Atomic and electronic structure of N-terminated GaN(000\bar{1}) (1 \times 1) surface

O Romanyuk\textsuperscript{1}, P Jiříček\textsuperscript{1} and T Paskova\textsuperscript{2}

\textsuperscript{1} Department of Optical Materials, Institute of Physics, ASCR, Prague, Czech Republic
\textsuperscript{2} Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27617 USA

E-mail: romanyuk@fzu.cz

Abstract. The atomic and electronic structures of the polar GaN(000\bar{1}) surface were investigated by x-ray photoelectron diffraction (XPD) and \textit{ab initio} density-functional theory (DFT) calculations. A well-ordered GaN(000\bar{1}) surface of a free-standing GaN wafer was prepared by sample annealing in a NH\textsubscript{3} atmosphere. A N-terminated bare (1 \times 1) structure was confirmed. An electronic band structure was investigated by DFT calculations. The surface state at the top of the valence band was localized for a relaxed (1 \times 1) structure. The energy loss function (ELF) was computed in the framework of the many-body perturbation theory. Plasmon loss peak positions were found to be in good agreement with reflection-electron energy loss spectroscopy (REELS) measurements.

1. Introduction

In recent years, many efforts have been focused on developing technology allowing semiconductor surface interfacing with biological macro objects for biomedical applications. The direct integration of the majority of semiconductor materials with biological objects is not possible, however, because of their toxicity [1]. A process of semiconductor surface bio-functionalization, i.e. surface passivation by hydrocarbons or large organic molecules, is required [2]. Knowledge about bare semiconductor substrate surfaces is necessary, therefore, for understanding the chemical reaction pathways and the absorption mechanisms on a surface during functionalization.

GaN is a promising candidate for semiconductor surface integration with biological objects: the functionalized GaN(000\bar{1}) surface is stable in an aquatic environment and leaches a negligible amount of toxic Ga into the biological objects [2]. In the present work, a GaN free-standing substrate surface was investigated.

The conditions for preparing the GaN(000\bar{1}) surface (Ga polarity) have attracted significant attention in the past [3]. Sharp (1 \times 1) diffraction patterns were observed after surface etching and a three-step annealing procedure. The atomic structure of the GaN(000\bar{1}) (1 \times 1) reconstruction was investigated by diffraction techniques [4], photoemission spectroscopy (PES) [5] and \textit{ab initio} calculations based on density functional theory (DFT) [6]. Under the most Ga-rich conditions, a pseudo-GaN(000\bar{1}) (1 \times 1) metallic surface was confirmed consisting of a Ga contracted bilayer [6]. Such a structure can be prepared by using a Ga flux and a low substrate temperature. On the other hand, the GaN(000\bar{1}) (1 \times 1) structure can also be prepared by sample annealing without Ga/N fluxes, i.e. out of equilibrium conditions [3].
The GaN(000 $\bar{1}$) surface (N polarity) shows a number of reconstructions depending on atomic flux and substrate temperature variations [7]. The bare GaN(000 $\bar{1}$) (1 \times 1) structure was found to be thermodynamically unstable under N-rich conditions [8]. However, a stoichiometric (1 \times 1) structure can be prepared by surface annealing without Ga/N fluxes [9]. Such a structure consists of a lower amount of Ga on the surface in comparison with GaN(0001) (1 \times 1) phases and could be potentially suitable for biological applications.

Photoelectron spectroscopy measurements were carried out on the GaN(000 $\bar{1}$) (1 \times 1) reconstruction [10, 11]. Differences in surface preparation conditions, i.e. annealing temperatures and Ar or N$_2$ ion sputtering procedures, have led to discrepancies in the reported atomic and electronic band structures of the GaN(000 $\bar{1}$) (1 \times 1) surface [11, 12]. The N-terminated and Ga-adlayer (1 \times 1) structure models have been suggested to explain the experimental data.

Recently, the atomic structure of the GaN(000 $\bar{1}$) (1 \times 1) reconstruction was investigated by quantitative low-energy electron diffraction (LEED) [9]. The Ga-adlayer model of the GaN(000 $\bar{1}$) (1 \times 1) structure was ruled out, whereas the N-terminated bilayer model was confirmed. Atomic relaxations were found to be in good agreement with DFT calculations.

Here, the atomic and electronic band structures of the GaN(000 $\bar{1}$) (1 \times 1) structure were investigated by XPD and DFT calculations, respectively. The electronic band structure of the relaxed N-terminated GaN(0001) (1 \times 1) surface was analysed. Based on electronic structure calculations, the dielectric properties of GaN were computed in the framework of a many-body perturbation theory (MBPT). An ab initio approach for dielectric function calculation was compared with the semi-classical theory for optical constant calculation from REELS spectra.

2. Experimental part

A GaN(000 $\bar{1}$) sample [13] was grown by hydride-vapor phase epitaxy (HVPE) on a sapphire substrate along the [0001] direction in a standard vertical reactor. The as-grown GaN substrate had a thickness of about 1.5 mm with a dislocation density of about $10^5$ cm$^{-3}$. Fe doping was used in order to compensate for the residual oxygen and silicon impurities, resulting in a free carrier concentration in the range of $10^{13}$ cm$^{-3}$. The GaN bulk wafer was self-separated from the sapphire substrate during the cooling down from the growth temperature. The N-side of the GaN substrate was mechanically polished and cleaned ex-situ in a HCl:DIH$_2$O (1:1) solution at 75°C for 10 min prior to loading into a ADES-400 angular-resolved photoelectron spectrometer. The GaN sample was degassed by flashing at 1000°C until the pressure inside the chamber was in the $10^{-9}$ mbar range. The GaN sample was heated indirectly through a sample holder consisting of a thin molybdenum plate; an electron beam was used to heat the plate, and the substrate temperature was monitored by an optical pyrometer. In order to obtain sharp LEED patterns, the sample was repeatedly annealed a few times for approximately 40 minutes at 1000°C in a NH$_3$ atmosphere of 2x10$^{-6}$ Torr.

Standard mode angular resolved photoelectron diffraction intensity measurements were performed for a photoelectron kinetic energy of 825 eV (MgK$\alpha$ excitation from the N 1s core level) in two higher symmetry azimuths, namely the [1000] and [1010] directions (figure 1). The polar angle $\theta$ of the electron emission (analyzer) was varied over a range of 0$^\circ$ - 69$^\circ$ in 3$^\circ$ steps.

3. Computational details

Photoelectron diffraction from a large atomic cluster (2000 atoms, parabolically shaped) with a single atomic photoemitting layer placed at different depths under the surface was evaluated. The angle resolved intensities from the N 1s level were calculated by the code EDAC [14] taking multiple electron scatterings into account. The order of elastic scatterings was increased so as to reach sufficiently good convergence. An inelastic electron mean-free-path of 25 Å was used for electrons emitted with 825 eV kinetic energy, eight phase shifts were used in the muffin-tin type description of the atoms and an inner potential of 11 eV was used.
Ab initio DFT calculations of the GaN electronic band structure were carried out using the ABINIT computer code [15, 16]. The generalized gradient approximation (GGA) was used for the exchange-correlation energy functional, and norm-conserving pseudopotentials [17] of the Troullier-Martins type [18] were used to describe the atomic species. The Ga 3d electrons were treated as core electrons. The electronic wave functions were expanded in a plane wave basis. The kinetic energy cutoff was set to 30 Ha, and a k point set corresponding to \(6 \times 6 \times 3\) for a bulk and \(6 \times 6 \times 1\) per \((1 \times 1)\) surface Brillouin zone (BZ) [19] was used. The converged lattice constants \(a=3.197\) Å and \(c=5.195\) Å were used. A \((1 \times 1)\) surface structure was constructed using the repeated supercell approach with a GaN slab thickness of 8 Ga-N bilayers. The vacuum gap thickness was 13 Å. The bottom Ga layer of the slab was passivated by pseudohydrogens with 1.25 electronic charges. The atomic coordinates were adjusted until the interatomic forces became smaller than \(10^{-4}\) Ha/Bohr, whereby only the three bottom layers (N-Ga-pseudo-H) were kept fixed.

The optical properties of the GaN were computed within a many-body perturbation theory implemented in Yambo computer code [20]. The relaxed ground state geometrical structure from ABINIT was used for the quasiparticle GW band structure calculations and the screening electron-hole interaction calculations, as well as for solving the Bethe-Salpeter equation by the Haydock recursion method [21, 22]. The screening function was calculated by using 40 k points in the irreducible BZ (in the convergence study, up to 112 k points were tested). Sixteen valence and sixteen conduction bands were found to be appropriate for the bulk dielectric function calculations. An energy onset of 0.5 eV for the energy loss function (ELF) curve was used to correct the volume peak plasmon position. An ELF resolution of 0.4 eV was used in the theoretical calculations, similar to the energy step used in the REELS measurements.

4. Results and discussion

In figure 1, a ball-and-stick model of the N-terminated GaN(000\(\overline{1}\)) \((1 \times 1)\) structure is shown. The direction to the neighboring atom within one atomic plane corresponds to the [1000] azimuth. The [10\(\overline{1}0\)] direction corresponds to the N-Ga atomic pair direction within an atomic bilayer.

Atomic structure of the GaN(000\(\overline{1}\)) \((1 \times 1)\) reconstruction is analyzed by XPD. In figure 2 a), the experimental and computed polar angle distributions of normalized XPD intensities are shown for [1000] \((\phi = 0^\circ)\) and [10\(\overline{1}0\)] \((\phi = 30^\circ)\) directions. The [1000] and [10\(\overline{1}0\)] atomic planes (perpendicular to the surface plane) of the GaN(000\(\overline{1}\)) \((1 \times 1)\) structure are shown in figure 2 b). The polar angles between the N emitters and the neighboring atoms are indicated. Since the GaN(000\(\overline{1}\)) \((1 \times 1)\) structure consists of two domains [9], the photoelectron intensities from the atomic planes rotated by 60° were averaged.

For the \(\phi = 0^\circ\) direction, the broad peak measured between 22°-32°, centred at 27°, could be interpreted as a convolution of the forward focusing peak intensity along the \(\theta = 24^\circ\) and \(\theta = 32^\circ\) directions (double layer). The peaks at 39° are close to the calculated peak position values at 42°. The experimental and theoretical peaks do agree at 51° and correspond to the N-N atomic pair direction. For the \(\phi = 30^\circ\) (90°) direction, the experimental peak positions at 26° are close to the N-N atomic pair direction at 28° [figure 2 b)]. The peak at 43° is a
Figure 2. a) Polar dependence of the XPD intensities measured on the GaN(0001) (1 × 1) surface along the [1000] (ϕ = 0°) and [1010] (ϕ = 30°) directions. Two symmetrical GaN planes are shown in b) with the corresponding polar angle θ values. The peak maxima in a) correspond to the forward focusing directions in b). An N 1s photoelectron kinetic energy of 825 eV (MgKα line) was used. The experimental and theoretical intensities were normalized. The experimental setup geometry is shown in c). The incidence angle of the photons was fixed to 20° from the surface along the [1000] direction.

convolution of the forward focusing peak intensity from the double layer along 38° and 47°. The experimental peak at 52° is close to the N-N pair direction at 55°. Thus, the experimental XPD curves agree qualitatively with the computed XPD intensities for the relaxed GaN(0001) (1 × 1) surface: the N-polarity of the GaN crystal was confirmed. The N-terminated bare structure is in agreement with our previous study [9]. The structure consists of an N-terminated, relaxed bilayer on the top of the surface. A Ga adlayer on the top of the N layer [11] was ruled out [9].

In figure 3 a) and b), the electronic band structures of the bulk GaN and of the relaxed GaN(0001) (1 × 1) surface are shown. There is a surface state s1 on the top of the valence band, which originates from the N 2p dangling bond orbital. The state is almost dispersiveless because of the weak interactions between the localized N dangling bonds [11]. This is a distinct feature of the bare N-terminated GaN(0001) (1 × 1) surface. This state is missing in case of the Ga-adlayer GaN(0001) (1 × 1) structure [11, 12] since there is no N dangling bonds on the surface.

The total densities of the states (DOS) of the GaN bulk crystal and the relaxed N-terminated GaN(0001) (1 × 1) surface are shown in figure 3 c) by red and black lines, respectively. In the case of surface DOS, the s1 peak is present on top of the valence band, while it is absent from the bulk DOS. A local DOS of the topmost N atom was computed to clarify the origin of the surface state. The N 2p orbital electron density is shown by the green line. There are a strong s1 peak and weak s2 and s3 peaks in the LDOS curve. The s2 and s3 peaks do overlap with the bulk Ga electronic states (B and C). Nevertheless, the surface state s1 is strong and can be used as a distinct feature of the clean N-terminated GaN(0001) (1 × 1) surface.
Figure 3. Electronic band structure of a) bulk GaN and b) GaN(0001) (1 × 1) surface. There is a surface state on the top of the valence band in b) marked by a green line. c) The total density of states of the bulk GaN (red line) and (1 × 1) surface (black line). The local DOS of the N 2p states is shown by a green line. These states are formed by N dangling bonds on top of the GaN(0001) (1 × 1) bare surface.

Molecular absorption during GaN surface functionalization alters the electronic structure and changes dielectric response of the clean GaN surface. Knowledge about the ELF of the clean N-terminated GaN(0001) substrate is, however, important for surface functionalization study. The ELF of GaN(0001) was recently investigated by REELS [23]. The ELF, $\text{Im}(-1/\epsilon)$, where $\epsilon$ is a dielectric function, was derived from REELS effective electron inelastic scattering cross-sections. Calculations were carried out within the framework of a semiclassical approach by using Drude-Lindhard type oscillator fitting [24]. Here, the ELF was computed from the first principles, thus avoiding the fitting procedures.

In figure 4, ELF curves derived from REELS spectra and computed by MBPT are shown. The plasmon loss peak positions at 9, 18.2, 23.5 and 28.5 eV agree well between the REELS- and DFT-derived curves. The peak intensities at 23.5 eV, however, are different. The peak corresponds to Ga 3d → 4p band transitions [25]. Agreement could not be improved by using modified pseudopotentials with the Ga 3d electrons as valence electrons. Such a difference can be explained by the presence of defects in the free-standing GaN substrate. Since N is preferentially desorbed from a surface during sputtering [3], an excess of Ga atoms (N defects) can be present on the surface. The appropriate annealing procedures in a NH$_3$ atmosphere could be required to recover the stoichiometry on the surface. In this sense, the ELF measured by REELS should approximate to the ELF derived by MBPT.

5. Conclusions
The atomic and electronic structure of a clean, ordered GaN(0001) (1 × 1) surface were investigated by XPD. The polar dependence of the photoelectron intensities was computed taking multiple electron scatterings into account. The theoretical peak position maxima agree with the measured maxima for the N-terminated GaN(0001) (1 × 1) reconstruction. The electronic band structure was computed in the framework of DFT. A surface state on the top of the valence
band was confirmed. The optical properties of GaN were derived by the MBPT. The loss peak positions derived by the MBPT were found to be in agreement with the REELS measurements.

**Acknowledgments**

Support by the Czech Academy of Sciences (No. M100101201) and by the Grant Agency of the Czech Republic (No. P204/10/P028) is gratefully acknowledged. The access to the MetaCentrum computing facilities provided under the programme ”Projects of Large Infrastructure for Research, Development, and Innovations” LM2010005 funded by the Ministry of Education, Youth, and Sports of the Czech Republic is highly appreciated.

**References**

[1] Kotov N A, et.al. 2009 *Adv. Mater.* 21 3970

[2] Jewett S A, Makowski M S, Andrews B, Manfra J and Ivanisevic A 2011 *Acta Biomaterialia* 8 728

[3] Hattori A N, Endo K, Hattori K and Daimon H 2010 *Appl. Surf. Sci.* 256 4745

[4] Yu Z X, Tong S Y, Xu S, Ma S and Wu H 2003 *Surf. Rev. Lett.* 10 831

[5] Widstrand S M, Magnusson K O, Johansson L S O and Oshima M 2005 *Surf. Sci.* 584 4169

[6] Rosa A L and Neugebauer J 2006 *Phys. Rev. B* 73 205346

[7] Ramachandran V, Lee C D, Feenstra R M, Smith A R, Northrup J E and Greve D W 2000 *J. Cr. Growth* 209 355

[8] Smith A R, Feenstra R M, Greve D W, Neugebauer J and Northrup J 1997 *Phys. Rev. Lett.* 79 3934

[9] Romanyuk O, Jiricek P and Paskova T 2012 *Surf. Sci.* 606 740

[10] Kowalski B J, Iwanowski R J, Sadowski J, Kowalik I A, Kanski J, Grzegory I and Porowski S 2004 *Surf. Sci.* 548 220

[11] Wang F H, Kruger P and Pollmann J 2001 *Phys. Rev. B* 64 035305

[12] Chao Y C, Stagarescu C B, Downes J E, Ryan P and Smith K E 1999 *Phys. Rev. B* 59 R15586

[13] http://www.kymatech.com

[14] Abajo F J G, Van Hove M A and Fadley C S 2001 *Phys. Rev. B* 63 075404

[15] Gonze X, et. al. 2002 *Comput. Mater. Sci.* 25 478

[16] Gonze X, et. al. 2005 *Z. Kristallogr.* 220 558

[17] Fuchs M and Scheffler M 1999 *Comput. Phys. Commun.* 119 67

[18] Troullier N and Martins J L 1991 *Phys. Rev. B* 43 1993

[19] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* 13 5188

[20] Marini A, Hogan C, Gruning M and Varsano D 2009 *Comp. Phys. Comm.* 180 1392

[21] Palummo M, Pulci O, Marini A, Reining L and Del Sole R 2006 *Phys. Rev. B* 74 235431

[22] Benedict L X, Shirley E L and Bohn R B 1998 *Phys. Rev. Lett.* 80 4514

[23] Romanyuk O, Jiricek P, Zemek J, Tougaard S and Paskova T 2011 *J. Appl. Phys.* 110 043507

[24] Yubero F, Sanz J, Ramiskov B and Tougaard S 1996 *Phys. Rev. B* 53 9719

[25] Bermudez V M 1996 *J. Appl. Phys.* 80 1190

---

**Figure 4.** Energy loss functions derived from REELS spectra by a semiclassical approach (solid line) and computed within the MBPT (dashed line). The plasmon peak positions agree well, whereas the peak intensities at 23.5 eV are different. Atomic disorder on the surface can explain this intensity difference.