Cross-sectional scanning tunneling microscopy study of InGaAs quantum dots on GaAs(001) grown by heterogeneous droplet epitaxy

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We present a cross-sectional scanning tunneling microscopy (STM) study of heterogeneous-droplet-epitaxy (HDE)-grown InGaAs quantum dots (QDs). We found that the structural properties of HDE-grown QDs such as size, shape, etc., are quite different from that of Stranski–Krastanov (SK)-grown InGaAs QDs. HDE-grown InGaAs QDs exhibit a reverse trapezoidal shape, opposite to the SK-grown QDs. In addition, the In concentration within individual HDE QDs is rather uniform, contrary to the case in SK QDs. These HDE QDs also show large size fluctuation. However, we found that there is a size dependence in the In concentration within the QD—the larger QD has lower In concentration, suggesting a self-compensation effect which gives rise to a sharp photoluminescence linewidth.
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III–V semiconductor quantum dots (QDs), often formed by using Stranski–Krastanov (SK) growth mode, have been emerging as an important materials system for next generation optoelectronic devices including lasers and photodetectors.[1–3] For optoelectronic applications, it is very important to control both the inter- and intraband transitions of the QDs by optimizing the growth parameters. Often, photoluminescence (PL) linewidths are used to monitor the quality of the QD samples.[4] Generally, a broad PL linewidth is attributed to the nonuniformity of QDs, including the size, shape, and composition inhomogeneities within the ensemble of QDs. Much effort has been made to improve the homogeneity of QD in order to obtain a sharp PL linewidth of the samples.[5–7]

Recently, heterogeneous droplet epitaxy (HDE)[8,9] was proposed to produce InGaAs QDs with narrow PL linewidth (21.6 meV).[10–12] In this letter, we present a study of HDE-grown InGaAs QDs using cross-sectional scanning tunneling microscopy (STM). We found that the structural properties of the QDs such as size, shape, In distribution, etc., are quite different from that of SK-grown InGaAs QDs. More importantly, we found a self-compensation effect between the size and In concentration of the QDs, which leads to a sharp PL linewidth despite a large fluctuation in the quantum dot size.

The InGaAs QDs structures were grown on GaAs(001) using HDE techniques in a RIBER-32P molecular beam epitaxy (MBE) system with As_4, elemental Ga, and In sources.[10–12] For the droplet formation, 2.5 ML of In and 50 ML of Ga were deposited sequentially at 200 °C without As_4 flux. After crystallization with As_4 flux at 200 °C, InGaAs QDs were formed by annealing at 500 °C and a 100 nm GaAs capping layer was grown at the same temperature. The details of the growth process were described in Ref. 12.

Electrochemically etched tungsten tips were cleaned *in situ* using electron bombardment. The samples were cleaved *in situ* in the STM chamber (base pressure $<4\times10^{-11}$ Torr) to expose the buried epitaxial structure on the (110) surface. STM images presented here were acquired at a sample bias of either -2.5 V (filled states) or $+2.5$ V (empty states) and at a tunneling current of 0.08 nA.

Figure 1(a) shows a cross-sectional STM image of HDE-grown InGaAs QDs. The QDs appear brighter than GaAs matrix. The contrast mechanism is similar to that described

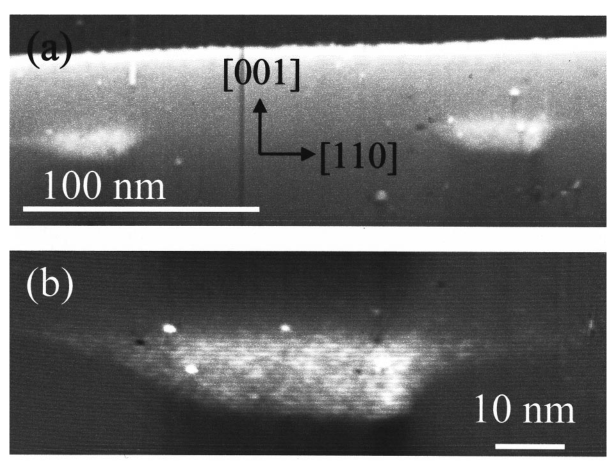

FIG. 1. (a) 250 nm×80 nm STM image of HDE-grown InGaAs QDs acquired at a sample bias of -2.5 V (filled states) and a tunneling current of 0.08 nA; (b) zoom-in view of a HDE-grown QD.

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previously.[13] Qualitatively, the In-rich regions appear brighter than Ga-rich regions. Figure 1(b) is a filled state STM image that shows a close up view of a typical HDE-grown InGaAs QD. By comparing with SK-grown InGaAs QDs, we note that HDE-grown InGaAs QDs exhibit different structural properties. First, these QDs have a reverse trapezoidal shape, opposite to that of SK-grown QDs. Second, most QDs do not have ''wetting-layer-like'' structures, instead they have tail-like extension at the top of individual dots. It has been shown that the droplet structure of InGa droplets along with highly dense Ga droplet successfully prevented the two-dimensional growth of InGaAs during crystallization under an As_4 flux.[12] Our observation confirms the previous result. Third, the HDE-grown InGaAs QDs show higher aspect ratio compared to similar sized QDs grown using the SK mode.

From STM observation, we also found that the size distribution of HDE InGaAs QDs is similar to that of QDs grown by SK mode. The size variations of observed QDs are as following: length: 35–48 nm; height: 7.9–10.7 nm; aspect ratio: 1:3.9–4.5.

Quantitative analysis of the In concentration within individual QDs is performed by using chemically resolved STM image where one can count individual In atoms. Shown in Fig. 2(a) is the empty state STM image of a QD. Because the cation-derived empty surface states for In and Ga are at different energy levels, the In atoms appear as locally bright spots in the empty state image.[14–16] Figure 2(b) is the local height image of Fig. 2(a) enhancing the local variation. One can count the individual In atoms in the QD. As shown in Fig. 2(c), except for a small fluctuation (most likely a statistical fluctuation due to the finite size effect), the In concentration is rather uniform, with an average value of 17%. This result of uniform In concentration is in total contrast to the result of nonuniform In concentration found in SK-grown InGaAs QDs.[13]

The PL measurement performed at 20 K for this sample shows that there is a sharp peak centered at 946 nm (1.31 eV) with a full width at half maximum (FWHM) 21.6 meV.[12] As mentioned previously, the size distribution of HDE InGaAs QDs is rather large. Assuming that different QDs have similar In concentration, a quick estimation based on the size fluctuation indicates that the FWHM of the PL peak should be larger than 50 meV. A question immediately arises: what is the origin of the sharp PL for these HDE InGaAs QDs?

Upon close examination of many individual QDs, we found that, while the In concentration within individual dots is uniform, the In concentration between different dots is different. In fact, there is a size dependence of the In concentration for different dots: the larger dot has lower In concentration, and vice versa. In Table I we show the results for four QDs of different sizes. In this table, we list the size of the QDs as well as their surface lattice constants along the [001] direction. The average surface lattice spacing along the [001] direction was obtained by measuring the top ten atomic rows (bilayers) across the center of a dot. It should be noted that the surface lattice spacing is larger than the nominal lattice spacing at the same In concentration due to the outward relaxation effect.[17,18] Nevertheless, for a small range of

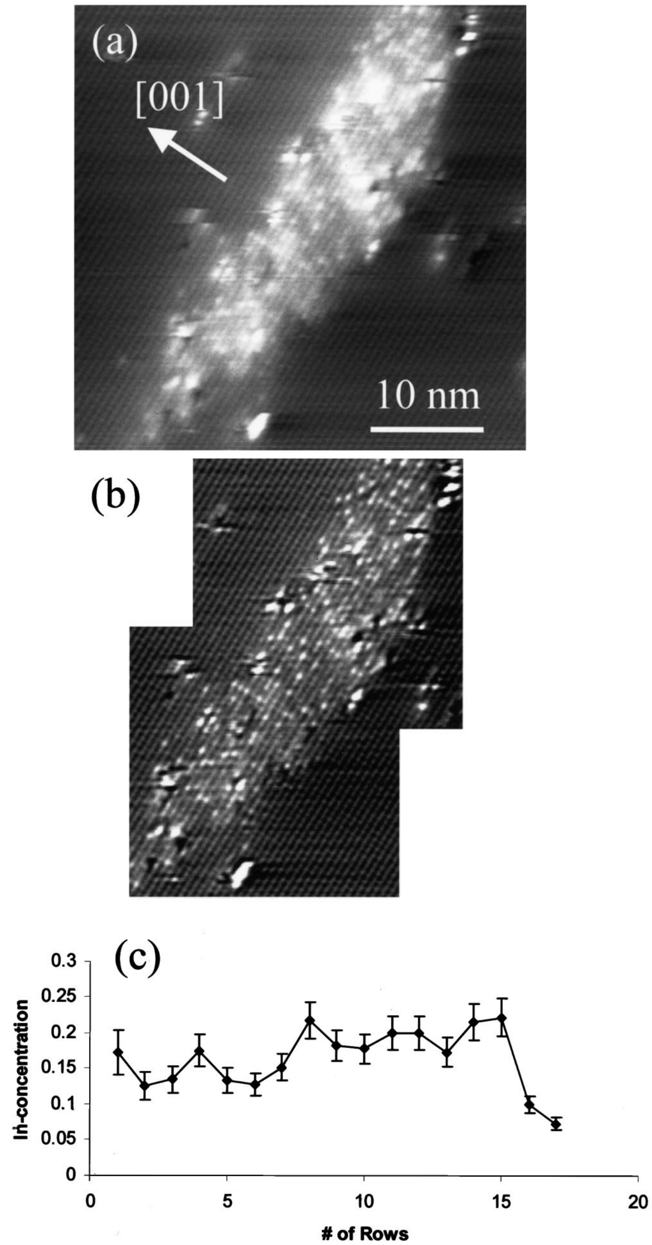

FIG. 2. (a) Empty state STM image of a HDE-grown QD acquired at a sample bias of 2.5 V (empty states) and a tunneling current of 0.08 nA; (b) enhanced display of (a) showing individual In atoms; (c) row-by-row In-concentration along the [001] direction of the quantum dot determined from the STM image.

concentration variation at low In concentration, its value scales linearly with the averaged In concentration within the QD.

Here we suggest that this size-dependence of In concentration in different HDE QDs is responsible for the sharp PL peak observed in HDE InGaAs QDs, despite a large size fluctuation. Although in a smaller dot the energy due to the size quantization is larger, this effect is compensated by the higher In concentration which lowers the band-gap energy of the alloy. We further estimate this effect quantitatively using Table I. Because the lateral dimension of the QD is much larger than its height, the largest contribution to the quantization energy comes from the confinement along the [001] direction. With an average height of 9.3 nm and a variation ± 1.4 nm along [001], assuming an effective mass of 0.054

TABLE I. Comparison for different HDE grown InGaAs QDs.

	Length (top) (nm)	Height (nm)	Average surface lattice spacing along [001] with respect to GaAs	Estimated In concentration (%)	ΔE_1 (meV)	ΔE_2 (meV)	ΔE_t $(\Delta E_1+\Delta E_2)$ (meV)
Dot 1	47.9	10.7	1.05	12	35.8	−19.2	16.5
Dot 2	36.9	9.5	1.054	14	13.8	−2.9	10.8
Dot 3	36.2	9.1	1.07	17	−19.3	4.0	−15.2
Dot 4	34.9	7.9	1.075	18	−30.3	31.5	1.2

ΔE_1: variation in band gap energy due to composition variation (relative to the average composition).
ΔE_2: variation in ground-state energy level due to confinement based on a simple 1D quantum well calculation (relative to the average QD height).

m_o for electron, the resulting fluctuation in the quantization energy for the electron would be about ± 25 meV (see ΔE_2 in Table I). On the other hand, the variation in the composition would result in about ± 30 meV in the band-gap energy for the alloy (see ΔE_1 in Table I), roughly compensating the variation in the confinement energy due to the size fluctuation.

To realize the self-compensation effect, two steps are very critical in sample growth procedure: the incorporation of In to Ga droplets forming InGa droplets and InAs–GaAs intermixing during the crystallization and annealing process at about 500 °C, in which the QD structures and their PL peak intensity, peak position, and FWHM are thought to be very stable.[19] In contrast, without cation intermixing, InAs QDs and GaAs QDs grown by modified droplet epitaxy, having similar or even better size distributions compared with HDE-grown InGaAs QDs, exhibit rather broad PL peaks of about 100 meV,[20–22] which are similar to those of the QDs grown by SK mode.[4]

One possible mechanism for the size-dependence of In composition in HDE QDs is related to the redistribution of the In atoms during the Ga deposition. We note that during the droplet formation, the amount of Ga deposited is much larger than that of In (50 MLs:2.5 MLs). As In adatoms have higher mobility than Ga adatoms, during the Ga deposition, In droplets may dissolve and In atoms may be incorporated into the adjacent Ga droplets to form Ga-rich InGa droplets. The Ga droplets and Ga-rich InGa droplet should exhibit similar shapes which are different from that of In droplets.[10] Transmission electron microscopy measurement also indicates after annealing the density of the QDs is higher than the density of In droplets,[12] implying that In droplets dissolve to form InGa droplets. If so, there should exist a size dependence for In concentration. In this case, if the interchange rate of Ga and In is the same for all droplets, then the larger droplets will have less In concentration compared with smaller ones.

Another possible mechanism may be connected with the surface segregation of In atoms during crystallization and annealing processes. During these processes In atoms segregate into the top of the surface for reducing the strain energy, resulting in InGaAs QDs formation.[11] Although the detailed mechanism of the segregation is not clear now, the size and the In composition of each QDs might be influenced by the segregation process.

In summary, XSTM has been employed to investigate InGaAs QDs grown by HDE methods. The size, shape, composition, strain, etc., are quite different from that of SK-grown InGaAs QDs. More importantly, it is found that the self-compensation between the size and indium concentration of the QDs appears to be the key factor that controls the sharpness of the PL linewidth in the investigated samples.

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