Effect of alcohol-based sulfur treatment on Pt Ohmic contacts to p-type GaN

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The effects of an alcohol-based (NH$_4$)$_2$S solution [t-C$_4$H$_9$OH+(NH$_4$)$_2$S] treatment on Pt Ohmic contacts to p-type GaN are presented. The specific contact resistance decreased by three orders of magnitude from 2.56×10$^{-2}$ to 4.71×10$^{-5}$ Ω cm$^2$ as a result of surface treatment using an alcohol-based (NH$_4$)$_2$S solution compared to that of the untreated sample. The O 1$s$ and Pt 4$f$ core-level peaks in the x-ray photoemission spectra showed that the alcohol-based (NH$_4$)$_2$S treatment was effective in removing of the surface oxide layer. Compared to the untreated sample, the alcohol-based (NH$_4$)$_2$S-treated sample showed a Ga 2$p$ core-level peak which was shifted toward the valence-band edge by 0.25 eV, indicating that the surface Fermi level was shifted toward the valence-band edge. These results suggest that the surface barrier height for hole injection from Pt metal to p-type GaN can be lowered by the surface treatment, thus resulting in a drastic reduction in specific contact resistance. © 2001 American Institute of Physics. [DOI: 10.1063/1.1358356]

Rapid progress has recently been achieved in obtaining high-brightness GaN-based light-emitting diodes (LEDs) in the visible and ultraviolet wavelength range. For the case of the highly efficient LED, several critical issues must be addressed, such as high-quality crystal growth, low-resistance Ohmic contact, and etching–sawing–cleaving for device processing. Low-resistance Ohmic contacts to p-type GaN are particularly crucial in improving the performance of optoelectronic devices as well as electronic devices.

The growth of heavily doped p-GaN (>10$^{19}$ cm$^{-3}$) and the absence of contact metals, which have a work function larger than that of p-GaN (the sum of the electron affinity of 4.1 eV and the band gap of 3.4 eV), have been realized as major obstacles in the achievement of low-resistance Ohmic contacts to p-GaN. To obtain a low-resistance Ohmic contact to p-type GaN, a variety of surface treatments of p-GaN using solutions such as KOH, aqua-regia solution, and (NH$_4$)$_2$S have been proposed. It has been reported that the surface treatment with a (NH$_4$)$_2$S$_x$$_t$ solution is particularly efficient in removing the native oxide on the p-type GaN surface, resulting in a low-resistance Ohmic contact to p-type GaN.

In the area of GaAs devices, several studies have reported that the alcohol-based (NH$_4$)$_2$S$_x$$_t$ solution removes the native oxide on the GaAs surface more efficiently than the normal (NH$_4$)$_2$S$_x$$_t$ solution due to the low dielectric constant of the alcohol-based (NH$_4$)$_2$S$_x$$_t$ solution, resulting in a larger improvement in device characteristics. Zhiyaev et al. have reported that the photoluminescence intensity of n-type GaN is considerably enhanced as a result of the surface treatment with an alcoholic sulfide solution. Our previous results also showed that, for the case of n-type GaN, the surface treatment with an alcohol-based (NH$_4$)$_2$S$_x$$_t$ solution removes the insulating layer on the n-type GaN surface more effectively than the normal, aqueous (NH$_4$)$_2$S$_x$$_t$ solution, leading to more enhanced electrical properties. In this letter, we report on an investigation of the effect of an alcohol-based (NH$_4$)$_2$S solution [t-C$_4$H$_9$OH+(NH$_4$)$_2$S] for use in the treatment of Ohmic contacts to p-type GaN by observing the oxide layer and the shift of the surface Fermi level, as evidenced by the x-ray photoelectron spectroscopy (XPS) spectra. In addition, the current–voltage (I–V) result showed that the specific contact resistivity for a sample treated with an alcohol-based (NH$_4$)$_2$S$_x$$_t$ solution is drastically decreased by three orders of magnitude over that of an untreated sample.

The p-GaN samples were grown on a c-face (0001) sapphire substrate by using a metalorganic chemical-vapor deposition system (Emcore DG125™). A 30-nm-thick GaN buffer layer was grown on the substrate at 500 °C, followed by the growth of a 1-μm-thick Mg-doped p-type GaN epilayer at a temperature of 1020 °C. Hall measurements showed that the bulk hole concentration was about 2×10$^{17}$ cm$^{-3}$. The GaN layer was degreased by treatment with trichloroethylene, acetone, and methanol for 5 min at each step, and then rinsed in deionized (DI) water for 10 min. Prior to the fabrication of the transfer length method (TLM) patterns, mesa structures were patterned by inductively coupled plasma etching (Oxford Plasma 100) using Cl$_2$/CH$_4$/H$_2$/Ar and the TLM patterns were defined by standard photolithographic techniques. The size of the pads was 100×200 μm$^2$ and the spacings between the pads were 5, 10, 15, 20, 25, and 35 μm. The samples were first etched in HCl:H$_2$O(1:1) solution for 1 min and then dipped into a 60 °C alcohol solution for 10 min, which was composed of 90 vol% tert-butanol (t-C$_4$H$_9$OH) and 10 vol% (NH$_4$)$_2$S. The residual solution was removed from the sample by rinsing the samples in DI water for 1 min. After the sulfur treatment, the samples were immediately placed in a vacuum chamber for metal deposition. The Pt (8 nm) films were then deposited on p-type GaN by electron-beam evaporation (PLS 500 model). I–V data were measured at room
temperature using a parameter analyzer (HP4155A). To characterize the chemical bonding at the interface between the Pt layer and sulfur-treated $p$-type GaN, XPS was performed using the Mg $K\alpha$ line (1253.6 eV) as an excitation source in an ultra-high-vacuum system with a base pressure of \( \sim 1 \times 10^{-10} \) Torr.

Figure 1 shows the $I$–$V$ characteristics of the samples which had been untreated and treated with alcohol-based \((\text{NH}_4)\_2\text{S}\) solution. While the $I$–$V$ curves of the untreated sample exhibit a nonlinear $I$–$V$ behavior, the $I$–$V$ curve of the alcohol-based \((\text{NH}_4)\_2\text{S}\) solution treated sample shows a linear behavior. Specific contact resistances for the samples were determined from a plot of the measured resistance versus the spacings between the TLM pads. The specific contact resistance was determined to be 2.56 \( \times 10^{-2} \) V cm$^2$ for the untreated samples and 4.71 \( \times 10^{-5} \) V cm$^2$ for the alcohol-based \((\text{NH}_4)\_2\text{S}\) treated samples, respectively. Compared to the untreated sample, the specific contact resistance decreased by three orders of magnitude as a result of the surface treatment using the alcohol-based \((\text{NH}_4)\_2\text{S}\) solution.

To investigate the mechanisms for the improvement of the Ohmic characteristics due to this surface treatment, XPS spectra were obtained from the Pt contacts (2.5 nm) on the sulfur-treated $p$-type GaN. Figure 2 shows the O 1$s$ core-level of the Pt/$p$-GaN interface for untreated and alcohol-based \((\text{NH}_4)\_2\text{S}\)-treated samples, respectively. As shown in Fig. 2, the O 1$s$ core-level peak for samples treated with alcohol-based \((\text{NH}_4)\_2\text{S}\) solution were significantly decreased compared to that of the untreated sample. This result shows that the oxide layer was efficiently removed from the $p$-GaN surface by the treatment with alcohol-based \((\text{NH}_4)\_2\text{S}\) solution. It has been reported that an interfacial oxide layer increases the barrier height for hole injection from metal to $p$-type GaN, leading to a detrimental effect on Ohmic contacts to $p$-type GaN$^{14}$ Hence, the improved Ohmic characteristics for samples treated with the alcohol-based \((\text{NH}_4)\_2\text{S}\) solution can be attributed to the removal of the interfacial oxide layer.

Figure 3 shows the Pt 4$f$ core level of Pt deposited on the $p$-GaN for two samples. As shown in Fig. 3, the Pt 4$f$ core level of the alcohol-based \((\text{NH}_4)\_2\text{S}\)-treated sample [Fig. 3(b)] shifts toward the lower-energy side compared to that of untreated sample [Fig. 3(a)]. The binding energy of the Pt 4$f$ core-level peak for Pt, which is known to be around 71 eV, is smaller than that of a core-level peak for the Pt oxide.$^{15}$ Therefore, the shift of the Pt 4$f$ core level to the lower-binding-energy side is due to the changes in the chemical bonding state of Pt at the interface, as a result of the alcohol-based \((\text{NH}_4)\_2\text{S}\) treatment. These results are in agreement with the O 1$s$ core level behavior, as shown in Fig. 2.

The O 1$s$ and Pt 4$f$ core-level spectra show that an alcohol-based \((\text{NH}_4)\_2\text{S}\) treatment is very effective in removing the surface oxide layer. However, it has been reported that the removal of the surface oxide layer itself does not guarantee a drastic reduction in the metal contact resistance.$^{16}$ An alcohol-based \((\text{NH}_4)\_2\text{S}\) treatment can also alter the surface electronic properties, and hence, the surface barrier height, which is closely related to the subsequent
metal contact behavior. It is known that the energy position of the Ga-based core-level peaks is one of the most accurate means of determining the shifts in the GaN surface Fermi-level position. Therefore, the surface Fermi-level position was determined by observing the Ga 2p core-level of an alcohol-based \((\text{NH}_4)_2\text{S}\)-treated sample. The Ga 2p core-level spectra of the Pt/p-GaN interface of the untreated and an alcohol-based \((\text{NH}_4)_2\text{S}\)-treated sample are shown in Fig. 4. Figure 4 shows that the Ga 2p core-level peak of the untreated sample [Fig. 4(a)] shifts toward the lower-energy side by 0.25 eV compared to that of an alcohol-based \((\text{NH}_4)_2\text{S}\)-treated sample [Fig. 4(b)]. This indicates that a small surface barrier height for hole injection from metal to p-type GaN can further reduce the specific contact resistance, as shown in Fig. 1.

It is well known that for GaAs, the sulfur passivation in a S-containing solution is essentially an etching process, during which a chemical reaction and dissolution alternately take place. A similar mechanism can be proposed for the alcohol-based sulfur passivation of p-type GaN. The native oxide layer on the GaN surface can be initially removed through the formation of gallium hydroxide, which is produced via the \(\text{OH}^-\) groups present in the solution when the GaN sample is dipped in the alcohol-based sulfur solution. The selective removal of surface Ga via gallium hydroxide in a sulfur solution can lead to the formation of Ga vacancies. It is well known that the Ga vacancies are able to act as acceptors in p-type GaN. Hence, the surface reactions of GaN with the sulfur solution can result in the formation of acceptor-like Ga vacancies, leading to a shift of the surface Fermi level toward the valence-band edge, as shown in the Ga 2p core-level spectra Fig. 4. A previous study reported that sulfur does not bond with nitrogen but bonds with gallium or occupies nitrogen-related vacancies. The S ions in the solution would then bond to the Ga atoms on the GaN surface, producing Ga sulfides. For the case of passivation of a GaAs surface by using \((\text{NH}_4)_2\text{S}\) solution, it has been reported that the sulfides, which are formed on the GaAs surface, are soluble in the sulfur solution. Hence, the simultaneous process of reaction and dissolution can leave a very thin sulfide layer on the sulfur-treated GaN surfaces. This very thin sulfide layer can play an important role in preventing the formation of oxide on the GaN surface on exposure to air prior to the metal deposition. These processes can lead to the effective removal of surface oxide, formation of Ga vacancies, and protection from the formation of the native oxide on exposure to air prior to metal deposition, thus resulting in enhanced Ohmic characteristics for the samples treated by an alcohol-based \((\text{NH}_4)_2\text{S}\) solution.

In summary, we report on an investigation of the effect of an alcohol-based \((\text{NH}_4)_2\text{S}\) solution treatment on Ohmic contacts to p-type GaN. Compared to the untreated sample, the specific contact resistance was drastically decreased by three orders of magnitude as a result of the surface treatment. The O 1s and Pt 4f core-level spectra showed that the alcohol-based \((\text{NH}_4)_2\text{S}\) treatment is very effective in the removal of the surface oxide layer. The Ga 2p core-level peak for the alcohol-based \((\text{NH}_4)_2\text{S}\)-treated sample showed a shift by 0.25 eV toward the valence-band edge compared to that for the untreated sample. The drastic improvement in the Ohmic characteristics of the alcohol-based \((\text{NH}_4)_2\text{S}\)-treated sample can be attributed to the effective removal of the surface oxide and the shift of the surface Fermi level toward the valence-band edge.

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