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GaAs(001): Surface Structure and Optical Properties

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The optical anisotropy of differently reconstructed GaAs(001) surfaces has been analysed both theoretically and experimentally. The atomic structures and RAS spectra are calculated from *first principles* for the As-rich c(4×4) and $\beta2(2\times4)$ as well as for the stoichiometric $\alpha2(2\times4)$ and the Ga-rich $\zeta(4\times2)$ surface phases. These results are compared with spectra recorded at low temperature (40 K). We find good agreement between the calculated and measured data, in particular for the As-rich surface phases. In marked contrast to earlier calculations we find the peak near the E_1 critical point energy, characteristic of the $\beta2(2\times4)$ surface, to originate from electronic transitions in bulk layers. The experimental data for the Ga-rich (4×2) surface phase are less well reproduced, possibly due to surface defects or structural deviations from the $\zeta(4\times2)$ model for the surface geometry.

1. Introduction

Optical spectroscopies are rapidly gaining importance for the *in situ* characterisation of static surfaces and the real-time monitoring of surface growth. That holds in particular for the reflectance anisotropy spectroscopy (RAS) often also termed reflectance difference spectroscopy which has become a widely used surface-characterisation technique. Among III–V materials the GaAs(001) surface is the most intensively studied example. The large number of stoichiometry-dependent surface reconstructions together with its technological importance for III–V based optoelectronics has made the GaAs(001) surface a popular model system also for the application of RAS [1–6, 8]. In recent years much theoretical work has been dedicated to explaining the GaAs surface optical properties. Most of these studies are based on a tight-binding approach to describe the electronic structure [1, 6, 9–12]. Other calculations model the effect of the surface termination of the bulk electronic wave functions [13] or the piezo-optical effect [14, 15]. Previous *ab initio* calculations of the GaAs surface optical properties [16–18] were for computational reasons restricted to rather thin slabs and used a relatively small number of basis functions. They were thus severely limited in their reliability. Moreover, these calculations suffer from the DFT-LDA band gap underestimation due to the neglect of electronic self-energy effects.

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The stoichiometry-dependent surface structures of GaAs(001) have been studied intensively over the last decade [19]. In spite of this, theoretical [20, 21] as well as experimental studies [22, 23] have only very recently indicated the existence of new structures for the stoichiometric (2×4) reconstructed α phase of GaAs(001) as well as for the Ga-rich (4×2) surface, distinct from the models accepted so far.

Based on these new findings concerning the surface structure we re-examine the GaAs(001) surface optical properties. To that end we combine *first-principles* calculations of the surface optical anisotropy with low-temperature RAS measurements. We discuss the origin of spectral features in the optical spectra in terms of surface and bulk related contributions and derive implications for the surface atomic structure.

2. Computational Method

We investigate the GaAs(001) surface by *first-principles* density-functional (DFT-LDA) calculations using nonlocal pseudopotentials and a real-space multigrid technique [24]. The electronic wave functions are mapped on a grid with a spacing corresponding to 4% of the GaAs bulk lattice constant. The surface is modelled by periodic super cells containing 12 atomic (001) layers and a vacuum region 8 atomic layers thick. Further details of the DFT-LDA calculations are similar those in Ref. [20].

The calculation of excitation energies within DFT-LDA neglects the quasiparticle character of electrons, leading to a distinct underestimation of excitation energies. In order to calculate optical spectra comparable with experiment, we replace the local exchange and correlation potential used in the DFT-LDA with the nonlocal and energy-dependent self-energy operator $\Sigma(\mathbf{r}, \mathbf{r}'; E)$. Specifically, we calculate Σ in the *GW* approximation, where it is expressed as the product of the single-particle propagator G with the dynamically screened Coulomb interaction W. Since the calculation of optical spectra is computationally expensive, due to the large number of electronic states involved, we use a model dielectric function [25] to calculate W. Our approach lifts the underestimation of transition energies. The E_0, E_1, E_0' and E_2 critical point (CP) energies of the bulk band structure are shifted from 0.6, 2.5, 3.9 and 4.1 eV to 1.4, 3.2, 4.7 and 5.0 eV, respectively. This is in good agreement with the values of 1.52, 3.04, 4.6–4.8 and 4.9–5.1 eV measured at low temperatures [26].

The electronic structure obtained within DFT-LDA or in the *GW* approximation is used to obtain the surface optical anisotropy [27, 28] in the independent-particle or independent-quasiparticle approximation. A detailed description of our method is given in Ref. [29]. The optical spectra presented here are calculated as accurately as our earlier results for InP [30] and GaP(001) [31] surfaces.

3. Surface Preparation

The GaAs(001) surfaces were prepared in ultra-high-vacuum by thermal desorption of a protective arsenic cap [32, 33]. The samples (capped homo-epitaxial epilayers) were grown by molecular beam epitaxy. After preparation the surfaces were investigated at room temperature by low energy electron diffraction and scanning tunneling microscopy. On such structurally well characterised surfaces RAS experiments were carried out at approximately 40 K. Such a low temperature was maintained since our calculations do not take temperature effects, affecting significantly both amplitudes and energy

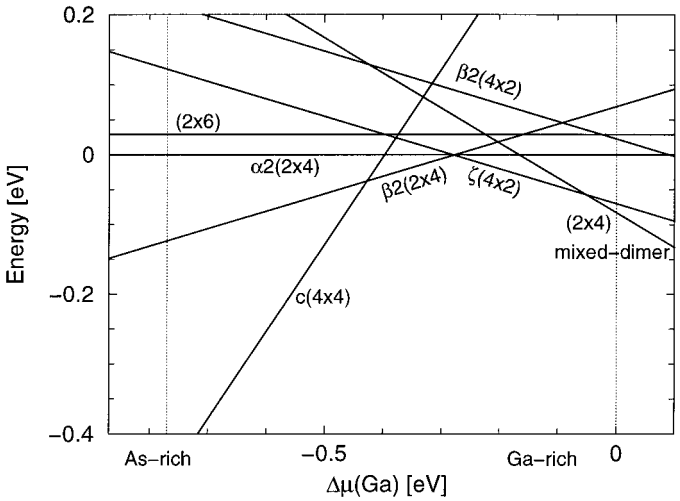

Fig. 1. Relative formation energy per (1×1) unit cell for GaAs surface reconstructions vs the cation chemical potential. Dashed lines mark the approximate anion- and cation-rich limits of the thermodynamically allowed range of $\Delta\mu$(Ga)

positions of characteristic features, into account. The temperature effects on the optical properties of bulk GaAs have been studied by Lautenschlager et al. [26]. Their results show that temperature effects influence the dielectric function only very weakly for temperatures below 80 K. Consequently, temperature effects should not play any considerable role in the data presented here.

4. Results and Discussion

Figure 1 shows the calculated phase diagram for GaAs(001). The energetically relevant geometries are sketched in Fig. 2. For extreme anion-rich surfaces the formation of three-dimer blocks of As on top of an As-terminated substrate in a c(4×4) symmetry is stable. Moderately As-rich surfaces are characterised by the β2(2×4) structure. As intermediate structures the $\alpha 2(2 \times 4)$ [20] and – possibly as transient phase – a (2×6)

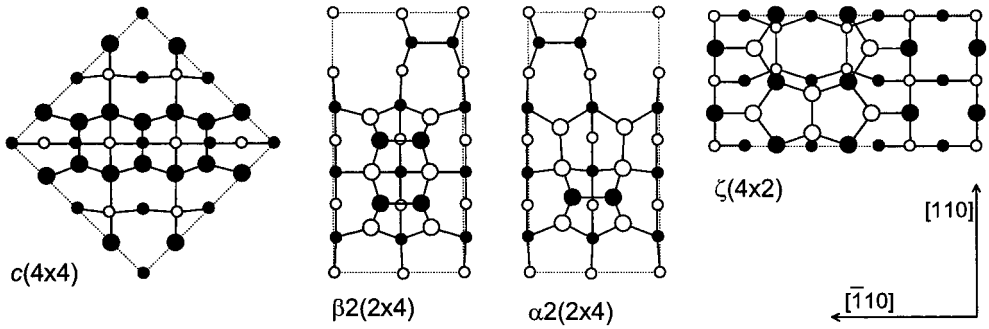

Fig. 2. Top view of relaxed GaAs(001) surface structures, ordered according to the Ga coverage. Empty (filled) circles represent Ga(As) atoms. Positions in the uppermost two atomic layers are indicated by larger symbols

structure may occur. Finally, Ga-rich surfaces form a $\zeta(4\times2)$ surface [21]. The calculations predict a (2×4) mixed-dimer structure as observed for InP and GaP surfaces [34] for extreme cation-rich surface preparation conditions. We are not aware of any experimental evidence supporting this computational finding. Rather, the formation of (4×6) symmetries is reported for extreme Ga-rich GaAs surfaces [19]. We probed a large number of (4×6) surface structures [34, 35]. However, all structures had to be dismissed on energetic grounds. This holds in particular for the formation of Ga clusters on top of a (4×2) reconstructed surface.

Our discussion of the surface optical properties focuses on the four main reconstructions shown in Fig. 2. In Fig. 3 we present the RAS spectra for these four surface models calculated in DFT-LDA. Obviously, the surface optical anisotropy is strongly related to the surface geometry and therefore well suited to monitor and control the GaAs growth. However, as shown in the right panel of Fig. 3, not only transitions between surface states contribute to the RAS. In particular we find that surface modified bulk electronic states give rise to a positive signal around the E_0'/E_2 bulk CP energies for all four surface models. This feature, denoted B2, is in particular characteristic for the (2×4) reconstructed surface phases. The insensitivity of the B2 peak to the adsorption of oxygen was already interpreted earlier as a strong indication of its bulk-related origin [8].

Positive, bulk-related contributions to the optical anisotropy also arise around the E_1 CP energy. In contrast, earlier tight-binding results [9, 10] associated the reflectance anisotropy near the E_1 energy to As-dimer related surface states. We find that the B1 feature near the E_1 CP energy is more influenced by surface reconstruction than the B2 peak. It is much more pronounced for the (2×4) surface reconstructions than for

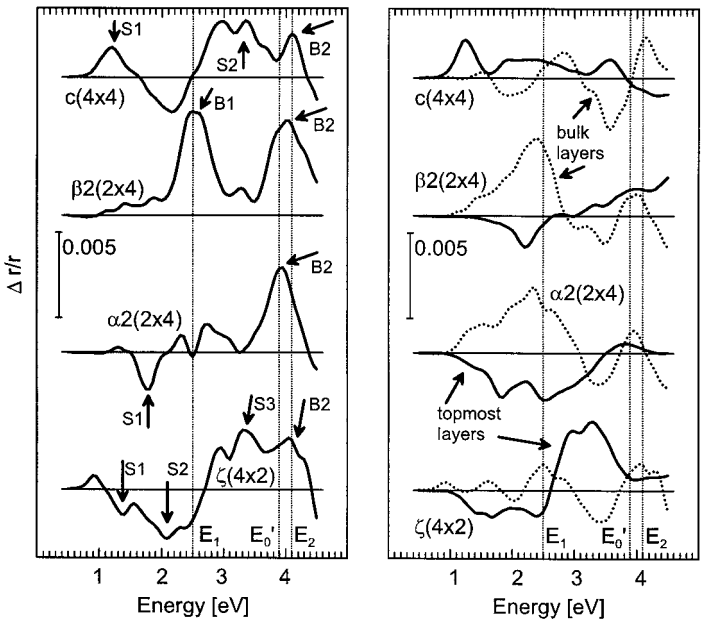

Fig. 3. RAS spectra [Re $\{(r_{[1\bar{1}0]} - r_{[110]})/\langle r\rangle\}$] calculated for GaAs(001) in DFT-LDA. The left panel shows the total signal, whereas solid/dashed lines in the right panel show separately the contributions of surface/bulk layers to the RAS. The calculated positions of bulk CP energies are indicated

the c(4×4) or (4×2) surfaces. In addition, strong negative anisotropy from the topmost atomic layers leads to a near cancellation of the optical anisotropy around the E_1 energy for the $\alpha2$ and ζ structures. Similar effects may also be responsible for the weakening of the B1 feature upon adsorption of oxygen, which was interpreted by Berkovits and co-workers [8] to indicate that the B1 optical anisotropy is due to As-dimer states. We would like to point out that our assignment of the B1 feature near the E_1 CP to bulk related states is also strongly confirmed by RAS-results on hydrogen-modified GaAs(001) surfaces which showed the B1 feature to be insensitive against exposure of several thousand Langmuir of atomic hydrogen to the (2×4) reconstructed surface, in spite of the concomitant destruction of the surface structure [7].

In addition to the optical anisotropies arising from electronic transitions between surface-perturbed bulk states there are strong anisotropies that are directly due to electronic surface states. These features have fingerprint-like character and may be used to determine the surface reconstruction. The As-rich c(4×4) reconstructed surface is characterised by positive anisotropies below the E_1 CP energy (S1) and between E_1 and E_0' (S2), which are mainly caused by As-dimer related states. Characteristic for the $\alpha2(2\times4)$ structure is the negative anisotropy for energies lower than the E_1 transitions. This negative anisotropy is also found for the corresponding structures at InP and GaP(001) surfaces [30, 31] and originates from electronic transitions involving the cation–cation surface bonds. Strong contributions of electronic surface states occur also for the $\zeta(4\times2)$ surface. The RAS features S1, S2 and S3 are superpositions of optical anisotropies related to numerous electronic transitions at the surface. No clearcut assignment to specific surface bonds is possible, however.

The inclusion of self-energy effects via the *GW* approximation leads to non-uniform shifts of the characteristic peaks to higher energies and also changes their line shape somewhat. This can be seen in Fig. 4, where we compare the spectra calculated in the *GW* approximation with the RAS data measured at low temperature. In case of the As-rich c(4×4) surface the relative positions of the anisotropy peaks with respect to the bulk CP energies and the magnitude of the anisotropy change only slightly upon inclusion of self-energy effects. Apart from the overestimation of the B2 feature we find nearly excellent agreement between *GW* calculations and the measured signal. Also in case of the GaAs(001) $\beta2(2\times4)$ surface the agreement between theory and experiment is very good. While the DFT-LDA calculations yield anisotropies B1 and B2 of comparable strength, the *GW* calculation increases the B1 anisotropy so that the relative ratio of the B1/B2 anisotropies comes close to the experimental value. The GaAs $\alpha2$ geometry is stable only in very narrow range of surface preparation conditions as can be seen from Fig. 1 (if it is at all an equilibrium structure) and was not observed in the present study. The presence of Ga–Ga bonds oriented along the [110] direction is known from earlier experiments, however, to induce a negative anisotropy for energies below the E_1 critical point energy [6, 36]. This negative anisotropy is indeed reproduced by our calculations (denoted S1 in Fig. 4). It is considerably increased and broadened upon application of self-energy corrections. Also in case of the $\zeta(4\times2)$ structure, the inclusion of self-energy effects affects strongly the surface-state-related optical anisotropies. The S1 signal increases, whereas the S2 feature diminishes, somewhat improving the agreement with experiment. The agreement between measured and calculated spectrum for the Ga-rich GaAs(4×2) surface remains unsatisfactory, however. Although it appears as if all experimental features are also present in the

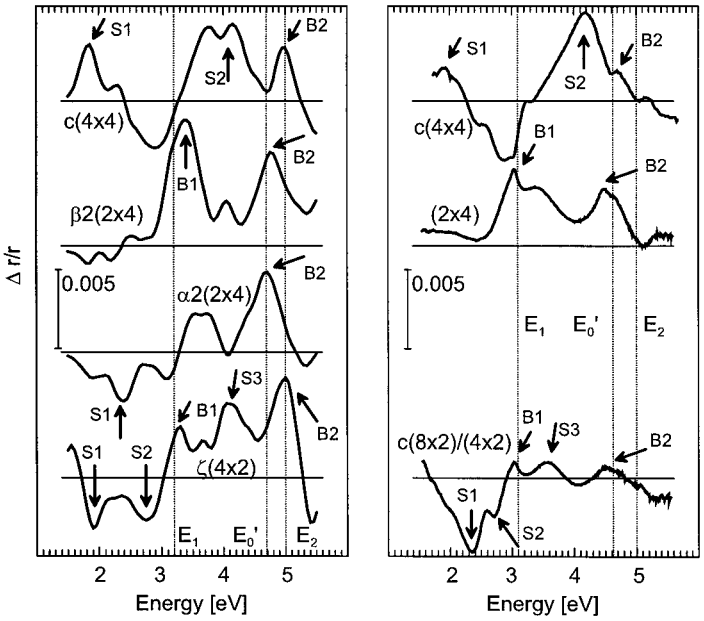

Fig. 4. RAS spectra [Re $\{(r_{[1\bar{1}0]} - r_{[110]})/\langle r\rangle\}$] calculated for GaAs(001) in *GW* approximation (left panel) are compared with the corresponding measurements (right panel). The RAS data were taken at a sample temperature of 40 K. The calculated/measured positions of bulk CP energies are indicated

calculated spectrum, the overall agreement with respect to the energy positions and magnitudes of characteristic peaks is poor.

One reason for this discrepancy could be that c(8×2) rather than (4×2) reconstructed domains [19, 21] are responsible for the measured signal. Unfortunately, our *ab initio* approach cannot presently be extended to the study of the RAS of c(8×2) reconstructed domains, due to the exceedingly large computational requirements of such a calculation. In order to estimate the influence of the reconstruction on the RAS spectrum we therefore performed semi-empirical tight-binding (TB) calculations on both reconstructions, using an sp3s* parametrisation and the method described in Ref. [37]. The results are shown in Fig. 5. We find only very limited agreement between the theoretical spectra obtained

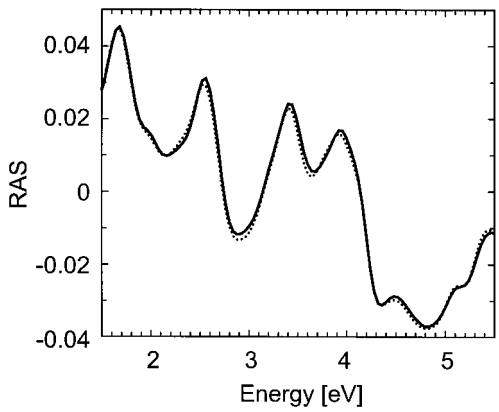

Fig. 5. Calculated Reflection Anisotropy Spectrum of the GaAs(100) c(8×2) and $\zeta(4\times2)$ surfaces, obtained within the nearest-neighbours TB method of [37]. Full line: c(8×2); dotted line: $\zeta(4\times2)$

within TB and those computed within DFT-LDA for GaAs(001) $\zeta(4\times2)$. That concerns both the magnitude of the optical anisotropy and, in particular for energies below the E_1 CP, its sign. A similar problem was encountered in the case of the Si(100) surface [38], where in DFT-LDA the RAS signal at about 1.5 eV, due to transitions across surface states, is opposite to that obtained by nearest-neighbours TB calculations. The sign of the RAS signal in TB coincides with that of a naive picture of the dimers considered as isolated Si_2 molecules, while in DFT-LDA the transitions polarised perpendicularly to the dimers dominate. This can be explained by the underestimation of the direct interaction between atoms belonging to adjacent dimers in the TB approach[2]). Nevertheless, the results shown in Fig. 5 indicate that the difference between the optical response of (4×2) and $c(8\times2)$ reconstructed GaAs surfaces should be very small. This is consistent with the fact that the local bonding configurations of both surface reconstructions are nearly identical.

On the other hand, computational and methodological insufficiencies of our *ab initio* approach could be responsible for the poor description of the RAS of the Ga-rich GaAs surface. We neglect the spin–orbit coupling, which for example results in there being no $E_1/E_1+\Delta_1$ splitting. For bulk GaAs the spin–orbit splitting in the valence band is Δ_0 = 0.33 eV at Γ and Δ_1 = 0.22 eV along the L direction. The low-energy features in the RAS spectra which are close in energy to the $E_0+\Delta_0$ bulk gap may therefore be considerably affected by the spin–orbit interaction. Furthermore, excitonic and local-field effects [39, 40] are missing in our study. In addition, we neglect the influence of surface induced strain fields, which may have a distinct influence on the optical anisotropy [41, 42]. However, it does not appear plausible that these effects limit the accuracy of our calculation more strongly in case of the Ga-rich (4×2) surface than in case of the more As-rich surface structures. At that point we can only speculate that the surface structure is not accurate. The rather complex $\zeta(4\times2)$ surface structure may either not be the true surface ground state, but by now we have not found an energetically more favourable structure, or the formation of this rather complex surface structure may be kinetically hindered, resulting in a surface with many defects. In that respect it is interesting to note that the measured RAS for the Ga-rich GaAs surface is better described by a superposition of the results calculated for the ζ and $\alpha2$ structures than by the calculations for the ζ structure alone. Detailed investigations on the influence of defects on the optical spectrum of Ga-rich GaAs surfaces are therefore presently being performed.

5. Summary

We presented a comparison between GaAs surface optical properties calculated from *first-principles* and low-temperature RAS measurements. We find that the RAS spectra contain contributions from electronic transitions between surface-perturbed bulk states that depend only weakly on the surface structure such as the optical anisotropy near the E_0'/E_2 energy. In addition, strongly stoichiometry-dependent features occur that are

[2]) In Si(100) the direct interaction between atoms belonging to adjacent dimers is about as large as the interaction between the p_z orbitals of the two atoms in a single dimer. Nearest-neighbours TB, however, strongly overestimates the latter interaction with respect to the former, because the two atoms in the same dimer are first neighbours, while atoms belonging to adjacent dimers are not.

due to electronic surface states. A very good agreement between experiment and theory is obtained for the $c(4 \times 4)$ and (2×4) surface phases, whereas the spectrum calculated for the $\zeta(4 \times 2)$ surface model describes poorly the corresponding measurements for Ga-rich surfaces. Surface defects appear presently as the most likely explanation for the observed discrepancies.

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