Characterization of Ga_2O_3 Single Crystal and Thin Film

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Abstract

Ga_2O_3 is a semiconductor with many yet unknown properties. Among its most interesting features are the fact that it is transparent, has a high band gap of 4.9eV, and yet remains conducting.Ga_2O_3 is solar-blind, remaining transparent in the visible range. This, combined with its conductivity makes it a potential material for a UV detector device and a solar cell coating. Characterization of Ga_2O_3 was done by using x-ray photoelectron spectroscopy (XPS), UV-visible spectroscopy (UV-Vis), and ellipsometry. XPS was used to identify the surface stoichiometry and nature of the interface when Ga_2O_3 was coated with a thin layer of Pd. Ga_2O_3 has an anisotropic crystal structure, leading to anisotropy in both its optical constants and conductivity. Ga_2O_3's anisotropy was observed with UV-Vis, and confirmed with Ellipsometry. Ellipsometry also made progress in identifying Ga_2O_3's complex index of refraction and dielectric constants in single crystal and in both amorphous and crystalline thin films. Additionally, ellipsometry was able to measure thin film thickness.

1 Introduction

Semiconductors have become familiarly known as an essential part of the modern world. Their device potential is immense, and only through careful study of physics have we been able to create devices which maintain life as we know it. Since many of these devices have been and will likely continue to utilize Silicon, it is important to find other materials which can be easily integrated into a Si device. Many semiconductor compounds have been discovered which do just that, and among the most well understood are in the III-V group. However there remains a class of III-VI materials which are fundamentally different and worthy of further study. Ga_2O_3, from the III-VI group, is particularly interesting for its device potential. Ga_2O_3 is both transparent and conducting with a relatively high band gap. Therefore, potential applications seek to exploit those properties. Since Ga_2O_3 is a solar-blind photoconductor, it can be used as UV-detector. Another potential application is doped Ga_2O_3 utilized as a transparent yet conducting layer on solar cells. Ga_2O_3's crystal structure, as seen in Figure 1 is anisotropic, and many properties of interest are related to its anisotropy.

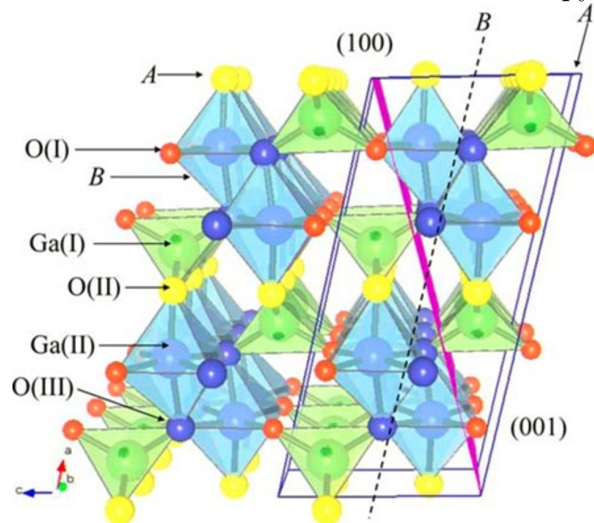

Figure 1: Structure of β-Ga_2O_3 [1]

Three experiments were used to better understand both Ga_2O_3 single crystal and thin film. XPS was first done as an introduction to a chemical compo-

sition identification, and depth profiling. Then, Ga_2O_3's optical properties were explored with UV-Visible Spectroscopy and Ellipsometry. Ga_2O_3's optical constants are closely related to its conductivity and transparency, but also depend on the anisotropic nature of the crystal structure. Therefore, examining optical constants in different orientations of Ga_2O_3's optic axis is a great area of interest.

2 Experiment

XPS

XPS is a surface analysis technique which attempts to identify compounds found within a few angstroms from the surface. A PHI VersaProbe Scanning XPS Microprobe was used to take measurements. The experimental setup is such that a sample is first placed in ultra-high vacuum (UHV), which was on the order of 10^{-7} Pa. The sample is then bombarded with a focused beam of x-rays from the Al k-α. Incoming x-rays excite electronic transitions from the core and valence electrons into states above the vacuum level, from which electrons then leave the sample. A detector is placed close to the sample and the electrons move into a cylindrical hemispherical analyzer (CHA) where their kinetic energy is determined. The non-negligible distance from the sample surface to the detector is the reason the experiment must be done in UHV; electrons cannot undergo an unknown number of interactions with air particles before their kinetic energy is measured or else the experiment's information has been lost. Once the kinetic energy of the ejected electrons has been measured, information about the atoms they came from can be extracted using a conservation of energy equation.

$$E_{binding} = E_{photon} - E_{kinetic} - \phi \qquad (1)$$

Where $E_{binding}$ is the electron's binding energy relative to the Fermi level, or its chemical potential. E_{photon} is the incoming x-ray's energy, $E_{kinetic}$ is the kinetic energy measured at the CHA, and finally ϕ is the work function of the spectrometer which is measured in advance.[3] Thus, the only unknown variable is $E_{binding}$.

The XPS user specifies in which range of binding energies to look, and at what resolution. At each binding energy the number of detected electrons (counts) per second is measured, and this forms the XPS spectrum. An initial survey scan is done which probes a wide range of binding energies. Tabulated XPS spectra are used as a guide for peak identification, as well as help from the Physical Electronics (PHI) Multi-Pak software. Once an area of interest is identified, the user can do a high resolution scan for a longer time over a small number of binding energies to more accurately see the peak's features. XPS peaks originating from core levels may exhibit double peaks due to spin orbit splitting.

When doing XPS on a poor conductor, charge neutralization is of concern. A semiconducting or insulating sample develops an area deficient in electrons due to the low mobility of electrons in insulators and semiconductors. XPS spectra of a sample which is not charge neutralized can show a shift in the binding energy due to the local electric field. The shift can be most easily identified in well-known transitions such as oxygen. Thus, a high resolution scan of oxygen can be done to check to see if neutralization is needed. To remedy a buildup of positive charges, an electron gun can be directed toward the sample to provide it with additional electrons to replace the ones it is constantly losing due to photoelectron excitation.

The XPS system is also equipped with an Ar sputter gun which can clear away surface layers of the sample. This capability allows for depth profiling and is a key tool in understanding semiconductor to metal interface composition. Sputtering and depth profiling was utilized in one ex-

periment where a thin film of Pd deposited on a single crystal of Ga_2O_3 was sputtered away gradually in a small area. An XPS line scan was done across the sputtered spot to ensure Pd had been sputtered away gradually in some areas and completely in the center. The purpose of doing this was for an application in a future experiment.

UV-Visible Spectroscopy

UV-Visible Spectroscopy (UV-Vis) was explored to measure band-gaps and to see anisotropy in a single crystal of Ga_2O_3. The experiment measured the percent of light transmitted (%T) through a sample as a function of wavelength. The user can control the range of wavelengths probed, although the system has a lower limit of about 200 nm and an upper limit of about 1000 nm. The experimental setup included a monochromatized Tungsten lamp and two detectors, all encased in a box to isolate the experiment from escaping or incoming photons. One detector has the purpose of providing a reference measurement. If a slide or holder is used to suspend the sample, the same type of holder is placed in the path of the reference beam so that its effects may be subtracted out of the final measurement. Here, a metal apparatus and magnets were used to suspend the single crystal, so the path of the reference beam was left blank.

Before introducing the sample into the system, all of the holders were put in the system and a background measurement was taken. The single crystal was then introduced and the percent transmittance was measured. Finally, the thickness of the crystal was measured with Vernier calipers. After (%T) data is acquired, band gap analysis can begin. To extract the band gap, the optical absorption coefficient, α is calculated:

$$\alpha = \frac{1}{d} \ln\left(\frac{1}{T}\right) \tag{2}$$

where d is the thickness, and T, the ratio of the transmitted intensity I to the reference intensity I_0. [4] The band gap is related to the optical absorption coefficient in the following way.

$$(\alpha h\nu)^p = (h\nu - E_g) \tag{3}$$

Where hν is the energy, α is the optical absorption coefficient from equation 2, and E_g is the band gap. Finally, p is a quantity which is either 2 or $\frac{1}{2}$ based on whether the electronic transition was direct or indirect. [4] Thus to extract the band gap one must first plot $(\alpha h\nu)^p$ on the y-axis, and $h\nu$ on the x-axis. A linear fit of the curve extrapolated down to the energy axis gives the energy at which the band gap can be found. To gain experience and confidence in its applicability, UV-Vis was first done on a rutile TiO_2 single crystal. Next, a single crystal of Ga_2O_3 was measured in the system. The Ga_2O_3 crystal was rotated perpendicular to the plane of incidence in 45° increments, and a spectrum was taken at each rotation of the crystal.

Ellipsometry

Ellipsometry is a quick and non-perturbative technique which can determine many properties of a sample. Ellipsometry can be used to determine optical properties such as the complex index of refraction, and through that the dielectric constants, thickness, crystallinity, and composition. Ellipsometry works by measuring amplitude and phase changes in light that is first incident on the sample, and then light that is reflected from the sample. Incident light is strictly linearly polarized, while reflected light is elliptically polarized. Polarization of light is defined in two directions; when the electric field is perpendicular to the plane of incidence (s-polarized) and parallel to the plane of incidence (p-polarized). In linearly polarized light, the electric field is in phase only along those two directions. Elliptically polarized light rotates its polarization direction, tracing out an ellipse.

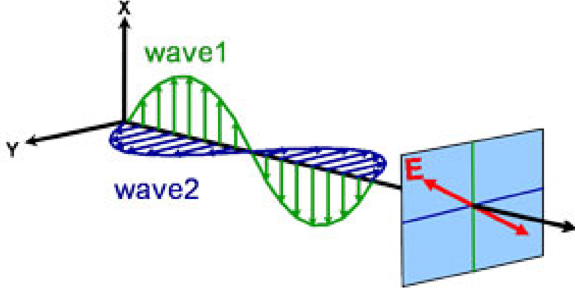

Figure 2: Linearly polarized light [2]

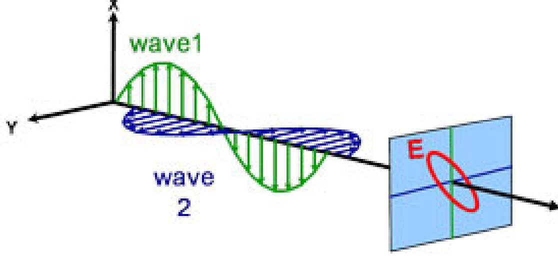

Figure 3: Elliptically polarized light [2]

The amount of p-polarized and s-polarized that is incident on the sample is known. In a generalized ellipsometric measurement, the system essentially measures the ratios of how much of the incident light kept its initial polarization and how much of it changed to a different polarization. More simply, a ratio of the Fresnel reflectivity equations, ρ is measured. This ratio is related to the light's amplitude and phase.

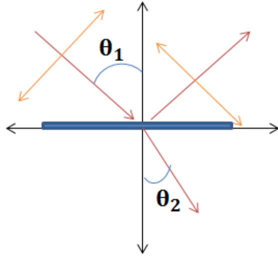

Figure 4: Path of light through a sample

$$\rho = \tan\psi e^{i\Delta} = \frac{r_p}{r_s} \tag{4}$$

Where ψ is the amplitude, Δ is the phase,

$$r_p = \frac{n_1\cos\theta_1 - n_2\cos\theta_2}{n_1\cos\theta_1 + n_2\cos\theta_2} \tag{5}$$

and

$$r_s = \frac{n_2\cos\theta_1 - n_1\cos\theta_2}{n_1\cos\theta_2 + n_2\cos\theta_1} \tag{6}$$

Of special interest are our material's optical properties including the complex index of refraction and complex dielectric constants. The complex index of refraction is defined as

$$\tilde{n} = n + ik \tag{7}$$

Where n is the familiar index of refraction, $v = \frac{c}{n}$, and k is the imaginary part. The complex dielectric constant is formulated similarly.

$$\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2 \tag{8}$$

The complex index of refraction and complex dielectric constant are related in a simple way.

$$\tilde{\varepsilon} = \tilde{n}^2 \tag{9}$$

The complex index of refraction is related to the optical absorption coefficient. A reformulation of Equation 2 gives the relation.

$$\alpha = \frac{4\pi k}{\lambda} \tag{10}$$

This relation links the complex part of the index of refraction to the band gap and the thickness.

The Ellipsometer used was made by the J.A. Woollam Company and data was acquired with the included CompleteEASE software. The measurements were done in generalized ellipsometry mode as it is the mode of choice for anisotropic samples. Generalized ellipsometry simply poulates more elements of the Jones matrix than standard ellipsometry. [5]

The system allowed for variable angle measurements, so measurements were taken at 55°, 65°, and 75° with respect to the plane of incidence. The sample was also oriented 0°, 45° and 90° with respect to the optic axis. This amount of rotation means the optical constants are over-determined.

Single crystal measurements were first carried out in an attempt to understand an ideal case. Thin films were then examined in hopes of determining their thickness and crystallinity. Thin film samples were nominally 100nm and were deposited on a Si substrate. One sample was annealed and

was thought to be polycrystalline, while the other remained amorphous.

Dielectric constants and the index of refraction can be extracted by fitting raw ψ and Δ vs eV data with a model using CompleteEASE software created by the J.A. Woollam Company.

3 Results

XPS

In the XPS experiment the Ar sputter gun was pointed toward the sample and was turned on in several locations for varying amounts of time. Slight misalignment of the gun from the target meant that the location sputtered was not the expected location. Several runs of the sputter gun were done to achieve a coherent area of sputtered surface. Immediately after sputtering a line scan consisting of 6 points was done from one side of the sputtered spot to the other.

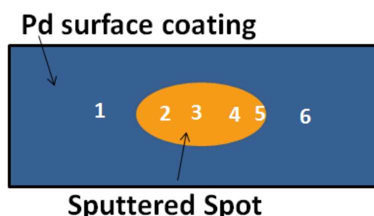

Figure 5: Cartoon of Sputtered Spot

A line scan was done across the sputtered spot in hopes of seeing a gradient, where Pd should be seen on the edges of the sputtered spot, but not in the center. At each point survey scans were done as well as high resolution scans of the Ga 2p transition, and Pd. Survey scans give a general idea of all compounds that are present, including impurities.

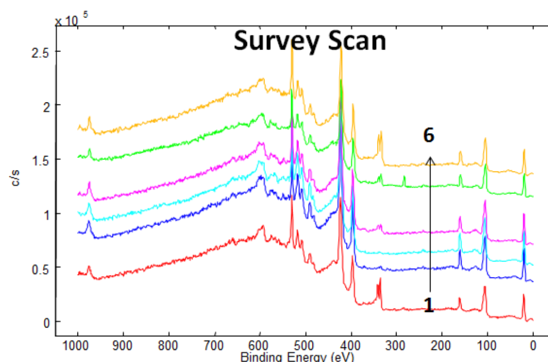

Figure 6: XPS Survey Line Scan

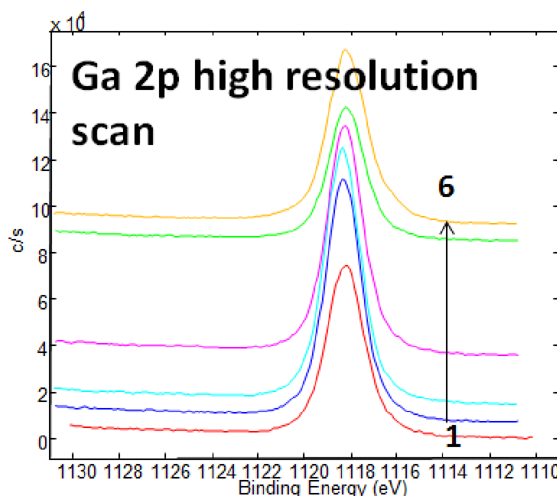

Figure 7: XPS Ga 2p High Resolution Line Scan

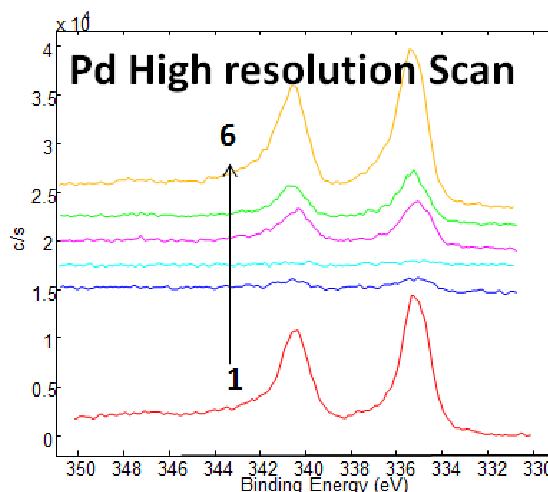

Figure 8: XPS Pd High Resolution Line Scan

Figure 5 is roughly representative of the location of the scans in relation to the sputtered spot. It was hoped to see a region

in the middle of the sputtered spot with no Pd, and that is what is seen in Figure 8. Ga 2p in Figure 7 is seen by XPS in all scans since the Pd film is thin enough for XPS to penetrate below it. The gradient of Pd achieves the experiment's goal of making a well in the Pd coating on the Ga_2O_3 single crystal. The sample will go on to an unrelated experiment now that the necessary well has been made.

UV-Vis

UV-Visible Spectroscopy was done on rutile TiO_2 single crystals on the (001) and (110) planes. There is no discernible difference in the onset energy for absorption between cleavage planes, so the (001) plane was chosen for further analysis.

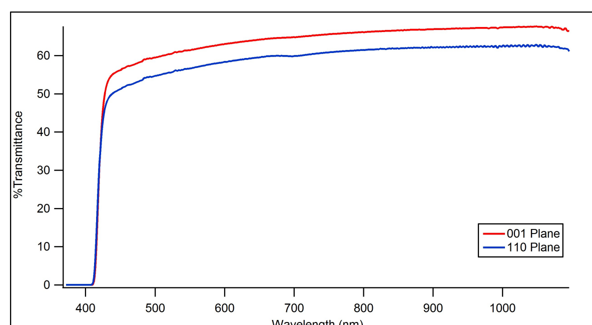

Figure 9: UV-Vis data for rutile TiO_2 single crystal

The crystal was measured to have a thickness of .66mm. The optical absorption coefficient was then calculated. Finally, Equation 2 was applied and the quantity $(\alpha h\nu)^2$ was plotted vs energy. The linear region was fit with a linear curve, and the band gap was found by extrapolating the curve down to the energy axis.

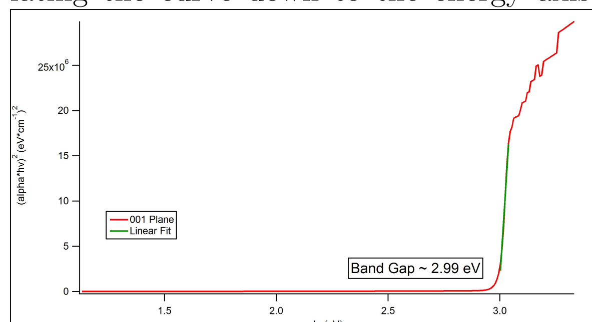

Figure 10: Linear fit to extract band gap for rutile TiO_2 single crystal

The band gap for rutile TiO_2 was found to be 2.99 eV. Next, a the Ga_2O_3 single crystal was put in the system and was rotated in the plane of the holder at 0°, 45°, 90°, and 135°. The thickness of the crystal was measured to be .48mm. The optical absorption coefficient was plotted on a log scale vs energy.

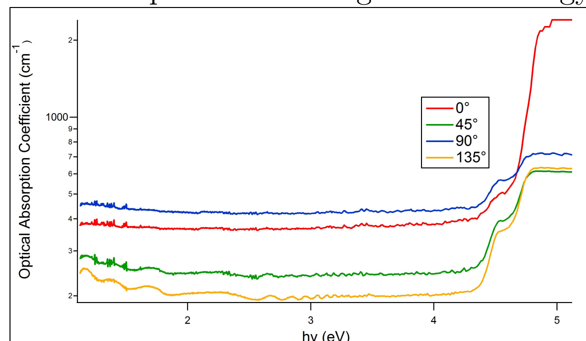

Figure 11: Optical Absorption Coefficient varying with rotations of single crystal Ga_2O_3

Although this highly anisotropic crystal could not be analyzed in the way described earlier, information can still be extracted. The varying of transmittance with rotations of the crystal verify Ga_2O_3s anisotropy with different band gaps in the two optical directions. More detailed features of the curve and band-gap extraction are a topic of further study.

Ellipsometry

Ellipsometry was first done on single crystal Ga_2O_3 in hopes of defining its properties for an ideal case. Data was taken at three orientations of the single crystal, and at three angles of incidence. One orientation of the crystal is shown in Figure 12. Without a complex analysis, it is immediately obvious that a the curves appear to be "turning on" somewhere just under 5eV, which is the location of Ga_2O_3's band gap as seen in the UV spectra.

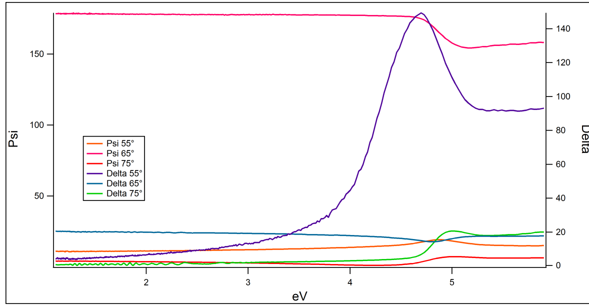

Figure 12: Raw Ellipsometry Data of Single Crystal Ga_2O_3

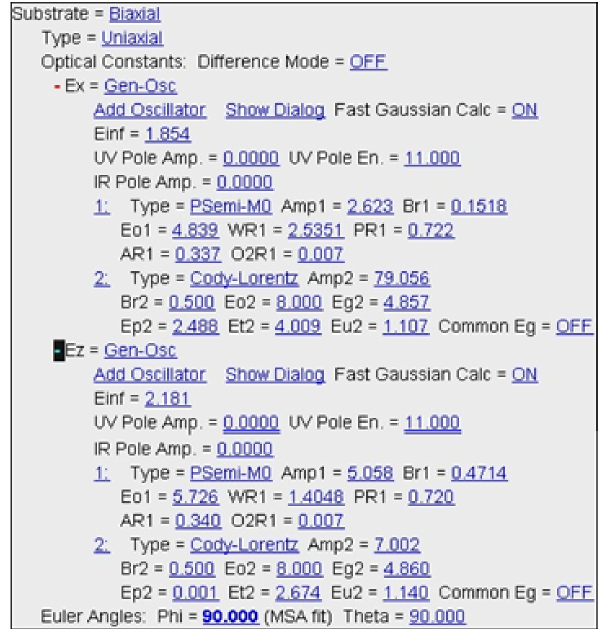

Figure 13: Parameters of the Model Fit in the CompleteEASE Software

To begin a real analysis of the optical properties, a multi-sample analysis is done which includes more than one orientation of the single crystal and all three angles of incidence. It was found that an individual crystal orientation could be modeled with great success, but applying the model to other orientations was much less successful. A model was found which did a satisfactory job of fitting all three orientations, and its parameters are seen in Figure 13. The crystal was modeled as uniaxial, and each orientation was modeled with two oscillators. The oscillators were Hersinger-Johs Parameterized Semiconductor Oscillator function (PSemi) and a Cody-Lorentz oscillator. The M0 type of Psemi oscillator is Kramers-Kronig (KK) consistent [6] KK consistency means the real and imaginary parts of the optical constants are mathematically tied, making a model fit more likely to be physically plausible.

After fitting the data, the optical constants can be extracted. Figure 14 plots the dielectric constants which result from the model described in Figure 13.

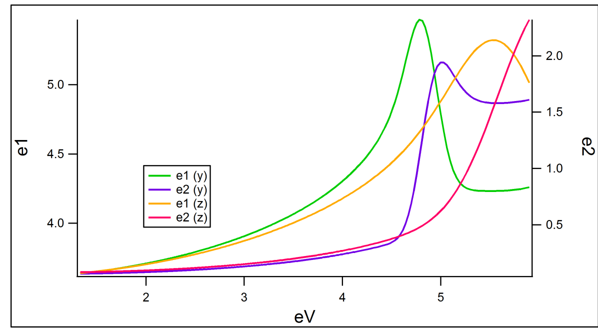

Figure 14: Dielectric Constants Of Single Crystal Ga_2O_3

To analyze thin film samples deposited on Si, the Si substrate was first measured with ellipsometry. Understanding the substrate helps in understanding thin film data in the case that it can be seen through the film. Si data was easily modeled and fit with a built-in Si model provided by the CompleteEASE software. This lead to an easy extraction of dielectric constants.

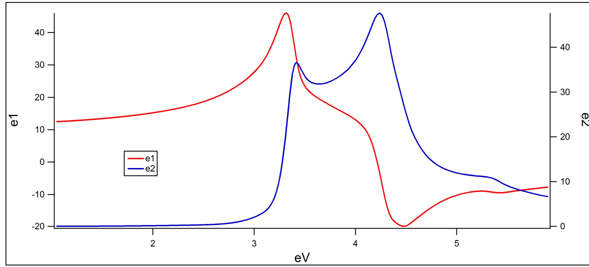

Figure 15: Dielectric Constants Of Si Substrate

These results agree strongly with values found in literature.[7] Thus, the substrate is understood.

Ellipsometry was done on two thin films deposited on the Si substrate; one which we believed to be amorphous and one which was annealed and thought to be polycrystalline. Both films were nominally 100nm. One goal of ellipsometry was to differentiate between amorphous and crystalline thin film samples. Indeed, the raw data appears to be different between the two samples.

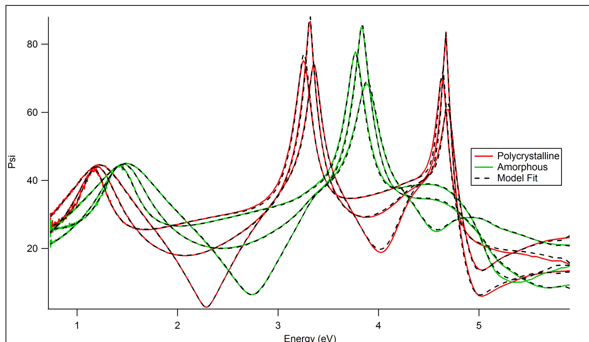

Figure 16: Raw Ellipsometric Psi data and model fits for both amorphous and polycrystalline data. Model fits differ between amorphous and polycrystalline samples

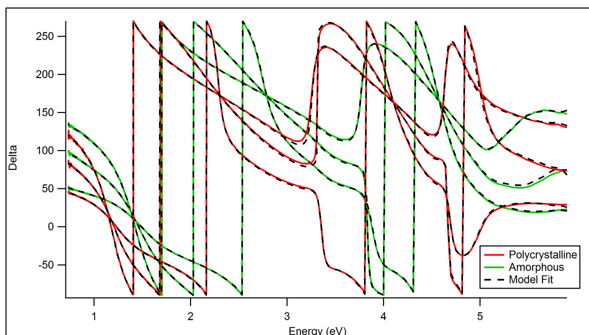

Figure 17: Raw Ellipsometric Delta data and model fits for both amorphous and polycrystalline data. Model fits differ between amorphous and polycrystalline samples

Although the data is different when looking at crystalline vs amorphous, this is not enough to categorize them, and, as we will see, the largest difference is due to their different thicknesses. The real test comes when extracting optical constants from fitting the data.

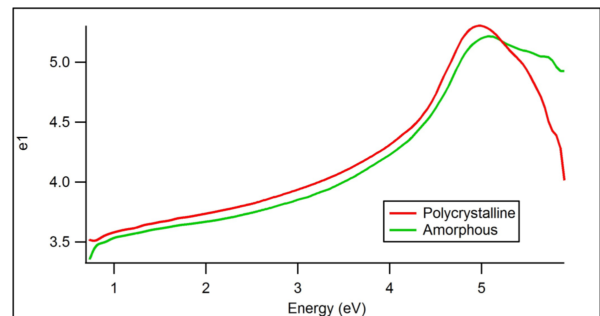

Figure 18: The real part of the dielectric constant for thin film Ga_2O_3 on Si

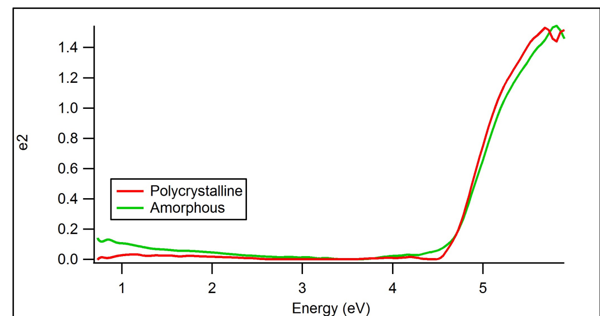

Figure 19: The imaginary part of the dielectric constant for thin film Ga_2O_3 on Si

Polycrystalline and amorphous films show little to no difference in their real and imaginary dielectric constants. Therefore, using ellipsometry as a method for categorization of crystallinity is still inconclusive. Fitting data with a model had the added advantage of being able to get a more reliable measure of thin film thickness and roughness.

	Thickness (nm)	Roughness (nm)
Polycrystalline	156	13.1
Amorphous	124	8

Since the nominal measurement of thickness was based off of a deposition rate, it is advantageous to exploit the ease and simplicity of an ellipsometry measurement to get a highly accurate thickness measurement.

4 Conclusion

The detailed study of the physics of semiconductors has lead to great advancements in device technology. Ga_2O_3 is a III-VI semiconductor material whose properties are intriguing and have capability to add functionality to the semiconductor device industry. Ga_2O_3's unique properties depend highly on the orientation, as it is anisotropic. XPS was shown to be a valid surface composition analysis technique. A sputtering system successfully made a well in a thin Pd coating on a Ga_2O_3 single crystal. A high resolution scan of Pd found that there was no Pd in the center of the well, and there were varying amounts at the other points. Therefore, the existence of the well was shown with XPS. UV-Vis found the band gap of a TiO_2 single crystal, and showed the anisotropy of Ga_2O_3. Ellipsometry sought to identify optical properties of Ga_2O_3 which are closely related to its transparency and conductivity. Optical constants were extracted for a single crystal sample and for two thin films with a Si substrate. Ellipsometry failed to definitively differentiate between amorphous and crystalline samples as their optical constants looked very similar. Ellipsometry did, however, provide a successful measure for thin film thickness and roughness.

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