# Phonon shifts and strains in strain-layered $(Ga_{1-x}In_x)As$

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We have measured the phonon frequencies (Raman technique) and the strains (x-ray rocking curve technique) of $(Ga_{1-x}In_x)As$ films on GaAs (100) substrates. Films with various $x$ values and various thicknesses were studied. The films range from perfect epitaxial to those that have relaxed by different amounts. The strain-induced frequency shift was calculated for each sample using the phonon deformation constants and measured strains. From the measurements and calculation, it is shown that the frequency shifts due to strain and the equivalent bulk frequencies for the phonon give internal agreement. This indicates that the Raman technique can be used for *in situ* monitoring of the growth process.

There is a great deal of interest in nonlattice-matched heterostructures[1] where, for example, one cubic semiconductor film of a given lattice constant is grown on a substrate of another cubic semiconductor with a different lattice constant.[2] For most device applications it is important that the nonlattice-matched films are epitaxial (or are pseudomorphic) with respect to the substrate. This avoids any lattice relaxation which leads to either interface misfit dislocations or a high density of threading dislocations.[3] Lattice relaxation[4] during growth will occur when the epilayer thickness exceeds some critical value $h_c$, which is equivalent to a critical strain energy.[1] At present reflection high-energy electron diffraction (RHEED) is the only practical *in situ* method for characterizing lattice constants during growth under high vacuum conditions.[5] Unfortunately, the $e$-beam energies used in RHEED are believed to adversely affect the surface properties and hence subsequent interface properties of the grown layers. Therefore, it is desirable to have an alternative method for *in situ* characterization which operates at low energy and power densities, and which can be used at ambient conditions. Raman spectroscopy is one possible candidate which meets these criteria.

We report studies of thin $(Ga_{1-x}In_x)As$ films grown on GaAs substrates with $x$ in the range $0 \leqslant x \leqslant 0.2$, and have measured the optic phonons (by the Raman technique) and the parallel and perpendicular strains in the film (by the x-ray rocking curve technique).[6] For a given value of $x$, we have measured films of various thickness, so that they are consequently strained by various amounts.

The films, similar to those reported previously,[3] were grown by molecular beam epitaxy (MBE) on (100) oriented GaAs faces. The x-ray rocking curve measurements were carried out using the Fe $K_{\alpha_1}$ radiation in a nondispersive double-crystal geometry.[6] To measure the lattice constants of the film, the 400 reflection was used to obtain the lattice constant normal to the sample surface, and the 422 reflection, with a large angle of incidence, to obtain the in-plane constant. The angular separation of the rocking curve peaks due to the misorientation of the film has been canceled out by taking an average of the two rocking curves differing by 180° in the sample plane. The Raman measurements were performed using a 5145-Å laser, in backscattering geometry, with a standard double monochromator.

Because the GaAs substrate is massive compared to the film, the substrate is assumed to retain its normal internuclear distances, with a lattice constant given as $a_s$. For the film we use the term parallel to denote lattice constants in the film parallel to the (100) plane of the substrate, thus $a_\parallel$ is the parallel lattice constant of the film. Similarly, $a_\perp$ is the perpendicular lattice constant of the film.

The seven single-crystal films of $(Ga_{1-x}In_x)As$ on (100) GaAs substrates that were studied are listed in Table I, where the value of $x$ and nominal film thickness, $h$, is given. Consider the three films of composition $x = 0.10$ as an

TABLE I. Various properties of our films are given. The first three columns list the sample number, the composition in $(Ga_{1-x}In_x)As$, and $h$ is the film thickness. The next three columns are: the measured x-ray strains, and the measured LO mode frequency in the film. The last three columns are calculated quantities: the elastic strain parallel ($\epsilon_{xx}$), and perpendicular ($\epsilon_{zz}$) to the plane, and the frequency shift.

| Sample | $x$ | $h$ | $\epsilon_\parallel^{xr}$ | $\epsilon_\perp^{xr}$ | LO | $\epsilon_{xx}$ | $\epsilon_{zz}$ | Freq. shift |
|---|---|---|---|---|---|---|---|---|
| No. 1 | 0.07 | 1000 Å | 0.00 | 1.21% | 291.8 cm$^{-1}$ | $-0.63\%$ | 0.58% | 2.03 cm$^{-1}$ |
| No. 2 | 0.07 | 1 $\mu$m | 0.42% | 0.71% | 289.9 cm$^{-1}$ | $-0.15\%$ | 0.14% | 0.49 cm$^{-1}$ |
| No. 3 | 0.15 | 1 $\mu$m | 0.61% | 0.91% | 288.3 cm$^{-1}$ | $-0.16\%$ | 0.14% | 0.50 cm$^{-1}$ |
| 387 | 0.10 | 1500 Å | 0.00 | 1.30% | 291.3 cm$^{-1}$ | $-0.67\%$ | 0.63% | 2.17 cm$^{-1}$ |
| 389 | 0.10 | 2500 Å | 0.32% | 0.98% | 290.0 cm$^{-1}$ | $-0.34\%$ | 0.32% | 1.03 cm$^{-1}$ |
| 388 | 0.10 | 1 $\mu$m | 0.46% | 0.79% | 288.9 cm$^{-1}$ | $-0.17\%$ | 0.16% | 0.55 cm$^{-1}$ |
| 390 | 0.20 | 400 Å | 0.00 | 2.46% | 291.6 cm$^{-1}$ | $-1.25\%$ | 1.21% | 4.06 cm$^{-1}$ |

example. For this composition we have grown one film with thickness less than the critical thickness $h_c$ and two with thickness greater than $h_c$. The critical thickness is defined as the maximum thickness at which a film can be grown in perfect epitaxy for a given substrate and given composition of the film. For each film we measure the relative unit cell size with respect to the substrate and obtain what is often called x-ray strain. For example, $\epsilon_{\parallel}^{xr} = (a_{\parallel} - a_s)/a_s$ and $\epsilon_{\perp}^{xr} = (a_{\perp} - a_s)/a_s$. These results are listed in the table. For perfect epitaxy $\epsilon_{\parallel}^{xr} = 0$, and this is found for the 1500-Å film (No. 387). We also list the measured position of the longitudinal optical (LO) phonon of this film; as the films become thicker this value decreases. The measured frequencies are plotted in Fig. 1 as solid circles. For example, for $x = 0.1$ there are solid circles corresponding to the frequency measured from each of these three films. These phonon frequency values make physical sense; the film with perfect epitaxy is under the largest compressive stress. Since, generally, compressive stresses shift the phonons to high energies, these films should have the largest frequency shift, as observed.

In order to calculate the phonon frequency shifts due to the strains in the film, we must determine the elastic strains. Clearly these are related to the measured x-ray strains. Physically we know that the largest negative in-plane elastic strain ($\epsilon_{xx}$) will be required to produce a perfect epitaxial film (i.e., a film with $\epsilon_{\parallel}^{xr} = 0$). Similarly, a perfect epitaxial film will have the largest strain perpendicular to the plane ($\epsilon_{zz}$). With the help of the elasticity theory, $\epsilon_{xx}$ and $\epsilon_{zz}$ can be calculated from the x-ray strain. For the case discussed



FIG. 1. Solid circles are the measured frequencies for the samples listed in Table I. For each sample, a bulk equivalent frequency (cross) is calculated from the Raman measured frequency and the x-ray measured strain, as described in the text.

here, for a two-dimensional stress in the $xy$ plane, from elasticity theory $\epsilon_{zz}/\epsilon_{xx} = 2\nu(1 - \nu)$ where $\nu$ is Poisson's ratio. Since $\nu \approx 1/3$, we have $\epsilon_{zz} \approx -\epsilon_{xx}$ and the deviations from this result shown in Table I are due to the fact that Poisson's ratio is not exactly $1/3$ and varies slightly with $x$.

Given the elastic strains, it remains for us to calculate the frequencies of the optic modes in the presence of the strains. Assuming the threefold degeneracy of the $k = 0$ optical phonons in a material with the diamond structure, in the presence of strain the frequencies of the optic modes are given by the following secular equation[7,8]:
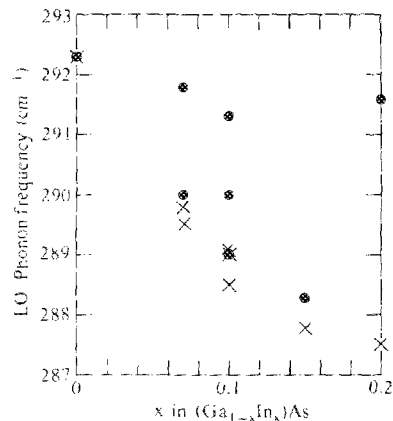
$$\begin{vmatrix} p\epsilon_{xx} + q(\epsilon_{yy} + \epsilon_{zz}) - \lambda & 2r\epsilon_{xy} & 2r\epsilon_{xz} \\ 2r\epsilon_{xy} & p\epsilon_{yy} + q(\epsilon_{zz} + \epsilon_{xx}) - \lambda & 2r\epsilon_{yz} \\ 2r\epsilon_{xz} & 2r\epsilon_{yz} & p\epsilon_{zz} + q(\epsilon_{xx} + \epsilon_{yy}) - \lambda \end{vmatrix} = 0. \qquad (1)$$

The eigenvalue is given by $\lambda = \Omega^2 - \omega_0^2$, where $\omega_0$ is frequency with zero strain and $\Omega$ is the strain-dependent frequency. The phonon deformation constants $p$, $q$, and $r$ describe the change of the spring constants with strain.[9] Since the frequency shift due to strain is small, we use the approximation $\Omega \approx \omega_0 + \lambda/2\omega_0$. In III-V semiconductors with the zinc blende structure, the long range Coulomb forces split the LO and transverse optical (TO) modes at small $k$. This splitting is small and is essentially independent of strain, so the strain-dependent frequency shifts are obtained by adding the LO-TO splitting to the frequencies obtained from Eq. (1).

The phonon deformation constants have been measured by applying uniaxial stresses to single-crystal samples with various orientations.[7,8,10] Hence, in subsequent experimental papers[11] the shifts have been expressed in terms of stress. However, since here we directly measure the strains, we can ignore the stress (which is applied to the film by the substrate). Then the eigenvalue of Eq. (1) for the LO phonon that we measure from (100) oriented faces is given by

$$\lambda = p\epsilon_{zz} + q(\epsilon_{xx} + \epsilon_{yy}), \qquad (2)$$

where $\epsilon_{xx} = \epsilon_{yy}$ for our geometry. Given the phonon defor-

mation constants $p$ and $q$, and using our measured strain (listed in Table I), the frequency shift, $\Omega - \omega_0$, is obtained and given in the last column in Table I.

We measure $\Omega$, calculate $\lambda$ (using the measured x-ray strain), and hence can determine $\omega_0$, which is the equivalent bulk frequency for the phonon; $\omega_0$ of course varies with $x$. The equivalent bulk frequency results are plotted in Fig. 1 as crosses. For each datum point (solid circles) we obtain a cross. As can be seen, these bulk equivalent frequencies are in good agreement with each other. For $x \approx 0.1$, we find that $h_c$ is between 1500 and 2500 Å; this is in reasonable agreement with published data.[12]

Thus, we have shown that Raman spectroscopy appears to be a suitable method for characterizing strain in strained-layer epitaxial systems. Since the Raman measurement uses an optical probe of lower energy than RHEED, it should be ideal as a damage-free, noncontaminating, *in situ* tool to characterize the state of an epitaxial layer during growth by MBE, metalorganic chemical vapor deposition, or other techniques.

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