Surface Stoichiometry and Evolution of Crystal Facet during Selective Area MOVPE

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In the selective area epitaxy (SAE) based on the metalorganic vapor phase epitaxy (MOVPE), the grown crystals in the open area of the masked substrate are surrounded by low-index crystallographic facets and their shapes can be controlled by changing the growth condition and/or the mask pattern. These grown facets are atomically flat, damage-free and highly symmetric. Ando et al. found that the SAE on GaAs(111)B substrate gives a wide variety of three-dimensional structures such as a tetrahedron, a hexagonal prism, and a regular triangle prism in a micron size and showed that the vertical sidewall facets function as the cavities of the ring-cavity micro-laser called "facet laser" [1-5].

Invited

In this paper, it is shown that the evolution of crystal facet in GaAs SAE on (111)B is closely connected with the surface phase during the growth which was determined by the *in-situ* surface photo-absorption (SPA) monitoring [6,7]. Based on the surface structure thus determined and the expected chemical property of the surface, we discuss the mechanism about how the facet evolves to form a three-dimensional structure on the GaAs (111)B. Furthermore, based on the SPA monitoring of GaN MOVPE surface [8,9], we also discuss the mechanism of the vertical facet formation during the SAE of GaN hexagonal micro-prisms on (0001) sapphire substrate [10].

Figure 1 shows the typical SPA reflectivity trace observed for the GaAs (111)B surface at 700°C in the MOVPE reactor using hydrogen carrier gas. The wavelength of the monitoring light is 470 nm. When the AsH₃ supply was turned off, a fast desorption occurs and then a slow desorption starts from an intermediate state. By comparing the SPA spectrum during the fast As desorption between in MOVPE and in molecular beam epitaxy (MBE), it was found that the initial surface was (2x2) As-trimer surface [11] and transformed into the intermediate $\sqrt{19x}\sqrt{19}$ surface by the As desorption. The slow desorption results in the formation of Ga-rich (1x1) surface. Therefore, the fast desorption corresponds to the desorption of As-trimers.

It was found that the growth shape was directly connected with the surface phase during the growth. Figure 2 shows the growth condition for the hexagonal micro-prism and for the tetrahedron in the substrate temperature-AsH₃ pressure diagram. The hexagonal micro-prism is surrounded by the six vertical {T10} facets, and the tetrahedron is surrounded by the three inclined {T10} facets. The boundary for the growth condition between the hexagonal prism and the tetrahedron agrees well with the phase boundary between the (2x2) and $\sqrt{19x}\sqrt{19}$ surface phases. Figure 3 explains schematically how the vertical and the inclined facets evolve depending on the growth condition. Using a higher AsH_3 pressures and a lower substrate temperatures (T_s), the GaAs (111)B surface becomes As-rich (2x2) consisting of As trimers. The (2x2) surface is chemically inactive and has a low sticking ability to Ga atoms due to a termination of As dangling bonds by the As trimers, resulting







Fig. 2 The growth condition for the hexagonal micro-prism and for the tetrahedron in the substrate temperature- AsH_3 pressure diagram.



Fig. 3 The mechanism for the evolutions of vertical and inclined facets on GaAs (111)B.



NH₃ partial pressure, P_{NH3} (atm)



in an extremely low growth-rate. In contrast, assuming the inclined { $\overline{110}$ } facets appear at the initial stage of SAE, since the As coverage on this surface is large enough to promote the lateral growth by incorporating Ga atoms into the active sites, the lateral growth proceeds on the { $\overline{110}$ } facets until the vertical { $\overline{110}$ } facets appear. As a result, the hexagonal prism grows. In a lower AsH₃ pressures and a higher T_s, the As trimers desorb to form $\sqrt{19x}\sqrt{19}$ surface consisting of a high density of As dangling bonds. However, since the As coverage of inclined { $\overline{110}$ } facets is small, the lateral growth is well suppressed. As a result, the vertical growth-rate on (111)B surface becomes larger than the lateral growth-rate on the { $\overline{110}$ } facets and the tetrahedron grows.

The SAE of wurtzite GaN also shows the facet evolution. Figure 4 shows the mapping of the facet shape on the T_s -NH₃ partial pressure diagram. The GaN hexagonal micro-prisms with smooth vertical $\{1\overline{100}\}$ facets grow at the temperatures above 1040° C (region I). At a lower substrate temperatures and a higher NH₃ partial pressures, the side facet changes from the vertical $\{1\overline{100}\}$ to the inclined $\{1\overline{101}\}$ plane (region III). In the intermediate region II, the shape maintains the hexagonal prism, but the lateral growth is enhanced. The lateral growth might be sensitive to the coverage of active nitrogen at the step-edges, i.e., the lateral growth almost stops at a lower coverage of active nitrogen which is realized above 1040° C. These observations are well understand by the result obtained by the SPA monitoring that the surface is Ga-rich above 900° C in hydrogen carrier gas.

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