Surface Evolution of GaP Grown on Si Substrates Using Metalorganic Vapor Phase Epitaxy

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GaP surface evolution on Si substrates in the initial growth stage was investigated using atomic force microscopy. The GaP was grown on 4°-misoriented Si substrates at 700–830°C using metalorganic vapor phase epitaxy. Island growth was predominant below nominal 5-nm thickness at 830°C. Several antiphase domains (APDs) grew to be 100 nm or longer at nominal 5 nm deposition. They were 5 nm higher than surrounding islands. The surrounding islands formed a layer at a nominal thickness over 5 nm. The layer grew vertically faster than the APDs. Several APDs grew laterally until a layer-thickness exceeded an APD height. The layer finally embedded the APDs. Self-annihilation of APDs was achieved below 40-nm thickness. Similar surface evolution was found at 770 and 800°C. The APD size decreased with decreasing temperature. Self-annihilation of APDs was achieved below 20-nm thickness at 770°C.

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1. Introduction

A GaP layer on a Si substrate is necessary for a GaPN on a Si substrate, which is attractive for optoelectronic integrated circuits (OEICs).¹⁾ Several researchers have produced high-quality GaP layers on Si substrates.²⁻⁶⁾ The authors also obtained a GaP layer having neither dislocations nor stacking faults on a Si substrate using metalorganic vapor phase epitaxy (MOVPE).⁷⁾ We deposited GaP layers on Si(100) substrates 4° misoriented toward [011] at 830°C with a high PH₃ flow rate. We found antiphase domains (APDs) at an initial growth stage. The APDs appear because GaP is polar whereas Si is nonpolar. The lattice mismatch between GaP and Si is 0.37%, which results in a critical thickness between 50 and 100 nm.⁴⁾ The APDs must self-annihilate below the critical thickness because they probably degrade a subsequent layer on a GaP layer.⁸⁾

No APDs were reported to be observed in GaP layers on Si(111) substrates.⁹⁾ In GaP layers on Si(100), however, APDs were found. Misoriented Si(100) substrates were used to suppress APDs as described below. Migration enhanced epitaxy (MEE) at 440°C on a 4° misoriented Si substrate suppressed APD evolution, resulting in the absence of APDs in a GaP layer 10 nm above the interface.¹⁰⁾ Our growth temperature is much higher than 440°C. Reportedly, few APDs were found in a GaP layer on a 4° or 6° misoriented Si substrate grown at 900°C with a V/III ratio of 1600 using MOVPE.¹¹⁾ The APDs, however, propagated to a surface in a layer on exactly oriented or 1° misoriented Si substrate. APDs self-annihilated in a layer on a 2° misoriented Si substrate during the early stage of growth. The growth parameters are

above our reactor limit. Self-annihilation of all APDs was reported to be achieved on a 0.12° misoriented Si substrate using MOVPE with the optimized Si surface pretreatment and optimized GaP growth conditions.⁵⁾ The Si surface pretreatment is an important topic. However, we remain unable to achieve a complete double-stepped Si surface even if we used 4° misoriented Si substrates. In this study, we investigated APD evolution during the initial growth stage in a sample prepared under the previously used growth conditions. We then varied the growth temperature between 700 and 830°C . We present a relation between APD evolution and growth parameters.

2. Experimental Procedure

Epilayers of GaP were prepared using a MOVPE on Si(100) substrates with 4° misorientation toward [011]. The MOVPE reactor was of the horizontal cold-wall type. Triethylgallium (TEG) and PH_3 were used as source materials. The substrates were degreased and etched using a method described by Ishizaka and Shiraki.¹²⁾ They were preheated at 925°C at 100 Torr in a H_2 flow for 30 min. The substrates were cooled to a growth temperature of $700\text{--}830^\circ\text{C}$. The reactor pressure was increased to 300 Torr. They were exposed to PH_3 for 15 s before GaP growth initiation. Growth was initiated by supplying TEG. The respective flow rates of TEG and PH_3 for GaP growth were 1.4×10 and $2.7 \times 10^3 \mu\text{mol/min}$. The total gas flow rate was $8.9 \times 10^{-2} \text{ mol/min}$. GaP structures were characterized using Nomarski interference microscopy and atomic force microscopy (AFM). A sample was characterized using transmission electron microscopy (TEM) operating at an acceleration voltage of 200 kV. A specimen for

cross-sectional TEM observation was prepared by mechanical grinding followed by Ar⁺-ion bombardment. GaP layer thickness was determined using AFM by observing a GaP layer, a part of which was removed in a solution of HCl:HNO₃:H₂O=3:1:1.

3. Results and Discussion

Figures 1 show AFM images of GaP on Si substrates grown at 830°C in the initial growth stage. Figures 2 show complementary AFM images of the morphologies of the samples depicted in Figs. 1. Figure 1(a) displays an AFM image after nominal 1 nm deposition. Many round islands were formed, some of which coalesced, forming a smooth surface locally. The island density was $7.0 \times 10^{10} \text{ cm}^{-2}$. Most islands were elongated slightly in the step direction. We are unable to determine APDs because the islands had small anisotropy. Figure 1(b) shows an AFM image of GaP on a Si substrate after nominal 3 nm GaP deposition. Many islands remained. Figure 2(a) shows an enlarged top AFM image of the sample. Most islands were elongated parallel to the step direction. There were small APD islands elongated perpendicular to the step direction,¹³⁾ the density of which was $6.0 \times 10^9 \text{ cm}^{-2}$. Figure 1(c) shows an AFM image of GaP after nominal 5 nm GaP deposition. A GaP layer covered the Si surface. The APDs were elongated perpendicular to the step direction. Figure 2(b) shows an enlarged AFM image of a fraction of Fig. 1(c). The APDs composed of three (115) planes as shown in Fig. 2(c). Some APDs with a 100–200 nm length were 5–10 nm higher than the neighboring surface. The APD size was much larger than that of the nucleated islands in Fig. 1(a). The APDs probably originated from antiphase terraces of a Si substrate. The

possibility exists that the APD size reflects the antiphase terrace size. Another possibility is lateral overgrowth of an APD over the neighboring islands. We cannot determine directly which mechanism is dominant at present. The APDs were inclined against the Si surface because the Si surface was misoriented. If APDs grew laterally in the step-down direction under the growth conditions in which the growth rate of APDs in the step-down direction is high, some APDs would be higher than the neighboring normal islands as shown in Fig. 2(b). The high APDs are expected to cover the neighboring islands after further growth. Figure 1(d) shows that the layer thickness almost reached a height of large APDs after 10 nm deposition. The shape of APDs remained similar. The result means that the layer growth rate was much higher than the vertical growth rate of APDs. Figure 1(e) shows a surface morphology of GaP after 20 nm deposition. A few APDs were observed in the figure, indicating that the layer covered most APDs during the last 10 nm deposition. The APD density was $3 \times 10^8 \text{ cm}^{-2}$. Figures 1(f) and 2(d) show the AFM image and enlarged top AFM image of GaP after 40 nm deposition. Almost all APDs were embedded in the GaP layer. In Fig. 1(f), the arrow indicates the GaP layer that almost covered an APD. The top of the APD was 20 nm below the neighboring (100) surface. The surface morphology images show that APDs are an origin of concave GaP surfaces.

Figures 1(b)–1(d) show that several large APDs grew rapidly; Figs. 1(d)–1(f) show that the APDs grew slowly. Large APDs probably grew freely until the layer thickness exceeded the height of the APDs. The layer probably blocked lateral growth of the APDs.

Figure 3 shows a fraction (surface coverage) of APDs and an APD density in the surface as a function of a GaP thickness. The APD density decreased during growth, probably because of the self-annihilation or coalescence of APDs. However, the fraction of APDs increased between 3 and 10 nm thickness. Some APDs grew rapidly. Both the density and fraction of APDs decreased above 10 nm thickness. Self-annihilation of all APDs proceeded above 10 nm thickness.

Figures 4 show (011) cross-sectional TEM images of the sample after 40 nm deposition. Figure 4(a) shows an image of a part of the sample; TEM observation was performed using (022) conditions. Neither dislocations nor stacking faults were found. Figure 4(b) shows a typical dark field image of a region of the sample. The TEM observations were performed under dark field conditions using (200) reflection to be sensitive to APDs.^{5,10)} Figure 4(c) depicts a dark field image of the same region of the sample taken under dark field conditions using (-200) reflection to prevent misjudgment due to a contrast resulting from surface roughness of the TEM sample.^{11,14)} Two large domains were found in Fig. 4(b). Figure 4(c) shows that contrasts of the domains were inverted using (-200) reflection. A difference between (200) and (-200) beam intensities were reported for GaP.^{11,14)} The domains were determined to be APDs. They were 20 and 30 nm high, whereas, they were 100 and 60 nm long in the [011] direction. The size and density were comparable to the AFM results on the large APDs that were observed at 10 nm deposition. TEM images show that most APDs were embedded in the 40 nm thick GaP layer. In cross-sectional TEM images, however, it was hard to find the small APDs that were observed in AFM images of the layers at 3 or 5 nm deposition. Figure

4(d) shows an enlarged image of Fig.4(b). Figure 4(d) indicates that contrasts were weak in the near boundary regions of the APD. The weak contrasts are possibly attributed to a short electron beam path in the near boundary region of the APD. The 5 nm or less high APDs will show extremely weak contrast because a size of a small APD is 10 nm or less in the electron beam direction.¹⁴⁾ We found several contrasts suggesting small APDs (not shown). However, the density of the small APDs that was determined using TEM was two times less than that determined using AFM. For the small APDs, further investigations will be required.

APDs must be smaller for smoother surfaces. Self-annihilation of an APD likely started at a point where the layer thickness exceeded the height of the APD. Earlier transition from island growth to layer growth is probably required to reduce the APD size because the APDs are expected to be smaller with less deposition. An increased PH₃ flow rate greater than 2700 $\mu\text{mol}/\text{min}$ will increase the nucleation density, which results in earlier transition to the layer. However, the flow rate of 2700 $\mu\text{mol}/\text{min}$ is our reactor limit. For this study, we varied the growth temperature between 700 and 830°C.

Figure 5(a) shows an image of GaP/Si after nominal 1 nm deposition at 800°C. Islands nucleated more densely on a fraction of the substrate than at 830°C; the island density was $1.2 \times 10^{11} \text{ cm}^{-2}$. The typical island size was 20 nm; the islands were smaller than those at 830°C. Several islands possibly coalesced in the step direction. The rms surface roughness was 0.31 nm, which was slightly less than that at 830°C. Figure 5(b) shows an image of GaP on the Si substrate after 10 nm deposition at 800°C.

The APDs were smaller than those at 830°C. The layer surface was higher than the APDs. The rms value of surface roughness was 1.7 nm. Figure 5(c) shows an image of GaP on the Si substrate after 20 nm deposition. The layer almost covered the APDs. The concave regions of the surface probably resulted from APDs. The rms value of surface roughness was 1.1 nm. Figure 5(d) shows an image of GaP on the Si substrate after nominal 1 nm deposition at 770°C. Island-like structure was visible on some of the substrate. The remainder of the surface resembled the substrate surface. Layer growth possibly occurred on some of the surface at the onset of growth, although we cannot confirm that GaP covered the surface. The rms value of surface roughness was 0.17 nm, which was similar to that of the substrate surface. Figure 5(e) depicts an image of GaP on the Si substrate after 10 nm deposition. As shown there, GaP covered the whole surface with structures elongated in the step direction. Visible APDs decreased rapidly when the temperature decreased from 800 to 770°C. The APD density was $2 \times 10^8 \text{ cm}^{-2}$. The APD size was 30–50 nm, which was less than that at 830°C. Figure 5(f) shows an image of GaP on the Si substrate after 20 nm deposition. No APDs were visible. Concave surface regions, which appeared at 800°C, were found also at 770°C. The bottoms of several concave surfaces were 5-nm deep. The depth was larger than that at 800°C, which suggests that embedding of APDs possibly proceeded slowly at 770°C. Previously, we reported⁷⁾ that the GaP morphology degraded under PH₃ flow rate of 1350 $\mu\text{mol/min}$ when the temperature decreased from 830°C. As described here, the results at 770 and 800°C under a PH₃ flow rate of 2700 $\mu\text{mol/min}$ indicate for the first time that the nucleation temperature can be lowered to less than 830°C without

degrading GaP morphology also in MOVPE with TEG and PH₃.

Figure 6(a) shows an image of GaP on the Si substrate after nominal 10 nm deposition at 740°C. The density of islands was $3 \times 10^{10} \text{ cm}^{-2}$. Some islands measured 200 nm long and 10 nm high. Layers are difficult to obtain below the critical thickness under the growth conditions. Figure 6(b) shows an image of GaP on the Si substrate after nominal 10 nm deposition at 700°C. Islands became larger with decreasing temperature from 740 to 700°C. Several islands were 1000 nm long or more (not shown). The temperature dependence of island density between 700 and 770°C was similar to that between 700 and 830°C using the PH₃ flow rate of 1350 $\mu\text{mol/min}$ described in the previous report.⁷⁾ Decomposition of PH₃ is low below 740°C.

The growth mechanism was similar qualitatively at 770, 800, and 830°C, except that the layer growth possibly occurred on some of the substrate at 770°C from the beginning of the growth. We summarized a fraction (surface coverage) of APDs at 770, 800, and 830°C as a function of a GaP thickness in Fig. 7(a). The fraction of APDs at 10 or 20 nm deposition decreased with decreasing temperature from 830 to 770°C. The reduction is possibly attributed to suppression of APDs' lateral growth by the layer because the size of APDs decreased with decreasing temperature from 830 to 770°C. The layer appeared after less deposition at the lower temperature. The Ga adatoms probably adhered more to the surface at a lower temperature, which contributed to the denser GaP nucleation. Most APD islands grew rapidly in the lateral direction before island coalescence. For the denser GaP nucleation, islands neighboring to APD islands were at a less distance from APD islands. The APD islands possibly coalesce other

islands at less deposition. The APD size at coalescence is expected to be smaller at a lower temperature. After island coalescence, a layer was formed. After island coalescence, the APDs should grow slowly in the lateral direction or start to self-annihilate.

Figure 7(b) presents a summary of the rms values of a GaP surface roughness as a function of a GaP thickness. The surface roughness increased at 800 and 830°C until layer growth became dominant. Then surface roughness decreased after large APDs started to self-annihilate. The smaller rms values of surface roughness at 800°C than those at 830°C were attributed to smaller antiphase islands at 800°C. The rms value of surface roughness at 10 nm thickness decreased with decreasing temperature from 830 to 770°C. The layer growth was probably dominant at 770°C after less GaP deposition. The layer growth might suppress the lateral growth of antiphase islands from the beginning of GaP deposition at 770°C. However, the rms value of surface roughness increased gradually although only a few APDs were found. The concave regions degraded the surface at 20 nm deposition. The self-annihilation probably proceeded slowly. Although nucleation at 770°C is favorable, post-nucleation growth conditions must be modified to improve the surface morphology.

4. Conclusions

GaP was grown on 4°-misoriented Si substrates at temperatures of 700–830°C using metalorganic vapor phase epitaxy. GaP surface evolution in the initial growth stage was investigated using atomic force microscopy. Island growth with a high density occurred

at 800 and 830°C. At 830°C, several APDs grew rapidly perpendicular to the step-down direction, becoming larger and higher than the surrounding islands during island growth. Layer growth appeared at a GaP deposition. The APDs grew laterally until the layer-thickness exceeded the APD height. The layer grew faster than the APDs, embedding finally the APDs. Qualitatively similar surface evolution was found also at 770 and 800°C, except that the layer growth probably occurred on a part of a Si substrate at the onset of the growth at 770°C. The APD size decreased when the growth temperature decreased from 830 to 770°C. Self-annihilation of APDs was achieved after 40 nm deposition at 830°C, whereas it was achieved earlier at 770 and 800°C than at 830°C. The layer growth probably started earlier at 770 and 800°C than at 830°C, which suppressed the APD lateral growth. The rms values of surface roughness of GaP/Si were lower at 770 or 800°C than that at 830°C. The initial growth at 770 or 800°C is favorable for the GaP/Si surface morphology.

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Figure captions

Fig. 1. $1 \times 1 \mu\text{m}^2$ AFM images of GaP on Si substrates grown at 830°C. GaP depositions were (a) 1, (b) 3, (c) 5, (d) 10, (e) 20, and (f) 40 nm.

Fig. 2. AFM images of GaP on Si substrates grown at 830°C: (a) enlarged top image of the sample after 3 nm deposition; (b) enlarged image of the sample after 5 nm deposition; (c) a schematic diagram of an APD; (d) enlarged top image of the sample after 40 nm deposition. In (c), the left sketch is a vertically enlarged sketch for comparison of AFM images with the right sketch.

Fig. 3. Fraction of APDs and APD density as a function of GaP thickness.

Fig. 4. Cross-sectional TEM images of the sample after 40 nm deposition: (a) image observed using (022) conditions; (b) image of a region of the sample observed using (200) conditions; (c) image of the identical region of the sample observed using (-200) conditions; (d) image of enlarged image in (b).

Fig. 5. $1 \times 1 \mu\text{m}^2$ AFM images of GaP on Si substrates: (a) after nominal 1 nm deposition at 800°C; (b) after 10 nm deposition at 800°C; (c) after 20 nm deposition at 800°C; (d) after nominal 1 nm deposition at 770°C; (e) after 10 nm deposition at 770°C; (f) after 20 nm deposition at 770°C.

Fig. 6. $1 \times 1 \mu\text{m}^2$ AFM images of GaP on Si substrates: (a) after nominal 10 nm deposition at 740°C; (b) after nominal 10 nm deposition at 700°C.

Fig. 7. Fraction of APDs, (a) and rms surface roughness, (b) of GaP on Si substrates as a function of GaP thickness. Closed circles, open circles, and rectangles are data for depositions at 770, and 800, and 830°C, respectively.

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