Observation of Interface Phonons by Light Scattering from Epitaxial Sb Monolayers on III-V Semiconductors

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Vibrations of Sb on (110) surfaces of III-V semiconductors (InP,GaAs,GaP) were investigated by Raman scattering from the submonolayer range up to a few monolayers. Interface phonons, involving the epitaxial first monolayer of Sb and the upper substrate layer, are observed. They are clearly identified by their coverage dependence. The peaks are most pronounced for Sb on InP. They fulfill the polarization selection rules for Sb chains along $(1\bar{1}0)$. Moreover, they reveal that for thicker Sb coverages the epitaxial structure of the first Sb monolayer remains intact.

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Because of their unique properties, III-V-semiconductor–antimony interfaces have attracted much attention.[1-12] Whereas most metals exhibit strong intermixing with III-V semiconductors, abrupt interfaces are found for Sb overlayers. In addition, epitaxial growth of the first Sb monolayer (ML) on (110) surfaces of InP (Refs. 1 and 2) and GaAs (Ref. 3) was deduced from LEED studies. The results were interpreted in terms of Sb zigzag chains along the $(1\bar{1}0)$ direction that essentially continue the truncated substrate structure (see Fig. 1). Angle-resolved ultraviolet-photoemission-spectroscopy results[4] support this model for Sb on GaAs(110) and GaP(110). Total-energy minimization calculations predict a similar structure for the first Sb monolayer on other III-V (110) surfaces.[5] For the GaAs/Sb system this model has been confirmed by scanning tunneling microscopy (STM), which also reveals a strong influence of the perfection of the Sb growth on the band bending at the interface.[6]

An effective method for preparing a highly ordered single Sb ML is the heating of a few ML of Sb on GaAs(110) at about 600 K, resulting in desorption of all Sb but the first ML,[7,8] which is stable[7] up to more than 800 K. Photoemission spectra of Sb on p-GaAs show a sharpening of the Sb spectral features after annealing, indicating an increase of order, accompanied by a decrease of band bending.[8] Similar results have been reported for InP.[9] Furthermore, the stability of the first Sb ML has been used to prevent an intermixing at the InP/Ag interface by introducing a thin Sb interlayer.[10]

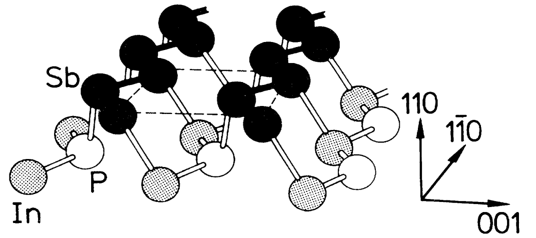

FIG. 1. Epitaxial Sb monolayer on InP(110): Schematic view of the zigzag chain structure, after Refs. 1-3. The dashed line indicates the surface unit cell.

On top of the epitaxial first Sb ML, amorphous Sb growth has been observed by Raman spectroscopy on GaAs as well as on InP.[11] At about 15 ML a phase transition from amorphous to polycrystalline Sb occurs.[11,12]

Besides the regular geometric structure, which is probed by STM and LEED, a highly ordered system like the epitaxial Sb monolayer should also exhibit specific dynamic properties. In this Letter we present the experimental observation of phonons of the epitaxial monolayer by light scattering. We have performed Raman scattering (inelastic light scattering) at Sb overlayers in the submonolayer and the monolayer region on InP(110) surfaces. For comparison, GaAs(110) and GaP(110) surfaces were also studied. The (110) surfaces were prepared by cleavage in UHV (base pressure 5×10^{-9} Pa). Sb was evaporated from a Knudsen-cell-like Ta oven. The substrate was kept at room temperature. After each deposition step Raman spectra were recorded with a laser power of 30 mW and a focus diameter of 0.1 mm. All spectra shown in this Letter were recorded with the 514.5-nm line of an argon-ion laser. More experimental details about *in situ* light scattering are given in Ref. 11.

In Fig. 2 Raman spectra of InP(110) with unannealed Sb coverages ranging from 0 to 1 ML are displayed. For the clean surface, only the InP TO and LO phonon lines at 305 cm^{-1} (37.8 meV) and at 345 cm^{-1} (42.8 meV) and weak multiphonon structures are observed. With increasing Sb coverage six new peaks evolve, marked by dash-dotted vertical lines in Fig. 2. Some of them are

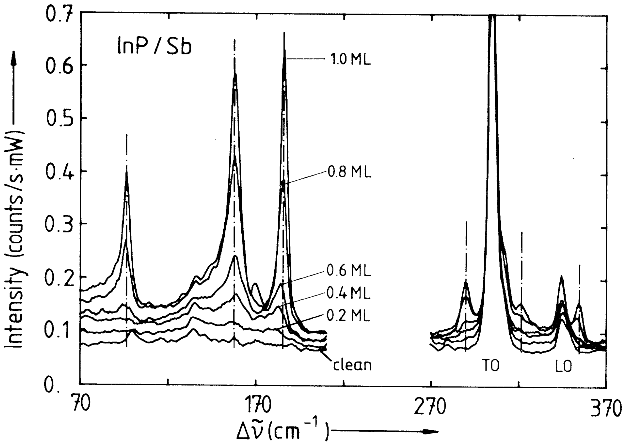

FIG. 2. Raman spectra of InP(110)/Sb for Sb coverages from 0 to 1 ML. The dash-dotted lines indicate the interface phonons.

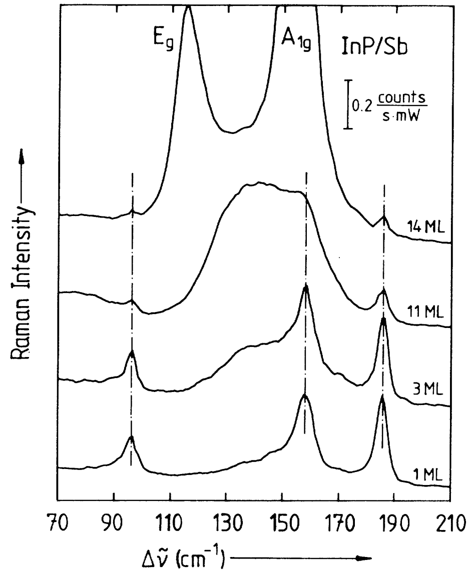

FIG. 3. InP/Sb Raman spectra for Sb coverages from 1 to 14 ML. Note that the interface peaks at 96 and 185 cm^{-1} persist even after the Sb crystallization.

even sharper than the substrate TO and LO lines; their linewidth is dominated by the spectral resolution (3 cm^{-1}) of the monochromator. Even more striking is the high intensity of these newly observed peaks, which is on the order of the substrate TO and LO intensities.

In Fig. 3 Raman spectra for higher Sb coverages are shown. While the new peaks decrease slowly, a broad band develops around 135 cm^{-1}, which is characteristic of amorphous Sb.[13] At about 13 ML this structure changes abruptly to the E_g and the A_{1g} phonon lines of crystalline Sb, revealing the well-known amorphous-to-polycrystalline phase transition of the Sb overlayer.[11] Note especially that two of the new peaks are still visible even after the overlayer crystallization. Their attenuation with increasing coverage is similar to that for the substrate TO line, which diminishes because of absorption of the incident and the scattered light in the Sb overlayer. The similar behavior of the new peaks shows that they are also attenuated in the overlayer, indicating that they originate merely from the interfacial region and have no contributions from the upper Sb layers.

In Fig. 4 the coverage dependence of the peak intensities is presented. They are normalized to the substrate-TO-phonon intensity. The new peaks develop essentially between 0.5 and 1 ML, indicating that they are not just due to the presence of adsorbed Sb but that they require the ordered structure of the epitaxial Sb monolayer. We therefore interpret them as collective vibrational modes of the substrate–Sb-monolayer system. In the following we will designate these modes as "interface phonons" and the corresponding Raman peaks as "interface peaks."

The observation of the interface peaks up to high coverages, shown in Fig. 3, indicates that the epitaxial structure of the first monolayer remains essentially intact, even after the crystallization. However, their intensity decreases slightly more than the TO line. This additional attenuation might be due to the creation of defects in the epitaxial monolayer or, alternatively, to a stronger damping of the vibrations because of the additional Sb coverage.

In order to study the polarization selection rules we tried to prepare a single Sb ML, as ordered as possible. Therefore, we annealed a sample with 4 ML of Sb at

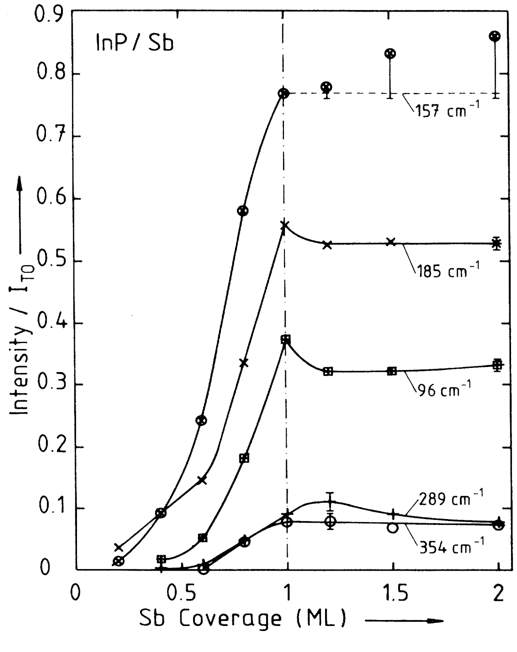

FIG. 4. Normalized interface-phonon-peak intensities.

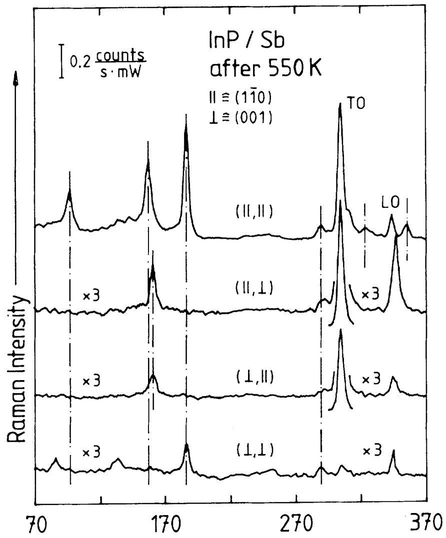

FIG. 5. InP/1-ML-Sb annealed: Raman spectra for different polarization configurations. The polarization notations $\parallel$ and $\perp$ give the direction with respect to the Sb chain direction $(1\bar{1}0)$.

550 K, as described above. Figure 5 shows the resulting Raman spectra for different polarization configurations of incident and scattered light. They are essentially the same as for the unannealed ML in Fig. 2, thus showing that the ML structure has not changed basically by annealing. In addition, we observe a strong polarization anisotropy: For the $(\parallel,\parallel)$ configuration much higher intensities occur than for $(\perp,\perp)$, where some peaks even vanish. These results are consistent with the polarization anisotropy expected for the Sb chains.

The interface peaks in Fig. 5 may be grouped according to their polarization dependence: Six peaks are found in the $(\parallel,\parallel)$ or in the $(\perp,\perp)$ configuration, which are called the "diagonal" configurations, while only two peaks are detected in the "nondiagonal" configurations with crossed polarizations. Furthermore, the peaks may be subdivided energetically: Some peak frequencies are in the "Sb range" around the E_g and A_{1g} optical vibrational frequencies of crystalline Sb (see also Fig. 3), others are located in the "InP range" close to the substrate optical phonons (TO and LO). In Table I the measured frequencies of all InP(110)/Sb ML peaks are listed. The observation of eight ML peaks cannot be explained by vibrations of only the two Sb atoms per unit cell: By also taking into account the first InP monolayer, one obtains four atoms per surface unit cell [two Sb, one In, and one P (see Fig. 1)], yielding nine optical ML phonons.

TABLE I. Measured frequencies (cm^{-1}) of the interface peaks for InP(110)/Sb. The peaks are grouped according to their frequency range and their polarization configurations.

	Sb range	InP range
Diagonal (A')	96,157,185	289,321,354
Nondiagonal (A'')	161	≈ 290

The point-group symmetry of the surface unit cell is C_s (or m). For the four atoms, group theory yields six optical eigenmodes of symmetry A' with atomic displacements perpendicular to the Sb chain direction $(1\bar{1}0)$ and three optical eigenmodes of symmetry A'' with displacements parallel to the chains. The Raman tensors for first-order allowed scattering for the A' and A'' modes can be found in Ref. 14. In our case their coordinate system is defined by the Sb chain direction, i.e., $x=(110)$, $y=(001)$, and $z=(1\bar{1}0)$. For backscattering at (110) surfaces, scattering from the six A' modes can only be obtained for diagonal polarization configurations, while the three A'' modes can only appear nondiagonal. This agrees very well with the experimental results: Eight out of nine possible optical modes are observed, six in diagonal and two in nondiagonal configurations. The missing one might be either masked by substrate contributions or accidently degenerate.

Therefore we conclude that the interface peaks are indeed due to allowed first-order Raman scattering by Sb interface phonons, involving the upper InP layer. Consequently, each ML peak position directly corresponds to a ML-phonon eigenfrequency. Unfortunately, no lattice-dynamics calculation is available at present to compare with the experimental results.

Comparison of the interface-peak intensities to the Sb-phonon intensities after crystallization shows that both have similar scattering efficiencies. This means that no significant surface enhancement occurs for the interface phonons. The resonance behavior of the interface phonons, however, is quite different from bulk Sb. This shows that the scattering processes invoke different electronic susceptibilities.

In similar experiments for 1 ML of Sb on GaAs(110) the interface peaks were generally less pronounced than on InP and at different frequencies, confirming the strong influence of the substrate material on the lattice dynamics of the Sb ML phonons. Only in the Sb range could ML peaks be detected; the most pronounced one was at 166 cm^{-1} for crossed polarizations.

From the lower interface-peak intensities we conclude that the Sb monolayer on GaAs(110) is much less ordered than on InP(110), even after 550-K annealing. This may be due to the different Sb-Sb distance: LEED results yield for Sb chains on GaAs, 2.80 Å (Ref. 3), and on InP, 2.84 Å (Ref. 2), which is closer to the Sb bulk value of 2.87 Å. Annealing at higher temperatures might improve the intensity and sharpness of the Sb interface peaks on GaAs.

The experiments on GaP(110)/Sb were complicated by the strong multiphonon signals of GaP, which may have masked interface peaks, especially for the (‖,‖) configuration. However, for crossed polarizations a sharp peak is found at 167 cm^{-1}.

A surface vibration, which might be similar to the Sb interface phonons, has been found on clean GaAs by inelastic He-atom scattering.[15] It was interpreted as a rotational vibration of the GaAs zigzag chains around their axis.[16] Such a vibration should also be possible for the Sb chains of the epitaxial monolayer. It would be one of the A' interface phonons and therefore correspond to one of the diagonal interface peaks.

In summary, we have presented the experimental observation of phonons of an epitaxial monolayer of Sb by light scattering. Specifically for InP(110)/1-ML-Sb the interface peaks are induced by allowed first-order scattering from interface phonons involving the epitaxial Sb monolayer and the first InP monolayer. Interface peaks are also found for GaP(110)/Sb and GaAs(110)/Sb. On GaAs they are less pronounced than on InP, indicating a lower perfection of the Sb monolayer.

The observation of such interface phonons is not restricted to materials whose bulk structure provides Raman-active phonons, such as Sb. In principle, for any ordered arrangement of atoms on a substrate the reduced symmetry allows the phonons to be Raman active. Even buried interfaces, which are usually inaccessible to surface-science techniques, can be analyzed in this way. Hopefully, lattice-dynamical calculations for monolayer configurations will become available in order to check on the structural models and to determine bond strengths from the measured Raman frequencies.

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