Optimal Stage Determination of Sapphire Nitridation Process Completion under High-Energy Electron Beam Influence

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***Abstract* – In this work, using the RHEED technique, the optimal stage of sapphire nitridation completeness was determined taking into account the electron beam influence on a nitridation process. It was found that as a result of the sapphire surface nitridation at the optimum stage of completion the AlN crystalline phase about one monolayer is formed on the surface. The AlN buffer layer growth under conditions of optimal stage of nitridation process completion is characterized by a smooth surface morphology and better crystalline perfection compared to AlN growth without nitridation or with excessive sapphire nitridation.**

***Index Terms* – NH_3-MBE, AlN, nitridation, inversion domains.**

I. INTRODUCTION

WIDE DIRECT BAND GAP (~3.4 eV), a high critical electric field strength ($\sim 3.3 \cdot 10^8$ V/m) and a high saturation rate ($\sim 2 \cdot 10^5$ m/s) make gallium nitride (GaN) and its solid solutions essential in optoelectronic and nanoelectronic applications, such as light emitting diodes (LEDs) [1], ultraviolet photodetectors [2] and high electron mobility transistors (HEMTs), which are actively used in microwave and power electronics [3, 4]. Sapphire (Al_2O_3) is the most common substrate for the epitaxial growth of III-nitride heterostructures due to optical transparency, high crystalline perfection and low cost. Before GaN epitaxial growth, an AlN buffer layer on sapphire substrates is formed [5, 6]. In order to match the AlN buffer layer with a foreign (with respect to III-nitrides) sapphire substrate, a nitridation process is carried out. This process occurs when the heated substrate is exposed in a flux of active nitrogen [7 – 12]. As a result, on the substrate surface the AlN crystalline phase is formed, which is structurally consistent with the subsequent AlN epitaxial film.

The nitridation process was firstly introduced by Kawakami et al. [13] when studying the epitaxial growth of AlN films, and then by Yamamoto et al. [14] when studying the nitridation effect on the InN growth. The significance of the nitride layer, formed as a result of sapphire nitridation, in controlling the GaN polarity was emphasized by Rouvière et al. [15], and more recently by Mohn et al. [16] and Stolyarchuk et al. [17].

Nitridation is a complex stepwise process. The authors [10] used reflection high-energy electron diffraction (RHEED) technique, recording the spots intensity associated with AlN and measuring the AlN lattice constant parameter. According to these results, it was found that the AlN formation during the nitridation process takes place in two distinct stages. First, the AlN formation process proceeds at a high rate, and then it slows down, reaching saturation. In [12], it was found that during AlN formation on the sapphire surface, the AlN spots width decreases, which the authors associate with an increase in the nuclei lateral size of the formed AlN phase.

The AlN formation rate depends on nitridation conditions. At a substrate temperature of 1120K in an ammonia flux of 20 standard cm^3/min under normal conditions (10^5 Pa, 298K) in the ammonia molecular beam epitaxy (NH_3-MBE) technique, according to Grandjean data, the process reaches saturation after 10 minutes from the nitridation initiation [10]. It was previously established that under NH_3-MBE conditions, the period of the fast nitridation stage varies from 120 seconds at the substrate temperature of 1270K and the ammonia flux of 400 standard cm^3/min up to 60 minutes at 770K and the flux of 12.5 standard cm^3/min, respectively [12]. In a series of works, it was shown that the structural perfection of subsequent III-nitride layers directly depends on the substrate nitridation conditions: substrate temperature, ammonia pressure, and substrate exposure time in ammonia flux [7, 10, 18, 19].

II. PROBLEM STATEMENT

Despite the fact that the nitridation conditions affect the rate of the process, the kinetic curve form remains unchanged [10, 12]. It is important to determine in which point of the nitridation kinetic curve the growth of the AlN buffer layer should begin. Usually, researchers focus on nitridation time. In [7 – 10], it was shown that there is an optimal nitridation time, and with a short and long nitridation time the layers' quality deteriorates significantly. Since time is not the only parameter that determines the choice of optimal nitridation stage before

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starting the buffer layer growth, this task requires choosing a universal criterion that takes into account the influence of all parameters (substrate temperature, ammonia flux, and nitridation time). Such a criterion is the stage of nitridation process completion [20]. To *in situ* determine the stage of nitridation process completion, one can focus on the diffraction spot intensity of the formed AlN crystalline phase using the RHEED technique [10, 12]. However, recent studies have shown that under the continuous exposure of electron beam to a substrate, the formation of the AlN crystalline phase is accelerated in the result of oxygen electron-stimulated desorption, and may differ by more than an order of magnitude from the nitridation process without electron beam [21].

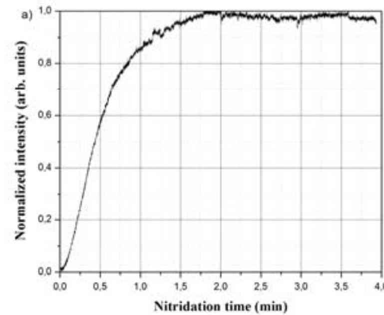
The aim of this work is to determine the optimal stage of sapphire nitridation process completion, taking into account the influence of high-energy electrons used in the RHEED technique.

III. EXPERIMENTAL SECTION

The studied samples were synthesized on a Riber CBE-32P molecular beam epitaxy machine adapted for ammonia MBE. Atomic aluminum was feed to the sapphire surface from SemiTEq effusion cells, which were specially designed to prevent the “creeping” effect in the atmosphere of residual ammonia. High purity ammonia of 99.999% was used as a source of active nitrogen, complete with additional purification filters from Entgris with a degree of ammonia purification better than 99.999999%. The ammonia flux into the chamber was set by a Bronkhorst flow regulator operating in the range of 8…400 standard cm^3/min under normal conditions. The substrates were heated by absorbing radiation from the heater with a ~0.4 µm thick molybdenum layer deposited on the reverse side of the sapphire substrate. Before the experiment, sapphire substrates were subjected to high-temperature annealing at a temperature of 1170K for 1 hour in order to preliminarily clean the surface from residual carbon and hydrogen contaminants. Then, the sapphire substrate was heated to 1110K and exposed in an ammonia flux. At the final stage, 1 µm thick AlN layer was grown in an ammonia flux of 15 standard cm^3/min at a substrate temperature of 1210K at the speed of 0.3 µm/h. The nitridated sapphire surface was investigated using reflection of high-energy electron diffraction and X-ray photoelectron spectroscopy (XPS), and AlN buffer layers with different inversion domains density were studied using atomic force microscopy and X-ray diffraction.

IV. EXPERIMENTAL RESULTS

The time dependence of the diffraction spot intensity of the formed AlN crystalline phase is displayed in the form of kinetic curves. Kinetic curve of the nitridation process at a temperature of 1110K and ammonia flux 25 standard cm^3/min is shown in Fig.1a. The AlN crystalline phase formation process on the sapphire surface first proceeds at a high rate, then it slows down and reaches saturation.



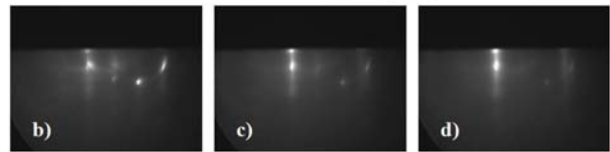


Fig. 1. Kinetic curve of the nitridation process at a temperature of 1110K and ammonia flux 25 standard cm^3/min (a), diffraction patterns from the initial sapphire surface (b), after 1 minute nitridation (c) and after 2 minutes nitridation (d).

Figure 1b-d shows the diffraction patterns (DP) from the initial sapphire surface and sapphire surface after 1 and 2 minutes nitridation, respectively. After 1 minute nitridation (Fig. 1c), DP shows spots from the sapphire surface in the [11–20] direction and a weak spot from the formed AlN. The low intensity of the AlN spot indicates an incomplete surface coating, or a small thickness of the AlN layer. After 2-minute nitridation spots from the AlN crystalline phase are much brighter on the DP, and the intensity of spots from sapphire is much lower.

However, according to the results of [21], the electron beam used in the RHEED technique accelerates the nitridation process during measurements in the beam exposure region and distorts the experimental data. The extrapolation of the measuring results of the beam influence on the nitridation process in this work made it possible to determine the acceleration coefficient of nitridation due to the effect of the beam.

Using the acceleration coefficient, which is determined by the current used by the primary electron beam, according to the method described in [21], the values along the time axis were recalculated for the nitridation kinetic curve. For this study, the acceleration coefficient was 10. This procedure made it possible to exclude the effect of high-energy electrons on oxygen desorption, as a result, reliable kinetic curves of the nitridation process were obtained and the effect of the stages of process completion on the AlN buffer layer growth was studied.

V. DISCUSSION OF RESULTS

On the experimental kinetic curves of the sapphire nitridation process, several points were selected (Fig. 2), from which the buffer layer nucleation began. If AlN

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growth begins on the nitridated sapphire surface at point 3, which corresponds to the deep nitridation of the underlying sapphire layers, 3D AlN with a high density of inversion domains is formed. In the case of choosing the initial point 2, corresponding to the AlN crystalline phase formation on the sapphire surface, during the growth of the AlN buffer layer, a two-dimensional film is formed with a smooth surface morphology and metallic polarity, as evidenced by reflective DP and 2×2 reconstruction. The epitaxial growth of AlN at point 1, corresponding to the non-nitridated sapphire surface, is characterized by coarsening of the surface, which subsequently leads to the polycrystal growth.

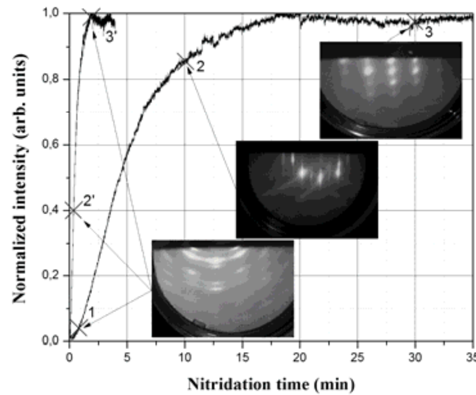

Fig. 2. The beginning of the AlN buffer layer formation at different stages of the nitridation process completion: at point 1, a polycrystalline AlN structure is formed, at point 2, a two-dimensional high-quality AlN crystalline structure is formed, with prolonged nitridation, a three-dimensional AlN structure with a developed surface morphology is formed. At points 2 'and 3' on the kinetic curve obtained under the influence of an electron beam, a polycrystalline structure is formed regardless of the choice of stage of completion.

For comparison, points 2' and 3' on the kinetic curve indicate the stages of nitridation completeness before its renormalization, not taking into account the beam influence. In this case, if the choice of the stage of completion is carried out, focusing on the kinetic curve without normalizing it with allowance for the accelerating coefficient, in all cases the growth of the AlN film leads to a polycrystalline structure (Fig. 2).

To study the effect of the stage of sapphire nitridation process completion on the surface morphology and structural perfection of the AlN buffer layer, III-nitride structures were grown on the initial (non-nitridized) and nitridated sapphire substrates at different stages of completeness.

The practical significance of the experiment was to obtain a high-quality AlN buffer layer. The high density of the inversion domains reduces the crystalline quality of the buffer layer, on which the perfection of further layers and the structure as a whole depends. To obtain a high-quality AlN layer, nucleation must begin at a certain stage of nitridation process completion.

Having studied the stages of nitridation process completion, an AlN buffer layer with a high crystalline perfection and a low density inversion domains were grown (Fig.3). The crystalline perfection of the layers was determined from measurements of the full width at half maximum (FWHM) from the rocking curves (Table I). The FWHM of the symmetric spot (0002), which reflects the micro-misorientation of the (0001) planes due to defects, mainly, vertical screw dislocations (ρ_{screw}), and the width of the skew-symmetric spot (10-13) (skew-geometry), which is sensitive to displacements, in particular, due to the presence of vertical edge and mixed type of dislocations (ρ_{edge}) were measured. The dislocation density was calculated by the formula of randomly distributed dislocations [22].

TABLE I
CRYSTAL PERFECTION AND DISLOCATION DENSITY IN THE AlN BUFFER LAYER

Deep nitridation		Optimal nitridation	
FWHM (0002)	$4.99 \cdot 10^{-3}$ rad	FWHM (0002)	$2.04 \cdot 10^{-3}$ rad
ρ_{screw}	$2.30 \cdot 10^{9}$ cm^{-2}	ρ_{screw}	$0.39 \cdot 10^{9}$ cm^{-2}
FWHM (10-13)	$7.31 \cdot 10^{-3}$ rad	FWHM (10-13)	$4.23 \cdot 10^{-3}$ rad
ρ_{edge}	$11.3 \cdot 10^{9}$ cm^{-2}	ρ_{edge}	$3.82 \cdot 10^{9}$ cm^{-2}

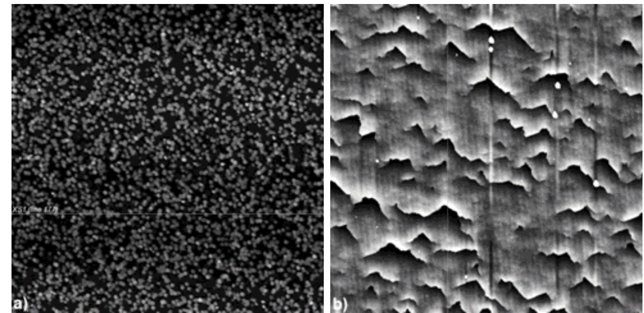

Fig. 3. 15 × 15 μm^2 AFM images of grown AlN films (1 μm) on a deep nitridated sapphire surface (a) and with the optimal stage of nitridation process completion (b). The Z height scales were 110 nm for (a) and 10 nm for (b) images. The height of the inversion domains on the first film surface was ~40 nm, there are no inversion domains on the surface image on the right, and the surface roughness was ~0.5 nm.

To obtain information about the thickness of the nitridated layer in the case of optimal stage of nitridation process completion, the nitridated sample was studied by XPS. The change in the chemical composition of the Al_2O_3 surface was recorded before and 10 minutes after nitridation at 1110K in 25 standard cm^3/min of ammonia. Fig. 4 shows spectra of the initial and nitridated surfaces of (0001) Al_2O_3. The inset to Fig. 4 clearly shows the appearance of the N1s nitrogen atom peak.

The thickness of the AlN layer synthesized in a result of nitridation was calculated by the formula below and was ~0.25 nm or ~1 monolayer,

$$I = I_0 (1 - e^{(-\frac{d}{\lambda})})$$

where I_0 is the calibration intensity of the N1s peak from the nitrogen atom in the AlN buffer layer, I is the intensity of the N1s peak from the nitrogen atom in nitridated Al_2O_3,

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d is the thickness of the AlN layer formed on the sapphire surface, λ is the characteristic electron escape depth.

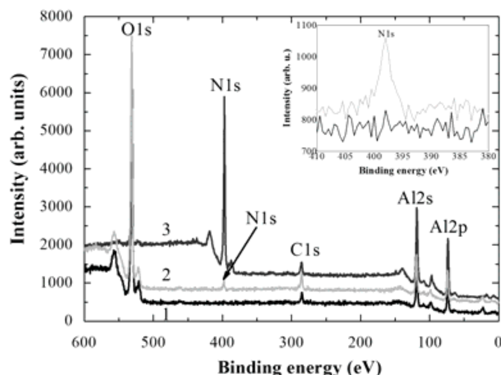

Fig. 4. XPS spectra of the samples: 1 — initial surface (0001) Al_2O_3, 2 — nitridated surface (0001) Al_2O_3, 3 — surface of the AlN buffer layer (0001). The inset shows the spectra of the initial (1) and nitridated (2) Al_2O_3 surfaces in the region of the N1s peak.

VI. CONCLUSION

In this work, the optimal stage of sapphire nitridation process completion is determined using the kinetic curves of the nitridation process, recalculated taking into account the coefficient of the electron beam influence on the nitridation process. It was established that sapphire nitridation with the formation of ~1 monolayer AlN on its surface provides the subsequent growth of AlN layers with a smoother surface and better crystalline perfection in comparison with deep sapphire nitridation. It is assumed that an increase in the thickness of the nitridated layer leads to the formation of a larger number of deflected AlN nuclei and an increase in the number of inversion domains. Also, the work demonstrated how distorted data can be obtained when determining the optimal stage of sapphire nitridation process completion, without taking into account the influence of the beam on the process itself.

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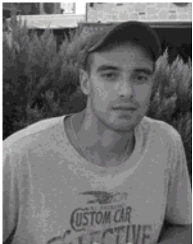

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