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Ordered domain structures of nitrogen-doped GaInP layers grown by organometallic vapor phase epitaxy

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Abstract Transmission electron microscopy (TEM) and atomic force microscopy (AFM) studies have been performed on organometallic vapor phase epitaxial GaInP heterostructures grown on (001) GaAs singular and vicinal substrates to investigate nitrogen doping effect on the ordering and domain structures. TEM results show that well-defined order–disorder–order heterostructures are formed when nitrogen doping level is high. This indicates that nitrogen hinders the occurrence of ordering. For the singular samples, ordered domain structures are found to be dependent on the nitrogen doping level of the underlying layer, on which they are grown. The doping dependence of ordered structures and the formation of anti-phase boundaries are described based on surface undulations (i.e., hillocks) and step configuration.

1 Introduction

Transmission electron microscopy (TEM) studies of ternary III–V semiconductor alloy layers grown on (001) binary substrates by molecular beam epitaxy and organometallic vapor phase epitaxy (OMVPE) exhibited the presence of atomically ordered CuPt-type structure, which is comprised of alternating {111}B monolayers of two binary components [1–9]. This phenomenon is of practical importance, because it influences the optical and electrical properties of group III–V alloy semiconductor layers. For example, the band gap energy of GaInP was found to be 160 meV lower in partially ordered materials than in totally disordered materials [4]. This is advantageous for devices, such as light emitting diodes [5] and high efficiency solar cells [6]. On the other hand, ordering was shown to provide the attractive opportunities of producing heterostructures [4] and quantum wells [7] by changing the band gap energy without altering solid compositions.

Mechanisms [10–12], by which CuPt-type ordering occurs in III–V compound semiconductors involve the roles of surface reconstruction as well as surface steps. For example, [110] steps were reported to assist the ordering process, but [−110] steps retard ordering. The degree of order (and hence bandgap) was shown to be greatly affected by growth conditions, e.g., temperature, growth rate, substrate orientation and doping level. Concerning doping, different types of dopants, such as Si, Zn, Te, P, and N, were introduced to investigate their effects on the degree of order in GaInP layers [13–17]. It was shown that the introduction of a high concentration of dopants during OMVPE growth results in a decrease in ordering. The effects were attributed to either the modification (and/or destabilization) of surface reconstruction, an increase in the diffusivity of group III atoms, or their combined effects.

In this work, TEM and transmission electron diffraction (TED) have been used to investigate the structural properties of N-doped GaInP layers grown on GaAs (001) singular and vicinal substrates. It is shown that the addition

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of N decreases the degree of order in GaInP and so can be used to grow order–disorder induced heterostructures. It is also shown that the ordered domain structures depend on the surface morphologies of GaInP layers.

2 Experimental

The N-doped GaInP layers were grown in a horizontal, atmospheric pressure organometallic vapor phase epitaxy (OMVPE) reactor using trimethylgallium (TAIGa), ethyl-dimethylindium (EDMIn), and tertiarybutylphosphine (TBP) with disilane as dopant precursor. The substrates were Cr-doped semi-insulating (001) GaAs and (001) GaAs misoriented by 3° in the [111]B direction, on which GaAs buffer layers were grown. This was followed by the growth of undoped GaInP/N-doped GaInP (GaInP:N)/ undoped GaInP heterostructures. The growth temperature was 620 °C, the growth rate was 1 μm/h, and the V/III ratio was 30. To investigate the effect of N doping on ordering and its associated structures, doping concentrations were varied from a DMHy/V ratio of 0–0.8. For transmission electron microscopy (TEM) examinations, two orthogonal [110] cross-section thin foil specimens were prepared using standard procedures and finished by Ar+ ion thinning with the specimen cooled to 77 K. Dark field (DF) and electron diffraction experiments were carried out using a JEM 2010 instrument operated at 200 kV. The thicknesses of the thin foils examined by TEM were in the range of 150–400 nm. The surface morphology was characterized using a Nanoscope III atomic force microscope (AFM) in the tapping mode.

3 Results and discussion

Figure 1 shows [110] TED patterns obtained from regions including the upper GaInP and middle GaInP:N layers of the GaInP/GaInP:N/GaInP heterostructures grown on singular (001) GaAs with different DMHy/V ratios of 0.2–0.8. (We could not take TED patterns from the sandwiched GaInP:N layers, because the smallest selective aperture of our electron microscope is larger than the thicknesses of the GaInP:N layer.) For all the samples, the patterns reveal the superlattice spots at ½(−111) and ½(1−11), each with its associated family of spots, indicating the occurrence of CuPt B-type ordering on (−111) and (1−11) planes. It is noted that the intensity of the superlattice spots (with reference to the main spots) becomes weaker with increasing DMHy/V ratio. In addition, the superlattice spots are elongated and tilted ∼7° from the [001] growth direction, but become circular with increasing DMHy/V ratio (i.e., N concentration). The elongation and tilting of the superlattice spots could be attributed to the elongated ordered domains and/or sharp planar defects in the ordered regions (i.e., anti-phase domain boundaries (APBs)) [18], as will be demonstrated by TEM results.

Similar TED examination was also performed on the heterostructures grown on vicinal (001) GaAs substrates with DMHy/V ratios of 0.6 and 0.8. Figure 2 shows [110] TED patterns from the upper two layers (GaInP and GaInP:N). For both the samples, the patterns exhibit only one variant of CuPt B-type ordering, indicating that CuPt-type ordering occurs only on the (−111) plane. Consistent with the results of the singular samples, the intensity of the superlattice spots becomes weaker with increasing N concentration, indicating that the N doping is effective in reducing the degree of order.

[110] TEM DF images were obtained using individual superlattice spots to investigate the ordered domain structures and APBs. Figure 3 shows ½(−33−1) and ½(−331) DF images obtained from the singular samples grown with different DMHy/V ratios. The DF images reveal the ordered domains as the bright areas. For the sample grown with a DMHy/V ratio of 0.2 (Fig. 3a), the ordered region contains fine modulations ∼5 nm wide and 80–150 nm long (indicated by the white arrows) titled 4–8° from the [001] growth direction, which is believed to be responsible for the elongation and tilting of the superlattice spots [3, 19]. There are also wavy inclined dark lines ∼9 nm across, corresponding to APBs (marked ‘P’). For the sample grown with a DMHy/V ratio of 0.4 (Fig. 3b), there are similar fine

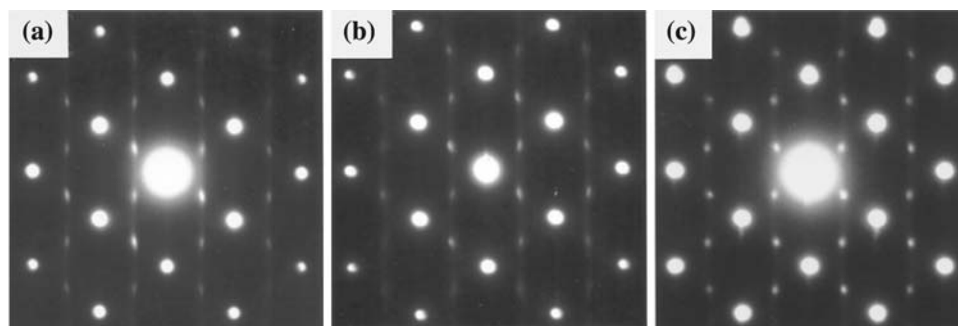

Fig. 1 [110] TED patterns obtained from regions including the upper GaInP and middle GaInP:N layers of the GaInP/GaInP:N/GaInP heterostructures grown on singular (001) GaAs with DMHy/V ratios of (**a**) 0.2, (**b**) 0.4 and (**c**) 0.8

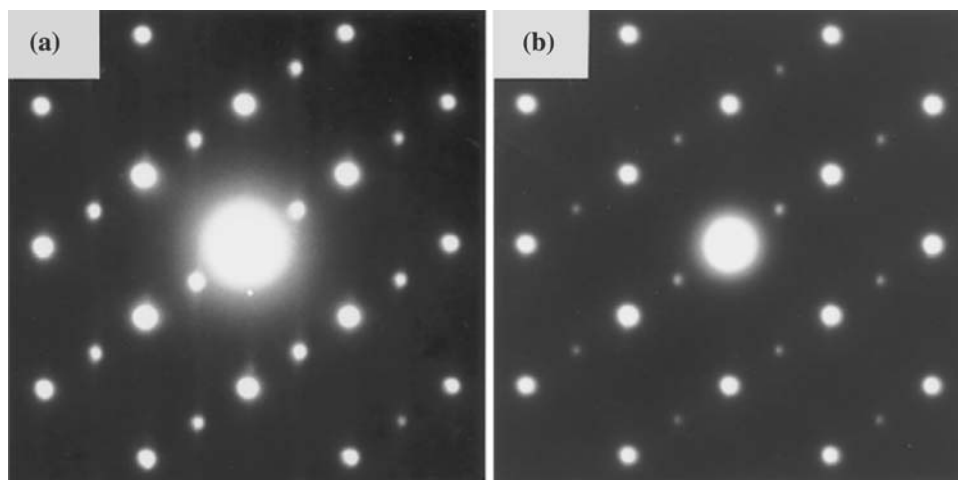

Fig. 2 [110] TED patterns from the upper two layers (GaInP and GaInP:N) of the heterostructures grown on vicinal (001) GaAs with DMHy/V ratios of (**a**) 0.6 and (**b**) 0.8

modulations in the ordered regions, which are slightly titled ~5° from the [001] direction. For the samples grown with ratios of 0.2 and 0.4, the ordered/disordered/ordered heterostructures are not well defined. However, for the sample grown with a ratio of 0.8, three layers are clearly visible; Fig. 3c and d show DF images from the same region taken using ½(−33−1) and ½(−331) superlattice spots. It is noteworthy that the ordered domain structure of the lower GaInP layer differs from that of the upper GaInP layer. For the lower GaInP layer, the ordered domain structure is fairly similar to those for the samples grown at the lower DMHy/V ratios. In other words, there are fine modulations in the ordered regions tilted 5–8° in an opposite sense. The upper layer, however, contains columnar-like ordered regions ~50–250 nm wide. Within the ordered regions there are a number of irregular wavy dark lines (3–40 nm wide), corresponding to APBs, as clearly shown in the inset of Fig. 3d. In addition, unlike the samples grown at the lower DMHy/V ratios, the two order variants in the upper GaInP layer occupy complementary regions, where the same points are indicated by the white arrows. It is noted that the GaInP:N layer reveals almost no contrast, indicating that N plays a role in reducing the degree of order. In addition, there are many stacking faults in the GaInP:N layer. This might be related to the roughening of the surface of GaInP during growth.

Figure 4 shows similar ½(−331) DF images obtained from the vicinal GaInP/GaInP:N/GaInP samples grown with DMHy/V ratios of 0.6 and 0.8. It is clearly shown that for the both samples, order/disorder/order heterostructures are formed, although the sample with the higher DMHy/V ratio shows the better structure. For the sample with a ratio of 0.6, the GaInP:N layer reveals weak bright contrast, namely, ordered micro-domains, indicating that the N

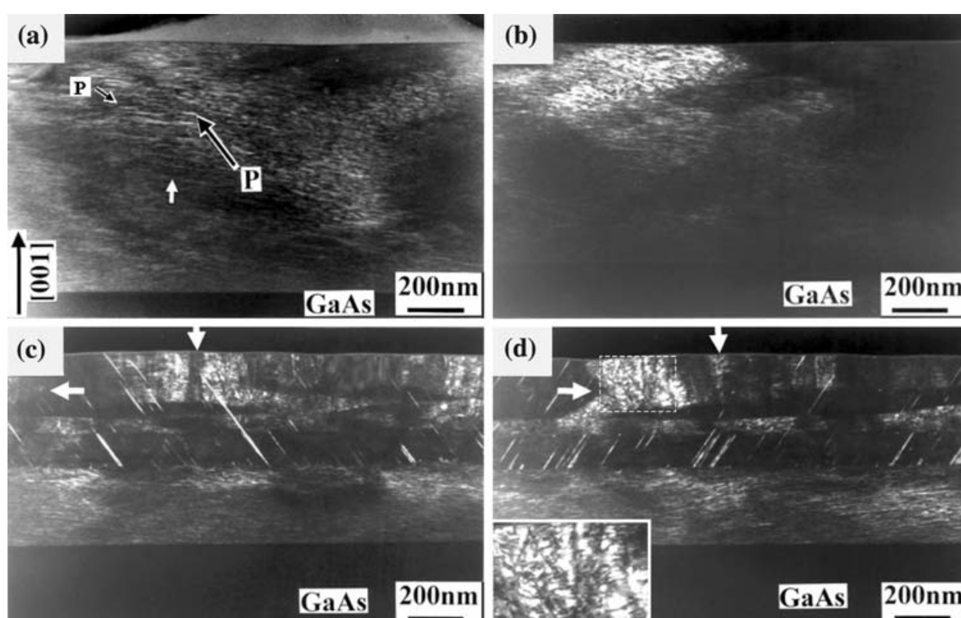

Fig. 3 ½(−33−1) and ½(−331) DF images obtained from the singular samples grown with different DMHy/V ratio of (**a**) 0.2, (**b**) 0.4, (**c, d**) 0.8

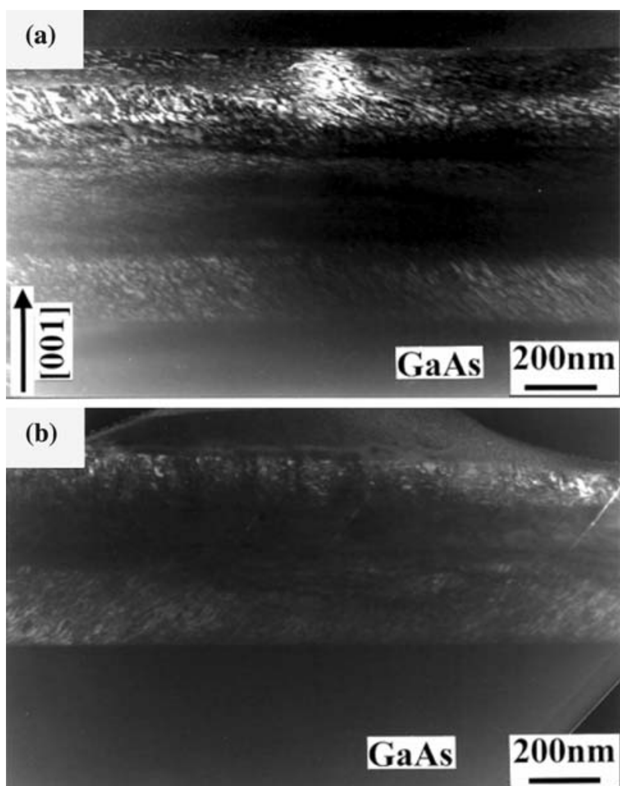

Fig. 4 ½(−331) DF images obtained from the vicinal GaInP/GaInP:N/GaInP samples grown with DMHy/V ratios of (**a**) 0.6 and (**b**) 0.8

content is not sufficient enough to completely hinder the formation of ordering. It is also noted that for the sample with a ratio of 0.8, the GaInP:N layer contains stacking faults. However, the density is much lower than that of the singular sample grown at a ratio of 0.8.

AFM was used to investigate the surface morphologies of the singular samples with different N concentrations. The results show that the surfaces become rougher with increasing DMHy/V ratio. This is in good agreement with the results previously observed Auvray et al. [20]. For example, the surface morphologies of the GaInP layers grown with and without N doping are shown in Fig. 5. For the undoped singular sample (Fig. 5a), the surface shows undulation with a root mean square (RMS) roughness of 2 nm. However, for the sample with DMHy/V ratio of 0.8 (Fig. 5b), there are hillocks elongated along the [110] direction. The hillocks are typically 0.7–2.2 μm wide and 1.8–5.9 μm long, and are facetted facing outwards.

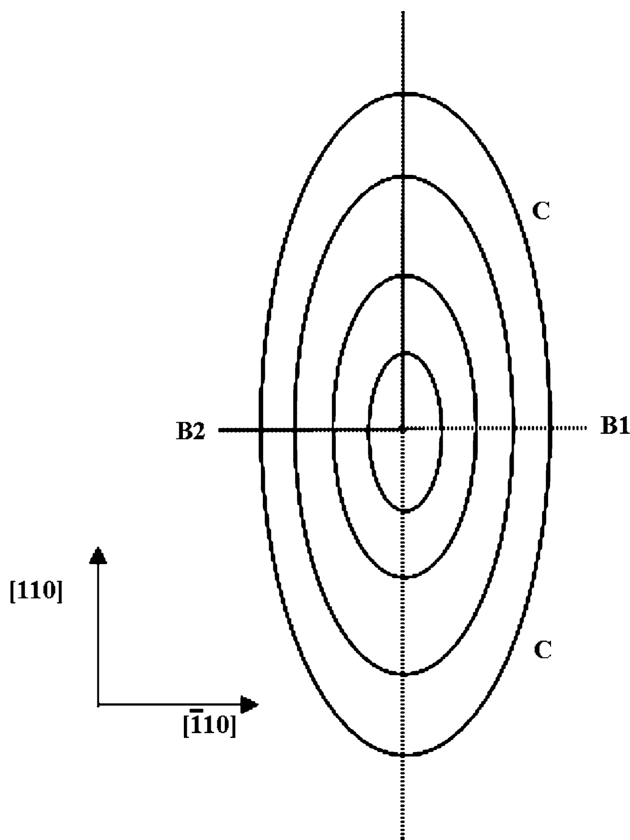

Fig. 6 A plan-view diagram of a possible step configuration of the singular sample, based upon the AFM results

The TEM results obtained from the N-doped GaInP and undoped GaInP layers exhibited characteristic features. First, the degree of order decreases with increasing

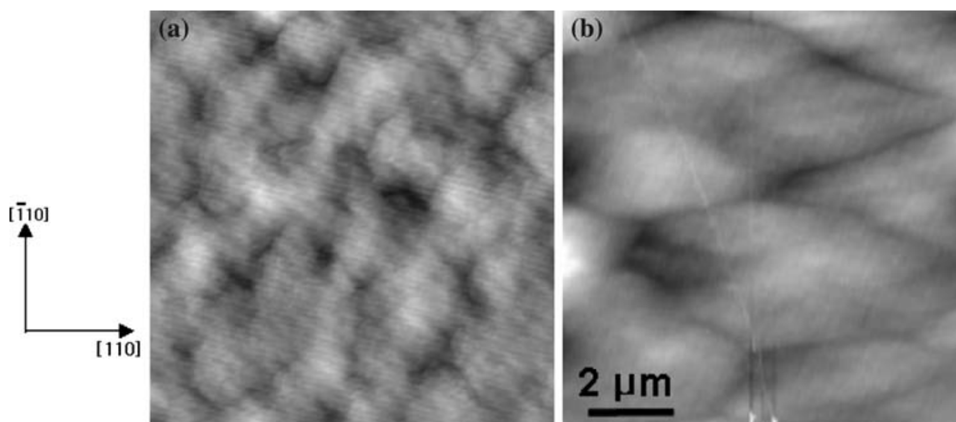

Fig. 5 AFM images of the surface morphologies of the GaInP layers grown with DMHy/V ratios of (**a**) 0 and (**b**) 0.8

DMHy/V ratio. This is consistent with the results previously observed by Chapman et al. [17] who deduced it from the photoluminescence peak energy. The decrease in the degree of ordering was attributed to the reduction of P dimers on the surface due to the presence of N that does not dimerize on the GaInP surface [17].

Second, the ordered domain structures of undoped GaInP are dependent on the underlying layer, on which they were grown. Unlike other layers, the upper GaInP layer grown onto the GaInP:N (with a DMHy/V ratio of 0.8) gives the ordered areas of two variants occupying complementary regions. This behavior may be explained as follows. In our previous work [3], we showed that surface atomic steps running along the [110] direction play a role in phase-locking the growth of successive atomic layers to give either the (−111) or the (1−11) ordered variant. And so the two separated columnar-like ordered regions may be associated with the surface hillocks. Figure 6 shows a plan-view diagram of a possible step configuration of the singular sample, based upon the AFM results. For simplicity, the surface of the sample is assumed to consist of elliptical hillocks with the longer sides running along the [110] direction, where the B1 and B2 areas slope downwards (in an opposite sense) and have atomic steps facing outwards. In B1 area, atomic layers nucleate at the steps and grow outwards to give ordered material of variant I. In a similar manner, atomic layers nucleate and grow in B2 area to give ordered material of variant II.

Third, the upper GaInP layer grown onto the GaInP:N layer contains numerous APBs. This may be explained as follows. The surface of the GaInP:N layer where the upper layer is grown has elliptical hillocks. As shown in Fig. 5, the hillocks have C areas that are inclined to the [110] direction and consequently this areas contain a number of kinks. Seong et al. [3], investigating the domain structures of ordered GaInAs OMVPE layers, showed that undimerised atoms could form at the step edge when the steps were not along the [110] direction and such atoms could lead to the formation of APBs [21]. Therefore, the increase in the density of APBs observed in the upper GaInP layer of the sample grown at 0.8 may be related to the increase in the C regions caused by the formation of surface hillocks, as shown in Fig. 6.

4 Summary

OMVPE GaInP order/disorder/order heterostructures grown on (001) GaAs singular and vicinal substrates at 620 °C were examined by TEM and AFM. TEM results showed that a high DMHy/V ratio of 0.8 is required to completely disorder GaInP layer and hence to form well-defined order/disorder/order heterostructures. It was also shown that for the singular samples, the ordered domain structures depend on the surface morphologies of the GaInP layer, on which they are grown. AFM results exhibited that the surfaces of the singular samples become rougher with increasing N content. The samples grown on the smooth surfaces produced ordered regions with fine modulations, while the samples grown on undulated surfaces with hillocks gave columnar-like ordered regions with a number of APBs. This behavior was explained in terms of the step configuration of the singular sample, where the facetted areas slope downwards (in an opposite sense).

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