Influence of the Elemental Composition on the Surface of the GaN Layer on the Surface Energy in Ammonia MBE

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***Abstract* — The paper presents the results of a study of the effect of the elemental composition on the surface of the GaN layer on its surface energy. It was found for the first time that formation of GaN quantum dots on the AlN surface can occur with an increase in the temperature of the GaN layer in the ammonia flow. An analysis of the chemical reactions taking place on the surface of the GaN layer was carried out, and the bare surface of GaN was also considered. Based on the chemical analysis performed, a particle was identified, namely hydrogen, whose intense desorption from the surface of the GaN layer leads to a decrease in the degree of filling of the uncompensated bonds of the bare GaN surface. Thus, a kinetic model of the 2D-3D transition was proposed, in which an increase in the surface energy of the 2D layer is associated with an increase in the degree of depletion of broken gallium bonds on the surface with hydrogen atoms.**

Keywords—GaN QDs, group III nitrides, 2D-3D transition, ammonia MBE.

I. INTRODUCTION

Low-dimensional semiconductor systems (two-dimensional quantum wells, filaments and dots) are actively investigated due to the possibility of controlling electronic properties using quantum-dimensional effects. Of particular interest are zero-dimensional nanoobjects or quantum dots (QDs), in which charge carriers are spatially limited in all three dimensions. QDs are actively used in various fields of science and technology, for example, in optoelectronics (InAs/GaAs QDs [1]), in spintronics (QDs based on Mn_xG_{1-x} compounds [2]), in biomedicine (QDs made of materials of II-VI groups [3, 4]), etc. GaN/Al(Ga)N QDs can serve as sources of single photons at room temperature [5, 6], to create light-emitting diodes and laser diodes in the UV and visible ranges [7, 8], as well as high-speed IR photodetectors [9].

QDs are usually formed during continuous growth of strained layers according to the Stranski-Krastanov (S-K) mechanism, which is based on the transformation of a two-dimensional (2D) layer into three-dimensional (3D) islands when the critical layer thickness is reached. In the equilibrium model proposed by Mariette [10], the 2D-3D transition becomes energetically favorable when the gain in relaxation of the elastic energy accumulated in the film exceeds the cost of creating new QDs surfaces. The formation of GaN QDs on the AlN surface during continuous growth of the GaN layer is not observed; for the formation of QDs, it is necessary to stop the growth of the layer and turn off the flow of active nitrogen (ammonia) [11]. Based on the equilibrium model, authors of [12, 13] assumed that switching off the ammonia flow leads to an increase in the surface energy of the film and to a decrease in the cost of forming QDs faces, as a result of which the relaxation of elastic energy and the formation of QDs become energetically favorable.

At present, the reason for the change in the surface energy remains unclear, as well as the processes on the surface of the GaN layer that cause this change. In works on theoretical calculations of the state of the GaN surface for various chemical potentials of Group III/V elements and hydrogen, which is a product of ammonia dissociation reactions, a change in the surface energy is often associated with a change in the elemental composition [14, 15].

In this work, it was found for the first time that the formation of GaN QDs on the AlN surface can occur without switching off ammonia, but with an increase in the temperature of the GaN layer.

The aim of this work is to analyze the elemental composition on the GaN surface with a change in temperature and its effect on the surface energy of GaN.

II. EXPERIMENTAL DETAILS

Experiments to study the 2D-3D transition were carried out on a Riber CBE-32 molecular beam epitaxy (MBE) unit with ammonia as a nitrogen source. The samples were grown on sapphire substrates with orientation (0001), which were preliminarily cleaned by annealing in a loading chamber at a temperature of 900±5 °C for 1 hour. Knudsen effusion cells

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were used as sources of aluminum and gallium. The substrate was heated due to the absorption of infrared radiation from the heater, for which the back side of the sapphire substrate was covered with a molybdenum layer 0.4 μm thick. The transition from 2D to 3D surface state was investigated in situ by reflection high-energy electron diffraction (RHEED) using the kSA400 system. The sequence of the experiment was as follows:

1. Nitridation of a sapphire substrate in an ammonia flow of 25 scm^3/min at a temperature of 835±5 °C.
2. Growth of a 350 nm thick AlN buffer layer at a temperature of 975±5 °C and an ammonia flow of 25 scm^3/min.
3. Formation of a 2 nm thick GaN layer under standard growth conditions (ammonia flow 275 scm^3/min, growth temperature 775±5 °C) at a growth rate of 220 nm/h.
4. Decrease of ammonia flux to 0, 15, 30 scm^3/min at 775±5 °C.
5. Subsequent increase in temperature at a rate of 20 °C/min, 6.2 °C/min and 9.3 °C/min for 0, 15 and 30 scm^3/min, respectively.

Heating was slow enough for the GaN layer to heat up to the specified temperature. The layer temperature was monitored with an Ircon pyrometer, a thermocouple, and an Ocean Optics USB4000 miniature spectrometer, which measures the temperature from the cathodoluminescence spectra of the growing layer and the thermal luminescence of the substrate, which is described in detail in [16]. The temperature is indicated with an error of ±5 degrees, because when determining the temperature using a spectrometer, the temperature of the metal film is actually measured, and the error also appears when normalizing the radiation spectra to the spectrum of an absolutely black body. The ammonia flow in the growth chamber was controlled using a flow controller operating in the range of 0-400 scm^3/min.

III. Experimental Results

Fig. 1 shows a diffraction pattern showing a transition from the 2D state of the GaN surface with a characteristic streaky pattern to a 3D state, which is characterized by the appearance of Bragg spots. The diffraction pattern in Fig. 1b refers to the case when the Bragg 3D spot was the most visible. Based on the readings of the spectrometer, the threshold temperature values were determined at which the 2D-3D transition occurred, the formation of QDs (T_L) began, and the temperature values were also determined for which the intensity of the 3D spot was maximum (T_H). With an increase in the ammonia flow, the temperature of the beginning of the 2D-3D transition increases, starting from the temperature T_L^1 = 790±5 °C for an ammonia flow of 0, and reaching T_L^2 = 812±5 °C and T_L^3 = 823±5 °C for ammonia flows of 15 and 30 scm^3/min, respectively. The temperature of the end of the 2D-3D transition also demonstrates a similar behavior; for larger values of the ammonia flux, it increases, T_H^1 = 804±5 °C, T_H^2 = 822±5 °C, and T_H^3 = 840±5 °C for ammonia fluxes of 0, 15, and 30 scm^3/min, respectively. A further increase in temperature leads to attenuation of the 3D reflection and restoration of the original 2D GaN surface, thermal decomposition of the GaN layer and restoration of the AlN layer, the latter can be seen in the diffraction pattern by an increase in the distance between the peaks of the 2D reflection intensity (Fig. 1c).

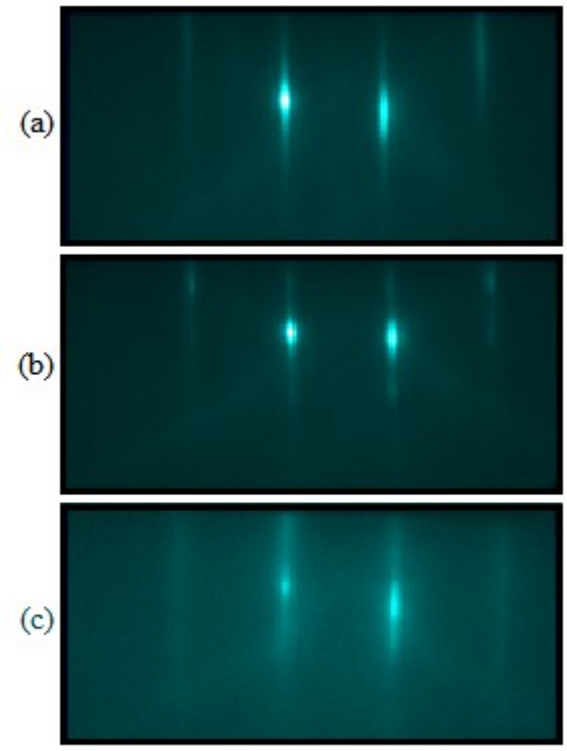

Fig. 1. RHEED patterns, showing the state of the surface of the GaN layer under different growth conditions: (a) – 2D surface of GaN at a temperature below 812±5 °C for an ammonia flow of 15 scm^3/min, which is characterized by observation of a streaky pattern; (b) – 3D state of the GaN surface at temperature 822±5 °C for an ammonia flow of 15 scm^3/min, with a characteristic Bragg spot; (c) – diffraction pattern of the AlN layer in ammonia flow of 15 scm^3/min, which is restored with a subsequent increase in temperature after 822±5 °C due to thermal decomposition of the GaN layer

IV. Discussion

To explain the results, we examined a bare GaN (0001) surface with metallic polarity. Confirmation of obtaining a Ga-polar surface is reconstruction (2 × 2), which manifests itself when GaN is cooled below 530 °C in an ammonia flow of 25 scm^3/min [17].

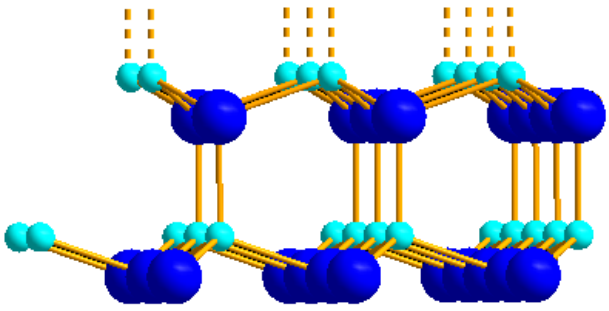

Fig. 2. Schematic diagram of the bare surface of GaN (0001) with metallic polarity. Small spheres are Ga atoms, large spheres are N atoms. The dashed line marks the uncompensated bonds of the surface gallium atom

On a Ga-terminated surface (Fig. 2), Ga atoms have triple coordination; each Ga atom is bonded to three N atoms and

has one more uncompensated bond. This surface is the least stable at any temperatures and flux ratios of group III/V, which was shown in a theoretical study of the state of the GaN (0001) surface under various growth conditions [17-19]. In addition, it was theoretically shown that the adsorption of ammonia molecules and radicals and hydrogen atoms [20-22] on the bare GaN (0001) surface always lowers the surface energy of the system, for example, the adsorption of an NH_3 molecule lowers the surface energy by 3.6 eV [21].

At typical growth fluxes of ammonia (275 scm^3/min), uncompensated bonds are saturated with a combination of $NH_3 + 3NH_2$ particles, and the unstable bare GaN (0001) surface is stabilized [15, 18]. As the temperature rises, the situation changes, the dissociation of ammonia molecules becomes significant, hydrogen is adsorbed without a barrier [21] on the GaN surface, and the combination of NH + H particles becomes stable [15, 18]. The surface is in equilibrium, the ammonia molecules coming from the gas phase dissociate, the adsorbed hydrogen is easily desorbed due to the low desorption energy and is then replaced by another adsorbed hydrogen. When ammonia is turned off, the equilibrium is disturbed, desorption of hydrogen is not compensated by its adsorption, the dangling Ga bonds are depleted, and the surface energy rises. As a result, the surface becomes unstable and reconstructed, a 2D-3D transition occurs.

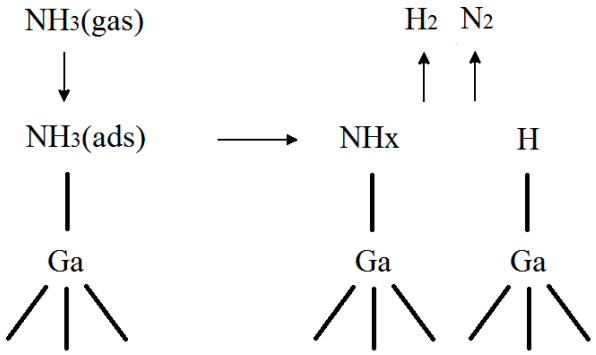

Fig. 3. Schematic representation of chemical reactions occurring on the surface of the GaN layer in an ammonia flow, where x = 1, 2

The main role of hydrogen desorption in the depletion of broken bonds follows from consideration of the chemical reactions (1-5) that occur on the GaN surface in ammonia with the gallium flow turned off. The reactions are shown figuratively in Fig. 3. The filling of the bare GaN surface begins with dissociative chemisorption (1), as a result of which NH_2 and H particles occupy uncompensated bonds. The NH_2 molecule can undergo decomposition, and when it collides with the adsorbed hydrogen, the NH radical and the hydrogen molecule H_2 are formed, which has a high binding energy (E_{bond} = 4.56 eV [23]) and cannot fill uncompensated bonds. The decomposition of the NH radical occurs in a similar way, as a result of which, in addition to the formation of molecular hydrogen, nitrogen is adsorbed on the surface. Thus, particles that can occupy broken bonds and lower the surface energy of the system are 4, namely NH_2, NH, H and N. It is energetically preferable for NH_2 and NH particles to dissociate through reactions (2) and (3) [20, 21], therefore, there is no desorption of these particles. The energy barrier for desorption of the nitrogen atom is 6.1 eV [24] which means strong binding of nitrogen with surface gallium atoms. On the other hand, hydrogen easily desorbs through recombination upon collision with adsorbed hydrogen [25, 26]. Hence, the main particle that determines the degree of saturation and depletion of uncompensated bonds is hydrogen.

$$(1)\quad NH_3^{gas} \rightarrow NH_2^{ads} + H^{ads}$$

$$(2)\quad NH_2^{ads} + H^{ads} \rightarrow NH^{ads} + H_2^{gas}$$

$$(3)\quad NH^{ads} + H^{ads} \rightarrow N^{ads} + H_2^{gas}$$

$$(4)\quad H^{ads} + H^{ads} \rightarrow H_2^{gas}$$

$$(5)\quad N^{ads} + N^{ads} \rightarrow N_2^{gas}$$

Taking into account the above, consider a 2D-3D transition with increasing temperature for the case of 0 scm^3/min. 2D-3D transition in this case is triggered not by switching off ammonia, but by a gradual increase in temperature. At temperatures below T_L, the surface remains flat, with Ga bonds saturated with NH_2 and NH_3 particles. As the temperature rises, dissociation of NH_2 and NH_3 molecules begins and the surface is filled with hydrogen. In the absence of ammonia, hydrogen desorption is not compensated by its adsorption, the GaN surface is depleted in hydrogen, and its surface energy increases, which leads to a 2D-3D transition. In an ammonia flow, the same degree of hydrogen depletion of the GaN surface is achieved at a higher temperature, therefore, the temperature of the onset of the 2D-3D transition increases.

Upon reaching T_H, the thermal decomposition of GaN begins to play an important role, which leads to the layer-by-layer decomposition of QDs and the restoration of the initial 2D GaN and AlN surfaces. As the ammonia flux increases, the temperature at which thermal decomposition becomes significant increases, as a result of which the upper boundary of the 2D-3D transition shifts. This behavior is consistent with the results of studies on the effect of ammonia on the thermal decomposition of the GaN [27] layer. When the GaN layer is completely decomposed, the original AlN surface is restored, the thermal decomposition of which requires much higher temperatures [28].

V. Conclusions

In this work, we analyzed the elemental composition of the GaN surface with a sequential temperature increase in the range from 775 to 890 °C for values of the ammonia flux of 0, 15, and 30 scm^3/min, as well as its effect on the surface energy of the GaN layer. It is shown for the first time that 2D-3D transition, i.e. the formation of GaN QDs occurs when the temperature in the ammonia flow rises, and not only when it is completely turned off. The temperature ranges of the 2D-3D transition were obtained from the diffraction patterns, and it was shown that for a larger value of the ammonia flux, both the lower and upper ranges shift upward. From a discussion of the chemical reactions taking place on the surface of the GaN layer, it was supposed that hydrogen is the main element responsible for saturation and depletion of broken Ga bonds. Based on the above, a kinetic model of a 2D-3D transition was proposed, in which the depletion of broken Ga bonds on the surface of the GaN

layer with hydrogen leads to an increase in the surface energy, as a result of which the 2D surface of the GaN layer is rearranged into 3D islands. According to the model, the shift of the boundaries of the 2D-3D transition with an increase in the ammonia flow is explained by the shift of the equilibrium point in temperature, at which desorption of the hydrogen begins to dominate over its adsorption from the ammonia flow.

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