

Optical response of semiconductor surfaces and molecules calculated from *first principles*

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Abstract *First-principles* pseudopotential calculations on the optical anisotropy of GaAs(001) surfaces and on the optical absorption of DNA base molecules are presented. It is found that both electronic surface states as well as surface-perturbed bulk wave functions contribute to the optical anisotropy of GaAs(001). The latter contributions are modified by surface electric fields, giving rise to signals which are both reconstruction and electric field dependent. Pronounced differences in the absorption behavior of the DNA base molecules suggest the possibility of a base discrimination by means of single molecule spectroscopy.

1 Introduction

Optical spectroscopies, such as reflectance anisotropy spectroscopy (RAS) have become very important for the real-time monitoring of surface growth. In addition, they are very helpful to investigate the interaction between surfaces and simple adsorbates or complex molecules. However, the full potential of optical spectroscopy can only be realized, if it becomes possible to calculate optical spectra with true predictive power. This is complicated by the computational expense required to calculate numerically converged optical spectra. Much methodological progress has recently been made in the accurate calculation of optical spectra of small clusters [1], bulk crystals [2, 3] and surfaces [4, 5, 6]. However, many questions still remain open.

One of these is the influence of electric fields on the surface optical response. Experimentally it has been known for a long time that electric fields, induced by, e.g., the pinning of the Fermi level at the sample surface (band bending) [7] or by a δ -doping layer [8], modify the RAS signal. The investigation of the mechanism behind the electric field induced modification of the optical signal may not only help to better understand the origin of specific RAS features, but should pave the way for applications, such as contact-less determination of the carrier concentration in a bulk material. Previous calculations [9, 10] modeled the electric field induced line shape changes around the E_1 and $E_1 + \Delta_1$ critical point (CP) energies of GaAs based on the piezoelectric effect. However, the influence of the surface reconstruction on the

field induced RAS changes or wider spectral ranges have not been considered. Here we present – to our knowledge for the first time – *first-principles* calculations on the interplay of surface geometry and surface electric fields in the reflectance anisotropy. The GaAs (001) surface with its large number of stoichiometry-dependent surface reconstructions (cf. Fig. 1) and its importance for III-V based optoelectronics has been chosen as model system.

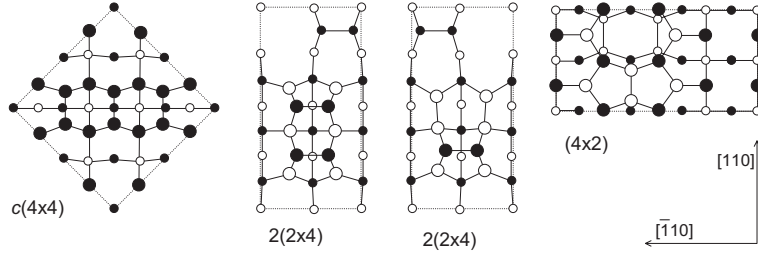


Fig. 1. Top view of relaxed GaAs(001) surface structures. Empty (filled) circles represent Ga (As) atoms. Positions in the uppermost two atomic layers are indicated by larger symbols.

Optical spectroscopy has also become a technique of common use for analyzing the adsorption of molecules on surfaces. The deoxyribose nucleic acid (DNA) base molecules adenine, guanine, cytosine and thymine form a particularly interesting class of molecules: due to their Watson-Crick complementarity they are well suited for molecular self-assembly processes, which are increasingly becoming a route to the fabrication of nanosize objects. Structures formed by these molecules may be used as templates to engineer macromolecules, molecular sieves or photonic materials with novel properties [11]. Other exciting applications which are presently being explored are nanomechanical devices [12] or DNA computing [13, 14]. The understanding of the optical spectra of isolated, gas-phase DNA base molecules is a necessary prerequisite to monitor self-assembly processes of these molecules by optical means. As a first step in that direction, we perform *ab initio* calculations of the absorption spectra of adenine, guanine, cytosine and thymine.

2 Computational Method

Density-functional theory in the local-density approximation (DFT-LDA) together with nonlocal norm-conserving pseudopotentials is used to determine the structurally relaxed ground state of the GaAs surface. A massively parallel, real-space finite-difference method is used to deal efficiently with the large unit cells needed to describe the surface. Thereby a real-space mesh is used

to represent the wave functions, the charge density, and the ionic pseudopotentials. The density functional equations are discretized using a generalized eigenvalue form:

$$H_{mehr}[\psi_n] = \frac{1}{2}A_{mehr}[\psi_n] + B_{mehr}[V_{eff}\psi_n] = \epsilon_n B_{mehr}[\psi_n] ,$$

where A_{mehr} and B_{mehr} are the components of the *Mehrstellen* discretization, which is based on Hermite's generalization of Taylor's theorem. It uses a weighted sum of the wave function and potential values to improve the accuracy of the discretization of the entire differential equation. Only nearest and next-nearest neighbor points are used in the discretization. This short-ranged representation of the equation leads to an efficient domain-decomposition-based implementation on massively parallel computers (for details see Refs. [15, 16]). Typical jobs utilize 32 to 128 PEs. The solution of the discretized equations is obtained on a grid fine enough to accurately represent the pseudopotentials and the electronic wave functions. We use a multigrid iteration technique that accelerates convergence by employing a sequence of grids of varying resolutions. Both the Poisson and the density functional equations are solved on coarser grids and the resulting corrections are transferred to the fine grid. This provides excellent preconditioning for all length scales present in our system and leads to very fast convergence rates. The operation count to converge one wave function with a fixed potential scales linear with the number of grid points. Further details of the DFT-LDA calculations are those in Ref. [17].

The electronic structure obtained within DFT-LDA is used to calculate the optical response: within independent-particle approximation the microscopic dielectric function is obtained from the Bloch band eigenfunctions $|n\mathbf{k}\rangle$ characterized by band index n , wave vector $\mathbf{k}$, and energy eigenvalue $\epsilon_n(\mathbf{k})$ using the Ehrenreich-Cohen Formula. For semiconducting systems the microscopic dielectric tensor is given by

$$\epsilon_{ij}(\omega) = \delta_{ij} + \frac{16\pi e^2 \hbar^2}{\Omega} \sum_{\mathbf{k}, c, v} \frac{\langle c\mathbf{k}|v_i|v\mathbf{k}\rangle \langle v\mathbf{k}|v_j|c\mathbf{k}\rangle}{[\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k})] \left([\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k})]^2 - \hbar^2 [\omega + i\eta]^2 \right)}.$$

The matrix elements $\langle v\mathbf{k}|v_j|c\mathbf{k}\rangle$ of the velocity operator v_j with the valence and conduction states are calculated in real-space. This does not only allow for an efficient parallelization, but also for a classification of the optical excitation processes according to their spatial localization. Of particular importance for the predictive power of the calculated spectra is their full numerical convergence. For the surface calculations we use $\mathbf{k}$ -point sets equivalent to 1024 points in the full (1×1) surface Brillouin zone and include all conduction states within an energy of 1 Ryd from the valence band maximum. Due to the memory requirements, calculations of this size can presently only be performed using massively parallel supercomputers such as the Hitachi SR8000.

From the dielectric tensor calculated for the supercells used to model the GaAs bulk and surface, we calculate the reflectance anisotropy according to the scheme devised by Del Sole and Manghi *et al.* [18, 19]. In general, optical spectra are strongly modified by many-body effects such as self-energy corrections and electron-hole attraction [2, 3, 6, 20]. However, RAS spectra are difference spectra, which are furthermore normalized to the bulk dielectric function. Due to the error cancellation, single-particle calculations within DFT-LDA are actually quite reliable in predicting surface optical anisotropies [21]. Therefore, we simply use the scissors-operator approach [22] to take self-energy effects into account. Excitonic and local-field effects are neglected.

A saw-tooth function added to the electrostatic potential is used to mimic the effect of an electric field. From the self-consistent solution of the Kohn-Sham equations the influence of the electric field on both the wave functions and the eigenvalues is obtained. The sign convention used here is such that the field points in the direction of the surface normal.

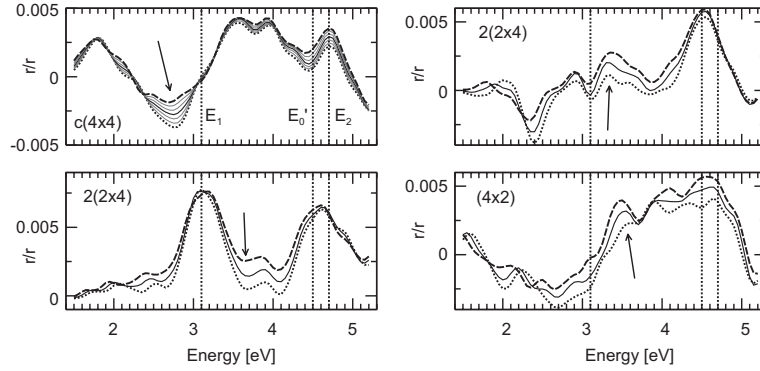


Fig. 2. Calculated RAS spectra for GaAs(001) surface reconstructions. For GaAs(001) $c(4\times 4)$ the field varies in steps of 0.005 V/Å. Thick solid/dotted/dashed lines correspond to the field magnitudes of 0.0/-0.015/0.015 V/Å.

To calculate the structurally relaxed ground state of the DNA base molecules we use the VASP (Vienna Ab-initio Simulation Package) implementation of the DFT in generalized gradient approximation (GGA) [23]. This implementation allows for the use of non-norm-conserving ultrasoft pseudopotentials of the Vanderbilt type. These pseudopotentials are extremely efficient for the calculation of systems containing first-row elements. The optical spectra of these molecules were calculated from all-electron wave functions obtained by the projector-augmented wave (PAW) method [24].

3 Results and Discussion

3.1 Optical Anisotropy of GaAs(001) surfaces

The stoichiometry-dependent surface structures of GaAs(001) have been studied intensively over the last couple of years. There now seems to be consensus on the geometries of the four main reconstructions shown in Fig. 1: $c(4\times 4)$ and $\beta 2(2\times 4)$ reconstructions occur for As-rich surfaces, a $\zeta(4\times 2)$ geometry is characteristic for Ga-rich surfaces, and stoichiometric surfaces form the $\alpha 2(2\times 4)$ structure [25].

The thick solid lines in Fig. 2 show the RAS spectra calculated for these surface models. Obviously, the surface optical anisotropy is strongly related to the surface geometry. The spectra calculated for $c(4\times 4)$ and $\beta 2(2\times 4)$ agree well with experiment [26, 27, 28]. The appearance of negative anisotropies for the $\alpha 2(2\times 4)$ structure at energies somewhat above 2 eV also agrees with the experimentally observed trend: annealing temperatures higher than those needed to prepare the GaAs(001) $\beta 2(2\times 4)$ surface lead to negative anisotropies for photon energies of about 2 eV [27].

The main experimentally observed RAS features for Ga-rich (4×2) reconstructed surfaces are negative anisotropies for photon energies below the E_1 CP and positive anisotropies for higher energies [26, 28]. They are reproduced by our calculation for the $\zeta(4\times 2)$ surface.

The influence of external electric fields ranging from -0.015 to 0.015 V/Å on the calculated RAS spectra is also shown in Fig. 2. In all cases the magnitude and to some extent the energy positions of specific RAS features are modified. A remarkable outcome of our study is the strong reconstruction dependence of the field induced RAS changes. For the $c(4\times 4)$ reconstructed GaAs surface, strong modifications of the RAS signal are observed for photon

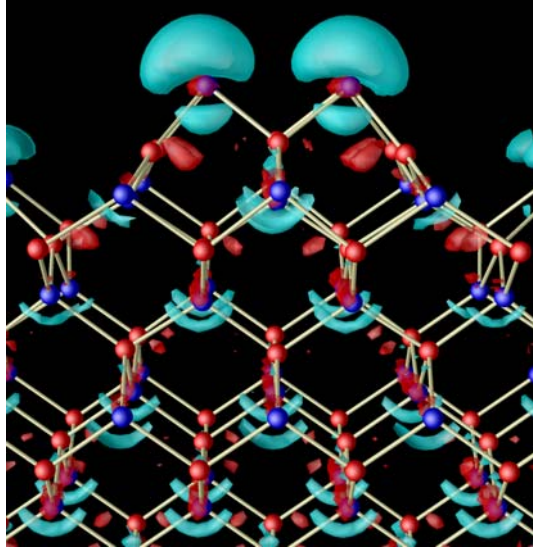


Fig. 3. Electron density transfer (red/blue isosurfaces indicate $\Delta\rho = \pm 10^{-4}e/\text{Bohr}^3$) induced by an electric field of 0.015 V/Å in a slab modeling the GaAs(001) $\beta 2(2\times 4)$ surface. Red (blue) balls represent Ga (As) atoms.

energies below 3 eV and at the E'_0/E_2 CP energies. The optical anisotropy of the (2×4) reconstructed $\beta 2$ and $\alpha 2$ surfaces, on the other hand, is mainly altered in the energy region between the E_1 and E'_0 CPs. Finally, nearly the entire RAS spectrum of the Ga-rich $\zeta(4\times 2)$ surface is modified by the application of an electric field. Our finding of a strong influence of the surface reconstruction on the field induced RAS is supported by recent experiments [29]. Although the influence of the electric field on the surface optical anisotropy is reconstruction-dependent, the spatial analysis of the origin of the RAS features shows that it is the optical signal from the layers underneath the surface, i.e. the so-called intrinsic anisotropy, that is affected by the field.

Our calculations indicate that the surface optical anisotropy for energies near the bulk CPs is a consequence of the anisotropically modified decay of the bulk Bloch states into the vacuum region. The surface induced deformations of the bulk-like wave functions are weighted differently by the x and y components of the transition operator, leading to an anisotropic optical response. Superimposed on the surface induced anisotropies of the electron wave functions are the electric field induced deformations. These are anisotropic too, as visualized in Fig. 3 for the electron density of the GaAs(001) $\beta 2(2\times 4)$ surface slab. We find that the changes of the combined density of states due to the electric field are negligible compared to the deformations of the wave functions resulting in modified transition matrix elements.

Our results on the influence of electric fields on the optical anisotropy of GaAs(001) surfaces cannot directly be compared with experiment. On one hand, this is due to computational shortcomings. We neglect the spin-orbit coupling and therefore cannot describe the $E_1/E_1 + \Delta_1$ splitting. The RAS features close to the $E_1/E_1 + \Delta_1$ energy are considerably affected by the spin-orbit interaction. Most measurements of the linear electro-optic effect focus specifically on these features. On the other hand, the comparison of experimental and simulated spectra is complicated by the facts that: (i) the magnitude of the surface electric field, induced by, e.g. δ -doping or space-charge layers is not known exactly, and (ii) most experiments are performed on surfaces, the geometries of which are not well characterized, e.g. oxidized surfaces.

In measurements done in air, Yang, Chen and Wong [30] found a linear relationship between the change in the RAS at the $E_1/E_1 + \Delta_1$ energy and the surface electric field. They determined a linear electro-optic coefficient of $0.46 \text{ \AA/V}$. In Fig. 4 we show the change of the RAS signal for the four surface reconstructions at energy positions indicated in Fig. 2, i.e., slightly below or above the E_1 transition as a function of the electric field. Clearly, the calculated change of the RAS is linear, as observed experimentally. The slopes of the curves in Fig. 4 are about $0.07 \text{ \AA/V}$, much smaller than the measured value of $0.46 \text{ \AA/V}$. The fact that the field needed in the calculation

to reproduce changes in the RAS comparable in magnitude to experiment is nearly one order of magnitude stronger than measured, is related to the large penetration depth of light. It amounts to about 170 Å for a photon energy of 3 eV [31], whereas our slab only models the uppermost 15 Å of the GaAs surface region.

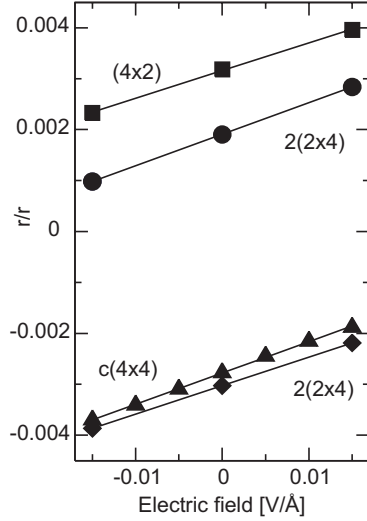


Fig. 4. Variation of the RAS calculated for GaAs(001) surface reconstructions at the photon energies marked by arrows in Fig. 2, for applied electric fields. The solid lines are a guide to the eye.

By varying the distance between the δ -doping layer and the surface, Sobiesierski, Westwood and Elliot [8] have shown that the surface electric field reaches far into the bulk and modifies the optical response along the full light penetration depth. The incoming light decreases in intensity as it penetrates the sample, therefore the ratio between the light penetration depth and the slab thickness gives an upper bound for the scaling factor needed to relate the calculated and the measured field sensitivity of the RAS. The value of the electro-optic coefficient calculated here is thus in the expected range. This agreement may be fortuitous, however, given the neglect of spin-orbit coupling in our study. Nevertheless, because both experiment and calculations find a linear relation between the changes of the optical anisotropy and the surface electric field, we expect our results, although obtained for comparatively strong fields, to correctly describe the basic mechanisms responsible for the field induced RAS changes.

3.2 Optical Absorption of the DNA bases

Figure 5 shows the absorption spectra of adenine, guanine, cytosine and thymine calculated within DFT-GGA. In all four cases the calculated onset of absorption occurs for photon energies slightly below 4 eV. The oscillator strength of the lowest optical transition, as well as the absorption behavior for higher energies, however, are strongly molecule specific. Guanine and thymine are characterized by relatively few and energetically well separated (by about one eV) optical transitions, whereas the energetical separation of the absorption peaks is much reduced in the cases of adenine and cytosine. The spectra presented in Fig. 5 refer to spin-averaged, zero temperature calculations. The influence of the quantized vibrations and rotations at finite temperatures will considerably broaden the spectra, as will the interaction with solvent molecules.

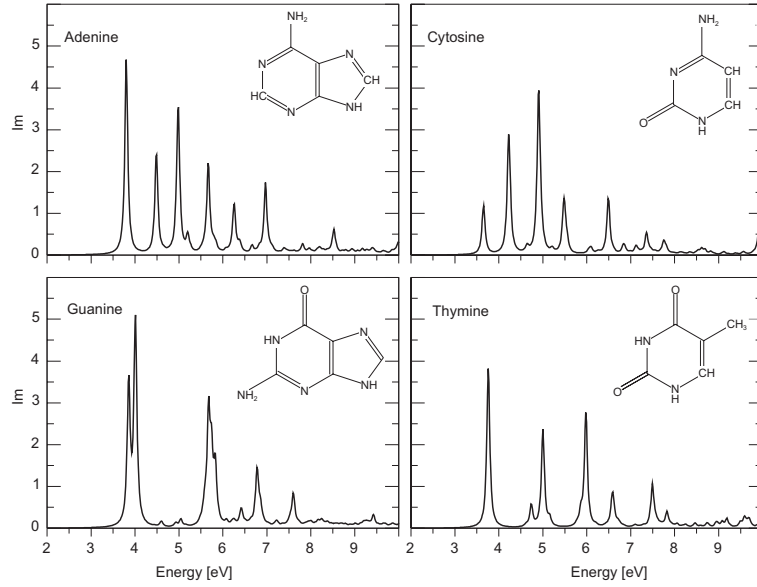


Fig. 5. Absorption spectra (in arb. units) of DNA base molecules calculated in the independent-particle approximation.

Further modifications of the spectra are due to many-body effects. In particular, electronic self-energy and electron-hole attraction effects change the spectra considerably. For the delocalized electron gas, these effects are usually calculated using a Green's function technique [1, 2, 3, 6]. In the present case, however, the localization of the electronic states allows for a numerically far less demanding treatment of these many-body effects: we investigated their influence by means of Δ SCF – also called constrained-DFT – calculations. Thereby the total-energy differences between the ground state and the optically excited states of the molecule are calculated. The electrons are allowed to relax, while the occupation numbers are constrained to the chosen configuration. We observe that the widening of the energy gaps due to the electronic self-energy is partially canceled by the gap narrowing due to the Coulomb attraction between electrons and holes. The net effect depends on the specific transition investigated and consists in an increase of the excitation energy by one to several tenths of an eV. If in addition to the electronic relaxation also the geometry of the molecule is allowed to relax, the energy shifts between light absorption and emission (Stokes shifts) can be calculated. These shifts are considerable. For guanine, for instance, we calculate a Stokes shift of about 0.7 eV for the transition between the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively). The molecular characters of the guanine HOMO and LUMO are depicted in Fig. 6. The HOMO consists of π orbitals formed by p_z states of carbon and nitro-

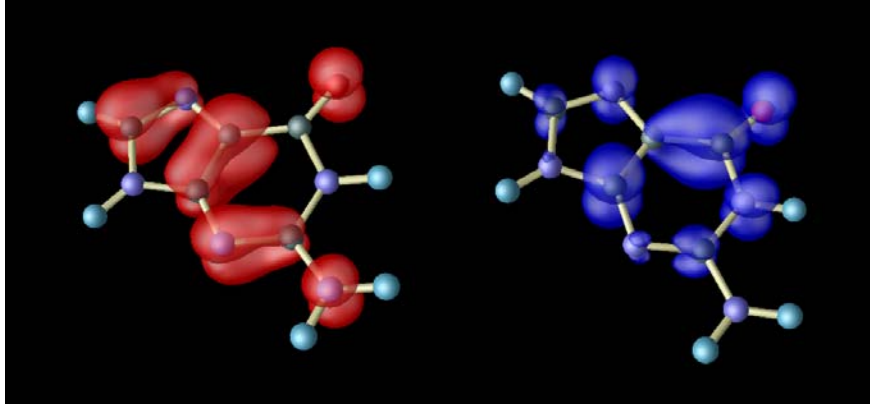


Fig. 6. Calculated charge density (isosurfaces $\rho = 0.05e/Bohr^3$) of the guanine HOMO (left) and LUMO (right).

gen atoms. However, there are also some lone pair-like contributions from the oxygen and the outermost nitrogen. The LUMO is formed by non-bonding or antibonding combinations of N, C, and O p_z states.

4 Summary

We have investigated the effects of reconstructions and surface electric fields on the optical anisotropy of GaAs(001). We find geometry-dependent surface-structure signatures which explain very well the experimental observations. Surface-perturbed bulk wave functions modified by electric fields via the linear electro-optic effect are mainly responsible for field induced modifications of the surface optical anisotropy. These modifications are strongly reconstruction-dependent. They are small, however, compared to the RAS signals due to the anisotropy of the surface itself.

We also investigated the optical absorption behavior of the DNA bases adenine, guanine, cytosine and thymine. Strong differences between the optical spectra of the four molecules are observed. At finite temperatures these differences will be somewhat masked by the influence of vibrational and rotational excitations. Nevertheless, a base discrimination by means of single molecule spectroscopy appears possible.

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