Semicond. Sci. Technol. **12** (1997) 550–554. Printed in the UK PII: S0268-1242(97)72479-9

Optical absorption and determination of band offset in strain-balanced GaInP/InAsP multiple quantum wells grown by low-pressure metalorganic vapour phase epitaxy

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Received 6 March 1996, in final form and accepted for publication 13 January 1997

Abstract. We report on optical absorption of the interband transitions in zero-net strained $Ga_xIn_{1-x}P/InAs_yP_{1-y}$ multiple quantum wells (MQW) grown by low-pressure metalorganic vapour phase epitaxy (LP-MOVPE), using tertiarybutylarsine as a group V source. Sharp interfaces are obtained using a growth interruption procedure. Analysis of this procedure with different interruption times leads to the same optimal times as those obtained for InP/InAsP superlattices grown in the same reactor. We have achieved the growth of modulation-free strain-balanced heterostructures, as indicated by cross-sectional transmission electron microscopy. High-resolution x-ray diffraction and optical absorption analysis demonstrate the high crystallographic and optical quality of these structures. The absorption spectrum of an $x = 0.06$, $y = 0.14$ sample was accurately fitted using the Bastard/Marzin model, and a strained conduction band offset of 94.0 ± 3.3 meV was deduced. This corresponds to about $75 \pm 3\%$ of the total strained bandgap difference.

1. Introduction

GaInP/InAsP multiple quantum wells (MQW) grown on InP substrates have recently been the subject of considerable interest [1–4], notably for the fabrication of high-performance optical modulators [5] and lasers [6]. The tensile strain of the GaInP barriers and the compressive strain of the InAsP wells can be adjusted to exactly compensate one another. One may expect that the critical thickness phenomenon that usually limits the number of layers that can be coherently grown, as in the InAsP/InP system, will not apply for the strain-compensated superlattices, provided that the thickness of each individual layer is below its critical value. This materials system will then be of practical importance for applications in optoelectronics, where one may need relatively thick strained MQW regions of tunable bandgap for excitonic absorption or emission. Of primary importance in the design of devices based on these heterostructures is the determination of materials parameters such as bandgap and band offset, once adequate control in the fabrication of these structures is obtained. To our knowledge, important device design parameters, such as the band offset, have never been reported for this system. Precise determination of this parameter requires a detailed knowledge of the structural parameters.

Some problems encountered in the growth of this structure, such as periodic lateral modulations, have been reported [3] for highly strained ($|\epsilon| \sim 1\%$) GaInP and InAsP layers grown on InP(001) by atmospheric

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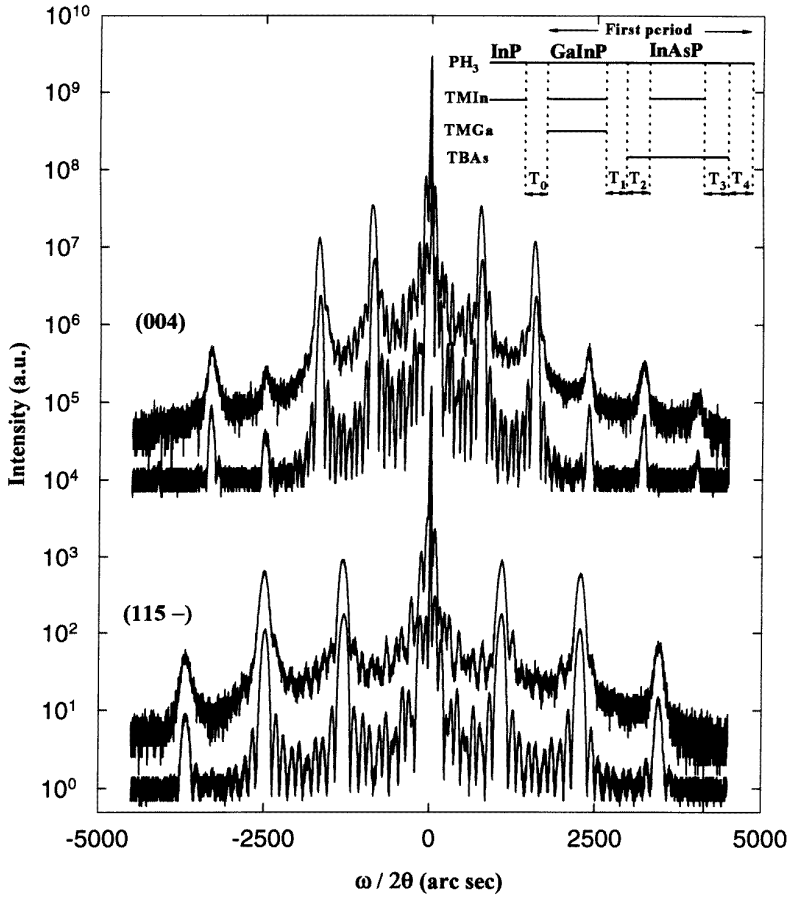

Figure 1. The (004) and (115—) HRXRD diffraction patterns for a 10-period strain-balanced $Ga_{0.06}In_{0.94}P$(11.2 nm)/$InAs_{0.14}P_{0.86}$(11.7 nm) MQW. The upper curves show experimental data; the lower curves are simulated (and shifted) rocking curves. The inset is a schematic representation of gas switching sequence and growth interruption times. The sequence used for this sample is (3; 3, 2, 1, 1).

pressure metalorganic vapour phase epitaxy (AP-MOVPE) at 650 °C. These do not appear [6] when the growth temperature is reduced to 550 °C.

It is generally understood [7, 8] that in a process similar to that of Stranski–Krastanov [9] growth, modulations in layer thicknesses are caused by the migration of the surface species during growth, reducing the amount of energy stored in the heterostructure. Experimental results of Smith *et al* [8], on a different material system ($In_xGa_{1-x}As/In_yGa_{1-y}As$) show that proper growth fluxes and reduction of growth temperature below a so-called roughening temperature, T_R, can prevent the migration of the species to yield nearly perfectly flat structures. In recent work, Bangert *et al* [10] have introduced the effect of misfit strain in the determination of T_R. They showed that for very small strain T_R increases significantly, and strongly depends on the material system.

Two approaches are therefore available to limit the formation of thickness undulations in GaInP/InAsP strain-compensated multilayers. Kasukawa *et al* [6] achieved modulation-free structures by significantly reducing the growth temperature. However, the crystal quality of GaInP is very sensitive to the growth temperature [11], and it is thus of practical importance to obtain laterally non-modulated structures at higher growth temperatures, near the optimized value of 640 °C.

In the present work, the strain in the layers has been reduced to $|\epsilon| \sim 0.4\%$ to obtain structures of high structural quality for the study of the optical properties, and for the determination of the GaInP/InAsP heterojunction band offset.

We present transmission electron microscopy (TEM) and high-resolution x-ray diffraction (HRXRD) results showing that high quality modulation-free strain-balanced GaInP/InAsP MQW on InP (001) can be obtained by LP-MOVPE at normal growth temperatures (620 °C), for structures with moderate strains in the individual layers. The measured structural parameters are used to adjust the optical properties of the samples with a Bastard/Marzin model [12, 13] using the band offset as the single fitting parameter.

2. Experiment

The LP-MOVPE growth of GaInP/InAsP heterojunctions was carried out on Fe-doped InP(001) substrates in a low-pressure (40 Torr) horizontal cold-wall reactor, described elsewhere [14]. Pure phosphine (PH_3), tertiarybutylarsine

(TBAs), trimethylindium (TMIn) and trimethylgallium (TMGa) were used as the reacting sources and Pd-purified hydrogen as the carrier gas, with a total gas flow rate in the reactor of 3000 sccm. A growth temperature of 620 °C was chosen, between 600 and 640 °C, the optimal growth temperatures for the InAsP/InP [15] and GaInP/InP [11] systems respectively, grown in the same reactor.

Cross-sectional TEM observations were performed on a Philips CM30 microscope operated at 300 kV. Samples with [1$\bar{1}$0] normals were prepared by mechanical grinding followed by room-temperature low-angle (4°) Ar^+ ion milling at 5 keV. The ion energy was gradually reduced to 2.5 keV during the final stages of thinning to minimize sample damage. The HRXRD analyses were performed with a Philips four-crystal diffractometer aligned in the (220) configuration. Absorption spectra were recorded using a Bomem DA3 Fourier transform infrared spectrometer.

3. Results and discussion

A series of 10-period MQW structures with 0.1 μm buffer and cap InP layers was grown to determine the optimal growth interruption times, which are particularly critical for preparation of abrupt interfaces [16], and to achieve the best strain compensation possible for moderate strain ϵ in the GaInP and InAsP layers. The gas switching sequence used for the GaInP/InAsP MQW growth, denoted $(T_0; T_1, T_2, T_3, T_4)$ (in s), is schematically represented in the inset of figure 1. The values of T_1 to T_4 are kept the same throughout the growth of the whole MQW, whereas the interruption time T_0 is used for the growth of the first GaInP layer on the InP buffer layer.

Figure 1 presents the symmetric (004) and asymmetric (115—) rocking curves of a strain-balanced 10-period GaInP/InAsP MQW. The simulation of the HRXRD spectra, based on the dynamical diffraction theory [17], gives Ga and As composition values x and y of 0.06 and 0.14 respectively, and thicknesses of GaInP and InAsP layers of 11.2 and 11.7 nm respectively. The simulations of the (004) and (115—) rocking curves, which assume sharp interfaces, were performed self-consistently with exactly the same parameters, to ensure their accuracy. The thickness values are in excellent agreement with those obtained from TEM measurements. The experimental curves show very sharp symmetric satellite peaks, with the zero-order peak almost exactly coinciding with that of the substrate. Their width and intensity are in excellent agreement with the simulation, attesting to the abruptness of the interface between GaInP and InAsP. The mean mismatch is 5.6×10^{-4}.

The high crystallographic quality of the structure of figure 1 was obtained using the optimal interruption times (3; 3, 2, 1, 1), which are exactly the optimal times obtained for InP/InAsP multilayers grown in the same reactor [15]. The structural quality seems to be more sensitive to the interruption times than for the InP/InAsP system. Figure 2 shows the effect of interruption times on the structural quality. In this figure, we have presented the (004) rocking curves of the structure of figure 1 grown using

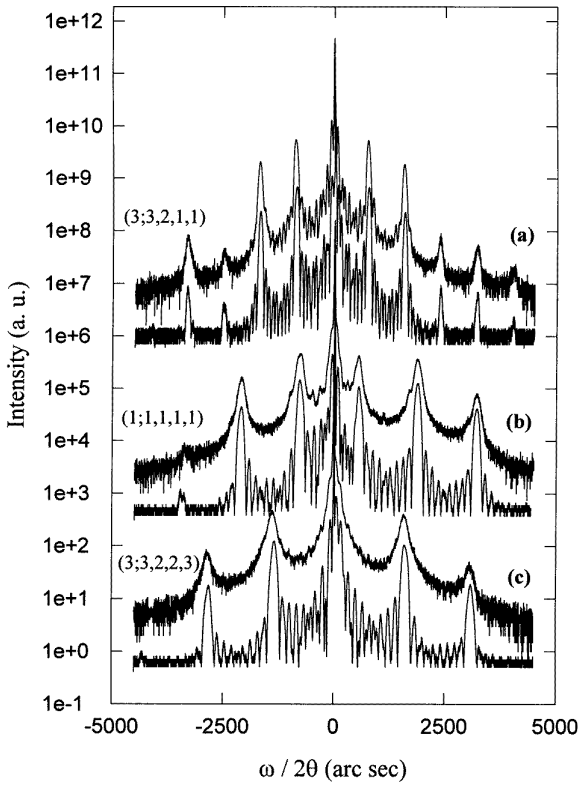

Figure 2. The (004) diffraction patterns for a 10-period MQW grown with different growth interruption times as shown in the figure. The three structures correspond to $Ga_{0.06}In_{0.94}P$(11.2 nm)/$InAs_{0.14}P_{0.86}$(11.7 nm) (a), $Ga_{0.10}In_{0.90}P$(6.8 nm)/$InAs_{0.14}P_{0.86}$(7.2 nm) (b) and $Ga_{0.08}In_{0.92}P$(6.1 nm)/$InAs_{0.15}P_{0.85}$(6.5 nm) (c). The upper curves show experimental data; the lower curves are simulated (and shifted) rocking curves.

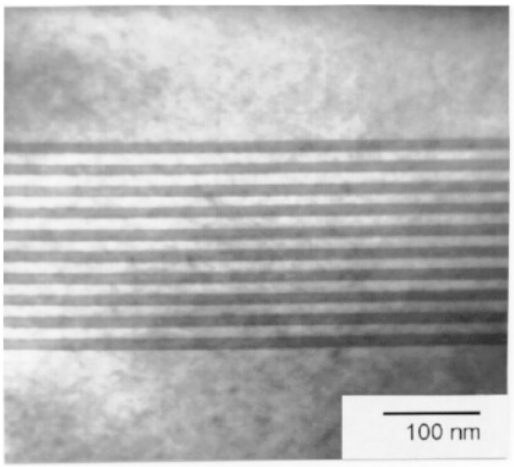

Figure 3. Bright field $g = (00\bar{2})$ near [1$\bar{1}$0] cross-sectional TEM image of the sample of figure 1. The clear and dark layers are GaInP and InAsP layers respectively.

the optimal interruption times, in comparison with those of MQW grown with decreased times (1; 1, 1, 1, 1) at the GaInP/InAsP interface, and increased times (3; 3, 2, 2, 3) at the InAsP/GaInP interface. The respective structures

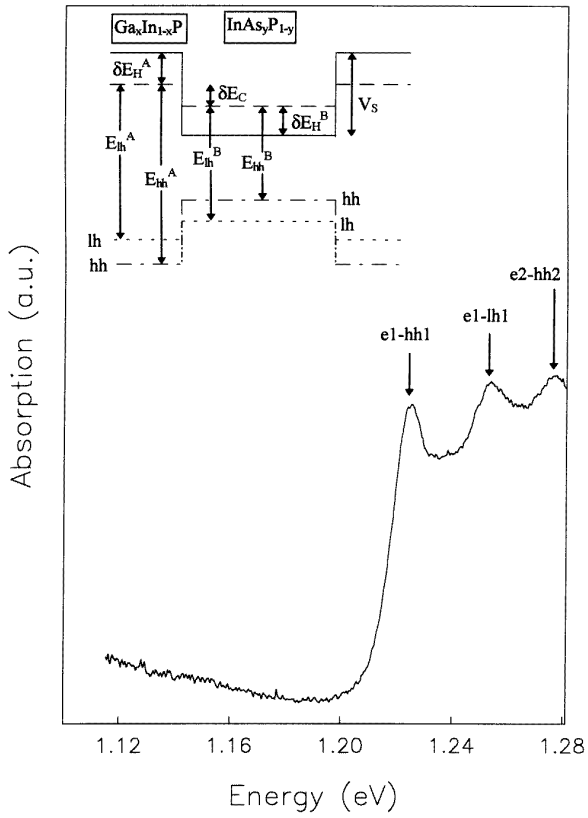

Figure 4. Room-temperature optical absorption spectrum of the sample of figure 1. The inset is a schematic representation of the band structure, A and B refer to the GaInP and InAsP materials respectively.

are a 10-period $Ga_{0.10}In_{0.90}P$(6.8 nm)/$InAs_{0.14}P_{0.86}$(7.2 nm) and $Ga_{0.08}In_{0.92}P$(6.1 nm)/$InAs_{0.15}P_{0.85}$(6.5 nm). The corresponding HRXRD rocking curves show even more broadening and intensity reduction of the satellite peaks than in the InAsP/InP case. For the non-optimal interruption times we cannot rule out the formation of intermediate quaternary layers or grading at the interface.

Figure 3 presents a $g = (00\bar{2})$ bright-field cross-sectional TEM image of the sample of figure 1, with the beam direction close to $[1\bar{1}0]$. All layers are very uniform in thickness, with parallel, well defined interfaces. No modulations are detected in the structure over the entire area observed by TEM. Diffraction contrast analyses also indicate that the MQW is of very high structural quality, as no threading or misfit dislocations were observed.

Figure 4 shows the optical absorption spectrum of the same sample at room temperature. The 7 meV width of the fundamental resonance, at 1.225 eV, is indicative of the very high optical quality of the sample. This spectrum has been fitted using the Bastard/Marzin [12, 13] model, by taking into account the bandgap variations due to the tensile strain in the InGaP barriers and the compressive strain in the InAsP quantum wells determined from the structural analysis. Binding energies of 3–6 meV and 5–10 meV are expected for light- and heavy-hole excitons respectively. Using these energy windows, and the fact that heavy-hole exciton energies should be approximately 1.5 times larger than light-hole exciton energies, the strained conduction band offset was determined by adjusting the measured excitonic energies with the calculated transitions. Thus, the strained conduction band offset is the only adjustable parameter†. For a detailed description of the calculations see [18, 19]. We reproduce in table 1 the relevant set of semiconductor parameter values used at 300 K. The bandgap bowing parameter is $c = 0.12$ eV for InAsP (see [18]) and $c = 0.88$ eV for GaInP (see [22]).

Table 1. List of physical constants for GaP, InAs and InP binary compounds that were used for the self-consistent numerical determination of the band offset at room temperature.

Parameter	GaP	InAs	InP
C_{11} ($\times 10^{11}$ dyn cm^{-2})	14.1[a]	8.02[d]	10.3[f]
C_{12} ($\times 10^{11}$ dyn cm^{-2})	6.22[a]	4.41[d]	5.83[f]
a (eV)	−9.6[b]	−6[b]	−8[g]
b (eV)	−1.65[b]	−1.8[b]	−1.55[b,g]
m_e^*/m_0	0.55*	0.023[b]	0.079**[a]
m_{hh}^*/m_0	0.54‡[b]	0.41[b]	0.65[b]
m_{lh}^*/m_0	0.16‡[b]	0.025[b]	0.12[a]
Δ (eV)	0.08[b]	0.38[a]	0.108[a]
$E_P = 2m_0P^2$ (eV)	22.2[b]	21.11[e]	17[e]
a_0 (Å)	5.4504[c]	6.0579[c]	5.8683[c]
E_g (eV)	2.78†[a]	0.36[b]	1.351[b]

* Calculated from E_P and formula 45, ch 2 of [12].
‡ Value at 77 K.
† Direct bandgap.
** Value at 4.2 K.
[a] [22].
[b] Madelung O (ed) 1982 *Physics of Group IV Elements and III–V Compounds* (Landolt-Börnstein New Series, group III, vol 17, pt a) (Berlin: Springer).
[c] Sirota A N, Antyukhov A M and Sidorov A A 1984 *Dokl. Akad. Nauk SSSR* **277** 1379 (1985 *Sov. Phys. Dokl.* **29** 662).
[d] Orlova N S 1989 *Cryst. Res. Technol.* **24** K39.
[e] [12].
[f] Jordan A S 1985 *J. Crystal Growth* **71** 559.
[g] Casey H C Jr and Panish M B 1978 *Heterostructure Lasers* (New York: Academic) p 9.

The band diagram is shown schematically in the inset of figure 4, where δE_H is the bandgap shift due to the hydrostatic component of the strain, E_{hh} and E_{lh} are the heavy- and the light-hole strained bandgaps, V_S is the strain-free conduction band offset and δE_C is the strained conduction band offset. The barrier layers are sufficiently thin to lead to significant overlap of the electronic wavefunctions, giving band widths of 0.4 meV and 5 meV for the $n = 1$ and $n = 2$ electronic levels, respectively. The peaks labelled e1–hh1 and e1–lh1 correspond to the transition between the $n = 1$ heavy-hole and light-hole levels respectively and the $n = 1$ electronic level, and the e2–hh2 peak corresponds to the

† This is not strictly true, as there may always be some discrepancy between the different values of the materials parameters quoted in the literature, which are obtained by different measurements. Our extensive previous work on InAsP [18, 19] and GaInP [20, 21], however, gives us enough confidence in the values used so that, in fact, the only parameter that we had to adjust in this work is the band offset.

transition between the $n = 2$ heavy-hole level and the $n = 2$ electronic level. The model accurately predicts all three peaks, with the best fit obtained for $\delta E_c = 94.0 \pm 3.3$ meV which corresponds to approximately 75±3% of the difference between the strained bandgaps and is consistent with the band offsets deduced for InAsP/InP heterojuctions [18, 19]. The excitonic binding energies deduced from the fit are 10 meV and 8 meV for the heavy- and light-hole excitons respectively, consistent with results for InAsP layers with small As content [18]. For the alignment that we obtained here the light-hole quantum well in the InAsP layer is shallow with offsets between 2 and 6 meV.

Since we have already observed type-II transitions for the light holes in GaInP/InP mutiple quantum well samples for similar Ga concentrations in the barriers, the GaInP/InAsP system is particularly appropriate for studying the differences between type-I and type-II transitions. Indeed, it should be possible to grow a series of samples with various InAsP well compositions for a given GaInP barrier layer to clearly indicate the transition from a type-I to a type-II light-hole system.

4. Conclusion

An adequate choice of growth parameters permitted the LP-MOVPE growth of high-quality modulation-free strain-balanced GaInP/InAsP MQW, with moderately strained layers. The crystallographic quality of this heterostructure is more sensitive to the interruption times than the InP/InAsP multilayers, but with the same optimal values. The Bastard/Marzin model, using precise structural parameters, allows an accurate identification of optical transitions corresponding to all peaks in the absorption spectrum, and determination of the band offset of the GaInP/InAsP heterojunction.

Acknowledgments

This work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada and the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (FCAR) du Québec. The authors thank L Isnard, R Lacoursière, J Bouchard and R Veillette for their technical assistance. One of the authors (YA) gratefully acknowledges the support of the Semlalia Faculty of Sciences, Marrakech. We acknowledge the comments from the reviewers which have helped to improve the presentation of our results.

References

[1] Woodward T K, Chiu T H and Sizer T II 1992 *Appl. Phys. Lett.* **60** 2846
[2] Chiu T H, Cunningham J E, Woodward T K and Sizer T II 1993 *Appl. Phys. Lett.* **62** 340
[3] Ponchet A, Rocher A, Ougazzaden A and Mircea A 1994 *J. Appl. Phys.* **75** 7881
[4] Jiang X S and Yu P K L 1994 *Appl. Phys. Lett.* **65** 2536
[5] Chin M K, Yu P K L and Chang W S C 1991 *IEEE J. Quantum Electron.* **27** 696
[6] Kasukawa A, Yokouchi N, Yamanaka N, Iwai N and Matsuda T 1995 *Japan. J. Appl. Phys.* **34** L965
[7] Cotta M A, Hamm R A, Chu S N G, Harriott L R and Temkin H 1994 *J. Appl. Phys.* **75** 630
[8] Smith A D, Briggs A T R, Scarrott K, Zhou X and Bangert U 1994 *Appl. Phys. Lett.* **65** 2311
[9] Tu K-N, Mayer J W and Feldman L C 1992 *Electronic Thin Film Science for Electrical Engineers and Materials Scientists* (London: Macmillan) ch 7
[10] Bangert U, Harvey A J, Dieker C, Hartdegen H, Vescan L and Smith A 1995 *J. Appl. Phys.* **78** 811
[11] Bensaada A, Cochrane R W, Masut R A, Leonelli R and Kajrys G 1993 *J. Crystal Growth* **130** 433
[12] Bastard G 1988 *Wave Mechanics Applied to Semiconductor Heterostructures* (Les Ulis: Éditions de Physique)
[13] Marzin J Y, Gérard J M, Voisin P and Brum J A 1990 *Semiconductors and Semimetals* vol 32 (San Diego, CA: Academic) p 56
[14] Cova P, Masut R A, Currie J, Bensaada A, Leonelli R and Tran C A 1991 *Can. J. Phys.* **69** 412
[15] Tran C A, Graham J T, Brebner J L and Masut R A 1994 *J. Electron. Mater.* **23** 1291
[16] Schneider R P and Wessels B W Jr 1990 *Appl. Phys. Lett.* **57** 1998
[17] Fewster P F 1984 *Philips J. Res.* **45** 620
[18] Beaudoin M, Bensaada A, Leonelli R, Desjardins P, Masut R A, Isnard L, Chennouf A and L'Espérance G 1996 *Phys. Rev.* B **53** 1990
[19] Desjardins P, Beaudoin M, Leonelli R, L'Espérance G and Masut R A 1996 *J. Appl. Phys.* **80** 846
[20] Bensaada A, Chennouf A, Cochrane R W, Graham J T, Leonelli R and Masut R A 1994 *J. Appl. Phys.* **75** 3024
[21] Bensaada A, Graham J T, Brebner J L, Chennouf A, Cochrane R W, Leonelli R and Masut R A 1994 *Appl. Phys. Lett.* **64** 273
[22] Madelung O (ed) 1987 *Intrinsic Properties of Group IV Elements and III–V, II–VI and I–VII Compounds* (Landolt-Börnstein New Series, group III, vol 22, pt a) (Berlin: Springer)