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Physicochemical Aspects of the Formation of AlN Crystal Film on the (0001)Al_2O_3 Surface

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Abstract

Temperature dependence of the formation of a two-dimensional crystalline AlN phase on the (0001)Al_2O_3 surface under ammonia flow was investigated. Two regions were experimentally detected in the temperature dependence of the process rate. Within the region of relatively low temperatures ($T < 940$ °C), the rate of AlN formation is limited by chemical reactions. A kinetic scheme of the process was proposed, and effective kinetic constants of the main stages of the process were determined. At a higher temperature ($T > 940$ °C), the formation of the ordered AlN phase is determined by a continuous two-dimensional phase transition in the lattice gas formed on the surface of AlN cells.. A three-parameter scheme is proposed to describe the process. A good agreement between theoretical and experimental isotherms was obtained for the following parameters of the lateral interaction between the filled AlN cells in the lattice gas: $E_i = 0.725$ eV – lateral repulsion of the neighbouring filled AlN cells; $U = -0.725$ eV – the energy of stabilisation arising during the formation of a filled cell; $V = 0.09$ eV – energy consumed for the formation of an intermediate metastable cell of the lattice gas. The critical temperature of phase transition is unambiguously determined by the established parameters of lateral interaction and is equal to 795 °C. The observed phase transition in AlN lattice gas is continuous because experiments were carried out at temperatures above the critical point.

Keywords: nitridation kinetics, two-dimensional AlN phase, lattice gas, lateral interaction, phase transition

INTRODUCTION

Initial stages of the generation of nitrides of the third group metals (A3-nitrides) on the substrates made of another single crystal material are very important for subsequent growth high-quality epitaxial layers suitable for the creation of modern element basis for ultraviolet optoelectronics, high-frequency high-power transistors and other electronic devices. Among the materials used as substrates for the epitaxy of A3-nitrides, such as silicon and silicon carbide, the most frequently used material is sapphire. It is generally accepted that the stage of substrate nitridation is extremely important [1, 2]. Sapphire nitridation is the formation of a thin AlN layer on Al_2O_3 surface through the interaction of the heated substrate surface with active nitrogen, the sources of which is ammonia or nitrogen plasma. Many works deal with sapphire nitridation (for example, [1–5] and references therein), but still some contradictions are present in the literature, and the process is to a large extent unclear yet. For instance, it was determined in [3] that the rate of AlN formation during nitridation decreases with an increase in process temperature, however, in [4], quite contrary, the rate of nitride formation increases with temperature. It is also well known that misalignment of lattice periods in the (0001) plane for the AlN film and the sapphire substrate (taking into account a 30° turn of the film lattice against the substrate) exceeds 12 % [2]. In [2], a process is described during which the nitridated layer is gradually changing its periodicity in the surface plane, *i.e.*, at first a strained pseudomorphous AlN layer with the same periodicity as that of the substrate is formed, and then, with an increase in layer thickness, the period changes nearly to the volume value for AlN. On the other hand, it was shown in [5] that the periodicity of nitridated layer for the thickness of less than one monolayer is already close to the volume-related value for AlN.

The formation of the new AlN phase on sapphire surface during nitridation points to the necessity of taking into account chemical transformations that have not been studied in detail until present. At the same time, the occurrence of the phase transition (PT) on the surface requires a corresponding consideration of the process from the point of view of the approaches developed for PT.

The goals of the present work were to carry out an experimental investigation of the temperature dependence of nitridation, to build a kinetic scheme of chemical reactions on the surface during nitridation, and to consider thermodynamic aspects of the formation of the AlN surface phase.

EXPERIMENTAL

Experiments were carried out in a three-chamber set-up CBE-32 (Riber, France) using ammonia as the source of active nitrogen. The basic pressure in the chamber was $1 \cdot 10^{-10}$ torr. The initial surface for nitridation was pure Epiready sapphire surface (0001)Al_2O_3, and the back side of the substrates was coated with a layer of molybdenum 450 nm thick to provide the absorption of light from radiation heater and forth e corresponding heating of the sapphire substrate. Preliminary purification of the substrate surface was carried out at a temperature of $T = 600$ °C for 1 h, and the final purification before nitridation was carried out in the growth chamber at 950 °C for 30 min. During nitridation, the substrate temperature was varied within the range 850–1050 °C with the fixed ammonia flow rate 25 cm^3/min.

Nitridation was controlled *in situ* with the help of reflection high-energy electron diffraction (RHEED) with the beam energy 10 keV. The evolution of the full diffraction pattern (DP) was recorded with the help of the kSA-400 system (k-Space Associates, the USA), which allows measuring the dependence of the intensity on time in any chosen area of the diffraction pattern. Reflections near the high-symmetry crystallographic directions were chosen for observation (the azimuthal deflection ~1–5°). The sapphire sample under investigation was a circle 4.5 mm in diameter. The small size of the sample provided morphological homogeneity, uniformity of the temperature and flow along the surface, and allowed decreasing the effects of surface charging under the action of the primary electron beam. In general, this resulted in good reproducibility of the experimental results.

RESULTS AND DISCUSSION

Kinetics of AlN formation

The initial surface of the sapphire substrate is rather smooth; measurements with the help of an atomic force microscope over the area of 5 × 5 μm reveal the mean square roughness of ~2 Å. After preliminary annealing in vacuum at 600 °C, the roughness of the sapphire surface did not change. A typical diffraction pattern of the surface near the azimuth <11–20> after the final annealing of the sample at 950 °C is shown in Fig. 1, *a*. The diffraction pattern corresponds to the usual non-reconstructed surface (1 × 1) (0001)Al_2O_3. Diffraction reflections of AlN arise during nitridation (see Fig. 1, *b)*, which is the evidence of the formation of the crystal phase. The intensity of these reflections increases with nitridation time, while the intensity of sapphire reflections decreases.

The changes of the chemical composition of Al_2O_3 surface after nitridation for 10 min at 880 °C were studied by means of X-ray photoelectron spectroscopy (XPS). The spectra of the initial (0001)Al_2O_3 surface and the surface after nitridation are shown in Fig. 2. The appearance of a peak of nitrogen atom N1*s* is well seen. The thickness of the AlN layer formed during nitridation is not more than two monolayers.

The curves of the change of the intensity of diffraction reflection from the new phase AlN with nitridation time for different temperatures are shown in Fig. 3, *a*.

At high temperatures, nitridation is completed, so it is possible to normalize all the curves by the maximal intensity at which the degree α of the transformation of surface Al_2O_3 layer into AlN was accepted to be unity. Then all the curves of intensity changes with time *t* should be interpreted as the curves of transformation degree $\alpha(t)$. The maximal transformation rate $d\alpha/dt$ (in s^{-1}) at a given temperature was determined from the kinetic curves. Two temperature regions were determined: below 940 °C the rate of AlN formation is essentially dependent on process temperature, while above 940 °C the dependence on temperature is absent.

It is evident that AlN is formed as a result of a definite sequence of chemical reactions; each of them requires surmounting a specific activation barrier.

This explains a substantial temperature dependence of the rate of AlN formation within the temperature range below 940 °C.

In our opinion, it is necessary to consider the following sequence of chemical reactions:

$$Al_2O_3 \rightarrow 2AlO + 0.5O_2 \qquad (1)$$

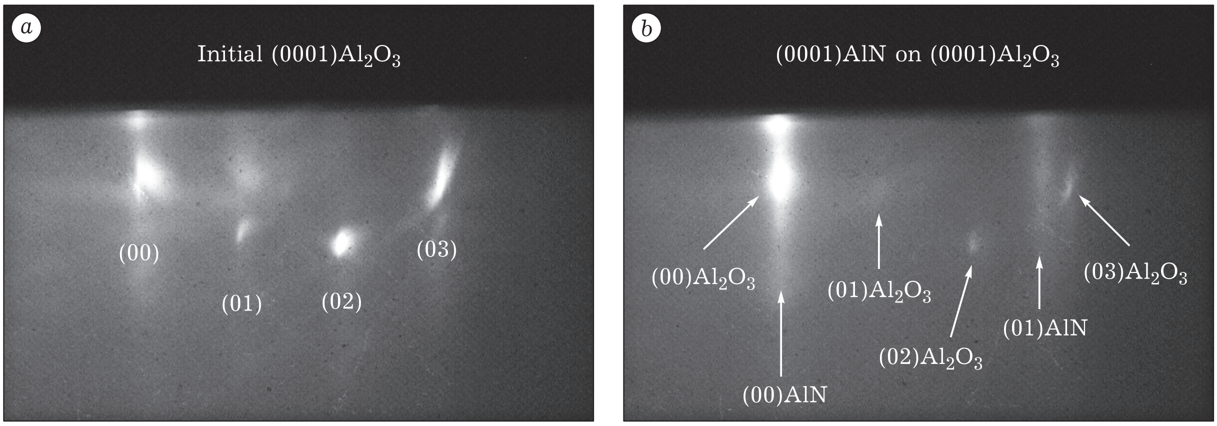

Fig. 1. Diffraction pictures: *a* – pure (0001)Al_2O_3 surface after preliminary annealing in vacuum, *b* – after nitridation: a fundamental (01)AlN reflection appeared.

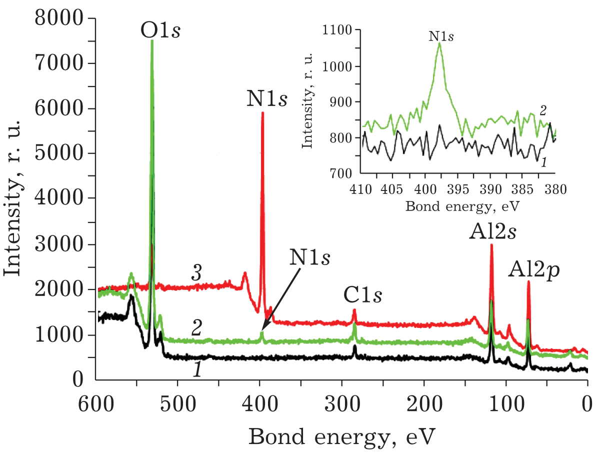

Fig. 2. XPES spectra of samples: *1* – initial (0001)Al_2O_3 surface, *2* – nitridated (0001)Al_2O_3, *3* – (0001)AlN surface. Insert shows the spectra of initial (*1*) and nitridated (*2*) surfaces Al_2O_3 in the region of the N1*s* peak.

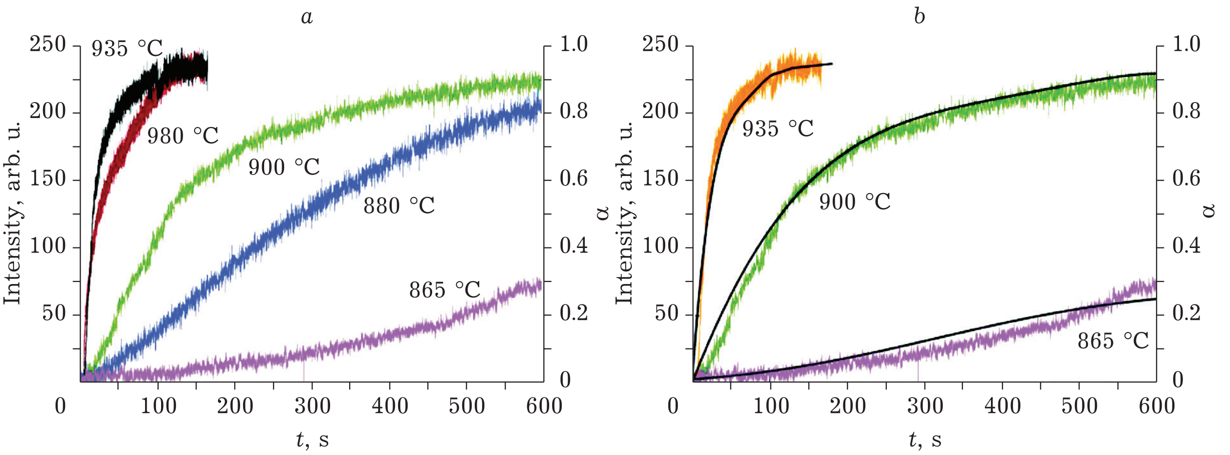

Fig. 3. Kinetics of AlN formation at different nitridation temperatures (*a*); comparison of calculated kinetic curves (black) and experimetnal ones (gray) at different temperatures (*b*).

This is partial reduction of surface aluminium from its oxide as a consequence of oxygen desorption from the sapphire surface, both at the stage of preliminary annealing in vacuum and at the stage of nitridation itself. Aluminium reduction was assumed in [6–8]. As a result, a definite amount of AlO is formed on the surface.

It is also evident that ammonia adsorption on the sample surface takes place:

$$NH_3^{gas} \xrightarrow{k_1} NH_2^{ads} + 0.5H_2^{gas}\uparrow \qquad (2)$$

This is a well known dissociative chemisorption of ammonia on various crystal surfaces with the formation of NH_2 radicals [9, 10].

The final step of the transformation is the formation of surface particles of aluminium nitride:

$$NH_2^{ads} + AlO \xrightarrow{k_2} AlN + H_2O \qquad (3)$$

It is also necessary to take into account recombination of adsorbed NH_2 radicals:

$$NH_2^{ads} + NH_2^{ads} \xrightarrow{k_3} N_2\uparrow + 2H_2\uparrow \qquad (4)$$

In general, the overall reaction of the interaction of sapphire with ammonia may be written as

$$4NH_3 + Al_2O_3 = 2AlN + H_2O + O_2 + N_2 + 5H_2 \qquad (5)$$

Within the approximation of the kinetic field-average equations, the equations for the rates of changes in the surface concentrations of $[NH_2]$, [AlO], [AlN] may be obtained:

$$\frac{d[NH_2]}{dt} = k_1P(1 - [NH_2]) - k_2[NH_2][AlO] - k_3[NH_2]^2$$

$$\frac{d[AlO]}{dt} = -k_2[NH_2][AlO]$$

$$\frac{d[AlN]}{dt} = k_2[NH_2][AlO]$$

Solving this system of equations numerically, we obtain a good agreement of the calculated kinetic curves with the experimental ones, if we accept the following values for the kinetic constants: $k_1P = 6 \cdot 10^4\exp(-E_1/kT)$, $k_2 = 7 \cdot 10^{19}\exp(-E_2/kT)$, $k_3 = 3 \cdot 10^{13}\exp(-E_3/kT)$, where $E_1 = 1.5$ eV, $E_2 = 5.3$ eV, $E_3 = 4.0$ eV, P is NH_3 pressure. Comparison between the calculated and experimental curves for several temperatures is shown in Fig. 3, *b*.

It should be noted that the constants in the proposed kinetic scheme provide a detaling of the complicated nitridation process but they are not the rate constants of elementary reactions, so it is not quite correct to render exact physical meanings to the obtained activation energies (as real activation barriers) and pre-exponential factors.

Phase transition on the surface

As we have already mentioned, within the region of high temperatures ($T > 940$ °C) the rate of AlN formation is independent of temperature, so, chemical processes do not limit the formation of AlN. In this case, the release of the crystal AlN phase is likely to be determined by the PT process. Phase transitions on the surface are usually only weakly dependent on temperature; moreover, PT are retarded with an increase in temperature, because stronger external actions (pressure or fields) are necessary for a PT to proceed.

The formation of AlN in nitridation will be considered within the model of a PT in the lattice gas [11, 12]. It is evident that separate AlN particles are accumulated on the surface at the start of nitridation, and this fact should be interpreted as the formation of the lattice gas of AlN. In the presence of a lateral interaction between the filled cells of the lattice gas, a PT into the dense crystal phase occurs. For a temperature higher than the critical point ($T > T_c$), the transition will be continuous, while for $T < T_c$ the transition will be discontinuous, or the first-order transition.

The isotherms of the PT in the lattice gas are described by Van der Waals type isotherms, for example, by one-parameter Fowler-Guggenheim isotherms [13], or more universal three-parameter isotherms [14–16]. A three-parameter isotherm that was used by us in this work is represented in the form:

$$\frac{\mu + \varepsilon}{kT} = \ln\left[\frac{\alpha}{1 - \alpha}\right] + \left[\frac{E_i\alpha}{kT} - \frac{U/kT}{1 + \exp[(V - U\alpha)/kT]}\right] \qquad (6)$$

where μ is the chemical potential of a cell of the lattice gas of AlN; α is the degree of surface filling with AlN cells (or transformation degree introduced above); ε is the vertical interaction of the filled cells with the substrate; U, V, E_i are the parameters of the lateral interaction of the filled cells of the lattice gas; k is Boltzmann constant.

The expression for the isotherm (6) should be considered as an implicit function α of argument $(\mu + \varepsilon)/kT$. It is usually sufficient to vary the argument within the limits from −5 to +5, to make the transformation degree vary from 0 to 1. An increase in the argument is connected with an increase in the entropy part of chemical potential μ with the accumulation of the filled AlN cells on the surface. There is a complete analogy between the PT in the lattice gas and in Ising model for an assembly of spin particles in the external magnetic field. Then, according to this analogy, the argument $(\mu + \varepsilon)/kT$ plays the role of the external field, while the parameters of lateral interaction play the role of the internal field. The negative sign of the argument points to the opposite directions of the external and internal fields.

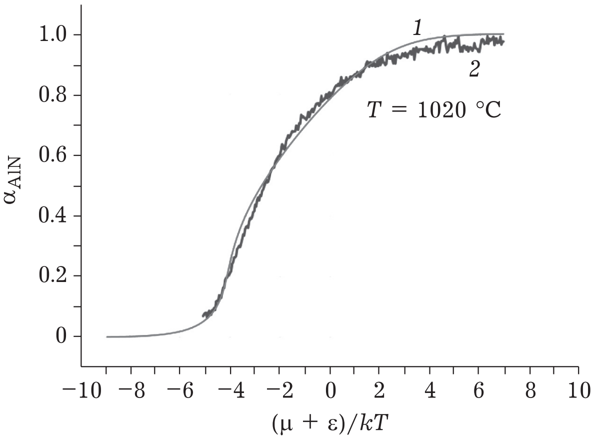

Fig. 4. Comparison between the calculated three-parameter isotherm (*1*) and experimental isotherm (*2*) obtained at T = 1020 °C.

Figure 4 shows a good agreement between the theoretical and experimental isotherms at 1020 °C and the following parameters of lateral interaction: E_i = 0.725 eV − lateral repulsion of the neighbouring filled AlN cells; U = 0.725 eV − stabilization energy arising with the formation of the filled cell; V = 0.09 eV − energy consumed for the formation of an intermediate metastable cell of lattice gas. The critical temperature of PT is unambiguously determined by the determined parameters of lateral interaction, our calculations give the point T = 795 °C. The observed PT in the lattice gas has a continuous nature because experimental temperatures are higher than the critical point. At lower temperatures ($T < T_c$), a PT of the first order with a jump of density should be observed, however, this discontinuity in the density of the lattice gas could not be observed in the experiment because the process within this temperature region is limited by chemical reactions.

CONCLUSION

Investigation of the temperature dependence of the rate of nitridation or the rate of the formation of the crystal hexagonal AlN phase on the surface under ammonia flow revealed a very complicated nature of the process. Two temperature regions were discovered. In the region of relatively low temperatures, the process is limited by chemical reactions, while at higher temperatures the formation of the ordered AlN phase is determined by the continuous phase transition in the lattice gas. A kinetic scheme of nitridation is proposed, effective values of kinetic constants are determined: $k_1P = 6 \cdot 10^4 \exp(-E_1/kT)$, $k_2 = 7 \cdot 10^{19} \exp(-E_2/kT)$, $k_3 = 3 \cdot 10^{13} \exp(-E_3/kT)$. A three-parameter isotherm is proposed, the parameters of the lateral interaction between the filled cells of AlN lattice gas are determined, the critical temperature of the phase transition is calculated (T_c = 795 °C).

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