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Raman spectroscopy for characterizing compositional intermixing in GaAs/AlGaAs heterostructures

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Compositional intermixing induced by the process of impurity-free vacancy (dielectric cap annealing induced) disordering in GaAs/AlGaAs is studied using Raman spectroscopy. The degree of intermixing in multiple-quantum-well structures was detected through the energy shift of certain Raman modes of the lattices. In addition, localized intermixing, with band-gap shifts as low as 6 nm realized in 1:1 band-gap grating patterns with different periods ($\geqslant 4$ μm), was also detected through the energy shift and the full width at half maximum of the structures's Raman modes. © *1999 American Institute of Physics.* [S0003-6951(99)01226-7]

Quantum-well intermixing (QWI) is a promising alternative to regrowth and overgrowth processes,[1] which are the main techniques used in realizing photonic integrated circuits.[2] Due to recent advances in QWI technologies, their use in novel applications, such as patterning asymmetric quantum wells for quasi-phase-matching applications, is being investigated.[3] For such an application, first-order intermixed gratings with periods $\cong 3$ μm are needed for wavelengths around 1.55 μm.[4]

Although spatially resolved photoluminescence (PL) measurements have recently been reported for band-gap gratings with similar periods, results showed that there is a lower limit on the size of the period that can be studied.[5] This is due to the finite diffusion length of the photogenerated carriers. Moreover, PL measurements provide little information apart from determining the band gap of the quantum wells (QWs). Raman spectroscopy, in contrast, can provide information about many parameters of semiconductor crystals, such as the lattice order and interface stress.[6] In addition, the spatial resolution of the Raman scattering measurements is only limited by the laser spot size, since the scattered light is produced only from the part of lattice illuminated by the laser. Raman measurements have served before as a sensitive technique for detecting and studying disordering in GaAs/AlGaAs heterostructures.[7] However, no exhaustive studies have previously been carried out on samples with a laterally structured band gap fabricated using QWI technologies.

In this letter we demonstrate three points. First, it is possible to detect compositional intermixing in GaAs/AlGaAs multiple-quantum-well (MQW) structures, down to at least 1 μm below the surface, using Raman spectroscopy. Second, we present provisional results on using Raman spectroscopy to quantify the degree of compositional intermixing in GaAs–AlGaAs heterostructures. Third, it is shown that Raman spectroscopy can clearly detect periodic band-gap grating structures, fabricated by intermixing. The experiments were designed to ensure that the Raman signal was collected from the QW/barrier interface, which is a necessary condition to obtain meaningful information about compositional intermixing from the Raman spectroscopy measurements. This was achieved by removing the dielectric caps and the top GaAs layer before testing, to reduce photon adsorption.

The structure used in this study was a MQW waveguide structure made of 76 periods of 2.8 nm GaAs QWs with 10 nm $Al_{0.4}Ga_{0.6}As$ barriers.[5] The 0.9 μm, upper, and 4 μm, lower, cladding regions were also $Al_{0.4}Ga_{0.6}As$. The wafer was capped with a top GaAs layer 100 nm thick. After cleaving, samples were annealed at different temperatures, between 900 and 960 °C, having been capped with 200 nm of electron-gun evaporated SiO_2. After intermixing, the SiO_2 cap was etched and the top GaAs layer removed from the samples to decrease the associated photon absorption. Raman scattering was induced using a He:Ne laser in a Renishaw Ramascope. The laser was linearly polarized in the sample $\langle 111 \rangle$ direction, with a spot size diameter of 340 nm and power density of 38 mW cm^{-2}. Detection of the Raman signal used no polarization selectivity in order to allow observation of both the TO and LO modes.[6] The PL background signal was removed from the Raman spectra and then the Raman peaks were curve fitted. The detected Raman modes are listed in Table I, and selected spectra are shown in Fig. 1. All the modes are intrinsic to the lattice, except for one mode that is probably associated with the doping species.[6–8]

In Fig. 2, the energy shift and the full width at half

TABLE I. Observed and reported Raman peaks for a MQW GaAs/AlGaAs undoped structure.

Peak	Observed energy (cm^{-1})	Closest reported (cm^{-1})	Phonon mode	Designation
1	382	382	AlAs like	LO $Al_{0.4}Ga_{0.6}As$
2	374	373	AlAs like	TO $Al_{0.4}Ga_{0.6}As$
3	367.8	…	…	…
4	275.1	275	GaAs like	LO $Al_{0.4}Ga_{0.6}As$
5	269	269	GaAs like	TO $Al_{0.4}Ga_{0.6}As$

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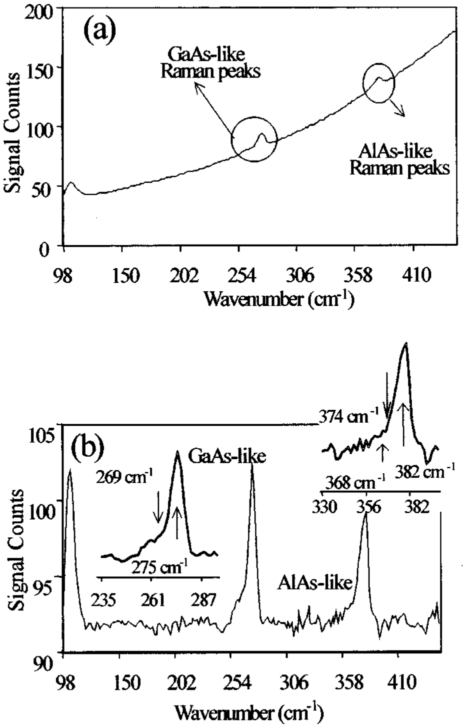

FIG. 1. Raman spectra from an as-grown MQW sample with the top GaAs contact layer removed. Raman spectra are shown (a) before and (b) after removing the PL background. The GaAs- and AlAs-like Raman modes are indicated.

maximum (FWHM) of the Raman peaks are plotted as a function of the degree of intermixing represented by the PL wavelength shift. Intermixing can be clearly seen through the energy shift of the TO GaAs-like Raman mode of the $Al_{0.4}Ga_{0.6}As$ layer. The sample annealed at 960 °C for 60 s exhibited a PL shift of 70 nm, with a change in the energy of the GaAs TO Raman peak of 4 cm^{-1} from that of the original sample,[9] which matches the energy of the TO GaAs-like Raman mode of $Al_{0.3}Ga_{0.7}As$. The expected Al composition resulting from intermixing of a thin, 2.8 nm GaAs QW and a thicker, 10 nm $Al_{0.4}Ga_{0.6}As$ barrier will be close to $Al_{0.3}Ga_{0.7}As$.[10] However, the other Raman modes of the $Al_{0.4}Ga_{0.6}As$ layer show no significant change. As for the unidentified (possibly impurity-related) Raman peak, although it exhibits substantial changes of up to 6 cm^{-1}, it shows no consistent trend as a function of the degree of QWI. The reason for not observing any intermixing effect on the Raman-mode energies, apart from the TO GaAs-like mode, is unclear and is not consistent with the compositional change in the lattice. Although this will be investigated in more detail, two factors might be contributing to such an observation.

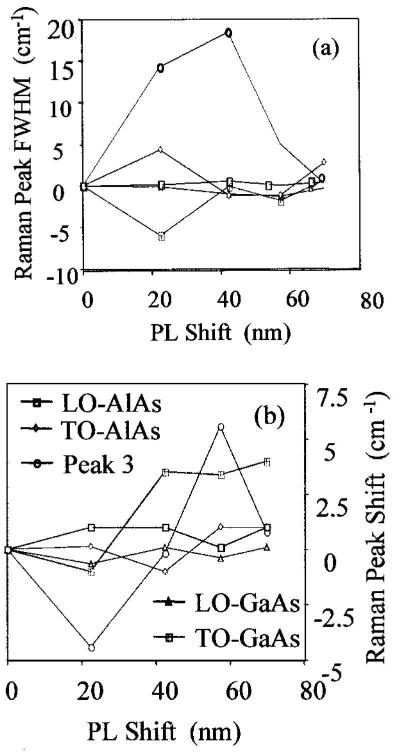

FIG. 2. Change in (a) FWHM and (b) energy shift for all detected Raman peaks as a function of PL wavelength shift.

(i) The photons used (632 nm) have absorption lengths of approximately 1 μm in the $Al_{0.4}Ga_{0.6}As$ upper cladding layer. Although relatively long, the absorption length is still finite and probably affects the strength of the detected signal. It should also be noted that the absorption of the backscattered Raman signal is smallest for the energies of the GaAs-like modes.

(ii) The strong PL generated by the HeNe laser will result in a poor Raman signal-to-background ratio. The PL signal, being smallest at the energies of the GaAs-like modes, as seen in Fig. 1(a), will have the least effect on such modes. The GaAs-like modes are, therefore, expected to be the most sensitive to small change.

A further sample, with band-gap grating periods between 12 and 22 μm and a 1:1 mark space ratio, was also studied. The gratings were fabricated by impurity-free vacancy disordering using SiO_2 and SiO_2:P caps to enhance and suppress intermixing, respectively.[11] The Raman and PL spectra were induced using an Ar^+ 514.5 nm laser with a ×50 objective, giving a spot size of 276 nm and power density of 83 $mW\,cm^{-2}$. The absorption length at this wavelength is ~400 nm in the $Al_{0.4}Ga_{0.6}As$ cladding layer. A scan of the PL peak across two periods of a 1:1 grating was carried out with a step size of 1 μm. A plot of the Raman peak shift as a function of position in the grating is shown in Figs. 3(a) and 3(b). As can be seen, the grating structure is clearly evident in the wavelength of the PL peak with a 6 nm shift seen between the intermixed and unintermixed regions. The Raman modes studied here were the GaAs-like LO and TO modes of the $Al_{0.4}Ga_{0.6}As$ cladding layer. The LO mode varies between 271.5 and 272.5 cm^{-1}, as can be seen in Figs. 3(c) and 3(d), which indicates a change in the AlGaAs composition between 45% and 35%.[12] It was also observed that the FWHM of this peak decreases from 15 cm^{-1}, in the region where there is minimal intermixing, to 11 cm^{-1}, where there is substantial intermixing. Less contrast was seen in the modulation in the energy shift of the TO mode when compared to that of the LO signal, as can be seen in Figs. 3(e) and 3(f). The TO-mode energy varies between 258 and 260 cm^{-1}, which implies a decrease in the effective Al fraction of the AlGaAs alloy inducing the Raman signal, suggesting that compositional intermixing is taking place between the GaAs QWs and the $Al_{0.4}Ga_{0.6}As$ barriers.[12] Also,

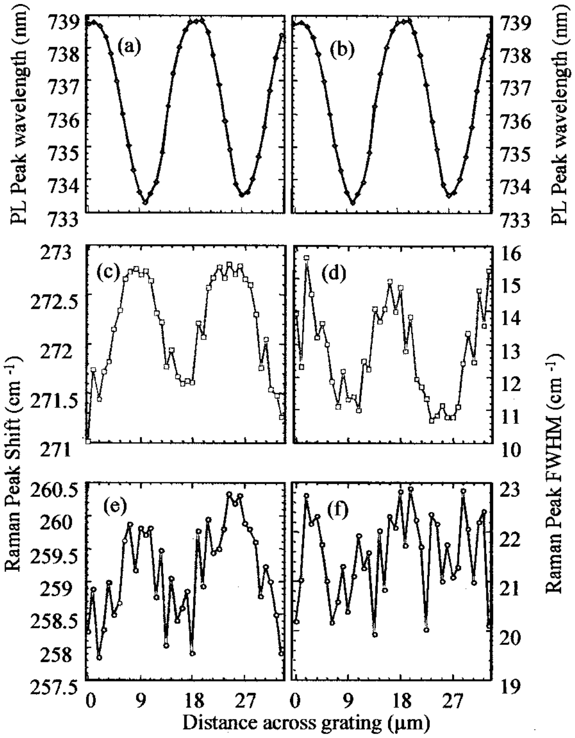

FIG. 3. (a) and (b) show the same PL shift line scan across two periods of an intermixed MQW annealed for 60 s at 950 °C with SiO_2/SiO_2:P caps. Scans of (c) the energy shift and (d) the FWHM of the LO GaAs like, and of (e) the energy shift and (f) the FWHM of the TO GaAs-like Raman peaks from the $Al_{0.4}Ga_{0.6}As$ cladding layer are shown.

the FWHM of this peak decreases from 23 cm^{-1} in the region where there is minimal intermixing, to 20 cm^{-1}, where there is enhancement in intermixing. The change in the FWHM of both Raman peaks is the opposite of that reported for a superlattice (SL) with the same effective AlGaAs composition as the SL.[13] In these studies, an increase of the FWHM from 11 cm^{-1} for the as-grown SL to 13 cm^{-1} for the intermixed SL was reported.[13] As can be seen in Fig. 3, the changes in the Raman shift and FWHM of these peaks coincide with the grating features, as identified by the variation in the PL peak. It should be also noted that, although the PL wavelength shift between both regions is only ~6 nm, the grating can still be clearly detected using Raman spectroscopy. The small differential band-gap steps within the grating are much smaller than those expected from the intermixing behavior of large areas, ~25 nm, which must be due to the short period of the grating. Feature-size-dependent intermixing has been observed in spatially resolved PL measurements, and will be reported elsewhere.[14]

In conclusion, we have demonstrated that it is possible to detect QWI using Raman spectroscopy in both large-area and laterally patterned structures. PL shifts <6 nm were detected through shifts in the Raman-mode energies and their FWHM. The technique is, therefore, suitable for characterizing QWI processes with high spatial resolution. Raman spectroscopy can also provide further information about the semiconductor lattice after intermixing by studying other features of the Raman-mode spectra, such as relative-mode amplitudes and integrated-mode area. To improve the probe depth and signal-to-noise ratio, lasers with wavelengths larger than that of the QW band gap (~900 nm) should be used in the characterization of GaAs/AlGaAs heterostructures. Such wavelengths will suffer no band-edge absorption and will induced no PL signal.

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