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# Pd/GaN(0001) interface properties[*]

M. Grodzicki, P. Mazur, S. Zuber, J. Pers[†], A. Ciszewski

Institute of Experimental Physics, University of Wroclaw, pl. Maxa Borna 9, 50-204 Wrocław, Poland

This report concerns the properties of an interface formed between Pd films deposited onto the surface of (0001)-oriented n-type GaN at room temperature (RT) under ultrahigh vacuum. The surface of clean substrate and the stages of Pd-film growth were characterized *in situ* by X-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), ultraviolet photoelectron spectroscopy (UPS), and low energy electron diffraction (LEED).

As-deposited Pd films are grainy, cover the substrate surface uniformly and reproduce its topography. Electron affinity of the clean n-GaN surface amounts to 3.1 eV. The work function of the Pd-film is equal to 5.3 eV. No chemical interaction has been found at the Pd/GaN interface formed at RT. The Schottky barrier height of the Pd/GaN contact is equal to 1.60 eV.

Keywords: *gallium nitride; palladium; metal-semiconductor junction*

## 1. Introduction

Gallium nitride (GaN) is a wide band-gap semiconductor extensively applied in modern optoelectronic devices. Its unique properties such as the direct band gap, high chemical resistance, a relatively high melting point and good thermal conductivity, make it a potential material for future engineering of high power and high frequency electronic devices such as semiconductor lasers, electroluminescence diodes, detectors, transistors, etc. [1–3]. Metal/GaN junctions are the necessary part of electronic devices as passive (ohmic) contacts for communication or the active (Schottky) contacts. Optimization of electrical behavior of GaN based devices requires elaboration of stable and reliable contacts. Palladium is widely used in electronic devices due to its high oxidation and corrosion resistance and the high work function. It is known as one of the candidates for the Schottky diodes on the n-type GaN substrate. The barrier height of those contacts ranges from 0.96 to 1.9 eV [4–6]. In this paper we report the results of our XPS, UPS, STM and LEED studies on the morphology of an interface and thin films of Pd on GaN(0001).

## 2. Experimental details

We used substrates, around 8 × 4 $\text{mm}^2$ in size, cut out from GaN(0001)/$Al_2O_3$ samples (from TDI Inc.). They consisted of an atomically flat, (0001)-oriented, n-type, Si-doped ($10^{18}$ $\text{cm}^{-3}$), and 10 μm thick epitaxial GaN layer grown on polished $Al_2O_3$(0001) templates. The substrates, Pd-films, and Pd/GaN interfaces were characterized by XPS using Al K$\alpha$ (1486.6 eV) radiation source, by UPS using He I line (21.2 eV) from a DC discharged lamp, and by STM applying tungsten tips.

Prior to measurements the GaN substrates were *ex situ* degreased in alcohol, next washed in distilled water and dried in air. Two separate ultrahigh vacuum (UHV) surface analysis systems with the base pressure $\sim 1.22 \times 10^{-8}$ Pa were used. The first one housed the STM head and LEED optics. The second housed the XPS and UPS spectrometers and was also equipped with LEED. Before Pd deposition (99.95 % purity from MaTecK), the substrate surface was cleaned *in situ* by cycles of annealing at 800 °C in order to remove surface oxides and carbon contamination. This was done by electron bombardment of the substrate

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[†] E-mail: jpers@ifd.uni.wroc.pl

from the backside. The Pd layers were deposited from an electron beam evaporator under operating pressure lower than $1.33 \times 10^{-7}$ Pa.

Geometrical configuration of the substrate and Pd-source differed in each of the UHV systems. An average Pd-layer thickness was quantified by two methods. It was done using a quartz microbalance in the first UHV system and by the XPS method [7] in the second one. In the former case the average thickness $d$ was determined from the dependence $d = \cos\theta \cdot \lambda \cdot \ln(I/I_0)$, where $\theta$ is the angle between the normal to the specimen's surface and the analyzer, $I_0$ and $I$ are the intensity values of the Ga-3d spectral line before and after the layer deposition, respectively, and $\lambda$ is the mean free path of the electron with kinetic energy of the Ga-3d line, which moves in Pd film. The value of $\lambda$ was taken from tabular data of [8]. Ion current of the Pd molecular beam was used to control the efficiency of evaporation. The amount of deposited Pd was controlled by evaporation time. All STM images were recorded with bias voltage and tunneling current ranging from 2.5 to 6 V and from 0.8 to 1.0 nA, respectively, and analyzed using the WSxM software [9]. Photoelectrons were collected by a hemispherical electron energy analyzer (Phoibos HAS-3500) with the pass energy of 10 eV in 0.1 eV steps. Optical axis of the analyzer entrance was normal to the substrate surface. The position of the Fermi level ($E_F$) was measured by UPS using a clean Au foil as reference. During the XPS and UPS experiment, the residual gas pressure in the chamber was measured by a quadrupole mass spectrometer. The same procedures of *in situ* annealing and Pd-deposition were used in both UHV systems. All measurements were done at room temperature (RT).

## 3. Results and discussion

Chemical composition of a fresh surface of the substrate as-introduced into the UHV system, just after the *ex situ* cleaning, revealed oxygen and carbon contaminants. In order to remove the contaminants it was necessary to anneal the substrate several times at 800 °C. Wide XPS spectra before and after Pd deposition are depicted for comparison in Fig. 1a and 1b, respectively. The spectrum in Fig. 1a indicates a good efficiency of the *in situ* cleaning procedure: oxygen and carbon spectrum lines are no longer there. The spectrum in Fig. 1b indicates the absence of any impurities except the deposited Pd, demonstrating a very good cleanliness control during Pd evaporation.

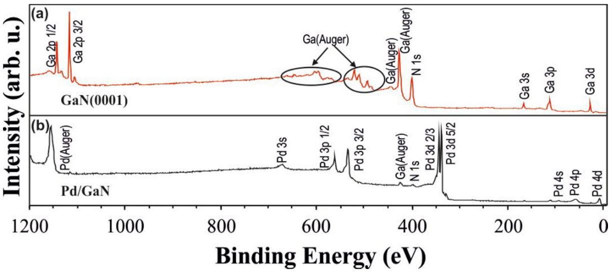


Fig. 1. XPS spectra of a wide band energy range (from 1200 to 0 eV): (a) clean GaN(0001) substrate, (b) after the Pd/GaN(0001) interface formation. Mean thickness of the Pd film is 5 nm.

STM analysis of the GaN(0001) surface topography shows the presence of terraces with 100 nm in width and ~1 nm in height (which corresponds to the double lattice parameter $c$ of GaN) (Fig. 2). A number of dislocation defects typical of GaN epitaxial layers on sapphire are clearly visible from the topographies in Fig. 2a. Diffraction pattern inset in Fig. 2a exhibits a hexagonal structure of the clean GaN(0001) surface.

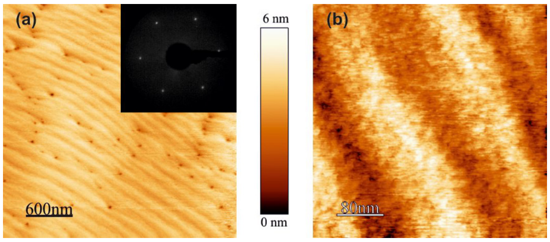


Fig. 2. STM images of GaN/$Al_2O_3$ topography registered after *in situ* cleaning: (a) imaged area $3 \times 3$ $\mu m^2$, (b) $400 \times 400$ $nm^2$. Inset in (a) shows LEED pattern of GaN(0001) surface taken at 80 eV.

Palladium does not wet the GaN(0001) surface. The STM topographies disclose a grainy structure of Pd film beginning from the earliest stages of growth. No diffraction pattern is observed after Pd deposition. The growth preserves the substrate surface terrace-step topography up to the mean thickness of 5 nm (see Fig. 3). A prolonged exposure to Pd beam, leading to thicker layers, ends with the decay of substrate-originated outlines of the terraces. Also numerous surface defects become covered. The Pd/GaN system appears very difficult to be STM imaged. This results from Pd accumulation on the scanning tip. Grainy structure of a metal film is an undesirable feature for most applications in modern electronics. It causes changes in electrical properties of the metal-semiconductor interface depending on the film thickness. We have checked how the *I-V* characteristics of the STM tip/sample contact changes with Pd coverage. Examples are shown in Fig. 4. The *I-V* curve evolves with the Pd film thickness from a poorly conducting contact between the tungsten tip and the clean GaN surface toward a better conducting Pd/GaN junction, whose conductance improves with increasing thickness of the Pd film.

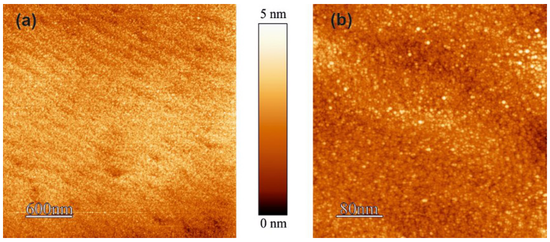


Fig. 3. STM topography of Pd film of mean thickness 5 nm on GaN which reveals a grainy morphology of the film. The surface terrace-step topography of the substrate is still visible. Imaging area equals 3 × 3 μm$^2$ for (a) and 400 × 400 nm$^2$ for (b).

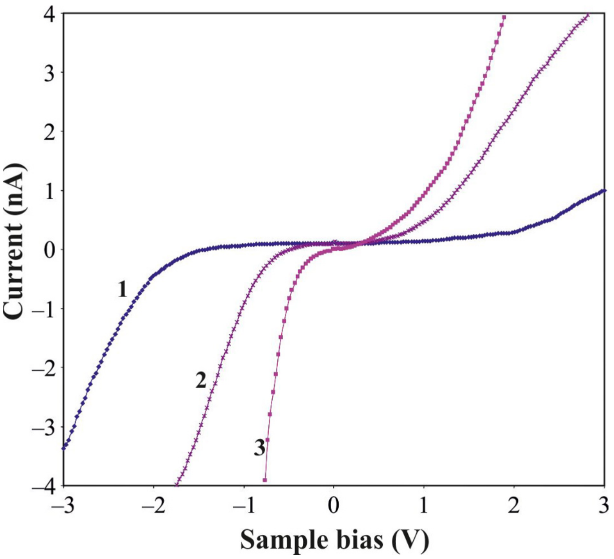
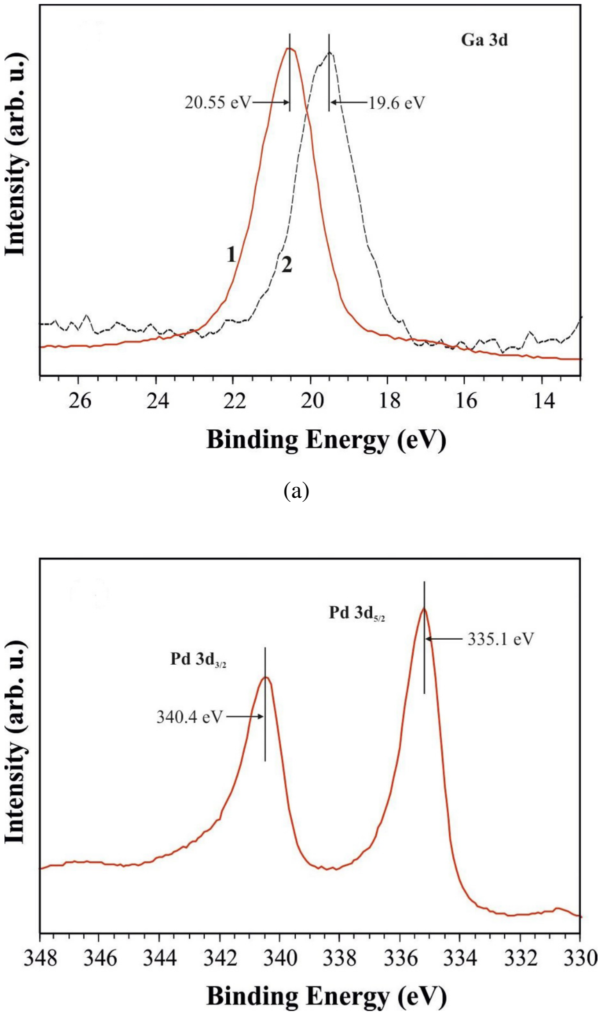


Fig. 4. The *I-V* characteristics of the STM tip/sample contact taken for the tungsten tip and the clean GaN (1); and for the Pd/GaN junction formed by Pd layers of 2.5 nm (2) and 5 nm (3) average thickness.

The physicochemical processes occurring at the Pd/GaN interface and the interface electronic properties were monitored by means of XPS and UPS. The signal of the substrate's spectral lines diminished with increasing evaporation time, while that from the Pd film increased. After deposition of a ~5 nm thick layer of Pd, the Ga3d line shifted by 0.95 eV from the position 20.55 eV toward the low binding energy (Fig. 5a). The peak half widths before and after Pd evaporation amounted to 1.7 eV. The position of peak was unchanged with continued evaporation, though its intensity decreased. Position of the Pd3d doublet amounted to 340.4 eV for the Pd3d3/2 line and 335.1 eV for the Pd3d5/2, which was in accord with tabular data [10], and the peak half width was 1.51 and 1.38 eV, respectively, see: Fig. 5b. We conclude that the shift observed for the Ga3d line is connected with the Schottky barrier formation in the Pd/GaN junction. Chemical interaction between Ga and Pd when Pd is deposited at RT and the adlayer is not annealed should be excluded since no chemical shift of Pd spectral lines has been noticed.

Essential changes were observed in the form of valence band, which is shown in Fig. 6. Prior to deposition of the metal, the band showed clearly a semiconductor's character. The position of binding energy at the valence band maximum (VBM) was at 2.75 eV below $E_F$, as determined from UPS measurements by extrapolation of the line fit to the leading edge of the spectrum. The relevant electron affinity amounts to 3.1 eV which has been calculated based on the relation $\chi = h\nu - W - E_g$,



(a)

(b)

Fig. 5. (a) The Ga3d normalized spectral line for the clean substrate (1) and after Pd deposition (5 nm thick film) (2). The Pd adsorption shifts the line position from 20.55 to 19.60 eV. (b) Position and shape of the Pd3d line for the same Pd film. The line remains at the same position as for bulk Pd.

where $h\nu = 21.2$ eV is the energy of the incident photons, $W = 14.7$ eV is the width of recorded spectrum from the VBM, and $E_g = 3.4$ eV is the band gap of the semiconductor.

After Pd deposition the band revealed a metallic character; a high density of states occurred in the range between the Fermi energy and the VBM of the semiconductor. The work function of the Pd metallic film was determined using the following expression: $\varphi_m = h\nu - W$. The value of $W$ was estimated to be 15.9 eV, which resulted in work function of 5.3 eV. This is a reasonable value since, according to literature data, the work function of palladium ranges between 5.1 and 5.5 eV depending on the crystallographic direction [11].

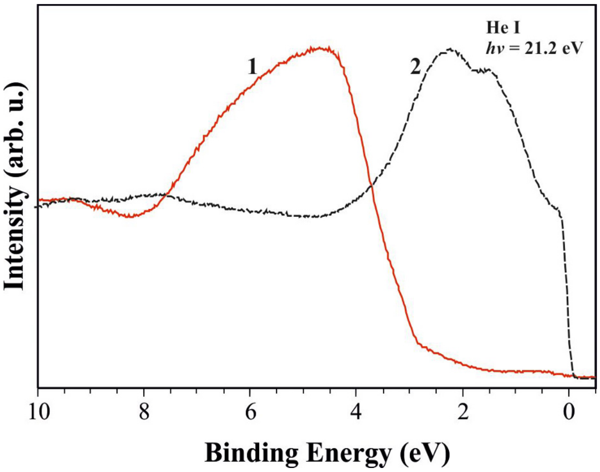


Fig. 6. The UPS valence spectra taken for the clean GaN (1) and after deposition of 5 nm thick Pd film (2).

The Schottky barrier height $\varphi_B$ is one of the key quantities that characterizes the properties of a metal/semiconductor junction. If there is no chemical interaction between metal and semiconductor, its magnitude can be determined from XPS measurements by employing the procedure of Waldrop et al. described for SiC [12]. Similar studies have also been carried out for the GaN semiconductor [13]. Since our XPS measurements excluded any Ga and Pd chemical interaction for the Pd layer deposited at RT, the Schottky barrier height $\varphi_B$ may be calculated from the formula $\varphi_B = E_g - E_F^S$, where $E_g = 3.4$ eV is the band gap of the semiconductor and $E_F^S = E_{Ga3d}^m - \Delta E$ with the $E_{Ga3d}^m$ being the binding energy of the Ga3d core level line as it is shifted due to charge transfer at the Pd/GaN interface following the Pd film deposition. The $\Delta E = 17.8$ eV defines the initial binding energy of the Ga3$d$ core level with respect to the VBM, which value is in accord with the previous data [14]. The barrier height at the phase boundary of Pd/GaN, as calculated basing on the above data, amounts to 1.6 eV. This value is consistent with the literature results [4–6].

## 4. Conclusions

Combined surface techniques of XPS, UPS, STM and LEED were used to investigate chemical and electrical properties of the Pd/GaN(0001) junction. The obtained Pd films have a grainy morphology beginning from the earliest stage of growth. Electrical conductivity of the Pd/GaN junction enhances with increasing thickness of Pd layer. The electron affinity 3.1 eV for the clean n-GaN surface as well as the work function of the Pd film equal to 5.3 eV have been calculated from the results obtained. The XPS measurements have excluded a chemical interaction at the Pd/GaN interface for the RT deposited Pd films. This allowed us to estimate the Schottky barrier height of the Pd/GaN contact, from the data acquired by using XPS and UPS, to be equal to 1.60 eV.

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## References

[1] KHAN M.A., SHUR M.S., KUZNIA J.N., CHEN Q., BURM J., SCHAFF W.J., *Appl. Phys. Lett.*, 66 (1995), 1083.
[2] PONCE F.A., BOUR D.P., *Nature*, 386 (1997), 351.
[3] TAN W.S., HOUSTON P.A., PARBROOK P.J., WOOD D.A., HILL G., WHITEHOUSE C.R., *Appl. Phys. Lett.*, 80 (2002), 3207.
[4] WANG L., NATHAN M.I., LIM T.H., KHAN M.A., CHEN Q., *Appl. Phys. Lett.*, 68 (1996), 1267.
[5] GUO J.D., FENG M.S., GUO R.J., PAN F.M., CHANG C.Y., *Appl. Phys. Lett.*, 67 (1995), 2657.
[6] RICKERT K.A., ELLIS A.B., KIM J.K. et al., *J. Appl. Phys.*, 92 (2002), 6671.
[7] TANUMA S., POWELL C.J., PENN D.R., *Surf. Interface Anal.*, 11 (1988), 577.
[8] POWELL C.J., JABLONSKI A., *NIST Standard Reference Data*, US National Institute of Standards and Technology, Gaithersburg, MD, 2010.
[9] HORCAS I. et al., *Rev. Sci. Instrum.*, 78 (2007), 13705.
[10] CRIST B.V., *Handbooks of Monochromatic XPS Spectra*, vol. 1, John Wiley & Sons Ltd., Chichester, 2000, 278.
[11] METHFESSEL M., HENNIG D., SCHEFFER M., *Phys. Rev. B*, 46 (1992), 4816.
[12] WALDROP J.R., GRANT R.W., WANG Y.C., DAVIS R.F., *J. Appl. Phys.*, 72 (1992) 4757.
[13] LIN Y.-J., HSU C.-W., *J. Electron. Mater.*, 33 (2004), 1036.
[14] WU C.I., KAHN A., *J. Vac. Sci. Technol. B*, 16 (1998), 2218.

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