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Se-induced 3d core-level shifts of GaAs(110)

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Abstract

We present ab initio pseudopotential calculations of 3d core-level shifts of the surface atoms for clean and Se-deposited GaAs(110) surfaces. We are able to explain the experimental findings for the clean GaAs(110) surface in the picture of the initial-state model. If relaxation effects are accounted for we find a distinct overestimation of the surface core-level shifts (SCLS) both for As and Ga atoms with respect to experimental results. We conclude that final-state effects play only a minor role in the dynamics of the photoemission process for the GaAs(110) surface. In order to clarify the surface chemistry of the Se/GaAs(110) system we determine the SCLS of the species involved for a series of structural models. Only one of these models gives rise to a reasonable agreement between calculated and measured SCLS. Therefore we strongly support a geometry where each surface As atom is substituted by Se and one further Se binds to the surface Ga atom.

1. Introduction

Currently there is a growing interest in the selenium and other group-VI atom deposition on the III–V compound semiconductor surfaces because of their passivating properties. Whereas the passivating action of a group-VI treatment is well known, especially for the polar GaAs(001) surface [1–3], the understanding of the actual formation process and the bonding of the adsorbate is far from being complete. The nonpolar GaAs(110) 1×1 cleavage surface represents a model face for such studies because of its smoothness on an atomic scale and is therefore discussed in the following. Tu and Kahn [4] found that upon deposition of Se the GaAs(110) 1×1 low-energy electron diffraction (LEED) pattern is conserved, but degrades rapidly as a function of coverage. When the coverage reaches one monolayer (1 ML or $\Theta = 1$, i.e. 2 Se atoms/1×1 unit cell) the LEED spots are sharpened, indicating either the formation of a stable monolayer or the saturation of the Se–As exchange in the first layer or first two layers of the substrate. The strong interaction between the GaAs(110) surface and deposited Se already for low coverages ($\Theta = \frac{1}{4}$) has also been shown in electron energy loss spectroscopy (EELS) experiments [4,5]. Very recent experimental studies by Schröter et al. [6] reported the conservation of the 1×1 LEED structure after extensive Se treatment and subsequent annealing for the GaAs(110) surface. Their core level studies indicate the existence of at least two distinct bonding sites for Se on the surface and As desorption upon annealing. The thickness of the reacted layer was roughly estimated to amount to 1–2 atomic layers. By means of angle-resolved photoemission spectroscopy (ARPES) the authors found

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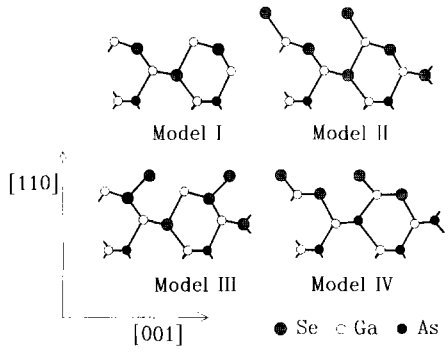

Fig. 1. Side view of four models for atomic arrangements at Se reacted GaAs(110) surfaces.

several rather dispersionless bands of surface bound states and resonances. On the basis of these experimental data Schmidt and Bechstedt [7] performed ab initio pseudopotential calculations for a variety of surface stoichiometries and structural models. For the Se-deposited and annealed GaAs(110) surface four structural models were investigated in more detail. These models can be seen in Fig. 1. On the grounds of their energetics and the agreement between calculated and measured band structures models I and IV were considered to be favourable. However, due to the existing difficulty with the correct choice of the appropriate chemical potentials and remaining discrepancies between calculated and measured band structures the question of the exact atomic surface structure could not be answered fully.

In this paper we make a different approach to gain information about structural properties of the Se-reacted GaAs(110) surface. We present ab initio calculations of the surface core-level shifts (SCLS) of the species involved in the surface reaction for the four structural models (Fig. 1). As a testing ground for the reliability of our calculations we use the free GaAs(110) surface, where a number of experiments on the SCLS have been reported [8].

2. Method

The ab initio pseudopotential approach which has been used for this work is described at some length in Ref. [7]. Therefore it may suffice to discuss here only the peculiarities which are connected with the calculation of SCLS.

In the photoemission process the photon energy is transferred to a core electron, which thereby obtains an energy above the vacuum level and can be detected as a photoelectron. The SCLS is defined as the difference in kinetic energy of an electron that has been emitted from a surface atom compared to one originating from a bulk atom. Usually, SCLS are interpreted in terms of the initial-state picture. Thereby the SCLS is explained by the energy difference of the core states localized at the surface and in the bulk, respectively. The single-particle energy eigenvalues of these core states depend on the chemical environment and therefore differ in general. The initial-state contributions to the SCLS are not directly accessible in pseudopotential theory, but can be calculated via the self-consistent potential extracted from a ground-state slab calculation [9]. The difference in the energy eigenvalues for the 3d states of surface and bulk atoms corresponds to the difference of the matrix elements of the respective Hamiltonians with the 3d orbitals localized at surface and bulk atoms. The initial-state SCLS is therefore given by:

$$\Delta E_{3d}^{is} = \langle \psi_{3d}(|\boldsymbol{R}_s - \boldsymbol{r}|)|V_{eff}(\boldsymbol{r})|\psi_{3d}(|\boldsymbol{R}_s - \boldsymbol{r}|)\rangle - \langle \psi_{3d}(|\boldsymbol{R}_b - \boldsymbol{r}|)|V_{eff}(\boldsymbol{r})|\psi_{3d}(|\boldsymbol{R}_b - \boldsymbol{r}|)\rangle. \quad (1)$$

The calculation of the SCLS in the initial-state picture as described above does not account for relaxation effects. In the photoemission experiment the initial state consists of a crystal in its ground state plus a photon, and the final state is a crystal with a core hole plus a photoelectron. If we assume the Fermi-level as a reservoir of electrons the crystal remains neutral. The charge of the core hole is compensated by a delocalized electron at the Fermi energy. The final-state SCLS can therefore be calculated as an energy difference between neutral slabs containing screened core holes at the surface or in a bulk-like environment of neutral slabs. Thereby the relaxation of the crystal electrons in the presence of the electron–hole pair is fully accounted for. For the explicit calculation we generated 'excited' Bachelet–Hamann–Schlüter-like pseudopotentials [10] in Kleinman–Bylander form [11,12] with a screened 3d core hole, i.e. the occupation of the 3d level is decreased by one, and the number of the 4p electrons is increased accordingly. This procedure

has been suggested by Pehlke and Scheffler [13] and more or less successfully applied to Si(100) and Ge(100) surfaces.

Our calculations were performed with periodic supercells, which contain 11 to 14 substrate(110) and adatom layers and a vacuum region equivalent in thickness to at least 6 GaAs(110) layers. For calculations of initial-state SCLS a 1×1 surface periodicity has been used whereas calculations of final-state SCLS have been done with 1×2 unit cells in order to minimize the interactions between the screened core holes in neighboured cells. In order to account for the electronic inequivalence of the two slab sides induced by the substitution of 'regular' by 'excited' atoms we apply a dipole correction to compensate for the artificial electrostatic field. All calculations were performed with an energy cutoff of 15 Ryd for the plane-wave basis set. The $\boldsymbol{k}$-space integration was performed by a summation over 4 special points in the irreducible part of the surface Brillouin zone. We have performed a series of tests with larger unit cells, higher energy-cutoff and more $\boldsymbol{k}$-points to make sure that our results are reliable.

3. Results and discussion

The GaAs(110) surface is probably the most intensively studied surface of binary semi-conductors. A series of experiments [8] arrived at quite similar results for the observed SCLS. The surface component of the Ga atom 3d photoelectrons is reported to have a 0.28 eV lower kinetic energy than the photoelectrons originating from bulk Ga atoms. For the As atoms a shift of about 0.37 eV in the opposite direction has been reported. In Fig. 2a we show our calculated results for the initial-state SCLS. These results were obtained for a relaxed surface geometry with geometrical details determined in perfect agreement with Ref. [14]. With respect to the innermost atoms we observe the surface components of the Ga (As) atoms to be shifted by -0.18 (0.36) eV. Thus our calculated values in the initial-state picture compare reasonably with experiment. If we consider the difference in binding energy between the first and second layer cation we observe a somewhat larger splitting of -0.22 eV which agrees slightly better with the experiment. It is interesting to note that the

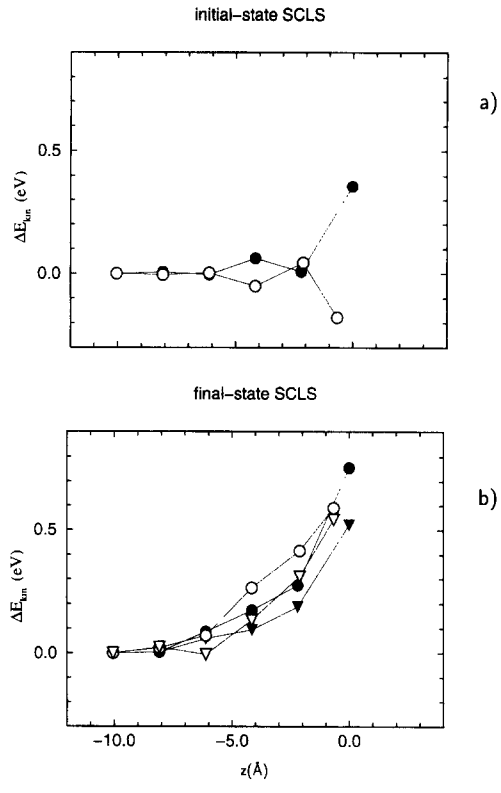

Fig. 2. Calculated SCLS for GaAs(110) in the initial and final-state picture. The energetic position of the 6th layer atoms has been chosen as energy zero. Ga (As) atoms are denoted by white (black) symbols. In case of final-state SCLS results for the electronic relaxation are denoted by circles whereas triangles are used for electronic and atomic relaxation.

core-level shifts both for anions and cations alternate in each layer. Obviously the change of the surface electronic structure due to the relaxation of the uppermost atoms influences the effective potential even several layers underneath the surface. However, the agreement between measured and calculated SCLS is not perfect. In particular the negative shift for the surface Ga atom is underestimated by about 0.1 eV.

One could assume that the remaining discrepancies are due to the complete neglect of relaxation effects. These effects are accounted for in the final-state picture. Our results for the final-state SCLS are shown in Fig. 2b. With black (white) circles the results for the SCLS of the anions (cations) in the frozen-lattice approximation are shown. In serious disagreement to experiment both surface components are now shifted to higher kinetic energies. If we

subtract the shifts due to initial-state effects we end up with the energies released upon the relaxation of the electronic wave functions. They amount to 0.40 (anion) and 0.77 eV (cation). Both the sign and the magnitude of the relaxation induced shifts can be understood in a simple physical picture. The accommodation of the screening electron is more easily done at the surface compared to the bulk, where the strong sp^3 hybridisation has to be disturbed. In particular the empty dangling bond at the surface Ga atom (the lowest unoccupied state in the GaAs(110) surface band structure, see e.g. Ref. [14]) allows a very efficient screening of the core hole in a surface cation. Therefore the relaxation of the electronic wave functions releases a particularly high amount of energy in case of surface Ga atoms. One possible reason for the complete disagreement between the calculated SCLS in the final-state picture and experiment could be that in addition to the electronic relaxation also the lattice relaxation has (at least partly) to be taken into consideration. In order to check this possibility we also performed calculations where all atoms in the slab were allowed to relax until they occupied their equilibrium positions. The results are shown in Fig. 2b by means of black (white) triangles for the anions (cations). Obviously the overestimation of the relaxation effects with respect to the experimentally determined SCLS is somewhat smaller, but the results are still by no means comparable to the experimental findings. Summarizing the results for the SCLS in the initial and final-state picture we conclude that the initial-state effects are most important for the explanation of the experimental data, at least in case of the GaAs(110) surface. The reason seems to be the dynamics of the photoemission process. Due to the relatively large band gap the screening is less complete and the relaxation of the electronic wave functions is too slow to have substantial influence on the kinetic energy of the photoelectrons. This interpretation is also consistent with earlier model calculations which explain the SCLS for III–V(110) surfaces

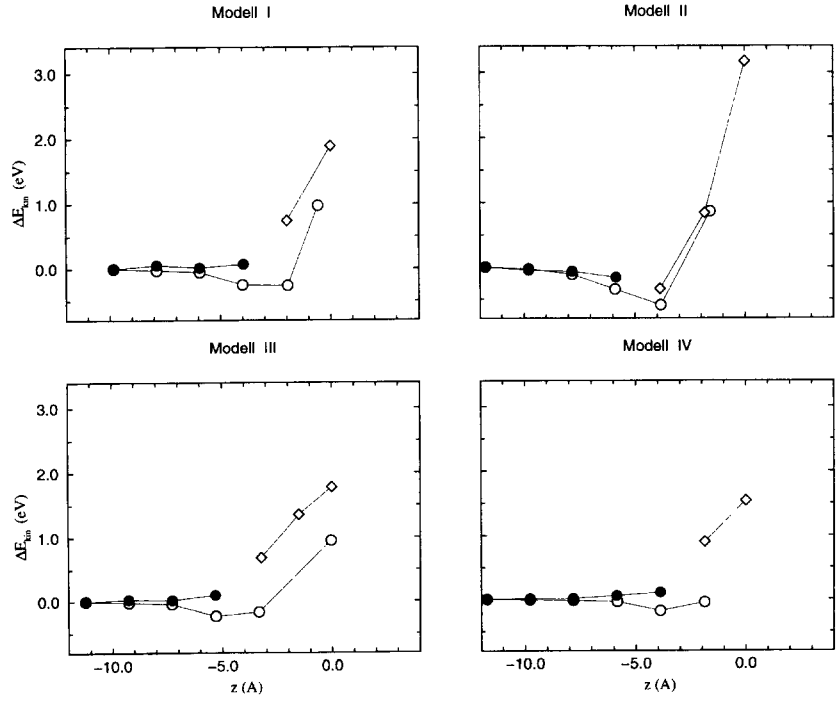

Fig. 3. Calculated initial-state SCLS for four structural models for the Se reacted GaAs(110) surface. Ga, As, and Se atoms are denoted by white circles, black circles and white diamonds. The energetic position of the innermost layer has been chosen as energy zero for Ga and As atoms. The energy zero for the Se atoms refers to a separate bulk calculation for Se in its trigonal modification.

solely on the ground of the different Madelung energies for bulk and surface [8]. It is interesting to note that Pehlke and Scheffler [13] also find a shift to higher kinetic energies for the photoelectrons originating from the surface atoms compared with the experimental findings for Si and Ge (100) surfaces. However, due to the smaller surface band gaps in these cases and the accordingly changed relaxation dynamics the explanation of the SCLS in the final-state picture is more satisfactory.

On the basis of the experience gained with the free GaAs surface we will restrict ourselves to the initial-state picture in the following discussion of SCLS for Se/GaAs(110). Characteristic features of the core level spectra for Se-deposited surfaces have been described recently by Schröter et al. [6]. Due to the Se treatment three components were reported to be necessary to fit the As component. They originate from bulk GaAs, As bound to Se, and liberated elemental As. Upon annealing to 710 K the latter two components nearly disappear and there is only the GaAs bulk component left. The Se induced change in the lineshape of the Ga 3d emission was said to be more complicated to analyze. Probably the Ga surface component is replaced by a reacted chemically shifted component at almost the same energy. Two components were needed to describe the Se signal. Using the energy position of the elemental Se as a reference they were reported to be 0.4 and 1.0 eV shifted to higher kinetic energy. As discussed above four structural models have been proposed to explain the experimental findings for the annealed Se/GaAs surface. These models are sketched in Fig. 1. For the relaxed geometries of these models [7] we calculated the initial-state SCLS. The results are shown in Fig. 3. For all four models we observe only moderate shifts for the As components which is in agreement with experimental findings. However model I, II and III have Ga surface components which are shifted to higher kinetic energies in contrast to the experimental statement. Model II and III can also be excluded since they show three Se 3d components with different energies (seperated by 0.5 and 2.3 eV for model II and 0.4 and 0.7 eV for model III). Only model IV is consistent with the experimental findings. The two Se 3d components are separated by 0.6 eV. In order to approximate the chemical shift with respect to elemental Se we calculated bulk selenium in its trigonal configuration. The two Se components of model IV are shifted by about 0.9 and 1.5 eV towards higher kinetic energy. This shift is somewhat overestimated compared to the experiment. The sign of the Se shift with respect to elemental selenium agrees well with electronegativity arguments and a detailed analysis of the electronic structure [7]. Se is more electronegative than Ga and As [15] and therefore additional charge is accumulated around the Se atoms. The charge accumulation decreases the binding energy of the core electrons. The surface Ga components of model IV are placed at slightly higher energies than found experimentally. However, this overestimation should perhaps not be taken too seriously since the experimentalists had difficulty to resolve the Ga signal. In agreement with the experiment we observe nearly no shift in the As signal.

4. Conclusions

We performed ab initio calculations of the SCLS for free and Se-treated GaAs(110) surfaces. For the free GaAs(110) surface we show that the experimental results can be understood in the initial-state picture. Inclusion of relaxation effects grossly deteriorates the results, indicating the different time constants for photoemission and relaxation processes.

On the basis of our calculated SCLS for different atomic configurations for Se/GaAs we can with certainty exclude three out of four discussed models. One model shows reasonable agreement in the calculated and measured SCLS. We therefore strongly support an exchange geometry where the surface As atoms are substituted by Se and further Se atoms are bound to the surface Ga atoms.

We have shown that the comparison of calculated and measured SCLS can be used as a powerful tool to determine surface chemistry and atomic structure.

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