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A study of transparent indium tin oxide (ITO) contact to p-GaN

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Abstract

In this study, indium tin oxide (ITO) thin film was evaporated on Mg-doped p-GaN layers with low $10^{17}/cm^3$, grown by metalorganic chemical vapor deposition (MOCVD) on (0001) sapphire wafers, and its contact properties were investigated. The sheet resistance (R_S) of the evaporated ITO films was several $k\Omega/\square$ before the annealing but the sheet resistance decreased to 40–50 $\Omega/\square$ after the annealing in N_2 using a rapid thermal annealing (RTA) system. *I–V* characteristics and contact resistivities of the evaporated ITO on p-type GaN were investigated as a function of substrate treatment, annealing time, and annealing temperature. The results showed that, in optimized conditions, the ITO contacts with the resistance in the range of low 10^{-1} Ω cm^2 could be obtained, and which is probably applicable as the ohmic contact for GaN-based light emitting diodes. Also, at these conditions, the measured optical transmittances of ITO film were above 90% at a wavelength of 420 nm (blue). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Indium tin oxide; Rapid thermal annealing (RTA) system; p-GaN; Transparent oxide contact

1. Introduction

Because gallium nitride (GaN) is an attractive material which has a wide direct band gap, GaN-based optoelectronic devices such as light emitting diodes (LEDs) and laser diodes (LDs) in blue and ultraviolet wavelength regions have been intensively researched and are also commercially available.

In the GaN-based LED fabrication, the p-contact is generally formed by depositing metal layers on p-GaN located at the top of GaN-based LED quantum well structure. Due to the high contact resistance to p-GaN originated from low doping density of p-GaN, many studies have been made to improve the poor electrical performance. Among these are the use of multilayer materials such as Ni/Au and Ta/Ti and the use of additive metal outline to increase the electron spreading area of p-GaN, etc. [1–4]. In general, Ni/Au ohmic contacts to p-GaN are widely studied in commercial GaN LEDs.

These metal contacts, however, are only partially transparent and most of the light generated in the LED cannot be emitted through the top of the devices even though the GaN-based LEDs are optically transparent. If the ohmic contacts could be formed by transparent conductive oxides instead of partially transparent multiplayer metals, the light emitting area can be increased so that light with a higher intensity could be obtainable, therefore, more efficient LEDs can be fabricated without the loss of contact area. However, up to today, only a few experiments on transparent conductive oxides have been carried out as the materials for ohmic contact to GaN-based LEDs.

ITO is a well known transparent conducting material with resistivity in the range of low 10^{-4} Ω cm^2 and with transmittance higher than 90% in the blue wavelength region at optimized conditions [5]. Therefore, ITO has been widely applied in various optoelectronic devices. In this study, ITO contact properties were studied by depositing ITO on p-GaN to investigate a possibility of forming transparent ohmic contact on p-GaN. Because the substrate pre-treatment before the contact formation is one of the most important factors

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Table 1
Substrate treatment conditions for p-GaN before ITO deposition

Treatment no.	Treatment
A	Acetone + Alcohol + HCl + 3HCl:HNO_3
B	Acetone + Alcohol + HCl + 3HCl:HNO_3 + $(NH_4)_2S$
C	Acetone + Alcohol + HCl + 3HCl:HNO_3 + KOH + $(NH_4)_2S$

in forming a good ohmic contact, the effect of substrate pre-treatment on the ITO contact properties was also investigated.

2. Experiment

In this study, Mg-doped p-GaN layers grown by metalorganic chemical vapor deposition (MOCVD) on (0001) sapphire wafers were used as the substrates. The carrier concentration of the p-GaN layer was in the range of low $10^{17}/cm^3$.

Before depositing the ITO layer on p-GaN samples, ultrasonic cleaning was carried out in organic solvents such as acetone and alcohol followed by a substrate cleaning to remove the possible thin gallium oxide layer on the surface of as-received p-GaN. In this process, the substrates were dipped in various solutions such as HCl, HCl/HNO_3 (3:1), KOH and $(NH_4)_2S$. HCl is the most widely used chemical for the removal of gallium oxide and HCl/HNO_3 is the solution used for the etching of GaN surface before GaN MOCVD growth. Recently, KOH has been reported as an effective solution in removing gallium oxide and in increasing the surface area by roughening the surface [6,7] and $(NH_4)_2S$ as a chemical in preventing from re-oxidation of the surface in addition to the removal of gallium oxide [8]. When the substrate was dipped in various solutions sequentially, every dipping process was followed by rinsing in the deionized water and blow-drying with N_2. Table 1 shows the summarized processes for the substrate treatment used in this study.

Indium tin oxide (ITO) films were deposited on p-GaN at room temperature using an electron beam evaporator with the deposition rate of 0.06 nm/s. As a comparison, ITO and 5 nm Ni/50 nm Au were also deposited on corning glass in addition to p-GaN. Deposited thickness of ITO thin films was 100 nm. To measure contact properties, a circular transmission line method (TLM) was used and its pattern was prepared by a lift-off process after patterning with a photoresist. Fig. 1 shows the circular electrodes patterns used in the experiment having 100 m in diameter and 5, 10, 15, 20, 25 and 30 μm of inter-electrode spacing. Deposited ITO films were annealed using a rapid thermal annealing (RTA) system at 500, 600 and 700°C of annealing temperature for 30, 60, 90 and 120 s in N_2.

Current–voltage (*I–V*) characteristics of the contacts and sheet resistance (R_S) of the deposited ITO were estimated using a HP4145B semiconductor parameter analyzer and a four-point probe, respectively, and UV spectrometry was used to investigate the optical properties of ITO and Ni/Au deposited on corning glass.

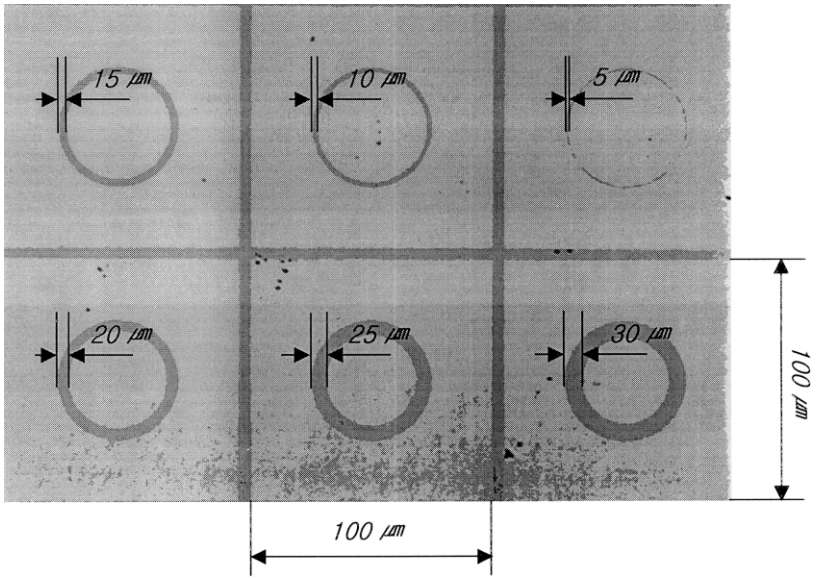

Fig. 1. Schematic illustration of circular electrodes patterns used in the experiment.

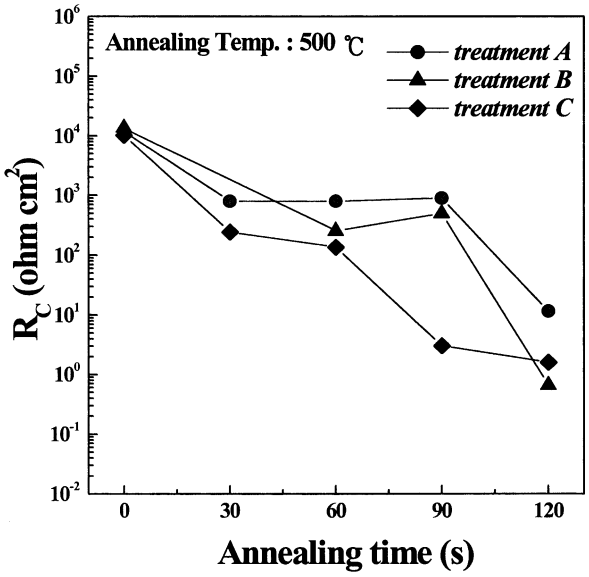

Fig. 2. ITO contact resistivities as a function of sample treatment and annealing time at 500°C of annealing temperature in a N_2 RTA system.

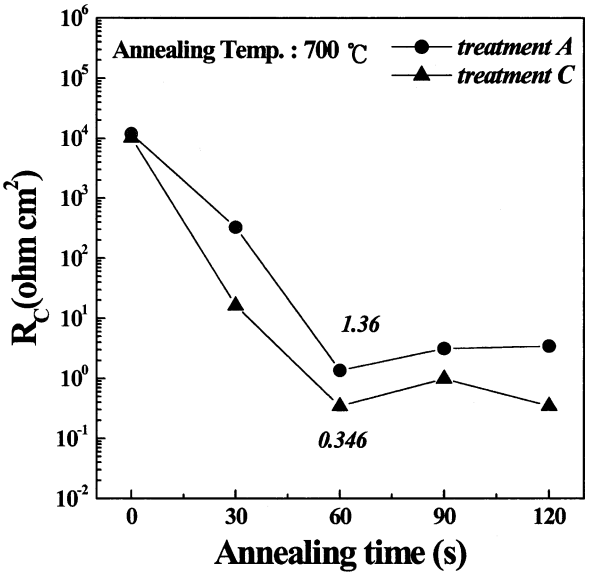

Fig. 3. ITO contact resistivities as a function of sample treatment and annealing time at 700°C in a N_2 RTA system.

Auger electron spectroscopy (AES) was used to investigate the interface properties of the contacts.

3. Results and discussion

Fig. 2 shows the effects of substrate treatment and annealing time in N_2 ambience on ITO contact resistivity on p-GaN at 500°C of annealing temperature. As shown in the figure, the ITO contact resistivity decreased with the increase of annealing time for all of the sample treatment conditions. However, as shown in the figure,

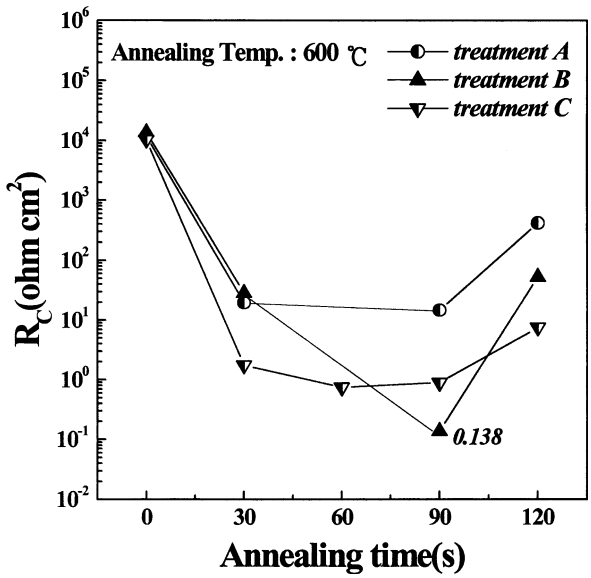

Fig. 4. ITO contacts resistivities as a function of sample treatment and annealing time at 600°C in a N_2 RTA system.

500°C of annealing temperature appears to be not enough for the formation of low contact resistance. Also, ITO contact formed after the sample treatment A showed the highest contact resistivity compared to other treatments.

Fig. 3 shows the effects of substrate treatment A and C and annealing time on ITO contact resistivity on p-GaN at 700°C of annealing time. Other conditions were the same as those shown in Fig. 2. As shown in the figure, the contact resistivity was also decreased with the increase of annealing time similar to the results shown in Fig. 1, however, the contact resistivity showed a minimum at 60 s of annealing time for both of the sample treatments A and C. The further increase of annealing time increased the contact resistivity slightly for both treatments. Also, similar to the case shown in Fig. 2, ITO contact formed after the sample treatment A showed higher contact resistivity than that formed after the sample treatment C. The lowest contact resistivities for the treatment A and C were 1.36 and 3.46×10^{-1} Ωcm^2, respectively. The higher contact resistivity by the sample treatment A compared to that by the sample treatment C is possibly related to the remaining oxide after the treatment A because HNO_3 in HCl/HNO_3 is an oxidizer, therefore, there is a possibility of forming a thin layer of Ga_xO_y which was known to increase the contact resistivity to p-GaN on the treated p-GaN surface before ITO deposition. Slightly high contact resistivity before the annealing for the sample treatment A may support this possibility.

When ITO contacts were annealed at 600°C as a function of annealing time, the contact resistivities also showed a minimum from 60 to 90 s for all of the sample

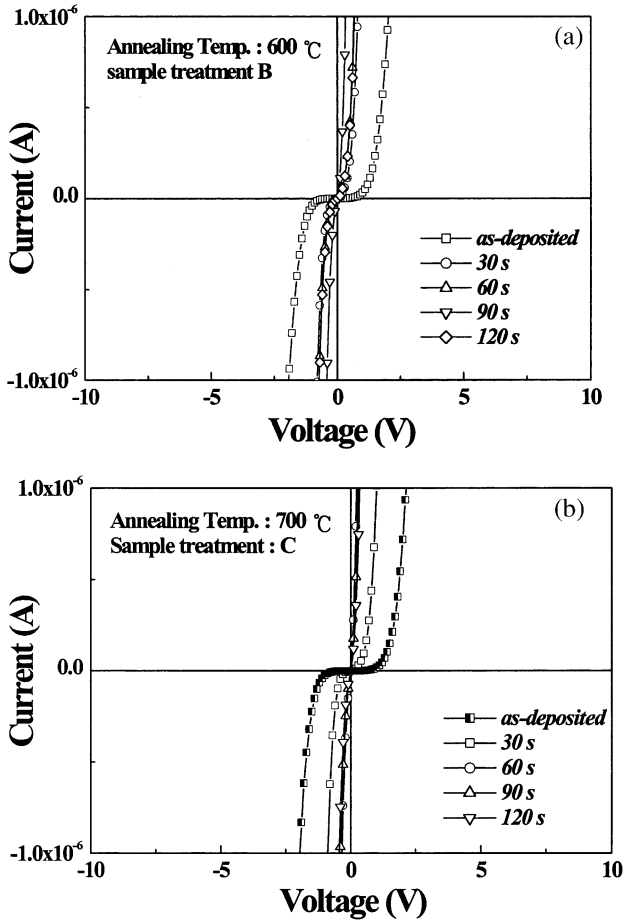

Fig. 5. (a) *I–V* characteristics of the ITO contact as a function of annealing time at 600°C for the sample treatment B. (b) (a) *I–V* characteristics of ITO contact as a function of annealing time at 700°C for the sample treatment C.

treatment conditions as shown in Fig. 4. In the case of the sample treatment B, the lowest contact resistivity of 1.38×10^{-1} Ω cm^2 could be obtained. Also, the ITO contact resistivities in the range of 10^{-1} Ω cm^2 could be obtained from 60 to 90 s of annealing for the sample treatment C. The lowest contact resistivity for the sample treatment B is not well understood, however, the low contact resistivities for the sample treatment C appears to be related to the effect of KOH in removing the gallium oxide formed during the previous step and in increasing surface area by roughening the surface.

Fig. 5a,b shows the *I–V* characteristics of ITO contact as a function of annealing time at 600°C for the sample treatment B (a) and those as a function of annealing time at 700°C for the sample treatment C (b). The *I–V* characteristics were measured between the ITO contacts with 20°C of interspacing. As shown in the figures, with the increase of annealing time at a given annealing temperature, the threshold voltage of the Schottky contact was decreased until the minimum contact resistivities were obtained and the further increase of annealing time increased the threshold voltage increase. Because the threshold voltage of the Schottky contact is related to the barrier properties of the contact, the minimum contact resistivities obtained appear to be related to the barrier height and width of the interfacial layer formed during the annealing and the specific sample treatment process.

Fig. 6 shows the depth profiles of Auger electron spectroscopy (AES) after 60 s of annealing at 600°C for the sample treatment A (a) and C (b). As a reference, the depth profiles of the as-deposited ITO after the each sample treatments were also included. Both figures show the diffusion of In, Sn and O into GaN and the diffusion of Ga into ITO after the annealing. It is supposed that, during the contact annealing, gallium atoms diffuse out from the GaN substrate to the ITO contact and create gallium vacancies and indium atoms diffuse from the ITO contact to gallium vacancy sites in addition to the diffusion of Sn and O to GaN, therefore, forming a mixed interfacial layer composed of $In_xGa_{1-x}N$, $In_xGa_yO_z$, etc., at the ITO/GaN interface. Also, it is possible that this mixed interfacial layer and created gallium vacancies could reduce the barrier height and decrease the sheet resistance of the substrate and the atomic concentration variations of ITO at the interface

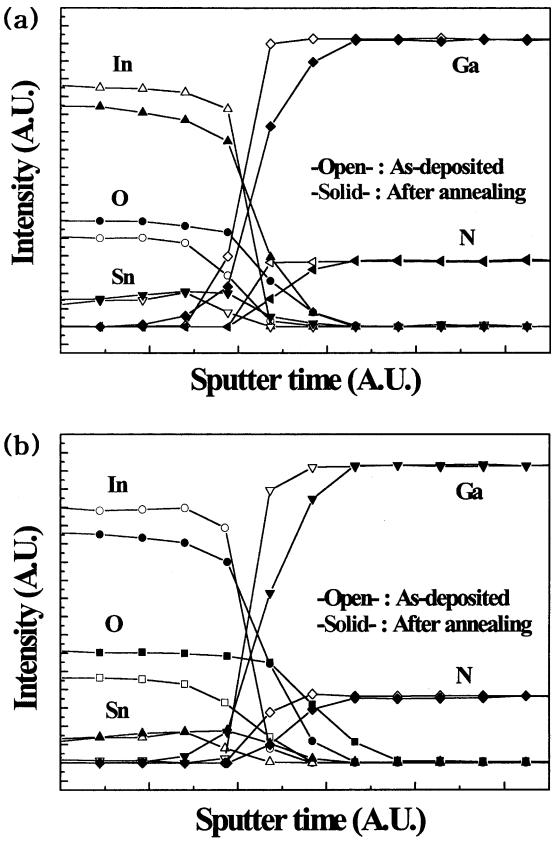

Fig. 6. AES depth profile of ITO films for the sample treatment A and C at 600°C for 90 s.

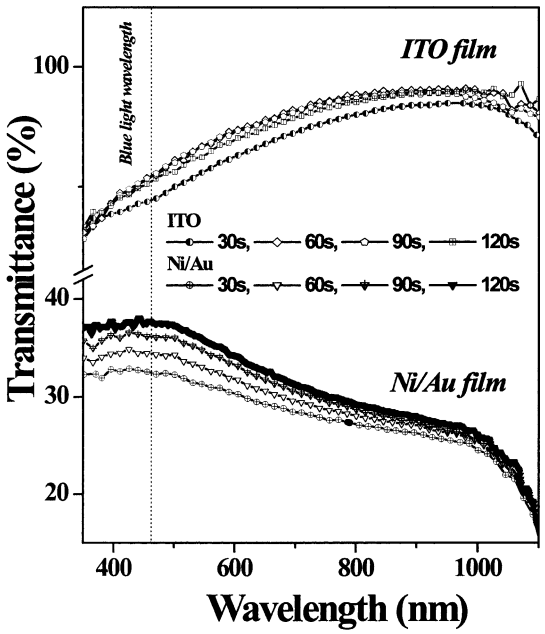

Fig. 7. Optical transmittance of the electron beam evaporated ITO and Ni/Au films with annealing time at 600°C. The thicknesses of ITO and Ni/Au films were 100 and 50:50 nm, respectively.

could also change the work function of the ITO near the interfacial layer [9,10]. Actually, it has been reported that the work function of $InGaO_3$ is approximately 5.4 eV [11], which is located between the work functions of p-GaN and ITO. However, the excessive intermixing of the materials at the ITO/GaN interface due to the excessive annealing will increase the barrier width, therefore, increasing the contact resistivity [12,13]. If the depth profile of the sample treatment A is compared to that of the sample treatment C after the annealing, the sample treatment C appears to be intermixed more than that of sample treatment A possibly due to the effect of formation of the rough surface by KOH during the treatment. Therefore, low contact resistance for the sample treatment A might be related to the increase in the area of the interfacial layer. The exact reason for the low contact resistivity for the microstructural change of the interlayer with the specific sample treatment and annealing condition needs more investigation and is currently under study.

Fig. 7 shows the optical transmittance of the evaporated ITO film on corning glass with increasing annealing time at 600°C in N_2. The measured optical transmittance of ITO film increased with the increase of annealing time up to 120 s and showed above 90% at 420 nm (blue) for the annealing time more than 90 s. The further increase of annealing time more than 120 s did not show any noticeable change in the transmittance. As a comparison, 50 nm Ni/50 nm Au, which is typically used for the ohmic contact to p-GaN, was deposited on corning glass and its transmittance was measured as a function of annealing time at 600°C. As shown in the figure, the transmittance of Ni/Au was generally less than 40%. The sheet resistance (R_S) of the ITO films deposited on corning glass was measured before and after the annealing at 600°C for 90 s, and the results showed the decrease of sheet resistance from several kΩ/□ before the annealing to 40–50 Ω/□ after the annealing in addition to the increase of optical transmittance with the annealing.

4. Conclusion

Electrical properties of ITO contact on p-GaN have been investigated as a function of different surface treatments to p-GaN, annealing temperature, and annealing time. The contact resistance initially decreased with the increase of annealing time and showed a minimum contact resistance at a certain annealing time and temperature. Also, the surface treatment before ITO deposition affected the contact resistance.

ITO contact resistivities in the range of low 10^{-1} Ω cm^2 could be obtained for certain conditions such as the surface treatment B (Acetone + Alcohol + HCl + 3HCl:HNO_3 + $(NH_4)_2S$) followed by the annealing at 600°C for 90 s and the surface treatment C (Acetone + Alcohol + HCl + 3HCl:HNO_3 + KOH + $(NH_4)_2S$) followed by the annealing at 700°C for 60 s, etc. The *I–V* characteristic of the deposited ITO contact was initially Schottky contact, however, at the optimized annealing conditions, the *I–V* curve showed a near-ohmic behavior possibly due to the formation of a mixed interface layer. Optical transmittance of the 100 nm ITO contact annealed at 600°C for more than 90 s was higher than 90% while that of 50 nm Ni/50 nm Au, typically used for the contact on p-GaN, is lower than 40%. Therefore, it is believed that if the ITO contact to p-GaN is formed after a proper surface treatment followed by adequate annealing, the ITO contact could be applicable as a transparent contact to p-GaN.

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References

[1] J.M. Delucca, H.S. Venugopalan, S.E. Mohney, R.F. Jr. Karlicek, Appl. Phys. Lett. 73 (23) (1998) 3402.
[2] J.S. Jang, I.S. Chang, H.K. Kim, T.Y. Seong, S. Lee, S.J. Park, Appl. Phys. Lett. 74 (1) (1999) 70.
[3] M. Suzuki, T. Arai, T. Kawakami, S. Kobayashi, S. Fujita, Y. Koide, Y. Taga, M. Murakami, J. Appl. Phys. 86 (9) (1999) 5079.
[4] T. Maragalith, O. Buchinsky, D.A. Cohen, A.C. Abare, M. Hansen, S.P. DenBaars, L.A. Coldren, Appl. Phys. Lett. 74 (26) (1999) 3930.

[5] J.W. Bae, H.J. Kim, J.S. Kim, N.E. Lee, G.Y. Yeom, Vacuum 56 (2000) 77.
[6] D.A. Stocker, E.F. Schubert, K.S. Boutros, J.M. Redwing, MRS Internet J. Nitride Semicond. Res. 4S1 (1999) G7.
[7] J.L. Lee, J.K. Kim, J.W. Lee, Y.J. Park, T.I. Kim, Solid State Electron. 43 (1999) 435.
[8] X.A. Cao, S.J. Pearton, G. Dang, A.P. Zhang, F. Ren, J.M. Van Hove, Appl. Phys. Lett. 75 (26) (1999) 4130.
[9] Y. Park, V. Choong, Y. Gao, B.H. Hsieh, C.W. Tang, Appl. Phys. Lett. 68 (19) (1996) 2699.
[10] C.-C. Chen, K.-L. Hsieh, G.-C. Chi, C.-C. Chuo, J.-I. Chyi, C.-A. Chang, J. Appl. Phys. 89 (10) (2001) 5465.
[11] T. Minami, T. Miyaya, T. Yamamoto, Surf. Coat. Technol. 108 /109 (1998) 583.
[12] Q.Z. Liu, S.S. Lau, Solid State Electron. 42 (5) (1998) 677.
[13] L.J. Brillson, Contact to Semiconductors Fundamentals and Technology, Noyes publications, 1993.