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RESEARCH ARTICLE

Influence of V/III ratio on QD size distribution

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Abstract The influence of V/III ratio on the formation of quantum dots (QDs) grown by metal-organic chemical vapor deposition (MOCVD) is investigated by atomic force microscopy (AFM) and photoluminescence (PL) measurements. As V/III ratio increases, the density of QDs decreases accompanied by the transition of QD size distribution from bimodal (at V/III = 9) to single-modal (at V/III = 15), and then to bimodal (at V/III = 25) again, which is attributed to the change of the indium-species migration length at different V/III ratios. There are PL spectrum redshifts and the PL peak intensity decreases as V/III ratio increases.

Keywords quantum dots (QDs), V/III ratio, QD size distribution, photoluminescence (PL)

1 Introduction

Quantum dots (QDs), new nano-materials have been intensively studied recently. Due to zero-dimensional structure and strong confinement effect of three-dimensional (3D) carrier, QD devices possess many unique properties, such as high gain, low threshold current density, high thermal stability and so on [1–5]. However, it is difficult to fabricate nanometer-scale QDs with high quality and good uniformity. In past years, some papers have reported a phenomenon of bimodal size distribution of QD. For example, Jung et al. [4,5] demonstrated that bimodal size distribution of indium arsenide (InAs) / gallium arsenide (GaAs) QDs grown under different temperature and In(Ga)As coverage. Arciprete reported the effect of annealing process on QD bimodal distribution [6]. Kim et al. [7] presented the influence of InAs coverage on the transition of size distribution and optical properties. However, less attention is paid to the effect of V/III ratio on QD bimodal size distribution. V/III ratio is the ratio of V group source flow rate to III group source flow rate in the QD forming process.

In this paper, we investigate the effect of V/III ratio on the bimodal distribution of InAs QDs by atomic force microscopy (AFM) and photoluminescence (PL) measurements. It is found that V/III ratio not only influences QD size distribution significantly, but also increasing V/III ratio leads to the redshift of PL spectrum and the decline of PL peak intensity.

2 Experiment

All the samples were grown by a Thomas Swan close-coupled-showerhead low-pressure metal-organic chemical vapor deposition (MOCVD) system. Trimethylindium (TMIn), trimethylgallium (TMGa) and arsine (AsH_3) were used as source materials. H_2 served as carrier gas.

For comparison, six types of InAs QDs, samples A-F were grown. Prior to InAs deposition, a GaAs buffer layer was grown at 680°C on (001) *n*-GaAs substrate, and then a GaAs barrier layer was grown at 505°C. At last, InAs QD samples at certain temperatures and V/III ratios were grown, in which samples A, B, and C were grown at 505°C with V/III ratios of 9, 15, and 25, respectively, while samples D, F, and F were grown at 497°C with V/III ratios of 15, 20, and 25, respectively.

AFM measurements were performed by a Veeco NanoScope MultiMode system in ambient conditions in contact mode. PL spectra measurements were carried out under the excitation of 514.5 nm Ar + laser, using a cooled InGaAs detector and lock-in amplifiers.

3 Results and discussion

From statistical analysis of AFM measurement results, QD size distribution and density can be obtained. Figure 1 presents the QD size distributions of samples A, B, and C. Upon increasing V/III ratio (sample A: 9, B: 15 and C: 25),

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QD density decreases (samples A: $1.31\times10^2/\mu m^2$; B: $1.17\times10^2/\mu m^2$ and C: $1.12\times10^2/\mu m^2$). This density variation can be explained by differences in indium-species migration length caused by different V/III ratios. At low V/III ratios, the density of indium adatoms on the growth surface is high, which effectively increases the migration length of indium-species before incorporation into the crystal and enhances the growth layer rearrangements into a more 3D-like topology [8], so QD density is high. Conversely, at high V/III ratios, the density of indium adatoms is low on the growth surface in the arsenic rich condition, which decreases the migration length of indium-species and is unfavorable to energy-minimizing rearrangements of the growth layer.

From Fig. 1, most of QDs in sample B are very small, whose diameter are below 40 nm, so sample B has single-modal QD distribution. However, in sample A and C, apart from smaller QDs, there are also lots of larger QDs whose diameter are above 40 nm, and sample A and C have bimodal QD distribution. We define that small modal QDs have diameter of 5–40 nm, large modal QDs have diameter of 40–80 nm, and give their percentage in Table 1. In Sample A with V/III ratio of 9, the distribution ratios of small modal and large modal QDs are 61.8% and 29%, respectively; in Sample B with V/III ratio of 15, the distribution ratios of small modal QD and large modal QD are 75.2%, 19.7%, respectively; in Sample C with V/III ratio of 25, small modal distribution ratio is 57.0% and large modal one is 30.3% (see in Table 1).

Obviously, V/III ratio affects QD size distribution (Table 1), and the results can be attributed to the migration length of indium-species. Sample A with V/III ratio of 9 has longer migration distance than that of sample B with V/III ratio of 15. There are also more indium atoms in sample A than those in sample B. In order to minimize strain and surface energy, some indium atoms incorporated into existing dots instead of forming new one, which will be more likely to form large QD in sample A compared with sample B. Large and small dots are both observed in sample A.

In sample B, short migration distance due to higher V/III ratio suppresses the transition from QD single-modal distribution to QD bimodal distribution. Nearly all of QD size are about 5–45 nm. QDs are of good uniformity.

When V/III ratio is further increased to 25 in sample C, migration distance gets shorter, which, could not produce enough suitable nucleation sites resulting in the reduction of small QD density. At the same time, with the increase of V/III ratio, wetting layer gets thicker. Nucleation sites are so few that there are excessive atoms on the growth layer. Some sites absorb more material. All these increase the densities of defect and large islands. Large QD in the sample C with the size 70–100 nm are large islands as shown in Fig. 1.

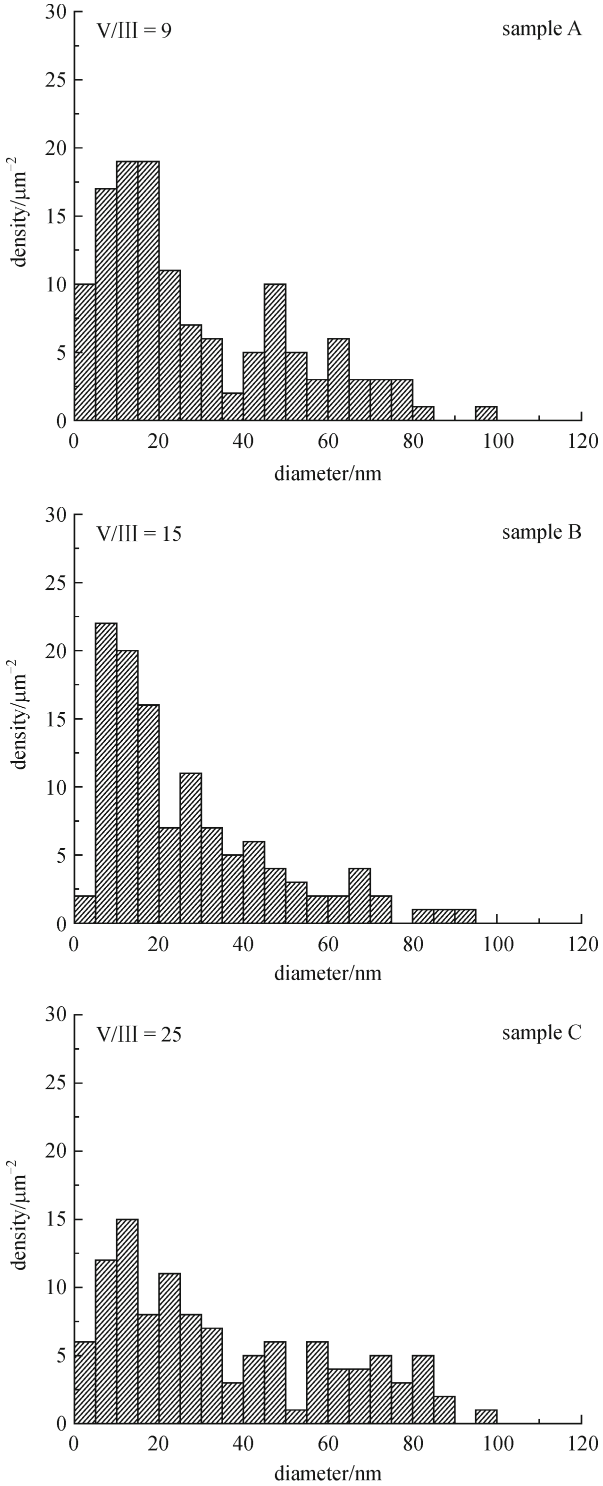

Fig. 1 Diameter distributions of samples A, B, and C

In order to further verify the results described as above, samples D, E and F at temperature 497°C with V/III ratios of 15, 20 and 25 were grown respectively. Figure 2 presents QD size distributions transition from single-modal to bimodal.

The samples grown at temperature 497°C have the same trend of density variation as samples grown at temperature 505°C. The higher V/III ratio (samples D: 15, E: 20, F: 25)

Table 1 Growth parameters and experimental results for samples A, B and C

sample	temperature/°C	V/III ratio	small modal/%	large modal/%	density/μm^{-2}
A	505	9	61.8	29.1	1.31×10^2
B	505	15	75.2	19.7	1.17×10^2
C	505	25	57.0	30.3	1.12×10^2

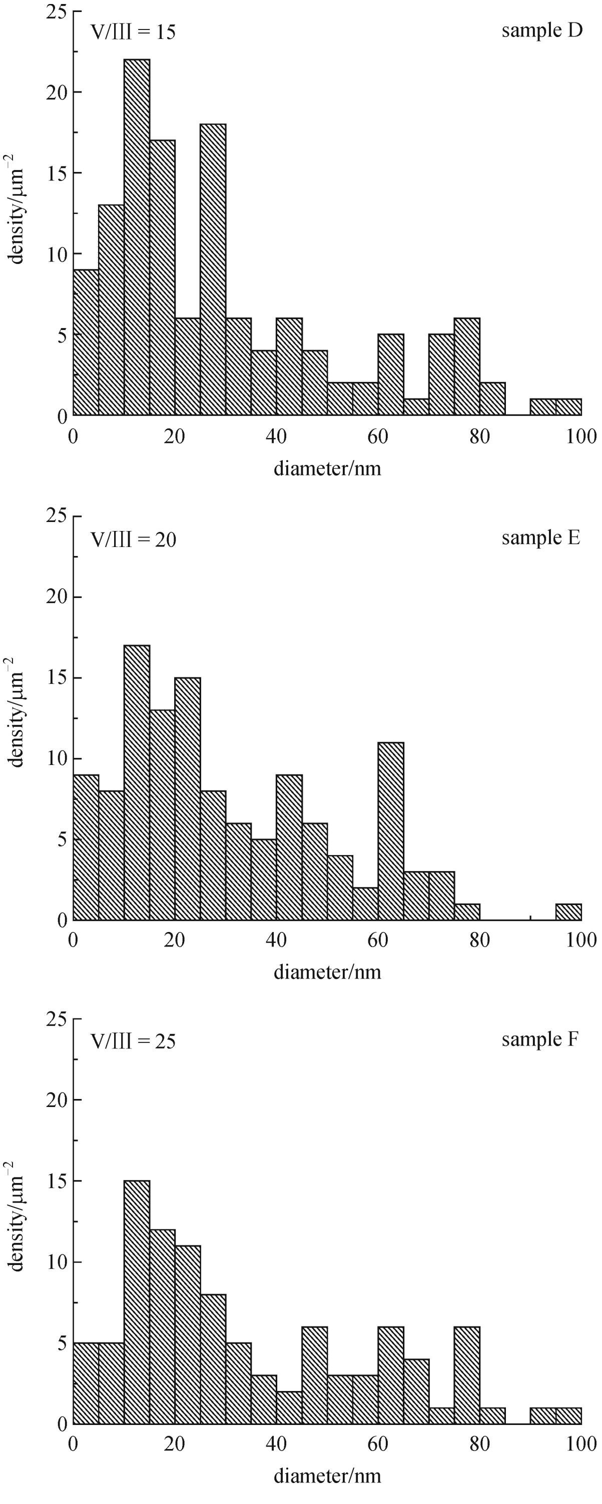

Fig. 2 Size distribution histograms of samples D, E and F

with the lower QD density (samples D: 1.30×10^2/μm^2, E: 1.21×10^2/μm^2 and F: 1.15×10^2/μm^2). When V/III ratio is greater than 15, upon increasing V/III ratio, QD size is changed from single-modal to bimodal distribution.

Table 2 lists experimental parameters and corresponding results of samples D, E and F. For sample D with V/III ratio of 15, small modal QD distribution ratio is 66.2% and large modal one is 23.8%. For sample E with V/III ratio of 20, the distribution ratio of small modal is 61.0%, which of large modal is 33.1%. For sample F with V/III ratio of 25, the distribution ratios of small modal and large modal are 60.2% and 31.6%, separately.

All the experimental results suggest that V/III ratio plays an important role in size distribution of QDs. To a certain degree, low V/III ratio will lead to high QD density and bimodal QD size distribution. With the increase of V/III ratio, short migration distance of indium-species can suppress the transition from single-modal QD distribution to QD bimodal distribution, and we find that QD size distributions of samples B and D are single-modal. But when V/III ratio further rises and exceeds a certain value, QD density decreases, meanwhile defect and big islands density augment and QD bimodal distribution reproduces.

At the same time, the effect of temperature on the size distribution of QDs can be obtained from results of samples B and D (QDs grown at different temperature with the same V/III ratio). With the growth temperature decreasing, QD density increases, more big size QDs appear and the QDs distributions transfer from single-modal to bimodal size which is similar to the results provided by Li et al. [9]. This can be explained that low growth temperature can suppress the diffusion of indium adatoms.

PL spectra for InAs QD with different V/III ratios at 15, 20 and 25 are demonstrated in Fig. 3. PL intensity of samples diminishes with V/III ratio increasing, which could be due to the decline of QD density. Compared with samples D and E, there is PL peak redshifts in sample F. It is well known that the large and small dots have different emission wavelengths, and the large dots have longer emission wavelength. So the raise in the density of large size QDs in sample F results in PL peak redshift [10]. When V/III ratio is 20 in sample E, QD bimodal distribution is not distinct, therefore, PL peak does not show redshift.

In fact, each PL spectrum can be fit into two peaks by Gaussian function, which can ascribe to the distribution of QD bimodal size. Take sample F for example, the Gaussian

Table 2 Growth parameters and experimental results for samples D, E and F

sample	temperature/°C	V/III ratio	small modal/%	large modal/%	density/μm^{-2}
D	497	15	66.2	23.8	1.30×10^2
E	497	20	61.0	33.1	1.21×10^2
F	497	25	60.2	31.6	1.15×10^2

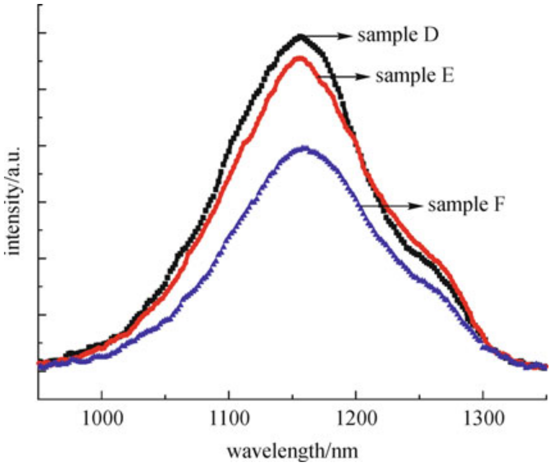

Fig. 3 PL spectra of samples D, E and F

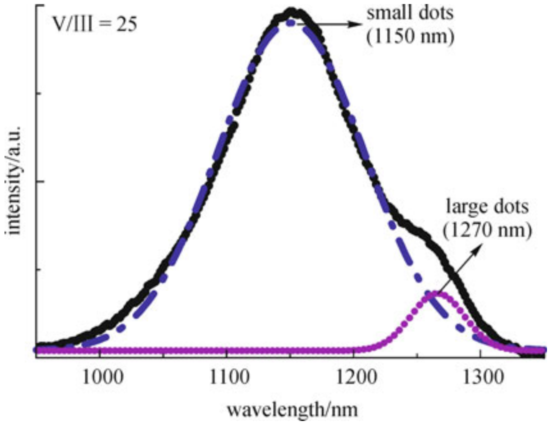

Fig. 4 Gaussian fitting PL of sample F

fitting line shapes of PL spectrum have double-peak (one centered at 1150 nm corresponding to small dots and the other at 1270 nm corresponding to large dots), as shown in Fig. 4.

4 Conclusions

In this study, the influence of V/III ratio on the size distribution and optical properties of self-assembled QDs by AFM and PL measurements have been investigated. V/III ratio plays an important role in size distribution of QDs. Upon increasing V/III ratio, QD density decreases accompanied by the transition from bimodal to single-modal size distribution, then to bimodal again. These results are attributed to the decrease of the indium-species migration length at high V/III ratios. To a certain degree, short migration distance of indium-species suppresses the transition from QD single-modal distribution to QD bimodal distribution. When V/III ratio exceeds some certain value, nucleation sites get fewer, while defects and large island density increase.

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