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Structural properties of GaAs nanostructures formed by a supply of intense As_4 flux in droplet epitaxy

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Abstract

We investigated detailed structural properties of GaAs nanostructures formed by a supply of intense As_4 flux to Ga droplets. Scanning electron microscopy (SEM) and cross-sectional transmission electron microscopy (TEM) revealed that whisker-like nanostructures had formed on the truncated cone-shaped bases after crystallization. Moreover, electron energy loss spectroscopy in scanning transmission electron microscopy (STEM-EELS) revealed that elemental Ga atoms remained inside the nanostructures while outside, some had crystallized into GaAs. These findings suggest that crystallization started at the edges of the droplets and the GaAs grew upward along the periphery of the droplets until the droplets were completely covered with crystallized GaAs.

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1. Introduction

The use of self-assemblies during crystal growth allows us to create high-quality quantum nanostructures without employing lithographical techniques. Therefore, self-assembly technologies have been intensively studied for basic physics and practical device applications [1]. Among the different techniques, droplet epitaxy is one of the most promising since various types of high-quality quantum nanostructures can be easily created, such as quantum dots (QDs) [2–4], double QDs [5], single quantum rings (QRs) [6–8], and concentric double QRs [9]. Although the characteristic properties of these quantum nanostructures have been demonstrated [5,9,10], their complex formation mechanisms are still a matter of concern [3,4,6,8,9]. Previous studies of the formation of single or double QRs revealed that crystallization at the bottom of the droplets (interface between the droplets and substrate) is not effective, resulting in the formation of well-defined central holes of the QRs [6,8,9]. This is consistent with the low solubility of As atoms in Ga droplets [11,12]. The As atoms attached to the droplet surface might migrate across the surface and crystallize into GaAs at the edge of the droplets [8]. However, we can also successfully form pyramidal- or cone-shaped QDs by supplying high-intensity As_4 flux to the Ga droplets, where the peaks of the nanostructures locate at the center of the original droplets. Therefore, we propose that effective crystallization could occur at the bottom of the droplets [4,6], which is inconsistent with the QRs formation. To solve the problem, more detailed studies of QD formation in droplet epitaxy are required.

In this study, we investigated the GaAs nanostructures formed by a supply of intense As_4 flux to Ga droplets, which were previously regarded as pyramidal- or cone-shaped QDs. By carefully analyzing the structural properties of the crystallized nanostructures, we found that whisker-like structures formed on the truncated cone-shaped bases. Moreover, elemental Ga atoms remained inside the structures covered with crystallized GaAs. From these results, a possible growth mechanism is proposed.

2. Experimental procedure

The samples were grown by conventional solid-source molecular beam epitaxy (MBE) on GaAs (0 0 1) substrate. To

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abruptly supply As_4 flux with precisely controlled intensity, a valved cell was used for the As source. After growing a 200-nm-thick GaAs buffer layer at 580 °C, As-stabilized c(4 × 4) surface was formed by reducing the substrate temperature to 325 °C. For Ga droplet formation, 10 ML (monolayer) Ga (0.5 ML/s) was supplied to the c(4 × 4) surface at this temperature without As_4 flux. On the c(4 × 4) surface, there was 1–2 ML of excess As layer. The first 1–2 ML of Ga changed into a two-dimensional GaAs layer and the remaining Ga formed droplets. The droplets then crystallized into GaAs by supplying As_4 flux of 2.5×10^{-4} Torr beam equivalent pressure (BEP) at 150 °C for 30 s, which are similar to the crystallization conditions of QD formation [4,6]. Finally, to remove the excess attached As atoms from the surface, the samples were annealed at 300 °C for 10 min under As_4 flux (1×10^{-5} Torr BEP), where the surface nanostructures almost retained their original shape. For structural characterization, the samples were observed by scanning electron microscope (SEM) and cross-sectional transmission electron microscope (TEM). Focused ion beam (FIB) milling was used to prepare the cross-sectional TEM samples. To protect the region of interest, the samples were coated with carbon followed by ion-induced carbon deposition using FIB before milling. To analyze the composition of the nanostructures, we also performed electron energy loss spectroscopy in scanning transmission electron microscopy (STEM-EELS). The nominal probe size was 0.2 nm in this study.

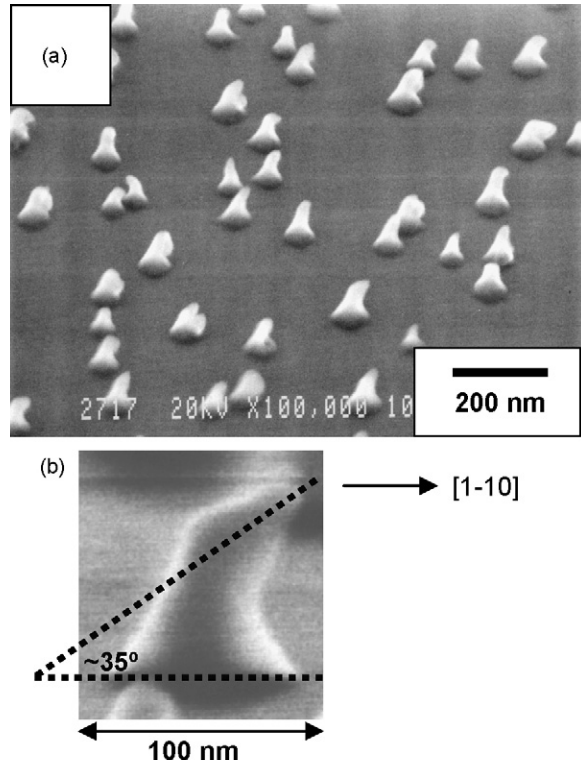

Fig. 2. (a) SEM image of nanostructures after crystallization at 150 °C followed by annealing at 300 °C. (b) Magnified cross-sectional SEM image of single nanostructure.

3. Results and discussion

Fig. 1 shows an SEM image of the surface after supplying 10 ML Ga to the c(4 × 4) surface at 325 °C. Many hemispherical shaped Ga droplets formed on the surface with a density of 1.3×10^{9} cm^{-2}. The average base size is 80 ± 8 nm and the size distribution is ~15%.

During the supply of As_4 flux (2.5×10^{-4} Torr BEP) at 150 °C, the reflection high-energy electron diffraction (RHEED) patterns changed from halo to spotty, indicating the crystallization of droplets into GaAs. The changing time of these RHEED patterns was only 1–2 s. Therefore, possible crystallization at this temperature should be completed after supplying As_4 flux for 30 s.

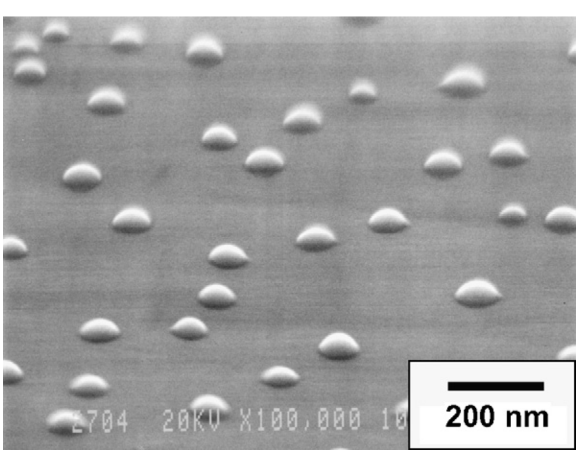

Fig. 1. SEM image of Ga droplets formed by supplying 10 ML Ga at 325 °C.

Fig. 2(a) shows an SEM image of the surface after crystallization at 150 °C followed by annealing at 300 °C. Nanostructure density (1.8×10^{9} cm^{-2}) is almost the same as that of the initial droplets, indicating that one droplet (Fig. 1) crystallized into one nanostructure (Fig. 2(a)). In this image, it is clearly visible that whisker-like structures formed on the truncated cone-shaped bases instead of maintaining the shape of the original droplets. Most of the whisker finally tilted along the ⟨1 1 1⟩B direction (~34° tilted from the perpendicular to the (0 0 1) surface toward the [1–10] direction as shown in Fig. 2(b)) [13]. These results reveal that the droplets do not crystallize into GaAs with nearly keeping their original shape [4].

To study these nanostructures in more detail, we also performed cross-sectional TEM and STEM-EELS analysis. Fig. 3(a) and (b) shows cross-sectional TEM images of the same sample as shown in the Fig. 2. We had expected the nanostructure to consist of only GaAs crystal. However, a clear contrast is visible at the center of the nanostructure, indicating the existence of different phases. To identify the origin of this contrast, we performed STEM-EELS analysis. Fig. 4(a) and (b) shows spectrum images of the nanostructure created by integrating the energy core-loss (L_{23} edges) signals of (a) Ga and (b) As, respectively. Except for the central region, the contrast in both the Ga and As spectrum images is almost the same as that of the GaAs substrate, indicating that these regions are GaAs. Conversely, the central region is clearly Ga-rich and As-poor. According to the phase diagram of the Ga–As system,