Structural analysis by reflectance anisotropy spectroscopy: As and Sb on GaAs(110)

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Abstract

We present calculated and measured reflectance anisotropy spectra (RAS) in the energy range from 1 to 6 eV of cleaved GaAs(110) surfaces covered with one monolayer of As and Sb in a (1 × 1) pattern. The spectral range and the accuracy of the data were improved and correlated for the first time with *ab initio* calculations of RAS spectra for the ECLS (epitaxial continued layer structure) and EOTS (epitaxial on top structure) surface models. The theoretical spectra for the two models completely differ and rule out the EOTS for both adsorbates. For Sb/GaAs(110) this finding agrees with the previous experimental and theoretical results reported on the structure. For As on GaAs(110) the ECLS structure was also suggested, but so far no direct proof for this model has been given. In this paper we show how RAS, thanks to its sensitivity to details of the surface structure and *ab initio* theoretical description, demonstrates its potential to conclusively determine surface structures.

1. Introduction

Reflectance anisotropy spectroscopy (RAS) since its first observation in 1966 [1] and the establishment of a robust and sensitive measuring technique in 1985 [2, 3] has been utilized in numerous surface studies. In the beginning it was mainly used to simply monitor surface modifications, but with increasing theoretical understanding of the spectral response [4–10] it was then applied successfully to extract quantitative information from the surface and has

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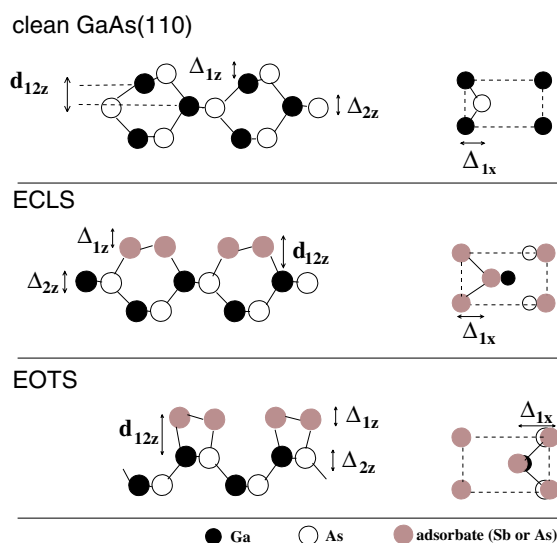
Figure 1. (a) Side and top view of the (a) clean GaAs(110) surface; and (b), (c) main structural models for Sb- and As-monolayers adsorbed on GaAs(110). (ECLS: epitaxial continued layer structure, EOTS: epitaxial on top structure.)

(This figure is in colour only in the electronic version)

become more and more a useful surface science tool. This success in understanding the origin of RAS is largely a success of *ab initio* theory which in many cases has given strong confidence to the interpretation of the spectra.

Clean (110) surfaces of III–V semiconductors like GaAs can be prepared by simple cleavage in vacuum. Therefore, many surface studies have been done on these systems, for example also the very first RAS measurements on III–V semiconductors [11]. Adsorbed group V monolayers on (110) surfaces of III–V semiconductors, especially on GaAs(110), have been studied for several decades as a prototype of a non-reacting interface and as systems with the possibility to adsorb exactly one ordered monolayer. In particular, Sb has been investigated quite intensively with respect to its structure by low-energy electron diffraction (LEED) [12, 13], x-ray standing wave (XSW) [14], grazing incidence x-ray diffraction GIXD [15], scanning tunnelling microscopy (STM) [16, 17], photo electron diffraction (PED) [18] and also RAS [4, 19]. Two structural models were finally mainly discussed: the EOTS (epitaxial on top structure) [20, 21] and the ECLS (epitaxial continued layer structure) [22] (figure 1).

While some of the results could be interpreted with both models, most of the studies, especially the diffraction techniques, as well as total energy calculations with tight-binding models [23] and *ab initio* pseudo potential [6, 24, 25] gave evidence to the ECLS. Tight-binding calculations of RAS seemed to indicate the ECLS too [4]. Thus for Sb/GaAs(110) the ECLS structure is now generally accepted.

For the system As/GaAs(110) much less is known. The much lower desorption temperature for As on GaAs(110) ($\approx$100 °C) than for Sb ($\approx$550 °C) of [26] was explained by much lower formation energies for As/GaAs compared to Sb/GaAs by *ab initio* density functional theory (DFT) calculations [27]. DFT calculations for the total energy [28] also predicted for extreme As rich conditions an As covered layer with ECLS structure [29]. RAS spectra of an arsenic rich structure were reported [30] to be different from the just

Table 1. Calculated and experimental structural parameters for GaAs(110), GaAs(110):As, GaAs(110):Sb surfaces. The latter two are calculated for the EOTS and the ECLS model (figure 1). The theoretical GaAs bulk lattice constant is 5.61 Å.

	Δ_{1x} (Å)	Δ_{1z} (Å)	d_{12z} (Å)	Δ_{2z} (Å)
GaAs(110) th.	1.18	0.68	1.46	0.10
GaAs(110) exp.	1.136	0.69	1.442	0.120
GaAs(110):As th. (ECLS)	1.58	0.05	2.05	0.09
GaAs(110):As th. (EOTS)	1.56	0.15	2.49	0.12
GaAs(110):Sb th. (ECLS)	1.99	0.06	2.38	0.10
GaAs(110):Sb th. (EOTS)	2.04	0.11	2.66	0.11

cleaved GaAs(110) and interpreted in terms of an As terminated structure. A very early IV-LEED study [31] and core level photoemission [26] suggested an ordered As coverage with a maximum of one monolayer, no excess As and no buckling. The core-level shifts of [26] were best matched with core-level shifts calculated by DFT for the ECLS model [27]. But the structure of As/GaAs(110) has not been definitely clarified.

The motivation of the present work is therefore to establish with these two similar systems another strong example of the possibilities of RAS as a structural surface science tool. The well characterized Sb/GaAs(110) will serve as a test case for our theoretical/experimental RAS approach and the As/GaAs(110) as a new case in order to use RAS for clarification of the structure. In addition to *ab initio* calculations, improved experimental RAS data were also taken, calibrated in amplitude and measured over an extended spectral range.

2. Theoretical considerations and geometries

Calculations have been performed within the density functional theory-local density approximation (DFT-LDA) [32]. Tests calculations performed within the generalized gradient approximation (GGA [33]) did not give important differences. We used a 18 Ryd cutoff in the kinetic energy, and nonlinear core corrections for the Ga pseudo potential were included. The surface structures have been optimized using 16 k-points in the whole BZ. We calculated the geometry of the two models which have been mostly discussed in the literature: the epitaxial continued layer structure (ECLS) and the epitaxial on top structure (EOTS) (figure 1).

The equilibrium geometries found for As or Sb (see table 1) are in agreement with previous calculations [25, 28]. The cases of As covered and Sb covered GaAs(110) are similar. With respect to the clean surface, the Ga and As surface atoms (now at the second layer) relax back to an almost ideally truncated bulk, whereas the ad-layer atoms (As or Sb) show almost no buckling. In the ECLS the distance between the second layer Ga atom and the Sb adatom is 2.62 Å, the same as in GaSb bulk. Also in the case of As on GaAs(110) in the ECLS model, the distance between the second layer Ga atom and the As adatom is equal to the theoretical Ga–As distance in bulk GaAs (2.43 Å). In the EOTS instead such distances are larger. At the clean surface, the bond between the second layer Ga and the first layer As is slightly stretched (2.45 Å) due to the buckling.

Our total energy minimization gives as a result that the ECLS structures have lower energy than the EOTS models: for GaAs:As the difference in energy is -1.3 eV/(1×1), and for the GaAs:Sb the difference is -1.0 eV/(1×1).

The reflectance anisotropy is defined here as

$$\frac{\Delta R}{R_0} = \frac{R_{[\bar{1}10]} - R_{[001]}}{R_0} \tag{1}$$

with R_0 being the average isotropic reflectance, and is calculated following [34].

The calculations have been performed using a grid of 70 k-points in the irreducible Brillouin zone and interpolating the energy bands using the triangle method (tetrahedron method in two dimensions) [35]. DFT wavefunctions have been used within the single-particle approximation, and the DFT single-particle energies have been corrected by 0.4 eV in order to account for GW, excitonic and local fields effects. Excitonic effects are not included explicitly. According to our calculations the As and Sb adsorbates do not give rise to extremely localized flat surface states in the gap. For this reason we expect excitonic effects to be important only for lineshapes but less important for the peak positions.

The calculated results are shown in figures 4 and 5 and will be discussed together with the experimental results.

3. Experiment

3.1. Reflectance anisotropy spectroscopy (RAS)

The reflectance anisotropy as defined in equation (1) measures the difference in the (intensity) reflectance R between the two perpendicular crystal axes [$\bar{1}$10] and [001] within the (110) surface. For quantitative comparison with previous data published we note that

$$\Delta R/R = 2\,\mathrm{Re}(\Delta r/r) \tag{2}$$

where r is the complex amplitude reflectance and Re indicates the real part.

The RAS measurements were performed with two setups. One, which was mainly used for Sb/GaAs(110), is capable of measurements in the spectral region of 0.8–6.5 eV. This RAS setup allows for a considerably larger spectral range than previous measurements due to MgF$_2$ Rochon polarizers, a CaF$_2$ photoelastic modulator and two detector systems. The principal measurable region is therefore expanded up to 9 eV, though oxygen adsorption limits the range to 6.5 eV if the RAS and the optical path to the windows of the preparation chambers are not nitrogen purged. The signals of this system were calibrated with a wedge made out of quartz, a material for which the bulk optical anisotropies are well known and $\Delta R/R$ can be calculated with very high accuracy from the optical constants. The As/GaAs(110) measurements, mainly performed on a molecular beam epitaxy (MBE) apparatus, were done with a Jobin Yvon RDS spectrometer positioned so as to make simultaneous RHEED (reflection high-energy electron diffraction) measurements possible. Since the polarizer in this RAS setup was made from quartz and the detector was a photomultiplier coupled by an optical fibre, the spectral range was limited to 1.45–5.25 eV.

All RAS measurements were made through low strain optical view ports.

3.2. Preparation of the Sb/GaAs(110)

The GaAs(110) surfaces were obtained by cleaving undoped GaAs in ultra-high vacuum (UHV) at a base pressure of 1×10^{-10} mbar. During Sb evaporation the sample was heated to 250 °C in order to avoid the formation of Sb crystallites or an amorphous Sb layer. The evaporation was stopped when subsequent RAS spectra taken during evaporation showed no differences any more. The presence of the Sb monolayer was verified with *in situ* Raman spectroscopy where the characteristic surface modes could be observed [36]. All the surfaces measured showed a (1 × 1) LEED pattern.

3.3. Preparation of the As-rich surface

The experiments for the preparation of the As-rich GaAs (110) were performed in an MBE chamber with a base pressure around 10^{-10} mbar, equipped with As$_4$ and Ga sources.
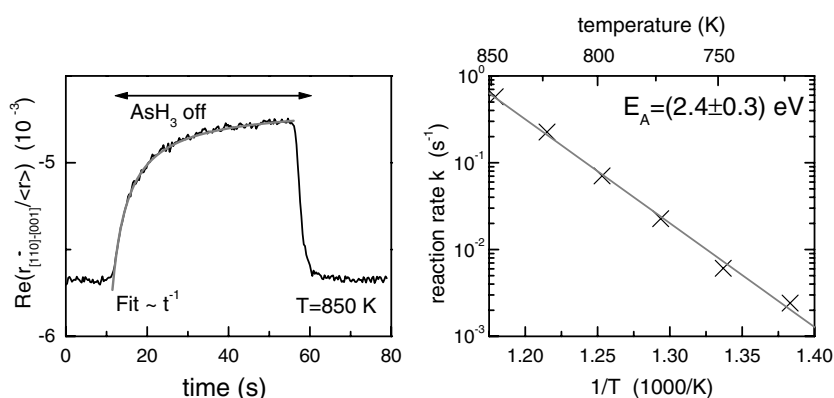
Figure 2. Arsenic desorption measured with RAS at a photon energy of 3.5 eV as a function of time after switching off the As (left) and activation energy of the desorption process derived from desorption experiments at different temperatures (right).

Si-doped (5×10^{17}) GaAs(110) substrates were used, which were then deoxidized around 600 °C, followed by a short buffer layer growth.

The preparation procedure for the As coverage was the following. After buffer growth the As$_4$ cell was set to 100 °C and the sample temperature slowly reduced. At room temperature a spectrum similar to the one of the cleaved surface with similar amplitudes was obtained. Then the sample was heated to 600 °C with the As cell set to 280 °C and afterwards the sample was cooled down. At 150 °C the As shutter was closed and the As cell was set to 100 °C again. The sample was cooled further to get sharper structures in the RAS spectrum. The symmetry in RHEED throughout the whole procedure remained always (1×1).

A comparable As-rich surface to the one in MBE was prepared in MOVPE in a horizontal flow quartz reactor with a vertical low strain window allowing for RAS measurements with the same system as used for the Sb layer. The gas flows for MOVPE buffer growth were 3 l min^{-1} H$_2$, 100 Pa AsH$_3$ and 0.5 Pa TMGa. After buffer growth the sample was cooled under AsH$_3$ to 200 °C, a standard procedure which yields the very As-rich so-called $d(4 \times 4)$ reconstruction on the GaAs(001) surface [37]. The resulting spectrum from the GaAs(110) prepared in this way (figure 2 in [30]) is very similar to the one shown in figure 3.

In MOVPE we were also able to rapidly change the As partial pressure by switching off the AsH$_3$ (not possible in the MBE because of the high As background pressure) and to observe the As desorption from the surface. Figure 2 shows a typical MOVPE transient. The desorption process is of second order (t^{-1}), which is typical for most higher index surfaces [30, 38, 39]. However, the activation energy taken from the measured Arrhenius plot in figure 2 of (2.4 ± 0.3) eV is much higher than for vicinal surfaces and close to the value of 2.6 eV for the GaAs(001) surface. This indicates that As is more tightly bound on the (110) surface than on the vicinal ones and the observed structure has a relatively low surface energy compared to other high-index surfaces. We note that this desorption energy is much lower than the calculated binding energy of 3.90 eV [27].

4. Results

Since the bulk of zincblende III–V semiconductors is optically isotropic, the reflectance anisotropy arises only from regions with broken symmetry, particularly surfaces, interfaces and perturbed bulk states. Features induced by surface electric fields, spin–orbit splitting, and finite wavevector effects may also contribute. The origin of certain features in the RAS spectra
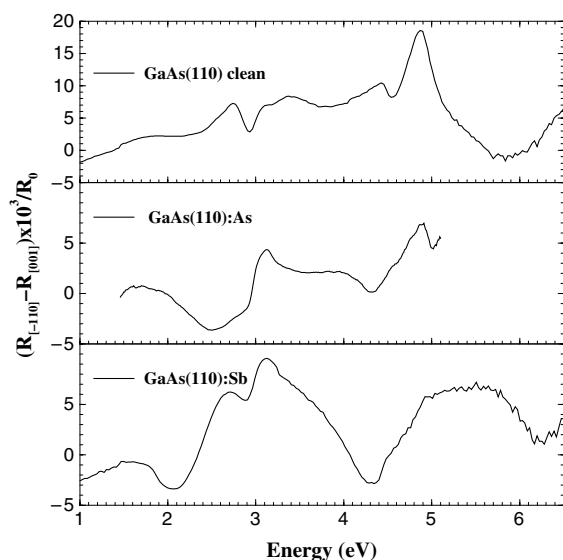
Figure 3. Experimental RAS spectra of GaAs(110). Top: clean surface, middle: As/GaAs, bottom: Sb/GaAs.

are not easily to determine, since the signal may arise from transitions between individual surface states, perturbed bulk states or both. To assign a specific structure of the RAS spectra to a certain transition one therefore has to compare the measured spectra to calculated ones.

The experimental RAS spectra are shown in figure 3 for the clean, As and Sb covered surface. Due to the improved spectral range of our RAS setup the spectra show more details than the previously published data [4], e.g. the pronounced maximum at 4.9 eV for the clean GaAs(110) and the broad maximum structure at 5.5 eV in Sb/GaAs(110) (figure 3).

All the surfaces have an identical (1×1) diffraction pattern, but the RAS spectra clearly differ. Thus, RAS is sensitive to the details of the surface layer. The spectra of the clean surface are already well understood, showing maxima due to surface state transitions at 2.5 and 2.7 eV as well as a broad maximum at 3.4 eV. The maximum at 4.9 eV was already predicted in earlier calculations and can be attributed to transitions between surface modified bulk states [7].

Although there are some similarities between RAS spectra of As and Sb terminated GaAs(110) (like the minimum structure below the E_1 bulk critical point around 3 eV) the spectra are clearly different. Sb/GaAs shows two broad maxima at 5.5 eV and around 3 eV and a minimum structure at 2 eV. As/GaAs instead shows only a broad minimum around 2.5 eV and the rising edge of the RAS is found around 3 eV.

One has to note that on all GaAs(110) spectra, independently of the adsorbed species, an anisotropy structure is found around 3 eV, in the region of the E_1 and $E_1 + \Delta_1$ bulk critical points. Hence this structure likely originates from bulk states modified by the surface and/or surface electric fields [40].

In order to determine which of the two concurring models of the surface structure is the valid one, we performed *ab initio* calculations of RAS spectra for the EOTS and ECLS adsorbate models (see figures 4 and 5).

Figure 4 shows the calculated spectra for the ECLS and EOTS structure together with the experimental curve for Sb/GaAs. The agreement for the ECLS is very good. The minima around 2 and 4.3 eV as well as the broad maxima around 2.8 and 5.5 eV are clearly reproduced. The main remaining differences in the details of the lineshapes are due to excitonic effects, temperature effects, and spin–orbit splitting, not included in the theory. Nevertheless, the agreement is even quantitative, not merely qualitative.
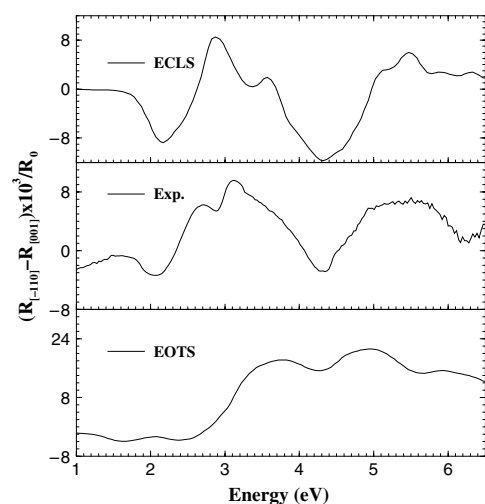
Figure 4. RAS spectra of Sb/GaAs(110). Top: calculated ECLS; middle: measured at room temperature; bottom: calculated EOTS.
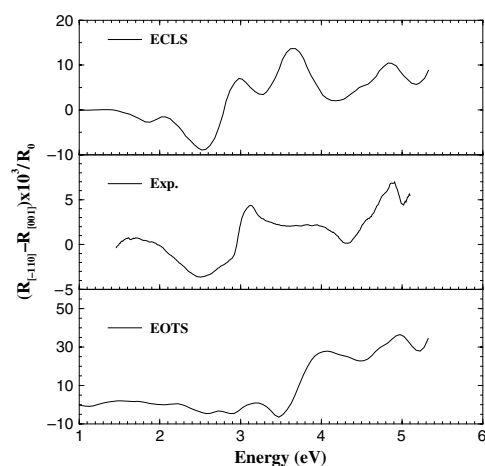
Figure 5. RAS spectra of As/GaAs(110). Top: calculated ECLS; middle: measured at 230 K; bottom: EOTS.

According to our calculation the EOTS structure should lead to a large positive anisotropy above 3.5 eV with no pronounced features. Also no minimum in the low energy range is predicted. Since this contrasts clearly with the measured spectrum, we can completely rule out the EOTS as a possible surface structure and confirm the ECLS model like in previous works.

Figure 5 shows the RAS spectrum of the As-terminated surface with the calculated RAS spectra for the ECLS and EOTS model.

The positions of the extrema to the calculated data for the ECLS model is very good; only the shoulder around 3.7 eV is enhanced in the theoretical spectrum and appears as a peak. Again the discrepancies in the lineshape may be due to excitonic effects, temperature effects (we calculate a $T = 0$ K spectrum), and an experimentally not so well defined As coverage. The latter may also be responsible for the fact that the RAS amplitudes of the measurements are smaller than the ones of the calculated spectrum. A possible explanation could be that the coverage with As is not 100%. Alternatively, at such temperatures disordered As may also stick to the surface and might decrease the amplitude.

The maxima of the EOTS calculation are at complete different positions and the overall shape is also very different. Therefore, the EOTS model must be excluded.

5. Conclusions

The adsorbate covered GaAs(110) surfaces clearly demonstrate RAS as a powerful surface science tool. All investigated surfaces in this work show (1×1) symmetry but very different RAS spectra. The successful identification of the ECLS model for Sb and As adsorbates is because of two facts: the extended spectral range and the possibility to calculate RAS spectra with a great accuracy. Steady improvements in computer power will make the calculations possible for more and more complex systems. By combining these two methods RAS will have a bright future, since it requires much less experimental effort when compared to other surface sensitive techniques like photoemission and STM; moreover, it allows for measurement in gaseous or liquid environments.

Acknowledgments

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