



Formation of High-Quality Ohmic Contacts to p-GaN for Flip-Chip LEDs Using Ag/TiN_x/Al

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We have investigated Ag (2.5 nm)/TiN_x (50 nm)/Al (200 nm) contacts for use in GaN-based flip-chip light emitting diodes (LEDs). The Ag/TiN_x/Al contact becomes ohmic with specific contact resistance of $4.4 \times 10^{-3} \Omega \text{ cm}^2$ when annealed at 430°C for 1 min in nitrogen ambient. It is shown that the continuous Ag interlayer is broken into Ag nanodots when annealed. It is also shown that the TiN_x barrier layer effectively hampers the indiffusion of Al toward GaN. Blue LEDs are fabricated using the annealed Ag/TiN_x/Al contacts and are compared with those made with the annealed Ni/Au/Al contacts.
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Realization of solid-state lighting is subject to the fabrication of high-brightness GaN-based light-emitting diodes (LEDs). For high-brightness LEDs, the achievement of high light extraction efficiency is essential. To improve light extraction efficiency and hence enhance device performance, LEDs with flip-chip geometry have been introduced.^{1,2} In flip-chip configuration, LEDs are fabricated with reflective p-type electrodes such as Ag, Al, and Rh layers.³⁻⁸ Among these, Ag layers are commonly used because they give high reflectivity and good ohmic behaviors to p-GaN.^{4,6,7} However, the Ag reflector has drawbacks such as poor adhesion to p-GaN and thermal instability.^{5,8} Al electrodes have good thermal stability and reflectivity comparable to that of Ag reflectors. However, Al reflectors have not been widely used because they produce poor ohmic contacts on p-GaN. Thus, instead of single Al layers, Al-based multilayers with Ni or Ni/Au contact layers were used to improve ohmic behaviors.^{4,8} Titanium nitride (TiN_x) is known to be one of the best diffusion barriers for electronic devices.^{9,10} TiN_x was also used as a contact layer for optoelectronic devices because of its low resistivity and high transparency.^{11,12} In this work, we have investigated Al-based reflective contacts to p-GaN using Ag interlayers and TiN_x barrier layers. The Ag/TiN_x/Al contacts become good ohmic with specific contact resistance of $4.4 \times 10^{-3} \Omega \text{ cm}^2$ when annealed at 430°C for 1 min in nitrogen ambient. LEDs fabricated with the annealed Ag/TiN_x/Al p-type contact layers give better electrical behaviors than those with the commonly used Ni/Au/Al contacts.

Metallorganic chemical vapor deposition grown 1.5 μm thick p-GaN layers ($4 \times 10^{17} \text{ cm}^{-3}$) were ultrasonically degreased using trichloroethylene, acetone, methanol, and deionized (DI) water 5 min in each step, followed by N₂ blowing. Prior to photolithography, the samples were treated with a buffered oxide etch (BOE) solution for 20 min and rinsed in DI water. Circular transmission line method (CTLM) patterns were defined by the standard photolithographic technique for measuring specific contact resistance.¹³ The outer dot radius was fixed at 75 μm and the spacing between the inner and outer radii varied from 4 to 25 μm . After the BOE treatment, Ag (2.5 nm) and TiN_x (50 nm) layers were deposited at room temperature by electron-beam evaporation. The TiN_x layers were deposited using a TiN electron-beam source (Super Conductor Materials, Inc., 99.99%) in vacuum to grow a nonstoichiometric phase with $x < 1$, because their resistivity is lower than that of TiN_x with $x > 1$.¹⁴ Prior to the deposition of 200 nm thick Al layers, the Ag/TiN_x samples were kept in air at room temperature for 10 h to introduce oxygen into TiN_x grain boundaries.⁹ For comparison, Ni (2.5 nm)/Au (2.5 nm)/Al (200 nm) layers, which are commonly being used for flip-chip LEDs, were also deposited by electron-beam evaporation. Some of the samples were then rapid-thermal-annealed at 430°C for 1 min in nitrogen ambient. Current-voltage (I-V) mea-

surements were performed 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 . The microstructure was characterized by transmission electron microscopy (TEM, JEOL 2010) operated at 200 kV. The interfacial reaction products were characterized by glancing angle X-ray diffraction (GXRD, Rigaku diffractometer (D/MAX-RC)) (using Cu K α radiation).

Figure 1 shows the typical I-V characteristics of Ag/TiN_x/Al and Ni/Au/Al contacts before and after annealing at 430°C, measured on the 4 μm spaced metal pads. For the Ag/TiN_x/Al contacts, the as-deposited sample shows nonlinear I-V behavior, but annealing results in ohmic behavior with specific contact resistance of $4.4 \times 10^{-3} \Omega \text{ cm}^2$.¹³ For the Ni/Au/Al contacts, the as-deposited sample exhibits near-linear I-V behavior. However, annealing causes the considerable degradation of its electrical characteristic. For comparison, Ag/Al contacts without TiN_x barrier layers were also formed. The Ag/Al contact showed nonohmic behavior when annealed at 430°C in nitrogen ambient. This implies that the introduction of TiN_x is important for forming ohmic contact and TiN_x serves effectively as a barrier layer.

To characterize interfacial reactions between the metal layers and p-GaN, AES examination was made of the Ag/TiN_x/Al layers before and after annealing at 430°C. For the as-deposited sample (Fig. 2a), individual Al, TiN_x, and Ag layers are well defined. Note that some amount of oxygen is present throughout the TiN_x layer, probably along the TiN_x grain boundaries. For the annealed sample (Fig. 2b), however, some intermixing between the metal layers occurred. For example, a small amount of Al diffused into the TiN_x layer. It is shown that some amount of Ga outdiffused into the Ag/TiN_x layer. This indicates the possible formation of Ga-Ag solid solution.^{15,16} In addition, it is expected that upon annealing the incorporated oxygen reacts with the TiN_x and forms Ti-oxide.

Figure 3 shows the cross-sectional TEM image of the Ag/TiN_x/Al contact annealed at 430°C. The Al and TiN_x layers were well-defined even after annealing. In addition, note that the continuous Ag layer was broken up into nanodots (7-13 nm in size) (indicated by the arrows) at the TiN_x/GaN interface, as shown enlarged in the inset.

Figure 4 shows GXRD results obtained from the Ag/TiN_x/Al contact before and after annealing at 430°C. For the as-deposited sample (Fig. 4a), in addition to Al, there are nitrogen deficient phases, such as Ti₂N and TiN_{0.9}. There exists a Ti-oxide phase such as Ti₂O₃, which is believed to form during the air exposure before the deposition of the Al layer. For the annealed sample (Fig. 4b), in addition to the Ti₂N phase, Ti-oxide phases, such as Ti₂O₃ and Ti₃O₅, are formed, as noted from the AES results. However, Ag was not detected in both samples. This may be because the amount of Ag is much smaller than those of the TiN_x or Al layers, leading to very weak diffraction peaks. Moreover, most of Ag peak positions are somewhat similar to those of Al diffraction peaks. For example, Ag

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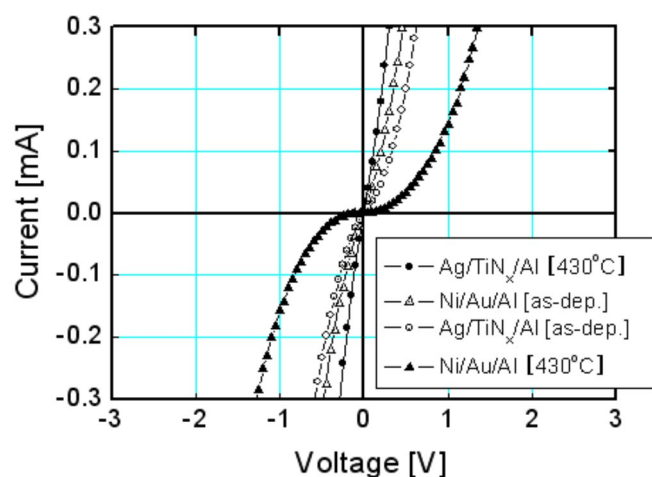


Figure 1. Typical I-V characteristics of the Ag/TiN_x/Al contacts and Ni/Au/Al contacts before and after annealing at 430°C for 1 min in nitrogen ambient.

(111), Ag (200), and Ag (220) peaks are expected to appear at diffraction angles of 38.102, 44.260, and 64.399°, respectively. Note

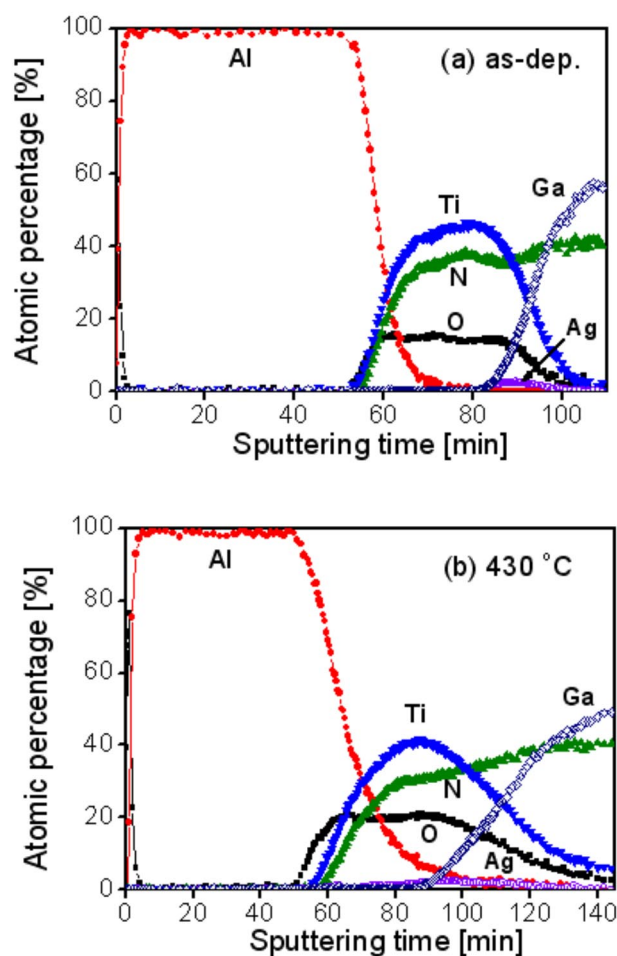


Figure 2. AES depth profiles of the Ag/TiN_x/Al contacts (a) before and (b) after annealing at 430°C for 1 min in nitrogen ambient.

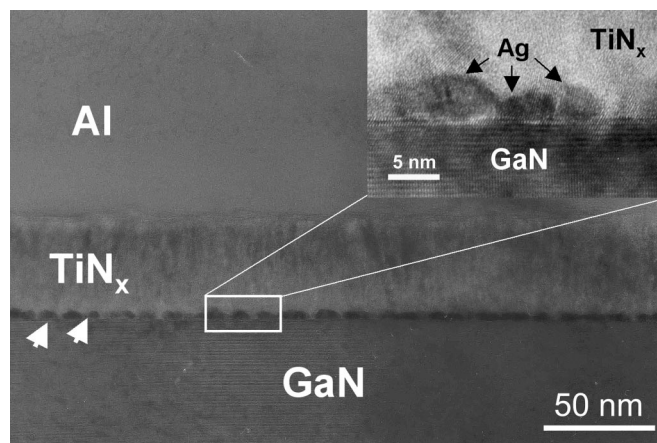


Figure 3. Cross-sectional TEM of the Ag/TiN_x/Al contact annealed at 430°C. Inset: HREM image of the interface region.

that the (111), (200), and (220) peaks of Al appear at 38.459, 44.705, and 65.072°, respectively (JCPDS card). Thus, the Ag peaks are believed to overlap with those of Al peaks.

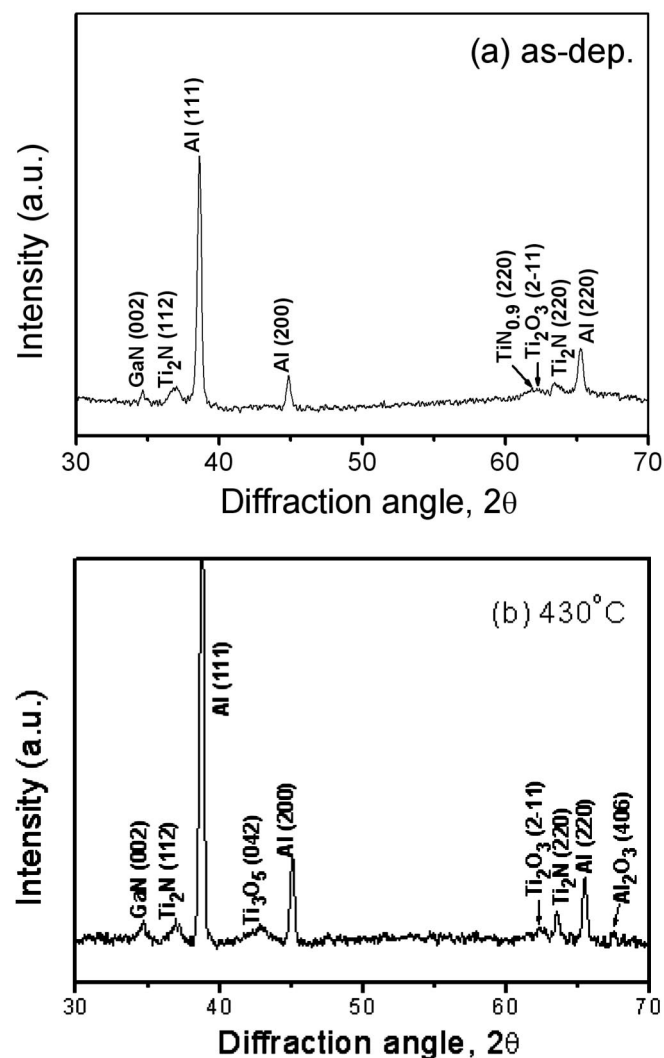


Figure 4. GXR D plots of the Ag/TiN_x/Al contacts (a) before and (b) after annealing at 430°C.

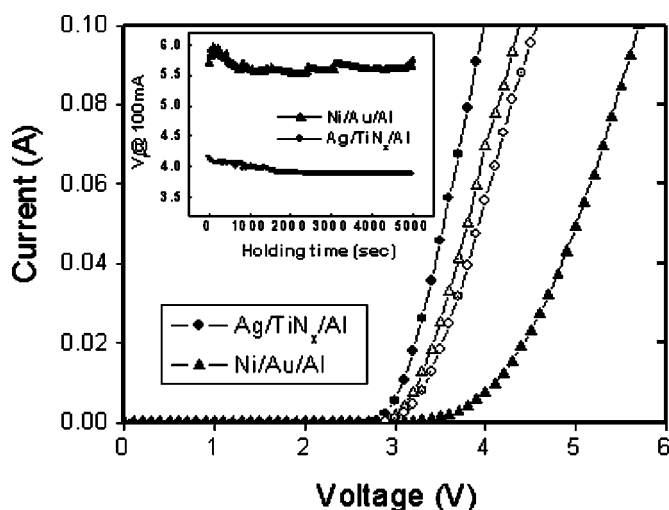


Figure 5. Typical (I-V) characteristics of GaN blue LEDs fabricated with the Ag/TiN_x/Al contacts (circles) and Ni/Au/Al contacts (triangles) before (open) and after (filled) annealing at 430°C. The inset shows the forward-bias voltage at injection current of 100 mA as a function of the holding time.

InGaN/GaN multi-quantum-well blue LEDs were fabricated using the Ag/TiN_x/Al and Ni/Au/Al contact layers (annealed at 430°C) and their performance was characterized (Fig. 5). For the LEDs made with the Ag/TiN_x/Al layers, forward-bias voltage becomes improved upon annealing at 430°C. For example, it is enhanced from 3.53 to 3.24 V at injection current of 20 mA. For the LEDs with the Ni/Au/Al layers, however, forward-bias voltage was degraded considerably upon annealing. These results are in good agreement with their I-V behaviors (Fig. 1). Forward-bias voltage at injection current of 100 mA as a function of the holding time is shown in the inset. For the Ni/Au/Al contact, the forward-bias voltage becomes unstable with increasing holding time. However, the Ag/TiN_x/Al contact exhibits relatively stable voltage. In addition, measurements¹⁷ showed that the LEDs with the annealed Ag/TiN_x/Al layers give series resistance of 9.66 Ω, while the LEDs with the annealed Ni/Au/Al layers show 15.39 Ω.

Although the Ag/TiN_x/Al layer was annealed at 430°C, only small amount of Al diffused into the metal layers. The XRD results showed the formation of the Ti-oxide phases. The oxides could stuff the TiN_x grain boundaries and so could hamper the diffusion of Al through the TiN_x film by grain boundary diffusion.¹⁰ The suppression of Al indiffusion toward the GaN plays an important role in forming ohmic contacts, since the indiffusion of Al could cause the formation of Al-nitride phases, generating donor-like nitrogen vacancies near the GaN surface, which is detrimental to p-type ohmic formation. This indicates that the exposure of the Ag/TiN_x layer to air is an effective process for forming ohmic contacts.

It should be noted that TiN_x (50 nm)/Al (200 nm) contacts before and after annealing 430°C produced nonohmic behavior (not shown), implying that the Ag interlayer plays an important role in forming ohmic contacts. Thus, the anneal-induced improvement of the electrical behaviors of the Ag/TiN_x/Al contacts could be explained as follows. First, the improvement can be related to the formation of the Ag nanodots at the TiN_x/GaN interface as shown by the TEM results. This leads to the formation of inhomogeneous Schottky barriers at the interface. According to the electronic transport theory at the metal-semiconductor interface with inhomogeneous Schottky barriers,¹⁸ the difference between the SBHs of the

Ag/GaN and the TiN_x/GaN and the size effect of the nanoscale Ag dots could result in the increase of the electric field at the interface, causing the lowering of the barrier height and hence the reduction of the contact resistivity.¹⁸⁻²⁰ Second, the out-diffusion of Ga caused by the formation of Ag-Ga solid solution^{15,16} results in the generation of deep acceptor-like Ga vacancies near the GaN surface and hence an increase in carrier concentration.²¹ Thus, the improvement could be attributed to the combined effects of the formation of the Ag nanodots and Ag-Ga solid solution.

In summary, the Ag/TiN_x/Al contacts were investigated to form ohmic contacts to p-GaN for flip-chip LEDs. The contacts produced ohmic behavior with specific contact resistance of $4.4 \times 10^{-3} \Omega \text{ cm}^2$ when annealed at 430°C for in nitrogen ambient, which is much better than that of the commonly used Ni/Au/Al contacts. It was shown that the exposure of Ag/TiN_x layers to air is effective in hindering the indiffusion of Al toward GaN and hence is helpful to p-type ohmic formation. Based on the TEM and AES results, the ohmic formation was attributed to the combined effects of the formation of the Ag nanodots and the Ag-Ga solid solution. Blue LEDs fabricated with the annealed Ag/TiN_x/Al p-type contacts showed forward-bias voltage of 3.24 V at 20 mA, while LEDs with the annealed Ni/Au/Al contacts gave 4.44 V.

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References

1. J. J. Wierer, D. A. Steigerwald, M. R. Krames, J. J. O'Shea, M. J. Ludowise, G. Christenson, Y.-C. Shen, C. Lowery, P. S. Martin, S. Subramanya, W. Gotz, N. F. Gardner, R. S. Kern, and S. A. Stockman, *Appl. Phys. Lett.*, **78**, 3379 (2001).
2. M. Koike, N. Shibata, H. Kato, and Y. Takahashi, *IEEE J. Sel. Top. Quantum Electron.*, **8**, 271 (2002).
3. P. M. Mensz, P. Kellawon, R. van Roijen, P. Kozodoy, and S. Denbaars, *IEEE Electron Device Lett.*, **33**, 2066 (1997).
4. D. A. Steigerwald, J. C. Bhat, D. Collins, R. M. Fletcher, M. O. Holcomb, M. J. Ludowise, P. S. Martin, and S. L. Rudaz, *IEEE J. Sel. Top. Quantum Electron.*, **8**, 310 (2002).
5. D. L. Hibbard, S. P. Jung, C. Wang, D. Ullery, Y. S. Zhao, H. P. Lee, W. So, and H. Liu, *Appl. Phys. Lett.*, **83**, 311 (2003).
6. J.-O. Song, D.-S. Leem, J. S. Kwak, O. H. Nam, Y. Park, and T.-Y. Seong, *Appl. Phys. Lett.*, **83**, 4990 (2003).
7. H. W. Jung and J.-L. Lee, *Appl. Phys. Lett.*, **85**, 4421 (2004).
8. H. S. Venugopalan, X. Gao, T. Zhang, B. S. Shelton, A. Dicarolo, I. Eliashevich, and M. Hsing, *Proc. SPIE*, **5187**, 260 (2004).
9. W. Sinke, G. P. A. Frijink, and F. W. Saris, *Appl. Phys. Lett.*, **47**, 471 (1985).
10. V. Fortin, S. C. Gujrathi, G. Gagnon, R. Gauvin, J. F. Currie, L. Ouellet, and Y. Tremblay, *J. Vac. Sci. Technol. B*, **17**, 423 (1999).
11. Y.-Z. Chiou, Y.-K. Su, S.-J. Chang, J. F. Chen, C.-S. Chang, S.-H. Liu, Y.-C. Lin, and C.-H. Chen, *Jpn. J. Appl. Phys., Part 1*, **41**, 3643 (2002).
12. C.-C. Liu, W.-T. Wang, M.-P. Hwang, and Y.-H. Wang, *Jpn. J. Appl. Phys., Part 1*, **43**, 594 (2004).
13. G. S. Marlow and M. B. Das, *Solid-State Electron.*, **25**, 91 (1982).
14. S.-K. Rha, S.-Y. Lee, W.-J. Lee, Y.-S. Hwang, C.-O. Park, D.-W. Kim, Y.-S. Lee, and C.-N. Whang, *J. Vac. Sci. Technol. B*, **16**, 2019 (1998).
15. A. E. Gunnes, O. B. Karlsen, A. Olsen, and P. T. Zagierski, *J. Alloys Compd.*, **297**, 144 (2000).
16. J.-O. Song, J. S. Kwak, Y. Park, and T.-Y. Seong, *Appl. Phys. Lett.*, **86**, 062104 (2005).
17. E. F. Schubert, *Light-Emitting Diodes*, Cambridge University, Cambridge (2003).
18. R. T. Lee, *Phys. Rev. B*, **45**, 13509 (1992).
19. S. K. Lee, C. M. Zetterling, M. Ostling, I. Aberg, M. H. Magnusson, K. Deppert, L. E. Wernersson, L. Samuelson, and A. Litwin, *Solid-State Electron.*, **46**, 1433 (2002).
20. J. I. Sohn, J.-O. Song, D.-S. Leem, S. Lee, and T.-Y. Seong, *Electrochem. Solid-State Lett.*, **7**, G179 (2004).
21. V. M. Bermudez, D. D. Koleske, and A. E. Wickenden, *Appl. Surf. Sci.*, **126**, 69 (1998).