ENGINEERING ZnO/GaN INTERFACES FOR TUNNELING OHMIC CONTACTS TO GaN

E. Kaminska[1], A. Piotrowska[1], K. Golaszewska[1], R. Kruszka[1], A. Kuchuk[1], J. Szade[2], A. Winiarski[2], A. Barcz[1,3], J. Jasinski[4], Z. Liliental-Weber[4]

[1]Institute of Electron Technology, Warsaw, Poland, Institute of Physics,
[2]University of Silesia, Katowice, Poland,
[3]Institute of Physics, PAS, Warsaw, Poland,
[4]Lawrence Berkeley National Laboratory, Berkeley, CA, USA.

ABSTRACT

We have investigated two approaches for the fabrication of thin ZnO films: sputter deposition from the ZnO target and thermal oxidation of vacuum deposited Zn. The microstructure and electronic properties after consecutive steps of the formation of n-ZnO/p-GaN contacts have been studied using electron transmission microscopy and x-ray photoelectron spectrometry. We have achieved ohmic contacts by Zn oxidation and explain their ohmic behaviour in terms of a tunnel n^+-ZnO - p-GaN junction.

INTRODUCTION

Transparent conducting oxides (TCOs) are becoming increasingly important in the modern semiconductor optoelectronics. Their exceptional combination of properties like low resistivity, high thermal stability, transparency to visible light and high work function might be essential for the development of transparent ohmic contacts to light emitting and light detecting GaN-based devices. Prior attempts to form transparent ohmic contacts to GaN had focused on ultra thin metal films. They were partly satisfying: higher transparency was achieved, but at the cost of increased contact resistivity and poor thermal stability. As for TCOs, indium tin oxide (ITO) has drown much attention for its application in GaN optoelectronic devices and also as current spreading layers in LEDs [1]. However, ITO in contact with p-type and n-type GaN exhibited non-ohmic behaviour [1, 2].

In this work we consider the use of a different TCO material, namely ZnO as a contact to p-type GaN. It has been chosen basing on the following premises. First, ZnO is very similar to GaN in terms of band gap, crystalline structure, optical properties and thermal stability. Second, we presume that the technology of a two-component compound could be easier to tailor as compared to the three-component one. We have used two approaches for the fabrication of thin ZnO films: sputter deposition from the ZnO target and thermal oxidation of vacuum deposited Zn. The electrical properties of ZnO/GaN contacts were assessed from conductivity, I-V-T and contact resistivity measurements. The modification of p-GaN surface by ZnO deposition processes and the structure of ZnO/GaN interface were investigated by X-ray photoemission spectroscopy (XPS) and transmission electron microscopy. For that reason, a particular care has been paid to the preparation of damage- and contamination-free GaN surface prior to ZnO deposition [3]. Basing on the obtained results, we demonstrate the feasibility of a tunnelling n+-ZnO/p-GaN contact, suitable for application as a transparent ohmic contact to p-type GaN.

EXPERIMENTAL PROCEDURE

GaN (0001) samples for this study were MOCVD grown on sapphire substrate. 2 µm thick p-type GaN epilayers were Mg doped to the free carrier concentration of $1\times10^{17}\,cm^{-3}$. Prior to ZnO fabrication the samples were degreased in hot organic solvents followed by 20 min. etch in thiourea-based solution $10\%(NH_2)_2CS : HCl : 15\%H_2O_2 = 20 : 1 : 1$ and immediately loaded into the vacuum chamber. The surface cleaning was completed by *in-situ* Ar^+ ion sputter etching at 300 V for 30 s. Analyses of the GaN surface subjected to the above two-step cleaning revealed terrace surface structure, characteristic of epitaxial GaN, with no trace of hydrocarbons or oxides.

Sputter deposition of ZnO was performed at room temperature in RF mode, at a working pressure of 4×10^{-3} Torr, using 6N-purity ZnO target and a magnetron cathode. ZnO films of a thickness of 50 to 150 nm were used throughout this study.

Zn films were deposited by thermal evaporation at a base pressure of 1×10^{-7}Torr. To promote uniform condensation of Zn on GaN substrate, an Au nucleation film was predeposited. The parameters of Au evaporation were optimised such as to form the Au deposit as thin as possible. AFM gave further evidence that Au formed on GaN surface an island-like structure. 50-100 nm thick Zn layers were chosen for further processing. Zn oxidation was carried out in a conventional furnace in flowing O_2 at 320^0C for 40 min.

Patterns for electrical measurements were fabricated by lift-off photolithography. The conductivity of thin ZnO films was assessed by measurements of sheet resistance and thermopower. Specific contact resistance was determined by circular transmission line method (CTLM). Following dimensions were used: r = 50 µm, and spacings 10, 20, 30, 45 and 60 µm. Optical transmission of ZnO films was measured by photospectrometry using ZnO films deposited on double-side polished sapphire substrates.

The cross-sectional TEM (XTEM) and high resolution imaging (HREM) were done using a Topcon 002B microscope operating at 200 keV. Fast Fourier transform (FFT) of HREM images were used to identify crystalline phases. XPS measurements were performed with a Physical Electronics PHI 5700 ESCA spectrometer, using monochromatised Al Kα (1486.6 eV) and non-monochromatised Mg Kα (1256 eV) radiation, respectively. The vacuum during the measurements was about 10^{-10} Torr. The atomic composition was obtained from Mg radiation spectra as for Al radiation the N (1s) line overlaps with the Ga LMM Auger lines.

RESULTS

Properties of ZnO films

Sputter deposited ZnO films showed n-type conductivity and a resistivity of $2\text{-}5\times10^{-2}$ Ωcm. They were colourless, with an average transmission above 88% in the wavelength range from 400 to 700 nm.

Zinc deposited at a pressure 1×10^{-7} Torr formed, upon oxidation, highly resistive ZnO. An increase of the working pressure above 10^{-6} Torr, by back-filling the deposition chamber with high-purity N_2, enabled to form conducting n-type ZnO films. In particular, Zn films deposited at $1\text{–}5\times10^{-5}$ Torr yielded after oxidation half-metallic n^+-ZnO with the resistivity below 10^{-3} Ωcm, and optical transmission above 70% in the visible wavelength range.

The thickness of oxidised zinc films increased by factor of 1.2 as compared to as-deposited ones.

Electrical properties of n-ZnO/p-GaN junctions

To evaluate the electrical properties of n-ZnO/p-GaN contacts, Au pads were deposited on ZnO surface. First, it has been proven that Au in contact with n-ZnO forms an ohmic junction. On the other hand our measurements of pure Au contacts on p-GaN sample revealed their rectifying properties, confirming thus the results reported by Mori et al. [5].

As for ZnO/p-GaN contacts their properties strongly depended on the method of ZnO fabrication. In spite of similar bulk conductivity $\rho \approx 2$–5×10^{-2} Ωcm, sputter deposited ZnO formed rectifying contacts with p-GaN, while oxidised Zn contacts displayed ohmic properties. Typical I-V plots for both types of n-ZnO/p-GaN contacts are juxtaposed in figure 1. The onset of the ohmic behaviour for oxidised Zn contacts was observed for $\rho \approx 1 \times 10^{-2}$ Ωcm and yielded the specific contact resistance of $r_c \approx 10^{-2}$ Ωcm^2. By decreasing the resistivity of ZnO below 1×10^{-3} Ωcm it has been possible to further decrease r_c to the low 10^{-3} Ωcm^2 range.

The measurements of the temperature dependence of r_c in the range from RT to 350 K have been performed. The data, shown in figure 2 in the form of the Arrhenius plot, indicate the activation energy of 201 eV that fits well to the activation energy of Mg in GaN [4].

Structure and electronic properties of n$^+$-ZnO/p-GaN junctions

The interface of the ZnO contact deposited by sputtering, shown in figure 3(a), is perfectly smooth, uniform and abrupt. Electron diffraction pattern corresponds to interplanar distances of hexagonal ZnO (a = 3.25 A, c = 5.20 A, space group No 186, P63mc). ZnO film is polycrystalline and highly textured, matching the GaN substrate. The microstructure of the oxidised Zn contact, presented in figure 4(a) is noticeably different. Au from the nucleation film recrystalised at the contact interface; developing elongated grains embedded in a ZnO overlayer. The crystalline structure of Au grains and ZnO film have been confirmed by HREM analysis assisted by fast Fourier transform procedure (FFT). It should be noted that in both ZnO contacts, regardless of the fabrication method, no sign of interfacial reaction has been found.
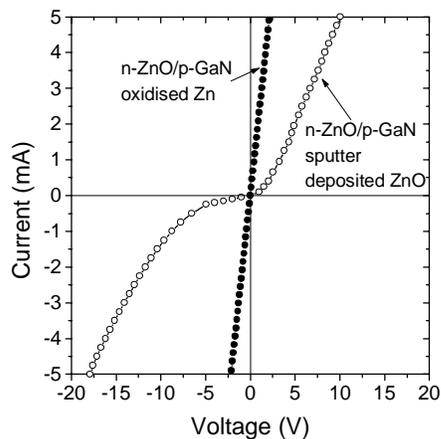

Figure 1. I-V characteristics of n-ZnO/ p-GaN contacts fabricated by ZnO sputter deposition (open circles) and oxidation of Zn (solid circles).
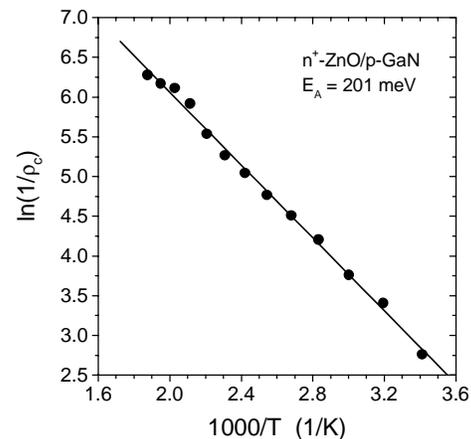

Figure 2. Resistivity of n-ZnO/p-GaN ohmic contact as a function of ambient temperature from the range RT - 300^{0}C.
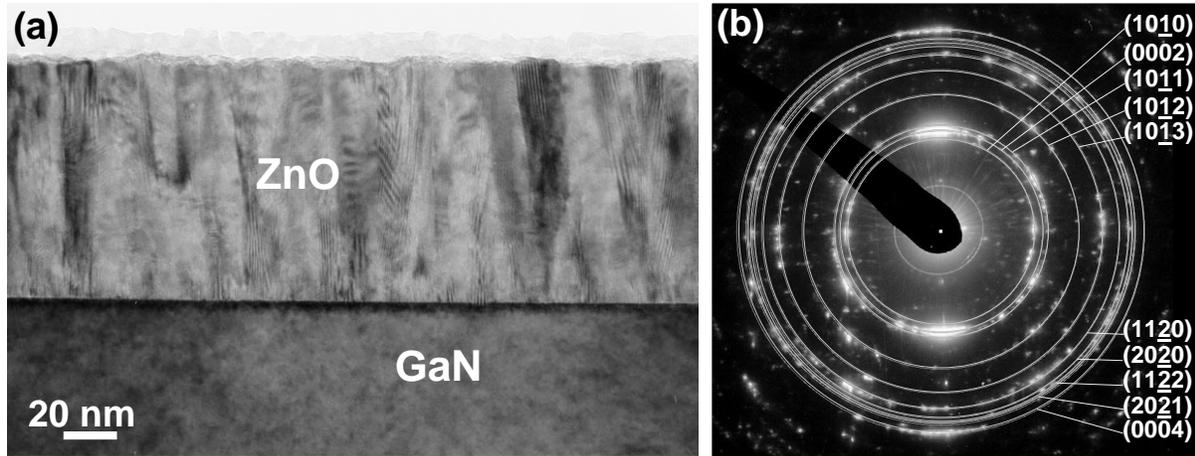
Figure 3. a) XTEM micrograph of sputter deposited ZnO film on GaN and b) corresponding electron diffraction pattern.
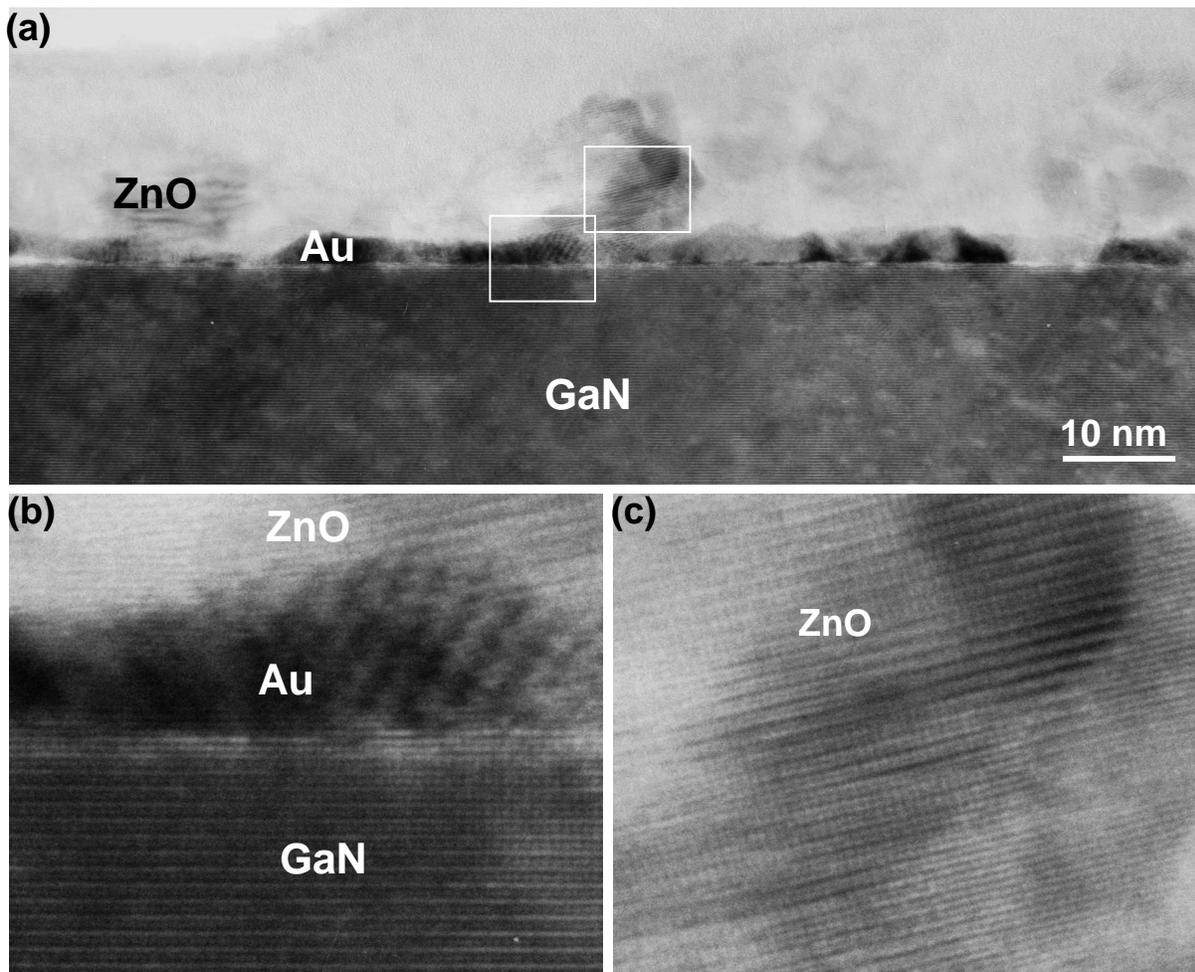

Figure 4. XTEM micrographs of oxidised Zn film on GaN: a) contact interface, b) HREM image of Au phase, c) HREM image of ZnO phase.

In figure 5 are juxtaposed results of XPS measurements performed after consecutive steps of the formation of oxidised Zn contact together with the spectrum obtained from sputter deposited contact. Specifically, the figure shows the photoemission spectrum of the Ga (3d) core level from the initial p-GaN surface and spectra of the Ga (3d) and Zn (3d) core levels following the predeposition of Au, deposition of Zn, oxidation of Zn and sputter deposition of ZnO on bare p-GaN surface. The double peak at the binding energy range 2 – 8 eV comes from Au (5d) states.

The displacement of the binding energy of Ga (3d) core level being the measure of the Fermi level shift at the p-GaN surface corresponds to the band bending at the interface caused by the given technological step. Zn (3d) core level, which appears in a high binding energy position of XPS spectra of the sample after Zn oxidation, corresponds to zinc reacted with oxygen. Since the original oxidised Zn film was too thick for assessing Ga (3d) core level, *in-situ* sputter thinning of ZnO down to 20 nm was performed enabling observation of both, Ga (3d) and Zn (3d) core levels. It should be noticed that neither the shape of the peak corresponding to Zn (3d) core level nor its position have been altered by the process of sputter thinning. The same procedure (not shown here) has been applied in the case of sputter deposited ZnO.

Regarding Ga, the gradual shift of the position of Ga (3d) core level to higher binding energies, resulting from subsequent deposition of Au and Zn followed by Zn oxidation indicates the pulling of the Fermi level at the interface downward. Careful measurements indicate that the Fermi level moves by ~0.7 eV after deposition of Au nucleation film. Zn overcoat induces additional shift by 0.1 eV. Oxidation of Zn film causes further displacement of the Fermi level by 0.4 eV. Thus, the final movement of Fermi level due to the formation of oxidised Zn on p-GaN surface corresponds to downward band bending by ~1.2 eV. The process of ZnO deposition by sputtering induces band bending by ~0.5eV.
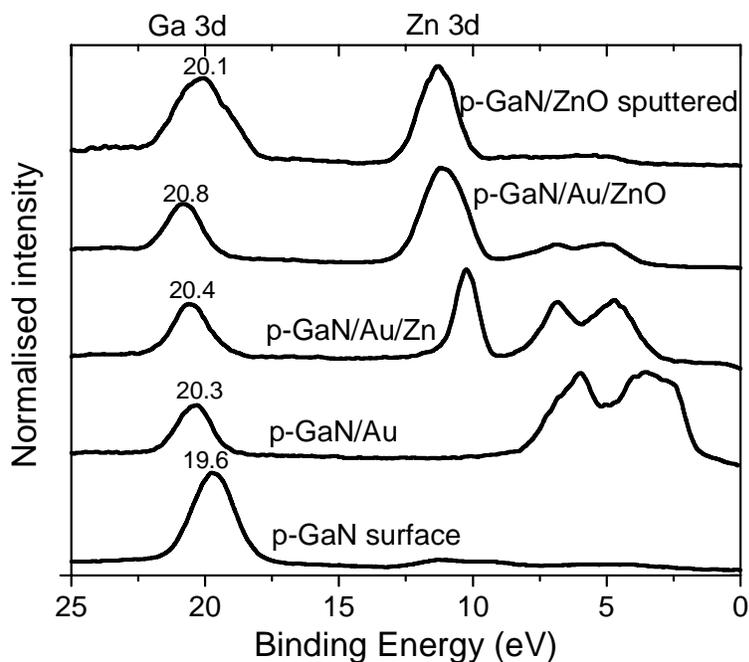

Figure 5. Evolution of the Ga (3d) and Zn (3d) core levels resulting from Au and Zn deposition, Zn oxidation as well as sputter deposition of ZnO.

DISCUSSION AND CONCLUSIONS

The properties of ZnO contacts to p-type GaN fabricated by two methods, a conventional sputter deposition from a compound target and oxidation of vacuum deposited Zn have been investigated. The most meaningful result, as far as electrical characteristics are concerned, is the ohmic behaviour of the latter contacts and rectifying of the former ones. The developed technological procedure of ohmic contact fabrication via oxidation of vacuum deposited Zn films was proven to play a crucial role for the final contact properties. While structural analysis revealed that two phases, namely Au and ZnO, coexisted at the contact interface, photoelectron spectroscopy gave measurable evidence of the particularly strong impact of the Au predeposition for the downward band bending at p-type GaN surface. Not less important are the consecutive technological steps giving rise to the additional band bending, resulting in final ohmic contact properties.

Since Au by itself does not provide ohmic contact to low-doped p-type GaN, the observed ohmic behaviour should be attributed to the formation of highly conducting n-type ZnO. The fact that n^+-ZnO forms with low-doped p-type GaN an ohmic contact suggests in turn, that a band bending at the ZnO side of the interface takes place as well. Klein has recently reported that thin films of transparent conducting oxides such as In_2O_3, in spite of highly doped bulk, develop at the surface a substantial depletion layer [6]. A similar behaviour could be expected in the case of ZnO. Enhanced upward band bending at the n^+-ZnO side together with downward band bending at p-GaN side would explain the observed ohmic behaviour in terms of formation of a tunnel n^+-ZnO - p-GaN junction. Also, experimentally assessed dependence of the specific contact resistance on the ambient temperature, with activation energy coinciding with that of Mg in p-GaN, may be interpreted in terms of tunnelling of carriers across the p-GaN/ZnO interface, limited by the bulk series resistance of p-GaN.

In contrast, conventionally sputter deposited ZnO causes much weaker band bending. This could explain the difficulties in achieving ohmic TCO-based contacts to p-GaN, even though highly conductive thin TCO films may be easily deposited by sputtering.

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