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COMMUNICATIONS

NiO–BASED CONTACTS FOR BLUE EMITTING DIODES

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Auger electron spectroscopy (AES) depth profiling in combination with the circular transmission line method (CTLM) contact resistivity measurements of the Au/NiO_x/p-GaN contact scheme with various content of oxygen in the NiO_x layer were used to explain the reduction of the contact resistivity as a result of its annealing in oxygen ambient. Au/NiO_x layers with a small concentration of oxygen in NiO_x were deposited on p-GaN by reactive dc magnetron sputtering and annealed in a mixture of O_2 and N_2, and in N_2 ambient. It was found that the Au/NiO_x/p-GaN structure with a low concentration of oxygen in the NiO_x layer provides a low resistivity ohmic contact, no matter if it is subsequently annealed in N_2 or O_2+N_2 ambient at 500 °C for 2 minutes.Auger depth profiles reveal that while annealing in O_2+N_2 ambient results in reconstruction of the initially deposited Au/ NiO_x/p-GaN contact structure into a NiO/Au/p-NiO/p-GaN structure, annealing in N_2 brings about reconstruction into Au+Ni/p-NiO/p-GaN.

K e y w o r d s: Auger electron spectroscopy, depth profiling, gallium nitride, nickel oxide

1 INTRODUCTION

Currently, there is a very high level of scientific and commercial interest in nitride semiconductors. Gallium nitride (GaN) is one of the most promising materials for use in high-temperature and high-frequency optoelectronic devices. Although many interesting results on GaN were obtained, many technical problems still remain unsolved in GaN based devices. One of the most serious problems is connected with producing ohmic contacts. Low contact resistance is an important factor for most electronic and optical devices in the field of wide-band semiconductors. Especially for p-type doped GaN laser diodes the contact resistance is more important because they require a high current density to operate. A lot of investigations have been made in the last few years, including a variety of metallization schemes and different surface pre-treatments such as cleaning procedures, annealing and sputter treatment [1-16]. However, due to its wide band gap and low doping level, low resistivity contacts to p-type gallium nitride are difficult to achieve. It was reported that by oxidizing a thin bilayer of Ni/Au under air or water vapour, low levels of resisivity could be achieved [7-16]. The reduction of the contact resistivity has been explained by various models. Ho *et al* [7-8] reported that a low-resistivity ohmic contact to p-GaN by oxidizing Au/Ni thin films could be primarily attributed to the formation of the NiO during the oxidation heat treatment. The NiO film prepared by oxidation of a Ni film was determined as a p-type conducting and thereupon an energy band model based on the Au/p-NiO/p-GaN heterostructure was proposed to explain the low resistive ohmic characteristic. Jang *et al* [12] attributed the lowering of the oxidized Au/Ni/p-GaN contact resistivity to the formation of Ga vacancies. Annealing under O_2 ambient causes preferential outdiffusion of Ni to the contact surface to form the structure of NiO/Au/p-GaN. Ga atoms are dissolved in the Au contact layer and the oxygen atoms incorporated during annealing promote the outdiffusion of Ga atoms from the GaN layer leaving Ga vacancies below the contact, which plays a role in increasing the net hole concentration. Koide *et al* [5,7] propose that oxygen aids in the removal of hydrogen from the p-GaN, resulting in a better activation of Mg acceptors in p-type GaN when the samples are annealed in air. In this study, we investigated the effect of NiO layer on the electrical properties of oxidized Au/Ni/p-GaN ohmic contacts. We employed AES depth profiling of the contact structure to search for correlation with its contact resistivity measured by CTLM. For this purpose we designed a novel NiO_x-based contact scheme (Au/NiO_x/p-GaN) with various concentrations of oxygen in the NiO_x layer deposited by dc reactive magnetron sputtering and subsequently annealed in N_2 and in a mixture of O_2 and N_2.

2 EXPERIMENTAL

GaN films were grown in AIXTRON 200 RF-S horizontal flow MOCVD reactor on (0001) sapphire substrates using trimethylgallium and ammonia as Ga and N precursors. To obtain state-of-the art material, the procedure of substrate nitridation, deposition of low-temperature GaN nucleation layer at 540 °C with subsequent annealing (recrystallization) and finally 1 μm GaN buffer growth at 1050 °C were used. Doping was achieved using bis-cyclopentadienyl magnesium (Cp_2Mg) during growth at 950 °C with flow rates 2000 sccm of NH_3, 5

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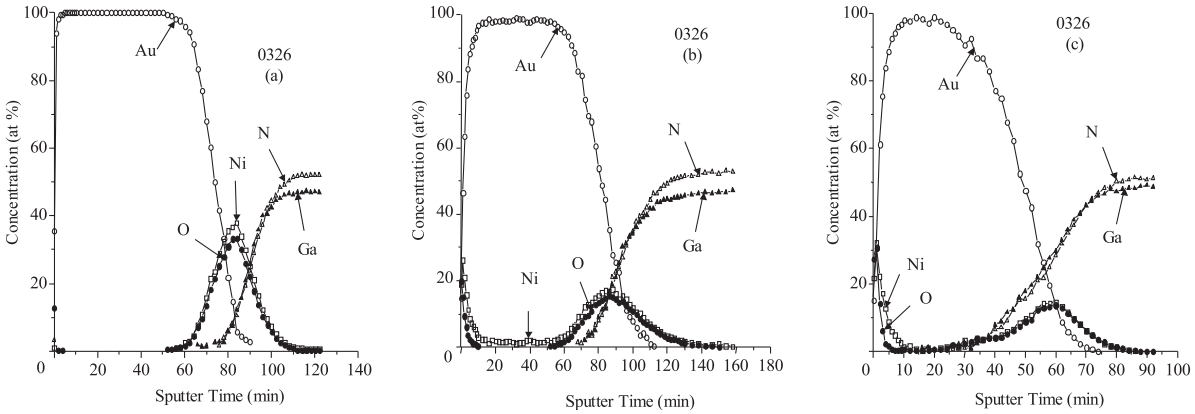

Fig. 1. AES depth profiles of Au/NiO_x/p-GaN contact structures (sample 0326) in which NiO_x was deposited at the highest content of oxygen in the working atmosphere (7 at%): (a) as deposited, (b) after annealing in N_2, and (c) in O_2+N_2 ambients. The contacts were annealed at 500 °C for 2 minutes.

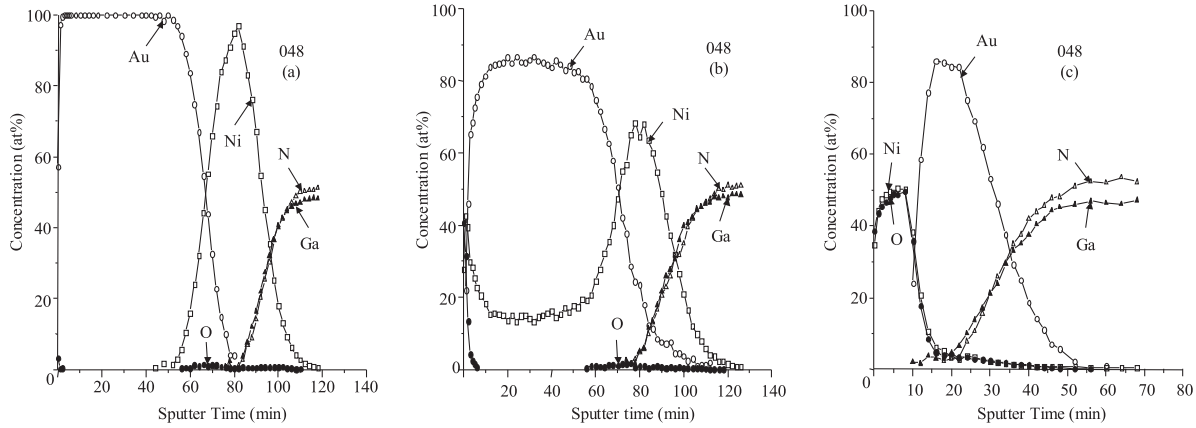

Fig. 2. AES depth profiles of Au/NiO_x/p-GaN contact structures (sample 048) in which NiO_x was deposited at 0.2 at% of oxygen in the working atmosphere: (a) as deposited, (b) after annealing in N_2, and (c) in O_2+N_2 ambients. The contacts were annealed at 500 °C for 2 minutes.

sccm of TMGa and 175 sccm of Cp_2Mg. After growth, the wafers were in-situ annealed in N_2 atmosphere at 780 °C for 15 minutes to activate the Mg and reduce compensation effects yielding 1 μm thick p-GaN layers with typical carrier concentrations around 7×10^{17} cm^{-3} and mobility around 10 cm^2/Vs. Prior to deposition of metal contacts, the p-GaN samples were degreased using organic solvents and deoxidised. Ni and Au thin films were deposited by dc magnetron sputtering. The NiO films were prepared by dc reactive magnetron sputtering from a Ni target in a mixture of oxygen and argon. The distance between the target and the substrate was approximately 75 mm. A sputtering power of 600 W 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. Ohmic contacts were characterized using a circular transmission line model (CTLM). For that purpose, circular test patterns were lithographically defined in the deposited metal layer. The samples were subsequently annealed in a rapid thermal annealing furnace at a temperature of 500 °C for 2 minutes. For each deposition sequence, one sample was left as deposited, one annealed in N_2 and one in O_2 and N_2, with a mixing ratio similar to ambient air. I-V measurements were performed on an HP 4155A semiconductor parameter analyzer 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 0 °with respect to the surface normal. Sputtering was performed by scanned Ar^+ ion beams with energy 1 keV and angle of incidence 80 °with respect to the surface normal. The energy resolution of the CMA was $\Delta E/E = 0.3\%$.

3 RESULTS

The oxygen content in the working atmosphere during the deposition of NiO_x and the contact resistivities of the Au/NiO_x samples annealed in N_2 and in O_2+N_2 are summarized in Table 1. The contact resistivity correlates with the content of oxygen in the working atmosphere: a lower content of oxygen leads to lower contact resistivities. The minimum contact resistivities were obtained in

Table 1. The oxygen content in the working atmosphere during the deposition of NiO_x and the contact resistivities of the Au/NiO_x samples annealed in N_2 and in O_2+N_2.

Sample	Oxygen content in atmosphere during deposition of NiO_x (at%)	Contact resistivity on annealing in N_2 (Ωcm^2)	Contact resistivity on annealing in O_2+N_2 (Ωcm^2)
0326	7	2.6×10^{-1}	1.2×10^{-1}
0327	2	4.9×10^{-2}	5.9×10^{-2}
0470	0.4	3.2×10^{-2}	1.8×10^{-2}
0480	0.2	7.9×10^{-4}	9.2×10^{-4}
0324	no oxygen	9.5×10^{-3}	2.9×10^{-3}
0514	0.2	1.4×10^{-1}	3.3×10^{-1}

samples deposited with the smallest content of oxygen for annealing in N_2 as well as in N_2+O_2. Table 1 presents also the contact resistivities of sample 0324 with pure Ni, instead of NiO_x, in the contact structure Au/Ni/p-GaN.

Figure 1 shows AES depth profiles of Au/NiO_x/p-GaN (sample 0326) in which Ni was deposited at the highest content of oxygen in the working atmosphere (7 at%). In the as deposited sample, both Au/NiO_x and NiO_x/p-GaN interfaces are abrupt and the composition of the NiO_x layer is close to the stoichiometry of NiO. Annealing in N_2 and in O_2+N_2 had no marked influence upon the composition and distribution of elements in the structure. NiO_x remained mainly on the surface of p-GaN. However, in both cases outdiffusion of Ni from the NiO_x layer occurred. Subsequently, in the sample annealed in O_2, nickel oxidized to form stoichiometric NiO. For both kinds of annealing, the contact resistivities are in the order of $10^{-1}\Omega cm^2$. Hence, direct connection of NiO with p-GaN in the scheme Au/NiO/p-GaN does not present an ohmic contact. As seen in Tab. 1, decreasing the content of oxygen in the deposition atmosphere (to 2 at%, 0.4 at% and 0.2 at%) and hereby also in the deposited NiO_x layers (to approx. 10 at%, 3 at% and 1 at%) lead to a lowering of the contact resistivities, this effect being similar for both modes of annealing (N_2 and O_2+N_2). Figure 2 shows AES depth profiles of the Au/NiO_x/p-GaN structure (sample 048) in which NiO_x was deposited at the lowest content of oxygen in the working atmosphere (0.2 at%). The content of oxygen in the deposited NiO_x layer was below 1 at%. Annealing in N_2 had a similar effect as in the contact structures with a higher, still understoichiometric content of oxygen (samples 0327, 047). A part of Ni outdiffused through the Au layer hereby forming a Au-Ni solid solution: This was reported also in [12]. Oxygen stayed in the remainder of the initial NiO_x layer between Au and p-GaN. Heat treatment in an oxygen-containing atmosphere resulted in outdiffusion of Ni to the surface with subsequent oxidation to NiO. The observed gradient in the composition of NiO within the Au layer towards the surface can be explained in such a way that Au does not form a continual layer. Due to surface tension, its morphology was reconstructed into discontinuous small pieces, which was reported also in [7]. In the region of Au we detect that portion of NiO which fills the space between the pieces of Au. One can deduce from the Auger depth profile that NiO is in intimate contact to p-GaN. Since there is no pile-up of NiO at the interface, one can infer that NiO does not create large particles but only a very thin layer between Au particles and p-GaN. The newly formed Au/p-GaN interface in the sample annealed in O_2+N_2 (Fig. 2c) is markedly broader than that of the same sample annealed in N_2 (Fig. 2b). In our opinion this is mainly caused by the porosity of the Au layer due to poor adhesion as a result of the balling-up effect. This has been confirmed by Park *et al* [14] by cross-sectional transmission electron microscopy (X-TEM) images. Voids on a similar interface have been observed by Ho *et al* [8] by X-TEM and by Narayan *et al* [15] by scanning TEM-atomic number (STEM-Z). They have interpreted their creation as transformation of Ni into NiO. Situation is different for the samples annealed in N_2. Here, the profiles of Au, Ni and p-GaN are steeper in the region of the interface than in the previous case. The Au layer and p-GaN substrate are separated by a nickel interlayer containing oxygen. As for the structure of this NiO_x layer, we assume that this is a mixture of Ni crystallites and smaller NiO crystallites. This assumption is based on our previous works [17, 18]: When depositing Ni with oxygen content corresponding to stoichiometric NiO layer on alumina and Si by dc reactive magnetron sputtering using deposition parameters similar to those used in the present work we found the NiO layer to exhibit fine crystallinity [17]. The NiO_x layer has a similar behaviour as that of semi-insulating polycrystalline silicon layers with a low oxygen content (SiO_x). These under-stoichiometric oxides were found to be composed of two phases: crystallites of Si and SiO_2 [18]. In the samples annealed in N_2, that part of the NiO_x layer which remained, after annealing, on its initial place at the interface with p-GaN is very likely a mixture of Ni and NiO crystallites. Thus, Ni and NiO are in intimate contact with p-GaN, and the model of the contact structure is Au+Ni/p-NiO/p-GaN. While studying the effect of various processes for cleaning the p-GaN substrate upon the contact resistivities we found that low energy oxygen dry plasma cleaning of the p-GaN

substrate resulted in low ohmic contact resistivity degradation. Table 1 summarizes the contact resistivities. In sample 0514 that was cleaned in this way, the magnitude of contact resistivity is higher by orders of magnitude than in samples with the same content of oxygen that were not exposed to plasmatic cleaning (see sample 048).

4 CONCLUSIONS

The measured contact resistivities indicate that the Au/NiO_x /p-GaN structure with a low content of oxygen in the Ni layer provides a low resistance ohmic contact regardless of its subsequent annealing in N_2 or O_2+N_2 ambient at 500°C for 2 minutes. Auger depth profiling reveals that annealing in O_2+N_2 ambient leads to a transformation of the deposited Au/NiO_x /p-GaN contact structure into NiO/Au/p-NiO/p-GaN, the NiO layer between Au and the p-GaN substrate being very thin. Hereby we have verified the model proposed in [7,8]. Annealing in N_2 results in reconstruction into Au+Ni/p-NiO/p-GaN. Thus in both cases, on annealing in N_2 as well as in O_2+N_2 ambient, the ohmic properties of the contacts are predetermined by creating a thin NiO oxide layer on the metal/p-GaN interface. AES concentration depth profiles of the contacts annealed in nitrogen have shown that good ohmic properties of the contact structures are not preconditioned by complete oxidation of the Ni layer. Lower contact resistivities in samples annealed in N_2 can be explained as follows: in this case, unlike on annealing in the N_2+O_2 mixture, no voids are created. Formation of voids is probably prevented by the created Au-Ni alloy, by the remainders of Ni layers (not yet spread by diffusion) and by NiO_x at the interface with p-GaN. Contact structures with a directly deposited NiO film, hence Au/NiO/p-GaN, have not exhibited good ohmic properties after annealing in N_2+O_2 mixture or in N_2, not even after prolonged annealing (longer than 2 minutes). The low energy oxygen dry plasma cleaning of the p-GaN substrate resulted in low ohmic contact resistivity degradation.

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