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Stable Low Resistance Ohmic Contacts To p-GaN

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ABSTRACT

Stable and low-resistance Ohmic contacts are especially important for laser diodes where high current levels are required. Good contacts are especially difficult on p-type GaN which was the motivation for this study. The GaN was epitaxially grown on (0001) sapphire substrates by MOCVD. Resistivity of this layer was 3.5 Ohm-cm and thickness was 2 microns. After conventional cleaning followed by treatment in boiling HNO_3 : HCl (1:3), metallization was by thermally evaporating 40 nm Au / 60 nm Ni or 70 nm Au / 55 nm Pd. Heat treatment in O_2 + N_2 at various temperatures followed, with best results at 600 °C or 700 °C, respectively. Best values of the contact resistance were 1.8×10^{-4} Ohm-cm^2 for Pd/Au and 2.65×10^{-4} Ohm-cm^2 for Ni/Au contacts. After repetitive cycling from room temperature to 600 °C, the Ni contacts were very stable and more stable than the Pd contacts. X-ray photoelectron spectroscopy depth profiling showed the Ni contacts to be NiO followed by Au at the interface for the Ni/Au contacts whereas the Pd/Au contacts exhibited a Pd : Au solid solution. Some contacts were quenched in liquid nitrogen following sintering. These contacts were much more uniform under atomic force microscopy examination and gave a 3 times lower contact resistance with the Ni/Au design. Current-voltage-temperature analysis revealed that conduction was predominantly by thermionic field emission.

INTRODUCTION

Great interest exists in the III-nitride semiconductors since the successful development in growth of GaN based materials and operation of electronic and optoelectronic devices such as blue and green light emitting diodes (LEDs) and laser diodes (LDs) [1,2]. The formation of stable and reliable low resistance ohmic contacts to p-type GaN has been a problem in achieving good performance of those devices. For devices with large contact areas such as LEDs and LDs, the specific contact resistance (ρ_c) between 10^{-4} to 10^{-6} Ωcm^2 is considered acceptable and for devices with smaller contact areas, values of ρ_c between 10^{-5} to 10^{-7} Ωcm^2 are necessary [3]. Bilayer metal schemes such as Ni/Au and Pd/Au were studied by many groups [4,5]. These have been studied due to the stable electrical and thermal properties and the high work function which is one criteria to form low resistance Ohmic contacts to p-type materials.

The effects of cryogenic cooling after heat treatment on the formation of Ni/Au and Pd/Au contacts are presented in this paper. We also compare these effects on forming Ni/Au and Pd/Au contacts annealed in a combined O_2/N_2 gas ambient. High temperature annealing may degrade homogeneity, possibly caused by spiking of metals between themselves or between metal and semiconductor due to the differences in thermodynamic properties of materials. Annealing was conducted in an oxygen and nitrogen mixed gas ambient as reported by Y. Koide et al. [4]. This is to remove hydrogen atoms contained in Mg-doped GaN epilayers. Removing hydrogen atoms results in the increase of the hole concentration and decrease of the contact resistance. Annealing in nitrogen gas ambient is believed to avoid nitrogen vacancies which act as doners. We expected that cryogenic treatment would reduce disadvantages from the discrepancy in thermodynamic properties of materials during cooling the heated samples to give improved Ohmic behavior. With cryogenic treatment, the changes of electrical and structural properties have been examined.

EXPERIMENTAL

The metal contacts were made on GaN films grown by metalorganic chemical vapor deposition (MOCVD) on (0001) sapphire substrates. The GaN films consisted of the Mg doped p-type GaN with a thickness of 2μm on a 30nm thick GaN buffer layer. The hole concentration of the p-GaN layer was 1.41×10^{17} cm^{-3} and the resistivity was 3.5 Ωcm. The samples were sequentially ultrasonically cleaned in trichloroethylene, acetone and methanol, then rinsed in 18 MΩ de-ionized (DI) water. The cleaned samples were chemically etched in boiling aqua regia of HNO_3 : HCl = 1 : 3 for 10 minutes to remove the native oxide and the contamination of the GaN surface as suggested by J. K. Kim et al [6]. Then, a photolithographic process was used to form the pattern for the circular transmission line method (c-TLM). In this pattern, the radius of the inner circular contact was 400 μm and the spacings between inner and outer circles ranged from 25μm to 75μm. Prior to the deposition of metal, the sample was etched in a warm solution of HNO_3 and HCl again. The warm solution means non-boiling aqua regia : a solution was boiled and cooled for 2~3 minutes since very hot solution ruins the photoresist. The Ni (30nm) / Au (15 nm) and the Pd (25 nm)/ Au (15 nm) contacts were deposited by thermal evaporation and completed by lift-off. The contacts were then annealed at temperatures ranging from 400 to 700 ^oC for 10 minutes in a conventional furnace in an oxygen and nitrogen mixed gas ambient. In order to study the effect of cryogenic treatment, some samples were subsequently cooled by dipping in liquid nitrogen after the heat treatment, then brought to room temperature in air. Sister samples were not quenched in liquid nitrogen.

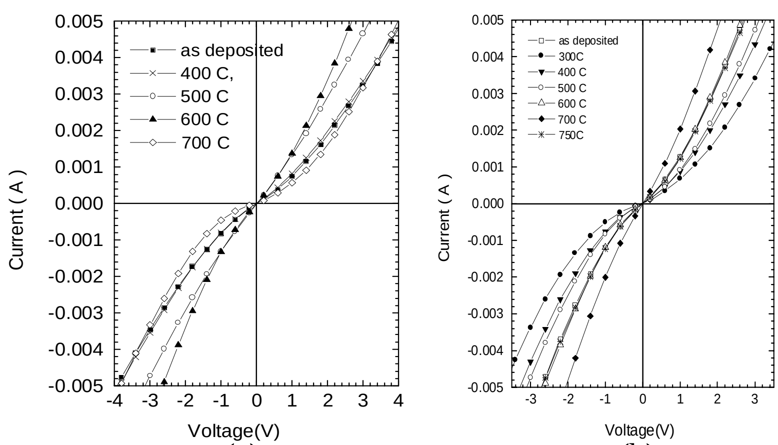
The current versus voltage (I-V) curves were measured as deposited and between each heat treatment interval. After each measurement of I-V curves, the specific contact resistance (ρ_c) was determined by use of the c-TLM. The samples with and without cryogenic treatment showing the lowest contact resistance were examined by scanning electron microscopy (SEM) images using a model Hitachi S-4000, atomic force microscopy (AFM) images using a model Quesant Res/stg, and electron spectroscopy for chemical analysis (ESCA) depth profiles using a model Surface Science SSX-100 with an ion energy of 4.5 keV, a raster size of 2x2 mm, a sputter time per step of 1~2 min. and a x-ray spot size of 1000 μm. Cross-sectional transmission electron microscopy (X-TEM) using a model JEM-2010 Electron Microscope was also employed to study the microstructure of metal/metal and metal/semiconductor interfaces.

RESULTS AND DISCUSSION

Electrical Properties

The samples chemically etched in boiling aqua regia of HNO_3 : HCl = 1 : 3 for 10 minutes prior to deposition of metals showed much improved I-V behavior and decreased specific contact resistance for both Ni/Au and Pd/Au contacts, but still showed nonlinear I-V characteristics. The current versus voltage curves for Ni/Au and Pd/Au contacts to p-GaN as a function of annealing temperature are shown in Figs. 1 (a) and (b). Annealed contacts shown in those two figures were treated in an O_2/N_2 ambient. For the as deposited case, both Ni/Au and Pd/Au contacts show similar characteristic of non linear I-V with a leaky Schottky behavior. However, the Pd/Au contact reveals a lower specific contact resistance of 7~10x10^{-4} Ωcm^2 compared to 4~6x10^{-2} Ωcm^2 for the Ni/Au contact in the linear region, although the work function of Ni (5.15 eV) is slightly higher than Pd (5.12 eV). These characteristics agree with previous studies [5]. The non linear I-V behaviors for Ni/Au contacts continued to improve by heat treatment up to a temperature of 600 ^oC shown in Fig. 1(a). For the Pd/Au shown in Fig. 1(b), the effect of annealing temperature on I-V characteristics is little different from the Ni/Au. Note that annealing at a temperature of 300 ^oC for the Pd/Au contact rapidly degraded the I-V curve compared to the as deposited contact, and continuing heat treatment until 600 ^oC improved the I-V behavior and decreased the contact resistance. Then, annealing at a temperature at 700 ^oC gave a much improved linear I-V curve and the lowest contact resistance. The reduction of the specific contact resistances to 9.84x10^{-4} Ωcm^2 for Ni/Au and 1.80x10^{-4} Ωcm^2 for Pd/Au were obtained by heat treatment at 600 ^oC and 700 ^oC, respectively. Lowering the contact resistance and improving linearity may come from a more intimate contact of metal with the semiconductor or any new phases having higher work function. Intimate contact leads to more current flow across the interface by breaking up some of the interfacial contamination between metal and semiconductor. Possible new compounds reduce the potential offset at the metal/semiconductor interface by forming a layer of a compound with higher work function or causing a highly doped region. We believe that the lower contact resistance of the Pd/Au contact with lower work function of Pd is due to a new phase with higher work function, which will be discussed from the ESCA profiles.

In contrast, the effect of cryogenic treatment on forming those two contacts is quite different as shown in Fig. 2. With further treatment by cooling in liquid nitrogen after the anneals, the Ni/Au contact exhibits better linearity of I-V characteristics and a contact resistance of 2.65x10^{-4} Ωcm^2. However, the Pd/Au contact shows opposite behavior to the Ni/Au contact such that cryogenic treatment degrades the specific contact resistance value to 3.34x10^{-4} Ωcm^2. The effect of cryogenic treatment on improving Ohmic behavior could be caused by some of the semiconductor dissolving in the metal on heating and recrystallization with a high concentration of the electrically active element in solid solution on subsequent cooling [7]. It could also be



(a) (b)

Fig. 1 Annealing temperature (in O_2/N_2 ambient) dependence of I-V characteristics of: (a) Ni/Au contacts and (b) Pd/Au contacts to p-GaN.

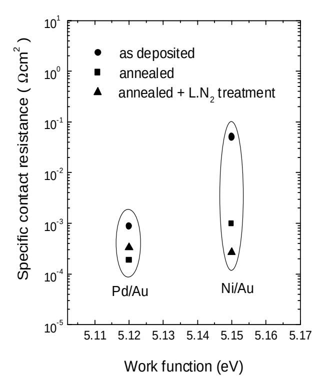


Fig. 2 Specific contact resistance for Ni/Au and Pd/Au contacts to p-GaN as a function of the work function of metal.

due to improved morphology as explained later. Therefore, the mechanisms and the reactions at the interface between metal and semiconductor for Ni/Au contact and Pd/Au contact would be different.

Temperature dependent I-V curves were observed on a Ni/Au contact annealed at 600 ^oC for 10 min. plus cryogenic treatment and Pd/Au contact annealed at 700 ^oC for 10 min plus cryogenic treatment. log(I) vs V and log(I) vs V curves (not shown) have similar behavior. The current of the Ni/Au contact is relatively stable over the whole voltage range compared to Pd/Au, although it's increase with temperature shows more dependence on temperature than the Pd/Au contact. The slopes of the log(I) vs. log(V) curve (not shown) range from 1.005 to 1.124 for the Ni/Au contact and from 1.222 to 1.625 for the Pd/Au contact. This is indicative that the Ni/Au contact has better Ohmic behavior and more thermal current than the Pd/Au contact. As a result, we would speculate that Ni, with a work function of 5.15 eV, formed a little lower barrier height with p-GaN than did Pd, with a work function of 5.12 eV. Increased sample temperature may increase carrier concentration and thin a barrier width, resulting in thermionic emission dominated current.

Structural properties

The microstructure for the Ni/Au contacts was observed by using XTEM as shown in Figs. 3, 4, 5 and 6. Fig. 3 shows a bright-field XTEM micrograph of the contact annealed at a temperature of 600 ^oC in O_2/N_2 ambient without cryogenic treatment. Fig. 3 (lower view) shows that the metal/GaN interface line is clear and sharp without forming new interdiffused compounds and the GaN surface is covered by two thin layers. By comparison to ESCA depth profiles studied in previous work [8], the top layer would be NiO formed by outdiffusion of Ni and reaction of Ni with oxygen during high temperature annealing and cooling in the O_2/N_2 ambient. This new phase shows a polycrystalline electron diffraction pattern in the upper view of

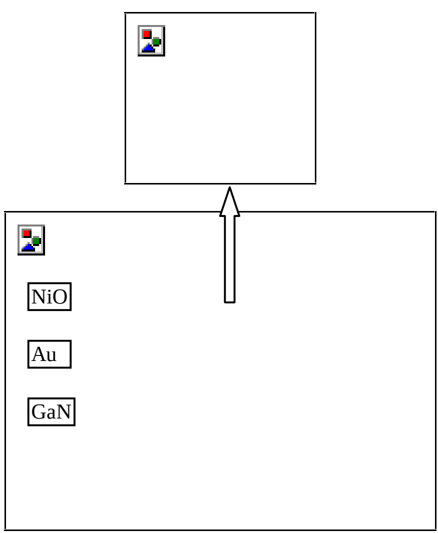


Fig. 3 XTEM image (lower view) and selective area diffraction pattern (upper view) for the Ni/Au contacts to p-GaN at 600 ^oC for 10 min. in O_2/N_2.

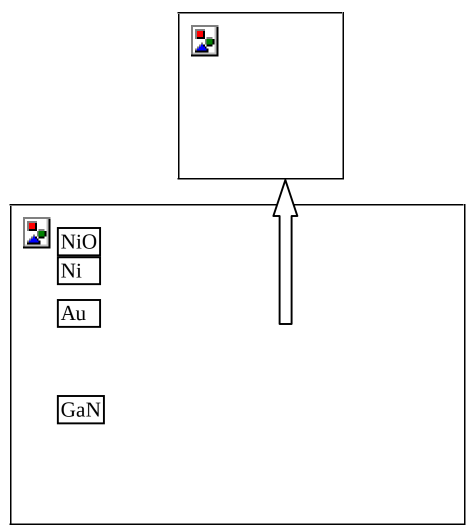
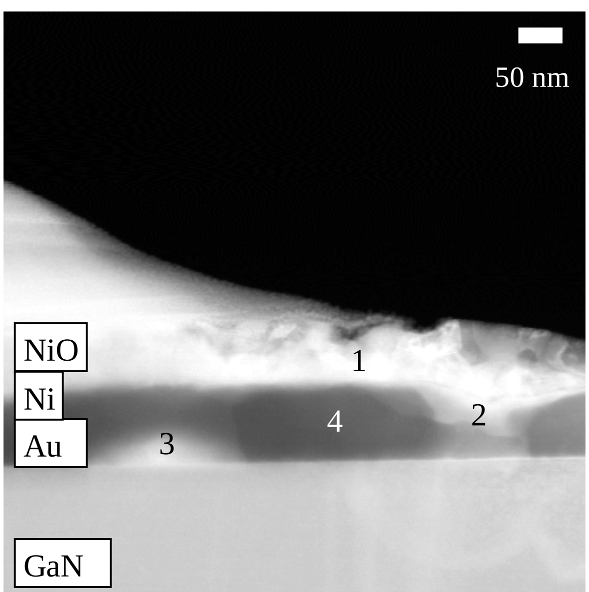


Fig. 4 XTEM image (lower view) and selective area diffraction pattern (upper view) for the Ni/Au contacts to p-GaN annealed at 600 ^oC for 10 min. in O_2/N_2 and cryogenically treated

Fig. 3. On the other hand, Au changes position with Ni and directly contacts the GaN surface as a result of the outdiffusion of Ni. This agrees with previous studies [8]. The XTEM images show segregation and porousness in Au layers due to poor adhesion as a result of the balling-up and the spiking effects. These effects are well known properties of Au metal during high temperature annealing and cooling process. However, for the contacts with cryogenic treatment illustrated in Fig. 4, the contact layer above the GaN surface includes three layers of different contrast : NiO, Ni, and Au layer from the top, respectively. This is confirmed by the comparison to energy dispersive x-ray (EDX) spectroscopy. Every EDX spectrum corresponding to probe points 1, 2, 3, and 4 depicted in Fig. 5 presents the different composition of each layer. EDX analysis of point 1 indicates an abundance of Ni and O and evidences the formation of a NiO phase in good agreement with previous results of ESCA depth profiles while point 2 shows an increase in Au. An abundance of Au has been detected in the cavity and the sublayer at the metal/GaN interface, points 3 and 4. This suggests that Au is responsible for a discontinuous metal layer and surface and interface roughness. It is believed that Ni was not completely reacted with oxygen but remained as a thin layer due to the rapid quenching. As a result, the new NiO and outdiffused Ni layers may protect the Au metal and minimize discontinuity and roughening of the surface, which might increase the contact resistance.

Compositional characteristic was also observed at the NiO/Ni/Au interface and the Au/p-GaN interface. There was no difference in EDX analysis indicating an abundance of Au at each NiO/Ni/Au interface. No evidence was shown for new compounds of Ni and Au. Fig. 6 shows an EDX spectrum of the Au/p-GaN interface. Each spectrum at points 1, 2, and 3 has a different composition of existing elements. A high resolution electron microscopy (HREM) image and EDX reveal the possibility of a Ga:Au transition metal in the Au/p-GaN interface layer (about 20 nm thick) but it is not clear.



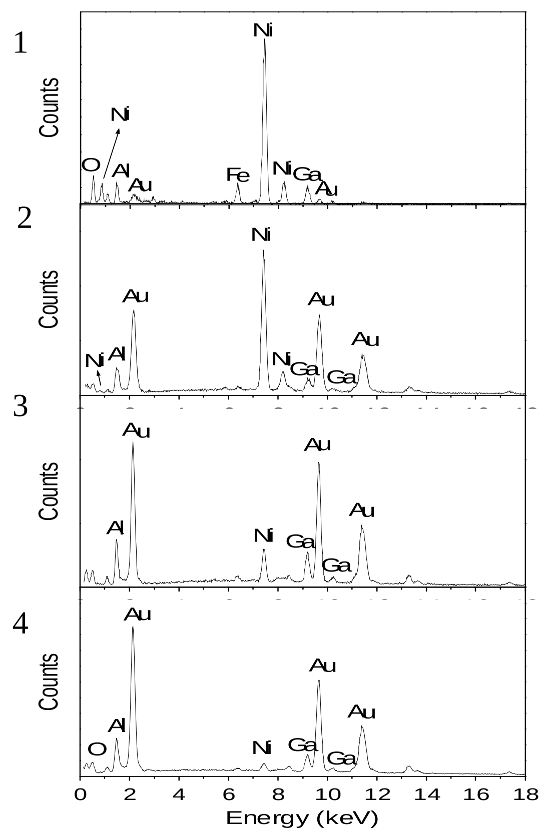
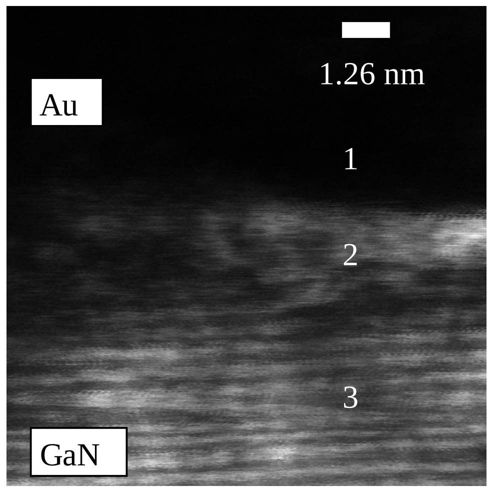


Fig. 5 XTEM image and EDX analysis for the Ni/Au contacts to p-GaN annealed at 600 ^oC for 10 min. in O_2/N_2 and cryogenically treated



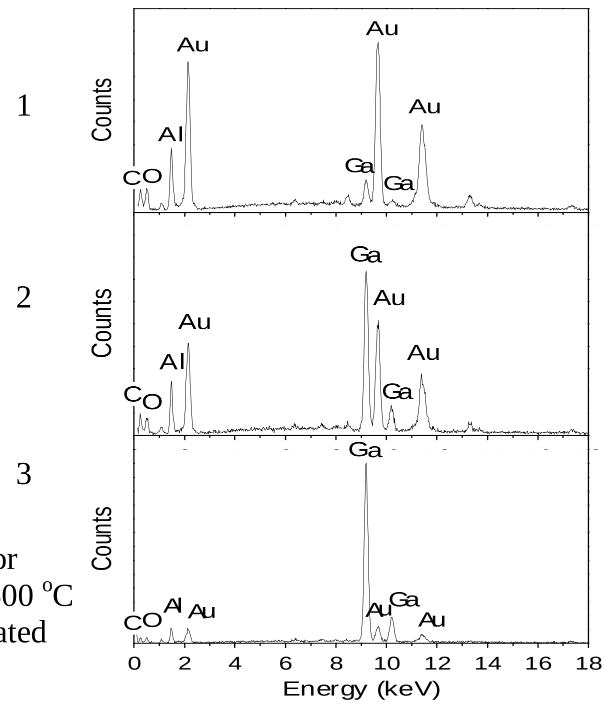


Fig. 6 HREM image and EDX analysis for the Ni/Au contacts to p-GaN annealed at 600 °C for 10 min. in O_2/N_2 and cryogenically treated

CONCLUSIONS

Both Ni / Au and Pd/Au contacts to p-GaN show Ohmic behavior with and without a cryogenic treatment. The cryogenic treatment on the Ni/Au contacts improves the I-V linearity and reduces the specific contact resistance from $9.84\times10^{-4}\ \Omega cm^2$ to $2.65\times10^{-4}\ \Omega cm^2$. The phases NiO and Au:Pd have been observed for both contact systems, respectively. Subsequent and fast cooling in liquid nitrogen after anneal affects the recrystallizing of NiO and Au:Pd solid solution produced from heat treatment, then improves surface morphology. The contact resistance is mainly improved by: i) high temperature annealing which forms new phases at the metal/metal interface and the metal and the GaN surface compared to the initial deposit; and ii) cryogenic treatment which affects both the recrystallization and surface morphology.

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