Effects of V/III ratio on ordering and antiphase boundaries in GaInP layers

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Transmission electron microscope (TEM) and transmission electron diffraction (TED) studies have been performed to investigate the effects of V/III ratio on ordering and antiphase boundaries (APBs) in organometallic vapor phase epitaxial $Ga_{0.5}In_{0.5}P$ layers grown onto (001) GaAs vicinal substrates at 670 °C. TED and TEM examination showed that the degree of order is higher in the layer grown using a V/III ratio of 160 than in the layer grown using a V/III ratio of 40. TEM results showed that the higher V/III ratio could be used to suppress APBs. In addition, the growth of order-induced heterostructures, where the V/III ratio is increased abruptly during growth, could be used to block the propagation of APBs. Mechanisms are proposed to explain these phenomena. © *1997 American Institute of Physics.* [S0003-6951(97)02623-5]

Since the first observation of CuPt-type ordering,[1] the degree of the order in (001) layers of GaAsSb,[1] InAlAs,[2,3] GaInP,[4–6] InAsSb,[7,8] and GaInAs[9,10] grown by organometallic vapor phase epitaxy (OMVPE) and molecular beam epitaxy (MBE) has been extensively investigated using transmission electron microscope (TEM) and transmission electron diffraction (TED) techniques. It is well known that CuPt-type ordering is a surface related phenomenon occurring during epitaxial growth.[11–14] Several models based on the $(2\times)$ surface reconstruction and the presence of [110] atomic steps have been proposed to explain the mechanisms by which the ordering occurs in the (001) layers of III–V compound semiconductors.[11–14] The models suggest that the surface structure during growth could play a crucial role in the ordering generation processes. TED examination has shown that such ordering typically occurs on two of the four possible {111} planes, i.e., the $(\bar{1}11)$ and $(1\bar{1}1)$ planes. TEM dark field (DF) examination has revealed the individual domains for the $(\bar{1}11)$ and $(1\bar{1}1)$ ordered variants in MBE and OMVPE III–V alloy layers.[4,6,8,10] The ordered domains generally contained a number of antiphase boundaries (APBs). Such defects are known to adversely influence the optical and electrical properties of the layers. For example, they are likely to decrease carrier mobilities, introduce deep energy levels, and decrease carrier lifetimes and so these defects are undesirable.[15] It is, therefore, very important to be able to control such defects to enhance device performance.

In this letter, a comprehensive TEM and TED study of CuPt-type ordering in OMVPE GaInP layers grown on GaAs (001) vicinal substrates is presented. Effects of V/III flux ratio on the degree of order and the density of APBs in the ordered GaInP layers and in order-induced heterostructures are described and possible mechanisms are discussed.

Nominally undoped $Ga_{0.5}In_{0.5}P$ layers were grown in a horizontal, atmospheric pressure OMVPE reactor using trimethylindium, trimethylgallium, and tertiarybutylphosphine (TBP). The substrates were Cr-doped semi-insulating GaAs misoriented by 3° in the $[1\bar{1}0]$ direction. A GaAs buffer layer ~30-nm-thick was grown first. This was followed by the GaInP layer grown at 670 °C with a rate of 0.5 μm/h. To explore the effects of V/III flux ratio on ordering, the two types of samples with order-induced heterostructures were grown using a change in input V/III ratio: the type I sample was grown using an input V/III ratio of 160 (termed ''high-V/III'') for 48 min, after which the input V/III ratio was reduced to 40 (termed ''low-V/III'') and growth continued for 36 min. Growth conditions for the type II sample were the same as those of the type I sample, except that the order of the GaInP layers was reversed. Two orthogonal $\langle 110\rangle$ cross-section thin foil films were prepared by mechanical polishing followed by Ar^+ ion milling using a liquid N_2 cold stage and examined using TEM and TED in a JEM 2010 instrument operated at 200 kV. The convergent beam electron diffraction technique was employed to determine the polarity between the [110] and $[\bar{1}10]$ directions, and the thin foil thickness.[10,16] The thicknesses of the thin foil films examined by TEM were mostly in the range of ~186–400 nm.

Figure 1 shows [110] TED patterns taken from the type I sample. The pattern [Fig. 1(a)] from the region including both low- and high-V/III layers shows the main spots and $1/2\{111\}B$ superlattice spots, indicating that strong CuPt-type ordering occurs on the $(1\bar{1}1)$ plane with much weaker ordering on the $(\bar{1}11)$ plane. The observation of both variants is somewhat surprising, since misorientation toward $[1\bar{1}0]$ typically produces only one variant.[4,11–14] This could be attributed to the presence of different types of steps on the substrates, i.e., the surface steps introduced by the misorientation and the thermal steps[17] occurring during epitaxial growth. The $(1\bar{1}1)$ variant, however, is overwhelmingly dominant over the $(\bar{1}11)$ variant. This is because the number of steps introduced by the misorientation is far greater than that of thermal steps. The $1/2(1\bar{1}1)$ superlattice spots are circular, indicating a low density of APBs in the ordered regions and/or the presence of large ordered domains.[8,10] However, the $1/2(\bar{1}11)$ superlattice spots are elongated and inclined, indicating either a high density of planar defects in

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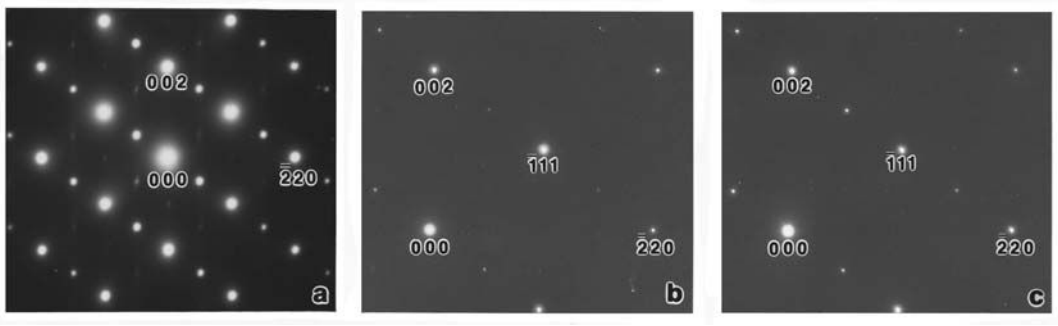

FIG. 1. [110] TED patterns from the type I sample. The pattern shows the main spots and 1/2{111}B superlattice spots.

the ordered regions or the presence of small and narrow ordered domains.[8,10]

Figures 1(b) and 1(c) show TED patterns obtained from the low- and high-V/III layers, respectively, using the smallest selected area aperture. Comparison of the patterns shows that the degree of order is higher in the high-V/III layer than in the low-V/III layer. The results could be interpreted as follows. The higher input phosphorus stabilizes the $(2\times)$ surface reconstruction where the surface is covered with $[\bar{1}10]$-oriented phosphorus dimers. Murata *et al.*,[18] using surface photoabsorption (SPA), showed that the concentration of the $[\bar{1}10]$-oriented phosphorus dimers, which are characteristics of the (2×4) reconstruction, is increased with increasing the TBP partial pressure. Since the $(2\times)$ reconstructed surface is required to produce CuPt ordering,[11–14] such a surface reconstruction leads to an increase in the degree of the order. This result is consistent with those obtained by Murata *et al.*[18]

A 1/2$(\bar{3}31)$ TEM DF image from the type I sample (Fig. 2) reveals the $(1\bar{1}1)$ ordered material as the bright regions. Within the ordered region, there are wavy inclined dark lines 5–15 nm across, corresponding to APBs, few of which propagate through the full layer thickness of ~0.7 μm at an angle of $\sim38°$ to the (001) plane. The density of APBs decreases throughout the layer. It is $\sim8.1\times10^9/\mathrm{cm}^2$ near the interface, $\sim2.0\times10^9/\mathrm{cm}^2$ near the interface between the low- and high-V/III layers, and $\sim1.5\times10^9/\mathrm{cm}^2$ in the middle of the low-V/III layer. Some of the APBs (marked ''J'') within the high-V/III layer have joined together and annihilated one another. Other APBs (marked ''T'') were terminated at the interface between the low- and high-V/III layers, indicating that an increase in the V/III ratio retards the propagation of the APBs. The result suggests that multilayers or artificial superlattice layers consisting of individual ordered layers grown using different V/III ratios may be used to suppress (or eventually eliminate) the APBs. Note that a large decrease in the APBs density occurs at the interface between the low- and the high-V/III layers. This may be related to the stabilized [110] steps due to the high TBP partial pressure.[19] Su and Stringfellow[19] suggested that the APBs arise from bunched steps. It was shown that an increase in the TBP partial pressure stabilizes the bilayer steps, consequently preventing step bunching.[20]

A similar 1/2$(\bar{3}31)$ DF image from the type II sample is shown in Fig. 3. Within the ordered region there are wavy APBs 5–15 nm across, several of which propagate through the full layer thickness of ~0.7 μm at an angle of $\sim37°$ to the (001) plane. The APB density again decreases throughout the layer, with values of $\sim7.5\times10^9/\mathrm{cm}^2$ near the interface, $\sim3.7\times10^9/\mathrm{cm}^2$ near the interface between the high- and low-V/III layers, and $\sim2.8\times10^9/\mathrm{cm}^2$ in the middle of the high-V/III layer. Some of the APBs join together and are annihilated (marked J). Very few APBs were terminated at the interface between the high- and low-V/III layers as compared to the type I sample, indicating that the inverted structure is less effective in suppressing APB propagation.

The effects of the V/III ratio on the degree of order were

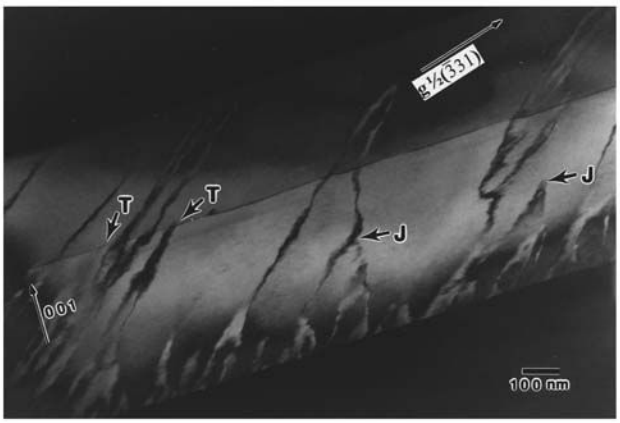

FIG. 2. 1/2$(\bar{3}31)$ TEM DF image from the type I sample showing the $(1\bar{1}1)$ ordered material. Wavy inclined dark lines 5–15 nm across correspond to APBs.

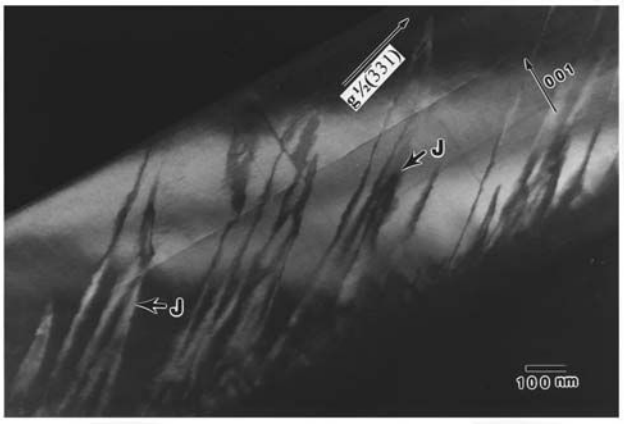

FIG. 3. 1/2$(\bar{3}31)$ DF image from the type II sample showing the $(1\bar{1}1)$ ordered material. There are wavy APBs 5–15 nm across, few of which propagate through the full layer thickness of ~0.7 μm at an angle of $\sim37°$ to the (001) plane.

investigated using a new TEM technique presented by Baxter *et al.*[6] for obtaining quantitative information on the degree of order in GaInP layers. The ratio of the intensity profiles in the $1/2(\bar{3}31)$ DF images (Figs. 2 and 3) and $(\bar{2}04)$ DF images (not shown) obtained from both type I and II samples showed that the degree of order is higher in the high-V/III layer than in the low-V/III layer. This is in good agreement with TED results [Figs. 1(b) and 1(c)].

Examination of the interfaces corresponding to the change in TBP flow rate in Figs. 2 and 3 reveals the change in order parameter as a change in brightness, although the change is small because the change in order parameter is small, as indicated by the 25–30 meV change in the band gap energy.[21] This preliminary data indicate that the change in order parameter is abrupt. The interfaces appear to be slightly wavy.

In summary, TEM results show that the density of APBs can be reduced by producing a change in order parameter via a change in the input V/III ratio during growth: Changing to a high TBP partial pressure appears to retard the propagation of ABPs, resulting in fewer APBs in the upper layer. DF results showed that the interfaces of the heterostructures were fairly sharp and abrupt although slightly wavy. TEM and TED results of both type I and II samples showed that the degree of order is higher in the high-V/III layer than in the low-V/III layer.

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