

## OHMIC CONTACTS TO p-GaN BASED ON THE SINGLE-WALLED CARBON NANOTUBES

Jozef Liday\* — Peter Vogrinčič\* — Viliam Vretenár\*\* —  
Mário Kotlár\* — Marián Marton\* — Vlastimil Řeháček\*

We have designed and verified a new structure for ohmic contacts to p-GaN, mainly for applications in light emitting devices based on a layer of single-walled carbon nanotubes (SWCNT) and metallic layers of Cr and Au, namely in configuration Au/Cr/SWCNT/p-GaN. The layer of carbon nanotubes was deposited on p-GaN by spraying a solution of synthesized SWCNTs, while the layers of Cr and Au were vapour deposited. The effects of the annealing temperature and time upon the electrical properties of Au/Cr/SWCNT/p-GaN contacts have been studied. It has been found that the contact structure provides a low resistivity ohmic contact after subsequent annealing in N<sub>2</sub> ambient at 700 °C for 1 minute.

**Key words:** p-GaN, single wall carbon nanotubes (SWCNT), ohmic contact, specific contact resistance, Au/Cr/SWCNT/p-GaN contact structure, RTA, Auger electron spectroscopy

### 1 INTRODUCTION

In recent years, much attention has been paid to semiconductor compounds based on gallium nitride used as short wavelength light emitting materials. Because of the low level of doping of p-GaN attainable by standard techniques, which hinders reaching a satisfactorily high hole concentration ( $> 10^{18} \text{ cm}^{-3}$ ) [1], ohmic contact to p-type GaN still constitute a problem. For efficient charge transport, such devices require good ohmic contacts with low resistance.

Numerous papers have dealt with improving 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 [2-7]. In the case of light emitting devices (diodes, lasers), when the ohmic contacts have to be also sufficiently transparent for visible light, this requirement has been satisfied by using very thin metallic contact layers on p-GaN. For improving the optical transparency of the contacts, metallization structures based on ZnO have also been used.

Nevertheless, from among all contact structures on p-GaN the Au/Ni/p-GaN [8-17] structure seems to be the most suitable thanks to relatively good values of the specific contact resistance and in the case of very thin layers also thanks to optical transparency.

Promising results were reached examining the effect of a NiOx layer with a low concentration of oxygen upon the electrical properties of ohmic contacts Au/NiOx/p-GaN [18]. It was found that a low-resistance ohmic contact was provided by Au/NiOx layers deposited by reactive magnetron sputtering and annealed not only in oxygen but also in nitrogen. In the latter case the results were even

better. Both annealing modes lead to 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.

A highly promising solution for obtaining low-resistance ohmic contacts to p-GaN with excellent optical transparency for visible light might be the use of carbon nanotubes (CNT). This material exhibits, depending on the orientation of the graphene plane, both semiconducting and metallic properties, whereas the semiconductor exhibits p-type conductivity. They have a low work function and high chemical stability. Additionally, they have excellent thermal and optical properties [19, 20]. The first applications of CNT for ohmic contacts to p-GaN showed that the specific contact resistance was lower than in the case of an Au/Ni contact [21].

The topic of this work is the design and verification of a new ohmic contact structure to p-type GaN, particularly for use in light emitting devices based on a layer of carbon nanotubes and metallic layers of Cr and Au. The layer of carbon nanotubes was prepared by spraying a solution, with optimized density and homogeneity, of CNT synthesized by standard laser ablation followed by a purification process. The specific contact resistance measured by the circular transmission line method (CTLTM) was correlated with the depth distribution of elements in the contact structure measured by Auger electron spectroscopy (AES). The effects of the contact structure annealing temperature and time were investigated.

Institute of Electronics and Photonics, Slovak University of Technology, Ilkoviova 3, 812 19 Bratislava, Slovakia, jozef.liday@stuba.sk;

\*\* Danubia NanoTech, s.r.o., Ilkoviova 3, 841 04 Bratislava, Slovakia

## 2 EXPERIMENTAL

Metalorganic vapour phase epitaxy (MOVPE) p-GaN layers with a thickness of 800 nm, carrier concentrations  $2 \times 10^{17} \text{ cm}^{-3}$  and mobility around  $5 \text{ cm}^2/\text{Vs}$  produced in the Magnetic Spin Materials Group at Johannes Kepler University in Linz were used for preparation of Au/Cr/SWCNT/p-GaN structures. The p-GaN layers were first sequentially ultrasonically treated for 5 minutes in each step in acetone, isopropanol, DI water, dried with compressed N<sub>2</sub> and then chemically etched in HCl:H<sub>2</sub>O (1:1) etchant to remove the surface native oxide. On such p-GaN layers, SWCNTs prepared by the standard laser ablation method followed by a purification process, were deposited. High-quality SWCNTs prepared in this way were deposited on p-GaN by spray coating using an off-the-shelf airbrush. As a solution, 2mg of SWCNTs diluted with 20 ml of N-methyl-2-pyrrolidone were tip-sonicated for 10 min. In order to accelerate the evaporation of the solvent and prevent formation of bigger droplets the substrate was heated up to 165 °C. The thickness of the SWCNT layer was approx. 75 nm. This thickness guarantees a sufficient (more than 60%) optical transmittance of the SWCNT layer [21].

After processing in HCl:H<sub>2</sub>O (1:1) etchant, patterns were created on the SWCNT layer by lift-off techniques that are needed for measuring the specific contact resistance by the circular transmission line method (CTLTM). In the end, metal thin films Cr (10 nm) and Au (50 nm) were deposited by e-gun evaporation at a pressure of approx.  $10^{-4}$  Pa. After rinsing out the photoresist from the patterns for CTLTM measurement, the SWCNT layer was denuded by etching in RF oxygen plasma using Plasma Etch PE-200 equipment.

After deposition the samples were subsequently annealed in N<sub>2</sub> in a rapid thermal annealing furnace at a temperature of 700 °C for 1 minute.  $I-V$  measurements were performed on a Keithley 2400 SourceMeter equipped with a MDC micropositioners 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 specific contact resistance was determined using the model of Marlow and Das.

To study the effects of the annealing temperature and time upon the specific contact resistance of Au/Cr/SWCNT/p-GaN contact, identically prepared samples were annealed, immediately after deposition, in a rapid thermal annealing furnace at temperatures from 300 °C to 700 °C for 1 to 3 minutes.

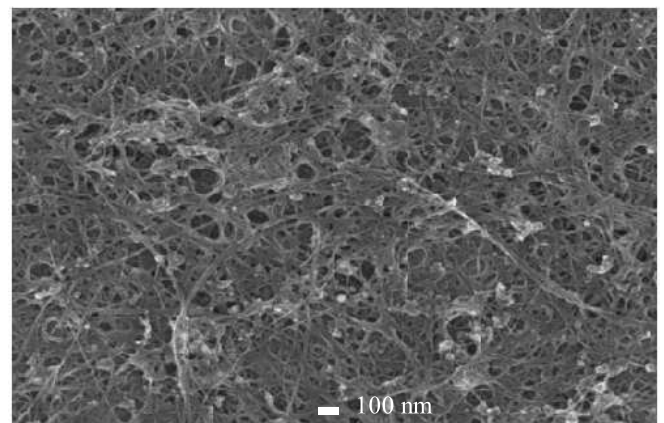
The properties of the layer of carbon nanotubes were examined on specially prepared samples. The specific resistance was measured in both longitudinal and transversal directions on a self supported SWCNT sample. The thickness was determined from cross-sectional SEM micrographs of SWCNT layers deposited on a SiO<sub>2</sub> substrate under identical conditions.

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<sup>+</sup> 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  $E/E=0.3\%$ . Auger depth profiling employed the Auger peaks of Au (239 eV), Cr (529 eV), C (270 eV), Ga (1070 eV), N (385 eV) and O (510 eV).

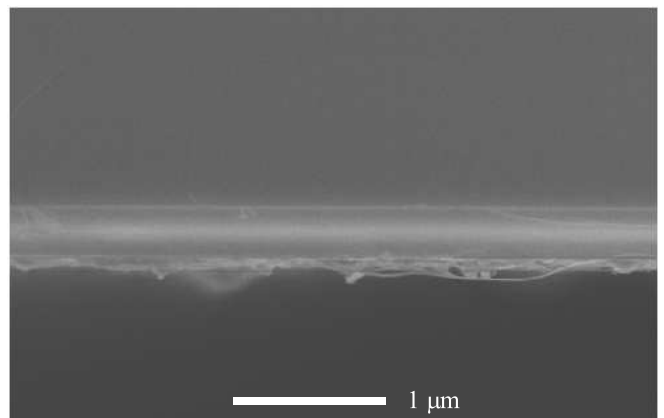
## 3 RESULTS

SEM image of the surface morphology of the SWCNT layer deposited onto SiO<sub>2</sub> substrate in Fig. 1 shows a homogeneous dense structure of a SWCNTs network. The thickness of the deposited layers examined by cross-section SEM analysis (Fig. 2) was around 75 nm. Resistivity of the self-supported SWCNT layers measured in the direction of the growth of the layers was about  $2.4 \times 10^{-3} \Omega \text{ cm}$ , in the cross-section approximately  $4.5 \times 10^2 \text{ cm}$ .



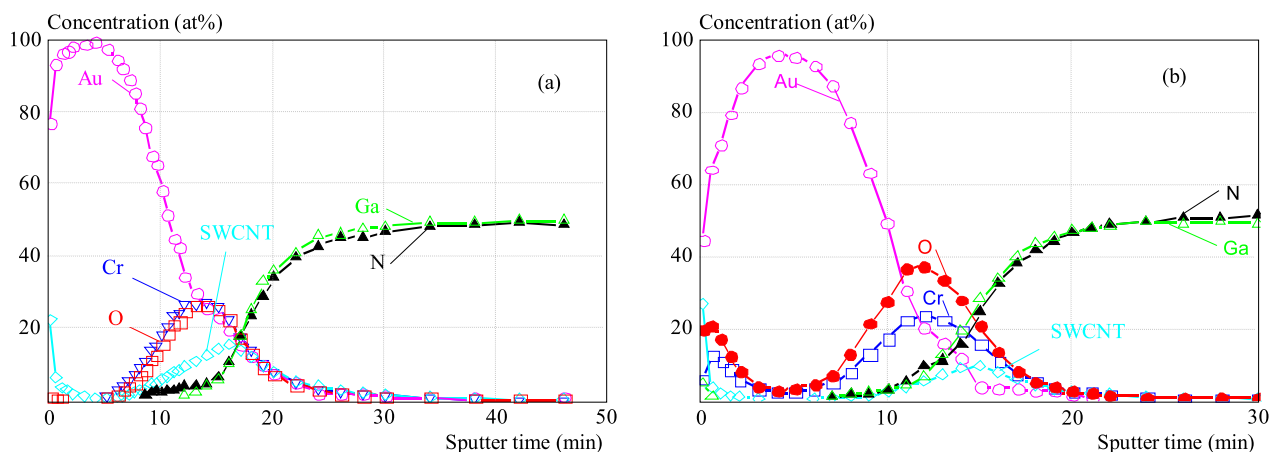
x 40.000 5.0 kV SEi SEM WD 4.1 mm

**Fig. 1.** SEM micrograph of the surface morphology of the spray-coated SWCNT layer



x 22.000 5.0 kV SEI SEM WD 2.4 mm

**Fig. 2.** Cross-sectional SEM micrograph of the spray-coated SWCNT layer



**Fig. 3.** AES depth profile of Au/Cr/SWCNT/p-GaN contact structure: (a) - as deposited, (b) - annealed in N<sub>2</sub> at 700 °C for 1 minute

**Table 1.** Specific contact resistances of as-deposited and annealed (in N<sub>2</sub> at 700 °C for 1 minute) Au/Cr/SWCNT/p-GaN contacts

Contact structure	Specific contact resistance ( $\Omega\text{cm}^2$ )	
	as-deposited	annealed 700 °C, 1min, N <sub>2</sub>
Au/Cr/SWCNT/p-GaN	$5.5 \times 10^{-1}$	$5.4 \times 10^{-3}$

Measurements of the influence of the annealing temperature and time upon the specific contact resistance of Au/Cr/SWCNT/p-GaN contacts on identically prepared samples revealed that the lowest value of contact resistivity was achieved after annealing in N<sub>2</sub> at 700 °C for 1 minute and these parameters were further used in the presented study.

Measurements of the contact resistivity of Au/Cr/SWCNT/p-GaN contacts by the circular transmission line method (CTLM) have shown that even non-annealed contacts have ohmic properties. The obtained results of the specific contact resistances of both annealed and as-deposited samples are summarized in Table 1.

Figure 3(a) shows the AES depth profile of the as-deposited Au/Cr/SWCNT/p-GaN structure. The profile proves the presence of oxygen bond to chromium with a composition close to the stoichiometry of CrO. CrO extends through the porous layer of SWCNT down to p-GaN. Annealing in N<sub>2</sub> at 700 °C for 1 minute resulted in out-diffusion of a portion of Cr through the Au layer to the surface with subsequent oxidation giving rise to Cr<sub>2</sub>O<sub>3</sub> stoichiometry, see Fig. 3(b). The observed high concentration of Cr<sub>2</sub>O<sub>3</sub> in the Au region is a consequence of the fact that due to surface tension in the Au layer its morphology changes to discontinuous pieces [8]. Cr<sub>2</sub>O<sub>3</sub> detected in the Au region consists of fine crystallites filling out the spaces between the pieces of Au. In the interface region in direct contact with p-GaN there is a layer of SWCNT and also oxidized chromium, Cr<sub>2</sub>O<sub>3</sub>. Thus the observed distribution of the components as a consequence of annealing may be explained by the polycrystalline structure of the contact consisting of Au, SWCNT and Cr<sub>2</sub>O<sub>3</sub>. Large grains of Au are, through SWCNT

and Cr<sub>2</sub>O<sub>3</sub> crystallites, in contact with p-GaN. As presented in [21, 22], individual semiconducting SWCNT or a mixture of metallic and semiconducting nanotubes exhibit p-type semiconducting behaviour. Similarly, Cr<sub>2</sub>O<sub>3</sub> is also a p-type semiconductor [23]. In the study of the Au/Ni-O/p-GaN structure [20] it was found that RTA 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/Cr/SWCNT/p-GaN contact structure is related, similarly like in the above case, to the existence of a similar contact scheme metal/p-SWCNT/p-GaN and metal/p-Cr<sub>2</sub>O<sub>3</sub>/p-GaN.

#### 4 CONCLUSION

We have studied a new contact structure, Au/Cr/SWCNT/p-GaN, based on a layer of carbon nanotubes and metallic layers Cr and Au, for ohmic contacts to p-GaN, particularly for application in light emitting devices. It has been found that the contact created by a layer of carbon nanotubes deposited on p-GaN by spray coating and covered by vapour deposited Cr and Au provides a low resistivity ohmic contact after subsequent annealing in N<sub>2</sub> ambient at 700 °C for 1 minute. It is believed that the ohmic nature is related to the existence of a contact scheme metal/p-SWCNT/p-GaN and metal/p-Cr<sub>2</sub>O<sub>3</sub>/p-GaN.

## Acknowledgements

The work was supported by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and of the Slovak Academy of Sciences No. 1/1197/12.

## REFERENCES

- [1] MURAKAMI, M. *et al* : Ohmic contacts for compound semiconductors, *Crit. Rev.in Solid State and Mater. Sci.* **23** No. 1 (1998).
- [2] YOUN, D. H. *et al* : Ohmic contacts to p-type GaN, *Jpn. J. Appl. Phys. Part 1* **37** (1998), 1768.
- [3] CHEN, L. C. *et al* : GaN-based light-emitting diodes with Ni/AuBe transparent conductive layers, *Solid State Electron* **47** (2003), 1843.
- [4] SONG, J. O. *et al* : Low-resistance Ni-Zn solid solution /Pd ohmic contacts to p-type GaN, *Semicond. Sci. Technol.* **19** (2004), 669.
- [5] SONG, J. O. *et al* : Formation of low resistance and transparent ohmic contacts to p-type GaN using Ni-Mg solid solution, *Appl. Phys. Lett.* **83** (2004), 3513.
- [6] SONG, J. O. *et al* : Low-resistance and transparent ohmic contacts to p-type GaN using Ni-Zn solid solution /Au scheme, *Appl. Phys. Lett.* **84** (2004), 4663.
- [7] CHAE, S. W. *et al* : Characteristics oh hydrogen storage alloy p-GaN ohmic contacts for InGaN LEDs, *J. Korean Phys. Soc.* **49** (2006), 899.
- [8] HO, J. K. *et al* : Low-resistance ohmic contacts to p-type GaN, *Appl. Phys. Lett.* **74** (1999), 1275.
- [9] HO, J. K. *et al* : Low-resistance ohmic contacts to p-type GaN achieved by the oxidation of Ni/Au films, *J. Appl. Phys.* **86** (1999), 4491.
- [10] KOIDE, Y. *et al* : Effects of annealing in an oxygen ambient on electrical properties of ohmic contacts to p-type GaN, *J. Electron. Mater.* **28** (1999), 341.
- [11] MISTELE, D. *et al* : Ohmic contacts for compound semiconductors, *J. Cryst. Growth* No. 230 (2001), 564.
- [12] CHEN, L. C. *et al* : Oxidized Ni/Pt and Ni/Au ohmic contacts to p-type GaN, *J. Appl. Phys.* **76** (2000), 3703.
- [13] JANG, H. W. *et al* : Mechanism for ohmic contact formation of oxidized Ni/Au on p-type GaN, *J. Appl. Phys.* **97** (2003), 1748.
- [14] WENZEL, R. *et al* : Ohmic contacts on p-GaN, *Mater. Sci. Semicond. Process.* **4** (2001), 357.
- [15] PARK, M. R. *et al* : Microstructure and electrical properties of low temperature processed ohmic contacts to p-type GaN, *ETRI Journ.* **24** (2002), 349.
- [16] NARAYAN, J. *et al* : Formation of epitaxial Au/Ni/Au ohmic contacts to p-GaN, *Appl. Phys. Lett.* **81** (2002), 3978.
- [17] WANG, S. H. *et al* : Environmental and thermal aging of Au/Ni/p-GaN ohmic contacts annealed in air, *J. Appl. Phys.* **91** (2002), 3711.
- [18] LIDAY, J. *et al* : Investigation of NiOx-based contacts on p-GaN, *J. Mater. Sci: Mater. Electron.* **19** (2008), 855.
- [19] POPOV, V. N. : Carbon nanotubes: properties and application, *Mater. Sci. Engin.* **43** (2004), 61.
- [20] ZHAO, J. *et al* : Optical properties and photonic devices of doped carbon nanotubes, *Analytica Chim. Acta* No. 567 (2006), 161.
- [21] LEE, K. *et al* : Single wall carbon nanotubes for p-type ohmic contacts to p-GaN light-emitting diodes, *Nano Lett.* **4** (2004), 911.
- [22] ZAHAB, A. *et al* : Water-vapor effect on the electrical conductivity of a single-walled carbon nanotube material, *Phys. Rev. B* **62** (2000), 10000.
- [23] H. CAO, H. *et al* : Sol-gel synthesis and photoluminescence of p-type semiconductor Cr<sub>2</sub>O<sub>3</sub> Nanowires, *Appl. Phys. Lett.* **88** (2006), 241112.

Received 3 January 2013

**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.

**Viliam Vretenár** (Ing, PhD), graduated in electromaterial engineering at STU in 2000 and received the PhD degree in solid state physics and acoustic from the Institute of physics SAS in 2006. He is engaged in application of CNTs and graphene in nanodevices, such as gas sensors, transparent conductive layers, supercapacitors, *etc.*

**Mário Kotlár** (Ing) graduated in electronics at STU in 2010. He is a research worker in the field of carbon nanotubes at Institute of electronics and photonics, FEIT STU. His work mainly deals with deposition and analysis of CNTs and other carbon nanomaterials.

**Marián Marton** (Ing, PhD), graduated in electronics at in 2004 and in 2008 he received his PhD in electronics and vacuum technology, both at STU. Currently his research deals with carbon nanomaterials, *eg* diamond, CNTs, CNWs and DLC.

**Vlastimil Řeháček** received his MSc in Nuclear Chemistry from the Comenius University in Bratislava in 1982 and his PhD in Electronics from the Slovak University of Technology in 2005. He is a scientific worker in Institute of Electronics and Photonics, FEIT STU. His current research interests include the development of voltammetric sensors, gas sensors and photolithography.