Optical Properties of NbO2 Films

A thesis submitted in partial fulfillment of the requirements for the degree of Bachelor of Science degree in Physics from the College of William and Mary

by

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451 Research Report

Abstract: The senior thesis research focuses on two different types samples of Niobium dioxide at two different thicknesses. Niobium dioxide is an interesting material due to its metal insulator transitions at approximately 1080 K. This transition occurs rapidly similar to other metal-insulator transitions and superconductivity transitions. We are interested in finding the optical constants of the materials through measuring the reflectance with FTIR and ellipsometry.

Introduction: Niobium dioxide is a material that goes through a insulator-metal transition at around 1080 K. This transition is believed to be facilitated by a dissociation of Nb-Nb bonds that in turns frees up an unpaired 4-d electron that contributes towards the electrical conduction and magnetic susceptibility[4]. As shown by Sakata, there are distinct changes in electrical conduction and magnetic susceptibility around the temperatures of the presumed phase transition[3]. These changes of the behavior of the material are significant in the fact that once the transition occurs they assume the behavior of a metal instead of a insulator[3].

In addition to the electrical and magnetic properties of the material there is also a structural transition. At room temperature the NbO_2 is deformed from a rutile structure[4]. The NbO_2 cell structure was measured to be tetragonal[4]. It was found that it undergoes a transition from deformed to a normal rutile structure at around 1125 K[4].

In our experiment we are concerned with measuring the optical constants of NbO_2. We are interested in the optical constants to find out which frequencies would be best to excite the material with ultra-fast optical pulses to excite a transition at a lower temperature than the transition temperature. Our analytic software focused on the optical constants of n and k, which represent the index of refraction and extinction coefficient respectively, but can easily be used to calculate conductivity(sigma) and permittivity(epsilon).

Sigma represents the conductivity of a material and in its most general form is seen with the current density and the electric field:

$$j = \sigma E$$

Similarly the permittivity is seen with the electric displacement and the electric field:

$$D = \varepsilon E$$

All the variables in these two equations are functions of frequency and sigma and epsilon are usually represented as tensors, but for simplicity sake we can also assume they are isotropic and are scalar functions(in certain cases). Using these relationships along with Maxwell's equations, it can be shown:

$$\varepsilon = \varepsilon_l + \frac{4\pi i\sigma}{\omega}$$

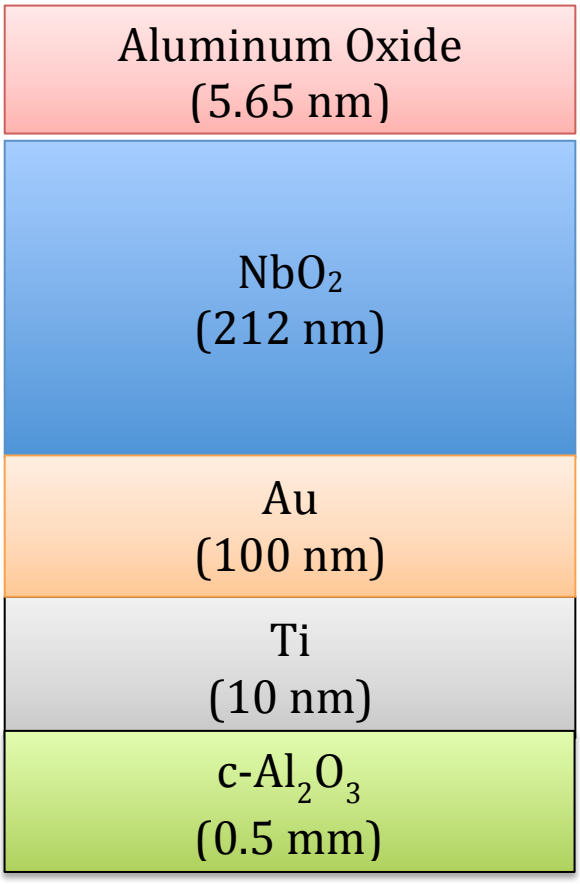
In addition we can connect the dielectric function the index of refraction and extinction coefficient:

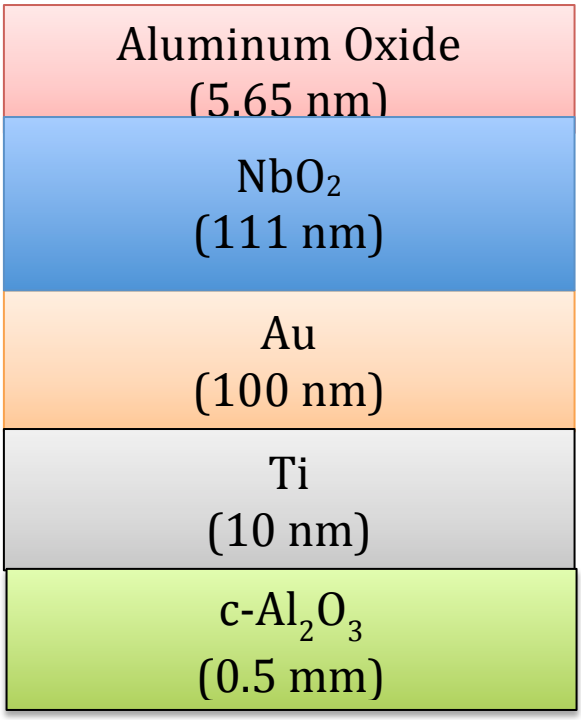
$$N = \sqrt{\varepsilon} = n + ik$$

We can finally relate these terms to the reflection(which we are measuring with FTIR) through the Fresnel equations.

By exploiting this relationship with the complex dielectric function we are able to measure n and k when we are able to measure a large swathe of reflection. This is the concept behind FTIR. The other experimental technique used is ellipsometry and exploits the polarization caused by the reflection of light off the material.

Our two sample's layering is shown below. The bulk of each sample is the NbO_2 and differs in the two samples by about 100 nm. The aluminum oxide capping layer is to prevent further oxidation of the NbO_2. During the modeling process each of the other layers have well known optical constants that allow us to implement their optical constants as part of our models easily and focus on modeling the niobium dioxide sample.





Spectroscopic Ellipsometry :

Ellipsometry is useful in that is uses polarized light to measure any phase shift and polarization due to reflectance off of a sample. This can be done without any necessary reference sample due to the fact that it compares the polarized light before reflecting off the sample and after reflecting off the sample. The measured values can simply be stated as the ratio of the Fresnel coefficients of the s-polarized light and the p-polarized light[2]. The full relation can be seen in equation number 1[2].

$$\rho = \frac{R_p}{R_s} = tan\,(\psi)\, e^{i\Delta} \qquad (1)$$

The two measured parameters are psi and delta. The tan(psi) function is related to the amplitude of the ratio of the Fresnel coefficients, while the $e^{i\Delta}$ term relates to any change in the phase of the polarization.

To solve for the respective psi and delta values the WVASE program solves for the Fourier coefficients from the ellipsometric data and also has the angle P, which is defined by the angle between the polarizer axis and the plane of incidence. With all this data, the psi and delta data can be defined by the following two equations[2]:

$$\alpha = \frac{\tan^2 \Psi - \tan^2 P}{\tan^2 \Psi + \tan^2 P},$$

$$\beta = \frac{2 \tan \Psi \cos \Delta \tan P}{\tan^2 \Psi + \tan^2 P},$$

We measured each of our samples at two different orientations to confirm that the samples are isotropic, meaning that the direction of the sample is invariant on the polarization of the light.

Once our data is measured, we used a previously designed model to match with our measured data. The model was designed by knowing all the layers of the sample and for most of the layers within our sample have well known optical constants that can easily be accounted for within the model. We are only concerned with finding the optical constants of the NbO_2 layer of our sample and that is what we fit to match our experimental data. So far in our research, we focused on the gold samples at 111 nm and 212 nm thickness, since the sapphire coated NbO_2 samples have a much more complicated electronic properties. Once we found a reasonable fit for both of our samples we compared the ellipsometric data to our FTIR data to confirm the reasonable measurement of the reflectance.

Fourier Transform Infared Spectroscopy (FTIR):

FTIR, while not as versatile as ellipsometry measurement, is able to measure into the mid-infrared(MIR) and far-infrared spectroscopy(FIR). FTIR measurements rely heavily on the basic set-up and application of the Michelson interferometer. The advantage of the Fourier transform spectroscopy is that it can measure numerous frequencies of light at the same time, that can be later analyzed using fourier transforms. The initial measurement of the intensity of light reflected is shown through the equation for the interferogram[1]:

$$\begin{aligned} I(x) &= \int_0^{\bar{\nu}_m} I(\bar{\nu})[1+\cos(2\pi\bar{\nu}x)]d\bar{\nu} \\ &= \int_0^{\bar{\nu}_m} I(\bar{\nu})d\bar{\nu} + \int_0^{\bar{\nu}_m} I(\bar{\nu})\cos(2\pi x)dx. \end{aligned}$$

Where ν is the frequencies being measured. The intefergram can then be converted to the fourier transform[1]:

$$\begin{aligned} F(x) &= \int_0^{\bar{\nu}_m} I(\bar{\nu})\cos\left[2\pi\bar{\nu}x-\phi\right]d\bar{\nu} \\ &= \int_0^{\bar{\nu}_m} I(\bar{\nu})\cos\phi\cos(2\pi\bar{\nu}x)d\bar{\nu} \\ &\quad + \int_0^{\bar{\nu}_m} I(\bar{\nu})\sin\phi\sin(2\pi\bar{\nu}x)d\bar{\nu}. \end{aligned}$$

Any loss of symmetry of the inteferogram can be represented with the change of phase and as a combination of the interferogram and sines and/or cosine function.

The downside of using FTIR is the face that it can only be used to measure the intensity, while the ellipsometry can measure polarization and any phase change in the polarization, but as noted before the ellipsometry does not measure as far as into the MIR and FIR where the phonons for NbO_2 are located.

Once the intensity of the reflection is measured multiple times, the spectrums can be averaged and transferred to the WVASE software. The reflection can be modeled using the same ellipsometric models established with additional oscillators at a lower wavelength.

Measurement Techniques:

For our FTIR measurements, we used a commercial Bruker spectrometer to measure reflection within the FIR and MIR frequencies. Each of our measurements for our samples were compared to a gold sample to find the absolute reflectance of our NbO2 samples. The gold sample was prepared by evaporating gold flakes onto a glass plate. Prior to measurement of each sample, the interferometer had to be adjusted to focus the source light onto the samples. This was achieved by adjusting the focusing lens with source light within the visible light spectrum. Once the source light was focused on the samples, we also maximized the source light while the Bruker was under vacuum to ensure the most accurate and noise-free data. These measurement techniques were replicated for each of the four samples.

The ellipsometric measurements are much simpler and only require the calibration of the device by measuring the delta and psi values of a well known sample such as silicon. Once the calibration is complete, we mount the NbO_2 samples and take the ellipsometric measurements. To ensure that the sample is isotropic we rotate the sample once and compare the ellipsometric data.

Analysis Techniques:

We used two primarily two scientific graphing and analysis programs for our measurements and modeling. During the FTIR measurement we used Origin and during the ellipsometric data as well as modeling for the niobium dioxide sample we used WVASE.

To begin our analysis we took an average of the data taken for both the 111 nm sample and the 212 nm sample and imported within a spreadsheet software, where we were able to further manipulate the data. We received two spectrums of data from FTIR measurements. We measured the mid infrared (MIR) spectrum and the far infrared (FIR) spectrum. When connected these two covered the frequency of the infrared spectrum. In the case of both of these reflection measurements the two spectrums did not line up exactly, so part of the manipulation was shifting either the MIR down or the FIR up. After initially moving the FIR up to match the MIR we changed to shifting the data to meet between the two spectrums. The difference in the reflections measurements was less than a percent, so we were able to justify these small shifts to form a continuous spectrum. In addition to making the spectrum continuous, we had to account for the gold within our sample. We simply took reflection data (that was measured for a previous experiment) and multiplied the data with our own spectrum. Since gold has near perfect reflection it only made a small, but still significant change to our data.

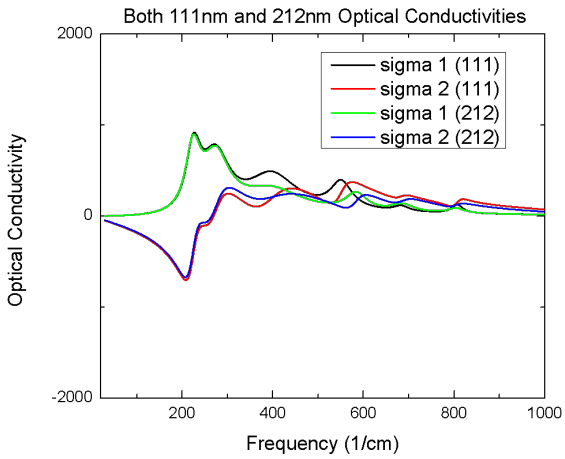
Once we had our full IR spectrum, we converted the file over to the WVASE modeling software to model the optical constants. The ellipsometric data had previously been modeled at an earlier time than this research was conducted, but the focus of this research was to model the IR data including any phonons that are present. To model the overall behavior of the IR spectrum we used a combination of

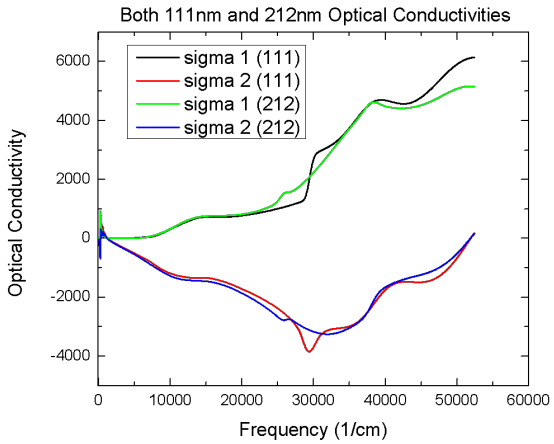
Lorentz and Tauc-Lorentz oscillators. To model the phonons we exclusively used the Lorentz oscillators.

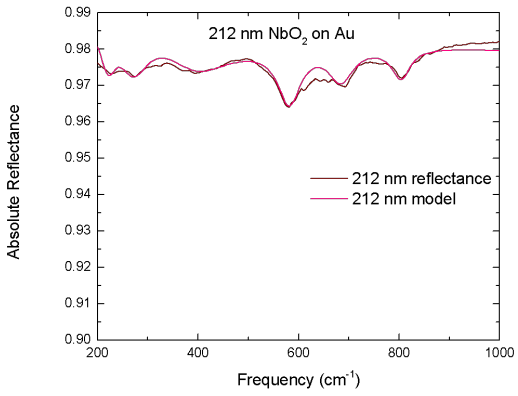
Results:

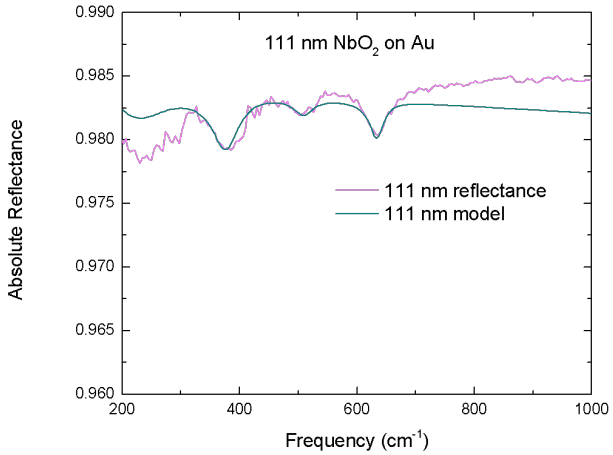
Initially the scope of this research project included analysis of both the gold samples and the sapphire samples, but due to our challenges and difficulty of the sapphire sample we were able to model the 111 nm and 212 nm samples. As of the last writing of the paper, the phonons of both the 212 nm and 111 nm samples have been roughly mapped out, with some need of fine tuning. The 212 nm sample is very closely fit across the larger behavior of the IR spectrum and most of the phonons. The 111 nm sample still needs work to fit the overall behavior of the IR spectrum. The phonons roughly correspond with frequencies seen in the 212 nm sample, but the strength of the phonons is still in question as for the model to fit perfectly the phonons are orders of magnitude larger than the corresponding 212 nm phonons. This is turn reflects on the optical constants of 111 nm being orders of magnitude larger than the optical constants of 212 nm. The nature behind these significant differences is not clear as there might be some measurement error in addition to some difference in strength due to the thickness of the samples. In addition to the difference in the strength of the phonons there is significantly more noise within the 111 nm sample that makes it difficult to determine the location of phonons within the model. Further research with these samples is required to determine the nature of these differences either through re-measurement of the sample or measurement

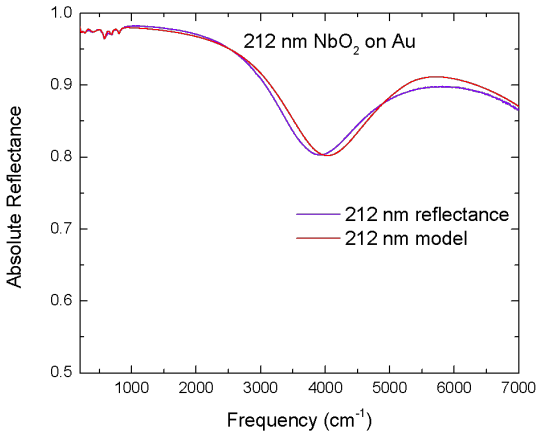
of different thickness sample to see if there is a further connection between thickness and strength of the phonons. There should be additional work to see if the other active layers such as gold and aluminum oxided have an effect. The gold might need to be more accurately modeled while the aluminum oxide may have phonons in the MIR and FIR region that can account for the discrepancies in our model.

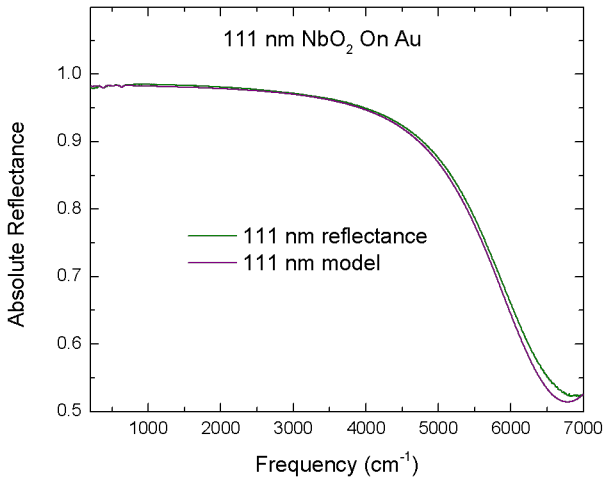









212 nm NbO2 on Au
212 nm reflectance
212 nm model
Absolute Reflectance
Frequency (cm-1)
1.0
0.9
0.8
0.7
0.6
0.5
1000
2000
3000
4000
5000
6000
7000


111 nm NbO2 On Au
111 nm reflectance
111 nm model
Absolute Reflectance
Frequency (cm-1)
1.0
0.9
0.8
0.7
0.6
0.5
1000
2000
3000
4000
5000
6000
7000

Refrences:

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