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Control of the morphology transition for the growth of cubic GaN/AlN nanostructures

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The Stransky–Krastanow growth mode of strained layers which gives rise to a morphology transition from two-dimensional layer to three-dimensional islands is studied in details for the cubic gallium nitride on cubic aluminum nitride (GaN/AlN) system grown by molecular beam epitaxy. Besides the lattice parameter mismatch which governs this transition, we evidence the importance of two other parameters, namely the substrate temperature and the III/V flux ratio. Tuning each of these two parameters enables to control the strain relaxation mechanism of a GaN deposited onto AlN, leading to the growth of either quantum wells or quantum dots. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1527975]

It is well known that some combinations of semiconductors having a lattice mismatch in the range of 2%–10%, can exhibit a sharp transition from a layer-by-layer growth [two-dimensional (2D)] to the formation of islands [three-dimensional (3D)]. This Stranski–Krastanow (SK) growth mode allows the relaxation of highly strained 2D layers through the free surfaces of 3D islands instead of generating misfit dislocations.[1] These islands are expected to be dislocation free and thus of high structural quality. Usually their typical sizes are on the scale of a few nanometers, so that these self-assembled quantum dots (QDs) are attractive nanostructures for both fundamental physics (interplays of quantum confinement effects, Coulomb blockade effects, etc.) and device applications (QD) lasers with higher gain, temperature-insensitive laser threshold, etc.).[2]

As for III nitrides, most of the work during the last years has been done with the wurzite structure. However, optical properties of wurzite nitride-based nanostructures are stongly influenced by the presence of a huge internal electric field (few MV/cm) which comes from the spontaneous polarization and piezoelectric effects. By contrast, in zinc-blende nitrides which are grown along the nonpolar [001] axis, no internal field is present. For optoelectronics devices this difference is important because the absence of internal field in the nanostructures allows expecting a larger optical efficiency. However, the structural quality for cubic nitrides layers is still a challenge which is difficult to solve due to the lack of appropriated substrates. To overcome this problem, the localization of the carriers into QDs appears to be a solution which suppress lateral carriers diffusion, and then reduce the probability for the carriers to be trapped by the large number of dislocations which act as nonradiative recombination centers.

The purpose of this letter is to study precisely the exact growth conditions in order to obtain such cubic GaN QDs. Especially, we evidence the strong influence of the two parameters which control the strain relaxation mechanisms, namely the substrate temperature and the III/V ratio during the MBE growth. This know-how allows us to develop a method to control both types of cubic nanostructures: QDs and QWs: the dimensionality of the grown GaN (2D QW or 3D QDs) is also assessed here by transmission electron microscopy (TEM) images.

The samples were grown by plasma-assisted MBE. The metal fluxes were provided by conventional effusion cells, while active nitrogen resulted from radio frequency dissociation of N_2 using a plasma cell. The used pseudosubstrates consist of a 3-μm-thick 3C-SiC layer grown by chemical vapor deposition on Si(100) substrates.[3] Both the surface morphology and the strain relaxation of the GaN layer were monitored *in situ* by using reflection high-energy electron diffraction (RHEED). A smooth cubic AlN buffer layers with a thickness of about (~40 nm) was first obtained for a growth temperature $T_S = 720\,^{\circ}\mathrm{C}$ under stoechiometric conditions. The roughness profile of AlN deduced from ($1\,\mu\mathrm{m} \times 1\,\mu\mathrm{m}$) topographic atomic force microscopy images shows superficial steps with a maximum height of 8 Å. The structural quality of the AlN buffer layer was checked by high resolution x-ray diffraction study[4] and the purity of the cubic crystallographic phase was assessed by Raman spectroscopy measurements.[5] The influence of T_S for the growth of GaN layer was performed for a temperature range [600–720 °C] under a slight Ga flux excess ($T_{\mathrm{Ga}} = 1035\,^{\circ}\mathrm{C}$) for three growth temperatures. The Ga flux effect, after depositing the AlN buffer layer, was studied at a growth temperature as high as $T_S = 720\,^{\circ}\mathrm{C}$ by varying the Ga flux in the range of the equivalent Ga cell temperature ($T_{\mathrm{Ga}} = 1030$–$1060\,^{\circ}\mathrm{C}$) during the GaN deposition. Note that substrate temperature was measured using a thermocouple which was in mechanical contact with the sample holder using a spring to ensure a good reproducibility of the temperature measurements. The N flux remaining constant during all these experiences (it corresponds to a growth rate of 0.34 (MLs/s) as measured through the RHEED oscillations. The TEM measurements were conducted using a JEOL 4000EX microscope operated at 400 kV, and the TEM images were taken in dark-field imaging conditions.

Figure 1 shows the *in situ* variation of both the morphol-

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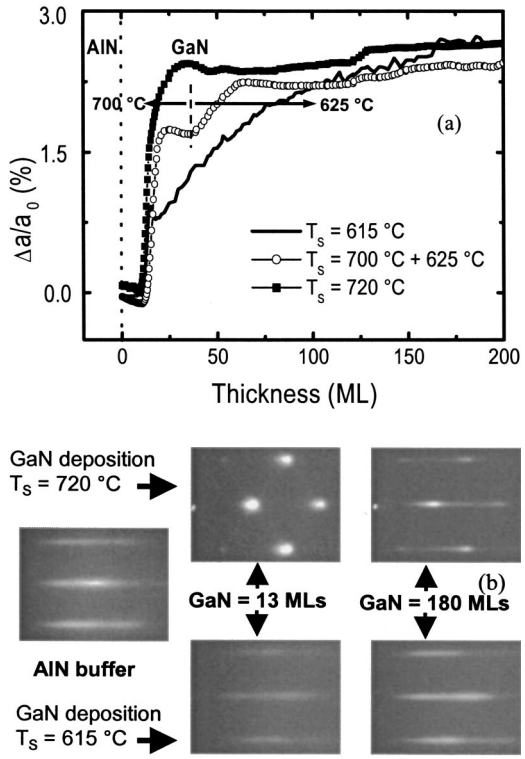

FIG. 1. RHEED observations of the change of the relaxation growth mode for GaN deposited onto AlN as a function of T_S: (a) the in-plane lattice parameter variation; and (b) the surface morphology. A 2D RHEED pattern is always obtained for GaN grown at T_S lower than 625 °C, whereas 3D RHEED pattern appears for $T_S = 720$ °C.

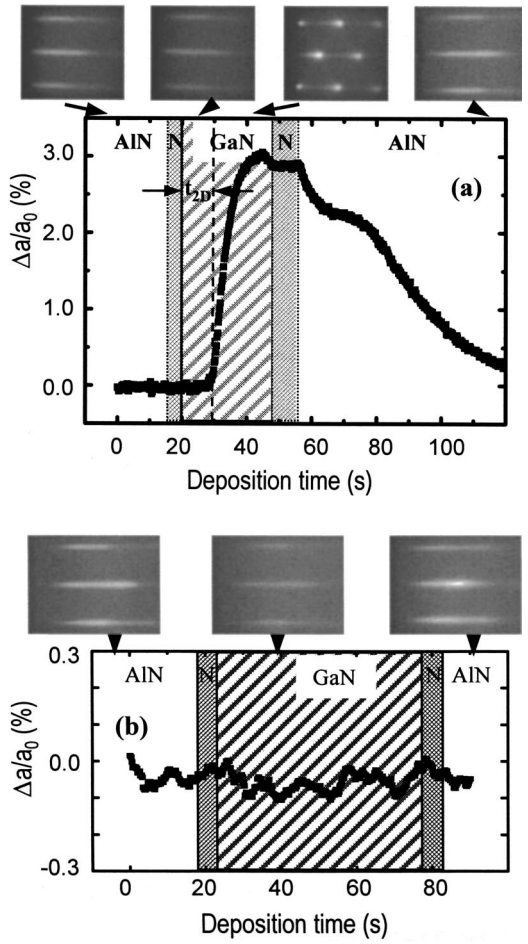

FIG. 2. Evolution of the in-plane lattice parameter and of the surface morphology during the deposition of GaN encapsulated by AlN layer: (a) for a flux ratio Ga/N~1 ($T_{Ga} = 1035$ °C); and (b) for a flux ration Ga/N ~2($T_{Ga} = 1055$ °C). The growth temperature was kept at 720 °C for both experiences.

ogy and the in-plane lattice parameter during the deposition of the GaN layer under slight Ga excess ($T_{Ga} = 1035$ °C) as a function of the substrate temperature. As it is clearly observed, when the substrate temperature is low ($T_S = 615$ °C), the in-plane lattice parameter variation corresponding to a full relaxation (2.8%) is gradually reached [Fig. 1(a)]. Meanwhile the RHEED patterns stay streaky indicating no change of the surface morphology during the whole growth process [Fig. 1(b)]. This 2D growth mode, even for GaN layers as thick as 180 MLs strongly suggests that the mismatch strain is relaxed through the formation of misfit dislocations in the 2D layer. The presence of such dislocations was evidenced by TEM,[4] although it is difficult to correlate their density with the thickness layer. This behavior corresponds then to a plastic strain relaxation.

On the contrary, for higher growth temperatures [$T_s = 720$ °C on Fig. 1(a)], the strain relaxation occurs abruptly during the first nanometers of GaN deposited layer. In addition a clear change of the surface morphology is observed thanks to the RHEED patterns (see the spotty RHEED diagram on Fig. 1(b) for a deposition of 13 MLs). Both these features indicate an elastic relaxation by forming coherent 3D islands which were clearly identified by AFM study.[6] For larger amount of GaN, however, these islands can increase and coalesce, given rise to a rough layer [see the RHEED diagram on Fig. 1(b) for 180 MLs]. The intermediate case between these two relaxation processes is also illustrated in Fig. 1 by changing the growth temperature during the GaN deposition.

These changes of the growth mode as a function of temperature can be related to some dynamics effect: when growing at low temperature, the mobility of the ad-atoms on the growth front is not sufficient to enable the growth of dots, so that plastic relaxation through the formation of misfit dislocations is favored. At higher temperature instead the dot formation is preferable as it was already observed for wurzite GaN/AlN system.[7]

An other important parameter which controls the growth and strain relaxation modes of cubic GaN on cubic AlN, is the Ga/N flux ratio. This is clearly evidenced on Fig. 2. Under stoechiometric conditions [Fig. 2(a)], the SK transition occurs after a time t_{2D} of 10 s corresponding to a 3 MLs deposition of GaN (see the 2D/3D transition on the RHEED pattern and the sharp increase of the in-plane lattice parameter). Then the time necessary to achieve a full relaxation of GaN is about 15 s corresponding to 4.5 MLs. After a growth interruption under nitrogen, it is possible to deposit AlN onto GaN QD layer and to recover a smooth surface layer with a AlN layer thickness of about 20 MLs (5 nm). This indicates that multilayer of GaN QD embedded in AlN barrier layers can be fabricated.

By contrast, it is possible with increasing the Ga flux, to delay the 2D/3D transition, and even to completely inhibit the dots formation when growing under very rich Ga conditions. Such a case is illustrated on Fig. 2(b): for Ga temperature as high as $T_{Ga} = 1050$ °C which corresponds to a Ga/N

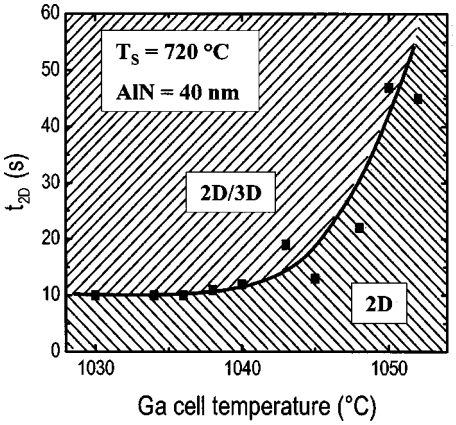

FIG. 3. Effect of Ga flux excess on the SK transition. The critical thickness of the 2D GaN layer (t_{2D}) is determined by the onset of the strong variation of the in-plane lattice parameter $\Delta a/a_0$ during the growth of GaN for various excesses of Ga. The growth temperature was kept constant ($T_S = 720\,°C$). The t_{2D} variation from 10 to 50 s corresponds to a variation of the 2D GaN thickness from 3 to 15 MLs.

ratio ≈ 2, we do not observe any variation of the in-plane lattice parameter, and any change of the RHEED pattern which stays 2D after the deposition of 15 MLs of GaN. Both these features indicate a layer-by-layer growth of a 2D GaN QW embedded into a AlN barrier.

The dependence of the SK transition on Ga coverage has been studied in more details by plotting the time t_{2D} corresponding to the onset of the SK relaxation versus the Ga temperature (Fig. 3). By changing the Ga flux by a factor 2, t_{2D} increases from 10 to 50 s, which corresponds to an increase of the critical thickness from 3 to 15 MLs. Note also that, in this set of experiments, the thickness of AlN was kept constant and thick enough in order to ensure the same 2D layer surface morphology before starting the GaN growth. Then the stacking fault density in AlN is expected to be the same for all the samples, and it cannot be explained the observed increase of the critical thickness. Variation of the critical thickness due to surfactant effects was already demonstrated for various systems such as Ge/Si[8] or InAs/GaAs,[9] hexagonal GaN/AlN,[10] but never a variation as large as a factor 5 was reported. Such behavior can be understood as due to a strong variation of surface energy when growing with a Ga excess. Indeed, it has been calculated[11] and observed experimentally[12,13] that, for hexagonal GaN grown under Ga-rich conditions, a 2 MLs Ga film is formed in order to stabilize the GaN surface. The fact that, in these conditions, a layer-by-layer growth mode is greatly favored as compared to the 3D one, can be assigned to a self-surfactant effect of Ga in the cubic GaN/AlN system: by forming a floating layer onto the surface, Ga adlayer lower the surface free energy, and then delays the islanding SK transition.

Having this know-how in hand, the growth mode of GaN on AlN can be either layer-by-layer or SK type, which allows us to grow either 2D QWs or 3D QDs just by varying the Ga/N ratio value. This is evidenced on Fig. 4 which shows the TEM images of samples grown at the same growth temperature ($T_s = 720\,°C$) but for two different Ga fluxes: for stoechiometric conditions [Fig. 4(a)], formation of GaN islands is observed on top of a 2D wetting layer. Although it is difficult to deduce the wetting layer thickness from these images, it is in qualitative agreement with the 3 MLs estimated from the RHEED data.

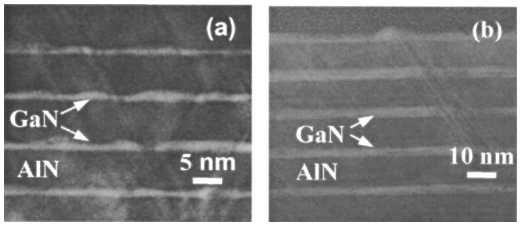

FIG. 4. Conventional resolution in dark-field cross-sectional TEM image for cubic GaN stacked nanostructures at the same temperature ($T_S = 720\,°C$) but for two different Ga flux excesses: (a) four QDs planes ~5MLs of GaN separated by ~36MLs of AlN spacer layer grown under stoichiometric conditions ($T_{Ga} = 1035\,°C$); (b) five QWs ~ 15MLs GaN separated by 36MLs AlN spacer layer under Ga-rich conditions ($T_{Ga} = 1055\,°C$).

By contrast, if the Ga temperature is increased ($T_{Ga} = 1055\,°C$), 2D GaN layers are obtained [Fig. 4(b)]: in the present case a stack of 5 GaN QWs having a thickness of 3 nm, and separated by 9 nm AlN spacer layers is shown.

In summary we have presented the crucial importance of the two growth parameters; namely the growth temperature and the III/V ratio, which control the strain relaxation mechanism of a cubic GaN layer deposited on cubic AlN. The SK transition is enhanced for high growth temperatures and stoechiometric growth conditions ($Ga/N \approx 1$), which enables the fabrication of stacks of GaN QD layers. Moreover, by increasing the Ga/N flux ratio, the SK transition can also be intentionally delayed and even inhibited, allowing the growth of coherent 2D GaN layers embedded in AlN spacer layers. This tuning of the growth mode just by changing the Ga/N ratio reveals the importance of the Ga excess, Ga adlayer acting as a self-surfactant effect in this cubic GaN/AlN system.

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