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Electroless nickel/gold ohmic contacts to p-type GaN

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Abstract

A solution based approach to forming ohmic contacts to *p*-type GaN is described. Electroless plated Ni/Au contacts are shown to compare favourably with traditional evaporated contacts, with contact resistivities, ρ_c, in the region of 10^{-2} Ωcm^2. These values are readily achieved after a rapid thermal anneal (RTA) in an O_2 atmosphere. The tunneling nature of the contact is confirmed via temperature dependant measurements. X-ray diffraction (XRD) measurements confirm the similarity between evaporated and plated contacts. Current–photocurrent (I–L) and current–voltage (I–V) measurements from light emitting diodes (LEDs) formed using an electroless *p*-type contact are shown. Electroless deposition of the contact metals allows for a reduction in processing time and cost.

The process of forming ohmic contacts to GaN continues to be widely studied and a variety of different metallisation schemes have been proposed[1–3]. The rationale for these schemes has often been availability of materials, processing capability and the particular application. A wide variety of techniques are also employed to aid the ohmic formation such as modification of the underlying contact layers to increase p-dopant concentration at the semiconductor surface[4],pre-treatment of the surface with plasma[5] or chemicals[6]. Due to the wide band-gap nature of GaN, high work function metals are required for use as a *p*-type ohmic contacts[7–9]. Of all the metal schemes proposed Ni/Au[10,11] has been shown to be a reliable contact readily producing contact resistivities in the region 10^{-4} Ωcm^2. This metal scheme also has the added advantage that when the deposit is thin enough and annealed at temperatures in the region of 500°C it becomes transparent. This is extremely desirable for light extraction from the top surface of the device.

Electroless deposition has previously been utilised on other semiconductors[12–14]. This work describes the formation of Ni/Au ohmic contacts to *p*-type GaN via electroless deposition. The material used for this study was from commercially supplied (Global Light, GmbH, Germany) LED wafers. The p-layer GaN is $\sim$ 150 nm thick with a hole concentration of 1 x 10^{17} cm^{-3}. The n-layer is $\sim$ 4 μm thick with an electron concentration of 1 x 10^{18} cm^{-3}. The structure was grown on a sapphire substrate and has an emission wavelength at 474 nm. The contact quality was tested using the circular Transmission Line Method (c-TLM). The samples were patterned for TLM measurements via lithography, with inner radii of 25 μm and outer radii ranging from 30 μm to 200 μm. Following patterning, the samples were prepared for electroless deposition by a standard two step process, wherein the *p*-type GaN is first sensitised in a $SnCl_2$ solution for 10 minutes at 40°C and then catalysed in a $PdCl_2$ solution for 20 minutes at 65°C. In the $PdCl_2$ solution the Sn^{2+} ions on the GaN surface are oxidised to Sn^{4+} and the Pd^{2+} ions are reduced to Pd which acts as the initial catalyst for reducing agent oxidation and metal ion reduction.

In electroless processing, Ni is most commonly deposited from an acid based bath containing a hypophosphite reducing agent which can co-deposit up to at 35 at.% phosphorus. We observed that good quality Ni/Au ohmic contacts could not be achieved using Ni deposited from such a bath. This may be due to chemical reactions during the annealing phase of the contact formation. For evaporated contacts it is necessity to anneal the deposits in oxygen at temperatures in the range 400 600°C to achieve ohmic contacts. The ohmic contact is understood to be formed through vacancy generation by oxidation of the Ni on the Ga sites as it diffuses into the GaN layer [15,16]. Electroless Ni-P which is amorphous upon deposition at 85°C,[17] crystallises to Ni_3P upon heat treatment above 240°C. Ghosh *et al*[18], have shown in the case of electroless Ni-P contacts to cadmium telluride (CdTe), that the contact deteriorates upon heating, due to the phase change as the temperature increases. It is therefore necessary to investigate an alternative electroless solution. Dimethyl amine borane (DMAB) based electroless plating solutions generally operate at neutral to mildly alkaline pH values. These solutions have the advantage of co-depositing only relatively small concentrations of boron ($<<1\%$) from the reducing agent. The electrical and microstructural characteristics are therefore much closer to that of pure Ni.

The Ni layer was deposited from a commercial DMAB based (Niposit 468, Shipley UK) solution at 60°C. Ni layers with a thickness of 90 250 nm were obtained 10 30 s after immersion in the bath. This corresponds to a deposition rate of $\sim 30\ \mu mhr^{-1}$, which is approximately four times faster than the longer term deposition typically achieved with this bath. This may be due to the initial catalytic oxidation of the borane at dispersed Pd nuclei which occurs at an accelerated rate by comparison with oxidation of borane at Ni sites[19]. This leads to the high deposition rate in the early stages. To form the Ni/Au bilayer the Ni deposit was rinsed and immersed in a commercial displacement Au bath (Ormex, Schloetter Ireland) at 80°C for 30 s. This commercial solution utilises the fact that Au is more noble and displaces Ni at its surface. Typical displacement rates yield 5 nm of Au in 30 s. The plated Ni/Au bilayer contacts examined in this work were ~ 100 nm thick. As-deposited the samples showed rectifying behaviour. This is expected given that the underlying mechanism for ohmic contact formation in the Ni/Au system is the formation of a transparent NiO_x which requires annealing the contacts in an oxygen environment.

To determine the optimum anneal temperature for the electroless plated contacts, a series of samples were annealed via a Rapid Thermal Annealer (RTA) at temperatures between 450–600°C for 60s in an O_2 atmosphere. I–V characteristics were measured for the contacts between ± 10 μA in 1 μA steps. The specific contact resistivity ρ_c and the sheet resistance of the p-layer was then extracted using the standard c-TLM formula[20]. The results of the anneal trials are shown in figure 1. This data indicated that the lowest specific contact resistivity values obtained, are for samples annealed at 500°C. This annealing temperature also corresponds to that utilised for evaporated Ni/Au contacts. The I–V characteristics with optimised activation and plating conditions and annealed at 500°C for one sample are presented in figure 2. Also presented with these I–V curves are the associated TLM fit, from which the parameters of interest are extracted. In order to extract accurate values of the contact resistivity, linear I–V characteristics are required and the associated data points must lie close to the calculated fitting curve. Accurate measurements of the inner and outer contact radii are also required. We have shown in previous work the importance of accurately measuring the contact radius when calculating contact resistivity values [21]. The ρ_c values for the sample in figure 2 was extracted to be 2.2 x 10^{-2} Ωcm^2. The extracted sheet resistance was 280–300 kΩ. All samples measured in this set had a specific contact resistivity in the range 10^{-2} Ωcm^2. This level of ρ_c is quite acceptable for use in low power devices such as LEDs adding only an additional 1.1 V to the operating voltage of a typical device driven at 50 Acm^{-2} for a ρ_c of 2.2 x 10^{-2} Ωcm^2.

In order to investigate the nature of the contact, I–V measurements were carried out at elevated temperatures. The samples were placed in a controlled environment and heated to 140°C. Standard I–V tests were carried out using the Cascade Microtech Probe station and the HP4156 parameter analyser. The ohmic nature of the contact was not affected by the temperature rise but there was a sharp drop in the voltage values compared to room temperature measurements on the same sample. Coupled with this drop in voltage was a drop in the point to point resistance (R$_{pp}$) values measured at each contact site. Using the R$_{pp}$ values from the high temperature I–V, the extracted ρ_c is found to be 2.5 x 10^{-2} Ωcm^2. This compares with 2.2 x 10^{-2} Ωcm^2 as calculated at room temperature. This temperature independence indicates that it is a tunneling type contact.

X-ray diffraction analysis was performed with a PANalytical X'Pert PRO MPD, equipped with Cu K-alpha radiation (1.5405Å) source. Stoller slits of 0.2 degrees were used, with a goniometer resolution of 0.001 degrees, to assess the similarity of the contacts achieved from the solution based electroless plated Ni/Au, with those achieved by vacuum deposition. The data in figure 3 is for a GaN substrate, evaporated Ni/Au contacts on GaN and electroless plated Ni/Au on GaN. Other than peaks representative of the GaN substrate it can be seen that for the annealed evaporated contact new peaks emerge at 38.3°, 52.9° and 58°. These may be attributed to Au[22] , Ni[23] and AuGa[24] . This last peak is more likely in the case of the evaporated contact which has a thinner Ni layer and more Au for interaction with the Ga of the substrate. In the case of the annealed electroless plated Ni/Au a small shoulder is observed at 38.3° which is realistic based on the thin 5 nm Au layer expected and the Ni peak at 52.9° is again observed. In addition there are 2 minor peaks at 43.3° which may be attributed to GaNi[25] which is more likely to be prominent for the plated contact where the Ni film deposited is approximately 95 nm and 47.8° which corresponds to the peak detected at 47.3° in the untreated GaN substrate[26] and is exaggerated by the lattice strain induced with the electroless Ni/Au film processing. NiO peaks were beyond the limit of detection for this setup and were not detected for either evaporated or plated contacts. The consistency of the XRD data indicates that the ohmic contact formation mechanism is the same for both the solution and vacuum deposited contacts.

Devices were fabricated using the developed electroless Ni/Au ohmic contact to the p-GaN. The *n*-type ohmic contact was a vacuum deposited metal stack Ti/Al/Pt/Au (3/50/30/200 nm). Standard lithography was used to define 200 μm diameter devices. The device L–I and I–V characteristics up to 20 mA were recorded. The results in figure 4, show consistent L–I and I–V characteristics capable of operation up to the standard driving current of 20 mA. These contacts were also shown to be stable over time with no loss of voltage or decrease in light output when operated at fixed current levels.

We have explored an alternative method of forming plated metal contacts to *p*-type GaN to serve as an ohmic contact. These preliminary results have shown that good ohmic contacts can be achieved through simple means. The contact resistivity values show very encouraging results and would be suitable for use in applications such as low-power LEDs. The possibility to further improve these contacts exists in the form of surface modification prior to metal deposition and the use of a specifically grown, highly p-doped surface. The contact resistivity is almost independent of temperature and shows the typical behaviour of a tunneling contact. The deposition process itself is low cost and extremely fast in comparison to other more commonly used deposition methods such as evaporation. The process could also be used to investigate other p-contact metals such as platinum. The method could also be extended to n-contact formation and to examine suitable metals schemes that could act as rectifying Schottky contacts on both p and n-type GaN.

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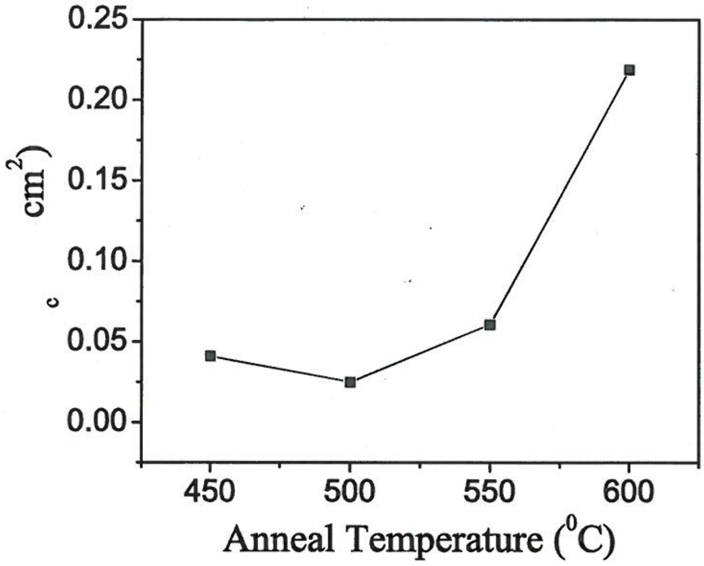
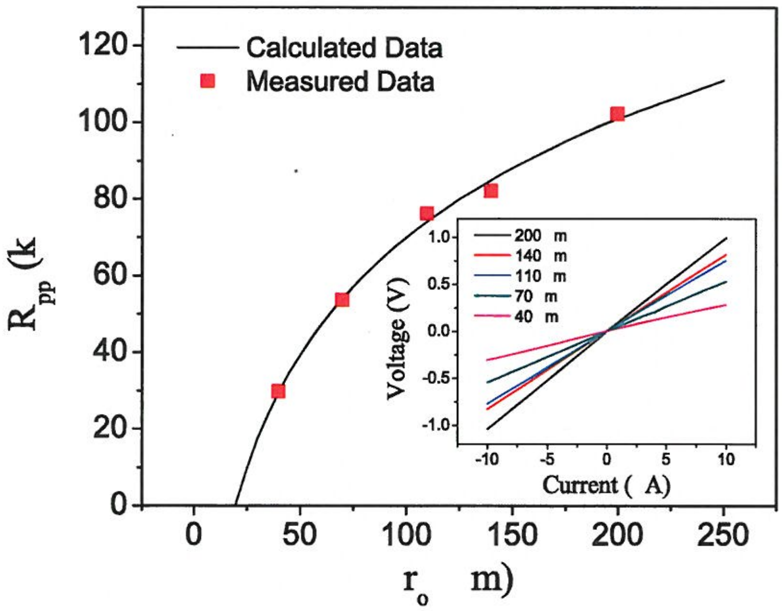
FIG. 1. The extracted ρ_c values versus temperature for nominally similarly plated samples. This data indicates an optimal annealing temperature of 500°C for our electroless contacts.

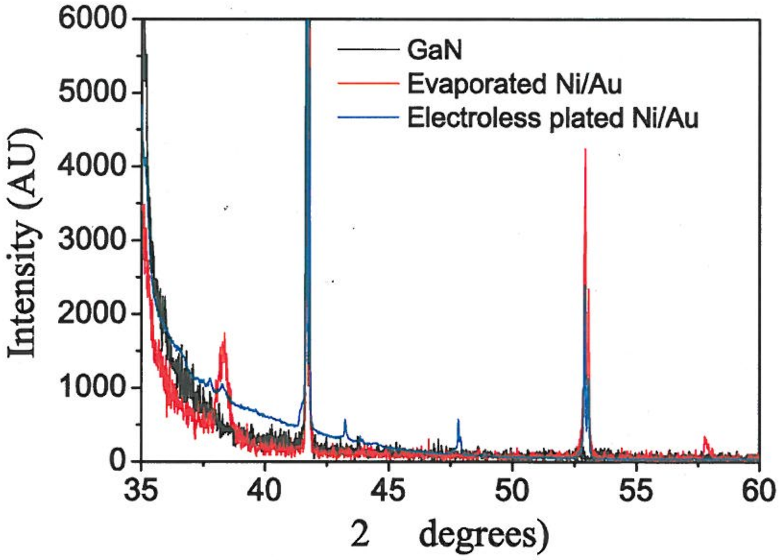
FIG. 2. The TLM fit from which the specific contact resistivity and the sheet resistance of the p-GaN are extracted. R_{pp} is the point to point resistance measured between contacts and r_o the outer contact radius. Also shown (inset) are the I–V characteristics for the sample.

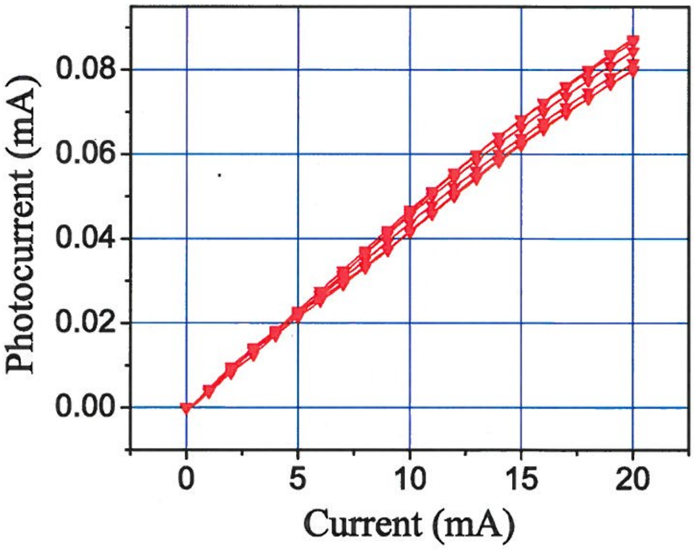
FIG. 3. XRD spectra for a bare GaN substrate and for substrates coated with evaporated Ni/Ai contacts and electroplated Ni/Au contacts. The XRD peaks observed for evaporated Ni/Au contacts are well matched to those from electroless deposits.

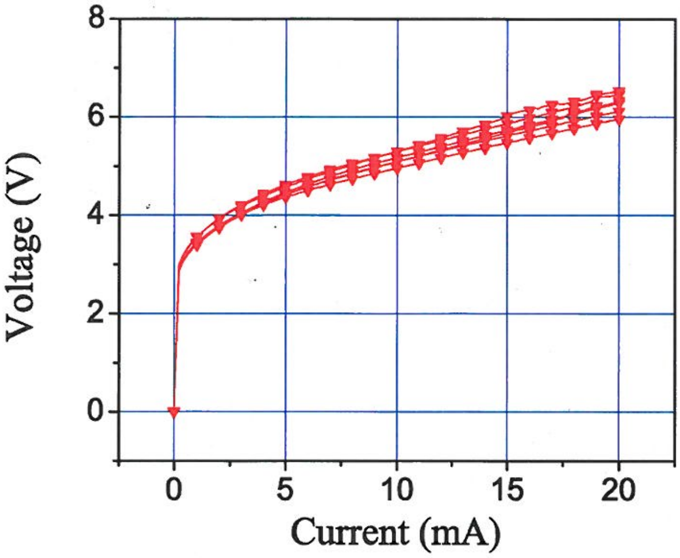
FIG. 4. (a) I–V plots from 200 μm diameter devices formed using electroless p-contacts and (b) L–I curves for the same devices.


0.25
0.20
0.15
0.10
0.05
0.00
c cm2)
450
500
550
600
Anneal Temperature (0C)


Calculated Data
Measured Data
120
100
80
60
40
20
0
Rpp (k
0
50
100
150
200
250
ro m)
200 m
140 m
110 m
70 m
40 m
1.0
0.5
0.0
-0.5
-1.0
Voltage (V)
-10
-5
0
5
10
Current (A)


GaN
Evaporated Ni/Au
Electroless plated Ni/Au
Intensity (AU)
6000
5000
4000
3000
2000
1000
0
35
40
45
50
55
60
2 degrees)


Photocurrent (mA)
0.08
0.06
0.04
0.02
0.00
0
5
10
15
20
Current (mA)


Voltage (V)
Current (mA)
8
6
4
2
0
0
5
10
15
20