Experimental evidence of two-dimensional–three-dimensional transition in the Stranski–Krastanow coherent growth

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The two-dimensional (2D)–three-dimensional (3D) transition has been studied for InAs and InP layers grown on (001) GaAs substrates by metalorganic vapor pressure epitaxy at different growth temperatures and growth rates. The combined use of scanning force microscopy and of Rutherford backscattering spectrometry allowed the determination of the surface morphology of the samples and of their equivalent layer thickness with a precision better than 0.1 monolayers (ML). The critical thickness for the 2D–3D transition has been found to occur after a deposition of (1.2 ± 0.1) ML for InAs/GaAs and after a deposition of (2.2 ± 0.2) ML for InP/GaAs, independently of the temperature and of the growth rate. For coverages slightly exceeding 1 ML, for InAs, and 2 ML, for InP, the surface of the samples appears partially covered by small bi-dimensional structures (platelets). The dimensions of the platelets appear to be independent of the system under study and consequently of the misfit. Moreover, their distribution on the surface appears to be strongly different from that of the islands after the 3D transition so that they cannot strictly be viewed as island precursors, as previously suggested. © *1997 American Vacuum Society.* [S0734-211X(97)03005-9]

I. INTRODUCTION

Recently a large amount of work has been devoted to the formation of quantum nanostructures for optoelectronic device production.[1] Among the different production techniques, special attention has been paid to the possibility of avoiding any pre- or postgrowth processing by exploiting strain-induced self-organization phenomena during epitaxial growth.[2–5] In fact, the epitaxial growth of materials with a high lattice mismatch with respect to the substrate has been observed to produce three-dimensional (3D) structures possibly leading to quantum dots. However, high quantum efficiency with zero-dimensional quantum confinement requires narrow nanoscale dot dimension distributions and large surface densities. The basic idea is to control the size distribution and density of the islands in the 3D growth by controlling the growth parameters.

It is now well established that, following the general classification of epitaxial growth into three different modes (Frank–Van der Merwe, Stranski–Krastanow, and Volmer–Weber[6]), the mismatched heteroepitaxial systems leading to the formation of self-organized islands follow the Stranski–Krastanow (SK) growth mode. This growth mode allows strain relaxation by developing a 3D morphology. Eaglesham and Cerullo,[7] while studying the first stages of island formation in the Si–Ge system, showed that despite "the primary driving force for island formation in SK growth (there) must be the ability of introducing dislocations in the islands"; the islands formed in the SK growth of Ge on Si are initially dislocation free. Their description appears to apply to other mismatched semiconductor couples and the SK growth in these systems is now currently reported as "coherent SK growth." Theoretical and experimental work has been devoted to the study of the morphological evolution of the deposited films mainly with the aim of explaining the shape[8] and the size distribution[9,10] of the resulting islands together with the critical thickness for the two-dimensional (2D)–3D transition.[11,12]

It is generally reported that in order to obtain small size, coherent and homogeneously distributed islands, the amount of the deposited material must slightly exceed the one required for the 2D–3D transition. It is therefore important to accurately define the critical thickness for the transition (d_c) in the systems under study together with its dependence on the growth parameters and on the lattice misfit.

We have focused our attention on the couple InAs/GaAs. This system exhibits a misfit of about 7% and it is widely studied for its promising properties for optoelectronic device applications. The critical thickness for the 2D–3D transition in InAs/GaAs has been reported to range from 1.5 to 2.0 ML.[13–19] All these studies have been performed on samples grown by molecular beam epitaxy (MBE) and the value for the transition is derived from the observed behavior of the reflection high energy electron diffraction (RHEED). However, no definitive results are reported about the dependence of the critical thickness value on the growth parameters.

On the other hand, the dependence of d_c on the misfit f has been predicted to follow very different power laws, i.e., $d_c \propto f^{-4}$ by Snyder *et al.*[12] and $d_c \propto f^{-8}$ by Spencer *et al.*[20] In

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these models a dependence on the growth velocity is also expected.

In the present work we studied the 2D–3D transition for InAs/GaAs samples grown by metalorganic vapor pressure epitaxy (MOVPE) for different values of the growth temperature T_g and of the growth rate v_g. All the samples were characterized *ex situ*: the absolute amount of the deposited material was measured by high sensitivity Rutherford backscattering spectrometry (RBS) while the evolution of the surface morphology was investigated by scanning force microscopy (SFM).

A set of InP/GaAs samples has also been grown to study the dependence of d_c on the misfit.

II. EXPERIMENT

InAs samples were grown on nominally (001) oriented GaAs substrates by MOVPE in an Aixtron reactor with hydrogen as carrier gas. The operating pressure was always kept at 20 mbar and the total flux of the reactants was 7000 sccm. The source materials were trimethylindium (TMIn) and arsine (AsH_3). A 200-nm-thick GaAs buffer layer was always grown on top of the substrate at 680 °C, using trimethylgallium (TMGa) and arsine. Then the temperature was lowered and the InAs layers were grown at different temperatures ranging from 400 to 500 °C. By varying the TMIn flow, while maintaining a constant AsH_3 flow, the *nominal* growth rates v_g ranged from 0.16 to 0.78 ML s^{-1} (1 ML InAs=0.303 nm). After the preselected growth time the TMIn flux and the heating lamps were contemporary shut down resulting in a postgrowth cooling of the samples with an initial rate of about 1 °C/s.

A set of InP epilayers was also grown on GaAs substrates (the InP–GaAs misfit is 3.8%). In this case T_g was fixed at 580 °C while v_g was varied in the same range as for the InAs samples.

RBS was used to measure the *equivalent layer thickness* of each sample. RBS spectra were recorded in depth-enhancing grazing incidence and emergence geometry[21] and were calibrated against Ta/Si standard samples whose absolute Ta content is known with an accuracy better than 2%. This procedure allows measurements of the *actual coverage* with a precision on the absolute value better than 0.1 ML. The RBS measurements give the number of In atoms per square centimeter, averaged on the sampled area that is of the order of 1 mm^2. Therefore no direct information on the nanosize distribution of the In atoms can be achieved by RBS.

The surface morphology of the samples was investigated by SFM with a Park Scientific Instruments microscope, model CP in the "contact mode." Ultralever© tips were used to minimize the tip-surface convolution resulting in measured lateral dimensions larger than the actual ones. In our experimental setup, by assuming the nominal value of 10 nm for the tip radius, the maximum overestimate in the lateral dimensions of the islands can be calculated to be about 5 nm. On the contrary, the island height, as measured by SFM, is not affected by the tip size.

It must be stressed that the present RBS-SFM technique is intrinsically very sensitive and precise, however it allows only *ex situ* characterization, so that postgrowth evolution of the sample morphology during the cooling time to ambient temperature cannot be excluded. Nevertheless, the sample morphology, at ambient temperature, has been found to remain the same, as observed immediately after the growth, for periods of the order of months. This excludes that relevant changes could be induced by the oxidation of the samples' surface exposed to air.

III. RESULTS

The SFM technique cannot distinguish between the atoms of the substrate and those of the epilayer, so that the evolution of the surface morphology before the 3D transition is somewhat speculative. Nevertheless, systematic observations of the morphology as a function of the coverage (which is accurately defined by RBS measurements) allow to draw the following conclusions:

(i) The GaAs buffer layers always show the same morphology as that of the substrate, i.e., flat terraces separated by atomic steps (about 0.3 nm high). From the average width of the terraces very low miscut angles (about 0.05°) of the substrates with respect to the (001) direction can be inferred.

(ii) For coverages d below 1 ML the substrate appears to be partially covered by the deposit, in fact from SFM images like that reported in Fig. 1 it appears that, superimposed to the regular terrace structure of the buffer/substrate, there is a network of *dark* wiggles which are 1 ML deep. Moreover, apart from the terrace steps, no relief structures are observed. Both these facts point to an incomplete 1 ML coverage of the substrate with no (negligible) regions with 2 ML coverage. One could argue that features as that shown in Fig. 1 could be interpreted as due to oxidation of the surface exposed to air. However, no such features are present after the 3D transition (Figs. 2 and 3), while they do also appear in the InP/GaAs system below the 3D transition [Fig. 5(a)].

(iii) For $1.00<d<1.15$ ML coverages (Fig. 2), the network of dark features disappears, indicating that the surface is completely covered by a 1-ML-thick layer. Moreover, many small *bright* structures are visible, whose distribution is homogeneous on the surface. These structures are approximately circular in shape, their diameters ranging from 10 to 30 nm, and they are 1 ML high. We refer to these structures as *bidimensional platelets* and we call this phase the *pretransition* phase. In fact our definition of the 2D–3D transition is related to the appearance of nanostructures which are at least 3–4 ML high (islands). As a matter of fact the fraction of surface covered by the platelets corresponds to the fractional coverage exceeding 1 ML, so that it can be considered as the fraction of surface covered by 2 ML of InAs.

(iv) For $1.15<d<1.22$ ML some islands appear on the

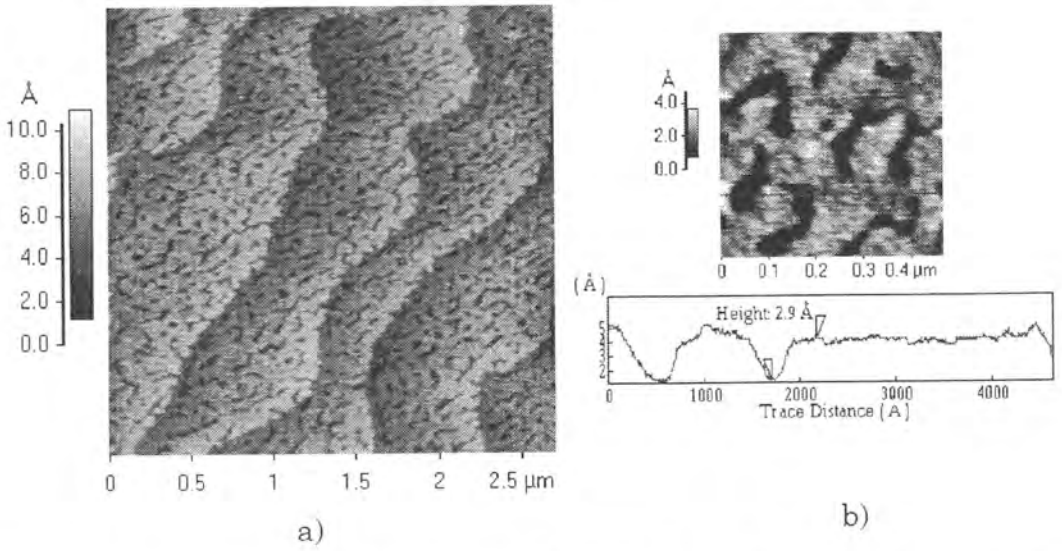

FIG. 1. SFM contact mode images of a InAs/GaAs sample: $T=500$ °C, $v_g=0.16$ ML s^{-1}, $d=(0.6\pm0.1)$ ML. Scan width (a) 2.8 μm and (b) 0.4 μm. The horizontal line scan in the lower part of (b) shows that the dark features are 1 ML deeper with respect to the lighter part of the image, indicating an incomplete monolayer coverage.

surface of the samples, their height being of the order of a few nanometers and their base diameters being of about 15 nm (Fig. 3). By increasing the coverage, the island density increases. Moreover, the islands increase their dimensions while maintaining an aspect ratio (height to diameter) at about 0.20.

The actual coverage, measured by RBS, of the samples grown at $T=500$ °C as a function of the growth time and for different values of the growth rate, is reported in Fig. 4. Open symbols refer to samples showing the island morphology while full symbols represent samples in which the 2D–3D transition did not yet occur. The error of the equivalent layer thickness determination is given by the size of the experimental points in the graph. The slope of the fitting straight lines gives the average growth velocity. The data deviations from the fitting lines correspond to the uncertainties on the values of the growth parameters that give departures of the *actual* growth rate from the *nominal* value. It is worth noting that both values (in units of ML s^{-1}) are *equivalent* growth rates, calculated from the coverage equivalent to the thickness that would be expected for a layer-by-layer growth. From the data of Fig. 4 no dependence of d_c on the growth rate can be detected. Also, for

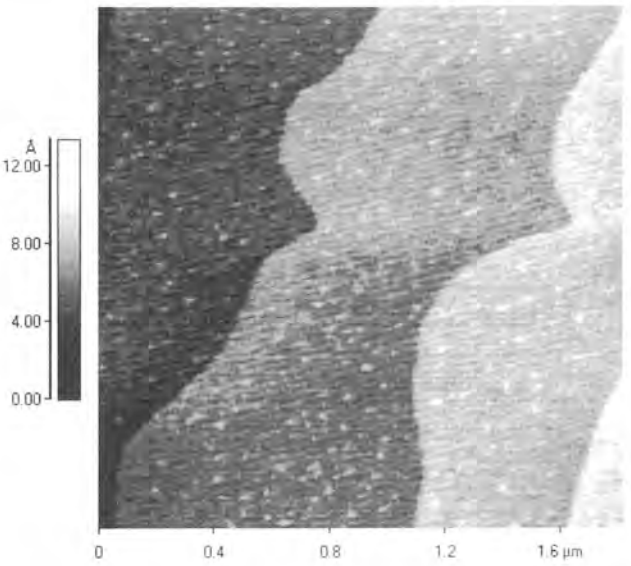

FIG. 2. SFM contact mode image of a InAs/GaAs sample: $T=500$ °C, $v_g=0.16$ ML s^{-1}, $d=(1.1\pm0.1)$ ML. The brighter features are 1 ML high.

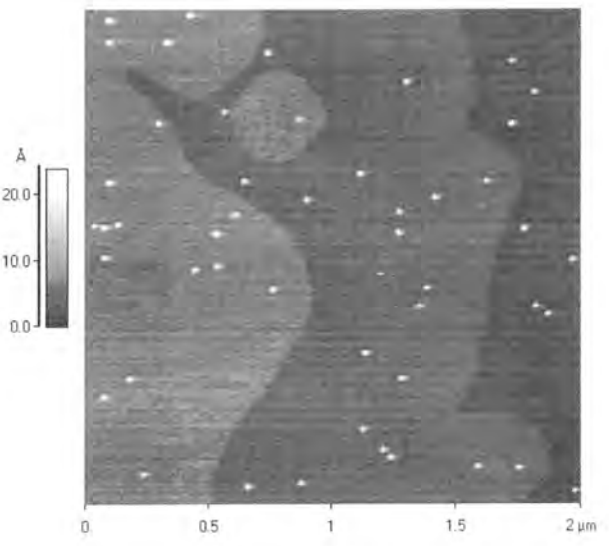

FIG. 3. SFM contact mode image of a InAs/GaAs sample: $T=430$ °C, $v_g=0.78$ ML s^{-1}, $d=(1.2\pm0.1)$ ML.

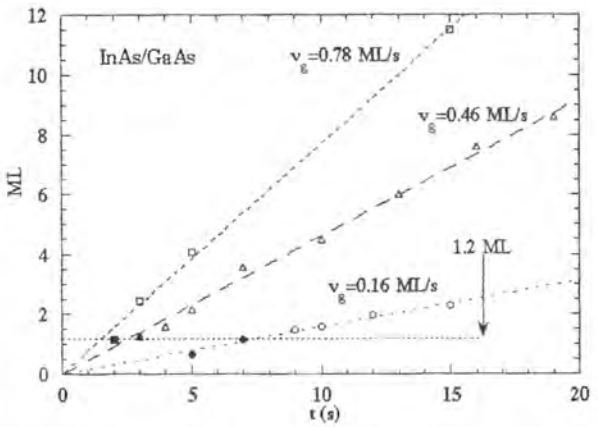

FIG. 4. Actual coverage of InAs/GaAs layers, grown at $T=500$ °C, as measured by RBS. The data concerns samples grown with different nominal growth rates as shown in the figure. Open symbols refer to samples showing the island morphology, while full symbols represent samples in which the 2D–3D transition did not yet occur. The equivalent coverage for the 2D–3D transition is also shown.

samples grown at $T=400$, 430, and 470 °C, no dependence of d_c on the growth rate can be detected. By considering the entire set of samples grown at different T_g and v_g, the transition is estimated to occur at $d_c=(1.2\pm0.1)$ ML where the error is the standard deviation of the overall observations. Being this error is the same order as that of a single measurement, we can conclude that, at least in the range of temperatures and of growth rates of this work, the d_c independence from the growth parameters is fully confirmed.

To study the expected dependence of d_c on the misfit of the material couple, a set of InP samples was also grown on GaAs. The equivalent deposited thicknesses ranged from 1.7 to 3.1 ML. As in the case of InAs samples, by considering the entire set of growths, the critical thickness for the 2D–3D transition can be estimated to be $d_c=(2.2\pm0.2)$ ML. As in the previous case the error corresponds to the standard deviation of the observations. Here it is greater than the uncertainty of the coverage measurement: in fact a small dependence of d_c on the growth velocity was detected, the critical thickness being slowly increasing with v_g.

The evolution of the surface morphology of the InP/GaAs samples is illustrated in Figs. 5(a) and 5(b), where SFM images of samples with equivalent thickness below and above 2 ML are reported. For deposited layers of equivalent thickness ranging from 1.5 to 2.0 ML [Fig. 5(a)] the surface of the samples is similar to that of InAs samples with a coverage below 1 ML. The replica of the substrate's atomic steps can be observed and a dense network of dark features is present, indicating that the coverage of the uppermost layer is incomplete. For deposits of equivalent thicknesses ranging from 2.0 to 2.2 ML [Fig. 5(b)] the *pre-transition* phase occurs. As in the case of the InAs growth, many small "bi-dimensional platelets" can be detected on the substrate which is completely covered by a continuous (2 ML thick) layer. The density, surface distribution, and individual dimensions of the platelets appear to be the same as (or very close to) those of the InAs/GaAs system.

By slightly increasing the coverage above d_c the first developed islands appear on the surface, i.e., the 2D–3D transition occurs.

Although the aim of this work was not to study the island nucleation mechanism and the evolution of their sizes, it must be stressed that the simple equilibrium model, reported in Ref. 10, gives predictions in perfect agreement with the experiment for both InP/GaAs and InAs/GaAs[22] systems.

IV. DISCUSSION

An accurate measurement of the critical thickness d_c for the 2D–3D transition has been performed giving a value of (1.2 ± 0.1) ML and of (2.2 ± 0.2) ML for InAs and InP, respectively. To our knowledge this it is the first time that the actual coverages are measured for each sample. In fact, the

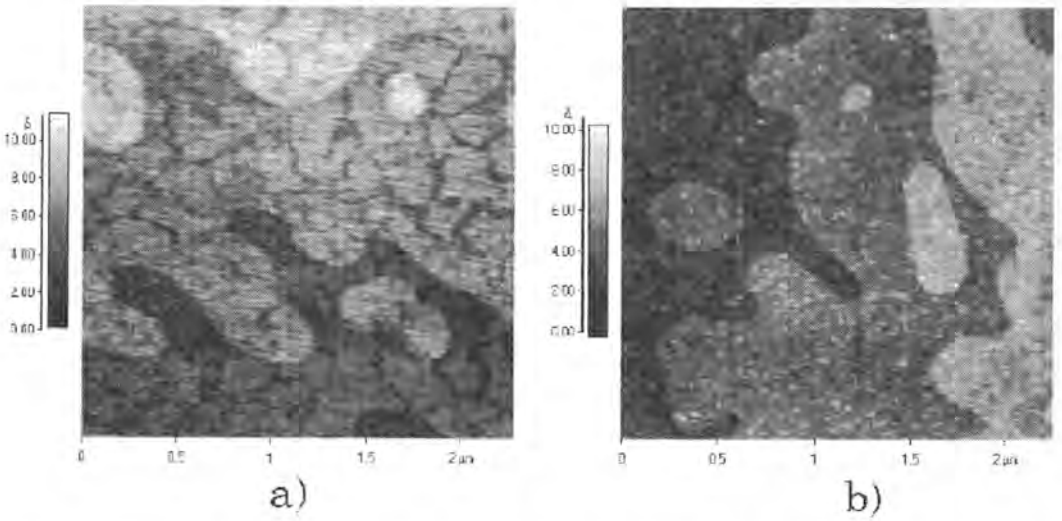

FIG. 5. SFM contact mode images of InP/GaAs samples (a) $T=580$ °C, $v_g=0.78$ ML s^{-1}, $d=(1.7\pm0.1)$ ML; (b) $T=580$ °C, $v_g=0.16$ ML s^{-1}, $d=(2.1\pm0.1)$ ML.

usual way of determining the coverage d is by computing it as the product of the nominal growth rate and the growth time t: $d = v_g t$, where v_g is measured by a separate calibration.

Our d_c values are smaller than those reported in the literature for MBE and MOVPE grown samples ($d_c \approx 2.0$ for InAs[13–19] and $d_c \approx 2.5$ ML for InP,[23] respectively). This discrepancy could be the result of the different definition of the 2D–3D transition used in this work. We define as critical thickness the maximum deposited equivalent layer thickness that results in samples where no 3D features can be observed at room temperature. Because we do not perform analysis *in situ* we cannot exclude that InAs/GaAs samples with an equivalent layer between 1.2 and 2.0 ML may appear 2D during the growth process, and that the 3D transition takes place during the postgrowth cooling down. In other words, our analysis gives an accurate value of the critical *coverage* d_c for the 2D–3D transition, while it cannot answer the question whether a larger coverage could persist *as a metastable state* during the growth process, so that thicker 2D layers might be detected by *in situ* measurements.

Such a picture would be compatible with the recent results of Steimetz *et al.*[24] that performed reflectance anisotropy spectroscopy (RAS) measurements on MOVPE-grown InAs/GaAs samples, reporting a critical thickness of about 2 ML. However, it must be noted that even the *in situ* determinations of the critical thickness are based on an *ex situ* calibration of the growth rate [obtained, for example, by photoluminescence (PL) or high-resolution x-ray diffraction HRXRD on different samples].

Alternatively one may explain the discrepancy by considering that all the measurements performed *in situ* (both RHEED in MBE and ellipsometry in MOVPE) do rely on signals averaged over wide sample areas, and this could shift d_c towards higher values. We, in fact, are able to detect, by SFM, very small departures from flat (2D) topography that should instead appear as a negligible signal change in RHEED or ellipsometry.

The calculation of the total island volume shows that the number of atoms contained therein corresponds to the fraction of deposited monolayers exceeding 1.0 ML for InAs and 2.0 ML for InP, respectively. This fact demonstrates that the growth for both systems is SK with 1 and 2 ML wetting layers, respectively.

Besides the absolute value of d_c, it is interesting to discuss its relation to the growth and to the material system parameters and to make a comparison with the predictions of the available models. We did not observe any dependence of the critical thickness on the growth parameters (growth rate and deposition temperature) for InAs/GaAs and a negligible dependence from the growth rate for InP/GaAs. Most of the experimental works concerning the critical thickness for the transition do not investigate such a possible dependence, whereas a strong dependence on the growth rate has been reported for a different system. In fact in an early work[25] Grandjean and Massies studied the epitaxy of $In_xGa_{1-x}As/GaAs$ ($0.35 < x < 0.53$) grown by MBE with different values of the growth rate. They report a noticeable trend towards higher d_c while increasing the growth rate and they conclude that this fact "is a confirmation that the mass transport at the surface is the key parameter which governs the growth rate in this highly mismatched system."

A dependence on v_g is predicted by some models. Spencer and Vorhees,[20] while studying the morphological instability of a growing strained film, leading to island formation, suggested that the critical thickness should scale with v_g/D_s (D_s is the surface mobility of the atoms), whereas following Snyder *et al.*,[12] it should scale with $\sqrt{v_g/D_s}$. Nevertheless, in Ref. 12 no such a dependence was observed even after a fivefold increase in the growth rate, which should lead at least to a factor of 2 in d_c.

However, the major feature to point out here is the dependence of d_c on the misfit. Spencer and Vorhees[20] and Snyder *et al.*[12] suggest, respectively, a dependence on f^{-8} and on f^{-4} for the critical thickness. Our experimental results, although related to only two systems, contradict these previsions and suggest a much different dependence which could be roughly f^{-1}. Also, the data reported in Ref. 25 could be better fitted by a quasi-linear inverse dependence on the misfit rather than by a higher power law. These facts suggest that the instability leading to island formation is a complex phenomenon which cannot be described only by kinetic or by energetic arguments, most probably an accurate description requires both approaches.

The role of the bi-dimensional platelets which appear on the surface of the samples immediately before islanding takes place is another important feature to discuss.

The existence of these structures was suggested in Ref. 9 in order to explain the size distribution of the InAs islands grown by MBE. In that article it was assumed that the 2D–3D transition should occur after a nominal deposition of 1.7 ML, in agreement with most literature data. Following Ref. 9, for energy minimization reasons, at 1.7 ML the platelets should spontaneously transform into 3D islands while maintaining the same number of atoms (about a few 10^4). This interpretation of the platelets as seeds for the islands is obviously strongly influenced by the value of d_c. As a matter of fact in our samples the number of atoms in the platelets is much lower and of the order of a few thousand atoms. Moreover, the surface density of the platelets just below and of the islands just above the transition is quite different, as shown in Figs. 2 and 3. As the amount of deposited material in the samples of Figs. 2 and 3 is the same within the experimental error, the growth of the islands appears to occur by transport and accumulation of the atoms of a few platelets and not of a single one.

A further confirmation of this growth mechanism comes from the InP system. In fact, the dimension of the platelets is the same as for InAs. On the contrary, the dimensions of the smallest islands are well described, for both systems, by the model of Ref. 10, which indicates that the volume of the InP islands is about 30 times the corresponding volume for InAs.

V. CONCLUSIONS

The 2D–3D transition for InAs/GaAs(001) samples grown by MOVPE has been studied. The experiments confirm that the system follows the SK growth mode with a measured critical thickness, d_c, of (1.2 ± 0.1) ML. This value is somewhat smaller than the one reported for similar layers grown by MBE. We may explain this discrepancy in terms of the different ways of determining d_c, by *in situ*, or by *ex situ* measurements, i.e., we may assume that *in situ* measurements are depicting metastable states, while our results are related to samples that reached thermodynamic equilibrium. On the other hand, one should also take into account that MOVPE and MBE growths are different physical processes (mainly in two aspects: MOVPE samples are grown in hydrogen atmosphere instead of high vacuum, and they undergo a slower cooling with respect to MBE samples), and one cannot exclude that a different d_c could arise from these facts.

We have also shown that, before the transition takes place, the surface of the samples is partially covered by small bi-dimensional structures which supply the material for the first developing islands, but which cannot be strictly considered as island precursors. In fact, the surface density of the platelets just before the 3D transition and the island density just after the 3D transition are quite different.

Last, we have demonstrated that the combined use of RBS and SFM is a powerful tool to obtain quantitative morphological information with submonolayer accuracy.

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[1]Y. Arakawa and H. Sakaki, Appl. Phys. Lett. **40**, 939 (1982).
[2]D. Leonard, M. Krishnamurthy, C. M. Reaves, S. P. Denbaars, and P. M. Petroff, Appl. Phys. Lett. **63**, 3203 (1993).
[3]J. M. Moison, F. Houzay, F. Barthe, L. Leprince, E. André, and O. Vatel, Appl. Phys. Lett. **64**, 196 (1994).
[4]S. Guha, A. Madhukar, and K. C. Rajkumar, Appl. Phys. Lett. **57**, 2110 (1990).
[5]J. Ahopelto, A. A. Yamaguchi, K. Nishi, A. Usui, and H. Sakaki, Jpn. J. Appl. Phys., Part 1 **32**, L32 (1993).
[6]A. A. Chernov, *Modern Crystallography III—Solid State Sciences* (Springer, Berlin, 1984), Vol. 36, p. 88.
[7]D. J. Eaglesham and M. Cerullo, Phys. Rev. Lett. **64**, 1943 (1990).
[8]J. Tersoff and R. M. Tromp, Phys. Rev. Lett. **70**, 2782 (1993).
[9]C. Priester and M. Lannoo, Phys. Rev. Lett. **75**, 93 (1995).
[10]M. Berti, A. V. Drigo, A. Giuliani, M. Mazzer, A. Camporese, G. Rossetto, and G. Torzo, J. Appl. Phys. **80**, 1931 (1996).
[11]C. W. Snyder, B. G. Orr, D. Kessler, and L. M. Sander, Phys. Rev. Lett. **66**, 3032 (1991).
[12]C. W. Snyder, J. F. Mansfield, and B. G. Orr, Phys. Rev. B **46**, 9551 (1992).
[13]D. Leonard, K. Pond, and P. M. Petroff, Phys. Rev. B **50**, 11687 (1994).
[14]H. Kitabayashi and T. Waho, J. Cryst. Growth **150**, 152 (1995).
[15]A. Madhukar, Q. Xie, P. Chen, and A. Konkar, Appl. Phys. Lett. **64**, 2727 (1994).
[16]Y. Nabetani, N. Yamamoto, T. Tokuda, and A. Sasaki, J. Cryst. Growth **146**, 363 (1995).
[17]A. Sasaki, Thin Solid Films **267**, 24 (1995).
[18]K. Nishi, R. Mirin, D. Leonard, G. Medeiros-Ribeiro, P. M. Petroff, and A. C. Gossard, J. Appl. Phys. **80**, 3466 (1996).
[19]Q. Xie, N. P. Kobayashi, T. R. Ramachandran, A. Kalburge, P. Chen, and A. Madhukar, J. Vac. Sci. Technol. B **14**, 2203 (1996).
[20]B. J. Spencer, P. W. Vorhees, and S. H. Davis, J. Appl. Phys. **73**, 4955 (1993).
[21]M. Berti, A. V. Drigo, and G. Torzo, Microsc. Microanal. Microstruct. **6**, 505 (1995).
[22]M. Mazzer (unpublished).
[23]M. Sopanen, H. Lipsanen, and J. Ahopelto, Appl. Phys. Lett. **67**, 3768 (1995).
[24]E. Steimetz, J. T. Zettler, F. Schienle, T. Trepk, T. Wethcamp, W. Richter, and I. Sieber, Appl. Surf. Sci. **107**, 203 (1996).
[25]N. Grandjean and J. Massies, Semicond. Sci. Technol. **8**, 2031 (1993).