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Ru/GaN(0001) Interface Properties

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We report the results of our studies of ruthenium layer structures adsorbed on GaN(0001). Ruthenium was evaporated at room temperature under ultrahigh vacuum conditions onto n-type GaN substrates epitaxially grown on sapphire. When X-ray photoelectron spectroscopy confirmed the presence of Ru bonds in the deposited adlayer, the ultraviolet photoelectron spectroscopy shown a peak at the Fermi level as well as lines originating from ruthenium. The height of the Schottky barrier was calculated based on the data measured by X-ray photoelectron spectroscopy and ultraviolet photoelectron spectroscopy and amounts to 1.5 eV. The work function of Ru adlayer is 4.4 eV, while the electron affinity of n-GaN(0001) substrate equals 3.4 eV.

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1. Introduction

Gallium nitride (GaN) and related compounds are very interesting because of their wide applications as ultraviolet light emitting devices as well as high temperature, high frequency and high power electronic devices. The interest in these materials is due to the fact that they have unique properties such as the direct band gap, high physicochemical resistance, a relatively high melting point and good thermal conductivity [1]. Ruthenium and its compounds are widely used in the electronic industry i.e. for lead-free thick-film resistor production [2] or as a material for fabrication of reliable contact to semiconductors [3, 4].

Metal/GaN interface is the essential part of the electronic device; on the one hand as ohmic, and the other as the Schottky contact, thus the characterization and understanding of the properties of the interface is very important. Electrical properties of ruthenium based contacts to n-GaN were investigated by measurement of $I-V$ curves and the metal was found to be a good candidate for the high temperature applications [4–7]. Despite the above, there has still been a deficit of basic research on pure Ru layers on GaN substrates reported thus far.

Herein we report the results of the studies of Ru/GaN(0001) interface by surface sensitive techniques.

2. Experimental

The n-type GaN(0001) used in this study was grown on an Al_2O_3(0001) substrate. An atomically flat, 10 μm thick epitaxial GaN layer was Si-doped ($n = 1-3 \times 10^{18}$ cm^{-3}). The sample around 5×8 mm^2 in size was degreased in isopropanol, then rinsed in distilled water and mounted with tantalum strips onto a molybdenum plate. The GaN surface was prepared by annealing up to 750 °C in an ultrahigh vacuum (UHV) condition. Ru thin film was deposited at room temperature (RT) on n-GaN substrates in UHV. Ruthenium was evaporated from a water-cooled electron beam evaporator. An ion current of the molecular beam (400 nA) was applied to control the growth rate equal to about 5 nm/min. Surface chemical analysis was performed by X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and low energy electron diffraction (LEED).

3. Results and discussion

XPS wide spectrum of fresh GaN(0001) samples placed into the UHV analytic system showed contaminants of oxides and carbon. To obtain the surface free of carbon and with a small oxygen impurity, the substrate was degassed at 500 °C and then annealed at 750 °C for 30 s several times. The LEED diffraction patterns for that prepared sample exhibited a (1×1)-GaN(0001) structure with sharp and bright spots.

Ruthenium layers were grown on a cleaned GaN(0001) surface gradually, their thickness increased with evaporation time (the stability of the source had been checked by controlling the ion current of the evaporated Ru molecular beam). The XPS signal of the substrate lines was decreased with increasing evaporation time, while that of the Ru adsorber increased. The XPS spectrum of the Ga 3d core level line for the cleaned GaN(0001) surface is shown in Fig. 1. The Ga 3d peak for the cleaned GaN surface at 20.2 eV with the full width at half-maximum (FWHM) equal to 1.8 eV is deconvoluted into three chemical components: the main, central component corresponds to Ga–N bond, the right one to Ga–Ga, and the left to Ga–O bonds, respectively (Fig. 1). The O 1s spectral lines recorded before and after annealing process shows that vestigial amount of oxygen remained on the cleaned surface (inset, Fig. 1). The Ga 3d for GaN(0001) covered with Ru layer shifts by 0.6 eV toward the low binding energy and its FWHM slightly increases to 1.9 eV. No diffraction pattern is observed after Ru deposition for any measured thickness of the adsorber. This indicates

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that the Ru layers have a disordered structure and/or grown in 3D mode forming randomly oriented and distributed grains on the surface. The position of the Ru 3*d* doublet shown in Fig. 2, amounts to 279.7 eV for the Ru $3d_{5/2}$ line and 283.8 eV for the Ru $3d_{3/2}$, and its FWHM is 1.5 eV. The result is consistent with the referential data [8].

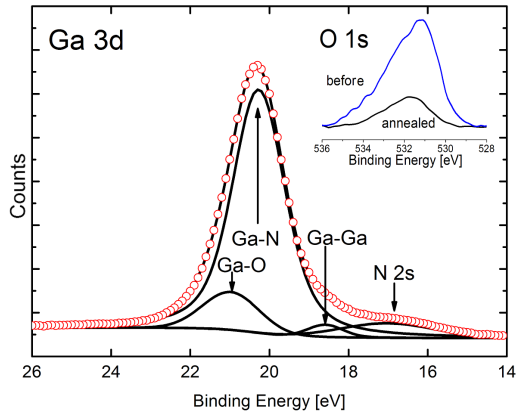

Fig. 1. Deconvolution of the Ga 3*d* peak of the XPS spectrum obtained for the cleaned GaN(0001) substrate. Three components have been fitted (solid line) to experimental data (red open circle). Inset: the O 1*s* lines recorded before and after annealing process.

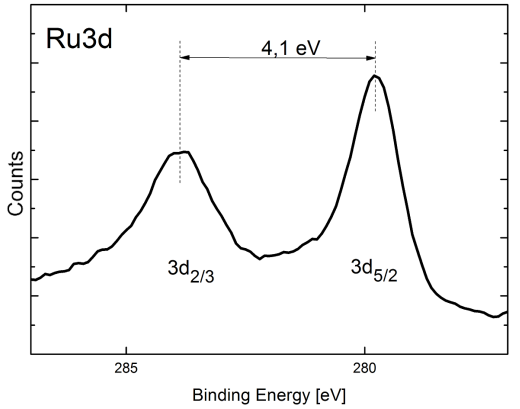

Fig. 2. XPS Ru 3*d* spectrum recorded for Ru film 5 nm thick deposited on GaN(0001) at RT.

Photoelectron spectrum of the valence band for the cleaned GaN(0001) surface and with the Ru overlayer is shown in Fig. 3. The position of the valence band maximum (VBM) for the substrate prior to deposition of the metal is found to be 2.6 eV below the Fermi level (E_{F}), as determined from UPS measurements by linear extrapolation of the location of the density of state edge at the point of background intersection and is 17.6 eV above the Ga 3*d* core level; very close to the value of 17.7 eV reported by Waldrop and Grant [9]. The shape of the valence band is typical for *n*-type semiconductors. The electron

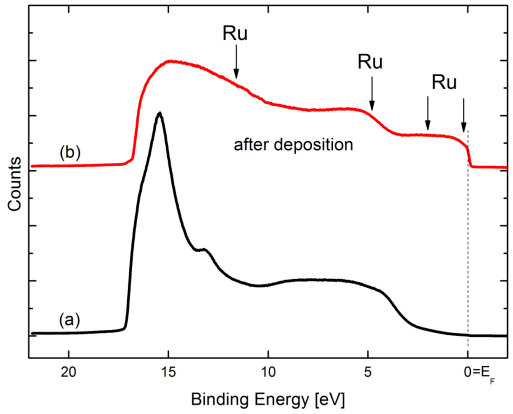

Fig. 3. UPS spectra of (a) cleaned GaN(0001) surface and (b) after deposition of 5 nm thick Ru layer. Arrows indicate positions of spectral lines originated from ruthenium.

affinity χ amounts to 3.3 eV which was calculated by the formula $\chi = h\nu - W - E_g$, where $h\nu = 21.2$ eV is the energy of the incident photons, $W = 14.5$ eV is difference between cut off energy and VBM, and $E_g = 3.4$ eV is the band gap of the GaN.

Deposition of Ru layers caused essential changes in the electron energy distribution collected by ultraviolet photoelectron spectroscopy. Major changes in the valence band are evident in the low binding energy parts, a high density of states arises in the range between the Fermi level and the position of the VBM of the cleaned GaN. The shape of the band reveals a metallic character. On the curve there are four characteristic maxima (marked by arrows): the first one at about 0.6 eV, the second at 2.0 eV, the third at about 4.8 eV and the fourth at 11.6 eV below the E_{F}. These positions are consistent with the literature data [8]. Minor differences in the spectrum also occur in the cut off energy which results in changes in the vacuum level. The work function of the Ru layers was determined using the following expression: $\varphi_m = h\nu - E_{cutoff}$. The latter value (cut off energy) was estimated to be 16.8 eV and it results in work functions of 4.4 eV. According to literature data [7, 10], the work function of ruthenium ranges between 4.5 and 5.9 eV depending on the crystallographic direction, thus the obtained value is appropriate.

The Schottky barrier height φ_B is the key quantity that determines the behavior of the metal/semiconductor interface. Its magnitude can be determined using XPS and UPS by the procedure of Waldrop et al. applied for SiC [11]. Similar studies have also been provided for the GaN semiconductor [12]. The magnitude of φ_B can be calculated from the formula $\varphi_B = E_g - E_{\mathrm{F}}^{\mathrm{S}}$, where $E_{\mathrm{F}}^{\mathrm{S}} = E_{\mathrm{Ga\ 3}d}^{\mathrm{m}} - \Delta E$. $E_{\mathrm{Ga\ 3}d}^{\mathrm{m}} = 19.6$ eV is the binding energy of the Ga 3*d* core level line for GaN, with overlayers of Ru as it is shifted due to electron charge transfer at the phase boundary of Ru/GaN. The ΔE defines the position of the Ga 3*d* peak for the cleaned semiconductor with respect

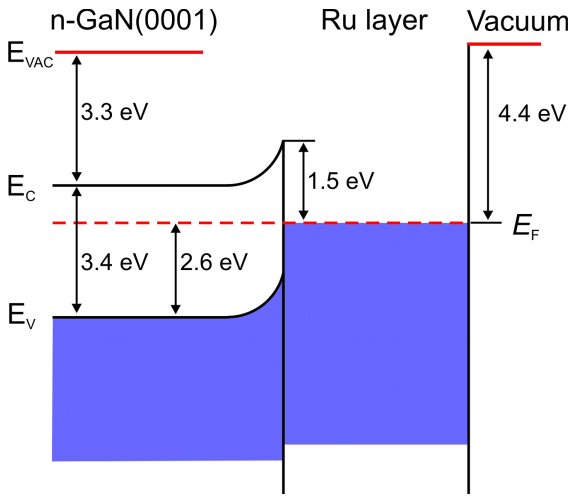

Fig. 4. Schematic energy diagram for the Ru/GaN(0001) interface elaborated based on measured data.

to the VBM, which was specified above in the text. The SBH at the Ru/GaN(0001) interface, as calculated basing on the data, amounts to 1.5 eV (Fig. 4) The obtained value is slightly higher than that calculated according to the Schottky–Mott rule: $\varphi_B = \varphi_m - \chi$, which amounts to 1.1 eV.

4. Conclusions

The n-type GaN(0001) surfaces were used to investigate the chemical and the electrical properties of the Ru/GaN interface. The electron affinity at the cleaned n-GaN(0001) surface amounts to 3.4 eV. LEED patterns shows a well-ordered (1×1)-GaN(0001) structure for the starting substrate. The work function of 5 nm Ru film on the substrate is 4.4 eV, as calculated from UPS spectra. The Ru layers do not grow epitaxially. The height of the Schottky barrier calculated based on the data measured by XPS and UPS equals 1.5 eV.

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