Determination of ordering effects on GaInP pressure coefficients

A.D. Prins[*1], **J.L. Sly**[2], **D.J. Dunstan**[1], **A. Nagata**[3], **C. Haslam**[4] and **T. Kobayashi**[3]

[1] Molecular and Materials Physics Group, Department of Physics, Queen Mary, University of London, London E1 4NS, UK.
[2] Department of Electrical Engineering and Electronics, University of Manchester Institute of Science and Technology, Manchester M60 1QD, UK.
[3] Department of Electrical and Electronics Engineering, Kobe University, Kobe 657-8501, Japan.
[4] CHESS PD Ltd, Guildford GU2 9TJ, UK

Received zzz, revised zzz, accepted zzz

PACS 81.05.Ea, 78.55.Cr, 07.35.+k, 71.20.Nr

We report the determination of pressure coefficients ~~between~~ for ordered and disordered GaInP samples measured in the same diamond anvil cell experiment at 10K. Results are compared to measurements using substrate calibration and data available in the literature. ~~Based on~~ Using previous theoretical calculations and experimental work we propose a linear model based on the band-gap reduction with ordering to calculate pressure coefficients. To date this is the only available method to quantifying this change. All layers measured were grown nominally lattice matched to GaAs.

Introduction

__GaInP lattice matched to GaAs is important for ~~visible~~ solid state devices operating in the visible region of the electromagnetic spectrum. Determination of fundamental parameters is essential for optimal device design and modelling [1], however the effects of long-range ordering complicate this system *(in what way, give some details)*. In III-V ternaries, the ~~O~~ordering of~~n~~ the group III sublattice can double the unit cell, halving the Brillouin zone and folding the electronic states of the L point back onto the Γ point. This folding repels like–symmetry states resulting in a lowering of the conduction band Γ state. The degree of ordering is often expressed statistically by an ordering parameter η with 0 being totally disordered and 1 being alternate monolayers of GaP and InP stacked along one or both of the two possible [111]B variants. This CuPt ordering alters the materials electronic properties giving an order dependent band-gap reduction (ΔE_{BGR}) and valence band splitting (ΔE_{VBS}). It is well known that under certain growth conditions GaInP grown by metal-organic-vapour-phase expitaxy (MOVPE) on [001] orientated GaAs substrates can form a partially ordered alloy with a maximum reported value of ΔE_{BGR} of 160meV [2]. Tilting the substrate toward one of the [111]B variant directions can enhance one order variant and suppress another. All data reviewed in this paper is from similar double variant ordered samples nominally lattice matched to GaAs. It is also possible to create quantum wells and superlattice structures by modulating the ordering with no change in material composition [3].

__Franceschetti *et al.* [4] calculated the pressure coefficients of optical transitions in (111) and other GaP/InP ordered superlattices using *ab initio* methods. They suggested the use of the "η^2 rule" of [5] to interpolate between their calculated values ~~for η=0 and η=1~~ of 8.2meV/kbar and 6.4meV/kbar for η=0

---

[*] Corresponding author: e-mail: a.d.prins@qmul.ac.uk

and η=1, respectively. Variation in sample growth conditions and composition along with a lack of consistent characterisation tend, however, to make sample comparison difficult. The maximum value of ΔE_{BGR} has been reported as 0.471 eV [6] but this value and the validity of the η^2 rule are questioned closely in [7]. The best fit to the current experimental data is found in [7] to be that proposed by [8] and gives a maximum value for ΔE_{BGR} of 0.223eV. Kippenberg *et al.* [9] showed by electroabsorption that ΔE_{BGR} is not due entirely to the shift in the conduction band, but that 22% of it comes from the valence band maximum being shifted up with ordering. They were able to apply exact linear fits against ΔE_{BGR} to the absolute band structure data measured. This method was also successfully used for the position of the X minima determined in our previous paper [10]. All these results would seem to suggest that the pressure coefficient dependence on ordering of [4] would be better interpolated using a linear fit against ΔE_{BGR} from 0 eV (η=0) to 0.223 eV (η=1).

__A decrease in the pressure coefficient with increasing order has indeed been reported by many authors, but there has to date been no attempt at comparison to quantify this change. Ignoring growth differences for the moment such comparisons would rely on fitting data from separate experiments and would be influenced by the pressure calibration in each. By measuring samples with different degree of ordering together [11], or by using substrate emission calibration, errors can be reduced and relative values determined. We report the determination of pressure coefficients between GaInP samples measured in the same diamond anvil cell (DAC) experiment at 10_K. The samples were from the same growth facility. We then examine these results against consistent data sets in the literature and our recently published work for other layers [10] using substrate calibration. All reported nominally lattice matched data at 300_K and below 25_K is then examined. A proposed method for calculating change based on our above discussion for [4] is given.

__To calculate ΔE_{BGR} values the band-gap of completely disordered material is taken to be 2.01 eV at 4.2K and 1.91 eV at 300K from [12], no value is given for 77K. DeLong *et al.* [12] used a large number of samples from a range of growth techniques coupled with double crystal X-ray diffraction (DXRD) measurements and annealing to determine these values.

Experiment

__The two GaInP samples investigated were grown by conventional MOVPE on Si-doped (001) GaAs substrates. The GaInP ~~, each~~ layer was approximately 1µm thick and nominally undoped. The degree of ordering in each sample was obtained by using different growth temperatures and substrate misorientations [10]. Double crystal X-ray diffraction (DXRD) showed lattice mismatch for both was < 0.1%. At 10K photoluminescence (PL) linewidths of less than 10 meV with energies of 1.945 eV (ΔE_{BGR}=0.055 eV) and 1.893 eV (ΔE_{BGR}=0.107 eV) for the disordered and ordered samples, respectively, were obtained. This amounts to an initial energy separation (ΔE) between the samples of 52 meV.

__The samples were thinned to 30_µm, then cleaved and loaded together along with a ~~a similar prepared~~ ruby chip into a diamond anvil cell. Argon was used as the pressure transmitting medium and pressure was calibrated using the substrate~~s sample~~ emission [13], cross referenced to standard ruby fluorescence [14]. PL was excited using the 488 nm line of an Ar^+ laser and high-pressure PL measurements were performed at 10 K.

Results and discussion

Fig. 1 shows the how the PL of both samples shifts to lower wavelength (higher energy) with increasing pressure, the determined pressure coefficients are 8.2 meV/kbar and 7.4 meV/kbar for the disordered and ordered layers respectively. This data may be plotted against pressure but by plotting against each others energy [11] errors in the pressure calibration can be ignored and relative values determined. Fig.2 shows the data plotted in this way. Fitting the gradient of this line, we obtain a value for the relative energy shifts of these two samples to be 0.9030_±_0.0196. We now assume for the time being that this ratio changes linearly with ΔE_{BGR}, to obtain a formulae for pressure dependence change with relative band-gap reduction (ΔE) between samples, we estimate error in this calculation and see how the results compare to our previous data sets and those in the literature.

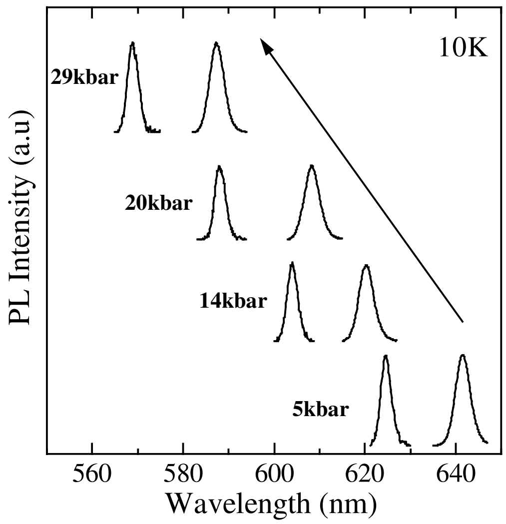

Fig. 1 Typical PL spectra under pressure for both samples measured together in the DAC.

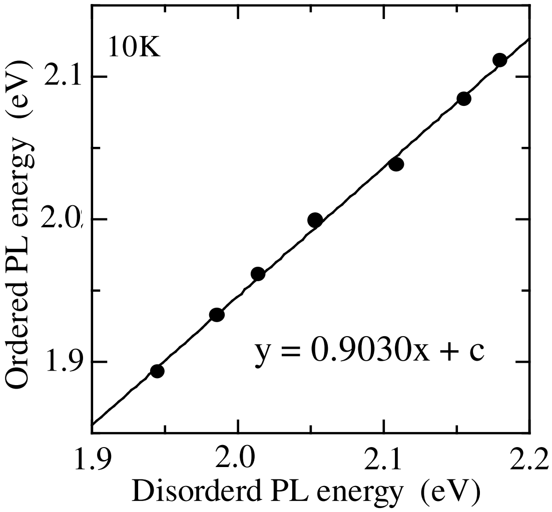

Fig. 2 PL Peak energies for the two samples plotted against each other. Determined gradient is given.

Assuming an error of ±0.01 eV in the determination of the value of ΔE the relative change in pressure coefficient with ΔE would be given by:

$$\frac{dE}{dP}(\Delta E)=\frac{dE}{dP}(\Delta E=0)\big(1-\big((1.886\pm 0.449)\Delta E\big)\big) \qquad (1)$$

w~~W~~here a positive value of ΔE is used for the decrease in band-gap from one sample to the other. The value of error in ΔE may be an overestimate, but is used since an exact measure of the lattice mismatch for the two samples measured in this work is not known.

To test the validity of this equation, we need to compare available data where pressure coefficients and starting energies of two or more samples are given. Where possible PL data should be corrected for lattice mismatch strains from DXRD data as well as exciton binding energies when measurements are taken at low temperature. To determine mismatch corrections we assume layers are fully strained and calculate the strain-induced shifts of the direct band-gap needed to reach lattice matching from [12]. The lattice-matched composition with GaAs is x = 0.52 at 2 K and 0.515 at 300 K [15]. The data sets that can be corrected are [10] at 2 K and those of Dong *et al.* [16] at 300K (solid points in Fig. 3). We also use the uncorrected data from [17] (431 K) and [18] (77 K), the latter can be used without knowledge of the band-gap for completely disordered material at this temperature since we plot energy differences between samples and ratios only. Data from [19] is not used since the two samples measured were not from the same growth method. Fig. 3 shows the pressure coefficient ratios of these four data sets (ratio is more ordered sample coefficient divided by that of the more disordered samples) plotted against the energy difference between samples from the same source. The solid line is plotted from equation (1) with the dashed lines showing the determined maximum error. A linear fit to the six data points with the Y-intercept fixed at 1 gives a line indistinguishable to that of the solid line. The measurement error in [10] is the only reported error and is shown as a vertical line in Fig. 3. The use of equation (1) appears to give a good fit to the available data sets.

(Author: Please fix the text folding in this page. In fact, since space is not a problem with this paper, you may prefer to leave the figure alone without the folded text.)

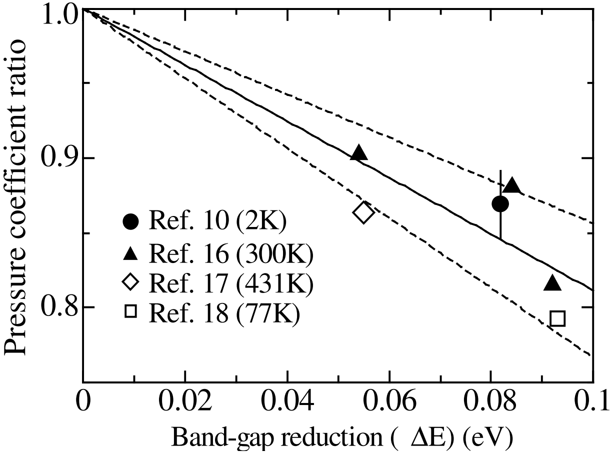

Fig. 3 Pressure coefficient ratios from various sources plotted against relative band-gap reduction (see text).

We now consider all the available pressure coefficient data (sets and individual points) in the literature at room temperature and below 25 K (but not 77 K) fro samples that are grown nominally lattice matched. We plot the quoted pressure coefficients against the value of ΔE_{BGR} determined from the energy difference from completely disordered material [12]. Fig. 4 shows a plot of all data (16 points), solid data points have been corrected for strain as described earlier. The only assumption made in Fig. 4 is that the absolute value of the 300 K band-gap determined by absorption [20] is offset to a lower energy to match our 300 K disordered value of 1.91 eV, such an offset is suggested in the paper.

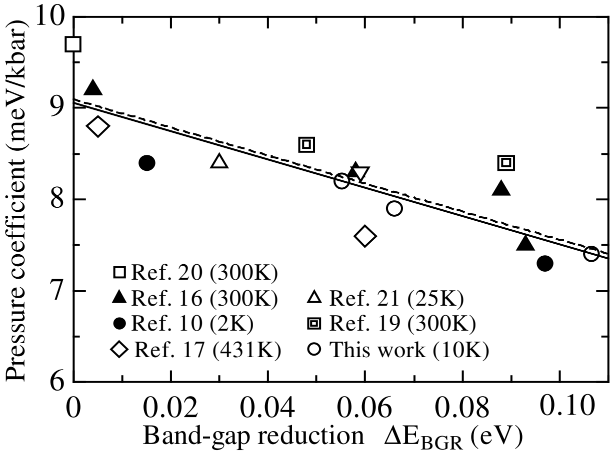

Fig. 4 Pressure coefficients from various sources plotted against band-gap reduction. Dashed line is linear fit whilst solid line is obtained using equation 1.

The data from ~~this current paper~~ the present work (open circles) also includes one extra point measured from another sample in a separate experiment. Whilst there is a large scatter in the data it seems clear that there is a definite trend and the large number of points allows a linear fit. The dashed line in Fig. 4 shows a fit to all the data points and gives:

$$\frac{dE}{dP}(\Delta E_{BGR}) = 9.095 - 15.357\Delta E_{BGR} \tag{2}$$

Applying equation 1 to our most disordered sample we obtain:

$$\frac{dE}{dP}(\Delta E_{BGR}) = 9.054 - 15.471\Delta E_{BGR} \tag{3}$$

~~And~~ T~~t~~his is plotted as a solid line on Fig. 4 (again almost indistinguishable). Separating the low and high temperature data sets does not affect the result of equation 2 greatly.

Using equation 1 to determine the pressure coefficient at ΔE_{BGR}= 0.223 eV relative to our measured point at ΔE_{BGR}= 0.055 eV we obtain a value of 5.6 ± 0.6 meV/kbar. This value agrees well with those calculated by [4] for a totally ordered layer and is close to the averaged value of the Γ and L minima pressure coefficients (about +9 and +4 meV/kbar respectively). Similarly using a value of ΔE_{BGR} = 0.471 eV we would obtain a pressure coefficient of 1.8 ± 1.5 meV/kbar which is a value less than that of the L minima and far below that of the Γ.

Conclusions

Using high pressure PL at low temperature on GaInP samples nominally lattice matched to GaAs and measured in the same DAC experiment we have been able to determine a value for the change in pressure coefficient with relative band-gap reduction (ΔE). The change appears to be linear with ΔE and this is backed up by comparing trends in our previously reported experimental work [10] and available data sets in the literature. Fitting all the available pressure coefficient data to the absolute band-gap reduction ΔE_{BGR} we have also found excellent agreement with equation 1. Based on this linear approach, our predicted pressure coefficient at the proposed maximum ΔE_{BGR} compared to the theoretical work of [4] would seem to back up the proposal of [7, 9] of a maximum ΔE_{BGR} value of 0.223 eV against earlier higher values [6].

Without a study of layers from different growth techniques coupled with consistent characterisation the current results present the best and only determination to date of the effects of ordering on the pressure coefficient of GaInP nominally lattice matched to GaAs. We propose a relative determination between samples from equation 1. Using the band-gap values for perfectly disordered material from [12] to calculate ΔE_{BGR} equation 3 may also be used to determine best suggested absolute values.

Whilst the nature of and the characterisation of this material system makes exact calculations for individual samples difficult, we believe we have identified trends in the system and presented a proposed model for determining these values which is in good agreement with current measured data.

Acknowledgements A.D. Prins acknowledges the support of the Japan Society for the Promotion of Science and wishes to thank Prof. P.Y. Yu (University of California) and also Y. Kagawa (Kobe University) for his technical assistance.

References

[1] A.T. Meney, A.D. Prins, A.F. Phillips, J.L. Sly, E.P. O'Reilly, D.J. Dunstan, A.R. Adams, and A. Valster, IEEE J. Selected Topics in Quantum Electron. **1**, 697 (1995).
[2] L.C. Su, S.T. Pu, G.B. Stringfellow, J. Christen, H. Selber, D. Bimberg, Appl. Phys. Lett. **62**, 3496 (1993).
[3] Y. Hsu, C.M. Fetzer, G.B. Stringfellow, J.K. Shurtleff, C.J. Choi, T.Y. Seong, J. Appl. Phys. **87**, 7776 (2000).
[4] A. Franceschetti and A. Zunger, Appl. Phys. Lett. **65**, 2990 (1994).
[5] D.B. Laks, S.-H. Wei, and A.Zunger, Phys. Rev. Lett. **69**, 3766 (1992).
[6] P. Ernst, C. Geng, F. Scholz, H. Schweizer, Y. Zhang and A. Mascarenhas, Appl. Phys. Lett. **67**, 2347 (1995).
[7] A. Mascarenhas and Y. Zhang, Chapter 11, Spontaneous Ordering in Semiconductor Alloys, edited by A. Mascarenhas, Kluwer Academic, New York (2002).
[8] Y. Zhang and A. Mascarenhas and L.-W. Wang, Phys. Rev. B **63**, R201312 (2001).
[9] T. Kippenberg, J. Krauss, J. Spieler, P. Kiessel, G.H. Döhler, R. Stubner, R. Winkler, O. Pankratov and M. Moser, Phys. Rev. B 60 4446 (1999); P. Kiesel, T. Kippenberg and G.H. Döhler, Chapter 13, Spontaneous Ordering in Semiconductor Alloys, edited by A. Mascarenhas, Kluwer Academic, New York (2002).
[10] A.D. Prins, J.L. Sly, D.J. Dunstan, A. Nagata and T. Kobayashi, J. Crys. Growth 268, 378 (2004).
[11] K. Inoue, J. Harada, T. Kobayashi, A.D. Prins, J.R. Downes, D.J. Dunstan, J.L. Sly, and M. Missous, Rev. High Pressure Science and Technology **10**, 148 (2000).
[12] M.C. DeLong, D.J. Mowbray, R.A. Hogg, M.S. Skolnick, J.E. Williams, K. Meehan, S.R. Kurtz, J.M. Olson, R.P. Schneider, M.C. Wu and M. Hopkinson, Appl. Phys. Lett. **66**, 3185 (1995).
[13] D.J. Wolford and J.A. Bradley, Solid State Commun. **53**, 1069 (1985).
[14] A. Jayaraman, Rev. Mod. Phys. **55**, 65 (1983).
[15] Y. Zhang and A. Mascarenhas, P. Ernst, F.A.J.M. Driessen, D.J. Friedman, K.A. Bertness, J.M. Olson, C. Geng, F.Scholz and H. Schweizer, J. Appl. Phys. **81**, 6365 (1997).

[16] J. Dong, G. Li, Z. Wang, D. Lu, X. Liu, X. Li, D. Sun, M. Kong and Z. Wang, J. Appl. Phys. **79**, 7177 (1996); J. Dong, Z. Wang, D. Lu, X. Liu, X. Li, D. Sun, Z. Wang and M. Kong Appl. Phys. Lett **68**, 1711 (1996).
[17] K. Uchida, P.Y. Yu, N. Noto, E.R. Weber, Appl. Phys. Lett. **64**, 2858 (1994).
[18] S.H. Kwok, P.Y.Yu, K. Uchida and T. Arai, Appl. Phys. Lett. **71**, 1110 (1997).
[19] D. Patel, J. Chen, S.R. Kurtz, J.M. Olson, J.H. Quigley, M.J. Hafich and G.Y. Robinson, Phys. Rev. B **39**, 10978 (1989).
[20] A.R. Goñi, K. Syassen, K. Strössner and M. Cardona, Phys. Rev. B **39**, 3178 (1989).
[21] J. Chen, J.R. Sites, I.L. Spain, M.J. Hafich and G.Y. Robinson, Appl. Phys. Lett. **58**, 744 (1991).