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Electrical Contacts to AlGaN for UV Detectors  

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Abstract
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Electrical contacts to AlGaN were investigated at The Pennsylvania State University. Ohmic contacts to n-type Al$_x$Ga$_{1-x}$N with x $\leq$ 0.4 were easily fabricated. For x $>$ 0.45, new contact metallurgies were required. For x = 0.6, V/Al/Pt/Au contacts with optimized layer thicknesses provided a specific contact resistance of 4 x 10$^{-5}$ Ohm-cm$^2$ when annealed at 750 °C for 30 s. For p-GaN, ohmic contacts with 10 nm layers of Ni and Au annealed in air for 10 min at 550 °C provided the lowest resistance obtained in this study. The environmental and thermal stability of these contacts was examined, providing further insight into the mechanism by which these contacts become ohmic and the reasons for their limited stability. For p-Al$_x$Ga$_{1-x}$N with x = 0.1 or 0.2, Ni/Pt contacts developed at Penn State provided the lowest resistance of all contacts examined. For x = 0.4 or 0.45, specific contact resistances as low as 2 x 10$^{-3}$ Ohm-cm$^2$ were measured after annealing Au contacts, but the resistance of the contacts and semiconductor increased dramatically upon exposure to sub-band gap light. Possible causes of this increase in resistance are discussed.
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1. Introduction

Along with the advancement of III-V nitride materials and devices has come the need for high performance electrical contacts to these semiconductors. This document contains the major findings of a study of contacts to AlGaN performed at The Pennsylvania State University during the period January, 1999–December, 2002 under AFOSR grant F496209910176. The findings are discussed in four sections, which cover ohmic contacts to n-AlGaN, Schottky barrier contacts to n-AlGaN, ohmic contacts to p-type GaN, and ohmic contacts to p-type AlGaN. We then comment briefly on metallurgical considerations for these contacts and worthwhile avenues for future investigations.

2. Ohmic Contacts to n-Type AlGaN

We were quickly able to fabricate ohmic contacts to n-type Al$_x$Ga$_{1-x}$N with $x$ approximately equal to 0.3. The simplest ohmic contacts are the Al/Ti/n-AlGaN contacts, and we were guided in these experiments by our early work on Al/Ti/n-GaN contacts [Kwak00] when choosing the metal layer thicknesses. For both AlGaN and GaN, it is important to avoid layer thicknesses that result in atomic ratios of Al:Ti greater than 3. Our explanation is that the reaction to form the ohmic contact is shallow (the metals react very slowly with the semiconductor), while interdiffusion between the metal layers is rapid (the metal layers mix completely). Hence, the phases formed in the metal contact are largely consistent with those on the Ti-Al phase diagram, with Al:Ti ratios greater than 3 providing excess elemental Al beyond that needed to form the most Al-rich intermetallic TiAl$_3$. The problem with excess Al is that it has a low melting point (660 °C), resulting in agglomeration of the contact metal and high metal sheet resistances if the contacts are annealed at too high of a temperature. For contacts to n-GaN, excess Al limits the lifetime of the contact subjected to high temperatures. For contacts to n-AlGaN, excess Al is even more problematic because we have no choice but to anneal the Ti/Al contacts at higher temperatures than required for contacts to n-GaN. The need for annealing the Ti/Al contacts to n-AlGaN at 800 °C or higher is caused by the more refractory nature of AlGaN compared to that of GaN as well as the reduced thermodynamic driving forces for reaction
with AlGaN. On the other hand, reducing the Al fraction in the contacts too far is also undesirable. If the contacts are too rich in Ti, even higher annealing temperatures are required than when the contacts contain more Al, as shown in Fig. 1. For Al/Ti/n-Al_{x}Ga_{1-x}N with \( x = 0.31 \), we recommend using Al(115 nm)/Ti (65 nm)/n-Al_{0.31}Ga_{0.69}N and annealing at 800 °C for 5 min or 900 °C for 30 s. For \( n = 2 \times 10^{18} \) cm\(^{-3} \), we measured a contact resistivity of \( 7 \times 10^4 \) Ω cm\(^2 \). The choice of annealing gas (N\(_2\) or Ar) was not an important variable.

We also examined multilayer contacts to n-AlGaN. For Au(50 nm)/Ti(50 nm)/Al (150 nm)/Ti (40 nm)/n-Al_{0.34}Ga_{0.66}N with \( n = 2 \times 10^{18} \) cm\(^{-3} \), we measured a contact resistivity of approximately \( 1 \times 10^5 \) ohm-cm\(^2 \) after annealing at 1000 °C for 30 s in N\(_2\) gas. If Au/Ti/Al/Ti/n-Al_{0.34}Ga_{0.66}N contacts are annealed in Ar, slightly lower contact resistivities can be achieved, but the layer thicknesses must be adjusted. Unfortunately, poorer surface morphologies are also observed.

Our efforts to study contacts to n-Al_{x}Ga_{1-x}N with \( x > 0.4 \) were stymied during the early years of this program by two difficulties we encountered. First, we observed a high degree of scatter in our contact resistance measurements, indicative of severe contact-to-contact non-uniformity. Through experiments with different surface preparations, contact metallurgies, and epilayers, we concluded that the problem was due to inhomogeneities in the epilayers themselves rather than deficiencies in our contact metallurgies or processing procedures. In some cases, cracks were visible in the epilayers, providing an explanation for our observations, but we were unable to explain the scatter in other cases. The other problem we encountered was high resistivities of the n-Al_{x}Ga_{1-x}N epilayers, particularly those with \( x \) near 0.6. For these epilayers, the sheet resistance of the semiconductor was so high that our measurements became less sensitive to the contact resistance than we would have hoped. As the program continued, we began to receive from both Emcore Corporation and the University of Texas n-AlGaN epilayers of high Al fraction that provided greater uniformity and lower sheet resistances.
Once we received high quality $n$-Al$_x$Ga$_{1-x}$N with $x = 0.4$ ($n = 9 \times 10^{17}$ cm$^{-3}$) from Emcore Corporation, we were able to conduct reproducible experiments [Schweitz01a]. We found that multilayer contacts such as Ti/Al/Pt/Au provide lower contact resistance than contacts that contain only Ti and Al, and we furthermore determined that Au plays an important role in achieving a low contact resistance. Interestingly, the Au does more than just lower the metal sheet resistance, which when high enough increases the measured contact resistance. The Au actually reduces the interfacial or specific contact resistance after it diffuses into the annealed contact. We also found that the specific contact resistance is very sensitive to the thicknesses of the metal layers in the contact. For the Ti (26 nm)/Al (74 nm)/Pt (50 nm)/Au (50 nm) contact, we measured a specific contact resistance of $5 \times 10^{-5}$ Ω cm$^2$ after the contacts were annealed in N$_2$ at 800 °C for 30 s.

We also examined four different pre-metallization surface preparation procedures, all of which included degreasing the sample in acetone (2 min) and methanol (2 min) followed by rinsing the sample in deionized water and blowing it dry with N$_2$ gas. This treatment was performed prior to photolithography. After the samples were patterned for lift-off but prior to metallization, they were treated in HCl (10%, 5 min), buffered oxide etch containing HF (10%, 5 min), H$_3$PO$_4$ (98%, 45 °C, 15 s), or no acid. After acid treatment, samples were rinsed in deionized water and blown dry. Based on these experiments, we selected the pre-metallization surface preparation that includes the buffered oxide etch for our future work on ohmic contacts to n-AlGaN, although we note that the benefit of using any acid treatment was minimal, and using H$_3$PO$_4$ actually results in a significant increase in the specific contact resistance, despite the fact it is reported to etch aluminum oxide.

As we began to work on ohmic contacts to Al$_x$Ga$_{1-x}$N with $x$ much greater than 0.4, we found not surprisingly that the specific contact resistance increased and higher annealing temperatures were needed. Thus far in this report, we have described variations on ohmic contacts that were already developed for n-GaN. For n-Al$_x$Ga$_{1-x}$N with $x$ near 0.6, we anticipated that new contact metallurgies might be required. We identified vanadium as a potential substitute for Ti. Like Ti, V forms metal nitrides with low work functions, and V is less refractory than other substitutes for Ti that we considered, such as Hf or Ta. On
the other hand, V differs from Ti in that no V-Al-N ternary phases have been identified, in contrast to the situation in the Ti-Al-N system [Schweitz01b]. The Ti-Al-N ternary phases have been reported to form at the interface of many Ti-bearing ohmic contacts to n-Al_{0.3}Ga_{0.7}N/GaN heterostructures. Hence, we expected the contact metallurgy to change in potentially important ways when we replaced Ti with V, although we did not know beforehand if this change would be beneficial or detrimental.

Our initial studies of V/Al/Pt/Au contacts were conducted on Al_{0.3}Ga_{0.7}N/GaN heterostructures because of the greater availability of high quality Al_{0.3}Ga_{0.7}N/GaN than high Al-fraction AlGaN at the time we began these experiments. We measured a specific contact resistance of $1 \times 10^{-5} \Omega \text{cm}^2$ when we annealed V (15 nm)/Al (85 nm)/Pt (50 nm)/Au (50 nm) contacts at 650 °C for 45 s on Al_{0.3}Ga_{0.7}N/GaN heterostructures. In contrast, Ti/Al/Pt/Au contacts with optimized layer thicknesses had specific contact resistances that were two orders of magnitude higher when they were annealed at temperatures below 800 °C. On the other hand, the specific contact resistance of the Ti/Al/Pt/Au contacts was lower than that of the V/Al/Pt/Au contacts when the Ti/Al/Pt/Au contacts were annealed above 800 °C.

The advantages of replacing Ti with V become much more important as the Al fraction in n-AlGaN increases, as demonstrated by studies we conducted on two high Al-fraction n-AlGaN epilayers. The first was a 600 nm n-Al_{0.4}Ga_{0.6}N layer ($n = 8 \times 10^{17} \text{ cm}^{-3}$) grown at Emcore Corporation. The second was a 400 nm Al_{0.6}Ga_{0.4}N layer from the University of Texas with the following doping profile: the top 85 nm was doped to provide a carrier concentration of approximately $8 \times 10^{19} \text{ cm}^{-3}$, the intentional doping was gradually reduced to zero over the next 15 nm, and the bottom 300 nm were undoped. The first samples underwent cumulative anneals in 50 °C increments between 600 and 900 °C for 30 s at each temperature, but additional samples were annealed at only one temperature for 30 s (referred to as a “direct” anneal).

Both Ti/Al/Pt/Au and V/Al/Pt/Au contacts were studied on both epilayers, and the specific contact resistances were sensitive to the thicknesses of the metal layers. Figure 2 shows the specific contact resistances for all layer thicknesses and annealing conditions
that lead to ohmic behavior (linear I-V curves) on n-Al_{0.44}Ga_{0.56}N. Based on our previous work on Au/Pt/Al/Ti/n-Al_{0.4}Ga_{0.6}N [Schweitz01a] and Au/Pt/Al/V/n-Al_{0.3}Ga_{0.7}N/GaN [Schweitz02], we already knew approximate optimal thicknesses for the first two layers when used with 50 nm each of Pt and Au. We therefore tested contacts with Ti (21)/Al (79), Ti (26)/Al (74), and Ti (31)/Al (69) as the first 2 layers beneath Pt (50)/Au (50), where all layer thicknesses are given in nanometers. Only the contact with 26 nm of Ti exhibited linear I-V curves over the whole range of annealing conditions tested. The contact with 21 nm of Ti became ohmic after annealing at 700 °C, while the contact with 31 nm of Ti never became ohmic. The Pt and Au layer thicknesses were also varied above the Ti (26)/Al (74) layers. For contacts with Pt (75)/Au (25) layers, linear I-V curves were never obtained, while the Ti (26)/Al (74)/Pt (25)/Au (75) contact provided the lowest specific contact resistance. Gold plays an important role in achieving a low contact resistance, as the most Au-rich contacts exhibited the lowest resistance. Two additional samples were annealed directly at 850 °C for 30 s without any intermediate steps, and the average specific contact resistance was 8 x 10^4 Ω•cm^2.

A similar procedure was followed for the V/Al/Pt/Au contacts, and the results are shown in Fig. 3. The layer thicknesses V (15)/Al (85)/Pt (50)/Au (50) provided lower resistance than V (10)/Al (90)/Pt (50)/Au (50) and V (20)/Al (80)/Pt (50)/Au (50). Furthermore, the minimum in the specific contact resistance of the sample with 15 nm of V occurred at a much lower annealing temperature than it did for the best Ti/Al/Pt/Au contact. Two additional samples with V (15)/Al (85)/Pt (50)/Au (50) were annealed directly at 700 °C for 30 s, providing an average specific contact resistance of 1 x 10^4 Ω•cm^2. The Pt and Au layer thicknesses were next varied above V (15)/Al (85). Contacts with Pt (75)/Au (25) were the worst among this group, while V (15)/Al (85)/Pt (25)/Au (75) contacts provided the lowest specific contact resistance, again demonstrating that increasing the Au layer thickness at the expense of the Pt layer was beneficial. The average specific contact resistance of two V (15)/Al (85)/Pt (25)/Au (75) samples annealed directly at 700 °C for 30 s was 1 x 10^5 Ω•cm^2, much lower than the value provided by the best Ti/Al/Pt/Au contact to n-Al_{0.44}Ga_{0.56}N in this work.
On n-Al$_{0.6}$Ga$_{0.4}$N, the V-based contacts outperformed the Ti-based contacts to an even greater extent. Three Ti-based contacts were tested: Ti (26)/Al (74)/Pt (50)/Au (50), Ti (26)/Al (74)/Pt (75)/Au (25), and Ti (26)/Al (74)/Pt (25)/Au (75), but only the contact with 75 nm of Au became ohmic, and only after it was annealed at 850 °C or above. Furthermore, its specific contact resistance always exceeded $10^3$ $\Omega \cdot \text{cm}^2$. On the other hand, all three of the V-based contacts became ohmic. These included V (15)/Al (85)/Pt (25)/Au (75), which became ohmic at 600 °C; V (15)/Al (85)/Pt (50)/Au (50), which became ohmic at 650 °C; and V (15)/Al (85)/Pt (75)/Au (25), which became ohmic at 700 °C. Moreover, lower specific contact resistances were obtained with all of the V-based contacts than with any of the Ti-based contacts. The lowest specific contact resistance was measured after annealing the V (15)/Al (85)/Pt (25)/Au (75) contact at 750 °C for 30 s, and the average specific contact resistance for two samples with V (15)/Al (85)/Pt (25)/Au (75) contacts annealed directly at 750 °C for 30 s was $4 \times 10^2$ $\Omega \cdot \text{cm}^2$. Note that the V/Al/Pt/Au contact that we have developed provides an important advantage over the Ti/Al/Mo/Au contact to n- Al$_{0.36}$Ga$_{0.44}$N reported by Adesida and co-workers [Selvanathan02] in that the Ti/Al/Mo/Au contact requires a pre-metallization plasma treatment of the surface. Our study demonstrates that changes to the contact metallizations commonly used on n-AlGaN of lower Al fraction are beneficial for contacting Al-rich n-AlGaN.

3. Schottky Barrier Contacts to n-Type AlGaN

An investigation of Schottky barrier contacts to n-AlGaN was initially conducted early in the program to study the influence of pre-metallization surface preparations on contacts to AlGaN. We suspected that surface preparation might be especially important for ohmic contacts to p-AlGaN, since it can be very important for ohmic contacts to p-GaN, but we had much more n-AlGaN available to us than p-AlGaN early in the program. Platinum and Au Schottky contacts were fabricated to n-Al$_{0.14}$Ga$_{0.86}$N and n-Al$_{0.17}$Ga$_{0.83}$N from ATMI, with similar results observed when additional experiments were conducted on material from the University of Texas. Although the influence of surface preparation on the electrical performance of the diodes was measured, we quickly discovered that the
diodes' electrical characteristics were extremely sensitive to the environment in which they were stored, so much so that the effect of surface preparation was obscured by this environmental effect.

As illustrated in Fig. 4, Au Schottky barriers deposited on n-AlGaN were initially leaky (exhibiting high reverse currents), but with exposure to laboratory air for a few days became well behaved (exhibiting reverse currents reduced by as much as four orders of magnitude). On the other hand, diodes stored in vacuum had stable but poor electrical characteristics, exhibiting the same high reverse leakage currents, low barrier heights, and high ideality factors as freshly prepared diodes. The change in the diodes upon exposure to air at room temperature is partially reversible when the diodes are later stored in vacuum or annealed at 150 °C in N₂, and it is completely reversed after annealing at 250 °C in N₂. We further observed that aging in dry O₂ for 2 hours was similar to aging in air at room temperature for 1 week.

The initial high reverse leakage current scaled with the area rather than the perimeter of the diodes and was greatly slowed when Au contacts were 500 nm rather than 50 nm thick, so we believe that gases must be diffusing through the noble metal contacts and that the buried AlGaN surface is highly active. Furthermore, our later experiments showed that dielectric passivation of the semiconductor surface between contacts does not prevent a fluctuation in electrical response, although these experiments were conducted on AlGaN/GaN heterostructures capped with a very thin layer of GaN, and the change in the diodes exposed to air occurs more slowly when the semiconductor is capped with GaN. In any event, these results lend further credence to our claim that diffusion of gases through the metal contact are responsible for the variation in electrical response.

From a practical point of view, we can conclude that Schottky barrier contacts to n-AlGaN will need to be sealed from their environment to avoid fluctuations in electrical characteristics as a response to their environment. However, we are currently trying to understand the mechanism for the aging, which we have also observed more recently in Co, Ni and Re contacts to n-AlGaN and have observed to a lesser extent in Schottky bar-
rier contacts to n-GaN. Growth of a dielectric layer between the metal and semiconductor due to diffusion of O₂ to the metal/semiconductor interface could lead to a reduction in current transport with aging, but it is surprising that such a layer could be reduced under the mild conditions observed to reverse the effects of environmental aging. Since we do not know if O₂ acts uniformly across the metal/semiconductor interface or primarily at defects in the semiconductor, we are currently conducting experiments on n-GaN epilayers grown at Sandia National Laboratories by cantilever epitaxy to learn if aging occurs at a different rate above regions of high and low defect density. These experiments are being completed by a student supported by a teaching assistantship.

4. Ohmic Contacts to p-Type GaN

At the start of the solar blind detector program, many participants indicated that they would need to make ohmic contacts directly to p-AlGaN, but p-AlGaN was not yet available. Toward the end of the program, most participants decided to contact p-AlGaN capped with p-GaN. During the course of this program, we studied contacts to both p-GaN and p-AlGaN.

During the first year of the program, we examined process variables that influence the electrical performance of contacts to p-GaN. These factors include the activation procedure of p-GaN grown by metal organic chemical vapor deposition, the contact annealing environment (including introduction of O₂), the pre-metallization surface preparation, the deposition method (evaporation, sputtering, or electrodeposition), and the identity of the metals in the contact. Effective activation of Mg in the p-type semiconductor, without damaging the semiconductor surface, is critical to making good contacts, and we found that even the presence of unintentionally incorporated O₂ in ultra high purity (UHP) N₂ increased the rate of activation of p-GaN at temperatures below 900 ºC, as compared to activation in UHP N₂ gettered by hot Ti sponge. Activation was even more rapid when low levels of O₂ were intentionally introduced. [Hull00]

Of all the ohmic contacts to p-GaN that we tested, the lowest specific contact resistance and most reliably linear current-voltage (I-V) curves we obtained were for Ni/Au contacts
annealed in air. This conclusion differs from those that we drew shortly before the start of the program, but we had not yet tested Ni/Au contacts with very thin Ni and Au layers. The procedure for fabricating these contacts is similar to that reported by Ho et al. [Ho99], although our best results were actually for Ni and Au layers that were each 10 nm thick, and we annealed the contacts at 550°C for 10 min in synthetic (dry) air. On p-GaN from Emcore Corporation (p = 5 x 10^17 cm^-3), we typically measured a specific contact resistance of 4 x 10^-3 Ω cm^2, although on p-GaN from ATMI we measured specific contact resistances as low as 4 x 10^-4 Ω cm^2.

The thin Ni/Au contacts annealed in air have been used by some of the solar blind detector program participants in their devices (at Northwestern), and we have published information on the environmental and thermal stability of the contacts [Wang02]. Through our study of the contact stability, we are also able to shed more light on the mechanism for the surprisingly low resistance of these contacts.

Our study of the environmental and thermal stability of the contacts was initiated because we observed that the thin Ni/Au contacts initially annealed in air did not retain linear I-V characteristics when they were stored in a laboratory drawer for one month. We therefore examined the stability of the contacts in different environments and were able to clearly correlate their degradation with exposure to water vapor. Degradation did not occur at room temperature when samples were sealed in evacuated quartz tube or held in dry O_2 or dry N_2. We also observed that the sheet resistance of the semiconductor did not increase upon exposure to a humid environment; rather, only the ohmic contact itself degraded. Using x-ray photoelectron spectroscopy (XPS), we furthermore correlated the degradation of the contacts to the incorporation of hydroxyl groups in NiO, which formed in the contact when it was initially annealed in air. When aged at 200°C for 1 day, however, the ohmic contacts were stable only when held in dry O_2. (Presumably dry air would be acceptable as well.) They degraded markedly when aged in an evacuated quartz tube, dry N_2, or N_2 saturated with water vapor at 200°C.

From a practical point of view, we conclude that the Ni/Au ohmic contacts annealed in air must be passivated or hermetically sealed after fabrication to protect them from hu-
midity. We also conclude that processing steps carried out at 200 °C or higher in the absence of O₂ must take place prior to the fabrication of the ohmic contact to p-GaN. From a scientific point of view, our observations also allow us to comment on the mechanism by which the thin Ni/Au ohmic contacts annealed in air. To do so, we must first describe what other researchers have reported in the literature.

The mechanism responsible for the low resistance of the annealed contacts has been the subject of several recent investigations, and two different explanations are suggested in the literature. Ho et al. [Ho99] attribute the low specific contact resistance to a favorable band line-up when p-type NiO patches are adjacent to the p-GaN. Their model draws upon microstructural characterization of the contacts, which indicates that Au-rich regions, an amorphous Ni-Ga-O phase, NiO, and voids can all be found at the interface with p-GaN after the contacts are annealed. [Chen99a, Chen99b] On the other hand, Koide et al. [Koide99] propose that oxygen instead aids in the removal of hydrogen from the p-GaN, resulting in better activation of the Mg acceptors in p-type GaN when the samples are annealed in air. The model proposed by Koide et al. is also consistent with microstructural characterization of their annealed contacts, which consist of NiO/Au/p-GaN layers, and their model is further supported by their observation of a reduced sheet resistance of the p-type GaN layer when annealing is performed in air. The contacts studied by the two different research groups differ in the layer thicknesses of Ni and Au prior to annealing, and an exceptionally low specific contact resistance of 4 × 10⁻⁶ Ω·cm² was reported only for the very thin Ni (5 nm) and Au (5 nm) layers reported by Ho et al.

Further investigations by Maeda et al. [Maeda99] and Qiao et al. [Qiao00] were aimed at clarifying the role of NiO by producing Au/NiO/p-GaN structures through a variety of methods, including direct deposition of NiO, Li-doped NiO, and oxidation of Ni layers prior to the deposition of Au. None of these contacts provided a particularly low resistance, casting doubt on the model by Ho et al. Taking a different approach, Chen et al. [Chen00] compared oxidized Pt (5 nm)/Ni (5 nm)/p-GaN and Au (5 nm)/Ni (5 nm)/p-GaN contacts and observed that the specific contact resistance of the Au/Ni/p-GaN contacts was approximately four orders of magnitude lower than that of the oxidized Pt/Ni/p-
GaN contacts. These contacts differed in their microstructure after annealing. The Pt/Ni/p-GaN contacts consisted of a layered NiO/Pt-Ni-Ga/(amorphous Pt-Ni-Ga)/p-GaN structure, compared to the mixed microstructure of NiO, Au, and amorphous Ni-Ga-O already reported for the thin Au/Ni/p-GaN contact. While the authors suggested that a more intimate metal/semiconductor interface and improved activation of the p-GaN could explain the ohmic nature of the higher resistance Pt/Ni/p-GaN contacts annealed in air, they believed that the dramatic four order of magnitude improvement in the Au/Ni/p-GaN contacts was due to the role of p-NiO as an intermediate semiconductor layer. Recently, Jan et al. [Jan01] have also correlated a low specific contact resistance with an enhanced hole concentration in the p-NiO within the contact using X-ray absorption near edge structure data.

Our experiments also point to the importance of p-NiO for the formation of a low resistance ohmic contact, because degradation of the contacts occurs precisely under the same conditions that cause a reduction in the hole concentration in p-NiO, as we have confirmed through experiments on NiO layers that we formed through sputter deposition of Ni films that we subsequently oxidized. NiO is a p-type semiconductor because holes are present in the oxide to charge balance non-stoichiometry caused by Ni vacancies, which have charges of -1 or -2 relative to the perfect, stoichiometric lattice. When our NiO films or when our contacts that contain NiO are annealed at 200 °C in an environment lean in O₂, the stoichiometry of the oxide is altered. The NiO film, which was previously rich in oxygen, loses oxygen, with a corresponding reduction in the Ni vacancy and hole populations. At room temperature, these reactions are slow, but in the presence of humidity, we propose that a reduction in the hole concentration occurs through the following point defect reaction, which is consistent with all our experimental results:

\[ H_2O(g) + h + O^{2-}_O \rightarrow 2HO_2 + V^{2+}_{Ni} \]

Should a contact other than the thin Ni/Au contact annealed in air be desired, we recommend the following alternatives that do not require annealing in air: Ni (20 nm)/Pt (100 nm) contacts annealed in N₂ at 600 °C for 3 min, which were developed at Penn State and have the added advantage of excellent thermal stability, or Pd (20 nm)/Au (100
nm) contacts deposited on p-GaN subjected to a boiling aqua regia pre-metallization surface treatment.

5. Ohmic Contacts to p-Type AlGaN

For p-Al_{x}Ga_{1-x}N with x approximately equal to 0.1 and 0.2 supplied by ATMI, we found that the best procedures we identified differed markedly from those favorable for p-GaN. Our most linear I-V characteristics were achieved for the Pt (1000 Å)/Ni (200 Å)/p-AlGaN contacts developed in our laboratory, even though these were not the best contacts we studied for p-GaN. For Al_{x}Ga_{1-x}N with x = 0.1, annealing at 600 °C for 2 minute in N₂ gas was optimal. For x = 0.2, we recommend 1 minute at 800 °C. Although useful for p-GaN, we did not achieve linear I-V characteristics for contacts annealed in O₂ or prepared with aggressive pre-metallization surface preparations, such as boiling aqua regia. The greater affinity of Al for oxygen may pose a problem when annealing contacts in the presence of O₂, and the reactivity of the AlGaN surface in air at room temperature may be the reason why our attempts to use aggressive pre-metallization surface preparations were not successful.

We also examined contacts to p-GaN/p-AlGaN layers above p-i-n detector structures. Our first experiments were halted when we discovered cracks in the nitride semiconductor and found that they greatly influenced our results. Current transport was impeded whenever cracks were positioned between contacts, but not when the cracks were parallel to them, leading to erratic data. We provided this information to BAE Systems, which had received these epilayers from Emcore Corporation, and they did not use these wafers for device fabrication.

We next received p-type epilayers from BAE Systems and Emcore Corporation that were not cracked. One epilayer was Mg-doped Al_{0.4}Ga_{0.6}N, and the other was Mg-doped Al_{0.4}Ga_{0.6}N with a cap that was intended to be 10 nm of p-GaN. However, we later determined by XPS that the cap was actually a less Al-rich AlGaN layer; some Al was still present even at the surface of the cap. We found that we could achieve contacts with a
lower resistance on epilayers that were not capped with p-AlGaN of lower Al fraction. In either case, it was necessary to anneal the Ni/Au and Ni/Pt contacts at or above 700 °C in N2 in order to achieve a low enough resistance to make measurements, and the Ni/Pt contacts provided resistances that were approximately four orders of magnitude lower than the Ni/Au contacts when the contacts were annealed at 800 °C. Unfortunately, in the samples without the more Ga-rich p-AlGaN cap, the resistance of the AlGaN layer increased dramatically, even as we took our measurements.

We also worked with Mg-doped Al0.6Ga0.55N from the University of Texas. Researchers at the University of Texas had previously confirmed the p-type conductivity of their epilayers through experiments with mesas and diodes of varying area. [Li01] We were surprised, however, that good (and stable) contacts were formed after annealing at only 300 °C. A Ni/Pt/Au contact had a lower resistance (4 Ω cm2) than did a Ni/Au contact. On the other hand, the contacts were severely degraded after anneals at 400–650 °C; in fact, annealing at these temperatures resulted in very rectifying contacts. We were initially puzzled by this dramatic difference between the behavior of contacts to Mg-doped Al0.6Ga0.5N from Emcore Corporation and Mg-doped Al0.45Ga0.55N from the University of Texas. As we continued to receive material from the University of Texas and conduct further experiments, however, we discovered that the behavior of the contacts and epilayers after very high temperature annealing behavior (at 800 °C or higher) was very similar, regardless of the source of material. We observed a dramatic drop in resistance after high temperature annealing. In either case, however, the resistance increased after the contacts were annealed and measured. Since this behavior was reproducible and observed on Al-rich p-AlGaN epilayers from two different growers, we examined it in more detail, focusing on single metal films for simplicity.

Figure 5 shows a sequence of I-V curves for Pd contacts to p-Al0.6Ga0.55N that were measured following an 800 °C anneal from zero to 120 min after annealing. The resistance of each I-V curve was calculated from Ohm’s law, employing the voltage measured across a pair of contacts at a current of 10 μA. This total resistance includes the resistance of a pair of contacts as well as the resistance due to the epitaxial layer between them, and
is shown as an inset in Fig. 5. The increase in resistance can be approximated by a simple exponential growth model with a time constant on the order of a few minutes.

Circular transfer length method (CTLM) measurements of the Au, Pt, and Pd contacts indicate an initial specific contact resistance as low as $2 \times 10^3 \ \Omega \ \text{cm}^2$ for Au contacts after annealing at 850 °C for 2 min and as low as 0.2 Ω cm² for Pd contacts after annealing at the same conditions. As the resistance increases, CTLM measurements indicate that both the specific contact resistance of the contacts as well as the sheet resistance of the p-AlGaN epilayer itself suffers an increase in resistance. Note that these measurements were based solely on the 4 μm and 50 μm gap contacts, due to the changes that occur in the sample during measurement. The low resistance obtained immediately following the initial high temperature anneal can be recovered following a moderate anneal of 500°C—well below the 800°C annealing temperature initially employed to achieve the low resistance. Following a reversal anneal, however, the increase in resistance occurs at approximately the same rate.

A series of experiments were next performed to determine the cause of the increase in resistance. A sample of Pd contacts on p-Al₀.₄₅Ga₀.₅₅N that had been annealed at 800 ºC was employed, and the increase in resistance between a pair of contacts with a 4 μm gap was investigated. Following each period of degradation, the sample was annealed at 500 ºC to revert it to its minimum resistance. The I-V curves of the contact were measured (under tungsten halogen illumination) either immediately following the 500 ºC reversal anneal, after storage in the dark for 30 min following annealing, or after being held under tungsten halogen illumination (maximum energy of 3.8 eV) for 30 min following annealing but prior to probing. Interestingly, the resistance of the samples began to increase only once the samples were illuminated, and the increase in resistance was not affected by current injection. From this experiment, we were able to conclude that the increase in resistance was induced by exposure to sub-band gap illumination. Red filtration of the illumination was next employed, with no measurable changes in the behavior of the contacts or p-AlGaN. Thus, the degradation appears to be induced by photons less energetic than 1.9 eV (the maximum energy of transmission of the red filter employed).
In order to eliminate environmental effects as the cause of degradation, dark storage was employed in either flowing N₂ or open to laboratory air. No measurable differences between the dark storage in N₂ and dark storage in air were observed, so environmental effects appear to be unimportant.

The optically induced degradation of the p-AlGaN with sub-band gap illumination, along with the thermal excitation that reverses the degradation, suggest that one or more optically excited metastable deep levels are responsible. A variety of phenomena in AlₓGaNₜₓ₋₄N alloys have been attributed to optically excited deep levels located within the band gap. Persistent photoconductivity (PPC) in both n- and p-GaN in particular has received a great deal of attention [Johnson96, Hirsch97]. The increase in resistance that we observe, which we will refer to as degradation, resembles an inverse PPC, whereby the p-AlGaN conductivity decreases with optical exposure and is reversed with thermal processing. The degraded state in this experiment seems to persist indefinitely at room temperature, however, even with the removal of illumination.

The DX center, well described for AlGaAs alloys [Chadi90], is one type of deep level that may account for the observed degradation. In GaN, oxygen that has been unintentionally incorporated into the lattice acts as a shallow donor [Neugebauer97], but is theorized to undergo a transition to a deep DX-like state in AlₓGa₁₋ₓN for compositions with x greater than 0.2 [Park97] to 0.4 [Van de Walle98]. The DX center is photo-excited to a shallow donor state and reverts to its deep level with the application of thermal energy, and it has been suggested that oxygen DX centers are responsible for PPC in n-Al₀.₃₅Ga₀.₆₅N at temperatures below 150K [McCluskey98]. If present in p-type AlₓGa₁₋ₓN, an excited DX center could compensate Mg acceptors, thus decreasing the carrier concentration and conductivity. Another possible mechanism for degradation arises from residual H within activated Mg-doped AlₓGa₁₋ₓN. The role of H in Mg-doped GaN and the thermal dissociation of Mg:H complexes to activate p-GaN have been well documented [Neugebauer95, Nakamura92], and residual H within the lattice might repassivate Mg acceptors during optical excitation, with reactivation following moderate annealing. However, we have been unable to distinguish between surface and bulk conduc-
tion thus far in our investigation. The charging of surface states has recently been shown to result in drain current collapse within AlGaN/GaN high electron mobility transistors, which is induced by deep biasing and is reversed with mild thermal anneals and optical excitation [Ventury01, Binari02]. A related surface conduction phenomenon might account for the observed degradation in the present investigation. None of the experiments performed in this investigation can confirm nor refute the proposed mechanisms for the observed degradation. Further experimentation, including an examination of passivated samples, is warranted.

6. Metallurgical Considerations

We were concerned early in our investigation that the low contact resistances we measured when we annealed ohmic contacts to AlGaN at high temperatures might have been accompanied by spiking of the metallization into the semiconductor. Therefore, we conducted experiments in which we used selective etchants to remove the patterned metallizations and performed AFM on the freshly exposed AlGaN surface. We did these experiments on late transition metal contacts to p-AlGaN and V/Al/Pt/Au contacts to n-AlGaN, and we learned that the reactions between the contact metals and semiconductor are actually very shallow, penetrating the semiconductor no more than tens of nanometers, without spiking of the metallization. The reactions between contact metals and AlGaN are less extensive than the reactions typically observed between contact metals and GaN, consistent with the reduced thermodynamic driving forces for reactions between metals on AlN compared to metals on GaN [Schweitz01b].

More recent studies conducted with the support of a seed grant from the Lehigh–Penn State Center for Optical Technologies have allowed us to further investigate the metallurgy of contacts to AlGaN, and we have discovered using scanning transmission electron microscopy and x-ray photoelectron spectroscopy that the reaction between contact metals and AlGaN can actually alter the composition of the AlGaN immediately beneath the contact through preferential incorporation of Ga in the contact metallization and enrichment of Al in the semiconductor. Alteration of AlGaN and AlGaInN semiconductor alloy
compositions during annealing of ohmic contacts will likely affect the electrical properties of these contacts and warrants further investigation.

7. References


[Ho99] J. Ho, C.-S. Jong, C. C. Chiu, C.-N. Huang, K.-K. Shih, L.-C.


8. Figures

Figure 1. Contact resistivity (or specific contact resistance) of Al/Ti/n-Al$_{0.31}$Ga$_{0.69}$N ohmic contacts as a function of annealing condition.
Figure 2. Specific contact resistance of Au/Pt/Al/Ti/n-Al_{x}Ga_{1-x}N contacts cumulatively annealed for 30 s at each temperature. All layer thicknesses are in nanometers.

Figure 3. Specific contact resistance of Au/Pt/Al/V/n-Al_{x}Ga_{1-x}N contacts cumulatively annealed for 30 s at each temperature. All layer thicknesses are in nanometers.
Figure 4. Thermally evaporated Au Schottky barrier contacts on n-AlGaN as deposited and (a) after 1 week of exposure to laboratory air and (b) after storage in vacuum for 1 week.
**Figure 5.** Sequence of I-V curves for Pd contacts to $p$-Al$_{0.45}$Ga$_{0.55}$N with a 4 μm gap following an 800°C anneal. Zero minutes represents the first probing after annealing. The inset plot shows the total resistance vs. time.
9. Publications and Presentations Resulting from the Award

Publications


Presentations


### 10. Personnel Associated with the Project

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<td>Kasper Schweitz</td>
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<td>1/00–12/01</td>
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S. H. Wang wrote his M.S. thesis based in large part on work performed as part of this program, earning the M.S. degree in Materials Science in May, 2001. Both Brett Hull and Eric Readinger will defend Ph.D. theses during 2003, and work performed on this program will be an important part of their theses. Many of the conclusions from their work so far are included in the technical discussion in this report. The title and abstract of S. H. Wang's thesis are also included on the following page. The complete theses (including those of Brett Hull and Eric Readinger when submitted) may be obtained from The Pennsylvania State University (Library Phone: (814) 865-2112).
11. Thesis Abstracts

**Ohmic Contacts to p-Type GaN**

M.S. Thesis in Materials Science  
Sammy H. Wang  
May, 2001

Abstract

Gallium nitride has been of interest in recent years for its great potential for short wavelength optoelectronic devices. However, one of the issues for improving GaN-based devices is the ohmic contact to p-type GaN. Low contact resistance can enhance the power efficiency. Therefore, a better understanding of the contacts is needed.

In the first part of this thesis, a comparison of the I-V curves and specific contact resistance of seventeen different metal contacts is performed, where some contacts were previously reported in the literature and some were designed in our lab. The optimization of these metal contacts was carried out by varying the thickness of the metal films, surface pretreatment, annealing temperature, annealing time and annealing environment. Among all the contacts tested, thin Ni/Au contacts annealed in air showed the best electrical performance.

The second part of this thesis focuses on the stability of these oxidized Ni/Au ohmic contacts. After the samples sat in the lab bench for one month, significant degradation occurred, e.g., the linear current-voltage curves became non-linear. To study the cause of the degradation, additional experiments were performed that clearly showed that water vapor was responsible for the room temperature degradation. A mechanism for the change in the electrical performance is proposed. The contacts were furthermore found to be unstable at 200 °C in all environments tested except for oxygen, and the contacts aged more rapidly under bias.
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