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Effects of plasma treatment on the Ohmic characteristics of Ti/Al/Ti/Au contacts to *n*-AlGaN

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The effects of surface treatment using Cl_2/BCl_3 and Ar inductive coupled plasmas on the Ohmic characteristics of Ti/Al/Ti/Au contacts to *n*-type $Al_xGa_{1-x}N$ ($x=0-0.5$) were investigated. Plasma treatment significantly increased the surface conductivity of GaN and $Al_{0.1}Ga_{0.9}N$, leading to improved Ohmic behaviors of the contacts. However, it reduced the surface doping level in $Al_xGa_{1-x}N$ ($x \geqslant 0.3$) and degraded the contact properties. Following a 900–1000 °C anneal, the Ti/Al/Ti/Au contacts to $Al_xGa_{1-x}N$ ($x=0-0.3$) became truly Ohmic, with specific contact resistances of $(3-7)\times 10^{-5}\ \Omega\ cm^2$, whereas the contact to $Al_{0.5}Ga_{0.5}N$ remained rectifying even without the plasma treatment. X-ray photoelectron spectroscopy measurements confirmed that the Fermi level moved toward the conduction band in GaN after the plasma treatment, but it was pinned by plasma-induced deep-level states in $Al_{0.5}Ga_{0.5}N$. This study emphasizes the need to mitigate plasma damage introduced during the mesa etch step for AlGaN-based deep-UV emitters and detectors. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2338434]

In the past several years, significant progress has been made in the growth and fabrication of deep-ultraviolet (UV) light emitting diodes (LEDs) and solar-blind photodetectors based on AlGaN with high-Al mole fractions.[1–5] The device performance, however, is limited by the lack of high quality Ohmic contacts to AlGaN materials. The contact resistance may make a major contribution to the device series resistance, causing severe Joule heating and premature device failure.[1–4] A number of Ti/Al-based metallization schemes have been developed to form low-resistance Ohmic contacts to GaN and low-Al AlGaN.[6–9] However, as the Al mole fraction and thus the energy band gap increases, it is increasingly difficult to produce low-resistance Ohmic contacts to AlGaN.[6]

To fabricate deep-UV LEDs on an insulating substrate such as sapphire, a mesa structure must be defined using plasma etching in order to expose the *n*-AlGaN contact layer. Plasma-induced damage in nitride materials may take various forms, leading to changes in their electrical properties.[10] Previous studies showed that plasma treatment can significantly improve the quality of Ohmic contacts to *n*-type GaN.[11,12] The preferential loss of N during plasma etching gives rise to a N-deficient heavily doped surface, which markedly enhances carrier tunneling at the contact interface.[10–13] To date, little effort has been directed toward a better understanding of the effects of plasma damage on the electrical properties of high-Al AlGaN and its Ohmic metallization.

In this letter, we report on a comparative study of the effects of Cl_2/BCl_3 and Ar plasma treatment on the Ohmic behaviors of Ti/Al/Ti/Au contacts to $Al_xGa_{1-x}N$ ($x=0-0.5$). It is found that, in contrast to shallow donors in GaN and low-Al AlGaN, plasma damage in $Al_xGa_{1-x}N$ ($x \geqslant 0.3$) acts as compensation centers and degrades the contact performance.

1 μm Si-doped ($n_{Si}=5\times 10^{18}\ cm^{-3}$) $Al_xGa_{1-x}N$ ($x=0$, 0.1, 0.3, and 0.5) epilayers were grown on 2 in. *c*-plane sapphire with a low-temperature buffer layer using low-pressure metal-organic chemical vapor deposition. The Al mole fractions were determined by the Ga and Al source flow rates, and the values measured by x-ray diffraction were within 4% of nominal. The room-temperature electron concentrations in GaN, $Al_{0.1}Ga_{0.9}N$, $Al_{0.3}Ga_{0.7}N$, and $Al_{0.5}Ga_{0.5}N$ were determined by Hall measurements to be 4.5×10^{18}, 3.5×10^{18}, 2.5×10^{18}, and $2.7\times 10^{18}\ cm^{-3}$, respectively.

Three sets of samples were prepared by dicing each 2 in. wafer into three equal pieces. All the samples were chemically cleaned using $HCl:H_2O$ (1:1) and buffered oxide etch (BOE) solutions. The first set, used as the control, was cleaned only, without any pre metal treatment. The second set was etched in a Cl_2/BCl_3 inductively coupled plasma (ICP) for 1 min using a typical AlGaN etching recipe (5 mTorr base pressure, 300 W source power, and 40 W rf chuck power). The third set was exposed to an Ar ICP for 1 min (8 mTorr base pressure, 500 W source power, and 150 W rf chuck power). A metal stack of Ti/Al/Ti/Au (30/120/30/200 nm) was deposited using e-beam evaporation and circular transmission-line-method patterns with 5–45 μm gaps were formed by lift-off. The samples were further cleaved into sections for 1 min rapid thermal annealing in N_2 at temperatures from 600 to 1000 °C. Current-voltage (*I-V*) characteristics of the contacts were measured before and after the annealing using the four-point probe technique. To investigate the surface chemical properties, clean unmetallized GaN and AlGaN pieces with and without ICP treatment were characterized using x-ray photoelectron spectroscopy (XPS) in an Axis Ultra delay-line detector system equipped with a monochromated Al $K\alpha$ x-ray source.

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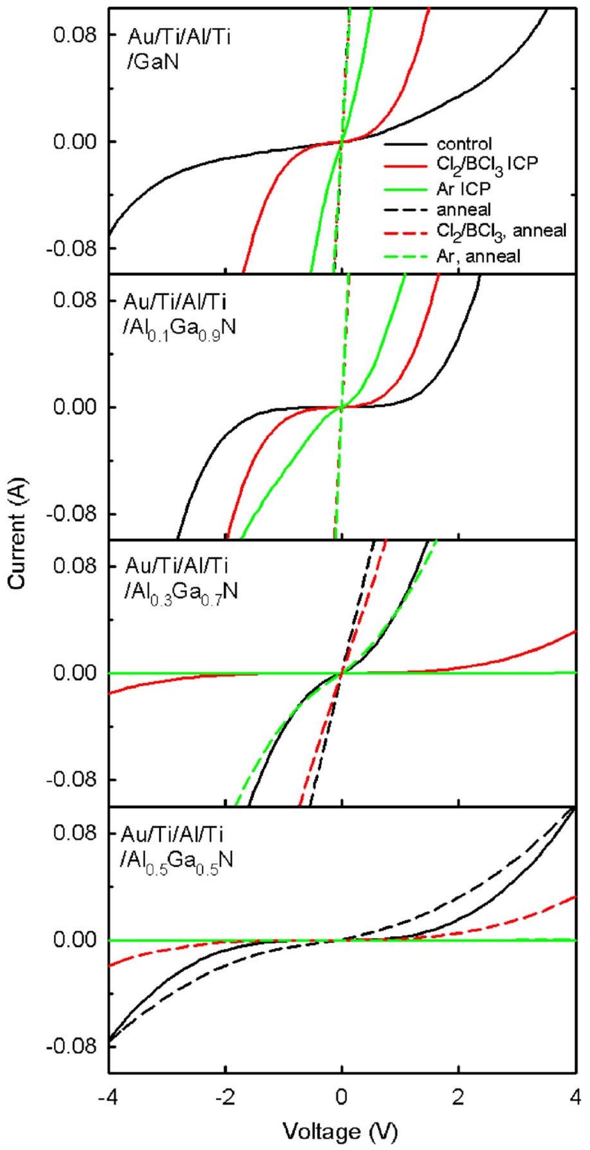

FIG. 1. (Color online) *I*-*V* characteristics of Ti/Al/Ti/Au contacts on control and ICP-treated $Al_xGa_{1-x}N$ (x=0–0.5) samples, before and after annealing at 900 °C in N_2.

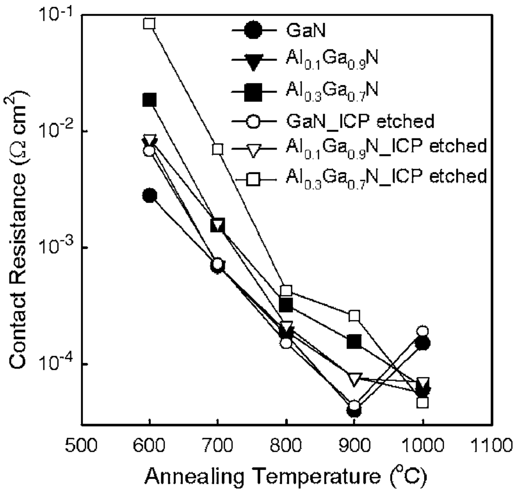

FIG. 2. Specific contact resistances of Ti/Al/Ti/Au contacts on control and Cl_2/BCl_3 ICP-treated $Al_xGa_{1-x}N$ (x=0–0.3) samples as a function of annealing temperature.

Figure 1 compares the *I*-*V* characteristics of the contacts on the control and ICP-treated GaN and AlGaN samples before and after annealing at 900 °C. The as-deposited contacts on all control samples exhibit rectifying contact characteristics. The plasma treatments remarkably improve the contact quality on GaN and $Al_{0.1}Ga_{0.9}N$, leading to less rectifying behaviors. This agrees well with previous findings that plasma etching creates N vacancies, which act as shallow donors and thus increase the surface doping concentration.[10–13] Note that Ar plasma has a greater impact on the electrical properties of the contacts than Cl_2/BCl_3 plasma. The as-deposited contact on Ar ICP-treated GaN exhibits near-liner characteristics. This is because that, during the Ar ICP treatment, a higher flux of more energetic ions was involved and plasma damage was accumulating without any concurrent etching of the materials. Upon annealing, all the contacts to GaN and $Al_{0.1}Ga_{0.9}N$ become true Ohmic, and the contacts on the control and ICP-treated samples have nearly identical *I*-*V* curves. Several solid-phase reactions which take place during the annealing have been considered to be responsible for the improvement in the contact properties:[6,7] (i) the dissolution of remaining native oxides by Ti, (ii) the outdiffusion of N and the subsequent formation of a N-deficient highly doped interfacial layer, and (iii) the formation of low-work function Ti–N and other interfacial alloys.

In contrast, the ICP treatment has an adverse effect on the contact characteristics of $Al_{0.3}Ga_{0.7}N$ and $Al_{0.5}Ga_{0.5}N$, as seen in the bottom part of Fig. 1. The contacts on the ICP-treated samples become more rectifying, indicating a degraded surface conductivity as a result of the plasma exposure. Angle-resolved XPS measurements revealed a N-deficient region in the vicinity of the surface. It is plausible that N vacancies are deeper-level states in AlGaN with a higher Al mole fraction, and plasma treatment introduces compensating defects rather than shallow donors. Upon annealing, the contacts on the untreated and Cl_2/BCl_3 ICP-treated $Al_{0.3}Ga_{0.7}N$ become Ohmic. However, plasma damage in the Ar ICP-treated $Al_{0.3}Ga_{0.7}N$ is so severe that it cannot be completely removed by annealing at 900 °C, and the alloyed contact remains to be leaky Schottky. In all cases, the contacts on $Al_{0.5}Ga_{0.5}N$ exhibit rectifying behaviors. The current is only slightly increased after annealing, supporting the above assumption that N vacancies generated in the alloying process have a limited contribution to the surface doping in $Al_{0.5}Ga_{0.5}N$. Increasing Si doping levels in epilayers and minimizing plasma damage are therefore essential for producing good-quality Ohmic contacts to AlGaN with a high Al-mole fraction.

Figure 2 shows the specific contact resistances of the contacts on the control and Cl_2/BCl_3 ICP-etched GaN, $Al_{0.1}Ga_{0.9}N$, and $Al_{0.3}Ga_{0.7}N$ as a function of annealing temperature. For the contact to GaN, the lowest contact resistance of $3.8\times10^{-5}\ \Omega\,cm^2$ is obtained after annealing at 900 °C. Further increasing annealing temperature leads to an increase in the contact resistance. The resistances of the contacts on all AlGaN samples decrease with increasing annealing temperature up to 1000 °C, suggesting a higher alloying temperature required for contacts to AlGaN. The lowest contact resistances after annealing at 1000 °C are also in the $10^{-5}\ \Omega\,cm^2$ range. The fact that the minimum contact resistance is nearly independent of the Al mole fraction (and thus the interfacial barrier height) confirms that the current trans-

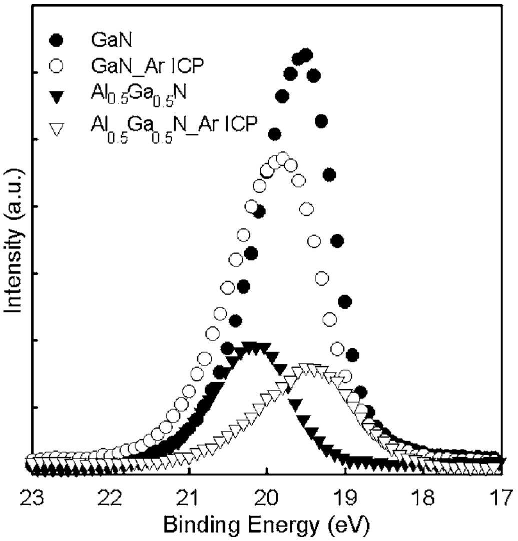

FIG. 3. XPS spectra of the Ga 3*d* core level for control and Ar ICP-treated GaN and $Al_{0.5}Ga_{0.5}N$ samples.

port at the contact interfaces is dominated by carrier tunneling due to a heavily doped interfacial layer. Note that the ICP treatment has a marginal effect on the contact performance on GaN and $Al_{0.1}Ga_{0.9}N$ after annealing. This suggests that while more N vacancies are created as a result of N outdiffusion during the annealing, other plasma-induced defects are largely annealed out. It is expected that a higher temperature is required to restore the contact property on AlGaN with a higher Al mole fraction due to the compensating nature of the plasma damage. Indeed, the contact on the ICP-treated $Al_{0.3}Ga_{0.7}N$ has a higher resistance than that on the untreated sample until the annealing temperature is raised to 1000 °C.

To gain a better understanding of the mechanisms underlying the different effects of plasma treatment, the surface stoichiometries and chemical bonding of the control and ICP-treated samples were characterized using XPS. Figure 3 shows the XPS spectra of the Ga 3*d* core level for GaN and $Al_{0.5}Ga_{0.5}N$ with and without Ar ICP treatment. The peak in the ICP-treated GaN shifts toward the higher binding energy by 0.26 eV, indicating that the surface Fermi level moves closer to the conduction band edge. A similar blueshift of the Ga 3*d* peak was observed in $SiCl_4$ plasma-treated GaN.[14] In contrast, the Ga 3*d* peak in $Al_{0.5}Ga_{0.5}N$ displays a shift toward the lower binding energy after exposed to Ar ICP, from 20.13 to 19.45 eV, implying a 0.68 eV downward move of the Fermi level. The measurement of O 1*s* spectra revealed an increase in the O concentration on the ICP-treated surfaces by a factor of ~3.7 on GaN and ~6.9 on $Al_{0.5}Ga_{0.5}N$. The higher O incorporation in $Al_{0.5}Ga_{0.5}N$ is expected, considering the higher propensity of AlN toward oxidation,[15] and may partly account for the degraded contact performance, as seen in Fig. 1. However, we found that the large redshift of the Ga 3*d* spectra in $Al_{0.5}Ga_{0.5}N$ remained after removing the oxide by HCl and BOE etching.

The dramatically different effects of plasma treatment on the Ohmic contact characteristics on GaN and $Al_{0.5}Ga_{0.5}N$ can be explained by the XPS results. The preferential sputtering of N during the ICP treatment creates N vacancies, which act as shallow donors in GaN and increase the surface doping concentration. This leads to an upward shift of the Fermi level and a thinner Schottky barrier for electron transport. The plasma treatment therefore remarkably enhances carrier tunneling, resulting in an Ohmic behavior of the as-deposited metal contacts. In the ICP-treated $Al_{0.5}Ga_{0.5}N$, the downward shift of the Fermi level suggests that plasma-induced defects act as deep-level centers, pinning the Fermi level. As a result, the Schottky barrier is increased and current conduction via tunneling is suppressed, leading to a more rectifying contact behavior, as shown in Fig. 1.

In summary, the effects of plasma treatment on the electrical properties of AlGaN surface are found to be a strong function of Al mole fraction. ICP treatment increases the surface doping level and improves the Ohmic characteristics of Ti/Al/Ti/Au contacts to GaN and low-Al AlGaN, but degrades the surface conductivity and Ohmic contacts on AlGaN with an Al mole fraction higher than 0.3. XPS measurements show that the Fermi level in GaN exhibits an upward shift after plasma treatment, consistent with the creation of N vacancy shallow donors. In contrast, the Fermi level in the ICP-treated $Al_{0.5}Ga_{0.5}N$ moves away from the conduction band edge, suggesting that plasma damage in high-Al AlGaN acts as deep-level compensation centers and must be minimized.

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