Nanodimensional AlN layers Grown on Silicon in the System H_2-HCl-Al-NH_3

Simion RAEVSCHI, Vasile BOTNARIUC, Leonid GORCEAC,
Stefan TIRON, Mihail KOMPAN[1], Yurii ZHILYAEV[1]

Moldova State University, Department of Physics, MD-2009 Chisinau, Moldova
[1]Ioffe Physico-Technical Institute, 194021 St Petersburg, Russia
raevskis@mail.ru

***Abstract* — There were obtained nanodimensional AlN layers on Si by HVPE (Hydride Vapor Phase Epitaxy) method. SEM (Scanning Electron Microscopy) images of AlN layers, and cross-sections of AlN/Si structures are shown. The structure of surface layers was investigated by AFM (Atomic Force Microscopy) method at the stage of forming continuous layer. AlN grains nucleation on the surface of silicon occurs according to the three- dimensional (Folmer -Weber) mechanism. Granules represent a statistically dispersed ensemble of particles distributed on the substrate surface. Two mechanisms have been identified for estimating grains in the transition from the germination stage to the stage of continuous layer formation.**

***Index Terms* — Aluminum nitride, gallium nitride, aluminum, gallium, ammonia, hydrogen chloride, hydrogen, epitaxy.**

I. INTRODUCTION

Nitrides of group III elements of the periodic system (AlN, GaN, InN) and their alloys are large forbidden band semiconductors with direct optical transitions that allows to produce efficient lasers and diodes radiating in the range of 200-2000 nm of the electromagnetic spectrum. Synthesizing these materials directly from the elements can be achieved at temperatures of the order of 2000 K and pressures higher than 1 GPa. Such conditions for obtaining massive crystals of required dimensions are expensive and difficult to accomplish. For this reason massive substrates of these compounds of required dimensions for producing suitable substrates are not available so far. As a consequence, all devices based on these compounds are created on heterogeneous substrates.

The gallium nitride is largely used in optoelectronics for producing luminescent diodes and lasers in the blue range of the visible spectrum. In the most of cases the operating structures of devices are deposited on sapphire or SiC substrates that are expensive and less accessible. Furthermore, the sapphire is an insulator with a relatively low specific thermal conductivity (0.5 W/ (cm.K), a large difference in lattice parameter compared to GaN (~ 14%), which limits the area of its use. Lack of necessary substrates is the main obstacle to wider implementation of this semiconductor in other areas (in devices operating at high frequencies and high power, in acoustic-electronics, at high temperatures and so on).

Other materials are also tried to be used as substrates, but the rigid conditions of obtaining the structures (high temperatures, aggressive chemical media et al.) reduce drastically the number of appropriate substances. In the last years, a special attention is paid to silicon as material for substrates. The silicon is characterized by a high melting temperature (~1700 K) and is thermodynamically stable up to high temperatures. Its crystallographic planes are of trigonal symmetry. The silicon is relatively cheap and accessible, and the integration of nitride and silicon technologies would have economical advantages. Obtaining of the epitaxial gallium nitride films directly on silicon encounters many obstacles, such as formation of Ga:Si eutectic drops and deterioration of the plate surface as a result of the interaction between Si and GaN. Another problem in obtaining quality epitaxial layers is determined by the large difference in crystalline lattice parameters of GaN (a_{GaN} = 0.3189 nm) and Si ($a_{Si(111)}$= 0.384 nm) of ~ 16.9%, favoring the generation of dislocations in the structure, even at the initial stage of deposition. However, the biggest problem is created by the large difference (of ~ 116%) between the coefficients of thermal expansion of GaN (0001) ($\alpha_a = 5.59 \cdot 10^{-6} K^{-1}$) and Si ($\alpha = 2.59 \cdot 10^{-6} K^{-1}$). As a result, when cooled, structures become mechanically strained, take a concave form, and cracks appear in layers. These are the main impediments to creating of devices with nitrides of group 111 elements on silicon.

Attempts to obtain epitaxial layers of GaN on Si have been performed by several methods. The most of positive results in the research were obtained when one or more intermediate (buffer) layers of accommodation were deposited at layer-substrate interface. To accommodate the layer-substrate more materials have been tried – AlAs, GaN, AlGaN, SiC, ZnO etc.

A suitable material to be used for this purpose is aluminum nitride. Some aspects concerning the epitaxy of aluminum nitride on heterogeneous substrates by various methods such as MBE (molecular-beam epitaxy), MOCVD (metal organic chemical vapor deposition), VRE (vacuum reactive evaporation) et al. are largely described in the literature, [1-3]. In this paper the results

of investigation of growth processes and some physical properties of AlN layers, obtained on Si (111) by the hydride vapor phase epitaxy (HVPE) method, are presented

The aluminum nitride forms continuous solid solutions with the gallium nitride. By changing the solution composition one can obtain materials with the forbidden energy band in the range of 3.5-6.2 eV. Such alloys would permit to create optoelectronic devices working in the UV spectrum range. For these and other reasons there are an increasing number of investigations of this compound in the last years. In the present work the AlN thin films are obtained and investigated in view of using them as buffer layers at gallium nitride epitaxy on heterogeneous substrates.

II. EXPERIMENTAL

Growth of the AlN and GaN layers on Si was performed by HVPE method in a quartz horizontal reactor at atmospheric pressure (~ 50 mm H_2 O) in a single technological process. The hydrogen purified with a palladium filter was used as transfer gas. Ammonia, hydrogen chloride, Ga (5N) and Al (5N) were used as precursors. Ammonia and hydrogen chloride were further purified of H_2O, O_2, CO_2, CO (with NUPURE CORPORATION, MODEL 600 filters). HCl flows in pipes of aluminum, gallium or corrosion were dissolved in 200 smlpm H_2. Total hydrogen consumption was 4.8 slpm and that of ammonia was 2.4 slpm. HCl consumption was around 5 smlpm at depositing of layers and ~ 50-100 smlpm at corrosion. During depositing, the substrates were rotated with a hydrogen flow of ~ 1 slpm at a speed of about 100 rpm.

Thermal profile in the reactor was provided with resistive heater. Temperature of Al, Ga sources was constant, around 1120 K. The depositing temperature was controlled by a thermocouple placed directly next to the substrate.

Depositing was performed on silicon wafers КЭФ 4, 5 on plane (111). Before loading into the reactor silicon was subjected to the following processing methods: i) boiling 10 min in CCl_4; ii) wash in de ionized water; iii) boiling 25 min in $1NH_4OH:2H_2O_2:5H_2O$; iv) wash in de ionized water; v) boiling 25 min in $1HCl:2H_2O_2:5H_2O$; vi) wash in de ionized water; vii) corrosion 2 min in $1HF:5H_2O$; viii) wash in de ionized water; ix) drying in propanol vapor, ~ 2 min.

The layers surfaces were investigated by SEM and AFM methods at room temperature under atmospheric conditions. AFM investigations were performed at an installation of NT-MDT Company using the silicon nitride indents.

III. RESULTS AND DISCUSSION

The AlN layers on Si (111) were obtained in the temperature range 500-1100^{0}C. When the temperature is lower than ~ 700^{0}C, they are like amorphous, porous white flakes, statistically dispersed on the surface of substrates. The layers are instable and can easily be removed from the surface of silicon. Therefore the main investigations were made at 800, 900, 1000, and 1100^{0}C, and for the process duration of 5, 10 and 20 min.

The AlN films obtained on Si are uniform, smooth like a mirror, without any cracks or eutectic traces. Dots with the size less than 1 μm can be seen on their surface in an optic microscope. On the layers deposited on two inches substrate there are seen concentric interference fringes – blue, green and dark-red, that is an evidence of the variable film thickness, less than 1 μm, along the substrate radius. At optimal reactant gas flows there were obtained also one-color films - blue and dark-red. The average thickness of AlN films dependence on the duration of depositing for layers obtained at different temperatures is shown in the Fig. 1. The thickness of layers obtained at 800^{0}C increases almost proportional to the depositing time. The depositing rate is determined by the Al mass transfer from the zone of the source to that of growth.

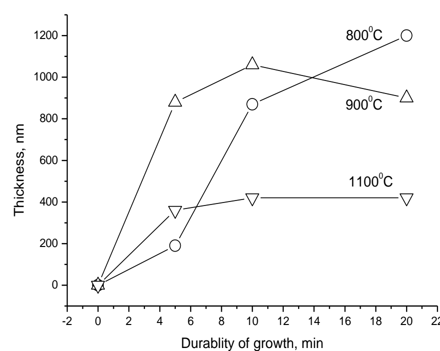

Fig.1. Dependence of the thickness of AlN layers, deposited on Si(111) by HVPE method, on the process duration at the given temperatures.

When the temperature is raising the depositing rate increases reaching a maximum value, then it decreases. The maximum of the depositing rate is observed at ~ 1000^{0}C where a layer of 1800 nm was obtained in 10 min. The depositing rate dependence on the temperature and time can be explained by the transition from the diffusion growth mechanism (at $T_g < \sim 800^0$C) to the kinetic one ($T_g > 900^0$C) determined by the processes occurring on the substrate surface. When the temperature is elevating, the porosity of films is decreasing and the dissociation coefficient of AlN is increasing, which results also in the diminution of the growth rate.

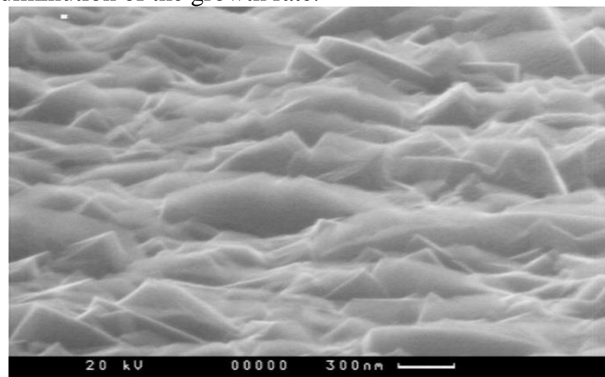

Fig.1. Image (SEM) of the surface of the AlN layer grown on Si at 900^{0}C, duration 5 minutes, (R376-4).

The variation of the thickness of the AlN layer along the surface is confirmed by measurements of the structure breakdown voltage. It is 400 V in the centre and 300 V on the periphery, i.e. the average value is 350 V. The average breakdown electric field is of the order of 350 V/150 nm ≈ 23 MV/cm, which is characteristic for dielectrics. The avalanche breakdown voltage is ~100 V for silicon with the resistivity of 4.5 Ω·cm and the impurity concentration of ~ 10^{15} cm^{-3} [4] . Therefore the voltage drop on the AlN layer does not exceed 250 V, and correspondingly the breakdown field

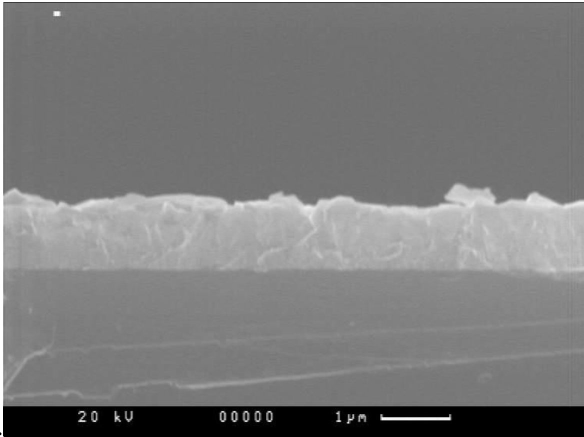

Fig.2. SEM image of the cross-section of the structure AlN/Si (111), (R376-1).

is less than 17 MV/cm. One has to mention that for massive AlN (6.2 eV) at 300 K the breakdown electric field is 1.2-1.8 MV/cm, and for SiO_2 is ~ 1 MV/cm.

The surface morphology of a film obtained at 900^0C is presented in Fig.1. The layers obtained under identical conditions, but at temperatures 800, 1000, 1100, and 1200^0C have a similar morphology. The AlN film of ~ 1 μm thickness is formed from structural components. The top surface of the layer has the relief shown in Fig. 2.

In Fig. 3 there are presented the AFM images of an AlN layer deposited on Si (111) by HVPE method in two projections. The layer surface is embossed, and the layer appears as a set of dispersed particles (dp), arranged disorderly. By geometrical dimensions (height, diameter), there are two main categories of particles: lighter particles with larger sizes, and darker smaller particles. The surface density of larger particles is much lower the density of small particles. The surfaces occupied by big and small dp on the substrate are not essentially different, the big/small ratio being 2/3. The height of large size dp lies in the range 110-320 nm and that of the small ones, 80-110 nm. The dp distribution
in two categories implies their geometric similarity and makes it easy to distinguish them in the curve of successively increasing peak heights depending on their number (Fig.4) .

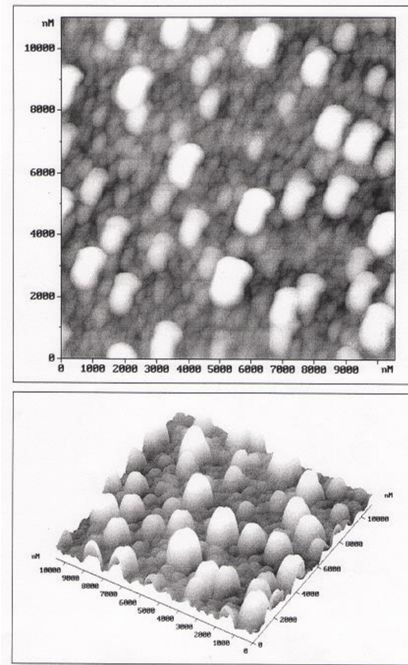

Fig.3. Surface image of AlN buffer layer grown on Si (111) at 1100^0 C (5 min), as observed by AFM.

Numbering of particles by size is motivated by the chaotic character of their arrangement on the substrate surface. It is also assumed that their geometric shape remains unchanged during the growth. This assumption is also partially confirmed by the forms of granules of different sizes that have different evolution time. As shown previously [2], the form of 111-N compounds granules changes only with change of the growth temperature or the concentration of precursor reactants. This paper presents the research results for layers obtained under stationary conditions of temperature and concentration of reactants. The figure shows a sharp threshold (130 nm) that separates the small size dp from those of large size. This threshold shows the change of layer growth mechanisms in the process of evolution from the initial stage of nucleation of granules to the subsequent stage of formation of larger dp - the stage of continuous layer deposition.
The estimated continuous layer thickness is ~ 70 nm. The height of large dp reaches ~ 300 nm after 300 sec of deposition (the dp growth rate reaches ~ 1 nm/sec). Taking into account the dp distribution by size one can say that the continuous layer is formed after ~ 200 sec of deposition, when there are changes as well in the mechanisms of layer growth.

Figure 5 shows the time dependence of the concentration of AlN dp deposited on the silicon surface. At the beginning of the process their concentration changes insignificantly. Dispersed particles grow only by size. The latency period of concentration evolution changes abruptly after a period of time of ~ 200 sec when a sudden increase takes place. After a very short time the dp concentration decreases sharply to the initial

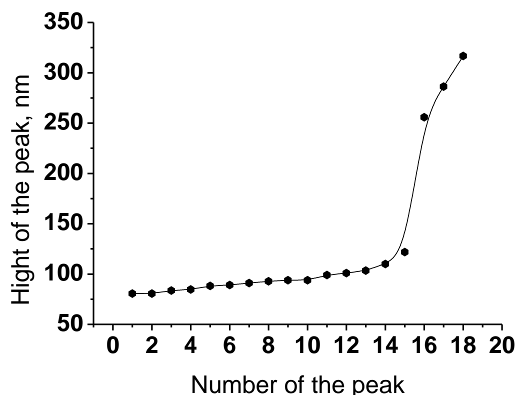

Fig.4. Distribution by height of AlN dispersed particles deposited on Si by HVPE method at 1100^{0}C, 300 sec.

level. Reducing the total concentration of the granules may be due to coalescence processes of dispersed particles of different sizes.

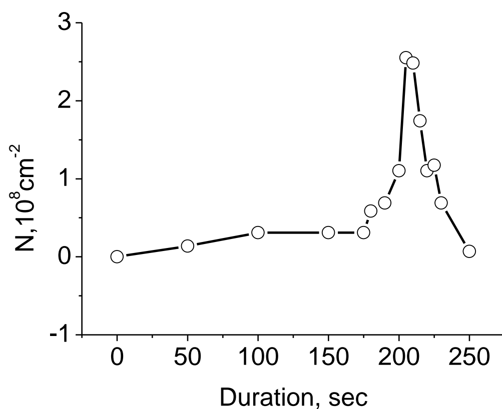

Fig.5. Change of concentration of AlN dispersed particles, deposited on silicon substrates at the initial stage of continuous layer formation.

Given the above, one can propose a model of AlN layer formation on Si (111). It is known that even the ideal surfaces of perfect crystal substrates obtained have terraces, steps, and contain surface defects with adatoms or dot vacancies, dislocations, linear and other defects. Roughness exceeds 10 nm even on the most perfect Si surfaces. Uneven real surface of substrates significantly affects the nucleation, and growth of the new layer, especially for heterogeneous layers. At the initial deposition stage the germination of layers occurs in the vicinity of defects. Defects are statistically distributed on the substrate surface, like the condensed granules of the new phase. The further granule size development is ensured not only by the flow of reactants from the gaseous environment, but also by the flow of compounds formed on the substrate due to surface diffusion processes. Similar mechanisms of mass transfer are also present at heteroepitaxy of GaN layers. The surface flow towards the initially formed centers is due to higher affinity between their substances as compared with the affinity between heterogeneous substances (AlN, Si). The growth rate of initially formed granules increases owing to increasing supersaturation over the granules surface as compared with the supersaturating over the substrate surface. At the initial stage of nucleation this difference is insignificant due to relatively low concentration of germination centers and small size of the granules. When the volume (surface) of granules increases, this difference becomes larger, and the flow of reactants to the surface of granules increases. The process of nucleation of new granules on the surface of substrate takes place continuously, but these smaller granules are absorbed by the larger size granules due to the coalescence processes.

Thus, the surface density of granules changes insignificantly during ~ 200 sec. After the substrate is coated with AlN, the surface diffusion mechanism is not more involved in granules development. At the intersection of surfaces of the originally formed larger granules appear sharp boundaries, favorable to nucleation of new granules. Thus, there appear two kinds of granules on the substrate surfaces – big ones evolving from the surface defects of the substrate, and small granules, formed later in the process of AlN layer thickness evolution.

IV.CONCLUSION

Using the HVPE method, thin AlN layers were synthesized on silicon substrates. The layer structure was investigated by AFM method. It was found that layers germination takes place according to the three-dimensional model, 3D. The formed granules are an association of dispersed particles, statistically distributed on the substrate surface. In the process of evolution from the initial discrete stage to the stage of continuous layer formation, a change of mechanisms of layers growth takes place.

The work was partially supported by Institutional 11.817.05.12A Project, funded by the Supreme Council of Research and Technological Development of the Academy of Sciences of Moldova.

REFERENCES

[1] [1] H. Ishikava, G-Y. Zhao, N. Nakada, T. Egawa, T. Jimbo, M.Umeno. GaN *on* Si *substrate wth* AlGaN/Al *intermediate layer*. Jpn. J. Appl. Phys. **38** (1999) pp.l492-l494, part 2 N5A.

[2] [2] И. А. Бобровникова, И. В. Ивонин, В. А. Новиков, В. В. Преображенский. *Theoretical and experimental study of surface processes at the molecular-beam epitaxy of gallium nitride,* ФТП, 2009, т.**43**, вып. 3, сс. 422 - 428.

[3] [3] A.Krost. *Metalorganic chemical vapor phase epitaxy of crack-free on* Si(111) *exceeding* 1 μm *in thickness*. Jpn. J. Appl. Phys., vol **39** (2000), pp.L1183-L1185, part2, N11B.

[4] [4] S.M.Sze. Physics of Semiconductor Devices. Secon edition. New York, Chichester, Brisbane, Toronto, Singapore, 1981.