Raman scattering determination of strain in CdTe/ZnTe superlattices

M. K. Jackson, R. H. Miles,[a] and T. C. McGill
T. J. Watson, Sr., Laboratory of Applied Physics, California Institute of Technology, Pasadena, California 91125

J. P. Faurie
Department of Physics, University of Illinois-Chicago Circle, Chicago, Illinois 60680

(Received 17 April 1989; accepted for publication 12 June 1989)

The strain configuration in CdTe/ZnTe strained-layer superlattices has been measured by Raman scattering near resonance. The ZnTe-like longitudinal optical phonon energy in the superlattice is significantly shifted from the bulk value to lower energies and the shift increases with increasing superlattice CdTe fraction. The observed shifts agree with calculations of strain shifts based on a free-standing strain distribution.

The wide band-gap II-VI semiconductors are of interest because of their potential use as visible light emitters, with application to short-wavelength optical storage and printing. The difficulties involved in doping these materials both *p* and *n* type to useful densities have hindered the development of homojunction devices. This has stimulated interest in heterojunction devices, such as superlattices.[1] CdTe/ZnTe is one system that has attracted attention as the two materials can be usefully doped opposite types and are readily grown by molecular beam epitaxy (MBE)[2] or organometallic vapor phase expitaxy (OMVPE).[3] Previous work has shown that CdTe/ZnTe superlattices display intense, visible photoluminescence orders of magnitude brighter than that from corresponding $Cd_xZn_{1-x}Te$ alloys,[4] while $Cd_{0.25}Zn_{0.75}Te$/ZnTe superlattices have recently demonstrated optically pumped, visible wavelength lasing at room temperature.[5]

An important issue in the fabrication of CdTe/ZnTe heterostructures is the accommodation by elastic strain of the large 6% lattice mismatch between the two bulk materials without formation of significant densities of defects. Methods which have been used to determine the strain configuration include photoluminescence (PL),[4] x-ray diffraction,[6] *in situ* reflection high-energy electron diffraction (RHEED),[6,7] transmission electron microscopy (TEM),[8] and resonance Raman scattering.[9] In this letter we present a study of strain in four CdTe/ZnTe superlattices by Raman scattering. We find that the strain shifts of phonon energies are consistent with a free-standing strain configuration. Unlike previous PL studies of the same samples[4] in which it was not possible to distinguish between unstrained and free-standing strain configurations, the Raman scattering data indicate that the superlattices are significantly strained.

The samples studied were grown on (100) GaAs substrates by MBE in a Riber 2300. Four samples were studied, with layer thicknesses from 23 to 56 Å, grown on a series of buffer layers that has been described previously.[4] The superlattices consist of between 150 and 200 periods, or a total superlattice thickness between 1.1 and 1.6 μm. The final buffer layer was CdTe for three of the samples and $Cd_{0.46}Zn_{0.54}Te$ for the fourth. Sample parameters are listed in Table I, along with the photoluminescence band gap observed at 5 K.

The Raman data were collected using the dye DCM in a cw dye laser. The laser energy was tuned with a three-plate birefringent tuning element, yielding a linewidth less than 1.5 cm^{-1} for all scans. Experiments were performed in a quasi-backscattering arrangement, with scattered light collected along the [100] growth direction. The incident beam was polarized along the [010] direction and no polarization analyzers were used on the collected light. Scattered light was dispersed with a double-pass spectrometer and detected by a GaAs photomultiplier tube and photon counting electronics. The incident laser energy for different scans was varied from just above the photoluminescence band gap to higher energies at which the scattered light became too weak to be detected. All data were taken at 5 K in an atmosphere of helium.

Typical Raman spectra for the four samples are shown in Fig. 1. The scattered intensity is shown as a function of the energy loss from the incident laser energy and is plotted in the range corresponding to single optical phonon scattering. The 0.8 Å resolution of the spectrometer is shown on the plots. All scans shown in Fig. 1 were taken with incident energies near resonance with the photoluminescence band gap. It can be seen that the peak occurring at the highest energy loss shifts to lower energy as the CdTe content progressively increases from samples 1 to 4. The spectra show up to four peaks or shoulders, with the maxima in the scattered intensity occurring at the peak with the greatest energy loss in the scans shown. Peaks occurring at lower energy loss are more prominent in the spectra for samples 2 and 3.

Between five and eleven Raman scans were collected for each sample, with varying laser energies. The values of the energy loss at the highest energy-loss peak in the scattered intensity were averaged for all scans taken on a given sample. The results are summarized in Table I and plotted in Fig. 2 for the four samples. The positioning of the points along the horizontal axis in Fig. 2 is simply to group the experimental and theoretical results according to the sample, which are ordered by increasing CdTe fraction. The position of the highest energy-loss peak clearly varies with the average CdTe content of the superlattice. The observed energy loss of this peak is the highest in sample 1, which has the lowest average content of CdTe, and is the lowest in sample 4, which has the highest fraction of CdTe. Results for samples 2 and 3 fall between those for samples 1 and 4, but the two are

---

[a] Present address: Hughes Research Laboratories, Malibu, CA 90265.

TABLE I. Sample parameters, observed PL band gaps, and LZ_1 phonon energies at 5 K. Samples are ordered by increasing average CdTe content.

Sample	Superlattice (CdTe/ZnTe) (Å)	Buffer layer	PL band gap (eV)	LZ_1 phonon energy (cm^{-1})
1	26/32	CdTe	1.87	202.4 ± 0.8
2	35/32	$Cd_{0.46}Zn_{0.54}Te$	1.74	199.0 ± 0.5
3	56/50	CdTe	1.69	199.5 ± 1.2
4	31/23	CdTe	1.81	197.4 ± 1.1

quite close in average composition and are difficult to distinguish from each other within the uncertainties in the measured values.

To compare the experimentally observed phonon energies with theory, we have estimated the expected energies in the superlattice of the lowest confined longitudinal optical (LO) and transverse optical (TO) phonons propagating in the growth direction. The energies of phonons in a strained superlattice are affected by both strain and confinement, but for our structures the main contribution to the shift from the bulk phonon energies is due to strain. Estimates of the effects of confinement on the LZ_1 mode (the highest energy confined ZnTe-like optical phonon) using a simple spring-mass model of the longitudinal phonons propagating in the growth direction give energy shifts less than 1 cm^{-1} for the samples studied. Confinement effects on the TO-phonon energies should be of a similar magnitude. This small contribution due to confinement has been neglected, which means that the lowest confined LO- and TO-phonon energies in the superlattice will occur approximately at the strained bulk LO and TO energies. The energies of the LO and TO phonons in strained bulk CdTe and ZnTe are calculated using the method of Ref. 10. From Ref. 9, the phonon deformation constants p and q are related to the Gruneisen parameter γ by $\gamma = -(p+q)/(6\omega_{LO}^2)$ and the shear deformation parameter a_s by $a_s = (p-q)/(2\omega_{LO}^2)$. We take[9] $\gamma = 1.2$ and $a_s = 0.6$. Bulk LO and TO energies are taken from Ref. 11 to be: ZnTe LO, 208 cm^{-1}; ZnTe TO, 180 cm^{-1}; CdTe LO, 170 cm^{-1}; and CdTe TO, 145 cm^{-1}.

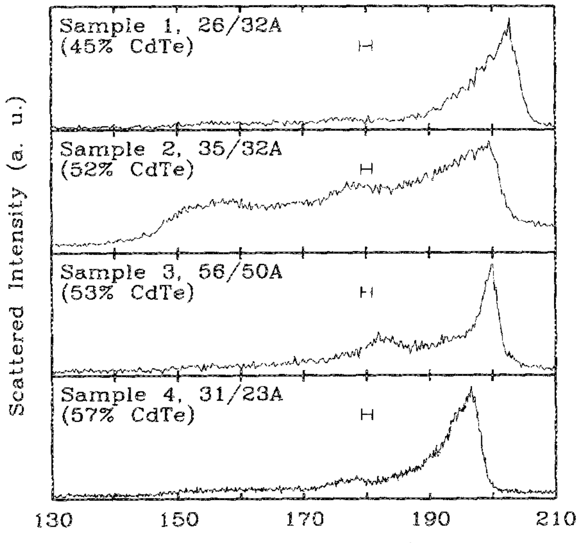

FIG. 1. Representative near-resonance Raman scattering intensity at 5 K vs energy loss for the four samples studied in the range of single optical-phonon scattering. The peak occurring at the highest energy loss shifts to lower energies as the average CdTe content increases progressively from samples 1 to 4. This is due to the increasing strain in the ZnTe layers, and shifts the ZnTe-like phonon energy from its bulk value of 208 cm^{-1}. The laser energies for samples 1–4 were 1.965, 1.833, 1.818, and 1.849 eV, respectively. The spectrometer resolution, sample layer thicknesses, and CdTe volume fraction are shown on each plot for reference.

The phonon energies for strained bulk ZnTe have been calculated for the four samples. The strain used in the calculation is that appropriate to a free-standing superlattice, i.e., the in-plane lattice constant is calculated to minimize the elastic energy of the whole superlattice. Values of the elastic constants for CdTe were taken from Ref. 12 and those for ZnTe from Ref. 13. In Fig. 2, we plot the LO (circles) and TO (squares) ZnTe phonon energies for the four samples. The open symbols are the bulk, unstrained phonon energies and the filled symbols are the bulk, strained energies using strains calculated for a free-standing superlattice.

We assign the highest energy-loss peak observed to the first confined ZnTe-like LO mode LZ_1. As the LZ_1 mode is expected to have the highest energy of all the superlattice phonons, assignment of the highest energy-loss peak observed to LZ_1 is unambiguous. However, assignment of the lower energy-loss peaks observed is much less certain, as they occur at energies which could be assigned to various superlattice phonon modes. The significant shift of the LZ_1 energy from the unstrained value of 208 cm^{-1} indicates that there is a high degree of strain in the superlattices. Comparing the theoretical estimates of the ZnTe phonon energies shown in Fig. 2 with the observed values, we see that there is good agreement with the strained LO-phonon energy calcu-

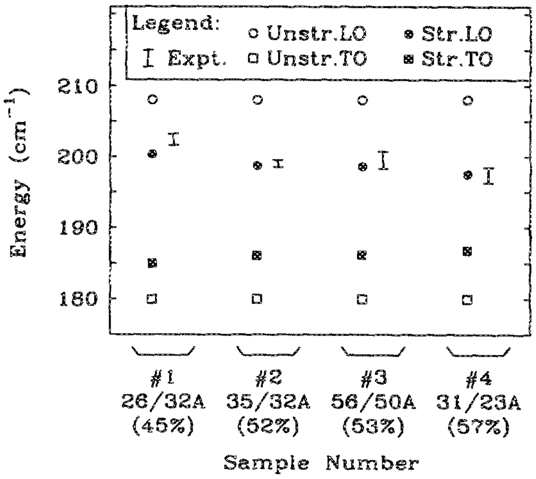

FIG. 2. Comparison of theoretical with experimental results for the four samples, which is ordered by increasing CdTe volume fraction. Data points are the experimentally observed LZ_1 energies. The circles and squares are the bulk ZnTe LO and TO energies, respectively. The open symbols are the unstrained energies and the filled symbols are calculated for strained bulk with strain appropriate to the free-standing superlattice.

lated for the free-standing strain configuration. This is consistent with previous conclusions[4,6] based on photoluminescence and x-ray measurements. If the ZnTe superlattice layers in our samples were strained to the buffer layer lattice constant, then the energy of the LZ_1 phonon would be the same for samples 1, 3, and 4, and would be much lower than the position observed. The calculated position of the LZ_1 phonon for sample 2, if it is assumed to be lattice matched to the $Cd_{0.46}Zn_{0.54}Te$ buffer layer, would be 195 cm^{-1}, which does not agree with the observed position.

Although interface modes in unstrained superlattices have been studied,[14–16] little work has been done in heavily strained superlattices. In unstrained superlattices, interface modes are located between the bulk LO and TO energies. As the highest energy-loss peaks observed in our samples occur in the range between the bulk ZnTe LO and TO energies where interface modes are expected to occur, there is a possibility that they are in fact due to an interface mode and not to a confined LO mode. If the interface modes in strained superlattices occur at energies determined solely by the bulk LO- and TO-phonon energies and are independent of the strain, then no shift with increasing average CdTe content should be observed, which does not agree with the observations. On the other hand, if the interface modes occur at energies determined by the strained LO and TO energies, then some dependence on the average CdTe content might be observed. However, by considering the strained ZnTe LO and TO energies shown in Fig. 2, we see that an interface mode occurring at some position midway between the two energies would be at an energy consistently lower than the observed peak positions. Hence, we think it unlikely that the highest energy-loss mode observed is an interface mode.

It should be noted that the free-standing strain configuration demonstrated in this letter is at variance with results reported in a previous CdTe/ZnTe resonant Raman scattering study.[9] Although direct comparison of the two studies is complicated by differences in sample thicknesses and growth conditions, previous structural studies[6] draw into question the conclusions of Ref. 9. Implicit in the derivation of strains from Raman peak shifts is the assumption of homogeneous strains within like superlattice layers. Structural studies[6] of the superlattices examined here reveal that strain relaxation is not confined to the superlattice/buffer-layer interface, as growth is highly dislocated and nonuniform within approximately one-half micron of this interface. However, a substantial improvement in crystal structure appears beyond this region as evidenced by TEM,[8] *in situ* RHEED,[6,7] and x-ray diffraction measurements.[6] As the samples used in this study consist of $1.1-1.6\,\mu m$ thick superlattices and the above band-gap light used is sensitive mainly to the surface region, the assumption of strain homogeneity in this work appears sound. The basis of this assumption of uniformity is less clear in the work of Ref. 9, however, as the samples studied were much thinner (less than $0.25\,\mu m$). Thus, while it is possible that the particular superlattice layer thicknesses chosen in Ref. 9 yielded one superlattice that was coherent with the buffer layer, it is unlikely that another superlattice which was shown to relax had a well-defined strain configuration so close to the superlattice/buffer-layer interface. The relaxation of a thin superlattice to a single free-standing lattice constant for all the superlattice layers would require the nucleation of a large number of defects only at the superlattice/buffer-layer interface, immediately followed by growth at a single in-plane lattice constant.

In conclusion, we have used near-resonance Raman scattering to measure the confined ZnTe-like phonon energy in four CdTe/ZnTe superlattices. Observed phonon energies are shifted from the bulk energies by amounts that increase with increasing superlattice CdTe content, and indicate that the superlattices are highly strained. Observed energies are in agreement with calculations of the expected phonon energies that account for strain, and indicate that the superlattices relax to a free-standing configuration.

The authors would like to thank D. J. Lockwood, J. Tsang, D. Z. Ting, H. Chu, and Y.-C. Chang for helpful discussions, and W. J. Boudville for assistance with computer graphics. This work was supported by the Defense Advanced Research Projects Agency and monitored by the Office of Naval Research under contract No. N00014-86-K-0841. One of us (M.K.J.) would like to acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada.

[1] R. H. Miles, J. O. McCaldin, and T. C. McGill, J. Cryst. Growth **85**, 188 (1987).

[2] G. Monfroy, S. Sivananthan, X. Chu, J. P. Faurie, R. D. Knox, and J. L. Staudenmann, Appl. Phys. Lett. **49**, 152 (1986).

[3] D. W. Kisker, P. H. Fuoss, J. J. Krajewski, P. M. Amirtharaj, S. Nakahara, and J. Menéndez, J. Cryst. Growth **86**, 210 (1988).

[4] R. H. Miles, G. Y. Wu, M. B. Johnson, T. C. McGill, J. P. Faurie, and S. Sivananthan, Appl. Phys. Lett. **48**, 1383 (1986).

[5] A. M. Glass, K. Tai, R. B. Bylsma, R. D. Feldman, D. H. Olson, and R. F. Austin, Appl. Phys. Lett. **53**, 834 (1988).

[6] R. H. Miles, T. C. McGill, S. Sivananthan, X. Chu, and J. P. Faurie, J. Vac. Sci. Technol. B **5**, 1263 (1987).

[7] G. Monfroy, X. Chu, M. Lange, and J. P. Faurie (unpublished).

[8] P. M. Petroff (unpublished).

[9] J. Menéndez, A. Pinczuk, J. P. Valladares, R. D. Feldman, and R. F. Austin, Appl. Phys. Lett. **50**, 1101 (1987).

[10] F. Cerdeira, C. J. Buchenauer, F. H. Pollak, and M. Cardona, Phys. Rev. B **5**, 580 (1972).

[11] D. J. Olego, P. M. Raccah, and J. P. Faurie, Phys. Rev. B **33**, 3819 (1986).

[12] H. J. McSkimin and D. G. Thomas, J. Appl. Phys. **33**, 56 (1962).

[13] D. A. Berlincourt, H. Jaffe, and L. R. Shiozawa, Phys. Rev. **129**, 1009 (1963).

[14] A. K. Sood, J. Menéndez, M. Cardona, and K. Ploog, Phys. Rev. Lett. **54**, 2115 (1985).

[15] S.-F. Ren, H. Chu, and Y.-C. Chang, Phys. Rev. B **37**, 8899 (1988).

[16] H. Chu, S.-F. Ren, and Y.-C. Chang, Phys. Rev. B **37**, 10746 (1988).