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Stranski-Krastanov growth mode during the molecular beam epitaxy of highly strained GaN

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It is demonstrated by *in situ* reflection-high-energy-electron-diffraction studies that the growth of hexagonal GaN on AlN occurs either purely in a layer-by-layer mode or in a Stranski-Krastanov mode, depending on the substrate temperature. Nanometric GaN islands embedded in AlN were fabricated by controlling the growth mode. Electron microscopy and atomic-force microscopy revealed that the dimensions of GaN dots could be varied down to values where zero-dimensional quantum effects are expected: the smallest dots were typically 10 nm wide and 2 nm high. These results open the way to the fabrication of quantum dots in materials with optical properties in the uv wavelength range. [S0163-1829(97)50740-5]

A great deal of work has been devoted recently to the elaboration of lattice-mismatched heterostructures, partly due to the progress in materials growth techniques. For semiconductor as well as for metallic systems, this interest is motivated by the possibility of tailoring the physical properties of the heterostructures by a suitable combination of materials. However, one major difficulty in achieving defect-free epitaxial growth of strained heterostructures is related to strain relaxation, which governs the growth mode. Depending on the interplay between elastic and plastic relaxation, three growth modes have been described, namely Frank-Van der Merwe (FvdM), Volmer-Weber (VW), or Stranski-Krastanov (SK). Schematically, the FvdM mode corresponds to a bidimensional (2D), layer-by-layer growth mode, the VW mode to 3D growth, and the SK mode to 2D growth of a few monolayers followed by 3D island formation.

In the FvdM growth mode, the increase in elastic energy as a function of the film thickness is balanced by the formation of misfit dislocations. This is the case, for instance, when ZnTe is grown on CdTe (6% mismatch). For a critical thickness of about 6 ML, plastic relaxation occurs through the formation of misfit dislocations but the growth remains layer by layer (2D), as shown by reflection-high-energy-electron-diffraction (RHEED) oscillations.[1]

Alternatively, Ge/Si (Ref. 2) and InAs/GaAs (Ref. 3) systems grow in the SK mode and relaxation occurs through 3D islanding after 2D growth of a few monolayers. This mode is often depicted as giving rise to two critical thicknesses: a first one resulting from elastic relaxation at the free surfaces of 3D islands that is followed, for further deposition, by plastic relaxation. Interesting specific consequences can result from the Stranski-Krastanov growth mode. For instance, in the InAs/GaAs system, quantum dots are now being grown[4] and the control of self-organization of large quantum dots assembly has become a subject of intense interest.

An emergent field in semiconductors physics is the III-V nitride semiconductors, which are widely studied for their potential as blue light emitter devices and UV emitters/detectors. As for other semiconductors, present and future applications require growth of high-quality lattice-mismatched heterostructures. In view of this, it is particularly important to understand the strain relaxation mechanisms during the first stages of growth.

Despite the importance of the subject, data concerning the growth mode or the critical thickness of nitrides, mainly AlN and GaN, are scarce and are generally obtained indirectly.[5,6] A notable exception is a critical thickness determination for GaN on sapphire by means of synchrotron x-ray diffraction.[7] However, in this case, the GaN was grown on a very thin AlN buffer on sapphire and the state of strain of AlN could probably bias the critical thickness determination. The recent report of GaN dots fabricated by metal-organic chemical-vapor deposition (MOCVD) on $Al_xGa_{1-x}N$ surfaces should also be mentioned.[8] In this case, the growth conditions were modified by adding TESi to the substrate surface which, according to the authors, changes the surface energy. However, the minimum size of the dots was 40 nm $\times$ 6 nm, too big to expect large quantum effects.

In this paper, we mainly report a real-time RHEED study of the molecular-beam epitaxy of wurtzite-type GaN on AlN (2.7% lattice mismatch). The RHEED streak spacing was measured as a function of the deposition time, leading to a quantitative determination of the in-plane lattice parameter variation and of the state of strain with respect to the substrate. More precisely, we demonstrate that GaN can be made to grow on AlN in a Stranski-Krastanov (SK) mode, with a 2D growth during about 2 ML followed by 3D island formation, which leads to the formation of very small dots, the dimensions and distribution of which can be varied with the growth conditions.

The occurrence of the SK growth mode was found to be temperature dependent and it was shown that growth was purely 2D at low temperature. In the temperature range where 3D islands formed, it was found that further GaN deposition resulted in island coalescence followed by a plastic relaxation through misfit dislocation formation. Conversely, we have shown that the growth of AlN on GaN is always 2D, with plastic relaxation occurring through misfit dislocation formation.

Our results then demonstrate that, through control of the epitaxial growth of nitride semiconductors, it should be possible to extend nanostructures physics to the ultraviolet wavelength range.

The growth of (0001) AlN and GaN with wurtzite structure was carried out by molecular-beam epitaxy on sapphire substrates. Atomic nitrogen was produced by a rf plasma source. After nitridation of the substrate by exposing it to nitrogen plasma, a thin (about 15 ML) AlN buffer was deposited at a substrate temperature T_s of 500 °C, followed by the growth of a 2-μm-thick GaN buffer at 650 °C and of a 200-nm-thick AlN layer. Note that the AlN layer was thick enough to be almost totally relaxed with respect to the GaN buffer, as could be deduced from the RHEED streak spacing value. Then the relaxation of GaN deposited on AlN was studied by RHEED (electron beam energy of 34 keV) using a charge-couple-device camera, a tape recorder, and software for quantitative image analysis. Whereas the RHEED pattern is streaky for 2D growth, occurrence of a 3D growth mode results in the conversion of streaks into a superposition of streaks and of Bragg spots. Evidence of a SK growth mode was found by recording the intensity of the RHEED pattern in a zone corresponding to the position of a Bragg spot as a function of the deposition time. Simultaneously, the streak separation in the RHEED pattern was measured to study the in-plane lattice parameter variations and the state of strain of the overgrown layer. Prior to these experiments, the growth rate was accurately determined by measuring RHEED oscillations.

The results are shown in Fig. 1. Depending on T_s, different behavior is observed: above 700 °C, the Bragg spot intensity increases after deposition of 2 ML, which is assigned to a 2D/3D growth mode transition. For further GaN deposition, the Bragg spot intensity remains constant, indicative of a persistent 3D growth mode. By contrast, at 620 °C, the 2D/3D transition is hardly observable and the rapid decrease of the Bragg spot intensity down to the value corresponding to the reflectivity of a smooth GaN surface (smaller than the reflectivity of the initial AlN surface) reveals a fast recovery of 2D growth. At intermediate temperatures, the intensity increase of the Bragg spot after deposition of two GaN monolayers is followed by a rapid decrease after deposition of about 6 ML, as evidence of island coalescence associated with smoothing of the RHEED streaks.

The three kinds of behavior corresponding to high T_s (>700 °C), low T_s (<620 °C) and intermediate T_s are also observed for the in-plane lattice parameter variation. In the intermediate T_s temperature range, a 1.4% relaxation assigned to island formation is followed by a *decrease* of the relaxation value corresponding to island coalescence. At high T_s, the relaxation rapidly reaches a plateau corresponding to a 3D growth mode whereas at low T_s the relaxation is small, correlated to a 2D growth mode. After island coalescence, a gradual relaxation was observed for long deposition times.

On looking more closely at the very first stage of the growth [see inset of Fig. 1(a)] one sees an oscillatory behavior of the RHEED intensity just before the large intensity increase associated with the formation of a Bragg spot. Consistent with the growth rate values determined for a thick GaN layer, the two RHEED intensity oscillations that are observed are unambiguously assigned to the deposition of two GaN monolayers followed by a transition to a 3D growth mode.

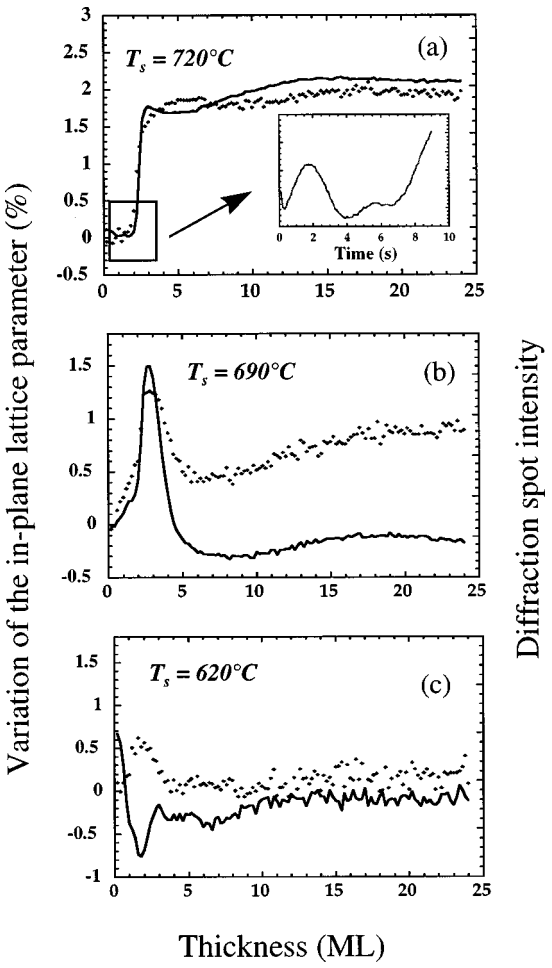

FIG. 1. Change in the in-plane lattice parameter (dotted line) and in the Bragg spot intensity (full lines) as a function of the deposition time of GaN on AlN. Note that the Bragg spot intensity is normalized to the streak intensity to take into account the change in the intensity of the RHEED diagram depending on the nature of the surface (AlN or GaN) (a) T_s=720 °C, (b) T_s=690 °C, (c) T_s=620 °C. Inset: oscillation of the RHEED diagram intensity (arbitrary units) as a function of GaN deposition time. Two oscillations are observed, corresponding to the 2D growth of two GaN monolayers. The large increase in intensity observed after 8 s corresponds to the roughening associated with 3D islanding.

The deductions from the RHEED experiments have been confirmed in two ways. First, GaN islands grown on AlN have been directly observed by atomic-force microscopy (AFM). Second, high-resolution electron microscopy (HREM) observation of a AlN/GaN superlattice and of GaN islands in AlN have confirmed that the SK growth mode was controllable by varying the growth temperature.

AFM measurements have been performed using a Nanoscope IIIA from Digital Instruments, in the tapping mode. The image of AlN shown in Fig. 2(a) is indicative of a smooth surface. Next, about four GaN monolayers were deposited on the AlN surface, as controlled by RHEED. Then both Ga and N fluxes were shuttered and the sample was cooled down to room temperature. The resulting GaN dots are shown in Fig. 2(b). They are typically 10 nm wide and 2 nm high. Their density (around 5×10^{11} cm^{-2}) was found to vary on the sample surface, possibly due to fluctuations in the nucleation process and/or inhomogeneities in the Ga flux.

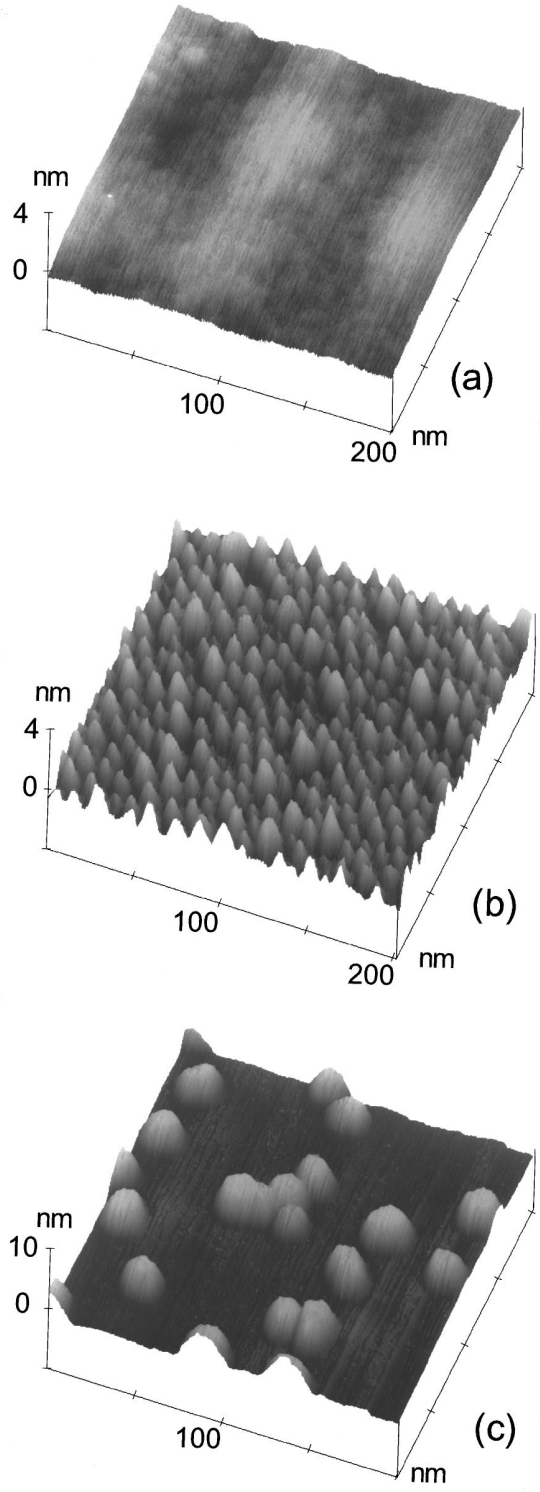

FIG. 2. (a) AFM observation of smooth AlN surface (root-mean-square roughness: 0.2 nm). The vertical scale is 4 nm/division. (b) GaN quantum dots formed by depositing the equivalent of four GaN monolayers on the smooth AlN surface immediately followed by cooling under vacuum. The vertical scale is 4 nm/division. The size of the dots is 10 nm wide and 2 nm high. (c) GaN quantum dots formed by depositing the equivalent of two GaN monolayers on the smooth AlN surface followed by exposure to N plasma during 50 sec, in order to allow structural reorganization. The vertical scale is 10 nm/division. The size of the dots is 25 nm wide and 5 nm high.

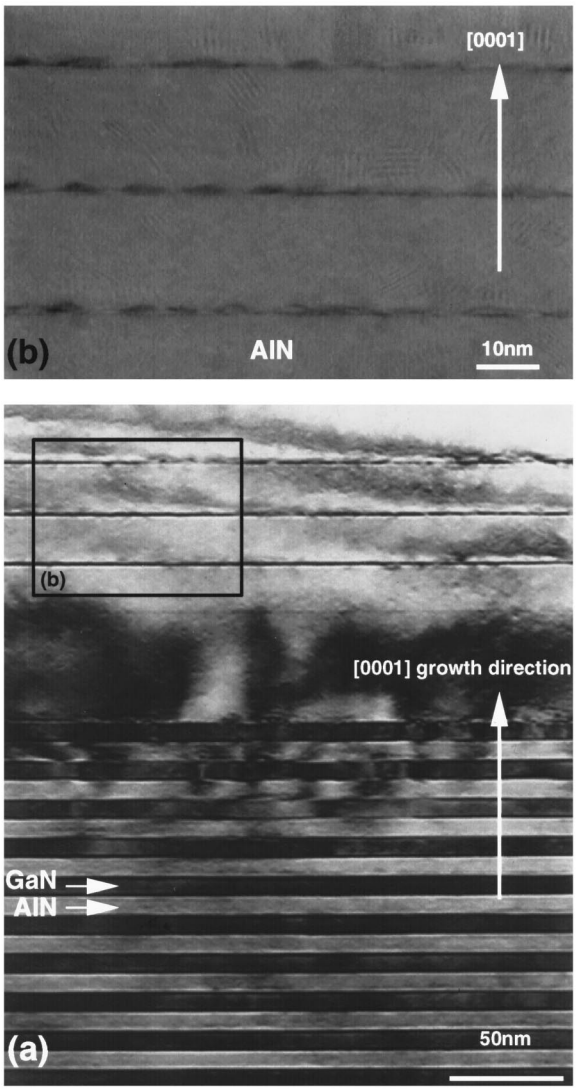

FIG. 3. (a) Two-beam bright field image [$g=(0002)$ of a GaN/AlN superlattice grown at 620 °C. The interfaces are perfectly abrupt at the monolayer scale. (b) The enlargement of the inset of Fig. 3(a) shows three layers of GaN dots capped by 20 nm of AlN. The size of the dots is consistent with AFM results, i.e., 10 nm wide and 2 nm high.

To illustrate the role of reorganization time under N plasma flux, Fig. 2(c) shows quantum dots realized at 710 °C by depositing a GaN quantity equivalent to 2 ML followed by exposure to N plasma during 50 s. Clearly, the dot density is smaller (5×10^{10} cm^{-2}) but their size is larger (25 nm wide and 5 nm high) than in the previous case, due to the reorganization process occurring under N plasma flux. In this particular case, the variation of the RHEED pattern observed during the reorganization process, namely, the appearance of inclined streaks associated with the formation of (10–13) facets, allows us to conclude that the dots are pyramids with sixfold symmetry. Then, the shape and the density of the dots were used to evaluate a total GaN quantity of about 2 ML which strongly suggests that during exposure to N plasma, dots grow to the expense of the surrounding 2D GaN layer.

Electron microscopy experiments were realized using a JEOL 4000FX microscope (Scherzer resolution about 0.17

nm) for high-resolution electron microscopy and conventional TEM observations. Cross sections were prepared using the standard techniques: mechanical polishing and argon ion milling.

In the same sample, an AlN/GaN: 8.5 nm/8.5 nm superlattice was first grown at 620 °C. For this growth temperature, as shown in Fig. 1, GaN islands rapidly coalesce leading to a 2D growth after a few monolayers. The resulting superlattice [low magnification TEM images in Fig. 3(a)] exhibits abrupt interfaces. This was confirmed by quantitative contrast analysis, which showed that no Al/Ga mixing occurred at the AlN-GaN interface. After completion of the superlattice, GaN islands embedded in AlN were achieved at a growth temperature of 700 °C. The growth was followed by RHEED and the GaN growth was interrupted after deposition of about 4 ML. Immediately after (with *no* reorganization time under N plasma flux) 20 nm of AlN were deposited to cap the islands and to smooth the sample surface. The operation was repeated three times. Electron microscopy results shown in Fig. 3(b) revealed that for this growth temperature GaN islands were formed, with dimensions consistent with AFM observations. Figure 3(b) also shows a continuous 2-ML-thick GaN layer corresponding to the 2D growth step before island formation, in agreement with RHEED experiments. A Burgers circuit drawn in the HREM images around the islands reveals that no dislocation is associated with the islands.

These results can be enlightened by noting that, due to the low ionicity of GaN, the bond bending energy is comparable to that of other III-V materials and higher than that of II-VI materials. In II-VI materials, plastic relaxation through misfit dislocation formation is favored by the low bond bending energy whereas island formation is promoted in InAs or GaN. For GaN, the elastic relaxation resulting from islanding is limited below 700 °C by the coalescence of the islands and the decrease in free surface which is demonstrated by the recovery of a streaky RHEED pattern. Then, for further GaN deposition, an additional relaxation process was observed and was tentatively assigned to the formation of misfit dislocations.

In conclusion, we have shown by a real time quantitative RHEED analysis combined with AFM and electron microscopy experiments that strained GaN layers experience a Stranski-Krastanov growth mode. Furthermore, it was found that the growth mode could be controlled by varying the growth temperature. As a consequence, the size of the GaN islands can be changed to fit desired physical properties. These experiments open the way to the realization of controlled production of quantum dots extending the wavelength domain to UV and far UV range.

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