

Heavy P-Type Carbon Doping of MOCVD GaAsP Using CBrCl₃

Christopher Heidelberger¹ and Eugene A. Fitzgerald

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

¹Corresponding Author: Phone: 617-253-6903, Email: chrish@mit.edu

Abstract

CBrCl₃ is shown to be a useful precursor for heavy p-type carbon doping of GaAs_xP_{1-x} grown via metalorganic chemical vapor deposition (MOCVD) across a range of compositions. Structural and electrical properties of the GaAsP films were measured for various processing conditions. Use of CBrCl₃ decreased the growth rate of GaAsP by up to 32% and decreases x by up to 0.025. The dependence of these effects on precursor inputs is investigated, allowing C-doped GaAsP films to be grown with good thickness and compositional control. Hole concentrations of greater than $2 \times 10^{19} \text{ cm}^{-3}$ were measured for values of x from 0.76 to 0.90.

Keywords: A1. Doping, A3. Metalorganic chemical vapor deposition, B1. Gallium arsenide phosphide, B2. Semiconducting III-V materials

1 Introduction

GaAs_xP_{1-x} is a ternary III-V semiconductor which has found many uses. Since the early 1970s, it has been widely used to fabricate red, orange, and yellow light emitting diodes [1,2]. It was studied for use as a graded base layer in heterojunction bipolar transistors (HBTs) in the 1990s [3]. More recently, GaAsP has become a material of interest for the high-bandgap cell in multi-junction photovoltaic systems [4–6]. For III-V on Si applications, it is useful because it is

a miscible alloy and nearly bridges the entire gap in lattice constant between Si and GaAs. Metalorganic chemical vapor deposition (MOCVD) has been the method of choice for most commercial growth of GaAsP and other III-V semiconductors.

Heavy p-type doping of GaAsP in excess of $1 \times 10^{19} \text{ cm}^{-3}$ is required in several device elements, such as Ohmic contact layers, tunnel junctions, and the base regions of HBTs. Carbon has an advantage over group II p-type dopants in its lower diffusivity [7] and higher solid solubility in GaAs [8]. There are several ways of doping with C in MOCVD. Various hydrocarbon sources have been used, including the methyl group from TMGa, but these generally require low growth temperatures and/or low V/III ratios and therefore result in a high density of deep-level traps and bad surface morphology [9,10].

CBrCl₃ and other halomethanes allow higher growth temperatures and V/III ratios so high-quality C-doped films can be grown [11]. However, they create reactive byproducts which can have two adverse effects on GaAs_xP_{1-x} growth: substantial growth rate reduction [12] and composition shift (change in x) [13]. Control over growth rate and composition is critical for device fabrication; therefore, it is important that we are able to understand the effect of C doping by CBrCl₃ on these parameters. In this paper, we report the thicknesses, compositions, and electrical properties of various C-doped GaAsP films.

2 Experiments

The epitaxial samples were prepared in a Thomas Swan/Aixtron cold-walled 6x2" MOCVD reactor, with a close-coupled showerhead configuration. Trimethylgallium (TMGa) was used as a Ga precursor and AsH₃ and PH₃ were used as group V precursors. In the 1980s, CCl₄ was originally used as a C precursor for MOCVD GaAs [11], but is now unavailable for

environmental reasons. Replacing one or more Cl atoms with Br yields compounds which are potential candidates; however, of these only CBrCl₃ is a liquid at room temperature, an important criterion for bubbler design. Hence, in this study CBrCl₃ was used as a C precursor, with a bubbler temperature of 26 °C. The total reactor pressure for all samples was 100 Torr, with N₂ used as carrier gas. Susceptor rotation speed was 100 rpm.

Samples were grown with a structure shown in Figure 1. Si substrates were used for all GaAsP samples because tensile GaAsP films grown on GaAs substrates had a tendency to crack, yielding inaccurate Hall effect measurements. N-type (100) Si substrates with a 6° offcut were used. The offcut is necessary to obtain single-domain GaAsP [14]. Si_{0.5}Ge_{0.5} was grown via a Si_{1-y}Ge_y graded buffer using a vertical-tube UHVCVD reactor. The wafers were then chemical-mechanically polished to remove surface roughness [15]. Next, in the MOCVD reactor, a Si_{1-y}Ge_y graded buffer was grown from y = 0.5 to y = 0.75, upon which an n-type GaAs_{0.74}P_{0.26} film was initiated at 725 °C and grown to 500 nm. Then, under a mixed AsH₃ and PH₃ overpressure, the growth temperature was lowered to the final growth temperature (600 °C or 650 °C). A C-doped GaAsP film was then deposited for 1000 s with a TMGa flow of 132 μmol/min and a V/III ratio of about 100. The C-doped GaAs and GaP films were grown directly on their respective n-type substrates rather than on Si.

Table 1 shows a summary of the process conditions for all of the C-doped GaAsP films, grown at a variety of temperatures, CBrCl₃ flow rates, and AsH₃ fractions. AsH₃ fraction, the chosen metric of As precursor in the gas phase, is defined as:

$$\text{AsH}_3 \text{ Fraction} = \frac{P_{\text{AsH}_3}}{P_{\text{AsH}_3} + P_{\text{PH}_3}}, \quad (1)$$

where P_{AsH_3} and P_{PH_3} are the input partial pressures of AsH₃ and PH₃, respectively.

Sample A was grown at a temperature of 650 °C, while all other samples were grown at 600 °C. Samples B–F vary AsH₃ fraction, and therefore the solid GaAs_xP_{1-x} composition, while keeping a constant CBrCl₃ flow. Samples G, C, and H vary the CBrCl₃ flow with a constant AsH₃ fraction. Sample J has multiple GaAsP layers with varying AsH₃ fractions and no CBrCl₃ flow. The AsH₃ fractions of 0.18–0.37 were chosen because at a growth temperature of 600 °C, they result in GaAsP compositions which span most of the direct band gap range [16]. The V/III ratio was kept constant while varying AsH₃ fraction.

Layer thicknesses were measured using cross-sectional SEM. High-resolution x-ray diffraction was used to measure film composition. (004) and (224) reciprocal space maps of the film and substrate were collected and used to find the in-plane and out-of-plane lattice constants of the C-doped GaAsP film using the methodology described in detail in Section 3.1 of Roesener et al. [17]. These values allowed for estimation of the relaxed lattice constant, using a Poisson ratio interpolated from the GaP and GaAs endpoints. The As content of the film was then calculated by Vegard's law. Hall effect measurements used the van der Pauw geometry and a permanent magnet with a field of 0.412 T. Indium was used to make contact to the GaAsP film. Given the finite size of the contacts, an error in Hall effect voltage of 5% was estimated [18]. Because of the pronounced effect of CBrCl₃ on GaAsP growth rate, the individually measured thickness of each sample was used in calculating its bulk carrier concentration. Leakage current into the n-type buffer layers and substrate was measured for representative Hall effect structures. Reverse bias leakage current from the p-doped GaAsP film into the n-doped substrate was less than 0.1% of the current between two Hall effect terminals at the same voltage. Therefore, any contribution of the n-type substrate to the sheet resistance or Hall voltage measurements was

deemed to be insignificant. C concentration in Sample H was measured using secondary ion mass spectrometry (SIMS), which was performed by Evans Analytical Group.

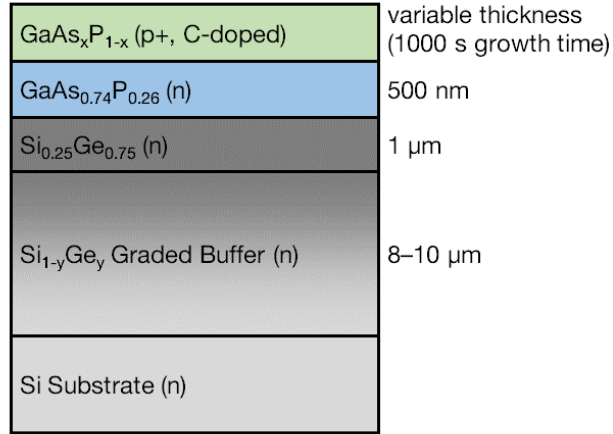


Figure 1: Cross-sectional schematic of the epitaxial samples.

Sample ID	Temperature (°C)	CBrCl ₃ Flow (μmol/min)	AsH ₃ Fraction
A	650	118	0.53
B	600	59	0
C	600	59	0.18
D	600	59	0.27
E	600	59	0.37
F	600	59	1
G	600	15	0.18
H	600	118	0.18
J	600	0	0.18, 0.27, 0.37

Table 1: List of GaAsP samples with growth conditions.

3 Results and Discussion

3.1 Effect of Growth Temperature

Sample A, grown at 650 °C, yielded a hole concentration of $9 \times 10^{17} \text{ cm}^{-3}$. This is too low for the applications discussed in Section 1. Growth temperatures of 650 °C and higher are

preferred for MOCVD growth of GaAsP. This is due to increased concentrations of impurities at lower temperatures as well as decreased PH₃ cracking efficiency [19,20]. However, it is known that a decreased growth temperature of 600 °C or lower produces the highest hole concentrations in C-doped GaAs [11,12]. Sample H, grown with the same CBrCl₃ flow rate as Sample A but at 600 °C, yielded a hole concentration of $2 \times 10^{19} \text{ cm}^{-3}$. This confirms that the active C doping of GaAsP also increases with decreasing growth temperature. The rest of this study focuses on a growth temperature of 600 °C because growth temperatures less than 600 °C are undesirable for the reasons mentioned above.

3.2 Growth Rate Reduction by CBrCl₃

The growth rate of GaAsP was decreased by the introduction of CBrCl₃. Figure 2 shows the growth rate reduction for a single AsH₃ fraction (0.18) as a function of CBrCl₃ flow. Lee et al. model the growth rate reduction of GaAs by CCl₄ as:

$$r = k_0[\text{CX}_4][\text{V/III}]^{-0.5} \exp\left(-\frac{E_a}{kT}\right), \quad (2)$$

where [CX₄] is the concentration of C precursor (CCl₄ in Lee et al.), E_a is the activation energy of formation of GaCl from Ga and Cl, and k_0 is a constant dependent on other factors [12]. The proportional dependence on C precursor concentration agrees with our data for GaAsP, suggesting that the growth rate reduction is caused by reaction of either Cl or Br byproducts with Ga or Ga precursor.

Growth rate reduction does not change appreciably with AsH₃ fraction at a constant CBrCl₃ flow rate, as shown in Figure 3. This is further evidence that the growth rate reduction is limited by the reaction of Br or Cl byproducts with Ga, and that group V species are not involved.

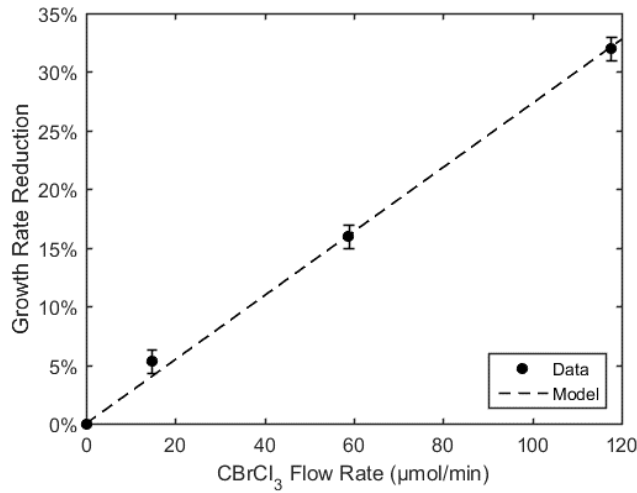


Figure 2: Reduction in GaAsP growth rate as a function of CBrCl₃ flow rate.

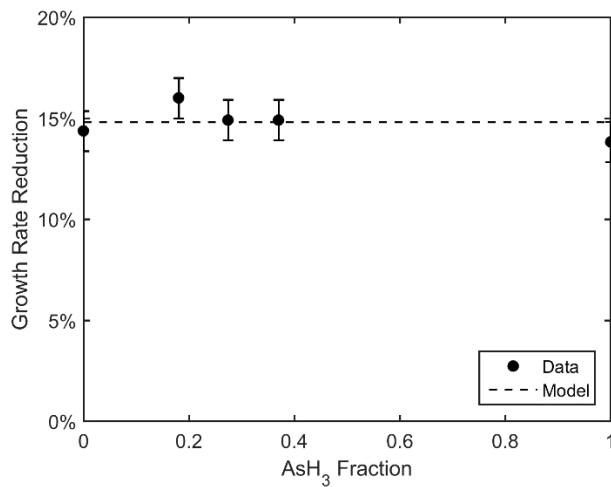


Figure 3: Reduction in GaAsP growth rate as a function of AsH₃ fraction.

3.3 GaAs_xP_{1-x} Composition Shift due to CBrCl₃

Figure 4a shows the GaAs_xP_{1-x} composition (x) with a constant AsH₃ fraction of 0.2 and a varying CBrCl₃ flow. The introduction of CBrCl₃ increases the As fraction in the solid phase (x). This trend was also observed by Tateno et al. for InGaAsP doped by CBr₄ [13]. The shift in x is approximately the same for all CBrCl₃ flows tested (15–118 μmol/min).

The incorporation of high amounts of C is expected to have an effect on the GaAsP lattice constant due to Vegard's Law [21]. However, this shift would be opposite in sign to the shift observed here, that is, towards smaller rather than larger lattice constants. In addition, the magnitude of the shift due to C incorporation is expected to be a small fraction (< 10%) of the observed shift, so it is ignored here.

GaAs_xP_{1-x} composition (x) versus AsH₃ fraction is shown in Figure 4b for both no CBrCl₃ and for a CBrCl₃ flow of 59 μmol/min. Smeets et al. model the relationship between the input partial pressures of AsH₃ and PH₃ and x as:

$$\frac{1-x}{x} = C \frac{P_{\text{PH}_3}}{P_{\text{AsH}_3}}, \quad (3)$$

where C is a fitting constant with an Arrhenius dependence and an activation energy close to that of the PH₃ cracking energy [22]. For the case of no CBrCl₃, this equation fits the data well with C equal to 0.075. For a CBrCl₃ flow of 59 μmol/min, the data is well-fit with an adjusted C of 0.066. Equation 3 with both values for C is plotted in Figure 4b. This modified model suggests that the CBrCl₃ is slowing the PH₃ cracking or otherwise consuming a certain fraction of PH₃, reducing the amount of elemental P available to enter the film. This could be due to formation of PCl₃, PBr₃, or similar species.

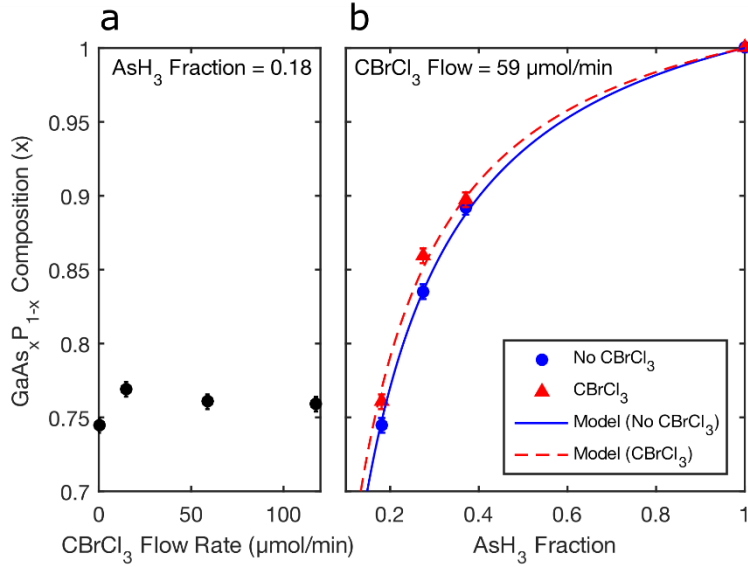


Figure 4: GaAsP composition (As fraction) versus (a) CBrCl₃ flow rate and (b) AsH₃ fraction.

3.4 Carrier Concentration and Mobility

Room-temperature hole concentration and mobility versus CBrCl₃ flow rate with a fixed AsH₃ fraction (0.18) are shown in Figure 5. A saturation of hole concentration at $2 \times 10^{19} \text{ cm}^{-3}$ is observed at high CBrCl₃ flow rates. The C concentration of Sample H (AsH₃ fraction of 0.18 and CBrCl₃ flow rate of 118 μmol/min) was measured by SIMS to be $4 \times 10^{19} \text{ cm}^{-3} \pm 1 \times 10^{19} \text{ cm}^{-3}$, corresponding to a dopant activation near 50%. The error in C concentration is large because of the unknown matrix effects of GaAsP compared to available GaAs standards. The dopant activation level of near 50% suggests that the saturation in hole concentration is due to a combination of multiple factors: a limitation in incorporation of C into the GaAsP film along with a reduction in dopant activation.

Figure 6 shows the room-temperature hole concentration and mobility as a function of AsH₃ fraction with a constant CBrCl₃ flow rate of 59 μmol/min. Hole concentrations for the three GaAsP samples are similar, while that of the GaAs and GaP samples are lower. Hole mobility increases almost linearly with increasing AsH₃ fraction. This behavior could be due to a

decrease in hole effective mass with increasing As concentration in combination with changing amounts of dopant scattering from incorporated C.

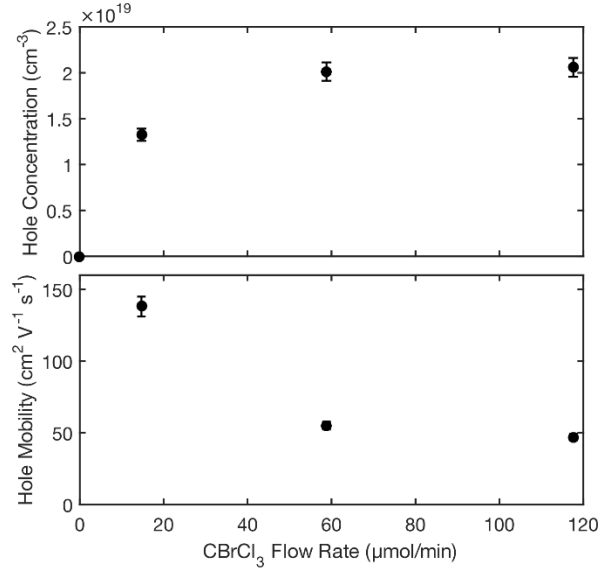


Figure 5: Hole concentration and mobility versus CBrCl₃ flow rate with a fixed AsH₃ fraction (0.18).

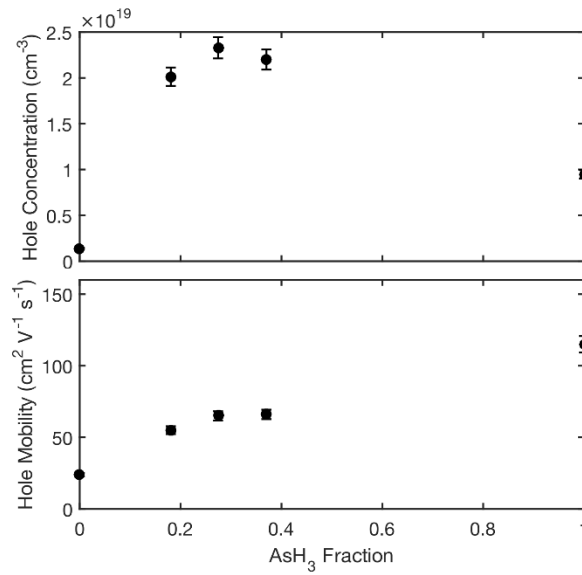


Figure 6: Hole concentration and mobility versus AsH₃ fraction with a fixed CBrCl₃ flow rate (59 μmol/min).

4 Conclusions

We found that CBrCl_3 can be used to grow GaAsP at a range of compositions with heavy p-type doping via MOCVD. The growth rate reduction of GaAsP due to CBrCl_3 was found to be proportional to CBrCl_3 flow rate and constant across GaAsP composition. This suggests that like for GaAs, the growth rate reduction is caused by the formation of GaCl or GaBr. GaAsP composition shifts towards GaAs due to CBrCl_3 , and was modeled using an adjusted equation from Smeets et al. By accounting for the growth rate and composition shifts, C-doped GaAsP films can be grown with the required precision. Hole concentrations of greater than $2 \times 10^{19} \text{ cm}^{-3}$ were achieved across a range of compositions with a CBrCl_3 flow rate of 59 $\mu\text{mol}/\text{min}$. At higher CBrCl_3 flows, the hole concentration saturated. Hole mobility increased linearly with increasing AsH₃ fraction.

5 Acknowledgements

This work was supported by the Center for Energy Efficient Electronics Science (NSF Award 0939514). This work was also supported by a research grant from the Singapore-MIT Alliance for Research and Technology Low Energy Electronic Systems Program, a program funded by the National Research Foundation of Singapore. This work made use of the MRSEC Shared Experimental Facilities at MIT, supported by NSF Award DMR-14-19807.

6 References

- [1] A. Bergh, P.J. Dean, Light-emitting diodes, *Proc. IEEE*. 60 (1972) 156–223.
- [2] M.G. Craford, W.O. Groves, Vapor Phase Epitaxial Materials for LED Applications, *Proc. IEEE*. 61 (1973) 862–880.
- [3] M. Ohkubo, N. Ikeda, T. Ninomiya, Graded-GaAs_{1-x}P_x base in heterojunction bipolar transistors with InGaP emitters, in: *Indium Phosphide Relat. Mater.*, 1995: pp. 456–459.
- [4] T.J. Grassman, M.R. Brenner, M. Gonzalez, A.M. Carlin, R.R. Unocic, R.R. Dehoff, et

- al., Characterization of metamorphic GaAsP/Si materials and devices for photovoltaic applications, *IEEE Trans. Electron Devices*. 57 (2010) 3361–3369. doi:10.1109/TED.2010.2082310.
- [5] K.N. Yaung, J.R. Lang, M.L. Lee, N. Haven, Towards high efficiency GaAsP solar cells on (001) GaP/Si, in: *Photovolt. Spec. Conf. (PVSC)*, 2014 IEEE 40th, 2014: pp. 831–835. doi:10.1109/PVSC.2014.6925043.
- [6] T. Milakovich, R. Shah, S. Hadi, M. Bulsara, A. Nayfeh, Growth and characterization of GaAsP top cells for high efficiency III-V / Si tandem PV, in: *Photovolt. Spec. Conf. (PVSC)*, 2015 IEEE 42nd, 2015: pp. 1–4. doi:10.1109/PVSC.2015.7355598.
- [7] B.T. Cunningham, L.J. Guido, J.E. Baker, J.S.M. Jr., N.H. Jr., G.E. Stillman, Carbon diffusion in undoped, n-type, and p-type GaAs, *Appl. Phys. Lett.* 55 (1989) 687–689. doi:10.1063/1.101822.
- [8] M. Konagai, T. Yamada, T. Akatsuka, K. Saito, E. Tokumitsu, K. Takahashi, Metallic p-type GaAs and GaAlAs grown by metalorganic molecular beam epitaxy, *J. Cryst. Growth*. 98 (1989) 167–173.
- [9] H. Zhu, Y. Adachi, T. Ikoma, Deep levels in MOCVD GaAs grown under different Ga/As mol fractions, *J. Cryst. Growth*. 55 (1981) 154–163.
- [10] M. Kushibe, K. Eguchi, M. Funamizu, Y. Ohba, Heavy carbon doping in metalorganic chemical vapor deposition for GaAs using a low V/III ratio, *Appl. Phys. Lett.* 56 (1990) 1248. doi:10.1063/1.103181.
- [11] B.T. Cunningham, M.A. Haase, M.J. McCollum, J.E. Baker, G.E. Stillman, Heavy carbon doping of metalorganic chemical vapor deposition grown GaAs using carbon tetrachloride, *Appl. Phys. Lett.* 54 (1989) 1905–1907. doi:10.1063/1.101237.
- [12] J.-S. Lee, I. Kim, B.-D. Choe, W.G. Jeong, Carbon doping and growth rate reduction by CCl₄ during metalorganic chemical-vapor deposition of GaAs, *J. Appl. Phys.* 76 (1994) 5079–5084. doi:10.1063/1.357219.
- [13] K. Tateno, C. Amano, Carbon doping and etching in Ga_xIn_{1-x}As_yP_{1-y} on GaAs substrates using CBr₄ by metalorganic chemical vapor deposition, *J. Electron. Mater.* 28 (1999) 63–68. doi:10.1007/s11664-999-0196-6.
- [14] Y. Bolkhovityanov, O. Pchelyakov, GaAs epitaxy on Si substrates: modern status of research and engineering, *Physics-Uspekhi*. 51 (2008) 437–456. doi:10.3367/UFNr.0178.200805b.0459.
- [15] M.T. Currie, S.B. Samavedam, T.A. Langdo, C.W. Leitz, E.A. Fitzgerald, Controlling threading dislocation densities in Ge on Si using graded SiGe layers and chemical-mechanical polishing, *Appl. Phys. Lett.* 72 (1998) 1718–1720. doi:10.1063/1.121162.
- [16] I. Vurgaftman, J.R. Meyer, L.R. Ram-Mohan, Band parameters for III–V compound semiconductors and their alloys, *J. Appl. Phys.* 89 (2001) 5815. doi:10.1063/1.1368156.

- [17] T. Roesener, V. Klinger, C. Weuffen, D. Lackner, F. Dimroth, Determination of heteroepitaxial layer relaxation at growth temperature from room temperature X-ray reciprocal space maps, *J. Cryst. Growth*. 368 (2013) 21–28. doi:10.1016/j.jcrysgr.2013.01.007.
- [18] R. Chwang, B.J. Smith, C.R. Crowell, Contact Size Effects on the Van Der Pauw Method for Resistivity and Hall Coefficient Measurement, *Solid. State. Electron*. 17 (1974) 1217–1227. doi:10.1016/0038-1101(74)90001-X.
- [19] M. Kondo, T. Tanahashi, Dependence of carbon incorporation on crystallographic orientation during metalorganic vapor phase epitaxy of GaAs and AlGaAs, *J. Cryst. Growth*. 145 (1994) 390–396. doi:10.1016/0022-0248(94)91081-2.
- [20] C.A. Larsen, N.I. Buchan, G.B. Stringfellow, Mass spectrometric studies of phosphine pyrolysis and OMVPE growth of InP, *J. Cryst. Growth*. 85 (1987) 148–153.
- [21] M.C. Hanna, Z.H. Lu, A. Majerfeld, Very high carbon incorporation in metalorganic vapor phase epitaxy of heavily doped p-type GaAs, *Appl. Phys. Lett*. 58 (1991) 164–166. doi:10.1063/1.104960.
- [22] E.T.J.M. Smeets, Solid Composition of GaAs_{1-x}P_x Grown by Organometallic Vapour Phase Epitaxy, *J. Cryst. Growth*. 82 (1987) 385–395.