Dynamics and structural assessment of open semiconductor surfaces: GaAs(110)

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We present a bond-charge-model slab calculation for the surface dynamics of GaAs(110), which represents an example of an open surface with unsaturated dangling bonds. The comparison to previously reported and some new He inelastic-scattering data for the low-frequency region provides information on the surface geometry.

In spite of the rapid, continuous progress of first-principles methods, triggered by the advent of supercomputers, there will always be a class of dynamical problems which are too large for *ab initio* treatments and still need to be handled with models where the role of electrons is properly accounted for. At present this problem still exists with extensively reconstructed surfaces, like Si(111)2×1, or open surfaces with unsaturated dangling bonds, like GaAs(110), where the perturbation with respect to the ideal surface involves many atoms, possibly distributed over several layers. Moreover there is still a need for simple realistic models. These provide a method for analyzing surface phonon data in terms of subtle features of the surface structure.

In the case of Si(111)2×1,[1] bond-charge-model (BCM) (Refs. 2 and 3) calculations provided a consistent description of the optical phonons and their dipole activity, and of the low-frequency dispersion curves measured by He scattering.[4] Moreover zone-boundary He-scattering data have been used to determine the tilt of the Π-bonded atomic chains.

This paper is devoted to a BCM study of an open surface, GaAs(110), which has a row structure similar to that of Si(111)2×1, but is unreconstructed, with a dangling bond above each As ion in the topmost chain. The analysis of the surface phonon-dispersion curves derived from previous[5] and newly analyzed He scattering data leads to a precise determination of the chain tilt, in excellent agreement with Duke *et al.* low-energy electron-diffraction (LEED) measurements.[6]

In recent years the properties[5–17] of GaAs(110) have been extensively investigated. The qualitative pattern of the equilibrium positions for the surface atoms is now fairly well established. The surface has the same periodicity of an ideal (110) plane, but it displays a relaxation of the topmost atoms, with As shifted above the ideal surface plane and Ga shifted toward the bulk. More precisely the relaxation consists in a nearly bond-length-conserving rotation of the surface $\langle 1\bar{1}0 \rangle$ chains by a tilt angle of about 30°, whereas the subsurface chains have a much smaller tilt.[14] Yet some uncertainty still exists with regard to the exact chain position and values of the tilt angle.

The surface dynamics of GaAs(110) has been studied by high-resolution He atom time-of-flight (TOF) inelastic scattering. The experimental details have been described in previous papers.[5,18,19] In order to test the BCM for vibrational and structural studies of open surfaces we were led to a refined analysis of the experimental data and a detailed examination of some weaker features in the TOF spectra (some of the TOF spectra showing new data are displayed in Fig. 1). The results are collected in Fig. 2 ($\bar{\Gamma}\bar{X}$ and $\bar{\Gamma}\bar{M}$): solid dots are the previous set of data (Ref. 5), open circles are features identified in the analysis, and solid triangles ($\bar{\Gamma}\bar{X}'$) display the He-scattering data of Doak and Nguyen.[9] In the $\bar{\Gamma}\bar{X}$ direction, along the surface chains, double peaks in the creation side are related to two closely spaced phonons both at about 8 meV at the zone boundary. Along $\bar{\Gamma}\bar{M}$, despite a lower signal-to-noise ratio, zone-boundary Rayleigh waves (RW) in the annihilation side[20] and a weak feature at ~14 meV corresponding to a gap mode, in the high-energy part of the creation side, are identified. The data of Doak and Nguyen[9] along $\bar{\Gamma}\bar{X}'$ (normal to the surface chains) consist of two surface acoustic modes with zone-boundary energies of 5.6 and 7.3 meV and some weaker peaks at about 10 meV near the zone center. We remark that $\bar{\Gamma}\bar{X}'$ is the only direction with a mirror plane symmetry. Thus all modes are either sagittal (displacement field in the scattering plane) or shear horizontal (SH: displacement field normal to the scattering plane), and scattering intensity from SH modes is symmetry forbidden for the planar scattering configuration. For the directions of our measurements the scattering plane is not a mirror symmetry plane: here He-scattering data require a more careful analysis, because SH and sagittal components can mix together.

GaAs(110) is similar to Si(111)2×1, where tilted chains are produced by the reconstruction (the two surfaces have indeed the same rectangular surface Brillouin zone). This similarity is reflected in the experimental surface phonon data, which show for both surfaces a low-frequency flat branch at about 10 meV, just above the RW.[4,5] The isolated chain dynamics on top of a rigid lat-

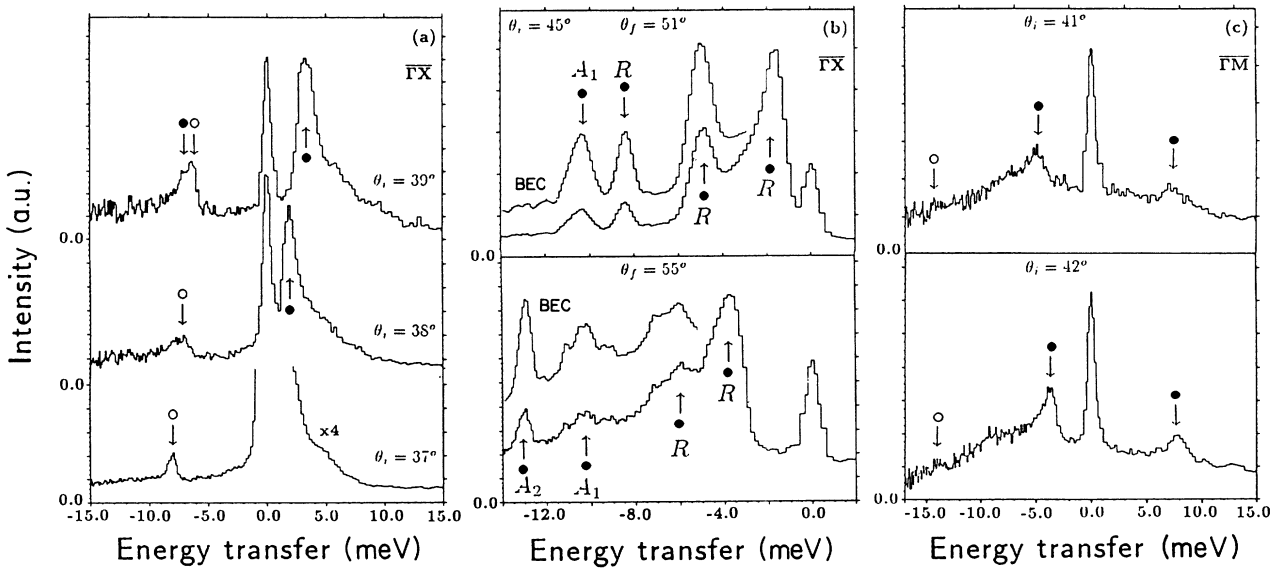

FIG. 1. A series of typical TOF spectra transformed to an energy scale for creation and annihilation of phonons along the $\bar{\Gamma}\bar{X}$ (a) and (b) and $\bar{\Gamma}\bar{M}$ (c) directions. The arrows with solids dots correspond to experimental data from Ref. 5, whereas the arrows with open circles are from a new analysis of the same experiments. In (b) the curves labeled by BEC are the usual TOF spectra Bose-Einstein corrected by dividing by the phonon occupation number on the creation side.

tice, as calculated by Wang and Duke for GaAs(110) with the sp^3s^* tight-binding model,[16] as well as our detailed BCM calculation for Si(111)2×1,[1] indicate that the new mode (at the zone center) is a bond-length-conserving libration of the topmost chain.

Our calculation for a slab of 23 atomic layers is performed in the framework of the BCM,[2,3] which is known to reproduce the bulk dispersion curves of GaAs with only six parameters.[3] In order to take into account the surface relaxation we modify the core positions at the surface and in the subsurface layer according to the widely accepted geometrical model proposed by Duke *et al.*[6] This latter provides a bond-length-conserving configuration (a rigid rotation by a tilt angle of 31.1°) which is particularly suitable to exploit the intrinsic dynamical features of this surface.

The surface bond charges (BC's) are placed where the charge-density maps exhibit their maxima[13] at distances from As and Ga ions in a 3:5 ratio.[3] The doubly occupied dangling bonds belonging to the As atoms[8] are also described by BC's.

The equilibrium conditions are imposed on all the surface cores and BC's: in this way values for the first derivatives of the central ion-ion and ion-BC potentials are obtained. Since the second derivatives are not affected by such a condition, we set them equal to the bulk values. This choice is supported by the bond-length conservation, which, however, cannot be taken as a sufficient condition for the use of bulk parameters. Another condition requires that the electronic configuration of the row BC be the same as in the bulk. However we have observed in the case of Si(111)2×1 that the transfer of the dangling electrons into the Π orbitals located at the row BC's affects the shear but not the radial force constants (FC's). This is due to the fact that a Π orbital has a nodal plane crossing the atoms and its overlap with the core states protruding in the bond direction is modulated by the shear but not by the BC radial displacement.

In the present heteropolar case, with a doubly occupied dangling bond, one deals with more atomiclike hybrid states. As we learn from Mailhiot *et al.* total-energy calculations,[17] the bond charges surrounding the top As ions are associated with the A_4 surface states at the top of the valence band, just below the As dangling-bond states (A_5). The surface relaxation, notably the chain tilt, is driven by the lowering and rehybridization of these branches and this should also provide the microscopic mechanism for the shear BC-ion FC changes implied in the equilibrium conditions. We actually have a moderate stiffening (~13%), in contrast to the case of Si(111)2×1, where the additional electron yields a substantial softening of the BC-ion shear FC. The change of FC's due to the relaxation-induced modification of the bond angles is accounted for by the geometric part of the Keating FC matrices, which are calculated for the actual bond configuration. In principle, Keating constants (β_1 and β_2) should themselves change with bond angles due to anharmonicity.[21] However Raman data for GaAs,[22] as well as more recent data for silicon and diamond,[23] under stress indicate that such corrections are small, and should stay within a few percent even if extrapolated to angle bending as large as 15°.

The results of our calculation for the lower part of the energy spectrum are shown in Fig. 2: solid lines are surface modes (dashed if weak) and shaded areas are the surface projection of the bulk bands. In the $\bar{\Gamma}\bar{X}$ direction the lower branch is the RW with a zone-boundary energy of 7.6 meV. Above the RW a second acoustic surface branch (R) is present with a zone-boundary energy of 8.2 meV; its character is SH along most of the $\Gamma\bar{X}$ direction (displacement field normal to the surface chains), and

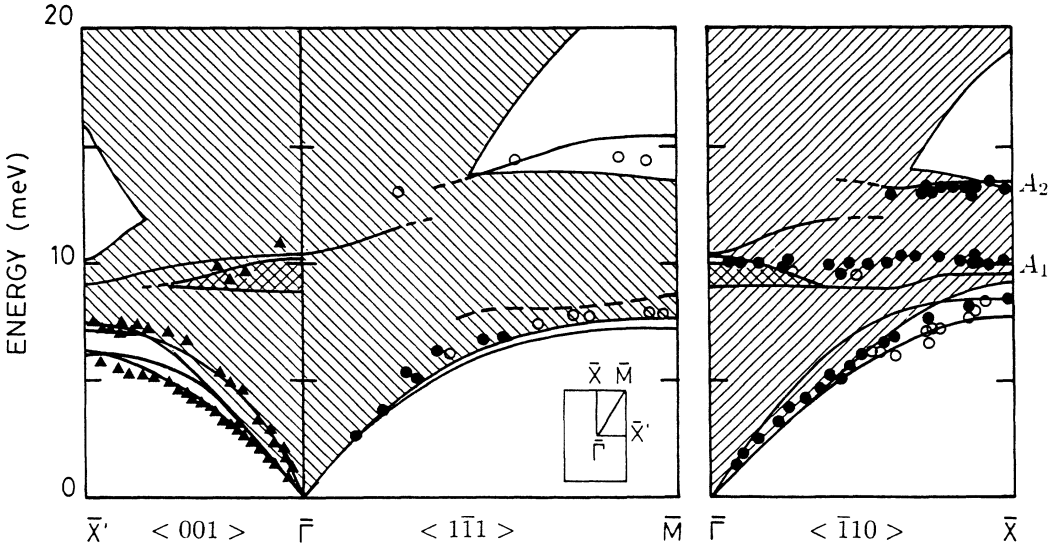

FIG. 2. Low-energy part of the phonon spectrum of GaAs(110). Shaded areas represent the surface projection of the bulk bands, solid lines and dashed lines correspond to the surface modes and to the resonances, respectively. Solid dots are experimental data from Ref. 5, triangles from Ref. 9. The open circles are from an analysis of the experiments of Ref. 5. The surface Brillouin zone is shown in the inset.

therefore cannot be detected by He-scattering experiments. Approaching the zone-boundary its polarization acquires a strong vertical component, and at the $\bar{X}$ point R consists essentially of a vibration of the Ga surface atoms normal to the tiled chain plane, yielding, in this way, a He-scattering cross section greater than the zone-boundary RW, which has only a small amplitude in the first layer. Indeed the experimental branch follows the RW for the major part of the $\bar{\Gamma}\bar{X}$ direction, and switches to R approaching the $\bar{X}$ point. This effect leads to the double-peak structure seen on the creation side [Fig. 1(a)]. The same polarization exchange mechanism occurs for the RW and the weaker resonance in the $\bar{\Gamma}\bar{M}$ direction, but here the weak structure cannot be experimentally resolved and lies at an average frequency.

Along $\bar{\Gamma}\bar{X}'$, our calculation reveals two acoustic surface branches with sagittal polarization—the RW and a longitudinal resonance—in excellent agreement with the data of Doak and Nguyen.[9] Along $\bar{\Gamma}\bar{X}$ we find a 13-meV flat branch (A_2) in very good agreement with experiment. A_2 lies in the TA-LA gap near $\bar{X}$, where it appears as a vibration of the As atoms normal to the tilted chain plane and of Ga atoms parallel to the chain. The same branch is found also along $\bar{\Gamma}\bar{M}$ in the gap.

A crucial aspect of this study is that, without any fitting of the model parameters, the 10-meV flat branch (A_1) is predicted in $\bar{\Gamma}\bar{X}$ and $\bar{\Gamma}\bar{X}'$ directions, about 1 meV below the A experimental data. A_1 is a true surface mode near the zone boundary, a broad resonance (dark areas in Fig. 2) at the zone center. The quasidegeneracy with the RW at the zone boundary, similar to that observed in Si(111)2×1,[4] is attributed to the folding of the RW.[1] Indeed also GaAs(110), though unreconstructed, has two molecules in the surface unit cell and almost equal ionic masses. Thus the following dynamical behavior is predicted for the modes R and A_1 at $\bar{X}$. In the *lower* mode only the Ga ions, which are the lighter, are moving whereas in the *upper* mode the heavier As ions are moving. Experimentally, A_1 is slightly more intense than R [Fig. 1(b)]. The two facts are consistent, since the He-scattering potential of the big As ion, on top of the chain, should be larger than that of the smaller Ga ions, located in a lower position. Such eigenvector inversion has been observed in GaAs bulk[24] and has been regarded as a crucial test for dynamical models.

As for Si(111)2×1, the gaps between A_1 and RW and between A_1 and A_2 depend crucially on the chain geometry. To study this we varied separately the two most important parameters of the surface relaxation, i.e., the value of the tilt angle and of the interchain distance. A bond-length-conserving decrease of the tilt angle, from 31° to 29°, enlarges the A_1A_2 gap by 1.1 meV, whereas a small decrease of the interchain distance as small as 2% with a fixed tilt angle lowers the RW by 1 meV. Both kinds of variations cause appreciable disagreement with experiment. We also made a calculation with Tong's configuration,[7] differing from Duke *et al.* geometry[6] for the absence of parallel displacements of the surface atoms, and found an unstable behavior of the RW near the $\bar{X}$ point. On the other hand, a slightly larger value of the tilt angle, ~33°, would produce the best fit of the two flat branches. In any case our analysis provides an excellent confirmation of Duke *et al.* geometry.[6]

In conclusion, we have demonstrated the validity of BCM for the surface lattice dynamics of heteropolar semiconductors, even in the presence of unsaturated dan-

gling bonds. The experimental features of GaAs(110) are nicely reproduced with no *ad hoc* parameter adjustment. From the best fit of zone-boundary phonons the geometrical parameters of the surface structure are determined in good agreement with the model of Duke *et al.*[6]

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