In-situ measurement of Indium segregation in InAs/GaAs submonolayer quantum dots

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Reflection high-energy electron diffraction was used to determine In segregation during the growth of InAs/GaAs submonolayer quantum dots by molecular beam epitaxy. The segregation coefficient R was estimated for the usual growth conditions, starting from a c4×4 reconstruction of the GaAs(001) surface, as well as for another set of very different growth parameters, yielding an initial 2×4 surface reconstruction that might provide quantum dots of better quality.

I. INTRODUCTION

Quantum dots (QDs) involved in solid-state devices are usually made from InAs material using the Stranski-Krastanov (SK) growth mode [1]. An alternative to grow such nanostructures in a much more flexible way, with a higher surface density, enhanced lateral confinement, and without wetting layer, is to use a submonolayer (SML) technique. The main idea behind the growth of InAs/GaAs SMLQDs is to deposit only a fraction of a monolayer of InAs material (generally between 30 and 50%), to nucleate a high density of small two-dimensional (2D) InAs islands on the GaAs surface, and then to cover it with a few monolayers of GaAs material. This cycle can be repeated as many times as necessary and, under the right growth conditions, the small 2D InAs islands of adjacent layers will stack vertically, due to the local strain field generated by the lattice mismatch between both materials. Each stack will behave as a single QD having the desired height (by varying the number of repetitions) and average composition (by varying the thickness of the GaAs spacer between two InAs layers) [2].

To predict the optoelectronic properties of such nanostructures from theoretical calculations, it is necessary to know their size and geometry, as well as their composition profile. These features can be roughly obtained from XSTM [3] or TEM [4] images, but the very low contrast of the SMLQDs in the images requires a sophisticated image processing and limits the quality of the results. In particular, the determination of the In-composition profile inside the SMLQDs is not straightforward as a consequence of the strong segregation of the In atoms that are also found in high quantity inside the surrounding GaAs layers. Generally, In segregation is well described by the phenomenological model of Muraki *et al.* [5] which defines a segregation coefficient R that expresses the fraction of In atoms that are transferred from one atomic layer to the next one during the growth of a thick InGaAs layer or its overgrowth by another material. Since the In segregation coefficient R is usually around 0.8 for the InGaAs/GaAs system, the actual composition profile of any In(Ga)As/GaAs layers is very different from the nominal one, meaning that segregation really needs to be taken into account in order to provide accurate calculations of the optoelectronic properties of such nanostructures.

A few years ago, Martini *et al.* [6] demonstrated that reflection high-energy electron diffraction (RHEED), an *in-situ* technique available in any molecular beam epitaxy (MBE) system, could be used to determine R during the deposition of InGaAs or its overgrowth by GaAs. They showed that the strong reduction of the intensity of the RHEED oscillations observed during the deposition of InGaAs layers was related to the gradual incorporation of the In atoms into the crystalline layers resulting from the segregation phenomenon [7]. This technique has several advantages. One can measure R *in situ* and in real time, during the growth of the sample itself, without any need for time-consuming *ex-situ* and destructive characterization techniques. Since the RHEED measurements take only a few minutes, tens of different growth conditions can be analyzed within a few hours. Finally, the RHEED technique is easy to use and provides a strong signal that is mostly sensitive to the top crystalline layer, leading thus to a segregation coefficient that can be determined with good precision.

As far as we know, SMLQDs are always grown under conditions similar to the ones used for SKQDs, *i.e.* a growth temperature between 480 and 520°C, a high As flux and starting from a c4×4 surface reconstruction. However, STM studies already showed that the deposition of InAs on GaAs(001) in such conditions doesn't form InAs islands but rather leads to the incorporation of the In atoms inside the deep trenches of the c4×4 surface reconstruction, resulting in a random alloying of the GaAs surface [8]. On the other hand, when InAs deposition starts on a GaAs(001) surface showing a 2×4 reconstruction, small 2D InAs islands are nucleated [9], as required for the formation of SMLQDs.

Therefore, in this paper, we investigated In segregation using the *in-situ* RHEED technique and we determined the segregation coefficient R for the conventional growth conditions starting from a c4×4 surface reconstruction. The study was then repeated for the 2×4 surface reconstruction that is supposed to nucleate 2D InAs islands. Since the 2×4 reconstruction can only be achieved with an extremely low As flux, the related growth conditions had to be drastically changed, what is expected to influence In segregation.

II. EXPERIMENTAL DETAILS

All the RHEED measurements were performed on an epi-ready GaAs(001) substrate. Before starting any measurement, a 100 nm-thick GaAs layer was grown at 570°C and then RHEED oscillations were acquired during GaAs homoepitaxy to check their symmetry. If necessary, the angle of incidence of the electron beam was slightly adjusted to get symmetrical oscillations. The deposition of In(Ga)As usually occurs at a temperature lower than 520°C in the presence of a relatively high As flux, which always leads to a c4×4 reconstruction of the GaAs(001) surface. To check In segregation for this surface reconstruction, we used growth conditions similar to the ones that are normally used in the literature to deposit the SMLQDs. In this work, we chose a growth rate of around 0.1 and 0.7 ML/s for InAs and GaAs, respectively, together with an As_2 flux corresponding to a deposition rate of 1.5 ML/s. This last value was estimated from the RHEED oscillations originated from the As_2 flux impinging on top of a Ga-rich surface. A valved As cracker was used to allow a fast change of the As_2 flux. As usual, all these RHEED measurements were performed with the electron beam along the [110] direction.

To get a 2×4 reconstruction, the As flux must be considerably reduced [10]. The c4×4 to 2×4 transition (and vice versa) is more easily detected when the electron beam is along the [010] direction (i.e. at 45° between the [110] and [-110] directions) because, in that case, the two surface reconstructions have a one-fold and four-fold periodicity, respectively [10]. Since the growth must occur under As rich conditions, such a low As flux requires lower growth rates for the InAs and GaAs materials used for the SMLQDs. Therefore, we used a growth rate of 0.015 and 0.1 ML/s for InAs and GaAs, respectively, together with an As_2 flux equivalent to a deposition rate of 0.15 ML/s. Due to the very low InAs deposition rate, the sample temperature was set to 480°C to minimize In evaporation from the surface.

III. RESULTS AND DISCUSSION

Usually, SMLQDs are obtained by alternating the deposition of a fraction of a layer of InAs material and a few GaAs monolayers. It is possible to monitor the growth of such layers with the RHEED system, but the very small amounts of InAs and GaAs materials deposited in each cycle make it impossible to determine R. However, since Martini *et al.* [6] already showed that In segregation could be accurately measured during the growth of a thick InGaAs layer (20 MLs of material are enough) or its overgrowth by a thick GaAs layer, we used the same technique here and monitored segregation during the deposition of 20 InGaAs monolayers using the specific growth conditions of the SMLQDs detailed above for both surface reconstructions.

Therefore, to measure the segregation coefficient R for the first set of growth parameters starting from a c4×4 surface reconstruction (0.1 and 0.7 ML/s for InAs and GaAs, respectively, and a high As_2 flux), we deposited a thick $In_{0.13}Ga_{0.87}As$ layer on a GaAs(001) substrate at 515°C with a growth rate of 0.8 ML/s and recorded the RHEED oscillations along the [110] direction (Fig. 1). One can see that their intensity has a much stronger decay than in the case of GaAs homoepitaxy [6]. The In composition x_n of the n^{th} $In_xGa_{1-x}As$ layer is given by the expression [5]

$$x_n = x_0(1 - R^n) \tag{1}$$

where x_0 is the nominal In composition, $1 \leq n \leq N$, and N is the total number of InGaAs layers deposited on top of the GaAs surface. Since for the InGaAs/GaAs system R≈0.8, there is a huge lack of In inside the first InGaAs layers (only 20% of the In atoms that were deposited actually remain in the first layer). The In concentration gradually increases in the next layers but it is only after roughly 20 MLs that its value reaches approximately the nominal value x_0. All the In atoms that are not incorporated into the crystal segregate towards the surface, leading to a growing population of In adatoms given by [5]:

$$x_{surf(n+1)} = \frac{R}{1-R} x_n \tag{2}$$

The segregation coefficient R is often expressed as a function of a parameter δ which is interpreted as the characteristic length (expressed in MLs) over which the effects of the segregation phenomenon can be effectively sensed [5]:

$$R = e^{-1/\delta} \tag{3}$$

Since the strong decay of our RHEED oscillations is due to the increasing In concentration in the InGaAs layers, the characteristic decay time of the envelope of the RHEED oscillations can be obtained by fitting the data of Fig. 1 with the expression [6]

$$I = I_0 + I_1 e^{-t/\tau} \tag{4}$$

where I_0 and I_1 are constants, t is the growth time, and τ is the decay constant that is the relevant fitting parameter. Both δ and τ are a direct measurement of the segregation strength and are related by the expression $\delta=\tau\times GR$ where GR is the growth rate of the InGaAs layers. By doing so, the In segregation coefficient of the RHEED data of Fig. 1 could be estimated as $R_{c4\times4}=0.77\pm0.01$. This value is in excellent agreement with previous ones obtained with other techniques [3,4].

The same procedure was repeated to investigate In segregation using the second set of growth parameters (0.015, 0.1, and 0.15 ML/s for InAs, GaAs, and As_2, respectively) necessary to start from a 2×4 surface reconstruction. In such conditions, segregation was stronger and was estimated as $R_{2\times4}=0.81\pm0.02$. Since it is a thermally activated process, we should expect a lower segregation coefficient for the 2×4 conditions resulting from the lower sample temperature. However, segregation also depends on the other growth conditions and, actually, a lower As flux and lower growth rates are known to enhance segregation [11]. Therefore, as both parameters were drastically reduced to reach the 2×4 conditions, their influence compensated the temperature reduction and provided a segregation coefficient larger than the one of the usual c4×4 conditions. The difference of segregation between both cases can be better evidenced when the RHEED curves are plotted together (Fig. 2). Since the growth rates are very different, both curves can only be compared when they are plotted as a function of the number of monolayers instead of growth time. When the segregation coefficient R is larger, more In segregates from one layer to the next one, and it takes a larger number of monolayers to reach the nominal composition x_0. As the curve related to the c4×4 conditions drops faster, it confirms that the segregation coefficient is smaller and that more In atoms are incorporated into each InGaAs monolayer, when compared to the 2×4 conditions, allowing the nominal composition x_0 to be reached faster.

Once the segregation coefficient has been experimentally determined, it is possible to estimate the real composition profile of the nanostructures. Most SMLQDs found in the literature use 4 to 6 repetitions of a basic cycle consisting of 0.3-0.5 ML of InAs material followed by 2-3 MLs of GaAs. Therefore, we simulated the In profile of SMLQDs consisting of 4 periods of 0.5 ML of InAs covered by 2.5 MLs of GaAs. When considering only one single SMLQD, the average nominal In concentration (i.e. without taking segregation into account) is 33.3% and is equivalent to the deposition of 1 ML of InAs followed by 2 MLs of GaAs. The simulation of the real In concentration in each monolayer of such a SMLQD can be done using Eq. 1 (with n=1), when depositing InAs, and Eq. (5), when depositing GaAs [5]:

$$x_n = x_0(1 - R^N)R^{n-N} \tag{5}$$

As there are 4 sequential depositions of InAs material, after the first InAs layer, the next ones must also take into account the increasing population of In adatoms present at the surface and given by Eq. 2. When using Eq. 5 to simulate the overgrowth of any InAs layer, *N* must be taken as 1 and *n* must be larger than 1 (n=2, 3 in our specific case). Figure 3 shows the actual In composition of the SMLQD when the segregation coefficient is $R_{c4\times4}$=0.77 and $R_{2\times4}$=0.81. One can see that both In profiles are similar and completely different from the nominal one, confirming that segregation has to be taken into account whenever the optoelectronic properties of such nanostructures need to be correctly simulated. The In concentration oscillates and gradually increases with the number of repetitions as a result of segregation that generates an increasing population of In adatoms at the surface before each new InAs deposition. Such behavior has already been observed experimentally, although not so clearly due to the limitations of the techniques that were used [3,4]. Our simulations also show that many In atoms are encountered beyond the location of the last InAs layer since all the In adatoms that accumulated at the surface were incorporated later into the following GaAs layers. Therefore, besides having a very different composition profile, such nanostructures are also slightly taller than expected, unless special flash-off techniques [12] are used to evaporate these extra In adatoms from the surface.

Finally, when comparing the RHEED results and the simulations of both extreme growth conditions investigated here, it is clear that In segregation in the presence of the 2×4 surface reconstruction is slightly stronger than for the c4×4 reconstruction, meaning that less In atoms will be incorporated into the InAs layers, yielding a slightly shallower potential well. However, according to previous STM studies, 2D InAs islands are only formed on top of the GaAs(001) surface when starting from a 2×4 reconstruction [9], while, for the c4×4 reconstruction, the In atoms are randomly incorporated leading thus to an alloying of the surface [8]. Since several types of devices [13,14] already showed a better performance using SMLQDs obtained with the usual growth condition (c4×4 reconstruction), these results can only be explained if a 3D confinement of the carriers is achieved, suggesting that some kind of quantum dots are effectively formed even with a 2×4 reconstruction. As, in these conditions, 2D InAs islands are not initially formed, it means that the QDs are somehow formed in another way, probably due to In segregation that locally accumulates In atoms (due to local strain conditions) and creates random InGaAs clusters that contain slightly more In than their surroundings. This is probably why XSTM [3] and TEM [4] images of SMLQDs obtained in such conditions always have low contrast and show nanostructures having a large variety of shapes and sizes, but nevertheless behaving as quantum dots due to the local modulation of the In concentration. On this point of view, the growth conditions providing an initial 2×4 surface reconstruction should produce better SMLQDs (even if segregation is slightly stronger) because real 2D InAs islands will be nucleated, leading to SMLQDs with a larger In content and a columnar shape resulting from the stacking of these small InAs islands.

IV. CONCLUSION

In conclusion, RHEED measurements were successfully used to quantify In segregation in InAs/GaAs SMLQDs grown in two very different conditions. When starting from a c4×4 surface reconstruction (usual growth conditions found in the literature), the segregation coefficient was estimated as $R_{c4\times4}$=0.77±0.01, while, starting from a 2×4 reconstruction, it was found to be $R_{2\times4}$=0.81±0.02. The small increase of In segregation in the second case was related to the very low growth rates and As flux needed to reach the 2×4 reconstruction. However, since previous STM studies showed that 2D InAs islands were only nucleated when starting from a 2×4 reconstruction, we believe that the second set of growth parameters should provide SMLQDs of better quality. Simulation of the In concentration inside the SMLQDs clearly showed that the composition profile is very different from the nominal one and confirmed that segregation needs to be taken into account to correctly predict the optoelectronic properties of such nanostructures.

V. ACKNOWLEDGEMENTS

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001 and by CNPq (grant 311687/2017-2).

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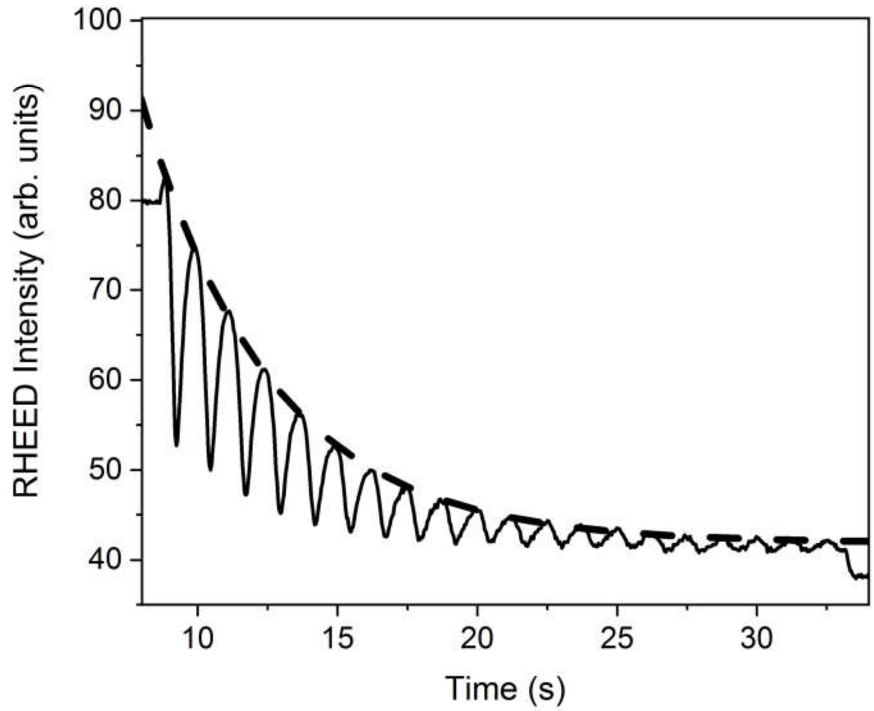

FIG. 1. RHEED oscillations during the deposition of $In_{0.13}Ga_{0.87}As$ at 515 °C starting from a c4×4 surface reconstruction. The best fit of the maxima using Eq. 4 is also shown (dashed curve).

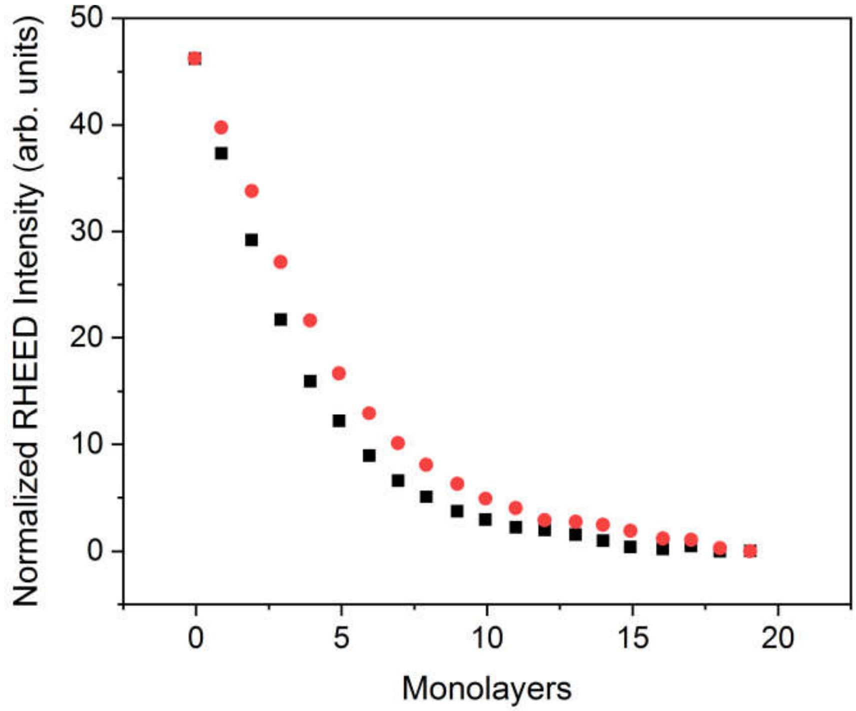

FIG. 2. Maxima of the RHEED oscillations starting from a 2×4 (red circles) and c4×4 (black squares) surface reconstruction plotted as a function of the number of InGaAs monolayers deposited on the GaAs(001) surface.

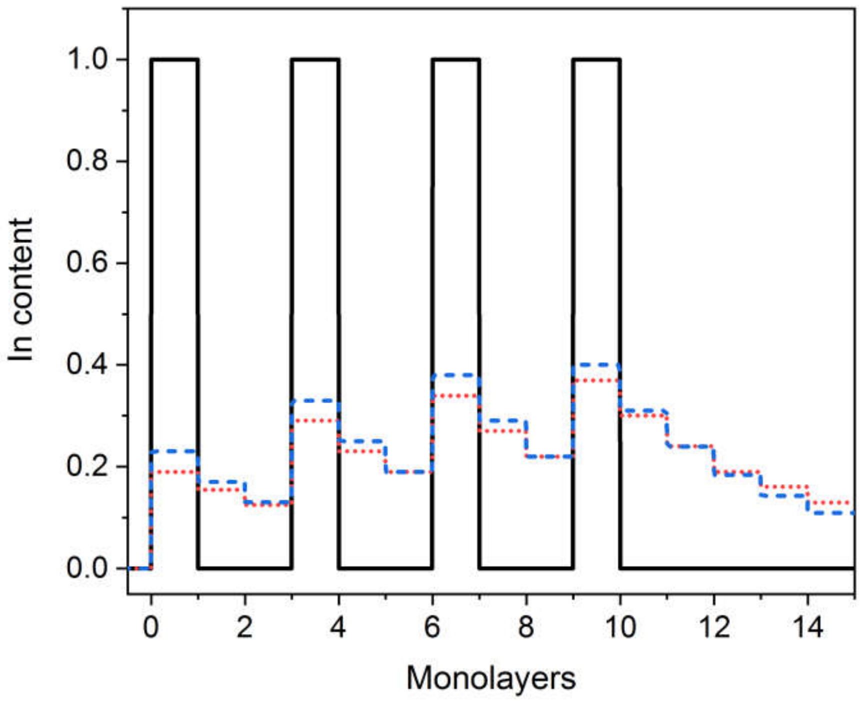

FIG. 3. Indium profile of a SMLQD consisting of four repetitions of 0.5ML of InAs followed by 2.5 MLs of GaAs, assuming a segregation coefficient R=0 (i.e. without segregation, black solid line), $R_{c4\times4}$=0.77 (blue dashes) and $R_{2\times4}$=0.81 (red dots).