

# Effect of growth rate on step structure and ordering in GaInP

Y. S. Chun, S. H. Lee, I. H. Ho, and G. B. Stringfellow<sup>a)</sup>

Departments of Materials Science and Engineering and Electrical Engineering, University of Utah, Salt Lake City, Utah 84112

(Received 9 August 1996; accepted for publication 16 October 1996)

CuPt ordering is widely observed in GaInP epitaxial layers grown by organometallic vapor phase epitaxy. The formation of this spontaneously ordered structure during epitaxial growth is intimately related to the atomic-scale physical processes occurring on the surface, specifically surface reconstruction and the attachment of atoms at steps. For growth on singular (001) GaAs substrates the surface structure, measured using atomic force microscopy, is seen to consist of small islands surrounded by either monolayer or bilayer steps. An increase in the growth rate from 0.25 to 2.0  $\mu\text{m/h}$  with a constant tertiarybutylphosphine partial pressure at 670 °C has no effect on either the degree of order or the step structure. Only the step spacing is observed to change. It decreases systematically as the growth rate is increased, following an approximate  $1/(\text{growth rate})^{1/2}$  dependence. As the growth rate increases, the time atoms have to rearrange before being frozen due to coverage by the next layer decreases. This leads directly to the dependence observed. These observations are consistent with previous observations which appear to show a close correlation between step structure (monolayer versus bilayer) and ordering, although the causative factor has not been determined. © 1997 American Institute of Physics. [S0021-8979(97)06802-3]

## INTRODUCTION

The CuPt ordered structure is typically formed in  $\text{Ga}_{0.52}\text{In}_{0.48}\text{P}$  layers grown on singular (001) oriented GaAs substrates by organometallic vapor phase epitaxy (OMVPE).<sup>1</sup> This phenomenon involves the formation of a monolayer superlattice structure along a particular  $\{111\}$  crystallographic plane. Theoretically, the periodic surface stresses resulting from the formation of  $[\bar{1}10]$  rows of  $[\bar{1}10]$ -oriented phosphorus dimers on the  $(2\times 4)$  reconstructed (001) surface result in a segregation of the subsurface group III atoms into alternating  $[\bar{1}10]$  rows of In and Ga atoms.<sup>2</sup> This results in the formation of the two B variants of the CuPt structure, with ordering on the  $(\bar{1}11)$  and  $(1\bar{1}1)$  planes, typically observed for layers grown by OMVPE. Surface steps are generally believed to be important factors in the epitaxial growth process. They may also be important in the formation of the CuPt ordered structure during epitaxial growth.<sup>3</sup>

The physical nature of the steps on the surface has, until recently, been largely unexplored, especially for growth by OMVPE. However, recent atomic force microscopy (AFM) studies indicate that the step structure strongly depends on the growth conditions. Kasu and Kobayashi<sup>4</sup> reported step bunching for GaAs layers grown by OMVPE on vicinal (001) substrates. Step bunching strongly depends on growth temperature, with no bunching at temperatures above 670 °C or below 550 °C. For GaAs, step bunching has also been observed to occur during annealing.<sup>5</sup> The superstep size was found to increase markedly as the annealing temperature was increased from 450 to 700 °C. GaInP layers grown by OMVPE on vicinal (001) GaAs substrates misoriented toward  $[\bar{1}10]$  were also found to have supersteps on the surface at temperatures in the range from 570 to 720 °C.<sup>6</sup> The superstep spacing was found to increase systematically with increasing temperature. The steps observed on the surfaces of

GaInP layers grown on singular (001) GaAs substrates are observed to change from monolayers at low temperatures of 520 and 570 °C to bilayers at 670 °C and above.<sup>8</sup> The step spacing is also observed to increase with increasing growth temperature.

The input phosphorus partial pressure is also found to affect the step structure for GaInP grown by OMVPE.<sup>7-9</sup> Mainly bilayer steps are observed on GaInP layers grown at 670 °C on singular (001) GaAs substrates with high phosphorus partial pressures and mainly monolayer steps are formed at low phosphorus partial pressures.<sup>7,8</sup> Bunching of steps is observed for GaInP grown on vicinal (001) substrates at low P partial pressures. The resulting supersteps are found to disappear at higher P partial pressures. This occurs at the approximate values at which the individual steps change from monolayers to bilayers on singular (001) substrates.<sup>9</sup> The degree of order observed in GaInP layers grown by OMVPE is also found to vary with the temperature and P partial pressure during growth. Murata *et al.*<sup>7</sup> observed that the degree of order decreases with increasing temperature in the range from 620 to 720 °C, a phenomenon that they interpreted as due to the decrease in the density of  $[\bar{1}10]$  P dimers, characteristic of the  $(2\times 4)$ -like surface reconstruction, with increasing growth temperature. They also found that below 620 °C, the degree of order decreases as the growth temperature decreases, even though the concentration of  $[\bar{1}10]$  P dimers on the surface increases. This was interpreted by Murata *et al.*<sup>10</sup> as due to formation of a second P layer in the "excess P" surface phase. An alternate interpretation is that this is due to kinetic effects.<sup>7</sup>

The degree of order was also observed to decrease markedly with decreasing input phosphorus partial pressure for both tertiarybutylphosphine (TBP) and  $\text{PH}_3$ . This is correlated with a decrease in the surface photoabsorption signal due to the  $[\bar{1}10]$  P dimers on the  $(2\times 4)$ -like surface.<sup>7-9</sup>

To summarize, it is believed that the formation of the  $(2\times 4)$ -like surface reconstruction is a key factor in the spontaneous formation of the CuPt ordered structure during the

<sup>a)</sup>Electronic mail: stringfellow@ee.utah.edu

OMVPE growth of  $\text{Ga}_{0.52}\text{In}_{0.48}\text{P}$ . However, the close correlation of the degree of order and the step structure suggests that the surface steps may also play an important role.

The growth rate is another parameter that has been found to affect the ordering process. Cao *et al.*<sup>11</sup> demonstrated that very high OMVPE growth rates of  $12 \mu\text{m/h}$  produced nearly completely disordered GaInP. This is easily explained in terms of kinetic factors, i.e., the surface atoms have insufficient time to reorganize into the ordered structure at these high growth rates. On the other hand, Kurtz *et al.*<sup>12</sup> and Su *et al.*<sup>13</sup> reported that the band-gap energy increased (the degree of order decreased) at very low growth rates when the layers were grown with a constant V/III ratio. This was attributed to a subsurface disordering (or annealing) process. The degree of order of GaInP grown on GaAs substrates misoriented toward (111)B or (111)A was also observed to decrease for low growth rates at a constant  $\text{PH}_3$  flow rate, although the changes were smaller in magnitude than when the V/III ratio was held constant.<sup>14</sup> No studies of the effect of growth rate on the surface structure have been reported.

This paper is concerned with the effects of growth rate on ordering and step structure, observed using atomic force microscopy (AFM) techniques, formed for  $\text{Ga}_{0.52}\text{In}_{0.48}\text{P}$  layers grown by OMVPE. The change in growth rate is found to be linked only with the step length on the surfaces of GaInP layers grown on singular (001) GaAs substrates. The growth rate, in the range of  $0.25\text{--}2.0 \mu\text{m/h}$  is observed to affect neither the step structure nor the degree of order.

## EXPERIMENT

The  $\text{Ga}_{0.52}\text{In}_{0.48}\text{P}$  layers were grown by OMVPE in a horizontal, atmospheric pressure OMVPE reactor using trimethylindium (TMIn) at  $25^\circ\text{C}$ , trimethylgallium (TMGa), and TBP at  $7^\circ\text{C}$  on singular (001) semi-insulating GaAs substrates. Substrate preparation consisted of degreasing followed by a 1 min etch in a solution of  $\text{H}_2\text{O}:\text{NH}_4\text{OH}:\text{H}_2\text{O}_2 = 12:2:1$ . The growth rate was varied from  $0.25$  to  $2.0 \mu\text{m/h}$ , keeping the TBP partial pressure constant at 1.5 Torr, at a growth temperature of  $670^\circ\text{C}$ . Before beginning the GaInP growth, a  $0.15 \mu\text{m}$  GaAs buffer layer was deposited using TMGa and arsine to improve the quality of the GaInP layers.

The solid composition of the GaInP layers was determined using Vegard's law, from x-ray diffraction measurements using  $\text{Cu } K\alpha$  radiation. The surface structure was characterized using a Nanoscope III AFM in the tapping mode. Etched single-crystalline Si tips were used with an end radius of about 5 nm, with a sidewall angle of about  $35^\circ$ . Scan rates of 1–2 lines per second were used and data were taken at 12 points/line and 512 lines per scan area. This technique has been demonstrated to allow imaging of features one atomic layer in height.<sup>15</sup> The 20-K PL was excited using the 488 nm line of an  $\text{Ar}^+$  laser. The emission was dispersed using a Spex Model 1870 monochromator and detected with a Hamamatsu R1104 head-on photomultiplier tube.

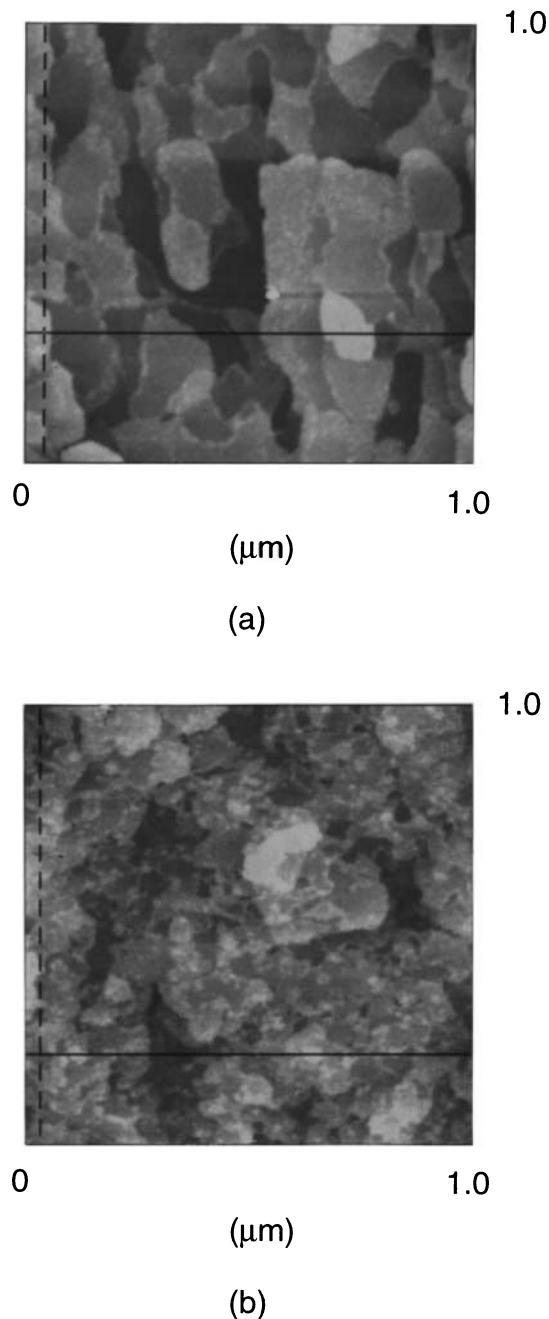


FIG. 1. Atomic force microscope images of GaInP layers grown on singular (001) GaAs substrates at  $670^\circ\text{C}$  at growth rates of (a)  $0.25$  and (b)  $2.0 \mu\text{m/h}$ . The solid lines are in the  $[110]$  direction.

## RESULTS AND DISCUSSION

AFM images of the GaInP layers grown at rates of  $0.25$  and  $2.0 \mu\text{m/h}$  with a constant TBP partial pressure of 1.5 Torr are seen in Fig. 1. The surface of the GaInP layer grown at  $0.25 \mu\text{m/h}$  is seen to consist of large, easily distinguished islands. For the sample grown at  $2.0 \mu\text{m/h}$  the islands are markedly smaller and the steps are clearly seen to be much more closely spaced. The islands are seen to be elongated in the  $[110]$  direction, similar to previous results.<sup>16,17</sup> Figure 2 shows section scans of the surfaces of these two layers. The steps on the samples grown at both growth rates are mostly  $\sim 6 \text{ \AA}$  in height, i.e., they are predominantly bilayer steps.

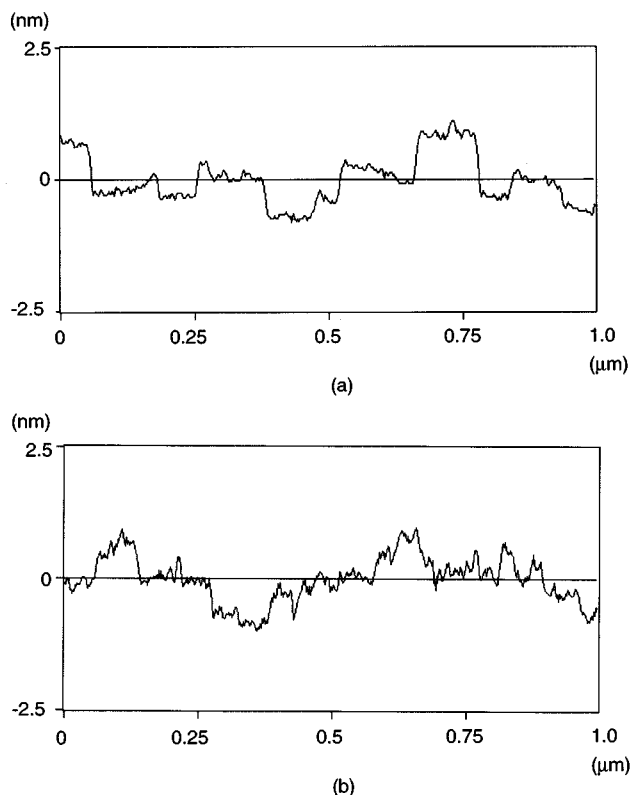


FIG. 2. Atomic-scale profiles of the surfaces of the GaInP samples shown in Fig. 1; (a) 0.25, (b) 2.0  $\mu\text{m/h}$  taken along the solid lines in Fig. 1.

The ratio of steps that are bilayers to the total number of monolayer and bilayer steps was determined by carefully counting 25  $1\ \mu\text{m}$  sections. Steps larger than bilayers were neglected. Figure 3 shows the fraction of bilayer steps versus growth rate. The fraction of bilayer steps is seen to be constant at about 68% regardless of the growth rate.

The 20-K PL peak energy was used to determine the degree of order in these samples using the equation:<sup>7</sup>

$S$ (degree of order)

$$= \sqrt{\frac{2005\text{-PL peak energy at 20 K (in meV)}}{471}}$$

As seen in Fig. 3, the degree of order is not affected by decreasing the growth rate, contrary to previous reports.<sup>12-14</sup> The fraction of bilayer steps and the degree of order are both observed to be independent of growth rate in the range from 0.25 to 2.0  $\mu\text{m/h}$ .

Our recent results<sup>8</sup> showed a qualitative link between the step structure and the degree of order as the temperature and TBP partial pressure were varied which is consistent with the results reported here. A clear and systematic increase in the percentage of bilayer steps was seen with increasing growth temperature, from  $\sim 20\%$  at 520  $^{\circ}\text{C}$  to 70% at 670  $^{\circ}\text{C}$ . This corresponds directly to a monotonic increase in the degree of order, measured using low-temperature photoluminescence, as the temperature is increased in this range, although the concentration of  $[\bar{1}10]$  P dimers determined from SPA results also decreases dramatically as the temperature increases. Both the degree of order<sup>7-9</sup> and the percentage of bilayer steps<sup>8</sup> are also seen to increase monotonically with increasing partial pressure of the P precursor. This appears to suggest a correlation between the step structure and the degree of order with changes in both the growth temperature and the P partial pressure, although interpretation of the data is complicated by the change in the concentration of  $[\bar{1}10]$  surface dimers with changing temperature and P partial pressure.

The data in Fig. 3 clearly demonstrate that the growth rate, in this range, affects neither the degree of order nor the step structure. This appears to be inconsistent with earlier reports of a decrease in the degree of order with decreasing growth rate for a similar range of growth rates.<sup>12-14</sup> Much of this seeming disparity arises because in the previous experiments of Kurtz *et al.*<sup>12</sup> and Su *et al.*<sup>13</sup> the growth rate was changed while keeping the V/III ratio constant. As a result, the phosphorus partial pressure was varied together with the growth rate. In fact, for the OMVPE growth of III/V materials at temperatures in the normally preferred mass transport range, as for all of the experiments considered here, a state approximating thermodynamic equilibrium exists at the solid/vapor interface. At the high input V/III ratios typically used, the V/III ratio at the interface is totally determined by the group V input partial pressures.<sup>18</sup> Thus, the change in the degree of order reported in Refs. 12 and 13 can be attributed to the change in the input P partial pressure. As discussed above, the decrease in the P partial pressure at the low growth rates will, itself, result in the decreased degree of order observed. Thus, in order to elucidate the effects of the growth rate it is vital that the group V flow rate be held constant, as in the present experiments. In later experiments, Kurtz *et al.*<sup>14</sup> observed a very small decrease in the degree of order as the growth rate was decreased while holding the  $\text{PH}_3$  partial pressure constant at a temperature of 675  $^{\circ}\text{C}$ . The small effect observed in these experiments may be due to a small change in the degree of decomposition of the

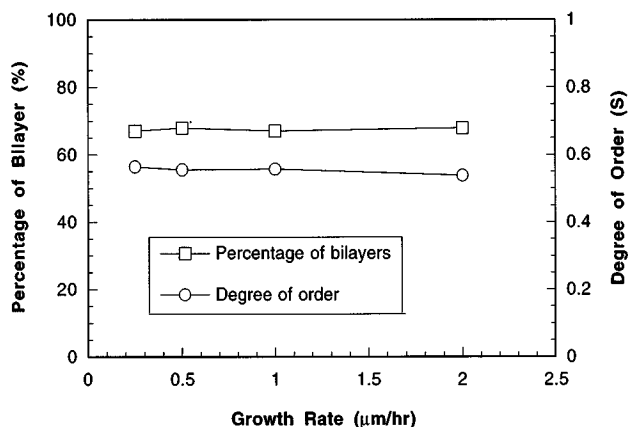


FIG. 3. Percentage of bilayer steps and the degree of order, determined from the PL peak energy, vs growth rate for GaInP layers grown at 670  $^{\circ}\text{C}$  with a TBP partial pressure of 1.5 Torr.

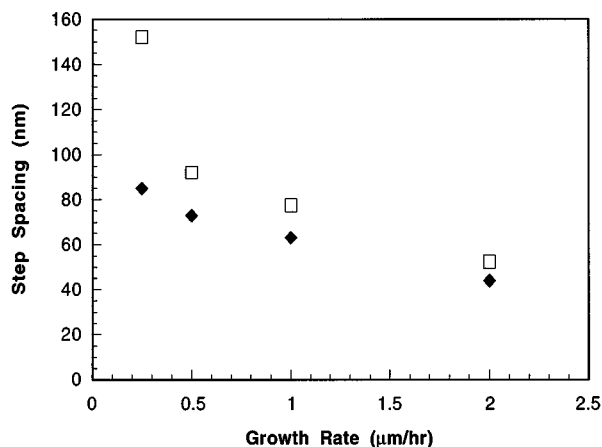


FIG. 4. Separation between  $[110]$  ( $\square$ ) and  $[\bar{1}10]$  ( $\blacklozenge$ ) steps vs growth rate for GaInP samples grown lattice matched to singular (001) GaAs substrates at 670 °C.

$\text{PH}_3$  caused by the decrease in the input TMIIn concentrations.<sup>19</sup>

It is likely that the disappearance of order observed by Cao *et al.*<sup>11</sup> at very high growth rates is truly due to the kinetic effects associated with the increase in growth rate, although, here again, the V/III ratio was held constant as the growth rate was varied and these high phosphine partial pressures led to a slight decrease in the degree of order.<sup>11</sup>

In Fig. 4 the spacing between  $[110]$  and  $[\bar{1}10]$  steps is plotted versus growth rate. These data confirm the observations in Fig. 1 that the islands are elongated in the  $[110]$  direction at low growth rates and become nearly symmetrical at high growth rates. It is seen that the (001) terrace width between steps is significantly decreased by an increase in growth rate. The data are generally consistent with previous observations of a  $1/(\text{growth rate})^{1/2}$  dependence.<sup>20</sup> The decrease in step length is thought to be due to a decrease in the length a group III adatom can diffuse before being covered by the next layer to grow. As the growth rate increases, the time atoms have to diffuse before being frozen due to coverage by the next layer decreases. This limits the widths of the terraces that can be formed. It is noted that the change in step spacing resulting from the changing growth rate has no observable effect on the degree of order in the GaInP.

## CONCLUSIONS

In summary, a variation of the growth rate in the range from 0.25 to 2.0  $\mu\text{m/h}$  is seen to have no effect on either the

step structure (bilayer or monolayer) or the degree of CuPt order produced during OMVPE growth of GaInP on singular (001) GaAs substrates when the TBP partial pressure is held constant. Increasing the growth rate affects only the step spacing due to a decrease in the time allowed for diffusion of the group III adatoms on the (001) terraces. Previous reports of a decrease in the degree of order of GaInP with decreasing growth rate while keeping the V/III ratio constant were, in fact, due to changes in the  $\text{PH}_3$  partial pressure.

## ACKNOWLEDGMENT

This work was financially supported by the National Science Foundation.

- <sup>1</sup>G. B. Stringfellow, in *Common Themes and Mechanisms of Epitaxial Growth*, edited by P. Fuoss, J. Tsao, D. W. Kisker, A. Zangwill, and T. Kuech (Materials Research Society, Pittsburgh, 1993), pp. 35–46.
- <sup>2</sup>S. B. Zhang, S. Froyen, and A. Zunger, *Appl. Phys. Lett.* **67**, 3141 (1995).
- <sup>3</sup>B. A. Philips, A. G. Norman, T. Y. Seong, S. Mahajan, G. R. Booker, M. Skowronski, J. P. Harbison, and V. G. Keramidas, *J. Cryst. Growth* **140**, 249 (1994).
- <sup>4</sup>M. Kasu and N. Kobayashi, *J. Appl. Phys.* **78**, 3026 (1995).
- <sup>5</sup>K. Hata, T. Ikoma, K. Hirakawa, T. Olkano, A. Kawazu, T. Ueda, and M. Akiyama, *J. Appl. Phys.* **76**, 5601 (1994).
- <sup>6</sup>G. B. Stringfellow, L. C. Su, Y. E. Strausser, and J. T. Thornton, *Appl. Phys. Lett.* **66**, 3155 (1995).
- <sup>7</sup>H. Murata, I. H. Ho, L. C. Su, Y. Hosokawa, and G. B. Stringfellow, *J. Appl. Phys.* **79**, 6895 (1996).
- <sup>8</sup>Y. S. Chun, S. H. Lee, I. H. Ho, and G. B. Stringfellow, *J. Cryst. Growth* (to be published).
- <sup>9</sup>Y. S. Chun, H. Murata, T. C. Hsu, I. H. Ho, L. C. Su, Y. Hosokawa, and G. B. Stringfellow, *J. Appl. Phys.* **79**, 6900 (1996).
- <sup>10</sup>H. Murata, I. H. Ho, and G. B. Stringfellow, *J. Cryst. Growth* (to be published).
- <sup>11</sup>D. S. Cao, E. H. Reihlen, G. S. Chen, A. W. Kimbal, and G. B. Stringfellow, *J. Cryst. Growth* **109**, 279 (1991).
- <sup>12</sup>S. R. Kurtz, J. M. Olson, and A. Kibbler, *Appl. Phys. Lett.* **57**, 1922 (1990).
- <sup>13</sup>L. C. Su, I. H. Ho, and G. B. Stringfellow, *J. Appl. Phys.* **75**, 5135 (1994).
- <sup>14</sup>S. R. Kurtz, J. M. Olsen, D. J. Arent, A. E. Kibbler, and K. A. Bertness, in *Common Themes and Mechanisms of Epitaxial Growth*, edited by P. Fuoss, J. Tsao, D. W. Kisker, A. Zangwill, and T. Kuech (Materials Research Society, Pittsburgh, 1993), pp. 83–88.
- <sup>15</sup>C. C. Hsu, T. K. S. Wong, and I. H. Wilson, *Appl. Phys. Lett.* **63**, 1139 (1993); H. Bluhm, U. D. Schwarz, F. Hermann, and P. Paufler, *Appl. Phys. A* **59**, 23 (1994).
- <sup>16</sup>M. Kasu and N. Kobayashi, *J. Cryst. Growth* **145**, 120 (1994).
- <sup>17</sup>L. C. Su and G. B. Stringfellow, *Appl. Phys. Lett.* **67**, 3626 (1995).
- <sup>18</sup>G. B. Stringfellow, *Organometallic Vapor Phase Epitaxy, Theory and Practice* (Academic, San Diego, 1989), Chap. 3.
- <sup>19</sup>S. R. Kurtz, D. J. Arent, K. A. Bertness, and J. M. Olson, *Mater. Res. Soc. Symp. Proc.* **340**, 117 (1994).
- <sup>20</sup>L. C. Su and G. B. Stringfellow, *J. Appl. Phys.* **78**, 6775 (1995).
- <sup>21</sup>L. C. Su, I. H. Ho, and G. B. Stringfellow, *J. Appl. Phys.* **75**, 5135 (1994).