

The electrical behavior of Pt₃In₇ and NiIn contacts to *p*-GaN

D. B. Ingerly^{a)} and Y. A. Chang

Department of Materials Science and Engineering, University of Wisconsin, Madison, Wisconsin 53706-1595

Y. Chen

Hewlett-Packard Company, 3500 Deer Creek Road, Palo Alto, California 94304-1392

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Based on the criteria for the solid-state exchange reaction with *p*-GaN, we have investigated the intermetallic compounds, Pt₃In₇ and NiIn, as possible ohmic contacts. The as-deposited contacts were found to be rectifying and using current–voltage characterization rapid thermal annealing of the contacts was shown to significantly decrease their resistance, with contacts annealed at 800 °C for 1 min yielding the lowest resistance. Pt₃In₇ contacts to *p*-GaN when annealed at 800 °C for 1 min exhibited a specific contact resistance (ρ_c) of $9.5 \times 10^{-2} \Omega \text{ cm}^2$ while NiIn was more than an order of magnitude lower at $8.0 \times 10^{-3} \Omega \text{ cm}^2$. The NiIn contacts also show a lower specific contact resistance than the more traditionally used Ni/Au contacts ($\rho_c = 1.3 \times 10^{-2} \Omega \text{ cm}^2$) processed under the same conditions. Atomic force microscopy was used to examine the morphology of the reacted contacts. While the Ni/Au contacts showed the formation of deep spikes (<200 nm) after annealing the NiIn contact showed a much smoother reaction region with no evidence of spiking. © 1999 American Institute of Physics. [S0003-6951(99)04517-9]

GaN is a wide band gap semiconductor with tremendous promise for optical applications. When alloyed with InN and AlN it can be used to fabricate high efficiency optical devices such as light emitting diodes (LEDs) and lasers that operate in the visible (yellow to blue) and ultraviolet (uv) ranges.^{1,2} The addition of blue and green LEDs to the already available reds, oranges, and yellows completes the visible spectrum, allowing LEDs to be used for applications such as traffic lights and large flat full-panel displays.^{3,4} Additionally, blue and uv lasers will have a significant impact on high-density information storage using magnetic and optical media.⁴ Aside from its applications in optoelectronics, GaN's wide band gap, good thermal conductivity, and chemical stability make it an ideal candidate for use in high temperature and high power electronic devices.^{5,6}

Despite the availability of commercial GaN based products, technical challenges still limit these devices. One major concern is the metal contacts to GaN semiconductors, because contacts with a high resistance can substantially reduce the performance of GaN based optical and electrical devices. In fact, the high resistance of the metal contact to *p*-type GaN is one of the most significant problems limiting laser diode performance.⁴

Currently Ni/Au is employed as an ohmic contact to *p*-GaN in most LED and laser applications.^{7,8} Despite being successfully used in these devices, the contacts typically exhibit a specific contact resistance (ρ_c) in the 10^{-3} – $10^{-2} \Omega \text{ cm}^2$ range^{9,10} and show poor thermal stability.¹¹ The standard approach used to form ohmic contacts to *p*-GaN has been to select metals with large work functions such as Pd, Pt, Ni, and Au and depositing them in multilayer combinations.^{10,12} However, none of these schemes has yielded a contact with the desired less than $10^{-5} \Omega \text{ cm}^2$ resistance typically considered device quality.

In an attempt to find new metallizations that could be used to form ohmic contacts to *p*-GaN, the solid-state exchange reaction was utilized. This reaction has been shown to be a systematic approach for tailoring metal/semiconductor contact properties.^{13–16} The complete thermodynamic and kinetic model for the exchange mechanism has been comprehensively set forth by Swenson, Jan, and Chang.¹⁷ Based on the exchange mechanism criteria, two intermetallic compounds, NiIn and Pt₃In₇, were selected as possible ohmic contacts to *p*-GaN.

Pt₃In₇ is an intermetallic compound with a Ge₃Ir₇ crystal structure and a peritectic melting point at 894 °C.¹⁸ The thermodynamically stable phase of NiIn has a CoSn (B35) crystal structure, however, the metastable B2 phase often forms and is the structure of the NiIn films used in this study. This B2 phase is thermodynamically stable at high temperature in Ni–In alloys that have 51% to 58% In.¹⁸ Both the Pt₃In₇ and NiIn alloys show good chemical stability and oxidation resistance.

The GaN substrates used in this study are 1.2- μm -thin films of single crystal GaN grown by metalorganic vapor phase epitaxy on sapphire (0001). The GaN epilayer is Mg doped and annealed at 850 °C for 5 min to activate the dopants. A *p*-type carrier concentration of $1.7 \times 10^{17} \text{ cm}^{-3}$ with a mobility of 8 cm/V s was measured by Hall probe at room temperature. Prior to lithography, the substrates were ultrasonically degreased with warm TCE, acetone, and methanol for 10 min each. These degreased substrates were then etched in HCl:H₂O (1:2) for 4 min and then rinsed in flowing H₂O for 10 min.

Using standard photolithography techniques the substrates were patterned with one of two masks. For the current–voltage (*I*–*V*) measurements, equally spaced circular dots 150 μm in diameter and 750 μm apart were used. For specific contact resistance (ρ_c) measurements a circular transmission line model (TLM) pattern similar to the one

^{a)}Electronic mail: ingerly@cae.wisc.edu

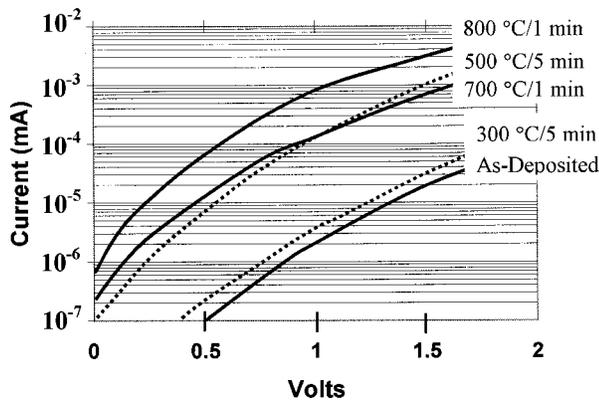


FIG. 1. I - V behavior of $\text{Pt}_3\text{In}_7/p$ -GaN contacts for different annealing conditions.

detailed by Marlow¹⁹ was utilized. Once patterned, the substrates were then placed in a $\text{HCl}:\text{H}_2\text{O}$ (1:3) solution for 60 s, blown dry with N_2 gas, and immediately loaded into a vacuum chamber with the background pressure less than 2×10^{-7} Torr.

The two metallizations investigated in this study, NiIn and Pt_3In_7 , were both deposited by sputtering from a compound target to a nominal 150 nm thickness. The Pt-In intermetallic film, deposited using direct current magnetron sputtering, has the actual composition of 31.5 at. % Pt and 68.5 at. % In as measured by electron microprobe analysis. After annealing, x-ray diffraction showed the films to be single phase with a Pt_3In_7 crystal structure under the sputtering conditions used. The annealed NiIn films (50:50 at. % ratio) were found to be in the metastable B2 crystal structure when deposited by radio frequency sputtering under the conditions used. As a control standard, Ni/Au contacts were also fabricated. These films were deposited by thermal evaporation, with Ni and Au film thickness of 10 and 100 nm, respectively.

After deposition, the photoresist was lifted off in an acetone bath leaving the patterned metal on the wafers. Following liftoff, the contacts were annealed in an AG Associated MiniPulse rapid thermal annealing (RTA) system with flowing high purity argon gas. The electrical properties of the contacts were measured with a Keithley Model 236 electrometer employed as a current source and voltage meter.

Figure 1 shows the electrical behavior of the $\text{Pt}_3\text{In}_7/p$ -GaN contacts under a wide range of annealing conditions from the as-deposited state up to 800 °C for 1 min. The I - V behavior was measured between two 150 μm diameter contacts spaced 750 μm apart. The I - V curves were symmetric around the origin, but only the portions of the curves corresponding to positive applied voltages are shown in the figure. Figure 1 clearly shows that as the annealing temperature is increased the contact resistance decreases until the lowest contact resistance occurs after annealing at 800 °C for 1 min. Contacts subjected to a higher annealing temperature, 850 °C for 1 min, showed a higher resistance than the samples annealed at 800 °C for 1 min. While only the I - V corresponding to the Pt_3In_7 contact is shown in Fig. 1, both metallizations exhibit the same relative changes in resistance versus annealing temperature, which suggests that the changes in I - V behavior are due to the same mechanism.

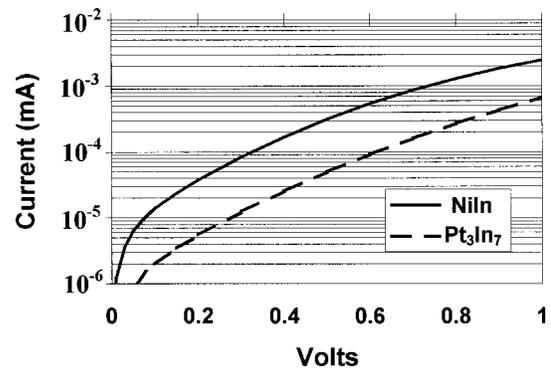


FIG. 2. Comparison between Pt_3In_7 and NiIn contacts annealed at 800 °C for 1 min.

Figure 2 shows a comparison of the I - V behavior for Pt_3In_7 and NiIn, both annealed at 800 °C for 1 min, which is the annealing condition yielding the lowest contact resistance, demonstrating that NiIn contacts have a much lower resistance.

It is difficult to compare the specific contact resistance for different metallizations reported by different researchers due to the wide variability in p -GaN substrates. These substrate differences can play an important role in the measured properties of the contacts. In order to allow a more universal comparison of the metallizations evaluated in this study we have used Ni/Au contacts as a standard.

Table I lists the ρ_c of contacts annealed at 800 °C for 1 min. These values are an average from three individual sets of measurements. All ρ_c values were measured at 5 V using the circular TLM pattern consisting of seven different contact pads with gap spacing ranging from 4 to 25 μm . The values determined are consistent with the I - V behavior shown in Fig. 2; with the NiIn contacts' ρ_c of $8 \times 10^{-3} \Omega \text{ cm}^2$ being more than an order of magnitude lower than the contact resistance of $9.5 \times 10^{-2} \Omega \text{ cm}^2$ determined for the Pt_3In_7 contacts. However, the most significant result of this study is NiIn contacts are shown to have a lower contact resistance than the Ni/Au contacts processed under the same conditions. While we did not attempt to optimize the annealing condition for the Ni/Au contacts in this study, the ρ_c of $1.3 \times 10^{-2} \Omega \text{ cm}^2$ is very comparable to the values reported by other researchers.^{9,10,12}

Atomic force microscopy (AFM) was used to evaluate the reaction morphology of the Ni/Au and NiIn contacts prepared and annealed under the same conditions. Wet etching was used to remove the metal film and expose the p -GaN surface. Figure 3 shows that deep pits (some more than 150 nm deep) were formed in the p -GaN after the Ni/Au contacts were annealed at 800 °C for 1 min; a result consistent with

TABLE I. Specific contact resistance of the annealed contacts. All contacts were annealed at 800 °C for 1 min.

Metallization	Specific contact resistance ($\Omega \text{ cm}^2$)
Pt_3In_7	9.5×10^{-2}
NiIn	8.0×10^{-3}
Ni/Au	1.3×10^{-2}

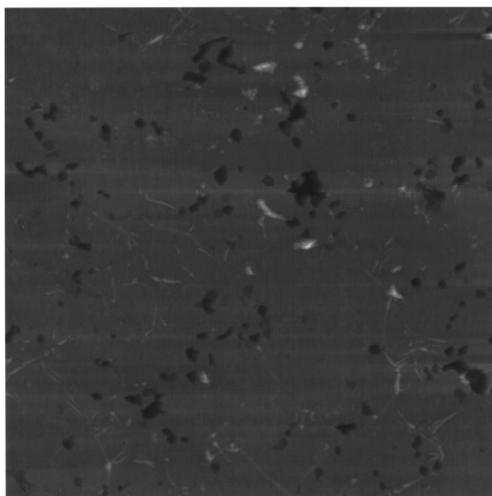


FIG. 3. AFM image of the annealed Au/Ni/*p*-GaN contact after etching the metal away. The image shows a $10 \times 10 \mu\text{m}$ area with the gray scale corresponding to a 150 nm of roughness.

the work of Venugopalan *et al.*¹¹ In contrast, the substrate surface corresponding to the NiIn contacts annealed at 800 °C for 1 min (Fig. 4) does not show these deep pits but rather a roughness consisting of perturbations on the order of about 20 nm. It is important to note that a *p*-GaN substrate subjected to the same wet etch process used to remove the metal from both annealed samples showed no change in surface morphology. These AFM results not only suggest that the Ni/Au and NiIn react very differently with the *p*-GaN substrate, but also that the NiIn contacts have a much more controlled and limited reaction depth. Auger depth profiling results on annealed Au/Ni and NiIn contacts were consistent with information gained from the AFM.



FIG. 4. AFM image of the annealed NiIn/*p*-GaN contact after etching the metal away. The image shows a $10 \times 10 \mu\text{m}$ area with the gray scale corresponding to a 50 nm of roughness.

The electrical and interfacial characterization conducted in this study demonstrates that NiIn has potential as an ohmic contact to *p*-GaN, and is potentially a more thermally stable contact replacement for Ni/Au. However, further research is required to determine what reactions occur during annealing and to identify what mechanism is responsible for lowering the resistance of the annealed contacts.

In summary, Pt₃In₇ and NiIn were selected based on the criteria for the exchange mechanism as possible ohmic contacts to *p*-GaN. RTA of the contacts was shown to decrease their resistance. For both metallizations, contacts annealed at 800 °C for 1 min had the lowest resistance of the annealing conditions examined in this study; in fact, Pt₃In₇ and NiIn demonstrated the same relative changes in resistance due to annealing. Pt₃In₇ contacts to *p*-GaN when annealed at 800 °C for 1 min exhibited a ρ_c of $9.5 \times 10^{-2} \Omega \text{ cm}^2$ while NiIn was more than an order of magnitude lower at $8.0 \times 10^{-3} \Omega \text{ cm}^2$. This is a particularly promising result since the ρ_c of NiIn is also lower than the more traditionally used Ni/Au contact ($\rho_c = 1.3 \times 10^{-2} \Omega \text{ cm}^2$) processed under the same conditions. AFM was used to examine the morphology of the reacted contact. While the Ni/Au contacts showed the formation of deep spikes (<200 nm) after annealing the NiIn contact showed a much smoother reaction region with no evidence of spiking.

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