Fabrication of Buried GaAlAs Microcrystal Structures by Droplet Epitaxy

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Abstract

We have already proposed a growth method for fabricating quantum dots named droplet epitaxy. However, at present, the photoluminescence of GaAs quantum dots fabricated by this method hasn't been distinctly observed yet. It might be due to the sulfur (S) remaining at the interface between the quantum dots and the substrate and/or due to the low temperature crystallization for the formation of the quantum dots.

We have proposed a new modified droplet epitaxy method to overcome these problems in the conventional droplet epitaxy and demonstrated the fabrication of high quality buried structures of GaAlAs microcrystals, which show photoluminescence. This modified method can successfully be used in the future fabrication of GaAs quantum dots.

Introduction

There has been considerable interest in semiconductor quantum dot structures, owing to their interesting physical properties and potential applications in high performance devices such as enhanced electron mobility device [1] and advanced semiconductor laser [2]. For quantum structure fabrication, it has been reported various method using metalorganic chemical vapor selective growth [3], electron-beam lithography [4], or self-organized growth [5].

Among these approaches, we have proposed the droplet epitaxy for the novel fabrication method of III-V compound semiconductor epitaxial microcrystals[6][7]. The conventional droplet epitaxy has the process of a sequential supply of Ga and As molecular beams on a sulfur-terminated (S-terminated) GaAlAs surface in the case of the fabrication of GaAs quantum dots. This method has some technical advantage for fabricating quantum dots with sharp size distribution and high density and applying for various III-V compound semiconductor in both lattice matched and mismatched one. However, at present, the photoluminescence (PL) of GaAs-GaAlAs quantum dots system fabricated by this method hasn't been distinctly observed yet. It might be due to the sulfur remaining at interface between the quantum dots and the substrate and/or the low temperature crystallization for the formation of the quantum dots. In the conventional droplet epitaxy, it needs to keep the S-terminated substrate surface at the temperature below about 200℃ during the formation of GaAs quantum dots.

In this work, for overcoming these problems, we propose a new modified droplet epitaxy method; sulfur-termination after the formation of metal droplets, such as Ga or Al, on GaAlAs surface and subsequent supply of As molecular beam to this surface, and demonstrate the fabrication of high quality buried structure of GaAlAs microcrystals. The purpose of this work is to investigate the effectiveness of the modified droplet epitaxy. Then we have fabricated GaAlAs microcrystals instead of GaAs microcrystals. Since the energy gap of the GaAlAs is different from that of GaAs, it might be easy to distinguish the photoluminescence peak from strong photoluminescence of underlying GaAs layer.

Experimental

The MBE system used in this work was a conventional system (RIBER32) linked to an UHV chamber for sulfur termination (S-termination). Elemental Ga, Al and As were used as the molecular beam source material. A valved Knudsen cell charged with elemental S was installed in the S-termination chamber.

The samples were grown on GaAs (100) semi-insulating substrates. After desorption of the native oxide on GaAs (001) wafer, $Ga_{0.70}Al_{0.30}$ As barrier layer with the thickness of 150 nm was grown on a 300 nm GaAs buffer layer including a GaAs/AlAs (5 ML/5 ML) 10 periods superlattice at 580℃. Then the substrate temperature was reduced to 510℃, $Ga_{(1-x)}Al_x$ droplets (x=0.03 and 0.10) were grown by the simultaneous supply of Ga and

Al molecular-beams without an As flux. The total amount of GaAl was equivalent to 5 monolayers (ML) of GaAlAs. Beam intensity and Al composition of GaAl were determined from the periods of the reflection high-energy electron diffraction (RHEED) specular beam oscillation during MBE growth of GaAs and GaAlAs. After the substrates were cooled down to about room temperature, As molecular beam was slightly irradiated on the surface until the surface reconstruction of the substrate disappeared. Next, samples were transferred into the S-termination chamber and exposed to the sulfur molecular-beam flux that had a beam equivalent pressure (BEP) of 1.0×10^{-6} Torr for 10 min at room temperature. The samples were transferred into the growth chamber again. Then, the samples were heated up to 400℃ and As molecular beam was irradiated on the surface to crystallize the droplets to GaAlAs microcrystals. After removing the S-adsorbed layer by raising the substrate temperature, a $Ga_{0.70}Al_{0.30}As$ barrier layer with 40 nm thickness and GaAs cap layer with 10 nm thickness were grown by migration-enhanced epitaxy (MEE) at 570℃ [8][9].

For comparison, the buried structure for $Ga_{0.90}Al_{0.10}As$ microcrystals, which size was almost same as GaAlAs microcrystals mentioned above, was fabricated by the conventional droplet epitaxy.

The structures produced on the surface of the samples were observed with a field emission-type high-resolution scanning electron microscope (HRSEM). For the photolumine-scence measurements of the buried structures, Ar^{+} laser was used as an excitation source and the spectra were observed by GaAs photodetector through a spectrometer. Laser beam diameter was about 0.8mm and the power was 15mW.

Results and Discussion

The original surface reconstruction of the $Ga_{0.70}Al_{0.30}As$ barrier layer was metal atom, such as Ga and/or Al, rich (3×6) at 510℃ without As flux. The RHEED pattern is clearly streaky and not halos, and no droplet was observed on the surface by HRSEM. After the supply of GaAl molecular beam, the halo and (4× 6) streaky pattern due to surface reconstruction appeared in the RHEED pattern. The halo is caused by the diffraction of GaAl droplets deposited on the substrate surface. These two surface reconstructions, (3×6) and (4×6), are originated from Ga-stabilized surface structures [10]. Although a little amount of supplied GaAl atoms was spent on changing the surface reconstruction, almost amount of supplied GaAl atoms was condensed as liquid droplets.

Surface morphologies of the samples observed by HRSEM during each stage of the growth process are shown in Fig.1. Many hemispherical shaped GaAl droplets were formed on the surface after the GaAl

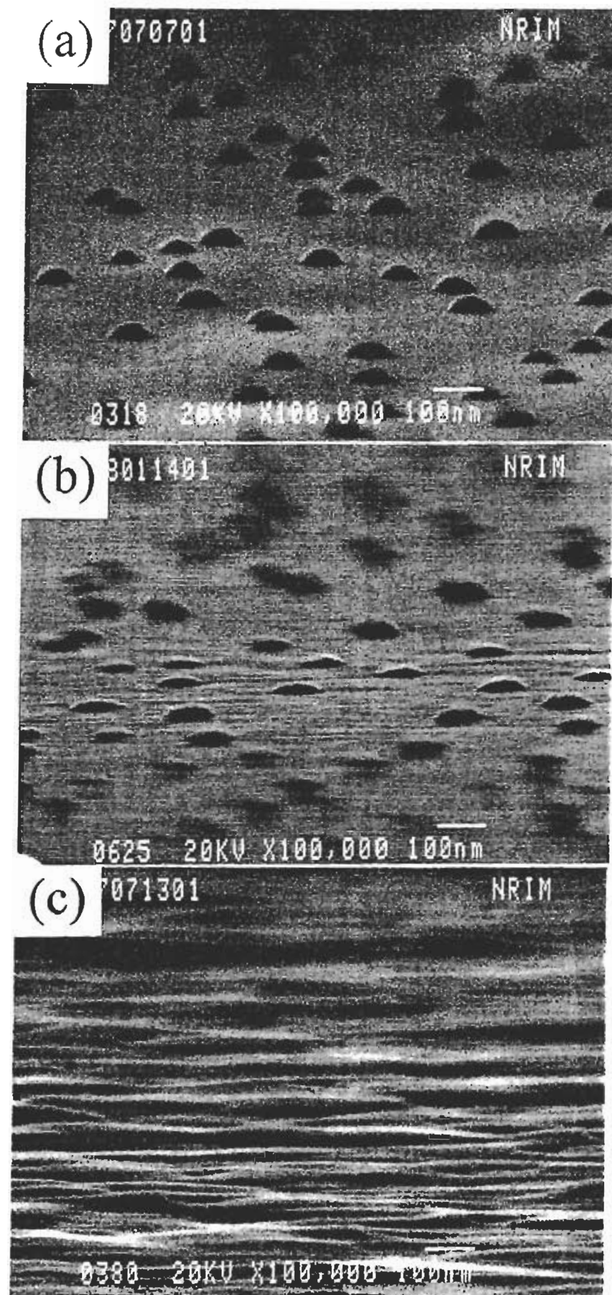

Fig.1 Surface morphologies of the samples; (a) $Ga_{0.90}Al_{0.10}$ droplets, (b) $Ga_{0.90}Al_{0.10}As$ microcrystals just before overgrowth, and (c) after the growth of overlayer.

deposition (a). The average diameter and the density of the GaAl droplets were 100nm and 4.5×10^{8} cm^{-2}, respectively. The standard deviation of the size distribution was about 10%. These GaAl droplets changed to GaAlAs microcrystals after the As flux supply (b). The base size, the standard deviation and the density of the GaAlAs microcrystals are very similar to those of GaAl droplets. The height of the microcrystals was about 30nm. The microcrystals had mainly {110} and {111} facets. These facts show that the S-terminated surface inhibits the two-dimensional growth during the crystallization of GaAlAs microcrystals from GaAl droplets. However, without S-termination, the two-dimensional growth occurs easily, forming GaAlAs layer instead of the microcrystals. The surface after the burying these microstructures by $Ga_{0.70}Al_{0.30}As$ barrier and GaAs cap layers is rather rough (c). The cross sectional TEM observation of buried structure revealed that the shape and size of buried GaAlAs microcrystals were almost same as those of GaAlAs microcrystals just before the growth of overlayer.

The procedure of As flux supply at room temperature is necessary to obtain uniform size GaAlAs microcrystals, otherwise the standard deviation of the size distribution is over 20 %. This may be related to the surface roughness with one monolayer height on the (2×6) S-stabilized surface fabricated by terminating the (4×6) GaAl-stabilized surface [11][12]. During this procedure, the RHEED pattern changed from the halo caused by GaAl droplets to the coexisting pattern of the halo and weak transmission spots from GaAlAs microcrystals. This fact means that a little amount of the GaAl droplets changed to GaAlAs. Before and after the following exposure to the sulfur vapor, no distinct change of RHEED pattern was not observed. After the supply of As flux at 400℃, the RHEED pattern changed to the coexistence of clear strong transmission spots which show <111> facets from GaAlAs microcrystals, weak twin spots and (2×6) streak from S-terminated substrate surface. The halo disappeared perfectly.

After the substrate heated up, (2×6) pattern changed to (2×1) or (2×4), that indicated S adsorption layer desorped from the surface, at about 520-550℃. This temperature corresponds to that mentioned in reference [13] for the removal temperature of adsorbed sulfur atoms.

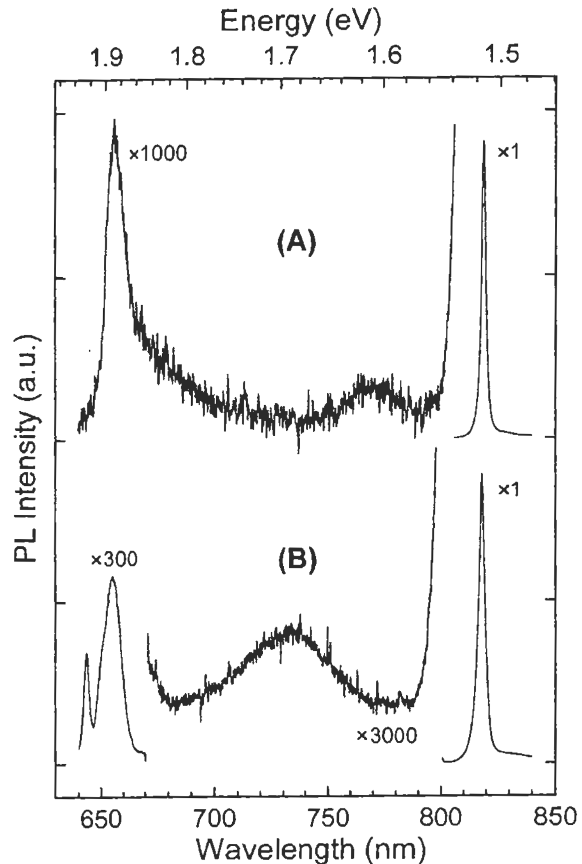

Fig.2 Photoluminescence spectra of buried structures observed at 15 K. Al composition of buried microcrystals are 3 % (A) and 10 % (B).

Again substrate was heated up, then the transmission diffraction spot and twin spot became weak gradually, on the other hand streaky pattern became slightly strong. This indicated that the two-dimensional growth began. Twin spots disappeared at the substrate temperature of 540-580℃. The growth of overlayer was performed at this temperature to bury the microcrystals.

Figure 2 shows the PL spectra observed for these samples. Distinct peak was observed between peaks of GaAs substrate and GaAlAs barrier layer. The peaks appeared at the photon energies of 1.608 eV and 1.692 eV for the buried structures of $Ga_{0.97}Al_{0.03}As$ and $Ga_{0.90}Al_{0.10}As$ microcrystals, respectively. These peaks are due to GaAlAs microcrystals. The energy gaps are 1.560 eV for $Ga_{0.97}Al_{0.03}As$ and 1.658 eV for $Ga_{0.90}Al_{0.10}As$, respectively [14][15]. Although the observed peaks sifted slightly higher energy than bulk materials, these differences may be caused by the quantum well effect [16] and/or compositional fluctuation in the microcrystals. We have also tried to measure the PL spectra of the buried

$Ga_{0.82}Al_{0.18}As$ microcrystals. However, in this case, it seemed that the peak of microcrystals might be hidden by that of GaAlAs buffer layer.

On the other hand, we couldn't distinctly observe the photoluminescence from the buried GaAlAs microcrystals fabricated by the conventional droplet epitaxy. From these experiments, we believe that this modified droplet epitaxy is better than the conventional droplet epitaxy for fabricating quantum dots.

Conclusions

We have proposed a new modified droplet epitaxy method to overcome the problems in the conventional droplet epitaxy and demonstrated the fabrication of high quality buried structures of GaAlAs microcrystals. We have observed the photoluminescence from the GaAlAs microcrystals fabricated by the modified droplet epitaxy method. This modified method can successfully be used in the future fabrication of GaAs quantum dots. In fact, in our preliminary results for the fabrication of 10 nm scale GaAs by using the modified droplet epitaxy, the photoluminescence peak from the GaAs quantum dots has been observed.

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References

1. H. Sakaki, Jpn. J. Appl. Phys. **28**, L314 (1989).
2. Y. Arakawa and H. Sakaki, Appl. Phys. Lett. **40**, 939(1982).
3. T. Fukui, S. Ando, and Y. Tokura, Appl. Phys. Lett. **58**, 2018(1991).
4. T. D. Bestwick, M. D. Dawson, A. H. Kean, and G. Duggan, Appl. Phys. Lett. **66**, 1382(1995).
5. D. Leonard, M. Krishnamurthy, C. M. Reaves, S. P. Denbaars, and P. M. Petroff, Appl. Phys. Lett. **63**, 3203(1993)
6. N. Koguchi, K. Ishige and S. Takahashi, J. Vac. Sci. Technol. **B11**, 787 (1993).
7. N. Koguchi and K. Ishige, Jpn. J. Appl. Phys. **32**, 2052 (1993).
8. Y. Horikoshi, M. Kawashima, and H. Yamaguchi, Jpn. J. Appl. Phys. **25**, L 868 (1986).
9. Y. Homma, H. Yamaguchi, and Y. Horikoshi, Appl. Phys. Lett. **68**, 63(1996).
10. L. Dawerits and R. Hey, Surf. Sci. **236**, 15(1990).
11. S. Tsukamoto and N. Koguchi, J. Cryst. Growth **150,** 33(1995).
12. S. Tsukamoto and N. Koguchi, Appl. Phys. Lett. **65**, 2199(1994).
13. H. Oigawa, J. F. Fan, Y. Nannichi, H. Sugahara, and M. Oshima, Jpn. J. Appl. Phys. **30**, L322(1991).
14. J. S. Blakemore, J. Appl. Phys. **53**, R123 (1982).
15. H. Shen, S. H. Pan, Z. Hang, J. Leng, and F.H. Pollak, Appl. Phys. Lett. **53**, 1080 (1988).
16. T. Ishibashi, Y. Suzuki, and H. Okamoto, Jpn. J. Appl. Phys. **20**, L623(1981).