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Composition of InAs quantum dots on GaAs(001): Direct evidence for (In,Ga)As alloying

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Scanning tunneling microscopy has been used to study the growth by molecular beam epitaxy of InAs quantum dots (QD's) on GaAs(001), with specific emphasis on measuring the volume of the dots at different temperatures as a function of InAs deposition. At low temperatures ($\sim$350 °C), the total QD volume is consistent with a classic Stranski-Krastanov mechanism since it is equal to the additional amount of InAs deposited after the two-dimensional (2D)→3D growth mode transition. By contrast, high substrate temperatures ($>$420 °C) result in QD's with a much greater volume, and the implication is that significant mass transport occurs to the dots from both the wetting layer and the substrate. The dots must contain both In and Ga and therefore the description of InAs/GaAs(001) QD formation as a classical Stranski-Krastanov growth process is incorrect. [S0163-1829(98)50448-1]

The drive for novel optoelectronic devices based on semiconductor nanostructures has led to enormous interest in understanding and controlling the growth of quantum dots (QD's) in semiconductor heteroepitaxy. The most widely studied epitaxial system is that of InAs on GaAs(001), for which the lattice mismatch is 7.1%. A transition from two-dimensional (2D) to three-dimensional (3D) growth is caused at least in part by the resulting strain.[1–6] Isolated, coherent 3D islands (QD's) can be formed prior to the incorporation of dislocations, which do not form until island coalescence is essentially complete. Although it is well established that the QD's rapidly achieve a saturation number density (N_S) prior to coalescence, and also have a relatively narrow size distribution, the precise mechanism by which they are formed is still poorly understood.[7–14] In particular, issues such as the shape and composition of the QD's are still the source of considerable debate in the literature, and they may impinge directly on the effectiveness of QD-based optoelectronic devices. Such issues clearly require more detailed study, in the regimes both before and after the QD's are covered with a GaAs capping layer.

The growth of InAs QD's on As-terminated GaAs(001) substrates is usually described rather simplistically in terms of a classic Stranski-Krastanov (SK) mechanism. However, a number of recent studies have shown that the growth mode is more complex and very sensitive to the deposition conditions, namely, substrate temperature,[15,16] V:III flux ratio,[17] and growth rate.[17] In this paper, we present *in situ* scanning tunneling microscopy (STM) measurements of InAs QD's grown on GaAs(001) by molecular beam epitaxy (MBE) focusing specifically on the volume of material within the dots and the effects of the growth temperature. We find that the total QD volume at low temperatures (350 °C) is consistent with a classic SK growth mode, i.e., it is equal to the additional amount of InAs deposited after the 2D→3D transition. By contrast, higher substrate temperatures ($>$420 °C) produce a total QD volume far greater than the amount of additional InAs deposited. The implication is that at high temperatures, the dots are not formed via the classic SK mechanism, but instead additional material is incorporated into the dots from the 2D wetting layer *and* the GaAs substrate.

The experiments were carried out in a MBE growth chamber (DCA Instruments), equipped with reflection high-energy electron diffraction (RHEED) and linked to an STM chamber (Omicron GmbH) via a gate valve. Epi-ready GaAs(001) substrates (n^+ Si-doped) were mounted onto molybdenum plates and transferred directly into the growth chamber via a fast entry lock. After initial thermal cleaning at 300 °C, the native oxide layer was removed under an As_2 flux at 620 °C. A 0.3-μm-thick buffer layer of GaAs was then grown at a substrate temperature of 570 °C, with a growth rate of 0.3 μm h^{-1}. The buffer layers were doped with Si ($n<1\times10^{18}$ cm^{-3}) apart from the last 500 Å, and annealed at 580 °C for several minutes under an As_2 flux before InAs deposition. The growth rate of InAs was set at 0.3 ML s^{-1}, with an As:In atomic flux ratio of 6:1 and a substrate temperature of 350–500 °C. The RHEED patterns were monitored throughout deposition and used to determine the 2D→3D growth mode transition, which is characterized by the sudden appearance of transmission electron diffraction spots in the RHEED pattern along the [110] azimuth. After InAs deposition, the sample was transferred immediately to the STM chamber (within a few seconds) and allowed to cool to room temperature (several minutes). This quenching process is much more rapid than generally achieved in a conventional MBE growth chamber and allows us to ''freeze'' the QD's for detailed STM imaging. Post-growth annealing and slow quenching rates both change the

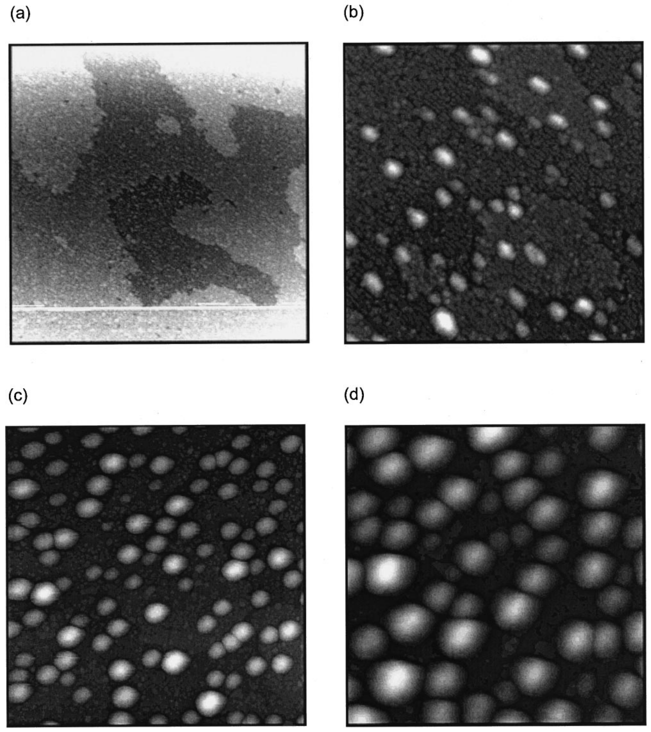

FIG. 1. Filled states STM images (1000×1000 Å^2) for a range of InAs depositions at 450 °C on GaAs(001); (a) 1.4 ML, (b) 1.7 ML, (c) 2.0 ML, and (d) 2.7 ML. The 2D→3D growth mode transition under these conditions occurs at 1.7 ML as determined from the change in RHEED pattern.

surface morphology. Constant current STM images were obtained with a sample bias of -3.5 V and tunneling currents of 0.05–0.2 nA.

The sequence of STM images (1000×1000 Å^2) in Fig. 1 illustrate how the surface morphology develops during the deposition of between 1.4 and 2.7 ML of InAs on GaAs(001) at 450 °C. For 1.4 ML of InAs the growth mode is still 2D and the corresponding STM image (a) shows three distinct terraces. This surface corresponds to the 2D wetting layer which at these temperatures is not pure InAs, but is a ternary alloy ($\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$), whose structure, thickness, and composition all depend strongly on the growth conditions, and the initial surface reconstruction of the GaAs substrate.[18–20] The STM image in (b) corresponds to deposition of 1.7-ML InAs and the onset of QD formation. The QD's appear as featureless white objects in the image because the gray scale has been adjusted to show contrast in the underlying 2D wetting layer. Two terraces are visible in this particular image, and the wetting layer has the rather disordered appearance characteristic of a (1×3) reconstruction, a structure known to be an $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloy, where $x \geqslant 0.3$ and is temperature dependent.[18] There is a rapid increase in the number density of the QD's as the InAs coverage is increased to ~2.2 ML (c). Coalescence of the QD's only begins to occur above about 2.7 ML (d) at this growth temperature. It should be noted that in the early stages of growth, the QD's are nearly all located at the lower side of step edges, although there appears to be no preference for nucleation at any specific step direction. Step decoration is not as obvious at higher coverages where the island density is large.

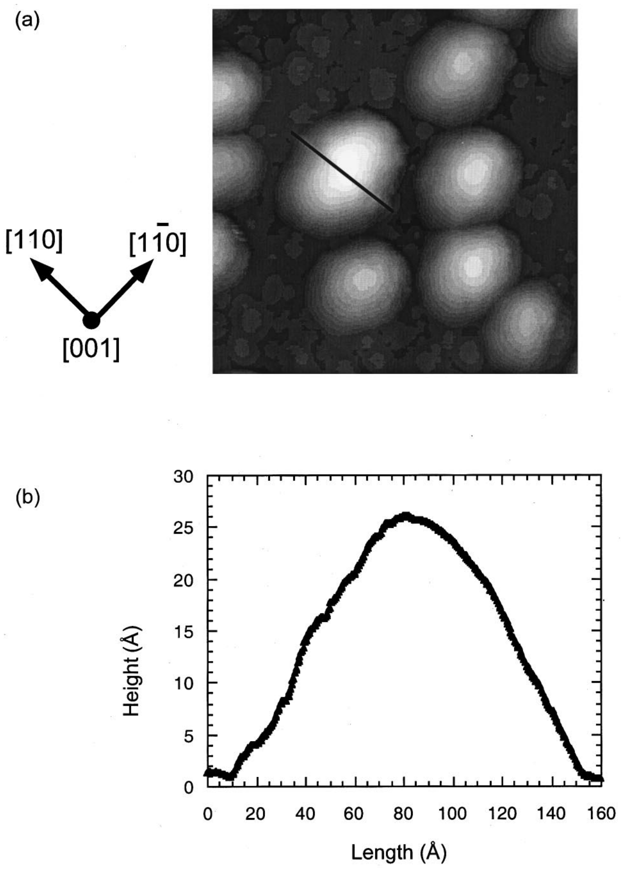

FIG. 2. (a) An STM image of a few QD's formed after the deposition of InAs on GaAs(001). (b) The cross section of the single QD was taken along [110] (solid line).

Substrate temperature has a significant effect on the volume of deposited InAs at which the 2D→3D growth mode transition occurs, as determined by RHEED. More InAs is required for the growth mode transition as the temperature is increased, ranging from 1.4 ML at 350 °C to 2.0 ML at 500 °C. High-resolution STM images of the 2D wetting layer prior to the growth mode transition show that the indium concentration in the $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ wetting layer is high at low temperatures, with the opposite true for high temperatures.[18,20] The strain gradient is therefore greater at low temperatures, consistent with the lower amount of deposited material required for the 2D→3D growth mode transition. Measurements of the RHEED specular beam intensity with increasing InAs deposition also indicate that the transition is not particularly sharp at low temperature, probably because of the poor lateral homogeneity of the indium concentration in the wetting layer. The 3D islands will be favored in certain local positions, which together with the kinetic limitations of adatom migration at low temperature, results in the rather sluggish transition. Temperature also has a significant effect on the saturation number density and size of the dots. A high density ($N_S = 2.6\times 10^{12}$ cm^{-2}) of small islands is formed at 350 °C, while a low density ($N_S = 5\times 10^{10}$ cm^{-2}) of larger islands exists at 500 °C.

The high resolution of the *in situ* STM can be used to obtain detailed and accurate information regarding the dimensions of the islands, more specifically their height *(h)* and diameter *(d)*. An STM image is shown in Fig. 2 showing a cross section of one island along [110]; in this case *h*

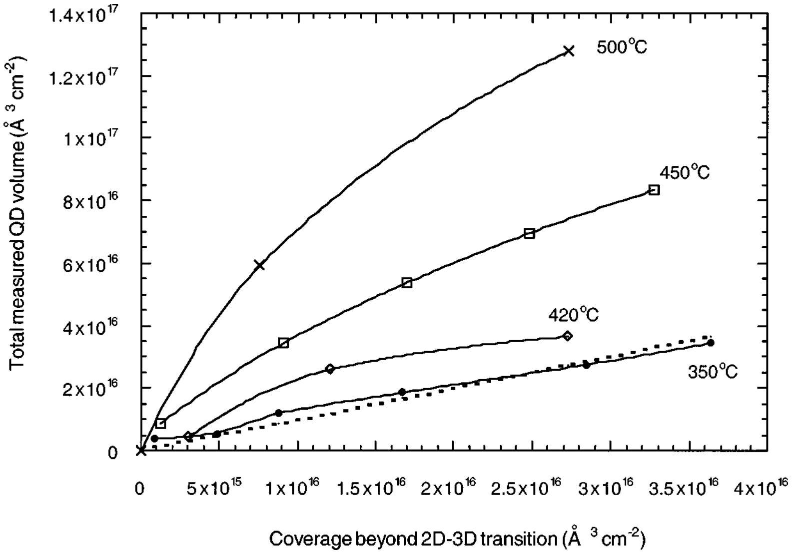

FIG. 3. The total measured volume of the InAs/GaAs QD's as a function of the amount of InAs deposited *after* the 2D→3D growth mode transition. The dashed line is the volume expected from classic Stranski-Krastanov growth, i.e., when the dots are simply composed of the additional amount of InAs deposited. The solid lines through the experimental data are simply guides to the eyes.

$=25$ Å and $d=140$ Å, but these values again vary significantly with growth temperature. Quantitative information regarding the volume of material in the dots can then be obtained from the measured dimensions. The total volume of the QD's is plotted in Fig. 3, at four different temperatures, as a function of InAs deposition *after* the 2D→3D transition (obtained from RHEED). The total volume of material in the dots at each particular deposition was obtained from the product of the number density and the average volume of each dot, where the volume is defined as $hA/2$, with A the area of each dot. Although other expressions, such as a planoconvex lens shape, have been used to estimate the volume in previous studies,[4,13] our studies showed negligible difference between the volumes obtained using the two expressions. Furthermore, direct numerical measurement of the QD volumes from the STM topographs shows that the above approximation for the dot volume is sufficiently accurate.

The data in Fig. 3 show clearly that the deposition temperature has a significant effect on the total volume of material in the dots; the higher the temperature, the greater the volume for a given amount of deposition. The dashed line represents the ideal SK case, where the QD volume is precisely that of material deposited after the 2D→3D transition. The experimentally obtained volumes for deposition at 350 °C follow this line very closely, suggesting classic SK behavior at this temperature. By contrast, deposition at higher temperatures leads to much greater volumes than expected from ideal behavior and the implication is that the additional material must be incorporated from another source, either the 2D $In_xGa_{1-x}As$ wetting layer or the GaAs substrate. Erosion of the wetting layer and incorporation of additional material in QD's has also been suggested by Leonard, Pond, and Petroff[4] on the basis of *ex situ* atomic force microscopy (AFM) measurements at a single growth temperature.

Using the volume data shown in Fig. 3, it is possible to estimate the absolute amount of material incorporated into the dots from the wetting layer and substrate. This is plotted in Fig. 4 at different temperatures as a function of the total amount of InAs deposited. The dashed line in the figure corresponds to the expected QD volume (in monolayers) if all the deposited material forms dots and there is no wetting layer (effectively Volmer-Weber growth). At low temperatures (350–420 °C), the measured QD volume is substantially less than the deposited volume, since the stability of the wetting layer accounts for about 1.5 ML of InAs. At 450 °C, the wetting layer is eroded as more material is deposited and by 2.7 ML, the volume of the QD's is equal to that of the deposited material. Erosion of the wetting layer is much more pronounced at 500 °C and even in the early stages of QD formation the volume of the dots is greater than the total deposited volume. The growth mode, however, is not Volmer-Weber, since a 2D wetting layer is always formed prior to the growth mode transition. Furthermore, high-resolution STM images taken after QD formation indicate the underlying surface has a (1×3) reconstruction consistent with the presence of at least 0.3 ML of In, even at 500 °C. As more InAs is deposited the QD volume increases dramatically, and prior to coalescence (beginning at 3.0 ML

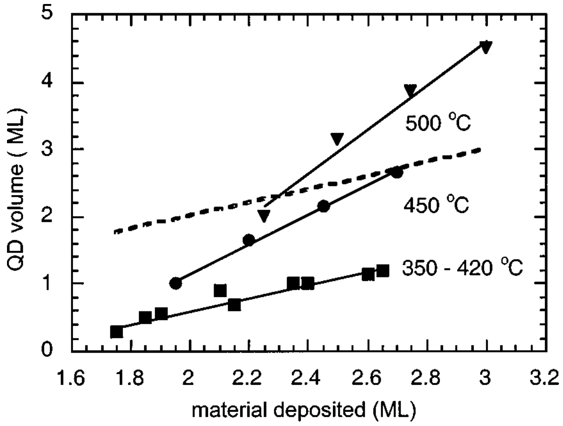

FIG. 4. The total volume of the QD's (monolayer equivalents) plotted as a function of the total volume of deposited InAs (monolayers). The dashed line represents the QD volume expected if all deposited InAs is incorporated into the QD's, and none into the wetting layer.

of deposited material at 500 °C), the QD volume is equivalent to 4.5 ML. This suggests that the QD's must contain at least 1.5 ML of GaAs from the initial substrate. This value is a lower bound since the existence of the (1×3) wetting layer reconstruction indicates that some of the deposited In is not incorporated into the dots. The stronger tendency to incorporate Ga from the substrate at higher temperatures is clearly shown by the increasing gradient of the QD volume plots in Fig. 4.

It is therefore evident that the formation of InAs quantum dots on GaAs(001) cannot be described in terms of a classical Stranski-Krastanov mechanism, at least at the growth temperatures generally used to produce quantum dot structures for device applications (∼500 °C). A substantial amount of additional material is incorporated into the dots with significant mass transport from both the wetting layer and the substrate. The dots must contain both Ga and In, with a gallium fraction of about 30% at 500 °C (3 ML of deposited InAs). Clearly, the situation is even more complex when the QD's are overgrown with GaAs, a necessary step in producing structures for optical applications. Obtaining information about the QD volume in these structures is much more difficult, although recent studies using cross-sectional STM (Refs. 21 and 22) and scanning transmission electron microscopy[23] (STEM) have shown that the dots are effectively embedded within the wetting layer and not on it, and they represent regions that are locally rich in indium. Energy dispersive x-ray analysis of capped dots suggested that QD's grown at 500 °C contain approximately 70% Ga and 30% In, the additional Ga in this study presumably arising from the capping process.[23] The presence of gallium in the QD's *even before* the capping process implies that the description of InAs/GaAs(001) QD formation as a simple Stranski-Krastanov growth process is incorrect.

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