Strain and phonon shifts in GaAs$_{1-x}$P$_x$ alloys

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We have studied the influence of an in-plane (001) strain on the energy position of the long wavelength optical modes of GaAs$_{1-x}$P$_x$ alloys. These alloys have a two mode behavior. We have observed that the strain-induced shift of the Raman peaks corresponding to the GaAs-like vibration is greater than that of the GaP-like vibration. This result shows that the two modes are not affected in the same way by the strain. © *1996 American Institute of Physics.* [S0003-6951(96)00613-3]

Ternary III–V semiconductors (AB_xC_{1-x}) can be classified according to the number of observed long-wavelength optical modes into two extreme categories: one-mode and two-mode behavior.[1] One-mode behavior is characterized by the appearance of only one couple of long-wavelength optical modes, with transversal (TO) and longitudinal (LO) character, over the entire composition range. Two-mode behavior is characterized by the appearance of two couples of LO and TO modes, one corresponding to the *AB*-like bond vibrations and the other the *AC*-like bond vibrations. The frequency of the modes depends on the composition (x) of the ternary compound and, in the case of strained heterostructures, on the strain field present in the alloy. The dependence of the frequency of the phonon on the strain is given in terms of the phonon deformation potentials.[2] These parameters have been measured in several binary III–V compounds[3] but no systematic study has been made for ternary compounds. The interest of this study is twofold: first, it is interesting to study if the phonon deformation potentials of the alloy are different to those of the two binary compounds, and second, in the alloy there are two different bond lengths, one corresponding to the *AC* bond and the other to the *AB* bond; the lengths of these two bonds do not vary very much over the entire range of alloy composition,[4,5] but it remains unclear how the strain modifies these two bonds. Recent results[6] suggest that the strain is mainly accommodated by one type of bond. Therefore, the two types of bonds will be submitted to different effective strains and, in the case of alloys with a two-mode behavior, the strain-induced shift of the two types of optical vibrations could be very different. The effect of strain on the long wavelength optical modes has been studied in systems where mainly one phonon mode is observed such as Ga$_{1-x}$In$_x$As alloys[7] and Ga$_{1-x}$In$_x$P alloys,[8] but not on systems having a two-mode behavior.

In this letter we presented a study of the phonon deformation potential of the GaAs$_{1-x}$P$_x$ alloy system. This alloy has a two-mode behavior.[9] In the backscattering geometry and for (001) surfaces, the Raman spectra are composed of mainly two peaks. One, located around 280 cm^{-1}, corresponds to the LO optical vibration of the GaAs sublattice. The other, located in the range of 350–404 cm^{-1}, corresponds to the LO optical vibration of the GaP sublattice. We have studied the modification induced by a (001) in-plane strain in both types of modes.

The different level of strain in the GaAs$_{1-x}$P$_x$ layers is obtained by growing layers of constant composition and different thickness on GaAs substrates. As lattice mismatch relaxation depends on layer thickness according to the constant product $\epsilon_{\parallel} d = K$, where $\epsilon_{\parallel}$ is the residual strain and d the thickness,[10] the residual strain in the GaAs$_{1-x}$P$_x$ layers will change from one layer to another.

The samples studied in this work consisted of a series of GaAs$_{1-x}$P$_x$ layers with phosphorus content of 10% and 23% ($x=0.1$ and $x=0.23$), and different thickness (500, 250 nm and 1000, 500, 400, 200 nm for $x=0.1$ and $x=0.23$, respectively), grown on semi-insulating GaAs (001) substrates by atomic layer molecular beam epitaxy (ALMBE).[11] Growth substrate temperature (T_s) was kept at 350 °C and a special group V element solid source with fast acting valves and cracking sections was used. Prior to GaAs$_{1-x}$P$_x$ layer growth, a 100 nm thick GaAs buffer layer was grown by conventional molecular beam epitaxy at $T_s = 580$ °C.

The experimental procedure that allows for the growth of GaAs$_{1-x}$P$_x$ layers with accurate control of alloy composition is based on the combination of ALMBE growth and *in situ* reflectivity difference characterization technique and has been previously reported.[12] This procedure allows us to grow GaAs$_{1-x}$P$_x$ layers with the desired phosphorus composition by an appropriate design of the opening time and duration of the pulses of the phosphorus cell.

All samples were characterized by double crystal x-ray diffraction in the (+/−) Bragg arrangement for the (004) reflection and in the $\theta+\phi$, $\theta-\phi$ for the (115) reflection. From the recorded data and by using a dynamical simulation program, we can obtain both the phosphorus composition, always in coincidence with the *in situ* determined composition, and the residual strain state $\epsilon_{\parallel}$ in the GaAs$_{1-x}$P$_x$ layers. $\epsilon_{\parallel} = (a_{\parallel} - a_0)/a_{0,}$ $a_{\parallel}$ being the x-ray measured in-plane lattice parameter and a_0 the unstrained lattice parameter of the alloy.

The Raman spectra were obtained at room temperature in the backscattering geometry using the 514.5 and 456.9 nm

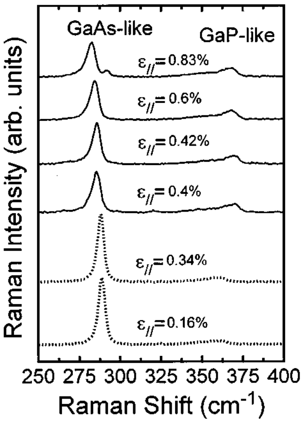

FIG. 1. Raman spectra taken at room temperature in the backscattering geometry. The exciting beam was 514.5 nm line. The full lines corresponds to the spectra of the samples having a composition (x) of 0.23, and the dashed lines to the spectra of those having a composition (x) of 0.1. The in-plane strain measured by x ray is also given.

lines of an Ar$^+$ laser. The experimental setup consisted of a triple stage monochromator and a diode array multichannel detector (Dilor XY in the ''high resolution'' mode). In this setup, the three monochromators operate in additive mode, and the resolution is limited by the geometrical parameters of the spectrometer and the diode separation, which altogether give 0.35 and 0.45 cm^{-1} for the 514.5 and 457.9 nm lines, respectively. Spectral linewidths were 1.38 and 2.1 cm^{-1} for these lines. For frequency calibration purposes, we used the Si and GaAs (LO) modes. The accuracy in the frequency values was finally estimated to be better than 0.4 and 0.5 cm^{-1} for the 514.5 and 457.9 nm lines, respectively.

In Fig. 1, we present the different Raman spectra obtained using the 514.5 nm line. As expected, we detect two peaks, one corresponding to the vibration of the GaAs sublattice and one corresponding to the vibration of the GaP sublattice. In one sample, we also detect the GaAs LO phonon Raman peak due to the small thickness of the epilayer. To check possible in-plane inhomogeneities, several spectra were taken at different points of the surface; within the experimental error, all the spectra taken in the same sample were similar.

In Figs. 2 and 3 we presented the frequency of the GaAs-like and GaP-like Raman peaks of Fig. 1 as a function of the measured in-plane strain, respectively.

The frequency shift of the Raman peak due to a biaxial strain in the (001) plane ($\epsilon_{xx}=\epsilon_{yy}$, with $\{x,y,z\}=\{[100],[010],[001]\}$ can be related to the phonon deformation potentials as follows:[2]

$$\Delta\omega=[(p+2q)/6\omega_0](2\epsilon_{xx}+\epsilon_{zz})$$

$$-[(p-q)/3\omega_0[(\epsilon_{xx}-\epsilon_{zz}),$$

where ω_0 is the frequency of the unstrained mode, p and q are the phonon diffraction potentials that describe the changes in the restoring forces, and ϵ_{ij} the components of the strain tensor. The first term of this expression corresponds to the shift induced by the hydrostatic component of the in-plane strain and the second one to the pure shear tetragonal strain component. If $\epsilon_{zz}=-2C_{12}/C_{11}\epsilon_{xx}$ (elastic theory), this expression can be written in terms of only one component of the strain tensor ($\epsilon_{\|}=\epsilon_{xx}$):

$$\Delta\omega=[(q-pC_{12}/C_{11})\omega_0]\epsilon_{xx}=\omega_0\alpha\epsilon_{\|}.$$

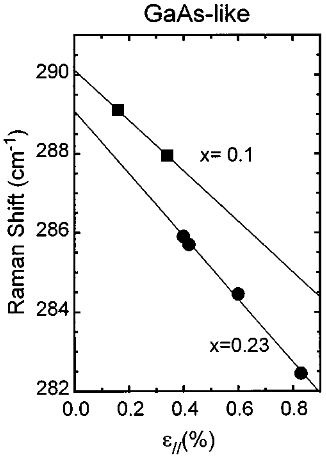

FIG. 2. Frequency of the GaAs-like Raman peak as a function of the in-plane strain. The full lines are a linear fit to the data. The full points correspond to the samples having a composition (x) of 0.23 and the squares to the samples which have a composition (x) of 0.1.

The lines in Figs. 2 and 3 correspond to a linear fit of the Raman shift to $\epsilon_{\|}$ as defined previously; the slope of this line is $\omega_0\alpha$, with $\alpha=(q-pC_{12}/C_{11})\omega_0^2$. The intersection with the y axis gives the frequency ω_0. The values of α obtained from that fit are presented in Table I. The α value for the two binary components are also shown in Table I.[13,14] Similar results are obtained using the 457.9 nm line, although the experimental values are slightly lower than those obtained using the 514.5 nm line (see Table I), which may be due to small in-depth strain inhomogeneities.[15,16] It is clear from the results of Table I that the strain-induced shift of the GaAs-like mode is greater than that of GaP-like mode.

The values of the phonon deformation potentials, p and q, for GaAs and GaP are very similar and the α parameter is

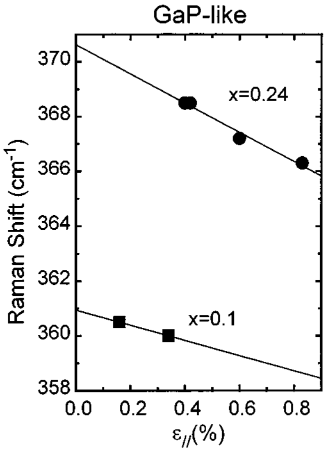

FIG. 3. Frequency of the GaP-like Raman peak as a function of the in-plane strain. The solid lines are a linear fit to the data. The filled circles correspond to the samples having a composition (x) of 0.23 and the squares to the samples having a composition (x) of 0.1.

TABLE I. α values of the GaAs-like and GaP-like vibrations for the two compositions studied here. The values obtained using the 457.9 nm line are given in parenthesis. For this line, due to worse signal to noise ratio, no reliable values were obtained for the GaP-like vibration of $GaAs_{0.9}P_{0.1}$. The values of α for the two binary compounds are also given.

	α GaAs-like	α GaP-like
$GaAs_{0.77}P_{0.23}$	−2.6(−2.3)	−1.3(−1)
$GaAs_{0.9}P_{0.1}$	−2.2(−2.2)	−0.8
GaP		−1.85[a]
GaAs	−1.8[b]	

[a]Balslev, Ref. 13.

[b]Wickboldt *et al.*, Ref. 14.

nearly the same for both binary compounds (see Table I). Therefore, we should expect an α value around −1.8 for the two phonon modes, contrary to what is experimentally observed: the α values of the GaAs-like modes are higher in the alloy than in both binary compounds, while the α value of the GaP-like modes are lower. The frequency shift of the phonon peak depends not only on the p and q values, or α values, which should be very similar for the two modes, but also on the real modification of the bond length and bond angles, which could be very different for the two types of bonds. Therefore, the different strain-induced shift of the two Raman peaks could be understood if the strain does not modify the two types of bonds in the same way.

The bond length modification has been measured in strained GaInAs.[6] According to this result, the strain present in these systems is accommodated mainly by the Ga–As bonds and not by the In–As-like bonds, which remain unchanged. Our results strongly suggest a similar behavior for the GaAsP alloy system. In our case, the strain is mainly accommodated by the GaAs bonds, in accordance with the larger elastic energy of GaP, calculated using the elastic theory, compared to that of GaAs for the same amount of in-plane strain; therefore, the deformation of the GaAs bonds is energetically more favorable. Using the same argument we should expect that, in the GaInAs alloys the strain should be accommodated mainly by the InAs bonds, contrary to what is observed in Ref. 6. The origin of this discrepancy is not well understood.

Using the α values of the binary compounds and the values of the unstrained frequencies obtained in Figs. 2 and 3, one can estimate the effective in-plane strain to which the GaAs-like and GaP-like vibrations are submitted, respectively. With this effective strain and taking into account the ratio between GaAs- and GaP-like bonds, one can calculate the values of the mean in-plane strain present in the samples. For a phosphorus content of 10% and 23%, these values are 12% and 24% higher than the values obtained by x-ray diffraction, respectively. This small discrepancy could be due to the fact that phonons are local probes and the microscopic distortion caused by the strain may not be of exact tetragonal symmetry.

In conclusion, we have studied the effect of an in-plane (001) strain on the longitudinal optical modes of $GaAs_xP_{1-x}$. The strain produces a much higher frequency shift for the GaAs-like modes than for the GaP-like modes. This different behavior strongly suggests that the strain is not accommodated in the same way by the two types of bonds present in the alloy.

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