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3d core-level shifts at Se/GaAs(110)

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Abstract

We determine 3d surface core-level shifts (SCLS) for clean and Se-deposited GaAs(110) surfaces by means of *ab initio* pseudopotential calculations. The experimental findings for the clean GaAs(110) surface can be described within the initial-state picture. If relaxation effects are taken into account we find a distinct overestimation of the SCLS for both As and Ga. We conclude that final-state effects play only a minor role due to the dynamics of the photoemission process for the GaAs(110) surface. The validity of the initial-state picture for III–V(110) surfaces is further corroborated by calculations on InP and GaP. In order to clarify the surface chemistry of the Se/GaAs(110) interface we calculate the 3d core level shifts of Ga, As and Se for four structural models of an exchange-reacted GaAs(110) surface. Only one of these models gives rise to a reasonable agreement between calculated and measured shifts. Our calculations support a geometry where each surface As atom is substituted by Se and one further Se binds to the surface Ga atom.

Keywords: Chemisorption; Density functional calculations; Gallium arsenide; Gallium phosphide; Indium phosphide; Low index single crystal surfaces; Photoelectron emission; Selenium; Semiconductor–semiconductor interfaces

1. Introduction

In general core states do not participate in the chemical bonding. However, core levels are influenced by the bonding, and, as localized spectators, provide a measure of the environment around an atom. On that account core-level spectroscopy is routinely used experimentally for the characterization of clean and adsorbate-covered surfaces. Compared to the huge amount of experimental studies, relatively little theoretical efforts have been made to quantify the different contributions to surface core-level shifts (SCLS). Pehlke and Scheffler [1] have pointed out that relaxation effects induced by the

screening of the photon-induced core hole play an important role for the SCLS, at least in case of (100) surfaces of Si and Ge. This calls into question the usual interpretation of SCLS in terms of initial-state effects due to charge transfer and/or the reduced coordination of surface atoms [2]. The aim of our work is (i) to investigate the origin of the SCLS at the clean GaAs(110) surface and (ii) to utilize the calculated shifts in the binding energies to cast light on the surface chemistry of the Se/GaAs(110) system.

In spite of a number of experiments [3–5] on the Se/GaAs(110) interface, the actual surface chemistry is far from being understood. Schröter et al. [5] showed recently that the 1×1 surface symmetry is conserved after extensive Se treatment and subsequent annealing of the GaAs(110) surface. Their

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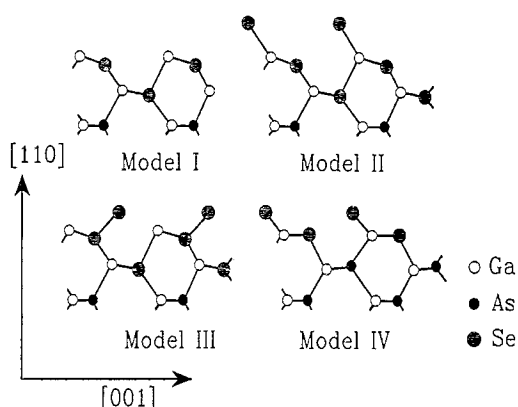


Fig. 1. Side view of four models for atomic arrangements at Se-reacted GaAs(110) surfaces.

core-level studies indicate the existence of at least two distinct bonding sites for Se on the surface and As desorption upon annealing. The reacted layer was estimated to be one or two atomic layers thick. In order to explain the experimental data, Schmidt and Bechstedt [6,7] 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 (cf. Fig. 1) were investigated in more detail. On grounds of their energetics and the agreement between calculated and measured bands models I and IV were considered to be favourable. However, due to the difficult choice of the appropriate chemical potentials and remaining discrepancies between calculated and measured surface bands, the question of the exact atomic structure could not be answered finally. Therefore, in this paper we probe the surface atomic structure by comparing calculated shifts of 3d photoelectrons with the experimental findings of Ref. [5].

2. Method

We employ an *ab initio* pseudopotential approach described at some length in Ref. [6]. In the following we will discuss only the peculiarities connected with the calculation of SCLS. In the photoemission (PE) process the photon energy is transferred to a core electron, which thereby obtains an energy above the vacuum level and can be detected as photoelectron. The kinetic energy of the photoelectron is given by

$$E_{\text{kin}} = \hbar\omega - \epsilon_i - \Phi + E_{\text{relax}}, \quad (1)$$

where $\hbar\omega$ denotes the photon energy, ϵ_i is the respective orbital energy, Φ denotes the work function and E_{relax} is the part of the final-state relaxation energy which is transferred to the photoelectron during the emission. 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 the bulk. Usually, SCLS are interpreted in terms of initial-state effects, i.e., explained by the energy difference $\Delta\epsilon_i$ of the respective bulk and surface core states [2]. The energy eigenvalues of these core states depend on the chemical environment and differ in general. These 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 groundstate slab calculation [8]. The difference in the energy eigenvalues for the 3d states of bulk and surface atoms corresponds to the difference of the matrix elements of the respective Hamiltonians with the 3d orbitals localized at bulk (R_b) or surface (R_s) atoms. The initial-state SCLS is thus given by

$$\begin{aligned} \Delta\epsilon_{3d} = & \langle \psi_{3d}(|R_b - r|) | V_{\text{eff}}(r) | \psi_{3d}(|R_b - r|) \rangle \\ & - \langle \psi_{3d}(|R_s - r|) | V_{\text{eff}}(r) | \psi_{3d}(|R_s - r|) \rangle. \end{aligned} \quad (2)$$

The calculation of the SCLS in the initial-state picture as above does not account for relaxation effects. However, from Eq. (1) it is obvious that also different relaxation effects E_{relax} in the bulk and at the surface may contribute to the SCLS. In the PE experiment the initial state consists of a crystal in its groundstate 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 for by a delocalized electron at the Fermi energy. If the photoelectron experiences the full amount of the relaxation energy released in response to the presence of the electron-hole pair, the final-state SCLS can be calculated as energy difference between neutral slabs containing screened core holes at the surface or in a bulk-like environment. For the explicit calculation we generated "excited" Bachelet-Hamann-Schlüter-type pseudopo-

tentials [9] in Kleinman–Bylander form [10,11] with a screened 3d core hole, i.e., the occupation of the 3d level is decreased by one, and the number of 4p electrons is increased accordingly. This procedure has been suggested by Pehlke and Scheffler [1].

Our calculations were performed with periodic supercells, which contain 11 to 14 substrate(110) and adatom layers and a vacuum region equivalent to at least six 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 core holes in neighbouring 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 k -space integration was performed by a summation over four 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 k -points to make sure that our results are reliable. The numerical accuracy of our results is about 0.05 eV.

3. Results and discussion

A series of PE experiments arrived at quite similar results for the SCLS of the free GaAs(110) surface [2]. The surface component of the Ga-atom 3d photoelectrons has 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. The change of the electronic structure due to the relaxed GaAs surface influences the effective potential even several layers underneath the surface. 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

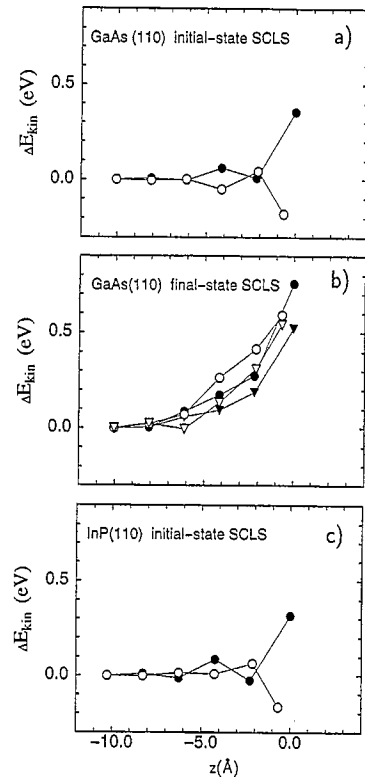


Fig. 2. Calculated SCLS for GaAs(110) in the initial- and final-state picture. The energetic position of the sixth layer atoms has been chosen as energy zero. In the case of final-state SCLS results for the electronic relaxation are denoted by circles whereas triangles are used for electronic and atomic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

-0.22 eV, which agrees slightly better with experiment. However, the agreement between measured and calculated SCLS is not perfect; the negative shift for the surface Ga atom is underestimated by about 0.1 eV.

One possible reason for this discrepancy could be 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 initial-state shifts calculated above, we end up with the energies released upon 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. In the final state the hole is screened. The screening charge is more readily accommodated at the surface compared to the bulk. 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. [12]) allows an efficient screening of the surface cation core hole. Thus the relaxation of the electronic wave functions releases a particularly high amount of energy in case of surface Ga atoms.

In search for an explanation for the disagreement between the calculated final-state SCLS and experiment we took on trial additionally the lattice relaxation into account, although its time constant should be large compared to the PE process. All atoms in the slab were allowed to relax until they occupy their equilibrium positions around the screened core hole. 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 energetical ordering of the SCLS is now even reversed compared to the experimental findings.

Summarizing the results for the SCLS in the initial- and final-state picture we conclude that initial-state effects are most important for the explanation of the experimental data for the GaAs(110) surface. The reason seems to be the dynamics of the photoemission process. Due to the relatively large bulk and surface band gap the screening is less complete and the relaxation of the electronic wave functions is too slow to influence the photoelectrons significantly. In order to corroborate our hypothesis, we calculated the initial-state SCLS also for InP and GaP(110) surfaces. In both cases we observe a similar degree of agreement with the experiments [2] as for GaAs(110). Results for InP(110) are shown in Fig. 2c. The interpretation of SCLS in terms of initial-state effects is also consistent with earlier model calculations which explain the SCLS for III–V(110) surfaces solely on the ground of the different Madelung energies for bulk and surface [2]. It is interesting to note that Pehlke and Scheffler [1] also overestimate the kinetic energies of surface photoelectrons for Si and Ge(100) surfaces. However, due

to the smaller surface and bulk band gaps in these cases and the accordingly changed relaxation dynamics, the explanation of the SCLS in the final-state picture is more satisfactory.

With respect to our results for the free surface we restrict ourselves to initial-state effects in the discussion of 3d shifts for Se/GaAs(110). Characteristic features of the core level spectra for Se-deposited surfaces have been described recently by Schröter et al. [5]. After Se deposition three components were needed to fit the As component, originating from bulk GaAs, As bound to Se, and liberated elemental As. Upon annealing the latter, two essentially disappear and there is only the bulk GaAs component left. The change in the lineshape of the Ga 3d emission was difficult to analyze. Probably the Ga surface component is replaced by a reacted chemically shifted component at almost the same energy. The Se signal consists of two components. With reference to elemental Se they are shifted by 0.4 and 1.0 eV to higher kinetic energy. Four structural models (Fig. 1) have been proposed to explain the experimental findings for the annealed Se/GaAs surface [6,7]. The calculated shifts in the binding energy for these models are shown in Fig. 3. For all models we

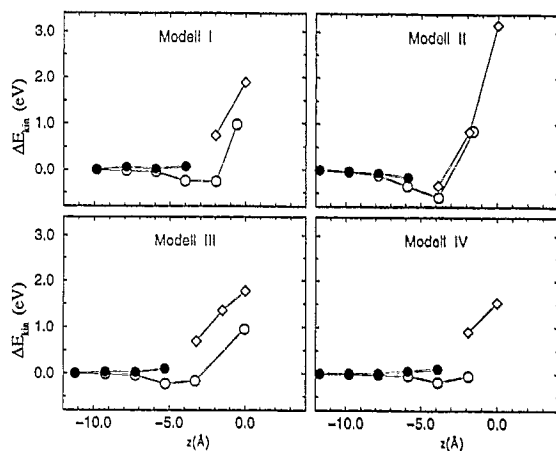


Fig. 3. Calculated initial-state SCLS for four structural models for the Se-reacted GaAs(110) surface. Ga, As and Se atoms are denoted by white circles, black circles and white diamonds. The energetic position of the innermost layer has been chosen as energy zero for Ga and As atoms. The energy zero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

observe small shifts for the As components in agreement with experiment. However model I, II and III have Ga surface components shifted to higher kinetic energies in contrast to the experimental statement. Model II and III can also be excluded on grounds of the three Se 3d components (separated 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 estimate 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 is slightly overestimated compared with experiment. The sign of these shifts with respect to elemental selenium agrees well with electronegativity arguments and a detailed analysis of the electronic structure [6]. Se is more electronegative than Ga and As, 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.

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 PE and relaxation processes. The initial-state picture seemingly holds also for other III–V(110) surfaces, as we have shown for InP and GaP.

On the basis of our calculated shifts 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.

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References

- [1] E. Pehlke and M. Scheffler, *Phys. Rev. Lett.* 71 (1993) 2338.
- [2] W. Mönch, *Semiconductor Surfaces and Interfaces* (Springer Verlag, Berlin, 1993), and references therein.
- [3] D.W. Tu and A. Kahn, *J. Vac. Sci. Technol. A* 3 (1985) 922.
- [4] C.R. Bonapace, D.W. Tu, K. Li and A. Kahn, *J. Vac. Sci. Technol. B* 3 (1985) 1099.
- [5] T. Schröter, A. Chassé, I. Eckardt, K. Tiedge, N. Wagner, D.R.T. Zahn, C. Nowak, A. Hempelmann and W. Richter, *Surf. Sci.* 307–309 (1994) 650.
- [6] W.G. Schmidt and F. Bechstedt, *Phys. Rev. B* 50 (1994) 17280.
- [7] W.G. Schmidt and F. Bechstedt, *Surf. Sci.* 331–333 (1995) 557.
- [8] J. Dabrowski, E. Pehlke and M. Scheffler, in: *Proceedings of the 21st International Conference on the Physics of Semiconductors*, Eds. P. Jiang and H.-Z. Zheng (World Scientific, Singapore, 1992) p. 389.
- [9] G.B. Bachelet, D.R. Hamann and M. Schlüter, *Phys. Rev. B* 26 (1982) 4199.
- [10] L. Kleinman and D.M. Bylander, *Phys. Rev. Lett.* 48 (1982) 1425.
- [11] X. Gonze, P. Käckell and M. Scheffler, *Phys. Rev. B* 41 (1990) 12264; X. Gonze, R. Stumpf and M. Scheffler, *Phys. Rev. B* 44 (1991) 8503.
- [12] J.L.A. Alves, J. Hebenstreit and M. Scheffler, *Phys. Rev. B* 44 (1991) 6188.