Interface mode in Si/Ge superlattices: Theory and experiments

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The Raman peak associated with Si-Ge vibrations in short-period Si/Ge (001) superlattices is studied both experimentally and theoretically. On the experimental side, we use a microprobe technique which allows us to investigate the longitudinal (L) and transverse (T) spectra, and find an unexpected behavior of the line shape and L-T splitting of this peak. By means of first-principles calculations, taking into account both strain and interface intermixing, we show that such behavior is consistent with the picture of an intermixed alloy layer at the interfaces, and we are able to identify the character and spatial localization of the individual atomic clusters contributing to the vibrations.

The study of optical phonons as "local probes" of the interface structure has proved to be very useful in GaAs/AlAs superlattices (SL's), where it has provided much information on atomic scale intermixing.[1] The question of the degree of interface abruptness in Si/Ge structures is also becoming very important, in view of the recent promising results on their optical and transport properties,[2] and the consequent search for further improvements. A reexamination of their Raman spectra, particularly the interface-related features, seems thus very timely.

Since the earliest Raman experiments, an "interface mode" has been detected in the phonon spectra of Si/Ge (001) SL's[3–7] besides the expected Si-like and Ge-like optical vibrations. The only allowed polarization in these conventional measurements [backscattering from the (001) surface] was the longitudinal polarization, where ideally abrupt SL's display no interface mode;[8] hence, the data have been interpreted as a clear indication that the interface cannot be sharp, and an intermixed SiGe alloy layer must be present. The assignment of this peak to an alloy mode was natural in view of the known spectrum of bulk SiGe alloys, which indeed shows a vibration associated with Si-Ge bonds in the same frequency range (~ 400 cm^{-1}).[9] A subsequent confirmation came from the evidence that the intensity of this peak increases drastically for interface smearing induced by annealing the as-grown samples.[10]

The recent availability of Raman microprobe techniques, which allow us to study both longitudinal (L) and transverse (T) polarizations, can now provide additional information on this peak.[11] The probe laser is focused to a sub-μm spot by a microscope objective, thus enabling additional scattering geometries such as from polished or cleaved sample edges.[12] For short-period $(\mathrm{Si})_m(\mathrm{Ge})_n$ SL's with $m,n = 3$–12 grown on Si, Ge, and $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ substrates,[13] the main new evidence concerns (i) the line shape of the peak, which is asymmetric in the L polarization but becomes broader and more symmetric in the T case [see Figs. 1(a) and 1(b)]; and (ii) the presence of a frequency splitting between the L and T polarizations, which is found to depend on the SL strain configuration; in particular, the splitting is negligible for Ge substrates, and increases to ~ 8 cm^{-1} for Si substrates (Fig. 2).

The question is whether and how this new evidence is compatible with the previous picture of an intermixed alloy layer at the interface. In this respect, two issues require some discussion. As to point (i), the polarization dependence is at variance with the behavior of the bulk alloy, where the same asymmetric line shape is found for both L and T configurations.[14] As to point (ii), the existence of a LO-TO splitting as a consequence of substrate-induced biaxial strain of the alloy layer is not surprising. However, if one assumes the simple model of 50-50% composition for the interface alloy layer, one would naively expect no splitting for a $\mathrm{Si}_{0.5}\mathrm{Ge}_{0.5}$ substrate, consistent with the fact that no splitting occurs in unstrained bulk alloys.

To clarify these issues, we have performed a theoretical study of the vibrational properties of $(\mathrm{Si})_n(\mathrm{Ge})_n$ SL's, taking into account both strain and interface intermixing. As in previous studies on $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ systems,[15] the calculations are based on interatomic force constants derived from first principles. The extension of such a scheme to SiGe systems, requiring higher-order corrections due to the different bond lengths, has been recently developed in Ref. 16. To model SL's with mixed layers, an artificial periodicity in the plane parallel to the interfaces has been assumed, with 18 atoms per bidimensional unit cell. Thus the three-dimensional cell needed to treat a SL with a period of N atomic layers contains $18 \times N$ atoms. In the alloyed planes, Si and Ge atoms are

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distributed at random according to the assumed concentration, and the calculated properties are averaged over ~ 10 different configurations.

In the right-hand panel of Fig. 1, we show the calculated Raman spectra for the $(Si)_8(Ge)_8$ SL.[16] In the ideal configuration (perfectly abrupt interfaces), the L spectrum shows Si-like confined optical modes (Si_1, Si_3, Si_5) and Ge-like quasiconfined peaks, with no sign of interface vibrations [Fig. 1(c)]. In the T polarization, instead, besides confined modes, the well known[8] "ideal" interface mode exists [Fig. 1(d)]. However, its line shape is in sharp contrast with experiment. We next present [Figs. 1(e) and 1(f)] results for the simple SL model system with two $Si_{0.5}Ge_{0.5}$ layers at each interface.[17] It appears that even this simple intermixing model is able to reproduce the different features of the SiGe-like peak in the two polarizations. Calculations for different interface composition profiles give essentially the same picture.

Coming now to Fig. 2, the shaded regions display the calculated frequency splitting for different strain configurations.[18] Again, the trend found experimentally is reproduced, including the "anomalous" finite splitting in the configuration corresponding to the $Si_{0.5}Ge_{0.5}$ substrate.

Our calculation can thus account for experimental results and trends. Moreover, it can also give insight into the microscopic origin of the observed features. Indeed, for given frequency and polarization, we can plot the local density of vibrational states, i.e. the contribution of the individual atomic layers to the vibration. This is shown in Fig. 3 for the $(Si)_8(Ge)_8$ SL. If we focus again on the interface mode,[19] we notice that its spatial localization is very different in the L and T cases.

In the L polarization, the SiGe-like peak is almost completely localized at each interface on the single alloy atomic plane closest to Ge. This can be understood in terms of recent results for the bulk alloy,[20] where the contribution of different five-atom clusters to the individual vibrations was analyzed; it was found that only

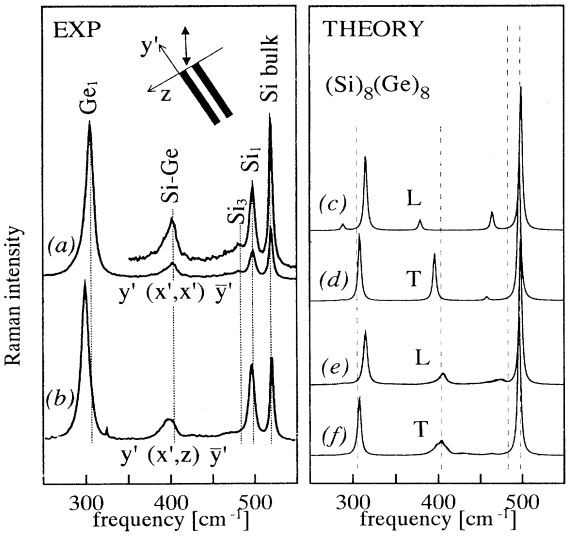

FIG. 1. Experimental [(a) and (b)] and theoretical [(c)–(f)] results for L and T Raman spectra of a (001)-oriented $(Si)_8(Ge)_8$ SL. The experimental scattering geometry is indicated in the inset; in (a) and (b) L and T polarizations are allowed, respectively. (c) and (d) refer to ideal SL's (no interface intermixing), while (e) and (f) are for a SL with two intermixed $Si_{0.5}Ge_{0.5}$ atomic layers at the interfaces. The vertical dotted lines are at the same frequencies in all panels and are drawn as a guide for the eye.

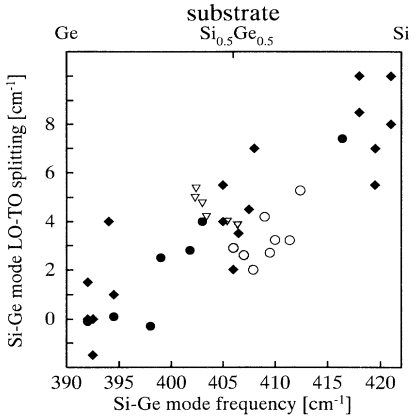

FIG. 2. Strain dependence of the LO-TO splitting of the SiGe-like interface mode (theory and experiment). The lowest horizontal scale gives the LO frequency of the same peak, which is a measure of the SL strain; the left-hand and right-hand extrema correspond to the lattice parameter of bulk Ge and Si. Triangles and open and full circles represent experimental values for different growth series. Diamonds are theoretical values corresponding to different SL intermixing configurations and lattice-matching to Si, $Si_{0.5}Ge_{0.5}$, and Ge substrates.

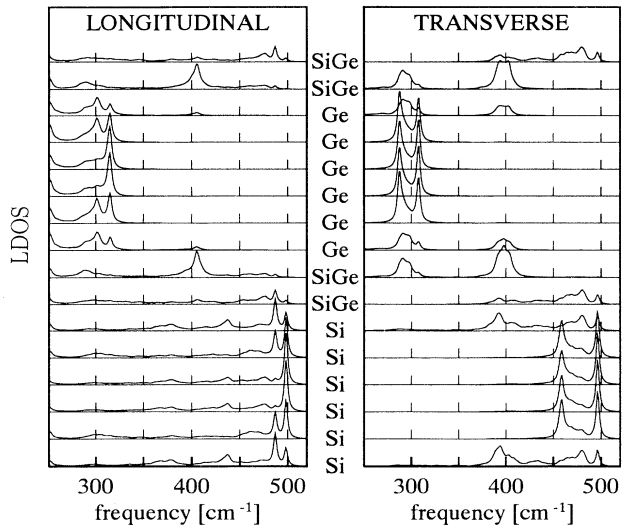

FIG. 3. Local density of states (LDOS) for L and $T1$ polarizations on the (001) atomic planes of a $(Si)_8(Ge)_8$ SL with two intermixed $Si_{0.5}Ge_{0.5}$ atomic layers at the interfaces (the composition of each plane is indicated).

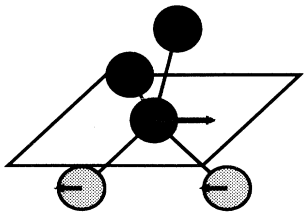

FIG. 4. Si_{2Ge} clusters (sketch) are mostly found across the interface planes between Si and SiGe. Hence they contribute mostly to the T polarization.

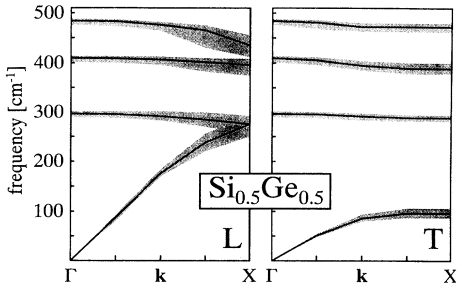

FIG. 5. L and T quasidispersion of the $Si_{0.5}Ge_{0.5}$ unstrained bulk alloy. Solid lines correspond to the frequency of the peak maxima in the spectral density of states (Ref. 22), with shaded regions indicating their width.

those clusters with a Si atom surrounded by at least two Ge atoms contribute to the 400 cm^{-1} vibration. Moreover, out of these clusters the ones which contain two Ge atoms only (Si_{2Ge}) do not contribute to the L spectrum in the SL geometry [the reason being that most of them are found across the interface, and are therefore oriented in such a way that their 400 cm^{-1} vibration is polarized parallel to the interface (see sketch in Fig. 4)]. In this framework, the localization of the L mode on one single plane is just a consequence of the fact that most of the longitudinally active clusters at 400 cm^{-1} are centered in that plane. The sharp localization and the small number of clusters contributing to this mode are thus responsible for its narrow line shape.

In the T polarization of Fig. 3 ($T1$) the spatial extension of the interface mode is very different, in that it involves four planes at each interface (reflecting the fact that Si_{2Ge} clusters are now active). These planes vibrate in pairs, according to the strength of the interplanar bonds,[8,21] each pair contributing with a very different line shape (in the $T2$ polarization, where the stronger interplanar bond occurs between the two alloy layers, only these two planes contribute a peak at $\sim$ 400 cm^{-1}). The T peak at $\sim$ 400 cm^{-1} is therefore a superposition of contributions coming from different pairs of planes and different clusters, which explains its broad Raman line shape (Fig. 1).

Coming now to the LO-TO splitting, this can be understood in terms of quasidispersions of the bulk alloys (Fig. 5).[22] Being confined to a well defined spatial region, the alloylike interface mode must indeed be associated to a *finite-q* vibration of the corresponding bulk alloy. This is already sufficient to explain the presence of a LO-TO splitting on the $Si_{0.5}Ge_{0.5}$ substrate, because L and T polarizations in the bulk are only degenerate at $q = 0$. Quantitatively, the calculated frequencies correspond to a smaller confinement wave vector in the L than in the T case, reflecting the different interface regions to which the L and T modes extend (see Fig. 3). Their strain dependence is also consistent with the calculated strain dependence of the bulk alloy dispersions. Before concluding, we will just mention that we have also tried different composition profiles, and found that the results are qualitatively similar and can be interpreted within the same scheme.[23]

In summary, we have shown that the anomalous behavior of the line shape and LO-TO splitting of the alloylike interface modes in "real" Si/Ge superlattices can be explained on the basis of an *ab initio* microscopic description of interface intermixing, which allows us to identify the character and spatial localization of the atomic clusters contributing to the vibrations.[24]

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[12]The experimental setup is the same as in Ref. 11. The power density was always kept below 10^5 W/cm^2 in order to preclude sample heating. The measurements were performed at room temperature with the 514.5 nm line of an Ar^+ laser and with a dye laser at 598 nm, using a triple grating spectrometer in the subtractive mode with a spectral resolution of 2.5 cm^{-1}. The signal was detected with a cooled photodiode multichannel detector.
[13]The samples were grown by low-temperature molecular beam epitaxy using Sb as a surfactant layer. For SL's with the largest periods, typical flux rates were $R = 0.17$ Å/s for Si and $R = 0.25$ Å/s for Ge, with substrate temperature $T_s \simeq 310\,^\circ$C. For thinner SL periods, $R \simeq 0.30$ Å/s and 0.28 Å/s for Si and Ge, respectively, with $T_s \simeq 320\,^\circ$C. The total SL thicknesses are between 0.2 and 1.0 μm.
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[18]The theoretical results are represented by broad dashed regions because of the broad line shape of the interface peaks; also, different thin SL's and different intermixing configurations give slightly different interface mode frequencies (full diamonds in Fig. 2).
[19]Si-like and Ge-like modes behave similarly to confined modes in other SL's; we will discuss the detailed confinement properties of T vibrations in a forthcoming paper.
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[21]In all III-V and group IV semiconductors, for a given transverse polarization the interplanar force constants C_n, are not symmetric with respect to a mirror plane centered on any (001) atomic layer; i.e, in the usual notation, $C_n \neq C_{-n}$. For the two transverse polarizations, $T1$ and $T2$, the interplanar forces are related by $C_n^{T1} = C_{-n}^{T2}$. See e.g., E. Molinari, A. Fasolino, and K. Kunc, Superlatt. Microstruct. **2**, 397 (1986), and references therein.
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[24]A more comprehensive study of the L and T phonon spectra, including acoustic modes as well as confined optical modes, will be presented elsewhere: R. Schorer, B. Abstreiter, S. de Gironcoli, E. Molinari, H. Kibbel, and E. Kasper (unpublished).