

Interaction of Oxygen and Water with Group III-Nitride (InN, GaN) surfaces

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Introduction

Group III-nitrides with wurtzite crystal structure are chemically stable semiconductors with high electron mobilities, high drift velocities and band gaps covering the spectral range continuously from the near infrared to the ultraviolet regime. These properties make them very promising materials for optoelectronic, transistor or sensor applications. For a successful design of electronic devices knowledge of both, bulk and surface properties, is essential. Changes in the surface characteristics are in particular caused by interactions with (gas) molecules. Investigations of the underlying processes are therefore mandatory for a basic understanding of the device behavior, including e.g. the operation principles of sensors and degradation mechanisms of devices. In this context oxygen and water are important molecules since they are always present under environmental conditions.

Experimental and theoretical investigations [1-12] of the interaction of GaN and InN surfaces with molecules have shown that these nitride surfaces are potentially reactive to molecular oxygen and water. For GaN the investigations mainly concentrate on 1×1 (0001) and $(000\bar{1})$ surfaces. However, theoretical calculations of Segev et al. [13] predict the 2×2 reconstructed GaN surface as the thermodynamically preferred one. The interaction of InN with water and oxygen with InN is even less studied and understood. Lebedev et al. [10] investigated the influence of surface oxidation on InN by an ozone-assisted oxidation process. They found out that the surface accumulation of the electrons can be successfully manipulated by the formation of a thin oxide layer.

However, to our knowledge no studies comparing the initial chemical interaction of oxygen and water for the different group III nitrides have been performed so far. Moreover, one might expect that surface reconstructions influence the chemical reactivity strongly since adsorption sites are occupied by adatoms leading to a change in the adsorption behavior compared to the unreconstructed surface.

In this study we present first new results of the interaction of GaN(0001)- 2×2 and InN(0001) surfaces with oxygen and water. We find strong differences in the reaction rates but rather similar adsorbate induced features in the valence band. Moreover, in case of the GaN(0001)- 2×2 surface the reconstruction is destroyed by the surface-molecule interaction.

Experimental

The GaN as well as InN films were grown by plasma-assisted molecular beam epitaxy (PAMBE) using Knudsen cells for metal evaporation and a SVTA RF 4.5 plasma source (13.56 MHz) for nitrogen supply. The growth was controlled in-situ by reflection high electron energy diffraction (RHEED).

As templates for the GaN films N-doped 6H-SiC(0001) samples were used. The grown GaN surfaces with a thickness of a few 100 nm exhibit a RMS roughness of less than 1 nm confirmed by atomic force microscopy (AFM) and a 2×2 surface reconstruction measured by RHEED.

The InN films were grown on Si-doped GaN/Al₂O₃(0001) templates from TDI, Inc. Due to the difficulty in growing high quality, smooth InN films, the samples investigated in this study exhibit a higher RMS roughness (3-5 nm) and the RHEED patterns reveal a 1×1 structure. Details of the growth and surface properties of the GaN and InN films can be found elsewhere [14,15].

After the MBE growth the samples were immediately transferred to the directly connected surface analysis chamber (base pressure of the entire system below 2×10^{-10} mbar) for characterization by X-ray photoelectron spectroscopy (XPS) using monochromated Al K α (1486.7 eV) and non-monochromated Mg K α (1253.6 eV) radiation. Furthermore, ultra-violet photoelectron spectroscopy (UPS) with photon energies of 21.2 eV (He I radiation) and 40.8 eV (He II radiation) was applied.

XPS measurements proof that the as-grown samples are virtually free of contaminations within the detection limit of this method (~ 0.1 at.%). In particular, no oxygen or carbon can be detected by XPS. Furthermore, the measured valence band structure by XPS and UPS agrees well with that previously reported for InN and GaN, respectively [1,14-16], with a valence band maximum 2.9 eV (GaN) and 1.45 eV (InN) below E_F determined from a linear extrapolation of the valence band edge in the monochromated XPS Al K α spectra.

The oxygen as well as the water (cleaned by several freeze-pump-thaw cycles) exposure was performed at room temperature by backfilling the analysis chamber with molecular oxygen and water, respectively. In our experiments partial pressures ranging from 5×10^{-9} to 7×10^{-8} mbar have been used (except for the very high exposure experiments, where the molecules have been

offered in the load lock system at ~ 1 bar). The exposure was calculated based on the measured partial pressure by a Bayard Alpert ionization gauge without any further corrections. Due to the unavoidable presence of hot filaments during the exposure, a partial activation of the offered molecules can not be ruled out completely.

Results and Discussion

Under exposure to oxygen or water at room temperature both types of nitride surfaces interact with the offered molecules. In Fig. 1 a monotonous increase of the O1s core level intensity measured by XPS is detected for all investigated cases. For a higher exposure, a saturation of the surface coverage is observed.

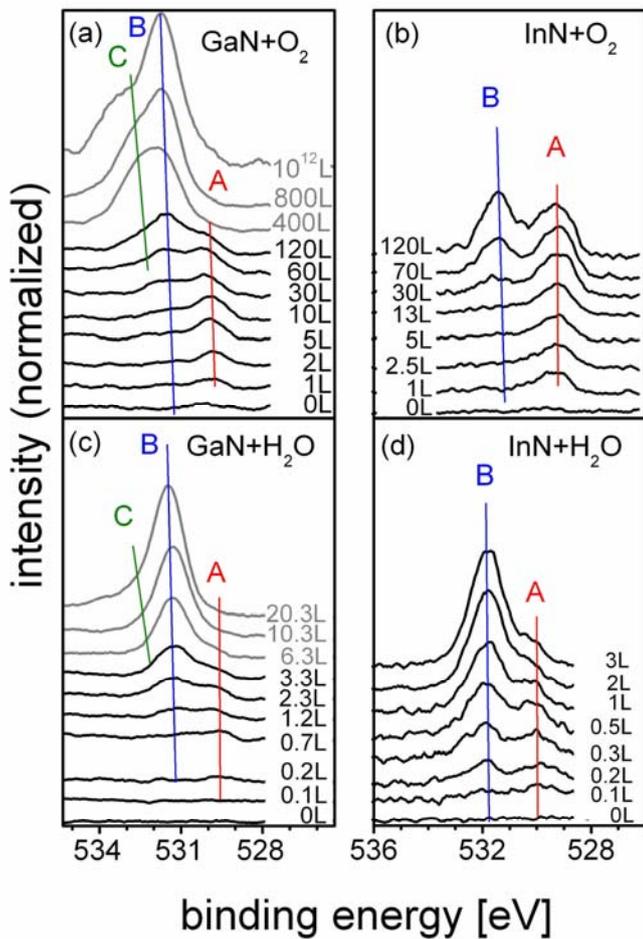


Fig.1: XPS O1s spectra for (a) GaN and (b) InN exposed to oxygen as well as (c) GaN and (d) InN exposed to water. In order to reduce the noise level, the shown spectra are partially smoothed.

The exposure dependencies in the O1s emission reveal some similarities. First of all, small exposures (around 1L) already lead to surface oxygen densities within the detection range of XPS. In all cases a peak denoted as “A” at a binding energy of about 530 eV is initially

detected followed by a peak “B” at around 532 eV. For higher exposures a third peak “C” at around 533.5 eV appears for the GaN surface. So far this state has not been detected for the InN surface.

The determined binding energies of the different chemical states (peak A, B, and C in Fig. 1) for the studied InN and GaN samples are summarized in table 1.

Peak	A	B	C
GaN+O ₂	530.5 eV	532.0 eV	533.5 eV
GaN+H ₂ O	530.5 eV	532.0 eV	533.5 eV
InN+O ₂	530.0 eV	532.0 eV	-
InN+H ₂ O	530.3 eV	531.9 eV	-

Table 1: O 1s binding energies for the different chemical states indicated in Fig.1.

To estimate the oxygen coverage on the GaN (InN) surfaces, we calculated the expected Ga2p (In3d) to O1s XPS peak area ratios using a simple two layer model as previously used e.g. in [3].

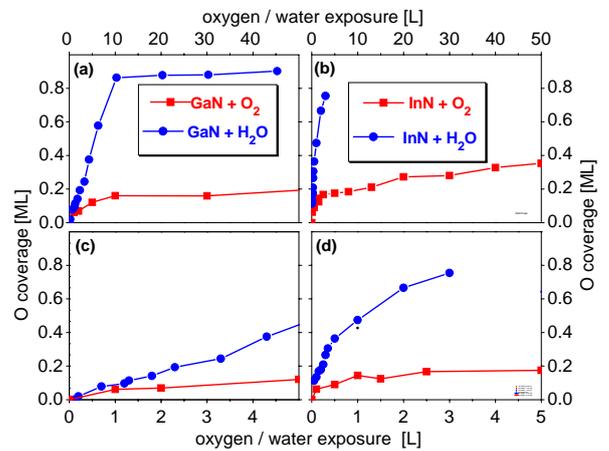


Fig.2: Calculated exposure dependent coverage for GaN (left side; (a) and (c)) and InN (right side; (b) and (d)) exposed to oxygen as well as water. In the upper part the behavior for the first 50 L is shown, whereas the lower part shows the low exposure regime (up to 5 L).

Besides the fact that GaN and InN surfaces strongly react with the offered molecules, some general trends can be deduced from the temporal changes upon exposure. First, the initial reactivity with water is much higher compared to that with oxygen leading to higher sticking coefficients for water than for oxygen. Secondly, the bare InN is more reactive compared to the GaN surface. Interestingly, for the interaction of water with GaN a plateau-like behavior is observed for exposures above 10 L. Such a plateau with an O-coverage of about 0.8 ML is also observed for the interaction of oxygen with GaN for exposures above ~ 1000 L. The available data for the interaction between water and InN presented here, suggest a

similar behavior. For very high exposures a very slow increase of the coverage with exposure is observed. Besides the investigation of the core level spectra, we have additionally studied the changes in the valence band structure. Fig. 3 shows the UPS (HeII) valence band spectra of as-grown GaN and InN in comparison to the corresponding spectra after exposure to oxygen and water, respectively (typical coverage 0.75 to 1.6 ML). In all four cases one observes the development of two states in the valence band at around 6 eV (denoted as O1) and 11 eV (denoted as O2) on GaN surfaces as well as 5.0 eV (O1) and 10 eV (O2) on InN surfaces. Note that the two states S1 and S2 detected at about 2 and 3 eV, respectively, are related to surface states of the GaN film. The state S1 at 2 eV is only observed for the 2×2 surface reconstruction as previously discussed [14]. Both states and the surface reconstruction disappear during the exposure as visible in UPS and RHEED (not shown). According to our XPS data, these two new valence band states are caused by adsorbed oxygen species. Impurities due to adsorption from the residual gas can be ruled out for the following reasons. First, the two states do not emerge after storage in the UHV system and secondly, XPS does not detect any chemical elements besides that of the nitride film and oxygen. In this context it is important to note that hydrogen can not be detected in our XPS measurements. The development of the two oxygen related features in the VB structure is in good agreement with former investigations of GaN and InN oxidation [1,10].

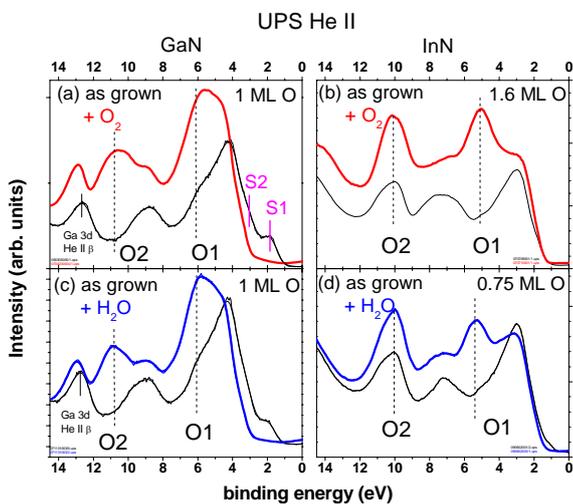


Fig.3: Comparison of the UPS HeII valence band spectra of GaN (left side, (a) and (c)) and InN (right side, (b) and (d)) before (thin black line) and after the exposure to oxygen (red thick line, (a) and (b)) and water (blue thick line, (c) and (d)). O1 and O2 are two oxygen related valence band states.

Starting with the as-grown surface, the two observed states O1 and O2 continuously gain in intensity with increasing exposure. Note that we are not able to detect any other new states in the valence band over the entire investigated exposure regime (in particular including low coverage). Thus, we conclude the exposure of both GaN and InN to oxygen and water results in identical adsorbed species at the surface. Since the formation of hydrogen and oxygen containing species under exposure to pure oxygen seems to be rather unlikely (even if hydrogen is a component of the residual gas), the detected adsorbate is very likely a pure oxygen species. This conclusion is further supported by previous studies on the water adsorption [17]: The adsorption of molecular water leads to a typical structure consisting of three peaks, which are obviously not observed, whereas the formation of OH-groups leads to a two peak structure with a typical relative peak height of about 1:3 ($3\sigma:1\pi$ emission) and a typical energetic separation of $\sim 3\text{--}4$ eV, which is also not in agreement with our experimental data. Moreover, additional experiments using high resolution electron energy loss spectroscopy (HREELS) for the oxygen exposed GaN surface show no evidence for the existence of OH-vibrational modes. However, for the unambiguously identification of the formed adsorbate species further experimental and theoretical efforts are of great importance. In particular, the comparison of the experimental data for the valence band structure with those from ab-initio calculations is expected to provide deep insight into the molecule surface interaction.

The interaction with molecules may also have impact on the electronic properties of the nitride films. In particular the surface band bending might be strongly affected. As can be seen in the valence band data for GaN (see Fig. 3 (a) and (c)) the oxygen as well as the water exposure has also an impact on the energetic position of the spectral features of GaN. Briefly, for GaN surfaces one observes a shift of both, the valence band maximum and the Ga 3d emission (as visible in the Ga 3d He II β emission) towards higher binding energies. The measured shift in Fig. 3 (a) and (c) is ~ 0.2 eV for oxygen and ~ 0.4 eV for water, respectively. In the case of InN no such shift is observed for the valence band maximum in Fig. 3 (b) and (d). The analysis of the In4d emission at a binding energy of ~ 18 eV (not shown), which can also be detected by UPS(HeII), is obscured by changes in the peak shape during interaction with the adsorbates. Moreover, it is important to note, that the observed peak shifts in case of GaN exhibit a rather complicated exposure dependency. For a more detailed discussion further experimental data have to be interpreted, which is beyond the scope of this manuscript. Nevertheless, the observed changes in the GaN indicate that both, oxygen and water, indeed can induce a change in the

band bending. Here a decrease of the initially typical upward band bending of GaN is observed.

Conclusion

We have investigated the interaction of GaN and InN surfaces with oxygen and water. In all cases a strong interaction with the bare surface is observed, whereas for high exposures the oxygen coverage increases only slowly. For both group-III nitrides the reactivity is much higher for water than for oxygen. Comparing the GaN(0001) and the InN(0001) surface, the InN is initially more reactive. For the initially 2×2 reconstructed GaN(0001) surface the reconstruction disappears during the interaction.

Even if differences in the reaction rate are observed for the four investigated systems, the resulting changes in the valence band are rather similar. In all cases two states separated by about 5 eV continuously gain in intensity over the entire studied exposure range. Therefore we conclude that in all cases the same adsorbate species is formed. This adsorbate species is most likely a pure oxygen species. In particular we have no evidence for OH formation or molecular water adsorption, which in particular should lead to different valence band structures. Furthermore, in case of GaN, we have shown that the adsorbates are able to influence the surface band bending.

For the exact determination of the formed species including the evaluation of the adsorption side and the changes in electronic properties, such as exposure dependent changes in band bending and work function, further experimental and theoretical efforts are of great importance.

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