PROFILING COMPOSITION VARIATIONS IN COMPOSITION-MODULATED GaP/InP SHORT-PERIOD SUPERLATTICES USING RESONANCE RAMAN SCATTERING

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ABSTRACT

We use resonance Raman scattering (RRS) and electroreflection (ER) measurements to profile the the composition and strain variations in laterally composition-modulated (CM) GaP/InP short-period superlattices (SPS's). The ER spectra of a $GaP_{2.2}/InP_{2.0}$ SPS give the fundamental band-gap energy at 1.69±0.05eV, which is about 210 meV lower than the band gap energy of a GaInP random alloy with the same overall composition. The RRS measurements reveal strong dependences of the phonon spectrum on the polarization and the excitation energy. In RRS spectra measured with the polarization of both excitation and scattered photons along the composition modulation direction, the GaP-like longitudinal optical (LO) phonon redshifts by 4.0±0.5 cm^{-1} near the resonance with the fundamental energy gap. On the other hand, when the polarizations are orthogonal to the composition modulation, the LO phonons redshift as much as 16 cm^{-1} at low excitation energies. A comparison of the experimental data with a model calculation gives the average In composition in the In-rich region as 0.70±0.02, and the average Ga composition in the Ga-rich region as 0.68±0.02. Our result also indicates that there are small volumes (less than 1% volume fraction) with very high In mole fraction.

INTRODUCTION

Spontaneous lateral CM in III-V alloys and SPS's has been studied extensively in recent years.[1-7] When a $(GaP)_2/(InP)_2$ SPS was grown by MBE on a (001) GaAs substrate, it was found that the cation composition is modulated along the [110] direction with a periodicity of ~100–200 Å, resulting in a lateral superlattice with alternating (110) layers of Ga-rich and In-rich material.[1] The interplay between the composition modulation wave and the concomitant coherency strain wave results in a lateral superlattice that has a band gap energy much lower than that of the random alloy with the same overall average composition, and the band-edge luminescence shows a strong anisotropy that is attributable to a lateral superlattice effect.[3,7] In understanding the effect of the CM phenomenon on the materials properties of alloys and SPS's, it is critical to know the actual extent of the composition variation. Energy-dispersive x-ray microanalysis has been used to estimate the variation of the local composition,[1,8] but this technique requires special sample preparation that does not preserve the integrity of the samples. Estimating the composition variation by comparison of the superlattice band-gap energy measured with optical techniques such as photoluminescence or modulation spectroscopy with that obtained from theoretical calculations usually does not yield a unique solution because many input parameters remain unknown.

The RRS technique can be used to estimate the composition variation by providing extra input in addition to the superlattice band-gap energy that is obtained from photoluminescence or modulation spectroscopy. For example, when the excitation laser energy is tuned away from resonances (*off-resonance*), the Raman spectrum of a composition modulated GaP/InP SPS should comprise signals from the Ga-rich as well as the In-rich regions of the sample. However,

Mat. Res. Soc. Symp. Proc. Vol. 583 © 2000 Materials Research Society

if the laser energy is tuned to be resonant with the fundamental band gap of the lateral superlattice, the Raman scattering signal should come predominantly from the In-rich region, because the ground-state electron and hole wavefunctions are both localized in that region, and so the optical transitions occur in the In-rich region. Consequently, the phonon frequencies would redshift towards those for In-rich compositions near the resonance. Thus, the phonon frequency shift near the resonance is a good measure of composition and strain in the In-rich region. Since the local coherency strain in the In-rich region depends on the composition in the Ga-rich region as well as that in the In-rich region, one can estimate the compositions in the In-rich region and in the Ga-rich region simultaneously, by comparing the phonon frequency shift with the superlattice band-gap energy.

EXPERIMENTAL

The samples were grown by a single-step gas source MBE process on (001)-oriented, on-axis semi-insulating GaAs substrates. Elemental Ga and In sources were used for group III fluxes, while P_2 cracked from phosphine was used as the group V flux. The substrate temperature was kept at ~530°C with a growth rate of ~1 μm/hr, as calibrated by reflection high-energy electron diffraction (RHEED) intensity oscillation measurements. The layer structure consists of a 0.2 μm undoped GaAs buffer layer, followed by 80 pairs of $(GaP)_{2.2}/(InP)_2$ short-period superlattice (SPS) layer. The thickness ratio of the GaP and InP layers, 2.2/2.0, gives an overall composition of $Ga_{0.52}In_{0.48}P$, which is nominally lattice-matched to the GaAs substrate.

The room-temperature polarized ER spectra were measured using a contactless ER technique.[9] RRS measurements were performed at room temperature in a quasi-backscattering geometry. The excitation source was either a Ti:sapphire laser (1.58–1.82 eV) or a dye laser with Rhodamine 6G dye (1.94–2.17 eV). The scattered photons were dispersed by a triple spectrometer and detected by a liquid-nitrogen-cooled CCD detector array. The details of the experiment have been published elsewhere.[10]

RESULTS

The average period of the lateral CM wave along the [110] direction was measured to be 135±15 Å using dark-field TEM images taken in $(\bar{1}10)$ cross section. No lateral contrast variation is observed in the (110) cross section. Figure 1 shows two ER spectra taken with the polarization aligned along the $[\bar{1}10]$ and [110] directions. Here, we take X=$[\bar{1}10]$, Y=[110], and Z=[001]. The sharp feature near 1.42 eV is due to the GaAs substrate. The broad feature near 1.69 eV is due to the optical transition across the fundamental band gap E_g' of the lateral superlattice in the SPS layer. This feature shows a strong polarization anisotropy: the signal is much stronger in the X-polarization than in the Y-polarization. This polarization anisotropy is a direct result of the lateral superlattice effect. The broad linewidth of this feature reflects the imperfect periodicity of the CM wave and the possibility that the

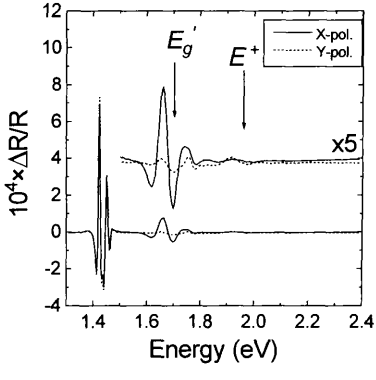

Figure 1 Polarized ER spectra taken with the polarization orthogonal (X) and parallel (Y) to the CM direction.

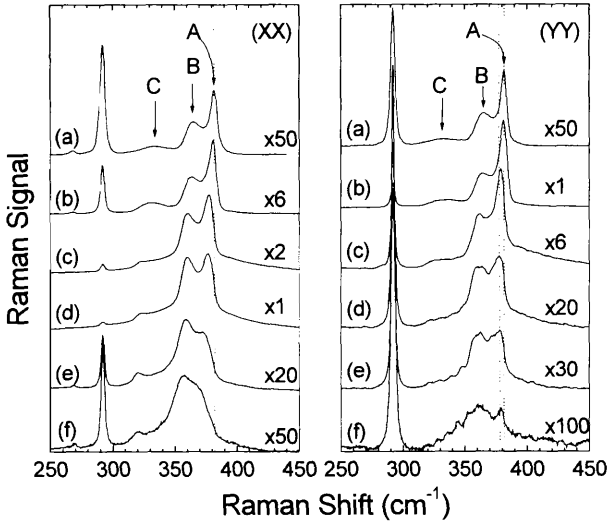

Figure 3 Series of polarized Raman spectra for (*XX*) and (*YY*) polarizations. The excitation energies are: (a) 2.410, (b) 2.008, (c) 1.768, (d) 1.712, (e) 1.625, and (f)1.602 eV for the (*XX*) polarization; and (a) 2.410, (b) 2.008, (c) 1.789, (d) 1.696, (e) 1.668, and (f)1.602 eV for the (*YY*) polarization. Each series is separately normalized with the factors on the right.

amplitude of the CM is not uniform throughout the sample. From these spectra, the superlattice band gap energy E_g' is determined to be 1.69±0.05 eV, which represents a 210 meV redshift relative to the band gap energy of the random alloy whose average Ga composition is 0.52. These results are similar to those obtained from earlier polarized photoreflectance measurements.[3] In addition, closer inspection of the expanded spectra indicates that there are additional spectral features at higher energies up to ~2.05 eV. We attribute these features to higher-energy transitions of the lateral superlattice. The strongest of these higher-energy features is the one at 1.9–2.0 eV, marked E^+. This one appears stronger in the *Y* polarization than in the *X* polarization, which is opposite to the behavior of the feature near 1.69 eV.

Figure 2 shows two series of Raman spectra taken in a quasi-backscattering geometry with (*XX*) and (*YY*) polarizations, where (*XX*), for example, refers to a configuration with polarizations of both the excitation and scattered photons aligned along the *X* direction. The "off-resonance" spectra (the top spectrum of each series), taken with the 5145-Å line of an Ar ion laser as the excitation source, are similar to that of a typical random alloy $Ga_{0.52}In_{0.48}P$:[11] a sharp GaP-like longitudinal optical (LO) phonon peak at 381.8 cm^{-1} (A), a relatively broader InP-like LO phonon peak at ~364 cm^{-1} (B), and a weak and broad transverse optical (TO) phonon peak at ~330 cm^{-1} (C) are observed. In addition, an LO phonon peak at 292 cm^{-1} and a much weaker TO phonon peak at 269 cm^{-1} from the GaAs substrate are seen. In the (*XX*) polarization, as the excitation energy is lowered, the Raman spectrum changes dramatically. All three phonon peaks A, B, and C move toward lower frequencies. In addition, the intensity of the InP-like LO phonon peak (B) increases relative to that of the GaP-like LO phonon peak (A) with decreasing excitation energy and the peak A becomes unresolved at the lowest excitation energies. On the other hand, in the (*YY*) polarization, the changes are less dramatic. The phonon peaks redshift

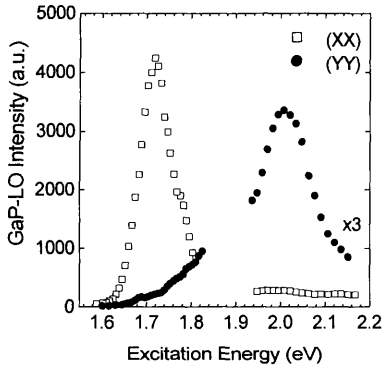

Figure 3 Intensity of the GaP-like LO phonon peak as a function of the excitation energy.

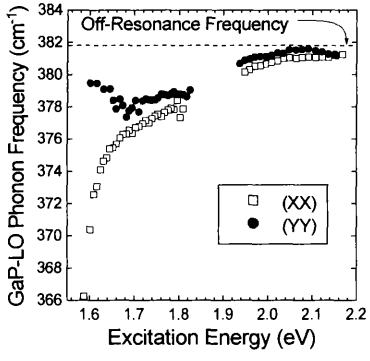

Figure 4 Frequency of the GaP-like LO phonon as a function of the excitation energy. (**Inset:** Comparison of the dependence of the calculated phonon frequency on the excitation energy)

initially with decreasing excitation energies, but blueshift back toward the "off-resonance" frequencies as the excitation energy is lowered below ~1.7 eV. Also, the InP-like LO phonon peak B does not completely dominate the spectrum as in the (*XX*) polarization at the lowest excitation energies, but the GaP-like LO phonon peak A is always resolved.

Figure 3 plots the intensity of the GaP-like LO phonon peak as a function of the excitation energy for the two polarizations. At ~1.72 eV, near E_g' observed in the ER measurement, a strong resonance is observed in the (*XX*) polarization. In the (*YY*) polarization, on the other hand, this resonance is very much weaker, and occurs at 1.69 eV. Near 2.0 eV, a moderately strong resonance due to the higher-energy transition E^+ is observed for the (*YY*) polarization, while a weaker resonance is seen for the (*XX*) polarization. In Fig. 4, the excitation-energy dependence of the frequency of the GaP-like LO phonon peak A is plotted for the two polarizations. In the (*XX*) polarization, the GaP-like LO phonon peak A shifts monotonically to lower energy as the excitation energy is lowered. At 1.72 eV, where the phonon intensity is maximum, the phonon frequency is 4.5±0.5 cm^{-1} lower than the "off-resonance" phonon frequency of 381.8 cm^{-1}. As the excitation energy is lowered further, the phonon peak moves further toward lower frequencies, and at the lowest excitation energy used (1.59 eV), this phonon peak redshifts by almost 16 cm^{-1}. In the (*YY*) polarization, the phonon peak frequency reaches a minimum near 1.69 eV, where it is redshifted by 4.0±0.5 cm^{-1}. At lower energies, the peak blueshifts as the excitation energy is further lowered.

DISCUSSION

The excitation dependence of the phonon frequency in the (*YY*) polarization is consistent with the scenario presented in the introduction: the phonon frequency is similar to that of a random alloy with the same overall composition when the excitation energy is away from the resonance, but is redshifted near the resonance at 1.69 eV. On the other hand, the excitation dependence of the phonon frequency in the (*XX*) polarization is anomalous in that even at low excitation energies the phonon frequency decreases monotonically as the excitation energy is lowered, i.e., moved

away from the resonance. This anomaly results from the inhomogeneity of the sample and the very strong resonance effect in this polarization. Since the period and the amplitude of CM are not uniform throughout the sample, there exist regions where the *local* In concentration is higher than the *average* In concentration of all the In-rich regions, $\langle x_{In} \rangle$. In these regions, the resonance occurs at a *local band-gap energy* that is lower than the spatially averaged band gap E_g' of 1.69 eV. When the excitation energy is in resonance with the *local* band gap of these regions, the Raman spectrum would be dominated by contributions from these regions due to the strong resonance in this polarization, and consequently, the phonons redshift to reflect the higher In content in these regions. As the excitation energy is further lowered, the volume fraction of such regions where the local band gap energy is in resonance with the excitation becomes very small, but the Raman contribution from these small volumes is still larger than that from the rest of the sample due to the strong resonance effect. This interpretation is supported by the fact that even at the lowest excitation energies, the Raman signal is significantly stronger in the (*XX*) polarization than in the (*YY*) polarization. It is also consistent with the changes in the shape of the Raman spectrum at lowest excitation energies, where the InP-like LO phonon becomes stronger than the GaP-like LO phonon, indicating that the signal is coming from very In-rich material. Within this interpretation, the volume fraction of these extra-In-rich regions can be inferred from the resonance plot of Fig. 3. For example, at the lowest excitation energy used, the phonon intensity is about 1% of that at the peak of the resonance. From this, one can infer that the very In-rich regions that yield a 16 cm^{-1} redshift of the GaP-like LO phonon occupy a small fraction on the order of 1% of the total sample volume.

On the other hand, since the resonance is weak in the (*YY*) polarization, the resonance behavior in this polarization is governed primarily by the volume distribution of the In-rich regions. Therefore, we take –4.0±0.5 cm^{-1} as the *average* phonon frequency shift of the GaP-like LO phonon that occurs due to the high In-concentration of the In-rich regions. In contrast, there is no comparable blueshift of the phonons in either polarization near the resonance at ~2.0 eV. The reason for this is as follows: for the lowest-energy transition, both the electron and hole wavefunctions are localized in the In-rich regions and thus the contribution to the Raman signal comes predominantly from the In-rich region when the excitation is in resonance with this critical point. In contrast, the electron and hole wavefunctions for the higher-energy states are not as strongly localized within the In-rich region. In fact, our calculations[7] show that the electron and hole states that are involved in the E^+ transition have wavefunctions that are significantly delocalized between the Ga- and In-rich regions. Therefore, Raman scattering near this resonance probes both the Ga- and In-rich regions simultaneously and no major shift in the phonon frequency is expected. This is consistent with previous resonance Raman measurements on AlGaAs alloys, where only Ga-rich regions could be detected.[12]

One can estimate the average In and Ga concentration in the In- and Ga-rich regions, $\langle x_{In} \rangle$ and $\langle x_{Ga} \rangle$, respectively, from the knowledge of: the period of the CM wave 135±15 Å; the average phonon shift $\delta\omega$ of GaP-like LO phonon, –4.0±0.5 cm^{-1}; and the average superlattice band-gap energy E_g' of 1.69±0.05 eV. Since both $\delta\omega$ and E_g' are functions of composition as well as the lateral coherency strain, which in turn is determined by the lateral composition variation, we estimated $\langle x_{In} \rangle$ and $\langle x_{Ga} \rangle$ by simultaneously fitting the phonon frequency shift and E_g' to a model calculation. We assume that the CM layer is strained in the [110] direction as discussed by Glas.[13] The strength of the lateral coherency strain in each In- or Ga-rich layer is then determined by the amplitude of the lateral composition modulation wave in each layer and the ratio of the width of the In-rich layer to that of the Ga-rich layer. Since the overall composition should be $Ga_{0.52}In_{0.48}P$, the width ratio is constrained by the amplitude of the lateral composition modulation wave in each layer. We assume that the composition modulation wave has an asymmetric sinusoidal form. The best fit to the experimental values of $\delta\omega$ and E_g' is

obtained for $\langle x_{In} \rangle = 0.70 \pm 0.02$ and $\langle x_{Ga} \rangle = 0.68 \pm 0.02$. (See Ref. 10 for a detailed account of the fitting procedure.)

It appears that the maximum phonon shift of 16 cm^{-1} in the (*XX*) polarization that we earlier interpreted as arising from small volumes with excessively high In compositions is inconsistent with this result, because a simple extrapolation would give x_{In} in such regions to be in excess of 1. However, it should be remembered that the above analysis assumes that the regions under consideration are coherently strained along the [110] direction. If the strain is locally relaxed, the same phonon shift would correspond to a much smaller composition amplitude swing $\delta x_{In} = x_{In} - 0.48$. For such extremely In-rich regions, the strain is likely to be incoherent because of the high elastic strain energy involved. For the case where the strain is fully relaxed, a 16 cm^{-1} phonon shift corresponds to a composition amplitude swing $\delta x_{In} = 0.25$, or $x_{In} = 0.73$, which is the lower bound for the In-composition in such excessively In-rich regions. In real situations, it is likely that the strain is partially relaxed, and therefore, x_{In} could be significantly large than this lower bound.

ACKNOWLEDGMENT

We thank F. Alsina for helpful discussions. The work at NREL was supported by the Office of Science (Materials Sciences Division) of the Department of Energy under Contract No. DE-AC36-83CH10093. The work at the University of Illinois was supported by the National Science Foundation and the Joint Services Electronics Program.

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