Strain driven migration of In during the growth of InAs/GaAs quantum posts

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Using an in-situ accumulated stress sensor, we observe a counter-intuitive reduction of the accumulated stress during In deposition on GaAs and have found, through modeling of the strain field, a hypothesis that quantitatively explains the experimental data. This effect is only observed during epitaxial growth of InAs/GaAs quantum posts, and not during growth of Stransky-Krastanov self-assembled quantum dots.

The behavior of In atoms during growth of InAs/GaAs quantum nanostructures has been a matter of debate during the last decade. García et al. suggested that the existence of a stress free In layer at the crystal surface could explain the evolution of the accumulated stress measured in-situ during the growth of InAs self-assembled quantum dots (QDs) on GaAs (001). Bottomley made a thermodynamical analysis of the InAs/GaAs (001) interface and extended such interpretation postulating the simultaneous formation of In and InAs liquid phases. To explain the QD size evolution during growth, the strain driven migration of In and Ga from the WL to the QDs and vice versa was postulated in different theoretical works. Joyce et al. made an study varying the InAs growth rate which suggested that, given enough time, the WL→QDs route would take place enhanced by the strain field gradients. From their work, they also concluded that slow growth rates should enhance the unmixing of In and Ga spices while fast growth rates would enhance their intermixing, not allowing the system to reach a thermodynamical equilibrium. Aditionally, Bottomley suggested that this In transfer from the WL might be favored by the existence of liquid phases at the surface. A direct experimental demonstration for such mechanisms could not be given at that moment, though.

Although the growth kinetics might have not been completely understood, the fundamental InAs and GaAs constituents have been alloyed since then in a variety of quantum nanostructures with diverse morphologies. InAs/GaAs epitaxial quantum posts (QPs) are an exemplary system where to study alloying, surface segregation and migration effects beyond the pioneering QD studies. In this letter, we present accumulated stress measurements recorded in-situ and on real time while growing InAs/GaAs QPs and QDs. Contrarily to other analytical techniques which are applied post-growth, our real time characterization enables the direct investigation of the growth kinetics shedding light over the role played by indium segregation and migration in both quantum nanostructures.

The QPs studied in this work have been grown using solid source Molecular Beam Epitaxy on GaAs (001) substrates with a thickness of 100 μm. This relatively thin substrates increase the sensitivity of the accumulated stress measurements. Substrate temperature and As beam equivalent pressure (BEP) are kept at 510 °C and 1.5×10⁻⁶ mbar, respectively. InAs and GaAs growth rates are 0.02 ML/s and 0.5 ML/s, respectively. As reported by other authors, our QPs are formed by deposition of a short period superlattice on top of a QD seed layer and therefore are related in nature to VCQDs. In such context, since QPs formation heavily relies on a strain driven process and an efficient migration of In adatoms towards energetically favorable sites, they are an exemplary system where to study alloying, surface segregation and migration effects beyond the pioneering QD studies. In this letter, we present accumulated stress measurements recorded in-situ and on real time while growing InAs/GaAs QPs and QDs. Contrarily to other analytical techniques which are applied post-growth, our real time characterization enables the direct investigation of the growth kinetics shedding light over the role played by indium segregation and migration in both quantum nanostructures.

To measure the accumulated stress, we record the de-
flection of two laser beams reflected on the surface of a cantilever shaped GaAs substrate. The reference beam impinges in the extreme where the cantilever is held to a hollowed Si wafer. The signal beam impinges at the opposite free standing extreme. Stress measurements can be recorded stably over time by measuring the deflection of these beams with a CCD camera and an optical spot tracking software. The sensitivity of our setup is currently 0.01 N/m, enough to detect small changes associated to surface reconstruction (typically of the order of 0.5 N/m) and real time monitoring of strained epitaxial layers.

Fig. (1h) shows the accumulation of stress induced by a single layer of InAs QDs capped with GaAs. The opening/closing sequence of As, Ga and In effusion cells was simultaneously recorded and is shown on top of the figure. As it was reported by Silveira et al, the deposition of 2 ML of InAs results compressive stress being accumulated in the following sequence:[16] Region I: The In cell is opened and InAs is deposited over the surface creating the wetting layer (WL) and increasing the compressive stress. The evolution is not linear meaning that InAs does not incorporate to the bulk GaAs following the constant rate deposition. Region II: at the critical coverage (1.67 MLs), the change in the RHEED pattern reveals that QDs nucleation begins before the In cell is closed. Ripening of the just formed QDs occurs during several seconds in arsenic atmosphere before the Ga cell is opened for capping. During this time, the accumulated stress diminishes slightly as it can be observed in the inset of Fig. (1h). Region III: the Ga cell is opened and the accumulated stress increases again indicating that some liquid In was available at the sample surface which is now incorporated as InGaAs in the capping layer. Finally, in Region IV the In has been exhausted and GaAs growth continues without further change in the stress.

The amount of indium segregated or incorporated in each region can be estimated quantitatively analyzing the accumulated stress measurements with a realistic strain calculation modeling. To do so, the six components of the strain have been found by minimizing the elastic energy density in a continuum three-dimensional discretization grid.[17] With this information, through the composition dependent stiffness constants at each grid point, the corresponding six components of the strain have been extracted. From these values, the in-plane stress is calculated as the average of $\sigma_{xx}$ and $\sigma_{yy}$ components, integrated on the whole plane at a position $z$ in the growth direction. This way, the stress introduced by each grown layer depends on the average InAs amount actually incorporated to that layer. Finally, the accumulated stress at a certain position $h$ (corresponding to a certain measurement time) has been obtained every 0.1 nm by integrating the in-plane stress from $z = 0$ (substrate) to $z = h$. The resulting curve $\Sigma \sigma$ vs $h$ is then weighted by the actual growth rates, leading to a curve $\Sigma \sigma$ vs time which can be compared directly with our experiment. Several simulations have been carried out assuming different In segregation profiles and thus wetting layer, QD and capping compositions. Fig. (1h) shows a set of representative in-plane stress contour maps calculated at different times of the growth sequence.

To restrict the degrees of freedom we have only considered segregation profiles which can be described by the Muraki’s model.[18] Namely, if $x_0$ is the nominal In composition of an In$_{x_0}$Ga$_{1-x_0}$As layer of nominal thickness N monolayers, the actual composition of the $n$th monolayer will be given according with this model by:

$$x(n) = \begin{cases} 
0 & \text{if } n < 0 \\
x_0(1 - R^n) & \text{if } 0 \leq n \leq N \\
x_0(1 - R^N)R^{n-N} & \text{if } n > N 
\end{cases}$$

where the segregation coefficient $R$ defines the fraction of In that is displaced from its nominal position. We can describe accurately the sublinear evolution of the accumulated stress curve that we observe during the WL growth introducing $x_0 = 1$, $N = 1.67$ MLs and $R = 0.5$ in Eq. (1) for $n < N$ (region I in Fig. (1a) and Fig. (1b)). It should be noted that here it is implicit an important intermixing between the incoming In atoms and Ga.
atoms from the substrate leading to a WL made of InGaAs of varying composition. In agreement with the observations made by García et al. less than 50% of the deposited In effectively contributes to the accumulated stress in such region. Above the critical thickness, the QDs begin to nucleate and the remaining 0.33 MLs, up to complete the deposited InAs thickness (2 MLs), are used to form the QDs during the elastic relaxation and ripening processes (region II in Fig. 1a and Fig. 1c-d). With such constraint, the formed QDs are simulated as InGaAs lens-shaped structures with a height of 4.5 nm and a diameter of 24 nm. We consider a linear In gradient from 80% in the base to 100% in the apex, as this is the usual profile observed by cross sectional scanning tunneling microscopy.[19] The simulation domain size is chosen to reproduce the typical areal density of this type of nanostructures ($10^{10}$ cm$^{-2}$).

The In not incorporated to the WL or the QDs is available for the capping once the Ga cell is opened (region III in Fig. 1a and Fig. 1c-g). Experimentally, we observe that In is exhausted after growing $\sim 8.5$ nm of GaAs. In the simulation, keeping $R=0.5$, the available In is incorporated to the bulk in just 2.5 nm (dashed curve in Fig. 1b) and do not reach the experimental accumulated stress of $-5$ N/m. Better results in the capping region are obtained increasing $R$ to 0.8 (dotted curve), although this clearly underestimates the stress introduced in region I and II. The best agreement between experiment and simulation in the whole range is obtained assuming that the segregation coefficient $R$ might vary from 0.5 to 0.8 during the capping (Fig. 2a). For simplicity, we introduce a linear variation of this parameter in region III giving rise to the thick continuous line in Fig. 1a. Typical Indium segregation coefficients in diluted InGaAs quantum wells ($x_{0} \sim 0.15$) and InAs QDs deduced from ex-situ analysis are between $R=0.7$ and $R=0.83$ thus consistent with our upper value.[18, 20]

This time dependent segregation coefficient $R$ demonstrates that during QDs capping In from the WL segregates to the sample surface. This is clearly shown in Fig. 2a where In becomes more spread as the growth proceeds. In this figure, the position of the growth front as a function of time is represented by the thick dashed line. In the framework presented by Joyce and Bottomley, the fast Ga growth rate will first produce a strong intermixing of Ga and In species leading to the partial melting of the WL due to the large biaxial stress. In this conditions, In will easily segregate and will result a dilute InGaAs alloy. In this case, an efficient migration of In in the liquid phase towards the QDs to increase their size or In content is not expected, given the fast growth rate of Ga and the absence of any other phenomena, such as strain fields of buried nanostructures.

Those strain fields are, in fact, the main driving force during growth of QPs and, as we show below, they have a strong impact in the In adatom migration. We have applied the same stress measurement and modeling described above to the growth of InAs/GaAs QPs. Fig. 3 shows the accumulated stress curve recorded over time for the QPs sample (small circles). The beginning of the curve is the seed QDs layer and the evolution is identical to regions I and II in Fig. 1a. During the first periods of the superlattice, growing Ga increases the accumulated stress by the incorporation of the liquid In at the surface, as it is observed in the reference QDs sample, and similar behavior is found when growing In, as expected due to their larger covalent radius. It can be seen in those first periods that during the growth pause under As flux, the accumulated stress decreases slightly ($\sim 0.2$ N/m per period). In principle, this small change, also observed in the QDs growth (inset of Fig. 1a), might be attributed to several factors such as a change in the surface reconstruction or to a small cooling of the sample when the In effusion cell is closed. However, it might also correspond to the detachment of In atoms from the WL and their migration to the sample surface or the QDs, where they introduce less stress.

The interpretation of such feature becomes clearer if we consider the following periods of the superlattice. From the 4th period and ahead, it is evident that the reduction of the accumulated stress is taking place also when In atoms are reaching the sample. This behavior is rather counter-intuitive since In growth should increase the stress accumulated in the sample. The reduction becomes larger as the growth proceeds and, conversely, the stress increase during the GaAs capping becomes smaller (inset of Fig. 3a). The latter effect suggest that each period there is less free In to be incorporated to the sample during GaAs capping, whereas the former indicates that the In detachment process is enhanced during the QPs growth. The combination of both processes points out an augmented efficiency of the migration of In atoms to-
FIG. 3. (a) Experimental and simulated accumulated stress curves of QPs. The inset shows the amplitude of the increase and the reduction of the accumulated stress as a function of the period number. (b) Detail of one period of the QPs growth. The inset shows the different stages of the process, with the amount of segregated In indicated in equivalent InAs thickness. Different colors indicate the In fraction and the arrows the In atoms route: A - Incorporation of In to the sample; B - segregation and migration of In incorporated in the last MLs; growth of the QPs; C - A certain amount of In keeps as a liquid phase in the surface.

wards places where they introduce less stress, which are the In rich columns that form the QPs.

More insight on the processes that are taking place can be obtained by the simulation of the QPs structure. For simplicity, we assume that a steady state has been reached with a constant amount of In segregating from layer to layer. The QPs are simulated as a stack of lens shaped QDs, 24 nm wide, 2 nm high, separated 1 nm from each other. This implies an overlap of consecutive QD layers, therefore the formation of the QPs. A homogeneous InGaAs alloy is assumed for the QPs (63% In). The surrounding matrix is modeled as a 1 nm thick InGaAs layer with 24% In that progressively reduces to 17% during the growth of the next InAs layer. For simplicity, we consider in the simulation a homogeneous InGaAs alloy although a more complex profile, similar to Muraki’s model, would be more realistic. Each period of this structure (QD + capping) has an In content equivalent to 0.2 nm of InAs once buried, similar to the nominal values used in the experiment. 0.06 nm of InAs segregates from layer to layer. The accumulated stress that results from this simulation is also depicted in Fig. 3a. As it can be seen, even with this idealized sequence, we can correctly reproduce the oscillations of the experimental curve.

Fig. 3b shows a detail of the curve corresponding to a single period of the deposited InAs/GaAs superlattice (indicated by a rectangle in Fig. 3a). The opening/closing sequence of As, Ga and In effusion cells are indicated. During region A in Fig. 3b, GaAs is growing and it incorporates most of the liquid In at the surface. In region B, InAs grows very slowly. At the beginning, the stress accumulates slightly and then it reduces. This reduction is more prominent for the last periods of the structure. We believe that at the beginning of the In growth stress increases due to a strong In-Ga intermixing and, as we explained above for the capping of the reference QDs (region III in Fig. 1a), this intermixing produces a partial melting of the surface. The fundamental difference with the growth of QDs is that now there are strong strain fields due to the buried QDs that favors the migration of this liquid In towards the top of them to form the QPs. This migration is indirectly incorporated in the simulation by assuming that part of the In deposited during region B keeps in a liquid solution and part lead to the formation of a new, very shallow QD, as explained in the previous paragraph. Since in the simulation the fraction of In that incorporates to the QPs is constant, the curve do not completely reproduce the experimental results shown Fig. 3, which is an evidence of the enhancement of the In migration with the number of periods.

The previous results show that the detachment of In atoms from the WL and the subsequent migration to the QPs is actually taking place, as suggested by Joyce, being such migration enhanced by the existing strain fields in the structure. The effect of the strain fields has been observed before in QDs and quantum wire bilayers through the variation of the critical thickness needed in the nucleation of the second layer, however in this work we demonstrate that part of the In that incorporates to the nanosstructure is actually being drained from the surrounding WL and not only from the incoming material [21, 22].

In summary, in this work we have used an in-situ accumulated stress measurement technique to study the growth of InAs/GaAs QPs and QDs. Our results demonstrate that there is an important loss of In from the WL during capping of the QDs, possibly due to a partial surface melting. This In redistribution is also present during QPs growth, where the strong strain fields enhance In migration across the liquid surface to the QPs and leads to the observed inversion of the accumulated stress curves.
Our results give an experimental demonstration of the processes suggested by Joyce and Bottomley and thus strongly complements the available knowledge on the growth of InAs/GaAs based quantum nanostructures.

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SUPPLEMENTARY INFORMATION

The in-situ accumulated stress measurement technique was introduced back in the early 90’s by Schell-Sorokin and Tromp. The kind of information that can be extracted ranges from the anisotropic strength of the surface reconstructions, the formation of quantum dots, the formation and evolution of dislocations and plastic deformation processes, material amorphization during ion bombardment or thermal expansion processes in thin films. In its basic form, it is based on measuring the relative deflection of two parallel laser beams reflected on the lever-shaped sample. One of the beams hits the lever end fixed to the sample holder, whereas the other one hits the free end. The relative change in the separation of the reflected spots $d(t) - d_0$ at a certain distance from the sample surface $L$ can be related with a change in the accumulated stress $\Sigma \sigma$ by means of the Stoney’s equation, leading:

$$\text{SUPPLEMENTARY INFORMATION}$$

$$\Sigma \sigma[h(t)] + [\Delta \tau_S] = \frac{M_S h_S^2}{12} \frac{d(t) - d_0}{d_H L}.$$  

(2)

where $h(t)$ is the thickness of the deposited layer at the time $t$, $h_S$ is the substrate thickness, $d_H$ is the initial separation of the laser beams and $M_S = C_{11} + C_{12} - 2C_{12}/C_{11}$ the biaxial modulus that relates the stiffness constants $C_{ij}$. As it can be seen, the magnitude measured in these experiments is the sum of the accumulated stress and the stress associated to changes in the surface reconstruction $[\Delta \tau_S]$, which is generally small.

The in-situ accumulated stress technique is sensitive only to the stress accumulated in the sample and hence
it can be used to distinguish if certain atomic species, namely In atoms, migrate during growth towards places where they introduce less stress. In this line, it is interesting to compare the stress that accumulates the In contained in 1 or 2 ML of InAs when it is incorporated in the form of pure InAs strained on GaAs or when it is spread in a more dilute, thicker, In$_x$Ga$_{(1-x)}$As layer. Fig. 4 shows the result of such comparison. The stress accumulated by the layer is calculated with:

$$\Sigma \sigma_L = M_L(x)\epsilon_L(x)t_L(x)$$

(3)

where $M_L(x)$, $\epsilon_L(x) = [a(x) - a(GaAs)]/a(x)$, $a(x)$ and $a(GaAs)$ are the biaxial modulus, the lattice mismatch and the lattice parameters of the alloy and the substrate, respectively. We use a linear interpolation of the stiffness and lattice constants of InAs and GaAs to calculate the alloy parameters. The layer thickness is given by $t_L(x) = \frac{a(x)N}{x}$, with $N$ the equivalent InAs monolayers (1 or 2 ML), in order to keep constant the amount of In. In rich layers introduce less stress than the same amount of In in a dilute alloy. Therefore, the observation of a reduction of the accumulated stress might be a fingerprint of the migration of In atoms to In rich regions.