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Analysis of the AIN phase transition on a sapphire surface within a universal 2D lattice gas model in MBE

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Abstract. The AlN phase transition on the (0001) Al₂O₃ surface was investigated. It was experimentally estimated that the AlN formation rate as a function of temperature has a different character in two temperature regions. In the region of relatively low temperatures (T <1210 K), the AlN formation rate is limited by chemical reactions. At higher temperatures (T >1210 K), the formation of an ordered AlN phase is determined by a continuous twodimensional phase transition within the filled AlN-lattice-gas cells formed on the sapphire surface. A three-parameter isotherm is proposed to describe the process. The observed phase transition in the AlN lattice gas is a continuous phase transition or a second-order transition.

1. Introduction

After Isamu Akasaki [1], Hiroshi Amano [2], and Shuji Nakamura [3] successfully obtained the first bright blue LEDs based on III-nitride semiconductor compounds with the use of a sapphire substrate, these semiconductors are considered as very promising materials for opto- and electronic applications. One of the most common substrates is a sapphire (Al₂O₃) substrate. Sapphire is transparent in the visible and UV wavelength ranges, has a rather high thermal conductivity (38.5 W m⁻¹ K⁻¹ at 300 K), is thermally stable, has high crystalline perfection and is much cheaper than SiC or native nitride substrates. Therefore, Al₂O₃ is a widely used substrate in the synthesis of heteroepitaxial structures (HES) based on III-nitrides, mainly for optoelectronic devices, as well as in the development of technologies for the growth of heteroepitaxial structures for high-electron mobility transistors (HEMTs).

The problem of III-nitride epitaxial growth on an Al_2O_3 substrate is associated with a number of technological difficulties due to the large mismatch between the lateral parameters of the crystal lattices of the grown AlN/GaN layer [4,5]. To minimize the lattice mismatch between III-nitrides and sapphire, the chemical transformation of the Al₂O₃ surface is carried out by exposing the heated substrate in a stream of active nitrogen with the formation of a thin AlN crystalline layer. This process is called "nitridation" and is an integral part of the technology for growing III-nitrides on sapphire. When crystalline AlN is formed, the unit cell is rotated by 30° relative to the Al₂O₃ unit cell, which leads to an effective mismatch of the lateral cell parameters up to $\sim 13\%$. As a result, it becomes possible to grow III-nitride epitaxial layers with reduced elastic stresses.

An adequate understanding of the physicochemical processes on the surface during the formation of semiconductor structures is in demand in many modern or just emerging technologies in such industries as electronics, optics, energy, chemical industry (for example, in catalyst development) and others. To achieve this understanding in each case, it is necessary to solve the complex problem of

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many-body interactions. Currently, significant progress has been made in understanding and numerical modeling of various processes on the surface of solids [6-9]. Methods based on various versions of lattice gas models (LGM) and Monte Carlo (MC) calculations allow one to describe a wide class of phenomena: equilibrium surface states, adsorption, diffusion, formation of ordered structures on the surface (reconstruction), phase transitions (PT) and critical phenomena on the surface, and many others.

Lattice gas models are one of the main tools for describing two-dimensional (2D) and threedimensional (3D) magnetic systems. For example, the Ising model is widely known, to which simple lattice gas models are completely equivalent. Lattice gas models are also widely used to describe various atomic processes (adsorption, formation of ordered structures, structural phase transitions) on metal surfaces. In particular, ideas are being developed not only about direct (for example, dipoledipole) lateral interactions between adsorbed particles, but also about indirect lateral electronic interactions caused by a metal substrate [10]. However, LGM is very rarely used to describe essentially analogous atomic processes on semiconductor surfaces. There are few such works [11-15]. It is believed that long-range elastic strains and stresses, as well as complex surface reconstructions, can be present, and often are, on semiconductor surfaces, and these limiting factors do not agree well with the lattice gas model. The authors of [16] also drew attention to the fact that LGMs are rarely used for modeling semiconductor surfaces. Modern scientific approaches in this field of research are reduced to the consideration of atomic processes on the surface of semiconductors mainly as reaction and diffusion kinetics, while the statistical thermodynamics of the semiconductor surface is not given due attention. As a result, the experimental data presented in different works contradict each other, moreover, contradictions are found within the same work. In addition, this leads to misinterpretations and significant errors in the description of the mechanisms and driving forces of surface processes.

It has been empirically established that a condensed (liquid or solid) phase often appears in the lattice gas of adsorbed particles. The formation of a condensed state is possible only in the presence of lateral attraction between adsorbate particles. However, direct interaction between the same type of adsorbed particles is repulsive. The problem arises of explaining the condensation in the lattice gas. Condensation occurs in a real 3D gas at sufficiently low temperatures, which is well described by a simple van der Waals model. In this model, within the framework of the mean field theory, both the potential of attraction and repulsion, which are described by two constants, are taken into account. By analogy with the van der Waals equation, a three-parameter isotherm was developed, which was successfully used to describe various 2D systems: for reconstruction phase transitions on GaAs (001) [14], InAs (001) [17], InSb (001) [18] surfaces, GaAs homoepitaxy [15], the formation of GaN quantum dots in the AlN matrix [19].

In this work, we investigated a universal 2D lattice gas model describing the AlN crystalline phase formation on the sapphire surface within the mean field theory, studied the nature and role of direct and indirect lateral interactions of the AlN lattice gas, and determined the critical temperature for estimating the magnitude of lateral interactions.

2. Experiment

The experiments were carried out on a CBE-32 (P) molecular beam epitaxy machine (RIBER) adapted for ammonia MBE. The base pressure in growth chamber was 1.0×10^{-9} Torr. As a source of active nitrogen, we used high-purity ammonia (99.999%) in combination with additional Entegris purification filters characterized by ammonia purification levels higher than 99.999999%. The ammonia flow into the chamber was set by a Bronkhorst flow controller operating in the range of 8... 400 sccm. In the experiments, we used 2-inch epi-ready (0001) sapphire substrates.

The process of exposure of the sapphire surface to the ammonia flow was monitored *in situ* by the reflection high-energy electron diffraction (RHEED) technique. An acquisition of the entire RHEED pattern evolution and the subsequent analysis of the behavior of diffraction spots were carried out by a CCD-based kSA 400 system (manufactured by k-Space Associates, USA) equipped with a high-resolution CCD camera with high-sensitivity optics specially designed for RHEED.

3. Results and discussion

To study the AlN phase transition on the (0001) Al₂O₃ surface, the AlN spot intensity as a function of time was obtained in the form of kinetic curves from diffraction patterns by the RHEED technique. It was measured at different substrate temperatures and is shown in figure 1. This experiment is described in more detail in [20]. The saturation area of the AlN spot intensity is clearly seen for the high-temperature curves. For the kinetic curves, the maximum rate $(d\alpha/d\tau)$ (in units of s⁻¹) for each temperature was determined, and this dependence is shown in figure 2. Two regions with different behavior of the AlN formation rate were found: a strong temperature dependence at relatively low temperatures (T < 1210 K) and a region with weak temperature dependence at higher temperatures (T > 1210 K). The mechanism of the AlN crystalline phase formation on the sapphire (0001) surface at low temperatures is described in more detail in [20].



Figure 1. Evolution of the AlN crystalline phase formation on the sapphire surface in a wide temperature range.



Figure 2. Temperature dependence of the maximum rate $(d\alpha/d\tau)$ of the Al₂O₃ surface layer transformation into crystalline AlN.

As was mentioned above, the AlN formation rate weakly depends on temperature at high temperatures (T > 1210 K) (see figure 1), and, therefore, chemical reactions do not limit the AlN crystalline phase formation. In this case, the appearance of the AlN crystalline phase can be limited by a surface phase transition in a lattice gas [17]. Phase transitions on the surface are usually weakly dependent on temperature. Moreover, the phase transitions "slow down" with an increase in temperature, since stronger external influences (pressures or fields) are required for a phase transition to occur.

To explain the AlN crystalline phase formation on the sapphire surface, it is necessary to consider a system of interacting particles - nitrogen atoms acting as an adsorbate and aluminum atoms acting as an adsorbent. In statistical physics, a system of interacting particles located in a periodic array of equivalent unit cells is called a lattice gas. The adsorption layer corresponds to a two-dimensional lattice gas model, which is one of the classical models of statistical physics. Over the past decade, a significant increase in interest in mean field theory, such as the LGM, has been observed due to the fact that it is very useful for the analysis of microscopic mechanisms of phase transitions on surfaces. We applied the lattice gas model [17, 21] to describe the AlN crystalline phase formation.

In the framework of LGM, lateral interactions between adsorbed particles are considered as parameters. The nature of lateral interactions can be varied. Van der Waals, dipole-dipole interactions are possible, as well as the interaction of adsorbed particles through the substrate (this interaction is often called indirect). Depending on the number of lateral interaction parameters used, the surface phase transition can be described by the PT isotherm in the lattice gas. The most common type of monomolecular adsorption isotherm is the Langmuir isotherm [18]:

$$P \cdot P_0^{-1} = \theta \cdot \left(1 - \theta\right)^{-1},\tag{1}$$

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where *P* is the pressure, θ is the surface coverage, and *P*₀ is given by [18]:

$$P_0(T) = \left(\frac{2\pi nkT}{h^2}\right)^{3/2} \cdot k_B T \cdot \exp(-\varepsilon / k_B T), \qquad (2)$$

for the case of monatomic gas adsorption, ε is the adsorption energy. This model describes the dependence of the equilibrium degree of surface filling on the adsorbate pressure for the case of a homogeneous surface, but it does not take into account the interaction of neighboring adsorbed components with each other. The appearance of a condensed phase is possible only in the presence of lateral attraction between the adsorbed particles. When adsorbed particles interact with each other, P_0 is an empirical parameter that is lower than the P_0 parameter of the Langmuir isotherm and usually lies in the range of $10^{-5} - 10^{-6}$ Torr. In this case, isotherms of the van der Waals type are used, for example, the one-parameter Fowler-Guggenheim (FG) isotherms [21], taking into account the parameter of the intermolecular interaction of neighboring components:

$$P \cdot P_0^{-1} = \theta \cdot (1 - \theta)^{-1} \cdot \exp(-4\theta E_i / k_B T), \qquad (3)$$

where E_i is the lateral attraction energy between adsorbed particles or between lattice gas cells. The GF isotherm can describe phase transitions of both the first and second order. However, the GF isotherm does not describe a first-order phase transition for the case of lateral repulsive interaction. Meanwhile, as a rule, pair interaction between identical particles, as in the case of chemisorbed nitrogen atoms, is repulsive [22]. Moreover, the GF isotherm is symmetric about the point $\theta = 1/2$, while the experimentally observed isotherms are always asymmetric [22]. Note that the asymmetric isotherm directly reflects the effect of complex interactions between adsorbed particles.



Figure 3. The schematic representation of a complex process of the AlN crystalline phase formation, including several stages: the formation of an intermediate lattice gas consisting of intermediate cells, the appearance of filled AlN-lattice-gas cells, and the crystalline AlN formation.

The lattice gas model can reproduce realistic phase transition isotherms only when many-body interactions are added to the model. We assumed that the AlN unit cell plays the role of a lattice gas cell. It seems reasonable to assume that the formation of a complex AlN unit cell consists of several stages (figure 3), including the appearance of intermediate metastable cells, which can be considered as the formation of an intermediate lattice gas consisting of intermediate cells. The introduction of an intermediate lattice gas allows many-body interactions to be taken into account phenomenologically [14, 15]. Thus, a two-dimensional system of adsorbed gas can be characterized by a state equation that expresses the relationship between pressure, surface coverage and temperature. Let us derive the equation of state. Using traditional statistical analysis, we have expressed the free energy F corresponding to the AlN lattice gas cells with a surface coverage θ in the form:

$$F = -\varepsilon\theta + k_B T \cdot \left[\theta \cdot \ln\theta + (1-\theta) \cdot \ln(1-\theta)\right] + \frac{1}{2} \cdot E_i \cdot \theta^2 - U \cdot \omega \cdot \theta , \qquad (4)$$

where ε is the so-called interaction energy of the filled cells with the substrate, E_i is the energy of paired lateral repulsion of neighboring filled cells of the lattice gas, ω denotes the surface coverage

with an intermediate lattice gas, which is then transformed into AlN-lattice-gas cells with the surface coverage θ , U is the stabilization energy arising at the filled cell formation. The free energy F_1 corresponding to the formation of a lattice gas consisting of intermediate cells with a coating ω is expressed as:

$$F_{I} = V\omega + k_{B}T \cdot \left[\omega \cdot \ln \omega + (1 - \omega) \cdot \ln(1 - \omega)\right] - U \cdot \omega \cdot \theta , \qquad (5)$$

where V is the energy expended to create a filled intermediate metastable lattice gas cell. Using the usual definition of the chemical potential $\mu = dF/d\theta$, minimizing expression (5) with respect to the concentration ω and taking into account the term $U\omega\theta$, we obtained the following equation of state:

$$\frac{\mu + \varepsilon}{k_B T} = \ln \left[\frac{\theta}{I - \theta} \right] + \left[\frac{E_i \theta}{k_B T} - \frac{U/k_B T}{I + \exp[(V - U\theta)/k_B T]} \right].$$
(6)

Let us recall that μ is the chemical potential of the AlN lattice gas cell; θ is the degree of filling the surface with AlN cells (or surface coverage introduced earlier); ε is the energy of interaction of the filled cells with the substrate; U, V, E_i are the parameters of the lateral interaction of neighboring filled cells of the lattice gas; k_B is the Boltzmann constant.

The equation of the three-parameter isotherm should be considered as an implicit function θ of the argument $(\mu + \varepsilon)/k_{\rm B}T$. Usually, it is enough to change the argument in the range from - 5 to + 5 for the degree of coverage θ to change from 0 to 1. An increase in the argument is associated with an increase in the entropy part of the chemical potential μ as the filled AIN cells accumulate on the surface.

The experimental kinetic curve in figure 4 demonstrates an S-like character (it looks like the curves in figure 1), so that at the initial section of the kinetic curve, the amount of the AlN crystalline phase increases exponentially with time. On the other hand, the chemical potential of a single AlN-lattice-gas cell is proportional to the logarithm of the concentration of AlN-lattice-gas cells ($\mu \sim \ln (\theta_{AlN})$), and, consequently, the chemical potential of an AlN-lattice-gas cell on the surface is proportional to the time ($d\mu \sim d\tau$). The experimental kinetic curve (figure 4) of the formation of an AlN-lattice-gas cell is actually a dependence of the AlN-lattice-gas cell density on the chemical potential μ , so the curve represents the isotherm of the phase transition.



Figure 4. Comparison of the calculated threeparameter isotherm (smooth curve) and the experimental curve (broken line).

Good agreement of the calculated isotherm with the experimental curve at $T_{exp} = 1290$ K (figure 4) was found by numerical fitting for the following parameters of lateral interaction: $E_i = 0.725$ eV, U = -0.725 eV, V = 0.09 eV. Usually, a symmetric isotherm has a value of the parameter E_i twice as large as U[19], but in this case we have an asymmetric isotherm, so these parameters can take close or even the same values. As can be seen from equation (6), the effective attraction increases sharply with increasing surface coverage θ .

The critical temperature $T_c = 1065$ K is determined by the parameters of lateral interaction. For temperatures above the critical one $(T > T_c)$, the transition will be continuous, and for $T < T_c$, the transition will be discontinuous or a first-order transition. The experimental temperature range is above T_c , and, therefore, the observed phase transition is a continuous phase transition, that is, a transition without an interface between the lattice gas and the condensed phase. At lower temperatures $(T < T_c)$, a first-order phase transition with a density jump should be observed. However, this discontinuity in the density of the lattice gas cannot be observed experimentally, because the process in this temperature range is limited by chemical reactions.

4. Conclusions

It was established that the AlN formation rate does not depend on temperature for the temperature range > 1210 K. In this range, the process is described as a phase transition in the framework of the lattice gas model. Good agreement between theoretical and experimental isotherms was obtained for the following parameters of lateral interaction between filled AlN cells in the lattice gas: the lateral repulsion of neighboring filled AlN cells $E_i = 0.725$ eV; the stabilization energy arising during the formation of a filled AlN cell U = -0.725 eV; the energy consumption for creating an intermediate metastable lattice-gas cell V = 0.09 eV. The critical temperature of the phase transition is 1065 K and uniquely determined by the found parameters of lateral interaction.

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