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Kinetics of Te doping in disodering GaInP grown by organometallic vapor phase epitaxy

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Te-doped GaInP epitaxial layers were grown by organometallic vapor phase epitaxy in an effort to clarify the Te disordering mechanism. CuPt ordered GaInP is produced under normal growth conditions. The addition of Te has been reported to induce disorder. One suggested mechanism for disordering GaInP is the increased step velocity caused by the addition of Te. To test this hypothesis, the effects of growth rate and growth temperature on the disordering effect of Te were studied. The Te/III ratio in the vapor and the partial pressure of the P precursor, tertiarybutylphosphine, were kept constant. The behavior of Te incorporation is found to be unusual. The decrease with increasing temperature is consistent with Te acting as a volatile impurity. However, the Te incorporation is also found to be inversely proportional to the growth rate, a characteristic of nonvolatile dopants. A suggested solution to this apparent contradiction is that the Te, which accumulates at step edges, is not able to keep pace with the steps when they move at the higher velocities. As the growth rate was decreased, with a corresponding decrease in measured step velocity, the degree of order was observed to increase, in support of this kinetic model. GaInP layers grown at higher temperatures were observed to become much less ordered. Analysis of these data indicates that the effect is due mainly to the effect of temperature on step velocity. The direct correlation between the step velocity and the degree of order, as these two growth parameters were varied, confirms that Te disorders GaInP for kinetic reasons. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1416857]

INTRODUCTION

The surface dynamics during vapor phase epitaxial growth are complex, involving processes such as adsorption, diffusion, and incorporation at steps.[1] Understanding of the surface processes is of both fundamental and practical importance, since these processes affect the bulk microstructure and hence the materials properties. For example, formation of the CuPt ordered structure, for GaInP grown under normal growth conditions, results in a reduction of the band gap energy by as much as ~160 meV.[2,3] The CuPt structure forms due to surface-driven processes during organometallic vapor phase epitaxial (OMVPE) growth. The (2×4) surface reconstruction in GaInP provides a surface thermodynamic driving force leading to long range CuPt ordered structures. The alternating surface stresses resulting from the $[\bar{1}10]$ P dimers on the GaInP surface thermodynamically stabilize the CuPt variants with ordering on the $(\bar{1}11)$ and $(1\bar{1}1)$ planes, the B variants, in the third layer below the surface.[4–6] This has been verified by surface photoabsorption (SPA) experiments showing a direct correlation between the concentration of $[\bar{1}10]$ P dimers and the degree of order (S).[7] The ordered structure is calculated to be unstable in the bulk.[6] However, the high diffusion barrier in the bulk freezes the ordered structure formed at the surface during growth, preventing the epilayer from reaching equilibrium.

Surface kinetics also plays an important role in the ordering process. The degree of order is reduced when layers are grown at high rates.[8] Rapid growth retards the ability of Ga and In atoms to exchange positions repeatedly at step edges, a process that is required to form an ordered structure. Steps also play an important role in the ordering process. [110] steps are known to assist ordering and $[\bar{1}10]$ steps retard ordering,[9] although the role of steps in the ordering process is not fully understood.

Addition of a donor, Te, during GaInP growth has been demonstrated to markedly reduce CuPt ordering.[10] Interestingly, the addition of Te does not change the SPA spectrum, a characteristic of the surface reconstruction; however, it does change the surface step structure, resulting in a significant increase of the $[\bar{1}10]$ step velocity. For singular substrates, the addition of Te causes the step velocity to increase by more than a factor of 20. A correlation between the step velocity and degree of order was taken as evidence that the disordering mechanism is related to the adatom attachment kinetics at step edges.[10]

Recently, the isoelectronic surfactant Bi has also been reported to affect the adatom attachment kinetics in GaInP.[11] Addition of Bi also changes the surface reconstruction as indicated by the SPA spectra. The peak at 400 nm due to $[\bar{1}10]$ P dimers decreases for Bi/III ratios in the vapor that causes disordering. Comparison between the effects for Te and Bi reveals that the amount of Te causing disordering in GaInP is 2 orders of magnitude lower than the amount of Bi

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required.[12] This indicates that the Te effect is due mainly to the accumulation of Te at the step edges, in agreement with the SPA evidence.

This article presents work designed to further our understanding of the disordering processes occurring at the surface during epitaxial growth due to the addition of Te. In order to clarify whether Te disorders GaInP kinetically, two growth parameters were varied, growth rate and temperature, with a constant Te partial pressure during growth.

EXPERIMENT

The GaInP layers were grown in a horizontal, infrared-heated, atmospheric-pressure OMVPE reactor. All layers were grown ~0.2 μm thick and lattice matched to semi-insulating GaAs (001) substrates. The lattice mismatch determined by x-ray diffraction was $\Delta a/a < 10^{-3}$ for all the layers used in this study. Trimethylgallium, trimethylindium, tertiarybutylphosphine (TBP), and diethyltellurium (DETe) were used as the group III, group V, and Te precursors, respectively. The partial pressure of TBP was kept constant, 8.4×10^{-1} Torr, during growth of all the layers described in this work. The three different growth rates, 0.3, 1.0, and 1.32 μm/h, were obtained by changing only the group III partial pressure at 620 °C. The V/III ratio at the interface was assumed to be constant.[1] To study the effect of growth temperature, layers were grown at 560, 620, and 680 °C with a growth rate of 1.0 μm/h.

The free electron concentrations were determined from room temperature Hall effect measurements using the Van der Pauw geometry. Photoluminescence (PL) measurements were performed at 12 K. The 488 nm line of an Ar^+ laser with a power of 10 mW focused to a 0.5 mm^2 spot was used to excite the samples. The PL signal was dispersed with a SPEX monochromator and detected with a photomultiplier tube using standard lock-in amplifier techniques.

The low temperature PL peak energy was used to determine the degree of order S using the following equation:[13]

$$\text{degree of order } (S) = \sqrt{\frac{2005\text{-PL peak energy (in meV)}}{471}},$$

where 2005 meV is the band gap of completely disordered GaInP and the maximum change of the band gap energy in GaInP has been measured as 471 meV.[14] This equation is correct for values of $S < 0.6$.[15]

The surface morphology, including the step structure, was characterized using a Nanoscope III atomic force microscope (AFM) in the tapping mode. Etched single-crystalline Si tips were used with an end radius of about 5 nm and a sidewall angle of about 35°. The samples were measured in air, so were covered by a thin, conformal oxide layer.

RESULTS AND DISCUSSION

The effect of growth temperature, from 560 to 680 °C, on the concentration of Te incorporated into the GaInP solid is shown in Fig. 1. A clear decrease in Te incorporation with increased growth temperature is observed. Dopant incorporation during the OMVPE growth of III/V semiconductors is often grouped into two categories. For volatile dopants, an equilibrium dopant surface coverage is established, which determines the dopant concentration incorporated into the solid. The dopant concentration is proportional to the pressure of the dopant precursor in the vapor and to the reciprocal of the vapor pressure of the dopant element.[16] In this case, the dopant incorporation is strongly temperature dependent and is independent of the growth rate. For nonvolatile elements, on the other hand, the dopant incorporation is nearly temperature independent, assuming that the dopant precursor is completely pyrolyzed. However, in this case the concentration incorporated into the solid is inversely proportional to the growth rate of the epitaxial layer.

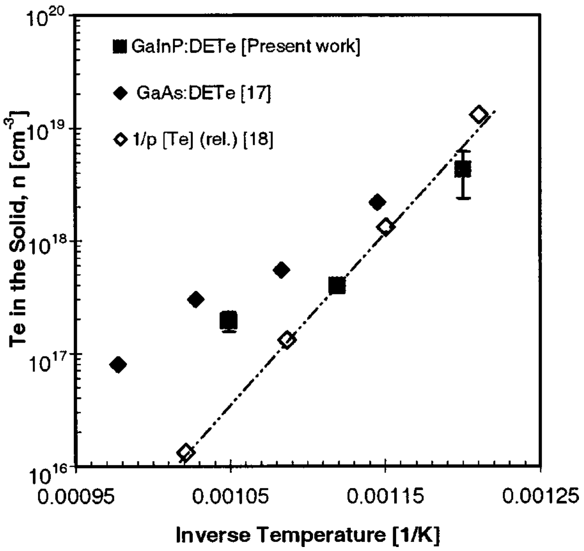

FIG. 1. Te concentration in GaInP as a function of growth temperature. The partial pressure of DETe was kept constant. Published data for DETe doping of GaAs (Ref. 16) and reciprocal vapor pressure of Te (Ref. 17) are included for comparison.

The temperature dependence of the Te incorporation seen in Fig. 1 appears to qualify Te as a volatile dopant.[16] This is consistent with expectations, based on the high vapor pressure of Te, and the results of Houng and Low published for GaAs,[17] which are also included in Fig. 1. It should be pointed out that the exponential temperature dependence is seen only for relatively low doping levels. When pushed to high levels, the amount of Te incorporated into the solid is limited by the solid solubility, giving a Te concentration that is nearly independent of both the precursor pressure in the vapor and the growth temperature.[18] The temperature dependence of Te doping observed in Fig. 1 is also consistent with data on the incorporation of Te into GaAs grown by MOMBE, which shows a strong, exponential decrease in Te doping with increasing temperature for temperatures of >540 °C.[19]

The dependence of Te concentration in the solid on the growth rate seen in Fig. 2 for a constant DETe partial pressure is confusing, since it clearly shows a decrease in Te incorporation with increasing growth rate, as expected for a nonvolatile dopant.[16] One way of trying to understand this

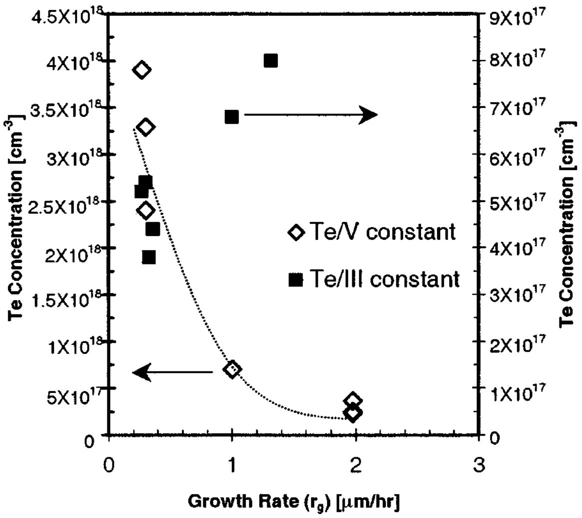

FIG. 2. Te concentration in GaInP vs growth rate for two conditions: (i) a constant $(\mathrm{Te/III})_v$ ratio and (ii) a constant $(\mathrm{Te/V})_v$ ratio. For constant $(\mathrm{Te/V})_v$, the Te concentration decreases approximately as (growth rate)$^{-1}$. A line is inserted to indicate the $1/r_g$ dependence. For constant $(\mathrm{Te/III})_v$, the Te concentration increases somewhat.

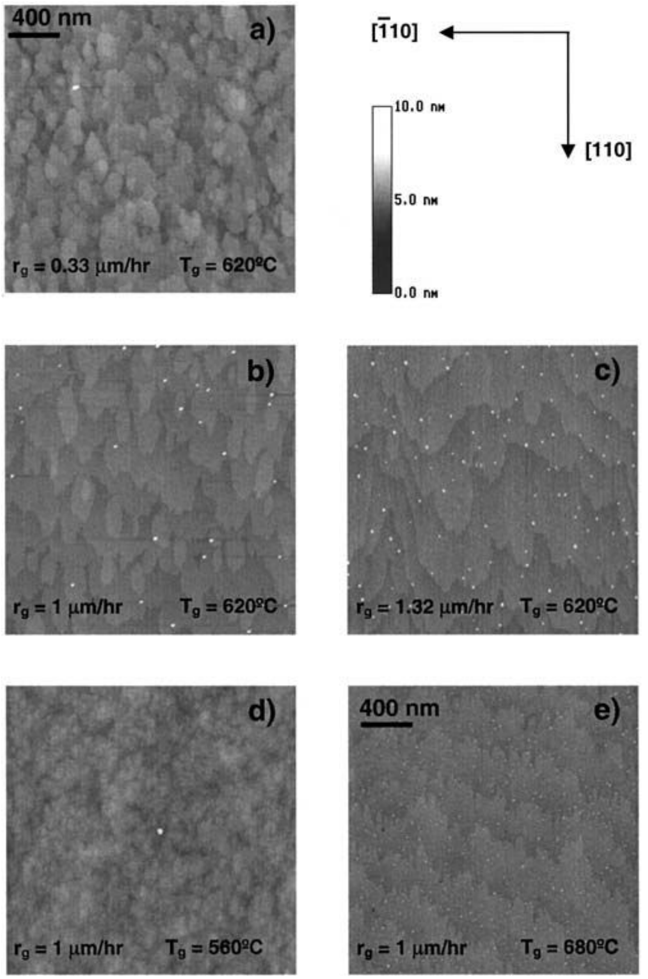

FIG. 3. AFM images of GaInP layers grown on singular (001) GaAs with a constant Te/III ratio in the vapor of 0.0007 and a TBP partial pressure of 0.84 Torr. The growth rate and temperature are included on each micrograph.

behavior is to consider the effect of step velocity on dopant incorporation.

The behavior reported above for Te is the opposite of that observed for Zn in GaAs, another volatile dopant, where an increase in step velocity is found to result in an increase in Zn incorporation into the solid, by a "trapping" mechanism.[20] One way of rationalizing the behavior of Te would be to consider a simple model where Te is incorporated into the solid only at step edges and an equilibrium is established between the Te concentration on the (001) terraces and in the vapor. At low step velocities, the Te concentration at the step edge will be proportional to the Te concentration on the terrace and the doping behavior will conform to that expected for a classical volatile impurity. However, since Te collects at the step edge and not on the (001) terraces,[10,12] it is possible that high step velocities will result in the Te atoms at the step edge being "left behind."

It is expected that the surface diffusion coefficients of dopants residing on the group V sites on the surface will be retarded by the two bonds formed to the underlying group III elements and the dimer bond formed to an adjacent anion. In addition, most of the group V sublattice sites on the surface will be occupied, which further retards the hopping rate. If, as a first approximation, the Te concentration at the step edge were taken to be inversely proportional to the step velocity in this regime, the concentration of Te incorporated into the solid, with a constant DETe partial pressure in the vapor, would be proportional to the reciprocal of the growth rate, the approximate dependence observed in Fig. 2 for constant Te and P partial pressures during growth. For a constant Te/III ratio, the effect of growth rate is compensated by increasing the DETe partial pressure. As seen in Fig. 2, the Te concentration in the solid changes only slightly when the growth rate, i.e., the group III partial pressure is increased.

Figure 3(b) shows an AFM image for a GaInP layer grown using "standard" conditions, a growth rate of 1.0 μm/h and a temperature of 620 °C. The value of $(\mathrm{Te/III})_v$ and the partial pressure of TBP were 0.0007, and 0.84 Torr, respectively. The average step spacing, obtained from a careful counting of the [110] step spacing along ten 2 μm AFM profiles, is approximately 220 nm. A very smooth surface with a relatively high step spacing along the [110] direction is observed. The steps are mainly of monolayer height. These results are consistent with those of a previous study.[10] The step spacing is clearly a function of the growth rate, as seen in Figs. 3(a) and 3(c). The layer grown at the lowest rate ~0.3 μm/h [Fig. 3(a)] still shows an island structure with an average step spacing of ~80 nm. For the highest growth rate of 1.32 μm/h, the surface morphology becomes smoother and the step spacing increases to ~270 nm [Fig. 3(c)]. This layer shows no islands on the surface. The step spacing, and hence the step velocity, increases as the growth rate increases because, as seen in Fig. 2, under these conditions (constant $(\mathrm{Te/III})_v$) the Te concentration increases as the growth rate is increased. The growth rate dependence of the step spacing is plotted in Fig. 4.

Figures 3(d) and 3(e) show AFM images for GaInP layers grown at different growth temperatures and a constant

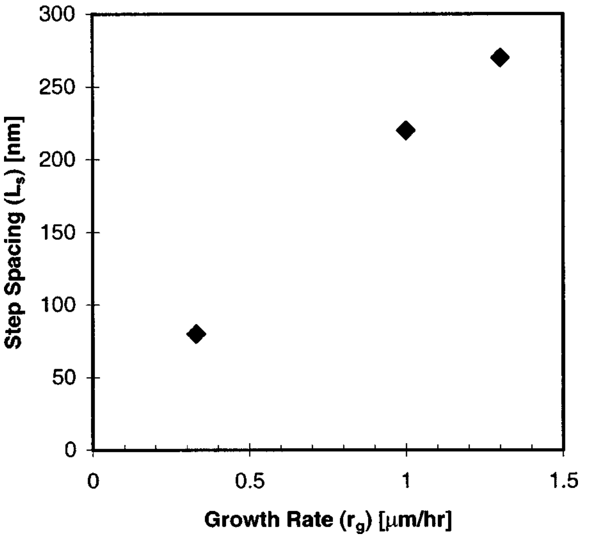

FIG. 4. Step spacing vs growth rate. As the growth rate is increased for constant $(\mathrm{Te/III})_v$, the Te concentration is also increased, leading to the larger step spacing.

growth rate of 1.0 μm/h. The surface of the layer grown at 560 °C [Fig. 3(d)] is composed of an island structure with a short step spacing as compared to the sample grown using the same conditions but a temperature of 620 °C [Fig. 3(b)]. The highest growth temperature of 680 °C produced a very smooth surface with no island structure [Fig. 3(e)]. The 120 °C difference in growth temperature produces a large change in step velocity. Note that it is not a change in the Te concentration in the samples that caused the change in step velocity. The Te concentration in the layer grown at 680 °C [Fig. 3(e)] was lower than in the layer at 560 °C [Fig. 3(d)], but it has a larger step spacing. Figure 5 is a semilog plot of step spacing versus reciprocal growth temperature. The activation energy obtained from the two lowest temperature data points is approximately 2.1 eV, which matches quite well with literature values for the activation energy for Ga surface diffusion on (001) GaAs.[21] This suggests that the temperature dependence of the step spacing is due to the temperature dependence of the surface diffusion of group III adatoms. Apparently, the elevated temperature increases the surface diffusion of group III adatoms, leading to a higher step velocity and a smoother surface until, at the highest temperatures used, the step spacing is determined by the unintentional substrate misorientation.

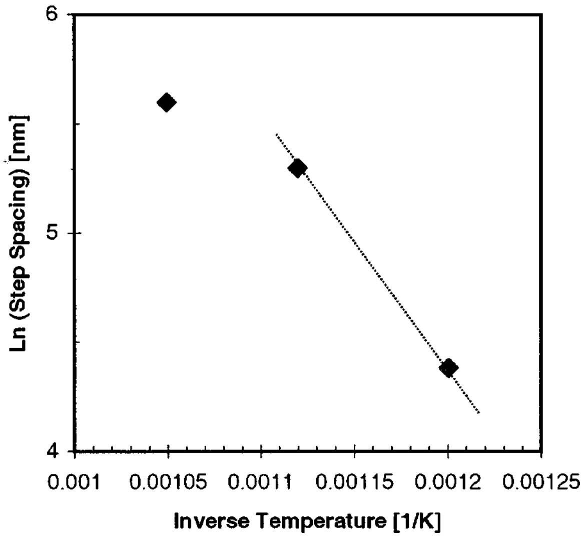

FIG. 5. Semilog plot of step spacing vs reciprocal growth temperature. The activation energy determined from the two lower temperature points is ~2.1 eV.

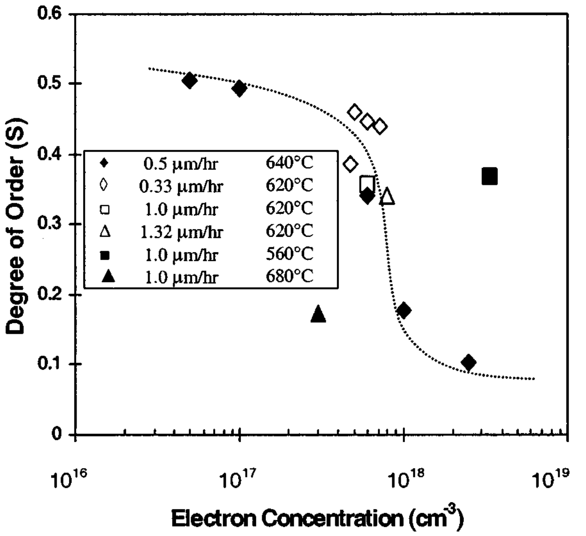

FIG. 6. Degree of order vs free carrier concentration in the bulk. The previous data (◆: grown at 640 °C, 0.5 μm/h) (Ref. 8) is included for comparison. A sharp transition in degree of order occurs when the Te concentration is near $6\times10^{17}\,\mathrm{cm}^{-3}$. A low growth rate (◇: 620 °C, 0.33 μm/h) produces more ordered materials than high growth rates (□: 620 °C, 1.0 μm/h and △: 620 °C, 1.32 μm/h). A high growth temperature (▲: 680 °C) produces much less ordered materials than a low growth temperature (■: 560 °C). Open symbols are for the samples grown at several growth rates.

Figure 6 is a plot of degree of order versus electron concentration due to Te doping. Previous data[10] (grown at 640 °C, 0.5 μm/h) are plotted for comparison. A sharp transition occurs in the degree of order near a Te concentration in the bulk of $6\times10^{17}\,\mathrm{cm}^{-3}$. The layers grown at the lower growth rate (0.3 μm/h) appear to be significantly more ordered on average. Clearly, in the transition region a reduced growth rate gives increased ordering. Note that from Fig. 1 we observe that the step velocity is also lower in these layers. Higher growth rates of 1 and 1.32 μm/h give a slight decrease in the degree of order. The samples grown at different rates using the same value of $(\mathrm{Te/III})_v$ resulted in a similar Te concentration in these layers of $\sim6\times10^{17}\,\mathrm{cm}^{-3}$.

Clearly, the growth temperature has a large effect on the degree of order. At a high growth temperature (680 °C: ▲) the GaInP is less ordered and more ordered material is produced at a lower growth temperature (560 °C: ■). It is well known that for undoped GaInP grown by OMVPE the maximum degree of order is obtained at a temperature near 620 °C.[16] For a constant value of $(\mathrm{Te/III})_v$ the layer grown at 560 °C, however, gives a slightly larger degree of order than for the layer grown at 620 °C. As discussed above, the Te concentration decreases significantly as the temperature is increased. Thus, these results reveal that the variation of the Te concentration in the bulk is not the factor that determines

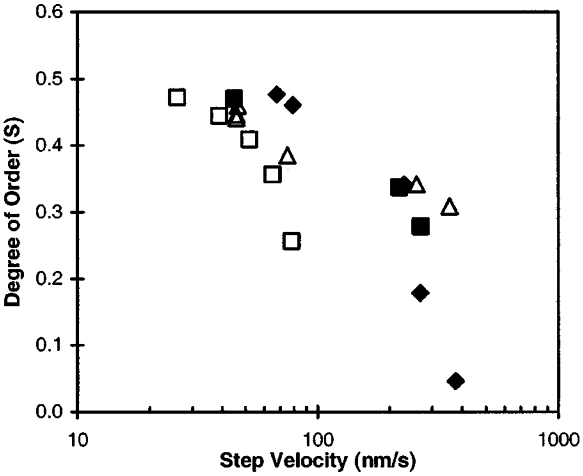

FIG. 7. Degree of order vs step velocity. The factors used to control the step velocity are: growth rate (□) (Ref. 8), addition of a constant Te partial pressure at several growth rates (△), addition of a constant Te partial pressure at several growth temperatures (■), and addition of various partial pressures of Te (♦) (Ref. 10).

the degree of order as the temperature is varied.

Examination of the dependence of degree of order on the two parameters, growth rate and temperature, reveals that in this study the only common feature for the series of Te-doped layers is that a larger step spacing correlates with a lower degree of order. To demonstrate this point, the order parameter is plotted in Fig. 7 as a function of the step velocity. The factors used to control step velocity in this plot are: variation of the growth rate;[8] variation of temperature T_g for a constant Te partial pressure; variation of growth rate r_g for a constant Te partial pressure; and variation of Te concentration in GaInP at a constant growth rate and growth temperature.[10] Note that the temperature effect on the degree of order has been factored out in this plot using data published for undoped GaInP.[22] The step velocity is proportional to the growth rate for vicinal substrates where the average step spacing is determined by the miscut angle of the substrate. The data clearly show that the step velocity has a significant effect on the degree of order as reported previously.[8] The ordering is retarded as the step velocity increases, due to the decrease in the ability of Ga and In atoms to repeatedly exchange positions at step edges before incorporation. The increased step velocity caused by the addition of Te also retards ordering, as reported earlier.[10] Remarkably, for samples grown with Te, Fig. 7 shows that a variation of either the growth rate or the growth temperature gives the same correlation between the decrease of the degree of order with an increasing step velocity. This strongly supports the previously suggested mechanism that an increase in step velocity caused by the addition of Te is responsible for the disordering.[10] Clearly, surface kinetics is the factor playing the most important role in disordering GaInP.

CONCLUSIONS

For normal growth conditions, ordered GaInP is produced during OMVPE growth. Growth rates giving faster step velocities have been observed to retard ordering due to the suppression of the ability of Ga and In atoms to exchange positions at step edges. The addition of Te was also observed to retard ordering. Addition of Te increases the step velocity by a factor of 20. Thus, the disordering effect of Te has been attributed to the increased step velocity. To test this disordering mechanism, the effects of two growth parameters, growth rate and growth temperature, were studied for a constant partial pressure of Te. For a constant value of $(\mathrm{Te/III})_v$, the degree of order increases as the growth rate decreases. This supports the step velocity model. A much larger effect is observed for a variation of growth temperature. High growth temperature produced much less ordered materials. Temperature also has a strong effect on step velocity. A common observation from the AFM images of the layers grown in this study is that less ordered materials always show larger surface step spacings. In fact, a clear relationship between the degree of order and the step velocity is observed. This is convincing evidence that Te disorders GaInP kinetically, i.e., by changing the step velocity.

A secondary observation is related to the temperature and growth rate dependence of Te incorporation. The temperature dependence of Te incorporation in GaInP is indicative of Te behaving as a volatile impurity, as expected. However, the inverse dependence on growth rate is indicative of the behavior expected for a nonvolatile dopant. The apparent contradiction is resolved by the suggestion that Te is not able to follow the step edges for high step velocities.

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[1] G. B. Stringfellow, *Organometallic Vapor Phase Epitaxy: Theory and Practice*, 2nd ed. (Academic, Boston, 1999), Chap. 3.
[2] L. C. Su, I. H. Ho, N. Kobayashi, and G. B. Stringfellow, J. Cryst. Growth **145**, 140 (1994).
[3] G. B. Stringfellow, in *Thin Films: Heteroepitaxial Systems*, edited by M. Santos and W. K. Liu (World Scientific, Singapore, 1998), pp. 64–116.
[4] G. B. Stringfellow, in *High Brightness Light Emitting Diodes*, edited by G. B. Stringfellow and M. G. Craford (Academic, Boston, 1997), Chap. 2.
[5] Y. Ueno, H. Fujii, K. Kobayashi, K. Endo, A. Gomyo, K. Hara, S. Kawata, T. Yuasa, and T. Suzuki, Jpn. J. Appl. Phys., Part 2 **29**, L1666 (1990).
[6] S. B. Zhang, S. Froyen, and A. Zunger, Appl. Phys. Lett. **67**, 3141 (1995).
[7] H. Murata, I. H. Ho, T. C. Hsu, and G. B. Stringfellow, Appl. Phys. Lett. **67**, 3747 (1995).
[8] D. S. Cao, E. H. Reihlen, G. S. Chen, A. W. Kimball, and G. B. Stringfellow, J. Cryst. Growth **109**, 279 (1991).
[9] H. Murata, I. H. Ho, Y. Hosokawa, and G. B. Stringfellow, Appl. Phys. Lett. **68**, 2237 (1996).
[10] S. H. Lee, T. C. Hsu, and G. B. Stringfellow, J. Appl. Phys. **84**, 2618 (1998).
[11] S. W. Jun, R. T. Lee, C. M. Fetzer, J. K. Shurtleff, G. B. Stringfellow, C. J. Choi, and T.-Y. Seong, J. Appl. Phys. **88**, 4429 (2000).
[12] G. B. Stringfellow, J. K. Shurtleff, R. T. Lee, C. M. Fetzer, and S. W. Jun, J. Cryst. Growth **221**, 1 (2000).
[13] P. Earnst, C. Geng, F. Sholtz, H. Schwezer, Y. Zhang, and A. Macarenhas, Appl. Phys. Lett. **67**, 2347 (1994).
[14] P. Ernst, C. Geng, F. Scholz, and H. Schweizer, Phys. Status Solidi B **193**, 2 (1996).
[15] R. L. Forrest, T. D. Golding, S. C. Moss, Z. Zhang, J. F. Geisz, J. M. Olson, A. Mascarenhas, P. Ernst, and C. Geng, Phys. Rev. B **58**, 15355 (1998).
[16] G. B. Stringfellow, J. Cryst. Growth **75**, 91 (1986).
[17] Y.-M. Houng and T. S. Low, J. Cryst. Growth **77**, 272 (1986).

[18] R. E. Honig, in *The Characterization of High-temperature Vapors*, edited by J. L. Margrave (Wiley, New York, 1967).
[19] M. Kamp, G. Morsch, J. Graber, and H. Luth, J. Appl. Phys. **76**, 1974 (1994).
[20] M. J. Anders, P. R. Hageman, and L. J. Giling, J. Cryst. Growth **142**, 292 (1994).
[21] M. A. Salmi, M. Alatalo, T. Ala-Nissila, and R. M. Nieminen, Surf. Sci. **425**, 31 (1999).
[22] H. Murata, I. H. Ho, L. C. Su, Y. Hosokawa, and G. B. Stringfellow, J. Appl. Phys. **79**, 6895 (1996).