Surface Phonons of InP(110) Studied by Raman Spectroscopy

K. Hinrichs, A. Schierhorn, P. Haier, N. Esser, W. Richter, and J. Sahm
Technische Universität Berlin, Sekretariat PN6-1, Hardenbergstrasse 36, 10623 Berlin, Germany

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We demonstrate that surface phonons of clean semiconductor surfaces can be studied by Raman spectroscopy. In this work the vibrational properties of clean InP(110) surfaces are investigated. Two surface phonons of A' symmetry at 254 and 270 cm^{-1} in the band gap between acoustical and optical bulk branches are observed in agreement with theoretical calculations. Because of their limited resolution previous high-resolution electron-energy-loss spectroscopy experiments found only one surface phonon mode near this energy range. Additionally, three other surface modes at 69, 146, and 347 cm^{-1} are identified by Raman spectroscopy. [S0031-9007(97)03816-7]

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Up to now surface phonons mostly have been studied by high-resolution electron-energy-loss spectroscopy (HREELS) and by helium atom scattering (HAS). Both techniques are well established experimental methods for mapping the surface dispersion band structure [1–4]. The main drawback of HAS is its limitation to low energy vibrations (below 250 cm^{-1}), whereas HREELS is used to monitor surface phonons with energies up to several 1000 cm^{-1}. Because of the larger penetration depth of photons compared to that of low energy electrons and atoms, optical methods seem to be less sensitive for surface properties than HREELS and HAS.

In recent years, however, resonant Raman spectroscopy (RRS) has been used successfully in surface physics. For resonant Raman conditions the incident optical quantum energy has to approach to an electronic surface state energy, leading to a strong enhancement of the Raman scattering cross section [5]. Because of different electronic band structures of bulk and surface, the corresponding vibrations show different energy dependences of the resonance behavior. Thus it was possible to determine surface vibrations of monolayer terminated semiconductor surfaces like Sb on InP(110) [6,7] and Sb on GaAs(110) [7] and As on Si(111) [7], respectively. Weak signals of adsorbate terminated semiconductors under nonresonant conditions were found for S on InP(001) [8] and H terminated vicinal Si(111) surfaces [9]. Raman signals from surface phonons of clean surfaces, however, have not been reported so far. Raman spectroscopy (RS) as an optical technique is sensitive to vibrations with near zero momentum; however, in general its energy resolution of a few cm^{-1} is distinctly higher than that of HREELS (approximately 30 cm^{-1} [1]). Another advantage of RS compared with particle scattering techniques is the possibility of exciting surface phonon modes polarized parallel to the surface plane.

It seemed of much interest to apply RS to clean InP(110) surfaces, because this surface has been investigated recently by several other methods. The studies of the vibrational properties of clean InP(110) surfaces include HREELS [1] on the one hand and various calculations on the other hand using the density-functional perturbation theory (DFPT) [10], the phenomenological bond-charge model (BCM) [11], and the pseudopotential frozen-phonon method [12], respectively. As a common result of these calculations there should be at least two A' surface modes within the band gap between the acoustical and optical bulk phonon branches (226 to 290 cm^{-1} at the $\overline{\Gamma}$ point). This result fits to former tight binding molecular dynamics simulations [13] which predicted two gap modes at 215 and 227 cm^{-1}. We refer more extensively to the BCM calculations [11] classifying three optical A'' and six optical A' modes at the $\overline{\Gamma}$ point. The optical A' modes are predicted to show up at 73 and 93 cm^{-1} (overlapping with the acoustical branches), at 227 cm^{-1} (lower gap mode) and 280 cm^{-1} (upper gap mode), 299 cm^{-1} (overlapping with optical branches), and 349 cm^{-1} (Fuchs-Kliewer phonon [14]).

In good agreement with these calculations HREELS showed surface phonon modes at about 77 and 341 cm^{-1} (Fuchs-Kliewer phonon), but only one gap mode at about 246 cm^{-1} at the $\overline{\Gamma}$ point. Additionally, a surface phonon mode at 158 cm^{-1} was found not being predicted at the $\overline{\Gamma}$ point by the calculations [1].

To properly discuss the Raman spectra it is necessary to consider surface geometry and selection rules for surface phonons determined by group theory. The surface geometry of InP(110) is very common for all III-V(110) compounds. Relaxation of the InP surface leads to a tilting of the V element outwards and of the III element inwards with a buckling angle of 27.1–31.1 degrees [10,15]. The top surface atoms are linked in zigzag chains in the $[1\overline{1}0]$ direction. The surface unit cell has a mirror plane parallel to the [001] direction (point group C_s). The vibrational modes A' (A'') conserve (break) the symmetry with respect to the mirror plane. According to the selection rules obtained from the Raman tensors [5,16] A' modes are allowed for the parallel polarization configuration of both the incident and the scattered light. In contrast A'' modes are allowed for the crossed polarization configuration only. Therefore,

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the symmetry of the surface phonon modes can be analyzed by the Raman selection rules. The displacement patterns of the two gap modes with A' symmetry according to the DFPT calculations [10] are shown in Fig. 1.

Clean InP(110) surfaces were prepared by cleaving differently doped (*n*- and *p*-type) InP crystals inside an ultrahigh vacuum (UHV) chamber at a base pressure of 2×10^{-8} Pa. For comparison, oxidized samples (destroyed surface symmetry) were investigated under identical conditions in UHV as the clean ones. In order to oxidize the surfaces the cleaved InP samples were exposed to atmospheric conditions for a short time in a load lock system connected to the UHV vessel. The Raman measurements were performed at room temperature using a standard Raman setup in near back scattering geometry with the incident beam at 40° to the sample normal. The large value of the refractive index of InP leads to the near back scattering geometry. Because of the electronic surface band gap for clean InP(110) at about 3 eV [17] a Krypton-ion laser operating at a photon energy of 3.000 eV (24203 cm^{-1}) was used as a light source to enhance the Raman scattering cross section. Photon energies at 2.603 eV (20997 cm^{-1}) and 2.543 eV (20492 cm^{-1}) were also used for comparison (nonsurface resonant conditions). At 3 eV the energy resolution was about 6 cm^{-1}. The scattered light was focused onto the entrance slit of a triple monochromator and detected by a liquid nitrogen cooled CCD array. The frequency scales of the Raman spectra were calibrated by using Kr^{+}-plasma lines. The scattered intensities were normalized to the Lorentzian fitted transversal optical (TO) phonon.

Raman spectra for the clean surface of the *n*-doped InP(110) for parallel and crossed polarization configurations of the incident and the scattered light are shown in Fig. 1. For these polarization configurations ($[1\bar{1}0] \parallel [1\bar{1}0]$ and $[001] \perp [1\bar{1}0]$) a number of peaks are observed. The most significant one at 305 cm^{-1} is the bulk TO phonon mode, which is symmetry forbidden for the ($[001] \parallel [001]$) configuration only. The other features in the Raman spectra of the clean surfaces not marked with dashed lines in Figs. 1 and 2 are due to multiphonon processes, in agreement with previously published Raman data [18–20]. In order to separate surface from bulk phonon modes two sets of Raman spectra were taken, one of the clean and one of the oxidized sample. Figure 2 presents Raman spectra of a sample before and after oxidation for the ($[1\bar{1}0] \parallel [1\bar{1}0]$) configuration and the difference spectrum (clean minus oxidized). The features at 69–82, 146, 254, 270 cm^{-1}, and a structure at 347 cm^{-1} marked by dashed lines can be assigned to surface phonon modes of A' symmetry. In the range between 298 and 317 cm^{-1} the difference spectrum is calculated with the Lorentzian fitted TO phonons of the clean and oxidized sample. The difference spectrum for the crossed polarization configuration, not presented here,

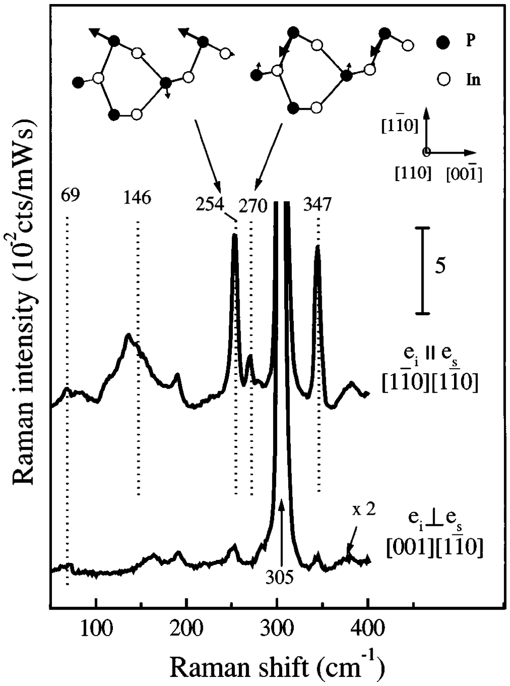

FIG. 1. Raman spectra of the clean InP(110) surface for the parallel ($[1\bar{1}0] \parallel [1\bar{1}0]$) and the crossed ($[001] \perp [1\bar{1}0]$) polarization configurations for photon energy of 3 eV. In the top part of the figure the atomic displacements of the lower frequency and higher frequency surface gap mode according to DFPT calculations [10] are shown.

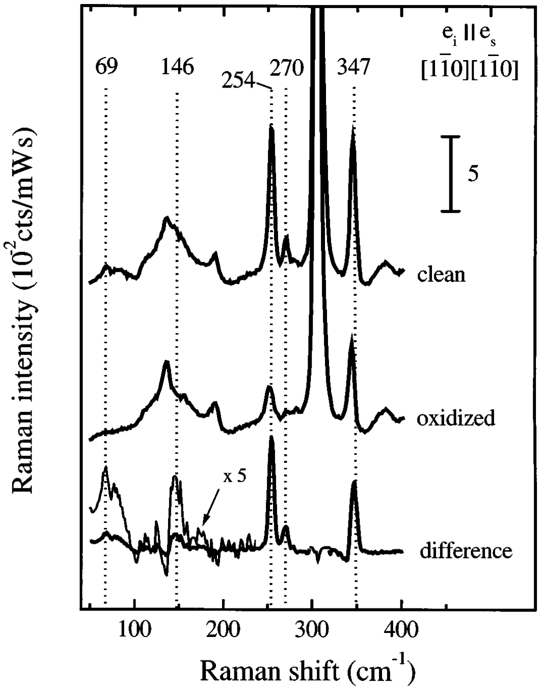

FIG. 2. Raman spectra of the clean (top) and oxidized (middle) InP(110) surface and the difference spectrum (bottom) for the parallel ($[1\bar{1}0] \parallel [1\bar{1}0]$) polarization configuration at a photon energy of 3 eV. The surface related features are marked by dashed lines.

shows only a weak structure at 69 cm^{-1} which might contain a possible A'' contribution. Additional Raman measurements with other samples (p-type) show very similar spectra except with the peak at 347 cm^{-1}. These Raman spectra also proved to be reproducible with intensities distinctly above the readout noise of the detector.

Figure 3 shows our results for the A' modes identified by RS together with surface phonon dispersion data according to DFPT calculations [10] and to HREELS [1]. In the following we will compare these data in detail starting at low energy.

The weak feature at 69 cm^{-1} (Fig. 2) is identified as a surface phonon mode with A' symmetry in good agreement with DFPT and BCM calculations [10,11] and HREELS [1] showing an A' surface phonon mode at 73–77 cm^{-1}. Tight binding calculations [21] predicted this mode at 63 cm^{-1}. The weak, but reproducible structure at about 82 cm^{-1} (Fig. 2) on the shoulder of the peak at 69 cm^{-1} could also be due to a surface phonon mode. In this energy range only the BCM calculations show an A' mode at 93 cm^{-1} at the $\bar{\Gamma}$ point. DFPT calculations also predict an A' mode at 93 cm^{-1}, but at the $\bar{X}'$ point of the surface Brillouin zone.

The weak structure at 146 cm^{-1} is assigned to a surface phonon mode. Near this position a surface phonon mode was identified by HREELS at 158 cm^{-1}, whereas theoretical calculations do not predict such a mode at the $\bar{\Gamma}$ point. The DFPT calculation denotes a surface phonon mode of this energy range apart from the $\bar{\Gamma}$ point in the direction to the $\bar{X}$ point. Taking into account the halfwidth of 18 cm^{-1}, which is nearly twice of that of other surface related peaks (254, 270, and 347 cm^{-1}), this peak could be due to a spectral superposition of two surface phonon modes or a coupling to bulk excitations.

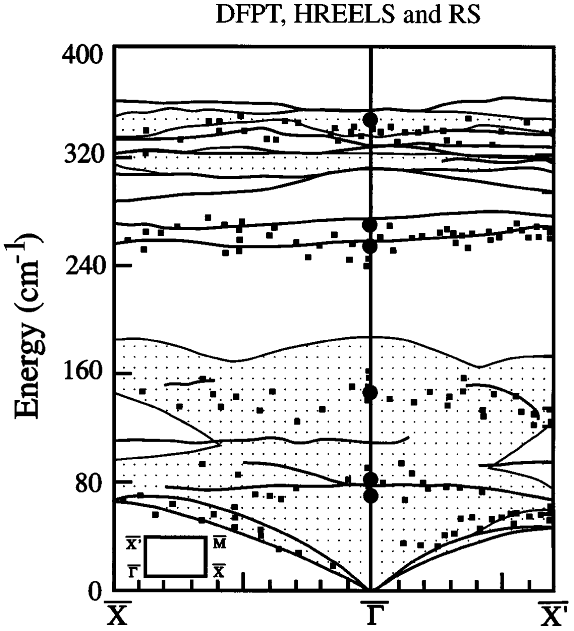

FIG. 3. Surface phonon dispersion of InP(110) calculated by DFPT [10] (solid lines) and results of HREELS [1] (squares) in comparison with present results from Raman spectroscopy (circles). The shaded areas represent the projected bulk phonon band structure.

The significant structures at 254 and 270 cm^{-1} are identified as two surface phonon modes located in the band gap between acoustical and optical bulk branches in agreement with theoretical results. DFPT calculations predict two surface modes at 258 and 273.5 cm^{-1} (Fig. 3) with eigenvectors in the mirror plane, dominated by vibrations in the first layer (Fig. 1). Taking into account that our measurements were performed at room temperature and the phonon energies calculated by DFPT are valid for 0 K, the calculated positions have to be diminished by about 4 cm^{-1} [10], which then gives an excellent agreement to our Raman results. Other theoretical calculations predict two surface gap modes near this energy range, too [11,12]. HREELS found only one phonon mode in this energy range around 246 cm^{-1} [1] due to the low energy resolution. The weak peak at about 251 cm^{-1} near the position of the lower frequency gap mode at 254 cm^{-1} observed in the spectrum of the oxidized sample is assigned to a well known multiphonon process [18–20].

The origin of the feature at 347 cm^{-1} is not fully clear (Fig. 2). There are two eigenmodes which could contribute, one is the bulk longitudinal optical (LO) phonon, the other a theoretically predicted surface eigenmode [10,11]. First order Raman scattering by LO phonons is not symmetry allowed at (110) orientated surfaces of zinc-blende compounds. However, forbidden LO scattering induced by impurities, finite wave vectors, and electric fields from the depletion layer is expected for parallel polarization configurations [5,22]. At first sight this seems to fit well the experimentally determined spectral position and selection rules (Fig. 2). However, the forbidden LO contributions would have to increase after oxidation due to the formation of band bending [22,23]. Under nonresonant conditions (2.543 and 2.603 eV) this expected behavior is found indeed (Fig. 4), whereas in the surface resonant case (3.000 eV) the intensity of the peak at 347 cm^{-1} decreases after oxidation (Fig. 4). Therefore, the feature in the difference spectrum (clean minus oxidized in Fig. 2) most likely arises from a superposition of two components, a forbidden LO phonon mode and a surface phonon mode (before oxidation), resonant at 3 eV. The small shifts ($\sim$1 cm^{-1}) of this structure before and after oxidation are within the energy resolution limit, thus an energetic separation of those two possible contributions is not clearly possible. A surface phonon mode at the $\bar{\Gamma}$ point is predicted at 353 cm^{-1} slightly above the LO phonon energy by DFPT calculations [10] and at 349 cm^{-1} by BCM calculations [11], but has been assigned to the Fuchs-Kliewer phonon. HREELS, however, yielded a value of 342 cm^{-1} for the Fuchs-Kliewer phonon being in between the TO and LO phonon energies of InP(110) [1]. In contrast the Raman spectra

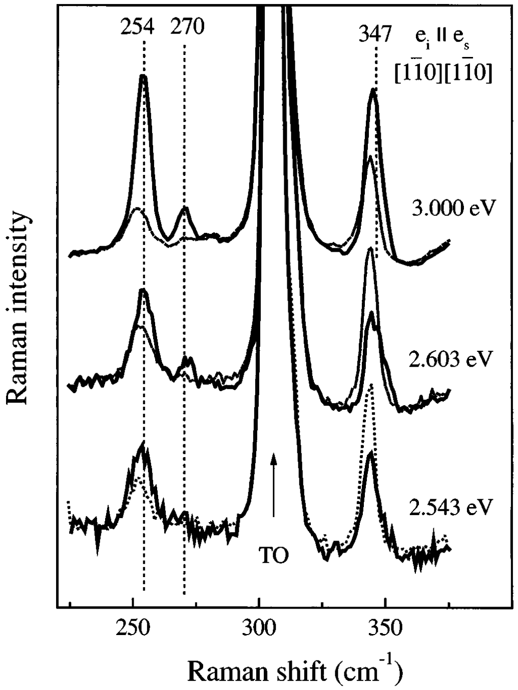

FIG. 4. Raman spectra of clean (solid lines) and oxidized (dashed lines) InP(110) surface for the parallel ($[1\bar{1}0] \parallel [1\bar{1}0]$) polarization configuration with incident light energies of 3.000 eV (24 203 cm^{-1}), 2.603 eV (20 997 cm^{-1}), and 2.543 eV (20 492 cm^{-1}).

(Figs. 1,2,4) do not show the Fuchs-Kliewer phonon within the energy range between the TO and LO phonons. Thus the 347 cm^{-1} peak is most likely a microscopic surface phonon mode. In order to investigate the resonance behavior of the surface phonons additional Raman measurements were performed with different photon energies (2.603 and 2.543 eV). The two gap modes were observed, when exciting with 2.603 eV, with a large decrease in intensity. When exciting with 2.543 eV the lowest (stronger) gap mode appeared only (Fig. 4). This indicates the resonance enhancement of the Raman scattering cross section for the incident light energy of 3.000 eV due to electronic surface transitions [17].

In conclusion, we identified surface phonon modes of InP(110) by Raman spectroscopy, the energy of which is in good agreement with other experimental results and with theoretical predictions. Raman spectroscopy was shown for the first time to be sensitive to surface phonon modes of clean semiconductors. For InP(110) two surface gap modes and three additional surface modes with A' symmetry have been observed using an incident light energy of 3 eV. Because of the excellent resolution it was possible to separate the two gap modes of InP. The two surface gap modes show a resonant enhancement of the Raman scattering cross section for an incident light energy of 3 eV. The results presented already outline new facilities of surface investigations by Raman spectroscopy. Thus the exact determination of positions and linewidths of these microscopic gap modes opens a new field of application in studying surface bonding, anharmonicity effects, and coupling to other excitations.

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