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## Intermixing and chemical structure at the interface between n-GaN and V-based contacts

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Abstract:

The interface between n-type GaN and V-based contacts was characterized by soft x-ray spectroscopy. We have investigated the chemical interface structure before and after a rapid thermal annealing (RTA) step, which is crucial for the formation of an Ohmic contact. X-ray photoelectron and x-ray excited Auger electron spectra suggest that RTA induces an accumulation of metallic Ga at the surface. Using x-ray emission spectroscopy, we find that the probed nitrogen atoms are in a VN-like environment, indicating that vanadium interacts with nitrogen atoms from the GaN to form VN.

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III-nitride semiconductors are important materials because of their increased use in optoelectronic devices such as light emitting diodes. Their performance depends on a low contact resistance. Thus, forming Ohmic contacts to nitrides is critical. Traditionally, Ti-based contacts were used [1]; more recently, good (*i.e.*, Ohmic) V-based contacts to n-type GaN and n-AlGaN alloys result in better contact resistances [2, 3] at lower annealing temperatures [2]. Since Galesic and Kolbesen [4] demonstrated the “nitridation” of metallic vanadium films (*i.e.*, the formation of VN) by rapid thermal annealing (RTA) in N<sub>2</sub> atmosphere, it has been hypothesized that VN is also formed at the interface between V-based contacts and n-Al<sub>x</sub>Ga<sub>1-x</sub>N after RTA treatment [3]. VN is stable [5] and has a low work function [6], thus it is suitable to form Ohmic contacts to n-GaN (whose electron affinity is about 4.0 eV) and n-Al<sub>x</sub>Ga<sub>1-x</sub>N (whose electron affinity is less than 4.0 eV) [7]. It was found that Al<sub>x</sub>Ga<sub>1-x</sub>N samples need higher RTA temperatures than pure GaN samples for optimal contact resistance [3]. It is speculated that VN is formed at lower temperatures for GaN (or greater Ga content in the alloy) [3], presumably since the bond lengths in GaN are longer than in AlN [8], and hence the bond is expected to be weaker.

The interface between the nitride layer and metal contacts after heat treatment has previously been investigated by (among others) energy dispersive x-ray spectroscopy [9, 10], glancing-angle x-ray diffraction [10], and Auger electron spectroscopy sputter depth profiling [10, 11]. A detailed photoemission investigation of the interface chemistry between low work function metals and GaN was performed by Wu and Kahn [12]. However, the chemical properties of the interface between *V-based contacts* and GaN, in particular the potential formation of VN, have yet to be explored. We have used surface sensitive x-ray photoelectron spectroscopy (XPS), x-ray excited Auger electron spectroscopy (XAES), and surface-near bulk sensitive x-ray emission spectroscopy (XES) to investigate the interface between a V/Al/V/Au

metal contact scheme (where Au is the top-most layer) and n-GaN before and after RTA treatment.

Si-doped GaN samples were grown on c-plane sapphire wafers by molecular beam epitaxy. The samples were chemically treated and V-based contacts were deposited by electron beam evaporation [3]. Two sets of metal contacts were analyzed (referred to as “thin” and “thick”): V(15Å)/Al(80Å)/V(20Å)/Au(100Å) and V(150Å)/Al(800Å)/V(200Å)/Au(1000Å), respectively. Both the thin and thick contacts on n-GaN were annealed by RTA at 650°C for 30 seconds in N<sub>2</sub> atmosphere. The specific contact resistivity was found to be on the order of 10<sup>-6</sup> Ω cm<sup>2</sup> [3].

All samples were sealed in inert atmosphere at Boston University and loaded into ultra-high vacuum (UHV, base pressure in the 10<sup>-10</sup> mbar range) at UNLV via a N<sub>2</sub>-filled glove box (*i.e.*, avoiding any air exposure). XPS and XAES were performed using Mg K<sub>α</sub> and Al K<sub>α</sub> radiation and a Specs PHOIBOS 150MCD electron analyzer. The electron spectrometer was calibrated using XPS and Auger line positions of Au, Ag, and Cu [13]. XES was performed at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, on Beamline 8.0.2. using a variable line spacing spectrometer [14]. The energy resolution is  $E/\Delta E > 1200$  and the spectrometer was calibrated using elastic scattered peaks at different energies (Rayleigh lines). For the XES experiments, the samples were briefly exposed to air prior to introduction into UHV.

Before RTA treatment, the XPS survey scans (not shown) of the n-GaN/V/Al/V/Au samples are dominated by Au features, as expected. After RTA treatment, elements from initially buried layers (*e.g.*, V, Ga, and N) can be observed in the survey scans.

The Ga  $2p_{3/2}$  XPS and Ga  $L_3M_{4,5}M_{4,5}$  XAES detail spectra from the bare (*i.e.*, contact free) n-GaN and the RTA-treated thick and thin samples are shown in Fig. 1(a) and 1(b), respectively. The Ga spectral features differ between the RTA-treated thick and thin samples, and both deviate significantly from the corresponding bare n-GaN reference. The Ga  $2p_{3/2}$  lines (Fig. 1a) of the RTA-treated samples are broader (than the n-GaN line). Furthermore, the thick RTA sample shows a pronounced shoulder at higher binding energies which is attributed to the presence of (at least) a second Ga species. We have thus performed a peak fit analysis (to be described in the following) that indeed indicates that both RTA-treated samples need to be described with (at least) two different Ga species (labeled I' and II), while the bare n-GaN reference can be well described with a single species (labeled I). For species I and I', we chose a Voigt line shape to describe Ga in compound semiconductor environments (GaN and Ga<sub>2</sub>O<sub>3</sub>, respectively). For feature II, we chose a Doniach-Šunjić (DS) line shape to describe Ga in a metallic environment. This choice of line shape and the assignment of species I, I', and II was motivated by the respective observed binding energies, the XAES spectra, and the modified Auger parameters (to be discussed below). We find that the overall quality of the fit improves by selecting the DS line shape for species II (compared to a Voigt). The fits on all three samples employed a linear background and were performed simultaneously by coupling the full width at half maximum (FWHM; Gaussian and Lorentzian for the Voigt line shape and overall FWHM for the DS line shape) and asymmetry factor (DS). The results of the fits are shown in Fig 1(a) as solid lines. The contribution of species II is dominant at the thick RTA sample surface, while the thin RTA sample surface is dominated by species I'. Both species (I' and II) in the Ga  $2p_{3/2}$  spectra of the RTA-treated samples show an energy shift compared to species I in the n-GaN spectrum. This energetic shift can be explained by a change in the Ga chemical environment

(from GaN to Ga<sub>2</sub>O<sub>3</sub>) after contact formation, as will be discussed below. Also, an interface-induced band bending due to the formation of a metal/semiconductor interface could be present.

The XAES Ga L<sub>3</sub>M<sub>4,5</sub>M<sub>4,5</sub> spectra are shown in Fig. 1(b). The spectrum of the bare n-GaN shows only one contribution to the Ga L<sub>3</sub>M<sub>4,5</sub>M<sub>4,5</sub> transition (I), while the XAES spectra of both RTA-treated samples show (at least) two different contributions (species I' and II). As in the case of XPS, the thick RTA-treated sample has a dominant contribution at higher kinetic energies (II), though a small contribution at lower kinetic energies (I') is observed. In contrast, the spectrum of the thin RTA-treated sample is a superposition of two species (I' and II), dominated by species I'.

To identify the two Ga species present, the modified Auger parameter ( $\alpha'$ ) was computed (using the sum of the Ga 2p<sub>3/2</sub> and Ga L<sub>3</sub>M<sub>4,5</sub>M<sub>4,5</sub> lines).  $\alpha'$  is independent of the Fermi level position (*i.e.*, independent of band bending and charging). Our  $\alpha'$  values are plotted and compared to previously published results for Ga-containing compounds [15] in Fig. 1(d). For the bare n-GaN, we find  $\alpha' = 2181.5 \pm 0.1$  eV. This lies between the previously reported values of GaN and Ga<sub>2</sub>O<sub>3</sub>. The O 1s XPS signal of all three samples is shown in Fig. 1(c). We note that the signal for the bare n-GaN is relatively small when compared to the RTA-treated samples. Thus, we interpret the observed  $\alpha'$  of n-GaN (species I) to be indicative of a GaN surface, possibly modified by some adsorbed water and/or OH formation at the surface from the above-mentioned chemical treatment.

For the two RTA-treated samples, a pair of  $\alpha'$  values can be derived (*i.e.*, for species I' and II). For the thin RTA sample, we find  $\alpha'$  values of  $2180.6 \pm 0.1$  eV and  $2184.7 \pm 0.1$  eV for species I' and II, respectively. For the thick RTA sample, we find  $\alpha'$  values of  $2181.0 \pm 0.1$  eV and  $2184.6 \pm 0.1$  eV for species I' and II, respectively. While species I' agrees well with

previously published values for  $\text{Ga}_2\text{O}_3$ , species II agrees well with metallic Ga [15], as shown in Fig. 1(d). The assignment of species I' to an oxide species is supported by the XPS O 1s signal increase for the RTA-treated samples (Fig. 1c). Besides the line shape analysis (as discussed earlier), our interpretation of species II as metallic Ga is further supported by Ref. 11, which reported that Ga is released from GaN when Al/n-GaN is annealed.

To investigate the potential formation of VN at the interface, XES was used to resolve the chemical environment of nitrogen and vanadium atoms at the buried interface between the V-based contacts and n-GaN. In Fig. 2(a), the N K XES spectra of the thick contact on n-GaN before and after RTA treatment are shown, along with reference materials (n-GaN and VN powder). The N K XES spectrum of the untreated contact sample is similar to that of bare n-GaN, as expected. Note the large magnification factor for the spectrum of the untreated contact sample ( $\times 470$ ), which is due to the fact that the n-GaN is buried under V/Al/V/Au layers with a total nominal thickness of 215 nm. In the spectrum of bare n-GaN (Fig. 2a, bottom), a weak emission feature at  $\sim 377$  eV can be observed, which stems from Ga 3d valence electrons relaxing into N 1s core holes (see enlarged inset in Fig. 2a). This feature indicates the presence of N-Ga bonds [16] (note that for the untreated contact sample, it is weaker than the noise level of the spectrum). In contrast to the untreated sample being similar to the n-GaN sample, the thick RTA sample is predominantly in a VN chemical environment. The feature indicative of N-Ga bonds (inset, Fig. 2a) and the prominent GaN shoulder at about 388.5 eV are absent in the thick RTA sample. A detailed noise-level analysis suggests that, for the thick RTA sample, the fraction of N atoms in a GaN environment (within the probing volume) is less than 20%. Thus, we find direct evidence for the formation of VN at the contact/GaN interface.

The RTA-induced formation of VN at the interface is also supported by the V  $L_{2,3}$  XES spectra in Fig. 2(b). The untreated sample displays a similar spectral shape to that of a V metal foil. The thick RTA sample shows an additional feature between 504 and 508 eV similar to the VN powder (Fig. 2b, top). To ascertain whether the spectrum of the thick RTA sample contains a VN contribution, the spectrum of the untreated sample (weighted by a factor of 0.6) was subtracted from the RTA-treated sample spectrum (Fig. 2b, 2nd from top). The difference spectrum shows two emission features which are similar to that of VN. Thus, we find that the V in the thick RTA sample exists in two forms: “unconverted” as metallic V and “reacted” as VN. Our observation of a GaN to VN transformation is also thermodynamically supported since the heat of formation of VN ( $\Delta H_{298} = -217.3$  kJ/mol) is favored over that of GaN ( $\Delta H_{298} = -109.7$  kJ/mol) [17]. The presence of metallic V is likely due to characteristics of the contact scheme: while the upper V layer remains metallic, the lower V layer at the V-GaN interface undergoes VN formation. Consequently, the metallic Ga signal in XPS and XAES is greater for the thick RTA sample than for the thin RTA sample (see Fig. 1a and 1b) since it has more V atoms available at the interface to form VN and hence able to “release” Ga.

In conclusion, we have investigated the interface formation between V/Al/V/Au contacts and n-GaN using soft x-ray spectroscopy. Our findings clearly show VN formation as a result of RTA treatment of V-based contacts on n-GaN. The presence of metallic Ga indicates that GaN serves as the nitrogen source for the observed VN formation. These findings provide new insight into the contact formation of GaN-based devices and the improved performance of V-based contacts.

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### Figure Captions

Fig. 1. Bare and RTA-treated thin and thick contacts on n-GaN: (a) Ga 2p<sub>3/2</sub> XPS spectra (dots) with respective fits (solid) and residuals, (b) Ga L<sub>3</sub>M<sub>4,5</sub>M<sub>4,5</sub> XAES spectra [for the thin RTA

contact sample the experimental data (dots) and a smoothed (solid red) line are shown], (c) O 1s XPS spectra, and (d) the corresponding modified Ga Auger parameters. In (d), hatched areas denote previously published values of Ga, GaN, and Ga<sub>2</sub>O<sub>3</sub> [14].

Fig. 2. (a) XES N K and (b) V L<sub>2,3</sub> spectra of n-GaN, thick contact sample before (“Untreated”) and after RTA, and VN powder as well as a V metal reference. The XES V L<sub>2,3</sub> spectrum labeled “Diff.” is the difference between the “RTA” spectrum and the “Untreated” spectrum (the latter multiplied by 0.6). For all spectra, multiplication factors are given that normalize the maximum count rate of all spectra to the same value. For the “Untreated” sample, the experimental data (dots) and a smoothed (solid red) line are shown. The inset in (a) shows the magnified region of the Ga 3d → N1s transition for the RTA-treated and n-GaN samples.



