Dispersion of GaAs(110) surface phonons measured with HREELS

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The surface-phonon dispersion of cleaved GaAs(110) surfaces was studied by use of high-resolution electron-energy-loss spectroscopy along the symmetry directions $\bar{\Gamma}\bar{X}$ and $\bar{\Gamma}\bar{X}'$, i.e., parallel and perpendicular to the surface Ga-As chains. The energy of the incident electrons was varied between 4 and 80 eV. Besides two acoustic-surface-phonon branches with energies lower than 9 meV, four almost flat phonon bands were recorded at 10.5, 16.5, 21.5, and 35.8 meV. The experimental results agree very well with recent *ab initio* calculations of GaAs(110) surface-phonon dispersion.

I. INTRODUCTION

The clean GaAs(110) surface is one of the most studied crystalline surfaces of binary semiconductors. However, only a few investigations discussed the vibrational properties. The first experimental studies of GaAs(110) surface-phonon dispersions were done with inelastic He atom scattering[1,2] along the main axes and the diagonal of the rectangular surface Brillouin zone (BZ). Two acoustic modes and two flat bands at about 10 and 13 meV were reported. These studies encouraged an intensive theoretical work especially on explaining the flat mode at 10 meV.

Different semiempirical models based on tight-binding methods,[3–5] on the bond-charge concept[6,7] and on nearest-neighbor force constants[8] were applied. In 1993, the first numerically demanding *ab initio* calculations of GaAs(110) surface phonons were published. Whereas Di Felice *et al.*[9] determined phonon energies only at the principal symmetry points in reciprocal space, Fritsch, Pavone, and Schröder[10] calculated complete surface-phonon dispersion curves up to energies of 40 meV.

The energy range above 13 meV is experimentally not accessible to He atom scattering but it may be studied with high-resolution electron-energy-loss spectroscopy (HREELS).[11–13] Clean and adsorbate-covered GaAs(110) surfaces were extensively investigated by HREELS but almost exclusively in specular scattering geometry, i.e., in the long-wavelength limit at the $\bar{\Gamma}$ point. Here, the predominant energy loss at about 36 meV is due to the optical surface or Fuchs-Kliewer phonon.[14,15] Numerical second derivatives of HREEL spectra revealed two additional modes at 17 and 23 meV (Ref. 16). A mode at 16 meV was only detected as an anti-Stokes line on the energy-gain side of a HREEL spectrum.[17]

Very few HREEL studies beyond the $\bar{\Gamma}$ point have been published. They examined the dispersion of free-carrier surface plasmons coupled to the optical-phonon mode on GaAs(110) (Ref. 18) and GaAs(001) surfaces.[19] However, these investigations were restricted to parallel wave-vector transfers in the very vicinity of $\bar{\Gamma}$.

In the present HREEL study, GaAs(110) surface phonons up to 40 meV excitation energy are examined throughout the whole surface BZ.

II. EXPERIMENT

The experiments were carried out under ultrahigh vacuum conditions at a base pressure lower than 10^{-8} Pa. GaAs(110) surfaces were prepared by cleaving rectangular bars of semi-insulating single crystals in a preparation chamber. Semi-insulating material was used to avoid free-charge carrier surface plasmon excitations which may broaden the peaks in the loss spectra[20,21] or even couple with phonon modes.[15,17]

After moving the samples into the analysis chamber, HREEL spectra were recorded by a spectrometer with a double cylindrical deflection monochromator and analyzer.[22] The instrumental energy resolution was typically 30 $\mathrm{cm}^{-1}=3.7$ meV. The primary energy E_p of the incident electrons was varied between 4 and 80 eV. In Fig. 1 an off-specular scattering geometry is explained. The angle of incidence ϑ_i was adjusted to between 47° and 60° whereas the detection angle ϑ_f of the scattered electrons was kept constant at 55° or 60°. The absolute value of the parallel wave-vector transfer $q_{\parallel}$ results from

$$q_{\parallel}=k_i|\sin\vartheta_i-\sin\vartheta_f|\ , \tag{1}$$

if the energy loss is much smaller than E_p (Ref. 23). The absolute value of the wave vector of the incident electrons is represented by k_i.

Due to the finite acceptance angle of the analyzer of approximately 2°, the error of $q_{\parallel}$ was estimated as $\pm 0.7\times 10^9$ m^{-1}. As the maximum count rates were in

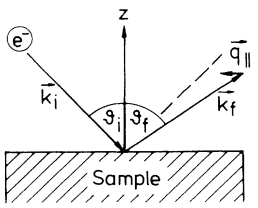

FIG. 1. Electron scattering geometry: $\mathbf{k}_i$ and $\mathbf{k}_f$ are the wave vectors of the incident and the scattered electrons, respectively; $\mathbf{q}_{\parallel}$ is the parallel wave-vector transfer. For $\vartheta_i\neq\vartheta_f$ the scattering geometry is off-specular.

the range of 10–100 counts per second for off-specular scattering geometry it takes a couple of hours to record a loss spectrum of good quality. In all spectra, surface-phonon modes were identified by Stokes and anti-Stokes structures on the energy-loss and -gain side, respectively.

III. RESULTS

The atomic arrangement of the relaxed GaAs(110) surface in real space as well as a quarter of the surface Brillouin zone are depicted in Fig. 2. The Ga-As zigzag chains in the $[\bar{1}10]$ direction are tilted, i.e., the upper Ga-As bonds are rotated with As atoms pointing outward. The tilt angle ω_1 and the normal displacement $d_{1\perp}$ between the upper arsenic and gallium atoms were determined by a variety of methods.[6,24,25] Their average values are 30° and 70° pm, respectively. The surface unit mesh and the surface BZ are rectangular and have the $(\bar{1}10)$ plane as a mirror plane. The notation for the symmetry points in the surface BZ was taken from Ref. 10. In some publications $\bar{Y}$ and $\bar{S}$ are used instead of $\bar{X}'$ and $\bar{M}$.

At $\bar{\Gamma}$, i.e., in the long-wavelength limit were $\vartheta_i \approx \vartheta_f$ and $q_\parallel \approx 0$, inelastic surface scattering of electrons is governed by a dipole interaction between the electric field of the incoming electron and a semi-infinite dielectric.[26] An energy-loss spectrum recorded in specular scattering geometry and at $E_p = 5$ eV is presented in Fig. 3. In addition to the strong optical surface or Fuchs-Kliewer phonon[14,15] at 289 $cm^{-1} = 35.8$ meV, weak and broad structures at approximately 170 $cm^{-1} = 21.1$ meV are clearly resolved on the gain as well as on the loss side. They may be identified with the 23 meV loss in the second-derivative spectra of del Pennino *et al.*[16] At $\bar{\Gamma}$, two additional losses at about 10 and 16 meV were only detected after taking the first derivative of the respective spectra.

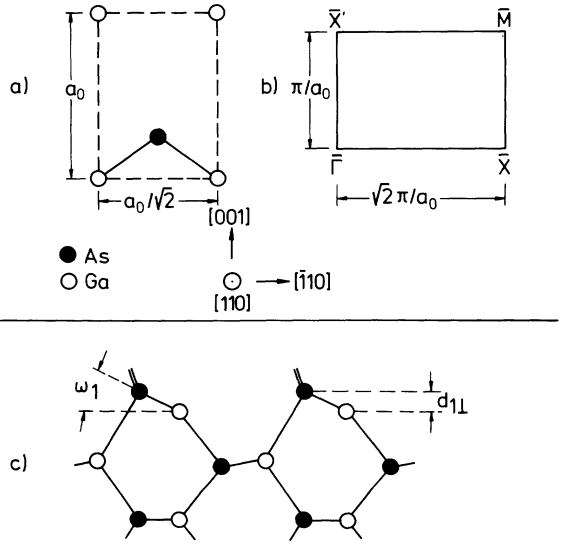

FIG. 2. Structure of relaxed GaAs(110) surfaces: (a) surface unit mesh; a_0 is the lattice constant; (b) a quarter of the respective surface Brillouin zone; (c) side view of the surface along the Ga-As chains in the $[\bar{1}10]$ direction. Closed circles represent As atoms, open circles Ga atoms.

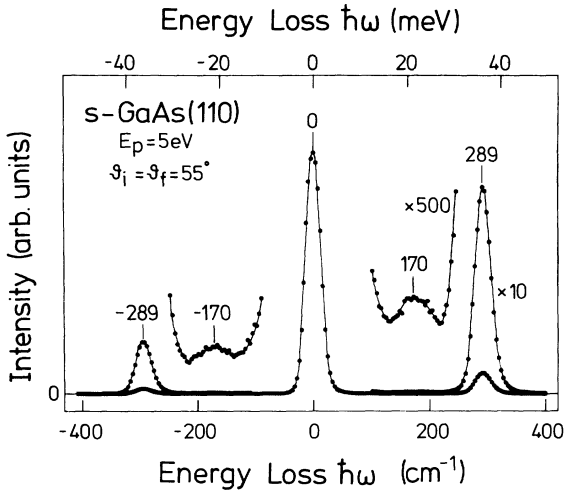

FIG. 3. HREEL spectrum in specular scattering geometry ($\bar{\Gamma}$ point). Two energy-loss and -gain features are observed: a surface-phonon mode at 21.1 meV (170 cm^{-1}) and the Fuchs-Kliewer phonon at 35.8 meV (289 cm^{-1}).

Energy and parallel wave vector are conserved with electron scattering at ordered surfaces.[13,23] Thus, surface-phonon dispersions $\hbar\omega(\mathbf{q}_\parallel)$ were investigated by recording energy-loss spectra in off-specular scattering geometry in $\bar{\Gamma}\bar{X}$ and $\bar{\Gamma}\bar{X}'$ directions, i.e., along and perpendicular to the Ga-As chains, respectively. The wave-vector transfer parallel to the surface $q_\parallel$ is scaled with the respective dimensions of the surface BZ, i.e., the normalized quantities are defined as

$$\zeta = \frac{q_\parallel}{7.9\times10^9\ \mathrm{m}^{-1}} \tag{2}$$

in the $\bar{\Gamma}\bar{X}$ direction and

$$\zeta' = \frac{q_\parallel}{5.5\times10^9\ \mathrm{m}^{-1}} \tag{3}$$

in the $\bar{\Gamma}\bar{X}'$ direction. Some measurements along $\bar{\Gamma}\bar{X}'$ also reached into the second surface BZ ($\zeta' > 1$).

A series of energy-loss spectra for $\zeta' = 0.5$ and various primary energies E_p is shown in Fig. 4. The detection angle ϑ_f of the scattered electrons was fixed at 60° with respect to the surface normal. The solid lines were calculated from the data by use of a Fourier transform filter.

With $E_p = 5$ eV, three loss and respective gain structures, S_1 at 10, S_3 at 21, and S_4 at 34.5 meV, are observed. With increasing the primary energy, a feature A at lower loss energies is noticed. It becomes stronger for higher impact energies and may be attributed to an acoustic-surface-phonon mode. The loss structure S_2 at about 16 meV is rather weak. At this point in the surface BZ it was only observed for $E_p = 60$ eV. Some features at 14 and 30 meV are marked but not labeled in Fig. 4 because they may be interpreted as combination losses of A and S_1 or $-A$ and S_4, respectively. This assignment is most likely since these losses disperse similarly to the acoustic phonon A.

The primary-energy dependence of the excitation cross section can only be described rather qualitatively as the background due to multiple phonon excitations is unknown. On the other hand, it was demonstrated that the cross section is an oscillatory function of E_p (Ref. 27). However, the acoustic mode A is obviously more intense at higher excitation energies.

In Fig. 5 electron-energy-loss spectra are shown which were recorded at fixed impact energy, $E_p = 80$ eV, and different $q_\parallel$ in the $\bar{\Gamma}\bar{X}$ direction. Only the predominant energy-loss and -gain structures A and S_2 are indicated. The energy of the acoustic surface phonon changes significantly with increasing $q_\parallel$ whereas the mode S_2 remains almost unshifted.

Summarizing the results leads to the dispersion of surface phonons displayed in Fig. 6. The open symbols represent weak structures in the energy-loss spectra. Their energetic positions were determined from the first derivatives which were numerically calculated. The data marked as squares are taken from spectra with $q_\parallel$ in the second surface BZ. Typical errors of $\Delta q_\parallel = \pm 0.7 \times 10^9$ m^{-1} and $\Delta\hbar\omega = \pm 1$ meV are displayed as bars.

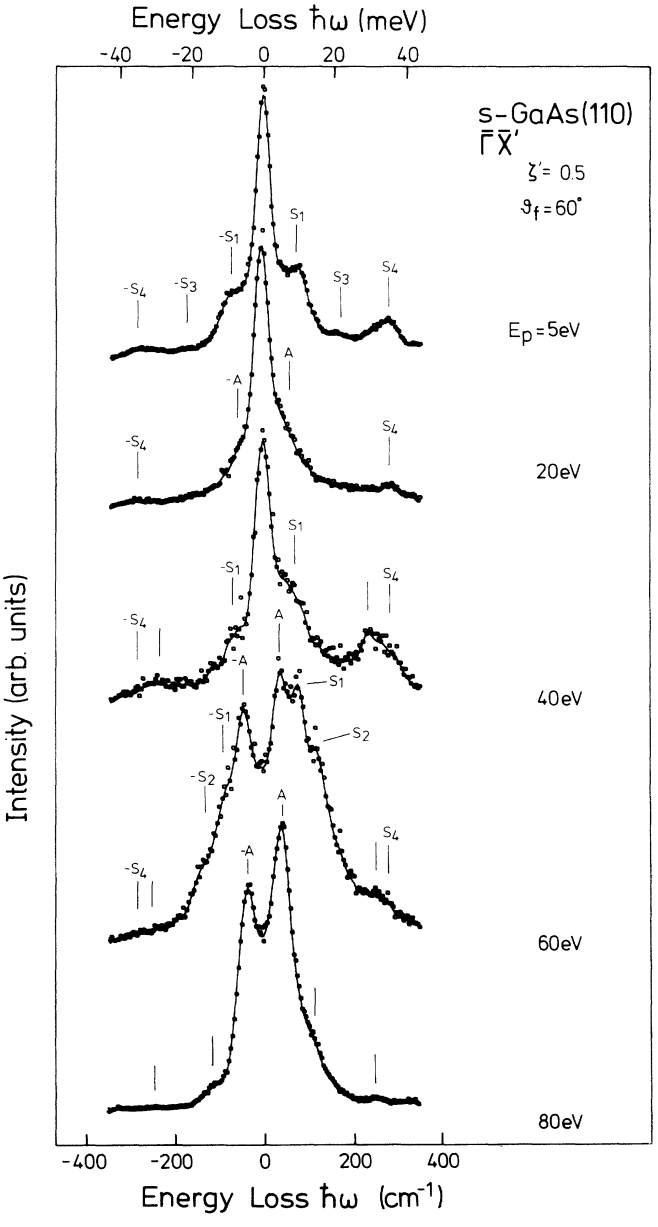

FIG. 4. Series of HREEL spectra along $\bar{\Gamma}\bar{X}'$ with fixed parallel wave-vector transfer at different primary energies E_p of the incident electrons. Five surface phonon modes, S_1 to S_4 and A, are observed. Structures without a label are interpreted as combination losses. Solid lines are approximations after Fourier filtering of the data.

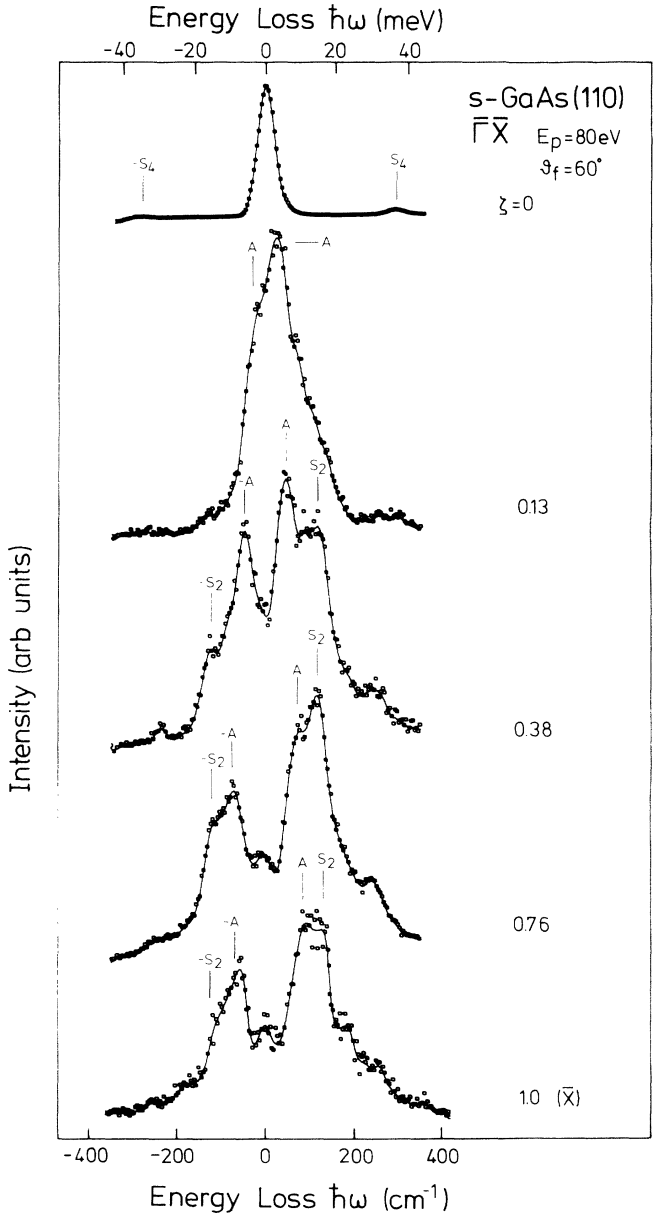

FIG. 5. Series of HREEL spectra along $\bar{\Gamma}\bar{X}$ at fixed primary energy E_p and varying parallel wave-vector transfer. The excitation energy of the acoustic surface phonon A changes significantly with increasing $q_\parallel$ whereas it does not in case of the optical phonon S_2.

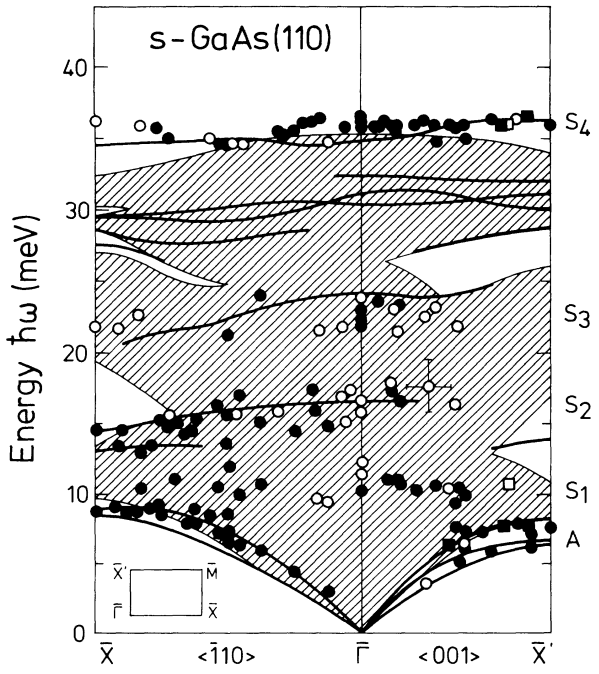

FIG. 6. Surface-phonon dispersion curves for GaAs(110) along $\bar{\Gamma}\bar{X}$ and $\bar{\Gamma}\bar{X}'$. Open circles represent weak structures which were observed in the first derivative of the respective HREEL spectra. Squares are deduced from spectra recorded at $q_{\parallel}$ in the second surface BZ. The projected bulk phonon bands (shaded area) and theoretical surface-phonon bands (solid lines) were taken from the *ab initio* calculation of Ref. 10. Labels S_1 to S_4 and A on the right side correlate the bands with the loss features in Figs. 4 and 5.

IV. DISCUSSION

Recently, Fritsch, Pavone, and Schröder[10] published *ab initio* calculations of GaAs(110) surface phonons. Their dispersion curves are displayed as solid lines in Fig. 6. The shaded area is also taken from Ref. 10 and represents bulk phonon bands which are projected onto the surface BZ.

The measured phonon spectrum of the relaxed GaAs(110) surface in Fig. 6 shows in principle two acoustic and four optical surface-phonon bands which agree very well with theory.

Along $\bar{\Gamma}\bar{X}'$, scattering of data below 10 meV suggests that at least two acoustic phonon modes are involved. The first-principle calculation predicts three acoustic surface modes where the middle branch at 6.1 meV has a shear horizontal polarization[10] and should, thus, not be found with HREELS. Inelastic He atom scattering experiments revealed two modes, the lower Rayleigh wave with 5.6 meV at $\bar{X}'$ and an upper branch with 7.3 meV at $\bar{X}'$ (Ref. 2). In Fig. 6 the upper branch of the experimental data reaches 7.2 meV and the lower one 5.7 meV when approaching the $\bar{X}'$ point. Therefore, it is likely that the two acoustic modes excited by HREELS are the same as those in Ref. 2.

In the $\bar{\Gamma}\bar{X}$ direction only one acoustic surface phonon with 8.6 meV at $\bar{X}$ is detected. Its dispersion agrees well with the one of the upper mode predicted by theory. This acoustic branch begins at $\bar{\Gamma}$ as a shear horizontal mode and acquires a strong vertical polarization approaching $\bar{X}$ (Ref. 10). Thus, it is well excited by electron scattering. Surprisingly, He-scattering experiments gave only the lower phonon branch[1] which may be identified as the Rayleigh wave. At $\bar{X}$, both modes are mainly polarized normal to the surface and, probably, they are both excited but not resolved by HREELS.

At about 10.5 meV, a phonon band with little dispersion is observed along both symmetry directions. For the last years its origin has been discussed controversially as it was already found along $\bar{\Gamma}\bar{X}$ and with poor intensity along $\bar{\Gamma}\bar{X}'$ with He scattering.[1,2] A tight-binding total energy approach suggested a mode with 9.3 meV at $\bar{\Gamma}$ which was attributed to a "chain bouncing," i.e., a normal vibration of the zigzag chains with respect to the substrate.[5] Bond-charge models revealed a true surface mode at the BZ boundary and a broad feature at $\bar{\Gamma}$ in the 10-meV range.[6] This mode was interpreted in terms of "backfolding" of an acoustic surface branch into a smaller BZ (Ref. 7). However, the recent *ab initio* calculations do not clearly identify a surface phonon mode at 10 meV. Fritsch, Pavone, and Schröder observed a broad feature in calculated differential reflection coefficients of inelastic He scattering due to phonon states which penetrate deeply into the bulk.[10] Di Felice *et al.* assume that states at 10 meV are mixed with bulk states.[9] Thus, the character of this loss is still under discussion.

In the upper energy range which is not accessible to He atom scattering, three more flat phonon bands are detected. As shown in Figs. 5 and 6, mode S_2, which is weak at $\bar{\Gamma}$, becomes more intense along $\bar{\Gamma}\bar{X}$. Its excitation energy shifts from 16.5 meV at the BZ center to 14.8 meV at the BZ boundary. The dispersion is well described by theory and refers to a motion of the topmost Ga atoms perpendicular to the chain direction.[10] A tight-binding approach suggested a bond-length conserving rotation of the upper Ga and As atoms at 16.3 meV at $\bar{\Gamma}$ (Ref. 5).

A second branch at $\bar{X}$ at lower energy which was detected with He scattering[1] cannot be safely separated from S_2 in Fig. 6 due to the limited energy resolution of HREELS.

Along $\bar{\Gamma}\bar{X}'$, the mode S_2 can only be followed up to the middle of the surface BZ which is also predicted by theory. For larger parallel wave-vector transfers, combination losses of A and S_1 modes above 16 meV make it impossible to identify the S_2 branch.

The surface-phonon branch S_3 in the range from 21 to 22 meV is predominantly detected at $\bar{\Gamma}$. As the Fuchs-Kliewer phonon it is the only mode which can be clearly resolved in specular scattering geometry. Therefore, the polarization of this mode should have a nonvanishing normal component. Theory proposes a weak and broad surface-phonon state at a somewhat higher energy referring to a motion of arsenic atoms perpendicular to the zigzag chains.[10,28]

The predominant loss structure at $\bar{\Gamma}$ is the optical surface or Fuchs-Kliewer phonon at 35.8 meV. The respec-

tive surface-phonon band was detected up to the surface BZ boundary along both $\bar{\Gamma}\bar{X}$ and $\bar{\Gamma}\bar{X}'$ and is almost flat. The calculations give a smaller excitation energy and a LO-TO splitting at $\bar{\Gamma}$ due to the finite number of layers per slab.[10] For very thick slabs a phonon energy of 35.2 meV at the BZ center is predicted and agrees with the experimental value.

Although loss structures around 30 meV are observed they are not associated with the calculated surface-phonon bands. Theory shows that these modes exhibit polarizations parallel to the surface with a maximum amplitude in deeper layers.[28] Therefore, the cross sections for the excitation of these modes by HREELS should be small or even vanish. This result supports the interpretation of the observed loss structures as combination losses.

V. SUMMARY

This study presents surface-phonon dispersions of the relaxed GaAs(110) surface. It is demonstrated that the cross section for phonon excitation is a function of the primary energy of incident electrons.

Two acoustic phonon bands are identified with 8.6 meV at $\bar{X}$ and 5.7 and 7.2 meV when the $\bar{X}'$ point is approached. Four flat surface-phonon bands are observed. Two of them, at about 10.5 and 36 meV, are observed along both symmetry directions. Another mode varies its excitation energy from 16.5 meV at $\bar{\Gamma}$ to 14.8 meV at $\bar{X}$ and is hardly detected in the $\bar{\Gamma}\bar{X}'$ direction. A surface mode in the range from 21 to 22 meV is mainly observed at $\bar{\Gamma}$. All surface-phonon bands agree very well with *ab initio* calculations.

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