Photoemission study of S adsorption on GaAs (0 0 1)

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Abstract. Angle-resolved photoemission spectra have been calculated with the one-step model for S/GaAs(0 0 1) and compared with experimental distributions. The data are analysed in terms of the ideal 1 × 1 and, furthermore, of the reconstructed 2 × 6 surface which is assumed to be closest to the experimentally realized structure. Emissions are characterized by electronic structure terms such as energy bands and orbital composition, though partly also by geometric properties. In particular, the determination of the second layer as consisting of Ga atoms has been achieved because of the distinct differences in the theoretical spectra with S–Ga and those with S–As bonds.
1. Introduction

Compound semiconductors of III–V composition play an essential role in technological development. The process of production for the technically most relevant GaAs(0 0 1) surface termination is still not satisfactorily understood, if it goes to the nanoscale regime. The main drawback is the instability of this surface towards various reconstructions, which demands efficient passivation methods. Sulfur passivation is occasionally discussed [1] and the investigation of such surfaces has drawn interest experimentally [2]–[7] and theoretically [8]–[13]. In the \textit{ab initio} calculations with density functional theory, the determination of the geometric structure has been of fundamental concern yielding also the electronic structure. A few surface structures of sulfur adsorbed on GaAs(0 0 1) seem to be accepted at present. Regarding the electronic structure, not much is known beyond the results concomitant with the geometric structure optimization. It is the aim of this paper to feed some material into this gap in knowledge from both experiment and theory.

The analyses of angle-resolved photoemission spectra try to access the electronic structure by a mapping to the valence band structure of bulk and surface. If there is a correspondence, then theory can also reveal the orbital and other wavefunction compositions of the states. If there is not, then some sort of trial and error analysis is necessary by comparing directly the experimental and theoretical spectra. Agreement will support the assumed theoretical basis; disagreement will require a refinement. In the former case, the states’ composition can be safely extracted again by theoretical means, although a simple association of a peak with an electronic state may not be possible. Interference of conduction states in the final state as well as weighting the transition by the magnitude of its matrix element disguise the transitions and mask the electronic structure [14, 15].

The present state-of-the-art of interpreting photoemission spectra is characterized by fully understood excellent results on one hand, such as for instance for simple metals and by very complex spectra with significant differences between the experimental and the theoretical intensities on the other, as in the case of compounds with surfaces which are unstable towards reconstruction. The uncertainties and problems originate partly from the deficiencies of the surface and its description and partly from the photoemission process itself. Experimental
as well as theoretical reasons may cause the difficulties. In the case considered here the surface reconstruction was experimentally attributed to a $2 \times 3$ with the possibility of $2 \times 6$. Theoretically, the $2 \times 6$ had been found to be the stable structure [13]. Thus, this investigation is aimed at the $2 \times 6$ reconstruction, though the large size of this unit cell required a simpler treatment regarding the calculational procedure and additional precursory investigations of the $1 \times 1$ ideal system.

This work is based on a comparison of experimental [16, 17] and theoretical angle-resolved photoemission spectra. Both show a lot of well-resolved features which are worth interpreting. As mentioned, the surface unit cell is not entirely out of the question and furthermore, the subsurface termination is not known experimentally so that one has to consider both Ga and As termination. The results should allow to decide upon the correct choice of the geometrical structure and to assess the usefulness of photoemission in combination with one-step calculations as a tool for adding further knowledge about it. They should reveal some of the states contributing to the bonding in the solid and at the surface.

2. Calculation method

Photoemission intensities are obtained within the one-step model. It consists of using the complete Golden Rule with scattering states as final states and bound states as initial states for the surface system. The matrix elements are calculated between them for the dipole operator of the incident light.

The initial states are described by their halfspace Green function which has been evaluated by a fast layer doubling algorithm for the surfaces in question. They use an LCAO representation with a parametrization of the Hamiltonian and overlap matrix according to the extended Hückel theory (EHT).

The final states use a step barrier for the solid–vacuum interface. For all systems a double-step potential at the surface has been investigated to simulate an uppermost layer potential different from the solid and vacuum potential, specifically using the different work functions of 5.25 eV for GaAs and 9.04 eV for sulfur to result in a potential well of 3.79 eV depth below the surface. The interior of the solid halfspace is described by an empirical pseudopotential. The wavefunctions join continuously the solid through the well with the vacuum and fulfil boundary conditions of outgoing states as time-reversed LEED states. Thus, they simulate the essential ingredients of the states emitted by the complete GaAs crystal including the surface and vacuum and selected by the detector. For the discussion of bulk properties, the complex bandstructure of the halfspace has been calculated.

The transition matrix elements utilize the dipole approximation with a constant vector potential and are calculated by integration in direct space. The case of unpolarized light has been applied according to experiment employing HeI radiation. For details of calculation and references see [18, 19].

3. Experiment

GaAs(0 0 1) wafers of p-type (Zn-doped, $7 \times 10^{18}$ cm$^{-3}$) were cleaned with trichlorehthane, isopropanol, acetone and mounted on molybdenum sample holders by indium.

After insertion into the ultrahigh vacuum (UHV)-system the samples were sputtered for 2–3 h by Ar-ions with an acceleration voltage of 1 keV and a current of 30 mA. Sputtering
and growth took place inside a standard molecular beam epitaxy (MBE)-chamber with a base pressure below $10^{-9}$ mbar before and $10^{-6}$ mbar during growth. The Ga and As sources are evaporating cells whereas, the S$\text{2}$-source is an electrochemical Knudsen cell. This is a galvanic cell Pt/Ag/AgJ/Ag$_2$S/Pt. An EMF is applied to the cell and regulates the S$\text{2}$-flow.

In order to obtain high-quality surfaces, at first a pure GaAs buffer layer of about 100 monolayers was grown under As-rich conditions. The growth was monitored by reflective high energy electron diffraction (RHEED). During this first phase, the temperature of the substrate was 565 $^\circ$C, the temperature of the Ga-source was 1025 $^\circ$C while the As-source was kept at 320 $^\circ$C. The surface showed the typical (2 × 4)-reconstruction. Afterwards, the growing of S-covered GaAs was initiated. For this, the Ga-shutter was kept closed and the Ga source was cooled down. The temperature of the As source was reduced to 240 $^\circ$C and the temperature of the sample to 500 $^\circ$C. The growth with S took place with a temperature of the S source of 225 $^\circ$C and a regulating voltage of 250 mV for 3–6 h. Both As and S shutters were opened for the whole time. Then the surface showed a change of the reconstruction from (2 × 4) to (2 × 3).

The angle-resolved photoemission spectroscopy (ARPES) was performed in a separate UHV-chamber with a base pressure of $5 \times 10^{-11}$ mbar directly connected to the MBE system. The chamber is equipped with a 180$^\circ$ spherical electron analyser mounted on a two-axes goniometer. The angular resolution was ±0.5$^\circ$ and the energy resolution was 63 meV. Off-normal emission energy-distribution curves (EDC) were taken at room temperature with an excitation energy of 21.22 eV (He I$_\alpha$) from a He-gas discharge lamp along the high symmetric directions $\Gamma J$ and $\Gamma J^\prime$ of the surface Brillouin zone.

4. Discussion of the ideal 1 × 1 surface

4.1. Bandstructure

In figures 1 and 2, the surface bandstructures of the ideal S covered 1 × 1 surfaces with adsorption on Ga and As termination are plotted. The surface states around the gap are the important features for a discussion of the differences in the context of photoemission and structure. The 1 × 1 geometry is schematically displayed in figure 3. A metallic surface state is obvious in the As terminated case and absent for Ga termination. With the sulfur overlayer missing, bandstructure calculation shows also a metallic surface state for Ga termination. Electron counting leaves 7/2 electrons of sulfur dangling bonds in the case of S/Ga and 9/2 in the case of S/As. Combining to an S-dimer a doubly filled dimer state leaves 5/2 electrons per sulfur in the former and 7/2 in the latter, i.e., a remaining half-filled metallic band in each case. However, the bandstructure calculation shows a balancing of the population between surface and bulk states different from the electron counting rule and most evident in the Ga terminated case. It also shows the general instability of the 1 × 1 surface structure and its tendency towards reconstruction even beyond simple S-dimerization starting from a 1 × 1 basis. Nevertheless, the presence of a metallic surface state in the experimental photoemission data, see figure 5, can be ruled out from the absence of a Fermi edge. Therefore, a first argument in favour of the Ga termination arises.

4.2. Angle-dependent emission: As subsurface layer

To further rule out the arsenic termination in sulfur adsorption, the respective angle-resolved spectra are depicted in figure 4 as a comparison between the experimental and the theoretical
Figure 1. Surface bandstructure of S adsorbed on an ideal Ga terminated GaAs(0 0 1) 1 × 1 surface.

Figure 2. Surface bandstructure of S adsorbed on an ideal As terminated GaAs(0 0 1) 1 × 1 surface.
Figure 3. Geometry of $1 \times 1$ sulfur adsorption on GaAs(0 0 1)/Ga.

Figure 4. Experimental (lines with scatter) and theoretical angle-resolved EDCs for non-normal emission from GaAs(0 0 1)–(1 × 1)As/S with polar angle as parameter and emission azimuth along $\Gamma$–$J$ ($0^\circ$ in bulk coordinates).
4.3. Angle-dependent emission: Ga subsurface layer

A comparison of the experimental spectra with those calculated on the basis of S adsorption on top of a Ga layer is found in figure 5. Note that the azimuthal 0° direction is fixed.
by the x coordinate of a bulk coordinate system and consequently an As top layer is
rotated by 90° with respect to a Ga top layer. The discrepancies found in the foregoing
subsection between experiment and theory using an As subsurface layer are resolved now to
a large degree:

(i) The main experimental peak around −1 eV now compares well with theory; only at angles
of 0° and 3° it seems to be suppressed. Because we associate this structure with a surface
emission, the observed agreement becomes important especially at high angles where an
enhanced surface sensitivity should be expected.

(ii) The step above −7 eV appears in theory for all angles and suits much better than in the
theoretical spectra for an As subsurface.

(iii) The experimental step (peak) between −2 and −3 eV is present in theory across the whole
range of spectra and partly reproduces the intensity, whereas for an As subsurface this occurs
merely for 27° and perhaps for 24°,

(iv) and to be more specific, the shoulder at −2 eV for 0° and 3° is entirely missing in the S/As
case.

(v) At angles of 9° and 12°, a theoretical peak appears at −2 eV for the S/Ga surface, which
seems necessary to fit the experimental shape but is absent for the S/As surface termination.

Thus, the overall shape of spectra agrees significantly better for this geometrical configuration
than for that before.

The misalignment in the position of the theoretical peak, mainly a sulfur surface state, close
to 0 eV for small angles is attributed to insufficiencies in the parametrization of the valence
bandstructure.

Atomic and orbital resolution yields that the dominant peak dispersing from 0 eV at 0° to
−1 eV at 24° (J point at 22.5° for small binding energy and ħν = 21.22 eV) in the theoretical
spectrum is a surface peak and consists mainly of S p_z orbitals.

Thus, most of the findings are in favour of a Ga termination of the adsorbing GaAs
halfspace.

4.4. Normal emission: Ga subsurface layer

The photocurrent in normal emission usually draws its most important aspects from the bulk
features of the bandstructure. In figure 6, electron distribution curves (EDCs) from normal
emission are displayed for various photon energies. Note that the calculation here employed
p polarized light instead of unpolarized used in the angle spectra series. Energies are marked
for comparison with the valence bandstructure through direct transitions. They are principally
possible, although frequently suppressed by smallness of the matrix elements and of the coupling
to the outgoing wavefunction. The multitude of transitions arises because of the many final states.

Weighting the final state band by its coupling to the vacuum, the complex bandstructure yields
a more realistic picture of transitions to be expected. Extracting the two most important direct
transitions leads to the energies marked by the intersections with the two lines crossing the spectra
in the plot. In particular, the direct transitions at the lower binding energy are well reflected
by the spectra, so around 22 eV at −1.5 eV and above 30 eV where the valence band energy
approaches −3 eV. It should be noted that the intensity of direct transitions and the distinctness
of their dispersion usually is much more pronounced than seen here, compare for instance with spectra of clean GaAs(0 0 1) [20].

The peak close to the valence band maximum seems to be associated with the surface state, partly a resonance, through the interval of photon energies from 10 to 22 eV. So it is hard to detect the uppermost valence band direct transition which should coincide at 10 eV photon energy with the surface peak. Besides this peak, no further surface peaks, present in the bandstructure according to figure 1, can be detected in the theoretical normal emission EDCs. Altogether, the spectra reflect some structures directly accessible through a bandstructure discussion, though the EDCs reveal additional peculiar features not easy to be traced back. This common experience in the case of complicated semiconductor spectra usually leads to a direct comparison with experimental EDCs which are still lacking here.
5. Photocurrent calculated for the $2 \times 6$ reconstruction

The surface geometry for the $2 \times 6$ reconstruction which is displayed in figure 7 has been taken from [13]. The electron counting associates seven electrons with each S-dimer in addition to five electrons filling the bonds to four Ga atoms in the subsurface layer by $5/4$ electrons each. Out of these seven electrons, two are distributed on the dimer bond and two on the dangling bond of each of both S constituents of the dimer, leaving one electron left over. With five dimers in the $2 \times 6$ reconstruction altogether five electrons are left over which are distributed on the four Ga corner atoms of the unit cell, which miss one bonding neighbour each. Thus, all states are doubly occupied and each S atom participates in a dimer and possesses one filled dangling bond.

Only a few ab initio calculations of the $2 \times 6$ reconstructed surface have been carried out in the literature. Our results for the photoemission spectra are displayed in figure 8 showing a slight improvement over the $1 \times 1$ calculation. In particular, the increased width of the main theoretical peak at low binding energies appears to be closer to the experiment.
The azimuthal anisotropy of the experimental spectra is rather small and scarcely discernible by inspecting the spectra directly. The anisotropy in the theoretical spectra is significantly higher. To shed some light on the directional dependence of emission, the modulus of the difference between the photocurrents in $\Gamma J$ and $\Gamma J'$ is shown in figure 9. Because other effects may play a role in contributing to the difference in the theoretical spectra, we confine the discussion to the peaks of the experimental difference spectra and associate these peaks with their fingerprints in the single theoretical spectrum. One should be aware that small experimental uncertainties as e.g. a shift in the kinetic energy determination may lead to the erroneous intensity differences. All difference spectra show rather clear and unique structures and, as demonstrated below, their peaks are obviously based on physics. We strongly believe that these kinds of spectra reveal additional valuable information which should be analysed.

**Figure 8.** Experimental (lines with scatter) and theoretical angle-resolved EDCs for non-normal emission from GaAs(0 0 1)–(2 × 6)Ga/S with polar angle as parameter and emission azimuth along $\Gamma – J$ (90° in bulk coordinates).
Figure 9. Anisotropy: absolute value of difference in experimental angle-resolved EDCs for non-normal emission from GaAs(0 0 1)–(2 × 6)Ga/S with polar angle as parameter between azimuth along Γ–J and along Γ–J′.

There appears a strong structure between −1 and 0 eV for a whole series of angles. Furthermore, two additional strong peaks are observed between −4 and −1 eV mainly at 24° and 27° polar angle. Looking at the theoretical spectrum separately, all these structures can be attributed to dominant sulfur p\textsubscript{z} emissions of the theoretical spectrum.

In a purely local orbital picture of only S p\textsubscript{z} emissions it would be difficult to understand how the geometric arrangement of the S atoms in the 2 × 6 unit cell can lead to this anisotropy. One has to look for the smaller orbital contributions to resolve this puzzle.

The peaks at −5.0 eV in the 18°–24° range and those at −3.7, −1.8 and −0.4 eV in the 27° experimental difference spectrum may serve as a specific example. From the density of states, a strong surface in-plane S p contribution at −4.6 eV to the −5.0 eV peak can be inferred. This orbital is directed along the dimer and the emission is associated with the dimer bond. The −3.7 eV peak contains contributions of in-plane S p and Ga p orbitals and corresponds to the backbond from S to Ga. Of course, both emission dimer and backbond must change when rotating the electron acceptance by 90°. The same is true for the peak at −1.8 eV which can be associated with in-plane As p and Ga p orbitals pointing from subsurface Ga to next layer As.
In short, the S dimer bond, the S–Ga back bond and the Ga bond to third layer As can be identified. Only those in-plane S p orbitals contribute which point parallel to the emission direction, the latter to be expected from simple atomic photoemission arguments.

The peak at $-0.4$ eV in the difference spectrum has no specific counterpart in the theoretical spectra. From its energy, one should associate it with the S dangling bond which points from the dimer in opposite direction. Already, at the discussion of normal emission, the energetic position of this surface state was questioned in view of the parametrization. Of course, a directional dependence of such a state has to be expected.

6. Summary and conclusions

A GaAs(0 0 1) surface with adsorbed sulfur has been investigated. Theoretical spectra calculated with the one-step model are compared to the experimental angle-resolved photoemission spectra. The agreement generally confirms the reliability of the \textit{ab initio} geometric model for the $2 \times 6$ reconstruction and establishes the presence of Ga as a subsurface layer. The emissions are identified by the associated transitions and traced back to the electronic valence states in favourable cases.

As a general feature, a dominance of sulfur adsorbate states is observed in the spectra. In particular, the dominant emission is due to sulfur p$_z$ orbitals. Then principally the surface geometry, i.e., the arrangement of sulfur atoms, should influence the spectra. Because of the small matrix elements for the in-plane orbitals, the directional dependence is suppressed in the spectra. However, utilizing the difference in the spectra for different azimuthal angles these small intensity emissions become observable. Minor structures are thus detected which reveal the orbitals’ direction and also geometric properties as the direction of the dimer.

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