Angle Resolved Photoemission Spectroscopy of GaN($10\bar{1}0$): Experiment and Theory

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We present synchrotron radiation excited photoemission spectra in off-normal emission from GaN($10\bar{1}0$) surfaces. The samples of GaN single crystals grown by high pressure, high temperature synthesis were cleaved under ultra high vacuum conditions. The experimental results were compared with calculated spectra within the one step model. We could identify emissions from surface states and resonances near the upper and lower valence band edge. The detected surface states confirm the assumed surface geometry.

I. INTRODUCTION

The most powerful experimental tool for examining the electronic structure of semiconductors is angle resolved ultraviolet photoemission spectroscopy (ARUPS). Because photoemission involves the excitation from initial bound states to outgoing scattering states, a full account of the experimental data can only be attained by comparison with photocurrents calculated within the one-step model. In the past the electronic structure of grown cubic GaN (001), (110) and wurtzite (0001) surfaces were studied by photoemission [1–4]. The nonpolar GaN ($10\bar{1}0$) cleavage plane offers an independent possibility of verifying the bulk band structure and to determine the specific surface states. Besides this a given surface geometry can be tested.

II. EXPERIMENTAL

The experiment was performed with the newly developed angle-resolved photoelectron spectrometer ASPHERE. It is a 180° hemispherical deflection analyzer with 100 mm main radius, a fringe field correction and adjustable angular resolution. Yet the best demonstrated energy resolution is less than $\Delta E = 10$ meV. The measurements were carried out at the DORIS III storage ring at the Hamburg Synchrotron Radiation Laboratory with the modified SX700 monochromator at the beamline BW3. The experimental angular resolution was set to 1° and the energy resolution to 50 meV.

The crystals used to prepare the GaN($10\bar{1}0$) surface were bulk GaN grown by high pressure, high temperature synthesis and the orientation was checked by Laue diffraction. Crystals were cleaved under ultra high vacuum conditions (giving an effective surface area of 1 x 0.1 mm) and transferred to the spectrometer keeping the sample in ultra high vacuum at all times. The samples were adjusted with p-polarized light incident along the ($\bar{1}2\bar{1}0$) direction under 45° with respect to the surface normal.

III. THEORY

We calculate the photocurrent within the one-step model. For details see references [5,7] and for its application to GaN (001) and (0001) surfaces see reference [1]. In this “golden rule” formulation of the photoemission process the initial states are represented by a Green’s function. This Green’s function is given here in the basis of a layer resolved linear combination of atomic orbitals. The associated Hamilton matrix is calculated according to the Extended-Hückel-Theory [7]. Its parameters are adjusted according to a self-interaction and relaxation corrected pseudopotential band structure calculation by Vogel *et al.* [8] using a genetic algorithm [9] for optimization. For the calculations of the Green’s function the surface model by Northrup *et al.* [10] is used.

The final state of photoemission is obtained as a scattering state with asymptotic boundary conditions. The wave function of the final state is determined by matching the solution of the complex bulk band structure to the vacuum solution, representing the surface by a step potential. The solution within the bulk is calculated by the empirical pseudopotential method, developed by Cohen and Bergstresser [11]. For GaN we use the pseudopotential form factors of Bloom *et al.* [12]. The damping of the wavefunction inside the crystal is described by the imaginary part of an optical potential.

The transition matrix elements between the final state and the layer Bloch sums of the initial state are calculated in real space. The decomposition of the matrix elements into contributions from atomic layers and orbitals are needed for a full analysis of the spectra.

IV. RESULTS AND DISCUSSION

In Fig. 1 we present the calculated surface band structure. Within the fundamental gap there are two dangling bond like surface states. The first one near 2.8 eV is related to Ga p_z orbitals and the second one (a) around the upper valence band edge to N p_z orbitals. The density of states (DOS) at the $\overline{\Gamma}$ point shows that beside the N p_z orbitals also N p_y orbitals contribute to the state (a) (Fig. 2). The three surface resonances (b, c, d) are mainly related to N p_x and p_y orbitals. The remaining resonance (e) is due to Ga s and N p_x orbitals.

In Fig. 3 we present experimental and calculated results for off-normal electron emission along $\overline{\Gamma X}'$ with an excitation energy of 78.6 eV. In the experimental spectra there are four main structures (I', II', III', IV'). Structure (I') is visible for all angles at binding energies between -1.2 eV for $\vartheta = 0°$ and -0.4 eV for $\vartheta = -9°$. A shoulder (II') with weak dispersion is found around the upper valence band edge. A dispersive structure (IV') can be seen between -6.4 eV binding energy at $\vartheta = 0°$ and -3.2 eV at $\vartheta = -9°$. An additional structure (III') is visible only for the angles $\vartheta = 4°$ and $\vartheta = 5°$. In the theoretical spectra structures (I) and (II) show the same dispersion as (I') and (II') and resolve them more clearly. Structure (I) gets contribution from N p_z orbitals which have the largest matrix elements. Especially for lower angles the emission originates from the N dangling bond which is labeled in the surface band structure (Fig. 1) with (a). Additional direct transitions from valence bands near the upper edge contribute to structure (I). This is also valid for structure (II) whose dispersion follows the upper edge of the projected bulk band structure. Further emissions (III) from N p_z orbitals appear for angles of $\vartheta = 4°$ and $\vartheta = 5°$. They explain the experimental structure (III'). A closer look at the matrix elements and the DOS shows this emission to be emerging from the second atomic layer. For negative angles, the strong emission in theory around -2.9 eV also originates from the N p_z orbitals. These emissions have no counterpart in the experimental spectra. Furthermore, theory shows a strongly dispersing structure (IV) between -6.2 eV at $\vartheta = 0°$ and -3.2 eV at $\vartheta = -9°$. The dispersion of structure (IV) evolves in the same manner as the surface resonance (e) (cf. Fig. 1), except for the peak at $\vartheta = -9°$ which is explained by the surface resonance (d). For angles around $\vartheta = 0°$ theory shows additional intensity near -7.0 eV binding energy. This intensity is explained by direct transitions from the lower valence band edge and is not seen in the experiment.

The comparison between experimental and theoretical photoemission spectra verifies the energy position and orbital composition of the dangling bond surface state (a, structure I) and a surface resonance (e, structure IV). Since the energy position of these two surface states sensitively depends on the surface geometry, we can verify the surface model proposed by Northrup *et al.* [10] used for calculating the photocurrents.

V. CONCLUSION

Photoemission spectra for GaN ($10\bar{1}0$) have been measured along the $\overline{\Gamma X}'$ direction of the surface Brillouin zone and are analyzed in the context of one-step model calculations. By comparison between theory and experiment we were able to identify emissions from a Nitrogen dangling bond state near the upper valence band edge. Furthermore, a strongly dispersing surface resonance was found. The existence of these two surface sensitive states validates the used surface geometry.

VI. ACKNOWLEDGEMENT

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[1] T. Strasser, F. Starrost, C. Solterbeck, and W. Schattke, Phys. Rev. B **56**, 13326 (1997); T. Strasser, F. Starrost, C. Solterbeck, and W. Schattke, to be published.

[2] S. A. Ding, G. Neuhold, J. H. Weaver, P. Häberle, K. Horn, O. Brandt, H. Yang, and K. Ploog, J. Vac. Sci. Technol. A **14**, 819 (1996).

[3] S. S. Dhesi, C. B. Stagarescu, K. Smith, D. Doppalapudi, R. Singh, and T. D. Moustakas, Phys. Rev. B **56**, 10271 (1997).

[4] S. A. Ding, S. R. Barman, K. Horn, and V. L. Alperovich, 23nd International Conference on the Physics of Semiconductors **1**, 525 (1996).

[5] J. Henk, W. Schattke, H.-P. Barnscheidt, C. Janowitz, R. Manzke, and M. Skibowsiki, Phys. Rev. B **39**, 13286 (1989).

[6] J. Henk, W. Schattke, H. Carstensen, R. Manzke, and M. Skibowski, Phys. Rev. B **47**, 2251 (1993).

[7] J. Henk and W. Schattke, Comput. Phys. Commun. **77**, 69 (1993).

[8] D. Vogel, P. Krüger, and J. Pollmann, Phys. Rev. B **55**, 12836 (1996).

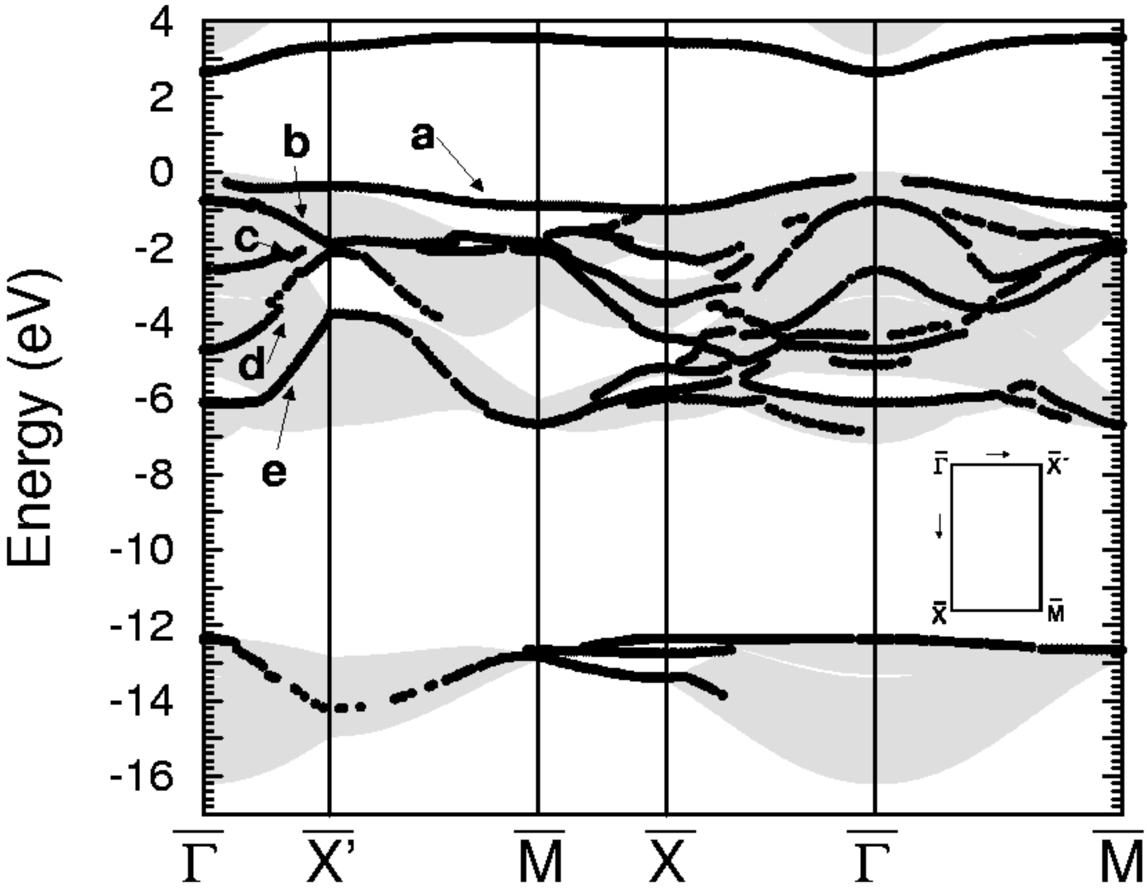
[9] F. Starrost, S. Bornholdt, C. Solterbeck, and W. Schattke, Phys. Rev. B **53**, 12549 (1996); **54**, 17226 (1996).

[10] J. E. Northrup and J. Neugebauer, Phys. Rev. B **53**, R10477 (1996).
[11] M. L. Cohen and T. K. Bergstresser, Phys. Rev. B **141**, 749 (1966).
[12] S. Bloom, G. Harbeke, E. Meier, and I.B. Ortenburger, phys. stat. sol. (b) **66**, 161 (1974).

FIG. 1. *Surface band structure of GaN*($10\bar{1}0$) *and the projected bulk band structure (shaded). The inset shows the surface Brillouin zone.*

FIG. 2. *Density of states at* $\overline{\Gamma}$ *for GaN* ($10\bar{1}0$). *On the left hand side the layer resolved DOS is shown, while on the right the DOS of the first two layers is further resolved into its atomic and orbital contributions.*

FIG. 3. *Theoretical spectra (left) and experimental (right) in off-normal emission along the* $\overline{\Gamma X}'$ *direction. Binding energies are referred to the valence band maximum (VBM). Lines indicate structures which can be found in both experiment and theory. Their dispersions are discussed in the text.*


Energy (eV)
a
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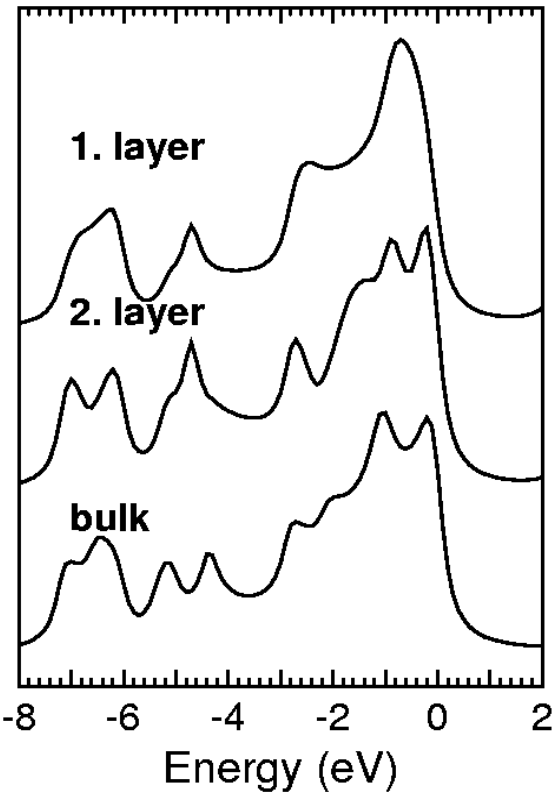
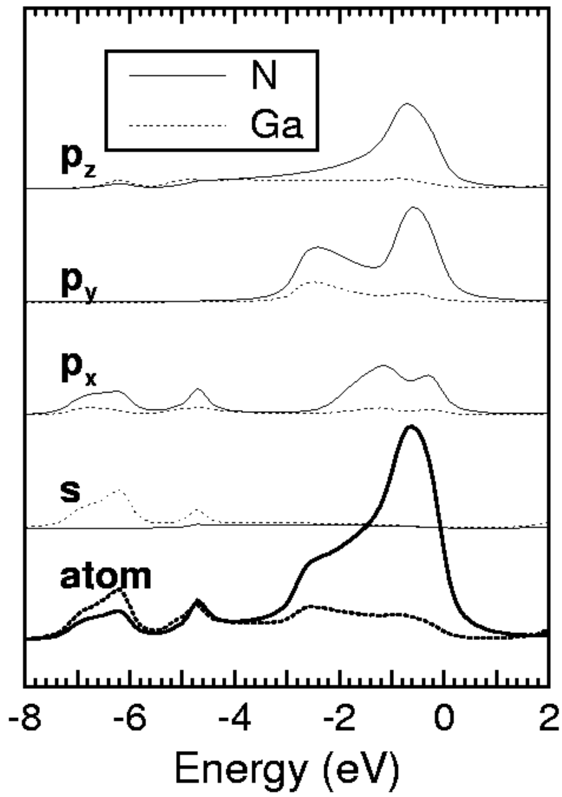
X
Γ
M


1. layer
2. layer
bulk
Energy (eV)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p_z
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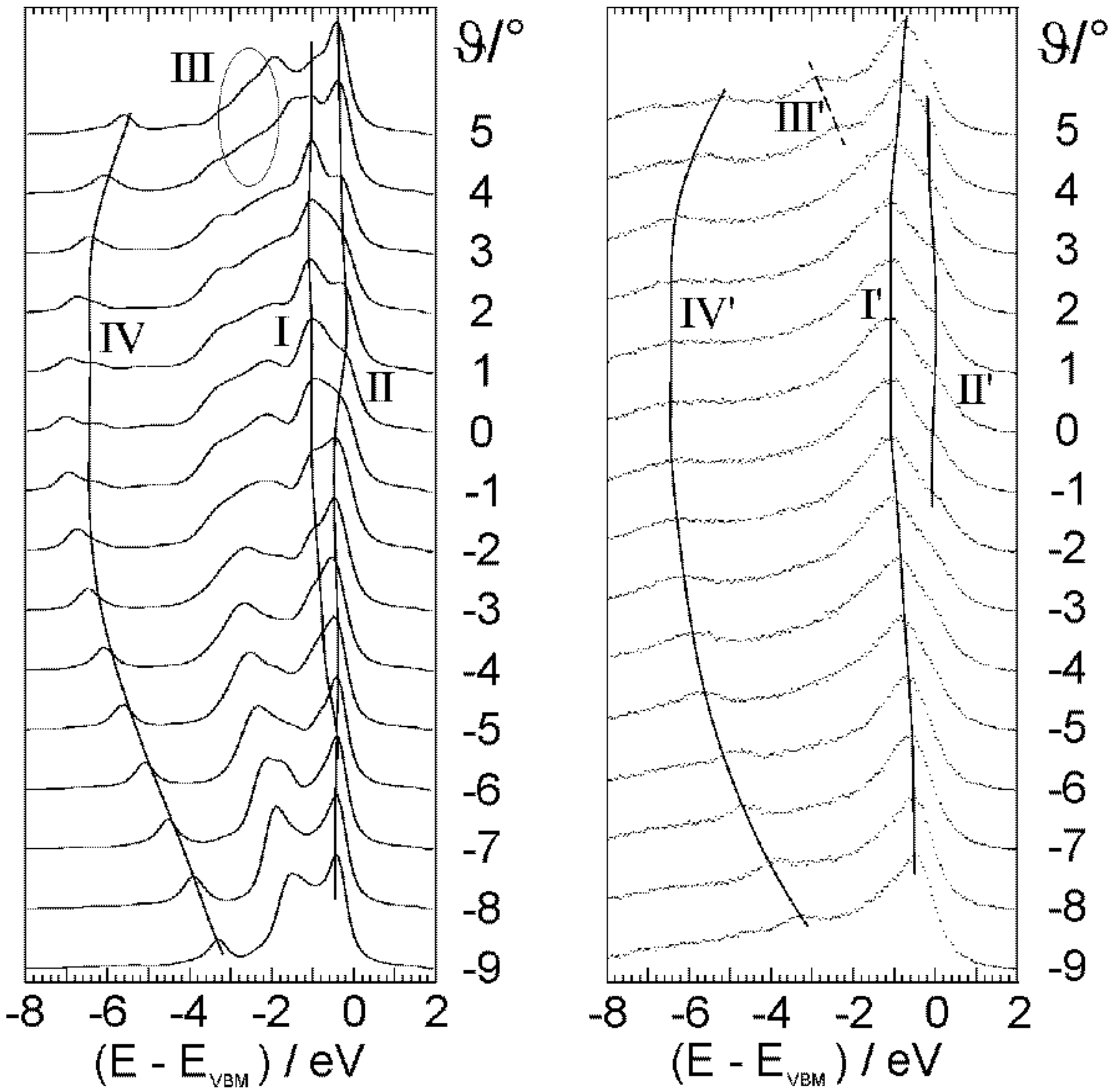

III
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(E - E_VBM) / eV