Ab Initio Calculation of Surface Phonons in GaAs(110)

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We have investigated the dynamics of the relaxed GaAs(110) surface using an *ab initio* linear-response approach in the framework of density-functional theory. The relaxation geometry was found by minimizing the total energy with the help of the Hellmann-Feynman forces. In terms of the electronic ground-state properties we have calculated the full phonon dispersion of GaAs(110) along high symmetry lines of the surface Brillouin zone by means of a self-consistent first-order perturbation scheme without any adjustable parameters. Our results are in excellent agreement with all available experimental data.

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The last years have witnessed a substantial progress in studies of the vibrations in crystal surfaces. Inelastic He atom scattering and electron energy loss spectroscopy have reached such a stage of sophistication that surface phonon dispersion can be measured with high precision for a great variety of systems. The need for microscopic models which describe correctly not only the structural but also the dynamical properties of crystal surfaces has intensified theoretical investigations on this topic. A short summary of what has been done so far is given in [1]. While model calculations can be used for a proper description of the force constants in the surfaces of ionic crystals, a self-consistent treatment of the electrons is necessary in metals and semiconductors. Up to now computationally demanding *ab initio* calculations of surface phonons have been done only for some metals [2–4] and elemental semiconductors [5]. In order to extend the self-consistent description to the surface dynamics of binary semiconductors, we have applied the density-functional linear-response approach proposed in [6,7] to GaAs(110). The method used is different from all former surface calculations of this type. By treating the electronic response with the help of the one-particle Green's function, the advantages of frozen phonon calculations [2] and of the dielectric function approach [3–5] can be combined in one formalism. The method has been applied very successfully to the bulk dynamics of a large number of elemental and binary semiconductors [6] and to other materials [8]. Especially in the case of GaAs all of the details of the bulk phonon spectrum (not only in high symmetry directions) have been reproduced. Therefore we have a reliable basis for our surface phonon calculation.

Among the surfaces of binary semiconductors, GaAs(110) has been studied the most, both experimentally [9–15] and theoretically [16–24]. It is now well established that the surface relaxation is mainly characterized by a bond-length–conserving rotation of the surface chains by a tilt angle of about 30° [9–11,16–19], with As shifted above the ideal (110) plane and Ga shifted towards the bulk. In contrast to the detailed examinations of the structural and electronical properties, up to now only a few investigations have been made on the surface phonons of GaAs(110).

On the experimental side inelastic scattering of He atoms has been used to explore the surface dispersion in the lower part of the frequency spectrum [12,13]. Harten and Toennies performed measurements along the chain direction and along $\overline{\Gamma}\,\overline{M}$ of the surface Brillouin zone [12]. They observed a distinct Rayleigh phonon branch in each direction, a flat branch at 13 meV in the vicinity of $\overline{X}$, and a weak dispersionless feature in the chain direction at about 10 meV. Doak and Nguyen [13] confirmed the results of [12]. Moreover, looking at the direction perpendicular to the surface chains, they found two acoustic surface modes with a zone boundary energy of 5.6 meV and 7.3 meV. The high frequency surface phonons were investigated by high resolution electron energy loss spectroscopy, which is dominated by the Fuchs-Kliewer mode at about 35 meV [14,15].

Most of the previous theoretical work on the dynamics of GaAs(110) is based on semiempirical approaches to describe the interatomic force constants. Santini and co-workers applied the bond charge model to GaAs(110) [20,21]. In [22] and [23] a tight-binding model was used to explore the surface dynamics. Das and Allen investigated the surface phonons by means of a nearest neighbor force constant model [24]. The calculations of [20–24] offer a rough insight into the microscopic nature of the dynamics in GaAs(110). Nevertheless, it is necessary to examine the surface vibrations starting from first principles in order to achieve correct force constants from a consistent description of the charge redistribution at the surface, due to the relaxation and atomic displacements. The only previous *ab initio* calculations on the dynamics of GaAs(110) were done by Di Felice and co-workers by performing Car-Parrinello molecular dynamics simulations for supercells containing five (110) layers [19].

With our calculation we have been able to go beyond such supercell calculations, which are restricted to a few high symmetry points. We have succeeded in determining from first principles the full phonon disper-

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TABLE I. Atomic geometry of the relaxed GaAs(110) surface, compared with low energy electron diffraction (LEED) and former calculations. The displacements of the top layer atoms are shown in the first two rows. The quantities $\Delta_{1,\perp}$, $\Delta_{1,\parallel}$, $\Delta_{2,\perp}$, $d_{12,\perp}$, $d_{12,\parallel}$ are defined in Fig. 1. All values are given in Å. The rotation angle is defined by $\omega = \tan^{-1}(\Delta_{1,\perp}/\Delta_{1,h})$.

	Theory				LEED	
	Present	Di Felice *et al.* Ref. [19]	Ferraz *et al.* Ref. [16]	Qian *et al.* Ref. [18]	Puga *et al.* Ref. [9]	Tong *et al.* Ref. [10]
As	$0.220\uparrow$	—	$0.235\uparrow$	$0.143\uparrow$	$0.193\uparrow$	$0.176\uparrow$
Ga	$0.435\downarrow$	—	$0.510\downarrow$	$0.442\downarrow$	$0.515\downarrow$	$0.510\downarrow$
$\Delta_{1,\perp}$	0.66	0.64	0.75	0.58	0.71	0.69
$\Delta_{1,\parallel}$	4.45	4.39	4.45	4.39	4.43	4.36
$\Delta_{2,\perp}$	−0.09	−0.06	−0.04	−0.07	−0.06	−0.03
$d_{12,\perp}$	1.47	1.47	1.46	1.44	1.45	1.47
$d_{12,\parallel}$	3.22	3.21	3.36	3.18	3.18	3.17
ω	29.3°	28.5°	31.6°	27.4°	30.1°	28.0°

sion parallel and perpendicular to the surface chains. The electronic problem was solved in the framework of density-functional theory in the local density approximation with the parametrization of Perdew and Zunger for the exchange-correlation potential [25]. For the expansion in plane waves up to 10 Ry we used the norm-conserving nonlocal pseudopotentials generated by Giannozzi [26]. With these pseudopotentials the bulk phonon frequencies and the bulk lattice constant are converged quite well even at such small cutoff energies. For sampling over the surface Brillouin zone we used six special points. The lattice constant of 5.613 Å was determined in bulk calculations. We introduced a periodic slab configuration consisting of periodically repeated nine-layer slabs separated by vacuum equal to three layers. Such a spacing turned out to be sufficient, as the electronic band structure remained unchanged, irrespective of an increase in the distance between neighboring slabs. Further evidence came from a phonon calculation performed for five-layer slabs showing no dispersion perpendicular to the surface. For symmetry reasons it is advantageous to use an odd number of layers per slab. In agreement with other calculations [16,17] we found that nine layers guarantee quite a good decoupling of the surfaces bordering one slab.

The determination of the relaxation geometry was done by minimizing the total energy with the help of the Hellmann-Feynman forces starting from the ideal surface. In order to find the zero-force configuration, we applied the modified Broyden scheme proposed in [27]. As pointed out in Table I, our results for the surface relaxation are in excellent agreement with experimental data and previous calculations, thus confirming the rotation-relaxation model. In a side view of the first three layers Fig. 1 illustrates the buckling of the surface chains by a tilt angle of about 30°.

The surface dynamics were treated by calculating the harmonic force constants of the fully relaxed nine-layer slab. In order to obtain the static linear electronic response to a lattice distortion in terms of the electronic ground-state properties, we used the density-functional perturbation scheme described in full detail in [7]. The key step of this method is that the variation of the charge density in response to an atomic displacement is calculated iteratively until self-consistency is achieved with respect to the screened perturbing potential caused by the lattice distortion. The calculated interatomic force constants decrease at least 2 orders of magnitude for atoms separated by more than three layers compared to the nearest neighbor interactions. Therefore the force constants of a nine-layer slab were used to model the dynamical matrices of a much larger slab containing 25 layers [28]. In order to obtain the full dispersion parallel and perpendicular to the surface chains, we used the interplanar force constants calculated from four dynamical

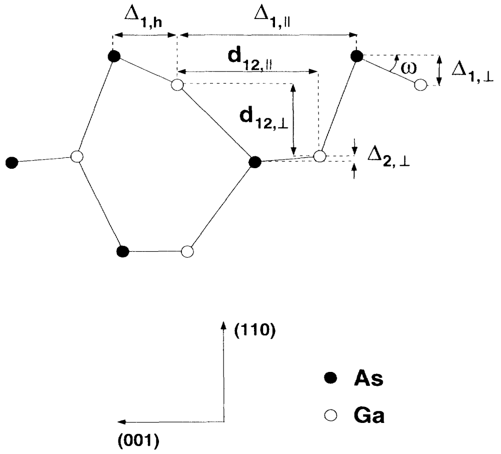

FIG. 1. Side view of the first three layers of the relaxed GaAs(110) surface. The relaxation parameters refer to Table I.

matrices in the $\overline{\Gamma}\,\overline{X}$ and three dynamical matrices in the $\overline{\Gamma}\,\overline{X}'$ direction.

Figure 2 summarizes our results. The large shaded area indicates the surface-projected bulk band structure. As can be seen, the calculated dispersion of the surface acoustic phonons is in excellent agreement with the He scattering experiments of [12,13]. The lowest mode in the $\overline{\Gamma}\,\overline{X}$ direction is the Rayleigh wave (RW) which starts at $\overline{\Gamma}$ as an in-phase vibration of the surface atoms normal to the (110) plane. Approaching the zone boundary, it switches to an in-phase vibration of the first layer As ions and second layer Ga ions perpendicular to the surface with an energy of 8.60 meV. The acoustic phonon above the RW begins for long wavelengths as a shear horizontal mode. In the vicinity of the $\overline{X}$ point, however, it acquires a strong vertical component with a displacement pattern complementary to the RW linked to the inequivalence of the surface atoms. In the vicinity of the $\overline{X}$ point we find a flat branch at 13 meV denoted as A_2 in the experiment of [12]. In very good agreement with [20], this mode is dominated by a vibration of the first layer Ga ions in the chain direction and of the uppermost As ions perpendicular to the surface chains. Our calculations do not reveal a clear surface state which would explain entirely the flat branch at 10 meV in the $\overline{\Gamma}\,\overline{X}$ direction referred to as A_1 in [12]. In order to clarify the origin of this feature, we have calculated the differential reflection coefficient of inelastic He scattering for constant-Q scans using Eq. (6.37) of Ref. [1]. Figure 3 shows three typical constant-Q scan curves for scans between the $\overline{\Gamma}$ point ($\xi = 0$) and the $\overline{X}$ point ($\xi = 1$). Besides the distinct peak of the RW, we observe a broad feature at 10 meV arising mainly from a series of states which penetrate deeply into the bulk. It is present in the regions indicated as dashed areas in Fig. 2. Near the zone boundary, the A_2 mode occurs as a further distinct peak. In comparison with the curves of [12], we find a good agreement for the width and relative intensities of all peaks.

In the $\overline{\Gamma}\,\overline{X}'$ direction our calculation yields three surface-localized acoustic phonons with a zone boundary energy of 5.78 meV, 6.13 meV, and 7.58 meV, respectively. The intermediate phonon branch displays a strictly horizontal displacement pattern in the chain direction, so that it cannot be detected in He scattering experiments. The other two branches are polarized normal to the surface chains. The upper phonon starts at $\overline{\Gamma}$ with atomic motions mainly parallel to the (110) plane. However, approaching the zone boundary, the top layer atoms are vibrating normal to the surface, while the second layer atoms are moving in the (110) plane. The lower acoustic phonon shows a complementary displace-

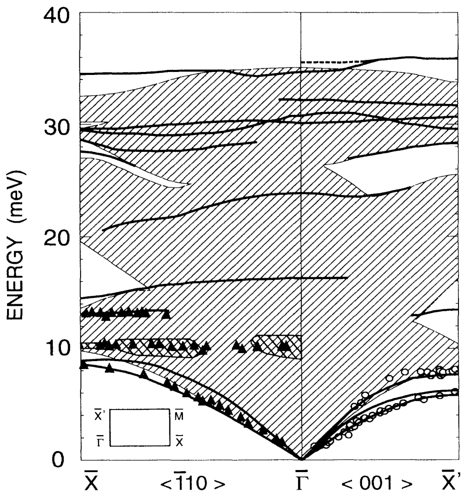

FIG. 2. Phonon spectrum of the relaxed GaAs(110) surface. The surface-projected bulk band structure is represented by the large shaded area. Surface-localized and resonant states are drawn as solid lines. The dashed areas at about 10 meV indicate the regions where the A_1 peak is present in our calculated constant-Q scan intensities. In the $\overline{\Gamma}\,\overline{X}'$ direction the two individual states of the highest surface phonon show an LO-TO splitting indicated by the heavy dashed line at about 35 meV. Inelastic He scattering data are depicted as triangles (Ref. [12]) and open circles (Ref. [13]). The irreducible wedge of the surface Brillouin zone is shown in the inset.

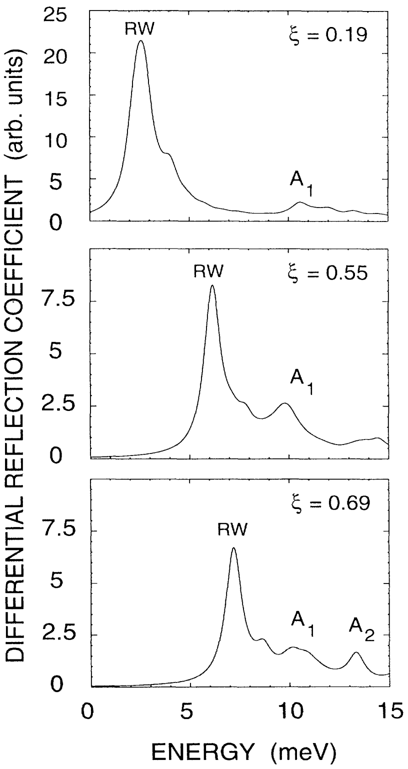

FIG. 3. Differential reflection coefficient calculated for constant-Q scans at three different points between $\overline{\Gamma}$ ($\xi = 0$) and $\overline{X}$ ($\xi = 1$).

ment pattern. This agrees very well with the results of [19] and with the observed scattering intensities of [13]. Because of the behavior of the lower phonon starting at $\overline{\Gamma}$ as a vibration mostly normal to the surface, and because of its group velocity near the zone center of about 2820 m/s, in accordance with continuum theory [29] we identify this branch as the RW.

In the lower part of the phonon spectrum an additional flat branch occurs in the $\overline{\Gamma}\overline{X}$ direction with an energy of 16.45 meV at $\overline{\Gamma}$ and 14.53 meV at $\overline{X}$. In the vicinity of the $\overline{X}'$ point our calculation places this phonon at 13.44 meV. It is dominated by a motion of the topmost Ga ions perpendicular to the chain direction. A similar mode was found in the molecular dynamics simulations of [19], although at smaller energies.

The most significant surface optical phonon of our calculation occurs above the bulk phonon bands. Its displacement pattern is dominated by an opposing motion of the first layer Ga ions and the second layer As ions perpendicular to the surface chains. The zone boundary energy of this mode is 34.40 meV at $\overline{X}$ and 35.70 meV at $\overline{X}'$. Approaching the zone center in the $\overline{\Gamma}\overline{X}$ direction, it touches the bulk continuum with an energy of 34.59 meV. For long wavelengths in the $\overline{\Gamma}\overline{X}'$ direction, however, we find an LO-TO splitting between the two individual states forming the pair related to the surface optical phonon. This is due to the symmetry which leads to an effect of the macroscopic polarization only on one of the two individual states. The higher mode is pure longitudinal optic and involves all layers of the slab. It matches the Fuchs-Kliewer mode at $\overline{\Gamma}$, with an energy of 35.33 meV. Because of the finite number of layers per slab, this LO mode is slightly split off the bulk continuum. For very large slabs its frequency converges to the bulk value of the longitudinal optic phonon lying at 35.2 meV, which is slightly underestimated due to the small cutoff energy of 10 Ry.

In conclusion, we have presented a completely self-consistent calculation of the surface geometry and surface dynamics of GaAs(110). We have achieved excellent agreement with the experimental data for the surface relaxation and all available experimental data for the surface phonons without adjusting any parameters.

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