Excellent Schottky Characteristics of Indium-tin-oxide Contact to n-type GaN

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Abstract—Excellent Schottky characteristics of indium-tin-oxide (ITO) contact formed on n-type GaN (n-GaN) were demonstrated. The post-thermal annealing of ITO contact sputtered on n-GaN led to a significant improvement in the Schottky characteristics, particularly pronounced in the air ambient than nitrogen ambient, e.g., the rectification ratio (measured at ± 1.0 V) was increased from 4.9 to 4240 after an optimized post-thermal annealing. Thermionic field emission model applied to the forward current-voltage curves of the ITO/n-GaN Schottky diodes also exhibited that the Schottky barrier height could be as high as 0.93 eV. The observed excellent Schottky characteristics with post-thermal annealing are attributed to the improved ITO crystallinity as verified by glancing X-ray diffraction method.

Keywords—indium tin oxide; Schottky contact; thermal annealing; thermionic field emission.

I. INTRODUCTION

Indium tin oxide (ITO) has been very widely used as the transparent conductive electrodes in organic and inorganic optoelectronic devices, particularly, in the light emitting diodes (LEDs) and solar cells because of its high optical transmittance in the visible wavelength and good electrical conductivity.[1-3] In GaN-based LEDs, ITO deposited on p-GaN is commercially used as the transparent conductive electrodes to spread the current more uniformly.[4-8] Due to this reason, a number of studies with respect to ITO contacts to p-GaN have been presented.[4-8] For example, Margalith et al.[4] showed that the ITO Ohmic contact to p-GaN could not be easily obtained due to the large work-function mismatch between ITO (4.6 eV) and p-GaN (7.5 eV), and more importantly, due to the sputtering ion damage produced at the p-GaN surface such as nitrogen vacancies and oxygen impurities acting as donors.[9] Therefore, ITO materials are usually deposited on p-GaN using an e-beam evaporator to avoid sputtering ion damage[10] and/or the modified p-GaN structures[11] such as strained layer or superlattices are used instead.

Despite such depth insight into ITO/p-GaN contact, the studies on ITO/n-GaN contact are very lacking.[12,13] This may be due to the lack of possible application of ITO/n-GaN contact system. However, it is worth noting that, if the ITO produces Ohmic contact to n-GaN, ITO can be used as the n-type transparent conductive electrodes of GaN-based LEDs, in which may lead to a enhancement of light extraction efficiency. Furthermore, ITO Ohmic contact can be also applicable in the photo-switching devices. Meanwhile, if the ITO yields non-Ohmic contact to n-GaN, namely, Schottky characteristics, ITO can be practically applicable in the photodiodes. These feasibilities indicate that the studies on the behavior of ITO contact to n-GaN are of particular interest. In this regard, we have investigated the electrical properties of ITO contact formed on n-type GaN as a function of post-thermal annealing conditions. It is shown that the ITO contact produces excellent Schottky characteristics after post-thermal annealing in air ambient.

II. EXPERIMENTAL PROCEDURE

A 2.8 μm-thick n-GaN (Si-doped)/1.95 μm-thick undoped GaN wafers grown on c-plane sapphire substrates by metal-organic chemical vapor deposition (MOCVD) were used for the contact study. Hall-effect measurements revealed that the carrier concentration $N=1.6\times10^{18}$ cm$^{-3}$, the Hall mobility $\mu=221$ cm$^2$V$^{-1}$s$^{-1}$, and the sheet resistance $R_{sh}=55.3$ Ω/sq. For the fabrication of Schottky diodes, first, the Ohmic metal pad was formed on the wafer using a Ti/Al (30 nm/70nm) layers, followed by rapid thermal annealing performed at 550 °C for 1 min in N$_2$ ambient. Note that, prior to the metal deposition, the sample surface was cleaned with the buffered oxide etchant for 5 min to remove native oxide and rinsed with deionized water. The conventional photolithography and e-beam evaporation techniques were used for the Ohmic-metal formation. Then, the 100 nm-thick ITO layer was deposited on the entire wafer using a radio frequency magnetron sputtering system, followed by a selective wet-chemical etching of ITO layer to form Schottky electrodes. The ITO sputtering was performed using the following condition, i.e., the composition of ITO target was 90 weight % In$_2$O$_3$ and 10 weight % SnO$_2$, the working pressure was 10 mTorr, Ar/O$_2$ gas ratio was 10:0, the rf power was 100 W, and the growth temperature was 500 °C. Hall-effect measurement of as-deposited ITO layer showed that $N=9.5\times10^{19}$ cm$^{-3}$, $\mu=7.4$ cm$^2$V$^{-1}$s$^{-1}$, and the electrical resistivity is $8.6\times10^4$ Ωcm. The completed device structure with a circular Schottky contact (diameter=50 μm) is shown in the inset of Fig. 1. To investigate the effect of post-thermal annealing, the devices were annealed at the temperatures of 400-800 °C for 1 min in nitrogen and air ambient. The electrical characteristics of ITO contact were evaluated using a parameter analyzer (HP4156A). The structural changes with post-thermal annealing were investigated using glancing X-ray diffraction (XRD) measurements.
III. RESULTS AND DISCUSSION

Figure 1 shows the typical semi-logarithmic $I-V$ characteristics of the ITO contact to n-GaN plotted as a function of annealing temperature and ambient. Note that the as-deposited ITO contact produces slightly rectifying behavior, indicating that the ITO Ohmic contact to n-GaN cannot be easily obtained in spite of high $N$ values of n-layer. Indeed, this result is somewhat different as compared with that of Sheu et al.,[12] reported that the as-deposited ITO produced Ohmic contact to n-GaN. The observed different behavior might be attributed to the different ITO deposition condition, i.e., the growth temperature of ITO was as high as 500 °C, in which high growth temperature is expected to influence the ITO crystallinity, as will be discussed later in details.

Interestingly, the post-thermal annealing led to a significant increase in the forward currents without regard to annealing ambient. This can be attributed to the improved electrical conductivity of ITO layer, e.g., the ITO layer annealed at 700 °C for 1 min in air ambient showed the reduced electrical resistivity of 3.5x10^{-4} Ωcm. Furthermore, for the sample annealed in N₂ ambient, the reverse currents also increased after thermal annealing, which seems to be negative effect in terms of rectifying behavior. In contrast, for the sample annealed in air ambient, the reverse current decreased with thermal annealing up to 700 °C, while that increased significantly above 800 °C. This indicates that the rectifying behavior of ITO contact to n-GaN can be significantly improved by the post-thermal annealing performed in air ambient.

Figure 2 shows the rectification ratio of ITO contact to n-GaN, as measured at ±1 V. As expected, the rectification ratio increased significantly with increasing annealing temperature, particularly pronounced at 600-700 °C. Notably, the samples annealed in air ambient always yielded higher rectification ratios than those annealed in nitrogen ambient. Consequently, the very high rectification ratio of ~4200 could be obtained for the samples annealed at 600-700 °C in air ambient.

To analyze the transport mechanism of ITO contact/n-GaN system, the forward $I-V$ curves were analyzed using a thermionic field emission (TFE) theory[14,15] because the calculated characteristic tunneling parameter ($E_{00}$) of 1.46 lies in the TFE regime, i.e., $kT/qE_{00} \sim 1$ for TFE, where, $k$ is the Boltzmann constant, $T$ is the temperature, $q$ is the electronic charge. Here, the $E_{00}$ was estimated according to

$$E_{00} = \frac{qh}{4\pi} \left( \frac{N}{\varepsilon_s \varepsilon_0 m^*} \right)^{1/2}$$

(1)

where $h$ is the Planck constant, $\varepsilon_s$ is the dielectric constant of the semiconductor ($\varepsilon_s=8.9\varepsilon_0$), and $m^*$ is the electron effective mass ($m^*=0.2m_e$). Thereby, the forward $I-V$ curves can be fitted with TFE model, i.e.,[14,15]

$$I = \frac{A^* e^{\Phi_B/qV}}{kT} \left[ \coth(\beta_0 V/2) - \frac{\beta_0 V}{2} \right]$$

$$+ A \frac{e^{\Phi_B/qV}}{kT} \left[ \coth(\beta_0 V/2) - \frac{\beta_0 V}{2} + 1 \right]$$

(2)

where $A$ is the contact area, $A^{**}$ is the Richardson constant (26.4 A/cm²K²), $\Phi_B$ is the effective Schottky barrier height, and $\xi$ is the energy difference between the conduction band edge and Fermi level.
Table I summarizes the Schottky parameters including the E₀₀, ideality factor (n), and Φ_B. Here, note that the n value, which was calculated using the relation of n＝(E₀₀/kT)coth(E₀₀/kT), was much larger than 1.0 for all cases, indicating that non-ideal carrier transport occurred at the ITO contact interface. According to previous studies,[15, 16] carrier transport through surface states associated with point defects such as nitrogen vacancies or oxygen interstitials (generated during ITO sputtering) or threading dislocations might be responsible for the non-ideal transport at the contact interface. Notably, however, the n value decreased significantly with post-thermal annealing, indicating that the density of surface states were reduced. It is also worth noting that the Φ_B of optimized ITO contact (annealed at 600 °C) is as high as 0.93 eV, which is much larger than the theoretically predicted value of 0.5 eV. This suggests that the thermodynamic reactions of ITO/n-GaN with thermal annealing led to an increase in the barrier height.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>E₀₀ (eV)</th>
<th>n</th>
<th>Φ_B (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.217</td>
<td>8.12</td>
<td>1.08</td>
</tr>
<tr>
<td>400</td>
<td>0.206</td>
<td>7.71</td>
<td>1.13</td>
</tr>
<tr>
<td>500</td>
<td>0.047</td>
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<td>0.78</td>
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<td>600</td>
<td>0.208</td>
<td>2.49</td>
<td>0.93</td>
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<tr>
<td>700</td>
<td>0.201</td>
<td>2.41</td>
<td>0.91</td>
</tr>
<tr>
<td>800</td>
<td>0.244</td>
<td>2.90</td>
<td>0.92</td>
</tr>
</tbody>
</table>

To support this hypothesis, XRD (θ-2θ) measurements were performed for the as-deposited sample and 700 °C annealed sample in nitrogen and air ambient, as shown in Fig. 3. Notably, the XRD peaks of In2O3 (222) and (444) planes increased significantly after thermal annealing, indicating that the density of surface states were reduced. It is also worth noting that the Φ_B of optimized ITO contact (annealed at 600 °C) is as high as 0.93 eV, which is much larger than the theoretically predicted value of 0.5 eV. This suggests that the thermodynamic reactions of ITO/n-GaN with thermal annealing led to an increase in the barrier height.

TABLE 1. SCHOTTKY PARAMETERS OF ITO CONTACT TO N-GaN ANNEALED IN AIR AMBIENT.

| ITO annealed in nitrogen, and air ambient, respectively, which is consistent with the Schottky characteristics. Therefore, the improved Schottky behavior with thermal annealing, particularly in air ambient, is due to the formation of ideal ITO-GaN interfaces accompanied with the regrowth of In2O3 (222) and (444) planes or improved crystallinity of ITO films.

IV. CONCLUSION

To summarize, excellent ITO Schottky contact to n-GaN could be demonstrated by post thermal annealing in air ambient. The rectification ratio could be as high as ~4200 after optimized post-thermal annealing condition, which was associated with the increased forward currents and the suppressed reverse currents. TFE model showed that the ideality factor was significantly decreased with post-thermal annealing, indicating a formation of ideal ITO/n-GaN interfaces. The Schottky barrier height could be also obtained to be as high as 0.93 eV. XRD analysis clearly showed that the improved Schottky characteristics would be correlated to the formation of ideal ITO-GaN interfaces accompanied with the regrowth of In2O3 (222) planes or improved crystallinity of ITO films. These results suggest that the ITO would be used as the transparent Schottky electrodes for photodiodes or optical sensors.

V. ACKNOWLEDGEMENTS

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