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IMPROVING THE OHMIC PROPERTIES OF CONTACTS TO P–GAN BY ADDING P–TYPE DOPANTS INTO THE METALLIZATION LAYER

Jozef Liday [*] — **Peter Vogrinčič** [*] — **Andrej Vincze** [**] — **Juraj Breza** [*] — **Ivan Hotový** [*]

The work investigates an increase of the density of free charge carriers in the sub-surface region of p-GaN by adding p-type dopants into the Ni-O layer of an Au/Ni-O metallization structure. We have examined electrical properties and concentration depth profiles of contact structures Au/Ni-Mg-O/p-GaN and Au/Ni-Zn-O/p-GaN, thus with magnesium and zinc as p-type dopants. The metallization layers were deposited on p-GaN by DC reactive magnetron sputtering in an atmosphere with a low concentration of oxygen (0.2 at%). The contacts were annealed in N_2. We have found that the structures containing magnesium or zinc exhibit lower values of contact resistivity in comparison with otherwise identical contacts without Mg or Zn dopants. In our opinion, the lower values of contact resistivity of the structures containing of Mg or Zn are caused by an increased density of holes in the sub-surface region of p-GaN due to diffusion of Mg or Zn from the deposited doped contact layers.

K e y w o r d s: p-GaN, ohmic contact, contact resistivity, Au/Ni-Mg(Zn)-O/p-GaN contact structure, annealing, Auger electron spectra, secondary ion mass spectra

1 INTRODUCTION

Great attention has been paid to gallium nitride for its various electronic and optoelectronic applications. One of the factors limiting the performance of this material is the possibility to create a low-resistance ohmic contact to GaN. In particular contacts with p-GaN still present a big problem, because of difficult achieving of high charge carrier concentrations ($> 10^{18}\mathrm{cm}^{-3}$) [1]. From among a number of metallization schemes till used, the best contact structure to p-GaN seems to be the Au/Ni structure, namely because of the relatively good values of contact resistivity 10^{-4} to 10^{-6} $\Omega\mathrm{cm}^2$ and its optical transparency. It was found that oxidation of such a thin Ni/Au bilayer in air or in water vapour brings about a change of Ni into NiO, diffusion of Au into the interface and at the same time an improvement in the transparency of the metallization layer [2-9].

While studying the effect of the NiO_x layer with a low concentration of oxygen upon the electrical properties of ohmic contacts Au/NiO_x/p-GaN [10] it was found that a low-resistance ohmic contact was provided by Au/NiO_x layers deposited by reactive magnetron sputtering and annealed not only in oxygen but also in nitrogen. Preliminary results have also shown that Ni-Mg-O and Ni-Zn-O layers with a low concentration of oxygen deposited on p-GaN by DC magnetron sputtering have, after annealing in nitrogen, an ohmic nature and in comparison with an identical metallization structure without addition of the group II element Mg or Zn they have a lower value of contact resistivity [11].

This work investigates the increase of the density of free charge carriers in the surface region of p-GaN by adding a p-type dopant into the Ni-O layer of the metallization structure Au/Ni-O and explores other relationships explaining the reduction of the contact resistance of oxidized Ni/Au ohmic contacts on p-GaN. The contact resistivity measured by the circular transmission line method (CTLM) was correlated with the depth distribution of elements in the contact structure measured by Auger electron spectroscopy (AES) and time of flight secondary ion mass spectrometry (TOF-SIMS).

2 EXPERIMENTAL

In this work, 800 nm thick δ-Mg doped GaN layers were used as p-GaN layers that had been grown (MOCVD) on a $1\,\mu$m thick GaN buffer layer deposited on (0001) sapphire substrates. After annealing in N_2 at 780 °C for 15 minutes they had a typical carrier concentrations around $7 \times 10^{17}\mathrm{cm}^{-3}$ and mobility around 10 cm^2/Vs.

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

Circular transmission line method (CTLM) patterns needed to characterize ohmic contacts were photolithographically designed for the measurement of contact resistivity. Metal thin films were deposited by DC magnetron sputtering. $Ni_{0.92}Mg_{0.08}$ (20 nm) and $Ni_{0.90}Zn_{0.10}$ (20

Slovak University of Technology, Faculty of Electrical Engineering and Information Technology, Ilkovičova 3, 812 19 Bratislava, jozef.liday@stuba.sk, [**] International Laser Centre, Ilkovičova 3, 812 19 Bratislava, Slovakia

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nm) thin films with and without small contents of oxygen were prepared by DC reactive magnetron sputtering from a Ni target containing 8 at% of Mg or 10 at% of Zn in a mixture of oxygen and argon or in pure argon. The upper Au layer (20 nm) was also prepared by DC magnetron sputtering. 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 deposition, the samples were subsequently annealed in N_2 or air in a rapid thermal annealing furnace at a temperature of 500 °C for 2 minutes. The samples with Ni-Mg and Ni-Zn layers deposited in pure argon without any oxygen content and afterwards annealed in air or N_2 served as reference samples allowing to find the effect of the additional Mg or Zn dopant upon the contact resistivity. 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. The total resistance was determined from the slope of the $I - V$ curves. 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 °C with respect to the surface normal. Sputtering was achieved by scanned Ar^+ ion beams with energy 1 keV and angle of incidence 60 °C 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), Mg (1186), Zn (994 eV), Ga (1070 eV), N (385 eV), O (510 eV) and C (270 eV).

SIMS depth profiling was conducted in an Ion-TOF SIMS instrument. High energy Bi^+ ions were used as a probe. For depth profiling, the high energy pulsed primary source (25 keV, 1 pA) was combined with low energy sputter guns at 1 keV (Cs^+, O_2^+) with angle of incidence 45 °C with respect to the surface normal. The sputtering ion beam is scanned over a 300×300 μm^2 area, while the primary ion beam is within an area of 80×80 μm^2 in the center of the sputtered crater.

3 RESULTS

Table 1 summarizes the measured values of contact resistivity of structures Au/Ni-Mg-O/p-GaN and Au/Ni-Mg/p-GaN, Au/Ni-Zn-O/p-GaN and Au/Ni-Zn/p-GaN, thus both with and without magnesium or zinc used as p-dopants of the Au/Ni-O/p-GaN structure. The contact structures containing magnesium and zinc exhibit lower values of contact resistivity than the undoped contacts.

One can see that whilst the Au/Ni-Mg/p-GaN structure deposited without the presence of oxygen in the working atmosphere and subsequently annealed in N_2 does not exhibit good ohmic properties, structure Au/Ni-Mg-O/p-GaN in which the Ni-Mg was deposited in the presence of a low content of oxygen (0.2 at%) had an ohmic nature after annealing under identical conditions. At the same time, the value of contact resistivity is lower than in the case of the Au/Ni-O/p-GaN contact. The situation is slightly different in the case of structures containing zinc dopant. The contact resistivity of Au/Ni-Zn-O/p-GaN contacts with the Ni-Zn layer deposited in the presence of a low concentration of oxygen (0.2 at%) is the same as in the same structure deposited without oxygen in the working atmosphere. The reason is the high ability of zinc to getter oxygen, thus also residual oxygen present in the working atmosphere in the course of deposition. Similarly, various gas ambient (N_2, air) during subsequent annealing of the contacts had no observable impact upon the magnitude of contact resistivity.

Figures 1(a) and 1(b) display AES depth profiles of the as deposited Au/Ni-Mg-O/p-GaN structure and of the structure after its annealing in N_2, respectively, in which Ni-Mg-O was deposited at a low content of oxygen in the working atmosphere (0.2 at%). Annealing in N_2 resulted in out-diffusion of part of Ni, Mg and O through the Au layer and, conversely, diffusion of part of Au up

Table 1. Samples, their preparation and contact resistivity

Sample	oxygen content in the atmosphere during deposition of Ni-Mg-O (at%)	oxygen content in the atmosphere during deposition of Ni-Zn-O (at%)	oxygen content in the atmosphere during deposition of Ni-O (at%)	Contanct annealing in N_2	Contanct annealing in air	Contact resistivity (Ωcm^2)
L8	no oxygen			yes		4.7×10^{-2}
L11	0.2			yes		9.0×10^{-4}
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}

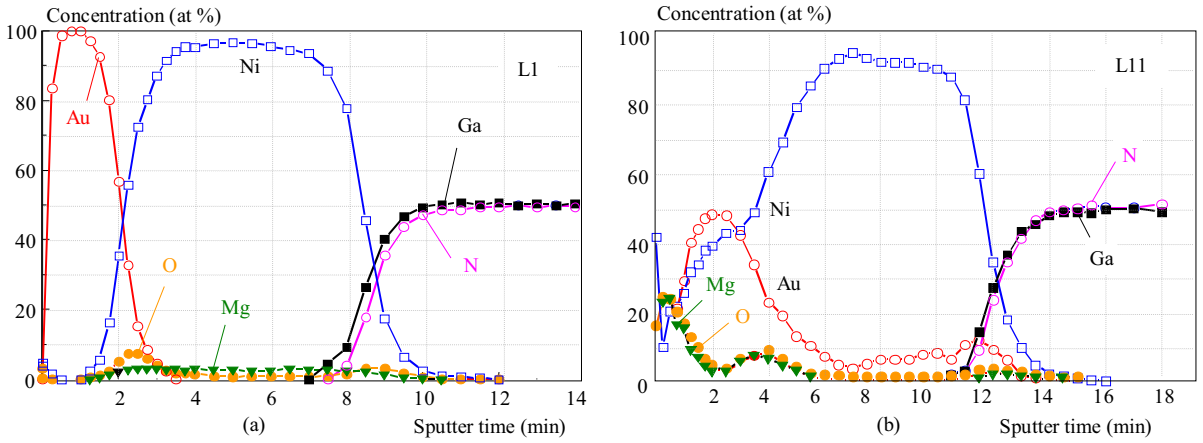

Fig. 1. AES depth profiles of Au/Ni-Mg-O/p-GaN contact structure. Ni-Mg-O was deposited in an atmosphere containing 0.2 at% of oxygen: (a) – as deposited, (b) – annealed in N_2 at 500 °C for 2 minutes

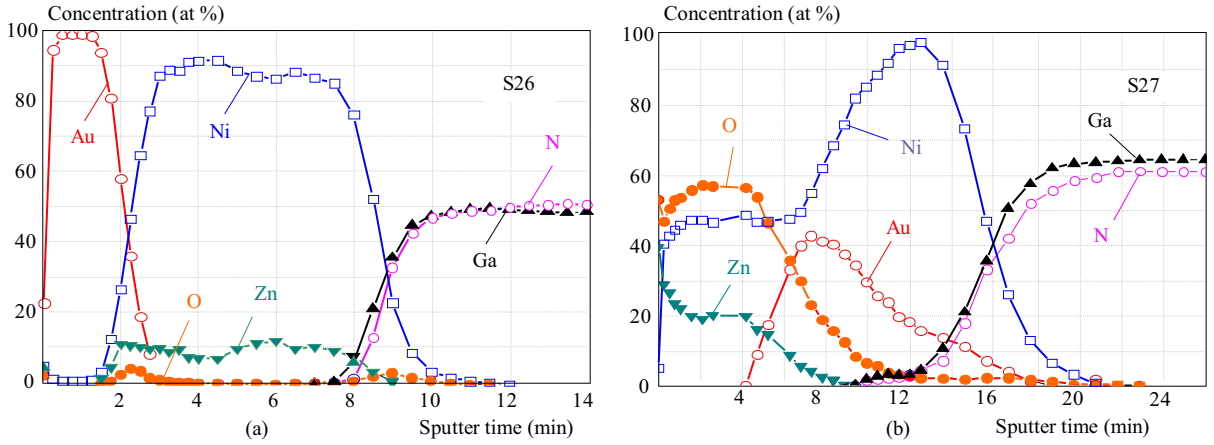

Fig. 2. AES depth profiles of Au/Ni-Zn-O/p-GaN contact structure. Ni-Zn-O was deposited in an atmosphere containing 0.2 at% of oxygen: (a) – as deposited, (b) – annealed in N_2 at 500 °C for 2 minutes

to the interface of the metallization layer with p-GaN. The depth distribution of Mg and O reveal that due to out-diffusion these elements were partially piled up in the vicinity of the Au/Ni-Mg-O interface. The almost identical concentrations and gradients of Mg and O in the contact structure point at the creation of MgO that precipitates mainly in the region of the initial interfaces and on the surface.

Figure 2(a) shows the AES depth profile of the as-deposited 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%). The depth profiles of Zn and of O exhibit pile-ups at the Au/Ni-Zn-O interface, oxygen is slightly piled up also at the Ni-Zn-O /p-GaN interface. Annealing in N_2 resulted in out-diffusion of part of Ni and Zn through the Au layer (Fig. 2(b)) 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 diffusion of zinc and brings about its oxidation. Oxygen diffused through the whole metallic layer down to GaN.

Comparison of the concentration depth profiles of Au/Ni-Zn-O/p-GaN contact annealed in nitrogen with an identical contact annealed in air (not shown here) 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 diffusion-broadening of the components as in the contacts annealed in the air. 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.

SIMS depth profiles of the same samples, namely Au/Ni-Mg-O/p-GaN and Au/Ni-Zn-O/p-GaN annealed in N_2 are presented in Figs. 3(a), (b) and Figs. 4(a), (b), respectively. The curves are in qualitative agreement with AES measurements. They reveal, however, also the distributions of elements with low concentrations. The depth profiles in Figs. 3(b) and 4(b) were measured by using oxygen ions as the primary sputter beam in SIMS measurements, whereby the yield of positive secondary ions of Ni, Ga, Mg and Zn was increased.

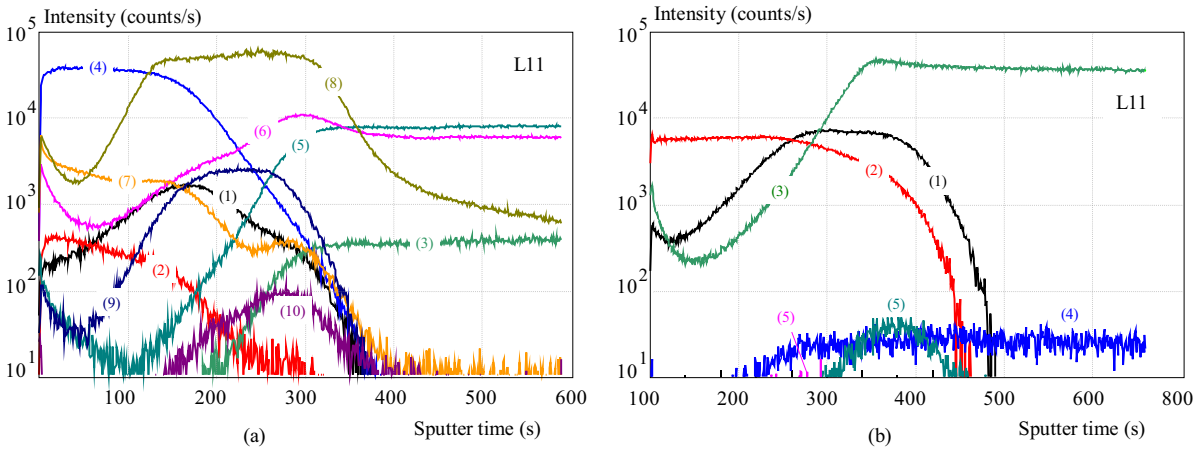

Fig. 3. SIMS depth profiles of Au/Ni-Mg-O/p-GaN contact structure of the same sample as in Fig. 1(b) — Ni-Mg-O deposited in an atmosphere containing 0.2 at% of oxygen; contact annealed in N_2 at 500 °C for 2 minutes:
(a) – negative secondary ions mass spectra obtained with Cs^+ primary ions; Legend: (1) – 39.97 MgO, (2) – 63.92 ^{64}Ni, (3) – 68.93 ^{69}Ga, (4) – 73.93 ^{58}NiO, (5) – 82.93 ^{69}GaN, (6) – 84.92 ^{69}GaO, (7) – 92.92 MgGa, (8) – 196.95 Au, (9) – 254.88 ^{58}NiAu, (10) – 281.84 GaAuO;
(b) – positive secondary ions mass spectra obtained with O_2^+ primary ions; Legend: (1) – 23.98 Mg, (2) – 57.94 ^{58}Ni, (3) – 68.93 ^{69}Ga, (4) – 82.93 ^{69}GaN, (5) – 92.92 MgGa, (6) – 254.88 ^{58}NiAu

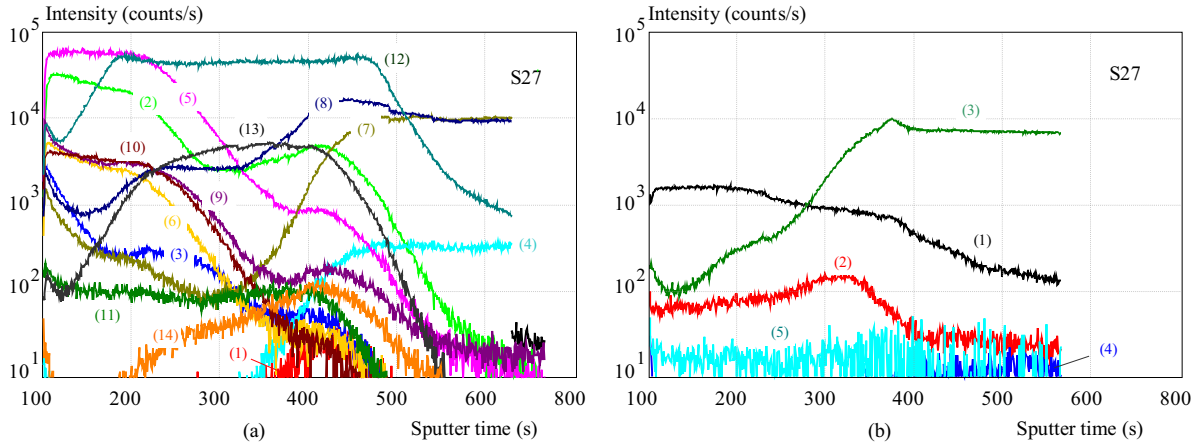

Fig. 4. SIMS depth profiles of Au/Ni-Zn-O/p-GaN contact structure of the same sample as in Fig. 2(b) — Ni-Zn-O deposited in an atmosphere containing 0.2 at% of oxygen; contact annealed in N_2 at 500 °C for 2 minutes:
(a) – negative secondary ions mass spectra obtained with Cs^+ primary ions; Legend: (1) – 39.98 MgO, (2) – 57.94 ^{58}Ni, (3) – 63.95 ^{64}Zn, (4) – 68.936 ^{69}Ga, (5) – 73.93 ^{58}NiO, (6) – 79.92 ^{64}ZnO, (7) – 82.93 ^{69}GaN, (8) – 84.92 ^{69}GaO, (9) – 92.92 MgGA, (10) – 93.93 ^{64}ZnON, (11) – 134.86 ^{64}Zn ^{71}Ga, (12) – 196.95 Au, (13) – 254.88 ^{58}NiAu, (14) – 281.87 GaAuO;
(b) – positive secondary ions mass spectra obtained with O_2^+ primary ions; Legend: (1) – 57.94 ^{58}Ni, (2) – 63.95 ^{64}Zn, (3) – 68.93 ^{69}Ga, (4) – 82.93 ^{69}GaN, (5) – 134.86 ^{64}Zn ^{71}Ga, (6) – 254.88 ^{58}NiAu

In Figure 3(a) one can see that the Au/Ni-Mg-O layer contains the Au-Ni composition detected in the whole metallic layer. During annealing in nitrogen, a portion of nickel and Mg dopant diffused through Au up to the top of the sample and oxidized giving rise to NiO and MgO. Part of the Ni-Mg-O layer, however, remained at its initial place between p-GaN and the layer of Au. Figures 3(a) and (b) prove the presence of Ga and GaO in the whole volume of the metallization layer. Oxygen supports diffusion of Ga from GaN, thus creation of acceptor-like Ga vacancies below the contact hereby lowering of the Fermi level. In the depth profiles in Fig. 3(a) using caesium ions as a sputter medium, Ga is detected also in the Mg-Ga composition and at the metal/p-GaN interface also in the form of AuGaO.

SIMS depth profiles of the Au/Ni-Zn-O/p-GaN contact annealed in N_2 presented in Figs. 4(a) and (b) show similar shapes of the dopant (in this case zinc) and of the other components as in the case of contact Au/Ni-Mg-O/p-GaN displayed in Figs. 3(a) and (b). In the depth profiles in Fig. 4(a), using caesium ions as a sputter medium, Ga is detected also in the ZnGa, MgGa and AuGaO compositions. The piled-up magnesium, detected in MgO at the layer/p-GaN interface, is in this case the dopant from the p-type layer of GaN. The SIMS profile of the Au/Ni-Zn-O/p-GaN contact shows also the ZnON composition.

In the study of the Au/Ni-O/p-GaN [10] it was found that annealing in nitrogen brought about its reconstruc-

tion into metal/p-NiO/p-GaN and the ohmic properties of the contacts were predetermined by creating a thin NiO oxide layer on the metal/p-GaN interface. AES and SIMS analyzes of Au/Ni-Mg-O/p-GaN and Au/Ni-Zn-O/p-GaN contact structures in this work revealed that due to annealing the initial layer transformed to a mixture of Ni, Au, Au-Ni, NiO, MgO in the first structure, and to a mixture of Ni, Au, Au-Ni, NiO, ZnO and ZnON compositions in the case of the second analyzed structure. Thus the observed distribution of the components as a consequence of annealing may be explained by the polycrystalline structure of the contact layer consisting of Au, Ni, NiO, MgO, ZnO and ZnON crystallites. Here, the NiO and ZnON grains are p-type semiconductors. The larger grains of Au and Ni are, also through the tiny grains, in contact to p-GaN and in the case of tiny grains NiO and ZnO the contact structure has the form of metal/p-NiO/p-GaN or metal/p-ZnO/p-GaN.

The ohmic nature of contact structures Au/Ni-Mg-O/p-GaN and Au/Ni-Zn-O/p-GaN is related to the existence of the contact scheme metal/p-NiO/p-GaN or metal/p-ZnON/p-GaN. The lower values of contact resistivity in Au/Ni-Mg-O/p-GaN and Au/Ni-Zn-O/p-GaN contacts in comparison with Au/Ni-O/p-GaN (see Tab. 1) are, in our opinion, caused by an increased concentration of holes in the sub-surface region of p-GaN, which is a consequence of dopant diffusion from the metallic contact layer doped by either magnesium or zinc.

4 CONCLUSION

We studied the contact structures Au/Ni-Mg-O/p-GaN and Au/Ni-Zn-O/p-GaN with magnesium or zinc used as p-type dopants intended to increase the density of free charge carriers in the surface region of GaN and to obtain 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. These structures were found to exhibit lower values of contact resistivity that otherwise identical contacts without addition of Mg or Zn. The ohmic nature of Au/Ni-Mg-O/p-GaN and Au/Ni-Zn-O/p-GaN structures is caused by their reconstruction into metal/p-NiO/p-GaN contacts, and in the case of the latter structure also into a metal/p-ZnON/p-GaN contact due to annealing in nitrogen. The ohmic properties of the contacts are predetermined by creating a thin p-NiO a p-ZnON oxide layer on the metal/p-GaN interface. The lower values of contact resistivity in Au/Ni-Mg-O/p-GaN and Au/Ni-Zn-O/p-GaN contacts in comparison with structure Au/Ni-O/p-GaN are, in our opinion, caused by an increased concentration of holes in the sub-surface region of p-GaN, which is a result of Mg and Zn diffusing from the contact layers doped by these dopants.

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Jozef Liday (Assoc Prof, PhD) graduated in solid state physics in 1968 and received his PhD in electronics and vacuum technology, both from STU, in 1985. His teaching and research activities include materials analysis, thin films and surface science.

Peter Vogrinčič (Ing), graduated in radio-electronics from the Slovak University of Technology in 1992. He is engaged in research, particularly in Auger analysis and depth profiling.

Andrej Vincze (PhD), graduated in Microelectronics from the Slovak University of Technology in Bratislava in 1999 and received his PhD degree from the STU at 2006. His work is focused to semiconductor and material analysis using SIMS at the International Laser Centre in Bratislava.

Ivan Hotový (Prof, DrSc) received his MSc in Electronics from the Slovak University of Technology in Bratislava in 1982 and his PhD in Electronics from the Slovak University of Technology in 1994. He is a scientific worker and lecturer at Department of Microelectronics, FEIT STU. His current research interests include the development of gas sensors, magnetron sputtering of metal oxide films and plasma etching of compound semiconductors.

Juraj Breza (Prof, PhD) born in Bratislava in 1951, graduated in solid state physics in 1974 and received his PhD in electronics and vacuum technology, both from STU, in 1982. Professor in electronics. His research and teaching activities include materials analysis, thin films, surface science and superconductor electronics.