Extended Abstracts of the 1992 International Conference on Solid State Devices and Materials, Tsukuba, 1992, pp. 582-584



# A Selective Growth of GaAs Micro Crystals on a Se-Terminated GaAlAs Surface from Ga Droplets for the Quantum Well Box Structure

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A selective growth of GaAs micro crystal was demonstrated on a Se-terminated GaAlAs surface. At first, Ga molecules were supplied to the Se-terminated GaAlAs surface to form Ga droplets. The surface consisted of Ga droplets and bared Se-terminated GaAlAs surface. In the following As molecule supply to the surface, GaAs micro crystals were observed to grow selectively from Ga droplets on the surface. The cross sectional investigations by the high resolution electron microscope revealed that a epitaxial growth of GaAs with (111) facets and a possibility of $Ga_2Se_3$ layer formation at the GaAs/Se-terminated GaAlAs interface.

## 1. Introduction

A recent advances in micro fabrication technique in semiconductor have enable the realization of fine structures where carriers are confined in low dimensions[1]. A structure with the carrier confinement in quasi-zero dimension is termed "the quantum well box". The quantum well box has been a leading candidate for an advanced semiconductor laser with a fine coherency and a low threshold current density[2]. In fabricating the quantum well box, an uniform size fine structure without defects or damages must be realized. For this purpose, the Droplet Epitaxy, implying a crystal growth from Ga or In droplets, has been proposed[3-7].

In our previous report that showed a selective growth of GaAs micro crystals on a ZnSe surface by the Droplet Epitaxy[3,4], the essential factors in the Droplet Epitaxy are that 1) a surface does not react with Ga atoms and 2) that the surface gives no sites for As molecule adhesion. Furthermore, 3)the substrate surface has a similar atomic configuration as that of GaAs surface for the epitaxial growth. Recently a sulfur terminated GaAs surface was reported to be chemically stable due to filled dangling bonds[8,9]. From these reports, group V elements such as S and Se seems to satisfy the required conditions for the Droplet Epitaxy.

In this paper, A GaAs micro crystal growth on Se-terminated GaAlAs surface was attempted. Surface morphologies were observed in every growth steps. Cross-sectional lattice images were examined to evaluate micro structures of GaAs micro crystals and atomic configurations at GaAs/Se-terminated GaAlAs interface.

## 2. Experiment

Si-doped GaAs(001) wafer was used as a substrate. After the usual degreasing and etching process, a GaAs buffer layer of 100 nm was grown at 580 °C. Subsequently GaAlAs layer in 20 nm was grown at the same substrate temperature. A composition of GaAlAs layer was $Ga_{0.85}Al_{0.15}As$. Se molecules were supplied to the surface at 300 °Cfor a few minutes till (2×1) reconstructed structure appeared, which was thought to be a symptom of the Se-termination[10]. An estimated equivalent pressure of Se molecules was about $5\times10^{-5}$ Torr at 150-160 °C sell temperature.

On the Se-terminated GaAlAs surface, Ga atoms were deposited at 150 °C for 3 second to form Ga droplets. The total amount of Ga atoms was estimated to be $1.4\times10^{15}$ atom/cm$^2$. The value, derived from the growth rate of the GaAs layer, corresponded to 2.2 monolayer of GaAs crystal. Following the Ga deposition, As molecules were supplied to grow GaAs micro crystals in a gradual increasing pressure of As molecules up to $3\times10^{-6}$ Torr for 30 min.

Ga atoms were also deposited on the As-stabilized GaAlAs surface at 150 °C for 3 seconds and a subsequent As molecule supply was carried out to compare the GaAs growth on Se-terminated GaAlAs surface.

The growth procedures were monitored by the reflection high energy electron diffraction (RHEED) and the surface morphologies were observed by the high resolution scanning electron microscope(HRSEM). High resolution transmission electron microscope (HRTEM) images of cross-section samples, observed from <110> and <100> directions, were examined to evaluate the interface structures between GaAs micro crystals and the Se-terminated GaAlAs layer. The HRTEM was operated at 400 kV with Cs=0.9 mm.

## 3. Results

The (2×4) pattern,observed after GaAlAs layer growth at 580 °,C changed to c(4×4) on reducing substrate temperature to 300 °C. When Se molecules were supplied to the surface at 300 °C, the surface reconstructed pattern changed into (2×1) pattern by about 2 minutes Se molecule supply. After the Ga supply to the surface, the RHEED patterns consisted of a slight halo pattern reflected from Ga droplets and the obscure (2×1) pattern reflected from Se-terminated GaAlAs surface. A subsequent As molecules supply to the surface altered the RHEED patterns to oblique streaks reflected from (111) planes and spotty diffractions from the GaAs micro crystals. By an observation from <1$\bar{1}$0> direction, some weak twin spots were found.

On the surface after the Se molecule supply, some small gray dots of 860 nm in average size ,thought to be segregation of Se atoms, were observed by HRSEM. The density of the dots was $4.4\times10^7$ dot/cm$^2$ and the average distance between gray dots was 1.5 μm.

Figure 1(a) and (b) show surface features after the Ga deposition. Ga droplets were observed as white dots. In these figures, hemispherical shaped Ga droplets were observed. The average diameter of the droplets was 30 nm and a size deviation was 14%. The average distance of the Ga droplets was 210 nm, that is, the density of the droplets was $2.3\times10^9$ droplet/cm$^2$. According to the amount of Ga atoms supplied to the surface, the Ga amount in 210 nm × 210 nm was estimated to be $6.3\times10^5$ atoms. Another

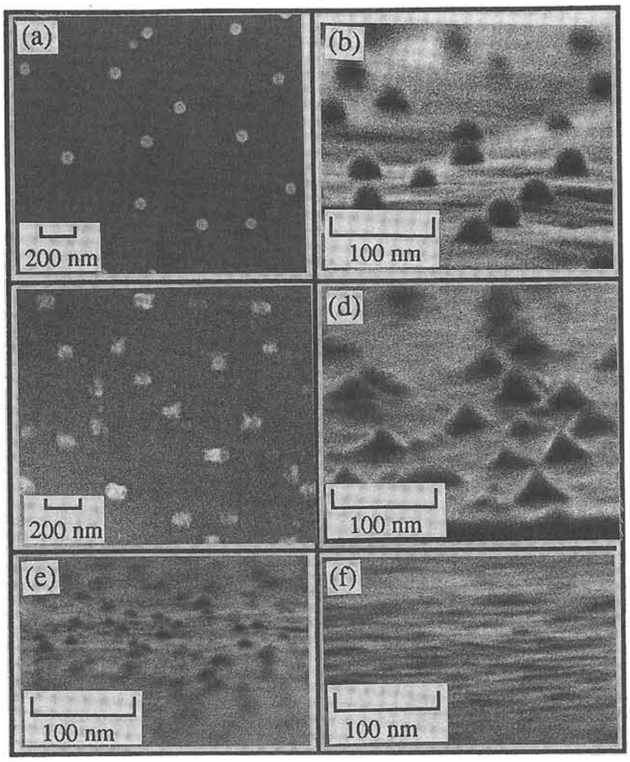


Figure 1 Surface morphologies on Se–terminated GaAlAs surfaces and As–stabilized GaAlAs surfaces.

(a) (b) Ga droplets on Se–terminated GaAlAs surface.
(c) (d) GaAs micro crystals on Se–terminated GaAlAs surface.
(e) Ga droplets after Ga deposition onto As–stabilized GaAlAs surface.
(f) A surface morphology after As molecule supply onto Ga droplets in (e).

calculation using the diameter of Ga droplets revealed that a Ga droplet contained $6.6\times10^5$ atoms in average. From these results, it was found that the Ga amount in a droplet was nearly consistent with the Ga amount deposited in 210 nm × 210 nm square.

Figure 1(c) and (d) are surface morphologies of the sample after As molecule supply. Many square shaped crystals covered with (111) facets were found on the surface. The crystals seemed to expand to <110> direction. These results could be understood as that the Ga droplets on Se–terminated GaAlAs surface grew to be GaAs micro crystals with As incorporating into Ga droplets. In the figures, a dominant size of the GaAs micro crystal was 45 nm in an average side length. The deviation of the length was 12%. The distance between large GaAs micro crystals was 200 nm and it was almost the same that the distance between Ga droplets. A GaAs micro crystal was estimated to involve $6.1\times10^5$ atoms in case that the feature of the crystal is assumed to be a pyramidal shape covered with (111) facets.

Figure 1(e) shows the Ga droplets observed after Ga deposition onto As–stabilized GaAlAs surface with the same manner on the Se–terminated GaAlAs surface. There observed droplets in smaller size with high density than those on Se–terminated surface.

Figure 1(f) shows a surface feature after As molecule supply onto Ga droplets on As–stabilized GaAlAs surface. Ga droplets disappeared on the surface, resulting in a GaAs layer with As incorporating as ever reported at a different substrate temperature[11,12].

By the HRTEM observations, pyramidal shape crystals without defects and truncated ones with twins were found. Figure 2(a) shows a micrograph of the pyramidal shape GaAs micro crystal observed from <110> direction. The crystal was also found to be covered with facets as observed by the HRSEM. The obtained lattice image indicated an epitaxial growth of the GaAs micro crystal on the Se–terminated GaAlAs surface. The interface between the micro crystal and the Se–terminated GaAlAs layer was flat and the lattices of GaAs and the Se–terminated GaAlAs were matched. In the image, a dark region, attributed to the stress induce by the lattice mismatch, was seen along to the GaAs/Se–terminated GaAlAs interface.

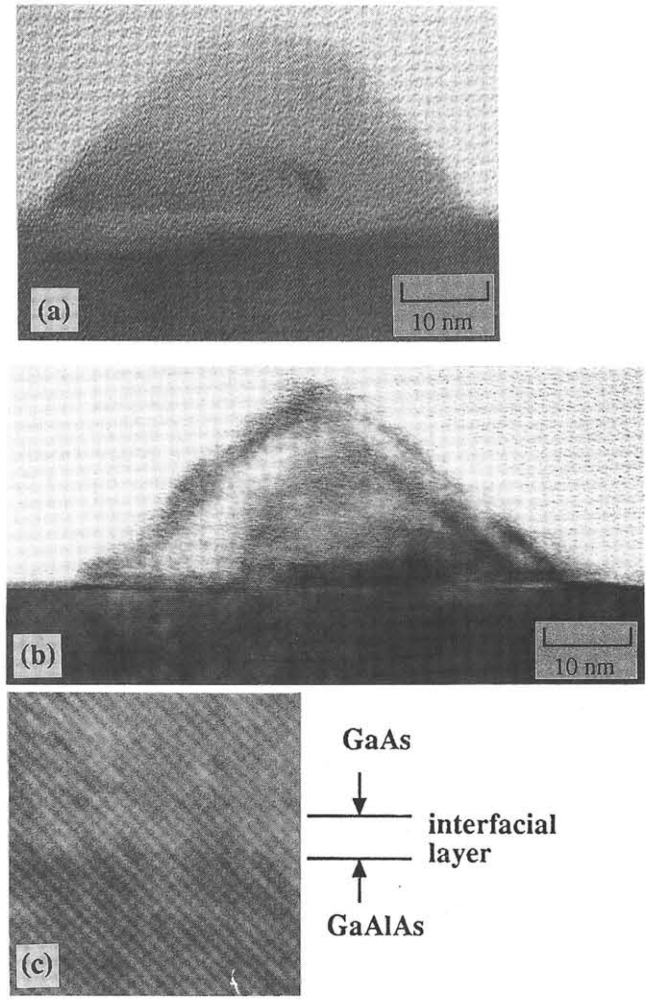


Figure 2 Structure observations of the GaAs micro crystals on Se–terminated GaAlAs surface.

(a) A lattice image of the GaAs micro crystal observed from <110> direction.

(b) A bright field image of the GaAs micro crystal observed from <100> direction.

(c) A lattice image of the GaAs/Se–terminated GaAlAs interface observed from <100> direction.

Figure 2(b) shows a bright field image of another GaAs micro crystal observed from <100> direction. The crystal exhibits a triangle shape. The angle of the top corner is 100 degree, being an obtuse angle, compared with the normally observed angle in a pyramid shape. This fact is attributed to the expanded shape of the micro crystal to <110> direction. Figure 2(c) shows a lattice image at the GaAs/Se-terminated GaAlAs interface observed from <100>direction. At the interface region, a bright region about in 1 nm was observed, meaning a possibility of $Ga_2Se_3$ layer formation[13)].

## 4. Discussions

As for a Se-termination of GaAs surface, Ohno reported that Ga-Se bonding is stable and Se atoms occupy bridge sites over Ga rows[14)]. Takatani et al. concluded that, in supplying Se molecule onto various reconstructed GaAs surfaces, every GaAs surface showed (2×1) reconstructed structure after Se molecule supply, even in the case that the surface was stabilized by As atoms[10)]. They speculated that the universal (2×1) structure of the surface was attributed to that As atoms were replaced by Se atoms due to the stable Ga-Se bonds. These results seems applicable to our Se-termination of GaAlAs surface. It is speculated that Ga-Se and Al-Se bonding are also formed after Se molecule supply onto GaAlAs surface and the bonded atoms compose the (2×1) reconstructed structure. Takatani et al reported a compound like $Ga_2Se_3$ after Se molecule supply onto GaAs substrate at 400 °C. They estimated the thickness of the compound to be a few atomic layer by means of a extended X-ray absorption fine structure (EXAFS) measurement[15)]. The $Ga_2Se_3$ layer is thought to be formed by the Se interdiffusion into GaAs layer and a replacing As sites with Se atoms. The thickness of the $Ga_2Se_3$ was consistent with the observed interfacial region at GaAs/Se-terminated GaAlAs interface. The coincidence seems to give a feasibility of $Ga_2Se_3$ formation. In our experiment, the observed Se segregation seems to exhibit a self-limiting adhesion of Se atoms as already mentioned by Farrell[16)]. At this moment, it is not clear in our case whether a surface layer such as $Ga_2Se_3$ exists after the Se termination at 300 °C.

The Ga amount in a droplet was nearly consistent with the Ga amount deposited in 210 nm × 210 nm square. This means that the deposited Ga atoms migrated on the Se-terminated GaAlAs surface and formed droplets without reacting with the underlying layer. The Se-terminated GaAlAs surface is expected to provide such an inert surface that Ga atoms does not react the GaAlAs layer when the Ga atoms are supplied at 150 °C.

A growth mechanism will be explained by the Vapor-Liquid-Solid mechanism[17)]. As molecule or As atoms dissolve into liquid Ga and grow GaAs crystal at the interface between liquid Ga and substrate. Then the GaAs micro crystals inherit a crystallographic information from the substrate, resulting in the epitaxial growth, as observed by HRTEM. In the growth process, a rapid growth to <001> direction and a slow lateral growth is considered[18)]. In the growth to <001> direction, atomic configuration is determined by the underlying two bonds. In the lateral growth to <110> direction, however, atomic configuration is determined by the bond configurations of both (111) plan of GaAs micro crystal and the Se-terminated GaAlAs surface. As a bond rotation is easily occurred on (111) plane[19)], a surface roughness of Se-terminated GaAlAs surface affects the bond arrangement, resulting in a twin formation. Some observed twin spots from <1$\bar{1}$0> direction is thought to be caused by a surface roughness.

Ohno reported that a equilibrium bond length between Ga and Se is 0.238 nm[14)]. Harrison estimated the equilibrium Ga-Se bond length to be 0.228 nm in case that Se atoms are involved in GaAs crystal[20)]. Both values are smaller compared with the bond length of Ga-As. An observed strain region in GaAs micro crystal, as indicated in the Fig.2(b), is attributed to the shorter equilibrium bond length between Ga and Se atoms.

On Se-terminated GaAlAs surface, the lateral growth of GaAs with As incorporating, as observed on the As-stabilized surface, did not occur. It means that the Se-terminated surface has also a low adhesivity to As molecules at 150 °C.

## 5. Conclusion

A GaAs micro crystal growth on a Se-terminated GaAlAs surface was attempted to fabricate the quantum well box structure. A selective growth of GaAs micro crystal growth with As incorporating into Ga droplets was observed on the Se-terminated GaAlAs surface. On a As-stabilized GaAlAs surface, Ga droplet disappeared after As molecule supply, resulting in a lateral growth of GaAs. Results of the lattice image observations gave a dominant GaAs micro crystal growth on Se-terminated GaAlAs surface.

Throughout the experiments and discussions, the GaAs micro crystal growth on a Se-terminated of GaAlAs surface was recognized to give a possibility to realize fine micro crystals in uniform size for the quantum well box structure.


## Acknowledgements

The authors are grateful to Satoshi Takahashi for the SEM observations. We would also like to thank Michihisa Iijima of Tokai University for his corporation.


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