Fabrication of GaAs Quantum Dots by Modified Droplet Epitaxy

Katsuyuki WATANABE^{1,2,*}, Nobuyuki KOGUCHI^{1,2} and Yoshihiko GOTOH²

¹National Research Institute for Metals, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

²Department of Materials Science and Technology, Science University of Tokyo, Noda, Chiba 278-8510, Japan

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We propose a modified droplet epitaxy method for fabricating self-organized GaAs/AlGaAs quantum dots (QDs) with a high As flux irradiation and a low substrate temperature. By our novel method, GaAs QDs were successfully formed, retaining their pyramidal shape, original base size and density of droplets, and preventing layer-by-layer growth. Quantum size effects of the QDs were distinctly observed by photoluminescence measurements. It was confirmed that this new modified droplet epitaxy method is promising for fabricating a high-quality GaAs/AlGaAs QD system.

KEYWORDS: quantum dots, self-organization, droplet epitaxy, MBE, GaAs, AlGaAs

Recently, various fabrication methods for semiconductor quantum dot (QD) structures have been reported.^{1–4)} Because of high structural crystallinity, high density and simple growth procedures, self-organized QDs grown by the Stranski-Krastanov (S-K) growth mode¹⁾ have become extremely attractive in the case of a lattice-mismatched system such as an InAs/GaAs system. On the other hand, in a lattice-matched system, several methods using selective growth on patterned substrates^{2,3)} and a lateral strain modulation with stresses⁴⁾ have been attempted.

We have proposed a novel self-assembled growth method, termed droplet epitaxy, for III–V compound semiconductor epitaxial microcrystals.^{5–7)} This method has some technical advantages for fabricating QDs with uniform size distribution in both lattice-matched and lattice-mismatched systems. However, for a GaAs/AlGaAs QD system, this method requires the sulfur-termination (S-termination) process^{6–8)} or an AlGaAs buffer layer grown at a low temperature,⁹⁾ resulting in poor crystallinity due to sulfur atoms remaining in the QDs or excess As atoms incorporated in the low-temperature growth (LT growth) layer. In particular, this LT growth layer shows high resistivity and has short carrier lifetimes,¹⁰⁾ thus deteriorating the properties of the QD laser.

In this paper, in order to overcome these problems, we propose a novel modified droplet epitaxy method using a high As flux irradiation at a low substrate temperature, without the S-termination process or the LT growth buffer layer. By this method, GaAs QDs were successfully formed, retaining their pyramidal shape, original base size and density of droplets, and preventing layer-by-layer growth. Moreover, quantum size effects of the QDs were distinctly observed by photoluminescence (PL) measurements.

The process was carried out with a Riber-32P molecularbeam epitaxy (MBE) system. After the desorption of native oxides on a GaAs (001) wafer, a 0.5- μ m-thick GaAs buffer layer and a 1.5- μ m-thick Al_{0.30}Ga_{0.70}As barrier layer were grown at 580°C. Then, the substrate temperature was reduced to 200°C with simultaneous decreasing of the As cell temperature below 100°C. Ga droplets were deposited by the Ga molecular beam without an As flux. The total amount of supplied Ga was 3.7 monolayers (ML). Next, an As₄ molecular beam was irradiated on the surface under the four different conditions discussed below. After an Al_{0.30}Ga_{0.70}As barrier layer with about 10 nm thickness was grown by migration-enhanced epitaxy (MEE)¹¹⁾ at the same temperature, the samples were again heated to 580°C, and a 90-nm-thick $Al_{0.30}Ga_{0.70}As$ barrier layer and a 10-nm-thick GaAs cap layer were also grown by MEE. The surface and cross section of the buried sample were observed with a fieldemission-type high-resolution scanning electron microscope (HRSEM). For PL measurements of samples, an Ar⁺ laser was used as an excitation source and the spectra were observed by a GaAs photodetector through a spectrometer. The laser beam diameter was about 0.8 mm and its power was 5 mW.

The reflection high-energy electron diffraction (RHEED) patterns were observed during each stage of the growth process, as shown in Fig. 1(1). The surface reconstruction of the AlGaAs barrier layer was As-adsorbed $c(4 \times 4)$ at 200°C. After the supply of the Ga molecular beam, this streaky pattern disappeared and halo patterns due to Ga droplets appeared (a). During the As₄ flux supply procedure, these patterns vanished and changed to the following four different patterns depending on the As₄ flux supply condition. First, with the As₄ flux of 4×10^{-7} Torr at the substrate temperature of 200°C, (1 × 3) streaks with nodes appeared (b). Second, with the As₄ flux of 4×10^{-5} Torr at the substrate temperature of 200°C, the coexisting pattern of transmission spots and {113} facets from GaAs microcrystals appeared (c). Third, with the As₄ flux of 4×10^{-5} Torr after decreasing the substrate temperature to 150°C, {111} facet patterns and weak twin spots of microcrystals were also observed (d). Last, with the low As₄ flux of 4×10^{-7} Torr at the substrate temperature of 150°C, the patterns became nodular streaks (e).

Surface morphologies observed by HRSEM are shown in Fig. 1(2). These images were obtained by tilting the substrate 30° from the cleaved plane. Numerous hemispherical-shaped Ga droplets with a density of about $3.5 \times 10^{10} \,\mathrm{cm}^{-2}$ were formed on the surface after the Ga deposition (a). The average diameter and size distribution of the Ga droplets are 10 nm and 23%, respectively. The surface flattened by layerby-layer growth was observed in the As flux supply condition of (b); a very similar phenomenon was observed in our previous work.5-7) With high As flux, numerical crater-shaped GaAs microcrystals are formed, and their diameter is larger than that of Ga droplets (c). Pyramidal-shaped QDs with a typical base size of about 11×16 nm and a height of 6 nm, with a more desirable shape than the crater one, are formed at even lower temperatures (d). Under the lower As flux at this lower temperature, crateriform roughnesses were barely

^{*}E-mail address: wkatsu@nrim.go.jp



Fig. 1. (1) and (2) are the RHEED patterns and surface morphologies of the samples at each stage of the growth process, respectively. In (1), upper column: the electron beam along [110]; lower column: the electron beam along [1 $\overline{10}$]. (a) is after the Ga deposition at 200°C. (b), (c), (d) and (e) are after subsequent As₄ molecular-beam irradiation with 4×10^{-7} Torr at 200°C, 4×10^{-5} Torr at 200°C, 4×10^{-5} Torr at 150°C, respectively.

observed (e). These base sizes were enlarged by a factor of \sim 3 as compared to that of (c). According to these results, it is obvious that both the supply of high As flux and the additionally low-temperature process are of significant importance for the growth of GaAs fine QD structures.

The growth mechanism is qualitatively explained by the following. When the As molecular beam was irradiated after the Ga droplets formation, the two-dimensional (2D) growth of crystallites progressed due to the repeated processes of As atom adsorption on the Ga-stabilized surface and subsequently, Ga atom migration from the droplets to the Asstabilized surface.⁷⁾ Under the first crystallization condition, the 2D growth was almost dominant (Fig. 1(b)). This result is similar to the generally known fact^{12,13} that layerby-layer growth occurs in the process of the appearance and annihilation of Ga droplets by As flux supply at the normal growth temperature of around 580°C. Three-dimensional (3D) growth progresses by As atoms incorporated into the droplet directly from the vapor phase. The high As flux irradiation leads to promoted 3D growth. Simultaneously, the 2D growth was restrained due to this increased consumption of Ga atoms in the droplets for 3D growth (c). Concerning the shape of microcrystals, it is reported that the crater shape originated from the diffusion of As atoms in the droplets.^{9,14)} Owing to the thermal activation process of the Ga migration, the 2D growth is suppressed more effectively at the lower substrate temperature. As a result, the pyramidal GaAs QDs were successfully formed under the conditions of (d). The lengths of QDs along [110] are larger than those along [110]. This might be due to the anisotropy of the Ga diffusion. Under only the condition of this lower temperature, the 2D growth



Fig. 2. High-resolution secondary electron image of the sample cross section shown in Fig. 1(d) after stain etching. QDs are indicated by arrows.

was not sufficiently prevented (e). From these results, it is evident that not only the As diffusion in the droplets but also the Ga migration from the droplets are important for the shape derivation. It is possible to estimate the length of the Ga flow as an increment of the radius of GaAs microcrystals compared to that of Ga droplets. The flow length decreased to about one-eighth with the increase of the As flux by two orders of magnitude, and one-third by reducing the substrate temperature from 200° C to 150° C.

Figure 2 shows a high-resolution secondary electron image of a cross section of the buried QD structure shown in Fig. 1(d) after stain etching. The triangular-shaped dark parts (indicated by arrows) correspond to GaAs QDs. Facets of $\{111\}$, which are consistent with the RHEED patterns, were observed. It is suitable to use the usual growth temperature of around 580°C in order to obtain a high-quality buried layer. However, when the substrate temperature was heated to 580°C without a capping layer, a 2D growth of naked microcrystals newly progressed. This phenomenon is explained by the following. When the size of the GaAs crystallites decreases, the As dissociation pressure rises in comparison with that of the bulk. Therefore, even under the As₄ flux atmosphere of normal MBE growth, As dissociation occurs. As a result, the Ga atom migrations on the substrate surface become newly active, resulting in the 2D growth. To avoid this problem in this procedure, first, only a 10-nm-thick AlGaAs layer, which is more than typical QD height, was grown at 150°C, and the embedding layer of the remainder was subsequently grown at 580°C. It is expected that the 2D growth occurs on the top part of the first thin capping layer and the buried microcrystals are not influenced during the heating process. From Fig. 2, it was revealed that the shape and density of the finally buried QDs were almost the same as those before the growth of the overlayer.

PL measurements were carried out at 20 K. Figure 3(a) shows the spectrum of the same sample shown in Fig. 2. Figure 3(b) is the PL spectrum of another QD structure with the density of $1.8 \times 10^{10} \,\mathrm{cm}^{-2}$, the typical base size of about 17×24 nm and the height of 10 nm. In these two cases, Ga droplets were deposited with a Ga flux equivalent to the GaAs growth rate of 1.0 ML/s (a) and 0.2 ML/s (b). The total amounts of supplied Ga are the same. Subsequently, the As₄ flux of 4×10^{-5} Torr was irradiated at the substrate temperature of 150°C. In (a) and (b), the peaks at about 1.51 and 1.96 eV originate in the GaAs bulk and AlGaAs barrier, respectively. Distinct peaks of GaAs QDs were observed around 1.76 eV (a) and 1.61 eV (b), and indicate the clear blue shift of 0.15 eV with the decreasing size of the QDs. The diamagnetic shifts of these PL peaks indicate that these peaks were due to QDs.¹⁵⁾ The full-widths at half maximum are 124 meV (a) and 102 meV (b), respectively. These broad



Fig. 3. Photoluminescence spectra of QDs. The typical size of the QDs of (a) and (b) are $11 \text{ nm} \times 16 \text{ nm} \times 6 \text{ nm}$ and $17 \text{ nm} \times 24 \text{ nm} \times 10 \text{ nm}$, respectively.

PL peaks might originate from a rather large size distribution of QDs. The relative PL intensities among the QDs, the GaAs bulk and the AlGaAs buffer layer differed between the two samples. The exact reason for this remains unclear. However, the structure of (b) includes a 20-nm-thick AlGaAs capping layer grown at 150°C, which is thicker than the 10 nm one of (a), because the QDs of (b) were bigger than one of (a). It appears that the difference in the relative PL intensities reflects that of the embedding process between these two samples.

We have previously reported that in the case of the Ga deposition on the As-adsorbed $c(4 \times 4)$ surface reconstruction, halo RHEED patterns of droplets appeared after the Ga deposition of 1.7 equivalent MLs corresponding to the surface coverage of As atoms for the $c(4 \times 4)$ reconstruction.⁷⁾ This finding indicates that a wetting layer of 1.7 ML thickness exists in these QDs structures. In order to confirm the existence of these structures, cross-sectional transmission electron microscopy studies are necessary. The emission of the wetting layer was not evident. This might be caused by the fact that the peak is hidden in the tail of the AlGaAs one or because the PL intensity is very weak. It is worth noting that the droplet formation on the AlGa-stabilized surface enables the fabrication of QD structures without a wetting layer.

In conclusion, we have investigated the modified droplet epitaxy method for fabricating GaAs/AlGaAs QDs. By high intensity As molecular-beam irradiation at a low substrate temperature, it was observed that the grown GaAs changed drastically from two-dimensional layers to three-dimensional pyramidal microcrystals suitable for QDs. Quantum size effects of the QDs were distinctly observed by PL measurements. In the future, it is believed that the quality of QD structures can be further improved by optimizing the growth conditions for droplet deposition, microcrystallization and embedding processes.

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