Raman Selection Rules for the Observation of Interface Modes in InAs/GaSb Superlattices

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We present a Raman study of elastic interface modes in InAs/GaSb superlattices from the viewpoint of their polarization selection rules. We show that one of the modes, which is strongly localized to the interfaces, can be used to probe sequentially grown interfaces in an independent and selective way. This opens up a promising new application area for Raman characterization of *AB/CD* superlattices.

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There are two distinct types of interface phonon modes (IFM) in semiconductor superlattices (SL's). The first type is the *electrostatic* IFM which exists when the dielectric function has opposite signs on each side of the interface (IF). These modes may be quite extended perpendicular to the interface and their frequencies lie between the bulk LO and TO frequencies. The electrostatic IFM's have been most widely studied in GaAs/AlAs SL's, and the selection rules for their observation in Raman spectroscopy are well established [1,2].

The second type of IFM exists primarily as a consequence of the elastic boundary conditions in SL's such as InAs/GaSb, which have layers containing no common cation or anion and so may be grown with "heavy" InSb- or "light" GaAs-like interfaces [3]. In this case, IFM's exist with frequencies either in the gap between the acoustic and optical branches of either material or above the optical branches. In the ideal SL, the type of IFM which is supported depends on whether the SL is grown with light or heavy interfaces. The two longitudinal IFM's with significant Raman cross sections are the strong GaAs-like IFM (~ 250 cm^{-1}), strongly localized to the interface with optic phonon displacements in the layers, and the weak InSb-like IFM (~ 180 cm^{-1}), which is more extended and with acoustic phonon displacements in the layer [3].

Since the first claim for their observation by Raman spectroscopy [4] IFM's in InAs/GaSb SL's have been used foremost to characterize interface composition [5–8], even without a clear understanding of which Raman configuration is optimal for observing the IFM's. In this Letter, we present a Raman study of IFM's in InAs/GaSb SL's from the viewpoint of their polarization selection rules. We begin by considering the orientation of the interfacial bonds in SL's grown with different combinations of heavy and light interfaces, which leads to a natural distinction between SL's grown with only heavy or only light interfaces, termed same interface-type structure (SIS), and SL's grown with alternating heavy and light interfaces, termed mixed interface-type structure (MIS). Results are presented on very high quality structures of both types, in which distinct but different selection rules may be observed for the GaAs and InSb IFM's. A model based on the modulation of the bond polarizabilities in the SL direction is presented in which the observations are consistent with the respectively strong and weak localization of the two IFM's. Finally, we demonstrate how the GaAs IFM can be used to probe the physical and structural properties of sequentially grown interfaces in an independent and selective way. Our results can easily be generalized to other *AB/CD* heterostructures, in which *AD* or *BC* interfaces support strongly localized modes. Measurements of this type are complementary to other more direct imaging techniques, such as scanning tunneling or transmission electron microscopies [9,10], and offer a clear, more rapid, and *nondestructive* means of detecting differences in quality of sequentially grown interfaces.

In the following, the group-III atom is chosen as the origin of coordinates, with the group-V atom at $(a_0/4)[111]$. We define x, y, z as the [100], [010], and [001] crystal axes, respectively; x' denotes [110] and y' stands for $[\bar{1}10]$. We also define the *A* interface to be produced when InAs is grown on GaSb, and the *B* interface that when GaSb is grown on InAs. Hence the orientation of bonds in the ideal SL's is as follows: The GaAs:*A* interface contains Ga-As bonds in the $(\bar{1}10)$ plane, while they are in the (110) plane for the GaAs:*B* interface. For a SIS with heavy IF's the situation is reversed, with In-Sb bonds in the (110) plane for the InSb:*A* IF and in the $(\bar{1}10)$ plane for InSb:*B*. Then, for a MIS two possibilities occur: (i) GaAs:*A* alternates with InSb:*B*, when the IF bonds are both in the $(\bar{1}10)$ plane and (ii) GaAs:*B* alternates with InSb:*A*, when the IF bonds are both in the (110) plane.

Four series of short period InAs/GaSb SL's have been grown by atmospheric pressure metalorganic vapor-phase epitaxy: SIS's with only light or only heavy interfaces, and MIS's with the first or the second alternation. The periods of all samples are in the range 8.5–10.5 nm. Other details of the growth procedure are described elsewhere [11]. The orientation of the samples is based on information supplied by the manufacturer of the substrate wafers and was verified in several cases by convergent beam electron diffraction. The high quality of the samples was proved by the observation of two doublets of folded longitudinal acoustic phonons (FLAP's) in SIS's and up to five well resolved doublets in MIS's, grown with the second alternation, when to our knowledge no more than two clear doublets have previously been reported. We have found that the MIS's grown with the first alternation turn out to be of poorer quality [11,12], and the reasons for this are discussed later. In the following, if not specified, only MIS's with second alternation are considered.

Raman measurements have been performed at 300 and 8 K in the true backscattering configuration from the (001) surface using different Ar^+ and Kr^+ laser lines for excitation and a Jobin-Yvon T64000 triple grating spectrometer with a multichannel charge coupled device detector. The typical bandpass was about 0.5 cm^{-1}.

Depending on the growth procedure up to three different types of IFM (184, 194, and 254 cm^{-1} at 8 K) have been observed. IFM1 at 254 cm^{-1} and IFM2 at 184 cm^{-1} have been assigned to longitudinal GaAs and InSb interface modes, respectively. Contrary to Ref. [5] the IFM at 194 cm^{-1} cannot be assigned to a weakly localized GaAs IFM, because it was observed in several SIS's with heavy IF's and it is absent in the very best SIS's and MIS's (Fig. 1). We suppose that the IFM at 194 cm^{-1} is in fact a disorder activated transverse InSb-like IFM. It is worth noting that while in previous studies [5–8] the InSb IFM2 was clearly observed only at low temperature, we have found it already at room temperature (Fig. 1), indicative of high interface quality.

In spite of a similar origin the GaAs-like IFM1 and the InSb-like IFM2 have different appearances in the $z(xx)\bar{z}$ and $z(xy)\bar{z}$ configurations as shown for a MIS in Fig. 1. We find that IFM1 seems to have nearly the same intensity in both $z(xx)\bar{z}$ and $z(xy)\bar{z}$, while in Ref. [7] it was observed only in $z(xy)\bar{z}$. At the same time IFM2 is negligible in $z(xx)\bar{z}$, contrary to previous observations [5]. The same behavior of IFM1 and IFM2 is observed in both SIS's and MIS's.

Figure 2 reveals the most striking results from MIS's. Unlike bulk LO phonons the IFM1 is clearly visible for $z(x'x')\bar{z}$ and completely vanishes for $z(y'y')\bar{z}$. At the same time the IFM2 has a similar intensity in both configurations (not shown in the figure) which resembles conventional nonresonant behavior of phonons in SL's. As the same configuration dependence of IFM's has been observed with excitation at 647, 496, 488, and 477 nm, the possibility of a resonant interference effect can be excluded. Moreover, on spectra taken near the E_1 gap of GaSb IFM1 exhibits quite different behavior which will be reported elsewhere. It is worth noting that room temperature spectra reveal the same behavior, although IFM1 is not so pronounced.

Contrary to its behavior in MIS's, IFM1 in SIS's shows the same intensity in both $z(x'x')\bar{z}$ and $z(y'y')\bar{z}$ [Fig. 3(a)]. More important from the viewpoint of future applications is that IFM1 has significantly higher intensity and is better resolved from the bulk LO tail in both of these configurations compared to the widely used $z(xy)\bar{z}$.

To evaluate the Raman activity of the IFM's we use the bond polarizability approximation [13–16]. The basic unit is a tetrahedron C_2AB_2 where in the case of the GaAs:B interface two A-B bonds represent Ga-Sb bonds, situated in the $(\bar{1}10)$ plane, and C-A represents As-Ga bonds situated in the (110) plane. In the principal-axes system of each bond the polarizability tensor of the bond is diagonal and is described by fundamental perpendicular ($\alpha_\perp$) and parallel ($\alpha_\parallel$) polarizabilities. After transformation of the two tensors, related to each A-B bond (or correspondingly C-A), into the crystal related axes and differentiating the resultant bond polarizability with re-

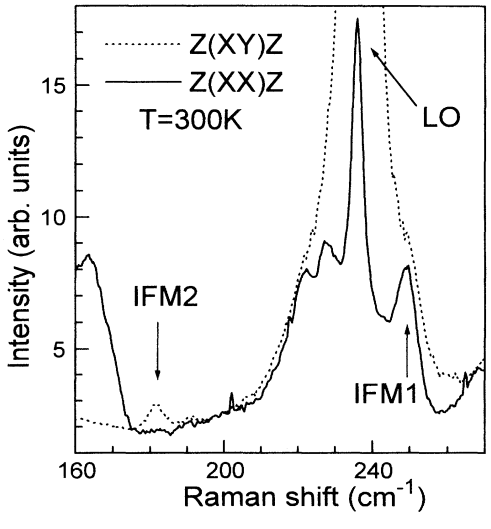

FIG. 1. Comparison between the $z(xx)\bar{z}$ and $z(xy)\bar{z}$ spectra for the GaAs-like mode (IFM1) and for the InSb-like mode (IFM2) in a MIS (laser at 647 nm).

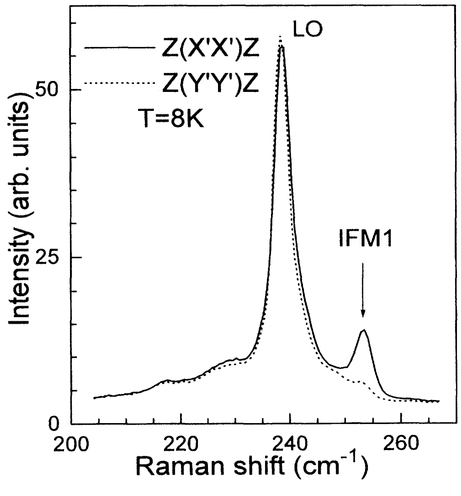

FIG. 2. Comparison between the $z(x'x')\bar{z}$ and $z(y'y')\bar{z}$ spectra for the GaAs-like mode in a MIS (laser at 488 nm).

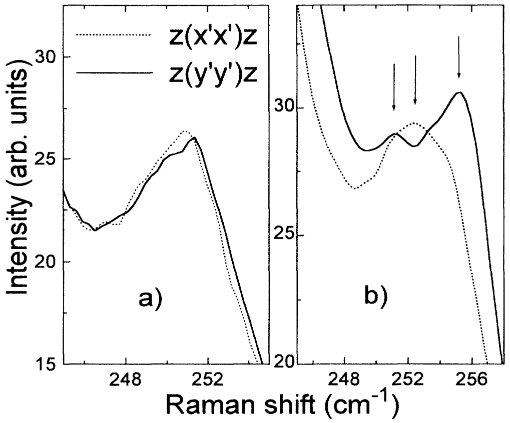

FIG. 3. The GaAs-like interface mode at 300 K from SIS's grown by different methods.

spect to the atomic displacement, a differential polarizability tensor for each bond pair is obtained:

$$P_{AB} = U_{AB}\begin{pmatrix} \alpha_{xx} & \alpha_{xy} & 0 \\ \alpha_{xy} & \alpha_{xx} & 0 \\ 0 & 0 & \alpha_{zz} \end{pmatrix},$$

$$P_{AC} = U_{AC}\begin{pmatrix} -\beta_{xx} & \beta_{xy} & 0 \\ \beta_{xy} & -\beta_{xx} & 0 \\ 0 & 0 & \beta_{zz} \end{pmatrix},$$

where α and β stand for GaSb and GaAs polarizabilities, $U_{ij} = (U_j - U_i)$ are the z projections of atomic displacements, and the longitudinal character of the vibrations has been taken into account. Assuming that (i) the fundamental bond polarizabilities α and β depend only on the bond length and (ii) the change in perpendicular polarizability with bond length is negligibly small in comparison with the change in the parallel one [16], it follows that $\alpha_{xx} \cong \alpha_{xy} \equiv \alpha$, and, correspondingly, $\beta_{xx} \cong \beta_{xy} \equiv \beta$. Finally, the Raman tensor for a IFM can be obtained by summing the elements of P_{AB} and P_{AC} over the SL supercell allowing for the chemical origin of each bond. In fact, the above assumption $\alpha_{xx} \cong \alpha_{xy}$ is very important for an explanation of our results and it means that the contribution from the pair of bonds to a Raman tensor in the $x'y'$-coordinate system has the following form:

$$R_{AB} \propto \begin{pmatrix} \alpha & 0 \\ 0 & 0 \end{pmatrix}, \qquad R_{AC} \propto \begin{pmatrix} 0 & 0 \\ 0 & \beta \end{pmatrix},$$

and, in other words, a particular pair of bonds contributes to the Raman scattering *when and only when* both incoming and outgoing radiation have a nonzero component of electric field in the plane containing the pair of bonds.

To illustrate the main idea we have first estimated the Raman intensity due to our tetrahedral unit: $I_{xx} = (\alpha U_{AB} - \beta U_{AC})^2$; $I_{x'x'} = (2\alpha U_{AB})^2$; $I_{xy} = (\alpha U_{AB} + \beta U_{AC})^2$; $I_{y'y'} = (2\beta U_{AB})^2$; $I_{x'y'} = 0$. In bulk material $\alpha = \beta$, $U_{AB} = U_{AC}$, and we recognize the usual selection rules. When a contribution to the Raman tensor from one of the pairs of bonds dominates (for example, $\alpha U_{AB} \gg \beta U_{AC}$), we obtain

$$I_{x'x'} \gg I_{y'y'}, \qquad I_{xx} = I_{xy} = \tfrac{1}{4} I_{x'x'}, \tag{1}$$

which indeed corresponds to the observed behavior of IFM1. Taking into account the real displacement pattern for the GaAs-like IFM with its strong localization at the interface [3], in summation over the supercell we have to include only the nearest neighbors to the Ga-As bond, namely, In-As-Ga-Sb. Since, In-As bonds are situated in the $(\bar{1}10)$ plane (relative to the tetrahedral unit under consideration), their contribution to the Raman tensor is similar to that of the Ga-Sb bonds. Then if $(\alpha U_{AB} + \gamma U_{DC} \gg \beta U_{AC})$ where γ and U_{DC} describe the polarizability and atomic displacement of In-As, we again obtain for the Raman activity of IFM1 the selection rules (1). The above mentioned constraint means strong modulation of polarizability in the growth direction and seems to be realistic in the particular wavelength range under consideration, if one takes into account that the Kr$^+$ and Ar$^+$ laser lines fall in the range close to E_1 and $E_1 + \Delta_1$ of GaSb and E_1 of InAs but are comparably far from E_0 and E_1 in GaAs.

It is important to note that the above consideration is valid for a MIS with a light B interface [Ga-As bonds in the (110) plane]. One could easily obtain that for a MIS with light A IF [Ga-As bonds in $(\bar{1}10)$ plane], the Raman intensities $I_{x'x'}$ and $I_{y'y'}$ interchange and IFM1 would be observed in $z(y'y')\bar{z}$.

Finally, for MIS's in the conventional xy-coordinate system the Raman tensors for the GaAs-like IFM localized to the GaAs:A or GaAs:B interfaces are given, respectively, by

$$R_A = \begin{pmatrix} -a & a \\ a & -a \end{pmatrix}, \qquad R_B = \begin{pmatrix} b & b \\ b & b \end{pmatrix},$$

where for a SL with perfect interfaces the cross section $a = b$.

For a SIS with light interfaces, the GaAs-like IFM gives rise to two almost degenerate modes (one antisymmetric A_1 and one symmetric B_2 mode). Using the same method we get the usual selection rules: the A_1 mode is active in $z(xx)\bar{z}$ and B_2 in $z(xy)\bar{z}$. Moreover, for a mode with a given symmetry the intensities in $z(x'x')\bar{z}$ and $z(y'y')\bar{z}$ are equal. Note that a particular pair of bonds still contributes to scattering in only one of $z(x'x')\bar{z}$ and $z(y'y')\bar{z}$ configurations, depending on whether the pair lies in the (110) or $(\bar{1}10)$ plane, respectively. Hence the A and B interfaces contribute independently to $I_{y'y'}$ and $I_{x'x'}$. This is quite significant since it shows that two sequentially grown interfaces may be probed independently, simply by selecting the correct polarization.

Thus far our model considers only ideal interfaces. In real systems, interfaces may not be ideal due to interdiffusion, steps, and other imperfections. Furthermore, interface A will not necessarily be of the same quality as interface B because of differences in the gas sequences and surface chemistry during growth. Because of its strong localization, the GaAs IFM is highly sensitive to this local interface environment [3,5,17]. Hence measurements in $z(x'x')\bar{z}$ and $z(y'y')\bar{z}$ should be able to detect differences in the quality of the two interfaces.

Using IFM1 as a probe we indeed find that depending on the growth procedure the A and B interfaces may have significantly different qualities [11,12]. In our best SIS's with light IF's IFM1 is sharp and nearly the same in both configurations [Fig. 3(a)], which suggests that the environments of both GaAs IF's are alike. In some SIS's with light IF's grown by different methods [9,10], IFM1 in $z(x'x')\bar{z}$ is qualitatively similar to that shown in Fig. 3(a), suggesting a comparable environment, but in the $z(y'y')\bar{z}$ configuration a broad line is observed consisting of two peaks shifted from the usual position of IFM1 [Fig. 3(b)]. As follows from Ref. [15], it means that the A interface is essentially nonuniform in terms of steps or interdiffusion. Generally we have found that GaAs:A and InSb:B are of poorer quality [11]. Therefore a MIS grown by the second alternation combines the best interfaces from the heavy and light SIS's and displays a significant improvement in periodicity and interface sharpness, as judged by FLAP's and IFM's respectively. As expected, MIS's with the first alternation of the worst light and heavy IF's turn out to be of poorer quality.

In the case of the heavy interface there are two clear distinctions: (i) IFM2 is essentially delocalized [3], so that significant contributions to the Raman tensor come from many layers in the supercell; (ii) the In-Sb bond polarizability is likely to be greater than that for Ga-As due to the proximity of E_1 or $E_1 + \Delta_1$ of InSb. As a result, contributions to the Raman tensor from bonds belonging to the (110) and $(\bar{1}10)$ planes are likely to be comparable resulting in the conventional selection rules $I_{xx} \approx 0$, $I_{x'x'} \approx I_{y'y'}$. It is worth noting that cancellation of the different contributions to I_{xx} should already occur for a single IF, as is indeed found in a MIS (Fig. 1).

In conclusion, we have performed Raman scattering measurements in GaSb/InAs superlattices with controlled interface composition and have determined the selection rules for observation of the interface modes. We have explained qualitatively the observed behavior of interface modes taking into account the degree of localization of the IFM at the interfaces and assuming that (i) the differential bond polarizabilities $\alpha_{xx} \cong \alpha_{xy}$ and (ii) there is a strong modulation of polarizability in the growth direction. We believe that strongly localized interface modes in other AB/CD superlattices (e.g., InAs/AlSb) could reveal similar behavior in Raman experiments, provided that modulation of polarizability across an interface can be guaranteed by choosing an appropriate laser wavelength. In such a case Raman scattering by strongly localized interface modes studied in the $z(x'x')\bar{z}$ and $z(y'y')\bar{z}$ configurations may also provide information about the nonuniformity of the interfaces and may be used to distinguish between sequentially grown interfaces.

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