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KINETIC PATHWAYS OF THE GROWTH MODE TRANSITION DURING Ge/Si(001) HETEROEPITAXY

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Abstract. *In situ* reflection high-energy electron diffraction, atomic force microscopy and photoluminescence spectroscopy have been combined to analyze the kinetics of the growth mode transition in the Ge/Si(001) system. By performing experiments in the dynamic growth regime and under growth interruption, we clearly establish the existence of intermediate clusters. We show that these clusters are metastable both in view of structural and optical properties. In particular, experiments performed with growth interruption have revealed that the two-dimensional wetting layers undergo a morphological instability well before reaching the critical thickness.

1. INTRODUCTION

The growth of Ge on Si is considered as a typical example of the Stranski-Krastanow (SK) growth and has been a subject of numerous investigations for many years in the past [1-3]. Because Ge has a lower surface free energy than Si, the growth of Ge on Si is expected to proceed via a layer-by-layer (2D) growth mode. However, since the lattice parameter of Ge is about 4% larger than that of Si, Ge grows on Si in a 2D mode only below a certain thickness, the so-called critical thickness, beyond which a transition to an island (3D) mode occurs. From thermodynamic considerations, today most scientists agree that the island formation is energetically favorable because the energy which is gained from a partial strain relaxation by elastic deformation of the islands and the substrate is large enough to outweigh the increase of the surface energy due to the increase of the surface area [4]. The kinetics of the growth mode transition from two-dimensional layers to islanding growth are, on the other hand, not fully understood. The general picture of the SK growth model is that the 2D-3D growth mode transition is sudden and spontaneous, as soon as the built-in strain energy exceeds the critical value.

A result of particular interest is the observation by the Lagally's group of elongated {105} faceted hut clusters, whose existence has been interpreted as an intermediate and metastable phase between 2D layers and macroscopic 3D islands [5]. Despite the important investigations of the hut clusters by different techniques [6-10], it is still unclear whether these clusters are formed before or after the growth mode transition. Furthermore, the metastability of the hut clusters has never been clearly demonstrated, neither in view of structural nor optical properties.

Following our recent observation of an intermediate phase between 2D layers and 3D islands during the Ge/Si growth [11], we have undertaken experiments with growth interruption in the regions near the growth mode transition. By combining structural and optical characterizations, we clearly establish the existence of intermediate clusters and show that they are metastable both in view of structural and optical properties. We provide evidence that the 2D

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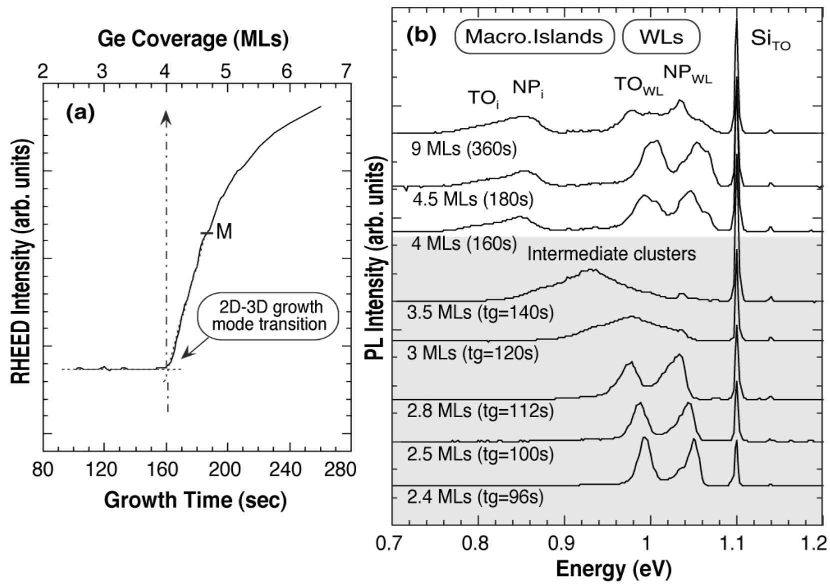

Fig. 1. (a) Variation of the RHEED intensity of a 3D spot as a function of the Ge growth time (lower axis) or the Ge coverage (upper axis). We note that to precisely determine the growth time (t_{Ge}) or the critical thickness (h_c), we searched the inflexion point M of $I(t_{Ge})$ and assumed that the critical thickness (h_c) corresponds to the intersection point of the tangent at M with the base line. (b) 11-K PL spectra illustrating three distinct stages of Ge growth in the dynamic growth regime when increasing θ_{Ge}; (i) growth of entirely pseudomorphic 2D layers up to 2.8 MLs; (ii) formation of intermediate clusters for θ_{Ge} in between 3 and 3.5 MLs; (iii) formation of 3D macroscopic islands for θ_{Ge} larger than 4 MLs.

layers sustain a morphological instability before reaching the critical thickness, and that pseudomorphic 2D layers are stable only for Ge coverages less than 60% of the critical thickness.

2. EXPERIMENTAL

Experiments were carried out in an ultrahigh-vacuum chemical-vapor deposition (UHV-CVD) system. Pure SiH_4 and hydrogen-diluted (10%) GeH_4 were used as gas sources. The system has a base pressure better than $1\cdot10^{-10}$ Torr, and the pressure during growth was about $5\cdot10^{-4}$ Torr. The growth chamber is equipped with a differentially-pumped reflection high-energy electron diffraction (RHEED) system, allowing us to probe the growing surface even at high partial pressures of hydrides. Ge deposition was carried out at 700 °C to avoid the formation of possible metastable layers due to a low-temperature growth. The Ge growth rate, estimated from RHEED oscillations at 550 °C, is ~1.5 monolayers per minute (MLs/min). We note that at high growth temperatures (larger than 700 °C), the Ge growth proceeds via step flow regime, no RHEED intensity oscillations can be observed. However, since the measured quantity is the variation of the RHEED intensity versus the Ge growth time (t_{Ge}), a possible uncertainty on the exact value of the critical thickness (h_c) at 700 °C compared to that at 550 °C does not affect our conclusions. Details of the experimental setup and growth conditions can be found elsewhere [12].

3. RESULTS AND DISCUSSION

In order to determine the existence of intermediate clusters between 2D layers and 3D islands, one of the most crucial steps is to determine the Ge coverage (θ_{Ge}) or the growth time (t_{Ge}) at which 3D islands are formed. This can be done by means of RHEED. It is now well established that the 2D growth regime is associated with the observation of streaky RHEED patterns due to reflection diffraction on a smooth surface, while the 3D growth is characterized by spotty patterns due to transmission diffraction through 3D islands [13]. The transition from 2D to 3D growth can be precisely determined by measuring the variation of the RHEED intensity of a bulk-type diffraction spot as a function of θ_{Ge} or of t_{Ge}. A typical result of such a measurement is reported in Fig. 1(a). The 2D-3D transition which is observed at t_{Ge}= 160 s appears to be very sharp as expected.

The corresponding critical thickness is 4 MLs. Fig. 1(b) shows the PL spectrum evolution of a Ge layer when θ_{Ge} increases from 2.4 to 9 MLs. The samples were capped with a 30 nm thick Si layer, which was grown right after suppressing the GeH_4 flux (*i.e. without growth interruption*). Such a growth condition is considered as the dynamic growth regime. The spectra in the shadow part of the figure correspond to the 2D growth regime while those in the upper correspond to the islanding mode. Apart from the narrow peak at 1098 meV which is attributed to the TO-phonon-assisted transitions in the Si substrate, the sample spectra with θ_{Ge} below 2.8 MLs *only* exhibit two main lines, labelled NP_{WL} and TO_{WL}, that are respectively attributed to the no-phonon line and its TO-phonon replica of the narrow Ge quantum well. This clearly indicates that in the dynamic growth regime the Ge 2D layers are stable for θ_{Ge} up to 2.8 MLs. For samples obtained after the 2D-3D transition (i.e., θ_{Ge} larger than 4 MLs), the spectra exhibit two series of lines that correspond to the Ge wetting layers (WLs) and Ge islands, respectively. The pair of lines located at high energies stems from the WLs while the two broader peaks observed at energies below 860 meV and labelled NP_i and TO_i can be respectively attributed to no-phonon and TO phonon-assisted transitions of *macroscopic* islands [11, 14, 15].

The feature of particular interest concerns the samples with θ_{Ge}= 3 and 3.5 MLs, that are obtained just before the 2D-3D transition. The spectra are completely different from those obtained both in the 2D and 3D growth regimes described above. They are dominated by an intense and very broad line while the WL's component has completely disappeared. This line is redshifted when θ_{Ge} increases from 3 to 3.5 MLs and then completely disappears after the onset of 3D island formation. We note that the weak peak observed at ~1034 meV is the replica of the Si_{TO} peak at zone center (O^{Γ}) [16].

The surface morphology corresponding to θ_{Ge}= 3 MLs (t_{Ge}= 120 s) is presented in Fig. 2(a). Whereas for Ge coverage below 2.8 MLs the surface is planar, the present surface exhibits islands with a very low density, near $6x10^7$ cm^{-2}. The island dimension is about ~1-2 nm in height and 40-50 nm in width. Displayed in the inset is an image of a single island. The island exhibits a truncated pyramidal shape with four sidewall facets formed by {105} planes and terminated on the top by a (100) plane. When θ_{Ge} increases from 3 to 3.5 MLs, both the island density and size increase very slightly while the island shape remains almost unchanged. The very slight increase of the island density can be correlated well with the RHEED results of Fig. 1(a), which indicates that the 2D growth is still maintained for θ_{Ge} up to 4 MLs. Actually, most of added Ge below the critical thickness goes in the WLs.

With a further increase of the film thickness up to the critical thickness, macroscopic islands are spontaneously formed. The corresponding surface morphology is presented in Fig. 2(b), which reveals the formation of islands with two different sizes and shapes, in agreement with previous works [17, 18]. Small islands are square-based {104}- and {103}-faceted pyramids while larger islands are multifaceted domes. The fact that the {105}-faceted islands are formed just before the formation of 3D islands indicates that they are intermediate between 2D layers and 3D macroscopic islands. These islands are found to completely disappear after the onset of the 3D island formation both from the optical and structural points of view. This provides a clear evidence that they are metastable against the formation of 3D islands. To clearly distinguish these intermediate islands from 3D islands, we refer to them as *"intermediate clusters"*.

The metastability state of intermediate clusters is further demonstrated in experiments with growth interruption (GI), where the GeH_4 flux is suppressed while the substrate temperature is kept constant. As described above, in the dynamic regime, the RHEED patterns corresponding to the intermediate-cluster surface are predominantly streaky. They are however found to gradually transform into spotty patterns within the first minute of GI, thus indicating the formation of 3D islands. Fig. 2(c) shows what has become the intermediate-cluster surface after 3 min of GI. The surface now exhibits islands, all of which have domed shape. The island dimensions, about 180 nm in base and 44 nm in height, are much larger than those of intermediate clusters. An interesting feature that can be observed in the inset of Fig. 2(c) is the existence of a depletion zone with a reduced Ge thickness around the islands. This indicates that Ge had diffused from the 2D layers towards the intermediate clusters to form larger islands. These results clearly demonstrate that the pyramidal clusters are metastable and are transformed into larger dome-shaped islands under GI. We note that a slight increase of the island density observed after GI may arise from a random nucleation process and an uncertainty of different measured surface areas. Fig. 2(d) shows the evolution of PL spectra with GI. In the lower curve, the PL of intermediate clusters is shown. Interestingly, the PL

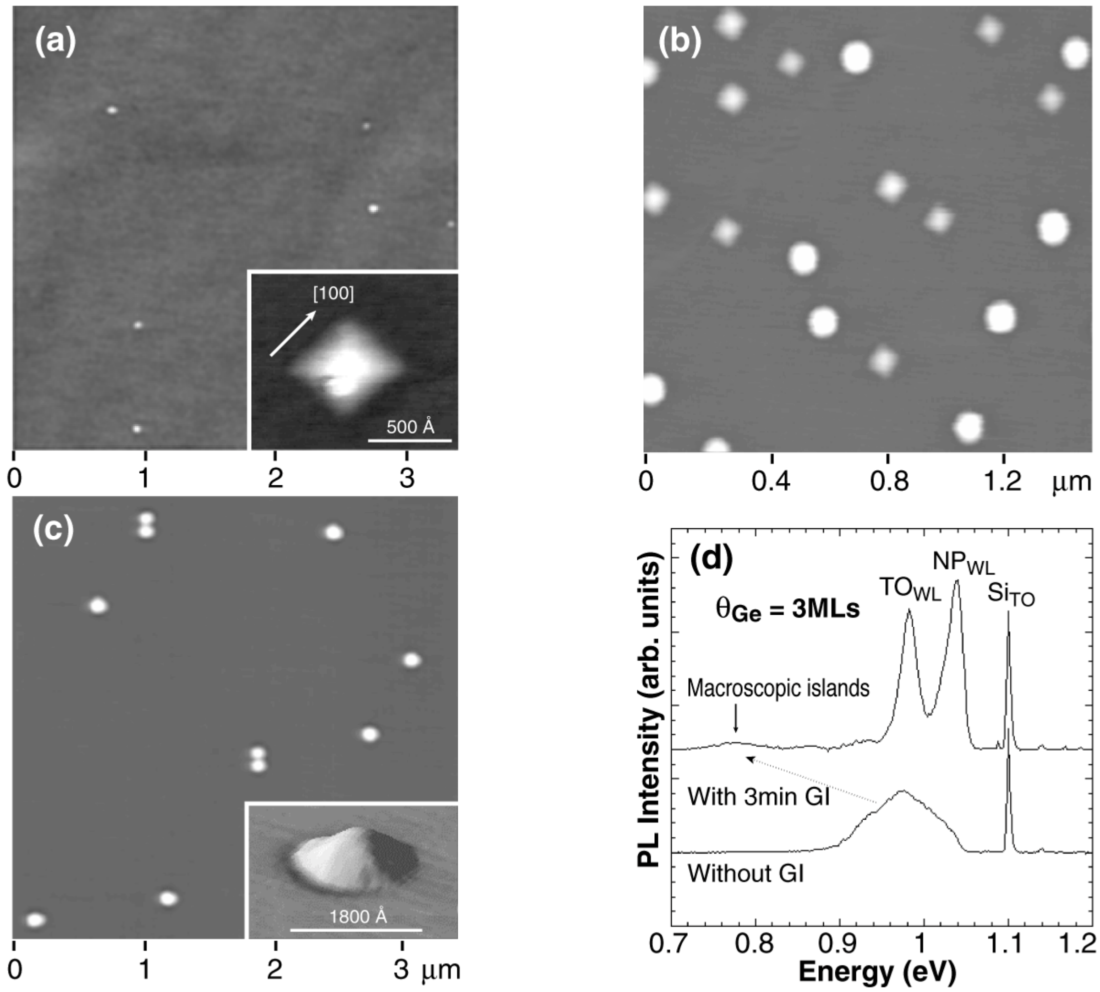

Fig. 2. Evidence on the metastability of intermediate clusters both in the dynamic growth regime and under growth interruption. (a) AFM image of a sample surface at θ_{Ge}= 3 MLs. The intermediate cluster are truncated pyramids formed by four {105} facets on a squared base and terminated at the top by a {100} plane. (b) AFM image of a sample surface at θ_{Ge}= 4 MLs, i.e. just after the 2D-3D transition. The surface exhibits macroscopic islands with two different sizes and shapes. The {105}-faceted intermediate clusters have completely disappeared. (c) AFM image of a sample surface at θ_{Ge}= 3 MLs after 3 min GI. Shown in the inset is an image of an isolated island. (d) 12-K PL spectrum of intermediate clusters without GI (lower curve) and with 3 min GI (upper curve).

of the sample obtained after 3 min GI (upper curve) reveals the electron-hole recombination simultaneously from the WLs and islands. The appearance of the WL component can be explained by the existence of a Ge depletion zone around the islands. Indeed, since the 2D layers around the islands have a smaller thickness than that in between the islands, the confinement energy becomes higher, leading hence to the formation of a potential barrier which prevents the carriers to be transferred from the WLs to the islands. The quenching of the wetting-layer component observed for intermediate clusters can be in the same way explained by an efficient transfer of the carriers from the WLs to the clusters.

In view of epitaxial growth, the intermediate clusters can be characterized by two main criteria. First, they are formed in advance of the 2D-3D growth mode transition. Second, they have a very low density, that varies only slightly when the Ge coverage increases from 3 MLs up to the critical value of 4 MLs. Furthermore, the island density has been shown to be independent on the growth temperature [11]. A possible mechanism leading to the formation of such clusters is that the 2D layer surface, before reaching the critical thickness, exhib-

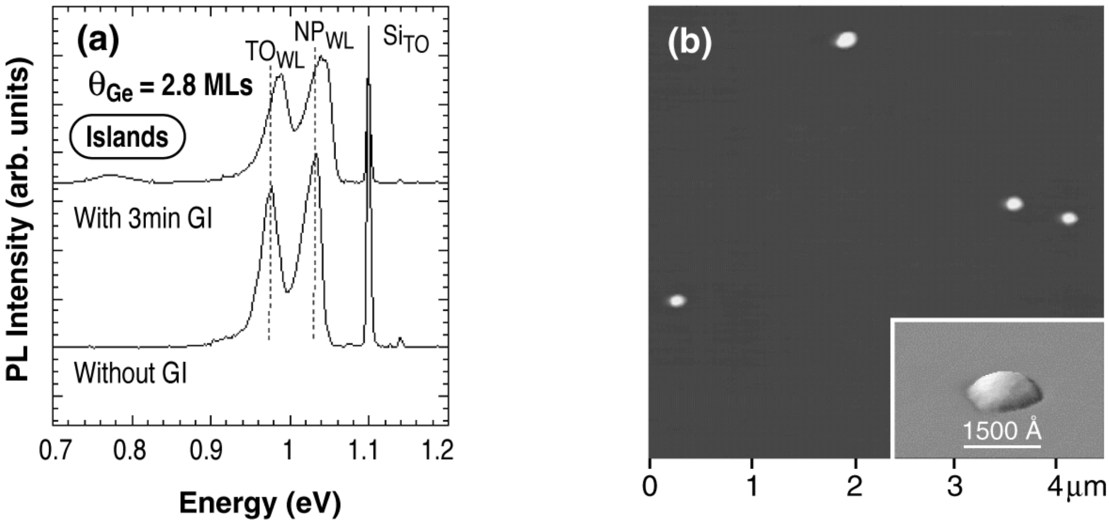

Fig. 3. Evolution of the PL spectra (a) and surface morphology (b) of a sample at θ_{Ge}= 2.8 MLs with GI.

its a local strain relaxation in some surface regions, providing preferential sites for cluster nucleation. To further illuminate this hypothesis, we have performed growth-interruption experiments on samples, which manifest a 2D growth behavior in the dynamic growth regime. Indeed, if the sample surface at these growth stages is morphologically unstable, it should evolve to a state where the total energy of the system is minimum.

Fig. 3(a) shows the change in the PL spectra with growth interruption for θ_{Ge}= 2.8 MLs. The lower curve corresponds to the sample without GI. The spectrum only reveals the presence of the WL's component, which clearly indicates that planar growth is still stable at this coverage in the dynamic regime. The spectrum of the sample with 3 min GI (upper curve) reveals, in addition to the WL's component, the appearance of a broad line located at lower energies. This later can be unambiguously attributed to macroscopic islands. The fact that the NP_{WL} and TO_{WL} lines exhibit a blueshift (of ~15 meV) clearly indicates that islands have been formed by consuming Ge from the 2D layers. Displayed in Fig. 3(b) is the surface morphology of the corresponding sample. While the sample surface at θ_{Ge}= 2.8 MLs without GI is very smooth, the present surface exhibits 3D islands in agreement with the above PL results. The island density is ~$2x10^7$ cm^{-2}, their dimensions are 150 nm in base and 40 nm in height. The decrease of both island density and dimensions, compared to those of Fig. 3(c), clearly reflects the decrease of the overall metastability of the layers when the Ge coverage decreased from 3 to 2.8 MLs.

This tendency is further confirmed for a Ge coverage reduced down to 2.5 MLs, as indicated in Fig. 4(a). The spectrum of the sample without GI, shown in the lower curve, exhibits only a pair of NP_{WL} and TO_{WL} lines indicating that the two-dimensional layers are in a stable state. The spectrum of the sample with 3 min GI (upper curve) simultaneously reveals the appearance of the island-related component and a blueshift of the WL component. This again indicates that the islands have been formed by consuming Ge from the WLs. A smaller blueshift of the WL lines, of ~7 meV, and also a higher energy of the island-related peak clearly indicate that the overall metastability state of the present layers is reduced compared to that with θ_{Ge}= 2.8 MLs.

To further understand the effect of GI experiments on the morphological state of the growing surface, we have carried out similar experiments on samples with θ_{Ge}= 2.4 MLs, i.e. with one tenth of ML smaller thickness than the above sample. The PL results are reported in Fig. 4(b). Interestingly, the growth-interrupted spectrum (upper curve) does not reveal any shift for both NP_{WL} and TO_{WL} lines. This is consistent with a complete absence of the island-related component. Furthermore, AFM measurements on the corresponding surface do not reveal any presence of islands, confirming that the surface remains planar after GI. These results demonstrate that the

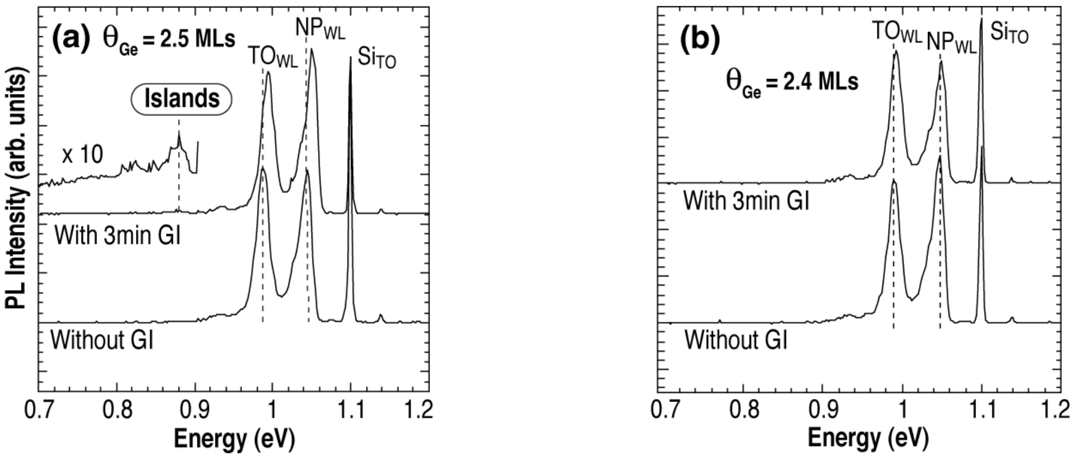

Fig. 4. (a) Changes in the 11-K PL spectra of a sample at θ_{Ge}= 2.5 MLs with growth interruption. (b) 11-K PL spectrum of a sample at θ_{Ge}= 2.4 MLs without GI (lower curve) and with 3 min GI (upper curve). No shift is observed on the WL lines after GI, indicating that the 2D layers are in a stable state both before and after GI.

2D layers with a Ge coverage of 2.4 MLs are in a stable state both before and after growth interruption. It should be pointed out that similar results are obtained for all layers whose Ge coverage is smaller than 2.4 MLs.

The above structural and optical results clearly indicate that the driving force leading to the island formation under GI experiments arises from the metastability of the 2D layers. Indeed, if a 2D system is in a metastable state, the decay towards equilibrium is governed by a nucleation process. The Ge wetting-layer surface is shown to undergo a morphological instability, the degree of which is found to increase with increasing the Ge coverage. Intermediate clusters are formed in the dynamic growth regime when the morphological instability of 2D layers becomes so high that a local strain relaxation of the surface lattice may occur in some surface regions. This would provide preferential sites for cluster nucleation. Of particular interest, pseudomorphic and stable 2D layers are obtained only for Ge coverage less than 2.4 MLs, i.e. less than 60 % of the critical thickness. These results also indicate that if thick 2D layers are needed in some applications, growth interruption during growth should be avoided.

4. CONCLUSION

To summarize, we have shown that experiments performed with growth interruption are an excellent approach to reveal the metastability state of 2D layers. Two important results concerning the kinetics of the Ge/Si 2D-3D growth mode transition have been revealed. First, the existence of intermediate clusters is clearly established. These clusters are shown to be metastable both in view of structural and optical properties. Second, the Ge wetting-layer surface is found to undergo a morphological instability well before reaching the critical thickness. By controlling the degree of instability of 2D layers, we have shown that islands with different sizes, shapes and optical properties can be formed. Our results indicate that the 2D-3D transition is not as spontaneous as currently believed in the Stranski-Krastanow description. It is believed that our finding on the instability of 2D layers well before the 2D-3D growth mode transition can be generalized to other highly lattice-mismatched heteroepitaxial systems.

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