Effect of Hydrogen Storage Materials on Ohmic Contact to p-GaN

Jun Cheol Bae, Dae-Woo Kim, Woo Jin Kim, Hong Koo Baik,
Sung-Man Lee*, Chang Hee Hong**
Thin Film Materials Lab., School of Materials Science & Engineering, Yonsei University, Seoul 120-749, Korea
*Department of Materials Science and Engineering, Kangwon National University, Chuncheon, Kangwon-Do 200-701, Korea
**Department of Semiconductor Science and Technology, Semiconductor Physics Center, Chonbuk National Univserity, Chonju 561-756, Korea

While GaN-based semiconductor materials have been used in commercial blue light-emitting diodes (LEDs)[1-3], development of blue or ultraviolet laser diodes (LDs) is still under way. Among many obstacles to manufacture LDs, one is lack of low-resistance ohmic contact materials for p-GaN. If contact resistance is high, device lifetimes cannot be long. Therefore, development of low-resistance ohmic contact materials for p-GaN is essential to manufacture LDs. The previous works to develop low-resistance ohmic contact materials for p-GaN are based on metals with high work function, but only contact resistance of $\sim 10^{-2}\,\Omega\mathrm{cm}^2$ have been obtained.[4,5] Many researches to reduce contact resistance for p-GaN have been extensively carried out, these are mainly divided into three parts. One is lowering the barrier height by surface treatment,[6,7] another is the increase of efficiency of Mg doping using metals that can getter hydrogen in p-GaN by annealing[8,9], and the third is producing heavily doped surface layer by solid state dopant (ex. Mg, Zn).[10,11] It has been well known that doping concentration is restricted below $10^{18}\,\mathrm{cm}^{-3}$ due to Mg-H complexes, therefore if these complexes are effectively broken using a material that has the strong bonding strength with hydrogen, electrical properties are improved by the increase of hole concentration. In this study, we used hydrogen storage material, Mg_2Ni and TiNi as the ohmic contact materials to break the Mg-H complexes, and investigated the relationship between the formation of hydrogen storage materials and the electrical properties.

Mg-doped p-type GaN epi-layer was grown by metalorganic chemical vapor deposition (MOCVD) on sapphire substrates using a thin GaN buffer layer. And its thickness is 2.5 ㎛. The hole concentration of the p-type GaN epi-layer was $6.8\times10^{16}\,\mathrm{cm}^{-3}$, hole mobility was $14.9\,\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{sec}$, and the resistivity of the p-type GaN epi-layer was $6.8\,\Omega\mathrm{cm}$. Native oxide layer was removed using aqua regia (HCl: HNO_3 =3:1) for 10 min. In order to investigate whether ohmic contact was obtained by using hydrogen storage materials, Ni(300Å)/Mg(300Å) and Ti(480Å)/Ni(300Å) were deposited on p-GaN. After metal layers were deposited, annealing was carried out at 400, 500, and 600℃ for 30sec in a flowing N_2 atmosphere. The electrical property of this contact was measured using HP 4145B at room temperature before and after annealing. The inter-diffusion during annealing was evaluated by Auger depth profile. X-ray diffraction was used to identify the phase evolution of Ni/Mg/p-GaN and Ti/Ni/p-GaN as a function of annealing temperature.

In order to examine the ohmic characteristics of Ni/Mg and Ti/Ni contact systems, the I-V measurements were carried out before and after annealing at various temperatures for 30sec and shown fig. 1. In as-deposited samples, both contact systems showed non-ohmic behavior, and it might be related to the high barrier height formed at the metal/p-GaN interface and the native oxide of p-GaN that was not removed clearly by aqua regia treatm ent. In Ni/Mg/p-GaN contact system, perfect ohmic characteristics was obtained after annealing at 400℃. However, after annealing at 500℃, I-V curves were degraded. These results were related to the phase ev olution occurred in Ni/Mg contact system during annealing, which was confirmed by Auger depth profile and X-ray diffraction. In Ti/Ni/p-GaN contact system, after annealing at 500℃, nearly ohmic behavior was obtained, and it was related to the formation of TiNi phase. The formation of TiNi by annealing at 500 was evidenced by X-ray diffraction pattern. Auger depth profile and X-ray diffraction were carried out to investigate interfacial reaction of Ni/Mg contact system, and shown fig. 2. In Auger depth profile of the as-deposited sample, the intermixing between Ni and Mg seemed to occur, however, kinetic energies of Ni and Mg showed both Ni and Mg were in pure metallic states. Thus, Ni and Mg were deposited in the form of layer-by-layer structure, and it was also confirmed by Auger depth profile of Ni(300Å)/Mg(1300Å)p-GaN, which showed no intermixing was occurred between Ni and Mg. After 400℃, Mg_2Ni was formed by the reaction between Ni and Mg, and remnant Ni was also observed. Therefore, there are two possible ohmic contact mechanisms. One is the Ni/p-GaN contact[12], and the other is Mg_2Ni/p-GaN contact. To investigate whether ohmic contact resulted from the Ni/p-GaN contact, Ni(1000Å) was deposited on p-GaN, and then annealed at 400℃ for 30sec. However, ohmic contact was not formed. In addition, considered that Mg_2Ni is well-know hydrogen storage material that has high hydrogen-storage capacity (3.3wt%) and can absorb hydrogen above 300°C,[13] it is clear that ohmic behavior of Ni/Mg/p-GaN contact system after annealing at 400°C resulted from the formation of Mg_2Ni/p-GaN interface. After annealing at 500°C and 600°C, I-V curve was a little degraded that might results from the decomposition of Mg_2Ni layer and the formation of $MgNi_2$ and MgO layers. M. Y. Song reported that oxygen, which existed in ambient, reacted with Mg_2Ni to form MgO and to segregate Ni: $Mg_2Ni + O_2 \rightarrow 2MgO + Ni$. The segregated Ni reacted with Mg_2Ni to form $MgNi_2$: $Mg_2Ni + 3Ni \rightarrow 2MgNi_2$. These two reactions decreased hydrogen-storage capacity of Mg_2Ni as the hydriding-dehydriding cycles increased. It indicated that I-V characteristics might be degraded by the decomposition of Mg_2Ni and the formation of $MgNi_2$. In Ti/Ni contact system, after annealing at 500°C, TiNi was observed by X-ray diffraction. TiNi is also hydrogen storage material that absorbs hydrogen starting at 500°C.[14] In other words, the formation of hydrogen storage material, TiNi was responsible for the improvement of electrical property of Ti/Ni/p-GaN contact system.

Ni/Mg and Ti/Ni contact systems showed ohmic behavior after annealing at 400°C and 500°C, respectively. From the results of materials reactions, ohmic characteristics resulted from the formation of hydrogen storage materials that have high hydrogen-storage capacity and absorbs hydrogen above 300°C.

REFERENCES

1. Dae-Woo Kim, Hong Koo Baik, Cha Yeon Kim, Sung Woo Kim, and Chang Hee Hong, Mat. Res. Symp. Proc., **482**, 1083 (1998)
2. C.Y. Kim, S.-W. Kim, C.H. Hong, D.-W. Kim, H.-K. Baik, and C.N. Whang, J. Crystal Growth, **189/190**, 720 (1998)
3. S. Nakamura and G. Fahsol, *The Blue Laser Diodes* (Springer, Berlin, 1997), Chap. 2
4. T. Mori, T. Kozawa, T. Ohwaki, Y. Yaga, S. Nagai, S. Yamasaki, S. Asami, N. Shibata, and M. Koike, Appl. Phys. Lett., **69**, 3537 (1996)
5. J. S. Jang, K. h. Park, H. K. Jang, H. G. Kim, and S. J. Park, J. Vac. Sci. Technol. B., **16**, 3105 (1998)
6. Jong Kyu Kim, Jong-Lam Lee, Jae Won Lee, Hyun Eoi Shin, Yong Jo Park, and Taeil Kim, Appl. Phys. Lett., **73**, 2053 (1998)
7. Jong-Lam Lee, Jong Kyu Kim, Jae Won Lee, Yong Jo Park, and Taeil Kim, Solid-State Electronics, **43**, 435 (1999)
8. Masaaki Suzuki, T. Kawakami, T. Arai, S. Kobayashi, and Yasuo Koide, Appl. Phys. Lett., **74**, 275 (1999)
9. Yasuo Koide, T. Maeda, T. Kawakami, S. Fujita, T. Uemura, N. Shibata, and Masanori Murakami, J. Electron. Mat., **28**, 341 (1999)
10. L. L. Smith, R. F. Davis, M. J. Kim, R. W. Carpenter, and Y. Huang, J. Mater. Res., **12**, 2249 (1997)
11. Doo-Hyeb Youn, Maosheng Hao, Hisao Sat, Tomoya Sugahara, Yoshiki Naoi, and Shiro Sakai, Jpn. J. Appl. Phys., **37**, 1768 (1998)
12. Jong Kyu Kim and Jong-Lam Lee, Jae Won Lee, Yong Jo Park, and Taeil Kim, J. Vac. Sci. Tech. B, **17**, 2675 (1999)
13. Jung Hoon Woo and Kyung Sub Lee, J. Electrochem. Soc., **146**, 819 (1999)
14. V.N. Fadeev and V.A. Syasin, Inorg. Mater., **32**, 1495 (1996)

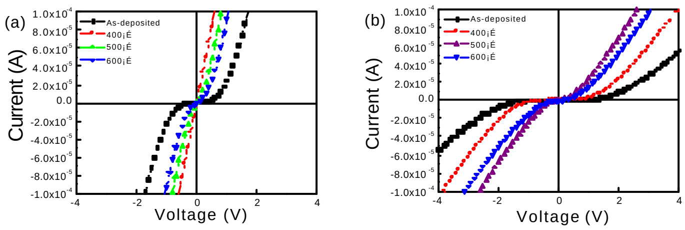

Fig. 1 I-V characteristics of (a) the Ni/Mg metallization and (b) the Ti/Ni metallization on p-GaN before and after annealing at various temperatures.

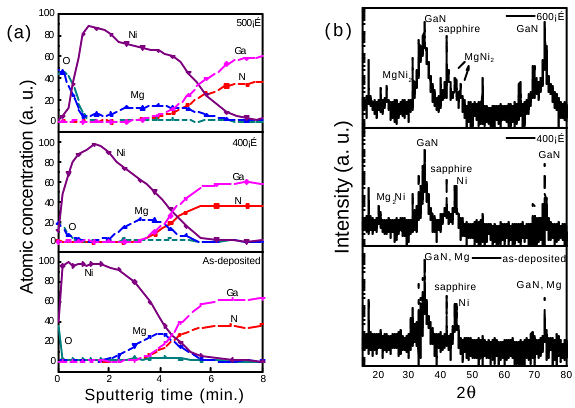

Fig. 2 (a) Auger depth profile and (b) X-ray diffraction patterns of Ni/Mg/p-GaN contact system before and after annealing.