

# Growth of dilute BGaP alloys by molecular beam epitaxy

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## ABSTRACT

Crystal growth of dilute BGaP alloys by solid-source molecular-beam epitaxy (MBE) equipped with electron beam evaporation system as the B source is investigated with changing growth condition of the growth temperature and the V/III ratio. The B composition for BGaP alloys increases with decrease of growth temperature and increase of III/V ratio.

The B incorporation into the GaP matrix is difficult compared to other group-III atoms (Al or In) incorporations due to bonds in the matrix are highly strained calculated by valence force-field model. The possibilities of forming and conserving B–P bonds opportunity increased with decrease of growth temperature and increase of the V/III ratio.

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## 1. Introduction

The monolithic integration of III–V compounds with Si is essential to realize the high speed optical interconnections between Si micro-processors. Especially, the pseudomorphic device structure without crystalline defects such as antiphase domains, stacking faults, threading dislocations and misfit dislocations (MDs) is vital to drive high performance of electrical and optical device [1]. In order to fabricate pseudomorphic III–V/Si heterostructure, GaP is a suitable III–V compound which has small lattice mismatch (0.37% at 300 K) with Si. Moreover, dislocation free GaP/Si templates are also possible to prepare by molecular beam epitaxy (MBE) [2]. However, the critical thickness without MDs caused by compressive strain of GaP/Si heterostructure has been achieved below 100 nm [3]. In addition, GaAsPN quantum well or InGaAsN quantum dot structure with III–V–N direct semiconductor are very prominent candidates of active material system for pseudomorphic optical device on GaP/Si template [4–8]. The lattice constants of these materials are larger than that of Si. Therefore, strain engineering is required to design and fabricate pseudomorphic optical devices on Si substrate.

The incorporation of B in III–V compound semiconductors decrease both the energy bandgap and the lattice constant caused by miscibility gap between the group-III atomic sizes of B and others such as Al, Ga and In. It has been applied for high strain and lattice-mismatch material systems such as BInGaAs/GaAs [9–12] and B(Al)GaN/6H–SiC [13–15]. In particular, BGaP alloy with 2.1% B composition can be lattice-matched with Si and BGaP could be used for strain compensation to strained GaP/Si heterostructure [16].

Therefore, separate confinement heterostructure (SCH) can be designed using III–V(–N) active layers for application of monolithic integration laser on Si substrate [17]. Liebich et al. have reported a SCH laser composed with GaAsPN multi-quantum well active layer and BGaP (B=3%) cladding layer on Si substrate by metalorganic vapor-phase epitaxy (MOVPE) [18].

B containing III–V semiconductors have been mainly reported by MOVPE growth technique, since obtained elemental B precursors are relatively easy for MOVPE growth in comparison to MBE growth. In case of MBE by using molecular cell, it is not easy to get desired beam flux due to low vapor pressure of solid B as experimentally tried several times by our group and reported by other group [19]. To overcome the above difficulty, an electron beam (EB) gun as the B source to MBE system is introduced. EB evaporation technique has an advantage over standard molecular cell for supplying low vapor pressure source, because of direct heating and low outgas.

In this article, we report epitaxial growth of dilute BGaP alloys by solid-source MBE equipped with EB gun as the B source. Growth condition dependence on B composition is investigated. In addition, immiscibility on dilute BGaP alloys due to the effect of the larger difference between the group-III atomic size of B and Ga is shown and discussed by calculated local strain energy.

## 2. Experimental details

A conventional solid-source MBE apparatus was employed for the growth of dilute BGaP alloys. To obtain high B flux, the EB gun (Oxford Applied Research EGCO4) filled with rod-shaped high purity B (6 N) [20] was used. Ga beam was supplied with group-III SUMO cell filled with metallic Ga (7 N). P<sub>2</sub> beam was supplied with an effusion cell using thermal decomposition of polycrystalline InP wafers (6 N). Beam equivalent pressure (BEP) for B and Ga was fixed

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at  $3.8 \times 10^{-9}$  and  $6.2 \times 10^{-8}$  Torr, respectively. All samples were grown on semi-insulating undoped GaP (001)  $\pm 0.5^\circ$  substrates. Prior to the growth, thermal cleaning was performed at  $630^\circ\text{C}$  under  $\text{P}_2$  beam irradiation. A  $0.1\text{-}\mu\text{m}$ -thick GaP buffer layer at  $580^\circ\text{C}$  under the P-stabilized ( $2 \times 4$ ) surface reconstruction, and then,  $0.1\text{--}0.2\text{-}\mu\text{m}$ -thick BGaP layers were grown under various growth parameters. In order to investigate B incorporation into BGaP layers, we varied on growth temperature from  $380$  to  $580^\circ\text{C}$ , and  $\text{BEP}_{\text{P}_2}/\text{BEP}_{(\text{B}+\text{Ga})}$  ratio (V/III ratio) from  $5$  to  $30$  ( $\text{BEP}_{\text{P}_2}$ :  $0.33\text{--}2.0 \times 10^{-6}$  Torr). The GaP growth rate was fixed at  $0.1\text{ }\mu\text{m/h}$ . The back pressure during crystal growth was approximately  $3.0 \times 10^{-8}$  Torr.

The surface morphology of BGaP layer was observed by atomic-force microscopy (AFM) (SII SPA-400). The B composition was estimated using dynamical simulation and Vegard's law. The perpendicular and parallel lattice constants of the BGaP epitaxial layer were determined from (004) symmetrical and (115) asymmetrical high-resolution X-ray diffractions (HRXRD) (PANalytical) with quadruple-crystal Ge (220) monochromator and X'Pert PRO MRD diffractometer. The lattice constants of free standing BP and GaP were  $4.546$  and  $5.451\text{ }\text{\AA}$  at  $300\text{ K}$ , respectively [21,22].

### 3. Results

Fig. 1 shows the growth temperature dependence of B composition with giving a line of the Arrhenius plot. The V/III ratio was fixed

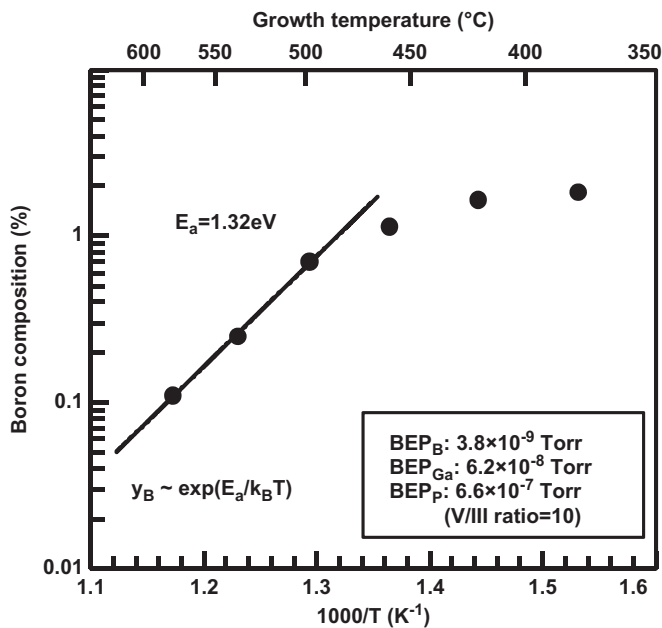


Fig. 1. Growth temperature dependence of B composition in BGaP with Arrhenius plot. The III/V ratio of 10 is kept constant.

at 10 in the present study. The B composition increases with decrease of growth temperature up to  $500^\circ\text{C}$ , and it was found to be saturated with further decrease of growth temperature. The B incorporation process is governed by a thermally activated desorption process of B species. The activation energy  $E_a$  of B desorption was estimated to be  $1.32\text{ eV}$  by using  $y_B = \exp(E_a/kT)$  fitted slope of the line connecting each data point. This observation may be due to the loss of B incorporation into GaP matrix. Fig. 2 illustrates the AFM images of BGaP layers grown at various temperatures. The surface grown at  $500^\circ\text{C}$  was very smooth with  $0.17\text{ nm}$  root-mean-square (RMS) surface roughness; however, the surfaces grown above and below  $500^\circ\text{C}$  were found to be very rough. The surface grown above  $580^\circ\text{C}$  might be compressed (B)GaP alloy with BP alloy due to the difference of lattice constants. On the other hand, the growth surface below  $460^\circ\text{C}$  is developed with poor surface migration of group-III atoms. It is well recognized that atomic surface migration is very important for high crystalline quality. The (004) x-ray rocking curve (XRC) was obtained with higher full-width at half-maximum (FWHM) value at lower growth temperature. XRC FWHM values of samples grown at  $580$ ,  $500$  and  $460^\circ\text{C}$  were  $12.9^\circ$ ,  $13.8^\circ$  and  $17.0^\circ$ , respectively. Despite the low growth temperature, it is possible to obtain a large B composition without significant degradation of crystalline at  $500^\circ\text{C}$ . It is concluded that the optimal growth temperature of dilute BGaP alloys for smooth surface and composition is  $500^\circ\text{C}$ .

Fig. 3 shows the V/III ratio dependence of B composition. The growth temperature was fixed at  $500^\circ\text{C}$ , and GaP surface

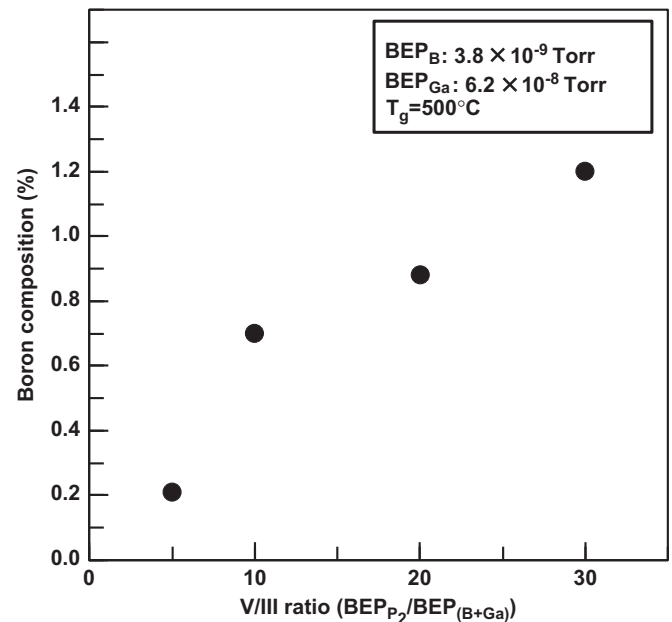


Fig. 3. III/V ratio dependence of B composition in BGaP at  $500^\circ\text{C}$ .

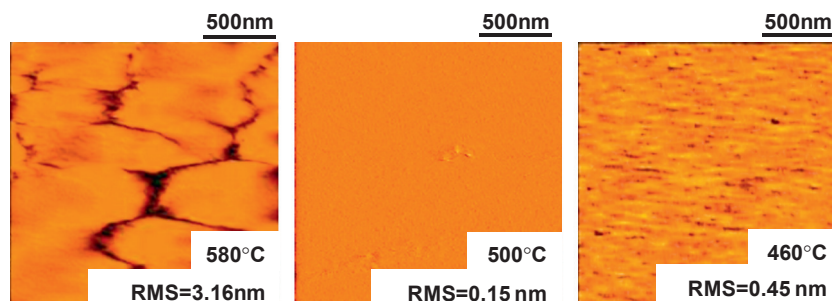


Fig. 2. AFM images of BGaP alloys grown with different growth temperatures: left  $580^\circ\text{C}$ , center  $500^\circ\text{C}$  and right  $460^\circ\text{C}$ .

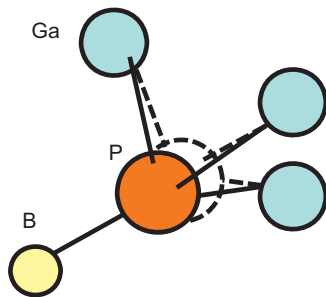
reconstruction of all samples before BGaP growth exhibited  $(2 \times 1)/(2 \times 2)$  reconstruction by reflection high-energy electron diffraction (RHEED) observation. The B composition increases with the increase of the V/III ratio. However, RHEED pattern revealed spot pattern for V/III ratio of 30, which indicated three dimensional growth. In equipment, an optimal GaP growth temperature and V/III ratio are approximately 580 °C and 10, respectively. Thus, V/III ratio of 30 at 500 °C is high. To summarize these points, the growth conditions of dilute BGaP with smooth surface and high B composition were considered appropriate for temperature of 500 °C and the V/III ratio of above 20.

#### 4. Discussion

In case of B incorporation into the GaP matrix, Ga–P bonds are strained because free standing B–P bond length is generally shorter than free standing Ga–P bond length, as illustrated in Fig. 4 for zinc-blend BGaP structure [23]. These values of atomic displacements can be estimated to calculate local strain energy  $E_{\text{strain}}(r_j)$  by valence force-field (VFF) model. The strain energy consists bond-stretching and bond-bending terms which can be written as [23–25]

$$E_{\text{strain}}(r_j) = \sum_{i=1}^4 \frac{3}{8r_{0ji}^2} \alpha_{ji} (r_{ji}^2 - r_{0ji}^2)^2 + \sum_{i=1}^4 \sum_{k=1}^4 \frac{3}{8r_{0ji}r_{0jk}} \beta_{ijk} (r_{ji}^2 - r_{0ji}r_{0jk} \cos \theta_{ijk})^2 \quad (1)$$

where  $i, j$  and  $k$  are the atomic labels,  $r_0$  is the equilibrium free-standing bond length,  $\theta_0$  is equilibrium bond angle,  $r_{ji}$  is the bond vector between atom  $i$  and  $j$ .  $\alpha$  is the bond-stretching constant and  $\beta$  is the bond-bending constant, which are related to the elastic stiffness constant. The strain energy  $E_{\text{strain}}$  is calculated as approximately 1.43 eV without localized effect of B atoms. The parameters and calculated results of bond lengths are shown in Table 1 with AlGaP and InGaP alloys of same impurity



**Fig. 4.** Bond configuration of zinc-blend BGaP structure. Dotted lines and solid lines indicate undoped and B incorporated GaP crystal structure, respectively. The Ga–P bonds are stretched due to B–P bonds which is shorter than Ga–P bond length shown in Table 1.

composition into the GaP matrix. The strain energy  $E_{\text{strain}}$  of BGaP is calculated to be much larger than that of AlGaP (5.44 meV) and InGaP (110 meV) by same method. It indicates that B incorporation into the GaP matrix is very difficult as compared to Al and In incorporation because the strain energy  $E_{\text{strain}}$  is the interaction parameter related immiscibility in thermodynamics [26]. Generally, higher interaction parameter means higher critical temperature and mixing instability at general III–V compounds [27,28].

In the initial B incorporation onto the GaP surface, B–P bonds are assumed to form compared to Ga–P bonds, preferentially, because the B–P single bond energy calculated by cohesive energy is higher than that of GaP [29]. However, BP bonds are metastable or unstable due to strain energy as reported previously. Therefore, dissociation of B–P bonds is caused by Ga displacement and thermal vibration [10]. In addition, atomic effective surface migration length of the MBE growth on substrate surface is short because of high vacuum pressure growth. Therefore, B atoms are assumed to desorb easily from the GaP surface.

A critical point of B incorporation feature was observed from the growth temperature dependence of B composition which is at 500 °C. Fig. 5(a) and (b) shows RHEED patterns along  $[1-10]$  azimuth from surfaces of GaP buffer layer before BGaP growth at 580 and 500 °C, respectively. These patterns demonstrated  $(2 \times 4)$  and  $(2 \times 1)/(2 \times 2)$  reconstructions at 580 and 500 °C, respectively. In general, the P surface coverage of  $(2 \times 1)/(2 \times 2)$  reconstruction (at 500 °C) is higher than that of  $(2 \times 4)$  reconstruction (at 580 °C) [30,31]. Although the supplied V/III ratio was fixed at 10, the virtual V/III ratio on the substrate surface at 500 °C is higher than that of at 580 °C. Therefore, the possibilities of forming and conserving B–P bonds increased with the decrease of growth temperature and increase of the V/III ratio.

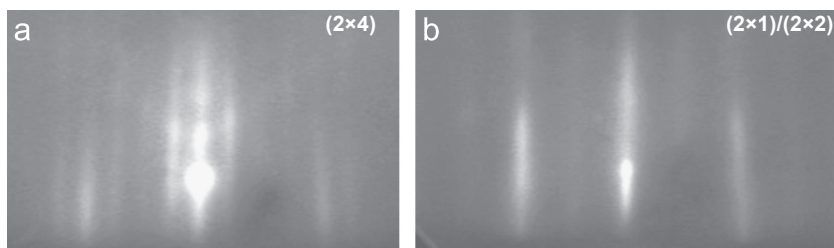
#### 5. Summary

The epitaxial growth of dilute BGaP alloys by solid-source MBE equipped with the EB gun as the B source is demonstrated. The B composition in the BGaP alloys is strongly influenced by growth parameters. B composition for BGaP alloys is found to increase with the decrease of growth temperature and V/III ratio. The growth surfaces obtained below 500 °C and V/III ratio over 30 is degraded, due to decreasing atomic surface migration.

**Table 1**

Force parameters ( $\alpha$ ,  $\beta$ ), free standing bond length ( $r_0$ ) and calculation result ( $r$ ,  $r_{\text{GaP}}$ ) for VFF model.  $r_{\text{GaP}}$  means calculated bond length of GaP in case of impurities atoms (B, Al, In) incorporation.

	$\alpha$ (N/m)	$\beta$ (N/m)	$r_0$ (nm)	$r$ (nm)	$r_{\text{GaP}}$ (nm)
GaP	44.49	10.70	0.2360	–	–
BP	69.27	30.59	0.1948	0.2072	0.2471
AlP	47.29	9.080	0.2367	0.2311	0.2360
InP	43.04	6.241	0.2541	0.2500	0.2317



**Fig. 5.** RHEED patterns along  $[1-10]$  azimuth from surface of GaP buffer layer before BGaP growth at (a) 580 °C and (b) 500 °C.

The B incorporation into the GaP matrix is difficult as compare to other group-III atoms (Al or In), and B–P bonds in the GaP matrix are unstable due to highly strained bonds by VFF calculation. Therefore, the formation and conservation possibilities of B–P bonds on the surface are increased with the decrease of growth temperature and the increase of the V/III ratio. Future study is carried on for increasing the B composition to perform strain compensation for GaP/Si templates.

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## References

- [1] H. Yonezu, *Semiconductor Science and Technology* 17 (2002) 763.
- [2] K. Yamane, T. Kawai, Y. Furukawa, H. Okada, A. Wakahara, *Journal of Crystal Growth* 312 (2010) 2179.
- [3] Y. Takagi, Y. Furukawa, A. Wakahara, H. Kan, *Journal of Applied Physics* 107 (2010) 053506.
- [4] B. Kunert, K. Volz, J. Koch, W. Stolz, *Journal of Crystal Growth* 298 (2007) 121.
- [5] K. Umeno, Y. Furukawa, A. Wakahara, R. Noma, H. Okada, H. Yonezu, Y. Takagi, H. Kan, *Journal of Crystal Growth* 311 (2009) 1748.
- [6] K. Umeno, Y. Furukawa, N. Urakami, R. Noma, S. Mitsuyoshi, A. Wakahara, H. Yonezu, *Physica E* 42 (2010) 2772.
- [7] N. Urakami, K. Umeno, Y. Furukawa, F. Fukami, S. Mitsuyoshi, H. Okada, H. Yonezu, A. Wakahara, *Physica Status Solidi C* 8 (2011) 263.
- [8] Y. Song, M.L. Lee, *Applied Physics Letters* 100 (2012) 251904.
- [9] J.F. Geisz, D.J. Friedman, J.M. Olson, S.R. Kurtz, R.C. Reedy, A.B. Swartzlander, B.M. Keyes, A.G. Norman, *Applied Physics Letters* 76 (2000) 1443.
- [10] M.E. Groenert, R. Averbek, W. Höslér, M. Schuster, H. Riechert, *Journal of Crystal Growth* 264 (2004) 123.
- [11] P. Rodriguez, L. Auvray, H. Dumont, J. Dazord, Y. Monteil, *Journal of Crystal Growth* 298 (2007) 81.
- [12] F. Saidi, R. Hamila, H. Maaref, Ph. Rodriguez, L. Auvray, Y. Monteil, *Journal of Alloys and Compounds* 491 (2010) 45.
- [13] T. Takano, M. Kurimoto, J. Yamamoto, M. Shibata, Y. Ishihara, M. Tsubamoto, T. Honda, H. Kawanishi, *Physica Status Solidi A* 180 (2000) 231.
- [14] T. Akasaka, T. Makimoto, *Applied Physics Letters* 88 (2006) 041902.
- [15] G. Orsal, N. Maloufi, S. Gautier, M. Alnot, A.A. Sirenko, M. Bouchaour, A. Ougazzaden, *Journal of Crystal Growth* 310 (2008) 5058.
- [16] B. Kunert, S. Zinnkann, K. Volz, W. Stolz, *Journal of Crystal Growth* 310 (2008) 4776.
- [17] B. Kunert, S. Liebich, A. Beyer, R. Fritz, S. Zinnkann, K. Volz, W. Stolz, *Journal of Crystal Growth* 315 (2011) 28.
- [18] S. Liebich, M. Zimprich, A. Beyer, C. Lange, D.J. Franzbach, S. Chatterjee, N. Hossain, S.J. Sweeney, K. Volz, B. Kunert, W. Stolz, *Applied Physics Letters* 99 (2011) 071109.
- [19] V.K. Gupta, M.W. Koch, N.J. Watkins, Y. Gao, G.W. Wicks, *Journal of Electronic Materials* 29 (2001) 1387.
- [20] Product information from Yamanaka Ceradine, Inc. <<http://www.yepc.co.jp/eng/>>.
- [21] A. Zaoui, F. El Haj Hassan, *Journal of Physics: Condensed Matter* 13 (2001) 253.
- [22] I. Vurgaftman, J.R. Meyer, L.R. Ram-Mohan, *Journal of Applied Physics* 89 (2001) 5815.
- [23] O. Rubel, I. Németh, W. Stolz, K. Volz, *Physical Review B* 78 (2008) 075207.
- [24] R.M. Martin, *Physical Review B* 1 (1970) 4005.
- [25] J.L. Martins, A. Zunger, *Physical Review B* 30 (1984) 6217.
- [26] T. Takayama, M. Yuri, K. Itoh, T. Baba, J.S. Harris Jr., *Journal of Applied Physics* 88 (2000) 1104.
- [27] K. Onabe, *Japanese Journal of Applied Physics* 22 (1983) 287.
- [28] T. Takayama, M. Yuri, K. Itoh, T. Baba, J.S. Harris Jr., *Journal of Crystal Growth* 222 (2001) 29.
- [29] W.A. Harrison, *Electronic Structure and the Properties of Solids*, W.H. Freeman and Company, United States of America, 1980.
- [30] O. Pulci, W.G. Schmidt, F. Bechstedt, *Physica Status Solidi A* 184 (2001) 105.
- [31] L. Töben, T. Hannappel, K. Möller, H.-J. Crowth, C. Pettenkofer, F. Willig, *Surface Science* 494 (2001) L755.