ANTIREFLECTION COATING APPLICATION OF GALLIUM ARSENIDE NATIVE OXIDE

A Thesis

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by

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______________________________
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In this thesis, the development of high surface quality, broad bandwidth, low cost antireflection coatings using the low optical index GaAs native oxide processed by a new oxygen-enhanced wet thermal oxidation method is demonstrated. The thicknesses and optical constants of the GaAs native oxide and the GaAs substrate used in the AR coating design have been determined by Variable Angle Spectroscopic Ellipsometry measurements within the visible light wavelength range at room temperature. The antireflection coatings have a simulated reflectance of <10% over bandwidths as large as 300 nm and a minimum reflectance of 2.3% for a design wavelength range of 400 to 800 nm. Good agreement between the simulated and measured reflectance data supports the validity of the modeling and indicates that a smooth interface is achieved between the semiconductor and the thermally grown native oxide.
This is for my loving family

and

my advisor Douglas C. Hall
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CHAPTER 1:
INTRODUCTION

1.1 Oxygen-enhanced Wet Thermal Oxidation Process

A tremendous amount of research has gone into efforts to develop high-quality native oxides on III-V compound semiconductors, (Ref. [1] and references therein), inspired by the desire to successfully replicate the applications of the silicon dioxide (SiO$_2$) for silicon device isolation and passivation. But, unlike the oxidation of the semiconductor Si, oxidation of the III-V compound semiconductors, such as GaAs, AlGaAs, InGaAs, involve multiple elements and the possibility of forming a soup of different oxides with an inhomogeneous distribution.

Among all the III-V materials, GaAs is the most widely deployed compound semiconductor. For the oxidation of GaAs, many approaches have been tried, including wet thermal, dry thermal, and room temperature anodization techniques. It has been found that a wet (H$_2$O vapor) ambient alone for oxidation of GaAs results in impractically slow, thermodynamically unfavorable reactions. Dry reactions of GaAs yield terminal oxides, rich in arsenic (As) oxides that are very dense. It is now understood that the As oxides can block the diffusion of oxidizing gases so that oxide growth becomes diffusion-limited and a terminal (maximum) thickness oxide result [2-
This understanding is one of the reasons why conventional wet or dry oxidation processes cannot produce a practical, device quality GaAs oxide.

In contrast, our newly developed oxygen-enhanced wet thermal oxidation process offers an effective way to achieve a high quality insulating native oxide on GaAs. In this process, the oxidant gas is formed of adding a trace amount of dry O\textsubscript{2}, typically less than 1%, to the conventional wet thermal oxidation ambient (H\textsubscript{2}O and N\textsubscript{2}). The ratio of the O\textsubscript{2} and N\textsubscript{2} flow rates is controlled by adjusting a mass flow controller (MFC) in the O\textsubscript{2} gas flow line relative to the fixed N\textsubscript{2} gas flow rates. The water vapor flows with the N\textsubscript{2} carrier gas from a bubbler containing deionized water at 95 °C. In our previous work, using this process, we have demonstrated the growth of a smooth, uniform, insulating native oxide of GaAs at the relatively high oxidation rate of 4.8 nm/min [5].

1.2 GaAs Native Oxide

Among all the oxidation conditions in the oxygen-enhanced wet oxidation process, the oxidation temperature and the ratio of the O\textsubscript{2} and N\textsubscript{2} flow rates are the two main conditions which most influence the surface quality and the oxidation rate of the GaAs oxide. We have successfully found a good oxidation condition of 420 °C, 2000 parts per million (ppm) O\textsubscript{2}/N\textsubscript{2} flow ratio with the fixed N\textsubscript{2} flow rates at 0.68 slm in our III-V oxidation furnace.

Characterization of the oxide surface is performed using an atomic force microscope (AFM) for GaAs oxides grown using different oxidation conditions with various oxidation temperatures and O\textsubscript{2} and N\textsubscript{2} flow rate ratio. As shown in Figure 1.1,
we have achieved a root mean square (RMS) roughness of 0.245 nm (Rq in the figure) over a 50 μm × 50 μm square area on the oxide surface. The sample is oxidized at 420 °C for 110 minutes at a 2000 ppm O₂/N₂ ratio, for an oxide thickness of 412 nm [5].

Figure 1.1. AFM scan of a 50 μm x 50 μm square area of the native oxide surface. The scale bar denotes a 0-2 nm height variation. The image is produced from a sample oxidized at 420 °C for 110 minutes at 2000 ppm O₂/N₂ yielding a 412 nm thick film [5].

Figure 1.2 (a) shows the relationship between the oxide thickness and the oxidation time. The thickness of the oxide is determined by measuring the etched oxide-semiconductor step height with a surface profilometer. The linear regression curve fits in Figure 1.2 (a) give oxidation rates of 1.4 and 4.8 nm/min at 1000 and 2000 ppm, respectively. We have grown GaAs oxide films as thick as 800 nm under the above oxidation conditions and an oxidation time of 185 minutes.

Metal-semiconductor Schottky diodes and metal oxide-semiconductor (MOS) capacitors using the oxides grown at 420 °C with a 2000 ppm O₂/N₂ flow rate ratio have
been fabricated by coworkers at Notre Dame to study the insulating property of the GaAs oxide film. As shown in Figure 1.2 (right), for a bias of +1 V, a 412 nm GaAs oxide reduces the leakage current density from $1.74 \times 10^{-3}$ to $6.35 \times 10^{-7}$ A/cm$^2$, or more than three orders of magnitude [5].

![Figure 1.2.](image)

The purpose of this thesis is to further characterize and optimize the oxygen-enhanced wet thermal process for oxidizing GaAs under the new clean room conditions in the Notre Dame Nanofabrication Laboratory, to further characterize the GaAs native oxide morphology and optical properties, and to explore the potential application of this oxide for realizing an antireflective thin film optical coating on GaAs. In Chapter 2, the
optimal conditions for growing the thermal GaAs native oxide are investigated through the use of AFM measurements of surface and interface roughness, and photoluminescence (PL) intensity and time-resolved PL (TRPL) lifetime measurement techniques. In Chapter 3, use of the variable angle spectroscopic ellipsometry (VASE) technique to measure the GaAs oxide thicknesses, and to extract the optical constants from the VASE data, is described. In Chapter 4, application of the GaAs oxide to realize an antireflection coating is demonstrated. The reflectance of the GaAs oxide layer is measured using an Ocean Optics spectrometer-based reflectance system, in good agreement with theoretical calculations using the optical constants extracted from the VASE measurement. Following the conclusion in Chapter 5, the Matlab script for the reflectance theoretical calculation is presented in Appendix I.
CHAPTER 2:
CHARACTERIZATION AND OPTIMIZATION OF THE GAAS NATIVE OXIDE

2.1 Atomic Force Microscopy Measurement

Good surface quality is a basic requirement for almost all materials used in microelectronic and optoelectronic device applications. The surface roughness is an effective way to characterize the overall surface quality of thin films. Taking GaAs oxide films as an example, for dielectric applications, a lower surface roughness correlates to a reduced level of defects that can affect the insulating layer leakage current. For optical film applications, lower surface roughness will reduce the optical loss due to scattering from surface reflection.

A high surface quality GaAs native oxide can be very difficult to achieve due to the fact that the GaAs oxidation process involves multiple elements and multiple correlated chemical reactions, such as: [3, 4]

Dry Reactions:

\[ 2\text{GaAs(s)} + 3\text{O}_2(g) \rightarrow \text{Ga}_2\text{O}_3(s) + \text{As}_2\text{O}_3(l) \]  \hspace{1cm} (2.1)

\[ 2\text{GaAs(s)} + 4\text{O}_2(g) \rightarrow \text{Ga}_2\text{O}_3(s) + \text{As}_2\text{O}_5(s) \]  \hspace{1cm} (2.2)

Wet Reactions:

\[ 2\text{GaAs(s)} + 6\text{H}_2\text{O}(g) \rightarrow \text{Ga}_2\text{O}_3(s) + \text{As}_2\text{O}_3(l) + 6\text{H}_2(g) \]  \hspace{1cm} (2.3)
\[2\text{GaAs}(s) + 8\text{H}_2\text{O}(g) \rightarrow \text{Ga}_2\text{O}_3(s) + \text{As}_2\text{O}_5(s) + 8\text{H}_2(g)\] (2.4)

A good balance of all the chemical reactions must be found through controlling the oxidation conditions in our process, including the oxidation temperature, the \(\text{O}_2/\text{N}_2\) flow rate ratio, and the water bubbler temperature which affects the water vapor flow. Below, we describe a series of oxidation experiments where AFM is used to characterize and optimize the surface quality of the GaAs native oxides.

2.1.1 Experimental Conditions

In previous work mentioned in Chapter 1, it was found that for GaAs oxidation, 420 °C is the optimal temperature for our oxygen-enhanced wet thermal oxidation process. In order to more fully investigate here the effect of the \(\text{O}_2/\text{N}_2\) flow rate ratio on the oxide surface quality at this temperature, a series of GaAs oxide samples are oxidized at 420°C, varying the \(\text{O}_2/\text{N}_2\) flow rate ratio from 1000 to 3000 ppm with 500 ppm intervals. The GaAs samples used in this study are all rectangular samples with sides 3 to 5 mm in length. The GaAs wafer consists of an epitaxial layer of n-type GaAs (Si, \(\sim 10^{16}\text{cm}^{-3}\) doped) grown on an n⁺-GaAs (100) substrate by molecular beam epitaxy (MBE) at RF Micro Device (Greensboro, NC). Because the surface roughness can increase with the thickness of the oxide under selected oxidation conditions, we adjust the oxidation times based on the measured growth rate with different \(\text{O}_2/\text{N}_2\) ratios to grow oxide films all having the same thickness of around 180 nm for the surface roughness measurements. For reference, Figure 2.1 shows an AFM scan of the GaAs sample measured before oxidation.
Figure 2.1. AFM scan of a GaAs sample surface before oxidation. The RMS surface roughness is 0.362 nm.

2.1.2 Surface and Interface Roughness

As observed in Figure 2.2 (a), when the GaAs oxide samples are taken outside of the cleanroom for AFM scans, they can easily pick up small dust particles from the air or incur surface damage during handling that may cause random, atypically high peaks, particularly in a large 50 μm x 50 μm square area AFM scan. Especially for a very smooth oxide surface, the RMS roughness is very sensitive to and significantly increased by these high peaks. In order to most accurately characterize the surface roughness, a smaller 10 μm x 10 μm area data window is selected within the full 50 μm x 50 μm AFM scans for the roughness calculation of all the oxide samples as shown in Figure 2.2 (b).
Figure 2.2. (a) 3D AFM image of a 50 μm x 50 μm square area of the native oxide surface. The image is produced from a sample oxidized at 420 °C for 60 minutes at 2500 ppm yielding a 240 nm thick film. (b) A 10 μm x 10 μm area of the same AFM scan is selected for the roughness measurement, which has a lower RMS of 0.139 nm compared to the 0.232 nm for the entire scan.

Figure 2.3 below is a plot of the surface roughness vs. O₂/N₂ flow rate ratio. All the AFM roughness data are measured over a 10 μm x 10 μm square area of the native oxide surface.
oxide surfaces. Plane fitting is applied to the image to correct tilt and bow of the scanning area for the roughness measurement [6]. The lowest RMS roughness is 0.139 nm from the oxide sample grown under the 2500 ppm condition. This value is 2.3 times lower than the 0.322 nm RMS surface roughness of the GaAs epi-layer before oxidation with the same scan area as shown in Figure 2.1, and ~1.8 times lower than our previous best published result 0.245 nm [5] obtained at a 2000 ppm O$_2$/N$_2$ flow rate ratio. The RMS roughness of the oxide sample in this work under the 2000 ppm condition is 0.204 nm, which is just 16.7% lower than the previously published result, which both shows the reproducibility of our oxidation process and the advantage of the better clean room conditions.

![Graph](image)

**Figure 2.3.** The surface roughness of the oxides under oxidation conditions at 420 °C with different O$_2$/N$_2$ flow rate ratio from 1000 to 3000 ppm. The thicknesses of all the oxide films are approximately 180 nm. A 10 μm x 10 μm area is selected for the roughness measurement.
To determine the roughness of the underlying oxide-semiconductor interface, we exposed the interface between the oxide and the GaAs material by completely etching away the oxide in buffered hydrofluoric acid. An etching time of over 5 hours is required to ensure complete removal of the oxide layer (proven by the fact that longer etching times result in no further change in the roughness data).

Again using an AFM scanning area of 50 μm x 50 μm on every sample, Figure 2.4 shows that the oxide/semiconductor interface roughness decreases with increasing oxygen content until reaching a minimum of 4.85 nm for an O₂/N₂ ratio of 2500 ppm. At 3000 ppm, AFM data shows the interface roughness increases again.

The accuracy of the interface roughness data of the 2000 ppm sample is supported by the Transmission Electronic Microscopy (TEM) image shown in Figure 2.7 for an oxide film grown under the same oxidation conditions. For comparison, this result is much lower than the interface roughness of ~20 nm observed in Ref. [7] for a GaAs oxide grown at higher oxidation temperatures of 450 and 475 °C in a moist N₂ environment.
Figure 2.4. AFM measurements of the roughness of the interface between the oxide and GaAs for varying oxygen content in the process gas. The oxides are removed by buffered hydrofluoric acid etching for at least 5 hours.

2.2 Oxidation Rates Under Different Oxidation Conditions

A stable and reproducible oxidation process must be able to precisely control the thickness of the oxide, especially for certain applications like an optical antireflection coating where a thin oxide film with a certain exact thickness is required. In this section, results of further investigations of the GaAs oxidation rates are presented. There are two reasons to do this investigation. First, the cleanroom conditions, which can have a strong influence on the process, have changed since our first work on GaAs oxidation was published [5]. Second, the VASE system here has replaced on prior profilometer
oxide thickness measurements, as better VASE modeling now provides us with more accurate results of the GaAs oxide thickness, especially for thin oxide films.

![Graph showing oxide thickness vs. O\textsubscript{2}/N\textsubscript{2} ratio for a 1 hour oxidation at 420 °C. The O\textsubscript{2}/N\textsubscript{2} ratio is varied from 500 to 7500 ppm.](image)

Figure 2.5. Oxide thickness vs. O\textsubscript{2}/N\textsubscript{2} ratio for a 1 hour oxidation at 420 °C. The O\textsubscript{2}/N\textsubscript{2} ratio is varied from 500 to 7500 ppm.

Ten samples oxidized for 1 hour each with varied O\textsubscript{2}/N\textsubscript{2} ratios varied from 500 to 7500 ppm are used to demonstrate the effect of O\textsubscript{2}/N\textsubscript{2} ratio on the oxidation rate.

Figure 2.5 shows the oxide thickness vs. O\textsubscript{2}/N\textsubscript{2} ratio, filling out the data in the inset Fig. 1.2. All the thickness data is from VASE measurement. As predicted in Ref. [5], beyond 5000 ppm O\textsubscript{2}/N\textsubscript{2} the production of hydrogen by the wet thermal oxidation reaction is suppressed such that a dense As oxide layer accumulates at the oxidation front, causing a transition to a diffusion-limited growth regime. As the more favorable dry oxygen reaction begins to dominate, insufficient hydrogen is produced to fully reduce arsenic...
oxide to more volatile species (As, AsH₃) that more readily aid the removal of As from the growing gallium oxide film.

In Figure 2.6, the linear fits of the oxide thickness vs. oxidation time show that the oxidation process has a reaction rate limited oxide growth mechanism at 1000, 1500, 2000 and 3000 ppm at 420 °C. The slopes of the linear fits show that the oxidation rate increases with the O₂/N₂ ratio from 2.0 nm/min at 1000 ppm to 6.1 nm/min at 3000 ppm. From this conclusion, we can consider the thickness of the 1 hour oxidation in Figure 2.5 as the hourly oxidation rate under each condition. Another conclusion here is that the line fit in Figure 2.5 above shows that the oxidation rate is linearly increasing with O₂/N₂ ratio within the reaction rate limited regime up to 3000 ppm.

Among all the experiments, the thickest GaAs oxide film obtained is 915 nm thick grown at 420 °C, 3000 ppm O₂/N₂ ratio for 3 hours. This thickness is consistent with the growth rate obtained from the linear fit to data obtained under this condition (the pink linear fit) in Figure 2.6. As in Ref. [5], we also observe an offset of around 10 minutes from the origin in all the linear fits (slightly different under different O₂/N₂ ratio), which indicates a slow gradual onset of the oxidation process. We can use the line fit equations of Fig. 2.6 to predict the oxidation time for processing oxide films of a certain desired thickness under the chosen oxidation conditions. The curve fit parameters and equations are shown at the upper left corner in Fig. 2.6.
Figure 2.6. GaAs oxide thickness measured for various oxidation durations and for 4 different ratios of O\textsubscript{2} to N\textsubscript{2} (the water vapor carrier gas) varied between 1000 and 3000 ppm with the linear fits.

To summarize, compared with our group’s published results for the first studies of GaAs oxidation [5], and taking advantage here of better clean room conditions, we have obtained more accurate and reproducible oxidation rates under various O\textsubscript{2}/N\textsubscript{2} flow rate ratios, which enables much more precise control of the oxidation process and the resulting oxide film thickness. While preserving the optimal oxidation temperature of 420 °C found in prior work, we have shown that a change of the O\textsubscript{2}/N\textsubscript{2} flow rate ratio from 2000 to 2500 ppm provides not only lower surface and interface roughness, but also a higher oxidation rate.
2.3 TEM Measurement and EDS Analysis

Figure 2.7 shows a TEM image of a thin oxide film with a thickness of 50 nm measured using VASE. The oxidation condition of this film is 420 °C, 2000 ppm O₂/N₂ for 26 minutes. This image clearly shows the thickness of the native oxide layer is 46+5=51 nm, only 3% difference from the VASE thickness fitting result, which strongly confirms the validity of the VASE fitting model and in this work for the GaAs oxide thickness measurements. The mixture of GaAs and the oxide can be clearly observed within the interface layer revealing the correct application of the effective medium approximation (EMA) layer used in the VASE thickness fitting model. The ~5.0 nm roughness of the interface between the oxide and the semiconductor is also very close to the AFM results of the interface RMS roughness shown in Figure 2.4 as well as the EMA layer thickness in the VASE fitting results.
Figure 2.7. TEM image of a 50 nm (VASE result) oxide film grown at 420 °C, 2000 ppm O₂/N₂ for 26 minutes. The line roughness of the oxide/GaAs interface is 5.01 nm as shown between two parallel lines.

The TEM image of Figure 2.7 also shows the partially crystalline structure of the native oxide, shown also in the following image (Figure 2.8) taken with a higher magnification. We also did energy-dispersive spectroscopy (EDS) analysis for the chemical composition of the oxide to better understand the oxidation dynamics. The five positions selected for EDS analysis are as follows: point 1 is inside the GaAs substrate, point 2 to 5 are all in the oxide layer moving from the interface towards the surface, with point 3 inside one of the darker areas observed in the TEM image. The results of the EDS analysis are listed in Table 2.1. The accelerating voltage of the microscope used in the EDS analysis is 300 keV and the beam current is 1 nA.
Figure 2.8. High magnification TEM image, showing the partial crystalline structure of the oxide and 5 positions selected for EDS analysis.

TABLE 2.1
EDS ANALYSIS OF THE GAAS NATIVE OXIDE

<table>
<thead>
<tr>
<th>Position</th>
<th>Ga (atomic %)</th>
<th>As (atomic %)</th>
<th>O (atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>47.86</td>
<td>52.13</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>36.49</td>
<td>0.34</td>
<td>63.16</td>
</tr>
<tr>
<td>3</td>
<td>38.89</td>
<td>~0</td>
<td>61.1</td>
</tr>
<tr>
<td>4</td>
<td>33.16</td>
<td>~0</td>
<td>66.83</td>
</tr>
<tr>
<td>5</td>
<td>29.91</td>
<td>~0</td>
<td>70.08</td>
</tr>
</tbody>
</table>
From Table 2.1, at point 1, the atomic percent ratio of Ga:As is very close to 1:1 for the GaAs substrate, which confirms the validity of this analysis set up. For points in the oxide layer, the atomic percentage of As are almost 0 except for position 2, which is consistent with the existence of a thin, dense, hard to remove arsenic oxide layer near the interface (observed, as described above, during an HF etching oxide removal process for AFM interface roughness measurements). The absence of As within the oxide at positions away from the oxidation front also confirms the reduction of As oxide by hydrogen produced by the wet oxidation reactions [3, 4] and subsequent removal through evaporation of more volatile elemental As or AsH₃.

The relatively high Ga:O ratio at point 3 shows that the darker area of the oxide has a more Ga rich composition, closest in stoichiometry to Ga₂O₃ (40%Ga, 60% O), which may indicate a more crystalline form of gallium oxide. Comparing the atomic composition of position 2, 4 and 5, we can see that the Ga oxide has a Ga:O ratio that decreases from the interface towards the surface within the oxide layer. The morphology and different orientations seen for the darker, possibly partially crystalline areas needs further exploration.

2.4 Photoluminescence and Time Resolved Photoluminescence (TRPL) Measurement

To characterize the passivation property of the GaAs native oxide, photoluminescence (PL) intensity and time resolved PL measurements are performed on samples with different top layers including the native oxide layer on GaAs substrate. For all cases, the wider bandgap of the overlayer serves to keep the excited electrons and
holes away from the surface. The following figure shows the sample structures, the 1000 nm thick n-type GaAs layer of all the samples are grown by MBE by RF Micro Devices (Greensboro, NC). The range of the PL intensity measurements are compared to a likely “known best” interface with Al$_{0.45}$Ga$_{0.55}$As on GaAs (sample G) and a likely “known worst” interface with air exposed native oxide on GaAs (sample A).

![Sample structures for the PL measurements.](image)

The PL intensity results are shown in Figure 2.10. A 488 nm Ar$^+$ laser excitation wavelength is used for all PL intensity measurements. The peak emission wavelength observed from the GaAs layer is 826 nm, corresponding to a photon energy of 1.501 eV. The band gap of GaAs at 300 K is 1.423 eV, which is about 3kT (T=300K) lower than the measured emission photon energy. This difference is attributed to the fact that in bulk
GaAs the mean energy of the excess carrier concentration distributions for electrons and holes are at \((E_c + 3/2kT)\) and \((E_v - 3/2kT)\) in the conduction and valence bands, respectively. The PL intensity of the thermal native oxide sample is almost as low as the worst known interface with the air exposed oxide interface, which is about 2 orders of magnitude lower than the best known AlGaAs/GaAs interface. This indicates the likely presence of a high level of interface states and suggests that the thermal native oxide cannot be used as a good passivation layer.

![Figure 2.10](image.png)

**Figure 2.10.** PL intensity data of samples with different top layers on GaAs. Samples with oxide top layers show a two magnitude lower PL intensity than other samples.

The time resolved PL measurement is used to measure the carrier lifetime in the GaAs layer of these samples. A longer lifetime indicates a better quality interface.
passivation by the top layer (i.e., a reduced level of nonradiative electron-hole recombination at the interface). The raw measured decay data are shown in Figure 2.11.

Figure 2.11. Measured decay data for (a) GaAs oxide grown at 420 °C, 2000 ppm O₂/N₂ and (b) InAlP on top of GaAs (sample C in Figure 2.8). In each figure, the red curve on the bottom is the instrument response function, and the blue curve on the top is the measured decay curve with overlapping fitting curve shown in black.
The following exponential decay function is used to fit the time resolved PL data:

\[ I(t) = \int_{t_0}^{t} IRF(t') \sum_{i=1}^{\infty} A_i e^{-t/\tau_i} dt' \]

where \( IRF \) is the instrument response function, and \( \tau_i \) is the carrier lifetime of the measured sample. For optimal results, two exponential decay components are used to get a good fitting of the experimental data. The intensity averaged lifetime is calculated using the following equation:

\[ \tau = \frac{l_1 \tau_1 + l_2 \tau_2}{l_1 + l_2} \]

The results are shown in Figure 2.12, where pie diagrams show the fractional intensities of the two decay components. For the thermal oxide samples, the fast decay components dominate with a lifetime less than 0.032 ns and a fraction of about 75%. In contrast, the slow decay component, with life times around 0.33 ns, are dominant in the other samples. This result is consistent with the decay curves shown in Figure 2.10, where it’s clear that the InAlP sample has a longer decay time. The height of the columns shows that the GaAs having grown thermal oxides have a lower intensity-weighted lifetime compared with the GaAs samples capped by epitaxially grown materials.
The carrier lifetime from time resolved PL measurements with different top layer materials upon a GaAs substrate. The columns show the calculated intensity weighted lifetime using Eq. 2.7. The pie diagrams show the fractional intensities of the two decay components (slow and fast), with the lifetime of the different components listed above.

The thermal oxides of GaAs don’t show as high a quality of interface passivation compared to the InGaAs and AlGaAs top layers, but is no more than 3X worse. For samples with the thermal oxide grown under different oxygen content, the intensity averaged lifetime of the oxide samples are all less than half of the lifetime of the samples with other materials. For the GaAs layer topped with the oxide, about 75% of the carriers have a very fast recombination time of ~0.03 ns, while only about 25% of the carriers recombine this fast for GaAs topped with an InGaAs or AlGaAs epilayer.
CHAPTER 3:  
VASE MEASUREMENT OF THE GAAS OXIDE

3.1 VASE Modeling and Thickness Measurement

A Variable Angle Spectroscopic Ellipsometry (VASE) system is applied in this work to measure the thickness and optical constants of the GaAs native oxide. The VASE measurement is more accurate than the profilometer previously used to measure the height of an etched oxide step, particularly for thin oxide films of thickness less than 50 nm. For the profilometer measurement, it is also very hard (due to the dense As rich oxide at the interface) to complete selectively remove the GaAs oxide to create an accurate oxide-GaAs step, which is something the VASE measurement doesn’t require. Because the VASE measurement is a nondestructive, non-contact thickness measurement, the same sample can be used for further AFM scan, photoluminescence, reflectance or other measurements. Finally, the VASE technique can also provide the optical constants of the oxide film.

3.1.1 Experimental Conditions

All the samples shown in Figure 2.5 for the oxidation rate measurement are measured by VASE. These GaAs native oxides grown under different oxidation conditions (introduce in Chapter 2) have thicknesses varying from ~ 5 nm to ~915 nm.
A VASE measurement is based on the simple equation

\[ \rho = \tan \Psi e^{i\Delta} = \frac{R_p}{R_s} \]  

(3.1)

where \( R_p \) and \( R_s \) are the total reflection coefficients for \( p \)- and \( s \)-polarized light. \( \Psi \) is the angle whose tangent is the ratio of the magnitudes of \( R_p \) and \( R_s \). And \( \Delta = \delta_1 - \delta_2 \), where \( \delta_1 \) is the phase difference between the \( p \)-polarized component and the \( s \)-polarized component of the incoming wave, and \( \delta_2 \) is the phase difference between the \( p \)-polarized component and the \( s \)-polarized component of the outgoing wave. So \( \Delta \) is the change in the phase difference that occurs upon reflection [8]. Within a certain range of photon energies and incident angles, the VASE system measures the \( \Psi \) and \( \Delta \) data and then a model is built to fit the sample structure by comparing the model-generated fitting data with the measured data. A good fitting with a low mean square error (MSE) value for a physically reasonable model will give accurate structure parameters for the sample, including the thickness, roughness and/or optical constants.

A significant advantage of VASE over single wavelength ellipsometry (SWE) [7] is that multiple angles of incidence (AOI) and multiple wavelengths are utilized. From our early work and other literature [5, 9], between 2~5 eV, the real part of the refractive index \( n = 1.7 \sim 2 \) for the GaAs oxide, and \( n = 3.5 \sim 4.5 \) for GaAs. So we choose the AOI to be 65° (close to the Brewster angle), 70° and 75° and a spectral range of 1.5 to 5.2 eV for the GaAs oxide sample measurements. In addition, the back side of the GaAs substrate is treated to minimize the backside reflection for optimal results [8].
3.1.2 VASE Thickness Fitting

![Diagram of GaAs oxide sample structure and VASE model structure for thickness fitting]

Figure 3.1. Left: GaAs oxide sample structure. Right: VASE model structure for thickness fitting

Figure 3.1 shows the sample structure and the structure for VASE modeling. A Cauchy parameterization model with an effective medium approximation (EMA) interface layer is used to fit the thickness of the GaAs native oxide film. The Cauchy dispersion relation is commonly used to describe the optical constants of materials below their energy bandgap with the expression

\[ n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \]  

(3.2)

where A, B, and C are fitting parameters [10]. A starting value of \( A = 1.72 \) is used based on prism coupling measurements of the GaAs oxide at 633 nm.

As the GaAs oxide is a transparent material, interference oscillations that are very sensitive to roughness are observed in the experimental data. For improved fitting results, considering the relatively high interface roughness of the GaAs oxide samples shown in Figure 2.3, an EMA layer which contains a mixture of the native oxide and GaAs is used between the Cauchy GaAs oxide layer and the GaAs substrate to model the interface roughness.
Parameter correlations are often a major problem during the VASE model fitting process. For example, in the Cauchy model, large negative values of the B or C parameters during the fitting indicate strong parameter correlations and often produce a nonphysical dispersion relationship for the material index. An effective way to reduce the parameter correlation is to limit the number of parameters by fitting the primary parameters first and then adding more parameters when we get closer to the actual solutions. In the EMA model layer, the constituent fraction of the two materials cannot be fit with the thickness simultaneously, so a value of 50% is initially set for the GaAs oxide.

A coupled “multi-sample analysis” of two oxide samples with 50.2 and 186.4 nm thick oxide films grown under the same conditions is shown below in Figure 3.2, which compares the model fit for each sample with the measured $\Psi$ and $\Delta$ spectral data. The dispersion formula and parameters used are given by:

$$n = 1.6425 + \frac{0.01238}{\lambda^2} + \frac{9.924 \times 10^{-5}}{\lambda^4}$$

where $\lambda$ is in nanometers. The total MSE value of the coupled fitting is 18.76. The thicknesses of the EMA layers of the two samples are almost the same, 5.727 and 5.441 nm respectively, which is very close to the interface RMS roughness value found by both TEM and by AFM (after oxide removal).
Figure 3.2. $\Psi$ and $\Delta$ spectral data and VASE model fitting for $\sim50.2$ nm (top) and $\sim186.4$ nm (bottom) GaAs native oxide films grown under the same condition of 420 °C, 2000 ppm O$_2$/N$_2$ with different times of 26 and 60 minutes, respectively. Coupled fitting MSE=18.76.
3.2 Extracting Optical Constants of the GaAs Oxide

After the thickness fitting, we can fix the thickness and extract the preliminary n and k values by point to point fitting across the entire wavelength range. For a physically meaningful result, the optical constants n and k must both smoothly decrease with increasing wavelength. If not, the thickness found previously is not correct and one must go back and fit the thickness again.

The preliminary n and k data might fit the experimental data well and yet not be physically reasonable. The complex dielectric coefficient \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \) are related to the refractive index n and extinction coefficient k by \( n + ik = \sqrt{\varepsilon_1 + i\varepsilon_2} \), and these must be Kramers-Kronig (KK) consistent to be physically reasonable [8]. To reduce the number of variables in our fitting process for optimal results, a general oscillator layer is used to parameterize the optical constants using the preliminary data as a reference.

The KK consistent oscillator used here is the Tanguy oscillator. The Tanguy model was developed by Tanguy [11, 12] and has five parameters: amplitude \( A_n \), energy of the fundamental bound state \( E_{gn} \) (bandgap), the unscreened binding energy \( R_n \), broadening \( \sigma_n \), and \( \ln(g_n) \). The general form of the Tanguy model is expressed by the following equations [11, 12]:

\[
\varepsilon = \frac{A_n\sqrt{R_n}}{(E+i\Gamma_n)^2}\left\{g\left(\xi(E+i\Gamma_n)\right) + g\left(\xi(-E-i\Gamma_n)\right) - 2g\left(\xi(0)\right)\right\} \tag{3.4}
\]

where \( g(\xi) = -2\psi\left(\frac{e^{\ln(g_n)}}{\xi}\right) - \frac{\xi}{e^{\ln(g_n)}} - 2\psi(1 - \xi) - \frac{1}{\xi} \tag{3.5} \)

\[
\xi(z) = \frac{2}{\left(\frac{E_{gn}}{R_n}z\right)^2 + \left(\frac{E_{gn}}{R_n}z + \frac{4}{e^{\ln(g_n)}}\right)^2} \tag{3.6}
\]
\[
\psi(z) = \frac{d(ln\Gamma(z))}{dz}
\]  

(3.7)

Figure 3.3 below shows the optical constants of the GaAs oxide with a minimum MSE value of 22.14 obtained during the above VASE modeling process. The sample we measured here is grown at 420 °C, with a 3000 ppm O₂/N₂ ratio for 42 minutes, reaching a thickness of 182.53 nm. Compared to the GaAs oxide grown using anodic oxidation [13], our GaAs oxide has a lower value for the optical constant (and so also for the dielectric constants). The optical constants of oxides grown with different oxygen content are slightly different, but with the same band gap of \(~4.1\) eV, as determined by where the extinction coefficient \(k\) and related optical absorption rapidly increase above zero.

![Figure 3.3](image_url)

Figure 3.3. Optical constants extracted from the VASE measurement of the 182.6 nm oxide sample grown under 420 °C, 3000 ppm for 42 minutes. The MSE value is 22.14.
In the VASE model, we use a parameterized GaAs layer model from the University of Nebraska at Lincoln (UNL) for the GaAs substrate. It has been shown by the small resulting MSE values to be an effective and accurate material model for GaAs thickness and optical constant fitting [10]. The optical constants of the GaAs substrate layer, shown in Figure 3.4, are also used below in the reflectance calculation and AR coating design.

Figure 3.4. Optical constants of GaAs substrate from UNL parameterized model layer [10].
CHAPTER 4:
AR COATINGS USING THE GAAS NATIVE OXIDE

4.1 Reflectance Calculation For a Single Layer GaAs Oxide Film Structure

From the extracted optical constants data from the VASE measurement, we have observed that the refractive index of the GaAs native oxide film $n_f$ is quite close to $\sqrt{n_s \cdot 1}$, the square root of the product of the indices of the GaAs substrate and the incident medium air, and the ideal theoretical refractive index value for a quarter wave thickness antireflective coating of thickness $\frac{\lambda_0}{4n_f}$ at the design wavelength of $\lambda_0$. Thus, a single layer antireflection (AR) coating is a promising potential optical application of the GaAs native oxides. AR coatings find application to solar cells or photodiodes to increase their light collection efficiency, to light emitting diodes (LEDs) to improve their light extraction efficiency, on the output facet of edge-emitting laser diodes to control the light output direction (in conjunction with a high-reflectance back facet coating), or on semiconductor optical amplifiers (SOAs) to prevent cavity resonance and lasing action.

Using the extracted VASE data, the reflectance of a GaAs native oxide film on a GaAs substrate is calculated here to further investigate the AR coating application.
4.1.1 Characterization Matrix Method

![Image of light beams](image)

Figure 4.1. Multiple reflected and transmitted beams for a single oxide layer on GaAs

The multiple reflections of the incident light beam that occur in the GaAs native oxide film for the case of a single film on an optically thick substrate (GaAs) are shown in Figure 4.1. We denote quantities relating to the ambient medium with the subscript ‘0’, the oxide film with ‘1’ and the GaAs substrate with ‘2’. The characteristic matrix of the stratified medium is defined in Born Wolf’s book for the purposes of determining the propagation of an electromagnetic wave [14]. The z-axis of a Cartesian reference system is defined as shown in Figure 4.1 for a TE wave propagating through the GaAs native oxide, which is a homogeneous dielectric film. We define

\[ p = \sqrt{\frac{E}{\mu}} \cos \theta \]  \hspace{1cm} (4.1)
where $\varepsilon$ is the dielectric constant, $\mu$ is the magnetic permeability and $\theta$ is the incident angle. The GaAs native oxide is a nonmagnetic material, so $\mu = 1$. In this case,

$$ p = \sqrt{\varepsilon} \cos \theta = n \cos \theta , $$

and the expression for the characteristic matrix is

$$ M(z) = \begin{pmatrix} \cos(k_0nz \cos \theta) & -\frac{i}{p} \sin(k_0nz \cos \theta) \\ -ip \sin(k_0nz \cos \theta) & \cos(k_0nz \cos \theta) \end{pmatrix} \quad (4.2) $$

where $n$ is the complex refractive index of the medium and $k_0 = 2\pi/\lambda$. The reflection coefficients can then be expressed as:

$$ r = \frac{(m_{11} + m_{12}p_2)p_1 - (m_{21} + m_{22}p_2)}{(m_{11} + m_{12}p_2)p_1 + (m_{21} + m_{22}p_2)} \quad (4.3) $$

with $m_{ij}$ being the elements of $M$ and $p_i$ being the $p$ value of each layer. The reflectance can then be derived as $R = |r|^2$. A Matlab script was written to perform this calculation directly using the optical constants of the two materials extracted from the above VASE measurement (see Appendix I).

4.1.2 Fresnel Equation and Infinite Reflected Beam Summation Method

Another way to calculate the reflectance is based on the Fresnel equations with the summation of all reflected beam components [10]. From Maxwell’s equations and the expression of the electromagnetic wave, it’s very simple to show that propagation of a wave across a film yields a resulting wave of the following form

$$ E_{after} = E_{before} \exp(-i2\beta) \quad (4.4) $$

where $\beta$ is the optical thickness of the film equal to $2\pi n_1 \cdot d \cos \theta/\lambda$. Then we can get the general form for the $n^{th}$ reflected beam:
\[ E_{n}^{r} = t_{10}t_{01}(r_{12})^{n-2}(r_{01})^{n-1}e^{-j(2n-2)\beta}E_{\text{incident}} \]  

(4.5)

with \( t_{ij} \) and \( r_{ij} \) being the transmission and reflection coefficient between layers \( i \) and \( j \).

Substituting the following relationships: \( r_{01} = -r_{10}, \ t_{10}t_{01} = 1 - r_{01}^{2} \) and summing the reflected beams we can get the expression of the reflectance

\[ R = \frac{E_{\text{total}}}{E_{\text{incident}}} = \frac{r_{01} + r_{12}e^{-i2\beta}}{1 + r_{01}r_{12}e^{-i2\beta}} \]  

(4.6)

where \( r_{01} \) and \( r_{12} \) can be easily calculated using the Fresnel equations. Practically, the VASE software has a built in program using this method to do the reflectance calculation for either a TE or TM mode.

Figure 4.2 shows the results of these two reflection calculation methods applied to the same GaAs native oxide sample. The calculated reflectance of a bare GaAs substrate is also shown in Figure 4.2 for comparison. The sample used here is the one with the best optical constants fitting mentioned in Chapter 3 for the 182.5 nm oxide. Comparing to the measured reflectance result, the second method has a better accuracy in the wavelength range of 400 to 800 nm. The disagreement of the calculated and the experimental results may be due to the non-specular, diffusive reflection (scattering component) from the rough interface, or the inhomogeneity of the oxide film (as discussed in Section 2.3).
Figure 4.2. Comparison of the two reflectance calculation methods and the experimental reflectance measurement. The oxide sample is grown under 420 °C 3000 ppm O₂/N₂ rate for 42 minutes which yields a 182.5 nm thick oxide.

4.2 AR Coating Films and Experimental Characterization

In an anti-reflection coating, the reflected waves from the oxide surface and from the interface of the oxide and GaAs must interfere destructively, which requires their phase difference to be odd multiples of π. The complete cancellation of the two waves, that is, zero reflectance, also requires that the two waves have the same amplitude, which can be expressed by the relationship of the refractive indices

\[ n_1^2 = n_0 \times n_2 \] (4.7)
Here we consider the simple structure of a single layer of GaAs oxide on the GaAs substrate. Within the visible light wavelength range, the index of the GaAs native oxide has a lower value of around 1.8 and the GaAs substrate has a higher index of around 3.8. Both of the reflection coefficients from the surface and interface are negative, denoting a phase change of 180°. If the two reflected wave from each interface have a phase difference of 180°, which occurs if the interface-reflected layer makes a round trip (2 passes) through a quarter wave optical thickness oxide film of index $\sqrt{n^2}$, the two waves will have opposite electric field vectors and will add destructively. Even though this is an approximate derivation from physical understanding, the conclusion is exactly correct. An accurate derivation considering the multiple reflections in the layer can be found in Reference [12]. In this case, minimum reflectance requires that the GaAs native oxide layer have a thickness $d$ of

$$d = m \left( \frac{\lambda}{4n} \right), \quad m = 1, 3, 5 \ldots$$  \hspace{1cm} (4.8)

where $n$ is the refractive index of the oxide. For fixed wavelength and oxide film refractive index, the reflectance is oscillating with the thickness of the oxide film, as shown below in Figure 4.3. The refractive indices of GaAs and the oxide used in the plot are 3.83 and 1.72 at 550 nm, respectively. The oxide thicknesses of 80, 240 and 400 nm give a minimum reflectance of 1.65% for this single oxide film structure, corresponding to $m$ is 1, 3 and 5 from equation 4.8, respectively. From Figure 4.2, we can also observe that the reflectance also oscillate with the wavelength if the film thickness is fixed. For example, at the reflectance minima point at $\lambda=274$ nm, the oxide thickness 182.5 nm is
approximately 5 (m=5) times the quarter wavelength optical thickness of 36.57 nm (182.5=5*274 nm/1.873/4), where n=1.873 in the refractive index from VASE).

![Figure 4.3. Reflectance of the native oxide film on GaAs @ λ=550 nm with different oxide thickness. Minimum of 1.65 % are at 80, 240 and 400 nm, maximum of 34.32% are at 160, 320 and 480 nm.](image)

In actuality, the optical constants n and k are functions of λ, as shown by the VASE measurement results of Figure 3.3 and 3.4. The decreasing trend of the indices of GaAs and the oxide within the visible wavelength range makes the minimum achievable reflectance vary over the AR coating design wavelength range. As can be observed in Figure 4.2, the antireflecting film order m=1 (that is, the thinnest, quarter wavelength optical thickness oxide film) should be chosen to realize the broadest low reflectance bandwidth [15]. Using the extracted optical constants from VASE, a sweep of the
reflectance vs. wavelength for different oxide thicknesses is performed with the results shown in Figure 4.4 below. Within the visible light wavelength range (400 ~ 700 nm), the 80 nm oxide gives the best average reflectance value, which is ~10% over bandwidths as large as 300 nm with a minimum of 2.3% at 555 nm. If we focus on the near infrared wavelength range 650 ~ 800 nm, a 100 nm thick native oxide film can provide an average reflectance of 3% with the minimum of 1.4% at 687 nm.

Figure 4.4. Reflectance simulation over 250 to 800 nm wavelength range with varied oxide film thickness from 50 to 100 nm.

For the single layer AR coating application, all the GaAs native oxide films of different thicknesses from 50 to 100 nm in Figure 4.4 were planned to be demonstrated experimentally here, especially the one with the optimal thickness of 80 nm. However, completion of the oxidations other than the first 50 nm thick sample was prevented by
an extended equipment outage during the summer and fall of 2012. The 50 nm sample was grown under the oxidation condition of 420 °C, and a 2K ppm O₂/N₂ ratio. From the observed linear oxidation rate of the GaAs oxidation process discussed in Figure 2.5, under these oxidation conditions, the fitting equation of the oxide thickness y (in Å) and the oxidation time x (in min) is y=38.239x-481.91. Aiming to grow an oxide of 50 nm, the calculated oxidation time should be 25 minutes and 40 seconds. The actual measured thickness of a GaAs native oxide film grown under these conditions is 50.1 nm, which proves the precise control of the oxide thickness achievable in this process.

4.3 Reflectance Measurements

Reflectance measurements are performed using a spectrometer and components from Ocean Optics Inc. to characterize the reflectance of the GaAs native oxide AR coating films. In this section, a brief overview of this system, its calibration and use for measuring reflectance is given, followed by a presentation of the experimental results, which are shown to have good agreement with the simulated reflectance spectra in the previous section.

4.3.1 System Introduction

Figure 4.5 below shows the diagram of the reflectance measurement system set up. The light source sends broadband white light via the input port of a fiber reflection probe onto the sample under test. The reflection / backscattering probe is coupled to the spectrometer and light source for measuring reflection or fluorescence from the sample surface. The reflection probe is mounted at a 90-degree angle and positioned
~5 mm from the sample surface. The output port of the reflection probe carries light from the sample to the spectrometer, which is connected to a computer via a USB cable for the data read out and analysis.

For this study, the reflectance of the single native oxide layer on the GaAs substrate is measured over the wavelength range of 400 ~ 800 nm. An Ocean Optics LS-1 Tungsten Halogen Light Source provides white light illumination over a wavelength range of 215 - 2000 nm and the Ocean Optics USB4000-UV-VIS spectrometer using a fixed grating and 3648-element linear CCD-array detector is preconfigured for spectral measurements from 200 to 850 nm with a spectral resolution of ~1.5 nm (FWHM). The reflection probe consists of a tight bundle of 7 optical fibers in a stainless steel ferrule -- 6 illumination fibers around 1 read fiber as shown in the inset to Figure 4.5. Each fiber is 200 μm in diameter. To align the sample for the measurement, an adjustable stage is used for the probe holder to gradually adjust the distance between the probe and tilt the sample to collect the maximum reflected power into the center read fiber.
Figure 4.5. Diagram of the reflection measurement system. Inset: the 6-around-1 design of the reflection probe.

Using this system, the reflection is expressed as a percentage ($%R_\lambda$) relative to the reflection from a standard reference substrate: [16]

$$%R_\lambda = \frac{S_\lambda - D_\lambda}{R_\lambda - D_\lambda} \times 100\%$$

(4.9)

where $S_\lambda$ is the sample intensity at wavelength $\lambda$, $D_\lambda$ is the dark intensity at wavelength $\lambda$, $R_\lambda$ is the reference intensity at wavelength $\lambda$. The dark intensity spectrum must be taken every time before each reflectance measurement.

4.3.2 System Calibration and Standard Reference Measurement

To calibrate the system, we use an Ocean Optics STAN-SSL low-reflectivity specular reflectance standard as a reference. This low reflectivity standard is a black glass standard especially for measuring surfaces with low specular reflectance values. It
has a ~4.0% reflectance across the 400-900 nm wavelength range as shown in the following figure.

Figure 4.6. STAN-SSL Specular Reflectance standard reflection measurement after system calibration, comparing with the provided calibration standard reference data.

The dashed line (almost overlapped with the dotted line) shows the measured reflectance data of the reference standard. The acquired data after calibration is just a little bit lower (decreasing from ~0.06% at 400 nm to ~0.03% at 900 nm) across the whole wavelength range (that is, ~1.5% down to ~0.75% relative error) compared to the standard reflectance reference data provided by the company, indicating the typical repeatability achievable with the measurement system. The slight error may come from a drift in the intensity of the white light source or other minor instabilities.
We must properly set the acquisition parameters of the signal processing functions in the Ocean Optics SpectraSuite software to increase the signal to noise ratio (S:N) through boxcar pixel smoothing and signal averaging to minimize the effects of drift in the dark signal or stray light correction.

For example, the S:N ratio improves by increasing the square root of the number of scans averaged, at the expense of longer acquisition time. This longer time may lower the measurement accuracy because the dark spectrum decreases as the spectrometer’s detector gets warmer. In practice, the entire acquisition time (which is the product of the value of “scans to average” and the “Integration time”) needs to be less than 2 minutes before taking a new dark spectrum. The integration time is analogous to the shutter speed of a camera and should be set for the great act accuracy so that the majority of the CCD array detectors reach raw counts of the photons detected near about 85% of their maximum capacity.

Boxcar smoothing is a technique that averages across the spectral data to increase the S:N. This technique averages a group of adjacent detector elements. A typical boxcar width setting of 4 is used for the measurements of this work, which averages each data point with 4 points to its left and 4 points to its right. The S:N will improve by the square root of the number of pixels averaged. A greater boxcar averaging width value could yield even smoother data and a higher signal-to-noise ratio, but would result in a loss in spectral resolution.
4.3.3 Reflectance of the GaAs Native Oxide AR Coating Film

Using this reflectance measurement system, the reflectance of a 50.1 nm GaAs oxide single-layer quarter-wave optical thickness AR coating is characterized. The measurement data, shown in Fig. 4.7, shows a very good match to the theoretical calculation reflectance data for wavelength over 500 nm, with a somewhat lower reflectance value measured for wavelengths shorter than 500 nm. The single oxide film does reduce the reflectance comparing with the reflectance of a bare GaAs substrate (also shown in Figure 4.7).

![Graph showing measured reflectance vs. calculated reflectance](image)

**Figure 4.7.** Measured reflectance of the 50 nm thick GaAs native oxide AR coating film vs. reflectance calculation results

The discrepancy between measured and calculated reflectance is in the range of 5.4% (=16.0% - 10.6%) at 425 nm and 1.2% (=13.8% - 12.6%) at 500 nm. The source of
the discrepancy is not well understood. Comparing Fig. 4.7 to the optical constants of GaAs shown above in Fig. 3.4 reveals that the feature at 425 nm in the reflectance data correlates to a critical point in the optical constants characterized by a peak in n and rise in k at the wavelength. As the calculated reflectance is thus more impacted by the optical properties of the GaAs (especially, the quite high index of this underlayer at this wavelength), it is possible that the lower experimental reflectance reveals a different composition interface layer against the oxide (either a lower index intermediate layer such as arsenic oxide), or increased scattering due to interface roughness that allows less penetration of the reflected wave into the GaAs.

Another possible source of the discrepancy may be the effects of surface roughness, as the portion of the incident power scattered from the surface will most likely not be collected by the probe detector. Because of the large spot size of the probe (about 1.5 mm if the distance between the probe and the sample is 5 mm), this lost power, which will lower the measured reflectance, might not be negligible. Finally, we can see from the TEM image that the oxide is not perfectly homogeneous, such that the optical constants throughout the oxide layer may not be the same as we extracted from the VASE, resulting in an error in the reflectance calculation.
CHAPTER 5:

CONCLUSION

In this thesis, we provided a valuable, thorough study characterizing the novel oxygen-enhanced wet thermal oxidation process as applied to the important compound semiconductor GaAs. The process conditions have been carefully characterized and optimized for a custom built III-V semiconductor wet oxidation system after its installation in the new Notre Dame Nanofabrication Facility clean room. Compared to our group’s previous published work [5], lower surface and interface roughness of the oxide has been demonstrated, as well as a higher linear oxidation rate. For a 420 °C process temperature, the optimal O$_2$/N$_2$ ratio for GaAs oxidation is found to be 2500 ppm in our system. Furthermore, the narrow gas mixture window for O$_2$-enhanced wet oxidation is clearly elucidated, with the observed transition from a linear growth regime at ratios up to 3000 ppm to a diffusion limited regime (and ultimately the formation of a dense terminal thickness oxide [5]) as the O$_2$/N$_2$ ratio is further increased to 7500 ppm.

A good VASE model has been developed to accurately fit the thickness and extract the optical constants of the GaAs native oxide film in the range of 1.5 to 5 eV. These optical constants have been used in the design of a GaAs native oxide anti-reflection coating. The TEM measurements of selected samples confirm the validity of
the VASE model for thickness measurement and the AFM interface roughness measurement.

Two methods are used in the simulation of the reflectance performance of the native oxide based on the optical constants from VASE. The experimental reflectance measurement using an Ocean Optics Reflectance Measurement system confirms the validity of the optical constants and the simulation methods. An oxide AR coating with reflectance less than 10% over a range of 300 nm has been simulated, with a minimum surface reflectance of $R = 2.3\%$ achieved (compared to the 32% reflectance of a bare GaAs substrate).
%% load GaAs and GaAs native oxide refractive index data using loadtest.m

clear all;
clc;

data=fopen('C:/Users/hall-lab/Documents/MATLAB/gaas-oxgenosc2.mat','r');

% Read and skip the header info
dataline1=fgetl(data);
dataline2=fgetl(data);
dataline3=fgetl(data);

% Read data and plot
n=1;
while ~feof(data) % Stop when reach the end of the data file
    gaasox(n,:) = str2num(fgetl(data));
    % gaasox(n,1)=1.24/gaasox(n,1)*1000;
    n = n+1;
end

% subplot(2,1,1);
% [AX,H1,H2] = plotyy(gaasox(:,1),gaasox(:,2),gaasox(:,1),gaasox(:,3));
% set(get(AX(1),'Ylabel'),'String','n')
% set(get(AX(2),'Ylabel'),'String','k')
% xlabel('Wavelength(nm)')
% title(dataline1)

% Open GaAs optical constant data file from VASE database
data = fopen('C:/Users/hall-lab/Documents/MATLAB/gaas_p.mat','r');

% Read and skip the header info
dataline1 = fgetl(data);
dataline2 = fgetl(data);
dataline3=fgetl(data);

% Read data and plot
n=1;
while ~feof(data) % Stop when reach the end of the data file
gaas(n,:)=str2num(fgetl(data));
% gaas(n,1)=1.24/gaas(n,1)*1000;
    n=n+1;
end

% subplot(2,1,2);
% [AX,H1,H2] = plotyy(gaas(:,1),gaas(:,2),gaas(:,1),gaas(:,3));
% set(get(AX(1),'Ylabel'),'String','n')
% set(get(AX(2),'Ylabel'),'String','k')
% xlabel('Wavelength(nm)')
% title(dataline1)

% Complex index for GaAs and GaAs native oxide N=n+ki
Ngaas=gaas(:,2)+gaas(:,3)*i;
Ngaasox=gaasox(:,2)+gaasox(:,3)*i;
% Input: index of each layer and the oxide thickness
Reflectance_calculator_wavelength(Ngaasox,Ngaas,182.527);

function
Reflectance_calculator_wavelength(Ngaasox,Ngaas,t_ox)
%Originally from Wangqing Yuan's Reflection_calculator.m
%PLTRANSMISSION Summary of this function goes here
% Detailed explanation goes here
% Born&Wolf principles of Optics, Chapter 1 and Chapter 14

%%% optical constant, complex index for each layer
n_oxide=Ngaasox; %need to match the wavelength range
n_GaAs=Ngaas; %need to match the wavelength range

% n_Ti=2.903+3.327i;
% n_Au=0.18296+5.1993i;
% n_SiN=2.0092;

N=3; % number of layer
AOI=0; % angle of incidence

%%% parameter
wavelengthrange=linspace(250,800,551); % for plot
R_matrix=zeros(551,1);

for wavelength=250:800  % wavelength range in nm
    n=[n_GaAs(wavelength-249);n_oxide(wavelength-249);1];

    %wavelength=808; % in nm
    %t_ox=linspace(0,500,501);
    %for count=1:501
        h=[0;t_ox;0];          % multiple layer structure
    in nm

    %% generate characteristic Matrix for each layer
    AOI=AOI*pi/180; % convert degree to rad
    Theta=zeros(1,N);
    Beta=zeros(1,N);
    Matrix_TE=zeros(2,2,N);
    Matrix_TM=zeros(2,2,N);
    for j=1:N
        Theta(j)=asin(n(1)*sin(AOI)./n(j));
        Beta(j)=2*pi/wavelength*n(j).*h(j).*cos(Theta(j));
        p(j)=n(j).*cos(Theta(j));
        q(j)=1./n(j).*cos(Theta(j));
        Matrix_TE(1,1,j)=cos(Beta(j));
Matrix_TE(2,2,j)=cos(Beta(j));
Matrix_TE(1,2,j)=-i./p(j).*sin(Beta(j));
Matrix_TE(2,1,j)=-i.*p(j).*sin(Beta(j));
Matrix_TM(1,1,j)=cos(Beta(j));
Matrix_TM(2,2,j)=cos(Beta(j));
Matrix_TM(1,2,j)=-i./q(j).*sin(Beta(j));
Matrix_TM(2,1,j)=-i.*q(j).*sin(Beta(j));
end

%% Final Matrix for transmision
FinalMatrix_TE=eye(2,2);
FinalMatrix_TM=eye(2,2);
for j=1:N
    FinalMatrix_TE=FinalMatrix_TE*Matrix_TE(:,:,j);
    FinalMatrix_TM=FinalMatrix_TM*Matrix_TM(:,:,j);
end

%% transmition and reflection coefficient
r_TE=((FinalMatrix_TE(1,1)+FinalMatrix_TE(1,2)*p(N))*p(1)-(FinalMatrix_TE(2,1)+FinalMatrix_TE(2,2)*p(N)))/((FinalMatrix_TE(1,1)+FinalMatrix_TE(1,2)*p(N))*p(1)+(FinalMatrix_TE(2,1)+FinalMatrix_TE(2,2)*p(N)));
t_{TE} = \frac{2p(1)}{((\text{FinalMatrix}_{TE}(1,1)+\text{FinalMatrix}_{TE}(1,2)*p(N))\times p(1)+ (\text{FinalMatrix}_{TE}(2,1)+\text{FinalMatrix}_{TE}(2,2)*p(N)))};

r_{TM} = \frac{(\text{FinalMatrix}_{TM}(1,1)+\text{FinalMatrix}_{TM}(1,2)*q(N))*q(1)-(\text{FinalMatrix}_{TM}(2,1)+\text{FinalMatrix}_{TM}(2,2)*q(N))}{((\text{FinalMatrix}_{TM}(1,1)+\text{FinalMatrix}_{TM}(1,2)*q(N))*q(1)+(\text{FinalMatrix}_{TM}(2,1)+\text{FinalMatrix}_{TM}(2,2)*q(N)))};

t_{TM} = \frac{2q(1)}{((\text{FinalMatrix}_{TM}(1,1)+\text{FinalMatrix}_{TM}(1,2)*q(N))*q(1)+(\text{FinalMatrix}_{TM}(2,1)+\text{FinalMatrix}_{TM}(2,2)*q(N)))};

R_{TE} = (\text{abs}(r_{TE})^2;
T_{TE} = \text{real}(p(N)*t_{TE}*\text{conj}(t_{TE}))/\text{real}(p(1));
\% \text{abs}(p(N)/p(1)*t_{TE}^2)
R_{TM} = (\text{abs}(r_{TM})^2;
T_{TM} = \text{real}(q(N)*t_{TM}*\text{conj}(t_{TM}))/\text{real}(q(1));
\% \text{abs}(q(N)/q(1)*t_{TM}^2)
R = (R_{TE}+R_{TM})/2;
R_{\text{matrix}}(\text{wavelength}-249)=R;
\% \text{end}
end

plot(\text{wavelengthrange},R_{\text{matrix}})
xlabel('Wavelength in nm');

ylabel('Reflectance');

title('Reflectance vs. Wavelength')

end
REFERENCES


