

Electronic, structural, and dynamical properties of the GaAs(110):Ge surface

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We have investigated the structural, electronic, and vibrational properties of Ge overlayers on the GaAs(110) surface in the framework of the density-functional theory within the local-density approximation. By minimizing the total energy with the help of the Hellmann-Feynman forces, we have found two different zero-force configurations for the GaAs(110) surface covered with one monolayer (ML) Ge as well as for two ML's Ge on GaAs(110). For both coverages the atomic equilibrium positions and most of the electronic surface states corresponding to the optimized structure with the lower energy minimum are very similar to those of the clean GaAs(110) surface. A thermodynamical analysis indicates an instability towards cluster formation. In the case of one ML Ge on GaAs(110) we have calculated the phonon-dispersion curves along high-symmetry lines in the surface Brillouin zone using first-order density-functional perturbation theory without any adjustable parameters. As well as the electronic properties, the features of the phonon spectrum mostly resemble those of the clean surface. Beside the appearance of an additional surface acoustic mode the main effect of Ge adsorption is a slight down-shift of the phonon frequencies. The dynamical analysis of the GaAs(110)-(1×1):Ge surface (1 ML) at $T = 0$ shows no instability towards reconstructions with periodicity along the high-symmetry directions $\bar{\Gamma}\bar{X}$ and $\bar{\Gamma}\bar{X}'$.

I. INTRODUCTION

Among the most important features of semiconductor devices are interfaces between different types of materials such as metals, oxides, and semiconductors. The progress in new preparation techniques such as molecular-beam epitaxy or metal-organic vapor phase epitaxy and the increasing sophistication of the analyzing methods (e.g., angle-resolved photoemission spectroscopy or scanning tunneling microscopy) have strongly enhanced the efforts towards a better understanding of adsorption processes and initial stages of the interface formation. With inelastic He-atom scattering and high-resolution electron energy-loss spectroscopy, it has become feasible to measure surface phonon dispersions up to a high degree of precision. Thus there is a demand for microscopic theories which not only correctly describe the structural and electronic properties but also the dynamics of surfaces with or without adsorbates. While for the ground state calculations density-functional theoretical methods have developed to standard techniques, studies of surface dynamics are still most commonly accomplished by model calculations. A summary of what has been done so far on the topic of surface dynamics is given in Ref. 1.

The clean GaAs(110) surface belongs to the most studied semiconductor surfaces, both experimentally and theoretically (a short survey of some previous work may be found in Ref. 2). It is well established that its relaxation mainly consists in a bond-angle relaxation in the first-layer Ga-As chains. It is characterized by a tilt-angle of approximately 30° , where the surface anions are lifted above the surface plane and the surface cations are pushed down below the surface plane. As the clean GaAs(110) surface is representative for the III-V semiconductor (110) surfaces, it constitutes an ideal system to examine. Recently, the linear-response approach proposed in Ref. 3 has been applied to calculate the phonon dispersion of this surface.² The results are in excel-

lent agreement with all available experimental data. We use the same method for the calculations of the GaAs(110):Ge system.

Adsorbed adlayers on semiconductor surfaces are of physical interest under various aspects. For instance, the adsorption of Al on GaAs(110) is relevant in connection with the formation of a Schottky contact.^{4,5} In the same context adsorbed alkali-metal in the monolayer regime have been investigated, too.^{6,7} As ordered overlayers of Sb and Bi on GaAs(110) are relatively easy to obtain,⁸ much work has been done on the adsorption of these group V elements.

In this paper we report our results from *ab initio* calculations for the GaAs(110) surface covered with one and with two monolayers (ML's) Ge. Because of the almost perfectly matching lattice constant and thermal expansion coefficient of the substrate and of the adsorbate, this system is an ideal candidate for studies of heterojunctions.

Experimentally the GaAs(110):Ge system has extensively been investigated by standard surface probing techniques such as photoemission spectroscopy, low-energy electron diffraction, Auger-electron spectroscopy, and scanning-tunneling microscopy (STM).⁹⁻¹⁵ The results of these studies have demonstrated that Ge forms ordered overlayers on GaAs(110) over a wide temperature range. At low coverage (below 10 ML's), however, the STM results of Ref. 15 clearly show that isotropic islands as large as 10 ML's in height nucleate upon deposition of Ge at elevated temperatures (≈ 700 K). Furthermore, it is known that at such temperatures the arsenic atoms segregate to the growing Ge surface.^{9-11,15} Chen *et al.*¹² reported uniformly deposited Ge layers on GaAs(110) even in the monolayer regime for a substrate temperature of 330 K. However, due to the low temperature, the crystal films turned out to be far from perfect.

The experimental evidence renders theoretical calculations of realistic systems in the ML coverage regime diffi-

cult. Nevertheless, the study of systems with only a few but ordered ML's Ge on GaAs(110) can provide valuable information upon the initial stages of the interface formation. In particular, a theoretical approach based on a semiempirical Hamiltonian has been applied to GaAs(110) systems covered with half a ML up to three ML's in order to study the precursors of the interface states of the Ge-GaAs(110) heterojunction.^{16,17} Very recently, a refined version of this method has been used to investigate Ge coverages up to twelve ML's and also the fully developed heterojunction.¹⁸ It has been found that the characteristic electronic interface features do occur already for the first Ge adlayer. The topic of electronic interface states in a $(\text{Ge}_9(\text{GaAs})_9)$ -(110) heterostructure has been addressed by Pickett and co-workers¹⁹ within local pseudopotential calculations.

The outline of the present paper is as follows. In Section II we summarize the essential points of our calculations. Sec. III contains our results in detail, divided into three parts. In the first part the structural properties including a stability analysis of the adlayer systems towards cluster formation are presented. The second part contains the discussion of the electronic properties for one and two monolayer coverage. The third subsection is devoted to the surface dynamics for one and two ML's Ge on GaAs(110) including a comparison with the results of the clean surface of Ref. 2. We conclude the paper in Sec. IV with a short summary.

II. METHODS OF CALCULATION

The electronic ground-state calculations were carried out within the scope of density-functional theory in the local-density approximation. Specifically, for a given atomic configuration, we solved the Kohn-Sham equations²⁰ with the parametrization of Perdew and Zunger²¹ for the exchange-correlation potential. The electron-ion interaction was described by norm-conserving nonlocal pseudopotentials generated by Giannozzi.²² Those pseudopotentials provide a good basis for the expansion in plane waves up to 10 Ry. In fact, the bulk phonon frequencies and lattice constants of GaAs and Ge are quite well converged even with such a small cutoff energy.

The geometry we used to describe the surface is a periodic array of Ge covered GaAs-“slabs” exposed to vacuum at both sides. In this sense a three-dimensional periodic system is retained, and hence, it is possible to apply the usual techniques for bulk calculations. A vacuum region equal to four interlayer distances proved to be sufficient for the wave functions of neighboring slabs not to “overlap”; the electronic band structure remained unaltered, irrespective of an increase in the spacing between the slabs. Due to symmetry reasons, it is convenient to consider an odd number of layers per slab.

For the ground-state calculations we have taken 11 layers, the outermost one or two layers consisting in the Ge adatoms. Hence, there are two identical surfaces per slab, i.e., each surface state occurs to be a pair of two individual states. The surfaces bordering upon one slab are sufficiently decoupled, as the corresponding energy bands of such a pair are fairly degenerate. The determination of the relaxation has been accomplished by minimizing the total energy with the help of Hellmann-Feynman forces. Specifically, starting with

appropriate initial atomic positions, the modified Broyden scheme proposed in Ref. 23 was applied in order to find a zero-force configuration related to at least a local minimum of the total energy. The symmetry of the GaAs(110):Ge surface has been assumed to be the same as the symmetry of the clean surface, i.e., only GaAs(110)- $p(1 \times 1)$ -Ge structures have been studied.

The dynamics of the one monolayer covered GaAs(110) surface has been treated in the framework of the first-order density-functional perturbation theory.^{3,24,25} Only recently, this method has been extended to the calculation of surface phonons.² The basic concept is that the variation of the ground-state wave functions caused by a lattice distortion, i.e., a phonon, is calculated iteratively until self-consistency is achieved with respect to the screened perturbing potential. The dynamical matrices in the harmonic approximation can be expressed solely in terms of the first-order deviations of the Kohn-Sham wave functions and the electronic ground-state properties.

We have carried out phonon calculations for a system of fully relaxed slabs containing seven layers GaAs and one ML Ge on the two substrate surfaces.²⁶ For the two ML case we have carried out the calculation for phonons at the \bar{X}' point with slabs containing only five substrate layers. As the interatomic force constants decrease at least two orders of magnitude for atoms separated by more than three interlayer distances, it is possible to extend the calculated dynamical matrices to those of slabs spanning much more than only nine layers without any further assumptions. More specifically; the force constants of the four outermost layers in a very thick crystal film are adopted from those of the small nine-layer slab. The remaining matrix elements for the inner layers of the extended system are determined from the values corresponding to atoms of the central plane of the nine-layer slab by exploiting the fact that subsequent (110) layers in the bulk material are related by symmetry operations of the crystal. This method has already been applied in Ref. 2. Our results confirm the reliability of this method, as the frequencies and displacement patterns of well localized surface phonons in our calculations remain unchanged for different slab sizes. The full dispersion relation in $\bar{\Gamma}\bar{X}$ direction (along the surface zigzag chains) and in $\bar{\Gamma}\bar{X}'$ direction (perpendicular to the chains) is determined by interpolation of four ($\bar{\Gamma}\bar{X}$) and three ($\bar{\Gamma}\bar{X}'$) dynamical matrices, respectively.

III. RESULTS AND DISCUSSION

A. Relaxation geometries

In a first approach the atomic equilibrium positions were determined by starting from an ideally continued GaAs(110) structure as input for the modified Broyden scheme. Due to the given symmetry, no Hellmann-Feynman forces and therefore no shifts occur in the direction of the surface zigzag chains.

For the relaxed systems we found the bond lengths to deviate no more than about 3% from the bulk value of GaAs. The latter was determined in bulk calculations to 2.431 Å which compares well with the experimental value of 2.448 Å.²⁷ Furthermore, the atoms in the fourth layer already resume the positions of the ideal structure and hence, the re-

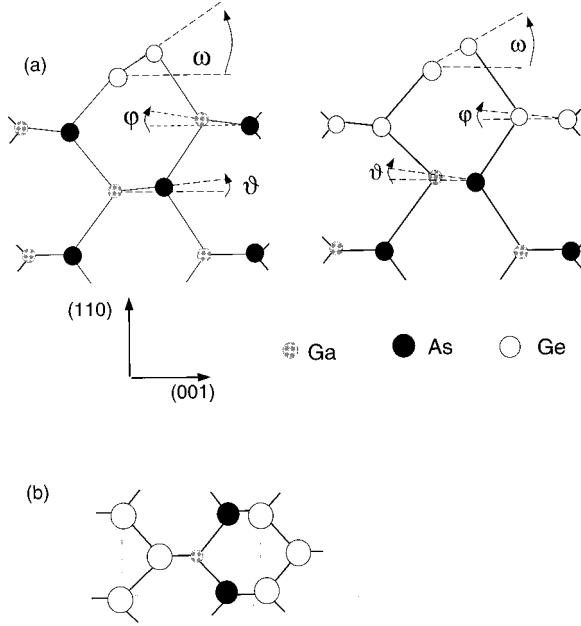


FIG. 1. Schematic diagram of the surface geometries for one and two monolayers Ge on GaAs(110). Positive tilt angles refer to counterclockwise inclined atomic chains. (a) Side view. (b) Top view.

laxation may conveniently be expressed in terms of the tilt angles of the atomic chains in the three outermost layers. Figure 1 qualitatively illustrates the atomic positions in this region. In analogy to the clean GaAs(110) surface, there is a pronounced relaxation in the outermost layer whereas the atoms in the deeper layers are already located fairly close to the ideal positions. The Ge atoms corresponding to As atoms in a hypothetically continued substrate are shifted outwards. The resulting tilt angle of the surface Ge chains is 36.1° for one and 31.5° for two ML's Ge on GaAs(110). In previous works using a semiempirical method,^{17,18} similar equilibrium positions are found to be only metastable. In contrast with our results the authors of Refs. 17 and 18 identify the configuration with the surface Ge chains inclined at an angle of approximately -30° as stable. Due to the higher total energy, we find the atomic positions corresponding to a negative tilt to be less stable.

Our results for the surface structures and the corresponding energy gain per surface unit cell with respect to the ideal configuration are summarized in Table I. The discussion of

TABLE I. Atomic equilibrium positions for one and two monolayers Ge on GaAs(110). The energy gain ΔE per surface unit cell is given with respect to the truncated ideal GaAs(110) structure. For the definitions of ω , ϑ , and φ we refer to Fig. 1.

Coverage	1 ML	1 ML (metastable)	2 ML	2 ML (metastable)
ω	36.1°	-29.9°	31.5°	-34.1°
φ	-5.9°	-1.9°	-4.0°	0.5°
ϑ	2.0°	0.0°	-0.7°	3.16°
ΔE (in eV)	-0.56	-0.26	-0.55	-0.39

the electronic properties in the next section will give more insight into the nature of the considered surface structures. This point is of fundamental interest for the investigation of the properties of the Ge-GaAs(110) interface.

From the experimental point of view one or two Ge adlayers on GaAs(110) are found to be unstable towards cluster formation. In order to address this point we use the calculated total energies to perform a thermodynamical analysis of the stability at $T=0$. In particular, this can be done following two different approaches.

Within the first approach³⁰ an instability is obtained if the surface free energy of the adlayer system becomes greater than that of the free GaAs(110) surface only partially covered with Ge clusters. In a first approximation, Ge clusters may be regarded to serve as a bulk Ge reservoir in both cases. Hence, the relevant quantity to be calculated is the surface free energy of the clean and covered surface in the presence of a bulk Ge reservoir. The surface free energy per (1×1) surface unit cell of the clean surface is given by

$$\Omega_S^{\text{GaAs}} = \frac{1}{2} (E_{\text{tot}}^{\text{GaAs}} - n_{\text{GaAs}} \mu_{\text{GaAs}}),$$

where $E_{\text{tot}}^{\text{GaAs}}$ is the total energy and n_{GaAs} the number of GaAs pairs per unit cell of the slab system. The chemical potential is denoted by μ_{GaAs} . The factor one-half accounts for the two surfaces per slab. Correspondingly, the surface free energy of the adlayer system is given by

$$\Omega_S^{\text{GaAs:Ge}} = \frac{1}{2} (E_{\text{tot}}^{\text{GaAs:Ge}} - n_{\text{GaAs}} \mu_{\text{GaAs}} - n_{\text{Ge}} \mu_{\text{Ge}}).$$

The chemical potentials are taken to be the same as in the bulk GaAs and Ge, respectively. They are defined by the total energy per unit cell divided by the number of GaAs pairs or Ge atoms. For the determination of the total energy of the bulk materials the same 10 Ry energy cutoff has to be used. Furthermore, a unit cell adapted to the slab symmetry is chosen, in order to guarantee an analogous \mathbf{k} point sampling as for the surface systems. For the surface free energy of the clean GaAs(110) surface, the present calculation results in a value of $\Omega_S^{\text{GaAs}} = 1.27$ eV per surface unit cell which is in good agreement with the experimental value²⁸ of 1.21 eV and with that of other pseudopotential calculations²⁹ (1.22 eV). In its more stable configuration, the surface free energy of the one (two) ML covered GaAs(110) surface is found to be 2.09 eV (2.13 eV) per surface unit cell. Therefore, the adlayer systems is thermodynamically unstable towards cluster formation as experimentally observed.

Within an alternative approach,³¹ one can compare the surface energies of a GaAs(110) system separated into the two phases of a clean surface (50%) and that of a two ML Ge covered surface with that of the entirely one ML covered surface. The surface energy for a slab with n_{GaAs} GaAs pairs and n_{Ge} Ge atoms per unit cell is defined by

$$E_S = \frac{1}{2} (E_{\text{tot}} - n_{\text{GaAs}} \mu_{\text{GaAs}} - n_{\text{Ge}} E_{\text{atom}}^{\text{Ge}}), \quad (1)$$

where $E_{\text{atom}}^{\text{Ge}}$ is the energy of a free non-spin-polarized Ge atom. We have calculated the atomic energy of Ge using a fictitious fcc cell with a next neighbor distance of 8 Å and a 10 Ry kinetic energy cutoff. The surface energy of the 50% two-ML covered surface can be estimated as

$$E_S^{0.5} = \frac{1}{2} \Omega_S^{\text{GaAs}} + \frac{1}{2} E_S^{2ML}, \quad (2)$$

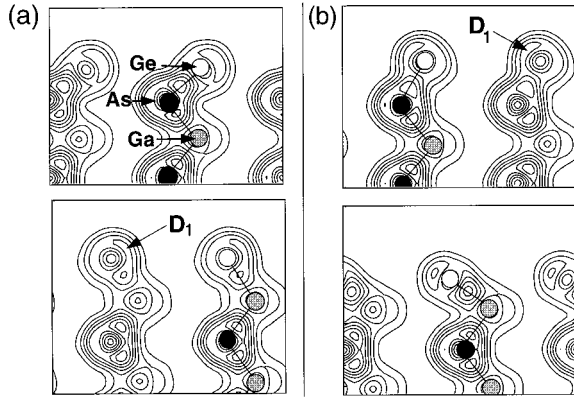


FIG. 2. Total pseudovalence charge density shown in the planes perpendicular to the surface containing Ga-As chains terminated by As-Ge bonds (upper graphs) or Ga-Ge bonds (lower graphs). (a) Stable atomic equilibrium positions. The Ga-bound surface atoms have “pseudoanionic” character as a result of an occupied dangling bond which can be identified by the little hump labeled as D_1 . The As-bound Ge atoms are “pseudocationic.” (b) Metastable configuration. Note the interchange in the ionic characters of the Ge atoms with respect to (a).

where E_S^{2ML} denotes the surface energy for the completely two-ML covered system. For the atomic positions with the lower total energy, the calculation results in a value of $E_S^{2ML} = -19.41$ eV ($E_S^{1ML} = -8.69$ eV) per (1×1) area for the two (one) ML covered GaAs(110) surface. Using Eq. (1) and Eq. (2) and the value of 1.27 eV per (1×1) area for Ω_S^{GaAs} , one finds the surface energy for the phase separated surface to be 0.38 eV lower in energy than the completely one-ML Ge covered surface. Therefore, this consideration favors the formation of clusters, too.

B. Electronic structure

The pseudovalence charge density of GaAs(110) covered with one ML Ge is shown in Fig. 2 for both of the equilibrium structures. Two different pairs of planes perpendicular to the surface are depicted in Fig. 2. One pair contains the GaAs chains terminated by As-Ge bonds and the other pair contains those terminated by Ga-Ge bonds. It is apparent that the charge densities of the two equilibrium structures differ significantly from each other in the surface region. As seen from the relative piling of the charges in the contour plots in Fig. 2, the heteropolarity of the substrate gives rise to a “pseudoionicity” of the adatoms. While the Ga-bound Ge atoms appear to be “pseudoanions” in the more stable structure, the As bound adatoms show pseudoanionic behavior in the other structure. The little humps labeled as D_1 in Fig. 2 indicate that the anionlike character originates in the occupied dangling bonds of the upwards shifted Ge atoms whereas the dangling bonds of the downwards shifted Ge atoms remain empty leading to a cationlike behavior. We only note that analogous features occur at the GaAs(110) surface covered with two ML’s Ge, too. Again the outward relaxed Ge atoms of the surface layer have doubly occupied dangling bonds. Under this aspect the Ge covered GaAs(110) surface is very similar to the clean surface, especially in the atomic configuration belonging to the lower minimum in the

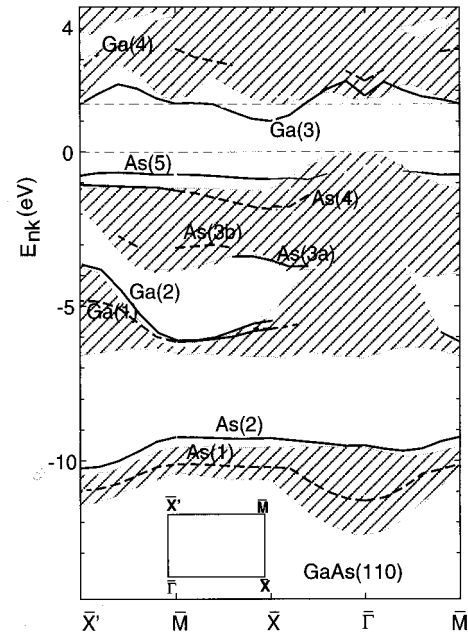


FIG. 3. Electronic energy dispersion of surface bound states (heavy solid lines) and resonances (dashed lines) of the clean, fully relaxed GaAs(110) surface. The irreducible wedge of the Brillouin zone is shown in the inset. The notations are taken from Ref. 34.

total energy. Here the “pseudo” anions (cations) are the immediate equivalents of the first layer As anions (Ga cations) of the free GaAs(110) surface.

As a result, most of the electronic surface states of the systems in question are closely related, which can be seen from the electronic band structure. The electronic band structure for the clean GaAs(110) surface is shown in Fig. 3. It has been calculated for a system of fully relaxed slabs containing nine atomic GaAs layers with a cutoff energy of 10 Ry. The atomic equilibrium positions are given in Ref. 2. The surface states are in good accordance with previous theoretical work (see, e.g., Ref. 32 and references therein). The one particle eigenvalue spectra of the (more stable) fully relaxed Ge covered GaAs(110) surfaces are shown in Fig. 4.

We will now discuss the surface electronic bands in the order of descending energies. The bands are characterized according to the shape of the charge distribution of the corresponding Kohn-Sham eigenfunctions. Analogous states in the systems with one or two ML’s Ge have the same labels. The band D_2 is associated with the unoccupied dangling bonds as is Ga(3) in Fig. 3. The occupied dangling bonds lead to the bands D_1 and As(5). Respectively compared to the clean surface state D_1 and D_2 show much more dispersion and the gap becomes very small. The states B_1 are back bonds and are located as As(4) at the outward relaxed surface (“pseudo”) anions. On the upper rim of the “stomach” gap near \bar{X} , we find p -like states orientated parallel to the surface (P). They are localized at the As ions of the second layer for one ML Ge [as are As(3a) and As(3b) for the free surface]. For two ML’s Ge they are placed at the Ga-bound Ge atoms. The state labeled as Ga(2) in Fig. 3 is s -like and placed at the first layer Ga ions. For one ML and two ML’s Ge coverage a similar state (denoted as Ga₂) appears in the first substrate

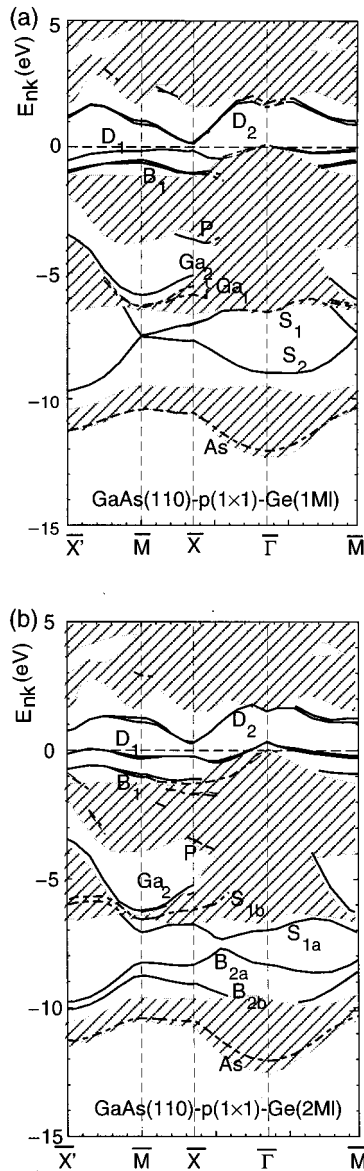


FIG. 4. Energy dispersions of surface bound states (heavy solid lines) and resonances (heavy dashed lines) of the stable equilibrium configurations. (a) GaAs(110)- $p(1 \times 1)$ -Ge (1 ML), (b) GaAs(110)- $p(1 \times 1)$ -Ge (2 ML).

layer, i.e., at the forming interface. Therefore these states can be identified as the precursors of an interface state of the forming heterostructure. In fact, they seem to be related to the interface state labeled as S_2 in Ref. 19. The next few resonances and surface bands cannot be described simultaneously and thus we have to distinguish between the different systems.

For one ML coverage the resonances Ga_1 arise from predominantly s -like Ga states of atoms in the third and deeper lying layers. S_1 is related to s -like states localized at the As-bound Ge atoms. A surface state with mixed character (approximately 50% Ge-Ga bond, 50% Ge s -like) gives rise to the band S_2 .

In the case of two ML's Ge coverage, there is a pair of resonances (labeled S_{1a} and S_{1b}) next to Ga_2 . S_{1b} is located at the outward relaxed ("pseudoanionic") Ge atoms, S_{1a} at

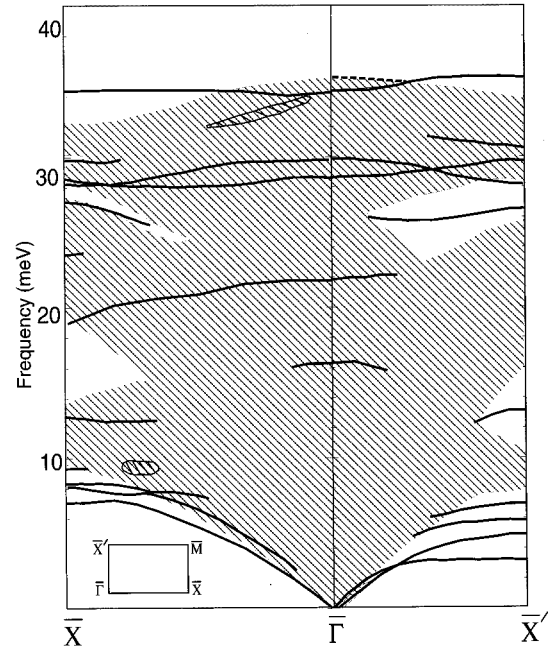


FIG. 5. Phonon spectrum of the relaxed surface system GaAs(110)- $p(1 \times 1)$ -Ge (1 ML) in the stable equilibrium configuration. The surface projected bulk structure is indicated by the large shaded area. Surface localized modes and resonances are drawn as heavy solid lines. The smaller hatched regions represent broad features with rather deeply penetrating surface states. The irreducible wedge of the Brillouin zone is shown in the inset.

the other Ge atoms of the surface layer. B_{2a} and B_{2b} are associated with the two distinguishable Ge-Ge back bonds to those to the Ga-bound Ge atoms being higher in energy. Note how the bands S_1 and S_2 in the one ML case and S_{1a} to B_{2b} for two ML's Ge start to form the characteristic gap (see, e.g., Ref. 19) between X' and M by filling up the heteropolar gap along the other high symmetry directions in Fig. 3.

Finally, there is a resonance labeled as As(1) for the clean and as As for the Ge covered surfaces. Its origin is an s -like state of the As ions in the second layer (clean surface) or in the first substrate layer (one and two ML Ge). It may also be identified as the precursor of the second s -like interface state S_1 of Ref. 19.

C. Vibrational properties

In the preceding section we have shown that the adsorption of one ML Ge on GaAs(110) results in structural and electronic properties which are very similar to those of the clean surface. Furthermore, Ga, Ge, and As are consecutive elements in the Periodic Table. Thus the mass of Ge is close to both the mass of As and Ga. From this one may expect that the adsorption of one ML Ge will not result in a completely new surface mode spectrum.

In fact, most of the predominant vibrational features of the clean GaAs(110) surface (see Ref. 2) can also be observed in the phonon dispersion for the system with one adsorbed ML Ge in the equilibrium configuration with the lowest energy. The latter is shown in Fig. 5 for wave propagation parallel ($\bar{\Gamma}\bar{X}$) or perpendicular ($\bar{\Gamma}\bar{X}'$) to the surface Ge chains. The large shaded area indicates the projected bulk

structure (PBS) of GaAs. The smaller hatched regions resemble broad features with several rather deeply penetrating surface modes. Above the PBS, similar to the clean surface and with almost the same energies, appears the significant branch of an optical surface mode. It is characterized by an opposing motion of the inward relaxed Ge ions and the second layer As ions. For long wave vectors in $\bar{\Gamma}\bar{X}'$ direction, it exhibits a splitting of the two individual states forming the pair related to this surface phonon. The mode at the upper rim of the PBS becomes macroscopic by coupling to the longitudinal optic bulk phonon. The other mode merging into the PBS remains localized at the first and second atomic layer.

In a similar fashion all of the other modes in the upper and intermediate energy regime correspond to modes of the clean surface. Most of the surface phonons of the Ge covered system, however, appear approximately 2 meV lower in energy.

More significant changes due to the adsorption of Ge are present in the region of the acoustic surface modes. In the $\bar{\Gamma}\bar{X}$ direction we find an additional branch beside two surface acoustic modes which are related to similar vibrations in the clean surface. This third phonon mode is crossing the upper mode at about 7.7 meV. It is dominated by a vibration of the second layer As ions normal to the (110) planes, and of the outward relaxed Ge ions parallel to the surface and perpendicular to the Ge chain direction.

In $\bar{\Gamma}\bar{X}'$ direction we identify four branches of surface phonons in the energy regime below the PBS, whereas only three surface acoustic waves were found in Ref. 2 for the clean GaAs(110) surface. A more detailed analysis reveals the origin of the additional phonon branch: The phonon with the zone boundary energy of 4.93 meV at \bar{X}' is analogous to the Rayleigh wave (RW) in Ref. 2. It starts at $\bar{\Gamma}$ with predominantly normal displacements and a group velocity of approximately 2.8×10^3 m sec⁻¹ in accordance with continuum theory.³³ Near \bar{X}' it is dominated by a vibration of the Ge atoms in the direction of wave propagation and a vibration of the second layer Ga and As ions with an additional component normal to the surface. The next higher mode with a zone boundary energy of 5.88 meV shows a complementary displacement pattern with the Ge ions vibrating mainly in the vertical direction. It corresponds to the third surface localized acoustic phonon in Ref. 2.

The mode with the lowest energy at \bar{X}' (at 3.20 meV) shows a strictly shear horizontal polarization. It is related to the intermediate acoustic branch at the clean surface. For the free surface its displacement pattern near the zone boundary is characterized by an in-phase vibration of the first layer Ga and As ions. The adsorption of one ML Ge does not alter the motion of the uppermost Ga and As ions, although they are second layer atoms in the covered system. This is because of the fact that in this special case the adsorbed Ge ions rigidly follow the vibration of the atoms in the first substrate layer. This explains the fairly low energy of 3.20 meV at \bar{X}' compared with the related branch of the clean surface which always runs slightly above the RW. The mode with the highest energy below the PBS is polarized strictly in the shear horizontal direction, too. The difference from the previous

mode lies in the movements of the Ge ions now being reversely phased to those of the substrate ions.

In order to investigate confined modes in the Ge overlayer as well as localized modes originating in the presence of both the surface and the interface, we have calculated the dynamical matrix at the \bar{X}' point of a relaxed GaAs(110):Ge system with five substrate layers and two Ge adlayers per slab. The corresponding phonon spectrum showed only marginal changes with respect to that of the one ML covered GaAs(110) surface. In particular, each of the surface phonons in the one ML covered surface is found also in the two ML covered system at hardly differing frequencies. No appreciable difference is also found for the corresponding eigenvectors of the Ge atoms in the second layer moving qualitatively as the corresponding Ge or As atoms. This indicates that these vibrations are caused by the presence of the surface rather than by the GaAs-Ge interface. The only new feature of the two ML case is the appearance of an additional optical surface localized mode with an energy of 34.3 meV, slightly above the PBS of GaAs(110). This mode consists of an SH-polarized opposing motion of the two second layer Ge atoms. Since the optical phonons of bulk Ge are somewhat higher in frequency than in GaAs,³ this surface mode might already be related to an optical phonon of bulk Ge confined in the overlayer.

Another interesting point to mention is that the results for the dynamical properties of the one ML system do not seem to show an instability towards reconstruction at zero temperature. In fact, the instability towards the formation of a superstructure along or perpendicular to the surface zigzag chains would result in the occurrence of imaginary frequencies for some phonon along the $\bar{\Gamma}\bar{X}$ direction or the $\bar{\Gamma}\bar{X}'$ direction. Since the calculated frequencies are well above zero, we expect the one ML covered GaAs(110)-(1×1):Ge surface at $T = 0$ to be dynamically metastable while the instability towards cluster formation is of thermodynamical origin. However, an instability towards reconstruction with periodicity in direction other than $\bar{\Gamma}\bar{X}$ and $\bar{\Gamma}\bar{X}'$ cannot be excluded by the present calculation.

IV. SUMMARY

In the present paper we have reported the results of an *ab initio* calculation of the relaxation geometries and electronic properties of the GaAs(110):Ge surface covered by one or two ML's Ge. For one ML coverage we furthermore have determined the surface phonon spectra of the fully relaxed system. As in previous model calculations^{17,18} we have found two atomic equilibrium positions corresponding to a positive and a negative tilt angle, respectively. In contrast to the investigations of Refs. 17 and 18, our calculation favors a positive buckling of the outermost Ge chains similarly to the relaxation of the clean GaAs(110) surface above negatively tilted Ge chains. From thermodynamical considerations it has been demonstrated that the ordered adlayer systems are unstable towards cluster formation as experimentally observed. Nevertheless, the investigation of the GaAs(110)-(1×1) surface with one and two adsorbed Ge layers provides interesting information under various aspects. As could be seen from the relative piling of the valence charge densities, all structures have in common an occupied (unoccupied)

dangling bond located at the outward (inward) relaxed Ge atoms of the surface layer. In the discussion of the electronic band structure, we have pointed out a variety of analogies between the Ge covered and the clean GaAs(110) surface. Additionally, for the two ML coverage, some precursors of interface states of the Ge-GaAs(110) heterojunction have been identified. As a result of the similar atomic and electronic structures, the phonon spectrum of the GaAs(110) surface covered with one ML Ge mainly resembles the features found for the clean surface in Ref. 2. Besides a shift towards lower energies for most of the modes, an interesting effect of the Ge adsorption upon the dispersion relations was the appearance of additional branches among the acoustic surface phonons. However, we found no evidence for early stages of the formation of interface modes at the Ge-GaAs(110) het-

erоjunction. The dynamical analysis of the GaAs(110)-(1×1):Ge surface (1 ML) at $T = 0$ did not show instability towards reconstructions with periodicity along the high-symmetry directions $\bar{\Gamma}\bar{X}$ and $\bar{\Gamma}\bar{X}'$.

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