DETERMINING THE EXTREME ULTRAVIOLET CONSTANTS OF THORIA BY SPECTRAL ELLIPSOMETRY.

by

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ABSTRACT

DETERMINING THE EXTREME ULTRAVIOLET CONSTANTS OF THORIA BY SPECTRAL ELLIPSOMETRY.

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We use spectroscopic ellipsometry on thin films of thorium oxide deposited on silicon wafers to determine the optical constants (n and k) of thorium oxide more precisely over the spectral range of 0.73-9.43 eV. We particularly focused on the 6.5-9.43 eV range. We found evidence of indirect band gaps at 7.5 and 7.9 eV. Our measurements also support the theory that the direct band gap is at 5.9 eV as claimed by William R. Evans in his senior thesis rather than 4 eV as clamed in T.R. Griffiths, and James Dixon (J. of Chemical Society, Faraday Transactions, 88, 1149-1160, 1992, and ref. cited within, especially ref. 2-9).

ACKNOWLEDGMENTS

I would like to thank my parents for all the support, help and encouragement they have given me all my life and while I worked on this project in particular. I would also like to thank my advisor, Dr. David Allred, for his guidance, expertise, and help. I would like to thank the other members of the BYU thin film group. The previous research they did and the questions they asked formed the foundation for this project. Also I would like to acknowledge Tom Tiwald and the J.A. Woollam company for giving us constant support and assistance throughout this project.

Contents

Chapter 1

Ultraviolet and Extreme Ultraviolet Optics

1.1 The push to shorter wavelengths

In the last 20 years, placing telescopes in orbit has opened to observation a world of nonvisible electromagnetic radiation that is blocked by the atmosphere. By observing the universe in the extreme ultraviolet (EUV) astronomers are gaining a greater understanding of many objects. Advances in the extreme ultraviolet are also of particular interest in computer-chip manufacturing, since the size of circuit features cannot be made smaller than the wavelength used in the lithographic process. Moving into the EUV has the potential to push back this limitation by an order of magnitude.

Just as an accurate understanding of the optical properties of glass and certain metals is essential to make quality lenses and mirrors for visible light, an accurate understanding of the optical properties of certain key materials like thoria is needed to make devices that can work well in the EUV. Thoria has a near-normal-incidence reflectance twice as high as standard materials at about 200 eV and has been investigated as a reflector at other photon energies throughout the extreme ultraviolet.

1.2 Properties of thoria in optics and EUV

Thoria has characteristics that make it useful for working with EUV. Thoria is more transparent in the optical and near UV spectral range than the other fluorite oxides. Several of its uses are based on this fact, including optical coatings and candoluminescence, which is the ability to thermally emit light at higher frequencies than would be given by a standard blackbody at the same temperature [1]. The optical properties of the oxides and fluorides of heavier group IV metals have also been studied for application as gamma radiation detectors and phosphors [2]. Thoria is the only stable oxide of thorium, and thorium oxidizes readily. Therefore, thorium and its alloys will likely have a thoria coating if exposed to oxygen. This will of course influence the optical properties.

1.3 EUV thin film research at BYU

Dr. Allred, Dr. Turley at BYU, and the students they work with, have a long track record of making EUV thin films. We became interested in using thoria for EUV and x-ray mirrors. However, when out group started researching thoria, it became apparent that the optical properties of thoria were not well known. We determined to measure the optical constants of thoria ourselves. For his senior thesis, William Evans used an ellipsometer at BYU to measure the optical constants of thoria from 1.2 to 6.5 eV which is the full range of the BYU ellipsometer. However, much of the interest in thoria (including the mirrors) centers on higher photon energies. To measure the constants of thoria at higher photon energies, we sent samples to the

J.A Woollam company. There, Tom Tiwald measured our samples on an ellipsometer with a wider spectral range. And for my capstone project we analyzed the data and determined the constants for thoria in the 6.5-9.4 eV range. We also obtained and analyzed data in the 0.73-6.5 eV range to support the conclusions made in Evans' thesis.

1.4 Ellipsometry

The optical properties of a material can be represented by a single complex number, $N = n + ki$ called the index of refraction. n determines the phase speed of the light in the material and k determines how strongly the material absorbs light. Ellipsometry is very good method for measuring these constants. Ellipsometry works by reflecting circularly polarized light off of a sample. When light is reflected at nonperpendicular angles, different polarizations will be reflected in different amounts. Since some components of the circularly polarized light get absorbed more than others, the light becomes elliptically polarized. By measuring the ellipticity of the reflected light we can calculate the optical constants.

Chapter 2

Experimental Details

2.1 Thin-film production

For our ellipsometry measurements we used silicon wafers coated with a thin layer of thoria. The thoria layers are thin enough for light to reflect off the silicon substrate. This allows us to measure how thoria absorbs light. The films were deposited in a vacuum chamber by sputtering. Sputtering works by bombarding a target of the material we wish to deposit with ions. The ions knock atoms out of the target, in our case thorium and oxygen atoms. These atoms travel through the chamber and are deposited on the substrate to form a coating.

The samples were deposited by reactive, radio-frequency (RF), magnetron sputtering using a US Inc. Mighty Mak 4-inch gun powered with a Plasmatherm 3 kW RF power supply. The target was a 101-mm diameter, 6.5-mm thick thorium disk. The silicon substrates were placed about 0.25 m from the target. The vacuum chamber was pumped down to less than $1 * 10^{-2}$ Pa (0.1 mtorr). A small amount of oxygen (about .33 Pa) was added to react with the thorium and form thorium oxide during the sputtering process. A small amount of argon was also added to the system. The total pressure was about 1.1-1.3 Pa (8-10 mtorr). Under these conditions the thoria deposited at about 1 nm/min.

The substrates were standard polished silicon wafers (100 orientation). Typical rms roughness for such wafers is 0.2 nm over 100nm by 100nm area. This was determined by atomic-force microscopy (AFM) on similar wafers. The sample's native silicon dioxide layers were estimated to be 2.0 nm thick.

2.2 Thin film characterization

To analyze the ellipsometry data, it was necessary to know the thickness of the thoria films. A quartz-crystal monitor was used while the films were deposited. An electric current caused the quartz to vibrate at its resonance frequency. The quartz was positioned so that it would gain a layer of thoria just like the samples. The added mass lowers the quartz's resonance frequency. This new frequency is compared with the frequency of another quartz crystal. From this we calculate the change in mass and, using the density of thoria, we can also determine its thickness.

We measured the near grazing x-ray reflection (XRR) spectrum of the reflectance sample to determine the thickness. We used a x-ray diffractometer (Scintag model XDS 2000), with Cu-K radiation (0.154 nm). To determine the thickness of the ThO_2 layers, we compared the position of interference minima in the measured XRR spectrum with those modeled for a range of Th thicknesses on 2 nm of SiO_2 (typical thickness of native oxide) on Si substrates. [2]

We also determined that the films were polycrystalline thoria with a preferred (111) and (110) orientations by measuring the x ray scattering of the two thickest films over the range 15° to 90°.

Surface roughness was measured with a Veeco Instruments Dimension 3100 Atomic

Force Microscope. The surface roughness, measured on a 1-micron by 1-micron area and averaged over two spots on each of four samples, was 5.1 ± 0.4 nm over 100nm by 100nm area and appeared to be independent of thickness. This value for roughness was used in modeling the films' ellipsometric data. [2]

2.3 Ellipsometry Instrument

The optical constants were first measured between 1.24 and 6.5 eV using a John A. Woollam Company M2000 Spectroscopic at BYU. Ellipsometric reflectance data was obtained on the silicon samples at angles between 67° and 83° from normal, taking measurements every degree. Normal-incidence transmission data was taken on similar samples deposited on quartz substrates instead of silicon. This data is extremely important for constraining k.

Optical constants were modeled with the WVASE software provided with the ellipsometer. We modeled the samples as a 1-mm Si substrate with a 2 nm SiO_2 layer coated by ThO_2 with a layer of roughness set at the root-mean-squared value determined by AFM. Initially, the thickness of the ThO_2 was set to the value given by XRD and then allowed to vary slightly to achieve a better fit. Allowing the thickness to vary like this allowed us to fit the measured data better and achieve a better measurement of thickness than from XRD alone. It also allowed us to measure the optical constants much more precisely. A "mean square error" (roughly equivalent of χ^2) less than 2.5 for the modeled optical constants was obtained. This means that the model fit the data very well. [2]

Extreme ultraviolet light is strongly absorbed by air and water vapor. Since the ellisometer at BYU operates in air it cannot take measurements above 6.5 eV. To get measurements at higher energies, we sent the samples to the J. A. Woollam Company.

Tom Tiwald, who works at J. A. Woollam, took measurements between .73 and 9.43 eV on a J. A. Woollam Company VUV-VASE. This ellipsometer sits in a chamber that is purged with nitrogen, which allows it to take measurements in the EUV. It uses both a deuterium and xenon source and both a photomultiplier tube and photodiode detectors to achieve such a wide spectrum. Measurements were taken at 65, 75, and 0 degrees from normal. Once again, constants were modeled using WVASE. The samples were modeled as a 1-mm-thick-silicon substrate coated with a layer of thoria. The roughness and thickness were again set to the levels given by the AFM and XRD then allowed to vary a little to achieve a better fit. A mean-square-error (χ^2) less than 3 was achieved.

Chapter 3

Results and Discussion

3.1 The Index of Refraction

In terms of the indices of refraction, ϵ_1 and ϵ_2 are respectively $n^2 + k^2$ and $2nk$. The values for n and k can thus be determined from ϵ_1 and ϵ_2.

Fig. 3.1 shows the real component of the dielectric constant and Fig. 3.2 shows the imaginary component of the dielectric constant. Both figures show the modeled values for three different samples and four measurements, as determined by fitting the ellipsometric data with a parametric model containing several oscillators, most based on the Lorentz approach. Markers (circles, squares, diamonds and X's) are placed every 10 data points. Note that ϵ_2 has two peaks. This shows up as two absorption features in k and α plots below.

Fig 3.3 gives the fit values of n and k from 0.73 to 9.43 eV for three different samples and four measurements. As one can see in the figure, except for the 357 nm sample, the refractive index measurements agree very well with each other.

Generally, n increases with energy. A maximum, followed by a drop in n is anomalous dispersion. For the three materials shown, the maxima lies between 7.2

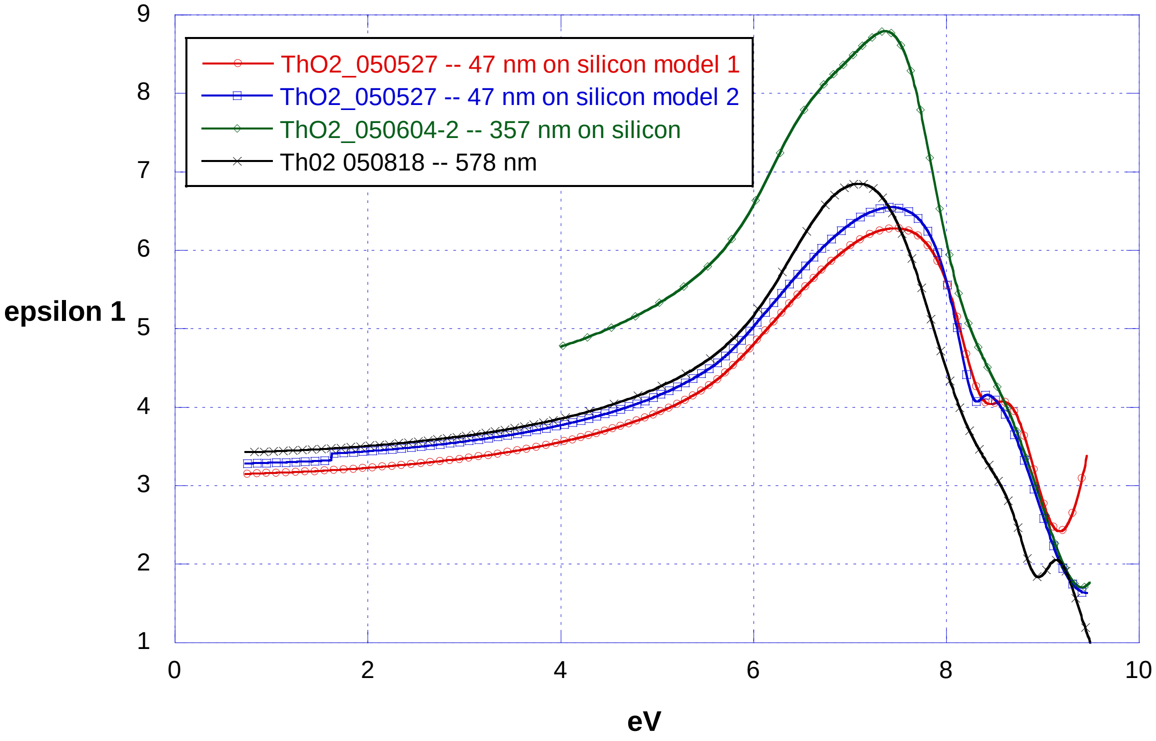

Figure 3.1

Thoria's dielectic constant ϵ_1 plotted against photon energy

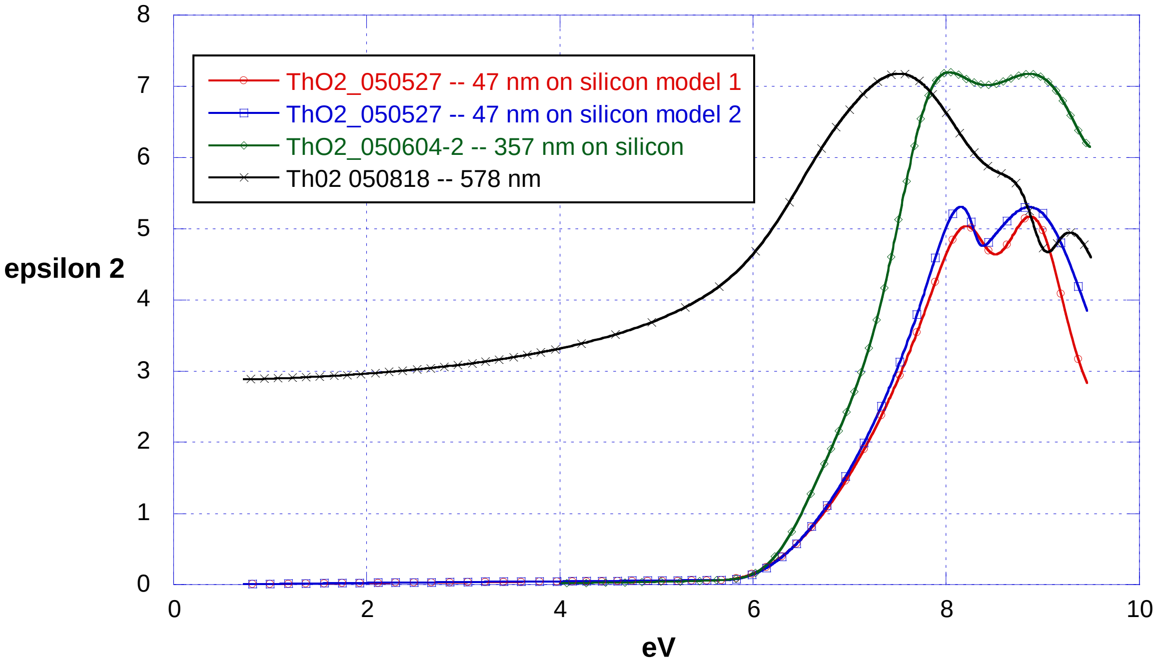

Figure 3.2

Thoria's dielectic constant ϵ_2 plotted against photon energy

to 7.8 eV, with the thickest sample showing the lowest energy maximum. After the region of fall there should be another area of partial recovery in n. A pattern of gradual rising index, followed by steeper falling, followed by recovery is characteristic of Lorentz oscillators. Variations on Lorentz models are used in parameterizing the data. In Fig 3.3 we see that in two of the measurements, n starts increasing again at the end of the range while the others do not. The presence or lack of this feature could be an artifact of the fit.

3.2 The Absorption Coefficient Alpha

Insulators like thoria can be treated as wide band gap semiconductors. For determining the band gaps and thinking about the physical properties of thoria, it is standard to work with the absorption coefficient, *alpha*. The absorption coefficient gives the

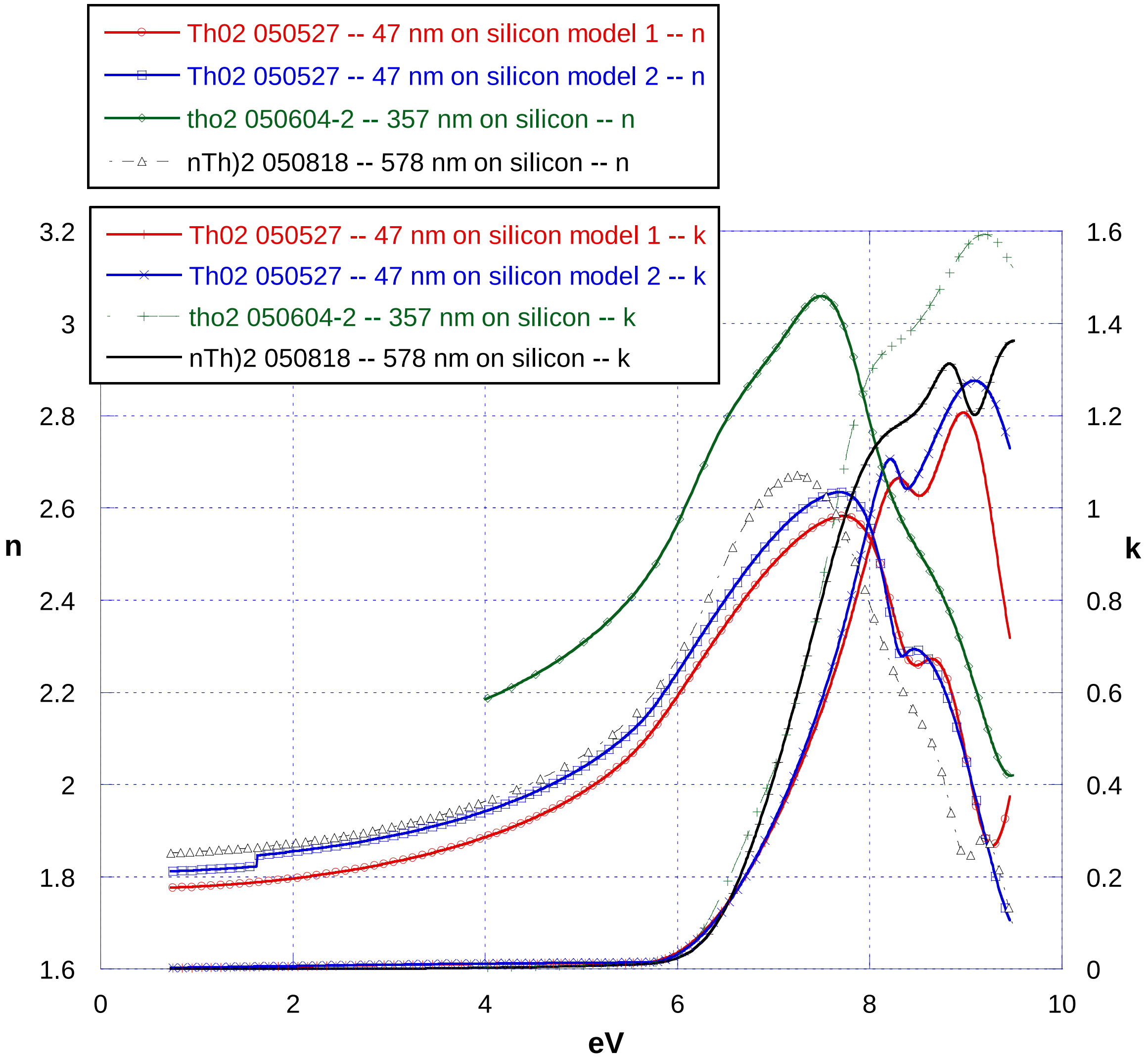

Figure 3.3

Thoria's optical constants n and k plotted against photon energy

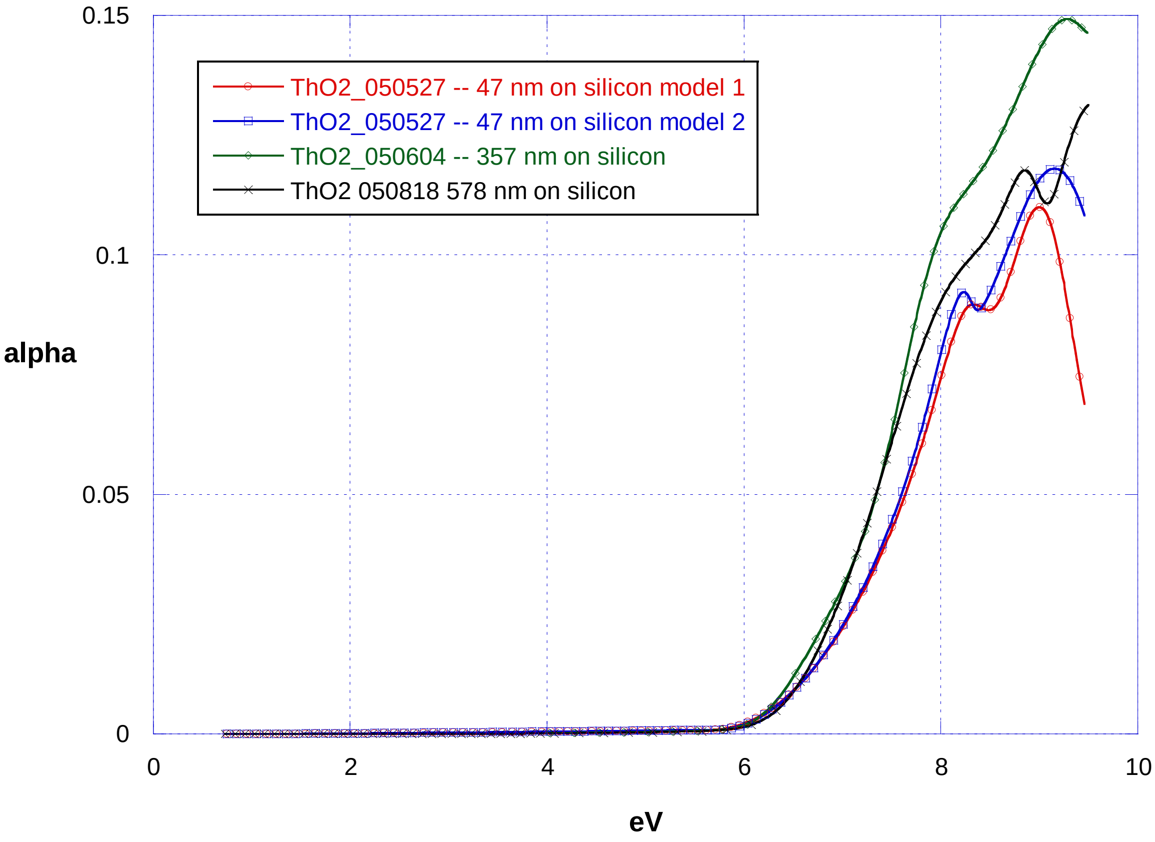

Figure 3.4

Thoria's α plotted against photon energy

intensity of a beam of light traveling through a material by the formula $I_1 = I_0 e^{(-\alpha * d)}$ were I_0 is the starting intensity and d is the distance traveled through the material. It is related to k and λ by the equation $\alpha = 4\pi k/\lambda$.

3.3 The band gap

Photons are absorbed by interacting with electrons. An electron absorbs the energy of the photon and moves to a higher energy state. To absorb the photon there has to be an empty state with a transition energy equal to the photon energy. Absorption properties are affected by a band edge. For semiconductor materials like Si and Ge, the absorption, which corresponds to the indirect gap, is less than about 10^{-5} nm^{-1}. Our samples are too thin to measure the absorption of such an indirect band gap. Some absorption is seen in this region, however. This is most likely due to isolated states in the forbidden gap.

Previous studies have found evidence that thoria possess a direct band gap at 5.9 eV [2], and thin-film samples are well suited to measurement of this feature. Absorption constants range in the 10^{-3} nm^{-1}, which can be measured with elliposmetry.

It can be shown that the probability of a photon imparting energy to an electron is directly proportional to $(\hbar\omega - Eg)^{1/2}$ were Eg is the minimum energy needed to make the jump. [3] Since the direct band gap easily dominates any other absorption processes going on in the range, it appears as a roughly straight line when $\alpha^{1/2}$ is plotted.

3.4 Interband absorption

It can be easily seen from the above graphs that the direct band gap is far from the strongest absorber. Electron states are often plotted by plotting the k vector of the state against energy. The k vector is related to the momentum of an electron in that state. As discussed above, the direct band gap describes transitions that occur when photons carry electrons from the maximum of the valence band in momentum space to the minimum of the conduction band which lies directly above the maximum. Given the right amount of energy, electrons can move straight up in the k-space plot because the new state has the same k vector and thereby the same momentum. However, the direct band gap is just a point, or small range of points, where electrons can cross. It generates a relatively small amount of absorption, in this case from about 5.7 to 7.3 eV.

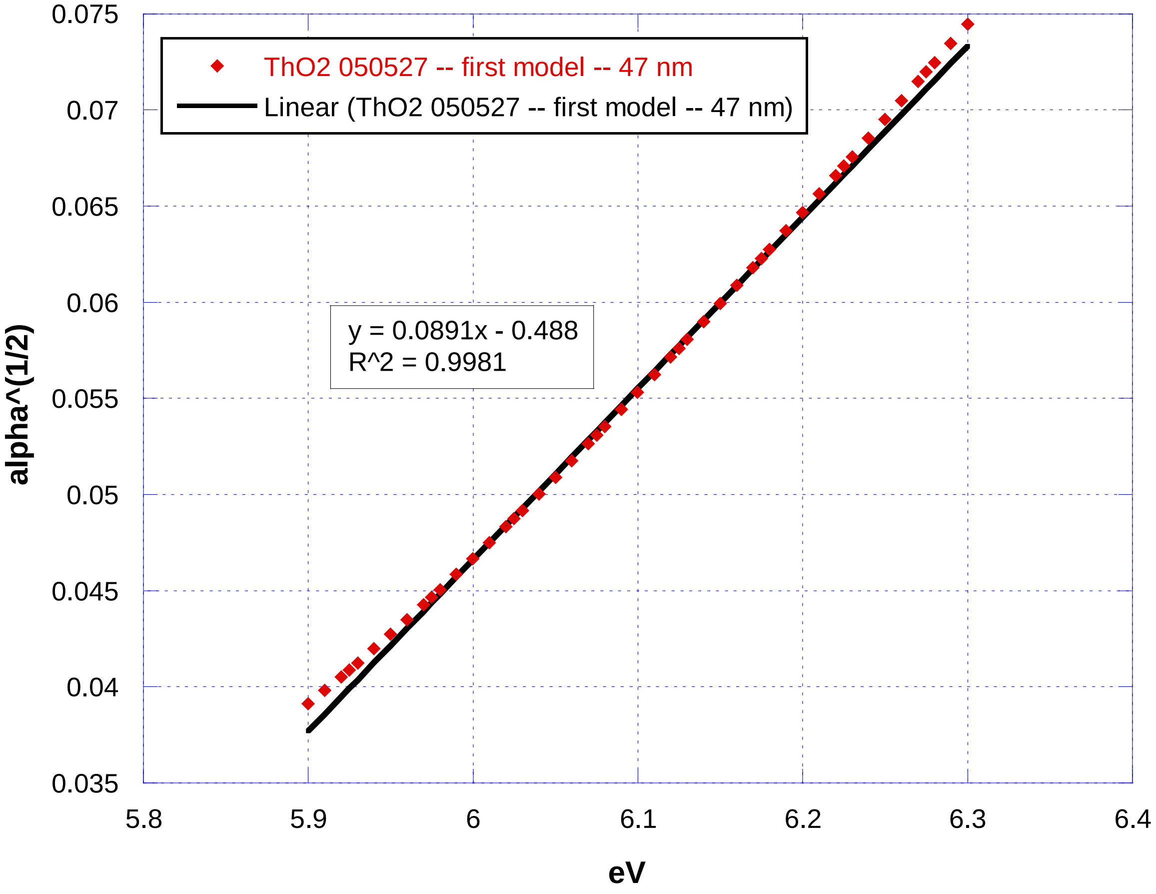

Figure 3.5

Thoria's band gap appears as a straight line when $\alpha^{1/2}$ is plotted. A trend line has been fitted and the formula is displayed on the graph. By extrapolating this line at the x axis we get 5.5 eV for the band gap energy

What do the two large absorption features at 8 and 9 eV in figure 3.4 correspond to? The rate at which electrons absorb photons is directly proportional to the number of electrons that can absorb the photon and the number of unoccupied states. One way to account for the maxima in figure 3.4 is to say that there are maxima in the joint density of states. This can occur if there are parallel lines between filled and unfilled bands in k vs. E plots. This means that there are photon energies which can excite electrons possessing a large number of k values. These are called interband absorption zones and seen in materials like Si. They may be responsible for the extremely high absorption rate we see in thoria at higher energies.

By plotting trend lines and extrapolating where they cross the axis, we estimate that the first interband absorption zone is at 7.5 eV and the second interband absorption zone is at 7.9 eV

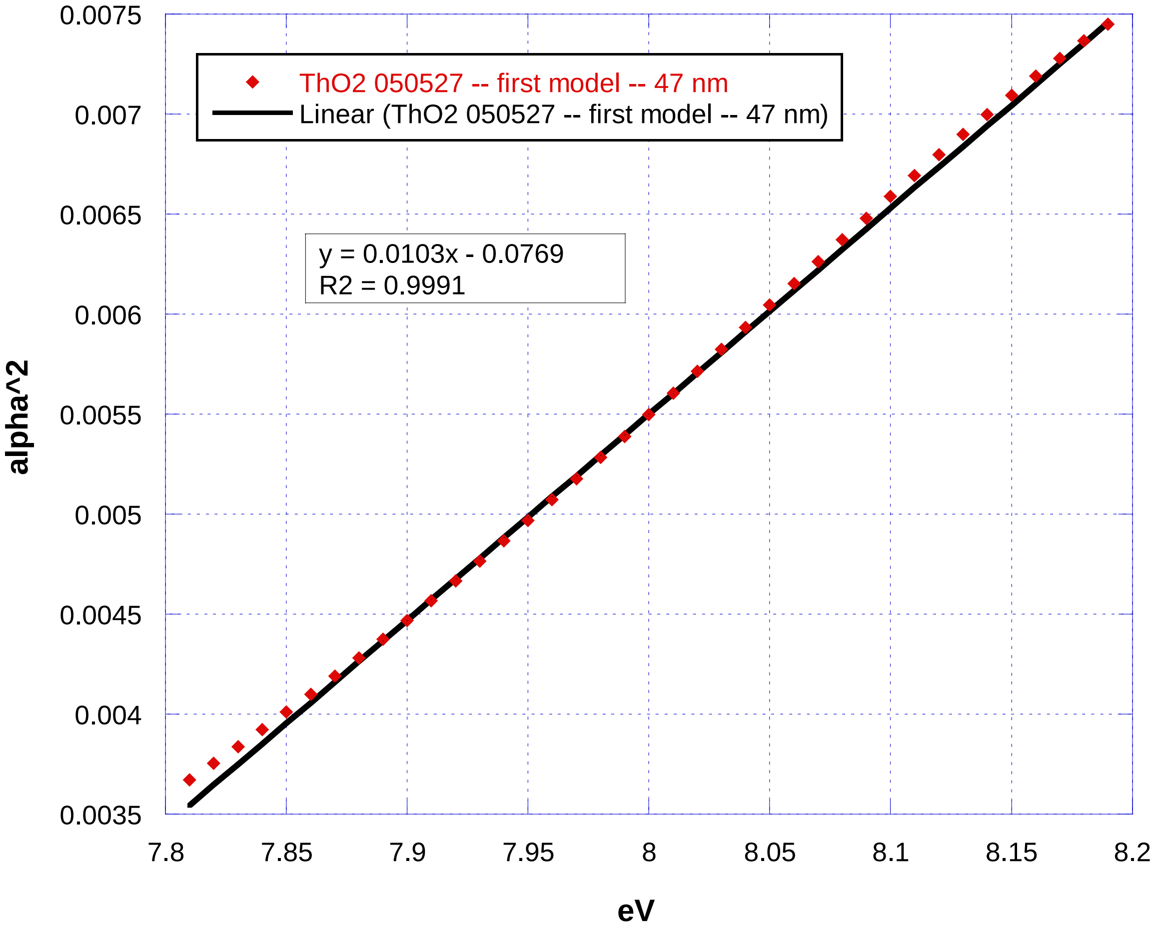

Figure 3.6

Thoria's first interband absorption zone appears as a straight line in α^2. By extrapolating the trend line at the x axis we get 7.5 eV for the absorption zone.

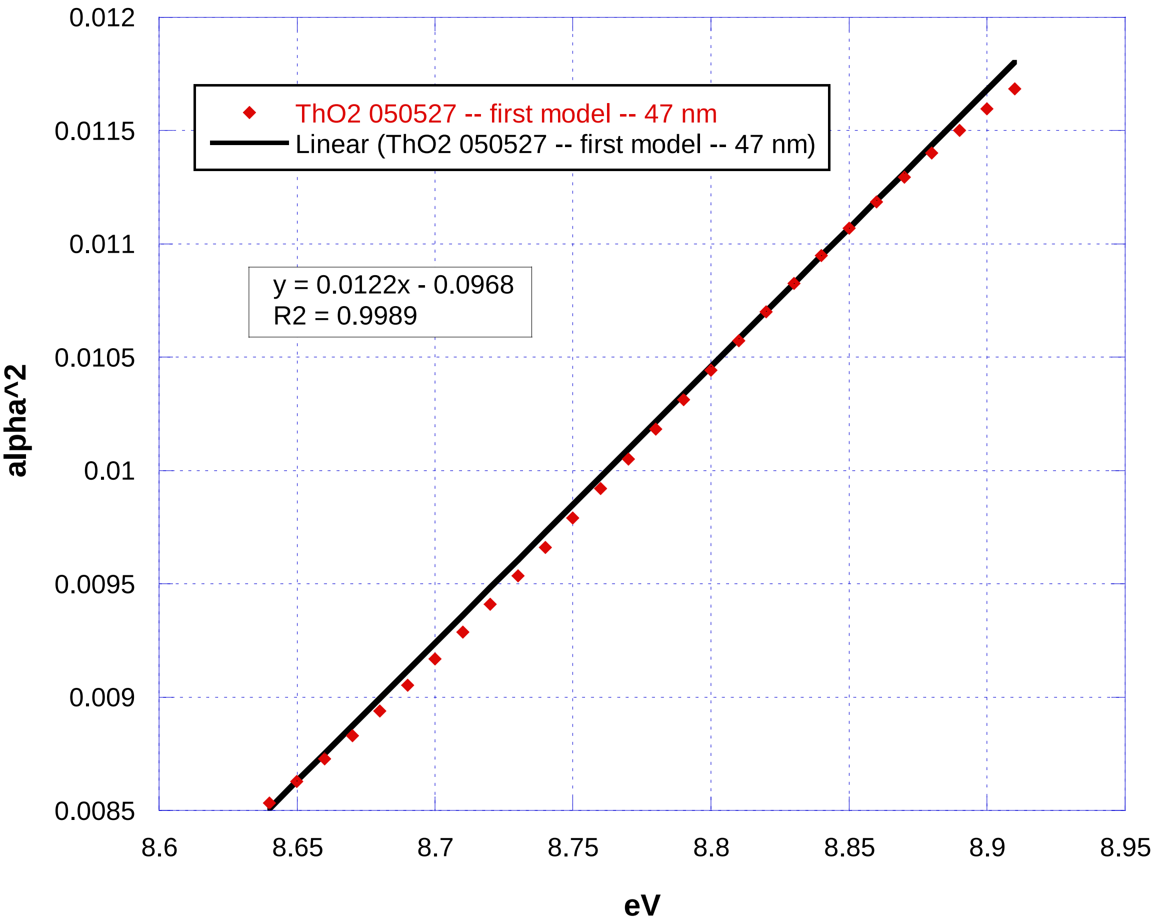

Figure 3.7

We calculate 7.9 eV for thoria's second interband absorption zone

Chapter 4

Conclusion

We have made great strides in increasing our understanding of thoria and its optical properties. We hope that these measurements will find use both here at BYU and in other places where people wish to use thoria in the EUV. However, this line of research is far from complete. Further research will be needed to determine with greater confidence that we are seeing interband absorption. Dr. Allred and Dr. Turly's group is interested in making mirrors over a range of frequencies in the EUV and soft x ray. Further measurements on different instruments will be needed to determine the optical constants above 9.43 eV.

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