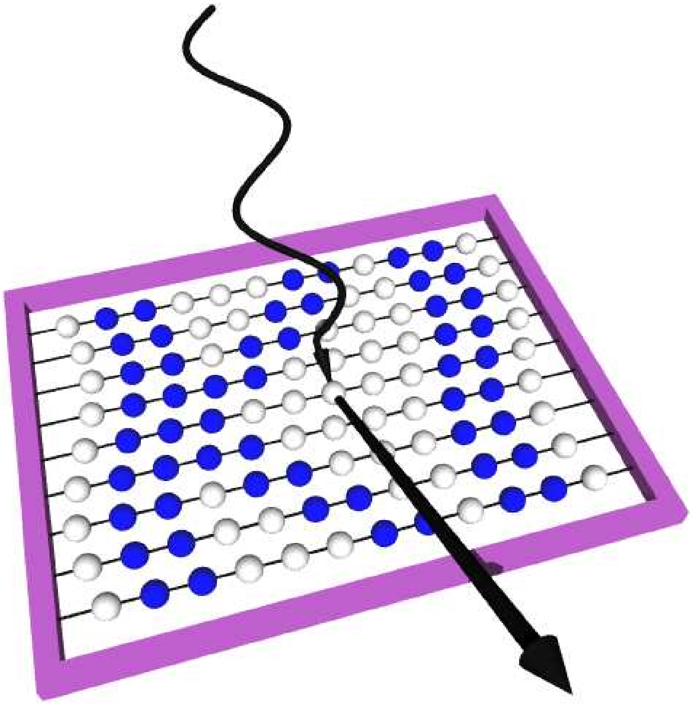
Valence band photoemission from GaN(001) and GaAs:GaN-surfaces



Posterpresentation by

T. Strasser, F. Starrost, C. Solterbeck and W. Schattke

at

Fourth Nordic Conference on Surface Science

May 29 - June 1, 1997 in Ålesund, Norway

Abstract

The most powerful experimental tool for examining the electronic structure of a semiconductor surface is the angle and energy resolved photoemission spectroscopy. We have calculated photoemission spectra for cubic GaN within the one-step model. It has been shown that for the III-V nitrides the wurtzite structure is more stable than the zinc blende structure, but Yang et al. demonstrate, that it is possible to grow films of cubic GaN on the GaAs(001) surface [1]. Cubic GaN is promising for an higher electron drift velocity and a lower gap than the wurtzite structure.

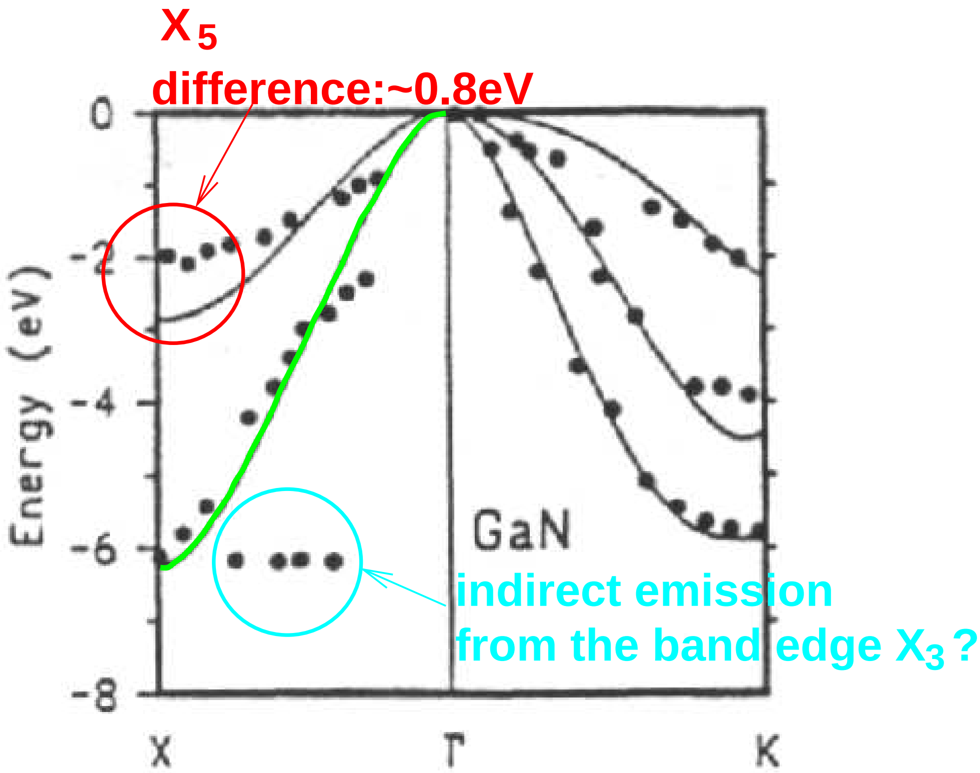
We present theoretical photoemission spectra in normal emission for the GaN(001) surface, calculated for photon energies from 10 up to 80 eV. By the use of the layer resolved density of states, we can identify emissions from a dangling bond like state, which is in resonance with the upper valence band edge, as well as emissions from the Ga-N bonds at higher binding energys. Furthermore the spectra show a intense Ga s peak, which is modulated by the matrixelements. Furthermore above 30 eV photon energy the theoretical spectra show strong dispersing structures, which can be interpreted as direct transitions. We are able to identify the initial states as well as the final states, being responsible for these structures. The calculated spectra are in good aggrement with ex data from Ding et al [2].

In a second step, we compare our results with theoretical spectra from a GaAs(001) surface. As for GaN, the spectra of GaAs are dominated by strong dispersing structures, but in contrast to GaN these features can be seen even for photon energies lower than 30eV. Because the system GaAs:GaN has reached technological interest, as e.g. by passivating the GaAs(001) surface by direct nitridation, we examine GaAs(001) surfaces, covered by a monolayer N, as well as by several layers of GaN. The assumed surface structure is included in the final as well as in the initial states. We investigate how the difference in the surface composition influences the electronic structure and, more important, we examine, how this difference influences the spectra. One overlayer of nitrogen on the GaAs(001) surface is sufficient to suppress the mos emissions from direct transitions of the GaAs bulk. The spectra are then dominated by emissions from the nitrogen dangling bond near the upper valence band edge. Furthermore we are able to identify emissions from the Ga-N bond, as well as from the Ga-As bonds from the lower lying layers. By changing the polarisation of the light, we can increase the emission from selected bonds within the second layer. Covering the GaAs surface with GaN layers, the emissions from GaAs disappear gradually. However, even with three layers of GaN we are still able to identify bonds between Ga and As. The spectra are dominated by emissions from nitrogen p_z-orbitals, as well as Ga s-Orbials. With every new layer of GaN the number of Ga s states involved increase in contributing to the density of states and even more pronounced to the spectra.

[1] H. Yang, O. Brandt and K. Ploog, phys. stat. sol. (b) 194, 109 (1996)
[2] S. A. Ding et al., J. Vac. Sci. Technol. A 14, 819 (1996)

Introduction

Discrepancies between recent experimental photoemission data and ab-initio bandstructure calculations (see the red circle in the figure below) cast serious doubt upon the validity of comparing experimental peak deconvolution directly with theoretical band position.

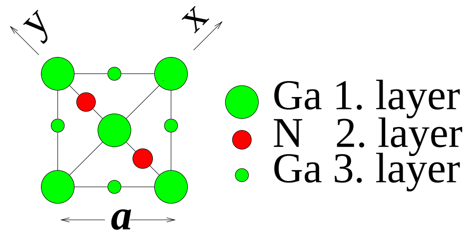


Comparision between an experimental GaN bulk band structure (dots) by Ding et al. with theoretical result by Vogel et al. (lines).

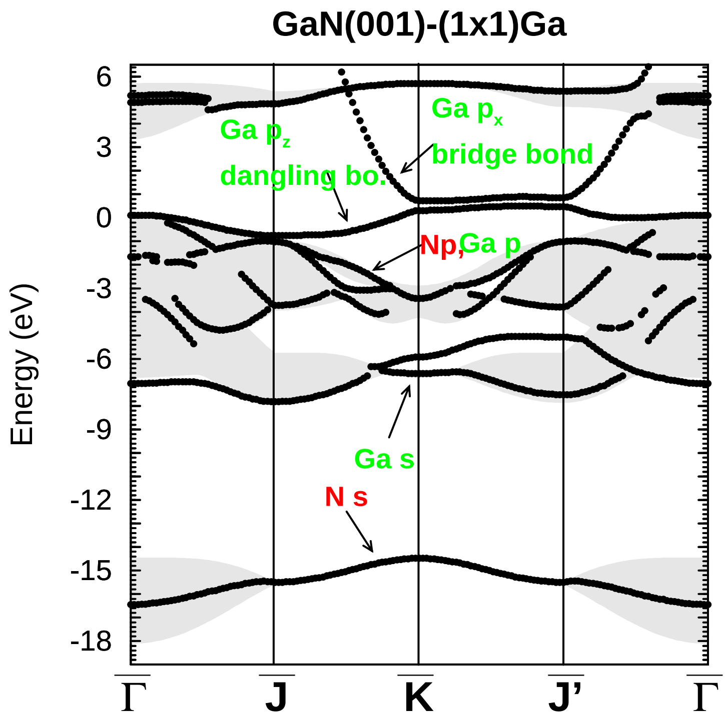
We present photoemission spectra determined within the one-step model in normal emission from cubic GaN and GaAs(001) surfaces. The structures in the spectra are compared with direct transitions as well as with emissions from surface states. Especially we analyse the orbital composition of the photocurrrent and associate structures in the spectra via structure plots with the participating initial and final bands. Furthermore we calculate photoemission spectra for a GaAs(001) surface, covered with up to three layers of GaN.

GaN(001)-(1x1)Ga

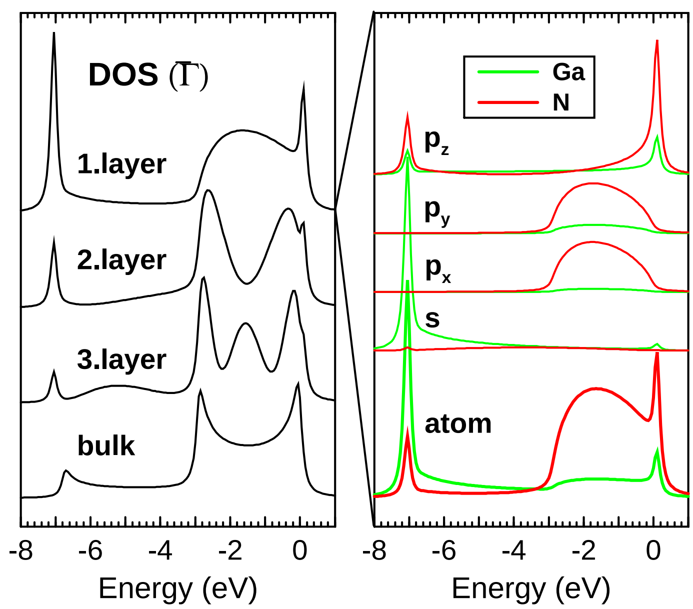
Geometry of the ideal and Ga-terminated GaN(001) surface:



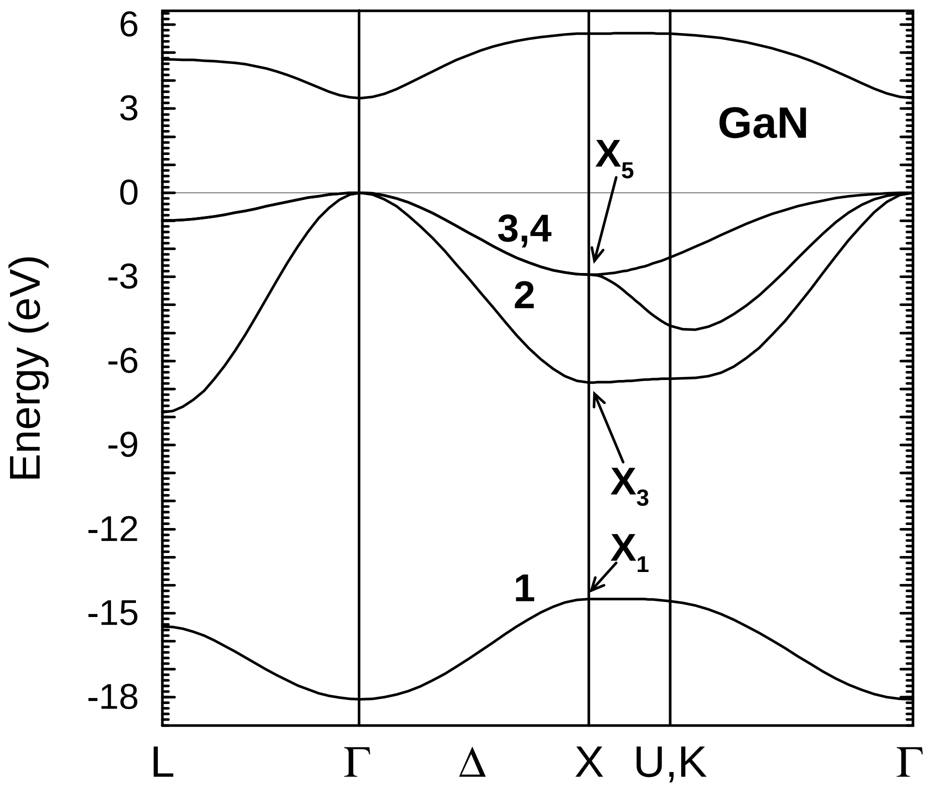
Surface band structure of the GaN(001) surface:



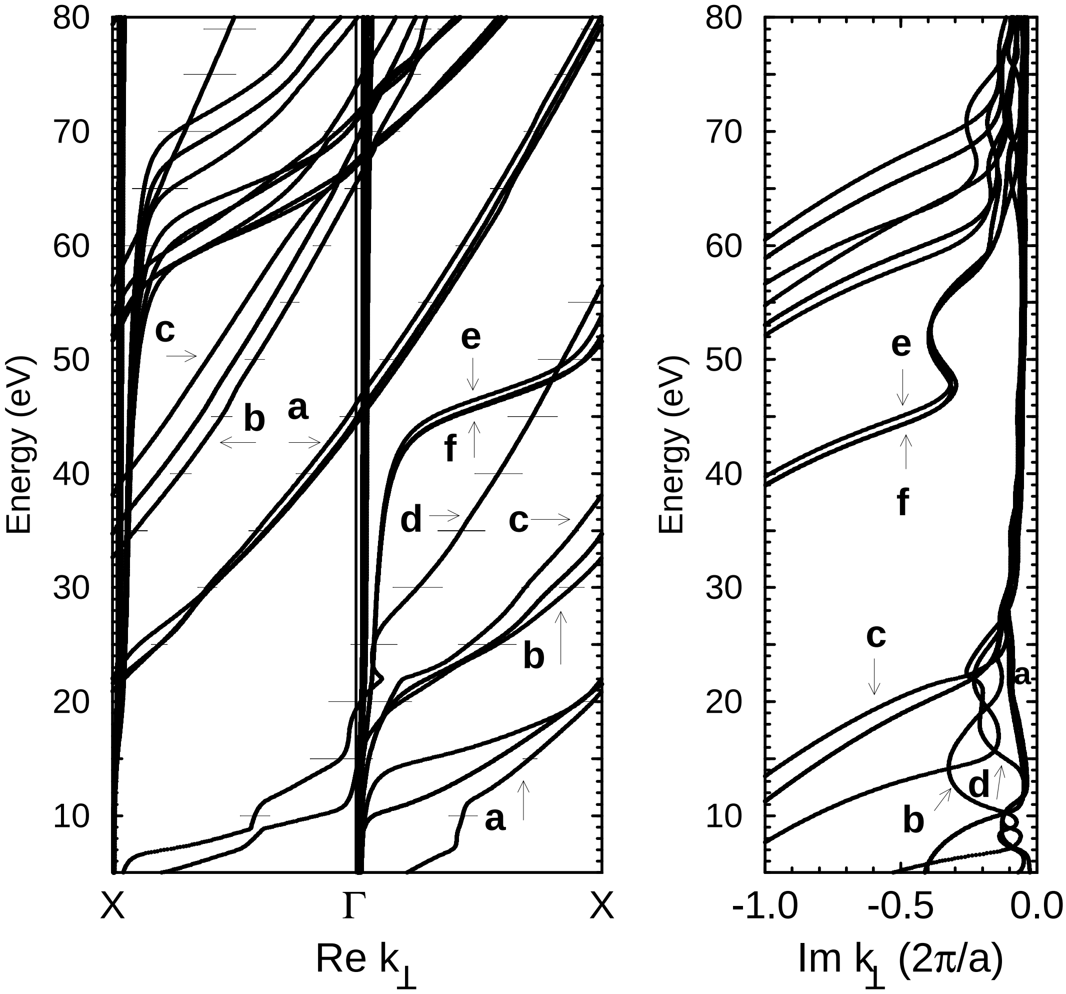
Density of states (DOS) at $\overline{\Gamma}$



GaN-Bulk valence band structure:



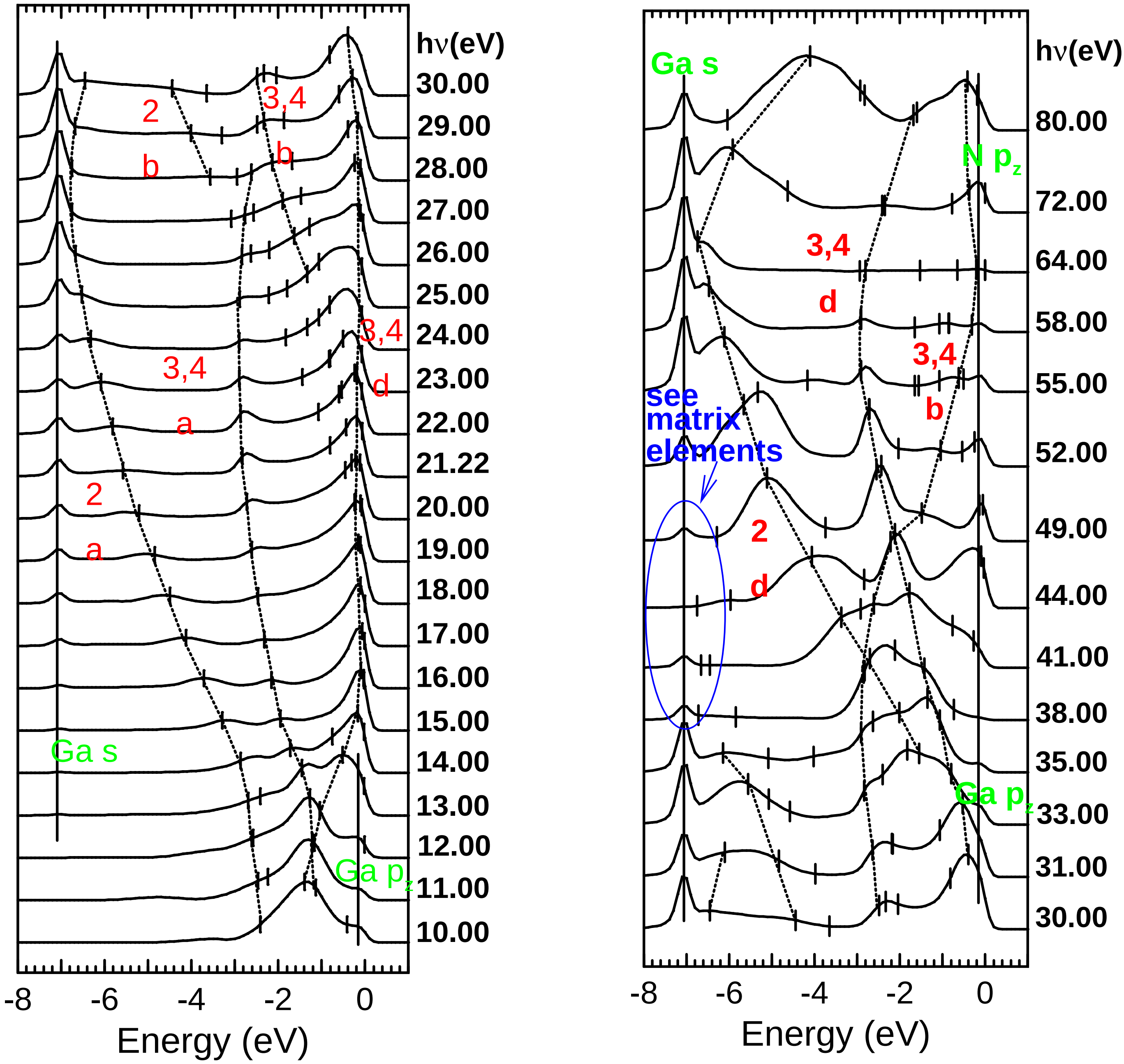
The complex final bands of the GaN(001) surface:



(Bars indicate the magnitude of the expansion coefficients of the final state with respect to the complex bulk bands.)

GaN(001)-(1x1)Ga

Theoretical photoemission spectra in normal emission:

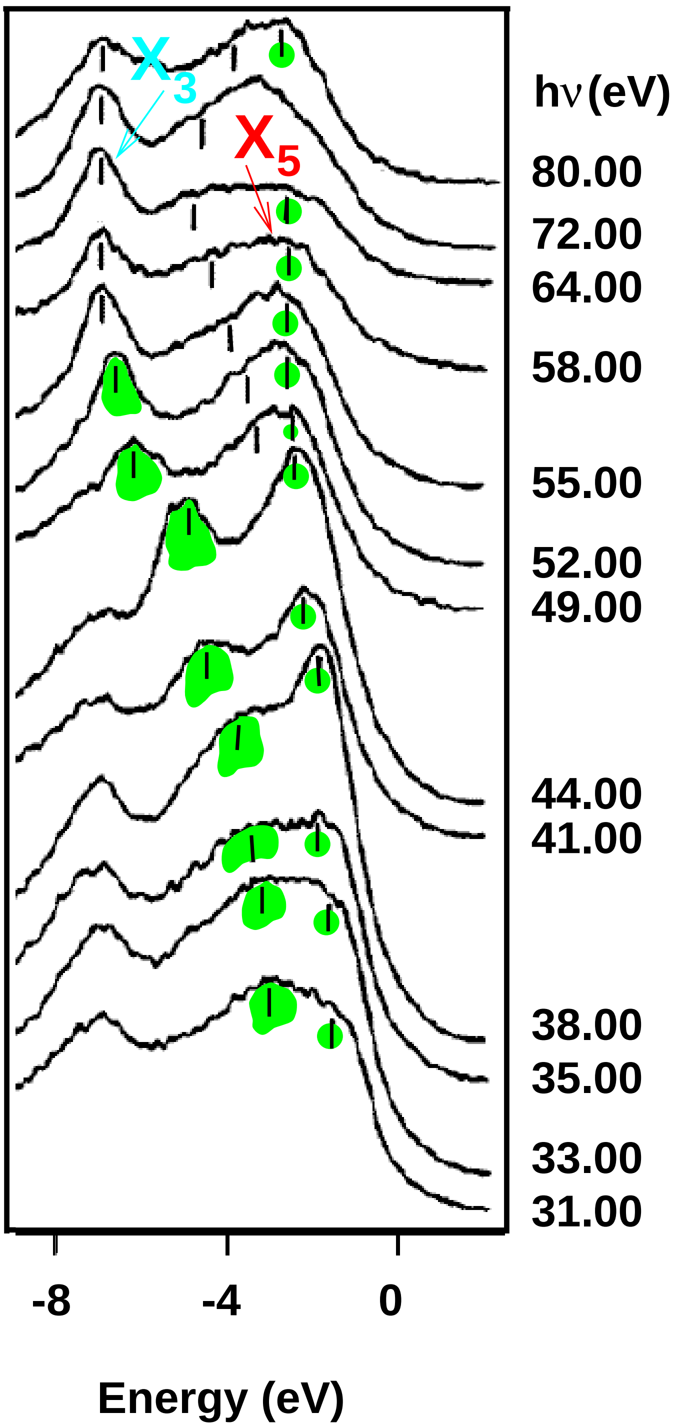


The radiation is incident in the yz-plane with p-polarization. Dispersive structures are marked by dotted lines and the corresponding initial and final bands are indicated (for notation see the bulk and the complex band structures). Non-dispersive structures are marked by solid lines and the corresponding atoms and orbitals are indicated. Bars indicate binding energies at which direct transitions would be positioned.

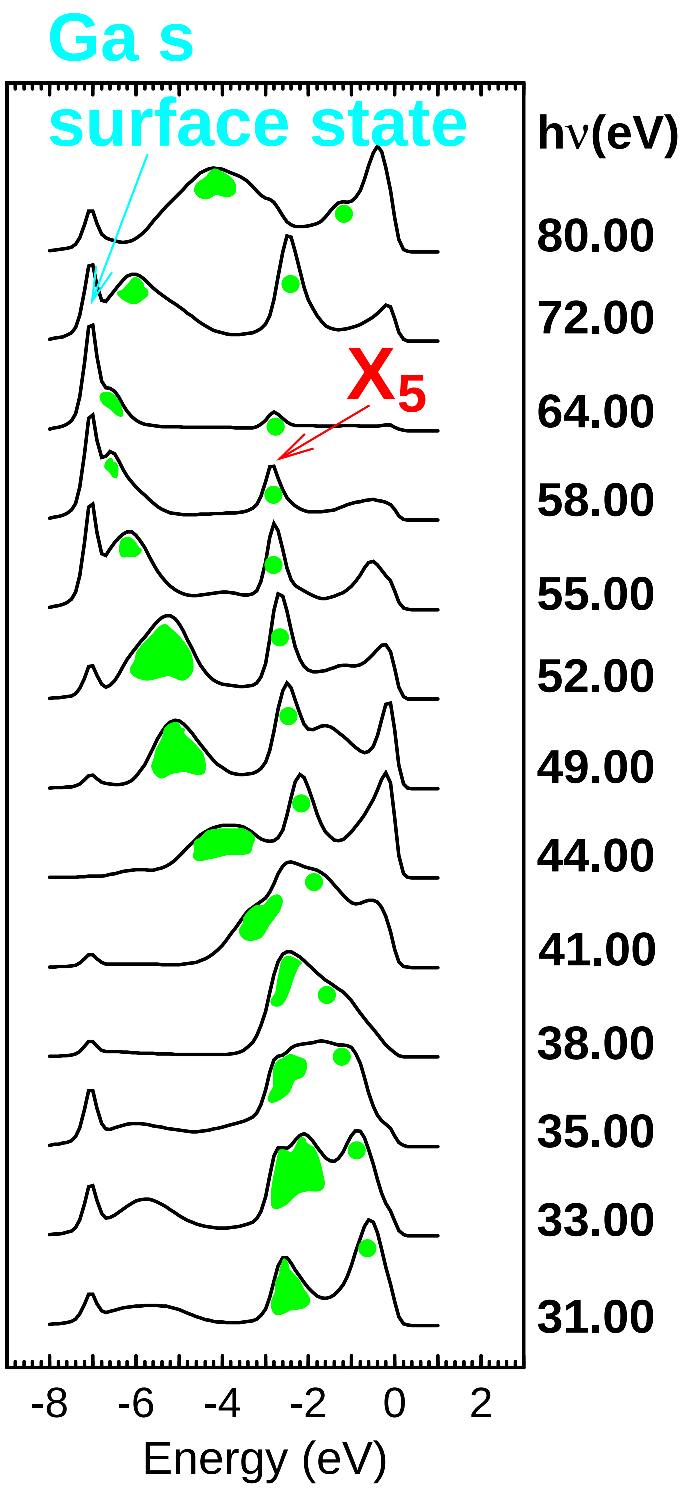
- Direct transitions clearly become visible for photon energies above 30 eV. This is consistent with the small imaginary parts of the final bands for energies greater than 30 eV.
- Due to its large expansion coefficients the final band (d) is responsible for the most prominent dispersing structures in the spectra.
- The emissions at -7.1 eV are clearly identified as being associated with a Ga s surface state. They show a strong modulation in intensity, which stems from the matrix elements. Emissions from the X_3 band edge can be excluded, because the band edge is localized at 200 meV lower binding energies.

GaN(001)-(1x1): Normal emission

Experiment by Ding et al.



Theory



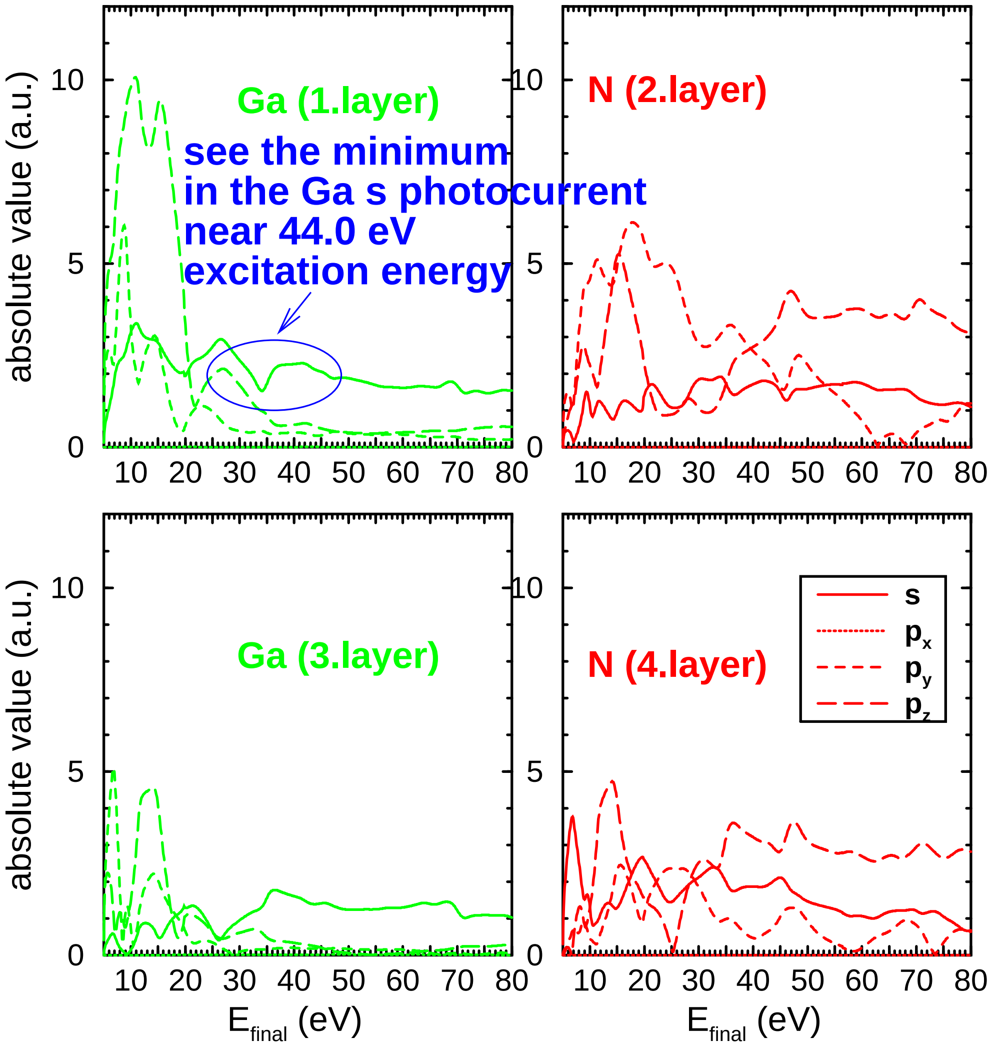
The theoretical spectra are calculated with unpolarized light incident along the yz-plane.

- Experiment and theory show the Ga s-related peak at -7.0 and -6.8 eV respectively. Both results show the decreasing intensity of this structure for photon energies around 44 eV. Experiment attributes this peak to indirect transitions from X_3, while theory shows that this structure is related to strong surface emissions.

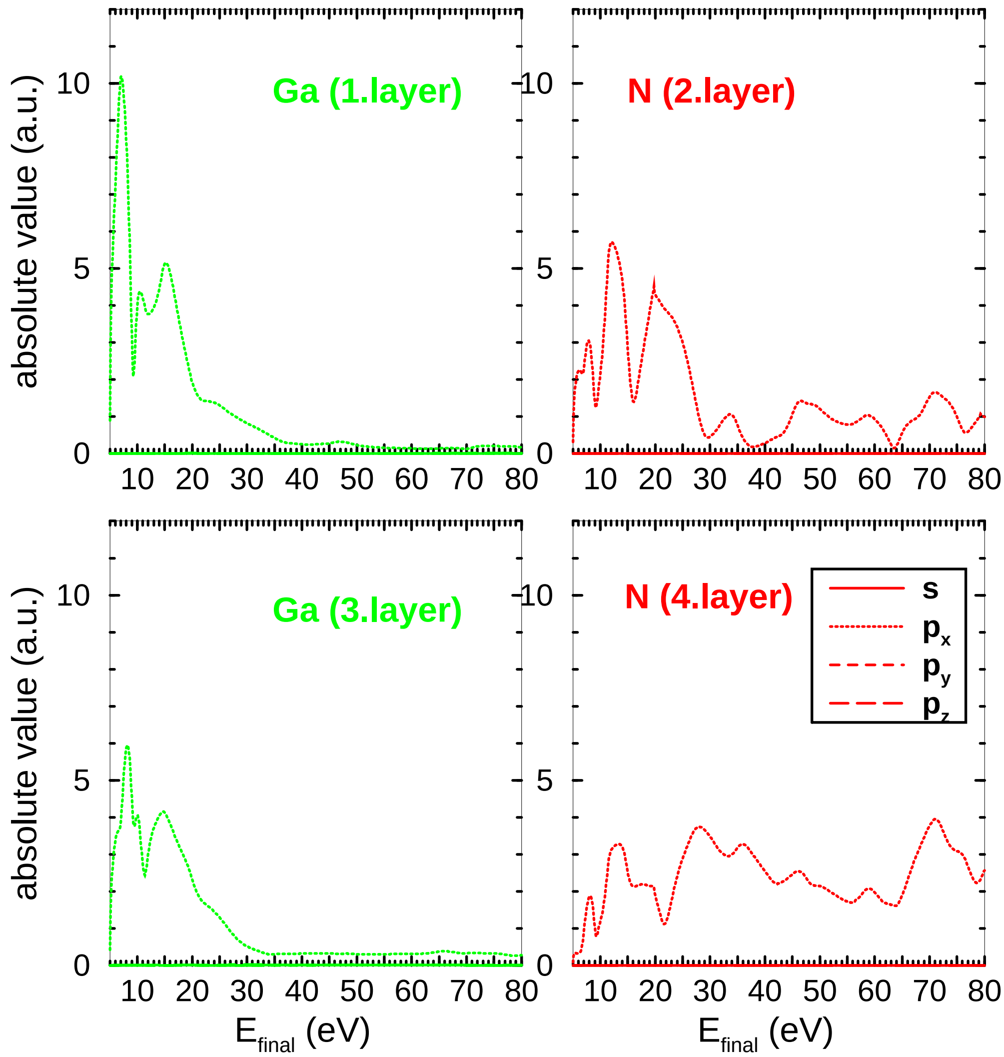
- Theory shows two strong dispersive structures (one between -2.5 and -6.5 eV and the second one at lower binding energies) which can be identified in experiment.

- Contrary to results from experimental peak deconvolution techniques the band edge X_5 may in fact coincide with the binding energy predicted by actual band structure calculations.

The matrix elements (p-polarization with light incident in the yz-plane)

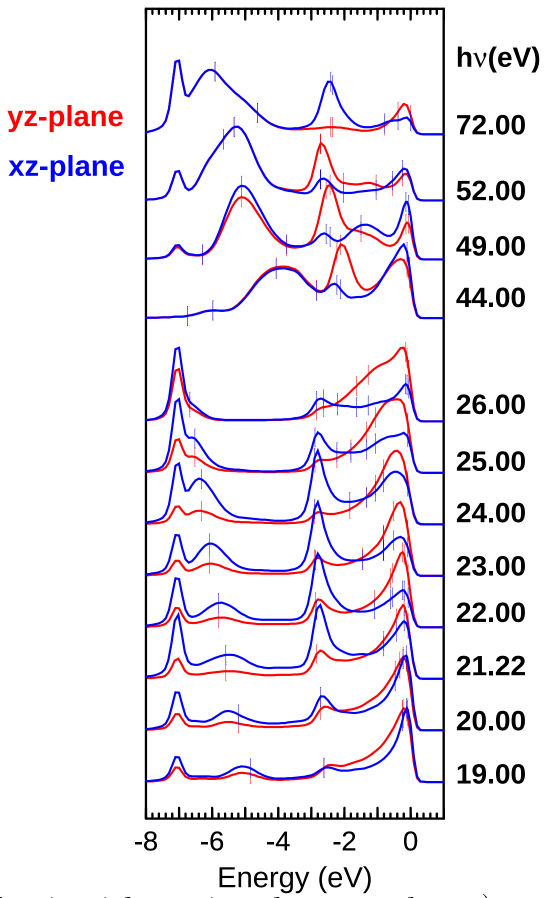


The matrix elements (s-polarization with light incident in the yz-plane)

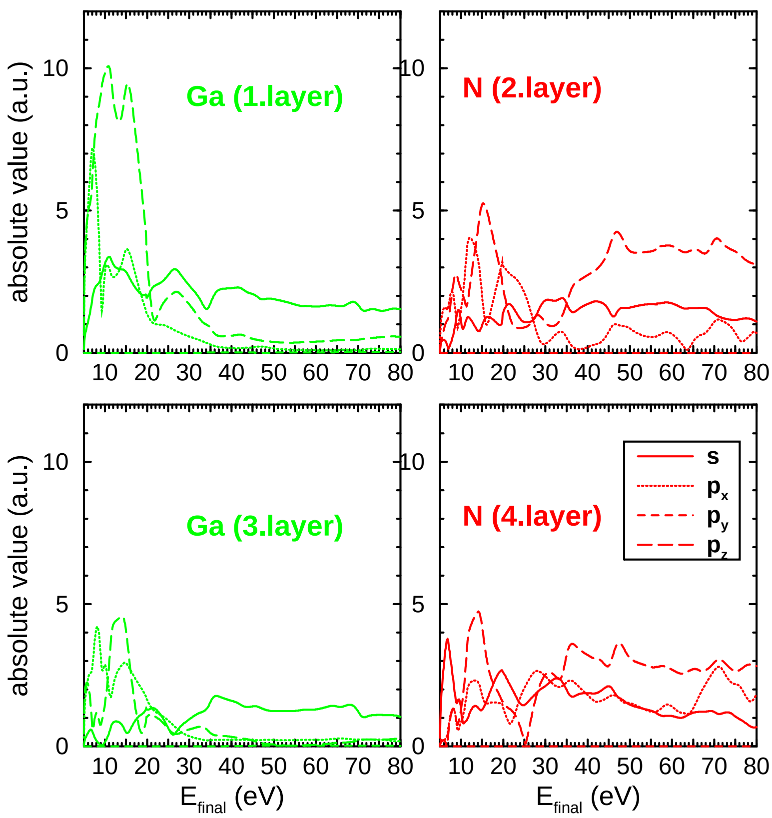


The influence of the direction of the light to the photocurrent (p-polarization):

- Turning the direction of the light in the xz-plane emissions near the band edge X_5 are enhanced.
- This is in accordance with a maximum in the matrix elements for the N p_x-orbitals for the first layer between 18 and 24 eV.

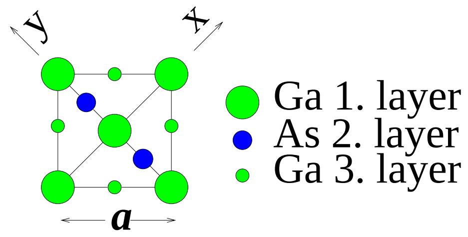


The matrix elements (p-polarization with light incident in the xz-plane)

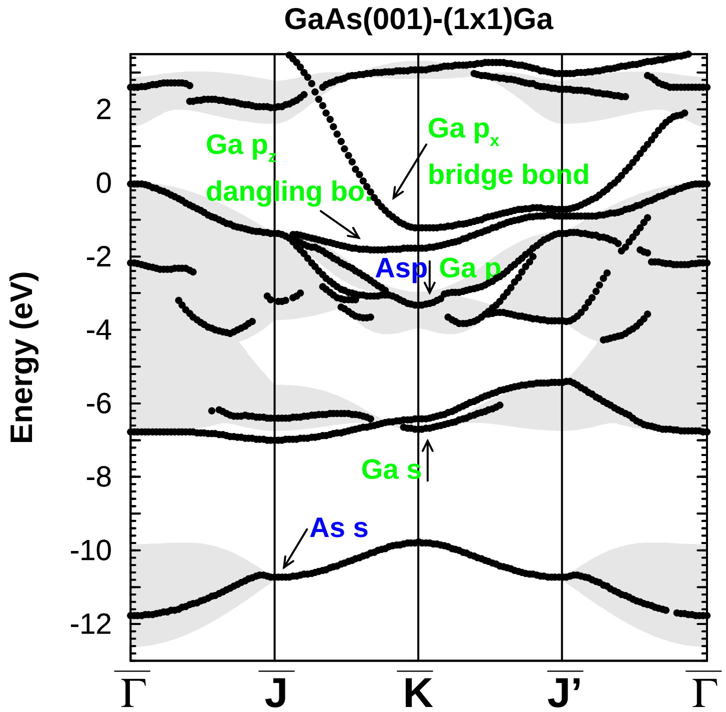


GaAs(001)-(1x1)Ga

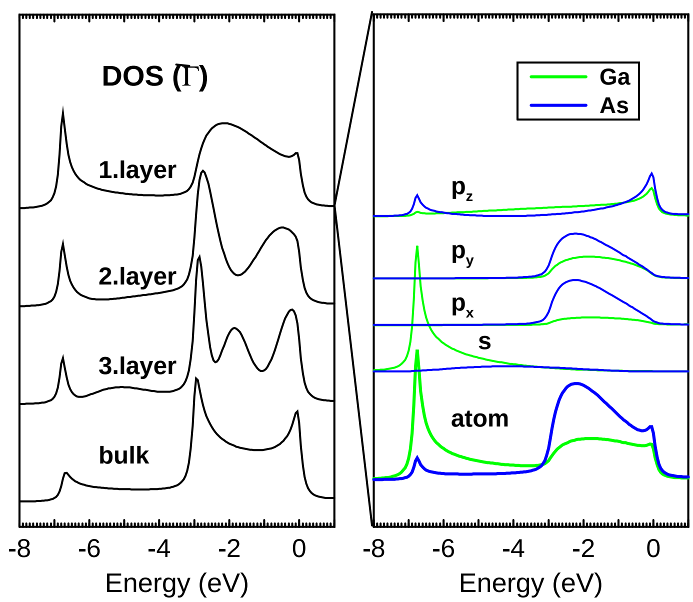
Geometry of the ideal and Ga-terminated GaAs(001) surface:



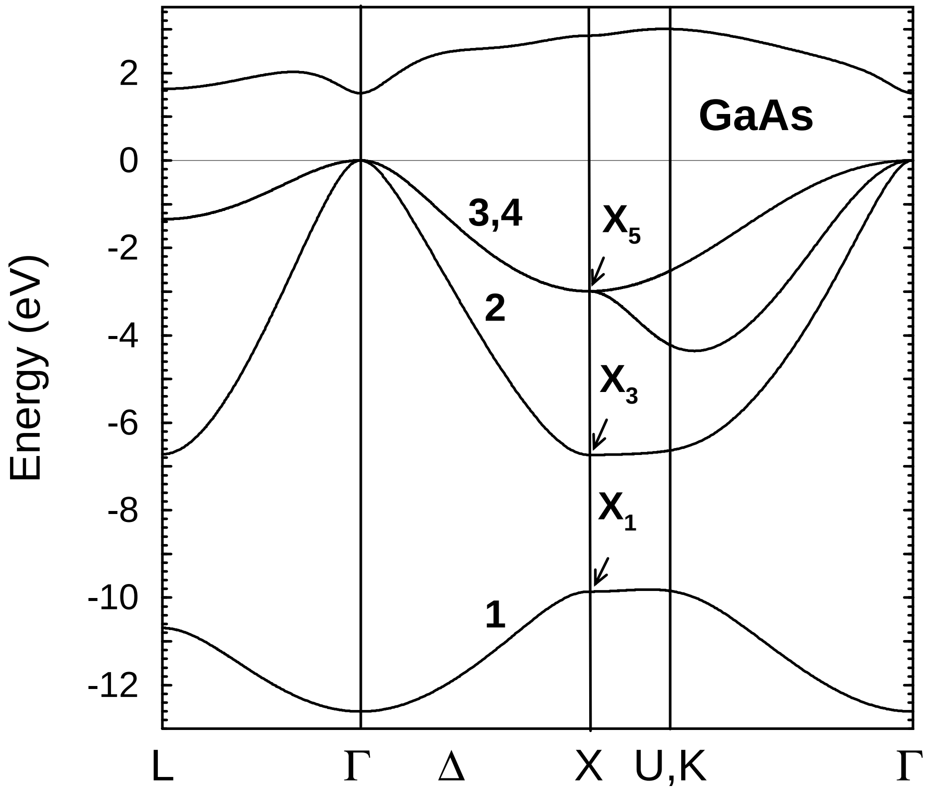
Surface band structure of the GaAs(001) surface:



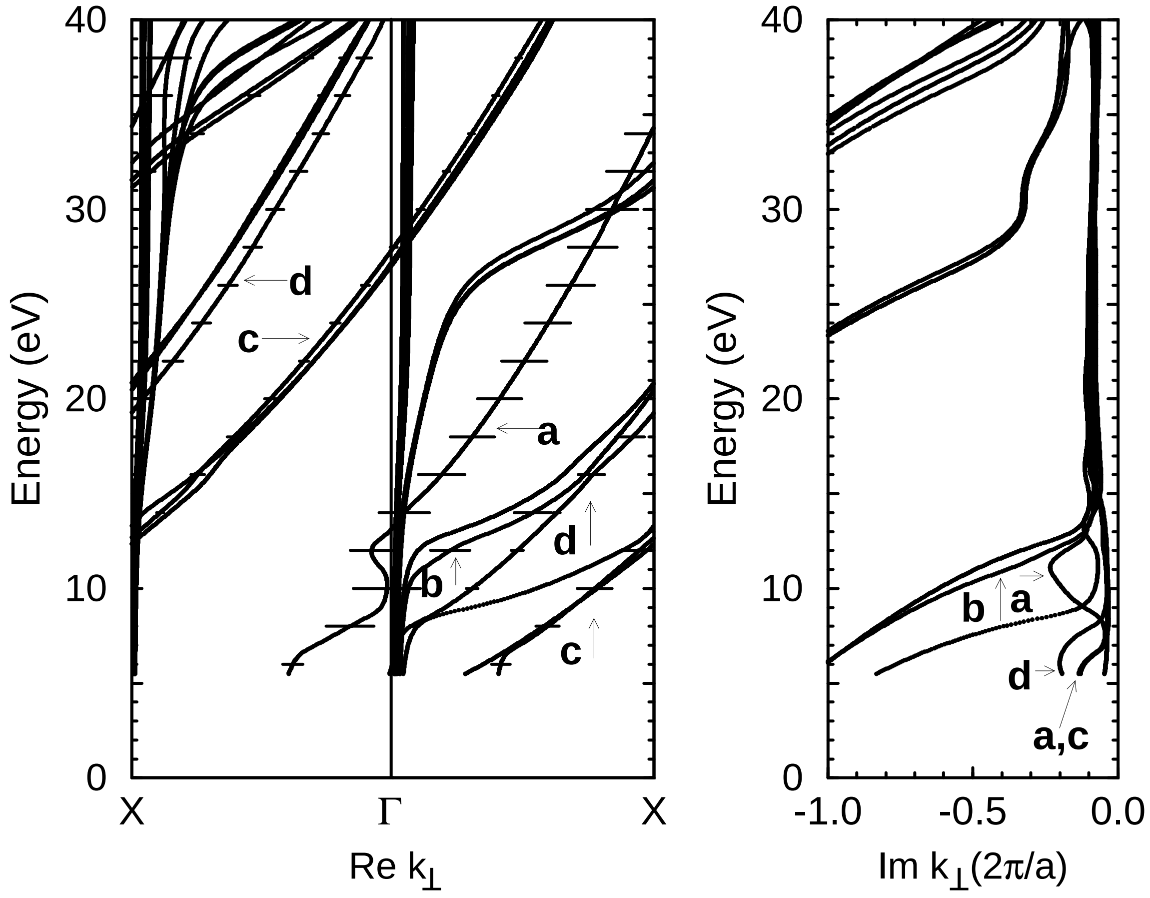
Density of states (DOS) at $\overline{\Gamma}$



GaAs-Bulk valence band structure:

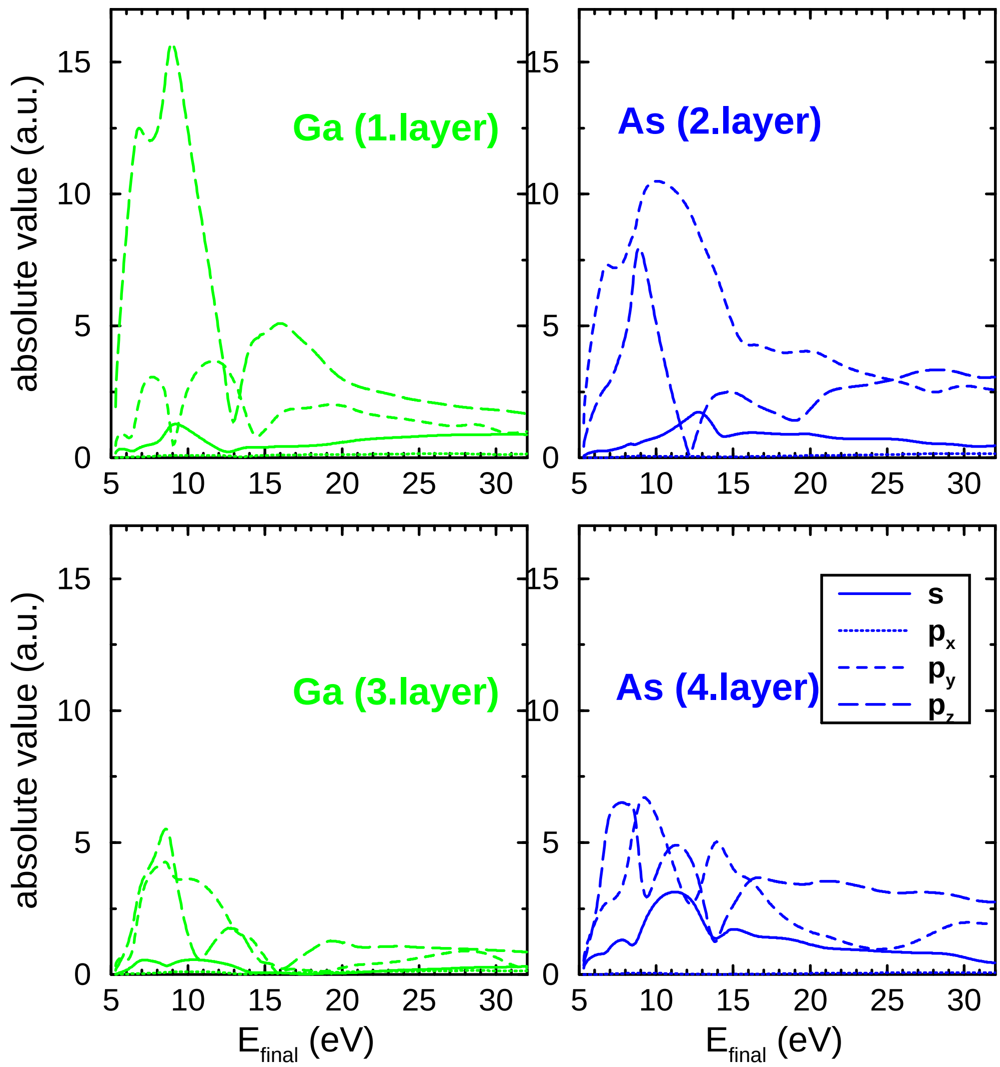


The complex final bands of the GaAs(001) surface:



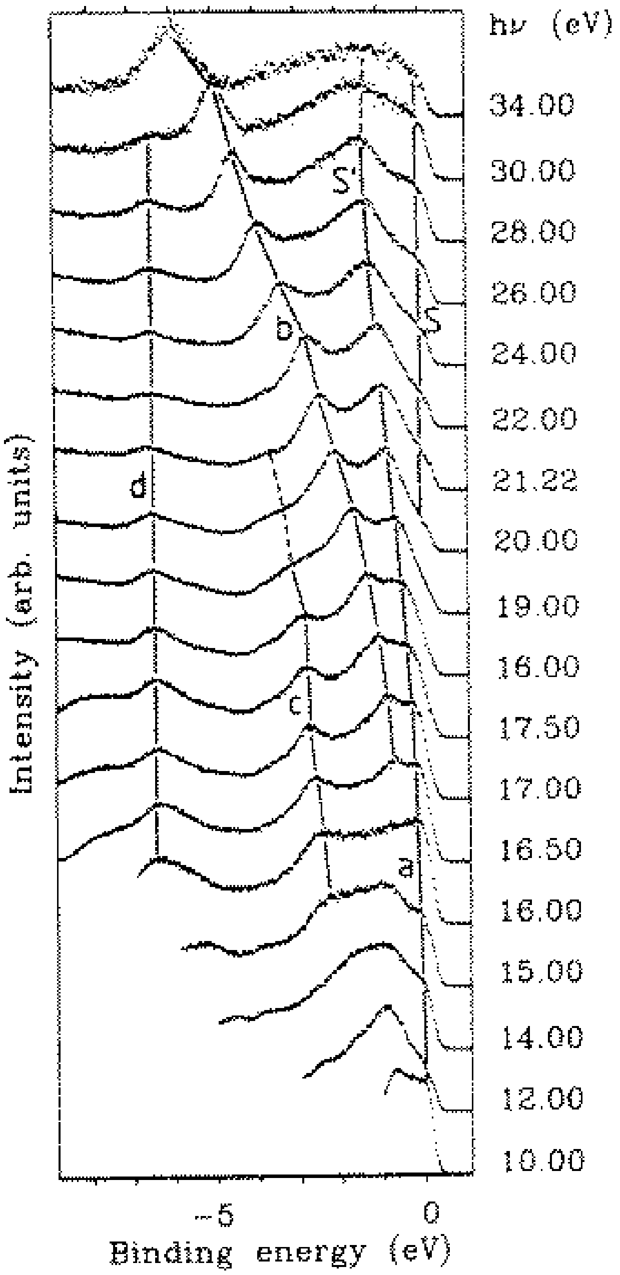
(Bars indicate the magnitude of the expansion coefficients of the final state with respect to the complex bulk bands.)

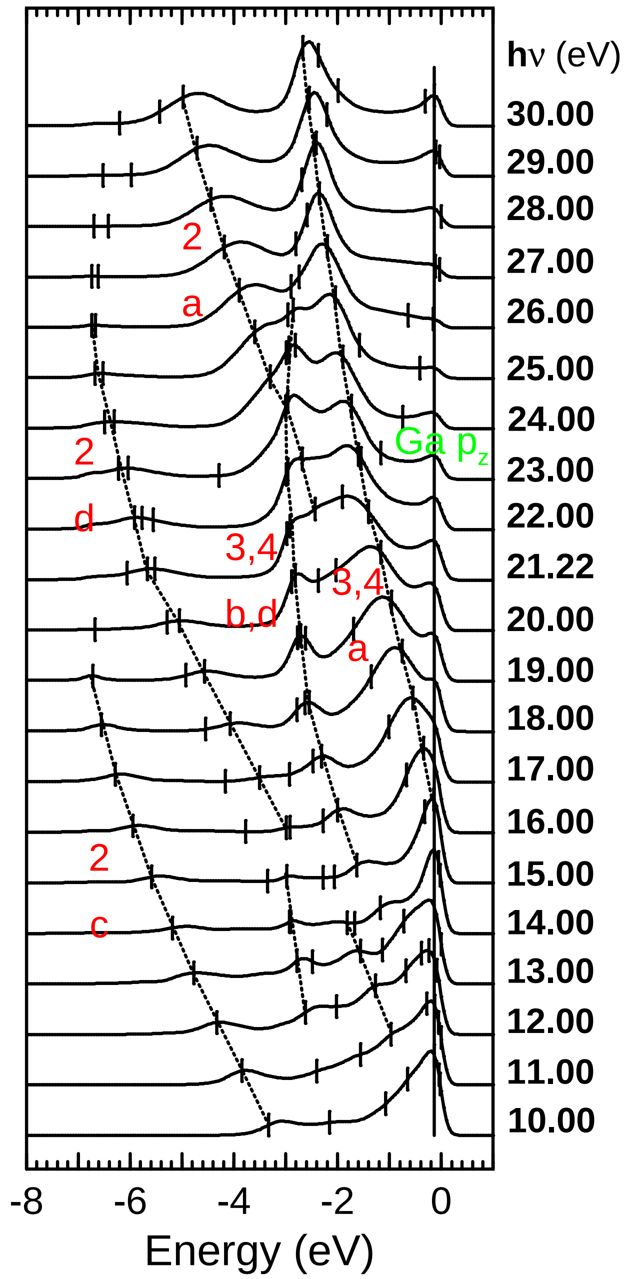
The matrix elements (p-polarization with light incident in the yz-plane)



GaAs(001)-Comparison with experiment

Experiment by Olde et al. **Theory**



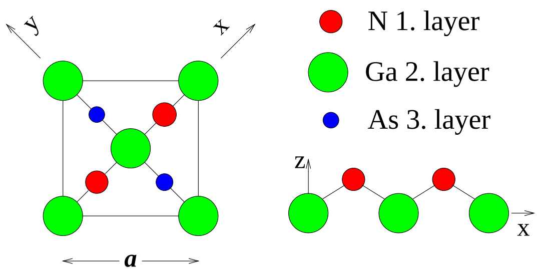


The theoretical spectra are calculated in normal emission with p-polarized light incident parallel to the yz-plane. The experimental results are from a GaAs(001)-c(4x4) surface (normal emission). Despite the different reconstructions, there are many structures in common between the GaAs(001)-c(4x4) and the GaAs(001)-(1x1) spectra. This is consistent with the known result, that the emissions from the (001) surface are dominated by the bulk.

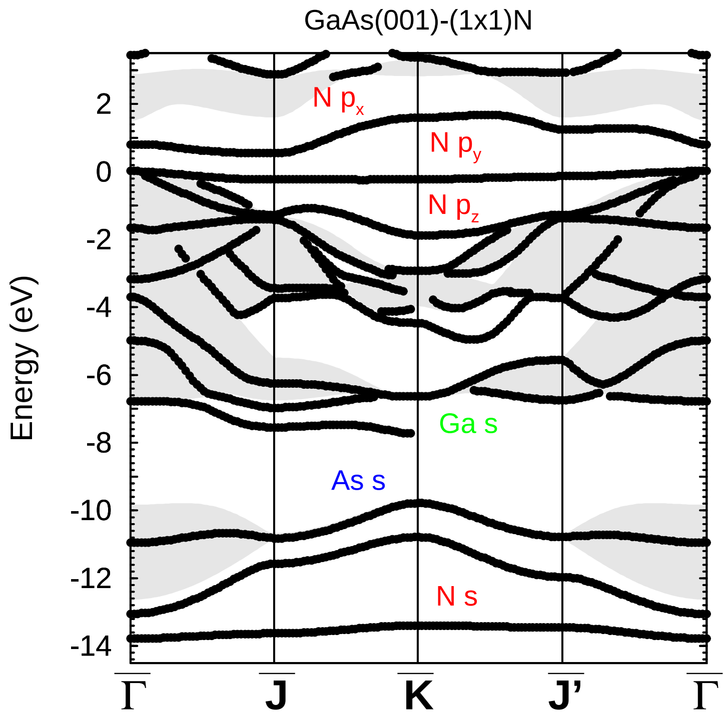
- In contrast to the GaN(001) surface the GaAs(001) surface shows strong dispersive structures also for photon energies lower than 30 eV. This is due to the fact, that the complex final bands of GaAs are only weakly damped at final state energies above 15 eV while those of GaN are strongly damped up to 28 eV.
- The experimental emission S' is not seen in theory. This is consistent with the experimental results which connect this emission with a surface state.

GaAs(001)-(1x1)N

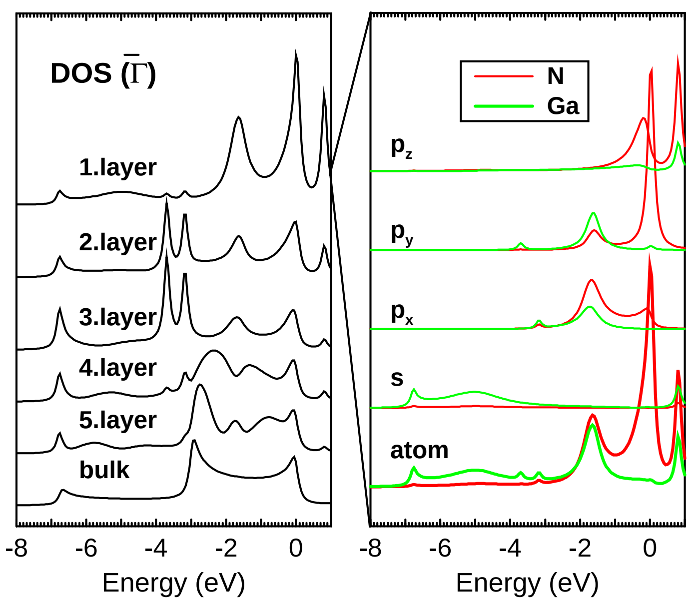
Geometry of the nitrogen covered GaAs(001) surface:



Surface band structure of the GaN(001)-(1x1)N surface:

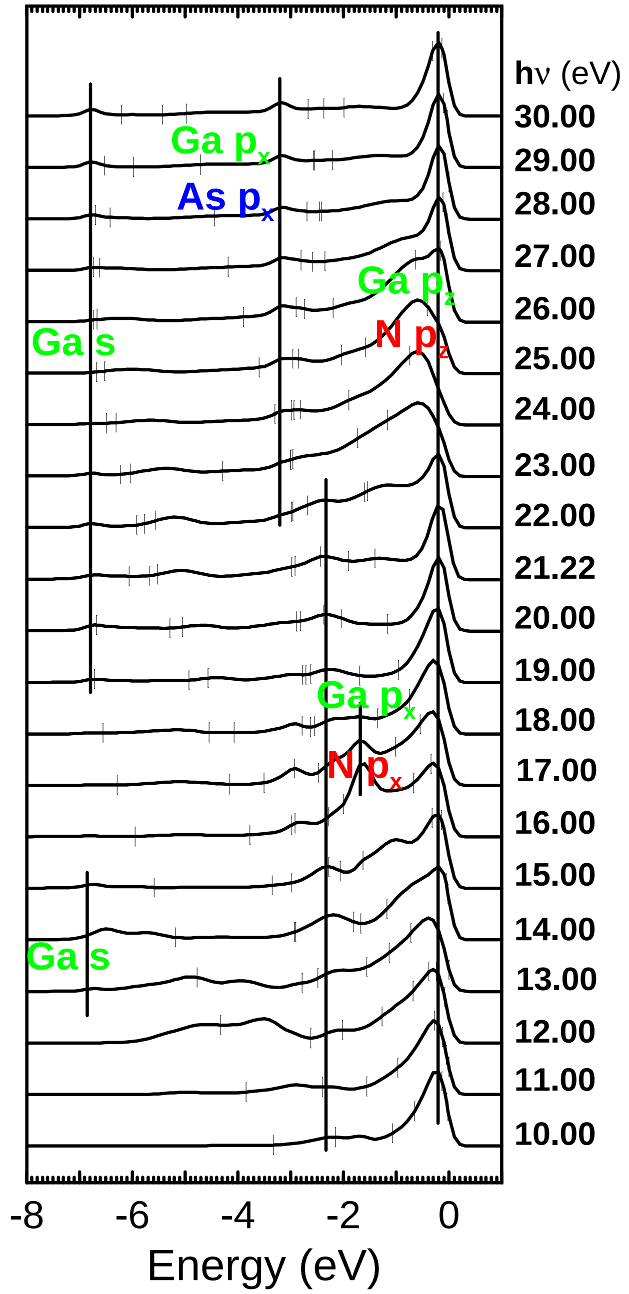


Density of states (DOS) at $\overline{\Gamma}$

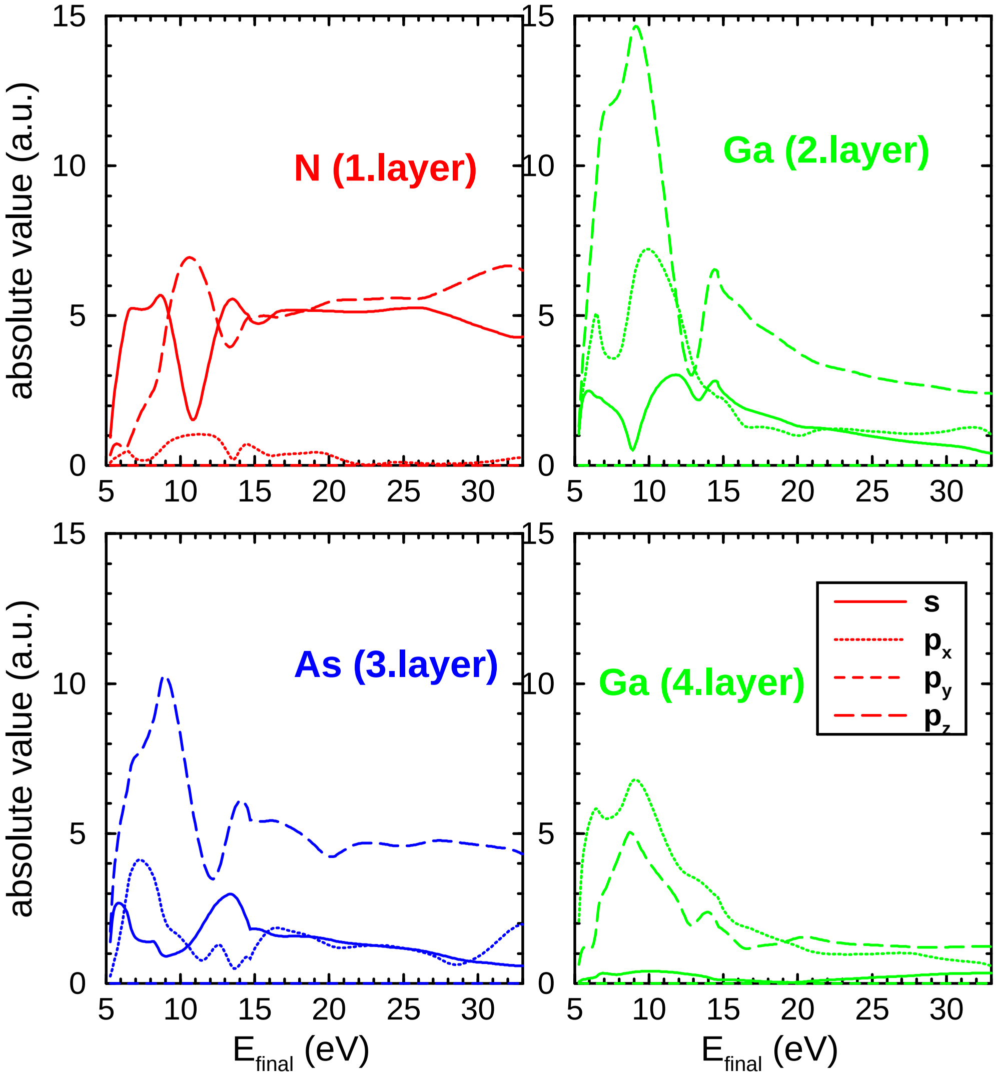


GaAs(001)-(1x1)N in normal emission:

- If the GaAs(001) surface is covered with a monolayer nitrogen, the emissions from the bulk are suppressed.

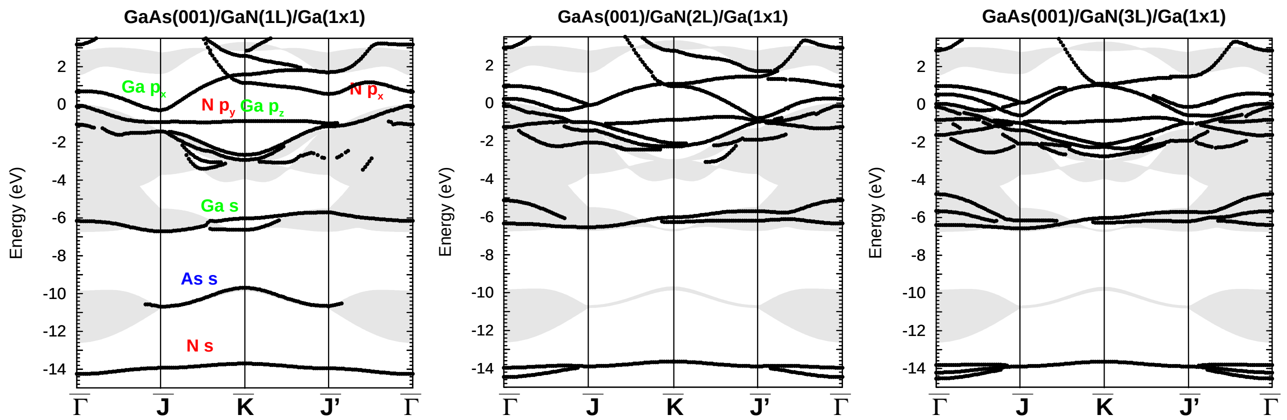


The matrix elements (p-polarization with the light incident in the xz-plane)

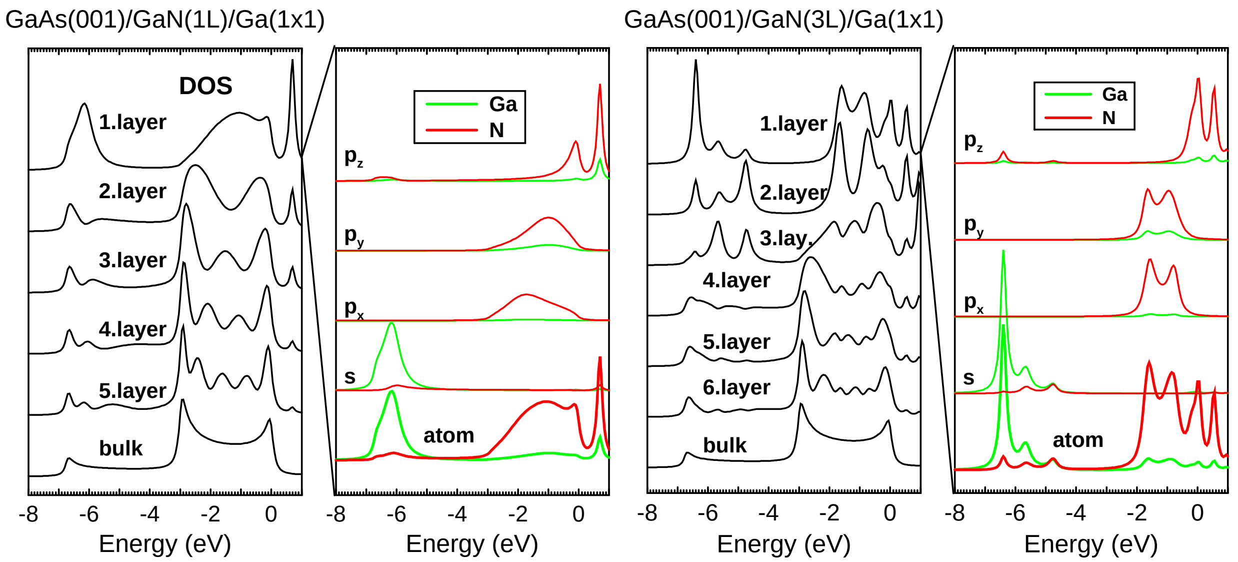


GaAs(001)/GaN(xL)/Ga(1x1)

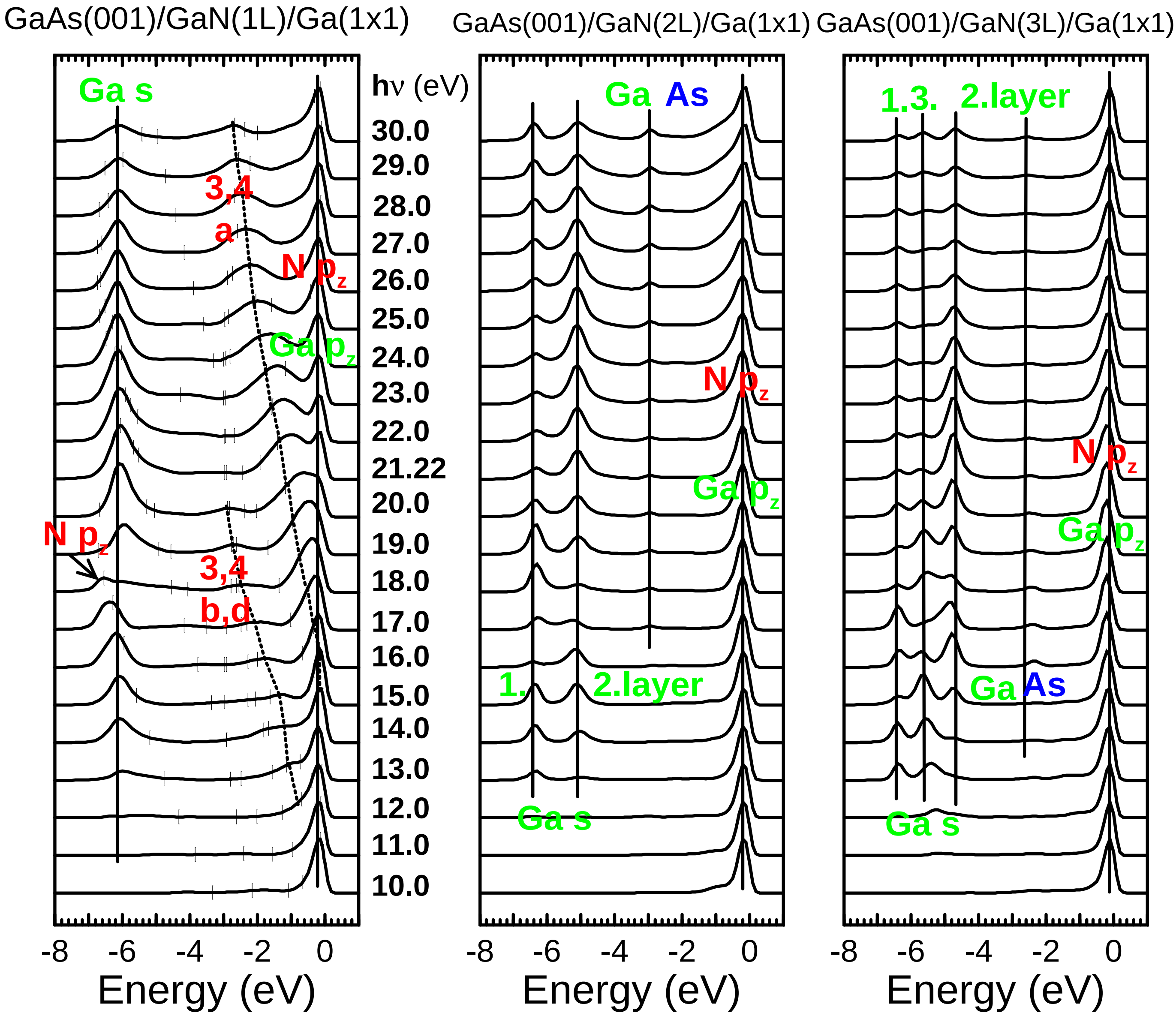
Surface band structures:



DOS at $\overline{\Gamma}$:

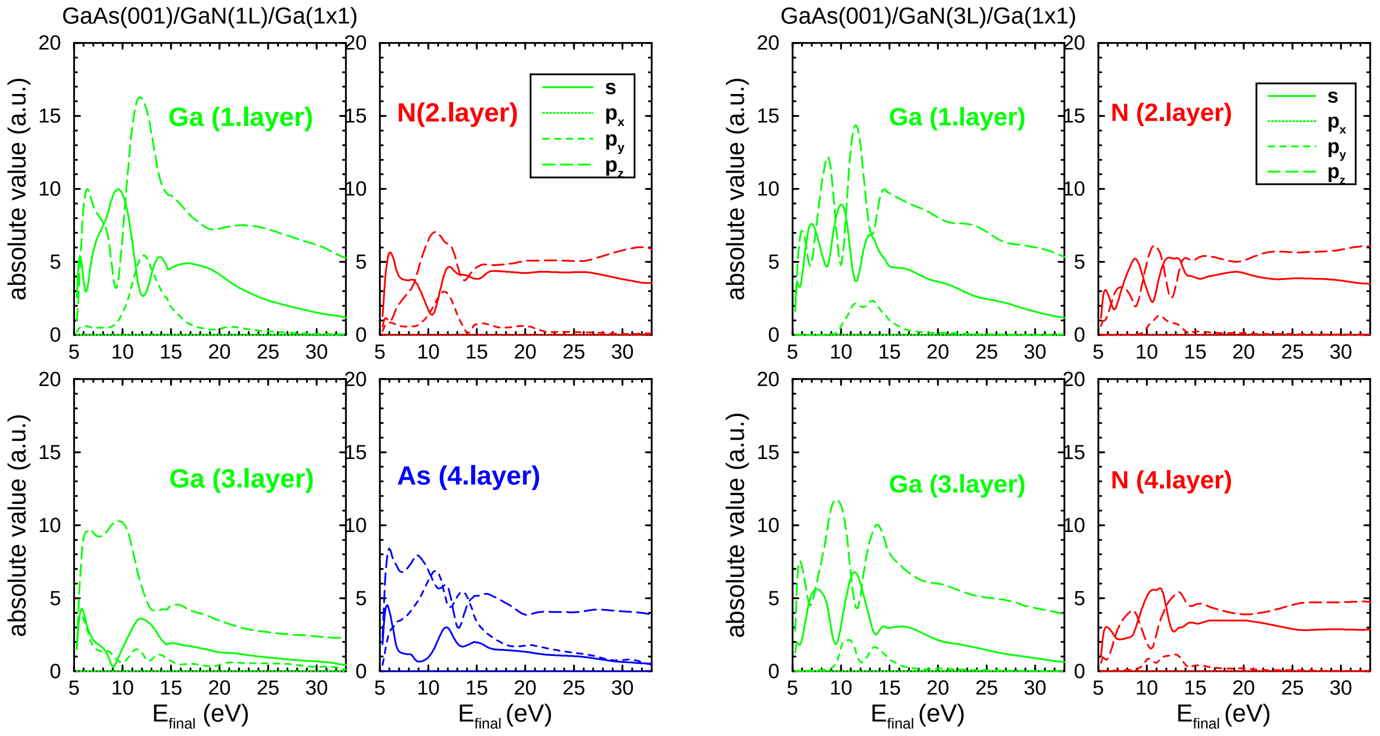


GaAs(001)/GaN(xL)/Ga(1x1) in normal emission



- With increasing coverage the transition from dispersive bulk induced spectra to extremely non-dispersive curves is observed.
- Single emissions can be related to orbitals localized in different GaN layers.
- Even with three overlayers of GaN one can still identify emissions from the Ga-As bond.

The matrix elements (p-polarization with the light incident in the yz-plane):



The one-step calculation

In the one-step calculation the photocurrent is given in a 'golden-rule"-formulation, summing over the transition probability from all occupied initial states $|\Psi_n(E)\rangle$ into the final state $|\Psi_f(E+\hbar\omega\rangle$:

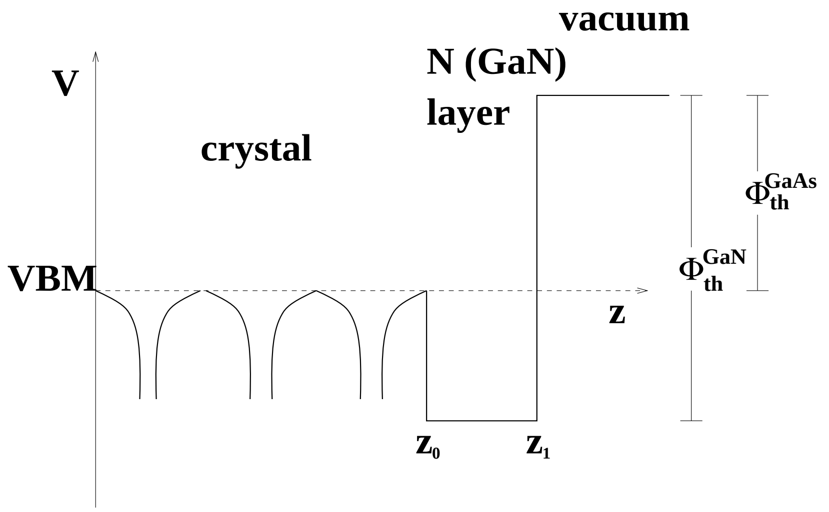
$$\vec{j} \sim \sqrt{E_{kin}} \sum_n^{occ} \left| \langle \Psi_f(E+\hbar\omega)| \, \vec{A}_0 \cdot \vec{p} \, |\Psi_n(E)\rangle \right|^2 \delta(E - E_n)$$

The initial states

The initial states are calculated by the empirical tight-binding method with a basis of layer resolved Bloch sums. We determine the transfer integrals according to the extended Hückel theory. Furthermore we use a half space Green's-function approach for getting the information about the initial states. The Green's matrix takes into account relaxation, reconstruction and adsorption at the surface.

The final states

The final state of photoemission is described as a time reversed LEED state, which is calculated using the concept of complex bandstructure basing on a local pseudopotential introduced by Pendry. To simulate damping processes an optical potential is introduced. The following picture shows the surface potential as used for the determination of the final state of the N or GaN layered surface.



Conclusions

- The theoretical spectra nicely reproduce most of the properties of the experimental spectra, like dispersion and intensities. In addition, they also allow to identify failures in the experimental band mapping and interpretation, thus rehabilitating the known theoretical bandstructures.
- A great advantage of our kind of theoretical analysis with tools like complex bandstructure, matrix elements and density of states is the clear identification of the origin of the emissions.
- Covering the GaAs(001) surface with GaN reveals well resolved emissions, especially from the dangling bond and the Ga s-orbitals, which can be attributed to the different layers of the GaN system. Even with three overlayers of GaN one can still identify emissions from the Ga-As bond.

References

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 (May/June 1996).

J. Olde, G. Mante, H.-P. Barnscheidt, L. Kipp, J.-C. Kuhr, R. Manzke, M. Skibowski, J. Henk, and W. Schattke, Phys. Rev. B **41**, 9958 (1990).

D. Vogel, P. Krüger, and J. Pollmann, Phys. Rev. B **55**, 1 (1997).

T. Strasser, F. Starrost, C. Solterbeck, and W. Schattke, Phys. Rev. B, submitted

Contact

Thomas Strasser
Institut für Theoretische Physik der Universität Kiel
Leibnizstr. 15
24098 Kiel
Germany
strasser@tp.cau.de
tel.: +494318801584