How kinetics drives the two- to three-dimensional transition in semiconductor strained heterostructures: the case of InAs/GaAs(001).

F. Arciprete, E. Placidi, V. Sessi, M. Fanfoni, F. Patella and A. Balzarotti

Dipartimento di Fisica, Università di Roma “Tor Vergata”,
Via della Ricerca Scientifica 1, I-00133 Roma, Italy.

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Abstract

The two- to three-dimensional growth transition in the InAs/GaAs(001) heterostructure has been investigated by atomic force microscopy. The kinetics of the density of three dimensional quantum dots evidences two transition thresholds at 1.45 and 1.59 ML of InAs coverage, corresponding to two separate families, small and large. Based on the scaling analysis, such families are characterized by different mechanisms of aggregation, involving the change of the critical nucleus size. Remarkably, the small ones give rise to a wealth of ”monomers” through the erosion of the step edges, favoring the explosive nucleation of the large ones.
In the previous decade the Stranski-Krastanov (SK) growth mode has been the subject of many experimental and theoretical studies. In the case of semiconductor heterostructures which are characterized by a large lattice mismatch, the strain built up during the layer by layer growth may bring about a drastic and sudden change in the growth mode; atoms start self-organizing in three-dimensional (3D) islands called quantum dots (QDs). InAs/GaAs(001) and Ge/Si(001) heterostructures are paradigmatic examples of these interfaces. The former with its lattice mismatch as large as 7%, undergoes the 2D-3D transition for a deposition of InAs lower than 2 ML.

Many attempts have been made to clarify the mechanisms underlying the 2D-3D transition. A recent significant result is due to Cullis et al. By studying the crucial role played by the In segregation in the 2D-3D transition for the InGaAs/GaAs(001) growth, they have reached an important conclusion: *When the average In concentration in the growing layer reaches a value in the range 80 – 85%, islanding begins.* This conclusion establishes a kind of thermodynamic constraint in order for the transition to take place. The model applicability has also been explored in the Ge/Si heterostructure. Among other established facts, it is widely accepted, where islanding is concerned, that the InAs/GaAs(001) film’s morphology during the transition is characterized by two distinct families of QDs: the so-called quasi-3D QDs, whose height and lateral dimensions range from 0.3 to 0.7 nm and from 10 to 20 nm respectively, and the mature QDs, whose height is higher than 2 nm and whose lateral dimensions range between 20 and 30 nm. Henceforth the former will be referred to as small and the latter as large QDs. Small QDs disappear very soon and the surface, before coalescence, turns out to be dotted with large QDs. Hitherto, what is the role played by the small QDs has not been well understood, and several conjectures have been put forward, often on the basis of untargeted data. In this Letter we present an accurate investigation of the kinetics of both small and large QDs for the InAs/GaAs(001) heterostructure grown by means of molecular beam epitaxy (MBE). In particular, we show that small and large QDs give rise to two distinct families: Remarkably, the small ones do not account for the number of all the large ones, although, in a certain way, the small QDs favor the explosive nucleation of the large ones. Hence, although energetics fixes the transition threshold, kinetics plays a fundamental role in determining its subsequent evolution. Although related to a specific system, the relevance of this result, is that it could be common to all highly-mismatched semiconductor heterostructures characterized by a similar phenomenology.
Because the system evolves within a very narrow range of coverage around the critical thickness,\[7, 8, 9, 10, 11\] we took advantage of the intrinsic non-uniformity of the molecular beams to grow a single sample where the InAs film thickness varies continuously along the sample surface. In this way a snapshot of the QD evolution is available and the system can be studied for InAs coverage increments as low as 0.01 ML. Furthermore, any problem of reproducible growth conditions is overcome. The investigated sample has been grown by means of an MBE reactor equipped with Reflection High-Energy Electron Diffraction (RHEED) for monitoring the growth. Prior to InAs deposition, a GaAs regrowth of approximately 500 nm was performed on the (001) oriented substrate, in As$_4$ overflow, at 590 °C at a rate of 1 µm/h. After 10 min post-growth annealing, the temperature was lowered to 500 °C for the InAs deposition. The growth was carried out without rotating the sample, so as to obtain the afore-mentioned non-homogeneous 2-inch sample. The impinging flux increases linearly along the [110] direction of the substrate,\[12\] from 0.011 ML/s to 0.030 ML/s, resulting in InAs coverage ranging from 0.87 ML to 2.40 ML for 80 s of growth. The In delivery was cycled in 5 s of evaporation followed by 25 s of growth interruption until the beginning of the 2D-3D transition was observed by RHEED at the center of the sample.\[8\] Atomic force microscopy (VEECO Multiprobe) was performed in air in the tapping mode by using non-conductive Si tips, on 20 different points of the sample for InAs coverage ranging from 0.87 to 2.22 ML.

Fig.1 shows AFM topographies (1.0 µm × 0.5 µm) for three significant InAs coverages: 1.54 ML, 1.57 and 1.64 ML in Fig. 1(a), (b), and (c), respectively. The images reveal a complex morphology of the WL, \textit{i.e.} 2D islands 1 ML high, and large terraces one step high. The first small QDs (Fig. 1(a) and (b)) are recognizable for coverage as high as 1.45 ML, whereas at higher InAs deposits the emergence and subsequent increase of the number of large QDs can be seen (Fig. 1(b) and (c)). Small QDs nucleate preferentially at the upper-step edges of 2D islands and terraces (Fig. 1 (a) and (b)) by reason of a favorable strain condition at those sites. They have been reported several times\[10, 11, 13, 14, 15\] and often been indicated as simple precursors of large QDs. We have already pointed out\[13\] that this simple picture is unrealistic and we will show below that the process involves a more complex kinetic mechanism.

The number density evolution of both small and large QDs\[16\] is summarized in Fig. 1(d) as a function on InAs deposition. The number of the small QDs begins to increase at
1.45 ML of InAs deposit and maximizes at 1.57 ML reaching the value of $1.1 \times 10^{10}$ cm$^{-2}$. Starting from 1.52 ML, the number of the large QDs increases gradually then, between 1.57 and 1.61 ML, undergoes a sudden rise, changing value by an order of magnitude. At higher coverages the density rise is much slower. The steady and gentle increase observable for coverages higher than 1.8 ML is due to the dependence of the density saturation value on growth rate.\[17, 18, 19\] In this region the density is of the order of $6 \times 10^{10}$ cm$^{-2}$.

The key point lies in understanding the transition process between 1.57 and 1.61 ML. The comparison of the number density of the two QD families rules out the possibility that the large QDs are merely the evolution of the small ones, i.e. the low density of the small QDs cannot account for the density evolution of the large ones. To gain an insight into the nature of these two families we have analyzed the scaling behavior of their size distribution. As a matter of fact, dynamic scaling theory makes it possible to determine one of the most significant parameters of film formation governed by nucleation and growth, namely the dimension of the critical nucleus, $i$.\[20, 21, 22\] This is done by comparing the experimental size distribution of QDs and its evolution during the first stage of film formation to the theoretical function that, in turn, depends upon $i$. To be specific, in the framework of dynamic scaling, the size distribution function of the number density of islands at coverage $\Theta$ is given by

$$N_i(u) = \frac{\Theta}{\langle s \rangle^2} f_i(u),$$

where $u = s/\langle s \rangle$, $\langle s \rangle$ being the island average size and $f_i$ is the scaling function that, according to Amar and Family, reads, for $i \geq 1$: $f_i(u) = C_i u^e e^{-i_0 u^{1/a_i}}$, where $C_i$ and $a_i$ are constants.\[22\] Dynamic scaling was first introduced to describe 2D islanding and was substantiated by computer simulations\[20, 21, 22\] and experimental studies both in homo\[23, 24\] and heteroepitaxial\[25, 26, 27\] growth. Ebiko et al.\[28\] were the first to show the applicability of Eq. (1) to 3D growth in semiconductor heterostructures, provided that $s$ was interpreted as the volume of the islands. Fig. 2 shows the scaled island volume distributions for the InAs deposits around the transition, from 1.45 to 1.82 ML. Both families have been included in the data analysis, taking care to separate the distributions related to the small and large QDs that are reported in Fig.2(a) and Fig.2(b) and (c) respectively. The scaling function for small QDs closely resembles that expected for a system with critical nucleus $i = 0$.\[22\] This implies the adatoms freeze spontaneously on the surface, giving rise to a nucleation center. Such a behavior can be explained by the presence of defects on the
surface, such as steps: actually, small QDs nucleate almost exclusively at the upper edge of steps and 2D islands (Fig.1). This fact indicates the presence of a minimum in the potential in the proximity of the step edge that makes the monomer stable. The scaling function does not change between 1.45 and 1.61 ML; for higher coverages the small QD density is negligible in respect to that of large QDs.

As far as large QDs are concerned, we distinguish two different types of behavior. Up to 1.57 ML of InAs deposit we observe a kind of mixed distribution function with an undefined value of \( i \), i.e. a transition region where large QDs belonging to \( i = 2 \) (Fig. 2(c)) and \( i = 0 \) coexist. The latter ought to be nothing but the grown small QDs. Starting from 1.59 ML (Fig.2(c)) the size distributions change completely, approaching a shape compatible with \( i = 2 \). A new aggregation mechanism is now operating whereby three atoms are required to form a stable nucleus. Fig.2(d) displays the comparison between the \( f_2(u) \) \((C_2 = 1.97, a_2 = 0.30)\) and the averaged experimental data; the agreement between the two curves is excellent. The different aggregation mechanisms allow us to maintain that large QDs are not merely the direct evolution of the small QDs.

Apparently, the number of atoms required to form a stable nucleus when \( i = 2 \) is three times greater than that for \( i = 0 \). On the basis of this obvious argument, we must expect that, at the onset of the \( i = 2 \) nucleation mechanism, an extra amount of free matter (diffusing monomers) is available on the surface. In Fig.3(a) the total volume of the large QDs is plotted as a function of InAs coverage. It is highly evident that the increase of the large dot volume in the transition region implies a quantity of matter well beyond that provided by the impinging flux \( F_o \) (lower line in the Fig. 3(a)). To be precise, in the range 1.6 – 1.8 ML the effective flux is \( F = 4.6F_o \). Above 1.8 ML, the volume increase reverts to being compatible with \( F_o \). The extra quantity of matter amounts to roughly 0.9 ML (Fig. 3(a)). We have already reported evidence of step erosion from QDs nucleated at step edges, setting a lower limit to 0.3 ML. A recent work confirms our finding: by looking at those data, an amount greater than 0.3 ML of eroded steps might be estimated. Even though the erosion could be responsible for the whole supplementary 0.9 ML, a further contribution could arise from substrate intermixing and In segregation.

The total volume contained in large QDs is determined by the equation: \( V_{large}^T = \rho_{large} \langle V_{large} \rangle \), where \( \rho_{large} \) is the density of the large islands and \( \langle V_{large} \rangle \) is the mean volume of the single large island. To specify how the variation of the large QD density and
mean volume contribute to the volume increase of $V_{large}^{T}$, we plot separately in Fig. 3(b) the two terms $\frac{d\rho_{large}}{d\Theta} \langle V_{large} \rangle$ and $\rho_{large} \frac{d\langle V_{large} \rangle}{d\Theta}$ as a function of $\Theta$. The derivatives of $\rho_{large}$ and $\langle V_{large} \rangle$ have been calculated numerically by interpolating the experimental data. During the first stage of transition the volume increase is mainly due to the sudden nucleation of large islands and it is only subsequently that single island growth prevails. At the transition the QD density explosion is then bound up with the substantial increase in the adatom density between 1.6 and 1.8 ML, as an increase in the effective deposition flux.

The growth instability leading to the 2D-3D transition is thermodynamic in character, this being caused, as pointed out by Cullis et al., Refs. 3, 4, 5 by the strain energy relaxation. The nucleation process begins at 1.45 ML of InAs deposition and, more importantly, a single monomer is enough to give rise to a nucleation center. In accordance with the model proposed by Dehaese et al., Ref. 32 at 1.45 ML the average concentration of In in the uppermost layer is certainly greater than 82%. However, our data clearly show that the nucleation is preferential at the step edges, an occurrence which we highlight further. Although the system, from the thermodynamic point of view, prefers to grow by forming 3D islands, the conditions for this to occur are met at step edges. On the other hand, at 1.59 ML, when the scaling analysis reveals that a stable nucleus needs three monomers ($i = 2$), large QDs first appear at steps and then all over the surface. Concomitantly, a great amount of monomers becomes available at the surface because of the step erosion due to small ($i = 0$) QDs, which in the mean time have increased in size. In the framework of the rate equation approach, Refs. 18, 19 the high monomer concentration $n_{1}$ promotes the nucleation process that is proportional to $n_{1}n_{2}$ ($n_{2}$ is the dimer concentration). However, this term competes with the dimer dissociation term proportional to $n_{2}$. Therefore kinetics implies that the observed explosive nucleation process can take place if the production of a high concentration of monomers occurs together with the dimer dissociation constant much lower than the nucleation constant. The conclusions are thus apparent: in order for 2D-3D sudden transition to occur, it is necessary that both energetic (In concentration at the growing layer) and kinetic conditions are favorable.

In summary, we have highlighted the fact that only an appropriate combination of thermodynamics and kinetics allows the InAs/GaAs(001) heterostructure to undergo a sudden nucleation and growth of large QDs. Once the appropriate In concentration has been reached, the $i = 0$ nucleation is favored thanks to steps. Moreover, the subsequent step
erosion produces a great amount of fresh monomers which, in turn, increase the probability of having the $i = 2$ (or, more generally, $i \neq 0$) nucleation over the entire surface.

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This result disagree with those of Ebiko et al. (Phys. Rev. Lett. 80, 2650 (1998)) and Krzyzewski et al. (Phys. Rev. B 66, 201302(R) (2002)) which found $i = 1$. However, we believe that this is a marginal point likely dependent upon substrate morphology (Leon et al. Phys. Rev. Lett. 78, 4942 (1997)). The important fact is the transition in the aggregation mechanism concomitant to the sudden increase in the density of large QDs.

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A. Figure caption

**Fig. 1** - AFM topographies (1.0 µm × 0.5 µm) for: 1.54 ML (a), 1.57 ML (b), and 1.64 ML (c) of InAs coverage. Panel (d) shows the number density dependence on InAs coverage of small and large QDs.

**Fig. 2** - Scaled distributions of the experimental island volume for: small QDs (a), large QDs in the range 1.54 – 1.57 ML of InAs coverages (b), large QDs in the range 1.59 – 1.82 ML of InAs coverages (c). Solid lines in panel (c) show the theoretical scaling function for \( i = 1, 2, 3 \). Panel (d) shows the average of the experimental distributions of panel (c) compared to the theoretical scaling function for \( i = 2 \).

**Fig. 3** - (a) Total volume \( V_{large}^{T} \) of large QDs plotted as a function of InAs coverage. The lowest line indicates the InAs flux \( (F_o) \) above the 2D-3D transition. The volume increase in the range between 1.6 – 1.8 ML is accounted for by the effective flux \( F \). (b) Derivative terms \( \frac{d \rho_{large}}{d \Theta} \langle V_{large} \rangle \) and \( \rho_{large} \frac{d \langle V_{large} \rangle}{d \Theta} \) of \( V_{large}^{T} \) plotted as a function of InAs coverage.
Fig. 1
Fig. 3