Dynamics of Ripening of Self-Assembled II-VI Semiconductor Quantum Dots

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We report the systematic investigation of ripening of CdSe self-assembled quantum dots (QDs) on ZnSe. We investigate the size and density of the QDs as a function of time after deposition of CdSe has stopped. The dynamics of the ripening process is interpreted in terms of the theory of Ostwald ripening. Furthermore, the experimental results allow us to identify the growth mode of the QD formation process. [S0031-9007(98)07378-5]

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Semiconductor quantum dot (QD) structures, with atomiclike discrete energy states, hold promise of novel optical and electronic device applications [1]. As an alternative to lithographic methods, QDs can be fabricated by the process of spontaneous self-assembled island formation driven by lattice mismatch between the QD material and the substrate. Such self-assembled QD formation is now well established in group IV, III-V [1], and more recently also in II-VI semiconductors [2,3], both by molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) growth methods. While there is considerable phenomenological experience in the growth of such QDs, many aspects of the mechanisms responsible for their formation still remain unknown.

One of the important open issues regarding the mechanism of self-assembly of the QDs concerns the stability of islands after the growth has stopped. Equilibrium calculations predict that the island stability depends on the amount of deposited material [4,5]: while there exist surface coverage windows where stable (nonripening) QDs may form, for sufficiently large coverages the islands will always undergo morphological changes with time, known as Ostwald ripening (OR) [6,7].

While theoretical equilibrium approaches can predict the onset of ripening [5], they cannot give information about its inherently nonequilibrium nature. To be sure, the theory of OR is rather well developed and understood [6,7], but little is known about the influence of strain [7], a factor of paramount importance for self-assembling QDs. Thus any information about the dynamics of the ripening process in QDs contributes not only to our understanding of the dot formation, but provides important insights into the fundamental questions of stability in strained nanoscale systems.

In this paper we report the systematic investigation of ripening of CdSe QDs on ZnSe [8]. This system manifests the ripening process in a striking way, at a rate and a scale that is particularly convenient to follow by atomic-force microscopy (AFM) measurements—and thus constitutes an ideal "laboratory" for investigating the issues of QD stability generally. Specifically, we investigate the properties of the CdSe islands (such as their density and size) as a function of time [9] after deposition has been stopped. We find that strain is responsible for the remarkable uniformity of the island sizes at the end of the deposition process. However, despite the known effect of strain in stabilizing the size of the QDs, we will show that the dynamics of the morphological changes which occur in CdSe QDs after growth is well described by the Ostwald ripening process [6]. Furthermore, the experimental results allow us to identify the nature of the equilibrium growth mode characterizing the QD formation process.

CdSe dots on ZnSe were fabricated in a Riber 32 R&D MBE machine equipped with elemental sources. A ZnSe buffer was first grown at 300 °C on (100) GaAs substrates to a thickness of approximately 2 μm. During the ZnSe growth, the reflection high energy electron diffraction (RHEED) pattern showed a streaky 2×1 reconstruction, with no evidence of transmission spots. The CdSe dots were typically grown at 370 °C and at a growth rate of 0.025 monolayer/s (ML/s). This slow rate was chosen so as to be as close as possible to equilibrium conditions. With such slow growth rate, we were also able to monitor the RHEED pattern very closely during CdSe deposition. After deposition of 2.5 to 3.0 ML of CdSe, we observed a clear transformation of the RHEED pattern from streaky to spotty, indicative of a transition from a 2D growth mode to the onset of island formation.

The uncapped samples were examined by AFM immediately (typically within one hour) after they were taken out from the MBE chamber, so as to minimize the effect of exposure to the atmosphere. Figure 1(a) is a top AFM view taken immediately after growth for the case of 3 ML of CdSe deposited on ZnSe. The image was taken as a phase image of the AFM tapping mode, so as to optimize the contrast between the islands and the background. The micrograph clearly shows circular islands with a reasonably uniform island size. The QD density obtained by deposition of 3 ML of CdSe is about 20 dots per μm^2, corresponding to the value of 2×10^9 cm^{-2}.

In order to study the stability of CdSe dots, we made repeated AFM scans of the same specimen at different times after growth, shown in the sequence of images

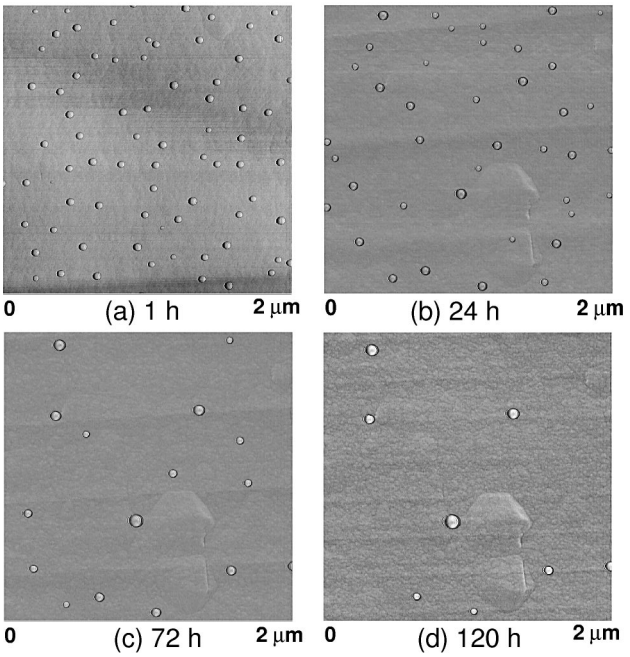

FIG. 1. Successive AFM images taken of CdSe QDs on ZnSe, showing the process of ripening. Scan (a) is taken immediately (within 1 hour) after taking the sample out of the growth chamber. Scans (b)–(d) are of the same region of the sample, taken 24, 72, and 120 h after the sample was removed.

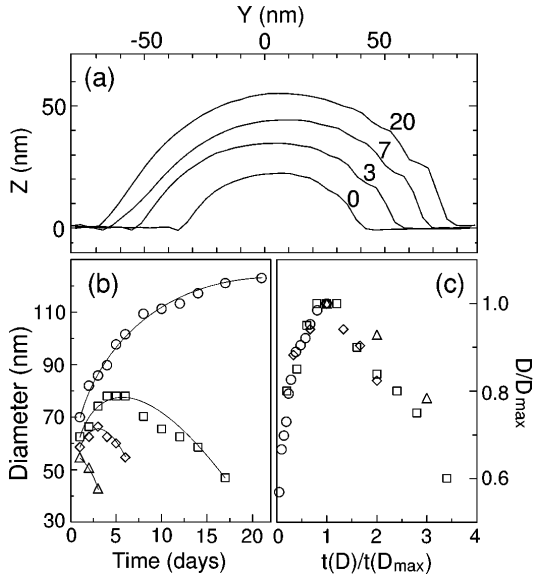

FIG. 2. (a) Time evolution of the profile of one individual dot over a period of 20 days. Note that the shape does not change. (b) Time dependence of dot diameter for dots of various sizes. Note that largest dots continue to grow, while the smallest dots disappear. (c) Self-similarity of the data from (b) after rescaling, as discussed in the text.

in Fig. 1(b)–1(d). Scans 1(b)–1(d), showing the same region of the sample, were taken 1, 3, and 5 days after growth. As is clear from the figure, the dots evolve in size as time progresses, without moving their original positions on the substrate. The fact that we observe some dots that clearly *grow* in size is strongly suggestive of Ostwald ripening [6] at room temperature.

Changes in the island volumes are often accompanied by modifications in the island shape as well. Indeed, ripening in the Ge/Si system is accompanied by a morphological transition from small *pyramidal* islands to larger *domes*, complicating the interpretation of the ripening process [10]. In the case of CdSe QDs, however, measurements at different stages of the ripening process indicate that the height-to-diameter ratio has an approximately constant value of 0.54 [11]; and, most important, we do not observe any morphological transitions during the ripening—the CdSe islands grow uniformly, keeping their shape unchanged [see Fig. 2(a)].

The behavior of CdSe QD size as a function of time is illustrated in Fig. 2(b), obtained as follows. In a given field of view, we picked individual dots and followed their size with time [as illustrated for a particular dot in Fig. 2(a)]. Note that the largest QDs (circles in the figure) continue to grow, the smallest (triangles) quickly disappear, and intermediate dots keep growing as long as there are smaller dots around; when those latter dots disappear, the intermediate dots become the smallest remaining size, and they are "consumed" eventually by the larger dots. Qualitatively, the behavior documented by Fig. 2 is fully consistent with the predictions of OR: large islands grow by accumulation of material from smaller islands, diffused along the substrate.

Classical Ostwald ripening predicts that the ripening process is scale-free and self-similar. This means that the curves of Fig. 2(b) can be described by the same function, and an appropriate rescaling of time and island size should collapse them into a single curve. Indeed, denoting by $t_{\max}$ the time when $D(t)$ reaches its maximum, and by $D_{\max}$ the diameter $D(t_{\max})$, plotting $(D/D_{\max})$ as a function of $(t/t_{\max})$ provides an excellent data collapse, as shown in Fig. 2(c).

To further quantify the dynamics of the observed ripening process, we investigated the island density, ρ, as a function of time. During ripening the uncapped CdSe dots undergo two changes: the total density of the QDs clearly decreases, and their size distribution broadens. Figure 3 shows the dependence of the dot density on time (log-log scale). The mean field theory of OR predicts that the time dependence of the average radius of the islands observed at a given time, $\overline{R}(t)$, depends on the mechanism of mass transport between the islands. In particular, if the process limiting the growth is surface diffusion, one finds that the average island size increases as $\overline{R}(t) \sim t^{1/4}$ for large t. However, if the limiting factor for mass transfer involves a kinetic surface barrier for the atom to detach from the edge of the island, one then obtains $\overline{R} \sim t^{1/3}$. Both results are for three-dimensional islands growing on a two-dimensional substrate [6]. Assuming that there is no evaporation (i.e., that atoms do not leave the substrate, but only diffuse along its surface), the total mass is

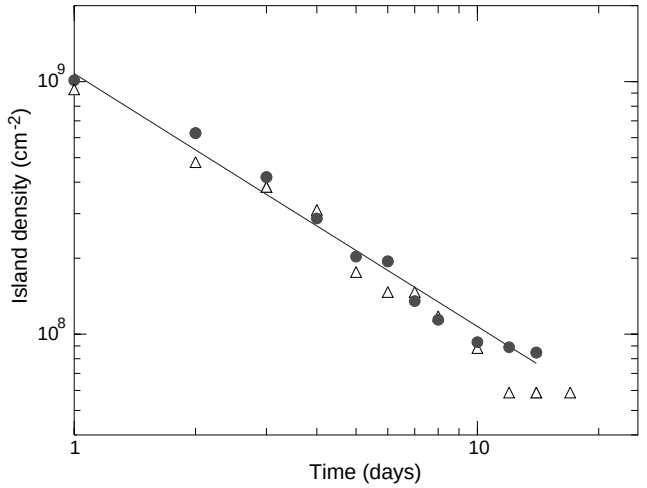

FIG. 3. Dependence of dot density on time due to ripening, shown on a log-log scale. The continuous fit has a slope of -1.0.

conserved, i.e., $\overline{V}\rho(t) = \text{const}$, where $\overline{V}(t)$ is the average volume of the islands at time t. Since the islands are three-dimensional and have a constant aspect ratio and the ripening process is self-similar, we then have $\overline{V}(t) \sim \overline{R}(t)^3$, i.e., $\rho(t) \simeq \text{const}\ \overline{R}(t)^{-3}$. This in turn gives $\rho(t) \sim t^{-3/4}$ for the diffusion-limited ripening process, and $\rho(t) \sim t^{-1}$ for interface-transfer-mediated growth. As Fig. 3 illustrates, prediction $\rho(t) \sim t^{-1}$ offers an excellent fit to the results observed on the CdSe/ZnSe system.

The agreement between mean field predictions of the OR and the observed ripening of CdSe QDs raises an important question regarding the mechanism of island formation. Both equilibrium and nonequilibrium theories predict that the origin of the striking size uniformity of the QDs obtained by heteroepitaxial growth (in contrast with homoepitaxial island formation [12]) lies in the influence of strain on the growth process. In particular, even when we limit ourselves to purely dynamical processes, it is expected that strain will affect the attachment/detachment process at the edges of the islands, thus biasing adatom diffusion away from the islands [7,13]. It would therefore not be at all surprising if the ripening of QDs did *not* follow the predictions of classical OR, since strain might change the universality class of the ripening process. However, in the case of CdSe QDs we find that ripening *does* follow the OR predictions, indicating that—while strain plays a crucial role in developing the size uniformity of the islands at the earliest stages of island formation—its importance is overshadowed by dynamical effects that dominate during ripening.

There is yet another feature of considerable importance that emerges from Fig. 2(b). It is clear that, even if the AFM images are taken within minutes after the CdSe dots are removed from the growth chamber, the dots will have already had some time to ripen in the chamber before they are taken out. It is evident, however, that *all* trends displayed in Fig. 2 can be extrapolated back, converging at approximately one value of the diameter [14]. This strongly suggests that the CdSe dots are really quite uniform at the moment of formation.

The above observation allows us to identify the growth regime in which the self-assembled QDs are formed in the CdSe/ZnSe system, in light of the equilibrium theories of growth [5]. The equilibrium calculation predicts three main growth modes that allow island formation: the Stranski-Krastanow (SK) growth mode, in which stable islands coexist with a wetting film [15]; the Volmer-Weber (VW) regime, in which stable islands grow directly on the substrate; and a ripening mode. Our results, demonstrating that CdSe/ZnSe islands begin to form only after the deposition of 2.5 to 3.0 ML of CdSe, clearly argue for the formation of a CdSe wetting layer [16], thus excluding the VW growth mode, and since the islands which we observe are not stable in time, the SK mode—as defined in Refs. [4,5]—can be excluded as well. Rather, our experimental results indicate a direct transition from the wetting film to islands that ripen, a transition that is predicted by the equilibrium growth theory labeled as "regime I" in Ref. [5].

Having made this conclusion, the remarkable uniformity of the islands at the end of the growth process [see Fig. 2(b)] may at first be puzzling. A closer look at the equilibrium theory indicates, however, that such uniformity at the transition from 2D growth to ripening is indeed to be expected. The stability of the islands against ripening is determined by the minimum of the *free energy per atom.* If the minimum is at some finite volume, the finite islands are stable and the system will not undergo ripening. If the minimum corresponds to $V = \infty$, ripening will take place. The dynamics of the island growth, however, depends on the *total energy* of a particular island, shown in Fig. 4. It can be seen that for large volumes the total energy decreases monotonically. To create an island, first one has to overcome the nucleation barrier at V_c. Since beyond the barrier the energy of the island is lower, the island will increase its size. If there were no metastable minimum after the energy barrier (see the dotted line in Fig. 4), islands would grow indefinitely; i.e., ripening would take place. However, a metastable minimum in the free energy function (at V_1 in Fig. 4) modifies the growth process (without modifying the equilibrium state of the system) by temporarily trapping the islands. The nucleated islands are small, and—in order to ripen—they must escape from the metastable state. The free energy of the strained QD system [5] indeed does predict the existence of such a metastable minimum at the 2D-to-ripening transition, which can explain the qualitative features of our experimental results. Until a critical thickness is reached (which is estimated to be about $H_c \simeq 2.5$ to 3.0 ML), no island formation is observed, all deposited atoms contributing to the wetting film. However, at H_c the system becomes unstable against island formation, and QDs begin to form. If there were no metastable minimum, the islands would ripen as soon as they form, leading to a

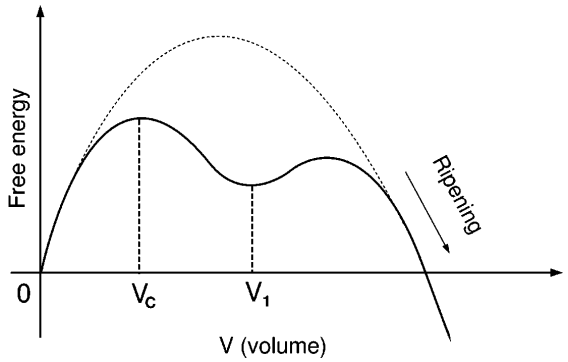

FIG. 4. Schematic illustration of the free energy of an island as a function of island volume V. The dotted line indicates the total free energy of strain-free island nucleation.

rather wide island size distribution even near H_c—a behavior that is not observed.

We conclude therefore that, after they form, the islands are trapped by the metastable minimum where they all have the same volume V_1. This explains the remarkable size uniformity of the islands when their size is extrapolated back to the end of the growth process (or the beginning of ripening), as seen in Fig. 2(b). The islands cannot start ripening until mass fluctuations in the system (driven by surface diffusion) allow them to overcome the energy barrier at volume V_1. Thus the islands escape the metastable minimum one by one, after which they undergo the normal process of ripening, moving down on the free energy curve [17]. Note that—while the existence of the metastable minimum is a direct consequence of the specific strain in the system—the asymptotic form of the free energy curve for $V \to \infty$ is *independent* of strain. Once the islands escape the metastable minimum, their ripening is expected to follow the dynamics predicted by the classical theory of OR; i.e., it is independent of strain. This explains the excellent agreement between the experimental results and OR, as shown in Fig. 2(c).

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[14] In the case of Fig. 2, the value is 58 ± 5 nm. This, however, includes a systematic error due to the AFM tip diameter. Taking that error into account, we have estimated the initial QD diameter value to be 35 ± 5 nm, as quoted in Ref. [11].

[15] Note that often in the literature the SK mode is used to describe both the growth regime when the islands are stable and that when ripening occurs, as long as a wetting layer is present. In contrast, here we use the SK mode to denote only that mode where the islands are stable, in line with Ref. [5].

[16] QD growth and wetting layer formation has been shown to depend on modes of growth and on substrate orientation. It is observed in all cases reported in Ref. [2], but in Ref. [3] QDs deposited on (111)*A* surfaces by atomic layer epitaxy are reported to form even for 1 ML deposition, and they do not form on (111)*B*. We emphasize that in the present analysis we restrict ourselves to effects observed in specimens grown under very slow (i.e., near-equilibrium) conditions on (100) ZnSe.

[17] Note that the existence of strain induced energy barriers and metastable states have been documented for various phenomena involving the formation of strained islands; see, e.g., Ref. [10] and D. Jesson *et al.* [Phys. Rev. Lett. **77**, 1330 (1996)].