In situ electron-beam processing for III-V semiconductor nanostructure fabrication

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Quantum dots (QDs) and quantum wires (QWRs) are promising for future optoelectronic device applications. To realize the expected performances of devices using such semiconductor nanostructures, the sites and sizes of the nanostructures must be effectively controlled. For this purpose, we have developed nano-fabrication technology using "*in situ* electron-beam lithography" and self-organizing molecular-beam epitaxial growth. Using this method, fine holes were formed on GaAs surfaces, and then a few monolayers of InAs were supplied to form QDs. It was revealed that the resulting QDs were selectively formed in the holes, without any QD formation in the flat region between the holes, because of accumulation of In atoms in the holes. This result demonstrates the usefulness of the *in situ* patterning/self-organizing growth approach for realizing arbitrarily arranged nanostructures.

1. Introduction

Semiconductor nanostructures, that is, quantum dots (QDs) and quantum wires (QWRs), are expected to realize breakthroughs in the performances of optical and electronic devices. In particular, QDs are promising for future optoelectronic device applications, such as high-performance lasers,[1] and have also attracted much attention from the viewpoint of scientific curiosity. Since self-organized growth methods such as Stranski-Krastanow (SK) mode growth enable high-quality QDs to be easily formed, they have been intensively studied and the uniformity of QDs has been considerably improved.[2,3] However, a method for controlling the sites of QDs has not been realized. It is desirable to obtain structures with arbitrarily designed QD sites and sizes in order to produce devices with high performances and novel functions. The site-control of SK dots has been examined using mesa- or hole-patterned substrates, obtained by conventional pattern etching and additional growth of buffer layers.[4-6] However, the precise control of individual dot-sites has not been realized since these *ex situ* process techniques result in relatively large patterns with submicron sizes and/or with size-fluctuations.

On the other hand, a through-ultrahigh-vacuum (through-UHV, or simply *in situ*) processes with a focused electron-beam (EB) are expected to enable the formation of ultrafine patterns without degradation of the processed surfaces.[7] Therefore, such processes are advantageous if applied to site-control methods for self-organized QDs.[8]

In this work we studied a site-control method for self-organized InAs QDs on GaAs substrates using "*in situ* EB lithography" and self-organizing growth by molecular-beam epitaxy (MBE). We successfully formed QDs with good optical properties selectively in patterned fine holes.

2. Experimental

Our approach was based on the *in situ* pattern-formation method for ultrafine structure fabrication, called "*in situ* EB lithography."[7] All of the processes were performed without air-exposure using a UHV-based multichamber system, comprising seven chambers used for MBE growth, surface-oxidation, Cl_2-gas etching, Auger electron-spectroscopy, EB patterning, sample exchange, and sample loading.The chambers were connected through UHV tunnels with gate-valves, and the base pressure for each chamber was lower than $1x10^{-9}$ Torr except for the loading chamber; thus the processed surfaces were kept clean. The details of this system have been described in previous publications.[7]

Figure 1 shows the fabrication procedure of the QD-structures used in this work. On nominally flat GaAs (001) substrates, square-mesa structures with sizes of 30 (m or 50 (m were formed by conventional wet-chemical etching. These pre-patterned substrates were loaded into the multichamber system, and a 500-nm-thick GaAs buffer layer (first buffer) was grown by MBE to prepare a clean surface (a).

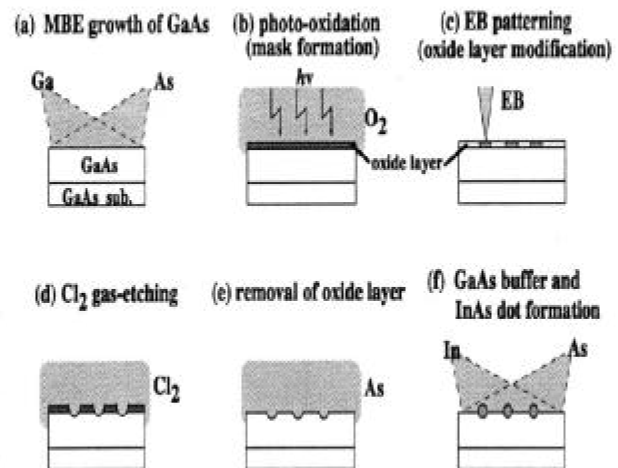

Fig.1. Procedure for fabricating the site-controlled InAs dots, including *in situ* EB pattern formation and self-organization by MBE. The InAs was delivered using a pulse molecular beam of 0.2 monolayer (ML) InAs, which was determined on the InAs substrates, with a growth interruption of 1 minute after each pulse.

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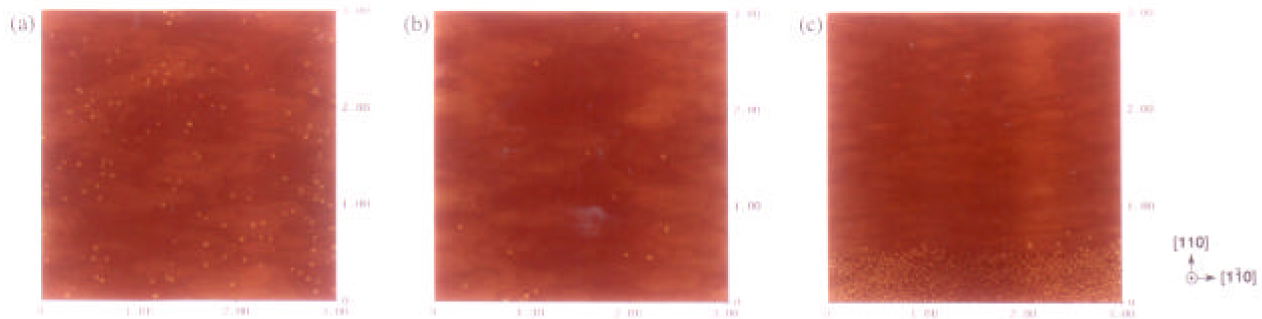

Fig.2. AFM images (3x3 μm^2) of the InAs dots formed on an unpatterned flat substrate (a), and on the center area (b) and on the edge area (c) of a square-mesa structure with a size of 50 μm.

Then, A thin photo-oxidized layer used as both an EB resist and an etching mask was formed on the surface (b). This process was performed by photo-irradiation using a halogen lamp under an oxygen-gas atmosphere of 1 atm for 1 hour. For pattern formation, direct EB writing on the oxide layer was conducted by using 1-nA-EB with a diameter of about 100 nm (c); followed by Cl_2-gas etching (2X10^{-5} Torr, 100°C, 15~30 minutes) for pattern transfer to a GaAs surface (d). EB irradiation with an appropriate dose locally modified the oxide layer, reducing its resistance to Cl_2 gas.[9].

This is a key process for "*in situ* EB lithography." In this work, holes were formed on the GaAs surface in matrix-arrays. Then, the remaining oxide layer was removed in the MBE chamber at 570°C under an As ambient (e). On the finely hole-patterned surface, QDs were formed through the SK growth mode by supplying InAs at 460°C (f). A thin GaAs buffer layer (second buffer) with a thickness of 10~20 nm grown at 550°C was occasionally introduced before supplying InAs, to improve the surface morphology and to prevent any undesirable influence of residual oxygen.

3. Results and Discussion

3.1. Effect of pre-patterned mesa-structures

Here, we describe the effect of fabricating pre-patterned square-mesa structures on the SK dot formation. Figure 2 shows *ex situ* atomic-force microscopy (AFM) images of InAs QDs formed on an unpatterned flat substrate (a), and on the surface of a square-mesa structure having a size of 50 (m (b), except for that of edge part. Also shown is those on the edge surface of the same mesa, the dimension of edge part being a few microns (c). In these cases, EB patterning was not performed.

The supplied amount of InAs was 1.4~1.6 ML, which is slightly more than necessary for the onset of SK islanding. The QD concentration was found to be remarkably dependent on the mesa size. While ~100 QDs were observed in (a), only a few QDs were found in (b) for the 50 (m mesa. On a smaller mesa of 30 (m (not shown), hardly any QDs were formed. At the edge of a mesa-structure, on the other hand, the QDs were densely formed, as shown in Fig.2(c). These results indicate a very long diffusion length of In adatoms on the GaAs surface or InAs wetting-layer surface.

The In adatoms diffused to the mesa edges with a high concentration of atomic steps, resulting in the formation of QDs there because of preferential nucleation for InAs growth. The diffusion length was comparable to the mesa width, that is, several tens of (m. Taking into consideration the fact that the diffusion length of Ga adatoms on GaAs surfaces was ~1 (m under the present growth condition,[10] that of In adatoms was found to be considerably larger. We believe that the long diffusion length of In-adatoms is caused by lattice mismatch.

The result that the formation of SK dots can be effectively suppressed around the central region on mesa structures indicates reduced growth rate of InAs there due to the incorporation of it into the mesa-edges, and gives a method for improving site-controllability of QDs, as described below.

3.2. QD formation in holes

InAs dot formation in the patterned holes fabricated by the procedure shown in Fig. 1 is described here. Figure 3 shows AFM images of parts (3x3 μm^2) of array-patterns with various amounts of supplied InAs. In these cases, the holes are relatively large (diameter, 200~400 nm; depth, ~50 nm), and the second buffer layer was not introduced. The inserts show reflection high-energy electron diffraction (RHEED) patterns monitored on unpatterned flat GaAs substrates, which were positioned adjacent to the patterned substrates on the same sample holders.

The image of a patterned surface without InAs supply is denoted as 0 ML (a); the corresponding RHEED pattern for the flat surface exhibited streak-characteristics with a c(4x4) reconstruction. When 1.0 ML of InAs was supplied (b), the AFM image remained almost unchanged, and dot growth was not observed. This is because the growth mode was still two-dimensional (2D), as confirmed by the streak-characteristics of the RHEED patterns. When 1.4 ML was supplied (c), however, three-dimensional (3D) growth (SK-islanding) started to occur on the flat surface, as confirmed by the chevron-like RHEED pattern.

At the same time, a few dots with a diameter of

about 100 nm were observed by AFM to be formed in each hole on the hole-patterned substrate. It is also noted that hardly any other dots, including SK dots, were observed in the flat region between the holes. Such selectivity of InAs-related dot-formation in the holes is caused by the preferential InAs nucleation due to the presence of a high density of atomic-steps.[11-13] In the flat region between the holes, accordingly, dot formation can be suppressed through the diffusion of In adatoms into the holes and the mesa-edges. When the amount of InAs was increased slightly, up to 1.8 ML (d), the dot size drastically increased. The average dot-volume was increased from $5x10^4$ nm^3 to $3x10^6$ nm^3 with only a slight increase in InAs amount from 1.4 ML to 1.8 ML.

The reason the dot size increased so remarkably is attributed to effective trapping of In adatoms in the holes and a stress-relaxation effect in the enlarged dots. The supplied In adatoms migrate on the GaAs surface and enter the holes, where they are less mobile due to the remarkably high concentration of localized steps. By supplying 1.8 ML of InAs, therefore, many small dots with a diameter of less than 100 nm are formed and coalesced to a smaller number of larger dots in order to minimize surface free energy. In addition, the effect of stress-relaxation[14] is believed to play an important role in the remarkable dot-enlargement.

The enlarged dots with a diameter exceeding 100 nm must be stress-relaxed, thus further preferential growth of InAs is caused on the their surfaces, while InAs growth is suppressed by stress on the surrounding substrates. Such behavior of dot-enlargement may have avalanche-like characteristics; thus only a slight increase in InAs amount causes remarkable dot-enlargement.

3.3. Site-controlled QDs with high quality

In order to improve the surface morphology and to obtain high-quality QDs, we introduced a thin GaAs buffer layer just before the InAs supply step. Around the center of mesa structures with a size of 50 μm, we performed "*in situ* EB lithography" to form 20x20 array patterns of small holes, and then a second buffer layer was grown, resulting in the formation of shallow (1~5 nm) holes with a size of 100~200 nm.

The use of this layer rendered the original holes shallower than before and elliptical along the [110] direction, because of preferential GaAs growth on B-steps[15] in the holes. Finally, 1.4~1.6 ML of InAs was supplied. Figure 4 shows AFM images of the resulting QDs formed in the arrayed holes with various depths. Each dot had a lateral size of 30~50 nm, and was identified as an SK growth QD by photoluminescence (PL) For holes of any depth, the QDs were selectively formed in the holes, without any formation in unpatterned flat regions. Such excellent site-selectivity of QDs in the holes is assisted by the incorporation of In adatoms at the mesa edges, as described in **3.1** Because of the large diffusion length, In atoms supplied on the mesa surface moved either into the fine holes or to the mesa edges, without any QD formation in flat regions.It was also revealed that the density of QDs in each hole was strongly dependent on the hole depth. In the holes with a depth of ~5 nm, a considerably high concentration of QDs (15~25 dots) were formed (a). The local concentration reached $1x10^{11}$ cm^{-2} measurement, as described later.

For the QDs with a diameter of 30 nm, this value is close to the concentration limit, which is hard to achieve on GaAs (001) flat surfaces. In shallower holes with a depth of ~3 nm, on the other hand, fewer QDs (5~15) were formed (b). When the hole depth was decreased further to about 1.5 nm, one or two dots were formed in each hole (c), and no dot was formed in holes with a depth of less than 1 nm (d).

These extremely shallow holes including 2 or 3 ML steps, as shown by the arrows in (d), are thought to be insufficient to confine the critical amount of In adatoms for nucleation of QD formation. Since all of the holes used in this work had the similar lateral dimensions, the dot concentration in each hole is thought to be determined by the depth of holes, that is, the local density of atomic steps in the holes.

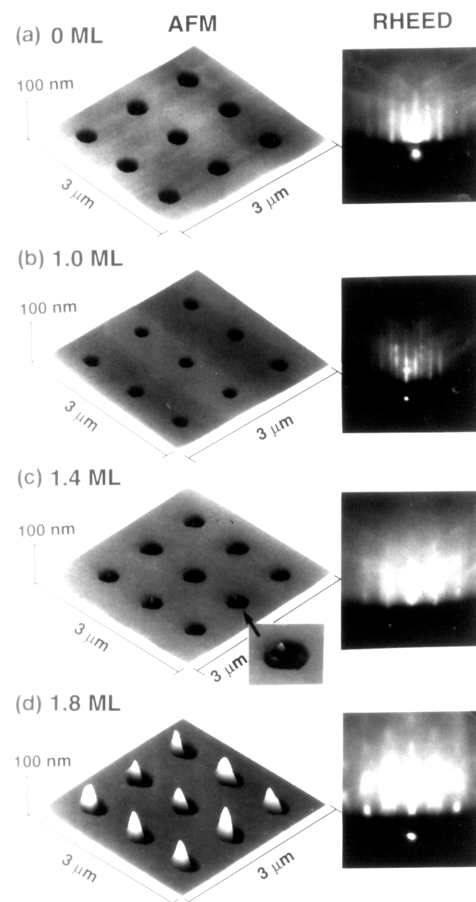

Fig.3. AFM images (3x3 μm^2) of InAs-related dot structures formed on the hole-patterned GaAs substrates together with RHEED patterns on unpatterned substrates for various amounts of supplied InAs: 0 ML (a), 1.0 ML (b), 1.4 ML (c), and 1.8 ML (d).

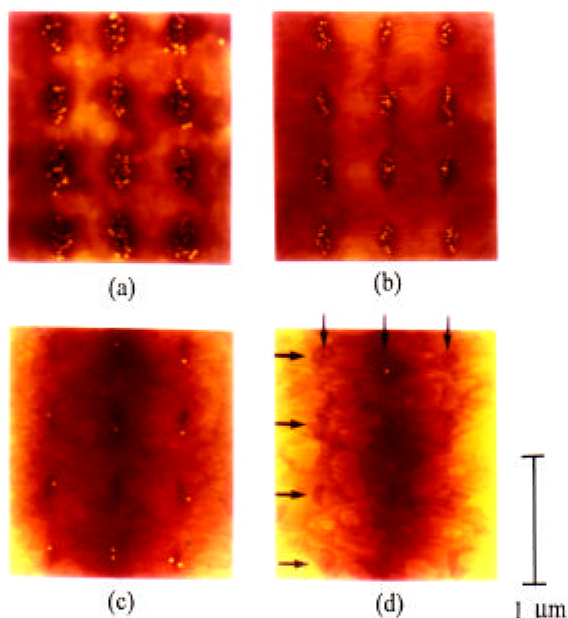

Fig.4 AFM images (2x2 μm^2) of the InAs dots, formed in the holes in the array. The hole depth was 5 nm (a), 3 nm (b), 1.5 nm (c), and 1 nm (d). The arrows in (d) indicate hole-positions in array.

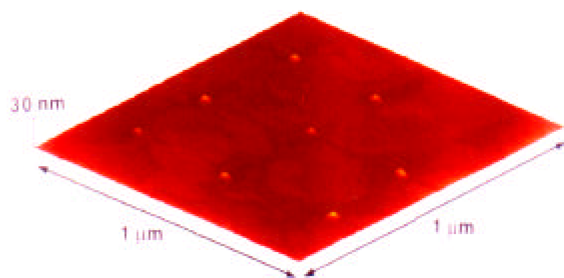

Fig.5 AFM image (1x1 μm^2) of InAs single QD array structure formed by an *in situ* patterning/self-organizing growth method.

Although SK dot formation around mono-atomic steps[11,12] or on multi-atomic steps[13] has been reported, its mechanism is not clear.

We speculate that the atomic steps act as barriers against the migration of In-adatoms; the adatoms locally accumulate in the regions surrounded by the steps, so that their concentration is dependent on the step density. Accordingly, InAs nucleation preferentially begins in the holes with localized steps, and results in the formation of dots with concentration depending on the hole depth.

We have revealed that it is important to precisely control the atomic steps to enable site-control of QDs, and have found that a single QD can be formed in a hole surrounded by 5~6 ML atomic steps. By forming such holes and supplying 1.4 ML of InAs, we successfully fabricated a single QD-array structure, as shown in Fig 5. This result demonstrates the feasibility of controlling individual QD formation-sites by using an *in situ* patterning/self-organizing growth approach. Further reduction of the array pitch will be attained by using EB with a finer diameter less than 100 nm. To fabricate QDs with further precisely controlled sites, other patterning methods using nano-probes, such as scanning tunneling microscopy lithography,[16,17] appear promising.

3.4. PL measurements

To measure the PL of site-controlled QDs, we fabricated buried QD structures. After forming site-controlled QD-arrays, which are similar to the structures shown in Fig. 4, a 100-nm-thick GaAs layer was grown on the array. Although we were unable to detect a PL signal from individual QDs, whose intensity seems to be below the detection limit of our PL system, we successfully measured PL for a sample having densely formed QDs (>10) in each hole, as shown in Fig. 6.

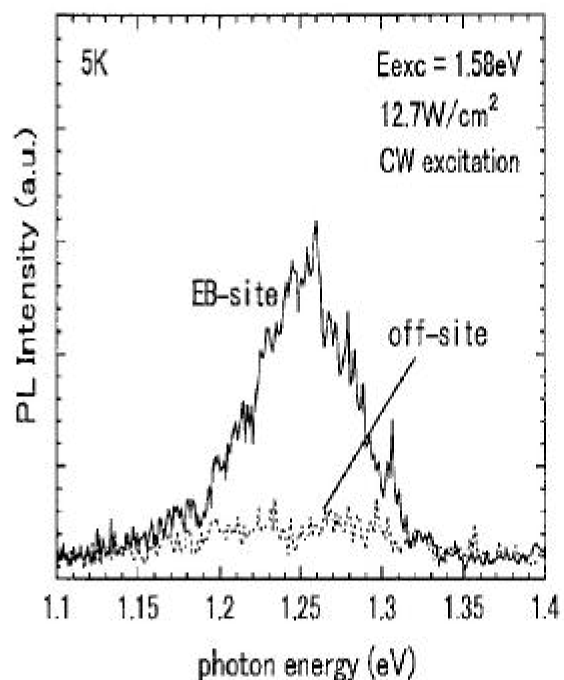

Fig.6 Microprobe-PL spectra of the site-controlled QD structure by exciting the QDs-formed area (EB-site) and non-formed one (off-site).

Using a Ti:Sapphire laser (E = 785 nm) with a beam focused to a diameter of 2 µm, we selectively excited different positions on the sample; that is, the hole-array patterned area and the unpatterned area. When we excited the unpatterned area including a negligible number of QDs, we did not observe any PL emission, as shown by "off-site" in Fig. 6. When we excited the hole-array patterned area, on the other hand, several tens of QDs (in several holes) were excited and distinct emission was observed (as shown by "EB-site,") around 1.25 eV, which is the typical emission energy for InAs SK QDs (Both the spectra were normalized by the emission intensities of GaAs buffer-layers).These results confirmed the good quality as well as the excellent site-controllability of our site-controlled QD

structures. In addition, the decay time derived from the time-resolved PL measurement for the same QDs depended on the emission energy, and was satisfactorily explained by assuming carrier tunneling among the high concentration of QDs in each hole.[18] This indicates lateral coupling among QDs in the holes, which was realized by our process. Based on these results, the *in situ* patterning/self-organizing growth approach was found to be useful in fabricating arbitrarily designed QD structures with high quality, which is useful for developing novel devices.

4. Summary

In summary, to realize arbitrarily designed InAs QD structures with high quality, a novel method for the site-control of InAs dots on GaAs substrates was studied. The method employs the through-UHV process, comprising *in situ* EB pattern formation and self-organizing MBE. By supplying 1.4 ML of InAs, which changed the growth mode from 2D to 3D on the flat surface, InAs QDs were selectively formed in the patterned holes while QD formation was effectively suppressed in the surrounding regions of the holes. Using shallow holes with a depth of 5~6 ML, we successfully arranged a single QD there. By microprobe-PL measurement, we confirmed emission from the site-controlled QDs in a buried structure.

Acknowledgments

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