashed lines represent computed values. The computed curves fall far outside the instrument measure error of the raw data, confirming an actual change in the optical properties of the exposed polythiophene film. Optimization was more quickly reached for the $\tan\psi$ data than for the $\cos\Delta$ data. Because each parameter was adjusted manually to achieve the least total squared error, this process was often time consuming, and optimization was usually ended once the $\tan\psi$ data were fit. The $\tan\psi$ curves fit the raw data within the 2% instrument error in the majority of the spectrum. However, the $\cos\Delta$ curves do not fit in some regions of the spectrum. It should be noted that at each time exposure, all five points are shown rather than a single point with statistical variation. Because some data points overlap, all five points are not necessarily seen at each time exposure in Figures 5 a-e. It was observed that the parameters taken from points near the wafer's edge, points 1 and 5 (see Fig 3 for point distribution) varied significantly from those taken from the central three points. Where this is the case, points 1 and 5 are distinguished in the figures. Because of this observation, it is felt that the values obtained from points 2,3, and 4 are more reliable. The error bars represent the variation as explained in the Background and Theory section.

Variations in index, extinction, absorbance

When all data points are concidered, there was no change in refractive index of 1.735 at 400 nm over the entire 60 minutes of exposure (Figure 5a). However, ignoring points 1 and 5, there is a change in index a 400 nm from 1.735 to 1.724, a 0.6% variation. At 600 nm, again ignoring points 1 and 5, there was a change in index from 1.7 to 1.713, then back down to 1.704 over the total exposure time (Figure 5b). The final value differs by only 0.2% of its initial value, however at 20 and 40 minutes of exposure the difference is 0.8%. At 800 nm, there was the most significant change in index from 1.67 to about 1.682 after the total exposure time, a change of 0.9% (Figure 5c). This may be of value because 800 nm is closer to the near IR wavelengths which would be used in wave guiding.

Now looking at the extinction coefficient, at 300 nm there was no conclusive evidence of a change from the initial value of 0.25 (Figure 5d). However, at 500 nm the extinction coefficient more than doubles from its initial value of 0.055 to about 0.12 (Figure 5e), a change of 218%. This increased attenuation may have a significant effect on near IR wavelengths propagating along the wave channel.

The changes in the extinction coefficient are complimented by corresponding results from the absorbance spectra shown in Figure 6. At 300 nm (Figure 6a) there is no noticeable change in absorbance between the unexposed and 60 minute exposure, while at 500 nm (Figure 6b) the absorbance changes from 0.4 to 0.6 after 60 minutes exposure. Remember that absorbance values are given as $\log_{10}\frac{I_{in}}{I_{out}}$ (equation 8), thus an increase in absorbance from 0.4 to 0.6 represents an actual change in absorption by a factor of 1.6. This is very near the factor of 2.18 increase observed in the extinction coefficient obtained from ellipsometry.

When the difference is taken between the unexposed and 60 minute UV exposure absorbance spectra lines, (Figure 6c), the maximum absorbance difference of 0.27 is seen to occur around 450 nm. This happens to be at a highly opaque region in the spectrum with absorbance at about 1.7. The absorbance difference trails off to a value of 0.06 at 700 nm which was the longest wavelength measurable by the Perkin Elmer Spectrometer. This region of the spectrum is much less opaque, with total absorbance at about 0.2.

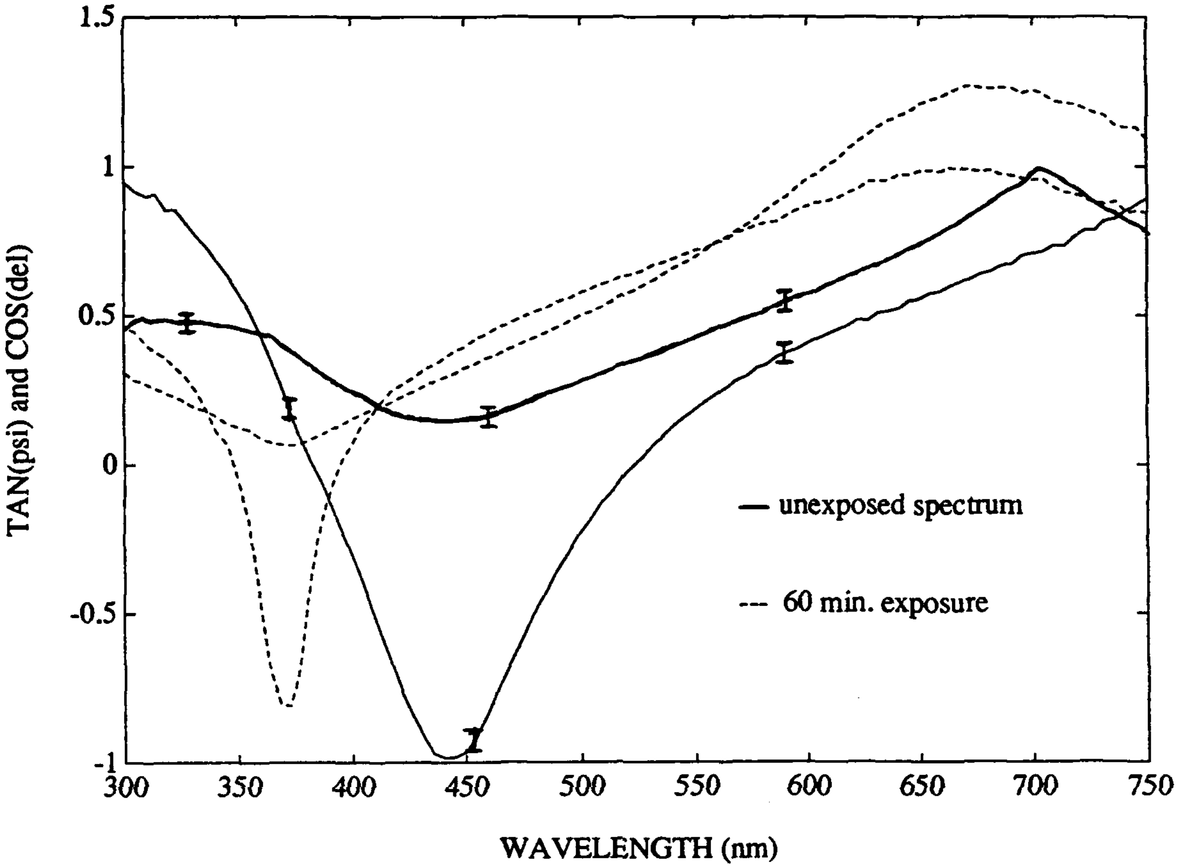


Figure 4: Sample tan ψ, cos Δ curves. Computed and raw values.

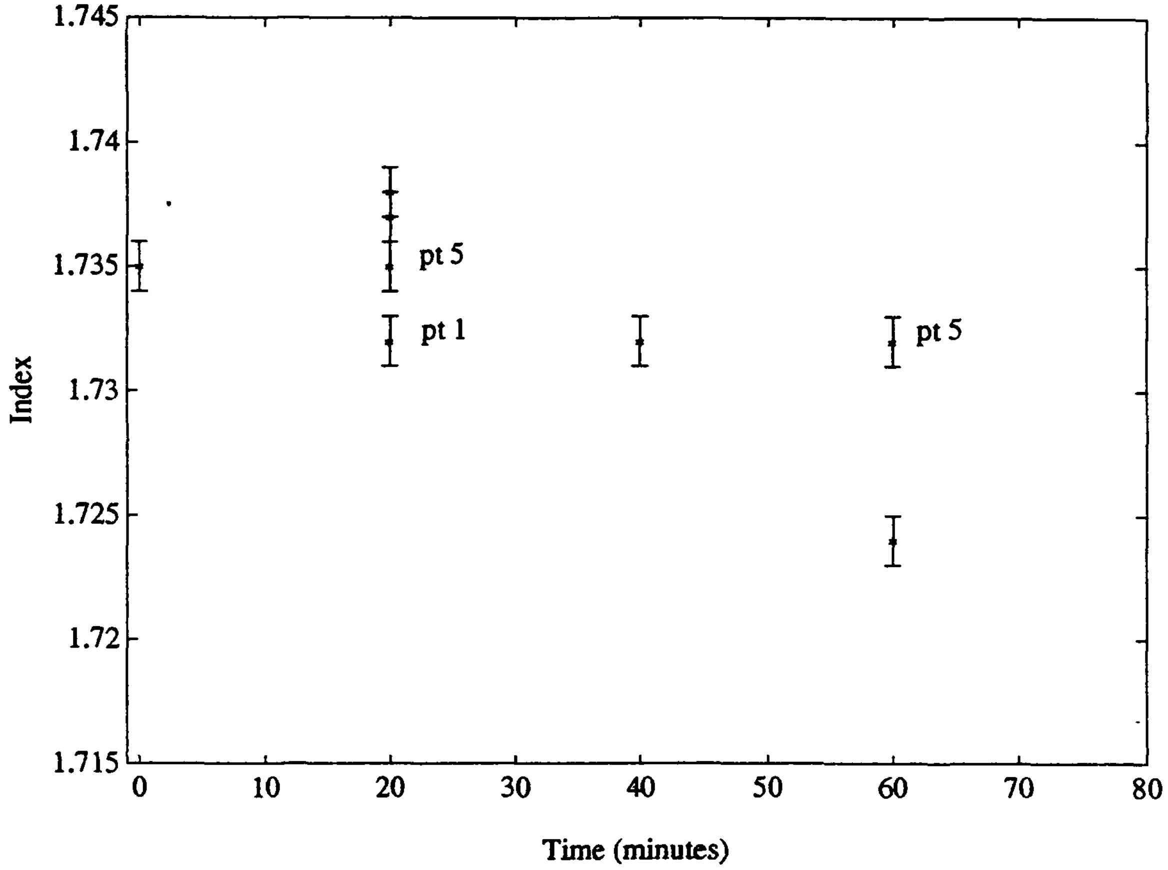


Figure 5a: Index of Refraction at 400 nm vs. Timed UV Exposure.

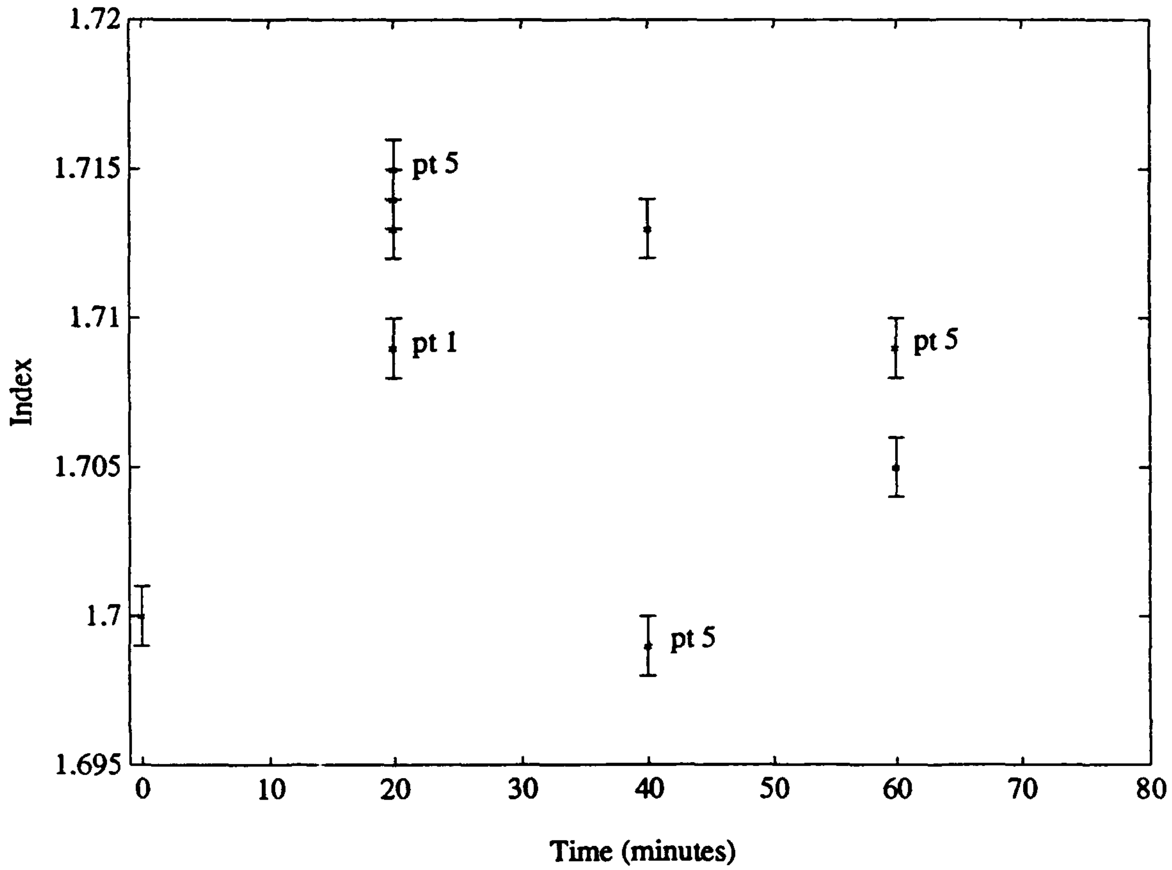


Figure 5b: Index of Refraction at 600 nm vs. Timed UV Exposure.

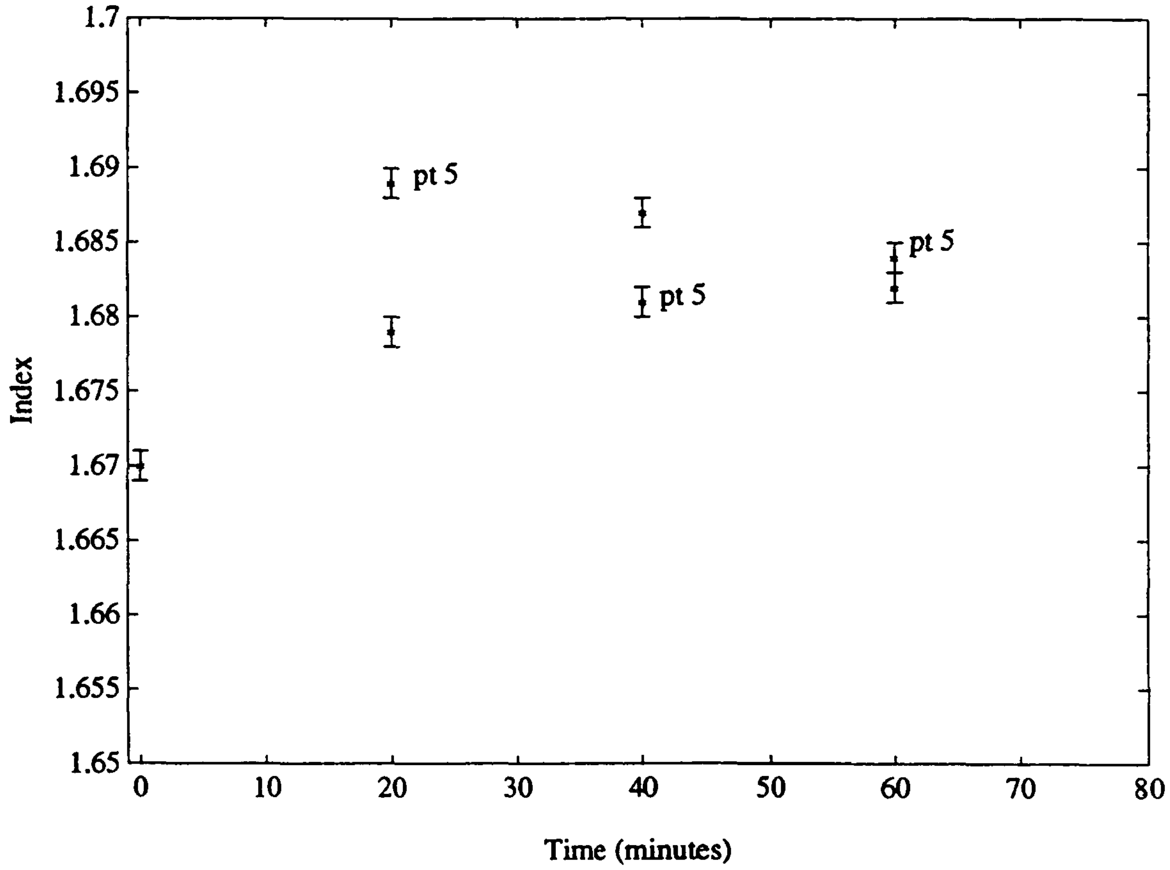


Figure 5c: Index of Refraction at 800 nm vs. Timed UV Exposure.

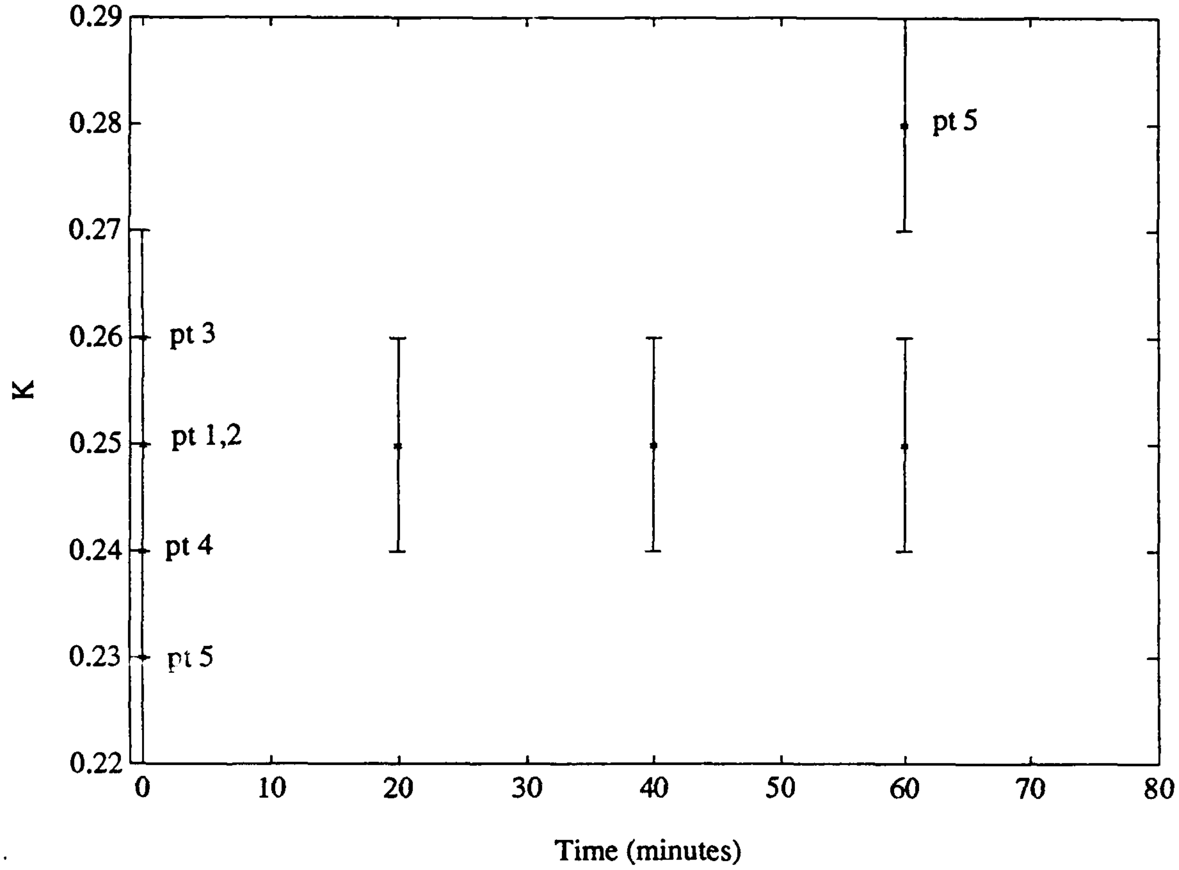


Figure 5d: Dispersion Coefficient at 300 nm vs. Timed UV Exposure.

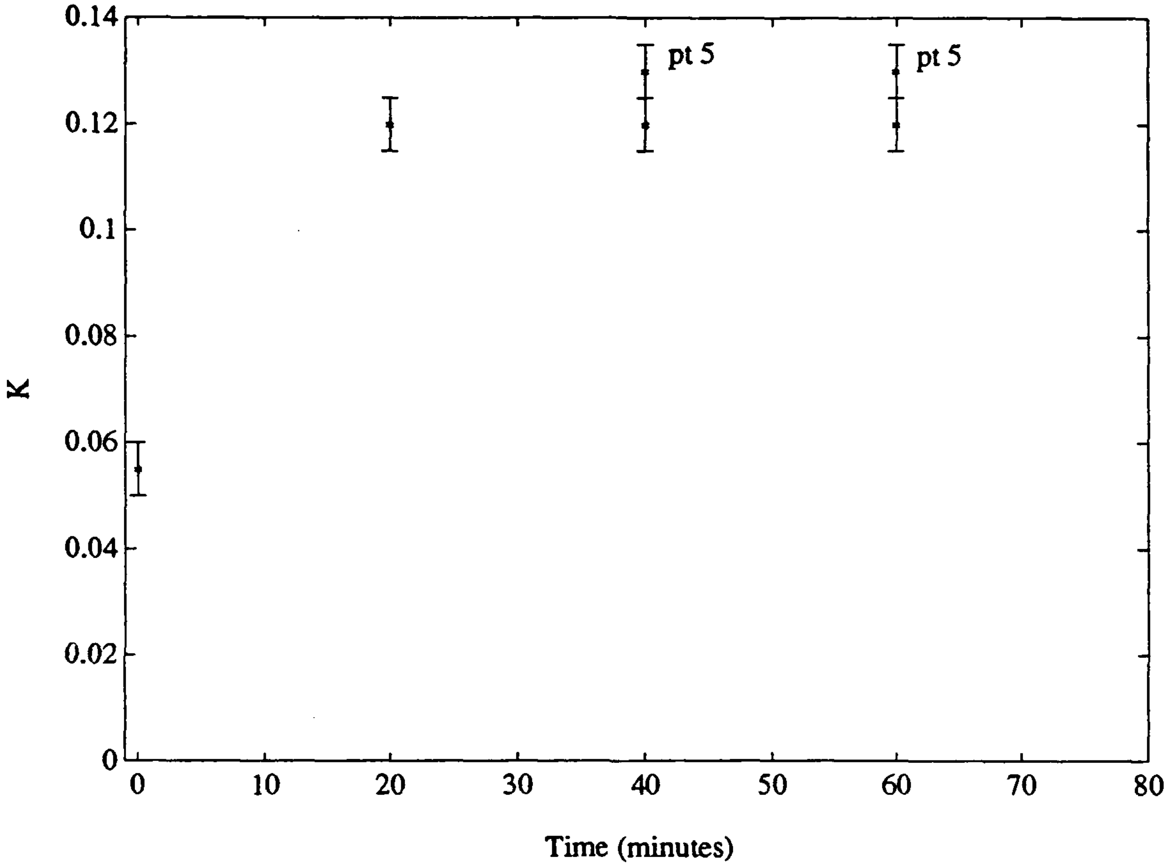


Figure 5e: Dispersion Coefficient at 500 nm vs. Timed UV Exposure.

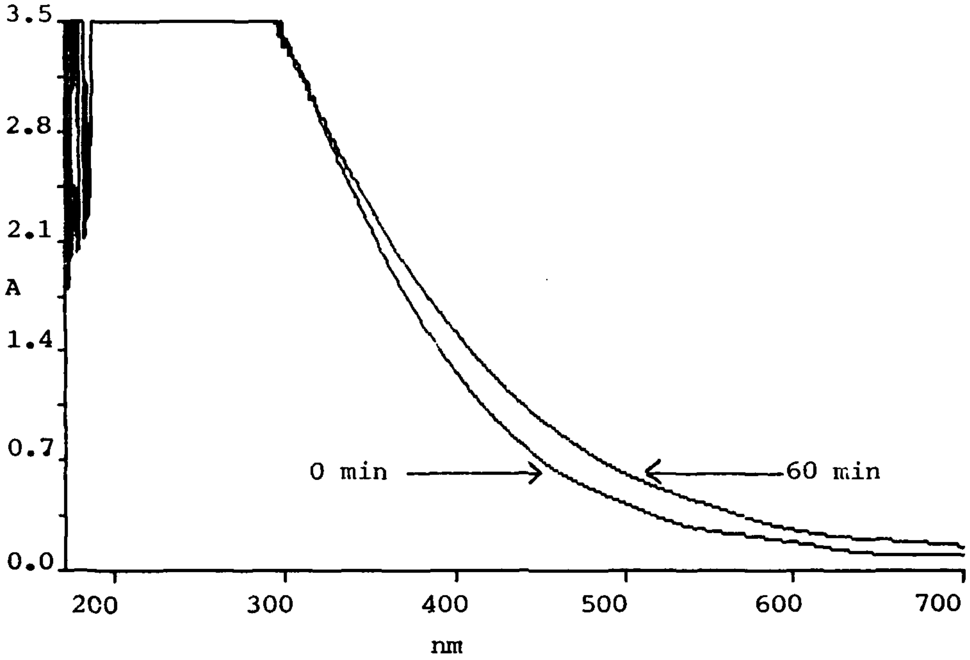


Figure 6a: Absorbance Spectrum vs. Wavelength.
Unexposed and 60 minute UV exposed spectra.

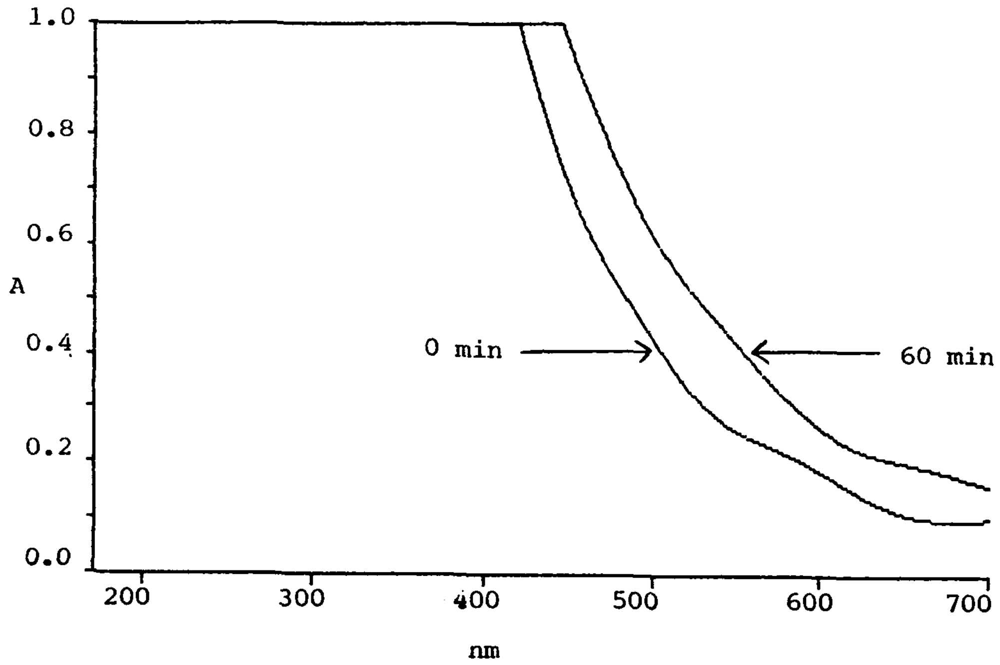


Figure 6b: Absorbance Spectrum vs. Wavelength.
Unexposed and 60 minute UV exposed spectra.

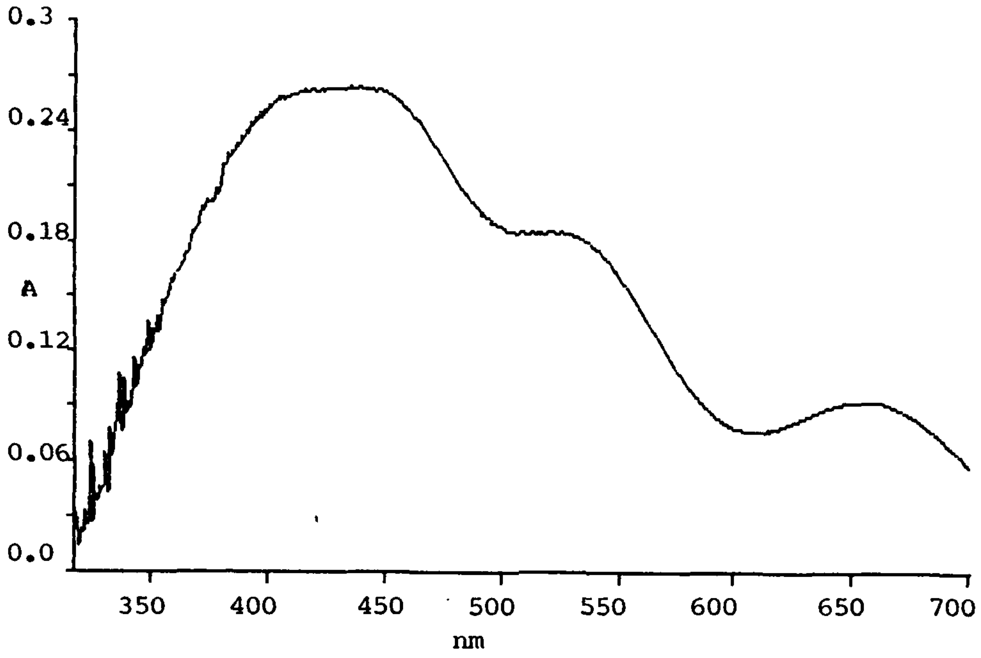


Figure 6c: Absorbance Difference vs. Wavelength.
Plot of the difference in absorbance between unexposed and 60 minute UV exposed polythiophene.

Thickness variations

As mentioned previously, a gradient in polythiophene thickness over the wafer was suspected because of interference rings visible on the surface. Ellipsometry confirmed this gradient as the film thickness was found to go from 148 nm at point 1, to a maximum of 151 nm at point 3, and decrease again to 136 nm at point 5. Independent SEM measurements are in agreement with the 150 nm range in thickness reported by ellipsometry. The mean thickness observed in the SEM images was 150 nm +/- 20 nm. The images also give no conclusive evidence of a surface layer on the polythiophene film which may or may not interfere with ellipsometric measurements.

Measurement of the 5-point pattern also revealed a uniform decrease in thickness over the entire wafer as a function of timed UV exposure. The time evolution for point 3 (Figure 3) is shown in Figure 7. This data is described best by an exponential function derived from equation (7) rather than a linear function. The four data points are fit to the time dependent thickness equation:

$$d(t)\,[\mathrm{nm}] = 30e^{-\alpha t[\mathrm{min}]} + 121 \tag{9}$$

$$\alpha = 0.045134\,[\mathrm{min}^{-1}]$$

where α represents a general decay coefficient. This curve is superimposed on the data points to illustrate the possible exponential nature of the observed thinning rather than a linear nature. It suggests a limiting thickness as $t \longrightarrow \infty$ of 121 nm, a loss of 20% of the initial film thickness.

The discovery of an exponential time dependence in film thickness suggests that outgassing or polymer cross-linking or both are predominant thinning mechanisms. This prompted further investigation into the thinning mechanism, which is the subject of Part II of this thesis.

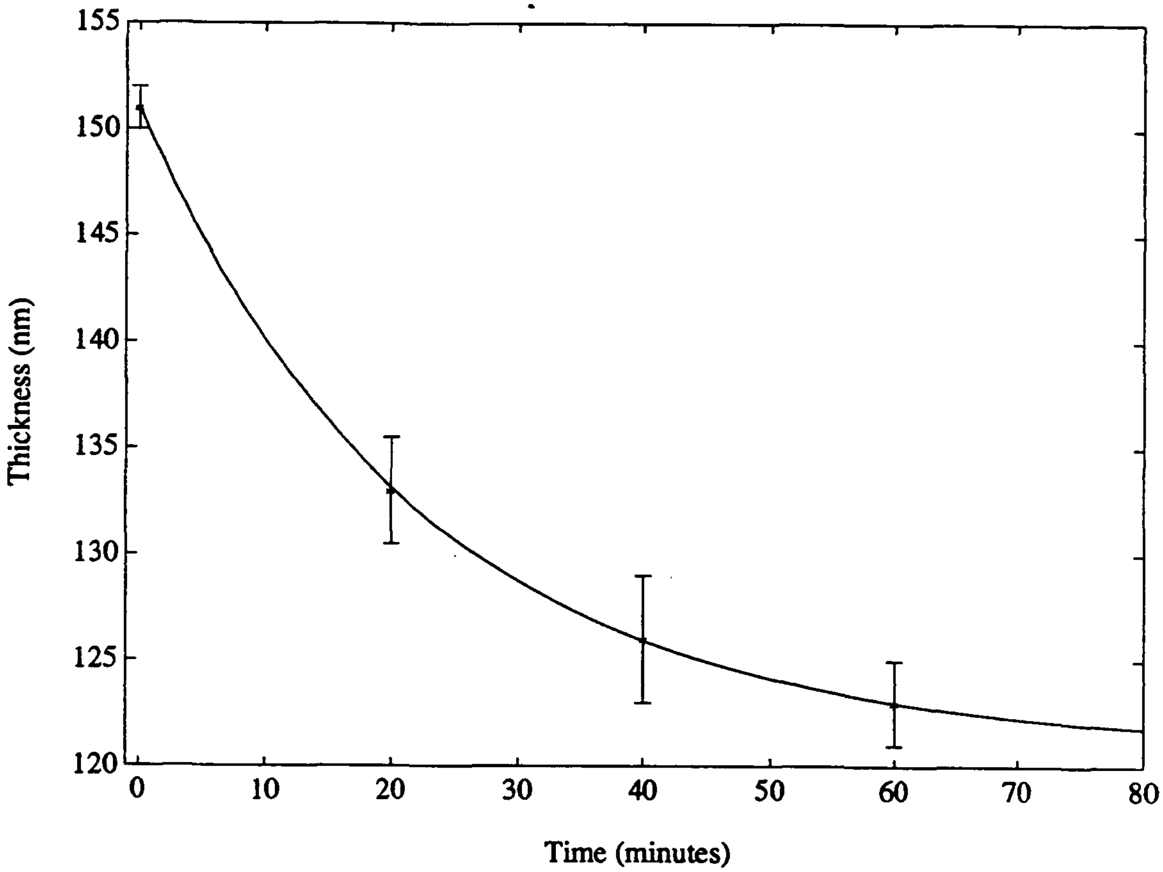


Figure 7: Polythiophene Film Thickness vs. Timed UV Exposure.
The solid line represents a curve fit to the raw data of the form:
$d(t)$ [nm] = $30e^{-\alpha t[\text{min}]} + 121$, with a decay coefficient $\alpha = 0.045134$ [min^{-1}].

Part II

Thinning of Polythiophene Films

Background and Theory

As mentioned in Part I, there are several mechanisms which could be responsible for the thinning of the polythiophene films over timed UV exposure. The results of Part I suggest that out-gassing and/or polymer cross-linking are the predominant mechanisms. Nevertheless, there is some reason to believe that ablation or evaporation of polymer material is also occurring.

Ablation and evaporation of polymer material

The evidence for ablation and/or evaporation of material is found in research done using UV laser ablation of polymers. Of course, laser ablation occurs at much higher intensities than encountered when using the JBA deep UV exposure tool. It is interesting to note, however, that research done in laser ablation more often reports values of fluence (energy/unit area) than intensities (energy/unit time-unit area). In this case, the total energy delivered per unit area by a laser pulse is about the same as that delivered by the exposure tool per second. A research group out of Prague, Czechoslovakia, reports a fluence threshold for ablation in PMMA of between 32 and 58 mJ/cm^2 (3:137). This group used an ArF Excimer laser, 193 nm, pulse width of 8 to 10 nsec FWHM.

Another team from Canada reports a fluence threshold for ablation in Polyimide of 17 mJ/cm^2 using a KrF Excimer laser, 248 nm, pulse width of 20 nsec FWHM (8:227). A threshold value of 23 mJ/cm^2 was used in their calculations; however, the 17 mJ/cm^2 threshold was the experimental result.

The JBA deep UV exposure tool delivers 35 mJ/cm^2 of 254 nm radiation every second for multiple seconds. If intensity is not the key factor, but rather total energy absorbed per unit area, this value is above the ablation threshold discovered by the other teams. Thus, it may be that ablation is occurring, but at a much lower rate than with high intensity laser pulses. Once again, ellipsometry is used to determine film thickness after various timed UV exposures, and the mechanism of decay is estimated from the nature of the thinning process, either linear or exponential.

Exposure of relative "thick" and "thin" films

It was decided that both a thick and thin polythiophene film (relative to the UV wavelength 254 nm) would be examined to see if each decreases by the same relative percentage of their respective initial thickness. Perhaps, as discovered in Part I, an annealed surface layer of approximately 121 nm forms which protects underlying material from further annealing. If this happens, the thick polythiophene film should decrease by a lesser total percentage than the thin polythiophene film.

Positioning error of samples

There are large variations in the thickness distribution found in the measurements taken on the thick sample which do not seem to be a problem with the thin sample. A good estimate for this variation can be obtained by considering the number of interference rings observed on the coated silicon wafers before they were cut into samples. Each interference ring observed corresponds to approximately 150 nm in thickness variation on the wafer. On the thinly coated silicon wafer, no interference rings were observed across the wafer diameter. This makes sense because the sample taken from the thickest portion of the film was only 87 nm thick, and one would not expect to see interference rings from such a thin film. If the thickness went to zero at the wafer edge, which it did not appear to do, this variation would correspond to a worst case thickness gradient of 3 nanometers per millimeter of displacement on the sample, assuming a linear gradient.

On the thickly coated sample, however, there were at least six very closely spaced rings observed on the wafer. This suggests that there were variations of approximately 900 nm from the edge to the center of the wafer. Assuming a linear gradient, this corresponds to 35 nanometers per millimeter of displacement on the sample.

Thus, when ellipsometric measurements were taken on each of the 5 by 10 mm samples, the results for the thick sample were much more sensitive to small variations in sample positioning on the ellipsometer. Even a small variation of 1 mm, which is a reasonable estimate for positioning error on this particular ellipsometer, could cause an error in measurement as much as 35 nm on the thick sample while only causing a 3 nm variation on the thin sample. The error shown in the Figures is only +/- 5 nm for the thick sample and +/- 1 nm for the thin sample, and these represent the instrument limited error propagation as described in the Background and Theory section of Part I. Adding the positioning error to the instrument error would increase the total error to +/- 40 nm at each data point for the thick sample, and +/- 4 nm at each data point for the thin sample. These estimates for positioning error are reported with the Figures, but not shown on the error bars. Only instrument limited error is shown in the Figures as error bars.

Experimental Setup and Procedure

Two polythiophene films are grown on 2" silicon wafers using Plasma Enhanced CVD (4:1-3). One film is grown to approximately 2 µm in thickness, and the other to approximately 100 nm. This time both samples are cut into 5 by 10 mm rectangles and mounted on standard SEM sample boats for ease of handling. This also insures that the ellipsometry is performed more precisely at the same point each time. A statistical sampling of points over the wafer is no longer needed. Once again, the samples are stored, whenever possible, in a room temperature, dry nitrogen chamber to avoid delamination caused by water vapor in the atmosphere.

The thick and thin samples are then exposed together under the JBA model 55 deep UV exposure tool at 35 mW/cm^2, 254 nm, with the following time intervals: 0, 5, 10, 20, 40, 50, 55, 60 minutes. Ellipsometric measurements are taken after each exposure, and the raw data curves are fit using the SIDISP program as before.

Results

The thick and thin samples were successfully exposed, measured, and analyzed as described in the preceding section. Once again, the curve fitting procedure yielded six fitting parameters, one of them being thickness. This thickness is plotted against timed UV exposure in Figures 8 and 9 for the thin and thick samples respectively.

The data for the thin sample (Figure 8) once again shows a convincing exponential time decay in thickness. The superimposed curve in Figure 8 is added to illustrate the exponential nature of this thinning. The time evolution in thickness is derived from equation (7), giving the following exponential function:

$$d(t)\,[\mathrm{nm}] = 32e^{-\alpha t[\mathrm{min}]} + 55 \qquad (10)$$

$$\alpha = 0.016347\ [\mathrm{min}^{-1}].$$

This equation suggests a limiting thickness as $t \longrightarrow \infty$ of 55 nm, a loss of 37% of the film's initial thickness. It should also be mentioned that the decay constant α is approximately three times smaller than that reported in Part I of this thesis, but nevertheless, the same order of magnitude.

The data for the thick sample (Figure 9) is less revealing of its nature of decay. The data points show a much wider spread in point to point variation than did those for the thin sample, as explained in the Background and Theory section of Part II. This makes it unclear whether the decay is exponential or linear, although if the total error of +/- 40 nm is added to the data points, there does appear to be a general decrease in thickness over time.

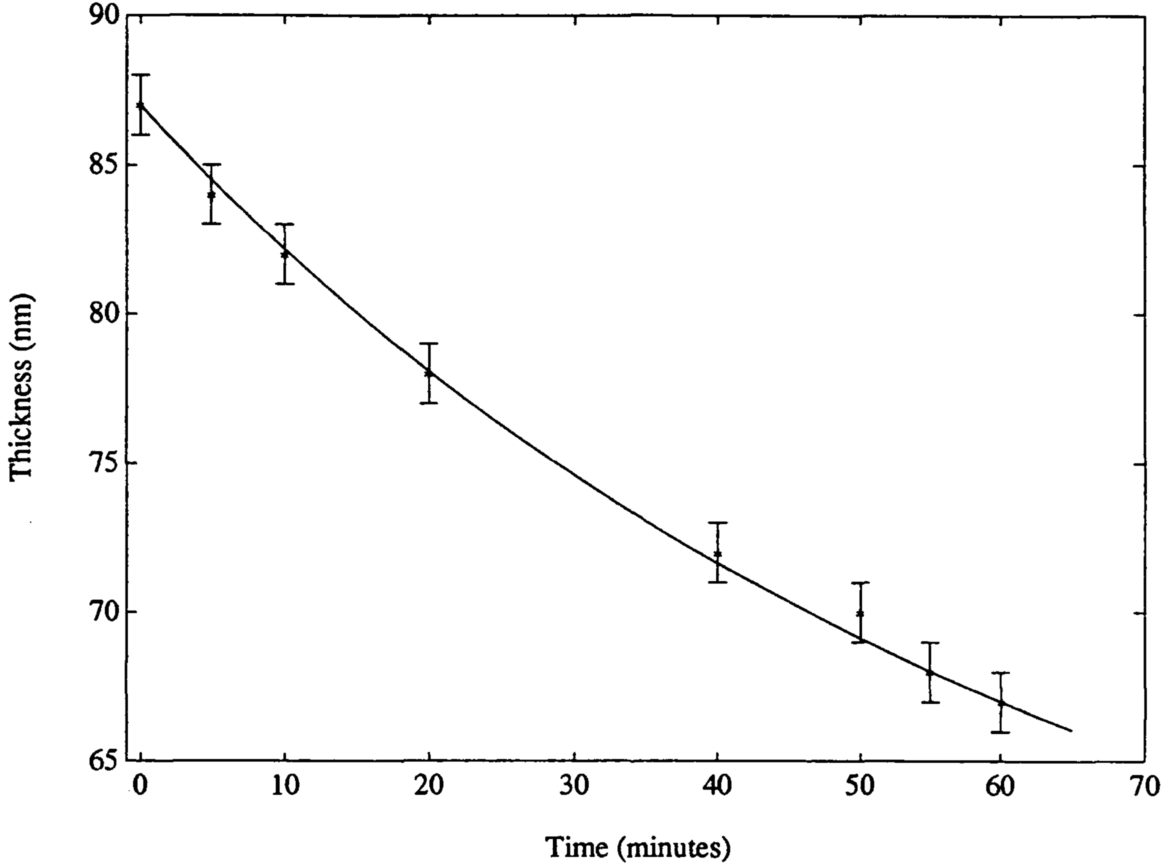


Figure 8: Polythiophene Film Thickness (thin sample) vs. Timed UV Exposure. The solid line represents a curve fit to the raw data of the form: $d(t)\ [nm] = 32e^{-\alpha t[min]} + 55$, with a decay coefficient $\alpha = 0.016347\ [min^{-1}]$. Only instrument limited error is shown. There is a possible additional sample positioning error of +/- 3 nm at each data point.

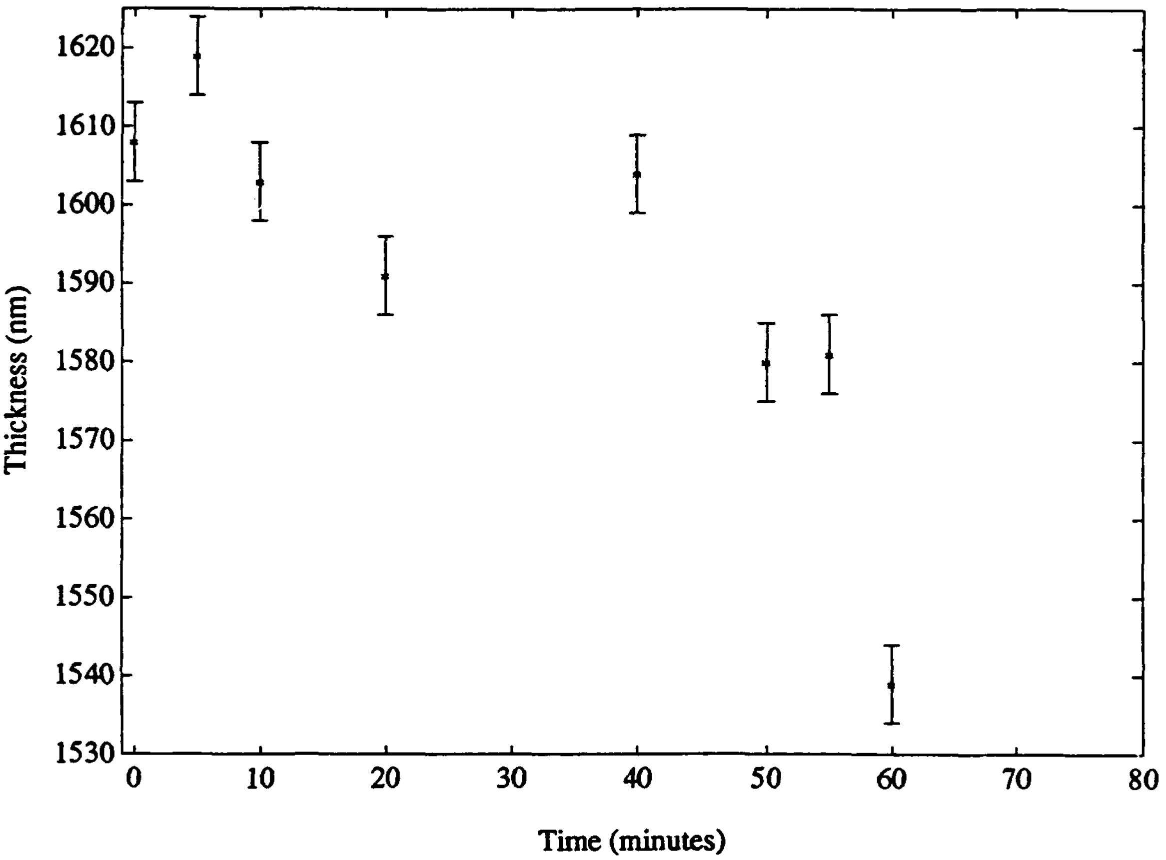


Figure 9: Polythiophene Film Thickness (thick sample) vs. Timed UV Exposure. Only instrument limited error is shown. There is a possible additional sample positioning error of +/- 35 nm at each data point.

Conclusions

The main thrust of the research accomplished in Part I was to investigate the possibility of changing the optical properties of polythiophene by exposure to UV radiation, a process known as photo bleaching, with the ultimate goal of producing wave guides in the near IR spectrum to be used in optical switching for optic logic elements (7:1). The results of Part I show a change in refractive index at 400 nm (0.6%), at 600 nm (0.2%), and at 800 nm (0.9%) for polythiophene exposed to UV radiation (254 nm, 35 mW/cm^2) for 60 minutes. The extinction coefficient does not change significantly at 300 nm, but at 500 nm it shows a large 218% increase. This large increase in the extinction coefficient is complimented by a corresponding increase in the absorbance spectra of 160% at 500 nm, while there is no increase in absorbance at 300 nm. The film was also observed to get thinner upon UV exposure as an exponential function of time. This supports the belief that the film is getting denser (assuming negligible loss of material); a result which should cause the refractive index, extinction coefficient and absorption to increase as observed. Thus, polythiophene does exhibit slight photo bleaching after 60 minutes of UV exposure, with the greatest effects being seen closer to the near IR wavelengths.

While the slight changes in refractive index are desirable for producing a "fiber"-with-"cladding" type optical wave guide, the large increase in extinction and absorption observed at longer wavelengths is unfortunate. Optical signals may be attenuated too greatly for practical use in logic elements. On the other hand, when the difference is taken between the absorbance spectra at 60 minutes and 0 minutes exposure (Figure 6c), there is a downward trend in absorption into the longer wavelengths. If this trend continues into the IR region of the spectrum, perhaps signal attenuation would not be so greatly affected. It would be a good idea for future research to investigate the near IR region of absorbance in UV exposed polythiophene, as this is the primary region of interest for wave guiding. Too much absorption at these wavelengths could negate the benefit gained by the slight variations observed in refractive index.

The main thrust of the research accomplished in Part II was to investigate the mechanism responsible for thinning of the polythiophene film observed in Part I. The thin, 87 nm sample once again displayed an exponential time decay. The data for the thick, 1.6 μm sample was inconclusive because of the large error suspected as a result of sample positioning combined with a large thickness gradient. Only a general decrease in thickness could be concluded due to this positioning error.

It is believed that ablation or evaporation of material would occur at a constant rate, yielding a linear functional dependence on time (5). On the other hand, the rate of outgassing would be dependent upon the amount of gases remaining in the material, and the rate of polymer cross-linking would be dependent on the number of unlinked polymers remaining. Either of these processes would, in their simplest form, yield an exponential functional dependence on time. This exponential decay was observed in the two independent measurements taken in Parts I and II; thus, there is strong evidence that outgassing and/or polymer cross-linking is the predominant source of the observed thinning process.

Materials that are trapped deeper within the polythiophene film would have greater difficulty escaping than materials nearer the surface. Therefore, one would expect a thinner film to be more easily depleted of trapped materials than a thicker film; meaning that thinner films should decrease by a greater percentage of their intial thickness than thicker films. The first sample in Part I had an initial thickness of 151 nm, and lost 20% of that thickness over the 60 minute UV exposure time. The thin sample in Part II had an initial thickness of 87 nm, and lost 37% of that thickness over the 60 minute UV exposure time. This evidence supports the hypothesis that out-gassing of trapped materials is the thinning mechanism.

If polymer cross-linking is also occurring, then it is reasonable to question whether the $\chi^{(3)}$ property of polythiophene has been altered by UV exposure. It is necessary to know exactly how UV exposure affects the optical properties of polythiophene in order to build appropriate optical switches. Destroying the $\chi^{(3)}$ property would eliminate photo bleaching as a method for production. Investigating the $\chi^{(3)}$ property after UV exposure should, therefore, be the subject for future research.

As a result of the research presented in Part I, it may now be desirable to build a wave guide "fiber" to determine whether the small changes in index observed after UV exposure are adequate for use in total internal reflection of near IR wavelengths. As described earlier, this could be accomplished by laying down an appropriate non-UV-transmitting mask on a polythiophene film, exposing it to between 20 and 60 minutes of UV radiation, then coupling a near IR source into this channel and testing for successful wave guiding. If wave guiding is not observed, this may be evidence that the near IR absorption is too great after UV exposure in accordance with the large increase observed in extinction coefficient and absorption. Perhaps, too, the refractive index boundaries within the material are not sharp enough for total internal reflection. The 20 to 60 minutes required for UV exposure may be long enough that the refraction boundary begins to blur and "undercut" the sharp edges of a mask deposited on top of the polythiophene.

Appendix A

Code for SIDISP and SIDISPEVAL

The codes for SIDISP and SIDISPEVAL given in this appendix were developed by Dr. James Targove, professor in the department of engineering physics, Air Force Institute of Technology, Wright-Patterson Air Force Base, Ohio. The code is run on Matlab and produces a set of theoretical curves which is matched against raw ellipsometer data taken from a thin film. The six parameters required as initial conditions for curve computation are: refractive index at 400 nm, 600 nm, and 800 nm; extinction coefficient at 300 nm, and 500 nm; and film thickness in nanometers. These parameters are then used in a mathematical model of an isotropic film deposited on a completely absorbing substrate. The actual SIDISP code only performs the task of asking the user to input the six parameters and plots the final data. This code looks for the raw ellipsometer data in a Matlab file also specified by the user. The Matlab data file must be in the form of a matrix in the following order: wavelength information in column 1; $\cos\Delta$ information in column 2; and $\tan\psi$ information in column 3. SIDISP calls upon the code SIDISPEVAL to do the theoretical computation in accordance with the described mathematical model.

SIDISP

```
echo off all
hold off
clear
%
% Program which plots experimental data against modelled data
% given a set of parameters. It calls fiteval for calculations.
global A B dat theta sub
input('input nx(800): ');
nx8=ans;
input('input nx(600): ');
nx6=ans;
input('input nx(400): ');
nx4=ans;
input('input k(500): ');
kx5=ans;
input('input(k(300); ');
kx3=ans;
input('input d (nm): ');
d=ans;
arg=[nx8 nx6 nx4 kx5 kx3 d];
input('Input data file name (MAT File):','s');
eval(['load ',ans]);
load si;
sub=si;
Data=a;
%Data(:,1)=Data(:,1)./1000;
[m,n]=size(Data);
for i=1:m;
   dat=Data(i,:);
   [temp,cosdel(i),tanpsi(i)]=sidispeval(arg);
end;
%axis([600,800,-1,1]);
clg
subplot(211);plot(Data(:,1),Data(:,2),Data(:,1),cosdel,'--');
title('FIT TO ELLIPSOMETRIC DATA');
xlabel('WAVELENGTH (nm)');
ylabel('cos(delta)');
%axis([600,800,0,5]);
subplot(212);plot(Data(:,1),Data(:,3),Data(:,1),tanpsi,'--');
xlabel('WAVELENGTH (nm)');
ylabel('tan(psi)');
axis;
pause;
%
```

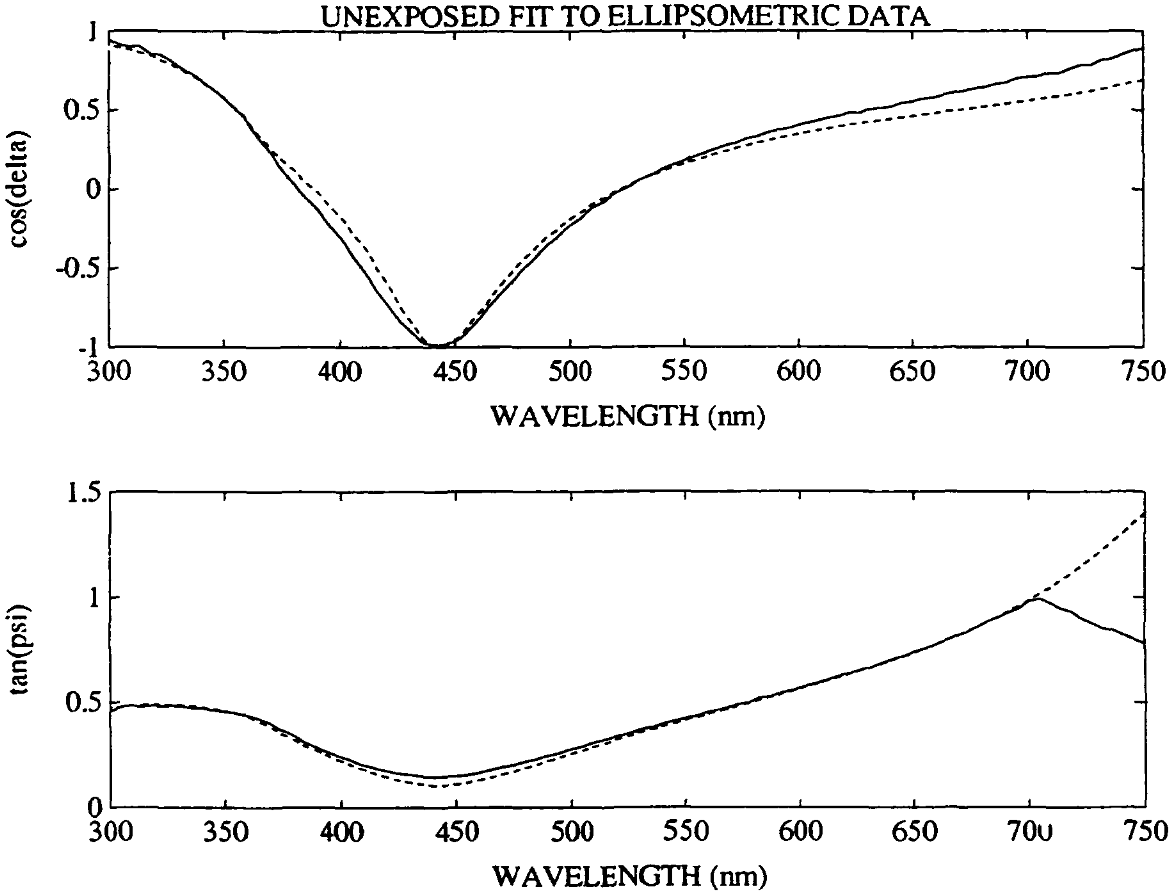
SIDISPEVAL

```
%%  ISOABS1
%
%  SE formulas for one thin, absorbing film on an absorbing substrate.
%
function [f,cosdel,tanpsi]=isoabs(arg);
i=sqrt(-1);
theta=70;
W1=theta*pi/180.;
W2=dat(1);
lambda=W2/1000;
temp=table1(sub,W2);
nsub=temp(1);
ksub=temp(2);
% comment out the next line for straight silicon substrate pdh
%nsub=1.47; ksub=0;
n8=arg(1);
n6=arg(2);
n4=arg(3);
k5=arg(4);
k3=arg(5);
d=arg(6);
temp=inv([1/.6^2-1/.8^2 1/.6^4-1/.8^4;1/.4^2-1/.6^2 1/.4^4-1/.6^4]);
temp=temp*[n6^2-n8^2;n4^2-n6^2];
B=temp(1);
C=temp(2);
A=n8^2-B/.8^2-C/.8^4;
nx=sqrt(A+B/lambda^2+C/lambda^4);
B=(k3-k5)/(1/.3^2-1/.5^2);
A=k5-B/.5^2;
kx=A+B/lambda^2;
%if W2>640
%kx=0;
%end;
% film n, k, d(nm), sub n,k
P=[nx kx d nsub ksub];
%  Calculate PSI, DEL
N1=P(1)-P(2)*i;
Ns=P(4)-P(5)*i;
THETA1=sqrt(N1^2-((sin(W1))^2));
COST1=THETA1/N1;
THETA2=sqrt(Ns^2-((sin(W1))^2));
COST2=THETA2/Ns;
B=2*pi*P(3)*THETA1/W2;
R0P=(N1*cos(W1)-COST1)/(N1*cos(W1)+COST1);
R1P=(Ns*COST1-N1*COST2)/(Ns*COST1+N1*COST2);
R0S=(cos(W1)-THETA1)/(cos(W1)+THETA1);
R1S=(THETA1-THETA2)/(THETA1+THETA2);
RP=(R0P+R1P*exp(-2*i*B))/(1+(R0P*R1P*exp(-2*i*B)));
RS=(R0S+R1S*exp(-2*i*B))/(1+(R0S*R1S*exp(-2*i*B)));
RHO=RP/RS;
tanpsi=abs(RHO);
cosdel=cos(angle(RHO));
f=(cosdel-dat(2))^2+(tanpsi-dat(3))^2;
```

Appendix B

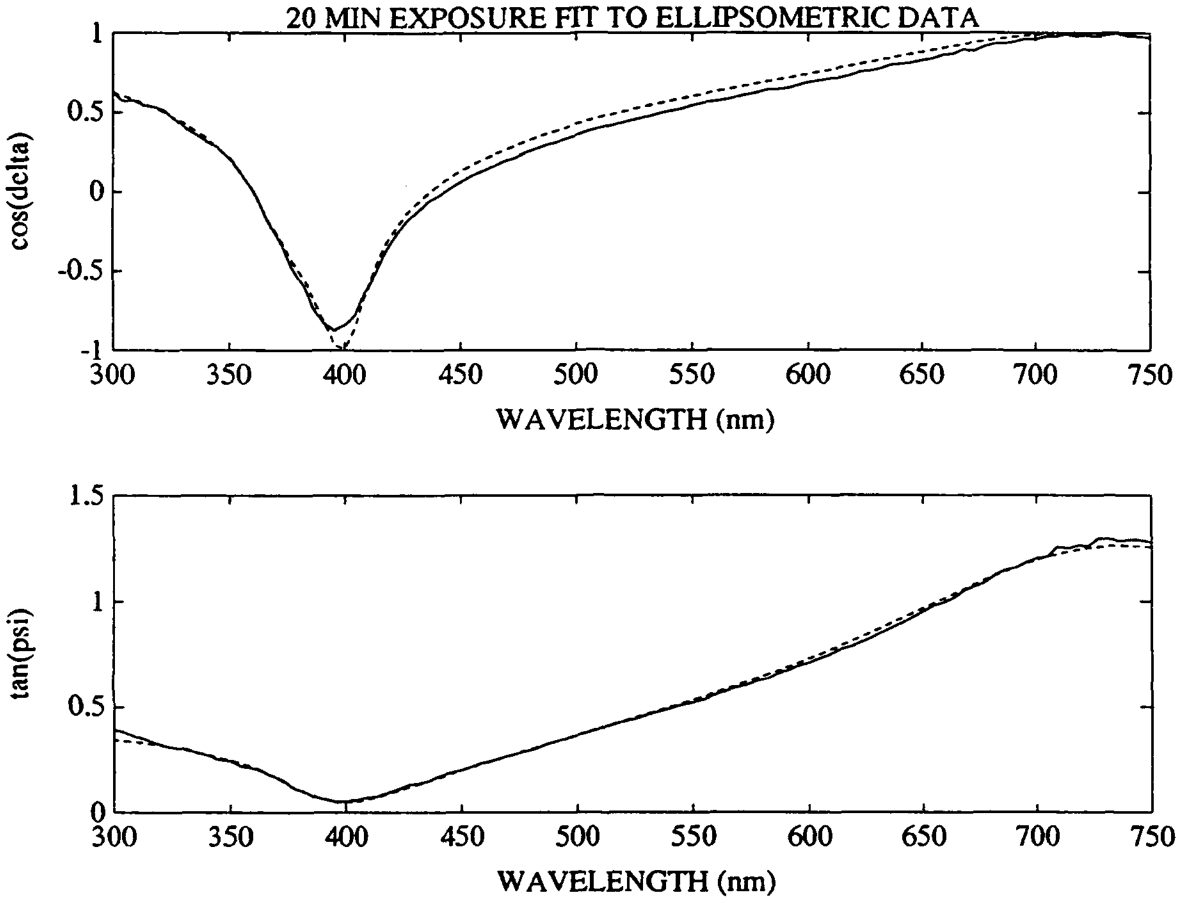
Computer Fitting to Raw $\cos\Delta$ and $\tan\psi$ Data

The plots presented in this appendix are an example of the SIDISP code output. The solid lines represent the raw ellipsometer data, and the dashed lines represent the theoretcial curve computed by the code. Each set of plots show various exposures times of a polythiophene film to UV radiation (254 nm, 35 mW/cm^2). Because the computed values for the $\tan\psi$ cuve converge more quickly to the raw $\tan\psi$ data, the fitting process was ended once convergence for this data was achieved within instrument limited error of 2%. As a result, the $\cos\Delta$ curves may not be within the 2% error in all regions of the spectrum.



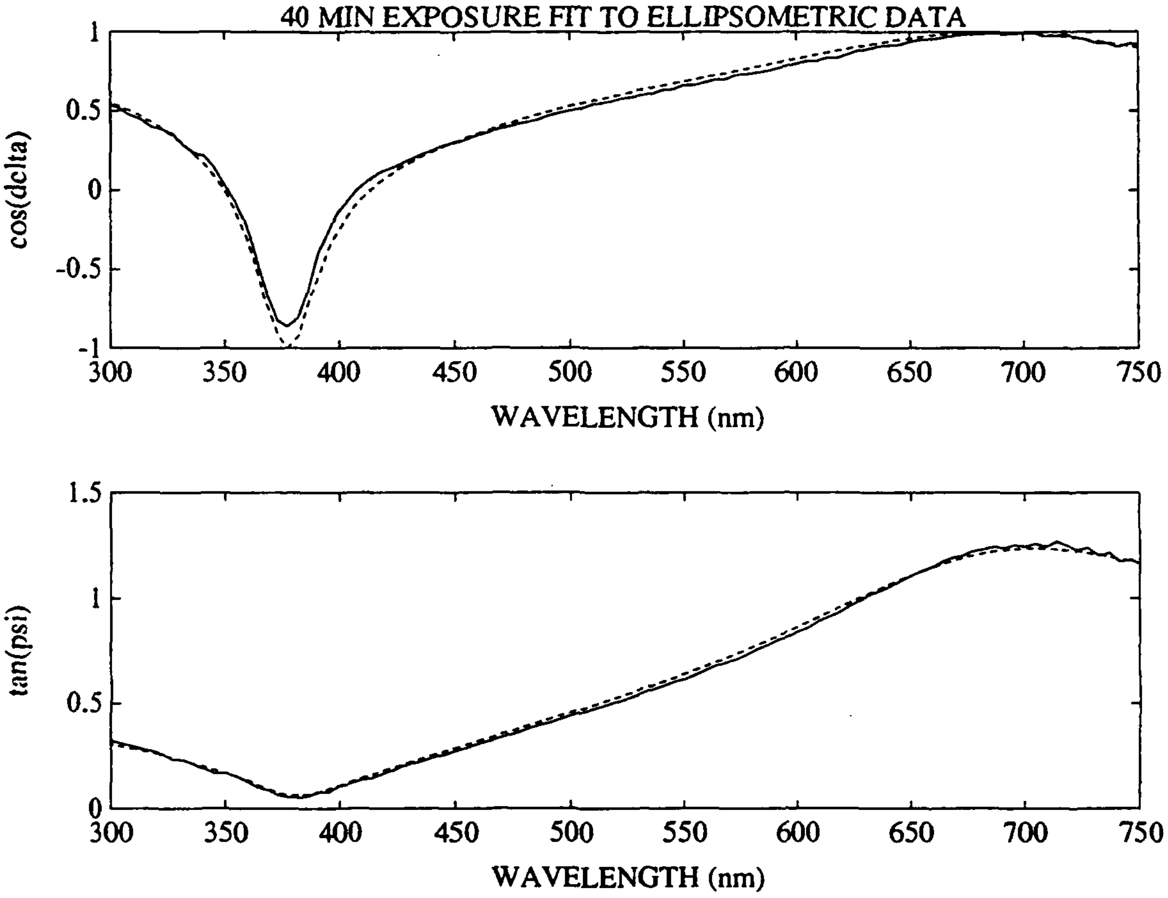
Unexposed Parameter Values

n(800 nm) = 1.67
n(600 nm) = 1.7
n(400 nm) = 1.735
k(500 nm) = 0.055
k(300 nm) = 0.26
d(nm) = 151


20 MIN EXPOSURE FIT TO ELLIPSOMETRIC DATA

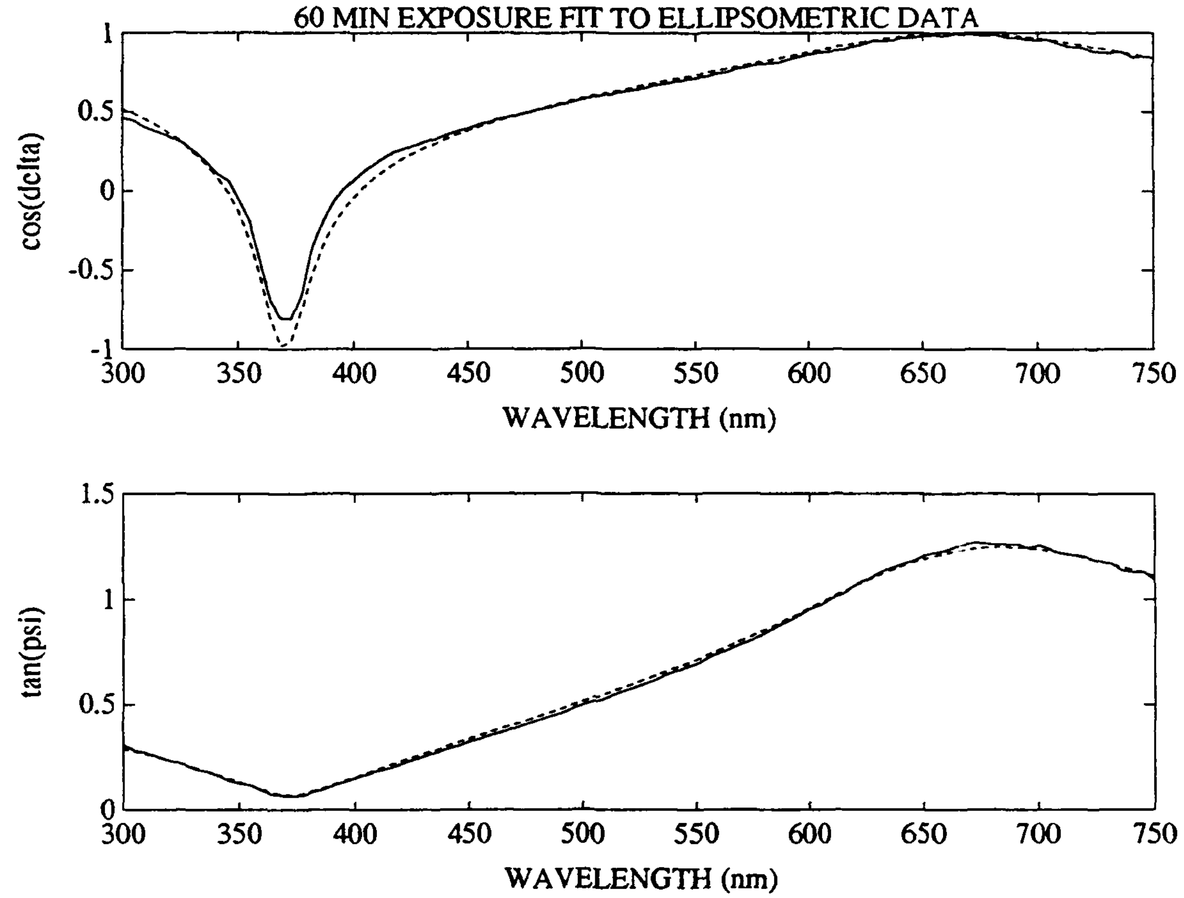
<u>20 Minute Expsosure Parameter Values</u>

n(800 nm) = 1.679
n(600 nm) = 1.713
n(400 nm) = 1.738
k(500 nm) = 0.12
k(300 nm) = 0.25
d(nm) = 133



40 Minute Exposure Parameter Values

n(800 nm) = 1.687
n(600 nm) = 1.713
n(400 nm) = 1.732
k(500 nm) = 0.12
k(300 nm) = 0.25
d(nm) = 126



<u>60 Minute Exposure Parameter Values</u>

n(800 nm) = 1.682
n(600 nm) = 1.705
n(400 nm) = 1.724
k(500 nm) = 0.12
k(300 nm) = 0.25
d(nm) = 123

Bibliography

1. Azzam, R. M. A. and N.M. Bashara. Ellipsometry And Polarized Light. New York: North-Holland, 1977.

2. Brittain, E. F. H. et al. Introduction to Molecular Spectroscopy: Theory and Experiment. New York: Academic Press, 1970.

3. Dienstbier, M. et al. "Study of UV Laser Ablation by Optothermal Methods," Applied Physics B, 51: 137-140 (1990).

4. Haaland, Peter and James Targove. "Flowing afterglow synthesis of polythiophene films," Applied Physics Letters, 61 (1), (6 July 1992).

5. Haaland, Peter, Captain, USAF, Associate Professor, Thesis Advisor, Department of Physics, Air Force Institute of Technology, Wright Patterson Air Force Base, OH. Personal Interviews, 1992.

6. Koran, G. and U.P. Oppenheim. "Laser Ablation of Polymers in Pressurized Gas Ambients," Applied Physics B, 42: 41-43 (1987).

7. Kutsche, Carl; Jim Targove; Peter Haaland. "Microlithographic Patterning of Polythiophene Films." Journal of Applied Physics, submitted June 1992.

8. Singleton, D.L. et al. "Dynamics of Excimer Laser Ablation of Polyimide Determined by Time-Resolved Reflectivity," Applied Physics B, 50: 227-230 (1990).

9. Skotheim, Terje A. Handbook of conducting Polymers. vol 1. New York: Marcel Dekker, Inc., 1986.

10. Stiller, Marc. "Excimer laser fabrication of wave guide devices," SPIE Proceedings, 1377: 73-78 (1990).

Vita

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Materials possessing strong chi(3) optical properties such as Polythiophene are sought for the production of optical switches. Polythiophene thin films produced by plasma enhanced CVD show a surface rms roughness of 10-15 angstroms over single square micron areas which is acceptable for wave guiding in the near IR. This reasearch investigates permanently changing the optical properties of such a thin film by exposure to UV radiation(254 nm, 35 mW/sqcm), known as photo bleaching, in hope of creating a refractive index boundary for use in total internal reflection. After 60 minutes exposurethe refractive index shows a slight increase of 0.9% at 800 nm. The extinction coefficient shows a change of 218% at 500 nm. There is a corresponding increase in absorbance of 160% at 500 nm, but this increase is seen to drop off at 700 nm. The thin films are observed to lose thickness exponentially over time as a result of out-gasing in the film. It is not known if the chi(3) property is affected after the 60 minute UV exposure.

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