

Transmission electron microscopy characterization of the initial stage of epitaxial growth of GaP on Si by low-pressure metalorganic chemical vapor deposition

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The initial stage of epitaxial growth of GaP on Si by low-pressure metalorganic chemical vapor deposition was characterized by transmission electron microscopy. The growth mode changes from three-dimensional to two-dimensional with increasing V/III ratio. GaP on Si grown at a low V/III ratio of 800 contains many dislocations, stacking faults, and microtwins; however, a significant reduction in the density of these defects is observed in GaP grown at high V/III ratio of 3200.

In recent years, the growth of III-V compound semiconductors on Si substrate has been actively studied. One problem in the heteroepitaxy of III-V compound semiconductors on Si is the three-dimensional island growth at the first stage of the growth. The generation of defects during island coalescence is one of several possibilities for defect generation. Structural defects are generated during island coalescence. If two-dimensional layer-by-layer growth on Si is realized from the beginning of the growth, the defect density could be lowered considerably.¹

The two-dimensional growth of AlAs on Si has been reported.² However, the growth mode of AlAs on Si is not an ideal layer-by-layer type growth. Ideal layer-by-layer growth of III-V compound semiconductors on Si has not been reported as yet. The difficulty in the realization of layer-by-layer growth of III-V compound semiconductors on Si could be due to a combination of lattice constant mismatch, surface contamination, etc.

Among the many III-V compound semiconductors, the lattice constant of GaP is close to that of Si (the lattice mismatch is about 0.37%) at room temperature. Therefore, the effect of lattice mismatch on the growth mode is expected to be minimized.

The problem in the growth of GaP on Si is that P atoms are less easily adsorbed on Si substrate even if PH₃ is introduced into the reactor prior to growth.³ We have proposed the use of AsH₃ preflow prior to the growth of GaP on Si.⁴ The crystal quality measured by the x ray full width at half maximum of GaP on Si improves by AsH₃ preflow prior to GaP growth. The As atoms are believed to absorb on the Si substrate compared to P atoms. However, the defect density is not sufficiently low. In this letter, the results of characterization by transmission electron microscopy (TEM) of the initial stage of epitaxial growth of GaP on Si grown under various V/III flux ratios is characterized.

GaP was grown by low-pressure metalorganic chemical vapor deposition (LPMOCVD). (100)Si substrates misoriented 2° off toward [011] were used. The source materials for Ga and P are trimethylgallium and PH₃, respectively. The pressure in the reactor during growth is maintained at 76 Torr. Before growth, the Si substrates were heated for 10 min at 1000 °C. The growth temperature was fixed at 900 °C, which is the optimized growth temperature for GaP in our laboratory. The V/III ratio was changed from 800 to 3200 by changing the PH₃ flow rate, keeping the TMG flow rate constant. The growth rate is about 15 nm/min under these growth conditions. Three-dimensional growth was not observed under these growth conditions for the case of GaP growth on GaP substrate. The growth times were 60 and 600 s. Cross-sectional samples were analyzed by TEM operating at 200 kV. The TEM samples were prepared by mechanical thinning by dimpling followed by ion milling.

Figures 1(a) and 1(b) show the cross-sectional TEM micrographs of GaP grown on Si using a V/III ratio of 800. The growth times are 60 s for Fig. 1(a) and 600 s for Fig. 1(b), respectively. The growth is in the form of separated islands and the average size of the islands increases with growth time. This result indicates that GaP tends to grow three dimensionally on Si.⁵ The defect distribution is not uniform in the GaP islands. In some islands large numbers of threading dislocations were formed whereas in other islands many stacking faults of microtwins were observed. Figure 2 contains a high-resolution TEM micrograph of the GaP/Si interface of the sample shown in Fig. 1. The structural defect is not seen in this high-resolution micrograph. The interface roughness between GaP and Si is about 5–6 atomic layers. It should be noted that there does not appear to be a GaP layer between the islands. Faceting was observed at island boundary either on (111) or (211) type planes.

The cross-sectional TEM micrographs of GaP grown on Si using a V/III ratio of 3200 are shown in Figs. 3(a) and 3(b). The growth times for Figs. 3(a) and 3(b) are 60 and 600 s, respectively. Island-type growth was observed

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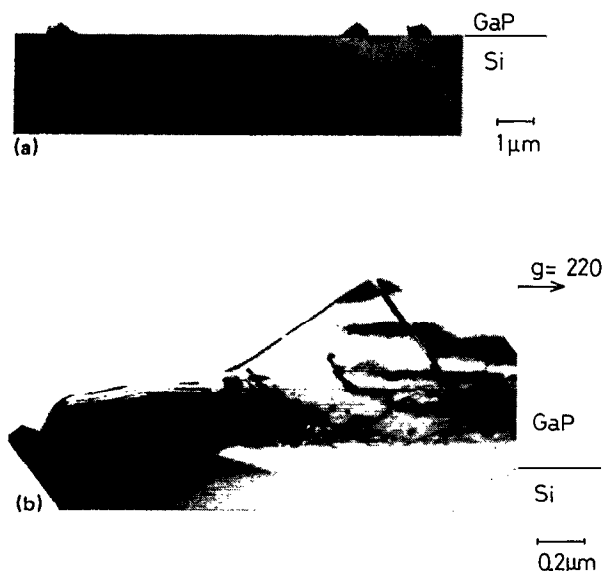


FIG. 1. Cross-sectional TEM micrographs of GaP on Si. V/III ratio is 800. (a) is zone axis image and (b) is (220) bright field image. The growth time is (a) 60 s and (b) 600 s.

for a growth time of 60 s. However, these islands appear to be connected by a very thin continuous layer of GaP. For the growth time of 600 s, almost complete coalescence of islands is observed with the formation of a smooth GaP layer. Few structural defects were observed in the GaP/Si grown using the V/III ratio of 3200.

At the initial stage of growth, GaP islands are formed for both the V/III ratios of 800 and 3200. The main difference between the GaP layer morphologies for different V/III ratios appears to be that for a V/III ratio of 800, the islands are separated without any interconnecting layer being present whereas the islands are connected by a thin layer when the V/III ratio is raised to 3200. Also the growth mode of the GaP on Si changes from three-dimensional to two-dimensional at much lower layer thickness, resulting in flat GaP layers when the V/III ratio is raised to 3200. For the case of the V/III ratio of 800, three-dimen-

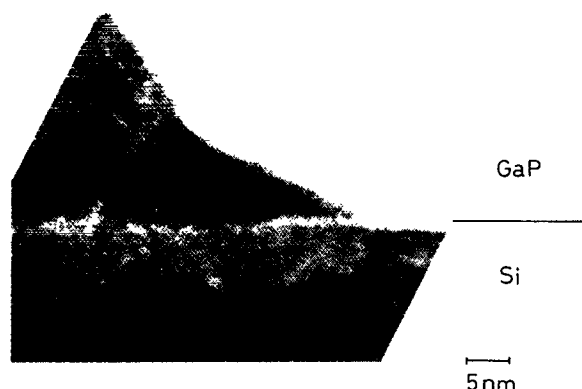


FIG. 2. High-resolution TEM micrograph of GaP/Si interface. V/III ratio is 800 and the growth time is 600 s.

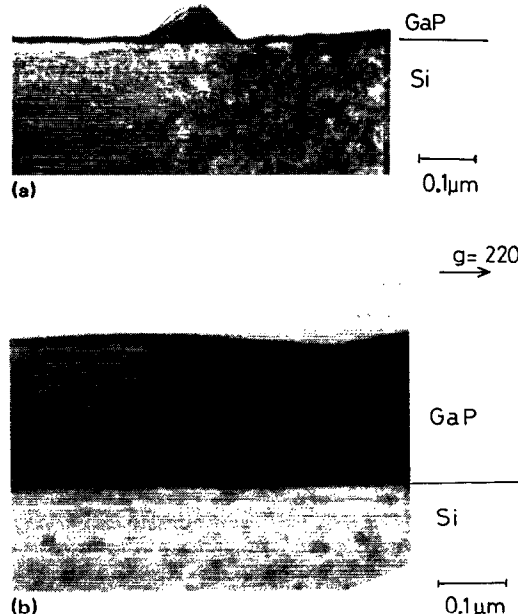


FIG. 3. Cross-sectional TEM micrographs of GaP on Si. V/III ratio is 3200. (a) is zone axis image and (b) is (220) bright field image. The growth time is (a) 60 s and (b) 600 s.

sional growth continues with the islands becoming larger with increasing growth time.

The transition of GaP from an island-type growth mode to a two-dimensional type growth is of interest and bears further discussion. For a low V/III ratio, the growth mode is entirely island type, with the island density being dictated by surface diffusion, nucleation site availability, etc., and can thus be well described as a heterogeneous nucleation process.

By increasing the V/III ratio to 3200, it is observed that the initial island density (for low growth times) is similar to the density obtained for a V/III ratio of 800.⁶ This result is very significant, because it indicates that at least in the very initial stages, a majority of the migrating species has a similar average mass to that obtained under the lower V/III ratio growth conditions. Hence the formation of islands is roughly similar in both cases. However the presence of the interconnecting layer indicates that perhaps the increase of P atoms absorbed on the Si surface captures the migration species, and that there is also a high molecular mass component among the migrating species, resulting in short migration length. The large clusters would necessarily have lower migration lengths and though initially small in number, with increasing growth time their number could increase, resulting ultimately in a continuous layer being formed between the islands. P atoms absorbed on the Si surface also shorten the migration length because migrating species are easily desorbed on the Si surface covered by P atoms rather than bare Si. Once formed, this layer could then promote two-dimensional growth, causing planarization of the epilayer and reduction of the surface area.

The reduction in structural defect density, for the case of the layer grown using a V/III ratio of 3200, could be explained by a mechanism similar to that proposed by George.⁷ In this mechanism, thermal annealing of structural defects during high-temperature growth is much more effective for the case of thin "connected island" layers than for thick layers formed by the coalescence of a widely separated island. Atomic rearrangements resulting in structural defect reduction are probably facilitated more easily for the case of thin layers than for thick layers, at high temperature.

In summary, the initial stage of growth of GaP on Si by LPMOCVD was characterized by cross-sectional TEM. The growth mode appears to be island type for a V/III ratio of 800. When the V/III ratio is increased to 3200, the growth mode changes from three-dimensional to two-dimensional for very low thickness of the GaP layer. A reduction in the migration length of the migrating species

was proposed to explain the change in the growth mode. A reduction in the defect density was observed with a more planar-type growth mode.

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