OHMIC CONTACTS TO p–GaN USING Au/Ni–Zn–O METALLIZATION

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We have studied the electrical properties and depth concentration profiles of Au/Ni-Zn-O/p-GaN and Au/Ni-Zn/p-GaN, thus of structures containing zinc as a p-type dopant utilized to increase the concentration of free charge carriers in the subsurface region of GaN and to gain a low-resistance ohmic contact. The layers were deposited on p-GaN by DC reactive magnetron sputtering. The prepared contact structures were annealed in N_2, structure Au/Ni-Zn/p-GaN also in O_2. The contact structures containing zinc exhibited lower values of contact resistivity in comparison with those without zinc. It was also found that the values of contact resistivity for both Au/Ni-Zn-O/p-GaN and Au/Ni-Zn/p-GaN were the same, thus it was not affected by the presence of a small content of oxygen (< 0.2 at%) in the working atmosphere during the deposition of layers. Similarly, various gaseous ambients (N_2 or a mixture of $N_2 + O_2$) during subsequent annealing of the contacts had no observable influence upon the magnitude of the contact resistivity. In our opinion the ohmic nature of the Au/Ni-Zn-O/p-GaN and Au/Ni-Zn/p-GaN contacts is related to a reconstruction of the contacts to a sequence metal/p-NiO/p-GaN due to annealing in nitrogen or in a mixture of oxygen and nitrogen and the ohmic properties of the contacts are predetermined by creating a thin NiO oxide layer on the metal/p-GaN interface. We believe that the lower values of the contact resistance in Au/Ni-Zn-O/p-GaN and Au/Ni-Zn/p-GaN contacts than in structure Au/Ni-O/p-GaN are caused by an enhanced hole concentration in the surface region of p-GaN due to zinc diffusion from the zinc-doped contact layer.

K e y w o r d s: p-GaN, Au/Ni-Zn-O/p-GaN contact structure, AES depth profiling, low resistance ohmic contact

1 INTRODUCTION

In recent years, much attention has been paid to semiconductor compounds based on gallium nitride used as short wavelength light emitting materials. For efficient charge transport such devices require good ohmic contacts with low resistivity. Whereas such contacts are easily prepared on n-type GaN, *eg*, by using metallization structures based on Ti/Al/Mi/Au [1], contacts to p-type GaN still pose an open problem. The reason is the low doping of p-GaN attainable by standard techniques, which hinders reaching a satisfactorily high hole concentration ($> 10^{18}$cm^3) [2].

Various materials and technologies have been used to fabricate ohmic contacts to p-type GaN, for instance Au, Ni, Ti, Pd, Pt, Au/Ni, Au/Pt, Au/Pd, Au/Cr, Cu/Ni, Au/Mg/Au, Au/Cr/Ni, Au/Ni/Pt, Au/Pt/Ni, Au/Pt/Ti, Au/Pt/Pd. Numerous procedures have been used to improve the ohmic properties of the contacts to p-GaN by increasing the charge carrier concentration in the surface region of p-GaN by means of group II dopants incorporated into the metallization layer [3–8]. For improving the optical transparency of the contacts, metallization structures based on ZnO have been used. From among the contact structures on p-GaN, the most advantageous appeared to be be composition Au/Ni/p-GaN, [9-18], because of its relatively good values of the contact resistance and good optical transparency. On annealing the contact in oxygen ambient, reduction of the contact resistance has been reported as explained by several models, see Ho *et al* [9,10], Koide *et al* [11] and Jang *et al* [14].

Promising results have been reached while examine the effect of a NiO_x layer with a low concentration of oxygen upon the electrical properties of ohmic contacts Au/NiO$_x$/p-GaN [19]. It was found that a low-resistance ohmic contact is provided by Au/NiO$_x$ layers deposited by reactive magnetron sputtering and annealed not only in oxygen but also in nitrogen, in the latter case the results are even better. Both annealing modes lead to a reconstruction of the initially deposited contact structure into a metal/p-NiO/p-GaN structure. The ohmic nature of these contacts is predetermined by formation of a thin oxide layer (NiO) at the metal/p-GaN interface. Preliminary results had also shown that Ni-Mg-O layers with a low concentration of oxygen enriched in Mg deposited on p-GaN by DC magnetron sputtering had, after annealing in nitrogen, an ohmic nature and a lower value of the contact resistivity [20] in comparison with an identical metallization structure without addition of the mentioned group II element. For this purpose, a layer of either Ni-Zn-O with a low content of oxygen or Ni-Zn was deposited on p-GaN by DC magnetron sputtering. In both cases zinc was used as a p-type dopant. The top Au layer

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Table 1. Samples, their preparation and contact resistivity

Sample	Oxygen content in the atmosphere during deposition of Ni-Zn-O (at.%)	Oxygen content in the atmosphere during deposition of Ni-O (at.%)	Contact annealing in N_2	Contact annealing in $N_2 + O_2$ mixture	Contact resistivity on annealing in N_2 (Ωcm^2)
S22	no oxygen			Yes	1.2×10^{-3}
S23	no oxygen		Yes		1.2×10^{-3}
S27	< 0.2		Yes		1.3×10^{-3}
L7		0.2			3.9×10^{-3}

was deposited in a similar way. The prepared structures were annealed in N_2, structure Au/Ni-Zn/p-GaN also in O_2. The contact resistance determined using the C-TLM method was correlated with the depth distribution of elements in the contact structures measured by Auger electron spectroscopy.

2 EXPERIMENTAL

GaN films were fabricated in AIXTRON 200 RF-S horizontal flow MOCVD reactor on (0001) sapphire substrates using the procedure of substrate nitridation, deposition of a low-temperature GaN nucleation layer at $540\,°C$ with subsequent annealing and, finally, growing a $1\,\mu$m thick GaN buffer at $1050\,°C$. Mg-δ doping was achieved by alternatively closing the trimethylgallium and opening the biscyclopentadienyl magnesium sources during the growth at $950\,°C$. The thickness of GaN:δ-Mg was around 800 nm. After annealing in N_2 atmosphere at $780\,°C$ for 15 minutes to activate the Mg, p-GaN layers were obtained with typical carrier concentrations around 7×10^{17}cm^{-3} and mobility around $10\,$cm^2/Vs.

To study the effect of the surface cleaning prior to lithography and contact metallisation, the samples were treated with buffered oxide etchant and irradiation by a UV lamp for 0 to 25 minutes.

The p-GaN layers were first sequentially ultrasonically treated for 5 minute in each step in acetone, isopropanol, DI water, and then they were dried with compressed N_2. Prior to lithography and contact metallization they were chemically etched by a buffered oxide etchant to remove the surface native oxide.

The circular transmission line method (CTLM) patterns to characterize ohmic contacts were photolithographically designed for measuring the contact resistivity. Metal thin films were deposited by dc magnetron sputtering. The $Ni_{90}Zn_{10}$ (20 nm) thin film with and without small content of oxygen was prepared by dc reactive magnetron sputtering from a Ni target containing 10 at% of Zn in a mixture of oxygen and argon or in pure argon, respectively. The distance between the target and the substrate was approximately 75 mm. A sputtering power of 600 W was used. Both argon inert flow and oxygen reactive flow were controlled by mass flow controllers. The total gas pressure was kept at 0.5 Pa.

After the deposition the samples were subsequently annealed in a rapid thermal annealing furnace at a temperature of $500\,°C$ for 2 minutes in N_2 or in a mixture of $N_2 + O_2$. I-V measurements were performed on a Keithley 237 parameter analyzer equipped with an MDC Duo Chuck by applying a voltage ramp from -10 V to $+10$ V and measuring the respective current. From the slope of the I–V curves, the total resistance was determined. The contact resistivity was determined using the model of Marlow and Das.

AES depth profiling was carried out in a Varian Auger electron spectrometer equipped with a cylindrical mirror analyzer (CMA) and EX 05 VG ion gun. A primary electron beam was used with energy 3 keV and angle of incidence 20° with respect to the surface normal. Sputtering was achieved by scanned Ar$^+$ ion beams with energy 1 keV and angle of incidence 60° with respect to the surface normal. The energy resolution of the CMA was $\Delta E / E = 0.3\,\%$. Auger depth profiling employed the Auger peaks of Au (239 eV), Ni (848 eV), Zn (994 eV), Ga (1070 eV), N (385 eV), O (510 eV) and C (270 eV).

3 RESULTS

Table 1 summarizes the measured values of the contact resistances of structures Au/Ni-Zn-Ox/p-GaN and Au/Ni-Zn/p-GaN containing zinc as a p-type dopant and of the Au/Ni-O_x/p-GaN structure without this dopant. The contact structures containing zinc have lower values of the contact resistance than the contacts without zinc. The contact resistances of Au/Ni-Zn-O_x/p-GaN and Au/Ni-Zn/p-GaN are the same, thus they were virtually not affected by the small content of oxygen (< 0.2 at%) in the working atmosphere during deposition.

Similarly, the different gaseous ambient (N_2 or a mixture of N_2 and O_2) during annealing had no influence on the contact resistivity.

Figure 1a shows the AES depth profile of the as-deposited Au/Ni-Zn/p-GaN structure. The depth profiles of the Zn dopant and of oxygen exhibit pile-ups at the Au/Ni-Zn interface, oxygen is slightly piled up also at the Ni-Zn/p-GaN interface. Annealing in N_2 resulted in out-diffusion of part of Ni and Zn through the Au layer (Fig. 1b) and vice versa, in-diffusion of Au and O to the interface of the metallization layer with p-GaN. The gradient of diffused Zn increases towards the surface of the sample due to the presence of oxygen that enhances the
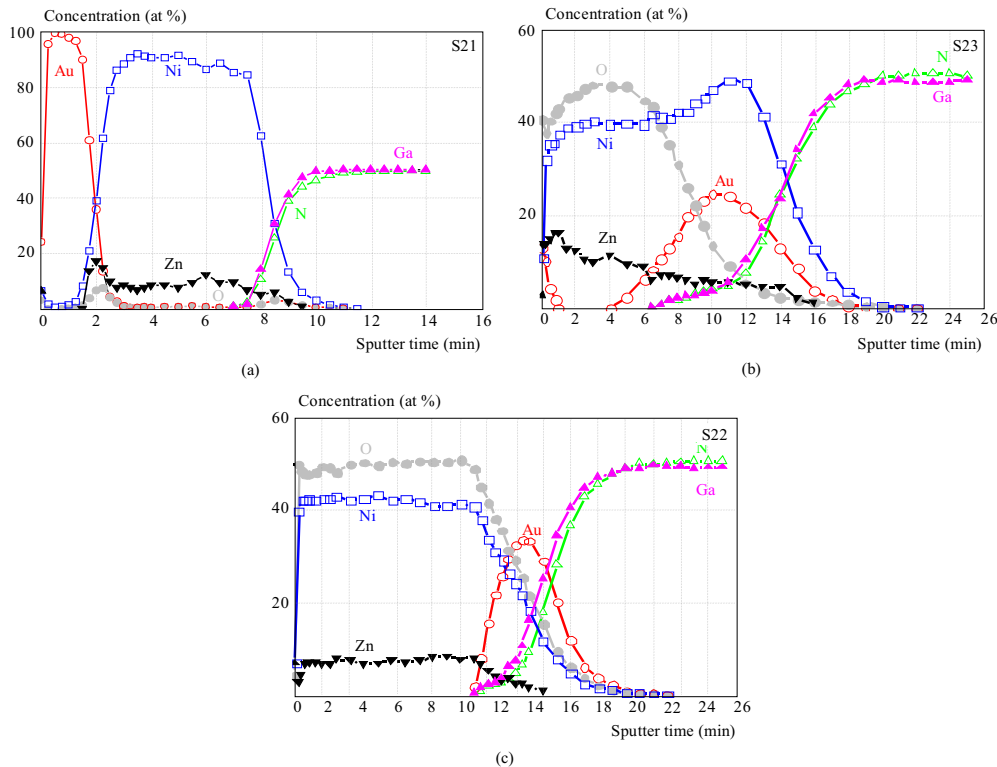
Fig. 1. AES depth profiles of Au/Ni-Zn/p-GaN contact structures: (a) – as deposited (sample S21), (b)– after annealing in N$_2$ at 500 °C for 2 minutes (sample S23) , (c) – after annealing in the mixture of N$_2$ and O_2 at 500 °C for 2 minutes (sample S22)
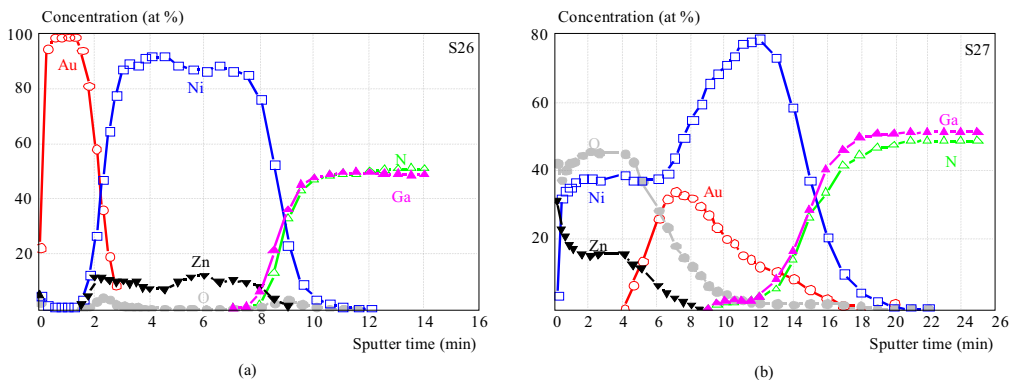
Fig. 2. AES depth profiles of Au/Ni-Zn-O/p-GaN contact structures (sample S26) in which Ni-Zn-O was deposited at 0.2 at% of oxygen in the working atmosphere: (a)– as deposited (sample S26), (b)– after annealing in N2 at 500 °C for 2 minutes (sample S27).

diffusion of zinc and brings about its oxidation. Oxygen diffused through the whole metallic layer down to GaN and oxidized the components of the layer, Ni and Zn. In Fig. 1c one can see that annealing of the identical Au/Ni-Zn/p-GaN structure in a mixture of oxygen and nitrogen resulted in complete out-diffusion of nickel and zinc, their oxidation from the oxygen in the gaseous ambient during annealing. Zinc is homogeneously distributed in the NiO layer and similarly like NiO it is in direct contact with GaN.

Figure 2 shows AES depth profiles of the Au/Ni-Zn-O/ p-GaN structure in which Ni-Zn-O was deposited at low content of oxygen in the working atmosphere (0.2 at%). Annealing in N$_2$ had a similar effect as in the contact structures Au/Ni-Zn prepared without adding oxygen into the atmosphere during deposition. The concentration profiles of Ni, O and Zn prove that in-diffused oxy-

gen supports out-diffusion of Zn and Ni and, at the same time, it causes their oxidation. In-diffused oxygen reached as far as the interface of the metallic layer with GaN.

Comparison of the concentration depth profiles of Au/Ni-Zn-O/p-GaN and Au/Ni-Zn /p-GaN contacts annealed in nitrogen with the profile of Au/Ni-Zn /p-GaN annealed in oxygen reveals that annealing in nitrogen atmosphere resulted in only partial diffusion of the components in the contact structures. The kinetics of the diffusion process indicates that a longer time of annealing would lead to similar diffusion-broadening of the components as in the contacts annealed in the mixture of oxygen and nitrogen. The measured, almost identical values of contact resistances of the structures annealed in the two gaseous ambients indicate that creation of an ohmic contact is not preconditioned by full mixing of the constituents of the metallic layers. Similarly like in the case of

Au/Ni-O/p-GaN layers [19], annealing results in recrystallization of the metallization layer. We assume that indiffused oxygen as well as oxygen embedded during deposition of the Ni-Zn-O metallic layer are bonded with part of Ni to give rise to NiO and the initial Ni-Zn-(O) layer is transformed by annealing into a mixture of Ni, NiO and ZnO crystals. In this way, the observed distribution of the components in the contact structure as a consequence of annealing may be explained by a polycrystalline structure of the contact layer composed of crystallites of Au, Ni, ZnO and NiO. The larger Au and Ni grains are in direct contact to p-GaN via tiny grains of NiO and ZnO.

In the study of the Au/Ni-O/p-GaN structure [14] it was found that annealing in nitrogen or in a mixture of oxygen and nitrogen caused reconstruction of the system into a metal/p-NiO/p-GaN sequence and that its ohmic properties were predetermined by creating a thin NiO oxide layer on the metal/p-GaN interface. In our opinion the ohmic nature of the Au/Ni-Zn-O/p-GaN contact structure is related, similarly like in the case discussed above, by the existence of an identical contact scheme. We believe that the lower values of contact resistivity in Au/Ni-Zn-O/p-GaN and Au/Ni-Zn/p-GaN than in structure Au/Ni-O/p-GaN (Table 1) are caused by an enhanced hole concentration in the surface region of GaN, which is a consequence of zinc diffused from the zinc-doped contact layer.

4 CONCLUSIONS

We examined Au/Ni-Zn-O/p-GaN a Au/Ni-Zn/p-GaN contact structures with zinc as a p-type dopant utilized to increase the charge carrier concentration in the surface region of GaN and to gain a low-resistance ohmic contact. The layers were deposited on p-GaN by DC magnetron sputtering. The prepared structures were annealed in N_2, the Au/Ni-Zn/p-GaN structure also in O_2. It was observed that the contact structures containing zinc exhibited lower values of the contact resistance that structures without zinc. It was also shown that the values of contact resistance of Au/Ni-Zn-O/p-GaN and Au/Ni-Zn/p-GaN were identical, thus they were not affected by the presence of a small amount (< 0.2 at%) of oxygen in the working atmosphere during deposition. Similarly, various gaseous ambients (N_2 or $N_2 + O_2$ mixture) during subsequent annealing had no observable affect upon the value of the contact resistance.

In our opinion the ohmic nature of the Au/Ni-Zn-O/p-GaN contact structures is related to reconstruction of the contact schemes into metal/p-NiO/p-GaN sequence due to annealing in nitrogen or in the mixture of nitrogen and oxygen, and the ohmic properties of the contacts are predetermined by creating a thin NiO oxide layer on the metal/p-GaN interface. We suppose that the lower values of contact resistivity in Au/Ni-Zn-O/p-GaN and Au/Ni-Zn/p-GaN structures as compared with Au/Ni-O/p-GaN are caused by an increased hole concentration in the surface region of p-GaN due to zinc diffusion from the zinc-doped contact layer.

References

[1] FAN, Z. *et al* : Appl. Phys. Lett. **68** (1996), 1672.

[[2] MURAKAMI, M. *et al* : Crit. Rev. in Solid State and Mater. Sci. **23** (1998), 1.

[3] YOUN, D. H. *et al* : Jpn. J. Appl. Phys. Part 1, **37** (1998), 1768.

[4] CHEN, L. C. *et al* : Solid State Electron. **47** (2003), 1843.

[5] SONG, J. O. *et al* : Semicond. Sci. Technol. **19** (2004), 669.

[6] SONG J. O. *et al* : Appl. Phys. Lett. **83** (2004), 3513.

[7] SONG, J. O. *et al* : Appl. Phys. Lett. **84** (2004), 4663.

[8] CHAE, S. W. *et al* : J. Korean Phys. Soc. **49** (2006), 899.

[9] HO, J. K. *et al* : Appl. Phys. Lett. **74** (1999), 1275.

[10] HO, J. K. *et al* : J. Appl. Phys. **86** (1999), 4491.

[11] KOIDE, Y. *et al* : J. Electron. Mater. **28** (1999), 341.

[12] MISTELE, D. *et al* : J. Cryst. Growth **230** (2001), 564.

[13] CHEN, L. C. *et al* : J. Appl. Phys. **76** (2000), 3703.

[14] JANG, H. W. *et al* : J. Appl. Phys. **94** (2003), 1748.

[15] EENZEL, R. *et al* : Mater. Sci. Semicond. Process. **0** (2000), 1.

[16] PARK, M. R. *et al* : ETRI Journ. **24** (2002), 349.

[17] NARAYAN, J. *et al* : Appl. Phys. Lett. **81** (2002), 3978.

[18] WANG, S. H. *et al* : J. Appl. Phys. **91** (2002), 3711.

[19] LIDAY, J. *et al* : Appl. Surf. Sci. **253** (2007), 3174.

[20] LIDAY, J. *et al* : J. Electrical Engin. **61** (2010), 374.

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