Influence of tellurium doping on step bunching of GaAs(001) vicinal surfaces grown by organometallic vapor phase epitaxy

S. H. Lee and G. B. Stringfellow[a)]
Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112

(Received 2 June 1998; accepted for publication 24 July 1998)

Atomic force microscopy has been used to investigate the influence of controlled tellurium (Te) incorporation on the step structure of GaAs grown by organometallic vapor phase epitaxy on vicinal (001) surfaces. Te doping, using the precursor diethyltelluride, is found to markedly decrease the surface roughness. Step bunching, observed for undoped layers, is totally eliminated. Only monolayer steps are formed for Te concentrations of $>4\times10^{17}$ cm^{-3}. A model is proposed to account for these effects and the results reported previously for GaInP. © *1998 American Institute of Physics.* [S0003-6951(98)03538-4]

As the basic aspects of epitaxial growth are explored, it becomes increasingly clear that the bonding at the surface, including both reconstruction and step structure, plays a key role. In particular, the step structure is found to be important for formation of the CuPt ordered structure often observed for epitaxial layers of III/V alloys.[1,2] Surface step structure determines the surface morphology. It also controls the local growth rates of the various facets on nonplanar substrates.[3] Thus, it is important for the formation of quantum wells[4] and self-assembled quantum dots.[5] Perhaps the most ubiquitous and important effect of the surface steps is related to dopant incorporation. Misorientation of the substrate to produce type A [with (111)A faces] and B [with (111)B faces] steps is found to change the distribution coefficients of many dopants by orders of magnitude.[6] However, these early studies of dopant incorporation did not include an examination of the actual step structures produced. This hinders the development of mechanisms to explain the effects observed. The purpose of this letter is to report the results of a study of the relationship between step structure and incorporation of the dopant Te during the organometallic vapor phase epitaxial (OMVPE) growth of GaAs on semi-insulating (001) substrates misoriented by 3° in either the A or B direction.

An early study of the effects of steps on the growth process clearly showed the difference between [110] and [$\bar{1}$10] steps.[7] Changing the growth conditions was found to strongly affect the step velocities. For nominally (001) GaAs layers grown by OMVPE, misorientation from (001) produces supersteps that may be several nanometers in height.[4,8,9] The steps were also observed to bunch during annealing, with no epitaxial growth.[10] Several factors are known to affect step bunching as it occurs during OMVPE growth: (i) Step bunching was observed on vicinal GaAs(001) surfaces only in the growth temperature range from 575 to 650 °C with misorientation angles of $\leqslant 7°$;[9] (ii) The step bunching was largely suppressed for high V/III ratios of 1500 and larger for GaInP layers;[11] (iii) The addition of certain dopants, such as O and Mg, with strong bonding at the steps, was found to roughen the surface and break the periodicity of step bunching for doping concentrations exceeding approximately 10^{18} cm^{-3}.[12,13] The addition of Zn and Se, dopants with weaker bonding at the steps, was observed to have little effect on root-mean-square (rms) roughness of the GaAs surface for doping as high as 10^{19} cm^{-3}.[12]

The step structures produced during the OMVPE growth of GaInP have also been studied in an effort to understand the effects of steps on the formation of the CuPt structure during growth.[1,2,14,15] As for GaAs, certain temperatures and V/III ratios were found to favor step bunching. The height of the supersteps formed during growth was found to decrease with increasing growth rate in a manner suggesting a surface diffusion limitation to the formation process. In addition, the individual steps produced during growth were found to be mainly monolayer (2.8 Å in height) or bilayer, depending on the growth conditions.[9]

In this study, Te-doped GaAs layers were grown in an atmospheric-pressure, horizontal OMVPE system on semi-insulating (001) GaAs substrates misoriented by 3° toward either the (111)A and (111)B direction, denoted 3^0_A and 3^0_B, respectively. This produces [$\bar{1}$10] (type A) and [110] (type B) steps, respectively. Trimethylgallium (TMGa) and arsine (AsH_3) input supply rates were 1.804 and 206 μmole/min, respectively. The dopant, diethyltelluride (DETe), diluted to 5 ppm in H_2 was added with mole fractions of 0, 5.32 $\times10^{-9}$, 1.61×10^{-8}, 4.81×10^{-8}, and 7.97×10^{-8}. The total H_2 flow rate was 4000 sccm. Approximately 250 nm thick GaAs layers were grown at a temperature 620 °C with a growth rate of 0.6 μm/h. The electron concentration was measured at room temperature using the Hall effect. The surface morphology, particularly 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, with a sidewall angle of 35°. Scan rates of 1–2 lines/s were used and data were taken at 512 points/line and 512 lines per scan area. The samples were measured in air, so were covered by a thin, conformal oxide layer.

Figure 1 shows the AFM images for layers with several values of electron concentration (from Te doping) for vicinal GaAs substrates having either A or B steps. Figures 1(a), 1(b), and 1(c) demonstrate the remarkable change in surface

[a)]Electronic mail: stringfellow@ee.utah.edu

 © 1998 American Institute of Physics
Downloaded 10 Oct 2007 to 155.97.12.90. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

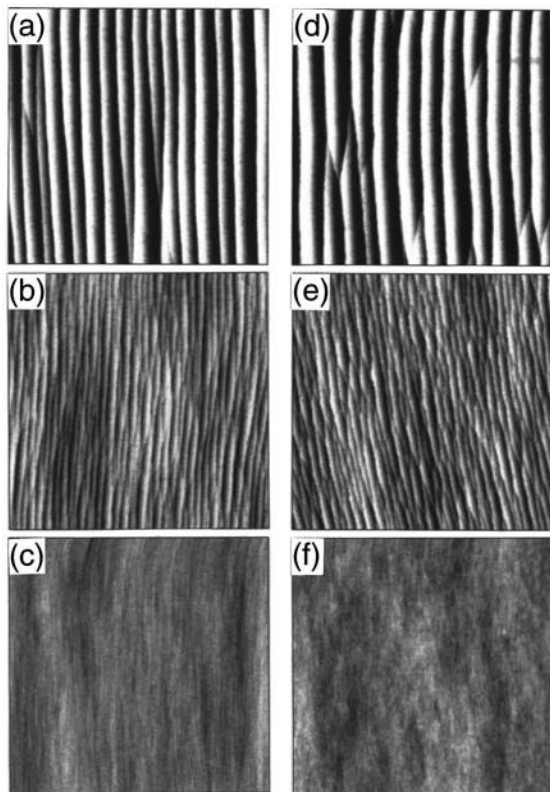

FIG. 1. AFM surface morphology vs electron concentration from Te doping for GaAs(001) vicinal substrates. (a), (b), and (c) are for undoped, $n=7.1\times10^{16}$, and $n=8.7\times10^{17}$ cm^{-3}, respectively, for 3_B^0 substrates. (d), (e), and (f) are for undoped, $n=1.2\times10^{17}$, and $n=8.9\times10^{17}$ cm^{-3}, respectively, for 3_A^0 substrates. The periodic steps are aligned approximately normal to the substrate misorientation direction. The scale is 1000×1000 nm for each image.

morphology with increasing doping level for substrates misoriented to produce B steps. Figures 1(d), 1(e), and 1(f) show the changes induced by Te doping for vicinal substrates with A steps. Figures 1(a) and 1(d) show the typical bunched steps observed for undoped layers having B and A steps, respectively. There are only two surface phases [a mixture of (001) and (11n) facets] observed for both the A and B misorientations. The AFM images show a marked decrease in step bunching with increasing Te doping concentration for both substrate types. This result is similar to the results reported previously for Te-doped GaInP vicinal layers grown at 670 °C.[14]

Figure 2 shows the average step height plotted as a function of electron concentration from Te doping. The average step height was obtained from a careful counting along ten 1 μm AFM section profiles. The step heights are 3.02 and 2.59 nm, respectively, for undoped layers having A and B steps. A significant decrease in step height was observed as the Te doping concentration was increased for both types of substrates. Note that the step height is reduced to about 0.29 nm, 1 monolayer, for electron concentrations exceeding 4×10^{17} cm^{-3}

Both thermodynamic[8] and kinetic[16] factors have been used to explain step bunching. Thermodynamically, the formation of bunched supersteps is similar to phase separation in the bulk. The free energy of the surface is reduced by formation of a two phase mixture of (001) and (11n) facets.

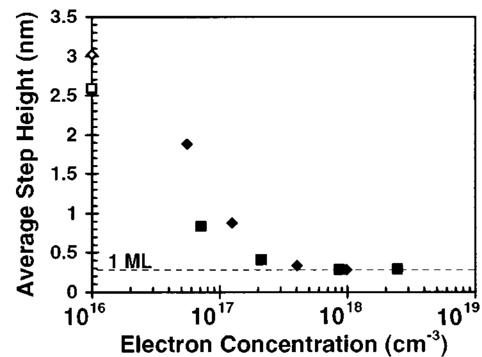

FIG. 2. Average step height vs electron concentration from Te doping for 3_B^0 (□), (■) and 3_A^0 (◇), (◆) substrates. Note that open symbols represent undoped samples, with $n<10^{16}$ cm^{-3}, shown for comparison.

The more common explanation of step bunching during epitaxial growth involves kinetics. Here, step bunching is attributed to a sticking coefficient at ''down'' steps that exceeds that at ''up'' steps.[16] For the opposite situation, where growth occurs predominantly by attachment at ''up'' steps, an array of ordered monolayer steps is formed. By using this kinetic explanation it is suggested that the addition of a sufficient quantity of Te to the solid produces a significant increase in the sticking coefficient at ''up'' steps. This is consistent with the marked increase in step velocity associated with the addition of Te for GaInP layers grown by OMVPE on singular substrates.[15]

Figure 3 illustrates the change in the facet orientation caused by the addition of Te to the system. The value of n for the (11n) facet is plotted versus the electron concentration. The n values were obtained from a careful counting of the angle between the (001) terrace and bunched facet along ten 1 μm AFM profiles. It changes noticeably at the same electron concentration producing the change in step height for both A and B step substrates. For undoped samples, the measured angle was 11.4±1.2°, corresponding to a (117) facet for both the 3_A^0 and 3_B^0 misorientations. This result is the same as that obtained for undoped GaAs layers grown by OMVPE at 600 °C on vicinal GaAs substrates misoriented to give B steps.[8] As the electron concentration is increased from 5.5×10^{16} to 7.2×10^{16} cm^{-3}, only the (117) and (119) facet are observed. The (119) facet, with a measured angle of 8.9°±0.9°, becomes dominant as the doping level is increased from 5.5×10^{16} to 7.2×10^{16} cm^{-3}. When the electron concentration reaches 2.1×10^{17} cm^{-3}, the bunched

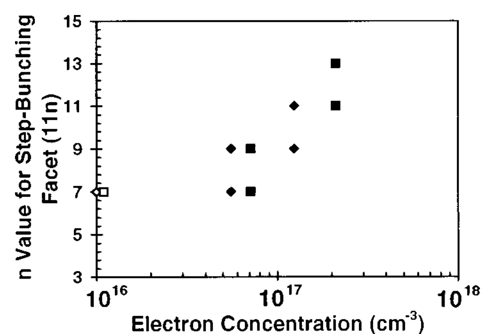

FIG. 3. n value for (11n) facets vs electron concentration from Te doping for 3_B^0 (□), (■) and 3_A^0 (◇), (◆) substrates. Note that open symbols represent undoped samples, with $n<10^{16}$ cm^{-3}, shown for comparison.

Downloaded 10 Oct 2007 to 155.97.12.90. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

facet angles indicate the formation of a mixture of facets with angles of around 7.3° and 6.2°, corresponding to $n = 11$ and 13, respectively. For even higher electron concentrations, the bunched facet angle becomes more difficult to measure due to the smoother surface and reduced terrace width. Clearly, the bunched facet angle becomes less steep as the Te doping level is increased. Apparently, only $(11n)$ facets with odd values of n are formed.

The effects presented here for GaAs layers can be compared with those reported previously for the addition of Te during the OMVPE growth of (001) GaInP. The $[\bar{1}10]$ step velocity, determined from the measured step spacing, increases sharply for Te concentrations exceeding 10^{18} cm^{-3}, with little change in the $[110]$ step velocity.[15] This indicates that Te doping has little effect on $[110]$ step propagation and that the addition of sufficient Te increases significantly the sticking coefficient at $[\bar{1}10]$ step edge [with (111)A faces]. Kaxiras *et al.* theoretically predicted at least two stable reconstructions on (111)A.[17] The predicted As trimer geometry is the most likely to be formed under OMVPE As-rich growth conditions, although it has not been observed experimentally.

To explain the data presented here, we postulate that the (2×2) reconstruction terminated by As trimers is formed on bunched step edges without Te dopant at a growth temperature of 620° and a V/III ratio of 114. The electron counting rule suggests the absence of dangling bonds on such reconstructed (111)A step edges. This gives rise to bilayer steps with relatively small sticking coefficients at both ''up'' and ''down'' steps, leading to step bunching, since a large energy barrier for attachment at ''down'' steps is not expected.[17] Added Te is postulated to preferentially attach at step edges. It is known to act as a surfactant molecular beam epitaxy (MBE) growth.[18] The electron counting rule suggests that, with no change in reconstruction, this will produce dangling bonds. This would be expected to destabilize the bilayer steps and increase the group III adatom sticking coefficients at monolayer steps, especially at ''up'' step edges[18] leading to an ordered step array. This would also explain the simultaneously reduction in step bunching and the degree of order in GaInP for a Te doping level exceeding 2×10^{17} cm^{-3}.[14]

In summary, the influence of Te addition on the step bunching of GaAs (001) vicinal surfaces has been investigated using atomic force microscopy. Te doping dramatically improves the surface morphology: (i) step bunching disappears and (ii) the step height on vicinal surfaces becomes approximately 1 monolayer for Te concentrations of $>4\times10^{17}$ cm^{-3}. The value of n for the $(11n)$ facets formed as a result of step bunching increases with increasing Te doping level. A qualitative model is suggested to account for these effects. Te is postulated to preferentially attach at the step edges. This leads to monolayer steps with higher group III adatom sticking coefficients at ''up'' steps, which suppresses step bunching. It also explains the results reported previously for ordering and step structure in GaInP.

This work was financially supported by the National Science Foundation.

[1] G. B. Stringfellow and L. C. Su, J. Cryst. Growth **163**, 128 (1996).
[2] S. H. Lee and G. B. Stringfellow, J. Appl. Phys. **83**, 3620 (1998).
[3] A. Yamashiki and T. Nishinaga, Cryst. Res. Technol. **32**, 1049 (1997).
[4] T. Fukui, J. Ishizaki, S. Hara, J. Motohisa, and H. Hasegawa, J. Cryst. Growth **146**, 183 (1995).
[5] M. Kitamura, M. Nishioka, J. Oshinowo, and Y. Arakawa, Appl. Phys. Lett. **66**, 3663 (1995).
[6] M. Kondo, C. Anayama, N. Okada, H. Sekiguchi, K. Domen, and T. Tanahashi, J. Appl. Phys. **76**, 914 (1994); M. Kondo and T. Tanahashi, J. Cryst. Growth **145**, 390 (1994).
[7] H. Asai, J. Cryst. Growth **80**, 425 (1987).
[8] M. Kasu and N. Kobayashi, Appl. Phys. Lett. **62**, 1262 (1993).
[9] M. Kasu and N. Kobayashi, Jpn. J. Appl. Phys., Part 1 **33**, 712 (1994).
[10] K. Hata, T. Ikoma, K. Hirakawa, T. Okaano, A. Kawazu, T. Ueda, and M. Akiyama, J. Appl. Phys. **76**, 5601 (1994).
[11] A. Gomyo, H. Hotta, F. Miyasaka, K. Tada, H. Fujii, K. Fukagai, K. Kobayashi, and I. Hino, J. Cryst. Growth **145**, 126 (1994).
[12] J. Li and T. F. Keuch, J. Electronic Mater. (to be published).
[13] S. Nayak, J. M. Redwing, J. W. Huang, M. G. Lagally, and T. F. Keuch, Mater. Res. Soc. Symp. Proc. **367**, 292 (1995).
[14] S. H. Lee, C. Fetzer, and G. B. Stringfellow, J. Cryst. Growth (to be published).
[15] S. H. Lee, T. C. Hsu, and G. B. Stringfellow, J. Appl. Phys. (to be published).
[16] R. L. Schwoebel and E. J. Shipsey, J. Appl. Phys. **37**, 3682 (1966).
[17] E. Kaxiras, Y. Bar-Yam, and J. D. Joannopoulos, Phys. Rev. B **35**, 9625 (1987).
[18] S. H. Lee and G. B. Stringfellow (unpublished results).

Downloaded 10 Oct 2007 to 155.97.12.90. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp