Low-Resistance Ohmic Contacts to Digital Alloys of n-AlGaN/AlN

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***Abstract*—Low contact resistance to digital alloys of n-type AlGaN/AlN with high average Al concentration is described. Low-energy electron diffraction was used to evaluate surface precleaning with HCl and buffered HF. The contact metallization consisting of a stack of Ti/Al/Ti/Au, 20/100/45/60 nm in thickness, was e-beam deposited and etch-patterned. The lowest specific contact resistance of $5.6 \times 10^{-5}\ \Omega \cdot \mathrm{cm}^2$ was obtained after annealing in N_2 ambient at 700 °C.**

***Index Terms*—AlGaN, GaN, light-emitting diode, ohmic contact, superlattices.**

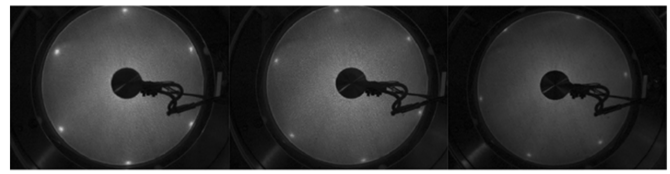

Fig. 1. LEED images of AlGaN surface at 47 V after cleaned with BHF only (a) and HCl only (b) and HCl and BHF together (c) for 10 min each.

I. INTRODUCTION

THE AlGaN-based optoelectronic devices operating in the ultraviolet spectral range of 250–300 nm require large bandgap cladding and contact layers. Short period superlattices of AlGaN/AlN, also known as digital alloys, can be used instead of random alloys but very little is known about formation of Ohmic contacts to them. Preparation of low-resistance Ohmic contacts to AlGaN, especially with high AlN content, is considered quite difficult. Contacts based on Ti/Al/Ti/Au are used on n-type GaN [1]–[8] and AlGaN [9]. The specific contact resistivity of 3×10^{-6} and $6 \times 10^{-5}\ \Omega \cdot \mathrm{cm}^2$ was demonstrated for GaN [3] and $Al_{0.6}Ga_{0.4}N$ [9], respectively. Recently, superior results obtained with V-based metallization were reported [10].

In this letter, we describe the use of Ti/Al/Ti/Au metallization to digital alloys of AlGaN/AlN with an average AlN content of 66%. This range of compositions is used in deep UV LED's operating near 280 nm. Digital alloys of AlGaN/AlN with an average composition between 0.55 and 0.75 can be prepared without changing the composition of the AlGaN well material [11]. Since the surface layer in these alloys is always AlGaN, it is expected that the fabrication of Ohmic contacts to alloys would be relatively insensitive to the average content of AlN. This is indeed the experimental finding and the Ohmic contact described here can be used for a wide range of digital alloy compositions.

II. EXPERIMENTS

Digital alloy samples of Al_xGa_{1-x} N/AlN used in our experiments were grown by gas source molecular beam epitaxy applications in light emitting diodes [11]–[15]. Samples consist of 200 periods of 0.9-nm-thick barriers of AlN and 0.5-nm-thick wells of AlGaN. The Al fraction in the wells is ~0.07, resulting in the average AlN content of $x = 0.66$. The layer was doped with Si to the average level of $2 \times 10^{19}\ \mathrm{cm}^{-3}$, as determined by secondary ion mass spectrometry. All samples were terminated with the well material, i.e., $Al_{0.07}Ga_{0.93}N$. The effective bandgap of these layers, determined by room temperature cathodoluminescence and optical reflectivity measurements, was found to be ~5.10 eV [11], [13], corresponding to the average AlN content of $x = 0.66$. The average AlN content, as well as the well and barrier thickness, were independently determined by X-ray diffraction measurements.

Surface cleaning is a critical procedure in achieving low contact resistance. The dominant contaminants on AlGaN are known to be oxygen and carbon. Oxygen is especially troublesome on layers with high AlN content since Al-oxides act as high-resistivity barriers in the contact. Surface cleaning of GaN and AlGaN with a range of acids, including HCl, HF, buffered HF (BHF), and bases such as KOH, has been reported by various groups but no single treatment has been found superior [16]–[21]. The cleaning process itself can result in surface contamination [16] and sensitive method of determining the surface condition is needed. We use low-energy electron diffraction (LEED), a standard high vacuum diffraction technique [22], to evaluate the effectiveness of different etchants. The surfaces of three samples, cleaved from a single wafer, were etched in room temperature HCl, BHF, and HCl and BHF together, for 10 min each. After etching and DI water rinse the samples were loaded into a LEED chamber. All three samples show well-defined diffraction spots due to the reciprocal lattice structure of the digital alloy, as shown in Fig. 1. The sample etched in BHF, Fig. 1(a), exhibited the brightest and best defined diffraction pattern, indicative of the highest surface quality. Diffraction pattern in this sample could be seen at a bias voltage as low as 34 V. The surface etched in HCl, shown in Fig. 1(b), is of lower quality, as judged by LEED images. A combination of HCL and BHF, shown in Fig. 1(c), was yet less effective. We

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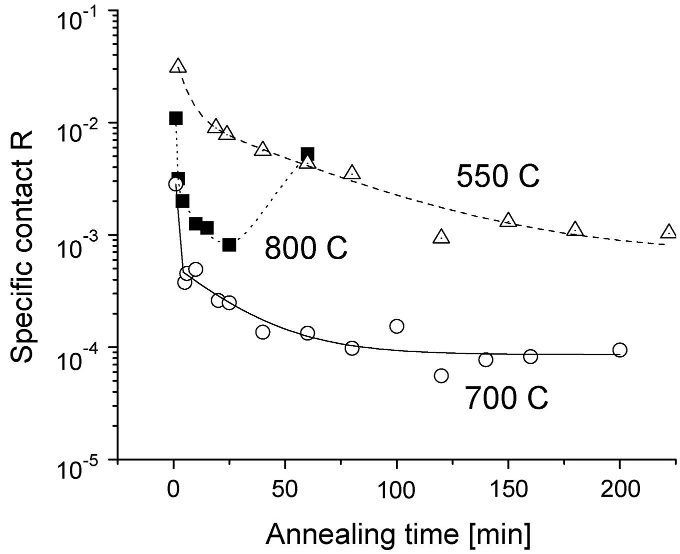

Fig. 2. Specific contact resistance versus annealing time at different temperature.

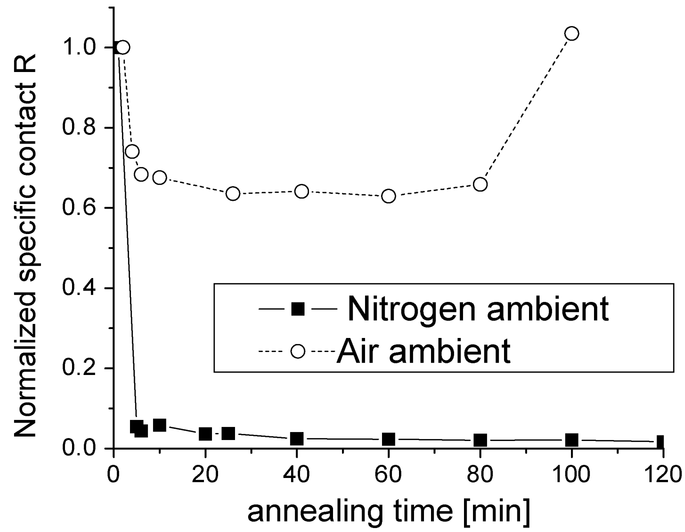

Fig. 3. Normalized specific contact resistance versus annealing time at 700 °C for different ambients.

have also examined surface cleaning of GaN with LEED and found HCl to be slightly more effective than HF or BHF. Our study of cleaning of AlGaN and GaN surfaces are consistent with previous Auger studies of AlN and GaN [16].

After surface etching each sample was loaded into an e-gun evaporator chamber for deposition of contact metals. A full surface layer of Ti(20 nm)/Al(100 nm)/Ti(45 nm)/Au(60 nm) was deposited at a base pressure below 2×10^{-7}torr [2], [23]–[25]. The metal was patterned using S-1813 photoresist (Shipley) and etched to produce a pattern for circular transmission line method (TLM) measurements. Metal liftoff technique was not used in this experiment since it does not yield reproducible results.

Samples with TLM patterns were furnace annealed for a period of 5–10 min in flowing nitrogen and air, and measured. Longer period anneals, up to 220 min at 550 °C (sample 1), 200 min at 700 °C (sample 2), and 60 min at 800 °C (sample 3) were carried out to evaluate metal-semiconductor interactions. In lower temperature anneals under nitrogen, below 700 °C, the specific contact resistance decreased rapidly during the first 5–10 min, as shown in Figs. 2 and 3. Longer anneals resulted in a slow decrease in contact resistance and eventual saturation. In anneals at 800 °C specific contact resistance reaches a minimum in about 25 min and then it increases. The specific contact resistance of $10^{-4}\ \Omega \cdot \mathrm{cm}^2$ was obtained after anneal at 700 °C for periods of 40 min and longer. The lowest contact resistance obtained in this letter was $5.6 \times 10^{-5}\ \Omega \cdot \mathrm{cm}^2$, also reached in anneals at 700 °C. This annealing temperature does not change the average composition of digital alloys, as determined by optical measurements.

We observe large differences in the annealing behavior in nitrogen and air. Fig. 3 plots the specific contact resistance, normalized to resistance after 1 min anneal, as a function of annealing time at 700 °C in nitrogen and air ambient. Annealing in nitrogen results in significant improvement in the specific contact resistance compared to samples annealed in air. In fact, longer term anneals in air, over 80 min, result in significant degradation of the contact resistance as shown in Fig. 3. We attribute this to the formation of an oxide barrier, as discussed below.

Samples with thinner Ti layer reached minimum specific contact resistance after shorter annealing times. For instance, when the thickness of the first Ti layer, deposited at the surface of the superlattice, was reduced from 20 to 10 nm, the minimum specific contact resistance was reached in half the annealing time. The thickness of this layer does not alter the contact resistance.

III. Result and Discussion

The metal sequence of the Ti/Al/Ti/Au metallization, and the individual layer thickness, was carefully designed. The first Ti layer is used to assure adhesion and to react residual surface oxides by forming TiO_2 (with the bandgap of 3.05 eV), an oxide with the bandgap smaller than that of GaN (3.5 eV), Ga_2O_3 (4.4 eV) and Al_2O_3 (8.8 eV) [26]–[29]. The Ti layer can also react with nitrogen in AlGaN and form TiN [4]–[7], [25], [30], [31], increasing the effective carrier concentration near the surface. Formation of Ohmic contacts with Ti layer alone, via formation of TiN, requires high annealing temperatures, 900 °C and above, [2], [30]. Interaction of Al with nitrogen in AlGaN occurs at lower temperatures and result in formation of Ohmic contact to AlGaN [5], [29], [30], and that is the reason for incorporating Al into the contact. In the absence of interfacial Ti, Al reacts with surface oxides forming insulating Al_2O_3. With the Ti/Al combination low-resistance contact is obtained after Al diffuses through the surface Ti layer. The anneal time is reduced for thinner Ti layers, as observed in our study. At moderate annealing temperature specific contact resistance decreases as this diffusion process takes place and then saturates. The second Ti layer, deposited over the Al layer, is used to form an oxygen barrier [7], [32], [33]. During annealing, the Al/Ti interaction results in formation of $TiAl_3$ which acts as an oxygen diffusion barrier [23], [24], [27], inhibiting formation of surface oxides of Al or Ti. [2] Even with this Ti barrier annealing in nitrogen produces lower contact resistance than annealing in air, as confirmed in our experiments. Another argument for annealing in nitrogen was provided by studies of Ti/Al couples showing oxidation of surface segregated Ti and formation of TiO_2 in 600 °C to 700 °C anneals [33].

REFERENCES

[1] M. E. Lin, Z. Ma, F. Y. Huang, Z. F. Fan, L. H. Allen, and H. Morkoc, "Low-resistance ohmic contacts on wide bandgap GaN," *Appl. Phys. Lett.*, vol. 64, no. 8, pp. 1003–1005, 1994.

[2] D.-F. Wang, F. Shiwei, C. Lu, A. Motayed, M. Jah, S. Noor Mohammad, K. A. Jones, and L. Salamanca-Riba, "Low-resistance Ti/Al/Ti/Au multilayer ohmic contact to n-GaN," *J. Appl. Phys.*, vol. 89, no. 11, pp. 6214–6217, 2001.

[3] S. Noor Mohammad, "Contact mechanisms and design principles for alloyed ohmic contacts to n-GaN," *J. Appl. Phys.*, vol. 95, no. 12, pp. 7940–7953, 2004.

[4] J. K. Kim, H. W. Jang, and J.-L. Lee, "Mechanism for ohmic contact formation of Ti on n-type GaN investigated using synchrotron radiation photoemission spectroscopy," *J. Appl. Phys.*, vol. 91, no. 11, pp. 9214–9217, 2002.

[5] A. N. Bright, P. J. Thomas, M. Weyland, D. M. Tricker, C. J. Humphreys, and R. Davies, "Correlation of contact resistance with microstructure for Au/Ni/Al/Ti/AlGaN/GaN ohmic contacts using transmission electron microscopy," *J. Appl. Phys.*, vol. 89, pp. 3143–3150, 2001.

[6] S. Ruvimov, Z. Liliental-Weber, J. Washburn, K. J. Duxstad, E. E. Haller, Z.-F. Fan, S. N. Mohammad, W. Kim, A. E. Botchkarev, and H. Morkoç, "Microstructure of Ti/Al and Ti/Al/Ni/Au ohmic contacts for n-GaN," *Appl. Phys. Lett.*, vol. 69, no. 11, pp. 1556–1558, 1996.

[7] N. A. Papanicolaou, M. V. Rao, J. Mittereder, and W. T. Anderson, "Reliable Ti/Al and Ti/Al/Ni/Au ohmic contacts to n-type GaN formed by vacuum annealing," *J. Vac. Sci. Technol. B, Condens. Matter*, vol. 19, no. 1, pp. 261–267, 2001.

[8] C. Lu, H. Chen, X. Lv, X. Xie, and S. Noor Mohammad, "Temperature and doping-dependent resistivity of Ti/AlPd/Au multilayer ohmic contact to n-GaN," *J. Appl. Phys.*, vol. 91, pp. 9218–9224, 2002.

[9] D. Selvanathan, L. Zhou, V. Kumar, J. P. Loung, M. A. L. Johnson, J. F. Schetzina, and I. Adesida, "Ohmic contacts on n-type $Al_{0.59}Ga_{0.41}N$ for solar blind detectors," *Electron. Lett.*, vol. 38, no. 14, pp. 755–756, 2002.

[10] J. H. Wang, S. E. Mohney, S. H. Wang, U. Chowdhury, and R. D. Dupuis, "Vanadium-based ohmic contacts to n-type Al0.6Ga0.4N," *J. Electron. Mater.*, vol. 33, no. 5, pp. 418–421, 2004.

[11] S. A. Nikishin, V. V. Kuryatkov, A. Chandolu, B. A. Borisov, G. D. Kipshidze, I. Ahmad, M. Holtz, and H. Temkin, "Deep ultraviolet light emitting diodes based on short period superlattices of AlN/AlGa(In)N," *Jpn J. Appl. Phys.*, vol. 42, pp. L1362–L1365, 2003.

[12] V. Kuryatkov, K. Zhu, B. Borisov, A. Chandolu, Ì. Gherasoiu, G. Kipshidze, S. N. G. Chu, M. Holtz, Y. Kudryavtsev, R. Asomoza, S. Nikishin, and H. Temkin, "Electrical properties of p-n junctions based on superlattices of AlN/AlGa(In)N," *Appl. Phys. Lett.*, vol. 83, no. 7, pp. 1319–1321, 2003.

[13] M. Holtz, G. Kipshidze, A. Chandolu, J. Yun, B. Borisov, V. Kuryatkov, K. Zhu, S. N. G. Chu, S. A. Nikishin, and H. Temkin, "Preparation of optoelectronic devices based on AlN/AlGaN superlattices," in *Mater. Res. Soc. Symp.*, 2003, Proc. 744 M 10.1.1.

[14] G. Kipshidze, V. Kuryatkov, K. Zhu, B. Borisov, M. Holtz, S. Nikishin, and H. Temkin, "AlN/AlGaInN superlattice light-emitting diodes at 280 nm," *J. Appl. Phys.*, vol. 93, no. 3, pp. 1363–1366, 2003.

[15] V. Kuryatkov, A. Chandolu, B. Borisov, G. Kipshidze, K. Zhu, S. Nikishin, M. Holtz, and H. Temkin, "Solar-blind ultraviolet photodetectors based on superlattices of AlN/AlGa(In)N," *Appl. Phys. Lett.*, vol. 82, no. 9, pp. 1319–1321, 2003.

[16] S. W. King, J. P. Barnak, M. D. Bremser, K. M. Tracy, C. Ronning, R. F. Davis, and R. J. Nemanich, "Cleaning of AlN and GaN surfaces," *J. Appl. Phys.*, vol. 84, no. 9, pp. 5248–5260, 1998.

[17] J. S. Jang and T.-Y. Seong, "Mechanisms for the reduction of the Schottky barrier heights of high-quality nonalloyed Pt contacts on surface-treated p-GaN," *J. Appl. Phys.*, vol. 88, no. 5, pp. 3064–3066, 2000.

[18] I. Waki, H. Fujioka, K. Ono, M. Oshima, H. Miki, and A. Fukizawa, "The effect of surface cleaning by wet treatment and ultra high vacuum annealing for ohmic contact formation on p-type GaN," *Jpn. J. Appl. Phys*, vol. 39, pp. 4451–4455, 2000.

[19] K. M. Tracy, W. J. Mecouch, R. F. Davis, and R. J. Nemanich, "Preparation and characterization of atomically clean, stoichiometric surfaces of n- and p-type GaN(0001)," *J. Appl. Phys.*, vol. 94, no. 5, pp. 3163–3172, 2003.

[20] J. Sun, K. A. Rickert, J. M. Redwing, A. B. Ellis, F. J. Himpsel, and T. F. Kuech, "p-type surface treatment for metal contact," *Appl. Phys. Lett.*, vol. 76, no. 4, pp. 415–417, 2000.

[21] A. P. Zhang, B. Luo, J. W. Johnson, F. Ren, J. Han, and S. J. Pearton, "Role of annealing conditions and surface treatment on ohmic contacts to p-GaN and p-AlGaN/GaN supperlattice," *Appl. Phys. Lett.*, vol. 79, no. 22, pp. 3636–3638, 2001.

[22] G. Ertl and J. Kupper, *Low Energy Electrons and Surface Chemistry*: VCH, New York, 1985.

[23] J. A. Bardwell, G. I. Sproule, Y. Liu, H. Tang, J. B. Webb, J. Fraser, and P. Marshall, "Comparison of two different Ti/Al/Ti/Au Ohmic metallization schemes for AlGaN/GaN," *J. Vac. Sci. Technol. B, Condens. Matter*, vol. 20, no. 4, pp. 1444–1447, 2002.

[24] J. Chen, D. G. Ivey, J. Bardwell, Y. Liu, H. Tang, and J. B. Webb, "Microstructural analysis of Ti/Al/Ti/Au Ohmic contacts to n-AlGaN/GaN," *J. Vac. Sci. Technol. A, Vac. Surf. Films*, vol. 20, no. 3, pp. 1004–1010, 2002.

[25] A. Motayed, R. Bathe, O. S. Diouf, R. D. Vispute, and S. Noor Mohammad, "Electrical, thermal, and microstructural characteristics of Ti/Al/Ti/Au multilayer Ohmic contacts to n-type GaN," *J. Appl. Phys.*, vol. 93, no. 2, pp. 1087–1094, 2003.

[26] J. Robertson, "Band offsets of wide-band-gap oxide and implications for future electronic devices," *J. Vac. Sci. Technol. B, Condens. Matter*, vol. 18, no. 3, pp. 1785–1791, 2000.

[27] F. Yun, M. A. Reshchikov, L. He, T. King, H. Morkoc, S. W. Novak, and L. Wei, "Energy band bowing parameter in $Al_XGa_{1-X}N$ alloys," *J. Appl. Phys.*, vol. 92, no. 8, pp. 4837–4839, 2002.

[28] M. Passlack, E. F. Schubert, W. S. Hobson, M. Hong, N. Moriya, S. N. G. Chu, K. Konstadinidis, J. P. Mannaerts, M. L. Schnoes, and G. J. Zydzik, "Ga_2O_3 films for electronic and optoelectronic application," *J. Appl. Phys.*, vol. 77, no. 2, pp. 686–693, 1995.

[29] B. P. Luther, J. M. DeLucca, S. E. Mohney, and R. F. Karlicek Jr., "Analysis of thin Al interface layer in Ti/Al and Pd/Al ohmic contacts to n-type GaN," *Appl. Phys. Lett.*, vol. 71, no. 26, pp. 3859–3861, 1997.

[30] B. P. Luther, S. E. Mohney, T. N. Jackson, M. Asif Khan, Q. Chen, and J. W. Yang, "Investigation of the mechanism for Ohmic contact formation in Al and Ti/Al contacts to n-type GaN," *Appl. Phys. Lett.*, vol. 70, no. 1, pp. 57–59, 1997.

[31] Y.-J. Lin, Y.-M. Chen, T.-J. Cheng, and Q. Ker, "Schottky barrier height and nitrogen-vacancy-related defect in Ti alloyed ohmic contacts to n-GaN," *J. Appl. Phys.*, vol. 95, no. 2, pp. 571–575, 2004.

[32] K. Nonaka, H. Fujii, and H. Nakajima, "Effect of oxygent in titanium on reaction diffusion between Ti and Al," *Mater. Trans.*, vol. 42, no. 8, pp. 1731–1740, 2001.

[33] A. M. Dhote, O. Auciello, D. M. Gruen, and R. Ramesh, "Studies of thin film growth and oxidation process for conductive Ti-Al diffusion barrier layers via *in situ* surface sensitive analytical techniques," *Appl. Phys. Lett.*, vol. 79, no. 6, pp. 800–802, 2001.