Se/GaAs(110): Atomic and electronic structure

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The molecular-beam deposition of selenium onto ultrahigh-vacuum cleaved GaAs(110) surfaces and subsequent annealing leads to the formation of a thin, stable, Se-rich reacted layer with distinct structural and electronic properties. We perform *ab initio* calculations based on density-functional theory of the Se-deposited GaAs(110) surface for different coverages, $\Theta = \frac{1}{4}, \frac{1}{2}, 1$, and $\frac{3}{2}$, and various structural models. In the $\Theta = \frac{1}{4}$ case we give a detailed analysis of the total-energy surface of the Se/GaAs(110) system. The highest adsorption energy is found for Se atoms bound in an interchain bridging position. For higher coverages we discuss a variety of adsorption models and compare these with exchange reactions in terms of the thermodynamic stability. We observe a tendency for an exchange of As and Se atoms in the uppermost layers and subsequent segregation of As at the surface. For the energetically most favored structures, we compare the calculated band structures with data from soft-x-ray photoemission spectroscopy.

I. INTRODUCTION

The interfaces formed when overlayers are deposited onto atomically clean surfaces of III-V compound semiconductors have attracted considerable interest. In the recent past a great deal of work, experimental as well as theoretical, has been published on the atomic and electronic structure of ordered overlayers of group-I, -III, and -V elements on III-V(110) surfaces. Only a few studies concerning the adsorption of group-VI elements have been reported. However, 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,[1–4] the understanding of the actual formation process, the bonding geometry of the adsorbate, and the related electronic structure underlying the passivation are far from being complete.[5] The same holds for the Fermi-level pinning in the case of group-VI adsorption on the GaAs(110) cleavage face.[6] 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[7] 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 Auger electron spectroscopy peak amplitudes show that upon the Se deposition the As peak saturates for lower coverages than the Ga peak ($\Theta \approx 2$), suggesting that free As, as a product of a possible interface exchange reaction, moves through the Se layers and segregates at the surface. 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 experiments.[7,8]

X-ray photoelectron spectroscopy (XPS) measurements by Sandroff *et al.*,[9] infer significant Se-As bond formation at the Se-treated GaAs surface. This is somewhat in contrast to the study of Tu and Kahn[7] and also to a recent study by Maeda *et al.*[10] The latter group proposed for the Se-treated GaAs(001) surface an atomic arrangement which is close to the Ga_2Se_3 structure. Scimeca *et al.*[4] found that deposition of Se on GaAs at room temperature yields As-Se bonding. At higher temperatures Ga-Se bonding accompanied with As-Se exchange was observed.

Very recent experimental studies by Schröter *et al.*[11] 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 were interpreted to indicate the existence of at least two distinct bonding sites for Se on the surface and in terms of an As desorption upon annealing. From the intensity variation of the bulk contributions to the core-level emission the thickness of the reacted layer was roughly estimated to amount to 1–2 atomic layers. An occupied part of the surface band structure was derived from angle-resolved photoemission spectroscopy (ARPES) investigations. The authors reported several rather dispersionless bands of surface bound states and resonances.

Schröter *et al.* have also proposed two models of the atomic arrangement at the well-ordered GaAs(110)1×1 surface after Se treatment and annealing. A Se-As exchange reaction in the first or in the first two GaAs(110) atomic layers together with an overlayer of adsorbed Se atoms were assumed. The Se-induced modulations of the measured angle-dependent photoelectron diffraction signals and the bulk core-level intensities have been

compared with theoretical calculations for these models. However, the angular dependences of the calculated patterns of the substrate signals on the model parameters were found to be too small to favor decisively one model over the other.

In this paper, we present accurate self-consistent calculations to determine the atomic structure and the electronic properties of the Se-treated (110) surface of GaAs for different coverages. The organization of the paper is as follows. Section II contains a brief review of the underlying *ab initio* theory. Section III reports the computed results for various coverages, geometries, and surface reactions. The results are discussed together with structural data available from experiment. A consistent picture of the Se adsorption and Se-As exchange after annealing is developed. In Sec. IV, calculated band structures are compared with ARPES results. The changes of the ionization energy in terms of the electron transfer are discussed. Section V contains a brief summary.

II. METHOD

Our calculations are based on the density-functional theory (DFT).[12,13] The electron-ion interaction is treated by norm-conserving, *ab initio*, fully separable pseudopotentials[14] as given by Stumpf *et al.*[15] The many-body electron-electron interaction is described within the local-density approximation (LDA), more precisely within the Ceperley-Alder scheme[16] as parametrized by Perdew and Zunger.[17] We use the repeated-slab method to simulate the semiconductor surface. The system is periodic parallel to the surface and we introduce an artificial periodicity perpendicular to the surface, defining a large three-dimensional unit cell. Our slab contains eight layers of GaAs(110) (1×1 and 1×2 surface periodicities as discussed later), both sides covered with Se or GaAs(110) layers, where the As atoms are partly or completely substituted by Se atoms. The total length of the unit cell in [110] direction equals 20 layers of GaAs(110), ensuring a vacuum region equivalent to at least six atomic layers. These parameters have been found to give well-converged results both with respect to the atomic geometry and the band structure. In the calculation of the Born-Oppenheimer surface of the total energy for a single Se atom adsorbed on a (1×2) unit cell of GaAs(110) we use only six layers of GaAs(110).

In order to test the Se pseudopotential, we performed a series of calculations for bulk selenium in its trigonal modification. For an energy cutoff equal to 18 Ry for the plane wave basis set, the ground-state properties of the crystallized Se as the equilibrium lattice constant, the bulk modulus, the total energy and the band structure were found to be well converged. The theoretical lattice constants $a = 4.34$ Å and $c = 4.93$ Å have been found in excellent agreement with experimental data (0.4% too small), but the calculated fundamental band gap $E_g = 1.25$ eV was determined too small (about 33%), as a well known DFT-LDA failure.[18] In an earlier study,[19] it has already been shown that the ground-state properties of GaAs are well converged using 18 Ry as an energy cutoff. This encouraged us to conclude that the choice of the number of plane waves corresponding to the energy cutoff of 18 Ry is adequate for the present study.

The $\mathbf{k}_{||}$ integration is replaced by a sum over four special points[20] in the irreducible part of the surface Brillouin zone (SBZ). In the calculation of the total-energy surface for a single Se atom adsorbed on a (1×2) surface unit cell only the mean-value point is used. With this $\mathbf{k}_{||}$-point sampling, as a test, the structural and electronic properties of the free relaxed GaAs(110) were determined in nearly perfect agreement with those derived by other authors.[19]

In order to determine the equilibrium positions, the atoms of the two innermost substrate layers are kept frozen whereas all other atoms are allowed to relax until the total energy and the forces are minimized. Simultaneously with the relaxation of the ions the single-particle wave functions are brought to self-consistency within a Car-Parrinello-like minimization scheme of the total-energy functional[21] using a modified computer code of Stumpf and Scheffler.[22]

In several cases, we also derive adsorption energies per adatom. These are calculated as the difference between the total energy of the covered surface and the sum of the total energies of the clean relaxed surface and the free Se atom. The adsorption energy is positive when the deposition process is favorable, i.e., energy is gained. The total energy of the free atom is calculated with the same energy cutoff and exchange-correlation functional as applied to the slab calculations, but spin-polarization effects are taken into account. In general the adsorption and cohesive energies calculated within such procedure are somewhat larger than experimental values, due to the application of the LDA.[23] Nevertheless, the results provide a consistent comparison between the different geometrical models considered in this paper.

III. STRUCTURE AND ENERGETICS

A. Submonolayer coverage

In order to get an idea about the preferred adsorption sites of selenium on GaAs(110) in the initial stage of the interface formation and to describe the diffusion behavior of Se atoms, we calculate the total-energy surface for one surface Se atom at more than thirty positions within the irreducible part of the GaAs(110) surface unit cell. We choose a 1×2 surface unit cell according to a coverage of $\Theta = \frac{1}{4}$, in order to reduce interactions between the adsorbed Se atoms and in order to allow the substrate to relax properly. In these calculations the adsorbate coordinates are fixed parallel to the GaAs(110) surface, whereas the adsorbate-surface distance as well as the atomic positions of the substrate are fully relaxed.

The resulting Born-Oppenheimer energy surface of such a test surface Se atom is shown in Fig. 1. We find a marked minimum of the total energy in a posi-

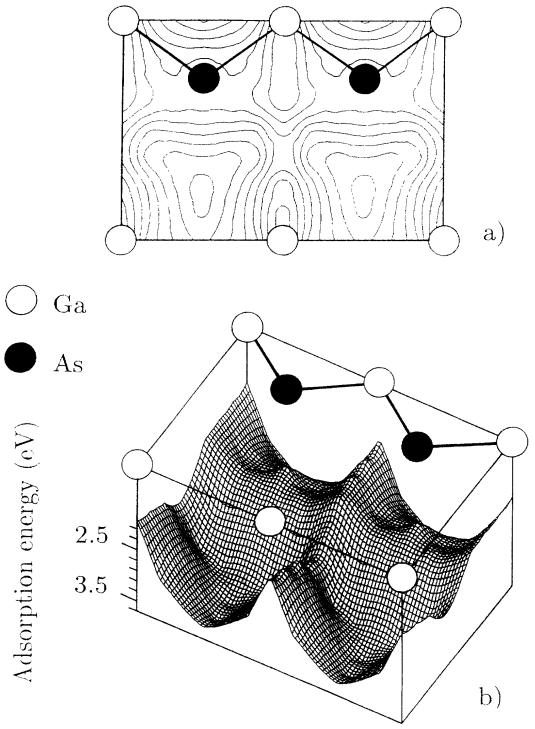

FIG. 1. The total-energy surface of the Se/GaAs(110) ($\Theta = \frac{1}{4}$) system is plotted (a) as a contour plot and (b) as a three-dimensional perspective view versus a (1×2) surface unit cell.

tion where the Se is threefold coordinated in between the As atom and the two Ga atoms belonging to neighboring Ga-As surface chains. The adatom is bound in an interchain bridging position which is roughly equidistant from the As and the Ga. The bond lengths to the substrate atoms, $d_{\mathrm{AsSe}} = 2.55$ Å and $d_{\mathrm{GaSe}} = 2.70$ Å, are somewhat larger than the sums of the covalent radii,[24] indicating the partially ionic character of the bonds. There are no scanning-tunneling microscopy (STM) studies of the initial stages of the selenium adsorption on GaAs(110). However, STM studies[25] of another group-VI element, atomic oxygen, suggest the same adsorption site as found to be energetically favorable for Se. A contradicting position has been derived from an earlier tight-binding calculation of Se adsorption on GaAs(110) by Menon and Allen.[26] They found that the Se atom binds above the surface at a Ga-Ga bridge site, midway between two Ga atoms. Considering Fig. 1, one observes that this position is 0.25 eV higher in energy than the threefold coordinated position. This discrepancy may be due to the non-self-consistency of the applied tight-binding method. In recent DFT-LDA calculations also the total-energy surfaces of sodium[27] and antimony[28] adsorbed on GaAs(110) have been calculated. For these adsorbates only small diffusion barriers (some tenths of an eV) in [1$\bar{1}$0] direction have been reported. Deep adsorption channels appear parallel to the Ga-As zig-zag chains, which are related to a strongly anisotropic adatom diffusion. These findings are in contrast to the behavior of selenium. The movement of Se atoms is prevented by surface energy barriers of about 1.1 eV in [1$\bar{1}$0] direction and 1.2 eV in [001] direction. Hence, a low-temperature formation of ordered Se adsorbates seems to be impossible, at least for low coverages $\Theta \leq \frac{1}{4}$.

The increase of the coverage from $\Theta = \frac{1}{4}$ to $\Theta = \frac{1}{2}$ by occupying both threefold coordinated adsorption sites in the (1×2) surface unit cell is accompanied by an increase of the adsorption energy per adatom by about 0.17 eV to 3.81 eV. The cohesive energy of bulk Se in its trigonal structure is only 3.44 eV applying the same calculational method. It gives an upper limit for the energy gain upon clustering. Its smallness can be interpreted in such a way that the formation of a two-dimensional overlayer of Se on the GaAs(110) surface is energetically preferred with respect to the formation of three-dimensional clusters, at least in the low coverage regime.

For $\Theta = \frac{1}{2}$, we end up with the atomic structure shown in Fig. 2. Its most important geometric parameters are given in Table I. In comparison with the (1×2) structure resulting in the $\Theta = \frac{1}{4}$ case, we observe a small decrease in the bond lengths. Both the As-Se bond as well as the Ga-Se bond are shortened by 0.03 Å. The resulting distances of 2.52 Å between As and Se and 2.67 Å between Ga and Se are larger than the sums of the covalent radii, $d_{\mathrm{AsSe}} = 2.36$ Å and $d_{\mathrm{GaSe}} = 2.42$ Å.[24] The differences indicate that the bonds between the adatoms and the substrate atoms are not completely covalent. The tendency for an enlargement of the bond lengths due to a remarkable ionic bonding contribution with respect to the sum of covalent radii is already observed for bulk Ga-Se materials. The in-plane bond length of the layered GaSe crystals amounts to $d_{\mathrm{GaSe}} = 2.46$ Å .[29] In the adsorption case, this effect is somewhat enhanced. Indeed, the valence electron density plotted in Fig. 3 indicates a rather ionic contribution to the bonds between selenium and the substrate atoms. The two electrons occupying

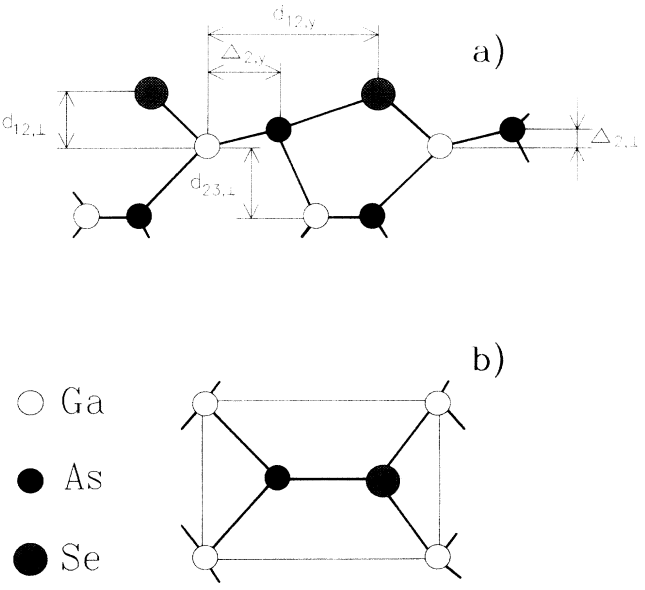

FIG. 2. Side (a) and top (b) views of the interchain bridging position of Se/GaAs(110)($\Theta = \frac{1}{2}$) system.

TABLE I. Structural parameters (in Å) of Se bound at the interchain bridging position on the GaAs(110)1×1 surface.

$d_{12,\perp}$	$d_{12,y}$	$\Delta_{2,\perp}$	$\Delta_{2,y}$	$d_{23,\perp}$
1.07	4.09	0.06	1.79	2.12

the dangling As bond at the free relaxed GaAs(110) surface are transferred to the adatom forming an octet shell. The sums of the ionic radii[30] of the substrate cations and the Se anion give rise to nearest-neighbor distances d_{AsSe} = 2.45 Å and d_{GaSe} = 2.60 Å, which are still somewhat smaller than the actual values. This may be understood by the fact that the surface Ga and As atoms are not completely ionized to Ga^{3+} and As^{5+}, as well as that the transfer of the two electrons from the substrate to the adsorbate is not complete due to relatively moderate differences between the electronegativities of Se and As as well as Se and Ga.[24] As a result of the electron transfer from the As dangling bond to the Se overlayer a reduction of the GaAs(110) surface relaxation occurs, similar to that in the case of other adsorbates as, e.g., Na.[31] In the $\Theta = \frac{1}{4}$ case the buckling of the substrate atoms underneath the selenium is reduced from 0.67 Å to 0.28 Å. For $\Theta = \frac{1}{2}$, the buckling of the substrate of 0.06 Å is nearly negligible (cf. Table I).

Starting from the atomic structure for $\Theta = \frac{1}{2}$ as shown in Fig. 2, exchange reactions at the surface are studied by interchanging the positions of the selenium atom and the arsenic atom in the first and second substrate layer, respectively. However, even after relaxation of the geometry the total energy per surface unit cell is increased by about 0.1 and 0.5 eV, respectively. Considering these energetical arguments, we do not expect the exchange reaction to be likely in an early stage of the adsorption.

B. Monolayer coverage

For the 1 ML coverage, i.e., two Se atoms per 1×1 unit cell (Θ=1), we consider five different structures which have been proposed in the past for the monolayer adsorption of Sb (Refs. 28, 32) and Al (Ref. 33) on GaAs(110). These are the so-called *epitaxial continued layer structure* (ECLS), the p^3 *structure*, the *epitaxial on top structure* (EOTS), and Se dimers in front of the Ga and As dangling bonds, respectively, and oriented in [001] direction. A top view of these structures is presented in Fig. 4. The ECLS, p^3*structure* and Se dimers in front of the Ga dangling bond yield with 3.42, 3.45, and 3.45 eV nearly the same adsorption energy per adatom. The EOTS with an adsorption energy of only 3.21 eV is somewhat less favorable. Se dimers in front of As dangling bonds give rise to the minimum-energy configuration and, therefore, with 3.63 eV, to the largest adsorption energy per adatom. The energy differences between the different structures are rather small compared for example with the case of Sb overlayers on GaAs(110).[28] We believe that this fact is related to the stronger ionic character of the adsorbate-substrate bonds and the unique direction of the electron transfer independent of the cation and anion character of the substrate atoms. Both effects give rise to an increase of the bond lengths and, in particular, to a rather insensitivity with respect to the bond angles in comparison to the more covalent Ga-Sb and Sb-As bonds. As a result Se zig-zag chains parallel to the [1$\bar{1}$0] direction and Se dimers in [001] direction in front of Ga dangling bonds have the same priority.

The adsorption energy per adatom of all considered Θ = 1 structures is lower than that found in the case of the $\Theta = \frac{1}{2}$ coverage. We relate this finding to the incomplete screening of the partially ionized Se atoms. Since both adatoms are slightly negatively charged, the repulsive Coulomb interaction has to be taken into the consideration. However, the adsorption energy of the minimum-energy configuration for Θ=1 remains about 0.2 eV larger than the cohesive energy per atom of 3.44

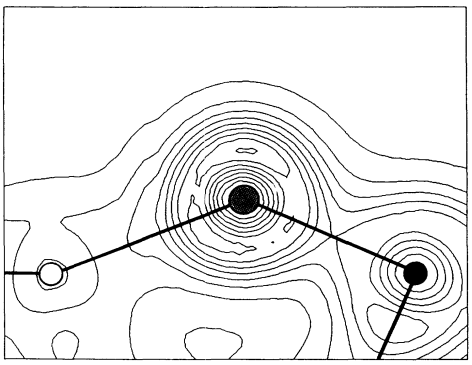

FIG. 3. Contour plot of the total valence pseudocharge density for a single Se atom per GaAs(110)1×1 surface unit cell adsorbed at the interchain bridging position. The contours (spaced by 0.015 $e\times$ Bohr^{-3}) are drawn along a folded plane perpendicular to the surface containing both the As-Se and Ga-Se bonds. Ga (As,Se) atoms are indicated by open (full, shaded) circles.

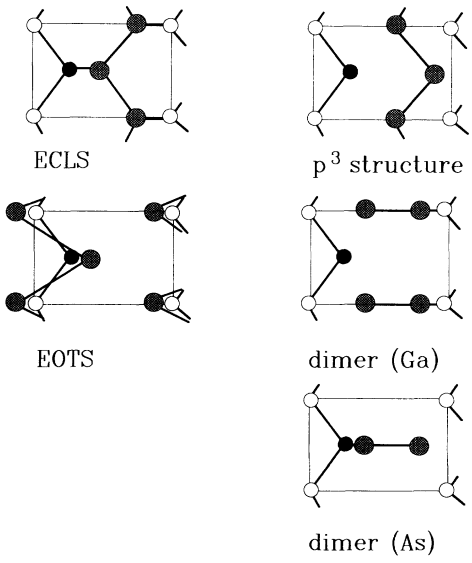

FIG. 4. Top view of different relaxed structures for a Θ=1 coverage of Se on GaAs(110)1×1. Ga (As,Se) atoms are indicated by open (full, shaded) circles.

eV obtained for bulk selenium. Consequently, we conclude that, similar to the $\Theta = \frac{1}{2}$ case, for a monolayer coverage no three-dimensional clustering of Se atoms should occur. This conclusion is quite in contrast to the Al adsorption on GaAs(110), where three-dimensional clustering of the Al atoms has been found to result in an appreciable energy gain.[33]

We have also studied an exchange of the neighbored Se and As atoms in the minimum-energy configuration for the $\Theta = 1$ coverage. However, as already stated in the $\Theta = \frac{1}{2}$ case, such a simple exchange reaction does not decrease the total energy of the system. On the contrary, even after geometry relaxation the adsorption energy per Se atom is lowered by about 0.1 eV. This behavior is once more quite different from that of Al adsorption on GaAs(110). Starting from the minimum-energy configuration for an ordered monolayer Al on GaAs, the Al-Ga exchange increases the adsorption energy by about 0.2 eV.[33] We relate this difference to the different numbers of valence electrons for As and Se. The additional electron makes the original tetrahedral coordination of the As site less favorable for Se atoms.

C. Exchange reaction

The preservation of the GaAs(110)1×1 LEED pattern[7,11] after Se treatment and subsequent annealing is a strong indication that the original zinc-blende structure of the surface nearly persists. Thereby, the actual occupation of the atomic sites remains unknown. However, there are several arguments that Se deposited onto GaAs(110) is likely to undergo an exchange reaction with As. In the bulk case, Se forms at least two stable compounds with Ga, GaSe, and Ga_2Se_3.[34,35] With heats of formation $\Delta H_f = -35$ kcal/mol and $\Delta H_f = -85$ kcal/mol (Ref. 34) they are more stable than GaAs [$\Delta H_f = -17$ kcal/mol (Ref. 35)] from the thermodynamic point of view. Another argument is based on the fact that the covalent radius of the Se atom is smaller than that of As.[24] Exchange reactions are supported by a thermal treatment of the overlayer.[4,7,11] The thermal activation allows us to overcome the energy barriers between adsorbate structures and exchange geometries. The same arguments are not valid for an exchange between Ga and Se because the electronegativity of Se is larger by 0.74 than those of Ga.[24] Thus, Se avoids to occupy a site in the cation sublattice.

The starting point of our considerations concerning As-Se exchange at the surface is the experimental finding of a nonmetallic surface after Se deposition and annealing. Neglecting at first complicated many-particle interactions, one expects that an even number of substrate anions is substituted by selenium atoms. Otherwise, the odd number of electrons per surface unit cell will most probably cause half-filled surface bands and, therefore, a metallic behavior of the surface. On the other hand, experimental results[11] indicate a reacted layer of a thickness equal to 1–2 ML. Such a nonmetallic surface with two reacted atomic layers is clearly represented by model I in Fig. 5, where Se atoms occupy the As positions in the uppermost surface GaAs(110) layers, maintaining $\Theta=1$. Moreover, shifted components in the core-level spectra have been related by Schröter *et al.*[11] to the occurrence of As bound to Se and liberated elemental As, which, however, desorbs after annealing. Considering this suggestion we also study the models II and III in Fig. 5, where an additional Se atom is adsorbed in front of one of the surface dangling bonds per cell, i.e., $\Theta = \frac{3}{2}$. After occupying the former As sites in the two outermost substrate layers by Se, it remains an open question where the additional Se atom eventually adsorbs, at the Ga or the Se surface atoms. For the sake of completeness, we also investigate a structure where only the As atoms of the outermost substrate layer are exchanged by Se atoms and the dangling bonds located at the topmost Ga atoms are saturated by Se atoms ($\Theta = 1$). Summarizing the selection procedure we end up with four possible structures which are shown in Fig. 5. The structural models II and IV have already been proposed by Schröter *et al.*[11]

The atomic arrangements, given in Fig. 5, are optimized until the total energy reaches a minimum, and their equilibrium geometrical parameters are determined. Unfortunately, the energies of the different structures cannot be immediately compared due to the exchange reaction. Only the adsorption energies of 3.47 or 3.28 eV of the additional third Se atom per cell in the models II and III can be directly discussed by subtracting the total energy of model I from those of the structure under consideration. With the cohesive energy of 3.44 eV for bulk trigonal selenium, we conclude that further Se deposition on an exchanged surface might still lead to an ordered overlayer, where the additional Se atoms bind to Ga atoms.

In general, the energetics of the exchange and adsorption processes depend on the initial and final stages of the exchanged and deposited materials, and in particular, on the energies of Se atoms in the appropriate reservoir and those of the As atoms appearing at the surface or desorbing from the surface. Strictly speaking, in order to assess energetically the exchange reactions, one has to take the chemical potentials of Se and As into account. Their knowledge is especially important in the cases where the total number of atoms of a certain species are different for two systems under comparison. However, since the processes which are taking place at the surface are not known exactly, the choice of the appropriate chemical potentials is rather complicated. A further problem arises from the fact that we are limited to zero-temperature calculations. Nevertheless, in order to get a rough idea about the energetics at the surface we made the following two assumptions: (i) before the exchange reaction takes place, the selenium is bound in its minimum-energy configuration for $\Theta = 1$, i.e., dimers in front of an As dangling bond at the surface and (ii) the liberated arsenic is added to a large As bulk reservoir. Both assumptions do certainly not describe exactly the processes which occur at the surface, but the systematic errors of both assumptions should cancel each other partly. Following the tendency of lowering the adsorption energy by increasing the coverage as observed in going from the $\Theta = \frac{1}{2}$ to the 1 and taking into account the relatively small cohesive

energy of bulk Se, one could argue that the bonding energy of Se, before the exchange reaction takes place, is overestimated. On the other hand, we would expect that the liberated As forms amorphous caps or sticks in small clusters on the surface, so that the assumed chemical potential of bulk As does certainly exceed the experimental value as well. Actually, we use the chemical potential of bulk As as calculated in a careful study by Qian *et al.*[36] Their DFT-LDA calculation has been performed with the same exchange-correlation energy, pseudopotentials of the same Bachelet-Hamann-Schlüter type,[37] and the same energy cutoff of 18 Ry for the plane wave basis set. These accordance in the technical data allows us to adopt their result.

Making the above mentioned assumptions about the chemical potentials, the energy gain for an exchange of the As atoms of the two outermost substrate layers with Se (model I) amounts to 0.19 eV per surface unit cell. If additional Se atoms are bound to the Ga and Se atoms at the surface (models II and III) energy gains of 0.03 and −0.15 eV per surface unit cell result. This means that an exothermic exchange reaction can occur if certain conditions concerning the chemical potentials are fulfilled. Whether or not remaining Se atoms are bound to the surface Ga atoms certainly strongly depends on the actual experimental conditions such as annealing temperature and Se coverage. The energy gain per surface unit cell released upon the formation of the model IV amounts to

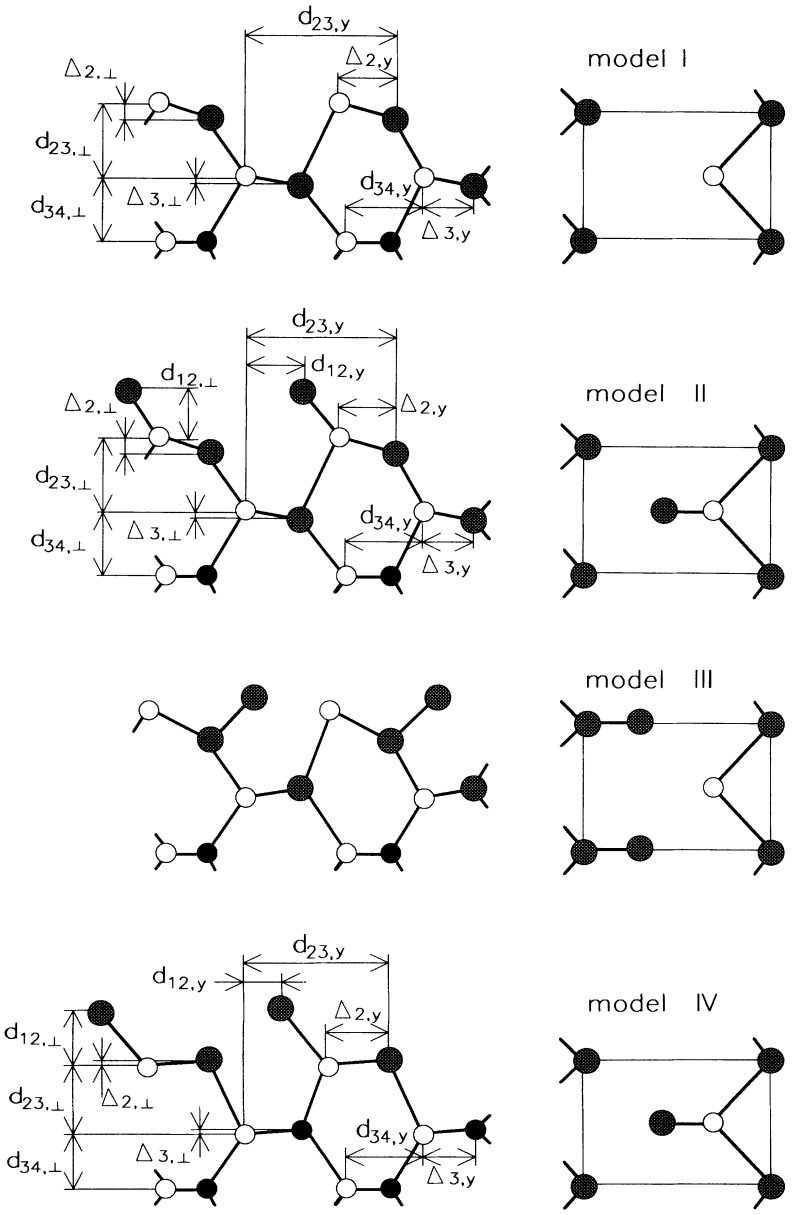

FIG. 5. Side and top views of four models for atomic arrangements at reacted GaAs(110) surfaces after Se-As exchange. Ga (As,Se) atoms are indicated by open (full, shaded) circles.

TABLE II. Structural parameters (in Å) of models I, II, and IV for an Se-As exchanged GaAs(110)1×1 surface.

	$d_{12,\perp}$	$d_{12,y}$	$\Delta_{2,\perp}$	$\Delta_{2,y}$	$d_{23,\perp}$	$d_{23,y}$	$\Delta_{3,\perp}$	$\Delta_{3,y}$	$d_{34,\perp}$	$d_{34,y}$
Model I			0.58	1.66	2.54	4.38	0.04	1.52	2.04	2.69
Model II	1.60	1.46	0.25	1.46	2.24	4.35	0.03	1.52	2.03	2.66
Model IV	1.89	1.43	<0.01	1.50	2.01	4.23	<0.01	1.40	1.96	2.77

0.16 eV. The geometry parameters of the three energetically favorable models I, II, and IV are listed in Table II. The most pronounced changes happen for the vertical distance $d_{23,\perp}$ of the Ga atoms in the first and second substrate layers which is considerably increased for models I and II. This is due to the reversal of the buckling in the first substrate layer after the As-Se exchange. In the case of model IV, this distance is closer to the ideal GaAs value, explaining the relatively high energy gain.

The geometry parameter are directly related to the bonding behavior of the surface atoms. As an example the valence charge density resulting for model I is given in Fig. 6. We find that the ionic character of the bonds is increased by the substitution of As by Se. However, the sp^3 character of the bonding orbitals is conserved within the lattice, as can be seen from the accumulated charge between Se and Ga. Because of the two additional electrons per surface unit cell, the relaxation in the first surface layer is different from the original one at the clean GaAs(110)1×1 surface. The rehybridization of the Ga atoms from sp^3 to sp^2 as observed for the free GaAs(110)1×1 surface[19] does not take place. There is no driving force for the topmost Ga atom to move inwards. On the contrary, a counterrelaxation appears. The bond lengths between the Ga of the second and third layer and Se vary between 2.29 and 2.49 Å nearly conserving the sum of the covalent radii of 2.42 Å (Ref. 24) in the innermost reacted layer. The bond lengths between the topmost Ga atom and the neighboring Se atoms are 2.59 and 2.84 Å, which are significantly larger than the sum of the covalent radii.

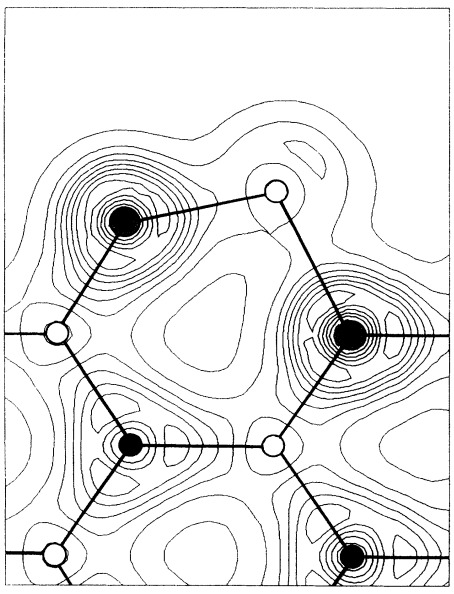

FIG. 6. Contour plot of the total valence pseudocharge density for Se/GaAs(110)1×1 (exchange model I in Fig. 5 with Θ=1). The contours (spaced by 0.015 e×Bohr^{-3}) are drawn along a folded plane perpendicular to the surface.

IV. ELECTRONIC PROPERTIES

A. Surface bands and orbital character

The identification of a certain structural model can be supported by studying the electronic properties. In Fig. 7, the band structures of the most favorable adsorbate structures (without any As-Se exchange) are plotted for the coverages $\Theta = \frac{1}{4}$, $\frac{1}{2}$, and 1. Only two-dimensional bands are selected, which describe bound states or at least nearly bound states for certain regions in the SBZ. For comparison, the experimental band-mapping results[11] for a coverage of about $\Theta = 1$ are indicated along ΓX and $\Gamma X'$. In principle, according to the electron counting model[38] all considered adsorbate structures should exhibit a nonmetallic character. The surface bands in the fundamental gap, which are mostly related to adsorbate-substrate bonds, should either be completely filled with electrons or empty. This holds in the $\Theta = \frac{1}{4}$ case. A small indirect gap $\Gamma - X'$ of 0.22 eV appears. The $\Theta = \frac{1}{2}$ adsorbate geometry deviates somewhat from our expectation. A negative indirect gap between the surface bands occurs at $\Gamma - X'$. However, this apparent metallicity may be interpreted as caused by the underestimation of the gaps within the DFT-LDA calculations.[18] For the half monolayer coverage the orbital character of the bands within the fundamental gap is explained in Fig. 8 for the states S_5 and S_6 near the Γ point. Both states are mainly related to orbitals localized at the adsorbate Se atom and the surface As atom. The energetically lower state S_5 has a pronounced p_z character. Energetically higher lying is the antibonding state S_6, where however also s orbitals contribute. Despite the full monolayer coverage ($\Theta = 1$), the most favorable Se dimers in front of As dangling bond produce a really metallic band structure. The surface bands exhibit a strong dispersion along high-symmetry lines of the SBZ. A considerable density of surface states appears in the fundamental gap. A vanishing or at least only tiny band gap has also been reported for Sb (Ref. 28) and Al (Ref. 33) dimers adsorbed on the GaAs(110) surface.

The dimer wave functions overlap along the [001] direction and therefore give rise to an one-dimensional metal.

Apart from a certain small shift, the occupied energy bands below the valence-band maximum (VBM) should be reliably reproduced within the applied DFT-LDA. That means, their calculated dispersion and orbital character should be observable in a band-mapping experiment like that by means of soft-x-ray photoemission spectroscopy in Ref. 11, as far as the underlying atomic geometries of the adsorbates are nearly correct. Such an agreement is, however, not observed in Fig. 7 between theory (solid lines) and experiment[11] (small filled circles). The calculated bands show a much stronger dispersion than experimentally observed. Also, the metallic behavior of the Se dimers on the surface contradicts the experimental findings. This is not surprising, since the ARPES data have been obtained for an annealed surface which was covered with a few monolayers Se before. On the other hand, the band structure calculations are performed for well-ordered submonolayer ($\Theta = \frac{1}{4}, \frac{1}{2}$) and monolayer ($\Theta = 1$) adsorbate structures. Therefore, the contradiction between the experimental results and the calculated surface bands for the ordered overlayer geometries is a further indication that these geometries are not stable at higher temperatures. So we consider the overlayer structures as transition states for the formation of a stable, reacted surface.

A more promising comparison is shown in Fig. 9. The occupied or half-occupied surface bands are represented for the $\Theta = 1$ exchange geometries of model I and model IV, being most favored from the energetical point of view. For comparison, the band-mapping results[11] are also indicated along ΓX and $\Gamma X'$. The most pronounced feature of the surface bands experimentally observed is their relatively weak dispersion along the symmetry lines in the SBZ. In the case of the complete Se-As exchange in the first two surface layers (model I), the four rather dispersionless bands from ARPES can be partly reproduced. The experimental peaks at about -6.5 and -3.5 eV compare well with the calculated surface bands S_2, S_3, and S_4, although the calculated bands S_3 and S_4 show a somewhat stronger dispersion. This could be an artifact of the slab calculation for the resonant states. Apart from a shift of about 0.3–0.7 eV the measured energies of -0.8 eV are described by the surface states S_5 and S_6. This energy shift equals roughly the uncertainty of the ARPES data of about 0.5 eV.[39] The highest occupied state S_7 is not observed experimentally. In Fig. 10

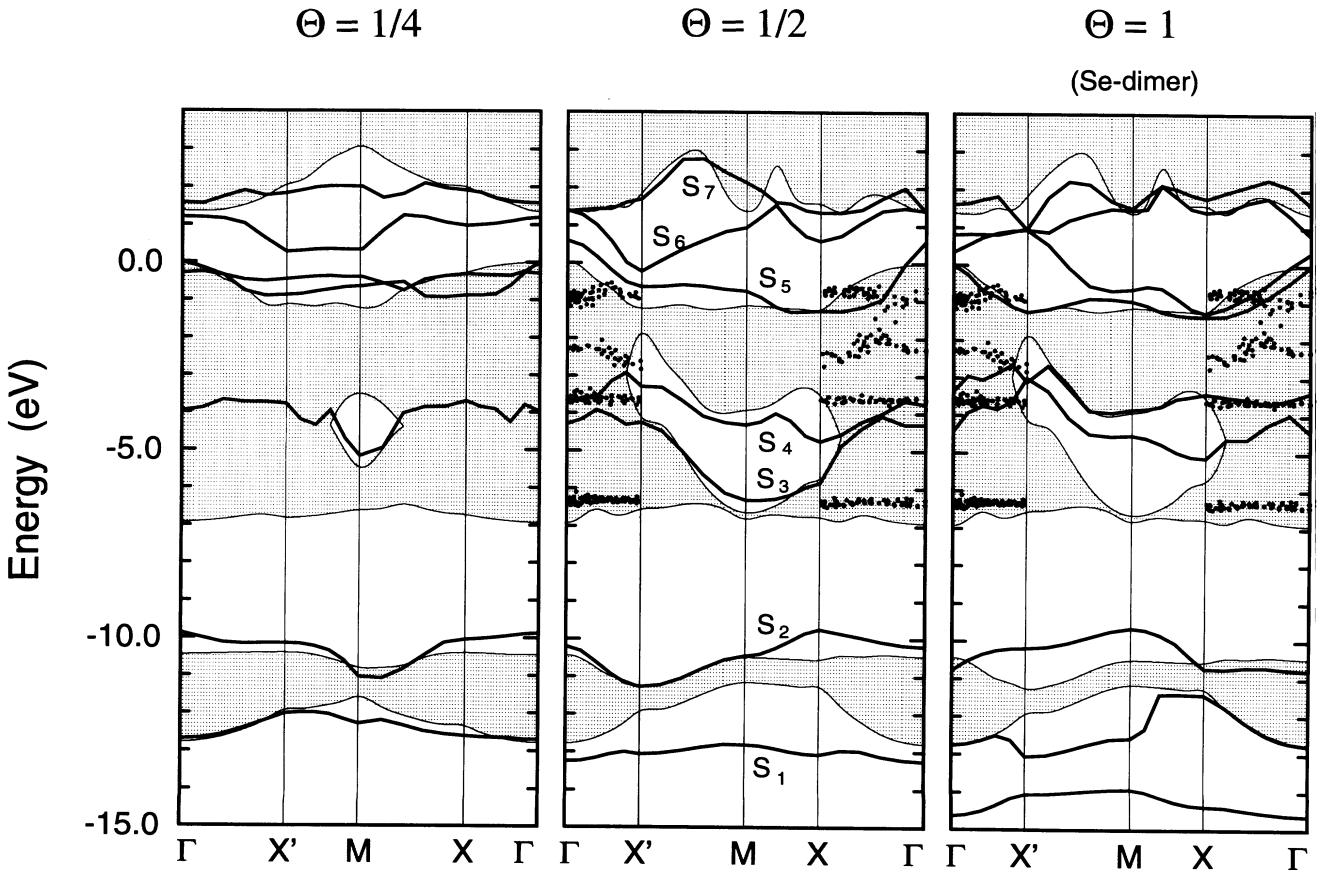

FIG. 7. Surface band structures of Se/GaAs(110)1×1 and 1×2 systems with the most favorable adsorbate geometry for different coverages $\Theta = \frac{1}{4}$ and $\frac{1}{2}$ (interchain bridging position), and $\Theta = 1$ (dimers in front of As dangling bonds) plotted together with the projected bulk band structure of GaAs (dotted region). The small full circles correspond to ARPES data of Ref. 11.

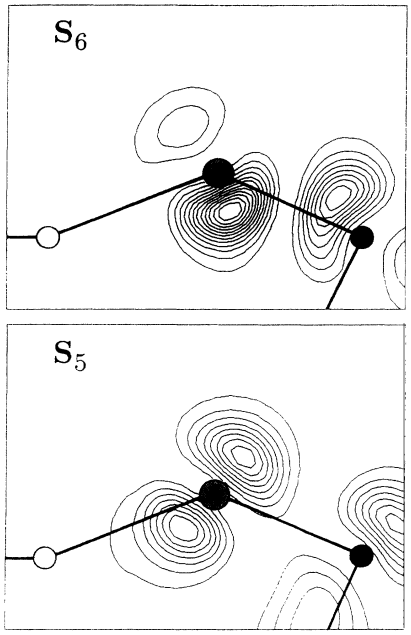

FIG. 8. Orbital character of the two states S_5 and S_6 near the Γ point in the fundamental gap for Se/GaAs(110) ($\Theta = \frac{1}{2}$) (interchain bridging position). The contours (spaced by 0.005 $e\times\text{Bohr}^{-3}$) are drawn along a folded plane perpendicular to the surface containing both the As-Se and Ga-Se bonds.

the corresponding wave functions for some of the surface states are given. Although mainly a bulk resonance, the Se derived state S_2 is partly localized at the surface. The three filled states which appear in the fundamental gap are mainly built up of p orbitals localized at the topmost Se. S_5 corresponds to p_z, whereas S_6 and S_7 are derived from p_y- and p_x-like states. These orbitals contribute to the Ga-Se bonding at the surface.

In Fig. 9 also the band structure of the exchange model IV, which is nearly as favorable as model I from the energetical point of view, is shown. In the energy region of about -6.5 eV, we do not find any state localized at the surface. The agreement between the measured energies at higher energies and the calculated bands is comparable to that discussed above for model I apart from the highest occupied band. This is due to the fact that the states S_1, S_2, and S_3 of model IV are similiar to S_4, S_5, and S_6 of model I both with respect to their orbital character and their dispersion. S_1 corresponds to a p-like state localized at the Se atom of the second layer, whereas S_2 and S_3 are localized at the topmost Se atom. The Fermi level is determined by the state S_3, which is occupied with one electron only. From this result, one may conclude a metallic behavior of the surface. However, we also see that this state has a very small dispersion over the SBZ which indicates that the corresponding wave function is built from practically nonoverlap-

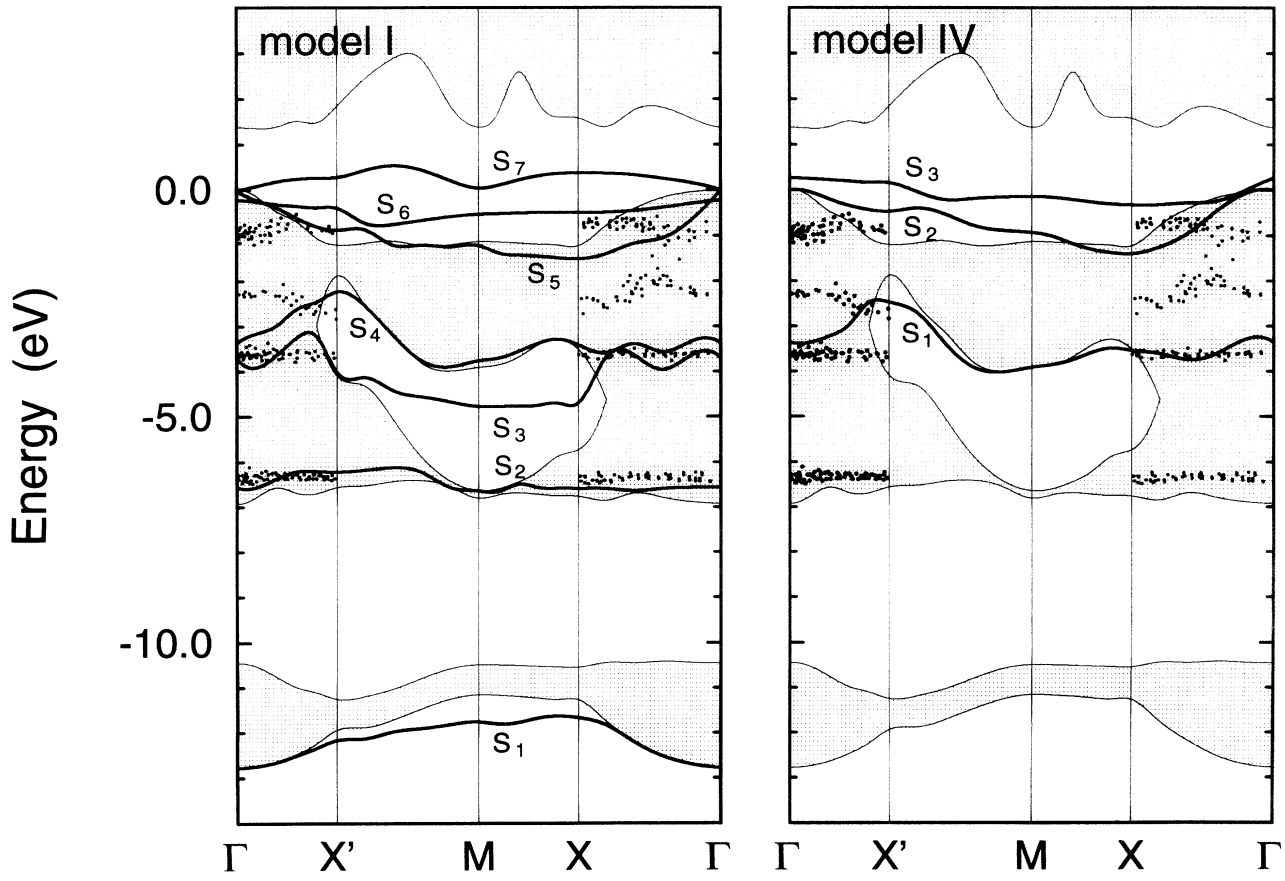

FIG. 9. Surface band structure of the Se/GaAs(110)1×1 system for two different exchange geometries (models I and IV) representing a coverage of $\Theta = 1$. The projected bulk band structure of GaAs is indicated by the dotted regions. The band-mapping results of Ref. 11 are represented by small filled circles.

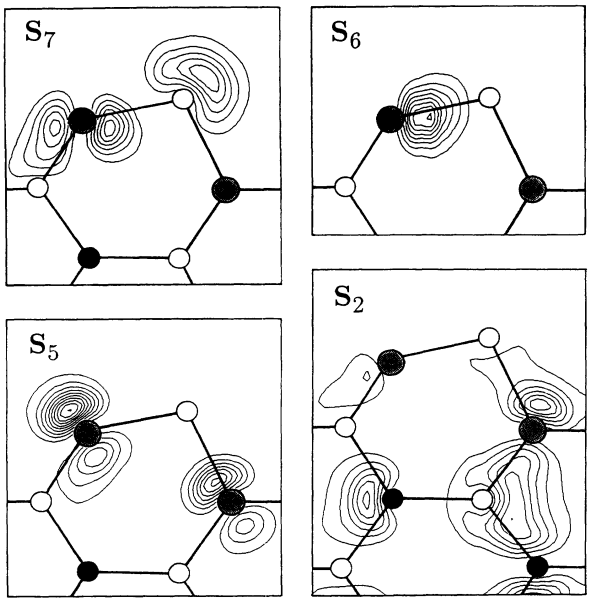

FIG. 10. Orbital character of wave functions at the X' point of the Se/GaAs(110)1×1 surface ($\Theta = 1$, exchange model I). The state S_2 and the three states S_5, S_6, and S_7 in the fundamental gap are drawn along a folded plane perpendicular to the surface. The contour spacing is 0.005 $e\times\text{Bohr}^{-3}$, apart from S_2 where 0.001 $e\times\text{Bohr}^{-3}$ are applied.

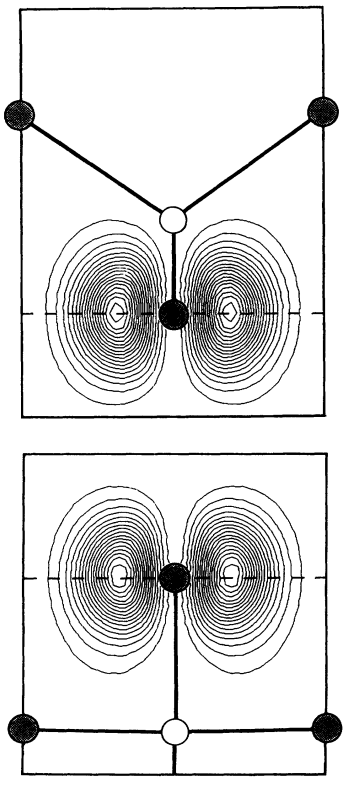

FIG. 11. Orbital character of the state S_3 at the X' point of the Se/GaAs(110)1×1 surface ($\Theta = 1$, exchange model IV). The state is plotted along a horizontal and a vertical plane which cross each other at the dashed lines. The contour spacing is 0.005 $e\times\text{Bohr}^{-3}$.

ping orbitals. The wave function analysis confirms this conclusion (see Fig. 11). The wave function of S_3 is a nearly atomlike p_y orbital which does not contribute to any bonding or antibonding combination. Perhaps, for this structure a similar argument holds as in the case of the alkali adsorption on GaAs(110).[31,40] The strong localization of the involved Se orbitals together with the strong electron-electron and electron-lattice interactions may induce a negative U behavior and the formation of bipolarons explaining the nonmetallic surface. Comparing the band structures both of models I and IV, we find some agreement with the experimental data. However, there remain open questions and a final decision about a certain structure cannot be made. We think that measurements of surface states along $X'M$ and MX would be very helpful to identify a certain structural model.

B. Surface dipole and ionization energy

A further quantity that has been proved useful in distinguishing between geometrical structures of interfaces is the ionization energy (cf., e.g., Ref. [31]) The change of the ionization energy of the system under consideration with respect to that of the clean GaAs(110)1×1 surface results from the variation of the surface dipoles. The macroscopic surface dipoles and the accompanying electrostatic potentials are obtained from the microscopic electrostatic potential evaluated in the DFT-LDA calculation by an average procedure. The potential is averaged along the (110) plane. In a second step, the dependence on the coordinate z perpendicular to the surface is smoothed passing the result through a convolution filter.[31]

Results for the potential changes $\Delta V(z)$ are presented in Fig. 12 for the energetically most favorable structures. The adsorption geometries [Fig. 12(a)] with interchain bridging positions ($\Theta = \frac{1}{4}, \frac{1}{2}$) and Se dimers in front of As dangling bonds ($\Theta = 1$) as well as the Se-As exchange models I, IV ($\Theta = 1$), and II ($\Theta = \frac{3}{2}$) [Fig. 12(b)] are considered. In all cases the potential changes roughly describe a dipole potential, at least far from the surface region. Within the surface region, where Se atoms are adsorbed or interchanged with As atoms, there are of course remarkable derivations from the simplified dipole behavior. They indicate that the macroscopic dipole observed far from the surface has a complicated microscopic origin. Relative to the formation of the dipole potential the variation of $\Delta V(z)$ are the largest for the adsorption geometries. They indicate the stronger local changes in the electron density for adsorption compared to the Se-As exchange. In any case, the potential changes are positive (negative) in the vacuum (GaAs bulk) region and, hence, are reversed in sign compared to the case of alkali metal adsorption.[31] The sign indicates that for the Se covered GaAs(110) surface electrons are transferred from the substrate to the selenium in agreement with the bonding behavior discussed above and the electronegativities.[24]

The consequences of the electron transfer along the

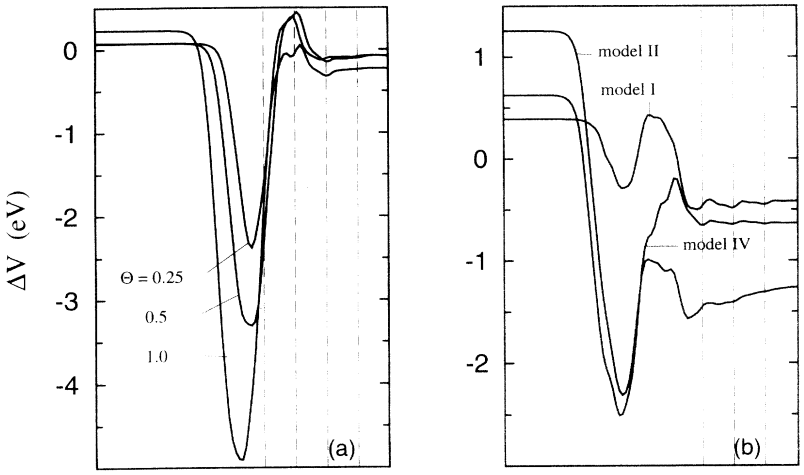

FIG. 12. Changes in the macroscopic electrostatic potential of a relaxed GaAs(110) surface induced by Se adsorption (a) or Se-As exchange reactions (b). Positions of the ideal nonexchanged GaAs(110) layers are indicated by dashed lines. The energy zero of the potential changes is aligned at $\frac{1}{2}[\Delta V(-\infty) + \Delta V(\infty)]$.

adsorbate bonds are represented in Fig. 13 for the ionization energy of the Se/GaAs(110) system. Due to the varying surface dipole $[V(\infty) - V(-\infty)]$, we observe a Se-induced increase of the ionization energy with rising coverage. This behavior is in agreement with the experimental findings for the adsorption of other group-VI materials as oxygen[41] and sulfur.[6] There the increase is explained by an electron transfer in acceptorlike adsorbate-related surface states near the VBM. The band structures in Figs. 7 and 9, however, show that the electronic behavior is somewhat more complicated, at least in the case of the selenium adsorption. The simple adsorption of Se atoms at the GaAs(110) surface produces only small changes in the ionization energy. For an overlayer coverage $\Theta = 1$, the value amounts to only 0.46 eV. The increase of the ionization energy is much more pronounced for the exchange of Se and As. In comparison with the clean GaAs(110)1×1 surface, model I ($\Theta = 1$) gives rise to an increase of 0.78 eV. The changes of the ionization energy increase to 1.26 and 2.52 eV for the models IV ($\Theta = 1$) and II ($\Theta = \frac{3}{2}$). Such clear differences in the ionization-energy changes should be useful to discriminate geometries and underlying adsorption or exchange processes as soon as experimental results are available.

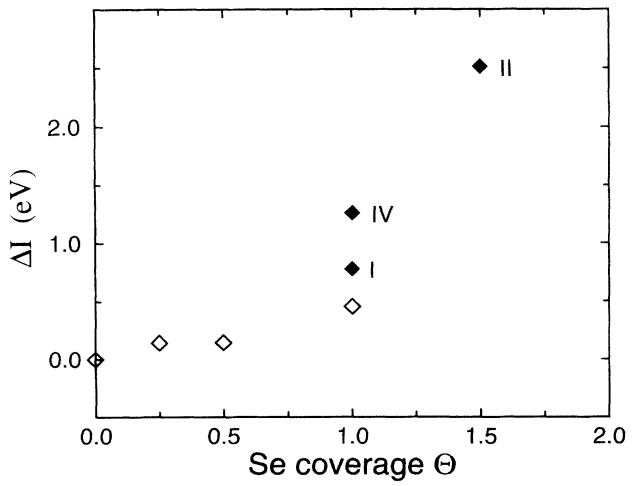

FIG. 13. Changes of the ionization energy with respect to that of the clean GaAs(110)1×1 surface. The most favorable adsorption geometries for $\Theta = 0, \frac{1}{4}, \frac{1}{2}$, and 1 are indicated by open diamonds, whereas the exchange geometries considered for $\Theta = 1$ and $\frac{3}{2}$ are indicated by the number I, IV, or II of the model.

V. SUMMARY

From a first-principles pseudopotential study, we have found several stable structures for Se chemisorption on GaAs(110) for coverages from $\Theta = \frac{1}{4}$ to $\frac{3}{2}$. In the low coverage regime Se occupies a threefold coordinated position between As and the two Ga atoms of the opposite GaAs chain. High diffusion barriers are observed both in $[1\bar{1}0]$ and [001] directions. Up to a coverage of $\Theta = \frac{1}{2}$, we find an attractive interaction between the Se atoms. Upon further adsorption of Se the interaction becomes repulsive. However, for 1 ML coverage the adsorption energy per Se atom is still higher than the cohesive energy of bulk Se. There is no energy gain when Se and As atoms are interchanged. If, however, the assumption is made that the liberated As forms large bulk As clusters at the surface, an As-Se exchange is energetically favorable. For low coverages, we find a pronounced ionic character of the bonding between substrate and adatom. The exchange models are characterized by a slightly more covalent bonding between selenium and gallium. For the energetically most favorable exchange geometries (model I and model IV) there is also some agreement between calculated surface bands and ARPES data. The ionization energy increases remarkably with increasing Se coverage with respect to its value for clean GaAs(110). This indicates the formation of a macroscopic surface dipole pointing into the substrate. Further experiments concerning the structural and electronic properties of this system are needed to favor decisively one of the proposed models.

ACKNOWLEDGMENTS

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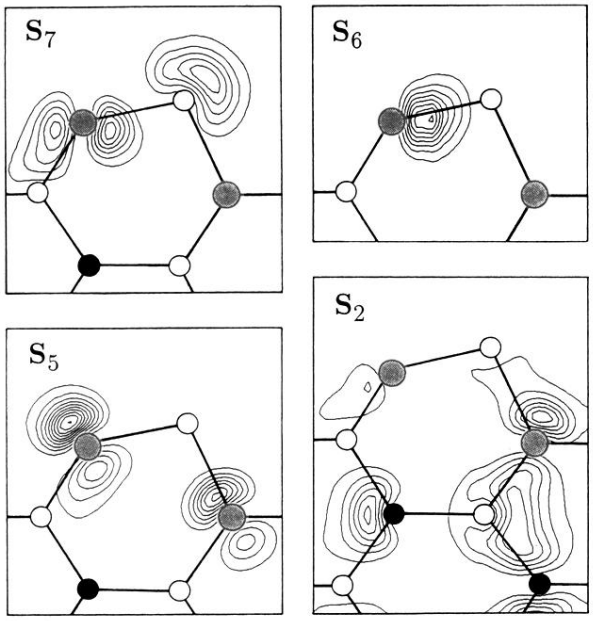

FIG. 10. Orbital character of wave functions at the X' point of the Se/GaAs(110)1×1 surface ($\Theta = 1$, exchange model I). The state S_2 and the three states S_5, S_6, and S_7 in the fundamental gap are drawn along a folded plane perpendicular to the surface. The contour spacing is 0.005 $e\times\text{Bohr}^{-3}$, apart from S_2 where 0.001 $e\times\text{Bohr}^{-3}$ are applied.

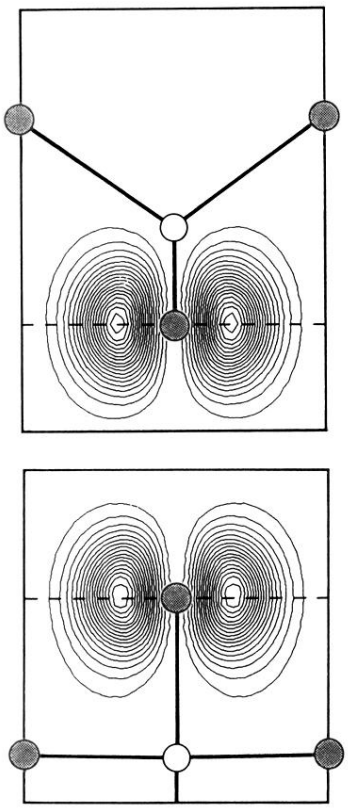

FIG. 11. Orbital character of the state S_3 at the X' point of the Se/GaAs(110)1×1 surface ($\Theta = 1$, exchange model IV). The state is plotted along a horizontal and a vertical plane which cross each other at the dashed lines. The contour spacing is 0.005 $e\times\text{Bohr}^{-3}$.

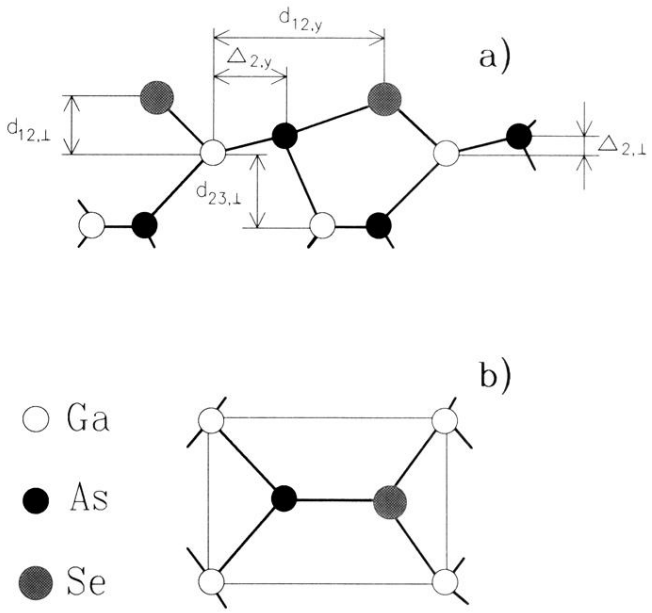

FIG. 2. Side (a) and top (b) views of the interchain bridging position of Se/GaAs(110)($\Theta = \frac{1}{2}$) system.

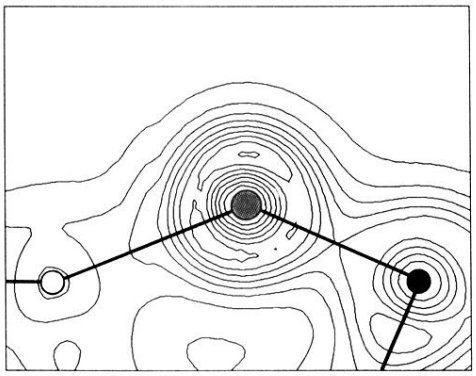

FIG. 3. Contour plot of the total valence pseudocharge density for a single Se atom per GaAs(110)1×1 surface unit cell adsorbed at the interchain bridging position. The contours (spaced by 0.015 $e\times$ Bohr^{-3}) are drawn along a folded plane perpendicular to the surface containing both the As-Se and Ga-Se bonds. Ga (As,Se) atoms are indicated by open (full, shaded) circles.

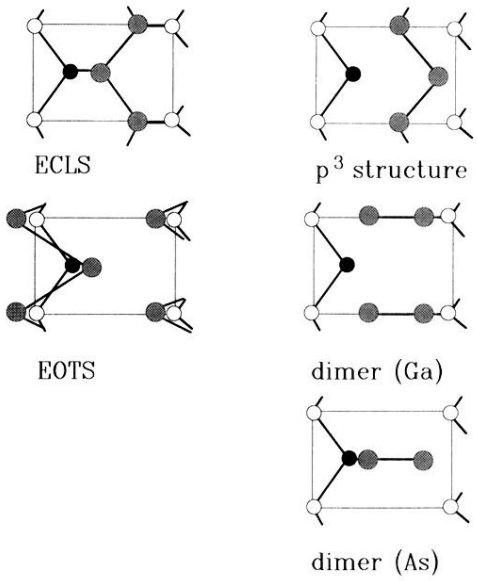

FIG. 4. Top view of different relaxed structures for a Θ=1 coverage of Se on GaAs(110)1×1. Ga (As,Se) atoms are indicated by open (full, shaded) circles.

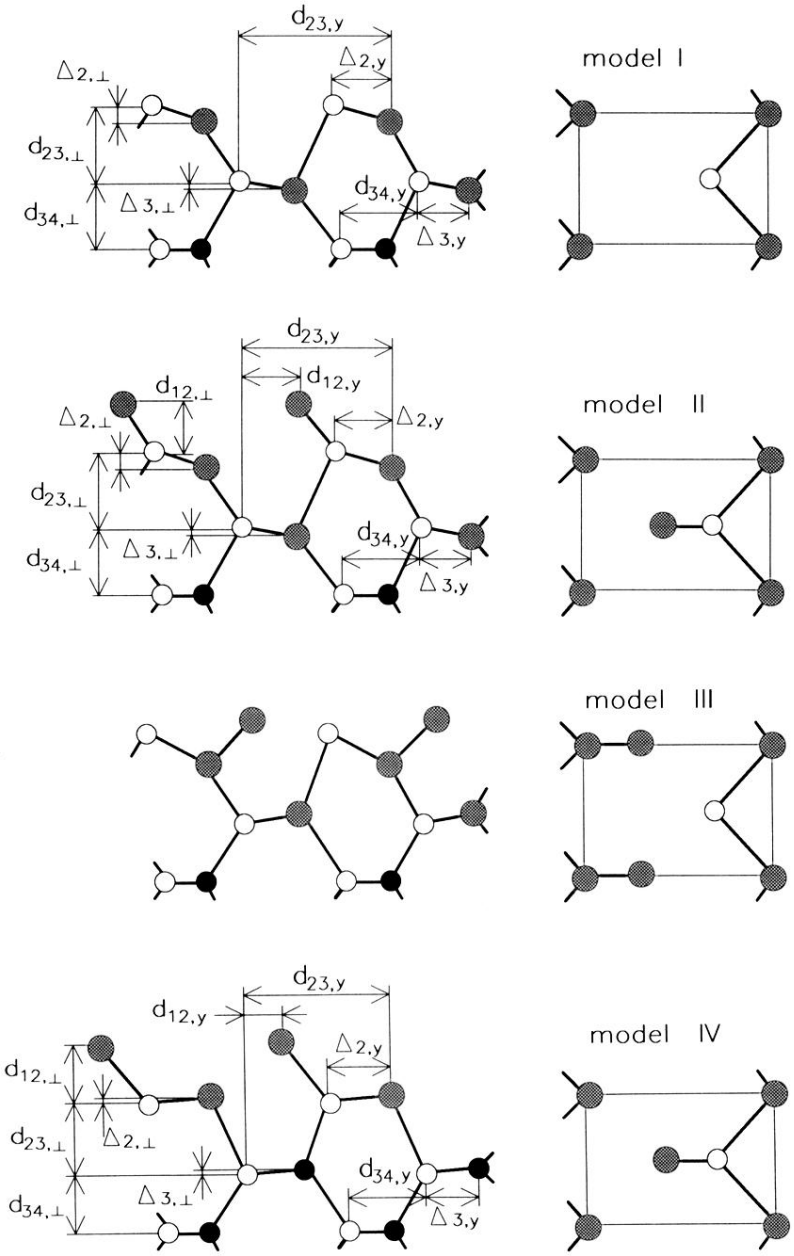

FIG. 5. Side and top views of four models for atomic arrangements at reacted GaAs(110) surfaces after Se-As exchange. Ga (As,Se) atoms are indicated by open (full, shaded) circles.

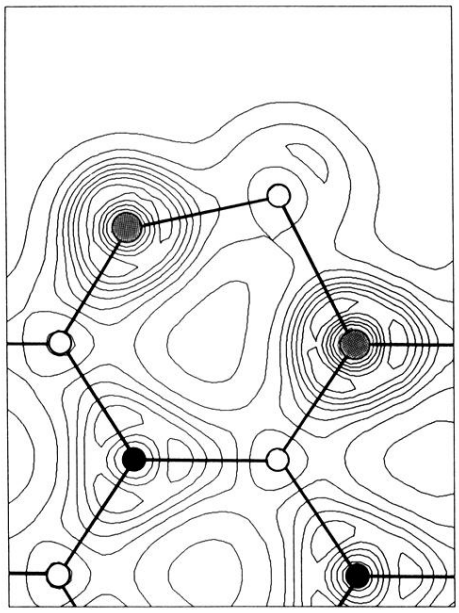

FIG. 6. Contour plot of the total valence pseudocharge density for Se/GaAs(110)1×1 (exchange model I in Fig. 5 with Θ=1). The contours (spaced by 0.015 $e\times\text{Bohr}^{-3}$) are drawn along a folded plane perpendicular to the surface.

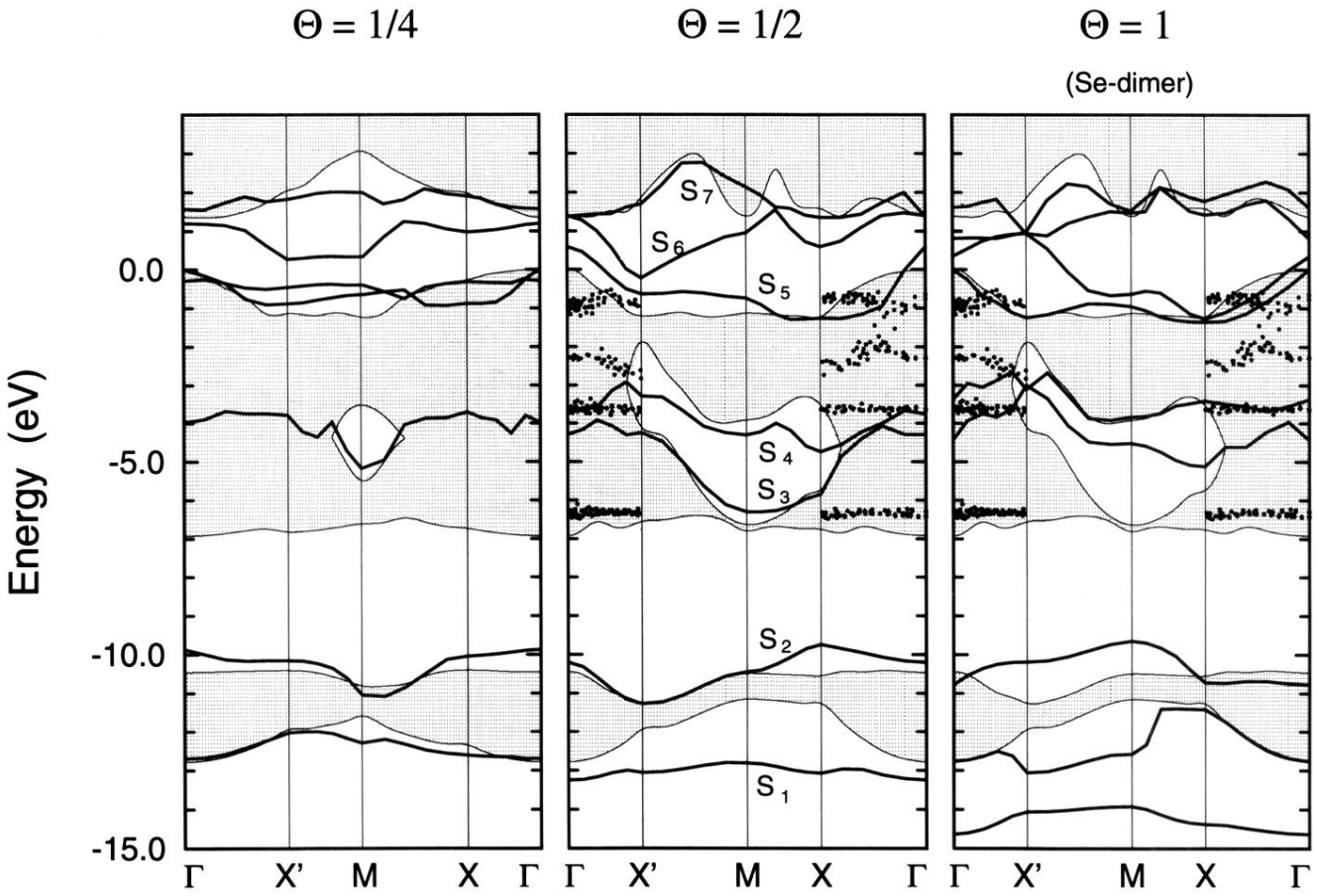

FIG. 7. Surface band structures of Se/GaAs(110)1×1 and 1×2 systems with the most favorable adsorbate geometry for different coverages $\Theta = \frac{1}{4}$ and $\frac{1}{2}$ (interchain bridging position), and $\Theta = 1$ (dimers in front of As dangling bonds) plotted together with the projected bulk band structure of GaAs (dotted region). The small full circles correspond to ARPES data of Ref. 11.

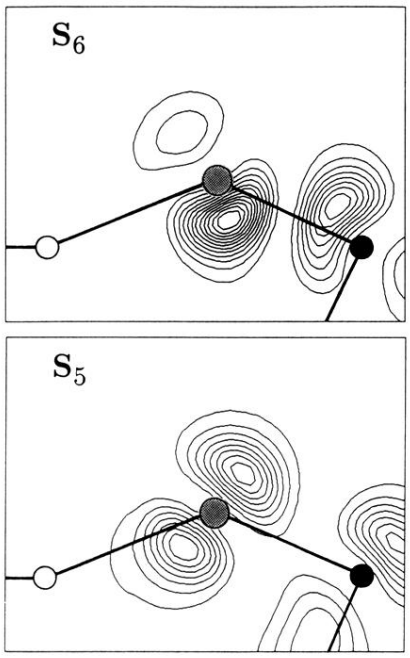

FIG. 8. Orbital character of the two states S_5 and S_6 near the Γ point in the fundamental gap for Se/GaAs(110) ($\Theta = \frac{1}{2}$) (interchain bridging position). The contours (spaced by 0.005 $e\times\text{Bohr}^{-3}$) are drawn along a folded plane perpendicular to the surface containing both the As-Se and Ga-Se bonds.

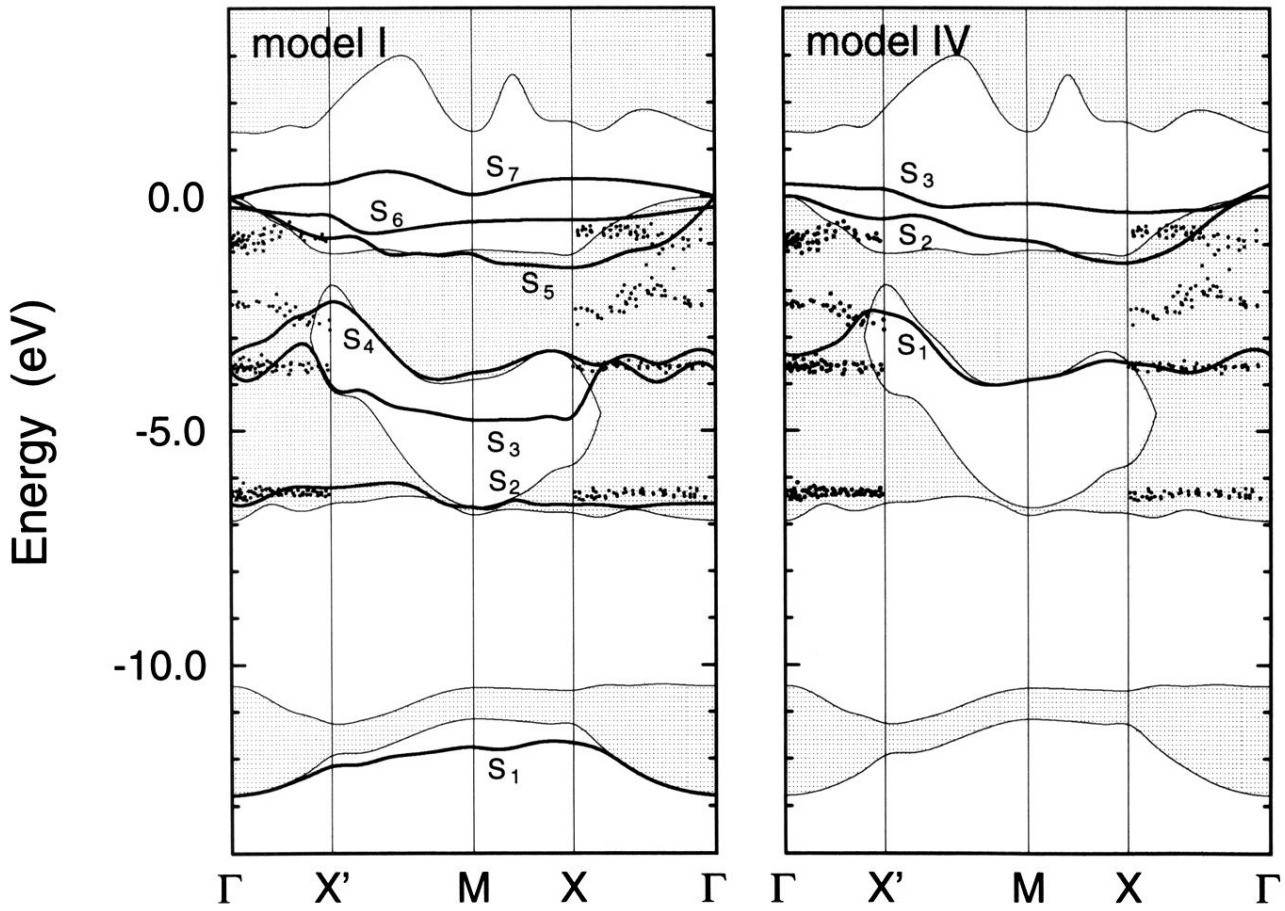

FIG. 9. Surface band structure of the Se/GaAs(110)1×1 system for two different exchange geometries (models I and IV) representing a coverage of $\Theta = 1$. The projected bulk band structure of GaAs is indicated by the dotted regions. The band-mapping results of Ref. 11 are represented by small filled circles.