Metal/GaN contacts studied by electron spectroscopies

J. Dumont, R. Caudano, and R. Sporken
Facultés Universitaires Notre-Dame de la Paix, Laboratoire Interdisciplinaire de Spectroscopie Electronique, Namur, Belgium
E. Monroy, E. Muñoz
Universidad Politecnica de Madrid, E.S.T.I., Ciudad Universitaria, Madrid, Spain
B. Beaumont, P. Gibart
Centre de Recherche sur l'Hetero-Epitaxie et ses Applications, CRHEA-CNRS, Valbonne, France

ABSTRACT

Au/GaN and Cu/GaN Schottky contacts have been studied using X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES). Clean and stoechiometric GaN samples were obtained using in situ hydrogen plasma treatment and Ga deposition. The growth of Cu and Au follows Stranski-Krastanov and Frank van der Merwe modes respectively. The interfaces are sharp and non-reactive. Schottky barriers of 1.15eV for Au/GaN and 0.85eV for Cu/GaN were measured using XPS.

INTRODUCTION

GaN and related wide band gap semiconductors are of particular interest in blue and ultraviolet (UV) optoelectronic applications and for high power and high temperature electronic devices. An impressive number of articles have been published over the past few years regarding the properties of GaN and GaN-based devices, but comparatively few detailed studies of metal/GaN interface formation have been reported. Kampen and Mönch [1] described the Schottky barrier height of ideal metal/GaN contacts based on the metal-induced gap states (MIGS) and electronegativity model:

$$\phi_{Bn} = \phi_{cnl} + S_{\chi}(\chi_m - \chi_s) \qquad (1)$$

While the difference χ_m - χ_s between the electronegativity of the metal and of the semiconductor is specific to each metal, the slope parameter S_{χ} and the charge neutrality level Φ_{cnl} are characteristic of GaN. They were calculated by Kampen and Mönch [1] who obtained S_{χ} = 0.29 eV/Miedema-unit. and Φ_{cnl} = 2.35 eV with respect to the top of the valence band. Bermudez [2] investigated the dependence of the structure and electronic properties of wurtzite GaN surfaces on the method of preparation. Ordered and unreconstructed surfaces were obtained. A bare surface barrier height was measured on these surfaces that depends on the annealing temperature and reaches 0.7eV for surfaces annealed at 700°C. When Mg was grown on wurtzite GaN surfaces, the energy difference between the Fermi level and the valence band maximum E_F-VBM increased with Mg coverage while no intermixing between Mg and GaN was observed [3]. Mohney and Lin [4] used a thermodynamical approach to predict the phase diagrams of many transition metal-Ga-N systems and to explain the electrical properties of the contacts.The structure and bonding at the metal/GaN interface are expected to affect electronic properties of the contact and in particular its barrier height and specific resistance. The present paper describes a compositional analysis of Au/GaN and Cu/GaN interface formation and the evolution of the Schottky barrier height during the interface formation. These studies are based on in situ XPS measurements.

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EXPERIMENTAL PROCEDURE

GaN epitaxial layers were grown at CRHEA (Valbonne, France) on (0001) sapphire substrates by metalorganic vapor phase epitaxy (MOVPE) at atmospheric pressure[5]. A 100 Å thick AlN buffer layer was used. Non intentionally doped samples showed n-type conduction, with a carrier concentration of about 10^{17} cm^{-3}, and a Hall mobility of about 130 $cm^2/V.s$. These samples had to be cleaned prior to metallization.

Several cleaning procedures will be discussed below. They usually involve wet chemical etching, followed by various treatments in ultra-high vacuum (UHV), such as annealing, exposure to atomic hydrogen, or exposure to a Ga flux. The atomic H was obtained from an RF plasma source (Oxford Applied Instruments, Model MPD20) operated at 175W RF power. The base pressure in the preparation chamber was 5 10^{-10} Torr. The plasma was ignited with nitrogen instead of hydrogen. The nitrogen was then gradually replaced by hydrogen. A flux of 9 sccm H_2 (purity N57), rising the pressure to 2 10^{-2} Torr, gave the brightest plasma (checked with a photodiode). During these treatments, samples were heated to 700°C. Ga was evaporated from a conventional effusion cell heated to 850°C. The Ga layer thickness, estimated from the XPS signals, ranged from 20 to 60Å.

Au and Cu were deposited by thermal evaporation from effusion cells equipped with BN crucibles. Background pressure was about 2 10^{-10} Torr prior to evaporation, and rose to 1 10^{-9} Torr during the metal deposition. Au was evaporated in a UHV chamber pumped by an ion getter pump and by a liquid-nitrogen cooled titanium sublimation pump. Cu was evaporated in a chamber equipped with a 380l/s turbomolecular pump. Evaporation rates range from 0.25 to 10Å/min, measured by a quartz microbalance. In both cases, the samples could be transferred between the evaporation chamber and the spectrometer under UHV.

Two instruments were used for the XPS measurements. The Au/GaN interface was studied with an SSX-100 spectrometer (Surface Science Instruments). This instrument uses a monochromatic and focused X-ray source (Al Kα, hν = 1486.6eV) and a hemispherical analyzer. For the measurements presented here, a spot size of 0.6 μm diameter and 55eV pass energy was used. The corresponding energy resolution, defined as the full-width at half maximum of the Au $4f_{7/2}$ core level peak, is about 1.1eV. A Scienta 300 photoelectron spectrometer was used to record XPS spectra during the Cu/GaN interface formation. This instrument uses a monochromatic Al Kα X-ray source with a rotating anode operated at 6 kW. Photoelectrons were detected by a hemispherical analyzer (150eV pass energy) and a two-dimensional position sensitive detector (micro-channel plate with CCD camera). The energy resolution obtained in these conditions is 0.3eV.

Auger electron spectra were measured with a PHI-595 Scanning Auger Microprobe. A primary energy of 12 kV and an analyzer resolution ΔE/E of 0.5% were used.

Quantitative data analysis required least squares fitting of the core level peaks. Fitting procedures for Ga3d, Au4f and N1s were already described elsewhere [6]. To fit $Cu2p_{3/2}$ and $Ga2p_{3/2}$ peaks a Shirley background and a Doniach-Sunjič function were chosen.

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RESULTS AND DISCUSSION

Cleaning of GaN surfaces

Several techniques were used to clean the GaN samples. Sample #1 was cleaned in KOH and aqua regia and then heated to 900°C under UHV. This treatment removes most of the carbon and oxygen. Sample #2 was first dipped into boiling HNO_3 and deionized water. As shown in figure 1, this chemical cleaning reduces the amount of gallium oxide but the amount of carbon is left unchanged. Moreover, even in argon atmosphere, the surface oxidizes fast again (in less than 1 minute) when the samples are loaded into UHV. Hence any ex situ cleaning must be followed by an in situ cleaning procedure. Both Khan et al. [7] and Bermudez et al. [2] have shown that atomically clean GaN surfaces can be prepared by Ga deposition and desorption. Here, we used atomic hydrogen (H*) from an RF discharge as an additional step to prepare clean and stoechiometric surfaces. Auger spectra in figure 1 (left) show that the H* treatment removes C contamination, while deposition of Ga followed by desorption at 950° removes the oxygen contamination. In order to obtain clean surfaces we combined the H* and Ga treatments. XPS shows that both O and C are now below the detection limit (figure 1, right).

Based on the distance between the valence band edge (obtained by linear extrapolation) and the Fermi level and knowing the value of the bandgap of GaN (3.4 eV), Fermi level is found at 0.9 ± 0.05 eV below the conduction band minimum for the bare surface. The Ga $3d_{5/2}$ core level peak from GaN appears at 17.6 ± 0.05 eV below the valence band edge, in good agreement with the value of 17.8eV (referred to the centroïd of the Ga 3d peak) reported previously [6].

Metal/GaN interface formation

Au/GaN results shown here are extracted from the article published by Sporken et al. [6] and are compared to the present study of the Cu/GaN interface formation. In this

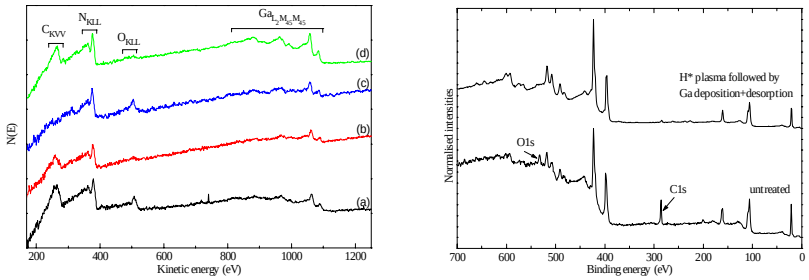

Figure. 1 *Left: Auger spectra of GaN cleaned following different procedures: (a) untreated; (b) cycles of boiling HNO_3 and deionized water; (c) same as (b), followed by H* exposure at 600°C;(d) same as (b) followed by Ga deposition and desorption at 950°C. Right: XPS spectra of GaN surfaces: (a) untreated; (b) cycles of H* exposure followed by Ga deposition + desorption.*

section, we first discuss the morphology of the interface and the growth of the copper layer using XPS core level intensities and shapes. Then, the Schottky barrier height measured by XPS is explained using the MIGS and electronegativity model.

First of all, since the lineshape of the XPS spectra from the substrate and adsorbate

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does not change during the growth of copper (figure 2), we conclude that the Cu/GaN interface is non reactive like the Au/GaN contact grown at room temperature [6].

Gold grows in a layer by layer (also called Frank van der Merwe or 2D) mode on GaN. This leads to exponential variations of the XPS signals from the substrate ($I \propto \exp(-z/\lambda)$) and adsorbate ($I \propto 1-\exp(-z/\lambda)$) with overlayer thickness. The attenuation length λ is related to the inelastic mean free path of the photoelectrons; it can be calculated using the equation [8]:

$$\lambda(nm) = 0.41\left[\frac{A(g\,mol^{-1})\,10^{24}}{\rho(kg\,m^{-3})\,N(mol^{-1})}\cdot E_{Kin}(eV)\right]^{1/2}, \qquad (2)$$

where A is the atomic mass, ρ is the bulk material density, N is Avogadro's number and E_{kin} is the kinetic energy of the photoelectron. For Au/GaN, excellent agreement is found between experimental and calculated XPS intensities [6]. For Cu/GaN, least squares fitting the experimental data (figure 3, left) using the exponential functions described above, with the photoelectron attenuation length λ as fitting parameter, gives reasonable values of λ (table I). However, the calculated curves do not reproduce the experimental data very well. This means that the growth is not perfectly 2D. Since we do not see a change in chemical bonding of the Cu, Ga and N, we suggest that the interface is still abrupt but islands are formed. Thus we fitted the data using a modified Stranski-Krastanov growth model. In this model, described more precisely by Sporken et al. [9] and later by Conard et al. [10], hemispherical islands grow on incomplete 2D layers. The substrate and overlayer intensities are calculated assuming that the 2D layer and the islands have the same density as bulk Cu. The fitting parameters are the thickness of the 2D layer, the number of islands per unit area and the attenuation length λ. As observed on figure 3 (right), the agreement is much better than for the simulation based on layer by layer growth. The number of islands obtained from the fit is about $1.10^{11}cm^{-2}$ and the 2D layer thickness is around 4.10^{15} atoms.cm^{-2} which corresponds to 5Å. However, the values of the attenuation length for Ga and N are much smaller than the theoretical values (see table I).

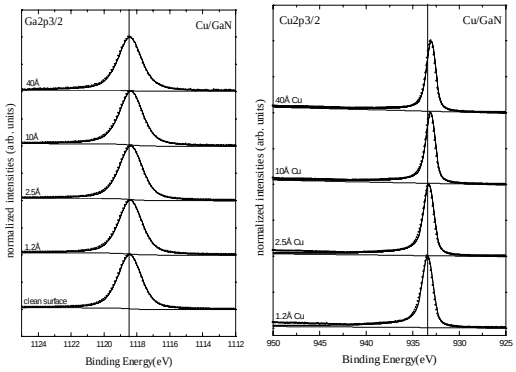

***Figure. 2**: Ga2p$_{3/2}$ and Cu2p$_{3/2}$ XPS spectra during formation of the Cu/GaN interface.*

This means that the XPS intensities of the GaN decrease to quickly with overlayer thickness. This may be due to an overestimation of the density of the 2D layer. It is likely indeed that the crystalline structure of the adsorbate is influenced by the GaN and that its

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density is different from the one of bulk copper. At the beginning of the growth, the copper atoms are distributed mainly on GaN adsorption sites. The lattice parameter of GaN is 3.19Å. On a GaN (0001) face, it is then expected that the 2D copper layer will have a preferred (111) orientation. A fit based on a number of atoms per Cu monolayer equal to 1.13 10^{15}cm^{-2} (i.e a Cu atom per adsorption site of the GaN (0001) face) gave us the same 2D layer thickness as before (5Å), but photoelectron attenuation lengths much closer to the theoretical values (table I).

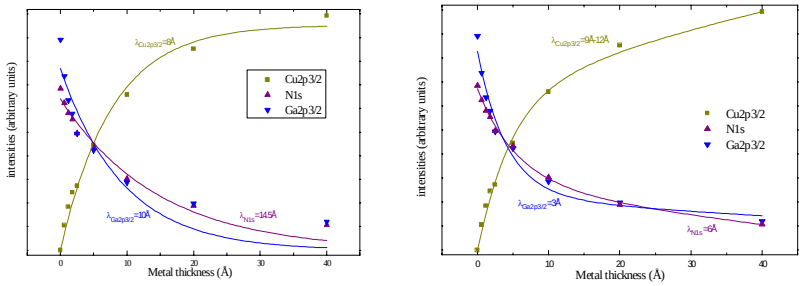

Figure. 3. *Experimental and calculated XPS intensities during the growth of Cu on GaN. Left: calculated intensities for layer by layer growth mode. Right: calculated intensities for modified Stranski-Krastanov growth mode .*

The distance between the conduction band minimum and the Fermi level was determined from the binding energy of the core level peaks ($Ga2p_{3/2}$ or Ga3d or N1s and $Cu2p_{3/2}$). Figure 4 shows the position of the Fermi level in the band gap. The clean surface shows a barrier height of 1.4 eV that decreases to reach the stable value of 0.84 eV after depositing 5.8 10^{15} atoms cm^{-2} of copper. This is similar to the Au/GaN interface formation [6]. During the formation of the Cu/GaN Schottky barrier (up to 5.8 10^{15}atoms cm^{-2}), the shape of the Cu $L_3M_{45}M_{45}$ Auger features changes (figure 4, right). This reflects changes in the electronic structure of the copper, which initially does not have full metallic character. Eventually, the Auger transitions reach a shape typical of metallic Cu.

Table I: *photoelectron mean free paths. 1st column: λ calculated using the Seah and Dench formula. [8] Other columns: values obtained from the XPS intensities. ρ_{2D} = density of the 2D layer; N_{2D} = number of atoms per unit area in the 2D layer.*

	Calculated value	Layer by layer mode	Layer + islands mode:$\rho_{2D} = \rho_{Cu}$	Layer + islands mode: $N_{2D} = N_{GaN}$
$\lambda_{Ga2p3/2}$	8Å	10Å	3Å	5Å
λ_{N1s}	15Å	14Å	5Å	10Å
$\lambda_{Cu2p3/2}$	11Å	9Å	12Å	12Å

The final Schottky barrier height of Cu/GaN and Au/GaN measured by XPS is 0.84eV and 1.15eV respectively. These values are close to results (0.82eV and 0.96eV) from the MIGS and electronegativity model using values for S_χ and Φ_{cnl} calculated by Kampen and Mönch [1]. These authors measured and calculated a barrier height of 0.82 eV for Ag/GaN, which is close to our result for Cu/GaN. Such agreement is predicted by eq. 1, since Ag and Cu have the same electronegativity.

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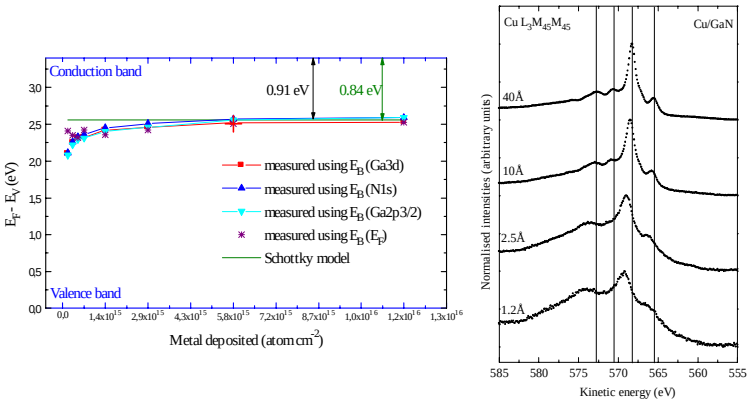

Figure. 4 *Left: position of the Fermi level with respect to the valence band maximum, as a function of Cu coverage. Right: Cu $L_3M_{45}M_{45}$ Auger features; evolution with copper coverage.*

CONCLUSIONS

Clean GaN samples were obtained using atomic H plasma and gallium deposition and desorption. Copper growth on these samples follows a Stranski-Krastanov growth mode. Analysis of the XPS intensities suggests that the 2D Cu layer has an in-plane lattice parameter close to the one of the GaN surface. A Schottky barrier height of 0.84 eV is measured for the Cu/GaN contact. This value agrees with the MIGS and electronegativity model.

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