EFFECTS OF NICKEL OXIDE ON NICKEL/GOLD CONTACTS TO P-TYPE GALLIUM NITRIDE

By

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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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Chair: Michael J. Kaufman
Major Department: Materials Science and Engineering

A determination of the role of NiO on the formation of Ni/Au ohmic contacts to p-GaN has been carried out by conducting a variety of deposition and annealing experiments followed by detailed characterization. Current-voltage (I-V) measurements for Au/pre-oxidized NiO/p-GaN contacts indicate contacts produced this way are not ohmic in nature but rather exhibit Schottky barrier behavior. The interface between NiO and p-GaN was analyzed using TEM and no reaction phase forms between Ni and p-GaN after annealing at 500°C in an oxidizing ambient although this treatment does convert Ni to NiO. The strain produced in the p-GaN upon Ni deposition is partially released during annealing in an oxidizing ambient for the samples containing either 600A or 1500A Ni while a similar annealing of the sample coated with 150A Ni sample did not result in measurable strain release in GaN. XRD analysis of the GaN sample coated with Ni50A/Au50A (the industry standard for producing ohmic contacts on p-GaN) indicated
that these contacts produce negligible strain in GaN. Based upon the experimental results, it is concluded that the NiO formed during annealing in an oxidizing ambient does not result in the low resistance ohmic contact behavior observed for Ni/Au contacts to p-GaN. Rather, the current path for the low resistance ohmic contacts of Ni/Au annealed in an oxidizing ambient appears to result from the direct contact between the Au phase and the p-GaN. Finally, it is shown that the optical transmittance of NiO produced by thermal oxidation is dependent on crystallographic orientation (texture).
GaN is an important material because it has a direct band gap which is suitable for blue and UV light emission. High temperature operation is another promising feature of GaN due to its wide band gap, high breakdown electric field and high saturation velocity. Therefore, many researchers have focused on GaN over the last few decades. In spite of the desirable features of GaN, there are two major processing challenges. One of them is related to epitaxial growth of GaN. The single crystal growth of bulk GaN is difficult because its melting temperature is high (~2500°C) and because nitrogen has a high vapor pressure at these elevated temperatures. Consequently, the exact stoichiometry of GaN is hard to achieve by growing from the melt. Therefore, GaN is usually grown epitaxially on the basal plane of sapphire (α-Al₂O₃) substrates. The difference in lattice constant between GaN and sapphire tends to result in high defect density in epitaxially grown GaN films. SiC (silicon carbide) is an alternative to sapphire but is rarely used because it is considerably more expensive. The other challenge for GaN is that it is hard to produce low resistance ohmic contacts to p-GaN. There are two major obstacles to achieving low resistance ohmic contacts. The first is related to the high work function of p-GaN since, to make ohmic contacts for p-type semiconductors, the work function of the metal should be higher than that of the p-type semiconductor. Unfortunately, no metal satisfies this criterion for p-GaN. The other obstacle for low resistance ohmic contacts is the high activation energy of the acceptor in p-GaN. Since
Mg has the lowest activation energy among possible p-type dopants. Mg is used as an acceptor for p-GaN. The activation energy of Mg (150meV - 200meV) is 3-5 times higher than that of dopants (~30-50meV) for Si. Further, the ionization efficiency of Mg is low (~6% at room temperature). Some researchers have tried to increase the Mg concentration in order to compensate for its low ionization efficiency. However, increasing the Mg concentration above certain levels does not improve conductivity but results in a decrease in hole concentration. The decrease in hole concentration can be explained by the solubility limit of Mg in GaN which is due to competing formation of Mg3N2. Finally, Some investigators have attempted to use Be as an acceptor and O as a reactive codopant to increase its activation efficiency.

In efforts to produce low resistance ohmic contacts to p-GaN, many different approaches have been tried and reported. In light of the Schottky barrier height of the junction, metals with high work functions should be used for p-GaN contacts because the Schottky barrier height decreases as the work function of the metal increases. Various metal contacts were applied to p-GaN. Other investigators have attempted to get rid of the native oxide between the metal and p-GaN because a native oxide between the metal contact and p-GaN increases the specific contact resistance. The surface treatment before the deposition of metal also has an effect on specific contact resistance. Other investigators have focused on the role of hydrogen in p-GaN since hydrogen reacts with Mg and makes Mg-H complexes which prevent Mg activation and decrease the hole concentration in p-GaN. The decrease in hole concentration results in an increase in specific contact resistance. Therefore, the removal of hydrogen from p-GaN is one approach for producing low resistance ohmic contacts to p-GaN. Finally, other groups
have focused on producing superlattice structures to increase the hole concentration in the near-surface regions. Thus far, InGaN/GaN and GaN/AlGaN/GaN superlattice structures have been reported.\textsuperscript{29-32}

The low specific contact resistance of Ni/Au contacts is obtained by annealing in an oxidizing ambient. Although many research papers have been published about Ni/Au contacts to p-GaN, the mechanism of low resistance ohmic contacts has not yet been positively identified.

In this research, a determination of the role of NiO on the formation of Ni/Au ohmic contacts to p-GaN has been carried out by conducting a variety of deposition and annealing experiments followed by detailed characterization. The optical transmittance of NiO produced by thermal oxidation is also discussed.
CHAPTER 2
THEORY AND BACKGROUND

2.1 Metal-Semiconductor Junctions

A metal-semiconductor junction may be ohmic or rectifying, depending on the nature of the semiconductor (p or n type) and the relative work functions of the two materials.

2.1.1 Rectifying Contacts

Figure 2-1(a) shows an energy band diagram of the junction between a metal and an n-type semiconductor. In this figure, $\Phi_M$ and $\Phi_S$ refer to the work function of the metal and the semiconductor, respectively. The work function of a material is the energy difference between the vacuum level and the Fermi energy level. In addition, $\chi$ is the electron affinity of the semiconductor and is the energy difference between the top of the conduction band, $E_C$, and the vacuum level. The metal-semiconductor (n-type) contact in which $\Phi_M > \Phi_S$ is called a Schottky barrier diode as shown in Figure 2-1(a) and this device shows non-linear I-V (current – voltage) characteristics. When the junction is formed, electrons flow from the semiconductor to the metal because they have higher energy in the semiconductor. This flow continues until the Fermi levels are aligned as shown in Figure 2-1(b). The electron flow from the n-type semiconductor to the metal leaves the surface of the semiconductor depleted of electrons and leaves behind positively charged donor ions in the semiconductor. In the near-interface region, the Fermi level of the semiconductor must move towards the valence band and induce upward bending of
the energy band as shown in Figure 2-1(b). The negative charge develops on the metal side because of the electron transfer from the semiconductor to the metal. Since these two types of charges exist on either side of the junction, the electric field directed from the semiconductor to the metal is produced. The equilibrium contact potential of the junction represents the difference between the work function potentials $\Phi_M$ and $\Phi_S$. The barrier height $\Phi_B$ for the injection of electrons from the metal to the semiconductor is given by

$$q\Phi_B = q\Phi_M - q\chi$$  \hspace{1cm} (1)
This type of metal-semiconductor contact is called a Schottky contact. A Schottky contact is also formed when a metal with a small work function compared with that of the semiconductor is deposited on a p-type semiconductor. This condition is shown in Figure 2-2. To align the Fermi levels in this case, electrons must flow from the metal to the semiconductor, resulting in a positive surface charge in the metal and a negative charge on the semiconductor. The negative charge exists within a depletion region in which acceptor ions are left uncompensated by the holes. The potential barrier is $\Phi_S - \Phi_M$ designated in Figure 2-2 (b).

### 2.1.2 Ohmic Contacts

An ohmic contact is a metal-semiconductor contact that has a negligible contact resistance relative to the bulk or series resistance of the semiconductor. This type of contact can be formed when metal-semiconductor junctions satisfy the following requirements: $\Phi_M < \Phi_S$ for n-type and $\Phi_M > \Phi_S$ for p-type semiconductors. When $\Phi_M < \Phi_S$ and the semiconductor is n-type as shown in Figure 2-3(a), the Fermi levels are aligned by the transfer of electrons from the metal to the semiconductor. This alignment raises the electron energies of the semiconductor relative to that in the metal at equilibrium as shown in Figure 2-3(b). There is no energy barrier to the flow of electrons from the metal to the semiconductor. When $\Phi_M > \Phi_S$ and the semiconductor is p-type (Figure 2-4), electrons flow from the valence band of the semiconductor to the metal. Since the valence band is not completely filled near the metal junction, electron-hole pairs in the valence band are formed by exciting valence electrons to higher available energy levels within the valence band, which results in a junction that does not provide a barrier to current flow.
2.2 Surface Pinning Effect

It is often observed that the Schottky barrier heights for various metals on a particular semiconductor (especially III-V compound semiconductors) are the same. This behavior is attributed to the presence of a large number of interface states in the band gap.
of the surface region of the semiconductor; these states arise from the surface dangling bonds and impurities. As a result, the addition or removal of electrons from the metal semiconductor

![Energy band diagram](attachment:energy_band_diagram.png)

Figure 2-3. Energy band diagram of ohmic contact for n-type semiconductor (a) before contact (b) after contact

semiconductor does not alter the position of the Fermi level at the surface and the Fermi level is said to be pinned. Figure 2-5 shows the surface pinning effects for III-V semiconductors. Since GaN does not show a surface pinning effect, the Schottky barrier

![Energy band diagram](attachment:energy_band_diagram.png)
height between the metal and GaN must be dependent on the work function of the metals.\textsuperscript{34}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure.png}
\caption{Energy band diagram of ohmic contact for p-type semiconductor (a) before contact (b) after contact}
\end{figure}

2.3 Native Oxide Effects

According to the metal-semiconductor band theory, the Schottky barrier height can be influenced by the native oxide thickness between the metal and the semiconductor. The effect of oxide thickness on Schottky barrier height can be represented by equation
According to equation (2), the Schottky barrier height increases with an increase in oxide thickness and high Schottky barrier heights result in high specific contact resistances.

Figure 2-5. Final $E_F$ position for a number of metals and oxygen on GaSb GaAs and InP. Note that there is little dependence on the chemical nature of the adatom.
2.4 Properties of GaN

GaN grown on sapphire substrate has the wurzite structure. The wurzite structure has a hexagonal unit cell and is similar to the zincblende structure. For wurzite, the stacking sequence of the (0001) plane is ABABAB, while for the zinc-blende structure, the stacking sequence of the \{111\} planes is ABCABC. The wurzite structure is shown in Figure 2-6 and the selected properties of GaN are presented in Table 2-1.\textsuperscript{36}

2.5 Gallium Vacancies in GaN

It has been reported that (1) Ga vacancies are not found in p-type or semi-insulating Mg-doped layers, (2) Ga vacancies are found in nominally undoped GaN layers, which show n-type conductivity due to residual oxygen, and (3) Ga vacancy concentrations are lower in samples, where the n-type doping is done with Si impurities and the amount of residual oxygen is reduced.\textsuperscript{37} It is also reported that Ga vacancies in GaN layers depend

![Figure 2-6. Wurzite structure of GaN](image-url)
Table 2-1. Selected properties of GaN

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (Å)</td>
<td>$a = 3.189$, $c = 5.186$</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>2500</td>
</tr>
<tr>
<td>Linear thermal expansion coefficient (°C$^{-1}$)</td>
<td>$\alpha_a = 5.59 \times 10^{-6}$, $\alpha_c = 3.17 \times 10^{-6}$</td>
</tr>
<tr>
<td>Energy gap (eV)</td>
<td>3.39</td>
</tr>
<tr>
<td>Breakdown field (V cm$^{-1}$)</td>
<td>$\approx 5 \times 10^6$</td>
</tr>
</tbody>
</table>

both on the Fermi level and the impurity atoms in the samples. The same general trend is found in the epitaxial layers as in the bulk crystals: Ga vacancies are formed only in $n$-type doping concentrations when oxygen is present. However, if similar doping is done with Si donors, no Ga vacancies are formed. This behavior can be explained through association of the observed Ga vacancies with complexes involving oxygen, such as $V_{Ga}$-$O_N$. Theoretically the formation energies of charged defects in thermal equilibrium depend on the position of the Fermi level in the energy gap, as shown in the calculated results of Figure 2-7. The negatively charged defects such as Ga vacancies have their lowest formation energy when the Fermi level is close to the conduction band, i.e. in $n$-type material. On the other hand, the formation energy of $V_{Ga}$ is high in semi-insulating and p-type material. These trends correlate with the experimental results showing that Ga vacancies are observed only in $n$-type material. It has been reported that N vacancies can act as donors in GaN with Ga vacancies acting as acceptors.

2.6 Nickel/Gold Contacts

Ni/Au is the most common metal for p-GaN contacts. The low specific contact resistance of Ni/Au contacts is obtained by annealing it in an oxidizing ambient. Ni has
a relatively high work function (5.01 eV) among possible metals, and hydrogen can be removed from the Mg-doped GaN by the deposition of a Ni film on the top surface of p-GaN and subsequent annealing in N₂ ambient.\textsuperscript{3,40} The specific contact resistance of Ni/Au contacts is sensitive to anneal condition.\textsuperscript{39,41,42} Annealing in an oxidizing ambient is more effective than annealing in a nitrogen ambient for producing low specific contact resistance. The microstructure of Ni/Au annealed in an oxidizing ambient was reported by Chen et al.\textsuperscript{43} Figure 2-8 shows an island-shaped Au phase with a small amount of Ni, NiO crystalline structure over Au island, and a small region of amorphous phase on the top of GaN substrate with a relatively large amount of Ga as well as Ni and O. A possible path for high current flow of Ni/Au contact was suggested and designated by arrow in Figure 2-9.\textsuperscript{44} Based upon TEM analysis,\textsuperscript{43} the authors suggested that, during annealing, Ni diffused out through the Au layer to react with oxygen and formed crystalline NiO as shown in Figure 2-10. Ho et al. suggested that NiO formation is one of the reasons for

![Figure 2-7. Formation energies of various defects in GaN as a function of the Fermi level, \( \mu_e \), according to theoretical calculations.](image)
Figure 2-8. TEM micrograph of Ni/Au on p-GaN after an oxidizing treatment at 500°C for 10min in air; a: Au includes a small amount of Ni, b: face-centered cubic NiO phase, c: amorphous regions consisting of a relatively larger amount of Ga as well as Ni and O.

Figure 2-9. TEM micrograph of Ni/Au on p-GaN after an oxidizing treatment at 500°C for 10min in air; the arrow indicates a possible path for high current flow.
Figure 2-10. Schematic illustration of the reaction mechanism and diffusion behavior during the oxidation of Ni/Au on p-GaN. (a) Early stage of oxidation reaction, (b) pronounced interdiffusion and crystalline NiO grow up to separate the Au-Ni alloy into discrete islands, (c) Au-rich islands building epitaxially on p-GaN and three possible reactions producing Ni-Ga-O phases and (d) oxidized contact scheme with optimum phase distribution.
low specific contact resistance because NiO was considered as a p-type semiconductor in direct contact with p-GaN. But this explanation is still controversial. Two different explanations have been suggested: (1) favorable band line-up when p-type NiO layers form between Au and p-GaN (Ho et al.)\(^{41}\), and (2) high hole concentration in p-GaN.\(^{45}\) The effects of NiO on specific contact resistance were reported by several researchers \(^{46,47}\) Several investigators examined the role of Au in Ni/Au contacts \(^{43-50}\) and reported that Au is necessary because Ni-only contacts showed high specific contact resistance compared to Ni/Au contacts.

2.7 Measuring Specific Contact Resistance

The specific contact resistance is determined by current-voltage (I-V) measurements using CTLM (circular transmission line method) patterns.\(^{51}\) For CTLM measurements, the total resistance, \(R_t\), between two electrodes separated by a circular gap is represented by equation (3).

\[
R_t = \frac{R_{sh}}{2\pi} \times \left[ \ln \left( \frac{R}{r} \right) + L_t \left( \frac{1}{R} + \frac{1}{r} \right) \right] \quad (3)
\]

where \(R_{sh}\) is the sheet resistance of p-GaN, \(R\) and \(r\) represent the radius of the outer and inner electrode, respectively, and \(L_t\) is the transfer length. The total resistance can be measured and plotted as a function of \(\ln(R/r)\). The fitting of this graph using the least squares method is conducted to get a linear curve of \(R_t\) vs. \(\ln(R/r)\). The slope of this fitted linear curve is the sheet resistance of the substrate and the intercept at \(\ln(R/r) = 0\) is \(R_{sh} \cdot L_t / (r \pi)\). The specific contact resistance can be calculated using the following equation:
The conductivity of NiO is due to non-stoichiometry. The formation of defects is the following:

\[
\frac{1}{2} O_2(g) \leftrightarrow O^x_a + V^{x}_{Ni}
\]

\[
V^{x}_{Ni} \leftrightarrow V^{+}_{Ni} + h^+
\]

\[
V^{++}_{Ni} \leftrightarrow V^{+}_{Ni} + h^+
\]

where

- \(O^x_a\): an oxygen anion on an anion site
- \(V^{x}_{Ni}\): a neutral Ni vacancy
- \(V^{+}_{Ni}\): singly charged Ni vacancy
- \(V^{++}_{Ni}\): doubly charged Ni vacancy

When oxygen is added to NiO, the nonstoichiometry is enhanced and the hole concentration increases.

2.9 Optical Properties of NiO

2.9.1 Optical Gap of NiO

It is known that the optical gap of NiO is 4.0eV. As shown in Figure 2-11, the optical absorption of NiO begins at 3.1eV and a first peak is at 4.3eV. A plateau in the absorption is maintained up to about 9eV and the absorption rises again beyond 9eV. The optical absorption of NiO, 4.0eV, comes from the point that the line with maximum slope of absorption intersects the averaged absorption between 4.3eV and 10eV. For semiconductors, the optical gap is defined as the difference between the smallest ionization and the smallest electron affinity energy, in other words, the energy one needs.
to create a free electron-hole pair in the solid. The optical gaps can also be observed in free molecules like NiCl₂ and NiBr₂. For these cases, the optical gap is the energy it needs to transfer an electron from a ligand orbital onto a metal orbital and is called a charge transfer gap.⁵⁴

Figure 2-11. Optical absorption coefficient of NiO. 4.0eV is the energy obtained by extrapolating the flat absorption between 4.3eV and 9eV, and intersecting it with the tangent at the steepest point of the absorption between 3.1eV and 4.3eV.

2.9.2 Nickel Oxide Deposited by Sputtering

Some researchers investigated the transmittance of NiO layer produced by RF reactive magnetron sputtering.⁵⁵-⁵⁸ In the research of Lu et al.⁵⁹ NiO films were deposited under different O₂/Ar ratios. According to their results, the transmittance of NiO films shows a strong dependence on the O₂/Ar ratio. With increasing O₂/Ar ratio, the transmittance decays as shown in Figure 2-12. It should be noted that all samples have Ni deficiency and atomic percent of oxygen increases with increasing oxygen flow ratio as shown in
Figure 2-13. The resulting high Ni vacancy concentration makes many charge transfer transitions, which promotes optical absorption in visible light.

Figure 2-12. Transmittance of NiO as functions of oxygen flow ratio at the substrate temperature of 400°C.

Figure 2-13. Atomic percent of oxygen in the deposited NiO films as a function of oxygen flow rate ratio.
CHAPTER 3
GOLD/PRE-OXIDIZED NICKEL OXIDE/P-GALLIUM NITRIDE CONTACTS

3.1 Experiments

3.1.1 Sample Preparation

3.1.1.1 Ni/Au ohmic contact

In order to confirm that Ni/Au annealed in oxidizing ambient shows ohmic contact characteristics under these experimental conditions, and that the quality of the p-GaN is sufficient to produce ohmic contacts, it is necessary to produce a reference sample. For this reference sample, Mg-doped p-GaN (hole concentration ~2x10^{17} cm^{-3}) was cleaned in an aqua-regia (HCl:HNO_{3} =3:1) solution for 5min at room temperature followed by a DI water rinse and a N_{2} dry followed. Ni 50A and Au 50A were deposited on pre-cleaned p-GaN by e-beam evaporation. and annealed at 500°C for 10min in air. E-beam deposition in this research was conducted under 2x10^{-6} torr base pressure. CTLM (Circular Transmission Line Method) patterns were made through a lift-off process.

3.1.1.2 Au/pre-oxidized NiO/p-GaN contacts

Mg-doped p-GaN was cleaned in the aqua-regia solution for 5 min at room temperature to remove the native oxide and/or contamination layers. A DI water rinse and N_{2} dry followed. 50A of Ni was then deposited on cleaned p-GaN by electron-beam (e-beam) evaporation. The deposited Ni was annealed at 500°C for different times (0, 10s, 20s, 60s, 120s, 180s and 300s) in air. 1000A of Au was deposited on top of the oxidized Ni by e-beam evaporation. CTLM patterns (Figure 3-1) were produced through a photo and dry etch process. AZ-1529 positive photoresist was coated (4000rpm, 40s) and
exposed under I-line ($\lambda=405$nm) for 105 s. Dry etching was conducted in an ICP dry etcher using Cl$_2$ and Ar gas to define the CTLM patterns. The experimental sequence of sample preparation is presented in Figure 3-2.

Figure 3-1. Schematic diagram of CTLM patterns
Cleaning: *Aqua-regia*  
\((HCl:HNO_3=3:1)\ 5\text{min}

Ni 50A deposition by *e-beam evaporation*

Anneal at 500°C in air for various time  
(0-300s)

Au 1000A deposition by *e-beam evaporation*

*Photolithography to make CTLM pattern*

Dry etch by *ICP dry etcher*

*Figure 3-2. Process sequence to make CTLM pattern for pre-oxidized samples*
3.1.1.3 NiO sheet resistance

The n-type Si (111) was oxidized at 950°C for 24h in air to form an SiO₂ surface layer in order to electrically isolate the deposited Ni from the Si. A 50Å Ni layer was then deposited on SiO₂ by e-beam evaporation using the same chamber as that used to deposit the Ni on the p-GaN for the Au/pre-oxidized NiO/p-GaN experiments. Therefore, the Ni deposited on SiO₂ has the same thickness and same characteristics as Ni on p-GaN for the Au/pre-oxidized NiO/p-GaN experiments. After deposition, the samples were annealed at 500°C in air for different times similar to those used for the Au/pre-oxidized NiO/p-GaN experiments. Since annealing was conducted with Au/pre-oxidized NiO/p-GaN samples, annealing conditions are the same as those for Au/pre-oxidized NiO/p-GaN samples. It is evident that characteristics of NiO for different anneal times should be the same as the NiO which was produced for Au/pre-oxidized NiO/p-GaN experiments. CTLM patterns were produced on the NiO layer through a lift-off process. Photolithography was conducted by using NR7-1500P negative photo resist and Au 700Å was deposited on patterned photo resist by e-beam evaporation. A schematic of the samples used for this experiment is shown in Figure 3-3. To measure the conductivity of NiO, four point probe and Hall measurement methods were attempted but useful data cannot be achieved through these measurements due to the high resistivity of NiO.

3.1.2 Analysis

3.1.2.1 I-V characteristics

I-V measurements were conducted using HP4155 Semiconductor Parameter Analyzer.
Figure 3-3. Vertical structure of CTLM patterns

3.1.2.2 AES analysis

A Perkin-Elmer PHI 660 Scanning Auger Multiprobe was used for depth profile analysis.

3.2 Ni/Au Ohmic Contact

Measured I-V curves of annealed sample are shown and compared with that of as-deposited sample in Figure 3-4. It is evident that the current increases and the I-V curve is almost linear after annealing implying that Ni/Au metal annealed in air shows ohmic contact characteristic as published by several researchers.

3.3 Au/pre-oxidized NiO/p-GaN Contact

3.3.1 Current-Voltage (I-V) Characteristics

I-V measurements were conducted and are shown in Figure 3-5. The as-deposited sample shows an almost symmetric but non-linear I-V curve (Figure 3-5 (a)), while the current is observed to increase for the sample that was annealed in air for 10s. After 20s annealing, the current decreases and there is no significant change until 300s annealing. I-V curves for all annealed samples in air shows rectifying I-V characteristics. It is clear that Au/pre-oxidized NiO/p-GaN contacts are not ohmic in nature but rather exhibit Schottky
Figure 3-4. Linear I-V characteristics after annealing at 500°C for 10min in air. (Ni50A/Au50A)

barrier behavior. In order to compare current among samples with different anneal times, the fourth largest circular pattern (electrode space is ~120µm) was selected from the CTLM pattern and I-V curves for that size are plotted in Figure 3-6. As can be clearly seen, the 10s-annealed sample shows the highest current values within the range of voltage measured (-2.0V – 2.0V). The currents measured at 1.0V, 1.5V and 2.0V are shown in Figure 3-7 (a), (b) and (c), respectively. The current changes at selected voltage with anneal times display quite similar trends. The average current value at 1.5V increases to 260µA for the sample annealed for10s from 170µA for the as-deposited sample, and then goes down to 50µA, the minimum current in this research, for the 20s-annealed sample. The sample annealed for 60s shows a slightly higher current (~20µA) compared with 20s-annealed sample and the current slightly goes down after 60s annealing. Since the current variation between 60s and 300s is negligible, it concluded that there is no significant change after 60s.
Figure 3-5. I-V curve for pre-oxidized samples annealed at 500°C in air for (a) 0, (b) 10s, (c) 20s, (d) 1min, (e) 2min, and (f) 5min.
3.3.2 Depth Profile Analysis

The depth profiles were investigated using AES (Auger Electron Spectroscopy) analysis and are shown in Figure 3-8. The as-deposited sample shows that pure Ni exists on p-GaN and Au is on Ni. After annealing for 10s, an oxygen peak was detected. The intensity of this peak is relatively low (~20%) compared with the pure Ni peak. In terms of peak position showing maximum intensity, the oxygen peak is seen near the interface between Ni and Au. It is evident through AES depth profiles that NiO layer was formed through oxidation of Ni at the surface during 10s annealing, but pure Ni still exists near the interface between Ni and p-GaN after 10s annealing. After 20s annealing, the oxygen peak is seen over the entire area of Ni and there is no significant change up to 300s annealing. The oxygen peak position showing maximum intensity is very close to that of Ni. Based upon these results, Ni was found to partially oxidize during 10sec annealing and oxidize fully after 20s annealing near the GaN interface.
Figure 3-7. Current measured at (a) 1.0V, (b) 1.5V and (c) 2.0V
Figure 3-8. AES depth profile for pre-oxidized samples with various anneal time. X-axis and y-axis represent sputter time (sec) and peak intensity (a.u.), respectively.

3.3.3 Post Annealing of Au/pre-oxidized NiO/p-GaN Samples

Since there is no heat treatment after the Au was deposited on the top of pre-oxidized NiO, Au/pre-oxidized NiO/p-GaN samples should not display any significant effect of the Au in terms of reaction during annealing. In order to investigate Au effect on the reaction and specific contact resistance, as-deposited and 10s-annealed samples (Au/pre-oxidized NiO/p-GaN) were annealed at 500°C in air for different times (up to 60min). I-V curves for as-deposited and 10s-annealed samples after post annealing are shown in Figure 3-9 (a) and (b) with the I-V curves before post annealing, respectively. As shown in Figure 3-9 (a), the current increases after post annealing but the I-V curve is not linear although it was annealed in air with Au on the top of Ni. In this case, it should be noticed that the Au thickness is too thick (1000A) to make the microstructure (layer inversion structure) that shows ohmic characteristics. 10s-annealed sample showing the highest current among Au/pre-oxidized NiO/p-GaN samples was also annealed at 500°C
Figure 3-9. Effect of post annealing on I-V characteristics for (a) as-deposited sample and (b) 10s pre-oxidized sample
in air and I-V curve is shown in Figure 3-9 (b). After post annealing (especially after 30min), the current decreased and I-V curves remain rectifying characteristics. It appears that oxygen in pre-oxidized NiO diffused to remaining pure Ni and produced NiO near the interface between Ni and p- GaN during post annealing. At the same time, oxygen in air reacts with Ni at the side-wall to produce NiO. These processes are shown in Figure 3-10 schematically. The fact that the 10s pre-oxidized sample remains rectifying with low current after post annealing is one of the proofs that pre-oxidized NiO/p-GaN interface does not make ohmic contact.

3.3.4 NiO Sheet Resistance

In order to investigate the effect of a NiO on determining specific contact resistance, it is necessary to investigate the conductivity of NiO formed by annealing Ni at 500°C in air for different times.

The sheet resistance of the substrate layer can be calculated from equation (3). The linear slope of the graph is $R_{sh}/2\pi$ when plotted with $R_t$ vs. $\ln(R/r)$.

![Diagram of reaction process during post annealing](attachment:image.png)

Figure 3-10. Reaction process during post annealing. (a) before post annealing (b) oxygen diffusion during post annealing. Oxygen flow is designated by arrow (c) NiO formation near the interface between Ni and p-GaN
In Figure 3-11, I-V curves for these samples with different annealing times (10s – 180s) in air are shown. For 10s-annealed sample, the I-V curve is linear up to ~0.4V, but over 0.4V, the current exponentially increases with applied voltage up to 2.0V. This phenomenon is similar to that of the negative applied voltage indicating that the I-V curves are symmetric about the origin (0 volts). In contrast, all samples annealed for 20s or longer show linear I-V characteristics. The non-linearity shown in the 10s-annealed sample can be explained by the fact that considerable amounts of pure Ni still exist under a thin NiO layer consistent with AES depth analysis. For low applied voltage less than 0.4V, the current is limited due to high resistance of NiO. As the applied voltage increases, the electric field applied through the thin NiO also increases. The increase of applied field can induce tunneling current between the Au and the remaining pure Ni through the thin NiO layer. The large number of free electrons in Ni and Au act as the source for the high tunneling current. As the annealing time increases, the thickness of the NiO layer also increases. After 20s annealing, most of the Ni was oxidized and current path between two electrodes is Au/ NiO /Au over the entire voltage range. Since linear I-V characteristics were achieved for 20s, 60s, 120s and 180s-annealed samples, the sheet resistance of NiO can be calculated by equation (3). For 10s-annealed sample, short voltage range, 0 to 0.4V, showing linear correlation between current and applied voltage was selected for sheet resistance calculation. Based upon equation (3), the linear fitting was conducted to calculate sheet resistance (Figure 3-12). From the slope of the fitted line, the sheet resistance was calculated and is shown in Figure 3-13. 10s-annealed sample shows the lowest sheet resistance, $9.92 \times 10^4 \, \Omega/\square$ among all samples. The sheet resistance started to increase to $4.72 \times 10^{10} \, \Omega/\square$ for the sample annealed for 20s and
Figure 3-11. I-V curves for NiO formed by annealing Ni at 500°C in air for (a) 10s (b) 20s (c) 60s (d) 120s and (e) 180s
Figure 3-12. Linear fitting of ln(R/r) vs. Rt curve for (a) 10s (b) 20s (c) 1min (d) 2min (e) 3min annealed samples
Figure 3-13. Sheet resistance of NiO formed by annealing Ni at 500°C in air for different times reached 6.04×10^{12} \Omega/\square for the sample annealed for 60s. After 60s, the sheet resistance decreased slightly reaching 2.05×10^{11} \Omega/\square at 180s. According to the sheet resistance data, it is suggested that one of the reasons for the high currents in the Au/10s pre-oxidized NiO/p-GaN sample is due to the low sheet resistance of the oxidized Ni layer (including pure Ni). The relatively low current in the sample annealed for 20s (Figure 3-7) can be due to the high sheet resistance of NiO. This sheet resistance increase can be one of the factors for the current decrease observed for Au/pre-oxidized NiO/p-GaN samples with increasing annealing time. It is noted that 10s pre-oxidized sample shows high current compared with the as-deposited sample shown in Figure 3-7 even though the 10s-annealed NiO should have higher sheet resistance compared with pure Ni. Therefore, lower current suggests that the reaction between Ni and p-GaN during annealing in oxidizing ambients is one of the important factors in determining specific contact resistance. Significantly, Ishikaws et.al^60 reported a very thin (~2nm) amorphous layer between the Ni and p-GaN after deposition of Ni on cleaned p-GaN and suggested
that this layer could be either a native oxide or a contamination layer as shown in Figure 3-14 (a). They also reported that this amorphous layer disappeared after annealing at 400°C for 10min as shown Figure 3-14(b). If their results are valid, a similar reaction is expected to have occurred in the 50Å Ni on p-GaN after annealing at 500°C for 10s. Thus, the native oxide or contamination layer removal could explain the observed high current in spite of the higher sheet resistance of the oxidized Ni layer compared to that of pure Ni for the as-deposited sample.

3.3.5 Rectifying Characteristics of Au/pre-oxidized NiO/p-GaN Contact

The rectifying characteristic of Au/pre-oxidized NiO/p-GaN samples can be explained using energy band diagrams. Figure 3-15 shows an energy band diagram for p-NiO/p-GaN contact. Figure 3-15(a) shows the equilibrium energy band diagram of p-NiO and p-GaN before contacting each other. The parameters used to construct this energy band diagram are listed in Table 3-1. According to the results of Nakayama et al., the
Figure 3-15. Energy band diagram of NiO and p-GaN (a) before contact (b) after contact

Fermi level of p-GaN is located at 0.13eV above the top of the valence band at 300K.

The Fermi level of undoped NiO is located at ~ 0.5eV above the top of the valence band.

Based upon these parameters, the offsets of conduction band and valence band can be calculated to be 2.7 and 2.1eV, respectively. For p-NiO connected to p-GaN, the energy band diagram was changed and is shown in Figure 3-15 (b). The p-NiO surface bands
bend upwards and p-GaN surface bands slightly bend downwards at the p-NiO/p-GaN interface. A notch for holes in p-NiO exists near the interface between p-NiO and p-GaN where holes are trapped because the Fermi level is located below the top of the valence band. Energy barrier height at the p-NiO/p-GaN interface can be calculated by Cserveny’s concept. Under forward bias conditions, which occurs when a positive voltage is applied to Au, holes which flow from p-NiO towards p-GaN meet an energy barrier (0.20-0.31 eV, which depends on the hole concentration of NiO) at the interface between p-NiO and p-GaN. Under reverse bias, there is relatively low energy barrier (0.07-0.18 eV) between p-NiO and p-GaN. Since CTLM pattern was used to measure I-V characteristics for pre-oxidized samples, the current path is Au/p-NiO/p-GaN/p-NiO/Au as shown in Figure 3-16. Since this current path consists of two p-NiO/p-GaN interfaces, one of the interfaces has a relatively high energy barrier and the other interface has a relatively low energy barrier whether positive or negative voltage is applied on Au. The Schottky barrier (0.27-0.49 eV) between p-NiO and p-GaN is the reason of non-linear I-V characteristics for pre-oxidized samples.

Table 3-1. Properties of p-GaN and p-NiO at room temperature

<table>
<thead>
<tr>
<th></th>
<th>$E_g$ (eV)</th>
<th>$\chi$ (eV)</th>
<th>$E_f-E_v$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-GaN</td>
<td>3.4$^{85}$</td>
<td>4.1$^{86}$</td>
<td>0.13</td>
</tr>
<tr>
<td>p-NiO</td>
<td>4.0$^{34}$</td>
<td>1.4$^{87}$</td>
<td>0.5$^{88}$</td>
</tr>
</tbody>
</table>

Since the current path has two interfaces (one has relatively high energy barrier and the other has relatively low energy barrier) whichever voltage applied, it is suggested that I-V curves for pre-oxidized samples should be symmetric. But I-V curves for pre-oxidized samples show asymmetric shape. This asymmetric behavior can be explained
Figure 3-16. Current path of CTLM patterns for pre-oxidized samples

by noting that the sizes of the two electrodes are different as shown in Figure 3-17. It is evident that the contact area and energy barrier combinations made asymmetric I-V curve for pre-oxidized samples. If p-NiO/p-GaN with small contact area has high energy barrier, and p-NiO/p-GaN with large contact area has low energy barrier, the current measured should be low compared with the opposite case in terms of combination of contact area and energy barrier height. Figure 3-18 shows a comparison of I-V curves

Figure 3-17. Different electrode size for CTLM patterns
with different voltage biases on the small electrode curve (a) and large electrode (b). The I-V curve with different voltage bias is consistent with the explanation that asymmetric characteristics of I-V for pre-oxidized samples is due to a combination of contact area and energy barrier height.

![I-V curve with different voltage bias](image)

Figure 3-18. I-V curve with different voltage bias (a) voltage on small electrode (b) voltage on large electrode
CHAPTER 4
REACTION BETWEEN NICKEL AND P-GALLIUM NITRIDE DURING ANNEALING IN OXIDIZING AMBIENT

As already stated, the theory for the low resistance ohmic contact behavior of oxidized Ni/Au contacts is still controversial. In fact, the presence of a reaction phase between the metal and semiconductor may play an important role in determining contact resistance\(^6\), i.e., the reaction between Ni and p-GaN during annealing could be one of the most critical factors in determining specific contact resistance on p-GaN metal contacts. Based on this possibility, the reaction between Ni and p-GaN during annealing has been the focus of numerous studies over the past several years.\(^6^2\)-\(^6^4\)

The phase diagrams for Ni-Ga and Ni-N are presented in Figure 4-1\(^6^5\) while the Ga-N-Ni ternary phase diagram at different N\(_2\) pressure was calculated and reported by S.E. Money et al.\(^6^6\) Several researchers have reported the reaction between Ni and p-GaN.\(^6^2\)-\(^6^4\) For example, Sheu et al. reported XRD results which indicated that Ni gallide (Ga\(_3\)Ni\(_2\), Ga\(_4\)Ni\(_3\)) and Ni nitride (Ni\(_3\)N) were formed during annealing at 500°C for 10 min in nitrogen ambient.\(^6^2\) Guo et al. analyzed the reaction between Ni and n-GaN, and reported that Ga\(_4\)Ni\(_3\) and Ni\(_3\)N formed during annealing at 400°C for 20min. in a nitrogen ambient.\(^6^3\) Surprisingly, Guo et al. reported a Ni-nitride (Ni\(_3\)N) peak just after deposition of Ni without any subsequent heat treatment. However, Venugopalan et al. also reported through XRD analysis that they could not observe a new reaction phase between Ni and GaN when it was annealed up to 600°C in a nitrogen ambient.\(^6^4\) They reported that a Ni-Ga solid solution was formed after a 600°C anneal while Ni gallide (Ni\(_3\)Ga) was reported
Figure 4-1. Phase diagrams of (a) Ni-Ga (b) Ni-N systems
after annealing at temperatures above 750°C. Thus, their results indicate that no reaction phase was formed between Ni and GaN at 400°C annealing in direct contrast to the report by Guo et al.

Besides this controversy over the formation of new reaction phases between Ni and GaN, it should also be pointed out that most of the annealing treatments in these studies were conducted in nitrogen or argon ambients. However, the annealing ambient for the standard Ni/Au contacts that show low specific contact resistance is an oxidizing (air) ambient. A very limited number of papers focused on the reaction phase between Ni and p-GaN during annealing in oxidizing ambients have been published.67

In the light of the reaction between Ni and p-GaN, the difference between oxidizing ambient and nitrogen or argon ambient is whether oxygen (or NiO) exists on the top of Ni or not during annealing. It is not clear whether oxygen actually plays a role in forming a reaction phase between Ni and GaN during annealing.

4.1 Experiments

4.1.1 Sample Preparation

Mg-doped p-GaN was cleaned using an aqua-regia solution for 5 min at room temperature to remove the native oxide or contamination layers. 1500Å of Ni was then deposited on the cleaned p-GaN by e-beam evaporation. This thickness was selected to ensure that there was enough starting materials for an interfacial reaction to develop. After deposition, the Ni-coated sample was annealed at 500°C for 4 min in air to produce NiO layer on the top of the Ni but not all of the way through. The annealing time was carefully controlled because longer times result in spalling of the Ni layer. After annealing in air, the sample was encapsulated in a quartz ampoule that had been purged
with Ar gas three times prior to sealing. The partial Ar gas pressure inside the quartz ampoule was selected to maintain approximately 1 atm during annealing at 500°C. The encapsulated sample was then annealed at 500°C for 24 hours in order to produce a sufficient amount of reaction product which could then be analyzed by TEM. After annealing, the quartz ampoule was broken and the sample was cooled in air.

4.1.2 Analysis

4.1.2.1 XRD measurement

X-ray diffraction was performed using an analytical high resolution X-ray diffractometer (Philips X’Pert MRD), operated with Cu Kα as the radiation source at 45kV and 40mA.

4.1.2.2 AES analysis

A AES Perkin-Elmer PHI 660 Scanning Auger Multiprobe was used for depth profile analysis.

4.1.2.3 TEM analysis

High resolution TEM (JEOL 2010F) with Oxford EDX detector was used for analysis of interfacial reaction between metal and p-GaN. The accelerating voltage was 200kV.

4.2 X-ray Diffraction Analysis

XRD analysis of the sample after annealing revealed the Ni and NiO peaks as well as GaN peak (Figure 4-2). One additional and relatively strong unknown peak was observed at a 2θ value of ~ 41.7; this peak position is the same as the Ni-nitride peak suggested by Guo et al.63 In order to investigate this unknown peak, XRD analysis was
Figure 4-2. XRD peaks for 24h-annealed and as-deposited samples (Ni1500A)

conducted for p-GaN without any layer on top of p-GaN and shown in Figure 4-3. The strong XRD peak at ~ 41.7° can be observed in Figure 4-3. Therefore, this peak didn’t come from Ni-nitride but from the substrate. The position of this peak matches the (0006) plane of sapphire based upon JCPDS index.

**4.3 Auger Electron Spectroscopy Depth Analysis**

AES depth profiles for the as-deposited Ni on GaN sample and the sample after annealing are shown in Figure 4-4. As can be seen, the Ni film exists on GaN before annealing. After annealing, the oxygen exists over the entire range of Ni. This means oxygen diffused towards the interface between Ni and p-GaN, and NiO was formed by oxidation of Ni during the 24h anneal.
Figure 4-3. Strong XRD peak at ~ 41.7° from GaN substrate

Figure 4-4. AES Depth profiles of (a) as-deposited sample (b) the sample annealed for 24h at 500°C. X-axis and y-axis represent sputter time (sec) and peak intensity (a.u.), respectively.
4.4 Transmission Electron Microscope Analysis

Since there was no evidence for a new reaction phase after 24h annealing based on XRD analysis, it can be suggested that the 4min annealing in air plus 24h annealing in Ar at 500°C either produces no new reaction phase between Ni and p-GaN, or that the reaction phase is very thin near the initial Ni/GaN interface. In order to investigate this possibility, TEM analysis was conducted to examine the interfacial region. The low magnification TEM image of the interface between Ni and p-GaN is shown in Figure 4-5 and indicates that fine-grain-NiO formed during annealing. Figure 4-6 shows an SAD (Selected Area Diffraction) pattern from NiO that is consistent with its fcc structure. The interface between NiO and p-GaN was observed at higher magnification and a thin, relatively bright layer was observed at the interface (see arrow in Figure 4-7). However, this layer appears to simply result from a slight overlapping of the two different crystal structures that meet at the interface. The other possible explanation for this layer’s formation is from damage or locally thin area, induced by ion bombardment during FIBing.\textsuperscript{68-70} In an effort to determine if there was anything at the interface, an EDX line scan was conducted across the interface (Figure 4-8). As can be seen, a strong Ni peak was detected on the NiO side of the interface with Ga and N peaks on the GaN side. A gradual transition from one side to the other was observed consistent with no additional phases at the interface. Thus, the HRTEM and EDX data indicate this bright layer is not a reaction phase indicating that no reaction phase forms between Ni and p-GaN after annealing at 500°C in an oxidizing ambient.
Figure 4-5. TEM image of NiO and p-GaN after 24h annealing

Figure 4-6. SAD pattern of NiO produced by annealing Ni 1500A
Figure 4-7. High magnification image of the interface between NiO and p-GaN

Figure 4-8. EDX analysis across the interface between NiO and p-GaN
CHAPTER 5
INTERPLANAR SPACING CHANGE OF GALLIUM NITRIDE DURING ANNEALING IN OXIDIZING AMBIENT

5.1 Selected Area Diffraction Patterns for GaN

SAD (selected area diffraction) patterns of GaN, previously discussed in chapter 4, were obtained in the as-deposited condition and after annealing at 500°C for 24h (Figure 5-1). Pure Au was used as a standard to calibrate the camera length. The d-spacings of the major GaN planes are provided in Table 5-1, where it is apparent that the interplanar spacing of the (0002) plane is lower after the 24h anneal while the (2110) plane has an increased d-spacing after annealing. Each plane is presented in Figure 5-2. It is evident that the interplanar spacing for the plane parallel to the surface, i.e., the (0002) plane, contracts during annealing, and that for the plane parallel to the c-axis, i.e., (2110).

Figure 5-1. SAD patterns of GaN (a) as-deposited (b) after annealing at 500°C for 24h
Table 5-1. Interplanar spacing comparison

<table>
<thead>
<tr>
<th>Plane</th>
<th>Before anneal</th>
<th>After anneal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0002</td>
<td>2.452</td>
<td>2.440</td>
</tr>
<tr>
<td>2110</td>
<td>1.609</td>
<td>1.634</td>
</tr>
</tbody>
</table>

Figure 5-2. Crystallographic view of (a) 0002 (b) 2110 planes of GaN expands during annealing.

5.2 X-ray Diffraction Analysis of Strain in GaN

The change in the interplanar spacings of GaN, produced after annealing at 500°C for 4min in air and the 24h in Ar, was analyzed by XRD. The as-deposited and annealed samples were compared with p-GaN with no metallic surface layer (Figure 5-3). The results show that the (0002) peak of GaN shifts 0.23° towards lower 2θ angles (higher d
Figure 5-3. GaN (0002) peak shift after Ni 1500Å deposition and annealing in oxidizing ambient spacing) after Ni deposition and reverses 0.07° upon annealing, consistent with the smaller d-spacing expected from the TEM analysis. The change in interplanar spacing was calculated and is shown in Table 5-2. It is noticed that the d-spacing of (0002) plane measured by TEM (Table 5-1) is smaller than that by XRD (Table 5-2). This phenomenon can be induced by several factors. One possibility is related to the lattice damage caused by Ga ions during FIB.

Table 5-2. Interplanar spacing of GaN (0002) plane

<table>
<thead>
<tr>
<th></th>
<th>Before anneal</th>
<th>After anneal</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>34.5</td>
<td>34.57</td>
</tr>
<tr>
<td>d-spacing</td>
<td>2.5975</td>
<td>2.5932</td>
</tr>
</tbody>
</table>
The other is that the oxidation of GaN can decrease the d-spacing of the (0002) plane. It was published that Gallium oxynitride had smaller (0002) plane d-spacing compared with that of GaN.\textsuperscript{71} It is also possible that this phenomenon is a measurement error from analyzing SAD patterns. Based upon both TEM and XRD analysis, deposition of 1500A Ni on cleaned p-GaN results in an elastic dilation in the [0002] direction of GaN. This tensile strain is partially released by annealing Ni in an oxidizing ambient as shown in Figure 5-3. The data show that Ni deposited on p-GaN has compressive stress along with p-GaN surface (parallel to surface) and this compressive stress makes compressive strain to the parallel plane to c-axis of p-GaN such as (2110) plane. Since the parallel plane to c-axis of GaN has compressive strain, GaN (0002) plane can have tensile strain after deposition of Ni. During annealing in an oxidizing ambient, the tensile strain in the [0002] direction of GaN is partially released due to either NiO formation or relaxation by annealing. The schematic diagram of this process is shown in Figure 5-4.
Figure 5-4. Schematic diagram of partial strain release of GaN after annealing in oxidizing ambient (a) before deposition of Ni (b) as-deposited (c) after annealing in oxidizing ambient
CHAPTER 6
EFFECT OF GALLIUM NITRIDE STRAIN ON CONTACT RESISTANCE

Lattice strain in GaN may affect contact resistance because strain in GaN, especially the near-surface regions of GaN, may shift the energy bands and/or produce defects at energy levels inside the band gap. The discrete deep levels within the GaN band gap can be formed due to (1) native defects, (b) metal-induced bonding and (c) reaction products. Deep level defects at the metal-GaN interface were reported by Brillson et al.; these metals on GaN induced new deep level emission across the band gap. Krispin et al. reported that the internal strain near the as-grown GaAs surface leads to the formation of an intrinsic defect within the band gap. Singh et al. also reported that the increasing strain with higher carbon fraction in SiC layer plays an important role in producing deep level defects. The defects may result in the production of charge trap centers or recombination centers near the surface. Auret et al. reported that sputter deposition of metal produces disorder in the semiconductor surface, which results in a new energy level in the semiconductor band gap; this new energy level may produce trapping or recombination centers. Other authors reported that the barrier heights of sputter-deposited Schottky contacts on p-type Si and GaAs are higher than those of similar metal contacts deposited by other less damaging processes. It was shown that this barrier height alteration was accompanied by the introduction of donor-like defects at and below the semiconductor surface.

6.1 Experiments
6.1.1 Sample Preparation

Pre-cleaned (aqua-regia, 5min at room temperature) p-GaN samples were coated with different thicknesses of Ni (150Å and 600Å) by e-beam evaporation to measure stress versus Ni film thickness.

6.1.2 Analysis

6.1.2.1 I-V characteristics

I-V measurements were conducted using HP4155 Semiconductor Parameter Analyzer.

6.1.2.2 XRD measurement

For the analysis of strain in GaN, X-ray diffraction was performed using an analytical high resolution X-ray diffractometer (Philips X'Pert MRD), operated with Cu Kα as the radiation source at 45kV and 40mA.

6.2 Current-Voltage Measurements and XRD Analysis

I-V curves for as-deposited samples with different Ni thickness all display non-linear behavior as expected (Figure 6-1). Further, it is evident that currents for the samples with 600Å of Ni are higher than those from samples with 150Å of Ni. XRD analysis (See Table 6-1 for details) was conducted on the samples coated with 0, 150 or 600Å of Ni. The 0002 GaN peaks (Fig. 6-2) for the different samples indicate that the Ni does cause this peak to shift to smaller angles (larger d-spacings). Furthermore, the shift of the peak is highest for the sample coated with 150Å of Ni indicating a larger strain in this sample. Based upon XRD analysis and I-V measurements, it is concluded that the increase of the strain in GaN induces the decrease of the current value.
Figure 6-1. I-V curves for different Ni thickness

Figure 6-2. XRD peaks of GaN (0002) plane
Table 6-1. XRD condition for the measurement of GaN (0002) peak

<table>
<thead>
<tr>
<th>Wavelength (Å)</th>
<th>1.54056</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step width (°)</td>
<td>0.002</td>
</tr>
<tr>
<td>Time per step (sec)</td>
<td>2.0</td>
</tr>
</tbody>
</table>

6.3 Effect of Annealing in Oxidizing Ambient on p-GaN Strain

The (0002) GaN peak shift after annealing in oxidizing ambient is due to the reduced stress caused either by annealing and/or by the formation of NiO. In order to investigate the effect of annealing on the strain produced by deposition of Ni, the samples with different Ni thicknesses were annealed at 500°C for 5min in nitrogen. Subsequent XRD analysis (Figure 6-3) indicates that the (0002) GaN peak for the 600A Ni sample shifted to higher 2θ (0.04°). However, the (0002) GaN peak from the 150A Ni sample showed a negligible difference after annealing.

These samples were annealed at 500°C for 10h in air to investigate whether or not the formation of NiO can release the strain. Grazing angle XRD patterns from the oxidized samples revealed only NiO peaks (Figure 6-4) indicating that the Ni was fully oxidized by this anneal. XRD analysis of the (0002) GaN peak (Figure 6-5) after annealing in oxidizing ambient indicates that the difference of peak position between the sample annealed in nitrogen and the sample annealed in air is negligible. Therefore, it is concluded that the strain release in GaN after annealing in oxidizing ambient is not due to the formation of NiO but due to just annealing.

6.4 Strain in GaN for Thin Ni

In order to investigate the GaN strain effect for thin Ni (less than 150A), 50A Ni
Figure 6-3. GaN (0002) peak comparison for (a) Ni 600A (b) Ni 150A before and after annealing at 500°C for 5min in nitrogen.
Figure 6-4. Grazing angle XRD analysis of NiO produced by annealing (a) Ni 150A (b) Ni 600A after 500°C for 10h in air.
Figure 6-5. GaN (0002) peak comparison for (a) Ni 600A (b) Ni 150A before and after annealing at 500°C for 10h in air
was deposited on pre-cleaned p-GaN. XRD analysis (Figure 6-6) revealed no peak shift suggesting that 50A of Ni is insufficient to produce any strain in the p-GaN. In terms of strain effect, the selection of thin Ni is needed to avoid energy band shift and/or the formation of energy level defects. Since Ni50A/Au50A coatings annealed in oxidizing ambient are the typical metal contacts used on p-GaN, it is necessary to investigate their influence on the lattice strain of GaN. For these experiments, Ni50A and Au 50A were deposited sequentially on pre-cleaned p-GaN by e-beam evaporation. After deposition, the sample was annealed at 500°C in air for 10min. XRD analysis was performed on (1) p-GaN before deposition, (2) as-deposited Ni50A/Au50A on p-GaN, and (3) after annealing (Figure 6-7). Since the (0002) GaN peaks do not shift between these three conditions, it can be concluded that Ni50A/Au50A contacts produce negligible strain in GaN.

A Au film 150A thick was deposited on Ni 150A in vacuum by e-beam evaporation to investigate the effect of Au in terms of strain release in GaN. The (0002) GaN XRD
peak (Figure 6-8) does not shift for the GaN coated with Ni150A/Au150A compared with that for the sample coated with 150A Ni only.

Figure 6-7. GaN (0002) peak comparison for Ni 50A/Au50A

Figure 6-8. GaN (0002) peak comparison for Ni 150A/Au150A
Based upon this XRD analysis, Au does not have a measurable effect on the strain of GaN for the sample of Ni150A/Au150.

6.5 Characterization of Split (0002) GaN Peak

As noted in Figure 6-8, the (0002) peak of GaN usually appears to be split into two peaks. This implies that the GaN has regions with different lattice parameters. GaN is grown on a buffer layer (AIN) on sapphire and the GaN is also divided into two regions. One is an undoped region located on the buffer layer and the other region is a Mg doped region (~2.5μm) at the top of the GaN deposit. In order to understand which peak comes from where in the GaN, the sample was covered with a thin piece of cellulose tape to decrease the penetration depth of the X-rays (see schematic in Figure 6-9). The XRD patterns from the untaped and taped samples (Figure 6-10) indicate that the intensity ratio of the split peaks is different between the two samples. Specifically, the first and second peaks were assigned and designated in Figure 6-10 for convenience. The relative

![Figure 6-9. Schematic X-ray penetration depth profile of (a) without tape and (b) with tape samples](image-url)
intensity ratio is defined as the intensity of the first peak divided by the intensity of the second peak. As shown in Figure 6-10, the relative intensity ratio is low for the taped sample compared with the untaped sample. This suggests that the higher angle peak comes from the Mg doped GaN whereas the first peak comes from the undoped GaN located below the Mg-doped region. Indeed, the relative intensity ratio $I_1/I_2$ decreases as the coating thickness is increased consistent with the conclusion that the second peak comes from the upper Mg-doped region. Kirchner et.al reported that the GaN lattice constants are slightly different when it has different carrier concentrations and the free electrons expand the lattice constant of GaN by the following equation:

$$\frac{\Delta V}{V} = -\frac{nD}{B}$$

where $V$: volume
n: free electron concentration
D: deformation potential of conduction band minimum
B: bulk modulus

Figure 6-11 shows the dependence of relaxed lattice parameters \( a \) and \( c \) on the free electron concentration.

Figure 6-11. Dependence of GaN lattice parameters on free electron concentration
CHAPTER 7
OPTICAL PROPERTIES OF NICKEL OXIDE PRODUCED BY THERMAL OXIDATION OF NICKEL

Since the band gap of GaN is suitable for the emission of blue light, one of the most important applications for GaN is blue light LD (Laser Diode) and LED (Light Emitting Diode). One of the reasons for adopting Ni/Au metal contacts annealed in oxidizing ambients is that the NiO produced during annealing has high transparency for blue light. NiO is a wide band gap semiconductor, with the absorption edge in the UV region and no absorption in the visible region. Although there should be no absorption in the visible region for NiO based upon the band gap value, some visible light is absorbed when it goes through NiO. It is known that Ni$^{3+}$ induces absorption in the visible region. Therefore, a high concentration of Ni$^{3+}$ ions in the NiO lattice decreases optical transmittance. Since high transparency is essential for better performance of blue light LEDs or LDs, the blue light transmittance of NiO annealed in different oxidizing ambients should be an interesting factor in terms of GaN applications.

Since NiO was produced through thermal oxidation for LD or LED applications, it is necessary to investigate the optical properties of NiO produced by thermal oxidation under various conditions.

7.1 Experiments

7.1.1 Sample Preparation

Ni 400A was deposited on a polished quartz plate by e-beam evaporation. Polished quartz plates were used as substrates because quartz plates are transparent to visible light.
Thus, 1/16" thick quartz plates were bought from Quartz Scientific Inc. Before the deposition of Ni, the quartz plates were cleaned by acetone, methanol and DI water, and dried with N$_2$ gas. After deposition, samples were annealed at 500°C for different times (from 15min to 24h), and at 600°C for different times (from 3min to 3h) in air, respectively.

7.1.2 Analysis

7.1.2.1 XRD measurement

X-ray diffraction was performed using XRD Philips APD 3720, operated with Cu Kα as the radiation source at 40kV and 20mA.

7.1.2.2 AFM measurement

The surface roughness was measured using Digital Instruments Dimension 3100 AFM and contact mode was applied.

7.1.2.3 Optical transmittance

Light of wavelength of 400-500nm was used to measure optical transmittance since the wavelength of blue light is ~450nm. The schematic diagram of the instrument used for optical transmittance measurement is shown in Figure 7-1. The optical fiber was used between the optical source and the sample plate to make a point source of white light.

7.2 Optical Transmittance of NiO Produced by Thermal Oxidation of Ni

The graphs in Figure 7-2 show transmitted intensity as a function of wavelength for the samples annealed at 500°C for different times. The curve showing the highest transmitted intensity is for the polished quartz plate without Ni. The curve showing the
Figure 7-1. Schematic diagram of the instrument for optical transmittance measurement
Figure 7-2. Optical transmittance of NiO oxidized at 500°C as a function of wavelength.

The lowest transmitted intensity (designated by arrow) is for the as-deposited sample without annealing. It is evident that the as-deposited sample is almost opaque over the wavelength range measured. The transmitted intensity of the polished quartz plate was selected as the reference and the transmitted intensities for other samples were normalized by dividing by the transmitted intensity through this plate (Figure 7-3). As shown in Figure 7-3, the sample annealed for 15min shows the highest normalized intensity and the sample annealed for 5h shows the lowest normalized intensity although all are in a narrow band. The normalized intensity for blue light at 450nm (Figure 7-4) has a U-shape with a minimum point at 62.2% for the sample annealed for 5h, compared with the high point at 69.5% for the sample annealed for 15min. For times longer than 5h, the normalized intensity increases to 66.2% for the sample annealed for 24h. For the samples annealed at 600°C the transmitted intensity varies with wavelength in a manner similar to the samples annealed at 500°C (Figure 7-5). Again, the normalized intensity and the intensity at 450nm are shown in Figure 7-6 and Figure 7-7, respectively. The significant trend for the
Figure 7-3. Normalized intensity of NiO oxidized at 500°C as a function of wavelength

Figure 7-4. Normalized intensity at 450nm for NiO oxidized at 500°C
Figure 7-5. Optical transmittance of NiO oxidized at 600°C as a function of wavelength.

Figure 7-6. Normalized intensity of NiO oxidized at 600°C as a function of wavelength.
Figure 7-7. Normalized intensity at 450nm of NiO oxidized at 600°C

samples annealed at 600°C is that the normalized intensity decreases as the anneal time increases. Only the 1h sample deviated from this trend in that it had higher transmittance compared with the sample annealed for 20min.

Many features such as film density, grain boundaries, surface roughness and crystal defects can act as scattering centers, and should be considered in determining light transmittance for thin films.

7.3 X-ray Diffraction Analysis

7.3.1 Grain Size Analysis

XRD analysis was conducted to investigate the grain size and crystal structures of NiO. XRD peaks for NiO (111) and (200) annealed at 500°C and at 600°C are shown in Figure 7-8 and 7-9, respectively. The grain size was calculated by equation (5) based upon measured XRD peaks.
Figure 7-8. XRD peaks of NiO annealed at 500°C; (a) (111) plane and (b) (200) plane
Figure 7-9. XRD peaks of NiO annealed at 600°C; (a) (111) plane and (b) (200) plane
\[ t = \frac{0.9 \lambda}{B \cos \theta} \]  

(5)

where \( B \) is the line broadening measured at full width half maximum and has units of radians, \( \lambda \) is X-ray wavelength, \( \theta \) is the Bragg angle and \( t \) is the average grain diameter.

The calculated grain size from XRD peaks is shown in Figure 7-10. It is observed that the grain size of the samples annealed at 600°C is larger than that of the samples annealed at 500°C. The grain size and normalized intensity at 450nm are summarized in Table 7-1. The normalized intensities of the sample annealed for 1h at 500°C and at 600°C are 66.0% and 68.5%, respectively. The measured grain sizes for the corresponding samples are 248Å and 299Å, respectively. According to grain size analysis, it is concluded that

Figure 7-10. Grain size comparison between 500°C and 600°C anneal.
Table 7-1. Grain size and normalized intensity for NiO produced by annealing Ni in an oxidizing ambient.

<table>
<thead>
<tr>
<th>Anneal temperature (°C)</th>
<th>Annealing time</th>
<th>Grain size (Å)</th>
<th>Normalized intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>15min</td>
<td>236</td>
<td>69.5</td>
</tr>
<tr>
<td></td>
<td>30min</td>
<td>244</td>
<td>66.7</td>
</tr>
<tr>
<td></td>
<td>1h</td>
<td>248</td>
<td>66.0</td>
</tr>
<tr>
<td></td>
<td>2h</td>
<td>245</td>
<td>63.0</td>
</tr>
<tr>
<td></td>
<td>5h</td>
<td>222</td>
<td>62.2</td>
</tr>
<tr>
<td></td>
<td>10h</td>
<td>200</td>
<td>62.8</td>
</tr>
<tr>
<td></td>
<td>24h</td>
<td>241</td>
<td>66.2</td>
</tr>
<tr>
<td>600</td>
<td>3min</td>
<td>258</td>
<td>71.6</td>
</tr>
<tr>
<td></td>
<td>5min</td>
<td>254</td>
<td>68.5</td>
</tr>
<tr>
<td></td>
<td>20min</td>
<td>256</td>
<td>67.2</td>
</tr>
<tr>
<td></td>
<td>1h</td>
<td>299</td>
<td>68.5</td>
</tr>
<tr>
<td></td>
<td>3h</td>
<td>317</td>
<td>63.1</td>
</tr>
</tbody>
</table>

The transmittance of NiO with large grains is higher than that with small grains. Since large grain size means relatively small grain boundary area and grain boundaries act as scattering centers for light transmittance, the samples annealed at 600°C show higher transmittance compared with those annealed at 500°C.
7.3.2 Effects of Preferred Orientation on Optical Transmittance of NiO

In an effort to determine if there was a preferred orientation/texture to the NiO film, the integrated intensities of the 111 and the 200 peaks for NiO annealed at 500°C were measured (Figure 7-11). The integrated intensity of 200 peak is always higher than that of 111 peak except for the sample annealed for 2h. The integrated intensity ratio, I_{111}/I_{200}, (Figure 7-12) for the sample annealed for 15min is 0.854. It increases with annealing time and reaches 1.040 for the sample annealed for 2h. After 2h, the integrated intensity ratio

![Image](image.png)

Figure 7-11. Integrated intensity of NiO annealed at 500°C in air decreases to 0.852 for the sample annealed for 24h. The integrated intensity ratio curve displays a convex shape having a maximum value for the sample annealed for 2h. The optical transmittance of NiO annealed at 500°C decreases as the annealing time increases to 5h, and then increases as anneal time increases as shown in Figure 7-4. The optical transmittance graph is concave with a minimum for the sample annealed for 5h. The correlation between optical transmittance and integrated intensity ratio indicates that
optical transmittance decreases as the integrated intensity ratio increases. It is suggested that optical transmittance decreases as the number of grains with (111) orientation increases compared with that of (200) orientation. This similar correlation can be seen for the samples annealed at 600°C. The integrated intensity and the integrated intensity ratio for NiO annealed at 600°C are shown in Figure 7-13 and Figure 7-14, respectively. In Figure 7-14, the integrated intensity ratio increases with annealing time up to 1.174 for the sample annealed for 20min and drops to 1.119 for the sample annealed for 1h. The integrated intensity ratio for the sample annealed for 2h is 1.333, which is the highest value among samples. The optical transmittance of NiO annealed at 600°C shows that it decreases with annealing time as shown in Figure 7-7. Only one deviation from this correlation is the sample annealed for 1h. For the samples annealed at 600°C, the optical transmittance decreases as the amount of grains with (111) orientation increases compared with that of (200) orientation. It is known that the change of atomic density
Figure 7-13. Integrated intensity of NiO annealed at 600°C in air

Figure 7-14. Integrated intensity ratio of NiO annealed at 600°C in air
may cause the alteration of optical properties such as refractive index.\textsuperscript{82,83} Ferreira et al. reported that the sample with relatively large amounts of (111) preferred orientation in NiO deposited by sputtering showed low optical transmittance.\textsuperscript{84} Thus, it can be concluded that having relatively large amount of grains with (111) orientation can decrease optical transmittance of NiO, which indicates that the optical transmittance of NiO is dependent on crystallographic orientation.

### 7.3.3 X-ray Peak Position of NiO

The other interesting point in the XRD analysis is the peak position of NiO. The (111) peak of NiO annealed at 500\(^\circ\)C with different anneal time was shown in Figure 7-8(a) and it is evident that the peak moved towards higher 2\(\theta\) values as anneal time increases until anneal time reaches 10h. The peak position is 43.36\(^\circ\) and 43.41\(^\circ\) for the sample annealed for 15min and the sample annealed for 10h, respectively. The peak position of the sample annealed for 24h is 43.35\(^\circ\) and is almost the same as that for the sample annealed for 15min. The (200) peak of NiO annealed at 500\(^\circ\)C is shown in Figure 7-8(b). The peak shift with annealing time for NiO (200) is similar to that for the (111) peak. For the samples annealed at 600\(^\circ\)C, the peak shifts of NiO (111) and (200) are similar to the samples annealed at 500\(^\circ\)C as shown in Figure 7-9. It is evident that the stress level of the NiO film changes with annealing time. However, in terms of relationship with optical transmittance, the XRD peak shift with annealing time does not show any systematic correlations.

### 7.4 Surface Roughness Analysis

Generally, one of the factors in determining optical transmittance is surface
roughness. In order to check if surface roughness plays a role in determining optical transmittance of NiO, AFM (Atomic Force Microscope) was used to get surface roughness of NiO annealed at 500°C. The contact mode was applied, and the average roughness data ($R_a$) and root mean square roughness ($R_q$) were determined (Figure 7-15).

![Graph showing surface roughness of NiO annealed at 500°C](image)

(a)

![Graph showing root mean square roughness of NiO annealed at 500°C](image)

(b)

Figure 7-15. The surface roughness of NiO annealed at 500°C (a) average, $R_a$ (b) root mean square, $R_q$. 
Surface images for no anneal, and after 15min and 1h anneals at 500°C are shown in Figure 7-16 (a), (b) and (c), respectively. $R_a$ is the most common index of surface roughness while $R_q$ is used in optical applications since it is more directly related to the optical quality of a surface. It is evident that the surface of the sample annealed for 15min is rougher than those of other samples. There is no significant difference in surface roughness for samples other than the sample annealed for 15min. Therefore, it can be said that surface roughness is not a critical factor in determining optical transmittance of NiO films produced by annealing Ni 400A at 500°C in air at 450nm wavelength.

![AFM surface images](image)

Figure 7-16. AFM surface image of (a) as-deposited Ni (b) NiO produced by annealing Ni 400A at 500°C in air for 15min. (c) NiO produced by annealing Ni 400A at 500°C in air for 1h.
CHAPTER 8
SUMMARY

In order to investigate the effect of NiO on specific contact resistance, 50A of Ni was deposited on cleaned p-GaN by e-beam evaporation. The deposited Ni was annealed at 500°C for different times (0, 10s, 20s, 60s, 120s, 180s and 300s) in air. 1000A of Au was deposited on top of the oxidized Ni by e-beam evaporation. CTLM patterns were produced through a photolithography and dry etch process. I-V curves for all annealed samples in air show rectifying I-V characteristics. It is clear that Au/pre-oxidized NiO/p-GaN contacts are not ohmic in nature but rather exhibit Schottky barrier behavior. Based upon AES depth analysis, it can be said that 50A Ni was partially oxidized during 10s annealing and fully oxidized after 20s annealing. According to the sheet resistance of the oxidized Ni layer, it is suggested that one of the reasons for the high currents in the Au/10s pre-oxidized NiO/p-GaN sample is due to the low sheet resistance of the oxidized Ni layer. The relatively low current in the sample annealed for 20s may be due to the high sheet resistance of NiO. For Au/pre-oxidized NiO/p-GaN contacts under forward bias conditions, which occurs when a positive voltage is applied to Au, the holes that flow from p-NiO towards p-GaN meet an energy barrier at the interface between p-NiO and p-GaN. Under reverse bias, there is a relatively low energy barrier between p-NiO and p-GaN. This Schottky barrier between p-NiO and p-GaN is the reason for the non-linear I-V characteristics for pre-oxidized samples.

There was no evidence for a new reaction phase between Ni and p-GaN after 24h annealing at 500°C based on XRD analysis. The interface between NiO and p-GaN was
observed using TEM and a thin, relatively bright layer was observed at the interface between NiO and p-GaN. The high resolution TEM image and EDX data indicate that this bright layer is not a reaction phase indicating that no reaction phase forms between Ni and p-GaN after annealing at 500°C in an oxidizing ambient.

The pre-cleaned p-GaN samples were coated with different thicknesses of Ni (150Å and 600Å) by e-beam evaporation in order to produce different stress levels. These samples were then subjected to both I-V measurements and strain analysis by XRD in an effort to determine the role of strain in the p-GaN on contact resistance. Based upon XRD analysis and I-V measurements, it is concluded that the increase in the strain in GaN induces a decrease in the current value. The effect of annealing in an oxidizing ambient on p-GaN strain was investigated and, according to the XRD results for the 150Å, 600Å, and 1500Å Ni deposits, it appears that the strain in GaN for 600Å and 1500Å Ni samples was partially released during annealing in an oxidizing ambient but the annealing for the 150Å Ni sample did not result in measurable strain release in GaN. A similar shift of the (0002) GaN peak was observed after annealing the 600Å Ni sample in a nitrogen ambient indicating that the strain release in GaN after annealing in an oxidizing ambient is not due to the formation of NiO but due to the relaxation associated with annealing. According to XRD analysis of the GaN sample coated with Ni50Å/Au50Å, it can be concluded that Ni50Å/Au50Å contacts produce negligible strain in GaN.

Based upon the experimental results, (1) Au/pre-oxidized NiO/p-GaN contacts are not ohmic in nature but rather exhibit Schottky barrier behavior, (2) no reaction phase forms between Ni and p-GaN after annealing at 500°C in an oxidizing ambient and (3) Ni50Å/Au50Å contacts do not cause significant strain in p-GaN and strain release in
GaN after annealing in an oxidizing ambient is not due to the formation of NiO but due to the relaxation associated with annealing. Thus, it is concluded that the NiO formed during annealing in an oxidizing ambient does not result in the low resistance ohmic contact behavior observed for Ni/Au contacts to p-GaN. It can be concluded that the current path for low resistance ohmic contacts of Ni/Au annealed in oxidizing ambients is due to the direct contact between Au and the p-GaN. Ni appears to serve as a necessary wetting layer that removes either the native oxide and/or the contamination layer on the p-GaN surface during annealing. After removal of these layers, the direct contact of Au on p-GaN is produced through a “layer inversion process”. It is known that the solubility of nitrogen in Au is negligible. It is also well-known that nitrogen vacancies in p-GaN act as compensation centers for holes. Therefore, the formation of nitrogen vacancies in p-GaN during annealing results in a decrease of hole concentration in p-GaN. Since Au/p-GaN direct contacts do not produce significant nitrogen vacancy levels during annealing due to negligible nitrogen solubility, the direct contact of Au/p-GaN can produce lower contact resistance compared with the direct contact of Ni/p-GaN.

In order to investigate the transmittance of thermally-oxidized NiO, Ni 400A was deposited on a polished quartz plate by e-beam evaporation. After deposition, samples were annealed at 500°C for different times (from 15min to 24hours) and at 600°C for different times (from 3min to 3hours) in air, respectively. According to grain size analysis, it is concluded that the transmittance of NiO with large grains is higher than that with small grains. This result can be explained by the fact that the large grain size means relatively small grain boundary area and less scattering by the grain boundaries. Since, the optical transmittance decreases as the amount of grains with (111) orientation
increases compared with that of (200) orientation, it can be concluded that the relatively large amount of grains with (111) orientation can decrease optical transmittance of NiO indicating that the optical transmittance of NiO is dependent on crystallographic orientation.
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Junghan was born in Seoul, Korea, in 1968. After he received his Master of Engineering in materials science and engineering from Korea University, Seoul, Korea, in 1993, he joined Samsung Electronics. He worked for the Semiconductor R&D Center in P.A. (process architecture) over 5 years. In 1999, he came to the United States to continue his study. He received his Master of Science in materials engineering from Purdue University in 2001.
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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