Adsorption of Hydrogen at GaN(000$\underline{1}$) Surface – Ab Initio Study

Maria Ptasinska[1], Jacek Piechota[1], and Stanisław Krukowski[1,2, *]

[1]Interdisciplinary Centre for Mathematical and Computational Modelling, University of Warsaw, Pawińskiego 5a, 02-106 Warsaw, Poland

[2]Institute of High Pressure Physics, Polish Academy of Sciences, Sokołowska 29/37, 01-142 Warsaw, Poland

Keywords: surface, density functional theory, gallium nitride, adsorption

ABSTRACT. Ab initio calculations are used to determine the basic physical properties of hydrogen adsorption at the N-terminated GaN(000$\underline{1}$) surface. It was shown that the Fermi level is pinned at the valence band maximum (VBM) for hydrogen coverage θ_H = 0.75 ML above which the Fermi level is shifted to the conduction band minimum (CBM). Application of the electron counting rule (ECR) indicates that for θ_H = 0.75 0.75 ML, the Fermi level is not pinned, located in the bandgap. Ab inito calculations confirmed that hydrogen adsorption energy depends on the Fermi level at the surface as predicted and explained earlier {Krukowski et al, J. Appl. Phys. 114 (2013) 143705-1-12 & 115 (2013) 043529-1-9}. The adsorption energy contains electron transfer contribution, below θ_H = 0.75 ML to VBM and above that coverage to CBM, thus it is $\Delta E_{ads}(H) \cong 5.8$ eV and $\Delta E_{ads}(H) \cong 3.1$ eV for a single H atom for these coverage ranges, respectively. Accordingly, the H_2 equilibrium pressure at GaN(000$\underline{1}$) surface varies from very low for $\theta_H < 0.75$ ML, about 10^{-20} bar to a fraction of a bar for $\theta_H > 0.75$ ML.

Introduction

The recent 2014 Nobel Prize in Physics awarded to Akasaki, Amano and Nakamura reflects not only their contribution to technological breakthrough in shortwave optoelectronics and understanding of the physical properties of nitride semiconductors but also the importance of the domain.[1] The cornerstones in the progress of understanding the basic properties were: the discovery of p-type doping by Amano and Akasaki[2], and the determination of the nature of p-type activation by hydrogen free annealing by Nakamura.[3] These discoveries laid foundations for fast development of new branch of optoelectronics, based on GaN/AlN/InN devices such as blue, violet and recently green laser diodes (LDs) marking the cornerstones of the progress in the domain.[5-9] Another application of these nitrides is the development of high electron mobility transistors (HEMTs).[10,11] Apart from typical electronic applications, a possible application of the latter structures includes molecular sensing, immensely important in biology, medicine and other areas.[12] All these devices were fabricated on a polar Ga-terminated GaN(0001) surface.

The opposite N-terminated surface, GaN(000$\underline{1}$), lagged behind for very long. It is well known that both gallium and nitrogen GaN polarity may be enforced on sapphire by appropriate nitridation before growth.[13-15] The growth experiments proved, however, that the obtained N-polar layers have significantly higher density of dislocations and other defects.[13,14] In addition, the coalescence of such layers to obtain a smooth layer surface is difficult.[16] Recent developments proved that successful coalescence of GaN islands may be achieved under the proper thermodynamic condition including III-V ratio and the presence of hydrogen.[17] The GaN(000$\underline{1}$) surface drew more attention only recently as single GaN crystals are available.[13] Thus an important step in development of N-polar technology has been achieved as the numerous growth experiments require easily accessible cheap substrates. At present, high quality GaN substrates are available at a very high cost, useful for the mature technology where the substrate cost is not important.[18] An additional important advantage of this orientation is that the N-polar GaN surface is chemically active so it can be etched easily allowing application of mechano-chemical polishing, using standard acid or base etchants.[19]

The N-polar growth orientation may be interesting for several important applications, such as a switched location of the two-dimensional electron gas (2DEG) at AlGaN-GaN heterojunctions to obtain higher mobility[20,21] or high efficiency visible light emitting diodes (LEDs).[22] Particularly interesting is the concurrent growth of N- and Ga-polar structures, opening a possibility of fabrication of lateral polarity junctions[23] nonlinear optical and acoustical devices[24] or even polarity selective patterning.[25] Thus the growth at the N-polar orientation presents interesting possibilities for optoelectronics and electronics.

An important feature of the growth at the N-polar orientation is extreme sensitivity of growth kinetics to thermodynamic conditions.[26] This is partially related to a strong interaction of the GaN(000$\underline{1}$) surface with hydrogen atoms.[27,28] The surface kinetic processes depend strongly on hydrogen originating from decomposition of ammonia and the from carrier gas.[29] Thus the investigation of hydrogen interaction with the GaN(000$\underline{1}$) surface is important from the point of view of basic understanding of its properties and may contribute also to the development of the technology.

The GaN(000$\underline{1}$) surface is chemically active, prone to oxidization, therefore experimental procedures should include characterization of the surface chemical state by Auger Electron Spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS).[29-32] The experimental data show a variety of structures at GaN(000$\underline{1}$) surfaces, such as 1 x 1, 3 x 3, 6 x 6 and c(6 x 6) reconstructions.[29] These structures are observed during or after the growth in MBE chambers; they are created in the case of surplus of gallium atoms at the surface reflecting a different arrangement of the surplus gallium atoms in several monolayers.

Electronic properties and their relation to the chemical state of the GaN(000$\underline{1}$) surface were thoroughly investigated using angle resolved photoelectron spectroscopy (ARPES).[22-26] The first measurement by Chao et al., indicated the presence of two surface states, the upper dispersionless at VBM, and lower, highly dispersive, extending down to 4 eV below VBM.[33] The two different

chemical states of the surface were positively identified, the first part is covered by gallium adatoms in the 'on-top' positions, and the second part is the clean surface with no adatoms.[34,35] The latter is characterized by the presence of almost dispersionless surface states band at the top of the valence band, related to N dangling bonds,[35,36] in a good agreement with ARPES data obtained by Chao *et al.*[33] The highly dispersive state was identified as related to Ga coverage of the GaN(000$\underline{1}$) surface.[37] The two different chemical states were confirmed in the Ga desorption kinetics measurements [38], low-energy electron diffraction (LEED)[39] and x-ray photoelectron diffraction (XPD).[40] Recent X-ray measurements indicated that the MOVPE grown GaN(000$\underline{1}$) surface is stoichiometric.[41] The stability of the clean GaN(000$\underline{1}$) surface was therefore confirmed and its basic electronic properties were identified by ARPES measurements.

The properties of the GaN(000$\underline{1}$) surface were also investigated using DFT calculations.[42-44] It was shown that at a clean GaN(000$\underline{1}$) or partially Ga occupied surface, a dispersionless state, originating from dangling nitrogen bonds, emerges at the valence band maximum (VBM), pinning the Fermi level.[42-44] Other DFT investigations lead to a conclusion that the GaN(000$\underline{1}$) surface stable structure corresponds to a Ga adatom in H3 position[45,46] or a Ga adlayer[46] depending on the gallium chemical potential layer. These findings are not compatible with the recent XPS measurements.[41] In the recent calculations, we have found that Ga adsorption leads to emergence of the donor state which pins the Fermi level at 1.1 eV above VBM which is compatible with the Fermi level pinned at the surface for p-type GaN and is inconsistent with n-type bulk.[47]

Recent investigations dramatically changed the overall picture of adsorption at semiconductor surfaces.[48-50] It was found that due to charge redistribution at the surface and between the surface and the bulk, the adsorption energy depends on the pinning of the Fermi level at the surface or, in the absence of pinning, on the doping in the bulk. Thus, for the first time, the electronic properties of the surface and molecular processes were intimately linked. This complicated picture requires a detailed analysis of the electronic properties of the surface. Such an analysis will be made below, for an important case of hydrogen adsorption at the GaN(000$\underline{1}$) surface.

Calculation procedure

In the calculations reported in this paper, the DFT based, commercially available code VASP (Vienna ab-initio simulation package) was used.[51-54] Depending on the size of the supercell used in the calculations, the following cut-off energies were used for the plane wave basis set: for 1 x 1 x 1 - E_{cutoff} = 700 eV, for 1 x 1 x 8 - E_{cutoff} = 600eV and for 2 x 2 x 8 - E_{cutoff} = 450 eV which were shown by Lepkowski and Majewski[55] to be sufficient for a simulation of the basic physical properties of GaN. In the test calculations for the elementary cell, i.e. the 1 x 1 x 1 cell, the Monkhorst-Pack grid (12 x 12 x 6) was applied during relaxation to the minimum energy position, while in the surface calculations, a 9 x 9 x 1 grid was used in the k-space integration.[56,57] The self-consistent field (SCF) loop was terminated when the difference between the two subsequent total energy values was smaller than 10^{-6}.

In all these calculations, Projected Augmented Wave ultrasoft pseudopotentials for Ga, N, H1.25 and H, employing the generalized gradient approximation (GGA) functionals with Perdew, Burke and Enzernhof (PBE) parameterization to exchange-correlation energy, were used.[58] As a quality test of the plane-wave expansion employed, the following lattice constant were obtained: a = 3.248 Å, c = 5.282 Å; and a = 3.197Å, c=5.203 Å, without and with *d*-electrons included explicitly in the valence band, respectively. These values, especially with *d*-electrons included explicitly, are in good agreement with the experimental data for GaN: a = 3.189 Å and c = 5.186 Å.[59] Slightly smaller values of the lattice constants, obtained with *d*-electrons use suggest that *d*-electrons may play an important role in bonding in GaN.

In the simulations of the surface properties, it is necessary to account for additional electrostatic dipole contribution from the polarity of GaN and also from the separation of the charge used for occupation of the surface states and screening by termination atoms. This is compensated using the Neugebauer and Scheffler dipole correction as implemented in VASP.[60] The vacuum thickness was 20 Å that combined with the dipole correction is sufficient to assure the independence of the slab replicas. In order to speed up the calculations, the initial relaxation of the atomic positions was made without a correction that considerably enhanced convergence of the SCF loop. The final relaxation steps were made using the full model, employing the correction, thus the final positions are precisely determined.

An analysis of the hydrogen adsorption at the GaN(0001) surface based on ab intio data

Determination of the basic features of the adsorption processes at semiconductor surface requires the three following steps:

- identification of the quantum states, both energy and the type, at the surface, existing and emerging due to the processes,

- determination of the possible Fermi level pinning at the surface states using the electron counting rule (ECR),

- verification of the ECR predictions by ab initio results for adsorption,

- determination of the equilibrium pressure of molecular hydrogen above the GaN(000$\underline{1}$) surface.

In the result, the possible coverage regions corresponding to the Fermi level, pinned at specified surface states, are marked. Following these procedures, by ab initio calculations the adsorption energies are determined for each region.

Quantum states at GaN(000$\underline{1}$) surface

As it was already determined by ab intio calculations, the clean GaN(000$\underline{1}$) surface is characterized by the presence of the dispersionless state, close to the valence band maximum, related to the broken bonds of nitrogen atoms.[42-47] In Figure 1, we present the results of spin polarized calculations determining the properties of the clean GaN(000$\underline{1}$) surface. As it is shown, the nitrogen s states are not involved in the creation of dispersionless states close to VBM. The state is related to p states i.e. effectively to the p_z broken bond state. Thus the basic results are confirmed in these calculations.

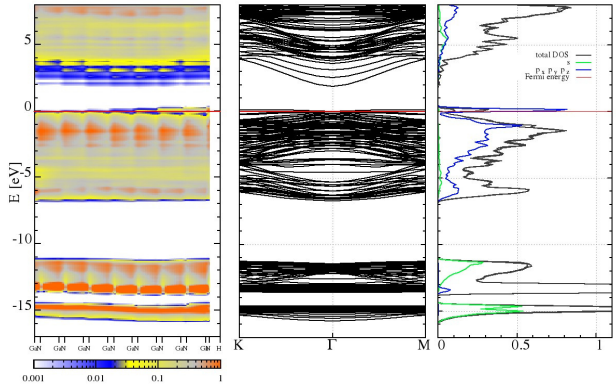

Figure. 1. Spatial distribution of band states in the direction perpendicular to the surface (left diagrams), band diagrams (middle) and density of states (DOS - right) of the 2 x 2 eight GaN atomic layers slab, representing the clean GaN(0001) surface. The DOS plot shows the states of the topmost nitrogen atoms: total - gray, s states - green, p states - blue line. The slab is terminated by hydrogen pseudoatoms, having Z = 5/4 electrons.

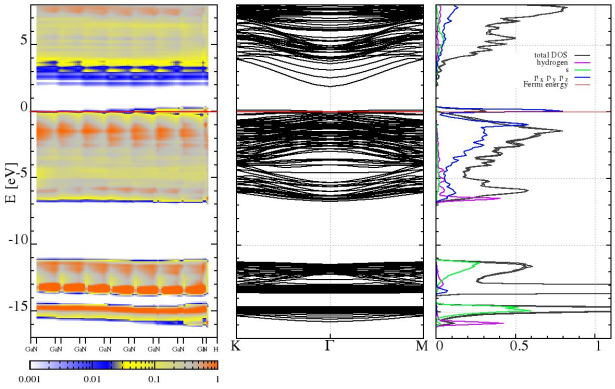

Figure. 2. Spatial distribution band states in the direction perpendicular to the surface (left diagrams), band diagrams (middle) and density of states (DOS - right) of the 2 x 2 eight GaN atomic layers slab with a single hydrogen adatom, representing the 0.25 ML hydrogen covered GaN(000$\underline{1}$) surface. The DOS line plot present the states of the topmost nitrogen atoms: total - gray, s states - green, p states - blue. In addition, the magenta line represents DOS of the H adatom. The slab is terminated as in Figure 1.

The spatial profile of the band diagram shows no electric field within the slab provided that the Fermi level is located at VBM, which is typical for p-type doping in the bulk. Since the nitrogen broken bond states are degenerate with VB, they should be occupied at standard experiment conditions.

In addition to the clean GaN(000$\underline{1}$) surface, the other important case is a single hydrogen atom attached at the slab surface. The simplest possible case assumes a single atom in a 2 x 2 slab, i.e. to θ_H = 0.25 ML uniform hydrogen coverage of the GaN(000$\underline{1}$) surface. This case is depicted in Figure 2. As it is shown, the hydrogen related states are located deep in the VB, thus they are fully occupied for all possible positions of the Fermi level at the surface. This is used below in the ECR analysis of the system.

ECR analysis of hydrogen at GaN(000$\underline{1}$) surface

The clean GaN(000$\underline{1}$) surface may be analyzed using standard tools. The nitrogen atom has four bonds in which all its 5 electrons are distributed. Therefore, each of eight states has 5/8 electrons which, for the two spin orientations, makes in average 5/4 electron for single broken bond. Thus for full occupancy an average 3/8 electrons for single state are needed that is equivalent to 3/4 electron for a single bond. In accordance to the results above, the three pairs of nitrogen states create bonds with neighboring Ga atoms and, as shown in Figure 1, they are located within VB. The remaining two p states have no overlap with the atoms, thus they represent a broken bond. As shown above, the dispersionless state is located at VBM. Thus the state is partially occupied and the Fermi level is pinned. The system is electrically neutral as shown in Figure 1 by a spatial band profile despite the existence of a polarization charge and related fields in nitrides as was discussed by Eller et al.[61] They argued that the polarization induced a surface charge may reach 10^{12} charge/cm^2, the value compatible with our earlier estimate of the surface charge at the GaN(0001) surface, equal to about 0.01 e_o/site and the site density 10^{15} cm^{-2}.[62] Hence the surface charge may compensate the polarization effects leading to flat bands in Figure 1.

The other case of interest is that of the H atom attached. The fraction of hydrogen occupied sites is denoted by α. Nitrogen contributes in average 5/4 electrons from the broken bond and one hydrogen electron to occupy 2 quantum states (for two spin orientations) that generates a surplus of 1/4 electrons so the hydrogen related states are donors. Nitrogen, with no atom attached, needs 3/4 electrons to occupy the two broken bond states. Thus the unoccupied nitrogen states are acceptors. The fraction of unoccupied nitrogen sites is denoted by β. Naturally, the recent results on bonding in GaN suggest that the nitrogen atom is not hybridized,[8] but the bonds are associated with four neighbors so, according to ECR, on average, 5/4 electron is associated with each nitrogen broken bond. The total number of electrons from the nitrogen atom is five, thus independent of the bonding, the number of electrons in the surface broken bond states is not changed. The bonding electrons occupy the surface states as these states are degenerate with VB:

$$\left(\frac{5}{4}+1\right)\alpha+\frac{3}{4}\beta=2(\alpha+\beta)=2 \qquad (1)$$

where the last equality stem from the normalization condition of the donor and acceptor states:

$$\alpha+\beta=1 \qquad (2)$$

The solution of these equations gives the ECR condition:

$$\alpha=\theta_H=\frac{3}{4} \qquad (3a)$$

$$\beta=1-\theta_H=\frac{1}{4} \qquad (3b)$$

where the single occupation of the surface sites by H adatoms is taken into account. Accordingly, it is expected that for hydrogen coverage below 0.75 ML, the Fermi level is in VB, for these above 0.75 ML, the Fermi level is in CB, while for 0.75 ML, the Fermi level is not pinned, in the bandgap. The ab initio results presented in Figure 3 verify these predictions.

As shown in Figure 3, the DFT based band diagrams confirm the Fermi level positions from the ECR predictions, it is located in VB, in the bandgap and in CB for the coverage equal to 0.5 ML, 0.75 ML and 1 ML, respectively. Thus the ECR scenario for the Fermi level position is confirmed by the DFT results.

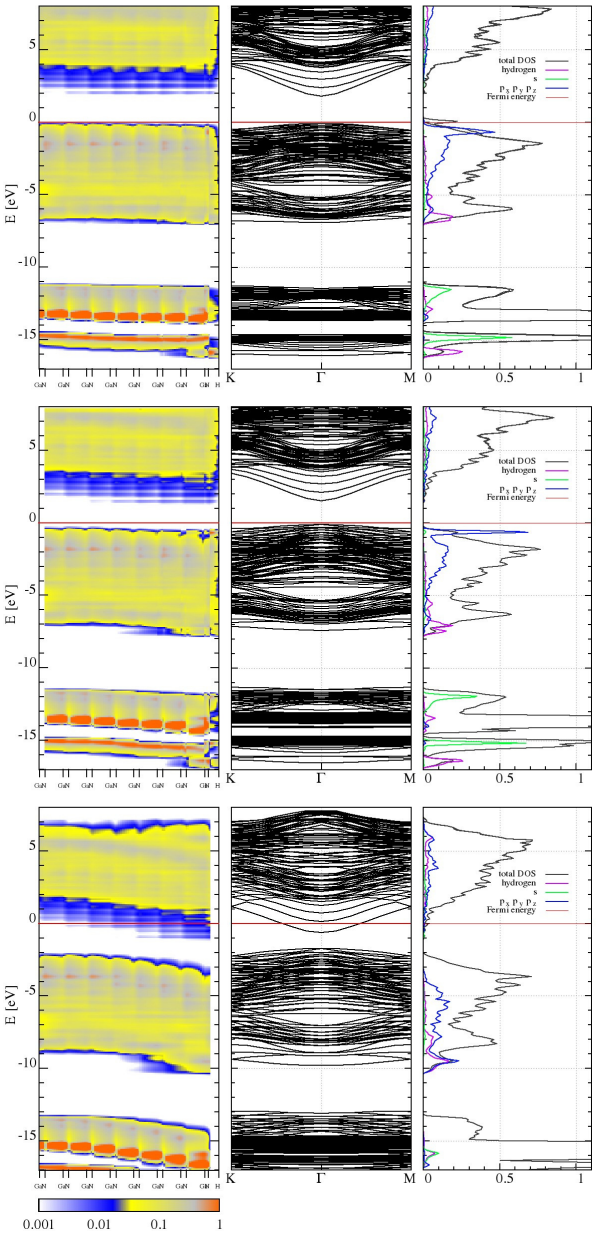

Figure. 3. Spatial distribution band states in the direction perpendicular to the surface (left diagrams), band diagrams (middle) and density of states (DOS - right) of the 2 x 2 eight GaN atomic layers slab with 2 (top row), 3 (middle row) and 4 (bottom row) hydrogen adatoms, representing 0.5 ML, 0.75 ML and 1 ML hydrogen covered GaN(0001) surface. The DOS line plots present the states of the topmost nitrogen atoms: total - gray, s states - green, p states - blue line. In addition, the magenta line represents DOS of H adatoms. The slab is terminated as in Figure 1.

Hydrogen adsorption at GaN(0001) surface

According to the predictions in Refs 48-50, the hydrogen adsorption energy remains constant for given pinning of the Fermi level, i.e. it is independent of the doping in the bulk and weekly changes with the coverage. Then, at the ECR coverage, the Fermi level at the surface undergoes a sudden jump to the new value corresponding to the new pinning point. At ECR coverage, the adsorption energy depends on the position of the Fermi level in the bulk which, in this particular case, translates into the dependence on the doping in the bulk. These data were verified by ab intio calculations in which the adsorption energy was calculated using the following formula:

$$\Delta E_{ads}(H) \equiv E(slab-H) - [E(slab) + E(H)] \quad (4a)$$

which could be also used for the adsorption energy of a hydrogen molecule:

$$\Delta E_{ads}(H_2) \equiv 2E(slab-H) - 2[E(slab) + E(H)] + \Delta E_{diss}(H_2)$$
$$= 2\Delta E_{ads}(H) + \Delta E_{diss}(H_2) \quad (4b)$$

where these energies are total DFT energies of the simulated systems and $\Delta E_{diss}(H_2)$ is the hydrogen molecule dissociation energy, equal to $\Delta E_{diss}(H_2)$ = 4.56 eV/molecule.[63] The adsorption energy of atomic hydrogen in function of the hydrogen coverage is presented in Figure 4.

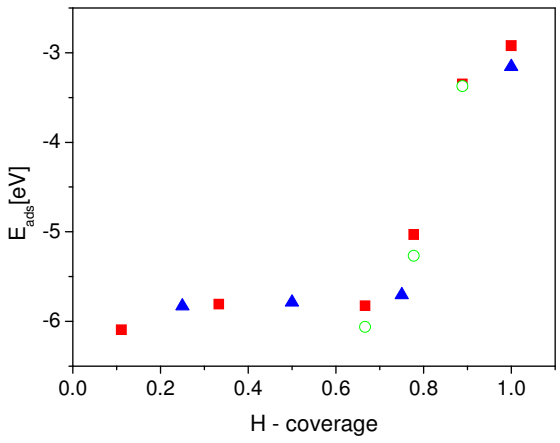

Figure 4. Adsorption energy of atomic hydrogen at the GaN(0001) surface for various hydrogen coverage. The blue diamonds and red squares are obtained using 2 x 2 and 3 x 3 slabs, respectively. The green empty circles denote a 3 x 3 slab with different hydrogen pseudoatom (Z = 1) termination.

As shown there, the adsorption energy of hydrogen is drastically different for the two coverage ranges. For the low coverage range, below θ_H = 0.75 ML, the hydrogen adsorption energy is $\Delta E_{ads}(H) \cong 5.8$ eV for a single H atom. The value is constant for the whole coverage range below 0.75 ML which excludes the commonly invoked interaction with the neighbors as the factor responsible for the variation of the energy value for higher coverage. Small variations observed for $\theta_H < 0.2$ ML are caused by numerical errors. In addition, as shown in Figure 4, the value is essentially identical for 2 x 2 and 3 x 3 slabs confirming that the result is not affected by the influence of the neighboring cells. Generally, the adsorption energy for the coverage $\theta_H < 0.75$ ML, $\Delta E_{ads}(H)$ is much higher than the hydrogen molecule dissociation energy, equal to $\Delta E_{diss}(H_2) = 4.56$ eV/molecule.[63] Such a large value of $\Delta E_{ads}(H)$ confirms a dissociative character of the process. Accordingly, the energy of adsorption of H_2 molecule may be deduced as 7.04 eV/molecule.

For higher coverage $\theta_H > 0.75$ ML, the adsorption energy is much lower. Due to the geometric restrictions, only few points were obtained and shown in Figure 4. The hydrogen adsorption energy is about $\Delta E_{ads}(H) \cong 3.1$ eV/atom. The adsorption energy of molecular hydrogen is therefore equal to 1.6 eV/molecule. The energy for high H coverage is much lower which is related to the fact that hydrogen attached to the surface contributes to one electron. A nitrogen broken bond contributes to 5/4 electron on average which sums up to 9/4 electrons to occupy 2 states of an H adatom. Thus an excess of 1/4 electron emerges and therefore the hydrogen adatom acts as a donor of electron which has to be transferred to the band states. Similarly, a nitrogen broken bond acts as an electron acceptor in agreement with the chemical behavior of nitrogen acting as the Lewis base ("B") and hydrogen as the Lewis acid ("A").[64] For coverage below 0.75 ML, the Fermi level is pinned below VBM, thus the target is the VB state. For coverage above 0.75 ML, the Fermi level is shifted above VBM, thus the target state is the CB state. Therefore, the energy gain related to the electron transfer is much higher for low coverage which explains the difference in adsorption energies presented in Figure 4. The difference is roughly equal to 2.8 eV which corresponds to the bandgap in the PBE approximation in analogy to similar results obtained for hydrogen and ammonia at the Ga-polar GaN(0001) surface.[49,50,66] Note that the transition is not related to the charge balance of the entire slab, as shown in Figure 4; the transition occurs for the same coverage, independent of the charge of the hydrogen termination atoms.

Equilibrium pressure of hydrogen above GaN(000$\underline{1}$) surface

Assumption of chemical equilibrium between the GaN(000$\underline{1}$) surface and the vapor entails equality of chemical potentials of hydrogen

$$\mu_H(a) = \mu_H(v) = \frac{1}{2}\mu_{H_2}(v) \qquad (5a)$$

where these symbols denote the chemical potential of adsorbed hydrogen at the surface, atomic and molecular hydrogen in the vapor consecutively. The chemical potential of adsorbed hydrogen may be expressed as:

$$\mu_H(a) = h_H(a) + Ts_H = h_H(a) + k_B T \ln\left(\frac{\theta_H}{1-\theta_H}\right) \qquad (6)$$

where the configurational entropy approximation is used for the entropy term and the vibrational contribution is neglected.[67] The chemical potential in the vapor may be expressed as:

$$\mu_H(v) = \frac{1}{2}\left[\mu_{H_2}(v)\right] = \frac{1}{2}\left[h_{H_2}(0) + \Delta\mu_{H_2}(T, p_{H_2})\right] \qquad (7)$$

where the latter term represent the thermodynamic potential of molecular hydrogen, given as (x = T/1000, where temperature is expressed in kelvins and pressure in bars):[67]

$$\Delta\mu_{H_2}(T, p_{H_2}) = -1.24x - 0.26x^2 + 0.025x^3 + k_B T \ln(p_{H_2}) \qquad (8)$$

Use of the chemical equilibrium assumption leads to the following dependence for the enthalpy difference for a single H_2 molecule

$$\Delta h_{H_2} = 2h_H(a) - h_{H_2}(v) = 2k_B T \ln\left(\frac{\theta_H}{1-\theta_H}\right) + \Delta\mu_{H_2}(T, p_{H_2}) \qquad (9)$$

which is expressed using DFT energies as

$$\Delta h_{H_2} = 2h_H(a) - h_{H_2}(v) = 2\left[h_H(a) - h_H(v)\right] + \Delta E_{diss}(H_2) = 2\Delta E_{ads}(H) + \Delta E_{diss}(H_2) \qquad (10)$$

where the enthalpy at 0K is replaced by DFT total energies. Using these relations, the final equation for the chemical equilibrium is obtained:

$$\Delta\mu_{H_2}(T, p_{H_2}) = 2\Delta E_{ads}(H) + \Delta E_{diss}(H_2) - 2k_B T \ln\left(\frac{\theta_H}{1-\theta_H}\right) \qquad (11)$$

which is used for determination of the pressure-coverage dependence for several selected temperatures presented in Figure 5. The latter term, which is usually of 0.1 eV order is sometimes neglected [67].

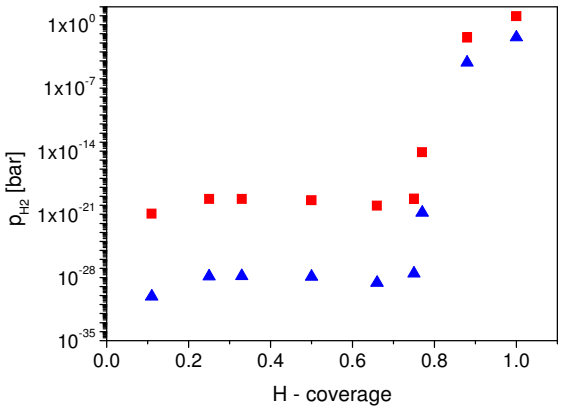

Figure 5. Equilibrium pressure of molecular hydrogen (H_2) above a hydrogen covered surface: red squares - 1300K, blue triangles - 1000K.

The equilibrium pressures were obtained for two benchmark temperatures: 1300 K corresponds to a typical GaN growth by MOVE or HVPE methods while 1000 K is in the range used for activation of the magnesium acceptor by annealing in a hydrogen free surrounding. The obtained data proves that the adsorption energy difference change related to the position of the Fermi level drastically changes the equilibrium pressure above the GaN(000$\underline{1}$) surface. Generally, due to large adsorption energies for $\theta_H < 0.75$ ML, the pressures are in range of 10^{-20} bar. A considerable decrease of adsorption energy for $\theta_H > 0.75$ ML induces a pressure increase by about 20 orders of magnitude to the typical experimental values, close to 1 bar.

Conclusions

The results described above may be summarized as follows. Ab intio calculations confirmed that at the clean GaN(000$\underline{1}$) surface, the Fermi level is pinned at VBM. They showed that hydrogen is attached at the GaN(000$\underline{1}$) surface in the atomic form. Adsorption of hydrogen at the surface creates surface states located deep in the VB. Thus all new states are occupied as the Fermi level is pinned at VBM at the GaN(000$\underline{1}$) surface. Application of ECR shows that adsorption of hydrogen creates a donor state which donates 1/4 electron to the unoccupied VB states. It showed that the critical coverage is at $\theta_H = 0.75$ ML at which the Fermi level is shifted from VBM to CBM.

The ab initio calculations confirmed earlier predictions that energy of adsorption depends on the pinning of Fermi level at the surface. As the H-related states donate electron to unoccupied states, the adsorption energy depends on the electron transfer energy gain. Therefore, adsorption energy for coverage range $\theta_H < 0.75$ ML is higher and is $\Delta E_{ads}(H) \cong 5.8$ eV for single H atom and $\Delta E_{ads}(H_2) \cong 7.04$ eV/molecule. For higher coverage $\theta_H > 0.75$, the adsorption energy is much lower as the electron transfer is to CB state. It is $\Delta E_{ads}(H) \cong 3.1$ eV/atom and $\Delta E_{ads}(H_2) \cong 1.6$ eV/molecule respectively.

Such a drastic energy difference affects the equilibrium pressure above the GaN(0001) surface. Generally, it is very low for $\theta_H < 0.75$ ML, about 10^{-20} bar. It is increased drastically for $\theta_H > 0.75$ ML where it attains the pressure equal a fraction of a single bar.

ACKNOWLEDGMENT The calculations reported in this paper were performed using the computing facilities of the Interdisciplinary Centre for Mathematical and Computational Modelling of Warsaw University (ICM UW), within the grant No. G47-3. This work has been partially supported by the Polish Ministry of Science and Higher Education within the SICMAT Project financed under the European Founds for Regional Development (Contract no. UDA-POIG.01.03.01-14-155/09)

REFERENCES

1. Ex: "The Nobel Prize in Physics 2014". Nobelprize.org. Nobel Media AB 2014. http://www.nobelprize.org/nobel_prizes/physics/laureates/2014/ (accessed Mar. 9, 2015).
2. Amano, H.; Kito, M.; Hiramatsu, K.; Akasaki, I. p-Type Conduction in Mg-Doped GaN Treated with Low-Energy Electron Beam Irradiation (LEEBI). *Jpn. J. Appl. Phys. (Lett)* **1989**, 28, L2112-L2114.
3. Nakamura, S.; Mukai, T.; Senoh, M.; Iwasa, N. Thermal Annealing Effects on P-Type Mg-Doped GaN Films. *Jpn. J. Appl. Phys. (Lett)* **1992**, 31, L139-L142.
4. S. Nakamura, S.; N. Iwasa, N.; M. Senoh, M.; T. Mukai, T. Hole Compensation Mechanism of P-Type GaN Films. *Jpn. J. Appl. Phys.* **1992**, 31, 1258-1266.
5. Nakamura, S.; Fasol, G.; Pearton, S.J. *The Blue Laser Diodes*; Springer: New York, 2000; pp 7-29.
6. Hirayama, H.; Maeda, N.; Fujikawa, S.; Toyoda, S.; Kamata N. Recent Progress and Future Prospects of AlGaN-Based High-Efficiency Deep-Ultraviolet Light-Emitting-Diodes. *Jpn. J. Appl. Phys.* **2014**, 53, 100209-1-10.
7. Khan, A.; Balakrishnan, K; Katona T. Ultraviolet Light-Emitting Diodes Based on Group III Nitrides. *Nature Photonics* **2008**, 2, 77-84.
8. Magnuson, M.; Mattesini, M.; Höglund, C.; Birch, J.; Hultman, L. Electronic Structure and Chemical Bonding Anisotropy Investigation of Wurtzite AlN. *Phys. Rev. B* **2009**, 80, 155105-1-6.
9. Lee, I. J.; Shin, H. J.; Chang, S. S.; M. K. Lee, M. K.; Kim, H. K. Identification of Hexagonal Polycrystal in Epitaxially Grown InN by Synchrotron X-Ray Diffraction and Near-Edge X-Ray Absorption Fine Structure Spectroscopy. *Appl. Phys. Lett.* **2003**, 82, 2981-2983.
10. Bouguen, L.; Konczewicz, L.; Contreras, S.; Jouault, B.; Camassel, J.; Cordier, Y. High Temperature Behaviour of AlGaN/AlN/GaN Hall-FET Sensors. *Mater. Sci. Eng. B* **2009**, 165, 1-4.
11. Shur M. S. Silicon and Nitride FETs for THz Sensing. *Proc. SPIE* **2011**, 8031, 80310J.
12. Wang, X.H.; Wang, X.L.; Feng, C.; Yang, C.B.; Wang, B.Z.; Ran, J.X.; Xiao, H.L.; Wang, C.M.; Wang, J.X. Hydrogen Sensors Based on AlGaN/AlN/GaN HEMT. *Microelectron. J.* **2008**, 39, 20-23.
13. Keller, S.; Fichtenbaum, N. A.; Wu, F.; Brown, D.; Rosales, A.; DenBaars, S. P.; Speck, J. S. ; Mishra, U. K. Influence of the Substrate Misorientation on the Properties of N-Polar GaN Films Grown by Metal Organic Chemical Vapor Deposition. *J. Appl. Phys.* **2007**, 102, 083546-1-6.
14. Sun, Q.; Cho, Y. S.; Lee, I.-H.; Han, J.; Kong, B. H.; Cho, H. K. Nitrogen-Polar GaN Growth Evolution on C-plane Sapphire. *Appl. Phys. Lett.* **2008**, 93, 131912.
15. Sun, Q.; Cho, Y. S.; Kong, B. H.; Cho, H. K.; Ko, T. S.; Yerino, C. D.; Lee, I. H.; Han, J. N-face GaN Growth on C-plane Sapphire by Metalorganic Chemical Vapor Deposition. *J. Cryst. Growth* **2009**, 311, 2948-2952.
16. Hussey, L.; Mita, S.; Xie, J.; Guo, W.; Akouala, C. R.; Rajan, J.; Bryan, I.; Collazo, R.; Sitar, Z. Lateral Epitaxial Overgrowth of Nitrogen Polar GaN on Smooth Nitrogen Polar GaN Templates by Metalorganic Chemical Vapor Deposition. *J. Appl. Phys.* **2012**, 112, 113513-1-5.
17. Song, J.; Yuan, G.; Xiong, K.; Leung, B.; Han, J. Epitaxial Lateral Overgrowth of Nitrogen-Polar (000-1) GaN by Metalorganic

Chemical Vapor Deposition. *Cryst. Growth Des,* **2014**, 14, 2510-2515.
18. Dwilinski, R.; Doradzinski, R.; Garczynski, J.; Sierzputowski, L. P; Zajac, M.; Rudzinski, M. Homoepitaxy on Bulk Ammonothermal GaN. *J. Cryst. Growth* **2009**, 311, 3058-3062.
19. Weyher, J. Defect Sensitive Etching of Nitrides: Appraisal of Methods. *L. Cryst. Res. Technol.* **2012**, 47, 333-340.
20. Keller, S.; Suh, C. S.; Chen, Z.; Chu, R.; Rajan, S.; Fichtenbaum, N. A.; Furukawa, M.; DenBaars, S. P.; Speck, J. S.; Mishra, U. K. Properties of N-polar AlGaN/GaN Heterostructures and Field Effect Transistors Grown by Metalorganic Chemical Vapor Deposition. *J. Appl. Phys.* **2008**, 103, 033708-1-4.
21. Wong, M. H.; Pei, Y.; Palacios, T.; Shen, L.; Chakraborty, A.; McCarthy, L. S.; Keller, S.; DenBaars, S. P.; Speck, J. S.; Mishra, U. K. Low Nonalloyed Ohmic Contact Resistance to Nitride High Electron Mobility Transistors Using N-Face Growth. *Appl. Phys. Lett.* **2007**, 91, 232103-1-3.
22. Keller, S.; Fichtenbaum, N. A.; Wu, F.; Brown, D.; Rosales, A.; DenBaars, S.P; Speck, J. S.; Mishra, U. K. Influence of the Substrate Misorientation on the Properties of N-Polar GaN Films Grown by Metal Organic Chemical Vapor Deposition. *J. Appl. Phys*. **2007**, 102, 083546-1-6.
23. Aleksov, A.; Collazo, R.; Mita, S.; Schlesser, R.; Z. Sitar, Z. Current-Voltage Characteristics of n/n Lateral Polarity Junctions in GaN. *Appl. Phys. Lett.* **2006**, 89, 052117-1-3.
24. Chowdhury, A.; Ng, H. M.; Bhardwaj, M.; Weimann, N. G. Second-Harmonic Generation in Periodically Poled GaN. *Appl. Phys. Lett.* **2003**, 83, 1077-1079.
25. Ng, H. N.; Parz, W.; Weimann, N. G.; Chowdhury, A. Patterning GaN Microstructures by Polarity-Selective Chemical Etching. *Jpn. J. Appl. Phys.* **2003**, 42, L1405-L1407.
26. Marchand, H.; Ibbetson, J. P.; Fini, P. T.; Keller, S.; DenBaars, S. P.; Speck, J. S.; Mishra, U. K. Mechanisms of Lateral Epitaxial Overgrowth of Gallium Nitride by Metalorganic Chemical Vapor Deposition. *J. Cryst. Growth* **1998**, 195, 328-332.
27. Yun, F.; Chevtchenko, S.; Moon, J. -T.; Morkoc, H.; Fawcett, T. J.; Wolan, J. T. GaN Resistive Hydrogen Gas Sensors. *Appl. Phys. Lett.* **2005**, 87, 073507-1-3.
28. Wang, Y.-L.; Chu, B. H.; Chang, C. Y.; Chen, K. H.; Zhang, Y.; Sun, Q.; Han, J.; Pearton, S. J.; Ren, F. Hydrogen Sensing of N-polar and Ga-polar GaN Schottky Diodes. *Sens. Actuators B* **2009**, 142, 175-178.
29. Sung, M.M.; Ahn, J.; Bykov, V.; Rabalais, J. W.; Koleske, D. D.; Wickenden, A. E. Composition and Structure of the GaN{000-1}-(1×1) Surface. *Phys. Rev. B* **1996**, 54, 14 652-14663.
30. Bermudez, V. W.; Koleske, D. D.; Wickenden, A. E. The Dependence of the Structure and Electronic Properties of Wurtzite GaN Surfaces on the Method of Preparation. *Appl. Surf. Sci.* **1998**, 126, 69-82.
31. Bellitto, V. J.; Thoms, B. D.; Koleske, D. D.; Wickenden, A. E.; Henry, R. L. HREELS of H/GaN(0001): Evidence for Ga Termination. *Surf. Sci.* **1999**, 430, 80-88.
32. Bermudez, V. M. Theoretical Study of Hydrogen Adsorption on the GaN(0001) Surface. *Surf. Sci.* **2004**, 565, 89-102.
33. Chao, Y. C.; Stagarescu, C. B.; Downes, J. E.; Ryan, P.; Smith, K. E.; Hanser, D.; Bremser, M. D.; Davis, R. F. Observation of Highly Dispersive Surface States on GaN(0001)1×1. *Phys. Rev. B* **1999**, 59, R15586-9.
34. Kowalski, B. J.; Plucinski, Ł; Kopalko, K.; Iwanowski, R. J.; Orłowski, B. A.; Johnson R. L.; Grzegory, I.; Porowski, S. Photoemission Studies on GaN(000-1) Surfaces. *Surf. Sci*. **2001**, 482-485, 740-745.
35. Kowalski, B. J.; Iwanowski, R. J.; Sadowski, J.; Kanski, J.; Grzegory, I.; Porowski, S. Surface States on GaN(000-1)(1×1) – an Angle-Resolved Photoemission Study. *Surf. Sci.* **2002**, 507-510, 186-191.
36. Plucinski, Ł; Strasser, T.; Kowalski, B. J.; Rossnagel, K.; Boetcher, T.; Einfeldt, S.; Hommel, D.; Grzegory, I.; Porowski, S.; Orłowski, B. S.; et al. Electronic Band Structure of Gallium Nitride: a Comparative Angle-Resolved Photoemission Study of Single Crystals and Thin Films. *Surf. Sci.* **2002**, 507-510, 223-228.
37. Kowalski, B. J.; Iwanowski, R.J.; Sadowski, J.; Kowalik, I.A.; Kanski, J.; Grzegory, I.; Porowski, S. Electronic Structure of GaN(000-1)-(1×1) surface. *Surf. Sci.* **2004**, 548, 220-230.
38. Choi, S.; Kim, T-H.; Wu, P.; Brown, A.; Everitt, H. O.; Losurdo, M.; Bruno, G. Band Bending and Adsorption/Desorption Kinetics on N-Polar GaN Surfaces. *J. Vac. Sci. Technol. B* **2009**, 27, 107-112.
39. Romanyuk, O.; Jiricek, T.; Paskova, T. Quantitative Low-Energy Electron Diffraction Analysis of the GaN(000-1)(1×1) Reconstruction. *Surf. Sci.* **2012**, 606, 740-743.
40. Romanyuk, O.; Jiricek, T.; Paskova, T.; Atomic and Electronic Structure of N-terminated GaN(000-1) (1 × 1) Surface. *J. Phys. Conf. Ser.* **2012**, 398, 012013-1-7.
41. Reddy, P.; Bryan, I.; Bryan, Z.; Guo, W.; Hussey, L.; Colazzo, R.; Sitar, Z. The Effect of Polarity and Surface States on the Fermi Level at III-nitride Surfaces. *J. Appl. Phys.* **2014**, 116, 123701-1-6.
42. Wang, F. –H.; Kruger, P.; Pollmann, J. Electronic Structure of 1×1 GaN(0001) and GaN(000-1) Surfaces. *Phys. Rev. B* **2001**, 64, 035305-1-8.
43. Wang, F. –H.; Kruger, P.; Pollmann, J. Surface Electronic Structure of GaN(000-1)-(1×1): Comparison Between Theory and Experiment. *Surf. Sci.* **2002**, 499, 193-202.
44. Strasser, T.; Solterback, C.; Starrost, F.; Schattke, W. Valence-band Photoemission from the GaN(0001) Surface. *Phys. Rev B* **1999**, 60, 11577-11585.
45. Van de Walle, C. G.; Segev, D. Microscopic Origins of Surface States on Nitride Surfaces. *J. Appl. Phys*. **2007**, 101, 081704-1-6.
46. Segev, D.; Van de Walle, C. G.; Surface Reconstructions on InN and GaN Polar and Nonpolar Surfaces. *Surf. Sci. Lett.* **2007**, 601, L15-L18.
47. Ptasinska, M.; Soltys, J.; Piechota, J.; Krukowski, S. Electronic Properties on GaN(0001) Surface – ab initio Investigation. *Vacuum* **2014**, 99, 166-174
48. Krukowski, S.; Kempisty, P.; Strąk, P. Foundations of Ab Initio Simulations of Electric Charges and Fields at Semiconductor Surfaces within Slab Models. *J. Appl. Phys.* **2013**, 114, 143705-1-12.
49. Krukowski, S.; Kempisty, P.; Strąk, P.; Sakowski, K. Fermi Level Pinning and the Charge Transfer Contribution to the Energy of Adsorption at Semiconducting Surfaces. *J. Appl. Phys.* **2013**, 115, 043529-1-9.
50. Kempisty, P.; Krukowski, S.; Adsorption of Ammonia at GaN(0001) Surface in the Mixed Ammonia/Hydrogen Ambient - a Summary of Ab Initio Data. *AIP Adv.* **2014**, 4, 117109-1-24.
51. Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, 47, 558-561.
52. Kresse, G.; Hafner, J. Ab Initio Molecular-Dynamics Simulation of the Liquid-Metal–Amorphous-Semiconductor Transition in Germanium. *Phys. Rev. B* **1994**, 49, 14 251-14 261.
52. Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mat. Sci.* **1996**, 6, 15-50.
54. Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, 54, 11169-11186.
55. Łepkowski, S. P.; Majewski, J. A. Effect of Electromechanical Coupling on the Pressure Coefficient of Light Emission in Group-III Nitride Quantum Wells and Superlattices. *Phys. Rev. B* **2006**, 74, 35336-1-8.
56. Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-zone Integrations. *Phys. Rev. B* **1976**, 13, 5188-5192.
57. Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations – a Reply. *Phys. Rev. B* **1977**, 16, 1748-1749.
58. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77, 3865-3868.
59. Leszczynski, M.; Teisseyre, H.; Suski, T.; Grzegory, I.; Bockowski, M.; Jun, J.; Porowski, S.; Pakula, K.; Baranowski, J. M.; Foxon, C. T.; et al. Lattice Parameters of Gallium Nitride. *Appl. Phys. Lett.* **1996**, 69, 73-75.
60. Neugebauer, J.; Scheffler, M. Adsorbate-Substrate and Adsorbate-Adsorbate Interactions of Na and K Adlayers on Al(111). *Phys. Rev. B* **1992**, 46, 16067-16080.

61. Eller, B.S.; Yang, J.-L.; Nemanich, R.J. Electronic Surface and Dieelectric Interface States on GaN and AlGaN *J. Vac. Sci. Technolo. A* **2013**, 31, 050807-1-29.
62. Kempisty, P.; Krukowski, S. On the Nature of Surface States Stark Effect at Clean GaN(0001) Surface. *J. Appl. Phys.* **2012**, 112, 113704-1-9.
63. Chase, M.; Davies, C.; Downey, J.; Frurip, D.; McDonald, R.; Sverud, A. JANAF Thermochemical Tables. *J. Phys. Chem. Ref. Data.* **1985**, 14, 1-1856.
64. Carey, F.A.; Sundberg, R.J. *Advanced Organic Chemistry, Part B Reaction and Synthesis*; Springer: New York, 2007; pp 481-502
65. Kempisty, P.; Strak, P.; Krukowski, S.; Ab initio Study of the Properties of GaN(0001) Surface at MOVPE and HVPE Growth Conditions. *Phys. Status Solidi C* **2012**, 9, 826.
66. Venables, J. A. *Introduction to Surface and Thin Film Processes;* Cambridge University: Cambridge, 2000; pp 109-116.
67. Krukowski, S.; Kempisty, P.; Jalbout, A.F. Thermodynamic and Kinetic Approach in Density Functional Theory Studies of Microscopic Structure of GaN(0001) Surface in Ammonia-Rich Conditions. *J. Chem. Phys.* **2008**, 129, 234705-1-12.