Exchange reactions versus adsorption geometries for Se/GaAs(110)

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We present the result of *ab initio* density-functional calculations of selenium deposited on the GaAs(110) surface. For the coverages $\Theta = \frac{1}{4}, \frac{1}{2}, 1$, and $\frac{3}{2}$ a variety of adsorption and exchange geometries are optimized. For submonolayer coverage a detailed analysis of the total-energy surface is given. For nearly effective monolayer Se coverage, Se-As exchange reactions are compared with adsorption geometries. We observe a tendency toward an exchange of As and Se atoms in the uppermost layers accompanied by a segregation of As at the surface. For the energetically most favored geometries we compare the calculated band structures with recent angle-resolved photoemission spectroscopy results.

The investigation of physical and chemical processes at interfaces between adsorbates and semiconductor substrates on a microscopic level is of considerable interest both for technological reasons and for fundamental aspects. Particularly, the details of the interface formation in dependence on the deposition parameters and the mechanism of band bending or saturation of surface states were not fully understood until now. One prototypical example in this direction is the deposition of Se or other chalcogen atoms onto GaAs surfaces. The passivating action of such a treatment is well known, especially for the polar GaAs(001) surface (cf. Refs. 1 and 2 and references therein). However, the understanding of the actual formation process, the bonding geometry of the adsorbate, the related electronic structure, and resulting passivating mechanism is far from being complete.

The nonpolar GaAs(110)-1×1 cleaved surface represents a model face for the passivation studies because of its smoothness on an atomic scale. Tu and Kahn[3] found upon deposition of about one monolayer (i.e., two Se atoms/unit cell or $\Theta = 1$) of selenium that the GaAs(110)-1×1 low-energy electron diffraction (LEED) pattern is reconstructed, indicating the formation of a stable Se overlayer of the same translational symmetry or the saturation of the Se-As exchange in the first substrate layer(s). Accompanying Auger electron measurements show that the As peak saturates for lower Se coverages than the Ga peak. This suggests that free As, as a product of a possible interface exchange reaction, segregates at the surface. The strong interaction between the GaAs(110) surface and the deposited Se for low coverages ($\Theta = \frac{1}{4}$) has been demonstrated by electron energy loss spectroscopy.[3,4] X-ray photoelectron spectroscopy (XPS) measurements have been interpreted in different directions. Sandroff *et al.*[5] infer significant Se-As bond formation at the Se-treated GaAs surface, in contrast to the study of Tu and Kahn[3] as well as in contrast to the recent investigation by Maeda *et al.*[6] The latter proposed the appearance of a Ga_2Se_3-like specimen at the Se-treated GaAs(001) surface. Very recent studies of Schröter *et al.*[7] reported the conservation of the 1×1 LEED structure after extensive Se treatment and subsequent annealing. The resulting changes of the line shape in the core-level XPS were interpreted by the existence of at least two distinct bonding sites for Se at the GaAs(110) surface and by As desorption upon annealing. The thickness of the reacted layer was roughly estimated to about 1–2 atomic layers. The occupied band structure, measured by angle-resolved photoemission spectroscopy (ARPES), exhibits several rather dispersionless bands of surface bound states and resonances.

In this paper, we present self-consistent *ab initio* calculations of the atomic structure and the electronic properties of the Se-treated (110) surface of GaAs for different coverages in the framework of the density-functional theory (DFT) in local-density approximation (LDA). For lower coverages, $\Theta = \frac{1}{4}$ and $\Theta = \frac{1}{2}$, we clarify the possible adsorption sites. For higher coverages, $\Theta = 1$ and $\Theta = \frac{3}{2}$, we study different Se-adsorption geometries and Se-As exchange reactions. The energetics of the accompanying growth processes is discussed in dependence on the initial and final stages of Se and As. The resulting band structure for the most favored atomic structures is compared with ARPES results and a possible passivating mechanism is considered.

The details of the calculations not specified here are like those in Ref. 8. The geometry chosen is that of a periodically repeated slab of eight GaAs(110) layers, both sides are covered with Se or GaAs(110) layers, where the As atoms are partly or completely substituted by Se atoms. The slabs are separated by a vacuum region of a thickness that is equivalent to at least six atomic layers. 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) the number of atomic layers within the slab is reduced to six. The pseudowave functions are expanded into plane waves up to an energy cutoff of 18 Ry. We replace the $\mathbf{k}_{||}$ integration by a sum over four special points in the irreducible part of the surface Brillouin zone (SBZ). In order to determine the equilibrium positions, the atoms of the two innermost substrate layers were 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 were brought to self-consistency within a Car-Parrinello-like minimization scheme of the total-energy functional[9] using a modified computer code of Stumpf and Scheffler.[10]

The stable atomic positions of Se on GaAs(110) are not known. We, therefore, evaluated the Born-Oppenheimer 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 considered a (1×2) surface unit cell according to a coverage of $\Theta = \frac{1}{4}$ in order to minimize the interactions between Se atoms. The adsorbate-substrate distance as well as the first substrate layers are allowed to relax fully. The resulting energy surface is plotted in Fig. 1. We find a pronounced minimum for a lateral position where the Se atom is threefold coordinated in between the As atom and two Ga atoms belonging to different Ga-As surface chains. This interchain adsorption position is rather equidistant to the three substrate neighbors. With $d_{\mathrm{AsSe}} = 2.55$ Å and $d_{\mathrm{GaSe}} = 2.70$ Å the bond lengths are somewhat larger than the sums of the covalent radii, indicating the partially ionic character of the bonds. There are no scanning-tunneling microscopy (STM) studies of the initial stages of the selenium adsorption. However, STM studies[11] of another group-VI element, atomic oxygen, on GaAs(110) suggest the same adsorption site.

In contrast to the cases of Sb (Ref. 8) and Na (Ref. 12) adsorption on GaAs(110), the total-energy surface in Fig. 1 has no deep channel parallel to the Ga-As zig-zag chains in the $[1\bar{1}0]$ direction. The movement of the Se atoms is prevented by energy barriers of about 1.1 eV in the $[1\bar{1}0]$ direction and 1.2 eV in the [001] direction. Hence, a low-temperature formation of an ordered Se adsorbate seems to be impossible, at least for low coverages. Nevertheless, a two-dimensional Se overlayer is energetically preferred to the formation of three-dimensional Se clusters. For coverages of $\Theta = \frac{1}{4}$ and $\frac{1}{2}$, where one Se atom occupies the defined adsorption site in one GaAs(110)-1×1 unit cell, we derive adsorption energies of 3.63 eV and 3.82 eV. These values are larger than the cohesive energy per atom of 3.44 eV calculated by the same method for bulk selenium in its trigonal structure as an upper limit for the energy gain upon clustering. The small increase of the adsorption energy with rising coverage from $\Theta = \frac{1}{4}$ to $\Theta = \frac{1}{2}$ indicates an attractive interaction between Se atoms in different (1×1) unit cells.

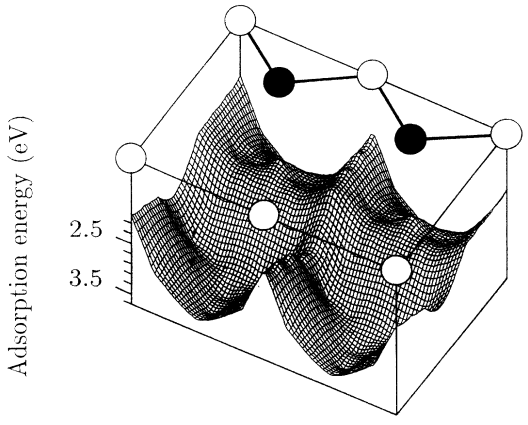

FIG. 1. The total-energy surface of the Se/GaAs(110) system for a coverage of $\Theta = \frac{1}{4}$ plotted as a three-dimensional perspective view together with the projected surface atoms in two GaAs(110)-1×1 unit cells. Open circles indicate Ga atoms, whereas dots mark As atoms.

For $\Theta = 1$, i.e., two Se atoms per GaAs(110)-1×1 unit cells, we consider five overlayer geometries that have been proposed for the description of the monolayer adsorption of Sb (Ref. 8) and Al (Ref. 13) on GaAs(110). These are the 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 (cf. Fig. 2). The adsorption energies 3.42, 3.45, and 3.45 eV of the ECLS, the p^3 structure, and Se dimers in front of a Ga dangling bond are nearly equal. The EOTS with an adsorption energy of 3.21 eV is less favorable. Se atoms in dimers in front of an As dangling bond give rise to an adsorption energy of 3.63 eV. The corresponding geometry should, therefore, be favored.

The energy differences between the various $\Theta = 1$ adsorption geometries are smaller than those observed in the case of the Sb adsorption.[8] We believe that this result is related to the stronger ionic character of the adsorbate-substrate bonds and the unique direction of the electron transfer independent of the cation or anion character of the substrate atom. 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. The adsorption energies per adatom of all considered $\Theta = 1$ structures are lower than those found for $\Theta = \frac{1}{2}$. We relate this finding to the incomplete screening of the partly ionized Se atoms. Since both adatoms are slightly negatively charged, the repulsive Coulomb interaction has to

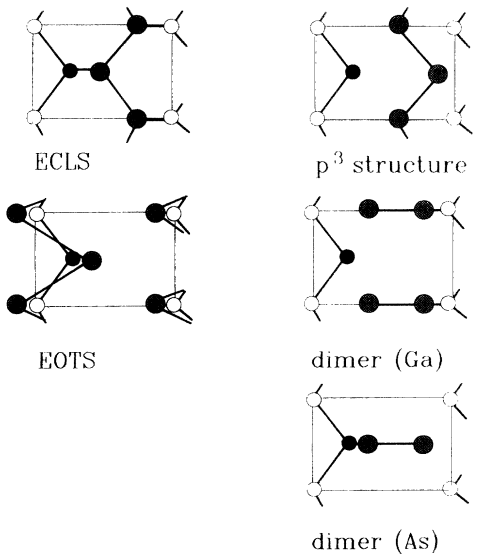

FIG. 2. Top view of the adsorption geometries considered for a $\Theta = 1$ coverage of Se on GaAs(110). Open (full) circles represent Ga(As) atoms, whereas the Se atoms are indicated by shaded circles.

be taken into the consideration. However the adsorption energy for the minimum-energy configuration for $\Theta = 1$ is still about 0.2 eV larger than the cohesive energy of bulk Se. Therefore, from the energetical point of view a three-dimensional clustering of the Se atoms is unlikely in the monolayer case.

The covalent radius of the Se atoms is somewhat smaller than that of the As atoms.[14] Therefore, an exchange reaction between surface As atoms and Se adatoms is possible, especially after thermal treatment of the overlayer as done within the overlayer preparation of Ref. 7. A Ga-Se exchange is unlikely, since the electronegativity of Se is larger than those of Ga and As.[14] Thus, Se avoids occupying a site in the cation sublattice. We study the four As-Se exchange geometries, the side views of which are presented in Fig. 3. Our selection of exchange geometries is based on the experimental finding of a nonmetallic surface.[7] Half-filled surface bands may be avoided by the Se substitution of an even number of substrate anions. This situation is represented by the model I of Fig. 3, where Se atoms occupy the As positions in the two uppermost surface GaAs(110) layers, i.e., $\Theta = 1$. We also study the models II and III in Fig. 3, where an additional Se atom per unit cell is adsorbed in front of one of the surface dangling bonds, i.e., $\Theta = \frac{3}{2}$. Model IV, where the exchange reaction is restricted to the first GaAs(110) layer and one adatom remains at the surface, has already been proposed in Ref. 7.

The atomic arrangements, given in Fig. 3, are optimized until the total energy reaches a minimum. The energetics of the exchange and adsorption processes depend on the initial and final stages of the exchanged and deposited materials, in particular, the energies of Se atoms in the appropriate reservoir and those of the As atoms appearing at the surface or desorbing from the surface. Unfortunately, their chemical potentials are not known exactly. A further complication arises from the limitation of our calculations to low temperatures. In order to give a rough idea we assume that the Se atoms are bound in the equilibrium adsorbate configuration for $\Theta = 1$, i.e., in dimers, before exchange and that the desorbed arsenic atoms go into a large bulk As reservoir. Regarding the arguments given above, the bonding energy of Se before the exchange reaction is overestimated. On the other hand, the assumed chemical potential of bulk As does certainly also exceed the experimental value, since the desorbed As forms small clusters, perhaps amorphous caps or sticks. A partial cancellation of the uncertainties is expected. Actually we use the chemical potential of bulk As as calculated by Qian *et al.*[15] Their DFT-LDA calculation is based on the same exchange-correlation potential, the same energy cutoff, and pseudopotentials of the same (Bachelet-Hamann-Schlüter) type. We find an energy gain of 0.19 eV per GaAs(110)-1×1 unit cell for an exchange of the As atoms in the two outermost substrate layers with Se atoms (model I). Thus, the exchange reaction is exothermic if the discussed conditions concerning the chemical potentials are nearly fulfilled. It should, therefore, be favored over the adsorption geometries. A considerably smaller energy gain of 0.03 eV is found for the geometry where an additional Se atom is bound to the Ga atom in the surface unit cell (model II), in contrast to model III, which is unfavorable in terms of energy. An energy gain of 0.19 eV is observed for the model IV (effectively $\Theta = 1$), where the anions are exchanged only in the first atomic substrate layer and the second Se atom per GaAs(110)-1×1 cell is adsorbed in front of a surface Ga dangling bonds. The released energy is only slightly smaller than for model I.

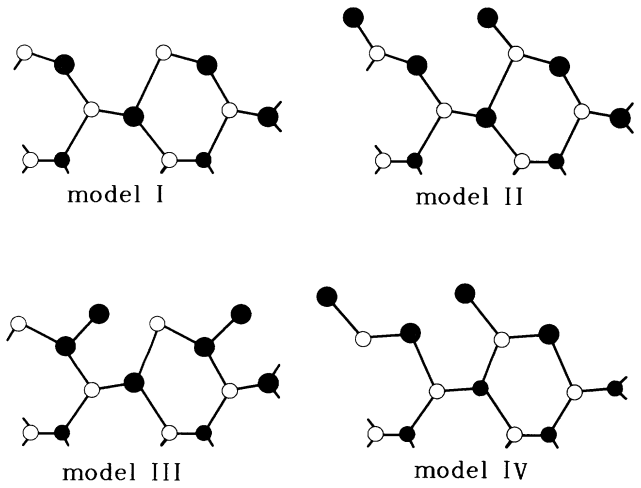

FIG. 3. Side view of the four exchange geometries considered. Open (full) circles represent Ga(As) atoms, whereas the Se atoms are indicated by shaded circles.

The crucial role of the chemical potentials for the likelihood of exchange reactions becomes obvious from further calculations. Starting from the minimum-energy configurations for ordered overlayers with $\Theta = \frac{1}{2}$ and $\Theta = 1$, i.e, the interchain bridging position or the Se dimer in front of As, we interchange the positions of Se and substrate As atoms. Thereby the As takes the former Se site, but is allowed to relax. We find that an exchange of Se in interchain bridging position with the As atom of the first and second substrate layer leads to a loss of energy of 0.13 and 0.50 eV, respectively, whereas an exchange of Se of the dimer configuration with the underlying As reduces the adsorption energy by 0.10 eV per adatom. This behavior is quite different compared to Al adsorption on GaAs.[13] Apparently, there is no strong tendency for Se to penetrate into the substrate in the low coverage case, and the processes on the surface are rather sensitive with respect to the experimental conditions.

Figure 4 shows the occupied or half-occupied surface bands for the favored $\Theta = 1$ exchange geometries, i.e., models I and IV in Fig. 3. 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 band-mapping results[7] are indicated along $\overline{\Gamma X}$ and $\overline{\Gamma X'}$. In the case of the complete Se-As exchange in the first two surface layers [Fig. 4(a)] the four rather dispersionless bands found experimentally can partly be reproduced. This holds especially for the features near −6.5 and −3.5 eV, which mainly arise from σ bonds between Ga and Se in the two outermost layers. We do not try to explain the features near −2.2 eV because of their strong resonance char-

acter. Apart from a small shift of 0.3 – 0.7 eV, the highest experimental band may be traced back to S_5 (Se p_z states) or S_6 (Ga-Se σ-bonding orbitals in the first atomic layer). Apparently, the calculated band S_7 has not been observed in the experiment. The band structure of the partially exchanged Se-As geometry of the model IV [Fig. 4(b)] cannot explain the lowest experimental band near −6.5 eV. The agreement for higher energies between the measured features and the calculated bands is comparable to that discussed for model I. Some bands can be identified by slightly shifting the energy and neglecting the stronger dispersion obtained in the calculations. However, the highest occupied band S_3 is only one half filled with electrons and, therefore, seemingly contradicts the experimental finding in Ref. 7 of a nonmetallic surface. This band is related to atom-like in-plane p orbitals which do not contribute to bonding or antibonding combinations. Consequently it is rather flat. Perhaps similar many-body arguments are valid as given in the case of the flat partially filled bands at the alkali-GaAs(110) surface.[12,16] The strong localization of the involved electronic 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.

In conclusion, we have presented *ab initio* studies of the structural and electronic properties of the Se-covered GaAs(110) surface, which give a rough picture consistent with the available experimental data. For low coverages we found Se adsorption in an interchain bridging position. For coverages of $\Theta = 1$ or somewhat higher we favor an exchange of Se and As atoms in the surface region. However the occurrence of the exchange reaction depends rather sensitively on the experimental conditions. From the energetical point of view and taking the experimental findings — 1×1 translational symmetry, two different Se adsorption sites, thickness of the reacted layer of one or two monolayers, As desorption upon annealing, and nearly dispersionless surface bands — into account, a geometry where the uppermost two surface layers are exchanged has to be favored. However, other geometries cannot be excluded. Further experimental and theoretical studies are needed to clarify the Se adsorption and the formation of stable reacted overlayer structures.

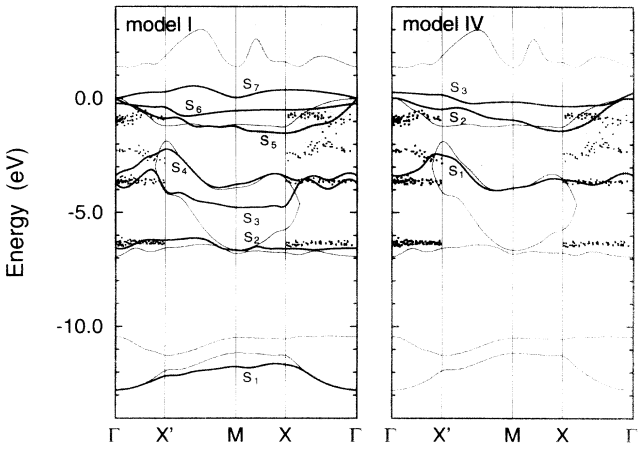

FIG. 4. Surface band structures of the Se/GaAs(110)-1×1 system for two different exchange geometries (models I and IV) representing a coverage of $\Theta = 1$. The projected bulk GaAs band structure is indicated by the dotted regions. The band-mapping results of Ref. 7 are represented by small filled circles.

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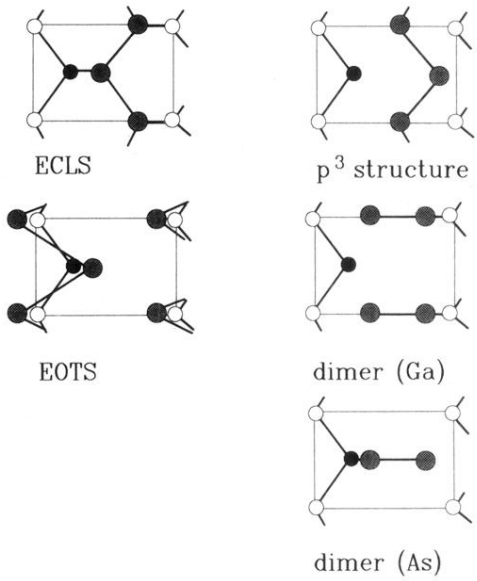

FIG. 2. Top view of the adsorption geometries considered for a $\Theta = 1$ coverage of Se on GaAs(110). Open (full) circles represent Ga(As) atoms, whereas the Se atoms are indicated by shaded circles.

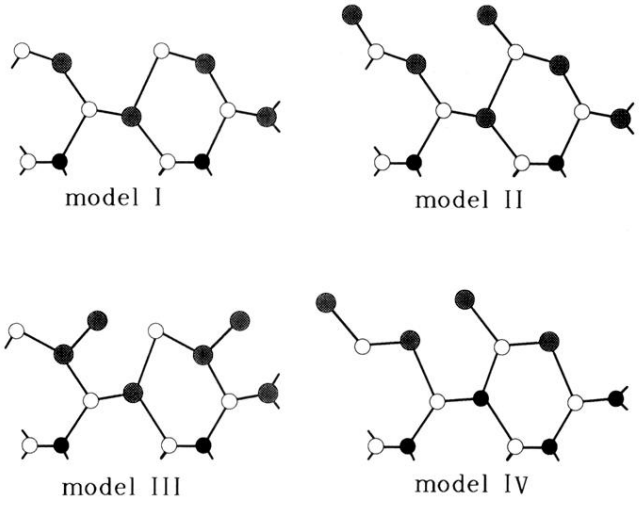

FIG. 3. Side view of the four exchange geometries considered. Open (full) circles represent Ga(As) atoms, whereas the Se atoms are indicated by shaded circles.

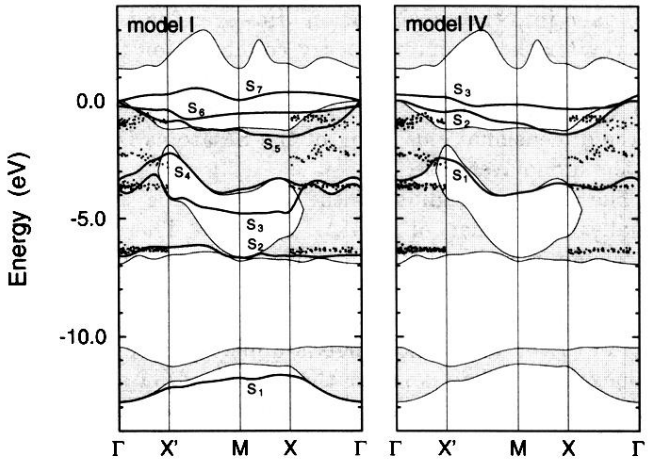

FIG. 4. Surface band structures of the Se/GaAs(110)-1×1 system for two different exchange geometries (models I and IV) representing a coverage of $\Theta = 1$. The projected bulk GaAs band structure is indicated by the dotted regions. The band-mapping results of Ref. 7 are represented by small filled circles.