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Transformation kinetics of a two-dimensional GaN thin layer grown on AlN surface during ammonia flow cycling

Y.E. Maidebura [1]✉, T.V. Malin [1], K.S. Zhuravlev [1]

[1] Rzhanov Institute of Semiconductor Physics, SB RAS, Novosibirsk, Russia

✉ maid@isp.nsc.ru

Abstract. In this work the transformation kinetics of GaN pseudomorphic layer and the lattice constant evolution of 2D GaN “frozen” layer under sequential switching off/on of ammonia flow at a growth temperature of 740 °C were investigated by reflection high energy electron diffraction method (RHEED). It was shown by the Bragg spot kinetics intensity of GaN layer that when ammonia flow is turned off, the intensity of Bragg spot reaches saturation and does not change during the exposure time in vacuum, while the maximum achieved intensity decreases when ammonia flow is turned off/on sequentially. Hence there is practically no effect of thermal decomposition on the change in the morphology of the GaN layer. It was found experimentally that the GaN layer formed with each cycle of 2D "frozen" is partially relaxed, which is explained within the Mariette equilibrium model. Thus, relaxation of elastic energy of 2D "frozen" GaN layer is due to the fact that some amount of 3D islands remains on the surface and the decrease of elastic energy value is caused by losses for islands faceting maintenance.

Keywords: GaN quantum dots, surface morphology, 2D-3D transition, surface processes, ammonia MBE, RHEED

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Кинетика преобразования тонкого двумерного слоя GaN, выращенного на поверхности AlN, при циклировании потока аммиака

Я.Е. Майдэбура [1]✉, Т.В. Малин [1], К.С. Журавлев [1]

[1] Институт физики полупроводников им. А.В. Ржанова СО РАН, г. Новосибирск, Россия

✉ maid@isp.nsc.ru

Аннотация. В данной работе была исследована кинетика трансформации псевдоморфного слоя GaN и изучена эволюция постоянной решетки слоя GaN при периодическом выключении/включении потока аммиака при ростовой температуре 740 °C. По кинетике преобразования слоя GaN было показано, что термическое разложение практически отсутствует и не влияет на изменение морфологии слоя GaN. Экспериментально было обнаружено, что образующийся с каждым циклом 2D "замороженный" слой GaN является частично релаксированным. Частичная релаксация объясняется в рамках модели равновесия Mariette, и связана с незавершенностью обратного перехода 3D островков в 2D слой.

Ключевые слова: квантовые точки GaN, морфология поверхности, 2D-3D переход, поверхностные процессы, аммиачная МЛЭ, ДБЭО

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Introduction

Group III nitrides such as InN, GaN and AlN, combined with solid solutions, can extend the spectral range of optoelectronic devices from infrared to ultraviolet, thus attracting significant research interest. A problem in III-nitrides based optoelectronic devices is the high density of dislocations and structural defects in grown heterostructures, acting as centers of non-radiation recombination and reducing the efficiency of optoelectronic devices. A possible approach is to use three-dimensional nanostructures, known as quantum dots (QDs), which act as traps for charge carriers and prevent them from diffusing to the non-radiation recombination centers.

The typical method of QDs formation is the Stranski–Krastanov (S-K) growth mechanism, where the transformation of two-dimensional (2D) layer into three-dimensional (3D) islands, i.e. 2D-3D transition, occurs during growth when the critical thickness of the growing layer is reached. It has been demonstrated in [1] that GaN QDs on AlN surface are formed by S-K mechanism when they are grown by molecular beam epitaxy (MBE) with plasma nitrogen source. GaN QDs formation by S-K mechanism has also been demonstrated using metal-organic chemical vapor deposition technology [2]. However, when GaN QDs are grown by ammonia MBE method, a 2D-3D transition with increasing 2D layer thickness is not observed and relaxation of elastic strains accumulated in the GaN layer occurs through the formation of mismatch dislocations. GaN QDs formation requires surface modification and an increase in surface energy, which occurs when the ammonia flux is switched off [3, 4] and is referred to as growth by the modified S-K mechanism.

In the case of growth according to the modified S-K mechanism, the process of GaN QD formation is reversible, i.e., turning on the ammonia flow after turning it off leads to reverse transformation of 3D islands into 2D layer (reverse 3D-2D transition) [5]. As shown in [6], with each ammonia turn-off/on cycle a portion of the GaN layer is formed that has a 2D surface morphology and is no longer transformed when ammonia is turned off. The reversibility of the 2D-3D transition has the potential to produce GaN QDs with a certain set of parameters (QD density and size), which is a significant technological challenge at the moment.

In this work, the kinetics of forward and reverse 2D-3D transitions and the lattice constant evolution of the GaN layer under periodic on/off ammonia flow were experimentally investigated and the experimental results were explained within the framework of the previously developed kinetic model and the Mariette equilibrium model.

Materials and Methods

The 2D↔3D transition was investigated on a Riber CBE-32 MBE machine with ammonia as the nitrogen source and Knudsen effusion cells as the gallium and aluminum sources. In situ reflection high energy electron diffraction (RHEED) has been used to investigate the transformation of GaN layer morphology. The evolution of diffraction patterns was analyzed using the kSA 400 system by k-Space Associates. The substrate temperature was measured using an Ircon pyrometer, thermocouple and Ocean Optics USB4000 miniature spectrometer. The ammonia pressure in the growth chamber was set and controlled using a mass flow controller.

The growth experiments were as follows. An AlN buffer layer of ~365 nm thickness was grown on a sapphire substrate with orientation (0001), on top of which a GaN layer of 2 nm thickness was grown. The gallium flow was then switched off, GaN growth was stopped and the GaN layer was kept in a flow of ammonia for 5 minutes to prevent surface modification. The ammonia flow was then switched off for 300 seconds to eliminate the effect of thermal decomposition and turned on for 120 seconds followed by a total of 4 more ammonia switch-off/on cycles with typical times of 60 and 120 seconds respectively.

Results and Discussion

Figure 1 shows the kinetics of the Bragg spot (black line) and rod (red line) intensities from GaN when the GaN layer is exposed to vacuum and subsequent on/off cycles of ammonia flow at a growth temperature of 740 °C. The insets in the figure shows the diffraction patterns for the two selected reflexes indicated by the yellow rectangles. The area for the 2D reflex measurement was chosen so that the Bragg spot contribution is minimal. The initial position of the red curve is explained by the fact that the measured rod-shaped 2D reflex is only distinguishable after the 2nd cycle of ammonia switching off/on. Consequently, the black and red curves represent simultaneously coexisting reflexes corresponding to the 3D and 2D surface states, respectively. Figure 1 clearly shows that when the ammonia flow is switched off, the intensity of the 3D reflex increases, then reaches saturation and remains unchanged after 300 seconds of exposure in vacuum, indicating the formation and stabilization of 3D islands. When the ammonia flow is turned on, the intensity of the Bragg spot decreases and increases sharply when it is switched off afterwards. As can be seen from the figure, the maximum achievable intensity of the Bragg spot decreases from cycle to cycle. This behavior indicates the presence of a mechanism other than thermal decomposition, which leads to a decrease of the Bragg spot intensity, as has been reported in [4, 5]. Conversely, the intensity of the 2D reflex decreases when ammonia is switched off and increases when ammonia is switched on again. As can be seen from the figure, with each cycle the 2D reflex becomes brighter and the maximum achievable intensity increases. This means that with each cycle the 2D part of the GaN layer develops, and it is no longer transformed when the ammonia flow is switched off. This behaviour is due to the fact that part of the NH_2, NH and N fragments move to energetically favorable positions on the GaN layer surface, desorption from which is significantly inhibited when the ammonia flow is switched off. Consequently, the surface energy of such a ‘frozen’ surface does not change when the ammonia is turned off and, according to the Mariette model [7], the surface remains 2D.

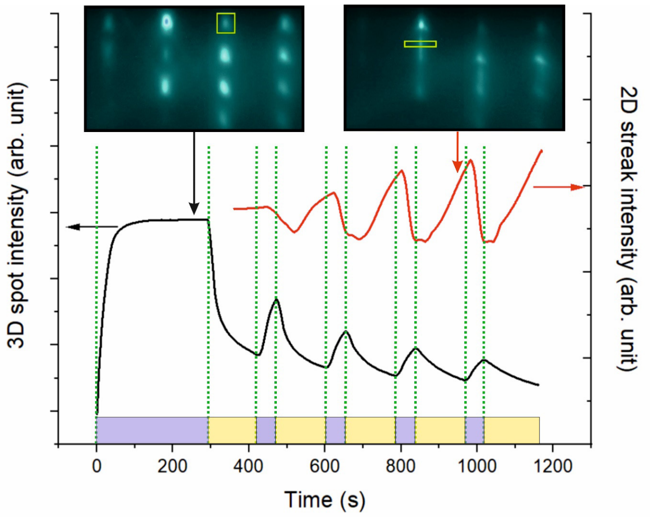

Fig. 1. Intensities of the 3D spot (black curve) and 2D streak (red curve) from the GaN surface with sequential switching off/on of the ammonia flow at T = 740 °C. The insets illustrate diffraction patterns for the two selected reflexes indicated by the yellow rectangles. The green dotted line indicates the ammonia flow off/on, and the purple/yellow areas indicate surface exposure in vacuum/ammonia, respectively

More surprisingly, the 2D layer, which no longer converts into islands, is partially relaxed. Assuming that the original GaN layer 2 nm thick is pseudomorphic and has a lattice constant of the buffer AlN layer (equal to about 3.12 Å at growth temperature), the in-plane lattice constant evolution of the 'frozen' GaN layer during the experiment was obtained from the relative spacing of the 2D reflex intensity peaks, shown in Fig. 2. The insets show GaN 2D reflex intensity profiles before and after 5 cycles of ammonia switching off/on. It should be noted that a reliable identification of the intensity peak position from a 2D partially relaxed GaN layer is only possible after two cycles of ammonia switching off/on. As can be seen from the figure, the lattice constant of the 2D 'frozen' GaN layer periodically increases and decreases. As the reflex from the 2D 'frozen' layer appears when the ammonia is turned on, its lattice constant decreases, i.e., the layer acquires elastic stress, and conversely, as the reflex intensity decreases, the lattice constant increases and relaxation of the elastic energy occurs. With each ammonia on/off cycle the stress in the layer increases and the lattice constant tends to that of the pseudomorphic GaN layer (3.12 Å). The partial relaxation of the 2D GaN layer can be explained in terms of the Mariette equilibrium model [7], according to which the 2D-3D transition occurs when the energy gain from the decrease of elastic energy stored in the pseudomorphic layer exceeds the energy loss in the creation of QD surfaces. Based on [6], after 5 cycles of ammonia switching off/on at 740 °C the fully original GaN layer is not recovered and the GaN layer morphology is a 2D layer on which lie 3D islands with characteristic lateral sizes of 100 nm. The total energy of such a surface, according to [7], consists of the elastic energy, the surface energies of the 2D layer and the facets of the 3D islands, which differs from a purely 2D layer by the presence of the surface energy of the facets. Then relaxation of elastic energy of 2D 'frozen' GaN layer is due to the fact that some number of 3D islands is kept on the surface and the decrease of elastic energy value is caused by the costs of maintaining faceting of islands.

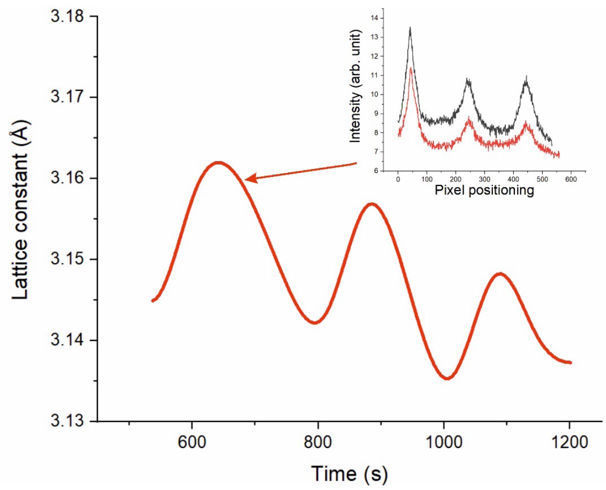

Fig. 2. Evolution of the lattice constant 2D 'frozen' GaN layer. The insets show GaN 2D reflection intensity profiles before and after 5 cycles of ammonia switching off/on

Conclusion

In this work, the transformation kinetics of GaN pseudomorphic layer and lattice constant evolution of GaN layer under periodic switching off/on of ammonia flux at a growth temperature of 740 °C have been experimentally investigated by RHEED method. It has been experimentally shown that when ammonia is turned off for the first time in vacuum (300 seconds), the Bragg spot intensity reaches saturation and does not change, whereas when ammonia is cycled, the maximum achievable intensity decreases with each cycle, indicating no thermal decomposition. It was also found that the 2D 'frozen' GaN layer, which does not transform into 3D islands and increases with each switch-off/ switch-on cycle, is partially relaxed. This behavior is related to the incomplete reverse transformation of 3D islands into a 2D layer and is explained within the Mariette equilibrium model, according to which part of the elastic energy is spent to maintain the faceting of the islands.

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THE AUTHORS

MAIDEBURA Yan E.
maid@isp.nsc.ru
ORCID: 0000-0001-6380-950X

MALIN Timur V.
mal-tv@isp.nsc.ru
ORCID: 0000-0001-6015-0631

ZHURAVLEV Konstantin S.
zhur@isp.nsc.ru
ORCID: 0000-0002-3171-5098

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