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Electrical Properties of Ti/Al Ohmic Contacts to Sulfur-Passivated N-Face n-Type GaN for Vertical-Structure Light-Emitting Diodes

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We investigate the electrical properties of Ti/Al ohmic contacts on $(NH_4)_2S_x$-passivated N-face n-GaN:Si (4.2×10^{18} cm^{-3}) grown by molecular beam epitaxy. It is shown that the passivation results in an increase in the photoluminescence intensity of n-GaN. Current–voltage (*I-V*) measurements show that the passivated samples experience a slight degradation in the electrical properties upon annealing at 300°C, while the untreated samples show some improvement although still nonohmic. Based on the *I-V* and X-ray photoemission spectroscopy results, we describe the possible mechanisms for the passivation and annealing dependence of the electrical properties of the Ti/Al contacts to the N-face n-GaN.

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For the realization of solid-state lighting, the fabrication of high performance GaN-based white light-emitting diodes (LEDs) is crucial. In this connection, vertical-structure LEDs, which can allow high external quantum efficiency, have been widely investigated.[1,2] For example, Wang et al.,[2] investigating the electrical properties of vertical GaN-based LEDs fabricated by Ni electroplating and laser lift-off techniques, reported that the n-type side-up vertical LEDs produced much higher output power as compared to conventional top-emission LEDs. Unlike top-emission LEDs, vertical LEDs require the formation of high quality ohmic contacts to both N-face n- and p-GaN.[2-5] Ohmic contacts to Ga-face n-GaN can be easily formed using Ti- or V-based schemes.[6-10] It was, however, shown that the formation of ohmic contacts to N-face n-GaN was difficult.[3-5] This was attributed to the absence of polarization-induced two-dimensional electron gas (2DEG) formed at the AlN/GaN interface due to the opposite directions of spontaneous polarization built from bulk to surface.[11] However, Jang et al.[5] used a 5 nm thick Pd interlayer to facilitate the formation of interfacial AlN, which played an important role in improving the electrical properties of Ti/Al contacts to N-face n-GaN when annealed at temperatures above 400°C.

For Ga-face n-GaN, sulfur passivation was widely performed to produce low resistance n-type ohmic contacts.[9,12,13] For example, Lee et al.[9] reported that nonalloyed Ti/Al contacts to $(NH_4)_2S_x$-treated n-GaN exhibited ohmic behavior with a contact resistivity of $\sim 10^{-5}$ Ω cm^2. Song et al.[14] also showed that nonalloyed Ti/Al contacts yielded a contact resistivity of $\sim 10^{-4}$ Ω cm^2 when surface-treated by a CH_3CSNH_2 solution. In this work, we passivated N-face n-GaN using an $(NH_4)_2S_x$ solution to modify the surface property and form low resistance Ti/Al ohmic contacts to N-face n-GaN. It is shown that the sulfur passivation causes an increase in photoluminescence (PL) intensity of n-GaN. It is also shown that the passivated contacts show better electrical behaviors than untreated samples before and after annealing at 300°C.

Molecular beam epitaxy (MBE) was used to grow a 35 nm thick GaN buffer layer on a sapphire substrate, which was followed by the growth of (~ 1 μm thick) N-face n-type GaN:Si layers ($n_d = 4.2 \times 10^{18}$ cm^{-3}). The N-face n-GaN layers were ultrasonically degreased with acetone, isopropyl alcohol, deionized (DI) water, and a mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) solution for 5 min in each step to remove organic contaminants. To eliminate the native oxide, the samples were further treated with a diluted HCl solution and rinsed in DI water. The samples were then prepared in two different conditions: (*i*) Untreated and (*ii*) dipped in $(NH_4)_2S_x$ (containing 6% sulfur) for 10 min at room temperature. After the treatment, the passivated samples were blown dry by N_2 gas. Circular transfer-length-method patterns were defined by using standard photolithography. The outer radii were fixed to be 200 μm and the spacings between the inner and the outer radii varied from 5 to 40 μm. The Ti(30 nm)/Al(200 nm) films were deposited by electron-beam evaporation under a base pressure of 2×10^{-6} Torr. Some of the samples were annealed at 300°C for 1 min in a N_2 ambient. For the fabrication of vertical-structure LEDs that were mounted on host substrates formed by wafer bonding or electroplating, keeping the processing temperatures low (below 300°C) is crucial to not damage the devices. This means that the formation of nonalloyed or low temperature ohmic contacts is essential. Current–voltage (*I-V*) data were measured at room temperature using a parameter analyzer (HP 4155A). PL measurement was performed at room temperature using the 325 nm line of a 30 mW He–Cd laser. X-ray photoemission spectroscopy [XPS, Sigma Probe (ThermoVG, U.K.) model] was carried out using an Al Kα X-ray source in an ultrahigh vacuum system with a chamber base pressure of $\sim 10^{-10}$ Torr.

Figure 1 shows the typical PL spectra of N-face n-GaN layers before and after sulfide treatment. The PL spectra show peak energies at the same wavelength of 365 nm (3.4 eV), where full widths at half-maximum are ~ 9.8 and ~ 12.0 nm for the samples with and without the sulfur passivation, respectively. It is shown that the passivation causes an increase in the PL intensity by $\sim 26\%$ as compared to that of the untreated sample. (Although samples from the same wafer showed a variation in the PL intensity, the passivated samples always exhibited higher intensity compared to the unpassivated ones.) Similar passivation-induced enhancement was previously reported for Ga-face n-GaN.[12-14] For example, Huh et al.[12] reported the enhancement of the PL intensity of Ga-face n-GaN by the $(NH_4)_2S$ treatment. Martines et al.,[13] investigating surface recombination and sulfide passivation, reported that the treatments caused the room-temperature excitonic PL intensity to increase and the improvements persisted for at least seven months in room air. They also reported that the effect of surface states on the Fermi level was significantly reduced by the treatment. Song et al.[14] also reported a remarkable increase in the PL intensity after the CH_3CSNH_2 treatment. Taking into account the fact that PL intensity

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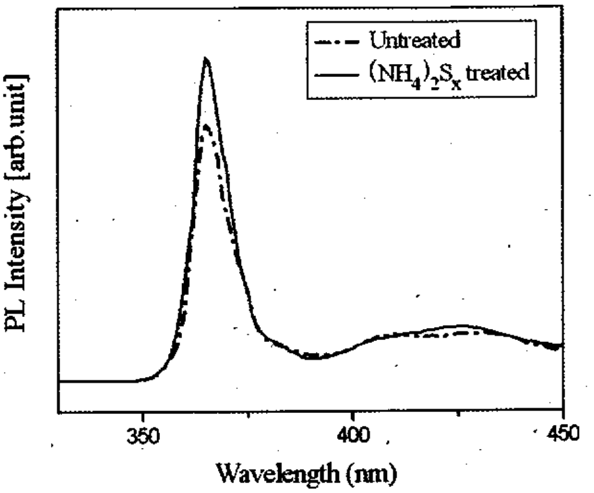

Figure 1. (Color online) PL spectra of N-face n-GaN layers before and after sulfide treatment.

is related to surface recombination velocity, the enhanced PL intensity of the passivated N-face n-GaN implies a decrease in the surface recombination velocity. In other words, the passivation causes the reduction of nonradiative transitions.[15] Furthermore, for both the samples, there is a broad peak around 425 nm. This peak is believed to be associated with the presence of Mg atoms, which were introduced unintentionally during growth.

Figure 2 shows the annealing dependence of the electrical properties of the Ti/Al contacts on N-face n-GaN before and after passivation. Before annealing, the passivated contact shows a good ohmic characteristic, while the untreated contact reveals nonohmic behavior. Upon annealing, the electrical behavior of the passivated samples is a bit degraded, while that of the untreated one is somewhat improved. However, the untreated sample reveals still nonlinear behavior. Measurements show that the specific contact resistances of the passivated sample are 2.6×10^{-4} and 5.5×10^{-4} Ω cm^2 before and after annealing. This is different from the electrical behaviors of Ti/Al contacts to Ga-face n-GaN, where the contact resistivity gradually decreased with increasing annealing temperature.[4,5,11]

To understand the chemical bonding states of Ga, XPS examination was made on the as-deposited Ti/Al contact samples on N-face n-GaN before and after passivation. Before starting analysis, the Ti layer was sputtered using Ar$^+$ ions to expose the interface region between the contact layer and the n-GaN. The peak of the C 1s line

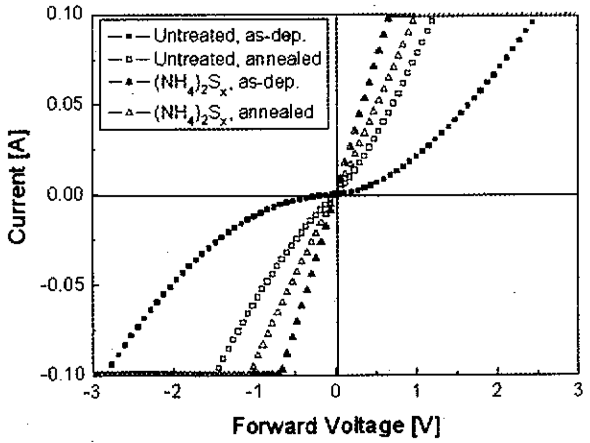

Figure 2. (Color online) The annealing dependence of the electrical properties of Ti/Al contacts on N-face n-GaN before and after sulfur passivation.

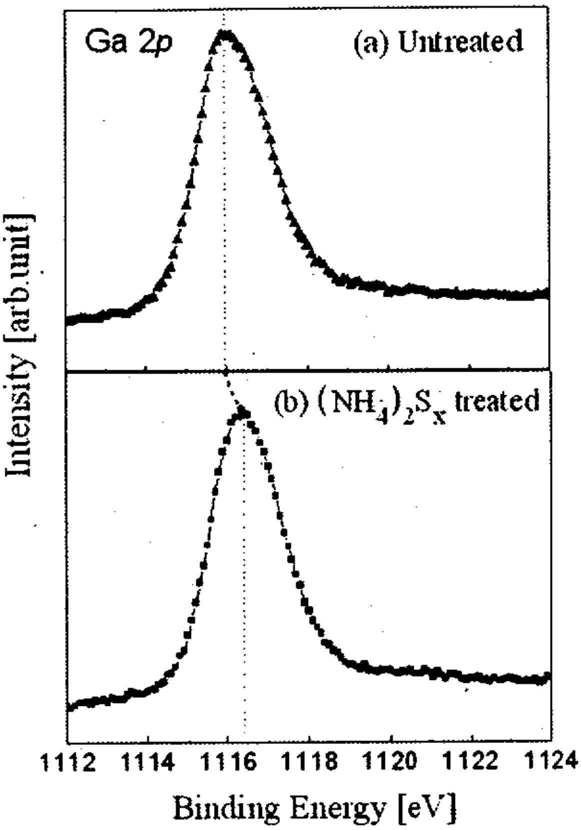

Figure 3. The Ga 2p core level for the Ti/GaN interface of samples before and after passivation.

(284.5 eV) was used as a reference for charge correction. Figure 3 shows the Ga 2p core level for the Ti/GaN interface regions of the samples before and after passivation. It is shown that the Ga 2p core level of the passivated sample shifts toward the high binding energy side by 0.5 eV, compared to that of the untreated sample. This implies that the sulfide passivation causes the surface Fermi level to shift toward the conduction- band edge, resulting in a reduction in the band bending in the n-GaN.[16,17]

Figure 4 exhibits the C 1s core-level spectra for the samples before and after the sulfur passivation. The untreated sample reveals a peak at around 531 eV. However, the passivated sample shows no oxygen-related peak. This indicates that the surface oxide was effectively removed by the surface treatment using an $(NH_4)_2S_x$ solution. This means that the sulfur layer formed on the n-GaN by passivation effectively prevents the formation of the surface oxide when the samples are exposed to air during the transfer for the measurements.

Electrical results showed that before passivation, the as-deposited contact gave a nonohmic behavior. This is different from the results previously reported by Kim et al.[18] and Jeon et al.,[19] who showed that nonalloyed Ti/Al contacts to N-face n-GaN were ohmic. This discrepancy could be attributed to a dry-etching process. In other words, unlike our MBE samples, the thin-film N-face n-GaN samples were dry etched after a laser lift-off process. Dry etching was believed to cause the generation of donorlike defects such as V_N or O_N at the sample surfaces,[18,20,21] which reduces the effective Schottky barrier height (SBH) and so lowers the contact resistance. The passivation-induced improvement of the electrical behavior (Fig. 2) could be explained as follows. The metal-semiconductor band theory[22] indicates that the effective SBH could be affected by the presence of a native oxide at the Ti/n-GaN interface. This implies that the successful removal of the surface oxide by the passivation (Fig. 4) can reduce the barrier height. As noted from the shift of the Ga 2p core level toward the higher binding energy (Fig. 4),

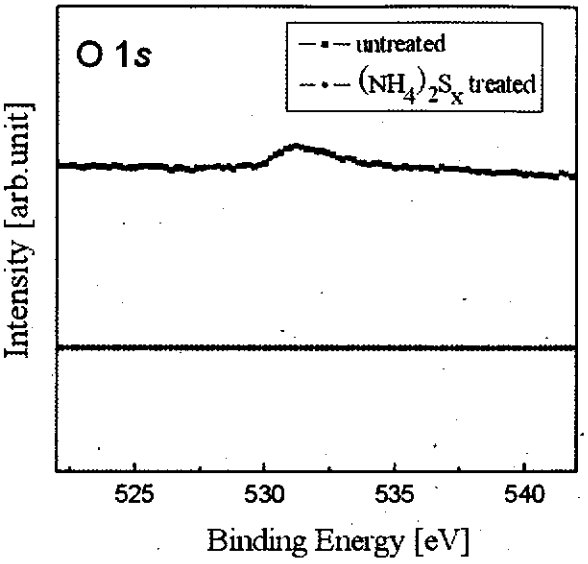

Figure 4. (Color online) The O 1s core-level spectra for samples before and after passivation.

the improvement may be attributed to the shift of the surface Fermi level. For N-face n-GaN, the exact reason why the sulfide passivation causes the surface Fermi level to shift toward the conduction-band edge is not clear at this moment. Offsey et al.,[23] investigating the surface characteristics of sulfur-passivated (001) n-GaAs by photochemistry, and Besser and Helms,[24] investigating the effect of sulfide treatment on the band-bending behaviors of GaAs:Si by PL, reported that the treatments resulted in the unpinning of the surface Fermi level by reducing the surface state density, leading to a reduction of the band bending. Thus, the surface Fermi-level shift observed in our passivated sample might also be explained in terms of the reduction in the surface state density, reducing the band-bending and so the surface barrier heights.[17] The annealing-induced degradation of the passivated sample (Fig. 2) may be explained as follows. For Ti/Al contacts to Ga-face n-GaN, the annealing-induced improvement was attributed to the generation of donorlike N vacancies and 2DEG.[6,11,25] For N-face n-contacts, the annealing-induced degradation was attributed to the absence of polarization-induced 2DEG.[11] These mechanisms are based on the presence of interfacial AlN formed as a result of annealing at temperatures above 400°C. Thus, considering the low temperature (300°C) used in this work, the annealing-induced degradation cannot be explained by the polarization effects. Recently, it was shown from the secondary-ion mass spectroscopy results that upon annealing at 300°C in a N_2 ambient, a TiN layer was more effective in preventing Ga atoms from out-diffusing from thin-film N-face n-GaN than a Ti layer.[19] This indicates that annealing the Ti/Al contacts at 300°C could cause the generation of Ga vacancies near the n-GaN surface regions. This is in agreement with phase equilibria in the Ga–Ti system,[26] showing that Ga–Ti alloy could form at 300°C. These acceptorlike Ga vacancies[17] could cause electrical compensation at the N-face n-GaN surface regions, reducing the electron concentration and so increasing the effective SBH. For the untreated sample, annealing slightly improved the electrical behavior, although still nonlinear and poorer than the passivated sample. This can be attributed to the combined effects of the dissociation of the interfacial oxide[27] and the formation of acceptorlike Ga vacancies, as described before. High resolution electron microscopy results (not shown) revealed the presence of oxide nanoclusters (~6 nm) at the interface. Further clarification of the precise mechanisms for the annealing-induced electrical behaviors is necessary.

In summary, we investigated the electrical properties of Ti/Al ohmic contacts to MBE-grown N-face n-GaN (4.2×10^{18} cm^{-3}) before and after sulfide treatment by means of *I-V* and XPS measurements. It was shown that the passivated samples produced much stronger PL intensity as compared to the untreated n-GaN sample. It was also shown that unlike the untreated samples, the passivated contacts produced ohmic behaviors with specific contact resistances as low as 2.6×10^{-4} Ω cm^2. For the passivated samples, 300°C annealing slightly degraded the electrical properties. Based on the *I-V* and XPS results, the possible mechanisms for the passivation and annealing dependence of the electrical properties of the Ti/Al contacts to N-face n-GaN were described.

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