

METROLOGY, STANDARTIZATION, AND CONTROL

Investigation of Gallium Nitride Island Films on Sapphire Substrates via Scanning Electron Microscopy and Spectral Ellipsometry

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Abstract—Gallium nitride (GaN) seed sub 100 nm layers deposited from triethyl gallium and ammonia on sapphire substrates in different modes during atomic-layer epitaxy (ALE) have been studied via scanning electron microscopy (SEM) and spectral ellipsometry. The seed layers are island films with different degrees of substrate surface coating, which consist of GaN crystallites having different sizes and average thicknesses from 10 to 40 nm. A program for processing SEM images has been developed, which allows us to quantitatively estimate areas of particles, inclusions, and phases present in films and on the substrate surface. The technique of processing the results of spectral ellipsometric measurements of island films composed of GaN crystallites on sapphire substrates using the Maxwell–Garnett model reveals the same tendency in the area of substrates coated with the films as the processing of SEM images. The developed program and technique made it possible to determine the optimal mode (among six implemented) of ALE of GaN seed layers on sapphire substrates for preparation of high-quality HEMT structures. They can also be efficiently used for studying any island films, layers with inclusions of physical and chemical phases, and systems of colloidal particles used for formation of microelectronic structures.

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INTRODUCTION

Gallium nitride (GaN) can be used for manufacturing devices, which, due to its set of physicochemical and electrical properties, are superior in functional characteristics to devices based on other semiconductors: silicon (Si), gallium arsenide (GaAs), silicon carbide (SiC), and aluminum nitride (AlN) (Table 1) [1, 2].

Currently, gallium nitride is the most promising material for high-temperature, high-voltage, microwave, and high-current integrated circuits (ICs), injection lasers, short-wavelength LEDs, and semi-

conductor devices, including high-electron-mobility transistors (HEMTs) [3–5]. The market size of semiconductor devices and microwave electronics systems based on nitrides of III-group materials (III-N compounds) exceeded 9 billion dollars in 2014 [6] and, according to actual forecasts [7], will achieve 38–40 billion dollars in 2020.

Preparation of single-crystal GaN substrates involves technological difficulties because of the high GaN melting temperature (~2500°C), high-equilibrium nitrogen pressure above the melt, and fairly low

Table 1. Main electrical parameters of GaN in comparison with some other materials used in microelectronics

Material	Band gap, eV	Relative electrical conductivity	Electron mobility, cm ² /(V s)	Break-down field strength, MV/cm	Electron velocity, 10 ⁷ cm/s	Thermal conductivity, W/(cm K)	Maximum operating temperature, °C
GaN	3.4	10.4	900	3.3	2.7	1.3	700
Si	1.1	11.8	1350	0.3	1.0	1.5	300
GaAs	1.4	12.8	8500	0.4	2.0	0.5	300
AlN	6.2	9.5	300	11.7	2.0	2.5	500
4H-SiC	3.26	10.0	650	2.0	2.0	4.9	600
6H-SiC	3.0	9.7	370	2.4	2.0	4.5	600

Table 2. Characteristics of substrates for epitaxy of GaN structures

Substrate material parameter	Substrate material		
	Si(111)	4H-SiC	sapphire
Cost of 1 cm ² , rel. units	1	100	10
Conductivity	Conducting	Semi-insulating	Insulating
Available plate diameter, mm	300	50–150	50–150
Thermal conductivity, W/(cm K)	1.5	4.9	0.47
Lattice mismatch (relative to GaN), %	+17	–3.5	–14
Mismatch in thermal expansion coefficients (relative to GaN), %	–50	–18	+3.0

Symbols + and – indicate that this parameter of the substrate material is larger and smaller in comparison with GaN.

GaN decomposition temperature ($\sim 1000^\circ\text{C}$) [8]; as a result, the cost of these substrates is high. In this context, the formation of high-quality gallium nitride layers on foreign substrates is an urgent problem [9].

To date, there are three main ways of preparation of heteroepitaxial structures (HESs) based on gallium nitride in commercial production; these ways differ in the substrate material (sapphire, silicon carbide, or single-crystal silicon). Substrates of these types differ significantly from gallium nitride in the lattice constant, coefficient of thermal expansion (CTE), and conductivity (Table 2) [10].

The production of GaN-based HESs on sapphire substrates, the structure of which (by the example of HEMT structures) is shown in Fig. 1, runs into the problem of gallium nitride and sapphire (Al_2O_3) lattice mismatch (Table 2). This leads to bending of the epitaxial layer–substrate system and causes high

mechanical stress and density of structural defects (dislocations) in HESs.

Conventional ways of solving the aforementioned problems consist of development of a system of compensating transition layers and application of local epitaxy methods. Implementation of these approaches implies the formation of a complex structure consisting of a many layers with different compositions and thicknesses and requires conditions for precise control of the growth (accurate to monolayer). This is a crucial factor for the traditionally organized process of growing HESs of nitride compounds based on conventional hydride–metal organic vapor phase epitaxy.

To solve the above technological problems, a reactor for realization of the combined method of preparing HESs of nitride compounds based on atomic-layer epitaxy (ALE) and conventional hydride–metal organic vapor phase epitaxy (epitaxy using organometallic compounds and hydride gases) was developed by AO Elma-Malakhit.

This approach to the technological process made it possible to use the advantages of ALE for precise deposition of GaN seed layers with a thickness of 10–50 nm on the substrate surface before growing thick (2–3 μm) epitaxial u-GaN structures (Fig. 1) [11].

Terms “seed (or nucleated) layer” and “seed (or nucleated) film” are generally accepted in microelectronics [12, 13]. The seed layer may be either a continuous or island film. In the case under consideration, seed layers are almost invariably island films due to the large lattice mismatch between GaN and sapphire and small (10–50 nm) layer thickness; island films are characterized by the following factors [13]:

(i) average area of the sapphire substrate surface coated with particles (grains and crystallites) of the GaN film;

(ii) distribution of the coating particles (grains and crystallites) of the GaN film over the sapphire substrate surface;

(iii) average area (diameter) of GaN particles (grains and crystallites) on the sapphire substrate surface;

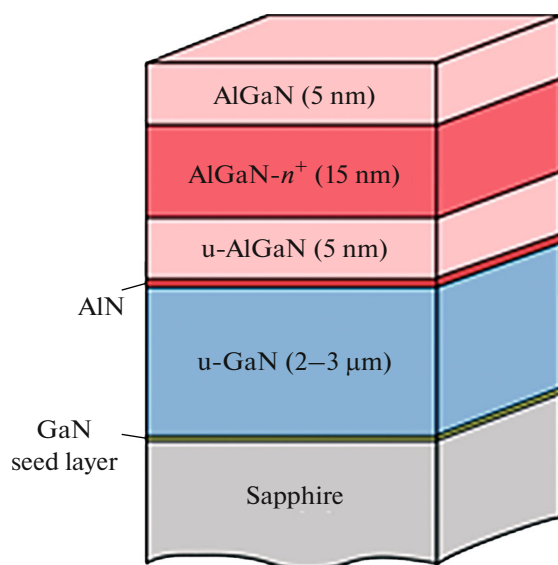


Fig. 1. (Color online) GaN-based HEMT structure on a sapphire substrate, 76.2 mm in diameter, with a thickness of 350–400 μm and orientation (0001).

Table 3. Modes of atomic-layer epitaxy of gallium nitride (GaN) seed layers from triethyl gallium (TEG) and ammonia (NH₃) on sapphire substrates in the upgraded reactor

Sample	Composition of the gas mixture in the reactor		Substrate holder rotation rate, rpm	Ratio of the NH ₃ and TEG feed times
	carrier gas	NH ₃ /TEG ratio		
Aix-26	N ₂	3×10^5	10	3.67
Aix-27	N ₂ /H ₂ = 3/1	3×10^5	10	3.67
Aix-29	H ₂	3×10^5	10	3.67
Aix-31	H ₂	3×10^5	10	22
Aix-32	H ₂	6×10^5	5.0	22
Aix-33	H ₂	1.5×10^6	10	22

(iv) average effective thickness of GaN film (crystallites) on the sapphire substrate surface.

Thus, island films are nanostructured systems, whose characteristics are responsible for the adsorption and reaction mechanisms in adsorbed layers [14, 15]. The set of these characteristics determines the surface functionality of seed layers, on which the qualitative and quantitative physicochemical properties of the grown HEMT structures depend (Fig. 1) [16].

For example, the quality of the HEMT structures that can be grown on the seed layer increases (tending to minimum defects and mechanical stress) with an increase in the area of the sapphire substrate surface coated with the GaN seed layer, an increase in the uniformity of layer distribution over the substrate surface, and a decrease in the area and thickness of GaN crystallites (Fig. 1) [13].

The first three characteristics of gallium nitride seed layers are measured and determined by processing of SEM images. The fourth parameter is measured using contact profilometers proceeding from the definition of the average effective film thickness.

The use of SEM images to determine the parameters of gallium nitride seed layers is an expensive, complex, and long-term procedure, which cannot always be used in production conditions.

Therefore, the purposes of this study were as follows:

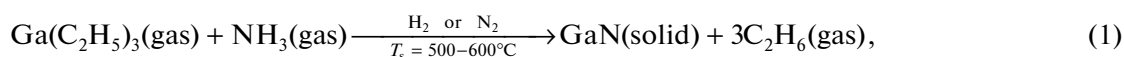
(i) to simplify the procedure of processing SEM images of seed layers in the form of island films and increase its efficiency;

(ii) to replace investigations of seed layers in the form of island films using SEM images (which are long term and, often, hard to access for production) with more rapid and available analysis via spectral ellipsometry;

(iii) to demonstrate the possibility of achieving the first two goals on samples of GaN seed layers using the ALE method with the aim of determining the optimal ALE mode for the seed layer formation with a maximum area of coating the sapphire substrate; this mode is necessary for preparing high-quality HEMT structures.

EXPERIMENTAL

To improve parameters of HEMT structures (Fig. 1) by increasing the quality and reproducibility of GaN seed layers deposited on sapphire substrates, we upgraded a reactor that is used for hydride–metal organic vapor phase epitaxy according to the patent [17]. ALE of gallium nitride seed layers from precursors (reagents) of triethyl gallium (Ga(C₂H₅)₃, TEG) and ammonia (NH₃) was performed on the upgraded reactor [18] according to the reaction



where H₂ or N₂ is a carrier gas and T_s is the substrate temperature.

In this study, GaN layers were deposited on 3-in [0001] sapphire substrates annealed for 20 min before the ALE. The ALE processes were carried out at $T_s = 524^\circ\text{C}$ on six samples in different modes.

In the upgraded reactor, the sapphire substrate on a rotating substrate holder successively passed through the TEG inlet region, blowing-off region, ammonia inlet region, and another blowing-off region. This method of formation of epitaxial gallium nitride layers is patented [17]. The ALE modes for GaN seed layers on six structure samples (sapphire–GaN seed layer) are given in Table 3.

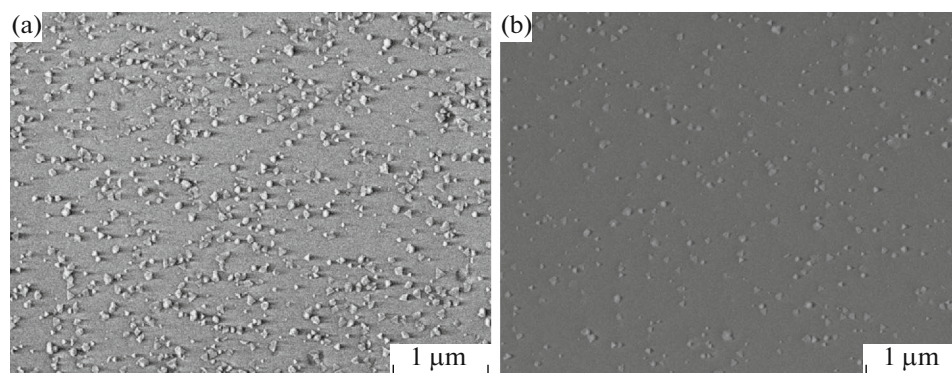


Fig. 2. SEM images of the surface of GaN seed layers on sapphire at identical magnifications for samples (a) Aix-29 and (b) Aix-32.

In this study, the structure samples listed in Table 3 were analyzed, concerning the seed layer parameters, using the following methods:

(i) SEM on a Jeol JSM-6490 LV electron microscope equipped with a Bruker Quantax XFlash energy-dispersive X-ray spectrometer and on an FEI Quanta 3D FEG electron microscope equipped with an attachment for generation of a focused ion beam;

(ii) spectral ellipsometry on Horiba Uvisel 2 and Horiba Auto SE ellipsometers.

RESULTS AND DISCUSSION

Results of Studying the Samples by Scanning Electron Microscopy

A scanning electron microscope makes it possible to investigate a surface of solids with a high resolution (up to 1 nm) and large focal depth, which allows us to visualize nanoscale structures. The use of this microscope with some other integrated systems and software provides an increase in the amount of information retrieved from the object of study; i.e., it allows us to:

- (i) determine the elemental composition;
- (ii) measure linear sizes;
- (iii) make hollows in the object and observe its structure along the depth, measuring thicknesses of the present layers;
- (iv) perform video recording in real time.

Surfaces of GaN seed layers on sapphire for two samples from Table 3 are shown in Fig. 2. We see that there are inclusions (crystallites) on the smooth sapphire substrate surface, which are individual GaN grains on the Al_2O_3 surface. To confirm this suggestion, the sample was analyzed by energy-dispersive X-ray microanalysis on a spectrometer entering the scanning electron microscope. The essence of the method consists of measuring the energy of the characteristic X-ray radiation excited by the SEM electron beam. The spectrum of the characteristic radiation is unique for each chemical element; therefore, the ele-

mental composition at the site of incidence of the electron beam can be unambiguously determined.

Since the region covered by the SEM electron beam significantly exceeded the crystallite size, the spectra should exhibit crystallite (Ga and N) and substrate elements (Al and O). This is confirmed via spectra from sample Aix-29 using energy-dispersive X-ray microanalysis (Fig. 3). These spectra indicate that crystallites are made of a GaN compound.

A common procedure of processing SEM images with the aim of revealing inclusions in films or particles on the substrate surface is the use of the standard Gwyddion program [19]. However, the application of this program for the samples is a semi-manual, long-term, and low-efficient procedure. Therefore, we developed a program of automatic processing of the SEM images of samples to analyze inhomogeneities and particles in films and on their surfaces [20].

The developed program includes procedures of filtering, correction, and increasing the contrast of SEM images of films and particles on the substrate surfaces, as well as calculating the percent ratio of regions with different color gradations. This program makes it possible to quantitatively estimate the areas of particles, inclusions, and phases present in the films and on the substrate surfaces.

Figure 4a shows the initial SEM image of the surface of sample Aix-26; this image processed using the standard Gwyddion program and the developed program is shown in Figs. 4b and 4c. We see that our program reveals gallium nitride crystallites on the sapphire substrate surface with a much higher contrast, compared with the standard Gwyddion program.

In addition, our program processes images automatically at a high speed, whereas the standard Gwyddion program requires some actions from an operator for choosing a procedure of processing crystallites (grains) and setting threshold values of filters, which slow down the processing rate. The percent ratio of the sapphire-substrate area coated with GaN crystallites (grains) was calculated based on the SEM

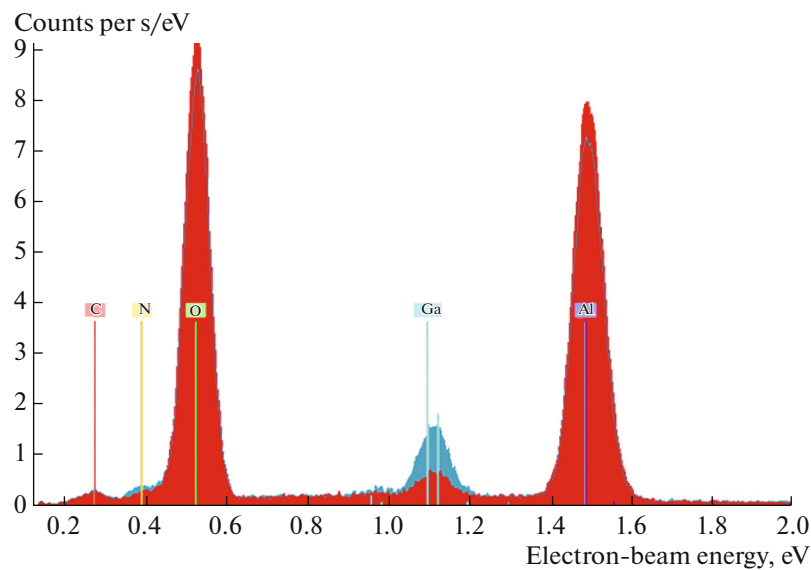


Fig. 3. (Color online) Spectra recorded from sample Aix-29 using energy-dispersive X-ray microanalysis: (red plot) sapphire substrate and (blue plot) crystallite on its surface.

images of the samples using the developed program; its values are given in Table 4 (column 2).

Modern SEMs are devices that are low-efficiency (because of the procedure of sample preparation), hard-to-access, and, often, expensive for production, which could not be supplied to all processing lines and manufacturing areas for producing HESs based on gallium nitride. Therefore, we made an attempt to carry out parallel investigations of samples using SEM image analysis and spectral ellipsometry.

Results of Studying the Samples by Spectral Ellipsometry

The general technique for determining the parameters of an optical system is as follows: a model is chosen after recording experimental data on the structure under study, the procedure of searching for the best correspondence is performed, and the results are analyzed. The process is repeated until the desired result is achieved.

Development of the structural model is a procedure of describing layers that are used for representing materials. A model of material is chosen for each layer from those existing in the library of the ellipsometer software or the data collected by a researcher. We must first set the characteristics of this material, then parameters for the described layer. This description of layers can take into account their various parameters (in particular, anisotropy, roughness, and presence of transition regions [21]).

To describe structural elements such as surface morphology, transition layers, and inclusions, the effective medium method is used in the DeltaPsi2 software on Horiba spectral ellipsometers, which allows us to make a choice between the two main versions [22, 23]:

(i) Maxwell–Garnett model, designed at describing small volume concentrations of noninteracting inclusions distributed in the main material;

Table 4. Comparison of the results of determining the sapphire-substrate surface areas coated with GaN crystallite layers for the samples under study, obtained based on processing SEM images and spectral ellipsometric measurements

Sample	Area of GaN crystallites on the substrate surface according to the results of processing SEM images, %	Area of GaN crystallites on the substrate surface according to the results of ellipsometric measurements, %	Ranges of the GaN crystallite layer thickness measured via mechanical profilometer, nm
Aix-26	7.1	11.5	30–40
Aix-27	7.2	11.5	30–40
Aix-29	9.0	13.0	30–40
Aix-31	5.3	5.5	20–30
Aix-32	2.6	4.5	25–30
Aix-33	1.2	1.2	10–15

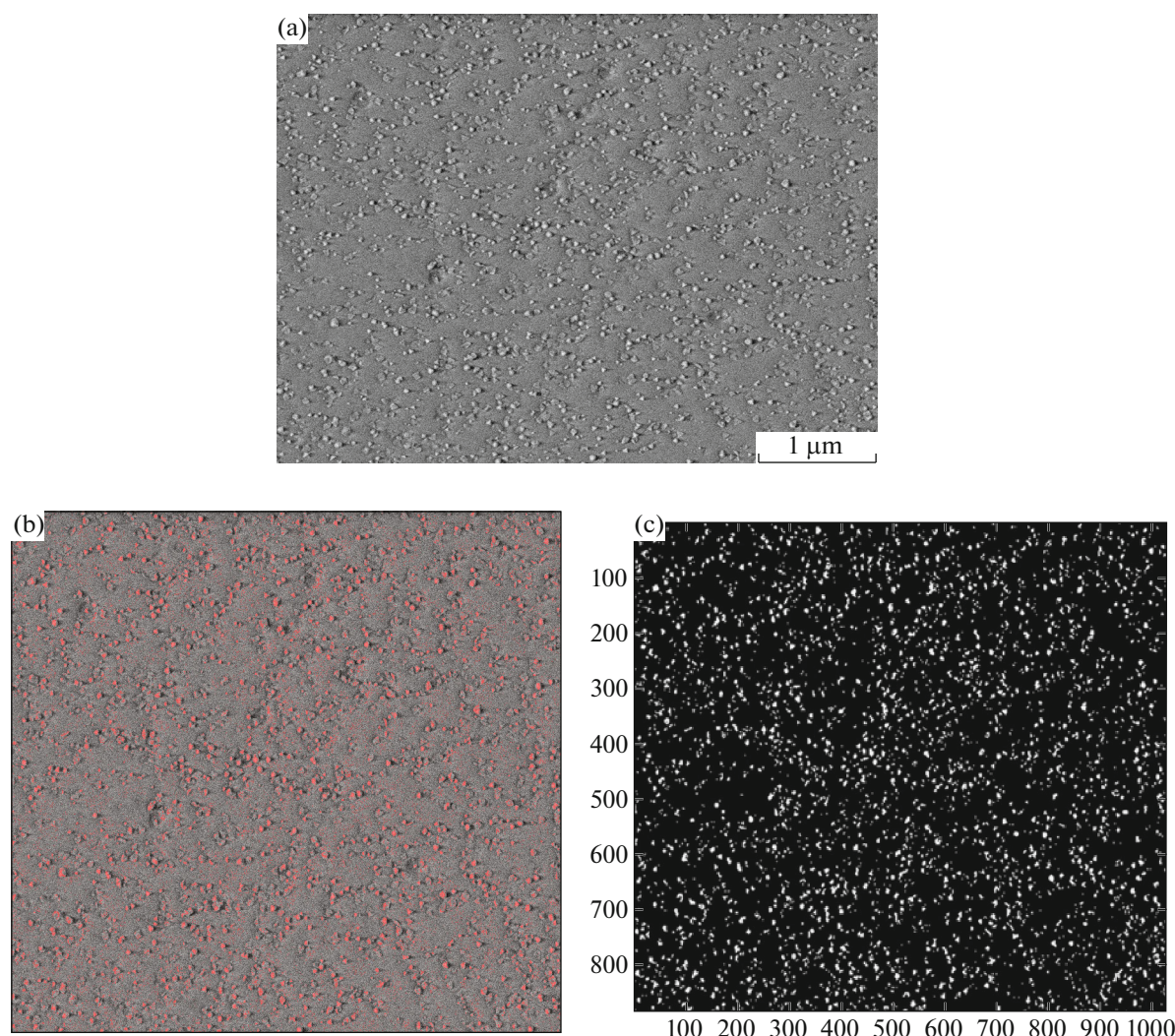


Fig. 4. (Color online) SEM images of the surface of sample Aix-26: (a) initial image, (b) image processed using the standard Gwyddion program (crystallites are shown red), and (c) image processed using the developed program.

(ii) Bruggeman model, appropriate for describing inclusions with different concentrations, which takes into account the interaction of these inclusions.

Since the SEM images of the sample surfaces (Fig. 2) exhibit the distribution of GaN crystallites (grains) on the sapphire substrate surface, we may conclude that GaN grains are individual inclusions of this material on the substrate; therefore, the use of the Maxwell–Garnett model appears most efficient.

When simulating the structure of a sample, this can be represented as a system consisting of two layers. The possible anisotropy is taken into account for the lower sapphire (Al_2O_3) layer, and the upper layer is a combination of some amount of GaN crystallites and air. Reflection from the rear side of the sapphire substrate was neglected in this model; however, the thickness of the GaN crystallite layer was fixed and the degree of coating the substrate surface with GaN crys-

tallites (grains) (i.e., the percent ratio of grains to air) was determined.

The average thickness of the GaN crystallite layer on the sample surface should be determined for substitution into the model. To this end, two cross-shaped stripes without GaN crystallites were formed on the surface of each sample parallel and perpendicular to the primary flat of the sapphire substrate. Using these stripes, multiple measurements of the GaN crystallite layer thickness with an Alpha Step 200 contact profilometer were performed on the surface of each sample.

According to measurement results, the height difference in the samples between the regions with GaN crystallites and without them (cross-shaped stripes) was from 10 to 40 nm (Table 4, column 4). Taking into account the measurement method and probe geometry, the GaN grains (crystallites) that are most protruding above the surface were detected as a single layer. Therefore, the height differences for the samples

are overestimated relative to the average thickness of the GaN crystallite layer, which was assumed to be 25 nm in the model for the entire set of samples.

The percent ratio of the sapphire-substrate area coated with GaN crystallites (grains) was calculated proceeding from the results of ellipsometric measurements (Table 4, column 3).

In [13] a GaN seed layer on sapphire substrates with a maximum area of substrate coating is optimal for producing high-quality HEMT structures. This is in agreement with the general laws of formation and growth of low-defect and low-stress film structures on substrates and sublayers with different structures and constitutions [24].

Thus, the data in Table 4 confirm that the method of processing SEM images and the spectral ellipsometry exhibit the same tendency when analyzing the samples. According to both methods, the best sample formed in optimal mode, characterized by a maximum sapphire-substrate area coated with the GaN crystallite layer, is Aix-29.

Therefore, the mode of growing the seed layer on sample Aix-29 presented in Table 3 is optimal among all implemented modes for forming high-quality HEMT structures.

CONCLUSIONS

A program for processing SEM images was developed to analyze inhomogeneities and particles in films and on their surfaces. This program, in contrast to the standard Gwyddion program, makes it possible to automatically estimate quantitatively areas of particles, inclusions, and phases present in films and on substrate surfaces based on SEM images. Thus, the efficiency of monitoring the parameters of island films increases.

We saw that processing of the results of spectral ellipsometric measurements of samples of island films and substrates with inhomogeneities and particles according to the Maxwell–Garnett model reveals the same tendency in their evolution as the processing of SEM images. This fact reveals the possibility of using a spectral ellipsometer as a basic tool to analyze these structures in commercial production (instead of the low-efficiency, hard-to-access, and generally more expensive scanning electron microscope).

As applied to the investigated samples of GaN seed layers grown via ALE, we conclude that the mode providing the maximum sapphire-substrate area coated with GaN crystallites (sample Aix-29) is optimal for preparing high-quality HEMT structures (among all implemented modes).

The techniques may be efficiently applied for studying nanolayers, colloidal particles, inclusions, and physical and chemical phases in films made of various materials used for formation of microelectronic structures.

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