Recent progress on the direct formation of GaAs/AlGaAs and InGaAs/GaAs QDs systems by droplet epitaxy are reviewed. The droplet epitaxy is promising for the fabrication of compound semiconductor quantum dots not only in a lattice-mismatched system but also in a lattice-matched system. By using this method, QDs samples without wetting layers are realized. We also review our recent progress toward the fabrication of site-controlled QDs by using droplet epitaxy on GaAs (001) with well-aligned nano-holes developed by combination of Atomic Force Microscopy (AFM) tip-induced oxidation and atomic hydrogen etching technique.

I. INTRODUCTION

There are several pioneering research works on the self-assembling formation of quantum dots (QDs). In the beginning of 1980s, two kinds of nucleation have been identified when InAs is grown on a GaAs substrate, depending on growth conditions [1–3]. For ultra-thin InAs films a two-dimensional (2D) growth is observed. When the layer thickness is increased, the strain in the epitaxial film induces a transition from 2D to a three-dimensional growth (3D) with island formation, which is known as Stranski-Krastanow (SK) growth mode. This has been evidenced by reflection high-energy electron diffraction (RHEED) observations [1]. Goldstein et al [4] observed photoluminescence (PL) originated from InAs islands formed in InAs/GaAs strained-layer superlattices. In 1993, Petroff’s group reported the direct formation of InGaAs QDs [5] based on the SK growth mode.

In 1990, we have proposed a novel self-assembling growth method, termed Droplet Epitaxy, for the direct formation of QDs [6]. We believe this was a first paper aiming the direct formation of QDs without using any lithography. The SK type growth occurs only in the lattice-mismatched system. Compared with the island formation based on the SK growth mode, the Droplet Epitaxy is applicable to the formation of QDs not only in lattice-mismatched but also in lattice-matched system. Another advantage of the Droplet Epitaxy is the possibility of controlling the thickness of the two-dimensional wetting layer that grows inevitably in the case of the fabrication of QDs by Stranski-Krastanow growth mode. In the case of Droplet Epitaxy, we can fabricate QDs without wetting layer. The process of the Droplet Epitaxy consists of forming numerous III-column element droplets such as Ga or InGa with homogeneous size of around 10 nm on the substrate surface first by supplying their molecular beams, and then reacting the droplets with As molecular beam to produce GaAs or InGaAs epitaxial microcrystals.

When QDs are formed on a planar substrate by using Droplet Epitaxy, however, they are randomly distributed in the location on the substrate. Self assembling quantum dots (QDs) has been attracted much attention to form structures with dimensions on the order of a few tens of nm that are necessary for the realization of advanced quantum devices such as quantum cellular automata (QCA) [7] or the quantum computer [8]. To realize these structures, it is necessary to control the location of QDs.

In this paper, we review the fabrication of GaAs/AlGaAs and InGaAs/GaAs QDs systems by Droplet Epitaxy and report on our recent progress toward the fabrication of site-controlled QDs by using droplet epitaxy on GaAs (001) with well-aligned nano-holes developed by combination of Atomic Force Microscopy (AFM) tip-induced oxidation and atomic hydrogen etching technique.

II. FABRICATION AND PHOTOLUMINESCENCE PROPERTIES OF GAAS/ALGAAS QDS

Our original idea for fabricating compound semiconductor QDs using metal droplets of constituent component came from the observation of the phenomenon that the excess amount of III-column element, which was sup-
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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 [11-0]. (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 and 4 × 10⁻⁷ Torr at 150 °C, respectively.

plied on the substrate surface during MBE growth of III-V compound semiconductor, condensed as homogeneous size numerous fine droplets at low substrate temperature. We thought that these droplets might change to the III-V compound semiconductor epitaxial microcrystals suitable for the QDs by subsequent V-column element molecular beam supply. However, two-dimensional lateral growth of GaAs was reported [9,10] in the case of the subsequent As molecular beam supply to the Ga droplets deposited on the GaAs substrate. One of the reasons of this lateral growth is As mono-atomic layer adsorption on the substrate surface during As molecular-beam supply. Then in our early efforts concentrated on searching suitable surface to prevent the mono-atomic layer adsorption of V-column element, which resulted in the two-dimensional lateral growth of III-V compound semiconductor. We have tried InSb on CdTe [6], GaAs on ZnSe [11] and GaAs on S- or Se-terminated AlGaAs [12–14] for the formation of lattice-matching QDs systems by the Droplet Epitaxy. Although we have succeeded in the fabrication of epitaxial microcrystals of InSb and GaAs by this procedure in our early experiments, strong photoluminescence from dots was not observed in these systems. This was caused by poor interface quality and/or poor crystallinity due to the low substrate temperature during crystallization of InSb or GaAs microcrystals.

Then we modified the procedure to overcome these problems, and observed strong photoluminescence from GaAs/AlGaAs QDs system [15–18]. Another reason of the lateral growth in the case of As molecular beam supply to the Ga droplets mentioned above is Ga atom migration from Ga droplets to the As stabilized surface, which was realized by the As mono-atomic layer adsorption. Figure 1 shows the RHEED pattern and surface morphology changes of the samples for the Ga droplets formation and subsequent As molecular beam supply of 4 × 10⁻⁷ or 4 × 10⁻⁵ Torr beam equivalent pressure at the substrate temperature of 200 or 150 °C in MBE chamber on the Al₀.₃₀Ga₀.₇₀As barrier layers which were grown on a GaAs (001) substrates. The detailed processes of the growth were described in the Ref.16. Total amount of supplied Ga was 3.7 mono-layers (ML). The 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 × 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 transmission spots with {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 a field-emission-type high-resolution scanning electron microscope (HRSEM) are shown in Fig. 1(2). Numerous hemispherical-shaped Ga droplets with a density of about 3.5 × 10¹⁰ cm⁻² were formed on the surface after the Ga deposition (a). The average diameter and size dis-
distribution of the Ga droplets are 10 nm and 23%, respectively. The surface flattened by layer-by-layer growth was observed in the As flux supply condition of (b); a very similar phenomenon was observed in our previous work [12–14]. With high As flux, ring-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 $11 \times 16$ nm and a height of 6 nm are formed at even lower temperatures (d). Under the lower As flux at this lower substrate temperature, crater form roughnesses were observed (e). 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 QDs structures.

The growth mechanism is qualitatively explained by the following. When the As molecular beam was irradiated after the Ga droplets formation, the 2D growth of crystallites progressed due to the repeated processes of As atom adsorption on the Ga-stabilized surface and subsequent Ga atom migration from the droplets to the As-stabilized surface [12]. Under the first crystallization condition, the 2D growth was almost dominant (Fig. 1(b)). This result is similar to the generally known fact [9, 10] that layer-by-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 $580 ^\circ C$. The 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). 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 $[100]$. This might be due to the anisotropy of the Ga diffusion. Even if the substrate temperature is low, the 2D growth was not sufficiently prevented with low As flux (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.

After the growth of QDs, an $\text{Al}_{0.30}\text{Ga}_{0.70}\text{As}$ barrier layer with about 10 nm thickness was grown by migration-enhanced epitaxy (MEE) [19] at the same temperature for the As molecular beam supply to the Ga droplets. The samples were again heated to $580 ^\circ C$, and a 90-nm-thick $\text{Al}_{0.30}\text{Ga}_{0.70}\text{As}$ barrier layer and a 10-nm-thick GaAs cap layer were also grown by MEE.

Figure 2 shows a HRSEM image of a cross section of the buried QD structure shown in Fig. 1(d) after stain etching. The triangular-shaped dark parts correspond to GaAs QDs. Facets of $\{111\}$, which are consistent with the RHEED patterns, were observed. 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.

Figure 3 shows the PL spectra of the same sample shown in Fig. 2 after post-annealing in the As flux at $760 ^\circ C$ for 60 min. The post annealing process was very effective to improve the PL properties of QDs. The PL intensity of QDs after annealing at $760 ^\circ C$ was enhanced by two orders of magnitude as compared to that of sample before post-annealing. Three dimensional confinement effects for excitons in this sample were confirmed by magneto-PL and micro-PL [17].

We have shown that GaAs QDs sample without wetting layer was successfully fabricated changing surface stoichiometry of the substrate just before Ga droplets deposition. Quantum Dots structures containing wetting layer with controlled thickness were also grown by droplets formation on GaAs quantum well of different width [20].

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**III. FABRICATION AND PHOTOLUMINESCENCE PROPERTIES OF INGAAS/GAAS QDS**
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Fig. 4. Bright-field plan-view TEM image of the uncapped samples with 50 MLs of Ga after the crystallization and the annealing process.

Fig. 5. Excitation power dependence of PL spectra for InGaAs QDs at 20 K.

[21–26] The Droplet Epitaxy is applicable to the formation of QDs in the lattice-mismatched system. Quantum dots systems for InGaAs/GaAs without wetting layer have been fabricated on GaAs (001) substrate by modified Droplet Epitaxy. Droplets of InGa alloy with highly dense Ga droplets have been formed by sequential supply of Ga, In and Ga molecular beams in the MBE chamber. These highly dense Ga droplets have successfully prevented the 2D growth of InGaAs during crystallization under As flux supply. The detailed processes of the growth were described in Ref. 21.

Figure 4 shows the bright-field plan-view TEM image of the uncapped samples with 50 MLs of Ga after the crystallization and the annealing process. Strong contrast originating from the strain field of InGaAs QDs with the density of \(7 \times 10^{9} \text{cm}^{-2}\) was observed in this image. The density value agrees well with the density of In droplets, indicating that the origin of InGaAs QDs is InGa droplets.

Figure 5 shows the PL spectrum on the GaAs-capped InGaAs QDs sample measured at 20 K. A sharp peak with FWHM of 21.6 meV was observed at 946 nm. This marked sharpness of the PL peak can be attributed to the size uniformity of the InGaAs QDs, which was originated mainly from the size uniformity of In droplets, or the self-compensation effect between the size of InGaAs QD and indium concentration [28]. Luminescence from the wetting layer was not observed even at high-power laser excitation. Luminescence from QDs was observed even at room temperature. Three-dimensional confinement effect for excitons in this sample was confirmed by magneto-PL.

IV. FABRICATION OF SITE-CONTROLLED III-V COMPOUND SEMICONDUCTOR QUANTUM DOTS BY DROPLET EPITAXY

When QDs are formed on a planar substrate by using Droplet Epitaxy, they are randomly distributed in the location on the substrate. We are now trying to fabricate the site-controlled QDs by using Droplet Epitaxy on GaAs (001) substrate with well-aligned nano-holes developed by combination of AFM oxidation and atomic hydrogen etching.

Figure 6 shows the schematic illustrations of the experimental procedures. (a) The nano-oxide dots patterning by the AFM tip-induced oxidation, (b) the nano-holes formation by using atomic hydrogen and (c) Indium droplets deposition on nano-holes by droplet epitaxy.

Fig. 6. Schematic illustration of the experimental procedures. (a) The nano-oxide dots patterning by the AFM tip-induced oxidation, (b) the nano-holes formation by using atomic hydrogen and (c) Indium droplets deposition on nano-holes by droplet epitaxy.
Fig. 7. AFM images for the oxide dots patterned by AFM tip-induced oxidation (a) and the nano-holes with cross-sectional profile after etched by atomic hydrogen (b).

Fig. 8. AFM image of InAs QDs fabricated by Droplet Epitaxy on nano-holes with hole-to-hole distance of 100 nm.

we have confirmed that this method was promising for controlling the sites of nano-structures.

V. CONCLUSION

Recent progress on the direct formation of GaAs/AlGaAs and InGaAs/GaAs QDs systems by Droplet Epitaxy are reviewed. In the Droplet Epitaxy, the process consists of forming numerous III-column element droplets such as Ga or InGa with homogeneous size of around 10 nm on the substrate surface first by supplying their molecular beams, and then reacting the droplets with As molecular beam to produce GaAs or InGaAs epitaxial microcrystals. The quantum dots systems of GaAs/AlGaAs and InGaAs/GaAs grown by this method show strong photoluminescence even at room temperature. The Droplet Epitaxy is promising for the fabrication of compound semiconductor quantum dots not only in a lattice-mismatched system but also in a lattice-matched system. We also review our recent progress toward the fabrication of site-controlled QDs by the combination of Droplet Epitaxy, well-defined Atomic Force Microscopy (AFM) tip-induced oxidation and atomic hydrogen-assisted oxide removing technique on GaAs (001).

ACKNOWLEDGMENTS


REFERENCES

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