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COMMUNICATIONS

APPLICATION OF CARBON NANOTUBES AND REDUCED GRAPHENE OXIDE LAYERS FOR OHMIC CONTACTS TO p–GaN

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Due to their properties, carbon nanotubes and reduced graphene oxide are highly promising materials for obtaining low-resistance ohmic contacts to p-GaN with good optical transparency for visible light. In this contribution we designed a combination of these two materials, along with a cap layer, to be used as structures for ohmic contacts to p-GaN. Carbon nanotube (CNT) and graphene oxide (GO) layers were deposited by spray coating using an off-the-shelf airbrush on p-GaN layers. The metallic layers of Au/Pd were vapour deposited. The structures for ohmic contacts were prepared in two configurations, namely as Au/Pd/r-GO/CNT/p-GaN and Au/Pd/CNT/r-GO/CNT/p-GaN. The prepared structures provide a low resistivity ohmic contact after subsequent annealing in air ambient at 600 °C for 3 minutes. The contact containing the sandwich CNT /r-GO/CNT interstructure exhibits lower values of contact resistance in comparison with the r-GO/CNT interstructure.

K e y w o r d s: p-GaN, ohmic contacts, carbon nanotubes, graphene, reduced graphene oxide (r-GO)

1 INTRODUCTION

Remarkable advances have been reached recently in the application of gallium nitride based semiconductor compounds in various optoelectronic applications. One of the factors limiting the reliability and performance of these devices is the possibility to create low-resistance ohmic contact to p-GaN.

A prospective solution for obtaining low-resistance ohmic contacts to p-GaN with excellent optical transparency might be the use of carbon nanomaterials (CNM), such as carbon nanotubes and reduced graphene oxide (r-GO). Depending on the orientation of the graphene plane, carbon nanotubes exhibit both semiconducting and metallic properties, whereas the semiconductor exhibits p-type conductivity. Due to their one dimensional structure CNTs exhibit field emission properties. The first applications of CNTs for ohmic contacts to p-GaN showed that the contact resistivity was lower than in the case of an Au/Ni contact [1, 2].

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 CNM and upper metallic layers Pd and Au. The quality of contacts in terms of their good ohmic behaviour evaluated by I-V curve measurements as well as the contact resistivities measured by the circular transmission line method (CTLM) were correlated with the micrographs obtained by scanning electron microscopy (SEM) and with the depth distribution of elements in the contact structure measured by Auger electron spectroscopy (AES). The effects of the various contact structure materials (layers of CNM), contact annealing temperature and time in air ambient were investigated. Measurements of the contacts by CTLM have shown good ohmic properties of the contacts based on layers of carbon nanomaterials and metals.

2 EXPERIMENTAL

Metalorganic vapour phase epitaxy p-GaN layers with a thickness of 800 nm on a GaN buffer grown on (0001) sapphire substrates, carrier concentration $2 \times 10^{17}\text{cm}^{-3}$ 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/Pd/CNT/r-GO/p-GaN and Au/Pd/CNT/r-GO/CNT/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_2 and then chemically etched in $HCl : H_2O$ (1:1) etchant to remove the surface native oxide. On such p-GaN layers, both CNT and GO layers were consecutively deposited by spray coating using an off-the-shelf airbrush. The high-quality CNT were prepared by the laser ablation method

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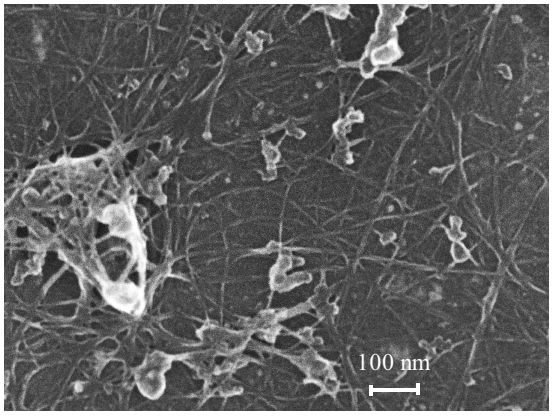

Fig. 1. The SEM micrograph of the surface morphology of the CNT/r-GO/CNT/ p-GaN structure

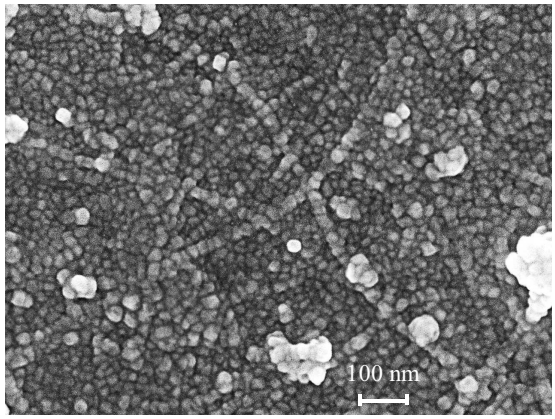

Fig. 2. The SEM micrograph of the surface morphology of the Au/Pd/CNT/r-GO/CNT/ p-GaN structure

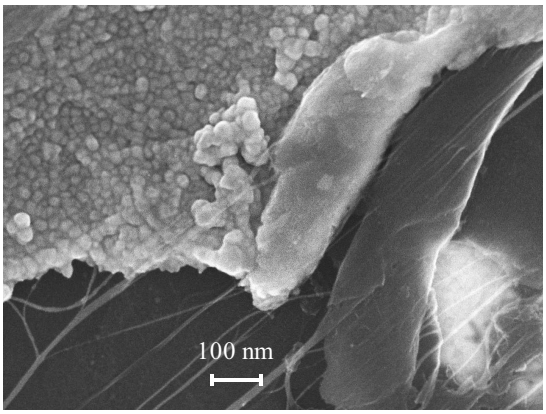

Fig. 3. The SEM micrograph of the cross-fracture of the Au/Pd/CNT/r-GO/CNT/ p-GaN structure

followed by a purification process. For spraying deposition, a solution of 2 mg of CNTs diluted with 20 ml of N-methyl-2-pyrolidone was tip-sonicated for 10 minutes. The substrate was heated to 165 °C in order to accelerate the evaporation of the solvent and prevent formation of bigger droplets. The deposited CNT layers were about 30 nm thick. For graphene layer, thermally reduced graphene oxide flakes were utilized. The graphene oxide flakes were prepared by chemical oxidation of graphite powder using the modified Hummer's method [3]. The synthesis method was described elsewhere [4]. The graphene oxide (GO) layer was deposited onto CNT layer using the spraying technique. A solution of 2 mg of graphene oxide flakes diluted with 20 ml of DI water was tip-sonicated for 10 minutes. During deposition the substrate was heated to 105 °C. Such a layered structure (r-GO /CNT/p-GaN) was annealed in order to reduce the graphene oxide layer into a graphene layer and so to obtain finally the graphene/CNT/p-GaN structure. Thermal reduction was performed by slow heating up to 850 °C in nitrogen atmosphere for several hours. The thickness of the r-GO layer was approx. 10 nm. Preparation of the CNT/r-GO/CNT/p-GaN was identical with that of the r-GO/CNT/p-GaN structure, however the cap layer of CNT was deposited onto the r-GO layer prior to annealing intended to reduce the graphene oxide layer into a graphene layer.

After processing in HCl : H_2O (1:1) etchant, photoresist structures for CTLM were patterned on either the r-GO layer (structure r-GO/CNT/p-GaN) or the CNT layer (structure CNT/r-GO/CNT/p-GaN) by optical lithography (lift-off technique). The next step was deposition of Pd and Au metallic layers in both contact structures. Thin films Pd (10 nm) and Au (50 nm) were deposited by e-gun evaporation at a pressure of 10^{-4} Pa.

After the layer materials were deposited, the samples were immersed in a liquid remover (acetone) and unwanted layer material (Pd+Au) with photoresist were lifted-off ultrasonically. After rinsing in DI water and drying, the process of making the structure for CTLM measurements was completed by creating a pattern also in the CNM layer (in one case CNT/r-GO/CNT and in the other one r-GO/CNT). The pattern for CTLM measurement was obtained by etching in RF oxygen plasma through a mask created in the metallic layer after removing the unwanted material in the Plasma Etch PE-200 apparatus. I-V measurements were performed on a Keithley 2400 SourceMeter equipped with MDC micropositioners by applying a voltage ramp from −10 V to +10 V and measuring the respective currents. 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 [5] and the measuring system described in [6].

To study the effects of the annealing temperature and time in air ambient upon the I-V curves and the contact resistivity, both types of contact structures, Au/Pd/CNT/r-GO/CNT/p-GaN and Au/Pd/r-GO/CNT/p-GaN, were annealed immediately after deposition in a rapid thermal annealing furnace at 500 °C, 600 °C and 700 °C for 1 to 5 minutes. The properties of the layer of carbon nanomaterials were examined on specially prepared samples. The thickness was determined both by profilometer Talystep and from cross-section SEM micrographs of CNT layers deposited on a SiO2 substrate under identical conditions.

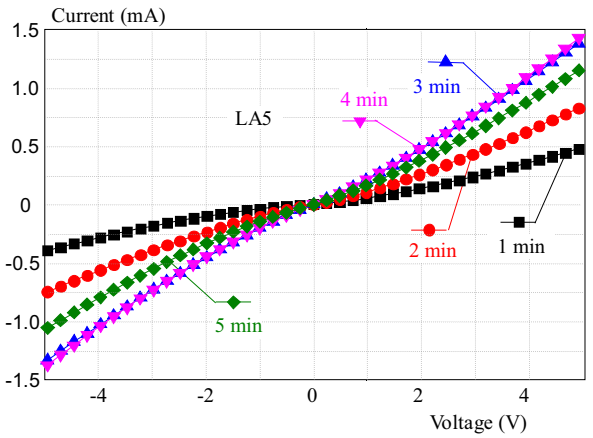

Fig. 4. $I - V$ curves of the Au/Pd/CNT/r-GO/CNT/ p-GaN contact annealed in air at 600 °C for time ranging from 1 to 5 minutes

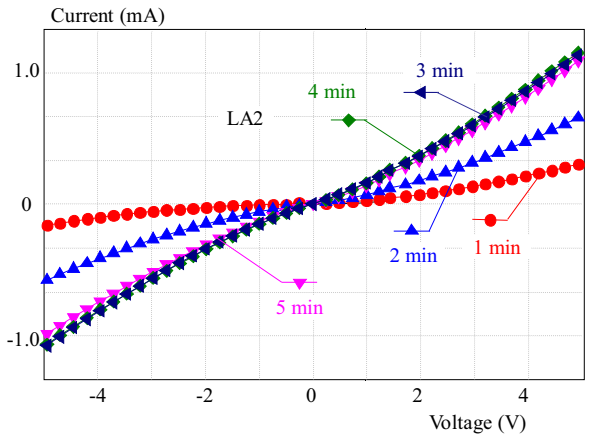

Fig. 5. $I - V$ curves of the Au/Pd/r-GO/CNT/ p-GaN contact annealed in air at 600 °C for time ranging from 1 to 5 minutes

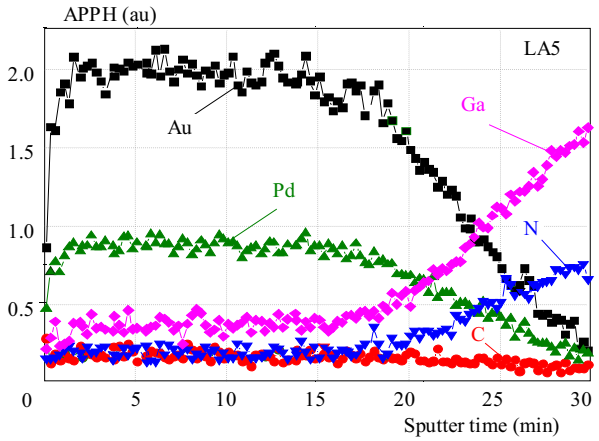

Fig. 6. AES depth profiles of Au/Pd/CNT/r-GO/CNT/p-GaN contact structure annealed in air at 600 °C for 3 minutes

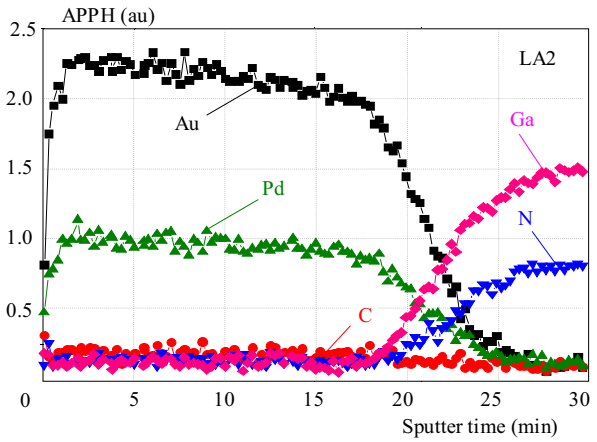

Fig. 7. AES depth profiles of Au/Pd/r-GO/CNT/p-GaN contact structure annealed in air at 600 °C for 3 minutes

Table 1. Contact resistivities of Au/Pd/CNT/r-GO/CNT/p-GaN and Au/Pd/ r-GO/CNT/p-GaN contacts annealed in air at 600 °C for 3 minutes

Contact structure	Contact resistivity (Ωcm^2)
Au/Pd/CNT/r-GO/CNT/p-GaN	7.5×10^{-3}
Au/Pd/r-GO/CNT/p-GaN	6.6×10^{-2}

AES analysis was performed with a Jeol JAMP 9510F scanning Auger microprobe equipped with an electrostatic hemispherical analyser and a multi-channel detection system. The electron gun operated at 10keV with a beam current of 5 nA. Auger depth profiling employed the Auger peaks of Au (69 eV), Pd (321 eV), C (263 eV), Ga (1060 eV) and N (375 eV).

3 RESUTLS

The SEM image (Fig. 1) of the surface of the CNT layer deposited onto GO/CNT/ p-GaN structure taken after subsequent annealing of the CNT/GO/CNT/ p-GaN structure shows a porous inhomogeneous structure of the CNT network. SEM micrograph of an identical structure covered by metallic layers of Au (50 nm) and Pd (10 nm) is shown in Fig. 2. Figure 3 is a SEM micrograph of the cross-fracture of the same sample shown in Fig. 2, thus of the contact structure Au/Pd/CNT/r-GO/CNT/p-GaN.

The average thicknesses of the deposited CNT and r-GO layers examined by profilometer Talystep and by cross-section SEM analysis were around 30 nm and 10 nm, respectively. The measured I-V curves of the Au/Pd/CNT/r-GO/CNT/p-GaN and Au/Pd/r-GO/CNT/p-GaN contact structures annealed in air at 600 °C in dependence on the annealing time are shown in Figs. 4 and 5. Evaluation of the I-V curves, mainly from the point of view of their slope and linearity, reveals that optimum annealing of both contact structures was achieved in air at temperature 600 °C for 3 minutes. It has been found [7] that the structure containing the CNT interlayer exhibits lower values of contact resistance in comparison with an otherwise identical contact without the CNT interlayer. In Figs. 4 and 5 one can see that in the case of contact structures Au/Pd/CNT/r-GO/CNT/p-GaN and Au/Pd/r-GO/CNT/p-GaN addition of a CNT layer between the cap metallic layer Au/Pd and the r-GO/CNT/

p-GaN structure brings about a higher slope of the I-V curves of contact structure (annealed in air at 600 °C for 3 minutes), thus improvement of the ohmic properties of the contact to p-GaN. The obtained results of the contact resistivities of Au/Pd/CNT/r-GO/CNT/p-GaN and Au/Pd/ r-GO/CNT/p-GaN contacts are summarized in Table 1. These results demonstrate that ohmic contacts with the CNT intermediate layer exhibit better ohmic properties.

Figures 6 and 7 show the AES depth profiles of Au/Pd/CNT/r-GO/CNT/p-GaN and Au/Pd/ r-GO/CNT/p-GaN contact structures annealed in air at 600 °C for 3 minutes. In both cases one can see that the metallic layers of Au and Pd are intermixed, most likely due to annealing, and through the CNM layers they got into direct contact to p-GaN. Based on our previous work [7] we believe that Au and Pd penetrated into the porous CNM layer already during the deposition of Au and Pd metallic layers. The observed distribution of the components in the contact can be explained by a polycrystalline structure of the contact layer composed of Au, Pd and CNT crystallites. In our opinion the ohmic nature of the Au/Pd/CNT/r-GO/CNT/p-GaN and Au/Pd /r-GO/CNT/p-GaN contact structures is related to the existence of a metal/p-CNT/p-GaN contact structure.

4 CONCLUSION

The Au/Pd/CNT/r-GO/CNT/p-GaN and Au/Pd /r-GO/CNT/p-GaN structures, based on a layers of carbon nanotubes, reduced graphene oxide and Au/Pd metallic layer were fabricated for ohmic contacts to p-GaN. CNT and GO layers were deposited by spray coating using an off-the-shelf airbrush, metallic layers were deposited by e-gun evaporation. Both of the structures exhibit ohmic properties. Measurements of the influence of the annealing temperature and time upon the contact resistivity showed that the lowest value of contact resistivity was achieved after annealing in air at 600 °C for 3 minutes, The structure with a CNT/r-Go/CNT layer between the metallic layer and p-GaN exhibited a slightly lower value contact resistivity. The obtained results are promising for fabrication of optically transparent ohmic contacts to p-GaN.

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