Formation of GaAs Quantum Dots by Low-Temperature Droplet Epitaxy

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Abstract

Direct formation of GaAs quantum dots on (Al,Ga)As layers grown at low substrate temperature was demonstrated through the sequential exposure of Ga and As molecular beams. The Ga droplets were initially formed on the LT-grown (Al,Ga)As layers having (1x1)surface structure.

The successive exposure of As beam reveals the facet formation along 〈111〉 in reflection high energy electron diffraction. From the observation of surface morphology by atomic force microscope, the existence of the GaAs quantum dots was clearly confirmed.

1. Introduction

One of the promising recent advances in the nanofabrication of quantum dots(QDs) with zero dimensionality exploits the natural consequences in the growth modes for hetero-epitaxial growth. It makes use of differences between the amount of strain due to lattice mismatch, and of the interfacial energies. Thermodynamic considerations of the initial stages of epitaxy have led to the distinction of three different growth modes[1]. In the Frank-van der Merwe (FM) mode the epitaxial material grows in a continuous two dimensional(2D) layer-by-layer way. The Stranski-Krastanov(SK) mode is an intermediate case, in which the first few monolayers nucleate in the 2D layer-by-layer way, but above a critical thickness three dimensional (3D) islands appear. It has been observed for various crystals of dissimilar lattice constant. A very large number of studies have been devoted to the QD fabrication by SK mode, for example, Ge on Si or InAs on GaAs semiconductors[2]. On the other hand, if the layer has a high surface free energy per unit area compared to the substrate, clusters or islands form and 3D growth occurs, *i.e*, Volmer-Weber(VW) growth mode. As for the lattice-matched system such as GaAs/(Al,Ga)As, SK growth mode is not available for the fabrication of QDs. Thus it is desirable to use VW growth mode rather than SK mode for such systems. If we are able to control the growth mode from FM to VW by changing the external growth parameters such as temperature or surfactant mediation, then one can extend the self-assembly phenomena to lattice-matched system. One of the promising techniques, droplet epitaxy, is based on incorporating the V-column element into III-column element droplets which have been deposited on the sulfur-passivated surface of the substrate [3]. In this process the presence of almost filled dangling bonds on the sulfur-passivated surface prevents the adsorption of foreign atoms. The inertness of the surface to the adsorption can drive a transition from 2D FM mode to 3D VW growth mode.

In this study we propose and demonstrate the direct formation of GaAs QDs on (Al,Ga)As layer by droplet epitaxy. The most distinctive process is that instead of the surface passivation by VI-column elements we use the semiconductor surface grown at low substrate temperature(LT) under far from equilibrium condition.

2. Experiment

The samples studied in this work were grown by molecular beam epitaxy(MBE)on semi-insulating (001)-oriented GaAs substrates. In the growth chamber, each sample was heated to 590℃ for oxide desorption. The films were grown using the tetramer arsenic source As_4 and its pressure was high enough to ensure (2×4)As stabilized surface reconstruction at normal substrate temperature. After the normal growth of a 0.5 -μmu-thick buffer layer at 580 ℃, ten period AlAs/GaAs superlattice were deposited as a buffer layer. After the growth of 1 μm-thick GaAs buffer layer, the substrate temperature was lowered to 250℃ under As beam exposure. Then following a 2000Å-thick $Al_{0.3}Ga_{0.7}As$ layer, the exposure of Ga beam of 9 equivalent monolayers was initially performed without As beam. After the exposure of Ga, the Ga shutter was closed, and then immediately As beam with 7×10^{-6} torr was exposed. The formation of GaAs QDs was observed by using *in-situ* reflection high energy electron diffraction(RHEED) pattern with the 10 keV incident electron beam. The samples were transferred from the growth chamber to an atomic force microscope(AFM) through air. The surface morphology was then examined in a constant height mode using a force of about 10 nN under ambient conditions.

3. Results and Discussion

A.Facet formation

Figure 1 shows the RHEED patterns obtained in the 〈110〉 and 〈1$\bar{1}$0〉 azimuth during the growth. At normal temperature (2x4)As stabilized surface is shown in Fig.1(a). As decreasing the substrate temperature to 250℃, the RHEED patterns gradually change from (2×4) to c(4×4) surfaces. The changes of surface reconstruction as lowering the substrate temperature is well-known behavior. After the deposition of LT-(Al,Ga)As, it shows immediately (1×1) surface structure, which is nominally observed in LT-MBE growth in Fig.1(b). When the Ga beam exposed on the surface of LT-(Al,Ga)As, the electron diffraction pattern shows a halo pattern caused by the formation of Ga droplets in Fig.1(c). By a subsequent exposure of As beam without Ga beam the halo pattern disappeared after ~20 s exposure. The RHEED pattern changed to one with spotty features with streaks along the 〈111〉 azimuth. As shown in Fig.1(d) the 〈111〉 streaks were clearly observed along the 〈110〉 azimuth rather than along 〈1$\bar{1}$0〉 azimuth. This change obviously indicated the facet formation. The facet planes of GaAs QDs are determined to be well-defined{111}. In contrast to the {113} or {115} of InAs QDs by SK growth mode, it is found that in the case of GaAs QDs, {111} is more favorable than {113} or {115}. Some twin spots were observed along both azimuths, and the important role of twin will be discussed elsewhere in detail.

These sequential changes of the RHEED patterns show that the 3D VW growth mode rather than 2D FM mode occurred on LT-(Al,Ga)As surface. This observation is consistent with that of GaAs QDs on sulfur-terminated GaAs surface during the growth [3]. And the halo surface structure appeared after Ga deposition on the As-adsorbed GaAs (100) substrate with the surface structure of c(4×4) at 250℃. During the same procedure on the c(4×4) As-adsorbed GaAs surface the halo disappeared and changed to (1×1)

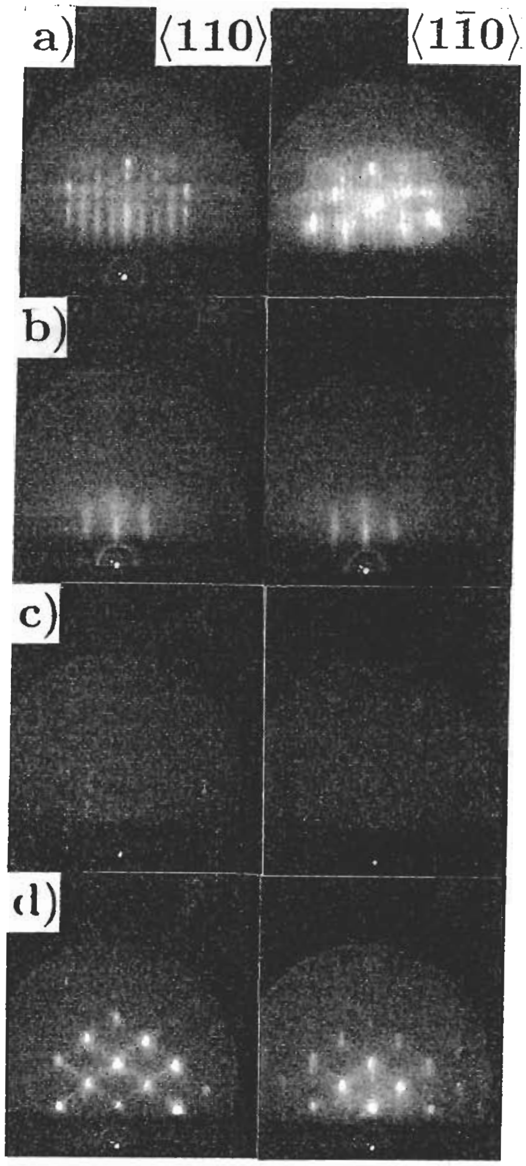

Fig.1 RHEED patterns during the GaAs quantum dots growth on LT-(Al,Ga)As layers observed along 〈110〉 and 〈110〉 azimuth. (a) is the pattern after GaAs buffer growth at 580℃. (b) is the pattern after LT-(Al,Ga)As growth at 250℃. (c) is the pattern after Ga deposition at 250℃. (d) is the pattern after As beam exposure at 250℃. Left column: electron beam along [110]; right column: electron beam along[1$\bar{1}$0].

streaks, which means no facet evolution. This result suggests that the surface structure of GaAs(001) surface plays the dominant role in the formation of facet in the initial stage of QDs growth. Furthermore the simultaneous exposure of Ga and As beams shows the 2D layer-by-layer growth of GaAs epilayers. Thus it is noted that the sequential exposure as well as the LT-grown (1× 1)surface is necessary to form the 3D microcrystals.

B.Surface morphology

In order to obtain the direct information on the resulting feature of GaAs QDs, we observed the AFM image. The AFM photograph was illustrated in Fig.2 for Ga-exposure of 9 equivalent monolayers. Prior to a detailed discussion on the QDs we will look at the surface morphology of LT-(Al,Ga)As layers showing the large mounds on the surface grown on flat surfaces. The elongated mounds are 10 nm high and 0.5 μm x 3.0 μm in planar dimension. It depends on the miscut angle of GaAs substrate and the substrate temperature. The anisotropy is along $\langle 1\bar{1}0 \rangle$ direction. As was pointed out by Johnson *et al.*, the mounds occur when samples are grown in a layer-by-layer mode and they are absent if the growth occurs by uniform step flow [4]. This is caused by Schwoebel barrier that does not allow any atoms to jump down a step and up steps [5]. If the step flow growth occurs when the atom reach a step edge before nucleating, the large scale mound can not be formed.

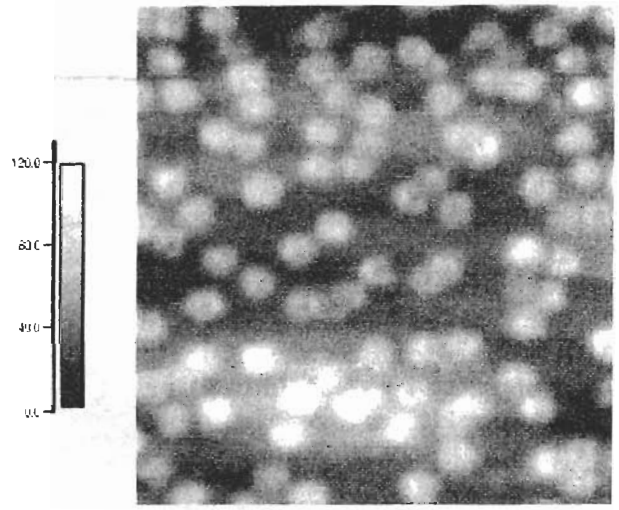

Fig.2 AFM images of a 1.2×1.2μm² surface area showing the result of formation of GaAs quantum dots.

The bright circular features represent the GaAs QDs which are spread over the mounds with uniform size of $80x80x5nm^3$. It is noted that the QDs were distributed randomly without any bunching behavior even around the edge of mounds where is the interface between the irregular mounds. As mentioned above, we pointed out the LT-grown (1×1) surface and sequential exposure for the formation of GaAs QDs. In other words it could be explained in terms of limited Ga migration on excess As-contained surface at low substrate temperature. Since the surface diffusion constant D is given by $D=D_0\exp(-E_s/kT)$, the Ga migration length on the (001) surface decreases exponentially with the substrate temperature[6]. When the Ga droplets initially formed on the (Al,Ga)As layer, those are practically immobile. In addition to the substrate temperature, the surface diffusion length of Ga adatoms is strongly influenced by the As pressure. Even though the detailed (1×1) surface structure of LT-GaAs is not understood yet, it is well-known that LT-GaAs contains excess As around 1~2 % or more in the lattice[7]. Thus we can deduce that the impinging Ga adatoms hardly migrate due to the excess As-contained (1×1) surface. When compared to c(4×4), (1×1) surface contains more As. This is reasonable because the As desorption temperature is around 250℃. Thus it is expected that Ga migration length of (1×1) surface is much shorter than that of c(4×4) surface. As we described above, the formation of {111} facets does not occur on c(4×4) surface. With the decrease in As pressure, we observed that the GaAs QDs enlarged and showed hemispherical structure. This result suggests that a higher As-pressure is needed for the formation of QDs with high aspect ratio.

The peculiar feature of QDs in this study is a small hole on the top of QDs illustrated as a dark spot in AFM photograph. In the conventional selective epitaxy of InP related compounds, *so-called* rabbit ear type morphology is shown due to the migration of reactants from the SiO_2 mask to (100) surface via (111)B surface as decreasing V-element partial pressure [8]. However in contrast, it shows *volcano type* as increasing the As-pressure. As illustrated in Fig.3, the growth mechanism could be explained in terms of As diffusion in liquid Ga droplets. First, Ga droplet initially deposited on the LT-(Al,Ga)As surface without As beam, and few monolayer-thick GaAs formed at

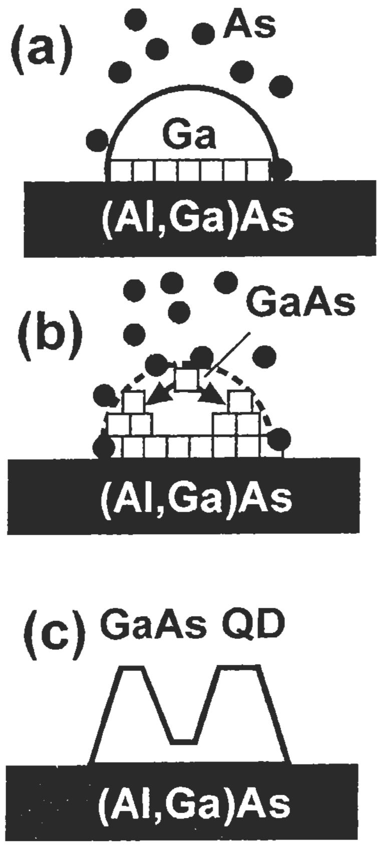

Fig.3 Schematic illustration of the sequential steps for the GaAs quantum dots. The hemisphere represents the Ga droplet on (Al,Ga)As layer. The solid circle and square represent the As and GaAs, respectively.

the hetero-interface because of the reaction between Ga and excess As on the surface. After the closure of Ga shutter As beam is exposed on the Ga droplets, and thus GaAs formed around the surface of Ga droplets in Fig.3(a). Second, under the As atmosphere the GaAs forms rapidly around the top surface of Ga droplets, and the dissolved As and GaAs diffused into the bottom hetro-interface. The formation rate of GaAs at the edge of Ga droplet is faster than that at the center area. Thus it is expected that the GaAs formed at the center area of Ga droplet moves to edge area in Fig.3(b). Finally, the volcano type is eventually formed in Fig.3(c). In this model the driving force of diffusion phenomena is the concentration gradient of As and GaAs in liquid Ga, and its situation is similar to the diffusion of As in Ga-rich solutions in liquid phase epitaxy.

In far-from-equilibrium MBE growth, the growth mode changes from 2D FM at high growth temperature to 3D VW growth at lower substrate temperature. This transition is due to the fact that sufficiently low temperature the adatoms on the surface become so immobile that they can not jump over local energy barriers. Insufficient mass transport causes the surface to be rough and to grow according to a 3D mode. Under high As atmosphere as well as low temperature, 3D VW growth can proceed in a special way resulting in the creation of pyramid or prism-like features on the surface.

3. conclusion

In conclusion, we demonstrated the formation of GaAs quantum dot on LT-(Al,Ga)As layers. Alternating supply of Ga and As beam source at low-substrate temperature reveals the formation of QDs. From the point of LT-process, it provides the useful fabrication technique for various nanostructures. Although the feature of the QDs is thought to be originated by the thermodynamic stability, further investigation is necessary to understand the surface structure of LT-GaAs and the nucleation site of GaAs QDs focused on the As sites.

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