Eur. Phys. J. B **24**, 3–6 (2001)

THE EUROPEAN PHYSICAL JOURNAL B

EDP Sciences

First-order Raman spectra from $In_{1-x-y}Ga_xAl_yAs$ epitaxial layers grown on InP substrates

M.M. Bülbül[1,2,a], G.D. Farrant[2], and S.R.P. Smith[2]

[1] Gazi University, Faculty of Arts and Sciences, Department of Physics, 06500, Ankara, Turkey
[2] Department of Physics, University of Essex, Colchester, Essex, CO4 3SQ, UK

Received 6 January 2001 and Received in final form 16 July 2001

Abstract. We report on Raman scattering by longitudinal optical phonons in $In_{1-x-y}Ga_xAl_yAs$ quaternary alloys lattice-matched to InP(with $x+y \cong 0.47$). The quaternary alloy samples were grown as epilayers on InP(001) substrates by molecular beam epitaxy. The Raman phonon spectra show a three-mode behaviour involving the InAs-, GaAs- and AlAs-like longitudinal optic phonon modes. The frequencies of GaAs- and AlAs-like modes vary linearly with the concentration of the Ga (or Al) while the position of the InAs-like phonon remains nearly constant. We show that the ratio of intensities of the modes is proportional to the corresponding ratio of their compositions. Disorder activated modes in the acoustic and optic regions due to the disorder in atomic arrangements of group III elements have also been observed. The mode frequencies have been modeled using the extended form of the Random Cell Iso-Displacement model (RCI), which provides a good description of the experimental results.

PACS. 78.30.Fs III-V and II-VI semiconductors

1 Introduction

The quaternary semiconductor system $In_{1-x-y}Ga_xAl_yAs$ is potentially of importance for optical communication devices such as optical emitters, waveguides, and detectors. The material is also very suitable for use in heterojunction bipolar transistors [1]. It can be grown lattice matched to InP for $x+y \cong 0.47$ [2], in which case the band-gap is adjustable between those of $In_{0.53}Ga_{0.47}$ As (0.76 eV, 1.63 μm) [3] and $In_{0.52}Al_{0.48}As$ (1.46 eV, 0.85 μm) [4]. Less is known about the physical properties of this quaternary system compared to well studied $In_{1-x}Ga_xAs_{1-y}P_y$ system (0.76–1.35 eV when lattice matched to InP). The lack of experimental studies is mainly related to the difficulty of preparing the crystal by liquid phase epitaxy (LPE). This is due to the fact that Al has a large distribution coefficient which makes it difficult to grow layers with uniform composition by the LPE method [5], whereas the virtual unity incorporation coefficients of the group III atoms in the molecular beam epitaxy (MBE) growth process allow great flexibility and control over alloy composition. Since only one group V element is used, and the group III sticking coefficients are easily kept to unity. High quality material has been grown by MBE with no evidence of alloy clustering [6]. Reported values for the double crystal X-ray diffraction linewidth and photoluminescence width are very narrow, and are not dependent on the Al mole fraction [7–9].

For these systems Olego *et al.* [10,11] have investigated compositional dependence of band gap energy, conduction band effective mass and lattice vibrations; Borroff *et al.* [6] have studied optical phonons; Cingolani *et al.* [12] have carried out experiments to determine excitons and electron-phonon interaction and Kobayashi *et al.* [13] have measured electroluminescence, transmissivity, photocurrent, and electroabsorption in an InGaAlAs/InP Type-II superlattice.

Raman scattering provides a simple and accurate way to characterise the alloys. Extensive Raman studies have shown this to apply to other III-V quaternaries [14] and ternaries [15–17]. In particular the analysis of our results relies mainly on previous work on the alloys $Al_yIn_{1-y}As$ [15,17] and $In_yGa_{1-y}As$ [16,18,19]. These ternaries exhibit two-mode behaviour, *i.e.*, their spectra show two LO (as well as two transverse optical) modes associated with the respective binary constituents for nearly the whole composition range.

To our best knowledge, there has been no theoretical calculation concerning phonon mode frequencies of $In_{1-x-y}Ga_xAl_yAs$ quaternary systems. In this work we present Raman scattering (RS) studies of optical phonon modes in these quaternaries. We investigate the alloy frequencies and relative intensities of the phonon modes. Furthermore, we obtained for the first time, good agreement with an analysis of the phonon mode frequencies based on the extended form of the RCI model of Zinger *et al.* [20].

[a] e-mail: mahir@quark.fef.gazi.edu.tr

Table 1. Basic parameters of the quaternary samples.

SAMPLES	x(Ga)	y(Al)
MBE542	0.37	0.09
MBE540	0.35	0.11
MBE539	0.32	0.15
MBE538	0.24	0.22
MBE537	0.10	0.37
MBE543	0.06	0.42

2 Experimental details

The $In_{1-x-y}Ga_xAl_yAs$ crystals investigated here were grown by MBE with nominal lattice matching to semi-insulating InP substrates with (001) surfaces. All layers have lateral compositional homogeneity and an average In content of about 0.53. The total layer thickness of the samples is about 1.5 μm. The basic parameters of the samples investigated are given in Table 1. The detailed growth process and some properties such as photoluminescence observations on these samples can be found in reference [21]. The Raman experiments were carried out at room temperature usually using either the 514.5 nm or 488 nm line of an Ar^+ laser operated at a power of approximately 200 mW. The spectra were recorded with spectral resolution between 1 cm^{-1} and 3 cm^{-1}. The scan speed of the spectrometer was usually about one minute per cm^{-1}. The scattered light was analysed by a Spex double monochromator spectrometer and detected by a standard photon counting technique. Spectra were mainly recorded in the, $z(x, x+y)\bar{z}$ and $z(x, y)\bar{z}$ backscattering configurations where z is normal to the layers with x and y are along the [100] and [010] direction (This notation $q_i(a_i, a_s)q_s$ refers to an incoming beam along the direction q_i with polarization a_i, and scattering beam along q_s with polarization a_s.) In this geometry, the selection rules for Raman scattering permit observation of LO modes with wave vector parallel to [001].

3 Results and discussions

3.1 Phonon modes

In this work, we study six $In_{1-x-y}Ga_xAl_yAs$ /InP samples. Figure 1 shows typical spectra, and Figure 2 plots the mode frequencies as a function of y(Al). The phonon behaviour of its boundary ternary alloys has been studied by several researchers. Raman scattering conducted by Emura *et al.* [15] concluded that the $Al_yIn_{1-y}As$ ternary alloy has two-mode behaviour including AlAs- and InAs-like longitudinal optic phonon modes. Kakimoto and Katoda [16] reported that the $Ga_{0.47}Al_{0.53}As$ ternary system also shows two-mode behaviour including GaAs- and InAs-like longitudinal optic phonon modes.

The spectra recorded from these samples show three strong phonon bands, namely LO_1, LO_2 and LO_3 at

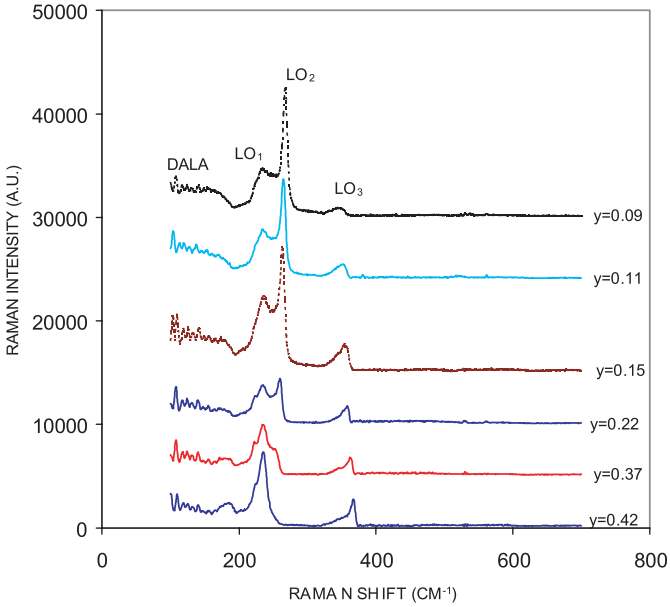

Fig. 1. First-order Raman scattering from different compositions of the $In_{1-x-y}Ga_xAl_yAs$ compounds at $T = 300$ K. The spectra are displaced vertically for clarity of presentation.

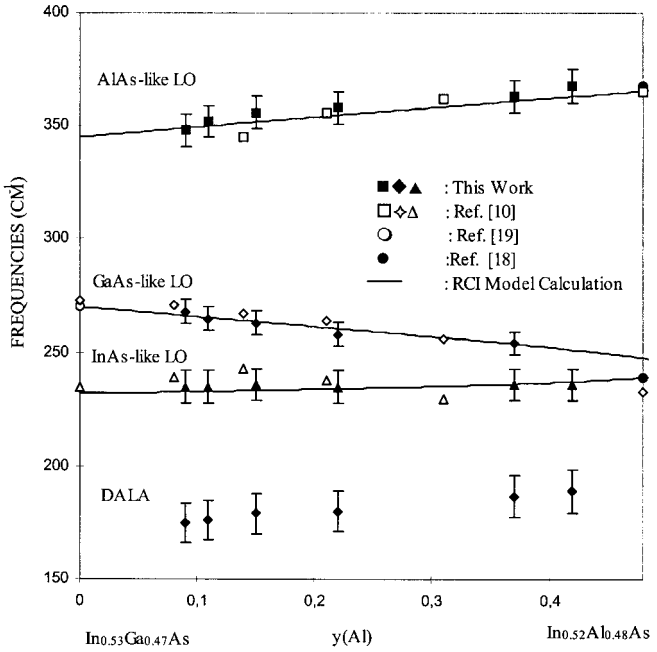

Fig. 2. Phonon frequencies of the quaternary compounds as a function of y(Al) at 300 K.

236–237 cm^{-1}, 253–268 cm^{-1} and 349–367 cm^{-1} respectively, which can be assigned to the InAs-, GaAs-, and AlAs-like LO phonon modes, respectively, by considering the ternary mixed alloy systems. Sample MBE543 has $x = 6\%$ (Ga), and its Raman spectrum is similar to that of its boundary $Al_yIn_{1-y}As$ ternary alloy [15]. Accordingly, this sample has two-mode behaviour including InAs-like and AlAs- like LO phonon modes.

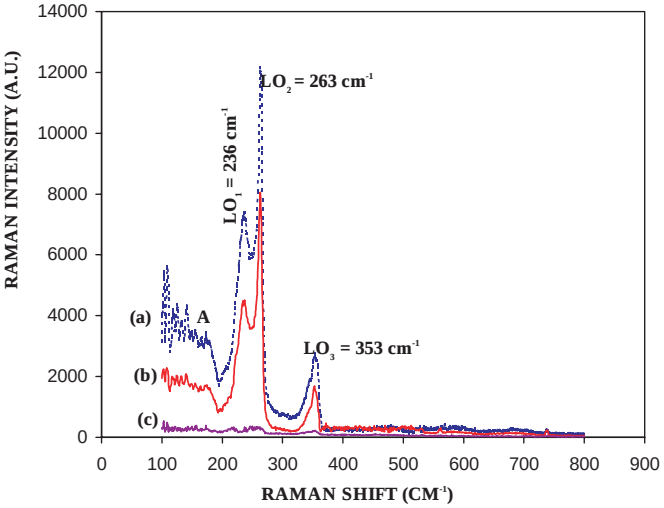

Fig. 3. Raman spectra of $In_{1-x-y}Ga_xAl_yAs$ quaternary sample, MBE539, with $x = 0.32$ and $y = 0.15$ in: (a) $z(x, x+y)\bar{z}$, (b) $z(x, y)\bar{z}$ and (c) $z(x, x)\bar{z}$ polarisation configurations.

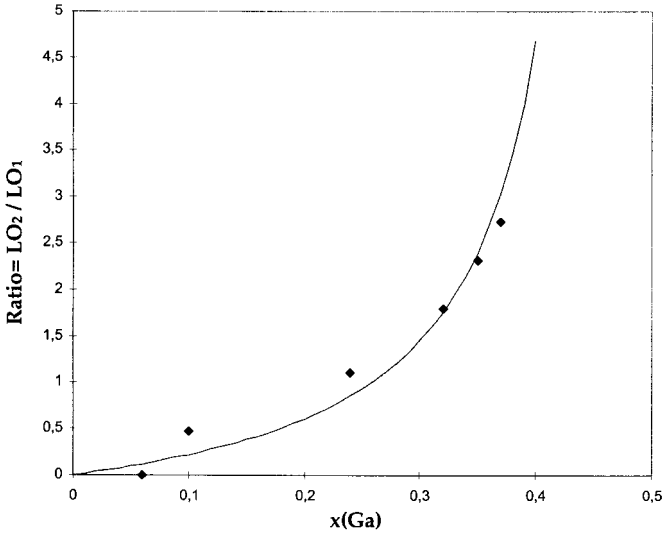

Fig. 4. Ratio of Raman peak intensities of GaAs- and InAs-like LO phonon modes. Solid diamonds represent experimental values while the solid curve was described by equation (1) with $g = 0.82$.

In all $In_{1-x-y}Ga_xAl_yAs$ quaternary samples the TO modes are not distinguishable in backscattering from the surface. To confirm the assignment of phonon modes, we have performed Raman scattering measurements on the sample MBE539, with $x = 0.32$ and $y = 0.15$ using a 488 nm laser line in three, the $z(x, x+y)\bar{z}$, $z(x, y)\bar{z}$ and $z(x, x)\bar{z}$ configurations in Figure 3. In the $z(x, x)\bar{z}$ configuration in Figure 3c, both longitudinal optic (LO) and transverse optic (TO) phonon modes are forbidden. The intense peaks observed with the $z(x, x+y)\bar{z}$ and $z(x, y)\bar{z}$ configurations almost entirely disappear in the $z(x, x)\bar{z}$ configuration as expected. The scattering selection rules valid for zinc-blende crystals predict that only LO phonon modes are allowed in the $z(x, y)\bar{z}$ backscattering configuration and that no first order scattering is allowed in the $z(x, x)\bar{z}$ configuration [22]. The spectra in Figure 3 were measured at a large angle ($\sim 60°$) of the incident light relative to the normal to the sample surface. In this case the wavevector of the incident light has a significant component in the (100) direction, parallel to the surface. This explains why these very small peaks still remain in the spectra. The relatively broad structures on the left side of the spectra at about 179–190 cm^{-1} are due to alloy disorder-activated scattering by longitudinal acoustic phonon (DALA) modes resulting from the relaxation of selection rules in the alloy sample [15,16,23]. We also show the acoustic band has a tendency to a positive shift with its maximum is at about 190 cm^{-1}. As y increases it is shown that the disorder-activated feature in the quaternary samples weakens considerably and the acoustic mode appears noticeable due to the fact that a long-range ordering becomes apparent.

Considering the dominant feature at about 254–268 cm^{-1} corresponding to the GaAs-like LO phonon mode, the spectra of the $In_{1-x-y}Ga_xAl_yAs$ samples ($y = 0.09$, $y = 0.11$, $y = 0.15$, $y = 0.22$) show that the intensity of the GaAs-like phonon mode (relative to that of the InAs-like phonon mode) decreases with increasing y, while the AlAs-like mode appearing at about 350 cm^{-1} becomes stronger with increasing y. However the InAs-like phonon-mode frequency depends very weakly on y. This is consistent with its weak dependence in $In_yAl_{1-y}As$ [15] and $In_yGa_{1-y}As$ [16,18]. The mode frequencies have also been modeled using an extended form of the Random Cell Iso-displacement (RCI), and provides a good description of the experimental results. Detailed explanation can be found in references [20,24,25].

The results indicate that the character of the phonon spectra of the quaternaries is of the three-mode type. In Figure 2, it is shown that the composition of y(Al) in $In_{1-x-y}Ga_xAl_yAs$ can be determined from the frequency positions of the compositional dependent LO phonon peaks as in the $Ga_{1-x}Al_xAs$ ternary system [26]. MBE537 was not provided with a quoted y, and we determined its composition from the frequency position of the GaAs-like LO phonon peak. In our next paper we will present the effect of the composition on the lineshape and profile of LO phonons in these samples. It will be shown that in the $In_{1-x-y}Ga_xAl_yAs$ alloy system the linewidth of the GaAs-like phonon mode becomes narrower when the sample composition is rich in Ga with narrowing of the AlAs-like LO phonon mode for high Al composition.

3.2 Intensity ratios

The relative intensities of the InAs-like, GaAs-like, and AlAs-like Raman peaks show further evidence of the three mode nature of these LO modes. The ratio $R = I_{GaAs}/I_{InAs}$ of the Raman intensity of these modes obtained from experiments is shown in Figure 4 as a function of x (the Ga concentration).

By using a mixed linear chain calculation, Barker and Sievers [27] show that the mode strengths are proportional

to the relative concentrations of the constituents. Thus, the ratio R will be of the form

$$R = g[x/(0.47 - x)] \quad (1)$$

where g is a fitting parameter determined by the intensity ratio and could be expected to be only weakly dependent on composition. The experimental results are well described by equation (1) with $g = 0.82$ as shown by the solid curve in Figure 4. However, we do not see the same kind of dependence for the ratio of the AlAs- and InAs-like phonon mode intensities, although Emura *et al.* [28] did observe a simple concentration dependence of this ratio in $In_{1-y}Al_yAs$.

4 Conclusion

We have shown that the Raman spectra of these quaternary samples display three mode behaviour involving the InAs-, GaAs-, and AlAs-like O modes. The ratio of intensities of these modes is proportional to the corresponding ratio of their compositions. It is noticed that the linewidth of the GaAs like phonon becomes narrower when the sample composition is rich in Ga, and the linewidth of the AlAs like LO phonon mode decreases at high Al composition. We have also shown that the compositions in the $In_{1-x-y}Ga_xAl_yAs$ system could be determined from the frequency of either the GaAs- or AlAs-like LO phonon peaks. However, no InAs-, GaAs-, and AlAs-like TO mode were clearly observed in the spectra, indicating that samples have quite good quality and are free of misorientation and surface roughness. Moreover, no LO and TO modes related to the InP substrates were observed in any of the spectra. The mode frequencies have also been modeled using an extended form of the RCI model, and provides a good description of the experimental results. Disorder activated modes in the acoustic and optic regions due to the disorder in atomic arrangements of group III and V elements have been distinctly observed.

We wish to thank S.J. Chua for provision of the samples we used in this work. This work was partially supported by TÜBİTAK Grants No. TBAG-1950 (100T073).

References

1. S. Hiyamizu, T. Fujii, S. Mato, T. Inata, Y. Nakata, Y. Sugiyama, S. Sasa, J. Cryst. Growth **81**, 347 (1987).
2. H.C. Casey Jr., M.B. Panish, *n Heterostructure Lasers* (Academic, New York, 1978).
3. T.P. Pearsal, IEEE J. Quantum Electron **QE-16**, 709 (1980).
4. M.R. Lorenz, A. Onton, *Proceeding of the Tenth International Conference of the Physics of Semiconductors*, 1970, edited by S.P. Kelly, J.C. Hensel, F. Stern (US Atomic Energy Commission, Oak Ridge, 1970), p. 444.
5. K. Nakajima, K. Akita, J. Cryst. Growth **54**, 232 (1981).
6. R. Borroff, R. Merlin, H. Chin; P.K. Bhattacharya, Appl. Phys. Lett. **53**, 1652 (1988).
7. Q.M. Praseuth, M. Allovan, M.C. Joncour, M.J. Gerard, P. Henoc, Inst. Phys. Conf. Ser. **91**, 225 (1988).
8. C. Cacciatore, D. Campi, C. Coriasso, C. Rigo, C. Allibert, Thin Solid Films **197**, 1 (1991).
9. E.G. Scott, D.A. Andrews, G.J. Davies, J. Cryst. Growth **81**, 296 (1987).
10. D. Olego., T.Y. Chang, E. Silberg, E.A. Caridi, A. Pinczuk, Inst. Phys. Conf. Ser. **65**, 195 (1982).
11. D. Olega, T.Y. Chang, E. Silberg, E.A. Caridi, A. Pinzuck, Appl. Phys. Lett. **41**, 476 (1982).
12. R. Cingolani, M. Lomascolo, R. Rinaldi, V. Spagnolo, G. Scamarcio, M. Ferrara. A. Hase, H. Hunzel, Solid State Commun. **84**, 679 (1992).
13. H. Kobayashi, Y. Kawamura, H. Iwamura, Jpn. J. Appl. Phys. **33**, 887 (1994).
14. R.F. Kopf, H.P. Perley, G. Livescu, Appl. Phys. Lett. **60**, 2386 (1992).
15. S. Emura, T. Nakagawa, S. Gonda, S. Shimizu, J. Appl. Phys. **62**, 632 (1987).
16. K. Kakimoto, T. Katoda, Appl. Phys. Lett. **40**, 826 (1982).
17. K.P.Jain, R.K. Soni, S.C. Abbi, M. Balkanski, Phys. Rev. B **32**, 1005 (1985).
18. D.F. Welch, G.W. Wicks, L.F. Eastman, P. Parayenthal, F.H. Pollak, Appl. Phys. Lett. **46**, 169 (1985).
19. T.P. Pearsall, R.Carles, J.C. Portal, Appl. Phys. Lett. **42**, 436 (1983).
20. G.M. Zinger, I.P. Ipatova, A.V. Subashiev, Sov. Phys. Semicond. **10**, 286 (1976).
21. S.J. Chua, A. Ramam, J. Appl. Phys. **80**, 4604 (1996).
22. W. Hayes, R. Loudon, *Scattering of Light by Crystals* (J. Wiley and Sons, New York, 1978).
23. V.P. Kunets, H. Kissel, U. Muller, C. Walther, W.T. Masselink, Yu.I. Mazur, G.G. Tarasov, Z.Ya. Zhuchenko, S. Lavoric, M.Ya. Valakh, Semicond. Sci. Technol. **15**, 1035 (2000).
24. T. Inoshita, J. Appl. Phys. **56**, 2056 (1984).
25. G.D. Farrant, Ph.D. Thesis, University of Essex (1998).
26. P. Parayanthal, F.H. Pollak, J.M. Wooddall, Phys. Rev. Lett. **40**, 895 (1982).
27. A.S. Barker, A.C. Sievers, Rev. Mod. Phys. **47**, 141 (1975).
28. S. Emura, S. Conda, Y. Matsui, H. Hayashi, Phys. Rev. B **38**, 3280 (1988).