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Reflective and Low-Resistance Zn/Rh Contacts to p-Type GaN for Flip-Chip Light-Emitting Diodes

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We report on the formation of high-quality ohmic contacts to p-type GaN ($5 \times 10^{17}/\text{cm}^3$) using a Rh (100 nm) layer combined with a 3 nm thick Zn interlayer for high-power flip-chip light-emitting diodes (LEDs). The as-deposited sample produces a nonlinear behavior. However, the samples annealed at 430 and 530°C for 1 min in air become ohmic with a contact resistivity of $\sim 10^{-5}\ \Omega\ \text{cm}^2$. Measurements show that the reflectivity of the samples annealed at 530°C is 73% at 460 nm. LEDs fabricated using the Zn/Rh contact layers give forward-bias voltages of 3.09-3.12 V at an injection current of 20 mA.
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High-performance flip-chip light-emitting diodes (LEDs) are of significant technological importance for applications in solid-state lighting.[1] In order to realize such LEDs, the development of p-type ohmic electrodes having high reflectivity as well as low contact resistance is crucial. Ag, Al, and Rh are known to be the best metallic reflectors. In particular, owing to its thermal stability, a Rh contact has been considered as a potentially important electrode for the fabrication of high-power flip-chip LEDs. Several attempts have been hitherto made to develop high-quality ohmic contacts to p-type GaN using Rh reflectors.[2,3] For example, Song et al.,[2] showed that nonalloyed Rh (10 nm thick) contacts yield a low specific contact resistance of $\sim 10^{-5}\ \Omega\ \text{cm}^2$, when the samples were two-step surface-treated using a buffered oxide etch solution prior to metal deposition. However, single Rh contacts suffer from thermal degradation when annealed at temperatures in excess of 300°C.[4] Recently, Lee et al.[3] used an 8 nm thick Pt interlayer to improve the ohmic behavior of Rh contacts and showed that Pt/Rh contacts give a specific contact resistance of $9.0 \times 10^{-5}\ \Omega\ \text{cm}^2$ and reflectance of 62% at 460 nm when annealed at 500°C. In this work, to improve the thermal stability of single Rh contacts, a Zn layer is added in-between a Rh layer and a GaN layer. Use of a Zn layer is advantageous since Zn atoms could act as an acceptor dopant[5] or transform into transparent conducting oxide, such as ZnO, when annealed in air. The results show that the Zn(3 nm)/Rh(100 nm) contacts produce specific contact resistances as low as $\sim 10^{-5}\ \Omega\ \text{cm}^2$, when annealed at 430 and 530°C for 1 min in air. GaN-based LEDs fabricated using the Zn/Rh ohmic contact layers give forward-bias voltages of 3.09-3.12 V at an injection current of 20 mA.

Metallorganic chemical vapor deposition (MOCVD) was used to grow 2 μm thick unintentionally doped GaN layers on (0001) sapphire substrates. This was followed by the growth of 1 μm thick p-GaN:Mg layer ($n_a = 5 \times 10^{17}/\text{cm}^3$). The GaN layers were ultrasonically degreased with trichloroethylene, acetone, methanol for 5 min in each step, and then rinsed with deionized water. After cleaning the samples using a buffered oxide etch (BOE) solution for 20 min,[6] the GaN layers were blown dry by nitrogen gas. Circular transfer length model (CTLM) patterns were defined by the photolithographic technique to measure the specific contact resistance. The outer dot radius was 75 μm and the spacing between the inner and the outer radii varied from 4 to 25 μm. Rh layers 3 nm thick Zn and 100 nm thick were deposited on the p-GaN by electron beam evaporation (PLS 500 model). Some of the samples were then annealed at 430 and 530°C for 1 min in air. Current-voltage (*I-V*) measurements were carried out using a parameter analyzer (HP 4155A). Auger electron spectroscopy (AES) was carried out using a PHI 670 Auger microscope with an electron beam of 10 keV and 0.0236 μA in an ultra-high vacuum (UHV) system with a chamber base pressure of $\sim 10^{-10}$ Torr. X-ray photoemission spectroscopy (XPS, PHI 5200 model) was performed using an Al Kα X-ray source (1486.6 eV) in an UHV system with a chamber base pressure of $\sim 10^{-11}$ Torr. Multiquantum-well LEDs were fabricated using Rh ohmic contacts combined with thin Zn interlayers and their electrical characteristics were characterized.

Figure 1 shows the typical *I-V* characteristics of the Zn (3 nm)/Rh (100 nm) contacts to p-GaN before and after annealing. The as-deposited sample exhibits nonlinear *I-V* behavior, because of the small work function of Zn, which is in contact with p-GaN. However, their *I-V* characteristics are significantly improved upon annealing. The specific contact resistance was determined from plots of the measured total resistance *vs.* the spacing between the CTLM pads.[7] Measurements showed that the specific contact resistance as low as 6.83×10^{-5} and $4.36 \times 10^{-5}\ \Omega\ \text{cm}^2$ is obtained from the contacts annealed at 430 and 530°C, respectively.

Figure 2 shows the reflectivity obtained from the Rh and ZnRh contacts. The ZnRh contact annealed at 530°C gives 73.5%, which is similar to that (72.6%) of the as-deposited Rh contact. It should be noted that the reflectivity of single Rh contacts becomes degraded upon annealing. This indicates that the use of the Zn interlayer effectively delayed the degradation of the reflectivity when annealed.

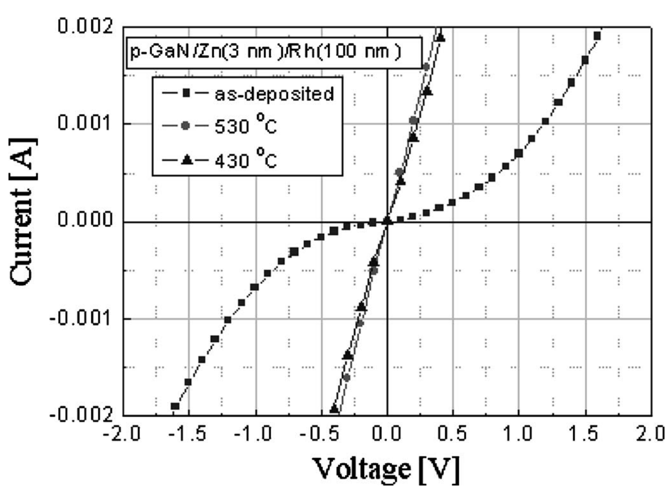

Figure 1. The typical *I-V* characteristics of the Zn (3 nm)/Rh (100 nm) contacts to p-GaN before and after annealing.

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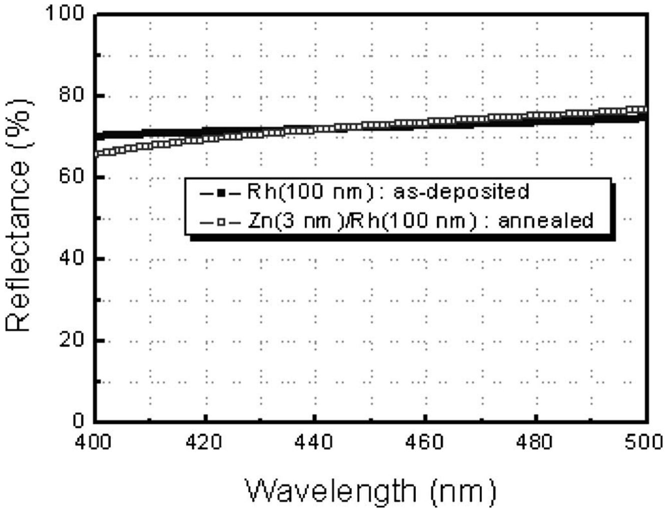

Figure 2. The reflectivity obtained from the Rh and ZnRh contacts. The ZnRh contact annealed at 530°C gives 73.5%, similar to that (72.6%) of the as-deposited Rh contact.

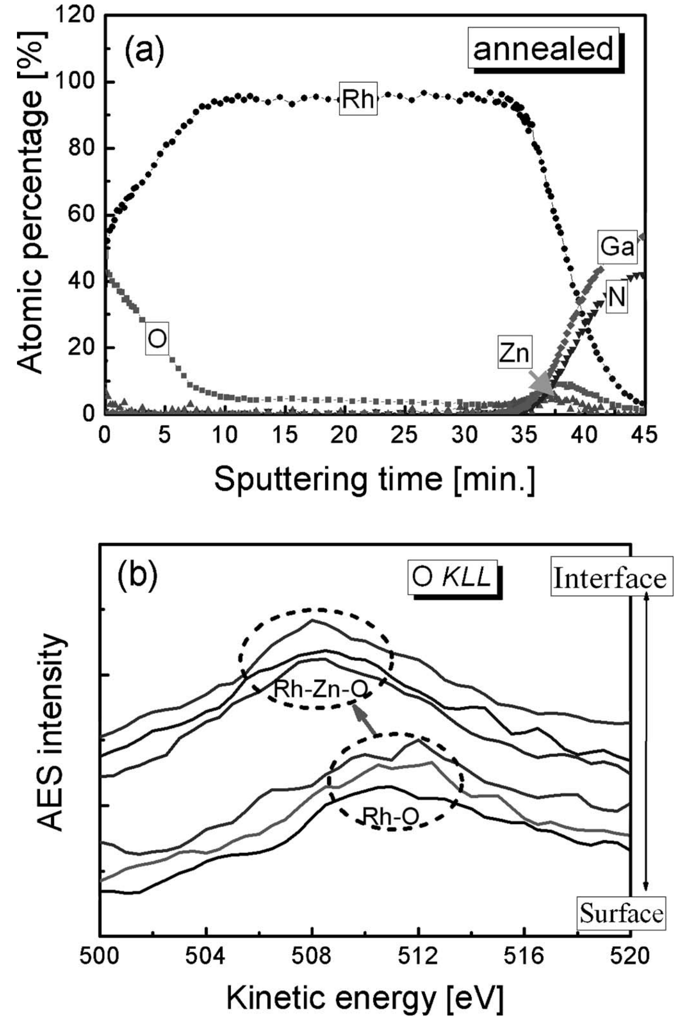

Figure 3. (a) Auger depth profiles of the Zn/Rh contacts annealed at 530°C. (b) The O KLL peaks obtained from the annealed sample.

Interfacial reactions between the Zn/Rh layers and GaN were examined by AES. For the as-deposited sample (not shown), each layer is well defined, indicating the absence of significant intermixing. For the sample annealed at 530°C (Fig. 3a), Zn mostly remained at the Rh/GaN interface region. It is noted that a large amount of oxygen was introduced into the contact layers from the annealing gas. Most of the oxygen is present at the sample surface region, although there is some at the metal/GaN interface. This is indicative of the formation of conductive Rh-oxide[8] at the sample surface and Rh-Zn-oxide at the interface. Figure 3b shows the O KLL peaks obtained from the annealed sample. It is noted that the O KLL peak shifts toward the lower energy side from ~511 eV at the sample surface region to ~508 eV at the interface region, as the sputtering time increases. The shift indicates that the different type of oxides is formed at the surface and interface,[9] as noted from the AES depth profiling result (Fig. 3a). A small amount of Rh was indiffused into the GaN, indicating a possible reaction between Ga and Rh, leading to the formation of the interfacial gallide phase, such as Ga-Rh alloy. It should be noted that Rh reacts with Ga and forms Ga-Rh phase even in the as-deposited sample.[2,10,11]

To characterize the chemical bonding states of Zn and Ga core levels at the interface between GaN and metal layers, XPS examinations were performed. Before beginning analysis, the metal layers were sputtered using an Ar^+ ion to expose the interface region between metals and GaN. Figure 4a shows the Zn 2p peaks obtained from the interfaces before and after annealing 530°C. For the annealed sample, the Zn 2p core level shifts toward the lower-energy side by 0.5 eV as compared to that of the as-deposited one. This indicates that a Zn-Rh-oxide, such as $ZnRh_2O_4$ phase, is formed,[9,12] as expected from the AES results (Fig. 3). Figure 4b shows the Ga 3d core level peaks from the samples before and after annealing.[c] The Ga 3d core level from the annealed sample shifts (by 1.19 eV) toward the low binding energy side as compared with that of the as-deposited sample. This indicates that annealing caused the surface Fermi level to shift toward the valence-band edge.[13-17]

Figure 5 shows the *I-V* characteristics of LEDs fabricated with the annealed Zn (3 nm)/Rh (100 nm) contact layers. The LEDs made with both the Zn/Rh contact layers give forward-bias voltage of 3.09-3.12 V at 20 mA. This is better than that of annealed Ni/Au contacts.

The Zn/Rh contacts produced good ohmic behavior, when annealed in air. Although the exact mechanism is not clear at this moment, the annealing effect may be explained as follows. First, the improvement could be due to the shift of the surface Fermi level toward the valence bandedge, leading to the reduction of the Schottky barrier height,[13-17] as noted from the shift of the Ga 3d level (Fig. 4b). The surface Fermi level shift could be caused by an increase in carrier concentration near the GaN surface. The formation of interfacial Ga-Rh phase (as noted from the AES results Fig. 3a)[2] results in the generation of deep acceptor-like Ga vacancies near the GaN surface.[14] In addition, the improvement may be in part related to the formation of transparent p-type $ZnRh_2O_4$ at the interface in contact with the GaN.[9,12] The presence of the $ZnRh_2O_4$ at the electrode/GaN interface may lead to the reduction of the barrier height and hence the reduction of contact resistivity.

To summarize, the Zn (3 nm)/Rh (100 nm) scheme was investigated to obtain thermally stable, reflective, and low resistance ohmic contacts to p-GaN for high-power flip-chip LEDs. The contacts produced specific contact resistance in the range of $\sim 10^{-5}$ Ω cm^2 when annealed at 430 and 530°C for 1 min in air. The samples annealed at 530°C produced reflectivity slightly better than that of single as-deposited Rh contacts. LEDs fabricated with the Zn/Rh p-contact layers gave forward-bias voltages of 3.09-3.12 V at 20

[c]During the XPS examination, the sample surface was Ar+ ion-sputtered, and Rh, Zn, and Ga photoelectron signals were carefully monitored. The Ga 2p core levels were finally collected when only the Ga photoelectron peak (*i.e.*, from Ga-N bonding) was detected. Thus, the Ga 2p peaks are believed to come from the surface region of the GaN, which is beneath the ohmic electrode.

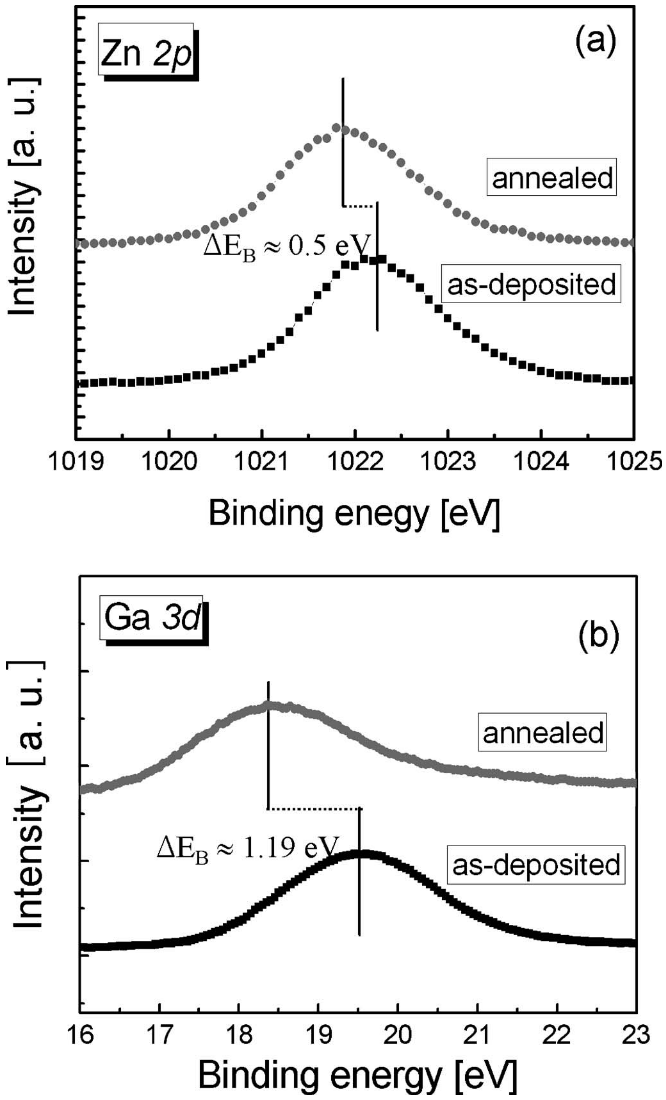

Figure 4. (a) The Zn 2p peaks obtained from the interfaces before and after annealing 530°C. (b) The Ga 3d core level peaks from the samples before and after annealing.

mA. This shows that the Zn/Rh contacts could be a promising scheme for the fabrication of high-power flip-chip LEDs.

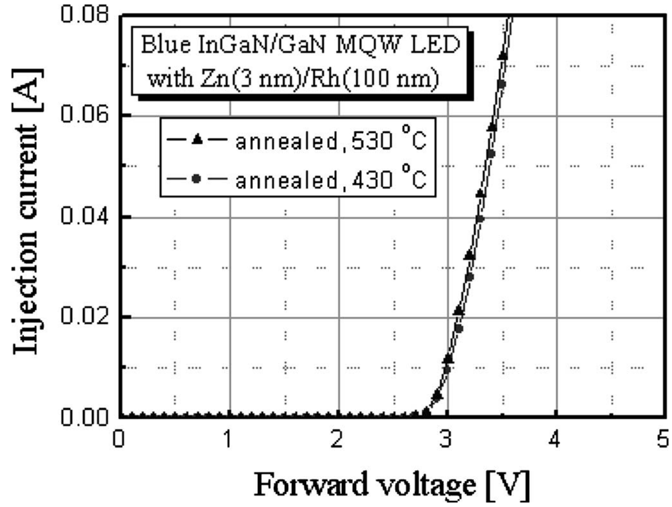

Figure 5. The *I-V* characteristics of LEDs fabricated with the annealed Zn (3 nm)/Rh (100 nm) contact layers.

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