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Growth regimes of aluminium nitride films on hybrid SiC/Si(111) substrates

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The nucleation mechanism of aluminum nitride films grown by the method of hydride vapor phase epitaxy on hybrid substrates 3C-SiC/Si(111) is theoretically analyzed. The temperature regions and vapor pressure regions of components are determined in which the island growth mechanism and the layer-by-layer growth mechanism are realized. The theoretical conclusions are compared with the experimental data. The morphology of aluminum nitride film on 3C-SiC/Si(111) at the initial growth stage is investigated by the method of scanning electron microscopy. The methods of controlling the change of the growth mechanism from the island growth to the layer-by-layer growth are proposed.

Keywords: aluminium nitride, gallium nitride, silicon carbide on silicon, method HVPE, nucleation, wide-bandgap semiconductors, heterostructures.

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1. Introduction

The formation of epitaxial layers of aluminum nitride (AlN) and gallium nitride(GaN) on silicon substrates is a promising area for device applications due to two reasons. Firstly, AlN and GaN layers can act as a basis for creation of device heterostructures on silicon. Secondly, since silicon can be easily removed, bulk layers of AlN and GaN may form and themselves act as substrates. Due to a large difference in the parameters of AlN, GaN and silicon lattices, as well as in their thermal expansion coefficients, it is virtually impossible to grow high-quality AlN and GaN layers directly on silicon substrates without special substrate preparation, as shown in many studies. Moreover, if growth takes place at a high temperature, silicon may chemically react with gallium, which significantly reduces the quality of epitaxial layers. In order to solve the latter problem, taking into account the fact that wetting of GaN is better on the AlN surface, first an AlN layer is usually deposits on the substrate, and then GaN is grown on it. This problem is solved by using different methods for creation of $\mathrm{Si}_x\mathrm{N}_{1-x}$ layers. However, in our opinion, a good buffer layer for growth of AlN and GaN films on silicon is a layer of nano-SiC grown by the coordinated atomic displacement method [1]. Detailed information about the advantages of AlN and GaN film growth on nano-SiC as compared to growth of such films on SiC films, grown by the standard technology, is given in the papers [1,2]. It should be noted that while methods of metalorganic vapor phase epitaxy (MOVPE) [3] or methods of molecular-beam epitaxy with nitrogen plasma activation (MBE PA) [4] are better suited for growth of AlN and GaN device heterolayers on hybrid nano-SiC/Si substrates (hereinafter „SiC/Si substrates“), the irreplaceable method for growth of thick AlN and GaN layers is, undoubtedly, the method of hydride vapor phase epitaxy (HVPE) [2].

It has been noted above that before growing a GaN layer, even if a buffer SiC layer is used, technologists usually grow AlN layers first and only then a GaN layer. This makes it possible to grow GaN films of higher quality. Therefore, structural quality of subsequent GaN layers considerably depends on structural quality of the AlN layer. Due to this, the goal of this paper is a study of the initial growth stages of AlN films grown by the HVPE method on hybrid SiC/Si substrates. It should be noted that the paper [5] suggested a model for nucleation and growth of AlN and GaN films on SiC/Si substrates and made qualitative assessments of the probability of implementation of different mechanisms for nucleation and growth of nuclei (islands) of such compounds based on the expressions for Gibbs energy of formation of three-dimensional and two-dimensional nuclei. However, this paper did not take into account the morphology of AlN islands, and did not take into account the impact of surface energies of different AlN faces on the nucleation process. In this paper the model [5] will be developed and quantitative estimates will be obtained for probabilities of nucleation of three-dimensional and two-dimensional islands both on the substrate singular surface and with presence of steps. Estimated data will be compared with the experimental results on the growth of AlN films on hybrid 3C-SiC/Si(111) substrates by the HVPE method.

2. Thermodynamics of formation of AlN nuclei, their equilibrium shape and critical size

Several papers [6,7] used the atomic force microscopy method to find that three-dimensional islands form at the initial stages of AlN film growth on a 6H-SiC(0001) substrate, grown by HVPE and MOVPE methods, i.e. the Volmer–Weber mechanism is implemented, and then these islands merge into a continuous layer. The paper [8] also found (by transmission electron microscopy) the formation of three-dimensional islands during MBE-growth on a vicinal substrate 6H-SiC (tilt 3–4° from the direction [0001]). At the same time, in case of growth on a singular face of the 6H-SiC substrate (0001), several first AlN monolayers were formed layer by layer, and then a transition to three-dimensional film growth occurred, which means the Stranski–Krastanov mechanism. The paper [5] estimated the probabilities of nucleation of three-dimensional AlN islands on 3C-SiC(111) (in the shape of a spherical segment) and two-dimensional islands (disk shaped) during growth by the HVPE method. The estimations have showed that the probability of three-dimensional island nucleation is significantly higher than that of two-dimensional islands.

It is well known that calculation of the nucleation barrier requires determination of the surface energies of the island faces and its binding energy to the substrate. The equilibrium shape of a crystal being in contact with the vapor phase can be found according to the known values of surface energies for low-index crystal planes, by using the Wulff construction [9]. To determine the crystal shape of III-nitrides, following the paper [10], we will take into account the values of surface energies for the faces $\{1\bar{1}00\}$ and $\{11\bar{2}0\}$, $\gamma_{(1\bar{1}00)}$ and $\gamma_{(11\bar{2}0)}$, as well as the value of the sum of surface energies for the faces (0001) and $(000\bar{1})$, $\gamma_{(0001)} + \gamma_{(000\bar{1})}$ [11–13]. It is found that the crystal cross-section in the plane, defined by the directions $[1\bar{1}00]$ and $[11\bar{2}0]$, is a regular hexagon the sides of which correspond to planes $\{1\bar{1}00\}$ [10]. If $\gamma_{(11\bar{2}0)} < 2/3^{1/2}\gamma_{(1\bar{1}00)}$, then the hexagon angles are truncated by $2/3^{1/2}\gamma_{(1\bar{1}00)} - \gamma_{(11\bar{2}0)}$, counting from the angle vertex. In the plane, set by the directions $[1\bar{1}00]$ and [0001], the crystal has a rectangular cross-section with a ratio of crystal height to its base diameter (diameter of an inscribed circle) equal to $(\gamma_{(0001)} + \gamma_{(000\bar{1})})/(2\gamma_{(1\bar{1}00)})$ [10]. The equilibrium shape of a crystal, being in contact with the surface, can be found using the Winterbottom construction [9]. In case of AlN crystal formation on the surface of 3C-SiC(111), it would appear reasonable that the crystallographic direction [0001] of AlN will coincide with the crystallographic direction [111] of 3C-SiC. In this case the lattice mismatch between the film and the substrate will be minimized (0.9%). As a result, we find that the AlN crystal is „sunk“ to the value of $(\gamma_{(0001)} - \gamma_i + \gamma_s)/(\gamma_{(0001)} + \gamma_{(000\bar{1})})$ in the substrate surface, where γ_i is the interphase energy for the film/subsrate interface, γ_s is the substrate surface energy. Thereat, the ratio of crystal height to diameter is equal to $\alpha = (\gamma_{(0001)} + \gamma_i - \gamma_s)/(2\gamma_{(1\bar{1}00)})$ on condition that $\gamma_{(0001)} + \gamma_i - \gamma_s > 0$ (in case of coherent autoepitaxy $\alpha = 0$, since $\gamma_s = \gamma_{(0001)}$ and $\gamma_i = 0$). It should be noted that since the planes (0001) and $(000\bar{1})$ are inequivalent, it is rather difficult to determine their surface energies separately. Therefore, surface energies of these faces will be estimated using an averaged value: $(\gamma_{(0001)} + \gamma_{(000\bar{1})})/2$ [10–12].

Value of γ_i is found by an *ab initio* calculation of the energy of film adhesion to the substrate [13]. For this purpose, the energy of a system consisting of a film and a substrate is calculated in two cases. In the first case, the film is mated with the substrate, in the second case a vacuum layer is located between the film and the substrate. The adhesion energy is equal to the difference of system energy in the second and the first configurations. Volumetric contributions to the system energy, as well as contributions by surfaces, retained upon film separation from the substrate, are identical in both cases (if a sufficiently thick film and substrate are considered). Therefore, the adhesion energy is equal to the sum of surface energies of the planes, formed upon separation of the film and substrate, minus the surface energy of the film/substrate interface. Considering the formation of an AlN film, we obtain the following formula for finding the interface energy $\gamma_i : \gamma_i = \gamma_{(000\bar{1})} + \gamma_s - \Gamma$, where Γ is the adhesion energy. Upon nucleation of an AlN film on AlN, we obtain a value $\gamma_i = 0$, which agrees with the models of film growth in case of homoepitaxy [14]. It should be noted that the used approach to determination of the crystal interface energy can be considered to be accurate in case of single-component crystals. In case of multicomponent crystals, the obtained calculation formula can be used for estimations only. This is due to the fact that the surface energies $\gamma_{(000\bar{1})}$ and γ_s cannot be determined accurately (if the substrate is a multicomponent crystal).

The AlN and SiC surface energies were calculated by the density functional method (DFT) in many papers (e.g., [11–13,15]). At the same time, there are almost no publications on calculations of adhesion energy for an AlN system on 3C-SiC(111) [13]. In this respect, the energy of AlN film adhesion to 3C-SiC(111) was calculated in this study by the DFT method using the Medea-VASP package. The modelled cell is shown in Fig. 1 (the total number of atoms is equal to 147). Atom configuration corresponds to the found minimum of system energy. Let us outline the typical properties of this configuration. Silicon atoms on the crystal interface are bound to nitrogen atoms and the first biatomic AlN layers repeats the sphalerite structure 3C-SiC. The first layer of atoms from the top consists of Al atoms. To find the system energy in this configuration, a vacuum layer 15 Å was placed above the AlN layer, while the broken bonds on the surface 3C-SiC$(\overline{111})$ were filled with hydrogen atoms. The PBE functionality (Perdew–Burke–Ernzerhof),

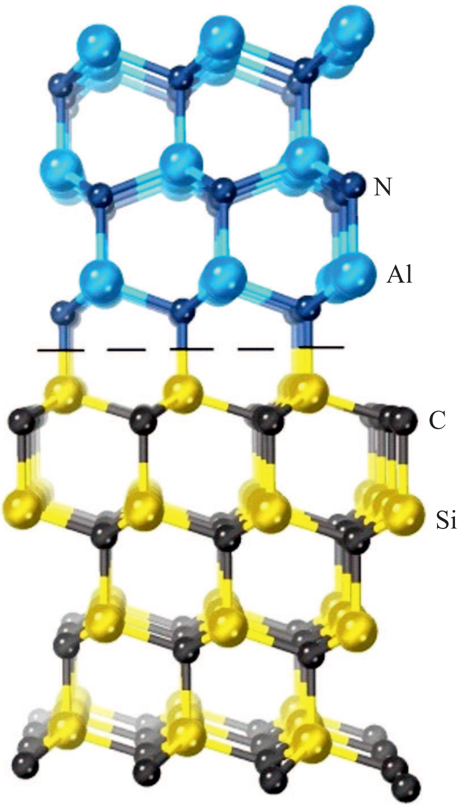

Figure 1. Structure of AlN and 3C-SiC(111) interface.

pseudopotentials and the plane wave basis were used during minimization of total energy. Plane wave cutoff energy was taken equal to 400 eV. To model the separation of the film and the substrate, bonds between silicon and nitrogen atoms (shown by the dashed line in Fig. 1) were broken. Then the AlN layer was moved to distance 5 Å from the layer of 3C-SiC. System energy was minimized in the two cases taking into account the surface relaxation. The calculated estimate of adhesion energy $\Gamma \sim 6.4\,\mathrm{Jm}^{-2}$ is by 18% lower than the adhesion energy value calculated in [13] with the same interface configuration ($\Gamma = 7.78\,\mathrm{Jm}^{-2}$). A difference in adhesion energy values, as in the case of surface energies of AlN and SiC crystals [11–13,15], is related to the use of different DFT methods and a different number of atoms in the modeled system. A large spread in surface energy values, obtained by *ab initio* calculation, will be observed if two surfaces, obtained by separation of the initial system, are not equivalent. The difference in calculations is usually considerably smaller for equivalent surfaces. Thus, the surface energy value of $2.4\,\mathrm{Jm}^{-2}$, which agrees well with the data given in the paper [11] ($2.32\,\mathrm{Jm}^{-2}$), was obtained for the faces $\{1\bar{1}00\}$ using the Medea-VASP program. Due to a large spread in the surface energy values for the crystal polar planes, it is rather difficult to calculate accurately the ratio of height of an AlN crystal, located on a 3C-SiC(111) substrate, to its lateral size. The estimates made with account of the reference data [11–13,15], make it possible to conclude that the value of α, i.e. the island height to diameter ratio, is in the interval of $0.1-0.7$. Since the obtained value of α is above zero, it means that, within the framework of the macroscopic nucleation model, the formation of three-dimensional islands is energetically more favorable than of two-dimensional islands. In a similar way, we find an interval of values for quantity $\Delta\gamma = \gamma_{(0001)} + \gamma_i - \gamma_s = 0.8-3.2\,\mathrm{Jm}^{-2}$. The value of $\Delta\gamma = 1.24\,\mathrm{Jm}^{-2}$, obtained by calculation [13], to which the values of $\alpha = 0.2$ and $\gamma_i = 1.65\,\mathrm{Jm}^{-2}$ correspond, will be used for further estimations of probability of three-dimensional and two-dimensional AlN island formation. In the paper [13] the surface energies of AlN and SiC faces ($\gamma_{(0001)} = 4.51\,\mathrm{Jm}^{-2}$, $\gamma_{(1\bar{1}00)} = 2.96\,\mathrm{Jm}^{-2}$, $\gamma_{(11\bar{2}0)} = 3.00\,\mathrm{Jm}^{-2}$, $\gamma_s = 4.92\,\mathrm{Jm}^{-2}$), as well as the adhesion energy were calculated by one DFT method, makes it possible to minimize the errors of calculations.

Islands of different shapes and dimensions may form on the substrate surface due to density fluctuations of deposited particles. Island shape during the island growth is determined both by thermodynamics (ratio of surface energies of crystal faces) and by process kinetics (ratio of growth rates of crystal faces) [16]. In this paper we will determine the thermodynamic (equilibrium) shape of the island, which makes the minimum contribution to the Gibbs energy of island formation.

Let us consider the formation of islands in the shape of a rectangular prism, the side surfaces of which is formed by the faces $\{1\bar{1}00\}$. Let the island height and base radius (radius of a circumscribed circle), expressed via the number of atoms, be respectively equal to n and m (so that the number of AlN pairs in the island is equal to $3m^2n$). Then the expression for Gibbs energy of three-dimensional island formation is as follows

$$\Delta G(m,n) = -3m^2n\Delta\mu + 3^{3/2}/2m^2a^2\Delta\gamma + 6mna\sigma_p, \quad (1)$$

where a and c are the AlN lattice parameters; σ_p is the interphase energy per unit length of the island perimeter, the calculations assume $\sigma_p = \gamma_p c/2$ and $\gamma_p = \gamma_{(1\bar{1}00)}$. It follows from the expression (1) that, as distinct from the classical nucleation theory [16,17], Gibbs energy of island formation is a function not only of island dimension, but of its shape as well. Therefore, size and shape of an island having a critical size are determined by finding the saddle point of the function (1):

$$m_c = \frac{2a\sigma_p}{\Delta\mu} \quad \text{and} \quad n_c = \frac{3^{1/2}a^2\Delta\gamma}{\Delta\mu}. \quad (2)$$

Having substituted (2) in (1), we find an expression for the nucleation barrier in the following form

$$\Delta G^* = \frac{2\cdot 3^{3/2}a^4\Delta\gamma\sigma_p^2}{\Delta\mu^2}. \quad (3)$$

Ratio of height of an island having a critical size to its lateral dimension is equal to $\alpha = cn/(2\cdot 3^{1/2}am)$

$= \Delta\gamma/(2\gamma_p)$, i.e. corresponds to the island of an equilibrium shape.

The work of formation of a two-dimensional AlN island in the shape of a regular hexagon on 3C-SiC(111) is equal to:

$$\Delta G(m) = -3m^2\Delta\mu + 3^{3/2}/2m^2a^2\Delta\gamma + 6ma\sigma_p. \tag{4}$$

From where

$$m_c = \frac{a\sigma_p}{\Delta\mu - 3^{1/2}a^2\Delta\gamma/2}, \tag{5}$$

$$\Delta G^* = \frac{3a^2\sigma_p^2}{\Delta\mu - 3^{1/2}a^2\Delta/\gamma/2}. \tag{6}$$

Let us now consider the AlN nucleation on a step formed by the faces (111) and $(11\bar{2})$ 3C-SiC. The work of formation of a two-dimensional AlN island in the shape of a regular hexagon on a step is equal to

$$\begin{aligned}\Delta G(m, l) = {} & -1/2\big(m(3m - 4l) + l|l|\big)\Delta\mu \\ & + 3^{1/2}/4a^2\big(m(3m - 4l) + l|l|\big)\Delta\gamma \\ & + a(3m - 2l)\sigma_p + a(2m - |l|)\sigma_i,\end{aligned} \tag{7}$$

where l is an integer that characterizes the shift of the island center in relation to the step edge; $\sigma_i = \gamma_{i(1\bar{1}00)}c/2$, where $\gamma_{i(1\bar{1}00)}$ is the energy of the AlN$(1\bar{1}00)$ and SiC$(11\bar{2})$ interface. It is assumed that the AlN faces $\{1\bar{1}00\}$ are parallel to the SiC planes $\{11\bar{2}\}$. By determining the saddle point of function $\Delta G(m, l)$, we find the critical island dimension and the nucleation barrier

$$m_c = \frac{a\sigma_p}{\Delta\mu - 3^{1/2}a^2\Delta\gamma/2} \quad \text{and} \quad l_c = -\frac{a\sigma_i}{\Delta\mu - 3^{1/2}a^2\Delta\gamma/2}, \tag{8}$$

$$\Delta G^* = \frac{a^2(3\sigma_p^2 + 4\sigma_p\sigma_i - \sigma_i^2)}{2\Delta\mu - 3^{1/2}a^2\Delta\gamma}. \tag{9}$$

Gibbs energy of three-dimensional island formation on a step $\Delta G(m, n, l)$ is found by multiplying the first, third and fourth terms in the right member of the equation (7) by the number of monolayers in the island n. Then the nucleation barrier and the critical island dimension are determined by the following formulas

$$m_c = \frac{2a\sigma_p}{\Delta\mu}, \quad n_c = \frac{3^{1/2}a^2\Delta\gamma}{\Delta\mu}, \quad l_c = -\frac{2a\sigma_i}{\Delta\mu}, \tag{10}$$

$$\Delta G^* = \frac{3^{1/2}a^4\Delta\gamma(3\sigma_p^2 + 4\sigma_p\sigma_i - \sigma_i^2)}{\Delta\mu^2}. \tag{11}$$

With subsequent growth of the AlN island, repeated nucleation on its faces is possible. Since the film grows layer-by-layer in case of autoepitaxy, two-dimensional islands will form. In this case, upon nucleation of nuclei in the shape of a regular hexagon on the face AlN(0001), Gibbs energy is equal to

$$\Delta G(m) = -3m^2n_0\Delta\mu + 6mn_0a\sigma_p. \tag{12}$$

Here, $n_0 = 2$, which corresponds to the formation of a stable polytype 2H-AlN, $\sigma_p = \gamma_{(1\bar{1}00)}c/2$. The critical dimension of the nucleus and the nucleation barrier are equal to

$$m_c = \frac{a\sigma_p}{\Delta\mu}, \tag{13}$$

$$\Delta G^* = \frac{3n_0a^2\sigma_p^2}{\Delta\mu}. \tag{14}$$

In case of nucleation on the faces $\{1\bar{1}00\}$, let us consider the nucleation of a rectangle-shaped island. Let the width (measured along the direction $[11\bar{2}0]$ in case of nucleation on the face $(1\bar{1}00)$) and the length of a rectangle (along the direction (0001)), expressed via the number of atoms, be equal to m and l, respectively, then Gibbs energy is determined by the expression

$$\begin{aligned}\Delta G(m, l) = {} & -ml\Delta\mu + ma\big(\sigma_{(0001)} + \sigma_{(000\bar{1})}\big) \\ & + lc\sigma_{(11\bar{2}0)} + ml\,\frac{ac}{2}\,\gamma_{(1\bar{1}00)},\end{aligned} \tag{15}$$

where $\sigma_p = 3^{1/2}a\gamma_p/2$. The island critical size is found using the formulas

$$m_c = \frac{c\sigma_{(11\bar{2}0)}}{\Delta\mu - ac\gamma_{(1\bar{1}00)}/2} \quad \text{and} \quad l_c = \frac{a\big(\sigma_{(0001)} + \sigma_{(000\bar{1})}\big)}{\Delta\mu - ac\gamma_{(1\bar{1}00)}/2}, \tag{16}$$

while the nucleation barrier, in this case, is equal to

$$\Delta G^* = \frac{ac\sigma_{(11\bar{2}0)}\big(\sigma_{(0001)} + \sigma_{(000\bar{1})}\big)}{\Delta\mu - ac\gamma_{(1\bar{1}00)}/2}. \tag{17}$$

3. Probability of nucleation of AlN nuclei with different ratios of component vapor pressures and temperature

Nucleation barrier height determines the probability of AlN island formation on the substrate surface and, thereby, determines the regions of existence of various AlN island growth regimes depending on substrate temperature and ratio of NH_3 and $AlCl_3$ pressures, i.e. on the ratio of components V/III. According to the paper [5], difference of chemical potentials in case of growth by the HVPE method can be calculated using the formula

$$\Delta\mu = k_{\mathrm{B}}T \ln \frac{p_{\mathrm{NH_3}}p_{\mathrm{AlCl_3}}K_{\mathrm{P,AlN}}}{p^2_{\mathrm{HCl}}}. \tag{18}$$

Here, $K_{\mathrm{P,AlN}}$ is the equilibrium constant for the chemical reaction $\mathrm{AlCl}_3^{(g)}+\mathrm{NH}_3^{(g)}=\mathrm{AlN}^{(s)}+3\mathrm{HCl}^{(g)}$, k_{B} is the Boltzmann constant. It should be noted that elastic energy per atom in an island (less than 0.01 eV per pair of AlN atoms)

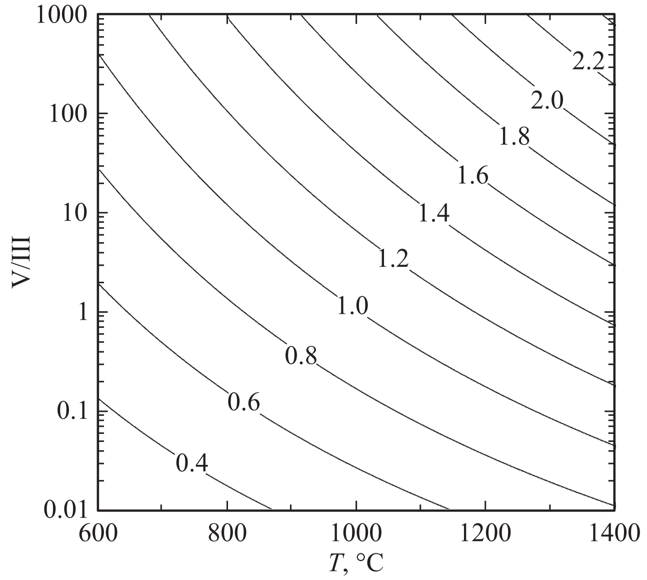

Figure 2. Difference of chemical potentials in eV in case of $p_{\mathrm{AlCl_3}} = 2 \cdot 10^{-3}$ atm, $p_{\mathrm{HCl}} = 6 \cdot 10^{-3}$ atm.

with the lattice mismatch of 0.9% is much smaller than the difference of chemical potentials and virtually does not affect the film nucleation thermodynamics. Elastic energy was estimated using the elastic constants obtained in the paper [18]. Figure 2 shows the dependence of chemical potential difference on temperature under various values of ammonia pressure $P_{\mathrm{NH_3}}$, in relation to the value of constant vapor pressure $P_{\mathrm{AlCl_3}}$.

The equilibrium constant for the chemical reaction $K_{\mathrm{P,AlN}}$ during plotting of the given dependence was calculated using the tabulated data given in [19]. Isolines $\Delta\mu = \Delta\mu_0$ in Fig. 2 are determined by the expression

$$T = \frac{\Delta H + \Delta\mu_0 N_{\mathrm{A}}}{\Delta S + R \ln(p_{\mathrm{NH_3}} p_{\mathrm{AlCl_3}} / p^3_{\mathrm{HCl}})}, \tag{19}$$

where ΔH and ΔS are the change in enthalpy and entropy during the reaction $\mathrm{AlCl}_3^{(g)} + \mathrm{NH}_3^{(g)} = \mathrm{AlN}^{(s)} + 3\mathrm{HCl}^{(g)}$, gas pressure in bar, N_{A} is the Avogadro constant, R is the universal gas constant. Thus, for instance, when ratio V/III decreases by a factor of 5 under the standard growth conditions $T = 1080^\circ\mathrm{C}$, $p_{\mathrm{AlCl_3}} = 2 \cdot 10^{-3}$ atm, $p_{\mathrm{HCl}} = 6 \cdot 10^{-3}$ atm, $p_{\mathrm{NH_3}} = 7 \cdot 10^{-1}$ atm [5], $\Delta\mu_0 = 1.77$ eV, temperature must be increased to 1206°C, in order to maintain the previous difference of chemical potentials. Pressure value estimates were obtained in the paper [5] for AlN growth by the HVPE method, ammonia flow being 1.2 slm and hydrogen chloride flow being 10^{-2} slm (above the aluminum layer). It should be noted that the formula (19) was derived using the equation $\ln K_{\mathrm{P,AlN}} = -(\Delta H - T\Delta S)/(k_{\mathrm{B}}T)$. Since the reaction enthalpy and entropy are slowly changing functions of temperature, then the calculations may use their fixed values respectively equal to $\Delta H = 42.3\,\mathrm{kJ} \cdot \mathrm{mol}^{-1}$ and $\Delta S = 84.4\,\mathrm{kJ} \cdot \mathrm{mol}^{-1}$, AlN film growth temperature being $T = 1080^\circ\mathrm{C}$.

AlN film growth regimes are determined by analyzing the value for the ratio of probability of three-dimensional and two-dimensional nuclei formation P_{3D}/P_{2D}. Ignoring the difference of nuclei growth speeds, the ratio P_{3D}/P_{2D} is determined by the following formula:

$$\frac{P_{3D}}{P_{2D}} \approx \frac{\exp(-\Delta G^*_{3D}/k_{\mathrm{B}}T)}{\exp(-\Delta G^*_{2D}/k_{\mathrm{B}}T)}, \tag{20}$$

where ΔG^*_{3D} and ΔG^*_{2D} are the nucleation barrier for three-dimensional and two-dimensional nuclei. The formula (20), after substitution of the formulas (3) and (6) into it (when considering nucleation on a singular face), or substitution of the formulas (9) and (11) (when considering nucleation on a step), shows that ratio P_{3D}/P_{2D} may take on values less than or equal to 1. The ratio P_{3D}/P_{2D} reaches the

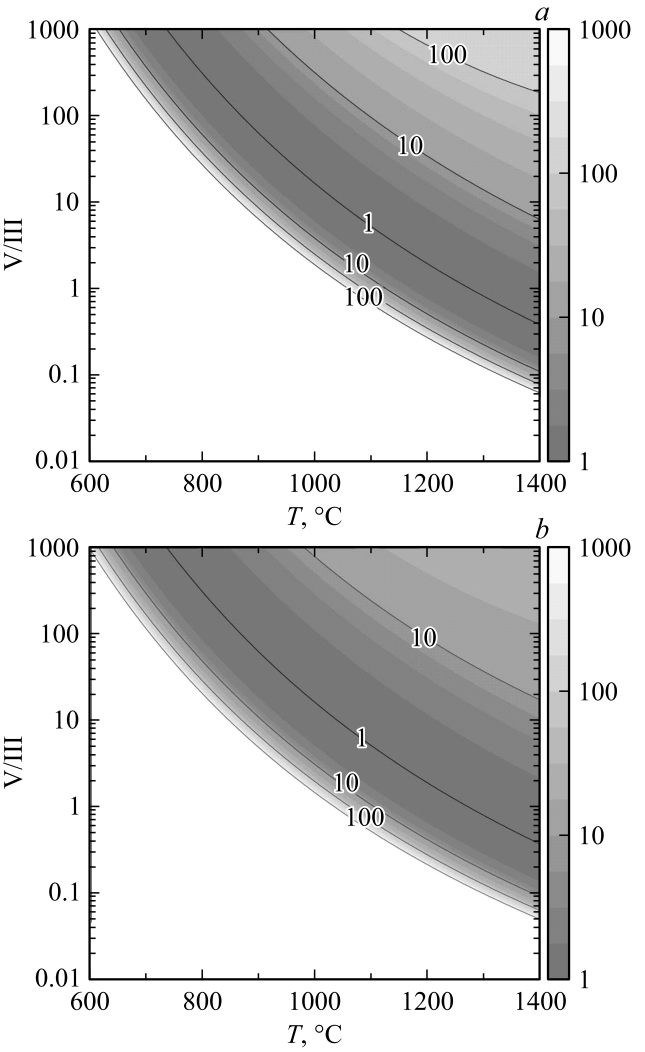

Figure 3. Ratio of probabilities of three-dimensional and two-dimensional nuclei formation P_{3D}/P_{2D} on an atomically smooth surface (*a*) and on a step (*b*) ($p_{\mathrm{AlCl_3}} = 2 \cdot 10^{-3}$ atm, $p_{\mathrm{HCl}} = 6 \cdot 10^{-3}$ atm) at different values of ammonia vapor pressure in relation to the value of constant vapor pressure $p_{\mathrm{AlCl_3}}$.

maximum on condition $\Delta\mu = 3^{1/2}a^2\Delta\gamma$. Figure 3 shows the dependences of the ratio of probabilities of AlN island nucleation P_{3D}/P_{2D} as a function of the value of ammonia vapor pressure $P_{\mathrm{NH_3}}$ in relation to the value of constant vapor pressure $P_{\mathrm{AlCl_3}}$ on an atomically smooth surface and on a step. Figure 4 shows the dependences of the absolute value of nucleation barriers in case of nucleation on an atomically smooth surface and nucleation on a step. The calculations used the reference data [13], as well as the assumption that $\gamma_i/\gamma_{i(1\bar{1}00)} \sim \gamma_{(0001)}/\gamma_{(1\bar{1}00)}$ (respectively $\gamma_{i(1\bar{1}00)} \sim 1.08\,\mathrm{Jm^{-2}}$). Thus, it follows from the data given in Fig. 3 that the ratio P_{3D}/P_{2D} under the standard AlN growth conditions by the HVPE method is equal to 28 in case of nucleation on an atomically smooth surface and 11 in case of nucleation on a step.

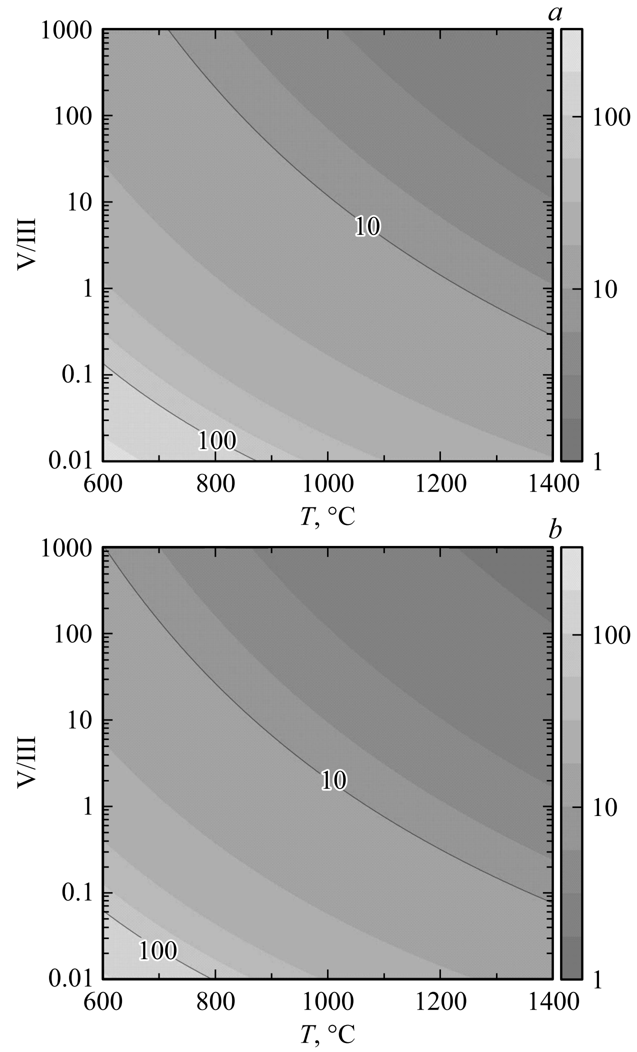

Figure 4. Nucleation barrier ΔG^*_{3D} in eV upon nucleation of three-dimensional nuclei on an atomically smooth surface (*a*) and on a step (*b*) ($p_{\mathrm{AlCl_3}} = 2\cdot10^{-3}\,\mathrm{atm}$, $p_{\mathrm{HCl}} = 6\cdot10^{-3}\,\mathrm{atm}$) at different values of ammonia vapor pressure in relation to the value of constant vapor pressure $p_{\mathrm{AlCl_3}}$.

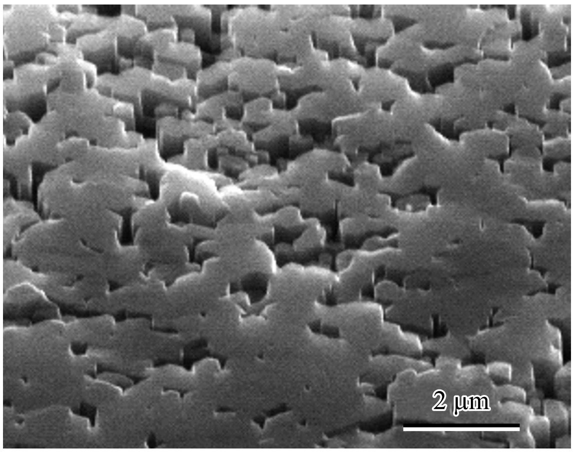

Figure 5. SEM-image of AlN film on the substrate surface 3C-SiC/Si(111).

This means that the formation of three-dimensional AlN islands on a SiC/Si(111) substrate under the aluminum chloride vapor pressure equal to $P_{\mathrm{AlCl_3}} = 2\cdot10^{-3}\,\mathrm{atm}$ in a wide temperature range is energetically more favorable as compared to formation of two-dimensional islands. The region, where the probability of two-dimensional island nucleation is close the probability of three-dimensional island nucleation, is determined by the condition $P_{3D}/P_{2D} \sim 1$. Substrate temperature at which the ratio $P_{3D}/P_{2D} = 1$ in case of nucleation on an atomically smooth surface and in case of steps is found from the equation

$$T = \frac{\Delta H + 3^{1/2}a^2\Delta\gamma N_{\mathrm{A}}}{\Delta S + R\ln(p_{\mathrm{NH_3}}p_{\mathrm{AlCl_3}}/p^3_{\mathrm{HCl}})}. \tag{21}$$

According to the obtained diagrams (Fig. 3), temperature must be increased in order to maintain the film growth regime upon a decrease of V/III flows. For instance, upon a 5-fold decrease of the flows ratio (in case of growth in the standard conditions), temperature must be increased to 1243°C.

The predominant formation of three-dimensional AlN islands is usually observed in case of growth by the HVPE method on substrates of sapphire and monocrystal silicon carbide. This fully agrees with the results of the developed model and the performed experiments (Fig. 5). An AlN film was grown by the HVPE method at the temperature of 1080°C for ~ 1 min. The carrier gas was argon (2 slm), reactant gases were ammonia (1.2 slm) and hydrogen chloride (10^{-2} slm above the aluminum layer). The AlN film morphology was studied by scanning electron microscopy (SEM) (Fig. 5). The AlN film at the initial growth stage consists of merged „microblocks“ resembling in shape a right-angle prism with a different number of side faces. It should be noted that a similar film morphology was found previously during GaN growth on SiC(111) by the MBE PA method [20].

The estimates of probabilities of nucleation on the AlN island edges (0001) and $\{1\bar{1}00\}$ make it possible to conclude that the nucleation barrier on face (0001) is by an order smaller than the nucleation barrier on the faces $\{1\bar{1}00\}$. This means that the ratio of island height to island lateral dimension must increase with time, which also agrees with the experiment results.

4. Discussion of results

Thus, the performed analysis shows that the Volmer−Weber mechanism is energetically most favorable at the initial stage of AlN film growth on SiC/Si(111). Predominance of the probability of Volmer−Weber mechanism implementation during AlN island growth on SiC/Si(111) as compared to the probability of layer-by-layer growth is related not only to the substrate nature, but also to the fact that chemical potentials were calculated by the formula (18) using the reaction constant $K_{\text{P,AlN}}$, calculated using the pressures of AlN formation reaction components in the vapor phase. To calculate the probability of two-dimensional nucleation, we must use not the pressure values for these components in the vapor phase, but the values of their concentration in the adsorbed state on the substrate surface. For instance, ammonia molecules on the substrate surface may dissociate into hydrogen and nitrogen molecules (atoms) [21]. As a result of dissociation, the chemical reaction constant may change its value. The chemical potential value also changes. However, it should be noted that $AlCl_3$ molecules form in the reaction zone with greater probability than AlCl and $AlCl_2$ molecules. $AlCl_3$ molecules are more stable in the region of the studied temperature intervals, as distinct from GaCl and $GaCl_2$ molecules, which in the presence of HCl may turn into $GaCl_3$ [21]. $AlCl_3$ molecules, as a rule, may form associative compounds of the $(AlCl_3)_2$ type only [21]. Thus, it can be assumed that $AlCl_3$ molecules, upon adsorption, do not dissociate into separate components, but, on the contrary, form associative clusters on the surface. $AlCl_3$ molecules, and the more so the associative compounds are less mobile on the substrate surface than in the vapor phase. Therefore, the above-mentioned calculation of chemical potentials, in our opinion, correctly reflects the process of AlN nucleation, which is also confirmed by the experiment. These issues will be studied in a separate report where we will strictly prove this conclusion.

5. Conclusion

The performed study has showed that AlN film growth by the HVPE method on hybrid SiC/Si(111) substrates in the current region of temperatures and pressures starts with nucleation of three-dimensional AlN nuclei. Diagrams were plotted for dependences of probabilities of island and two-dimensional nucleation in a wide range of growth temperatures and V/III flow ratios. It was found that nucleation of two-dimensional AlN islands on a SiC/Si(111) substrate starts dominating over nucleation of three-dimensional nuclei, in particular, at temperatures which exceed ∼ 1200°C. Special reactor types are required for growth at such temperatures. However, AlN film nucleation by the Volmer−Weber mechanism has an important advantage. Indeed, the primary defects, namely cracks, arise not only due to a difference in film and substrate lattice parameters, but also due to a difference in thermal expansion coefficients of materials at the stage of heterostructure cooling from the growth temperature to room temperature. Deformations during structure cooling can be rather significant in case of good contact between the substrate and the film, which ensures layer-by-layer growth. In case of formation of separate (with a small density) three-dimensional islands, the interphase contact area will be lesser than in case of layer-by-layer growth of a layer. Consequently, thermal deformations will also be smaller. The paper [5] showed that three-dimensional AlN nuclei may act as seeds (substrates) for subsequent growth of a GaN layer on their surface, but this time according to the two-dimensional mechanism. This layer forms in the shape of a flattened „cap“ on the top of a pyramidal AlN island. The mechanism of transition from island growth to two-dimensional growth was theoretically described in the series of papers [22–24], while an analysis of possible layer growth change by the example of GaN growth on AlN is given in the paper [5]. Implementation of the said mechanism requires reduction of the interphase energy between the edge of an AlN island and a two-dimensional GaN step (two-dimensional island), nucleating on its surface. This can be done by changing the growth conditions or by adding small amounts of surfactants to the vapor phase. For instance, a monolayer of metallic indium can be deposited after the growth of an AlN nucleating layer [25].

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Conflict of interest

The authors declare that they have no conflict of interest.

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