

Interlayer formation due to arsine stabilisation during interruptions of MOVPE–growth of InGaP

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Introduction

Heterointerfaces are the basis of band–gap engineering used for electronic and optoelectronic devices. The optimisation of these interfaces is a challenge, especially when switching between As and P occurs. Unintentional interlayer formation during metalorganic vapor phase epitaxy (MOVPE) of GaAs on InGaP has often been reported [1–5]. Such interlayers can drastically change the electrical and optical properties of device structures. The growth of GaAs on InGaP is usually preceded by switching from PH₃ to AsH₃ and a stabilization of the surface under group V–hydrides. Depending on the time of purging with group V–hydrides and their concentration during growth interruptions the formation of interfacial layer can be modified. Beside the As–P exchange at the GaAs–on–InGaP interfaces several studies discuss the influence of indium–carry–over on the formation of unintentional interlayer. These interlayers give often rise for an additional low temperature photoluminescence (PL) peak around 1.4 eV [1–4]. Thus, additional interlayers are often deposited [1,2,4] or the gas switching/purging sequences [3] are optimised to avoid these additional PL peaks. Capacitance–voltage (C–V) studies with metal–semiconductor contacts on isotype heterojunctions are known to provide reliable values for the band offset. Therefore we use in addition to PL also C–V measurements to detect the inadvertent interlayers at the GaAs–on–InGaP or InGaP–on–InGaP interfaces by their conduction band offsets DE_C [5,6].

Experimental procedure

The InGaP/GaAs layers were grown in a horizontal MOVPE reactor (Aix 200) at 70 hPa on (100) n–GaAs substrate using TMGa, TMIIn, Si₂H₆, PH₃, and AsH₃ as precursors. Nearly disordered InGaP was grown at 580°C with a V/III input ratio of 70 and a growth rate of 2.5 μm/h. The InGaP growth was interrupted by switching off TMGa, TMIIn and PH₃ and replacing them by AsH₃ (10 sccm/min in 7 l/min total hydrogen flow) for 60 s. The InGaP growth was restarted by replacing the AsH₃ directly by PH₃ for 0.5 s and then switching on TMGa and TMIIn again at the same time. Thickness, composition and strain of the interlayers as well as of the InGaP layer were determined by high resolution X–ray diffraction at the symmetric (004) reflection. The lattice mismatch of the InGaP layer was smaller than $5 \cdot 10^{-4}$. The 514.5 nm line of a cw Ar+ laser was used for excitation in low temperature photoluminescence (PL). In order to determine the electronic properties of the interfaces by the C–V method (measurement frequency: 1 MHz), the layer structures were Si–doped with carrier concentrations in the 10^{17} cm^{-3} range (cf. Ref. [7]). The As, In, Ga and P concentrations were measured by SIMS [8].

Results and discussion

Fig. 1 shows the depth profile of the electron concentration n of an InGaP layer with growth interrupts under AsH₃ flux. The horizontal dashed line marks the Si doping level. Remarkable peaks accompanied by strong depletion in the adjacent InGaP are formed as the results of interrupts. Fig. 2 shows the corresponding SIMS depth profiles. It is evident that the As–related signal is drastically enhanced at the position of the growth interruptions, in contrast to the In–related one. As the result of the growth interruption under AsH₃, an As–enriched quaternary (In,Ga)(As,P) interlayer is formed. The positions of the As–related peaks agree with the positions of the maxima of the electron concentration in Fig. 1. The thickness of the quantum well (QW) formed as the results of interrupts can be estimated from the SIMS depth profile in Fig. 2 to be below 7 nm with an As concentration y of about 0.08. (3.2 nm steps between measurement points). The As carry–over into the succeeding InGaP layer after each

interruption extends over more than 20 nm with $y > 0.01$.

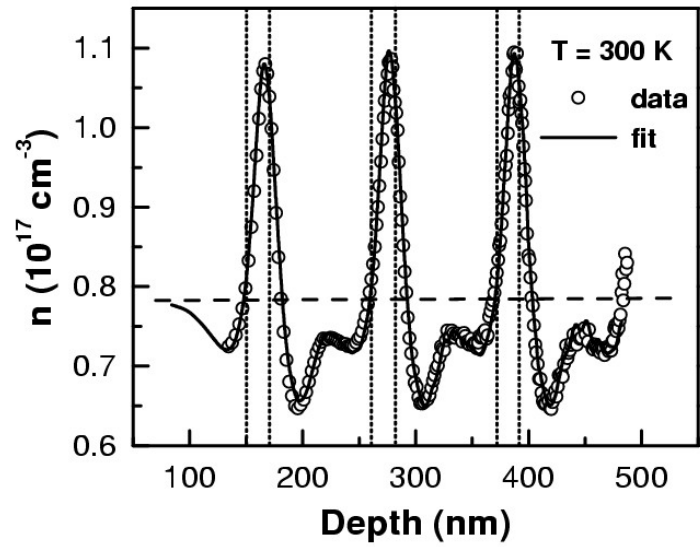


Fig. 1: C–V depth profile of the electron concentration n for an InGaP layer deposited with several growth interruptions under AsH_3 flux, (measured at 100 kHz and 295 K). Solid line: simulated best fit, horizontal dashed line: doping level in InGaP, vertical dotted lines: marker for the interfaces of the interlayers.

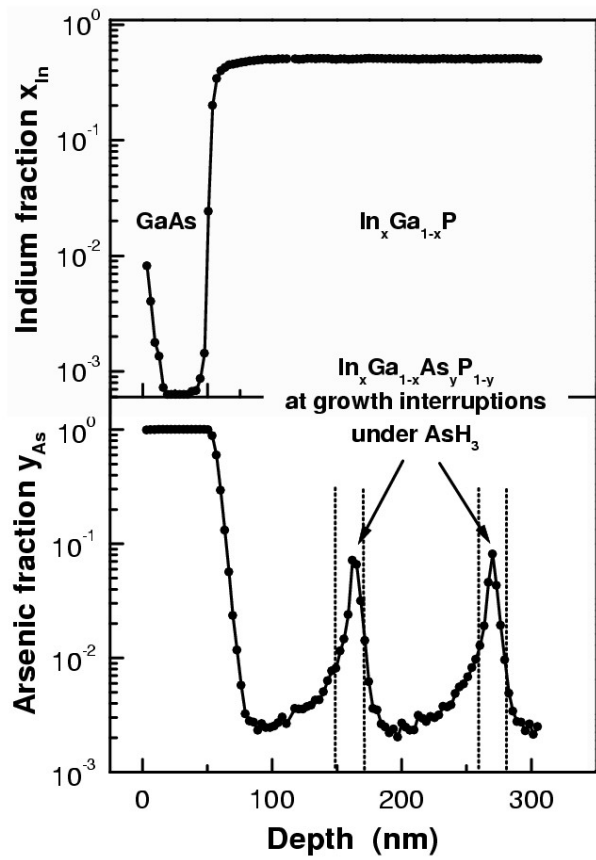


Fig. 2: SIMS depth profiles of the In and As concentrations for the InGaP sample (caped by GaAs) shown in Fig. 1. Vertical dotted lines: marker for the interfaces of the interlayers.

The compressive stress of the interlayers is so high, that they are clearly visible also in X–ray rocking curves. Their extension can be well fitted with 5–6 nm width and an As concentration between 0.15 and 0.08.

Further information on the interlayer is obtained by comparing measured and calculated electron distributions. With the same set of parameters for all interruptions, the fit to the measured electron distribution n shown in Fig. 1 as a line is perfect. The effective conduction band offset DE_C for the interface between interlayer and InGaP is found to be about 28 meV. The effective QW thickness is found to be about 20 nm, in reasonable agreement with the value estimated from SIMS measurements. The vertical dotted lines in Figs. 1 and 2 indicate the thickness of the interfacial layers as determined by simulation of the C–V data.

The 10–K–PL spectra of the InGaP layer are shown in Fig. 3. Additional peaks around 1.76 eV appear in addition to the typical emission of the InGaP band–to–band transitions of ordered (1.937 eV) and disordered component (1.973 eV). The additional peaks can be assigned to the unintentional interlayer formed by the growth interruptions. The (In,Ga)(As,P) QW thickness can be estimated to be 5.1 nm by band–gap calculations assuming rectangular potential wells for the electrons and holes using the determined band–gap shift of 217 meV and a DE_C of 28 meV from the C–V measurement. The valence band offset used in the calculation is 189 meV. For weakly ordered $In_{0.48}Ga_{0.52}As_yP_{1-y}$ layers, the band gap difference with respect to (In,Ga)P is given by /9/:

$$E_g \text{ (eV)} = 1.19y - 0.09y^2 \quad (1).$$

The As content would then be about $y = 0.185$ for a 5 nm thick As–containing interlayer. This is a bit higher than the results determined from SIMS and X–ray simulations but still in reasonable accordance.

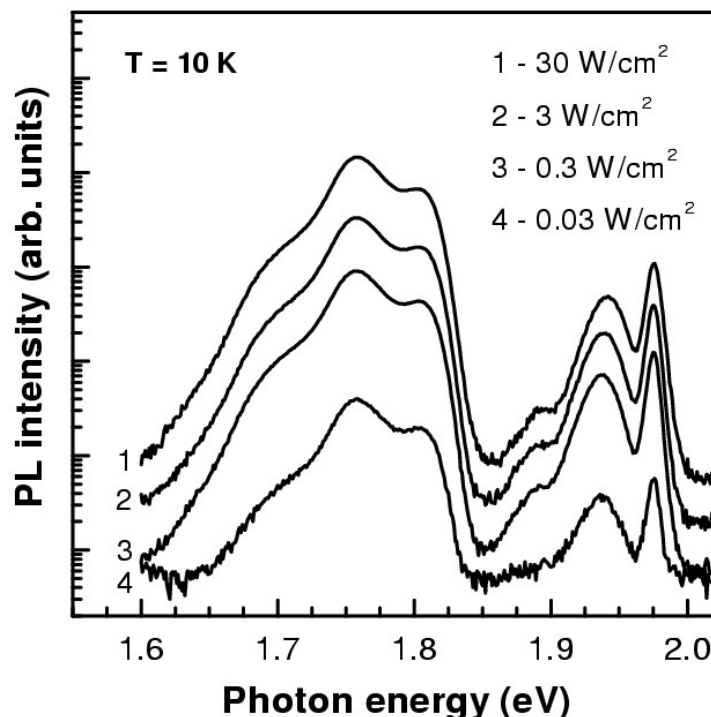


Fig. 3: Low–temperature PL spectra of the InGaP sample shown in Figs. 1 and 2 for several excitation densities.

The surprisingly high thickness of the interlayers suggests that, besides the As–P exchange, an additional interlayer growth takes place during or/and after the growth interruptions. The conduction band offset of 28 meV

detected by the C–V measurement is too small for possible InGaAs or InAsP interlayers, which could be grown during the arsine stabilised growth interruption with excessive indium on the InGaP surface and/or from hot reactor parts.

Conclusions

Interlayer formation as a result of prolonged stabilisation under arsine instead of phosphine during interruption of InGaP MOVPE growth was found. The measurements support that the unintentionally formed interlayer is an As rich (In,Ga)(As,P) layer with a thickness of about 5 ± 2 nm and an As content of about $y = 0.10 \pm 0.05$. The SIMS depth profile shows that As carry-over occurs into the succeeding InGaP layer over an extension of up to 20 nm with $y > 0.01$ after each arsine stabilized growth interruption.

References

- /1/ F.E.G. Guimarães, B. Elsner, R. Westphalen, B. Spangenberg, H. J. Geelen, P. Balk, *J. Cryst. Growth* **124** (1992) 199.
- /2/ R. Bhat, M.A. Koza, M.J.S.P. Brasil, R.E. Nahory, C.J. Palmstrom, B.J. Wilkens, *J. Cryst. Growth* **124** (1992) 576.
- /3/ R.C.Y. Tsai, M. Moser, C. Geng, V. Härle, T. Forner, P. Michler, A. Hangleiter, F. Scholz, *J. Cryst. Growth* **145** (1994) 786.
- /4/ Yong–Hwan Kwon, W.G. Jeong, Yong–Hoon Cho, Byung–Doo Choe, *Appl. Phys. Lett.* **76** (2000) 2379.
- /5/ A. Knauer, P. Krispin, V.R. Balakrishnan, M. Weyers, *J. Cryst. Growth* **248** (2003) 364.
- /6/ P. Krispin, A. Knauer, S. Gramlich, *Appl. Phys. Lett.* **80** (2002) 2493.
- /7/ P. Krispin, A. Knauer, S. Gramlich, *Mater. Sci. Eng. B* **88** (2002) 129.
- /8/ RTG Mikroanalyse GmbH Berlin, Schwarzschildstr. 1, D–12489 Berlin, email: rtg@bbtt.de
- /9/ E. Kuphal, *J. Cryst. Growth* **67** (1984) 441.