HTML ABSTRACT + LINKS

Effects of Br and Cl on organometallic vapor phase epitaxial growth and ordering in GaInP

A. D. Howard, L. W. Rieth, D. C. Chapman, R. R. Wixom, and G. B. Stringfellow[a)]
Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112

B. J. Kim and T. Y. Seong
Department of Materials Science and Engineering, Kwangju Institute of Science and Technology, Kwangju 506-712 Korea

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CuPt ordering in GaInP has significant effects on the electrical and optical properties. In fact, band gap reductions as large as 160 meV are potentially useful for devices. Thus, control of ordering is important. This has led to the investigation of surfactants that affect the surface processes during growth with little incorporation into the solid. A potentially interesting class of surfactant elements are those from group VII, that are known not to be incorporated during growth, but to change the dynamics of surface processes. This article describes the results of the addition of Cl and Br during the organometallic vapor phase epitaxial growth of GaInP. The addition of Br in small concentrations is observed to systematically decrease the amount of CuPt ordering observed directly via transmission electron diffraction and photoluminescence measurements. A ratio of Br/III of 0.042 is found to virtually eliminate ordering. The reduction in order parameter is not found to correspond to a decrease in the 405 nm peak measured during *in situ* surface photoabsorption measurements. This indicates that a change in surface reconstruction is not responsible for the decrease in order parameter. However, both Cl and Br are found to significantly roughen the surface morphology. Atomic force microscopy shows that facets are formed that increase in height and angle to the (001) growth surface as the surfactant concentration increases. This is postulated to be the origin of the reduction in order parameter, since previous studies have indicated that an intentional misorientation of the substrate in either the A or B direction leads to a decrease in order parameter. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1643783]

INTRODUCTION

GaInP grown by organometallic vapor phase epitaxy (OMVPE) is one of the most useful III/V semiconductor alloys. It is used in the highest efficiency light emitting diodes[1] and solar cells.[2] The GaInP/GaAs system is also becoming more widely used for the highest performance electronic switching devices.[3]

A striking feature of GaInP, along with other III/V alloys, is that the properties, for a fixed solid composition, are dependent on the growth conditions.[4] This is because a particular microstructure, termed CuPt ordering, results in, for example, a significant decrease in the band gap energy, as compared with that of alloys with a random distribution of the Ga and In atoms (the disordered alloy). In fact, a 160 meV reduction in band gap energy has been observed in GaInP that is only partially ordered, lattice matched to GaAs.[5] The microstructure, and hence the band gap energy, is dependent on growth parameters such as growth rate[6] and temperature.[7] More significantly, recent work has demonstrated that surfactants, added in minute quantities during OMVPE growth, can also cause disordering of GaInP.[8] For example, a heterostructure can be created where the material in both layers is GaInP lattice matched to GaAs. By adding a small amount of Sb to the surface during growth, the heterostructure can be made to have a band gap difference between the two layers of 135 meV.[8]

Two mechanisms have been observed to cause disordering when surfactants are added to the system. For Sb[8] and N,[9] the disordering mechanism is related to a change in the surface reconstruction of the nominally (001) GaInP. For Te, disordering appears to be related to an increase in the step velocity.[8] High step velocities hinder Ga/In exchange at the advancing step during normal OMVPE growth, similar to the disordering induced by the use of very high growth rates.[6] The surfactants N,[9] Sb,[8] As,[8] Bi,[8] and Te,[8] have been systematically studied in GaInP.

It is very likely that surfactants sometimes inadvertently present during growth have similar effects that have been ignored in the past. One class of such potential surfactants is the halides. Cl is often used as a transporting agent during epitaxial growth.[10] It is also sometimes used during OMVPE growth.[11] Both Cl and Br have been added to OMVPE growth systems to increase the selectivity of growth on patterned substrates.[12,13] In addition CX_4, where X can be Cl or Br, is used extensively for C doping of GaAs, AlGaAs, GaInAs, and InP.[14,15] Both CCl_4 and CBr_4 have been observed to increase the lateral velocity of steps during OMVPE growth of GaAs.[16] This suggests that they may affect ordering in GaInP.

[a)]Author to whom correspondence should be addressed; electronic mail: stringfellow@coe.utah.edu

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This paper describes the effects of the addition of CCl_4 and CBr_4 during the OMVPE growth of GaInP. The surface morphology and solid composition are both dramatically affected by the addition of CCl_4. Addition of CBr_4 has little effect on solid composition, but does lead to roughening. Most importantly, for GaInP grown lattice matched to GaAs substrates, the addition of Br is found to produce a systematic reduction in the CuPt order parameter and the band gap energy.

EXPERIMENT

GaInP:Br and GaInP:Cl samples were grown by OMVPE in a horizontal flow, infrared heated, atmospheric pressure reactor. Trimethylgallium (TMGa) and trimethylindium (TMIn) were used as the group III sources and phosphine (PH_3), carbon–tetrachloride (CCl_4) and carbon–tetrabromide (CBr_4) were used as the V and surfactant sources, respectively. The carrier gas was H_2 purified with an Aeronex GateKeeper filter. All growths were done at 620 °C and the growth rate was 2 μ/h. The V/III ratio was kept constant at 80. In a typical sample, a 150–200 nm thick GaInP layer was grown followed by a 250 nm thick GaInP:Br layer. For the Br study, the CBr_4/III ratio was varied from 0.004 to 0.042. Growth was done on singular (001) GaAs substrates.

Samples were then characterized by x-ray diffraction and photoluminescence (PL). PL was done at 20 K, excited with the 488 nm line of an Ar^+ laser with a power of 10 mW focused to a 0.5 mm^2 spot size. The order parameter was estimated quantitatively from the PL peak energy and qualitatively using transmission electron microscopy (TEM). The degree of order (S) was calculated for the undoped GaInP samples as

$$S=\sqrt{\frac{2005-\text{PL peak energy at 20 K}}{471}}.$$

For TEM experiments, two orthogonal $\langle 110\rangle$ cross-section specimens were prepared using standard procedures and finished by Ar^+ ion thinning with the specimen cooled to approximately 77 K. TEM and transmission electron diffraction (TED) examination were performed using a JEM 2010 instrument operated at 200 kV. The thicknesses of the thin foils examined by TEM were in the range 150–400 nm.

Atomic force microscopy (AFM) was done using a Digital Instrument Dimension 3000 system. Scans were done in tapping mode using etched Si tips with a 5 nm radius.

RESULTS AND DISCUSSION

The addition of Cl produces a dramatic reduction in In incorporation into the GaInP, as seen in Fig. 1. In this plot, the In distribution coefficient, $(x^s_{\mathrm{In}}/x^s_{\mathrm{Ga}})/(p^v_{\mathrm{In}}/p^v_{\mathrm{Ga}})$,[17] is plotted versus the ratio of 4 times the input partial pressure of either CCl_4 or CBr_4 to the input partial pressure of the In precursor. In this plot, the intercept, where the In distribution coefficient goes to zero, is equal to the reciprocal of the number of In atoms removed from the surface per Cl or Br atom in the vapor. For Cl, using just the data points at chlorine/In ratios of 0 and 1.6 yields a value of 1/2. In other words, each molecule of CCl_4 introduced into the vapor removes two atoms of In from the surface during growth. This is similar to previous observations for GaInAs and InP: The addition of Cl was observed to selectively remove In from the surface.[12,18] For these growth conditions, the effect of Br is much smaller, as seen in Fig. 1; however, the highest ratio of the partial pressures of CBr_4 to TMIn is <0.01. This contrasts with the data of Arakawa *et al.*,[13] who reported a significant decrease in In incorporation caused by the addition of CBr_4 in AlGaInAs alloys grown by OMVPE at a temperature of 680 °C. They reported that the Br removed only the In atoms from the surface, with each CBr_4 molecule removing two In atoms. Keiper *et al.*[19] reported that Br selectively removes In from InGaAs and Tateno *et al.*[15] reported a reduction in growth rate for CBr_4 addition during GaAs and AlGaAs growth by OMVPE. Our results for GaInP show that each molecule of CCl_4 removes two atoms of In from the surface, while for these conditions Br has no observable effect on In incorporation.

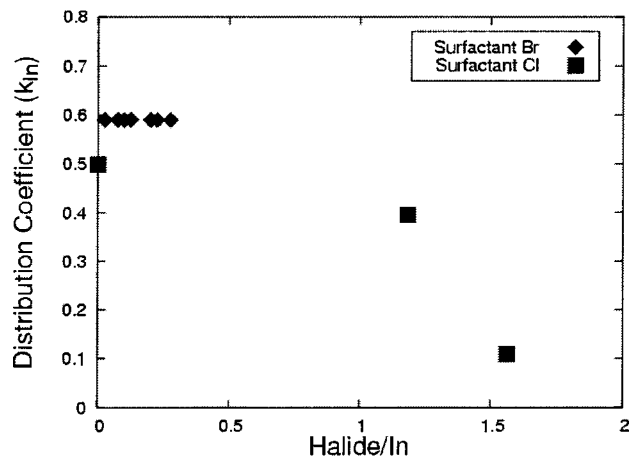

FIG. 1. In distribution coefficient $(x^s_{\mathrm{In}}/x^s_{\mathrm{Ga}})/p^v_{\mathrm{In}}/p^v_{\mathrm{Ga}})$ vs the ratio of four times the input partial pressure of CBr_4 to the input partial pressure of the In precursor.

Both CCl_4 and CBr_4 produce significant roughening of the surface during OMVPE growth, as seen in the AFM micrographs reproduced as Fig. 2. These measurements indicate that the rms roughness of the surface increases to 40–50 nm when CBr_4 is added to the vapor with a Br/III ratio of 0.03–0.04. For GaInP grown without Br, the roughness is more than 1 order of magnitude smaller (typically< 1 nm). The AFM micrographs indicate the presence of a high density of hillocks with faceted sidewalls. A similar roughening of the surface has been reported for GaAs grown with CCl_4 added.[20]

The faces of the pyramidal structures formed during growth in the presence of Br can be identified by simply determining the angle between adjacent points in an AFM scan. Specifically, the 512 data points from each of five line scans in the 8×8 μm AFM images were used to create the histograms shown in Fig. 3. The data shown are for scans in the $[\bar{1}10]$ direction. It is seen that the pyramidal angles increase significantly with increasing CBr_4 in the vapor. In fact, symmetric lobes are generated with an angle that increases with increasing CBr_4 concentration. For the highest

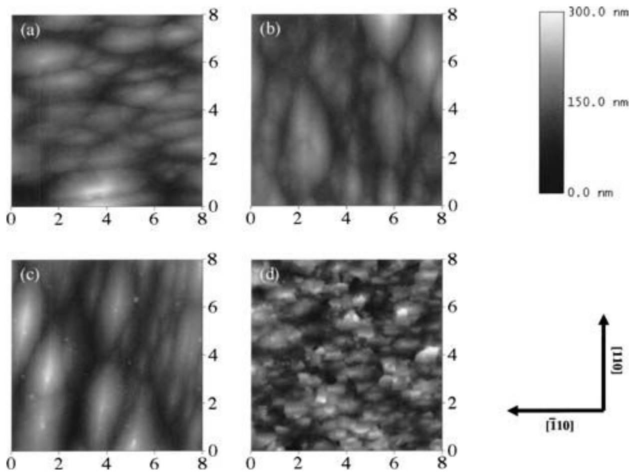

FIG. 2. AFM images of GaInP samples with four values of CBr_4 partial pressure: (a) 0.004, (b) 0.011, (c) 0.034, and (d) 0.042.

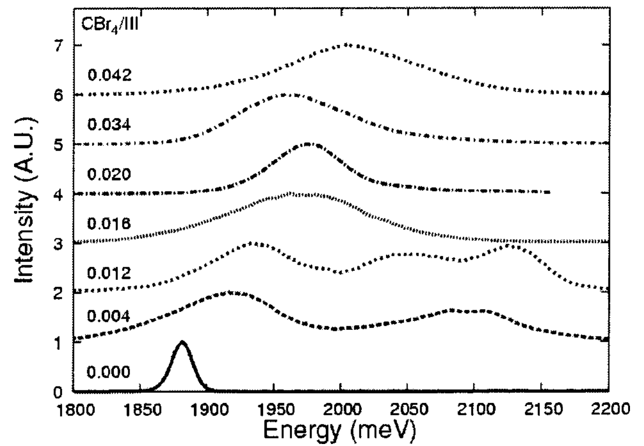

FIG. 4. Low temperature photoluminescence (PL) spectra for several ratios of CBr_4/III in the vapor. The lowest energy peak is due to the ordered GaInP.

concentration, the lobes occur at 7°–8° from the (001) growth plane and there are a significant number of planes generated with angles exceeding 10°. For scans in the orthogonal scan direction, a significant increase in the number of planes at high angles is also observed. For the highest CBr_4/III ratio of 0.042, the fraction of planes with angles of 10° and higher is even higher than for the $[\bar{1}10]$ scans.

The 20 K PL results for samples with several values of CBr_4 concentration in the vapor during growth are shown in Fig. 4. The lowest energy peaks are due to the ordered GaInP layers. They show a steady progression to higher energy as the amount of CBr_4 added during growth is increased. X-ray diffraction scans show clearly that all of the layers are lattice matched to the GaAs substrates. Thus, the increase in PL peak energy is attributed to a decrease in the degree of CuPt order.

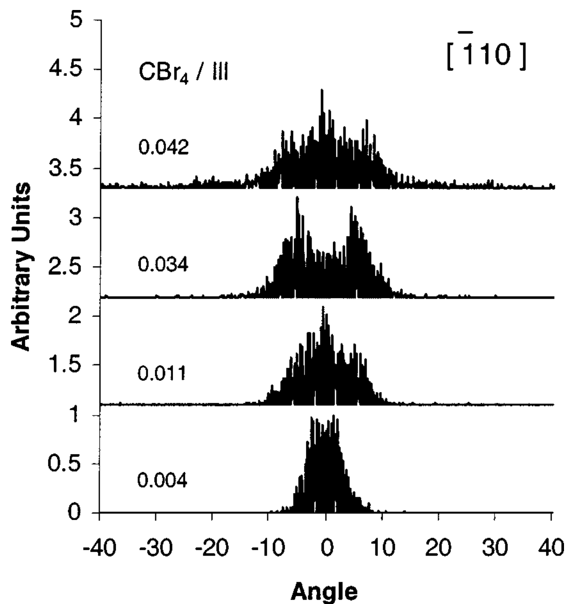

FIG. 3. Histogram for $[\bar{1}10]$ AFM scans showing the angles of the facets produced at the edges of the pyramids formed on the surface for four CBr_4/III ratios.

One other feature of the PL spectra is the presence of peaks with energies exceeding 2 eV, the band gap of completely disordered GaInP lattice matched to GaAs, for the layers with low CBr_4/III ratios in the vapor. The origin of these peaks has not been unambiguously determined. However, similar high energy peaks are observed in GaInP grown with DMHy added during growth. The DMHy removes In from the system due to parasitic reactions,[9] producing Ga-rich layers near the substrate. The TEM cross sections appear to indicate the presence of a distinguishable layer near the substrate for some samples grown with CBr_4 present.

The degree of order (S), obtained from the PL spectra for GaInP layers lattice matched to the GaAs substrates is plotted versus the CBr_4/III ratio in the vapor in Fig. 5. The data show a clear decrease in the degree of order with increasing concentration of CBr_4 in the vapor. Ordering is nearly completely destroyed in the sample grown using a CBr_4/III ratio of 0.042. This result is supported by TED results. The TED patterns for samples with CBr_4/III ratios of 0.034 and 0.042 are shown in Figs. 6(a) and 6(b). It should be noted that the degree of order can be estimated qualitatively from the intensity ratio of the ordered superspots to the zincblende

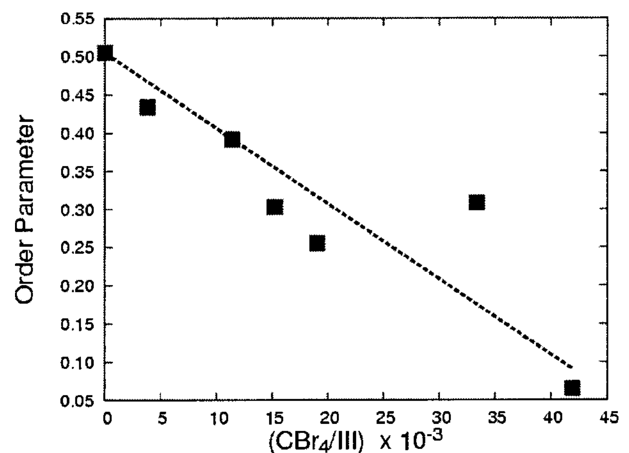

FIG. 5. Degree of order, from the PL peak energy, versus the CBr_4/III ratio in the vapor.

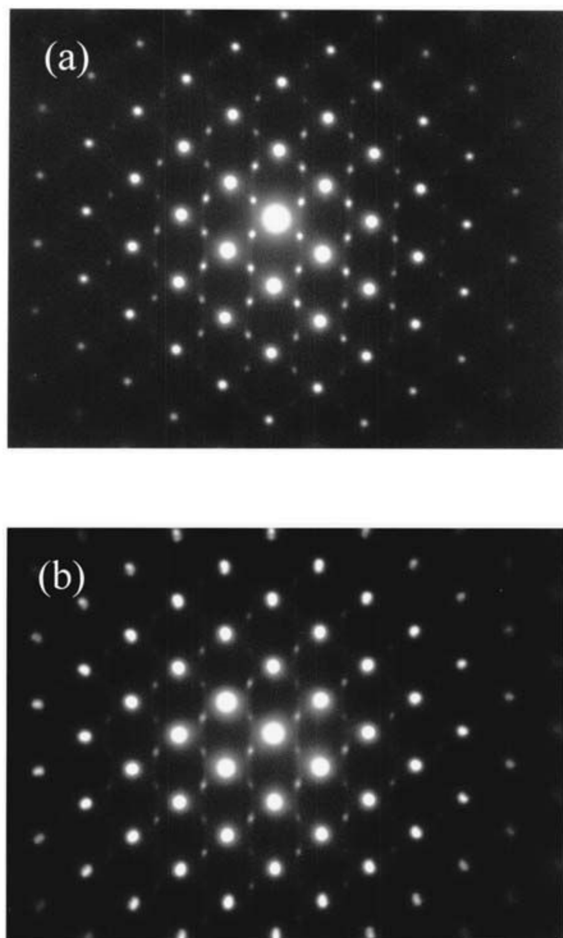

FIG. 6. Cross sectional transmission electron diffraction patterns showing the CuPt order induced superlattice spots for two GaInP samples with CBr_4/III ratios of 0.034 (a) and 0.042 (b). The order parameters from low temperature PL spectra are 0.308 for (a) and 0.065 for (b), which is consistent with the reduction in superspot intensity observed.

spots. The exposure was increased for the sample with CBr_4/III=0.042 [Fig. 6(b)] due to the weak ordering. This gives stronger zincblende spots. Clearly, the intensity of the superspots, due to CuPt ordering, as compared to the zincblende spots, decreases markedly as the Br concentration increases. Consistent with the PL data, the TED results for the sample with CBr_4/III=0.042 [Fig. 6(b)] shows that the ordering is nearly completely eliminated.

At this point, an important question relates to the mechanism by which the addition of Br to the system during OMVPE growth decreases the degree of order. Two main mechanisms by which surfactants disorder GaInP have been identified, as discussed in the Introduction: a decrease in the concentration of P dimers (thermodynamic) or an increase in step velocity (kinetic).

The results of *in situ* surface photoabsorption measurements indicate that the addition of Br to the system after growth of a GaInP layer has no affect on the peak at 405 nm, due to the $[\bar{1}10]$P dimers which drive the ordering process.[4,8] This indicates that the displacement of P dimers by Br is not the disordering mechanism. Other groups have reported that the reconstruction of As-terminated (001) GaAs $(2\times n)$ surfaces is not affected by chlorine adsorption.[20,21]

The step velocity is, of course, controlled by the ratio of growth rate to step density. The increasing angle of the pyramid sides with increasing Br in the vapor suggests that the step velocity is actually decreasing as Br is added to the system. Thus, the kinetic mechanism, described above, must also be eliminated from consideration.

There is one additional disordering mechanism that should be considered in this case, and that is disordering due to surface roughness. The CuPt ordering mechanism is dependent on having an ordered array of $[\bar{1}10]$P dimers on the surface.[22,23] Roughening of the surface would, thus, be expected to interfere with ordering. More specifically, it is well established that misorientation of the growth surface from (001) by more than a few degrees gives a decrease in the order parameter[24] in GaInP grown by OMVPE. Thus, for Br, which roughens the surface during growth, a third possible disordering mechanism is related to the roughness and/or the orientations of the facets formed on the sides of the hillocks during growth. As seen in Fig. 3, examination of the AFM images shows a clear increase in the misorientation of the pyramidal surfaces from (001) with increasing Br concentration in the vapor. The ordering was reported[24] to decrease markedly for misorientation angles of $>6°$, and to virtually disappear for misorientation angles of 10° or higher in either the [110] or $[\bar{1}10]$ direction. Thus, the decrease in order parameter due to the addition of Br during growth is most likely due to some combination of increasing roughness and the increasingly dominant pyramidal structure formed as a result of the roughening.

An open question is why Br and Cl cause an increase in roughness and the pyramidal growth. One possibility is that Br gathers at step edges, increasing the Ehrlich–Schwoebel (ES) barrier. It has been established that the ES barrier results in "slope selection" during epitaxial growth by creation of an uphill diffusion bias. The ES barrier inhibits diffusion of adatoms from the top of two-dimensional islands, resulting in mound formation[25,26] and roughening of the surface. The slope of these growing mounds will continually increase, until mass transport off of the mounds completely compensates the uphill current and a stable slope is created.[27] Growth will then occur via the step-flow mode on these quasivicinal surfaces.

SUMMARY

In summary, Cl and Br are both found to have significant effects on the OMVPE growth process and the properties of the resultant GaInP epitaxial layers. Cl is found to lead to the removal of In atoms from the surface, resulting in a marked decrease in the In distribution coefficient during growth. The results are interpreted to indicate that each Cl atom added to the system during growth results in the removal of two In atoms. The effect of Br on the Ga/In ratio in the solid for the conditions used in these experiments was observed to be negligible; however, the highest CBr_4 concentrations represented only 4% of the group III atoms present during growth. The addition of either CCl_4 and CBr_4 was shown to result in a significant roughening of the surface morphology, with the formation of pyramids having faces with increasing angles to

the (001) surface. The major conclusion of this work is that the addition of CBr_4 during OMVPE growth results in a reduction in the degree of CuPt ordering in the GaInP layers lattice matched to the GaAs substrates. SPA data indicate that this is not due to a reduction in the concentration of P dimers on the surface. The mechanism due to increasing step velocity is also eliminated because the increasingly rough surface as the concentration of Br in the vapor is increased results in a decrease in the average step velocity, since the growth rate was unchanged. The results suggest a third mechanism, namely that the roughness, in particular the orientations of the surfaces at the edges of the hillocks on which growth occurs, becomes higher with increasing Br concentration in the vapor. Since, the degree of order has previously been found to decrease with increasing misorientation angle, the results indicates that the disordering due to Br addition during growth is due to the increasing roughness produced.

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[1] G. B. Stringfellow and M. G. Craford, *High Brightness Light Emitting Diodes* (Academic, San Diego, 1997).
[2] T. Katamoto, E. Ideda, and H. Kurita, Appl. Phys. Lett. **70**, 381 (1997).
[3] T. P. Chin, J. C. P. Shang, J. M. Woodall, W. L. Chen, G. I. Haddad, C. Parks, and A. K. Ramdas, J. Vac. Sci. Technol. B **13**, 750 (1995); J. Shirakashi, T. Azuma, F. Fukuchi, M. Konagai, and K. Takahashi, J. Cryst. Growth **150**, 585 (1995).
[4] G. B. Stringfellow, in *Thin Films: Heteroepitaxial Systems*, edited by W. K. Liu and M. Santos (World Scientific, Singapore, 1998), Chap. 2.
[5] L. C. Su, S. T. Pu, G. B. Stringfellow, J. Christen, H. Selber, and D. Bimberg, Appl. Phys. Lett. **62**, 3496 (1993).
[6] L. C. Su, I. H. Ho, and G. B. Stringfellow, J. Appl. Phys. **75**, 5135 (1994).
[7] L. C. Su, I. H. Ho, and G. B. Stringfellow, J. Cryst. Growth **146**, 558 (1995).
[8] G. B. Stringfellow, J. K. Shurtleff, R. T. Lee, C. M. Fetzer, and S. W. Jun, J. Cryst. Growth **221**, 1 (2000).
[9] D. C. Chapman, L. W. Rieth, G. B. Stringfellow, J. W. Lee, and T. Y. Seong (unpublished).
[10] G. Beuchet, in *Lightwave Communications Technology*, edited by W. T. Tsang (Academic, San Diego, 1985), Chap. 4.
[11] G. B. Stringfellow, *Organometallic Vapor Phase Epitaxy: Theory and Practice* (Academic, San Diego, 1999), pp. 514–518.
[12] K. Naniwae, K. Kurihara, K. Nishi, and S. Sugou, J. Cryst. Growth **248**, 400 (2003).
[13] S. Arakawa, M. Itoh, and A. Kasukawa, J. Cryst. Growth **221**, 183 (1992).
[14] T. F. Kuech and J. M. Redwing, J. Cryst. Growth **145**, 382 (1994); N. I. Buchan, T. F. Kuech, G. Scilla, and F. Cardone, *ibid.* **110**, 405 (1991).
[15] K. Tateno, Y. Kohama, and C. Amano, J. Cryst. Growth **172**, 5 (1997).
[16] S. I. Kim, M. S. Kim, S. M. Hwang, B. D. Min, C. S. Son, E. K. Kim, and K. K. Min, J. Cryst. Growth **170**, 665 (1997).
[17] G. B. Stringfellow, *Organometallic Vapor Phase Epitaxy: Theory and Practice* (Academic, San Diego, 1999), p. 78.
[18] K. Hong and D. Pavlidis, J. Electron. Mater. **25**, 449 (1996).
[19] D. Keiper, R. Westphalen, and G. Landgren, J. Cryst. Growth **197**, 25 (1999).
[20] Q. Fu, L. Li, M. J. Begarney, B. K. Han, D. C. Law, and R. F. Hicks, J. Phys. IV **9**, Pr8-3 (1999).
[21] S. M. Mokler, P. R. Watson, L. Ungier, and J. R. Arthur, J. Vac. Sci. Technol. B **10**, 2371 (1992).
[22] R. Ososio, J. E. Bernard, S. Froyen, and A. Zunger, Phys. Rev. B **45**, 11173 (1992).
[23] S. Matsumura, N. Kuwano, and K. Oki, Jpn. J. Appl. Phys., Part 1 **29**, 699 (1990).
[24] H. Murata, S. H. Lee, I. H. Ho, and G. B. Stringfellow, J. Vac. Sci. Technol. B **14**, 3013 (1996).
[25] C. Orme, M. D. Johnson, K.-T. Leung, B. G. Orr, P. Smilauer, and D. Vvedensky, J. Cryst. Growth **150**, 128 (1995).
[26] B. G. Orr, M. D. Johnson, C. Orme, J. Sudijono, and A. W. Hunt, Solid-State Electron. **37**, 1057 (1994).
[27] S. Schinzer, S. Kohler, and G. Reents, Eur. Phys. J. B **15**, 161 (2000).

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