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Strain relaxation of AlN epilayers for Stranski–Krastanov GaN/AlN quantum dots grown by metal organic vapor phase epitaxy

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Abstract

We report a study of self-assembled GaN/AlN quantum dots (QDs) grown by metalorganic vapor phase epitaxy. We have investigated the impact of the AlN template quality on the nucleation of QDs obtained by the so-called Stranski–Krastanov growth mode transition. It is shown that the AlN epilayer deposited on GaN exhibits different relaxation steps. A rather inefficient plastic relaxation first occurs in the early few nanometers. Then, as the growth proceeds cracks are generated to further release the elastic energy. However, Raman spectroscopy indicates that strain relaxation takes place only nearby the cracks. Consequently, a third relaxation process occurs as the AlN layer thickness still increases. It is characterized by V-shape pits at the AlN surface likely originating from opening of threading dislocation terminations. Atomic force microscopy and micro-photoluminescence studies indicate that these topological defects act as preferential nucleation centers competing with the GaN QD formation.

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1. Introduction

During the past decade, group-III nitride heterostructures have been intensively investigated because of the huge interest for short wavelength optoelectronics. Among others, self-assembled GaN/AlN quantum dots (QDs) are a prototypical system for fundamental studies of quantum confined structures, as well as for the development of QD based optoelectronic devices [1,2]. GaN dots can be formed on AlN surfaces, thanks to the so-called Stranski–Krastanov (SK) growth mode transition. The 2.4% lattice mismatch between GaN and AlN is large enough to produce strain-induced three-dimensional (3D) islanding once the critical thickness is reached [3]. However, the AlN/GaN system has a lower lattice mismatch than its well-known InAs/GaAs counterpart (7.2%). As strain is crucial for the SK growth mode regime, the formation of GaN QDs may strongly depend on the strain state of the AlN epilayer. In other words, if the AlN template is tensilely strained, the lattice mismatch with GaN might not be sufficient to produce 3D islanding.

Due to the rarity of 2 in AlN substrates, GaN QDs are usually fabricated on AlN templates, which in turn are deposited on GaN buffer layers on sapphire, silicium or SiC substrates [1–4]. The strain state of the AlN epilayer thus depends on its relaxation processes. When deposited on GaN, the critical thickness for plastic relaxation is as small as 3 nm [5], but complete relaxation is limited due to the dislocation mediated process, which is rather inefficient in wurtzite crystals [6]. As a consequence, AlN epilayers usually exhibit a residual tensile deformation leading to the formation of cracks when increasing the layer thickness [7].

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In the present work, we investigate the influence of the AlN template layer on the formation of GaN QDs. We first study the relaxation of the AlN epilayer grown on GaN using micro-Raman spectroscopy, as previously done in the case of AlN grown on Si [8]. The additional contribution of atomic force microscopy (AFM) allows discussing the competition between different mechanisms of strain relief. Then, the interplay between the AlN strain state and the QD islanding is investigated by means of AFM and room temperature (RT) micro-photoluminescence (μPL) experiments.

2. Experiment

The samples were grown in an AIXTRON 200/4 RF-S metalorganic vapor phase epitaxy (MOVPE) reactor on 2 in. *c*-plane sapphire substrates. A quasi-relaxed 300 nm thick AlN layer ($c_{AlN} = 4.98$ Å, as determined by X-ray diffraction averaged over a large area) was deposited at 1120 °C on a 2 μm thick GaN template. The active region consists of five periods of GaN/AlN QDs. For each period, 2 nm GaN was grown at 960 °C with a 200 nm/h growth rate. The GaN QDs were obtained using a V/III ratio of 2500. Detailed information on the growth kinetics and energetics for the formation of such SK QDs by MOVPE can be found elsewhere [9].

The top layer of QDs, left uncapped, was characterized by AFM. The local deformation of the AlN layer was investigated by means of micro-Raman mapping (spot size 1 μm) using 1 μm steps. RT spectra were recorded with a Renishaw spectrometer under the 2.41 eV excitation line of a cw Ar^+ laser using the Z (XX) $\bar{Z}$ scattering configuration. Besides, RT PL spectra were acquired using a Dilor spectrometer, using an excitation energy of 3.70 eV. In this case, the spot size on the sample surface was about 3 μm and the mapping was performed using steps of 4 μm.

3. Discussion

With the aim of growing AlN on GaN templates ready for SK GaN QD fabrication, the AlN thickness must be large enough to allow maximal strain relaxation. Its minimum value was found to be 300 nm [10]. For such a thickness, we observe cracks whatever the growth conditions. The strain profile of the AlN epilayer was investigated by micro-Raman spectroscopy. The E_2 (AlN) mode authorized by the selection rules is observed. No signature of the GaN QDs could be obtained by this way because of their small volume. We show in Fig. 1(a) the frequency variation of the non-polar E_2 (AlN) phonon mode obtained when scanning perpendicularly to a crack.

3.1. Relaxation of the AlN/GaN template

Assuming that the E_2 phonon frequency for an unstrained AlN layer is 656 cm^{-1} at RT [11], we find that the strain of AlN is tensile far from the cracks, as expected

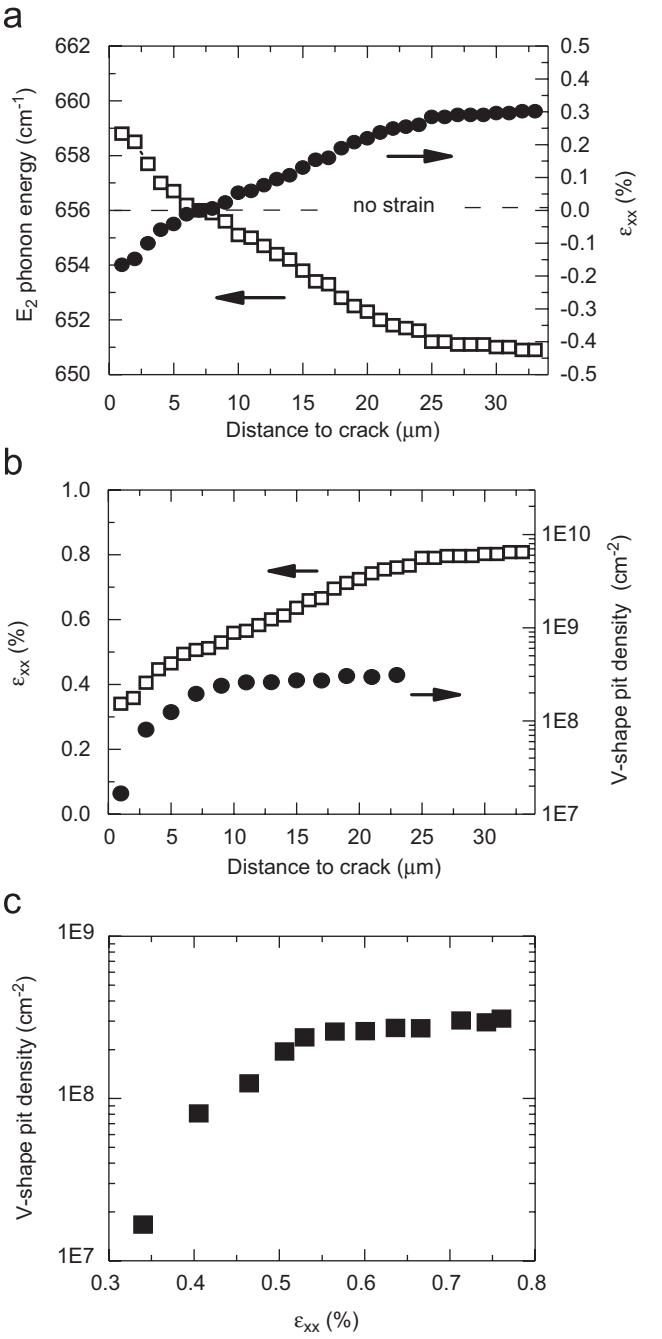

Fig. 1. (a) Room temperature position of the E_2 (AlN) phonon mode, and the respective strain vs. the distance to a crack. The dotted line corresponds to relaxed AlN; (b) calculated strain profile at growth temperature compared to the V-shape density; and (c) V-shape density vs. strain.

from the incomplete plastic relaxation. The in-plane component ε_{xx} of the strain tensor can be easily estimated because the internal stress is likely biaxial. In this case, the out-of-plane strain ε_{zz} is proportional to ε_{xx} and, for a given phonon, the frequency shift induced by strain can be written as

$$\delta\omega = \left(2a - \frac{2C_{13}}{C_{33}}\, b\right)\varepsilon_{xx}.$$

Using the deformation potentials a and b of the E_2 phonon determined by Gleize et al. [12], together with the elastic constants C_{13} and C_{33} given by Deger et al. [13] for AlN, we derive the strain variation shown in Fig. 1(a). We find $\varepsilon_{xx} = +0.30\%$ far from the cracks. Obviously ε_{zz} is negative, corresponding to a compressive stress along the z-direction. Note that, even in this region where the tensile strain of AlN is maximal, the in-plane lattice mismatch between the GaN QDs and the underlying AlN layer is far from negligible (more than 2%). Further, it is worth observing that the E_2 (AlN) phonon frequency measured exactly on the crack is higher than that of the relaxed material (see Fig. 1(a)), suggesting that the local stress is slightly compressive. This might be surprising because we grow the AlN layer on a thick quasi-relaxed GaN buffer layer characterized by a larger in-plane lattice parameter. Additional compressive strain near the cracks could be mainly due to the sample cooling after the growth. Indeed, the thermal expansion coefficients α_{AlN} and α_{GaN} of AlN and GaN, respectively, are significantly different from that of sapphire. We can calculate within the linear approximation the compressive strain due to the substrate when cooling down the sample from 1120 °C to RT by using the formula:

$$\delta\varepsilon_{xx} = (\alpha_{AlN} - \alpha_{sapphire})\Delta T,$$

where $\alpha_{AlN} = 2.9 \times 10^{-6}\,K^{-1}$, $\alpha_{sapphire} = 7.5 \times 10^{-6}\,K^{-1}$ [14,15], and ΔT is the absolute difference in temperature. We find $\delta\varepsilon_{xx} = -0.50\%$ when the sample is cooled down. The strain profile at 1120 °C, deduced from that at RT by a translation of +0.50% is displayed in Fig. 1(b). Thus, the AlN is in slight tension (+0.3%) at the crack border. Furthermore, cracking has only a local effect and does not allow the relaxation of the whole layer. Therefore, the tensile strain far from the cracks is as high as +0.8% at growth temperature (1120 °C).

It is interesting to compare the strain profile with the surface morphology. An AFM image of the AlN surface is presented in Fig. 2. Cracks and two other types of surface structures are observed. The first ones are spiral hillocks corresponding to screw dislocations [16] which are regularly distributed across the sample; their average density being about $2.5 \times 10^8\,cm^{-2}$. Moreover, we observe V-shape pits likely related to the openings of threading dislocations reaching the surface [17]. Their spatial distribution is noticeable: nearly no pits are found in the areas close to the crack, while their density increases significantly when moving away from the crack (Fig. 1(b)). It is thus obvious that these openings were created after the sample cracked. We display in Fig. 1(c) the variation of the average density of pits as a function of the strain profile: a clear correlation is evidenced. It is thus proposed that the pit formation might be a secondary route for strain relaxation.

To summarize, we suggest that strain relaxation of an AlN layer grown on a GaN template occurs as follows: the growth starts pseudomorphically and beyond a critical thickness of 3 nm dislocations are created allowing plastic relaxation [5]. However, they do not fully relax the tensile strain and elastic energy builds up as the growing layer thickness increases [6]. Above a certain thickness, the release of the elastic energy is achieved by the formation of cracks. However, strain relaxation takes place only nearby the cracks leaving large regions in-between under tensile strain. Then, the layer thickness still increasing, the built-in elastic energy increases too and V-shape openings appear, enabling a third relaxation process.

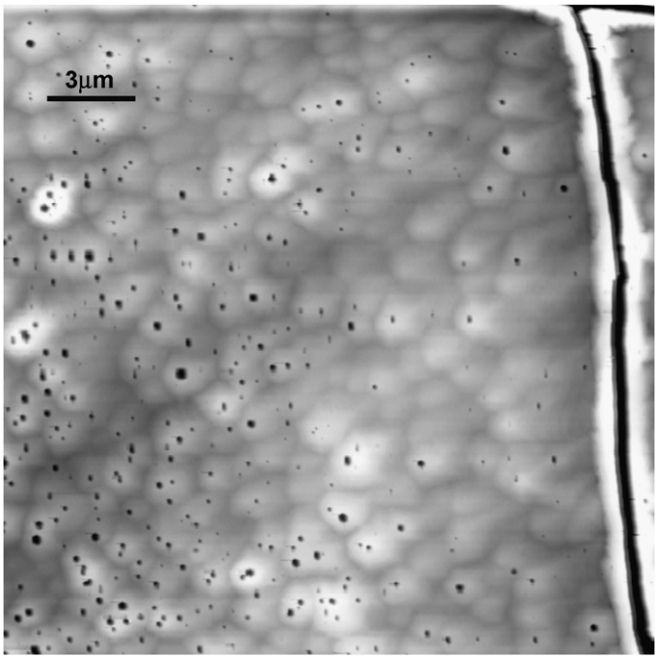

Fig. 2. . AFM image of the AlN surface near a macroscopic crack.

3.2. Self-assembled GaN/AlN QDs

Spatially resolved 300 K PL spectra measured at different distances from a crack are presented in Fig. 3. The broad PL band periodically modulated by Fabry–Perot interference is ascribed to the luminescence issued from the GaN QDs. The emission energy is significantly red-shifted compared to the GaN buffer layer energy, found at 3.42 eV at RT, due to the quantum confined Stark effect [2]. The spectra displayed in Fig. 3 peaking near 3 eV were obtained using a rather high excitation power density of about $500\,W/cm^2$, screening partially the built-in field in the QDs otherwise emitting at 2.6 eV under weak excitation [9,18]. As the excitation energy (3.7 eV) is lower than that of the wetting layer (~4.1 eV) [9], carriers are created only inside QDs. They will generally remain localized in the dots due to a reduced escape rate thus limiting non-radiative recombinations on dislocations. As a result the QD PL intensity should depend essentially on their density. When moving away from cracks (~10 µm), we observe an important decrease of the QD luminescence intensity, which indeed suggests a decreasing QD density.

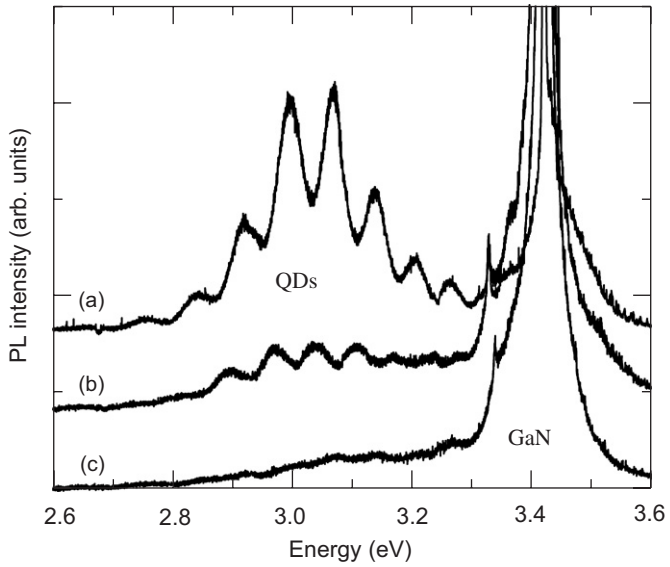

Fig. 3. Spatially resolved PL spectra under the 500 W/cm^2 excitation at 3.70 eV: (a) near a crack (1 μm); (b) intermediate location (5 μm); and (c) far from cracks (9 μm). Note that for spectrum (c) a small PL signature of the QDs is still observed.

AFM imaging was then carried out to confirm this density decrease (Figs. 4(a)–(c)). We observe on the first image islands of micrometric size (Fig. 4(a)), whose density increases with the distance to the nearest crack. Interestingly, their size and distribution correlate well with the dislocation opening density. Actually, the surface free edges in the AlN pits are powerful sinks for Ga adatoms [19] resulting in growth of pyramids of GaN. Using a higher magnification (Fig. 4(b)) we also observe bright spots corresponding to a dense coverage of QDs exhibiting an average height of about 4.7 nm. Their local density ($\sim 1 \times 10^{10}$ cm^{-2}) remains roughly the same between two cracks. However, a depletion zone, where no QD is present, is evidenced near the aforementioned micron size islands (Fig. 4(c)). As their density increases with the distance to the nearest crack, the overall QD density gradually decreases, which explains the vanishing of the luminescence intensity when getting far from a crack (Fig. 3). The depletion zone is due to surface diffusion of Ga adatoms towards the macroscopic islands which likely offer preferential nucleation sites. The SK relaxation regime thus competes with the adatom depletion near all large

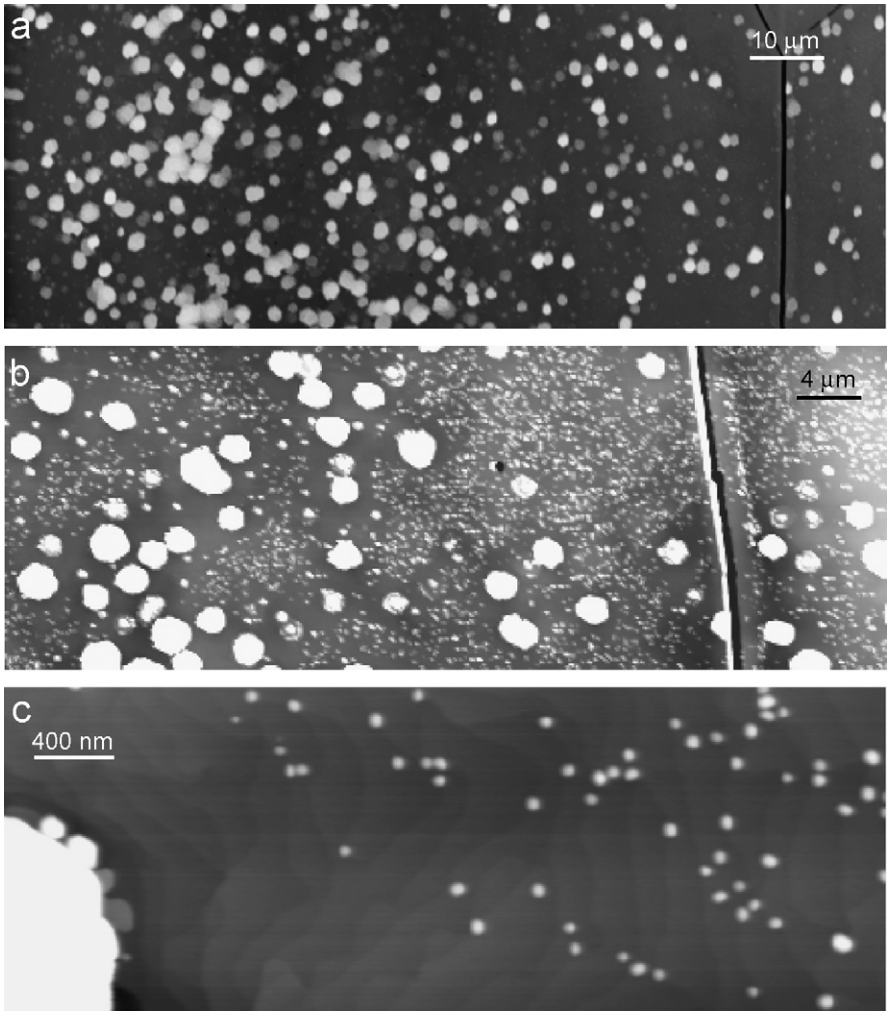

Fig. 4. AFM images of the sample surface after the deposition of the active layer: (a) series of cracks and large islands at low magnification; (b) decrease of the QD density near the large islands; and (c) QDs around a large island.

islands. This illustrates the importance of the AlN template strain and surface state on the growth of SK GaN/AlN QDs. From our observations, a surface diffusion length of 500 nm is deduced for a growth temperature of 960 °C and a low ammonia flow.

4. Conclusion

To summarize, a correlation between the AlN template relaxation and the formation of SK GaN QDs was obtained using AFM, μPL and μRaman spectroscopy. A qualitative model for the relaxation of AlN epilayers grown on GaN is proposed. The morphology of the AlN surface is a key parameter controlling the dot density. Such a behavior might be used to voluntary tune the dot density via the growth on pre-patterned surfaces.

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