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Chemical kinetics of the Si(111) surface nitridation process at temperatures below the structural phase transition $(7 \times 7) \rightarrow (1 \times 1)$

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A study of the influence of the conditions of silicon nitride crystalline phase formation on the process kinetics as a result of controlled nitridation of the reconstructed (7×7) Si(111) surface at varying substrate temperatures in the range 700−800°C has been carried out. From the analysis of the diffraction patterns obtained by the reflection high-energy electron diffraction technique, it is found that the formation kinetics of the two-dimensional (8×8) crystalline phase in the temperature range of 700−800°C differs from that of the high-temperature nitridation and exhibits normal activation-reaction behaviour, indicating the presence of an activation barrier. The activation barrier of 0.6 eV associated with the formation heat of a mobile silicon atom from the adatoms of the (7×7) structure involved in the formation of the SiN (8×8) crystalline phase on the ordered silicon (7×7) superstructure has been determined and a kinetic scheme of the process has been proposed.

Keywords: ammonia molecular beam epitaxy (NH_3-MBE), nitridation kinetics, crystalline SiN (8×8), Si(111) silicon, RHEED.

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1. Introduction

Today a quantum leap has been made in design and fabrication of such devices as light-emitting diodes [1–4], photodetectors [5,6] and field effect transistors [7,8] based on heteroepitaxial structures of gallium nitride and aluminum nitride (GaN, AlN) on various substrates including silicon (Si). The growth of GaN and AlN layers on Si substrates is especially relevant due to the possibility of integrating the technology of III-nitrides epitaxy into the mature silicon technology. Additionally, quite high thermal conductivity, high crystal quality and availability of the large diameter wafers in the market make silicon an attractive substrate material for III-nitride applications in the terminal devices.

Early experiments relating to straight growth of AlN on Si(111) at relatively high temperatures (> 1000°C) demonstrated formation of an amorphous layer of Si_xN_y at AlN/Si interface which resulted in epitaxial growth of the low quality structures [9]. Moreover, in paper [10] it was illustrated that AlN/Si interface sufficiently impacts the leakage currents and carriers transport across the epitaxial structure during operation of the terminal devices. Later it was found that formation of the amorphous layer of Si_xN_y may be prevented by way of a short-term nitridation of silicon substrates in the ammonia flow prior to the growth of crystalline AlN. Nitridation of Si — a process which, in certain conditions (surface temperature and ammonia dose) provides formation of a thin (1−2 monolayer) crystalline layer of SiN with a typical superstructure (8×8) and prevents diffusion of Si into the growing AlN film [11]. This approach is of high relevance when growing III-nitrides by method of ammonia molecular beam epitaxy (NH_3-MBE), since this method allows exact controlling of the minor ammonia flows in the growth chamber. In paper [12] it is mentioned that crystalline islands of SiN formed as a result of controlled nitridation of Si surface, upon subsequent deposition of Al, turn into epitaxial islands of AlN, from which AlN of high structural quality subsequently grows. The authors also emphasize that subsequent GaN layers of the best quality were obtained when growth began after preliminary exposure of the Si(111) surface in ammonia flow [12]. The final compressive stress of GaN grown on such an AlN layer remains high enough to compensate for the tensile component caused by cooling of the sample, which in turn prevents the formation of cracks, and also leads to reduced dislocation density [12].

Despite the fact that in many literature sources describing the growth of monocrystalline films of III-nitrides on Si(111) substrate by MBE method the nitridation stage is distinguished as one of the most crucial stages, the mechanism of SiN crystalline layer formation during nitridation of Si is still underestimated. The paper [13] outlines the method of reflection high-energy electron diffraction (RHEED) used in the study of kinetics and thermodynamics of Si(111) surface nitridation at fixed flow of ammonia and varied substrate temperature in the range of 850−1150°C. Two different nitridation stages were revealed: the stage of formation of an ordered 2D crystalline phase of SiN occurring as a result of Si atoms interaction on the surface with ammonia molecules, and the stage of amorphous phase Si_3N_4 formation occurred through interaction of chemisorbed ammonia molecules with Si atoms integrated in the crystalline lattice. It was found that the rate of SiN ordered crystalline phase formation declines with the temperature growth, and the rate of Si_3N_4 amorphous phase formation is increased [13]. This result indicates the necessity of nitridation process shift towards the lower temperatures area to exclude/inhibit the process of formation of amorphous phase of Si_3N_4 at the interface of AlN/Si(111). In recent study [14] the authors investigated the effect of controlled nitridation of Si(111) surface on the epitaxial growth of nucleation layers AlN-on-Si with low tensile stresses on the ordered crystalline phase of silicon nitride formed in low ammonia flow and at substrate temperatures of 700−900°C, including also temperatures below 820°C (i. e. below the temperature of the superstructure transition on a pure silicon surface $(7\times7)\rightarrow(1\times1)$). It was found that decrease of temperature from 900 to 700°C reduces the permanent tensile stress of the nucleation layers of AlN by almost 30%, caused by presence of active amorphous phase of Si_3N_4 at AlN/Si interface. The obtained results demonstrate that one of the main causes of cracks formation in III-nitride layers, grown on silicon substrates, is formation of stretched AlN layers with high content of amorphous phase of Si_3N_4 at AlN/Si interface which is specific for silicon nitridation at high temperatures (> 800°C).

This study was aimed at defining the kinetics and formation mechanisms of crystalline phase of silicon nitride with (8×8) superstructure during nitridation of the reconstructed surface of silicon surface (7×7) at technically acceptable temperatures for the upcoming epitaxial growth of III-nitrides. Since the ordered silicon surface with the superstructure (7×7) is evidently differing from the silicon surface (1×1) at temperatures above the superstructure transition, the mechanisms of silicon nitride crystalline phase formation are expected to be different as well. By understanding the mechanisms of forming the crystalline and amorphous phases of Si_xN_y at various temperatures will allow control the nitridation process and increase its reproducibility.

2. Experiment procedure

The experiments were carried out using the ammonia molecular beam epitaxy system Riber Compact-21 NH_3-MBE with the use of silicon Si(111)-substrates with a diameter of 2″ from SILTRONIX, (France). Preparation of silicon substrates for nitridation began with preliminary low-temperature chemical cleaning of surface using the modified Shiraki method [15]. After that, the substrates were immediately placed into the load chamber of MBE system for their storage in vacuum. Prior to being placed into the growth chamber the silicon substrates have been thermally treated in the pre-annealing chamber at a temperature of 450°C for 2 h in residual atmosphere at a pressure level of $(2-5)\cdot10^{-8}$ Torr to remove residual hydrocarbons from the surface and prepare Si(111) surface for the upcoming process operations. Further, the substrate was annealed for 20 minutes in the growth chamber in conditions of ultra-high vacuum at a temperature of ~ 1100°C. The base pressure in the chamber was $1.0\cdot10^{-9}$ Torr. The presence of atomically pure and ordered silicon surface after preliminary thermal treatment was registered during the substrate cooling below 820°C which was manifested as a specific superstructure transition $(1\times1)-(7\times7)$ on the diffraction patterns (DP) using RHEED method. The DPs of the samples surfaces were registered using analytical system kSA 400 equipped with a high-resolution CCD camera and appropriate software (k-Space Associates, USA).

The substrate was heated by absorption of radiation from the heater. The heater is made as a graphite spiral. The radiation spectra of the heated substrates were recorded using a small-size instrument „Ocean Optics USB4000“, provided with a multi-channel silicon photodetector.

The active nitrogen was sourced from high-purity ammonia (99.999%) in complex with additional purification Entegris filters designed to provide the degree of purification of the ammonia higher than 99.999999%. The ammonia flux to the chamber was set by a mass-flow controller Bronkhorst designed to operate within the range 8−400 sccm.

After the silicon substrates had been prepared the surface Si(111) was subjected to nitridation to study the DP evolution with time using RHEED method during formation of crystalline and amorphous phases of silicon nitride at various temperatures of substrate 700−800°C. To do this, the intensity of diffraction spots of newly formed crystalline silicon nitride was measured. The diffraction spot intensity versus time depicted as the kinetic curves, allows studying the kinetics of the chemical reaction in the presence of crystalline and amorphous phases. The process of plotting the kinetic curves is described in detail in the studies [13,14].

3. Experimental results

Let’s consider the temperature dependence of the rate of (8×8) superstructure formation during silicon surface nitridation. We should remind that earlier our team has been studying the kinetics of SiN 2D layer formation with (8×8) structure at temperatures above the temperature of $(7\times7)\rightarrow(1\times1)$ phase transition on the pure Si(111) silicon surface [13]. In paper [13] a model was suggested describing formation of an ordered nitride layer when the adsorbed ammonia radicals are interacting with the mobile silicon atoms on the surface (not to confuse with the stationary silicon atoms in DAS-model of (7×7) structure) in the absence of the activation barrier. It should be noted that DAS is a widely used abbreviation of the well-known „dimer-adatoms-stacking fault“ model for the superstructure (7×7). The suggested model allowed to explain the

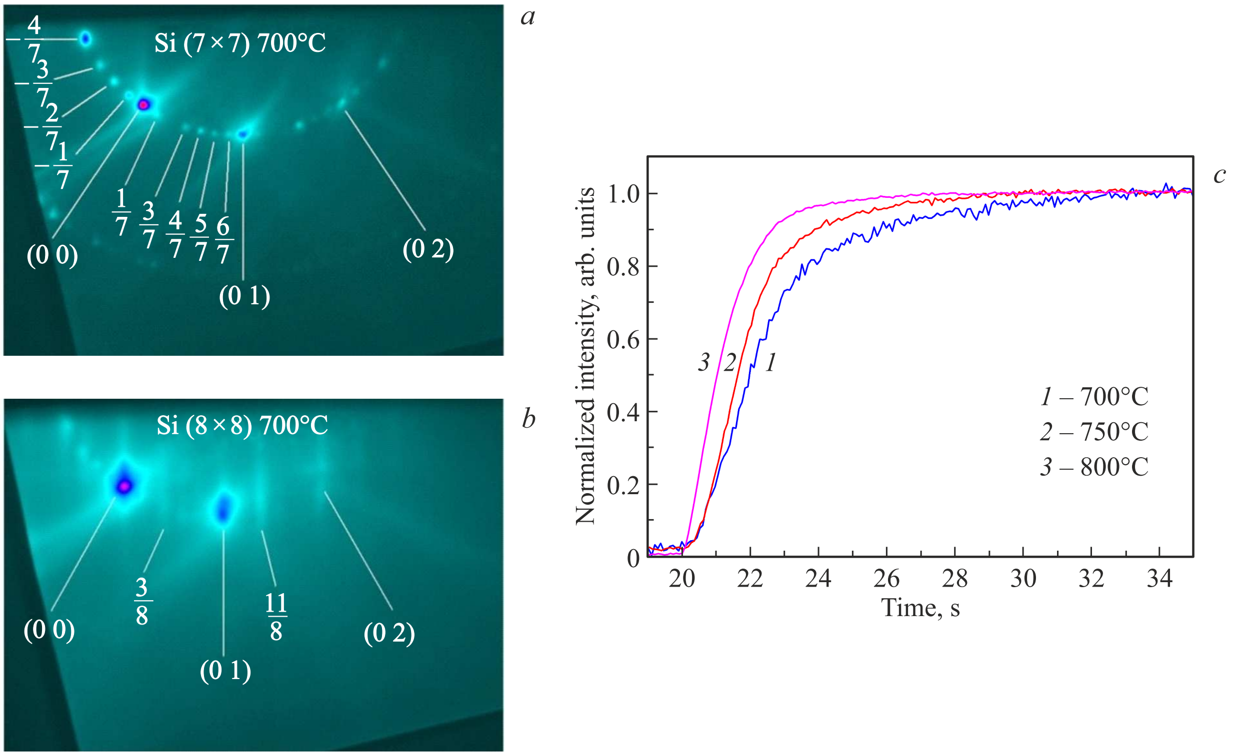

Figure 1. *a* — DP of (7×7) silicon superstructure with the substrate temperature of 700°C before the substrate exposure to ammonia flow. *b* — DP of nitridized silicon surface in ammonia flow 27 sccm with reconstruction (8×8). *c* — experimental kinetic curves of silicon surface nitridation in ammonia flow 27 sccm at various substrate temperatures, °C: *1* — 700, *2* — 750, *3* — 800. (A color version of the figure is provided in the online version of the paper).

formation of a meta-stable graphene-like structure (8×8) g-Si_3N_3 at initial stages of Si(111) surface nitridation in ammonia for the studied temperature range > 850°C, as well as to consider the kinetic and thermodynamic aspects of formation of this crystalline phase [13,16–18]. Our team recently has experimentally studied the formation of various crystalline and amorphous passivation layers of SiN on the surface of AlGaN/GaN heterostructures with 2D electron gas using methods of X-ray photoelectron spectroscopy (XPS), UV photoelectron spectroscopy (UPS), including angle-resolved spectroscopy (ARPES/ARUPS) [19].

In this study we investigated the kinetics of (8×8) superstructure formation within the temperature range below 820°C. While preparing the silicon surface to nitridation process after high-temperature (> 1100°C) annealing in the growth chamber the substrate was cooled down to the operating temperatures 700–800°C. During the substrates cooling in conditions of ultrahigh vacuum when the temperature declined below ~ 820°C (temperature of the superstructure transition $(1 \times 1) \rightarrow (7 \times 7)$), on DP we could observe the reconstruction transition from (1×1) structure to the highly ordered superstructure (7×7). DP of silicon superstructure (7×7) at the substrate temperature 700°C before exposure to the ammonia flow is shown in Figure 1, *a*.

The process of silicon (111) surface nitridation started from the supply of ammonia flow onto the prepared surface at the substrate temperature of 700–800°C. When ammonia was introduced into the growth chamber, the diffraction pattern showed the appearance of fractional spots corresponding to the formation of a superstructure (8×8) characteristic of the ordered two-dimensional crystalline phase of silicon nitride (Figure 1, *b*). With further nitridation of the silicon surface the intensity of reconstruction spots (8×8) on DP was growing until it entered the saturation plateau. This situation is absolutely different from the high-temperature conditions, where the intensity of the resulting fractional spots of reconstruction (8×8) on DP first increases sharply, and then there is a slow decrease in the intensity of all spots on DP due to the formation of an amorphous silicon nitride layer on the surface. The observed effect was explained by the fact that the diffraction spots of the formed phase (8×8) are appeared as a result of interference of plane waves scattered from a new ordered array of silicon nitride atoms on the surface, whereas the atoms of the formed amorphous phase are disordered, which results in incoherent scattering of electrons in (random) arbitrary directions, reducing the intensity of all spots on the DP.

The diffraction spots intensity versus time, i. e., experimental kinetic curves of silicon surface nitridation, shown in Figure 1, *c*, were plotted using kSA 400 software and hardware complex (k-Space Associates, USA), which allows

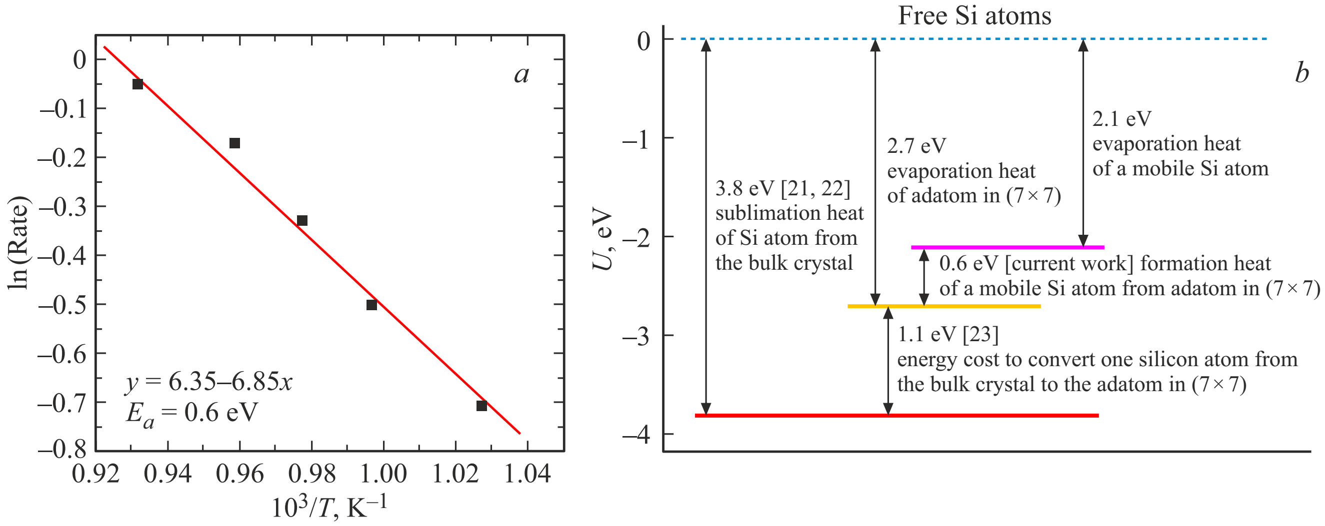

Figure 2. *a* — Arrhenius dependence of the crystalline phase SiN (8×8) formation rate on the temperature of the reconstructed silicon surface (7×7). *b* — schematic energy diagram for silicon atoms in different states of crystalline Si(111) and on its surface.

recording the evolution of the diffraction pattern during Si surface treatment with ammonia and then processing the DP record. In processing a DP area was selected with 11/8 spot (Figure 1, *b*), peculiar to SiN, and the variation of this spot intensity with time was registered. The fractional spot 11/8 of structure (8×8) was selected due to its visual brightness compared to other SiN spots. From the DP analysis, it was found that the behavior of the rate of formation of a two-dimensional crystalline phase (8×8) in the temperature range 700–800°C, i. e. below the structural phase transition $(7 \times 7) \rightarrow (1 \times 1)$ (as a characteristic transition of the pure silicon surface) differs from the kinetics of high-temperature nitridation above this transition. Variation of the rate of crystalline phase SiN (8×8) formation with temperature in Arrhenius coordinates at relatively low temperatures (700–800°C) in ammonia flow 27 sccm is illustrated in Figure 2, *a*. The procedure to evaluate the rate of crystalline phase SiN (8×8) formation in the process of Si(111) surface nitridation is outlined in details in paper [20]. The increased ammonia flow (27 sccm) was chosen intentionally so that the rate of formation of the crystalline phase of silicon nitride would certainly be limited only by mobile silicon adatoms on the surface, and not by adsorbed ammonia radicals.

The manifestation of normal activation-reaction kinetics (i. e., the reaction rate rises with increasing temperature), indicating the presence of an activation barrier, is shown in Figure 2, *a*. From Arrhenius dependence we could define the effective activation energy $E_a \approx 0.6$ eV. The pre-exponential multiplier makes $\sim 5 \cdot 10^2\,\mathrm{s}^{-1}$. The defined effective activation energy can be considered as necessary average energy cost for overcoming the barrier when converting stationary silicon adatoms in DAS structure (7×7) into weakly bound or mobile adatoms, which then participate in the formation of structure (8×8), given that earlier it has been discovered that the reaction of (8×8) formation during interaction of mobile silicon adatoms with ammonia at higher temperatures had a non-activation kinetics [13].

The energy diagram for silicon atoms (the average total energy of a single silicon atom when interacting with surrounding silicon atoms in a crystal lattice) in various states of crystalline Si(111) and on its surface is schematically shown in Figure 2, *b*. If for zero or a reference point of our system we select a group of resting silicon atoms (zero kinetic energy) located far enough apart from each other to neglect their interaction (zero potential energy), then the „effective“ energy diagram of atoms on the surface can be represented as follows: the highest energy cost 3.8 eV per 1 atom corresponds to sublimation of an atom (or the work required to remove a silicon atom from the crystal at a sufficiently large distance) located in the volume of the silicon crystal [21,22]. Level 2.7 eV (by 1.1 eV higher compared to the sublimation energy for the bulk silicon atom) corresponds to the evaporation heat of adatoms of structure (7×7), then 1.1 eV — energy cost required to bring the silicon atom from the lattice site to the position of adatom of structure (7×7). This is consistent with the data provided by Chao et al. [23] obtained from calculations: the difference between the bond energy of bulk atom (−4.62 eV) and adatom of DAS-structure (7×7) (around −3.55 eV) is about 1.1 eV. Even if there is an error in determining the absolute values of energy, this difference, obtained from the same calculations, seems to be quite justified. Mobile silicon adatoms are even higher in energy, while 2.1 eV (3.8−1.7 eV) — the energy costs required for evaporation of a mobile silicon atom from the surface (111) of Si crystal. Then, 0.6 eV (2.7−2.1 eV) corresponds to the heat of formation of mobile silicon atom from the adatoms of structure (7×7). This value is consistent with experimental activation energy defined in this study. Note also that the value of $1.1 + 0.6 = 1.7$ eV is well consistent with the previously estimated value of the formation heat of mobile silicon adatoms when they are generated on the surface from the lattice sites at elevated temperatures > 850°C [13]. It is also worth mentioning that earlier Uchida et al. [24] also have studied the differences between stable (stationary) and diffusing silicon atoms adsorbed on surface Si(111) — 7×7 by method of scanning tunneling microscopy. In this paper, in particular, the estimates are given for activation barriers for the abrupt transitions of single Si adatoms between different positions within one of the halves (fault or unfault) of the unit cell of DAS structure (7×7); the values given range from 0.31 to 0.78 eV. Moreover, the activation energy required for a hop of single adatom between adjacent halves of DAS-structure was found — 1.14 eV [25]. Thus, the value of 0.6 eV, assessed in this paper is within the scope of values discussed in the literature.

In a broader and, probably, the more exact sense, the effective activation energy of 0.6 eV found in these experiments — is an energy required to provide conditions for successful formation of the structure cells (8×8) based on the existing structure (7×7). We should remind that the structure (7×7) of pure silicon surface still remains a stable phase in the studied temperature range 700–800°C. In general, the transformation of a complex silicon superstructure with a large surface unit cell into another large unit cell (8×8) of silicon nitride is not a simple chemical reaction or a single action, and such a complex process most likely involves many simpler sub-stages or elementary acts. However, the suggested approach allows formulating a simple kinetic model of the nitridation process and explaining the occurrence and also considering the activation barrier in this reduced temperature range 700–800°C compared with the elevated operating temperatures [13].

Then the kinetics of nitridation of the silicon surface with the superstructure (7×7) in the range of studied temperatures can be described within the framework of a mean field model, assuming a simplifying assumption about the activation of the structural transition due to the transformation of fixed adatoms of structure (7×7) into mobile and chemically more active silicon adatoms with subsequent non-activation formation of the structure (8×8) in their interaction with ammonia. The components participating in the process and reaction between them on the surface are schematically illustrated in Figure 3. The following chemical reactions are included in the kinetic scheme: dissociative chemisorption of ammonia onto the silicon surface Si(111) (1), the total process of formation and accumulation of Si-N bonds from mobile silicon adatoms and chemisorbed ammonia, followed by their ordering into the structure (8×8) (2):

$$\mathrm{NH_3^{gas}} \xrightarrow{\substack{\mathrm{diss}\\ \mathrm{chem}}} \mathrm{NH_2^{ads}} + \frac{1}{2}\mathrm{H_2^{gas}} \uparrow, \tag{1}$$

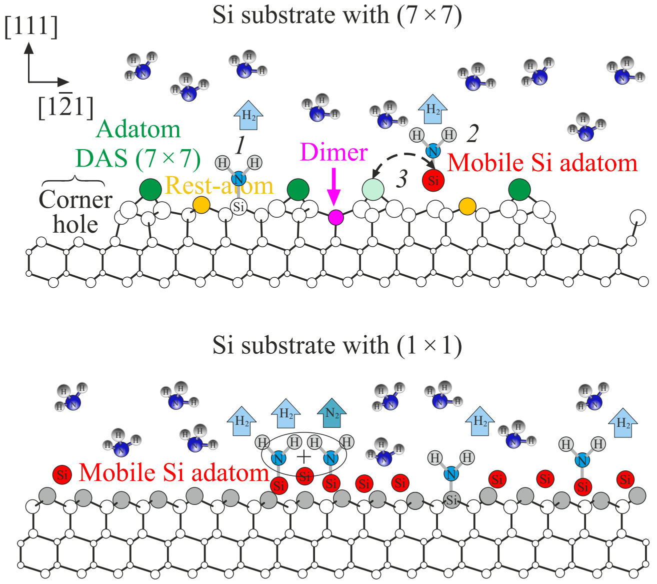

Figure 3. Schematic representation of the nitridation process of silicon surface with superstructure (7×7) in the upper part of the Figure, where the considered components and chemical reactions are shown: dissociative chemisorption of ammonia onto the surface Si(111) (*1*), formation of bonds Si-N from the mobile silicon adatoms with their further ordering into the structure (8×8) (*2*) and the process of generation/recombination of mobile silicon adatoms $\mathrm{Si^{mob}}$ on the surface of superstructure (7×7) (*3*). The scheme of nitridation of silicon surface with structure (1×1) is given for comparison.

$$\mathrm{NH_2^{ads}} + \mathrm{Si^{mob}} \rightarrow \mathrm{SiN^{[8\times 8]}} + \mathrm{H_2^{gas}} \uparrow. \tag{2}$$

Additionally, we introduced a process of generation/recombination of mobile silicon adatoms $\mathrm{Si^{mob}}$ on the surface of superstructure (7×7) (3):

$$\mathrm{Si^{7\times 7}} \leftrightarrow \mathrm{Si^{mob}}. \tag{3}$$

Despite the fact that only one effective stage has been added to the kinetic scheme proposed here — reaction (3), associated with the activation energy $E_a \approx 0.6$ eV defined in this paper, the situation at low temperatures changes in comparison with the kinetic model described in paper [13]. We should remind that in the area of high temperatures (> 820°C) the two-dimensional ordered crystalline phase SiN is formed without activation energy as a result of interaction of active (mobile) adatoms of Si, which are initially present on the surface in abundance with the chemisorbed ammonia radicals. In parallel, the amorphous phase $\mathrm{Si_3N_4}$ is being formed at a low rate as a result of deeper interaction of ammonia radicals with Si atoms from the crystal lattice. In the low temperature area (below the superstructural transition (7×7) → (1×1)) to form an ordered two-dimensional crystalline phase SiN, according to our model, the silicon adatoms in the DAS structure (7×7) are first transformed into more active mobile adatoms on the surface, after that, the formation process (8×8) is going similar to a high-temperature process. However, the formation of the amorphous phase Si_3N_4 can be neglected due to an even greater decrease in the speed of this process, due to the previously demonstrated high activation energy of this process, i. e., 2.4 eV [13]. Moreover, in the experimental diffraction patterns and in kinetic curves the formation of amorphous phase of Si_3N_4 was not observed at all.

Then, given the above, the rates of change in the concentrations of intermediates of these reactions and the rate of formation of final structure (8×8) can be described by the following system of differential equations, where the change in surface coating by adsorbed ammonia radicals is described by equation (4):

$$\frac{d[\mathrm{NH}_2^{\mathrm{ads}}]}{dt} = k_{1,\mathrm{ads}} \cdot F_{\mathrm{NH}_3} \cdot (1 - [\mathrm{NH}_2^{\mathrm{ads}}]) - k_{2,\mathrm{des}} \cdot [\mathrm{NH}_2^{\mathrm{ads}}]^2 - k_3 \cdot [\mathrm{NH}_2^{\mathrm{ads}}] \cdot [\mathrm{Si}^{\mathrm{mob}}], \quad (4)$$

$$\frac{d[\mathrm{SiN}]}{dt} = k_3 \cdot [\mathrm{NH}_2^{\mathrm{ads}}] \cdot [\mathrm{Si}^{\mathrm{mob}}], \quad (5)$$

where $d[\mathrm{NH}_2^{\mathrm{ads}}]/dt$ — rate of concentration change of ammonia radicals adsorbed on the silicon surface, $k_{1,\mathrm{ads}}$ — constant of ammonia adsorption rate on free adsorption sites $(1 - [\mathrm{NH}_2^{\mathrm{ads}}])$, F_{NH_3} — flow of NH_3, $[\mathrm{NH}_2^{\mathrm{ads}}]$ — ammonia radicals concentration, $k_{2,\mathrm{des}}$ — constant of ammonia radicals recombination rate followed by desorption of reaction products in the form of hydrogen and nitrogen molecules, k_3 — constant of crystalline silicon nitride formation rate, $[\mathrm{Si}^{\mathrm{mob}}]$ — concentration of mobile adsorbed silicon atoms not integrated in the crystalline lattice on the surface, $d[\mathrm{SiN}]/dt$ — rate of (v_{SiN}) change of crystalline silicon nitride concentration with time. All concentrations are normalized to a total number of adsorption sites on the surface.

If we consider $F = k_{1,\mathrm{ads}} \cdot F_{\mathrm{NH}_3}$ as a flow of ammonia molecules (radicals) adsorbed as a result of dissociative chemisorption, which participate in the formation of the crystalline phase of SiN, then the constant before the flow of active ammonia becomes identically equal to one. In addition, at relatively low temperatures, we may assume the relatively low desorption of ammonia and the second member of the equation will be $k_{2,\mathrm{des}} \cdot [\mathrm{NH}_2^{\mathrm{ads}}]^2 \to 0$ (obviously, it will be less than the values obtained at temperatures $\geq 850\,^\circ\mathrm{C}$) (4). However, the exact value of constant $k_{2,\mathrm{des}}$ is unknown in advance, and this parameter can be varied within relatively narrow limits close to zero. The constant k_3 is considered temperature-independent (activation energy $E_{a3} = 0$), as per previous results presented in paper [13], and is probably quite high, comparable to a unit, which implies a high probability of formation of bond Si-N in collision on the surface of mobile Si adatoms with adsorbed ammonia radicals. Thus, a pair of interrelated differential equations describing the behavior of silicon adatoms in structure (7×7) and of mobile adatom may be expressed as follows:

$$\frac{d[\mathrm{Si}^{\mathrm{mob}}]}{dt} = k_4 \cdot [\mathrm{Si}^{7\times7}] - k_5 \cdot [\mathrm{Si}^{\mathrm{mob}}] - k_3 \cdot [\mathrm{NH}_2^{\mathrm{ads}}] \cdot [\mathrm{Si}^{\mathrm{mob}}], \quad (6)$$

$$\frac{d[\mathrm{Si}^{7\times7}]}{dt} = -k_4 \cdot [\mathrm{Si}^{7\times7}] + k_5 \cdot [\mathrm{Si}^{\mathrm{mob}}], \quad (7)$$

where $k_4(T) = k_{04} \cdot \exp(-E_a/k_{\mathrm{B}}T)$ — temperature-dependent process of stationary Si adatom transformation into a mobile adatom on the surface with a structure (7×7), k_5 — probability of reverse process — connections of mobile adatom of Si to the appropriate site on the unit cell (7×7) into a position of the stationary adatom. The coating of surface with crystalline surface SiN (8×8) may be described by equation (5). Here we completely neglected the SiN decomposition, since the values of the growth surface temperature are relatively low.

The nitridation process of the pure silicon surface begins, as usual, at the moment of ammonia supply. So far, at a given temperature, an equilibrium (steady-state) concentration $[\mathrm{Si}^{\mathrm{mob}}]$ has been formed on the surface, which is determined by the ratio of constants k_4 (can be taken from the temperature dependence experiment) and k_5 (can be taken from correction for the shape of kinetic curves) and is expressed by the equation (8):

$$[\mathrm{Si}^{\mathrm{mob}}] = \frac{k_4 \cdot [\mathrm{Si}^{7\times7}]}{k_5(1 + \frac{k_4}{k_5})}. \quad (8)$$

The calculation results according to the suggested scheme in Mathcad software may be summarized as follows: 1) set of efficient constants was selected as follows: $k_{1,\mathrm{ads}} = 1$, $k_{2,\mathrm{des}} = 0.1$, $k_3 = 1.7$, $k_4(T) = k_{04} \cdot \exp(-E_a/k_{\mathrm{B}}T) = 1.8 \cdot 10^3 \cdot \exp(-0.67/k_{\mathrm{B}} \cdot (T+273))$, $k_5 = 0.6$; 2) a sufficiently rapid formation of the stationary concentration of $[\mathrm{NH}_2^{\mathrm{ads}}]$ was illustrated (Figure 4, *a*); 3) the experimental temperature dependence of the rate of formation of structure (8×8) at temperatures $T \leq 800^\circ\mathrm{C}$ is reproduced quite well (Figure 4, *b*). It should be emphasized that the experimental kinetic curves (zigzag curves with noise) are compared with the calculated ones (smooth curves), where only the surface temperature varies (the constants are fixed). It is seen that experimental and calculated curves have good consistency.

Thus, the proposed relatively simple kinetic scheme of the nitridation process of the reconstructed surface $\mathrm{Si}(7 \times 7)$, although it does not allow us to accurately determine the elementary kinetic constants, nevertheless it becomes possible to properly describe the set of experimental kinetic data obtained in this study.

4. Conclusion

In this paper, the formation kinetics of a two-dimensional crystalline SiN layer with the structure (8×8)

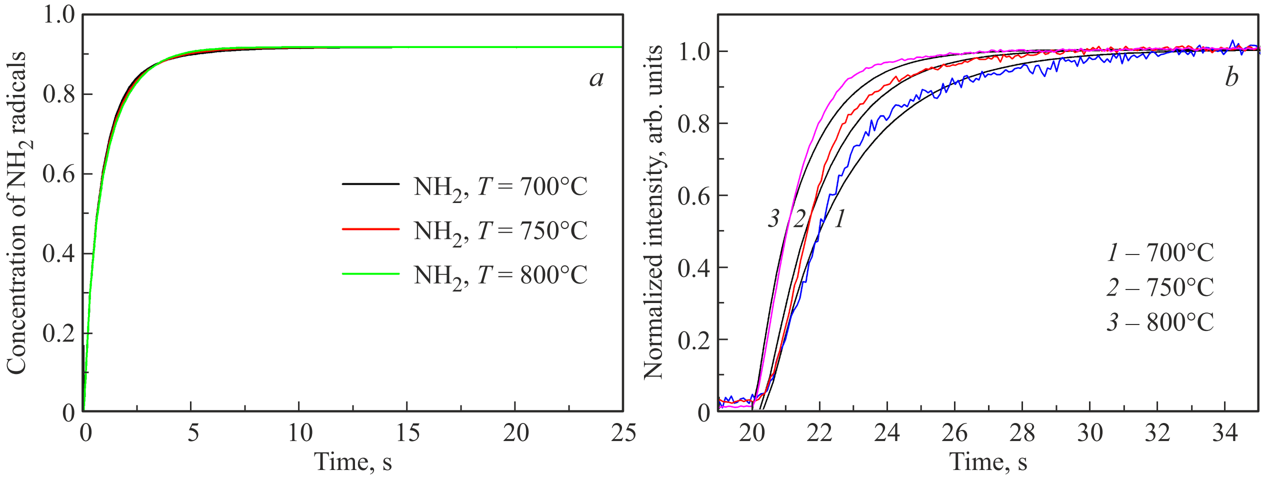

Figure 4. *a* — calculated time dependence of concentration of radicals NH_2, adsorbed on the silicon surface. *b* — comparison with calculated curves (smooth curves) of the experimental kinetic curves (zigzag curves with noise) obtained *in situ* through RHEED method during nitridation of silicon surface in ammonia flow 27 sccm at different substrate temperature, °C: *1* — 700, *2* — 750, *3* — 800.

at temperatures below the structural phase transition $(7 \times 7) \rightarrow (1 \times 1)$ on a pure Si(111) surface is investigated. It was found that the way the two-dimensional crystalline phase (8×8) is formed in the selected temperature range differs from the high-temperature nitridation as a manifestation of normal activation-reaction kinetics (i. e., the reaction rate increases with increasing temperature), indicating the presence of an activation barrier. From the analysis of kinetic curves of Si surface nitridation, the activation barrier 0.6 eV was determined, considered as the necessary energy costs for the transformation of stationary silicon adatoms in DAS structure (7×7) into mobile adatoms, which subsequently participate in the formation of the structure (8×8), in contrast to the non-activation kinetics of the reaction formation of (8×8) during interaction of mobile silicon adatoms with ammonia at high temperatures $> 850°C$. A mechanism is suggested for the formation of silicon nitride crystalline phase with the superstructure (8×8) during nitridation of the reconstructed surface (7×7) of a silicon substrate; The mechanism is presented as a graphical scheme including chemical reactions of dissociative chemisorption of ammonia on the reconstructed surface Si(111), formation of bonds Si-N from mobile silicon adatoms with their subsequent ordering into the structure (8×8) and the process of generation/recombination of mobile silicon adatoms Si^{mob} on the surface of the superstructure (7×7).

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] S. Zhou, X. Zhao, P. Du, Z. Zhang, X. Liu, S. Liu, L.J. Guo. Nanoscale, **14** (13), 4887 (2022). DOI: 10.1039/D1NR08221C

[2] V. Jmerik, D. Nechaev, A. Semenov, E. Evropeitsev, T. Shubina, A. Toropov, M. Yagovkina, P. Alekseev, B. Borodin, K. Orekhova, V. Kozlovsky, M. Zverev, N. Gamov, T. Wang, X. Wang, M. Pristovsek, H. Amano, S. Ivanov. Nanomaterials, **13** (6), 1077(2023). DOI: 10.3390/nano13061077

[3] J.W. Yang, A. Lunev, G. Simin, A. Chitnis, M. Shatalov, M. Asif Khan, J.E. Van Nostrand, R. Gaska. Appl. Phys. Lett., **76** (3), 273 (2000). DOI: 10.1063/1.125745

[4] B. Fan, X. Zhao, J. Zhang, Y. Sun, H. Yang, L.J. Guo, S. Zhou. Laser Photon. Rev., **17** (3), 2200455 (2023). DOI: 10.1002/lpor.202200455

[5] A. Osinsky, S. Gangopadhyay, J.W. Yang, R. Gaska, D. Kuksenkov, H. Temkin, I.K. Shmagin, Y.C. Chang, J.F. Muth, R.M. Kolbas. Appl. Phys. Lett., **72** (5), 551 (1998). DOI: 10.1063/1.120755

[6] T. Li, Y. Lu, Z. Chen. Nanomaterials, **12** (23), 4169 (2022). DOI: 10.3390/nano12234169

[7] K.-S. Im, S.P. Reddy Mallem, J.-S. Choi, Y.-M. Hwang, J.-S. Roh, S.-J. An, J.-H. Lee. Nanomaterials, **12** (4), 643 (2022). DOI: 10.3390/nano12040643

[8] T. Egawa, N. Nakada, H. Ishikawa, M. Umeno. Electron. Lett., **36** (21), 1816 (2000). DOI: 10.1049/el:20001282

[9] H. Lahrèche, P. Vennéguès, O. Tottereau, M. Laügt, P. Lorenzini, M. Leroux, B. Beaumont, P. Gibart. J. Cryst. Growth, **217** (1–2), 13 (2000). DOI: 10.1016/S0022-0248(00)00478-4

[10] H. Umeda, A. Suzuki, Y. Anda, M. Ishida, T. Ueda, T. Tanaka, D. Ueda. *2010 Int. Electron Devices Meeting, 2010*, Technical Digest (San Francisco, CA, USA, 2010) p. 20–5. DOI: 10.1109/IEDM.2010.5703400

[11] S. Pal, C. Jacob. Bull. Mater. Sci., **27** (6), 501 (2004). DOI: 10.1007/BF02707276

[12] A. Le Louarn, S. Vezian, F. Semond, J. Massies. J. Cryst. Growth, **311** (12), 3278 (2009). DOI: 10.1016/j.jcrysgro.2009.04.001

[13] V.G. Mansurov, T.V. Malin, Y.G. Galitsyn, A.A. Shklyaev, K.S. Zhuravlev. J. Cryst. Growth, **441**, 12 (2016). DOI: 10.1016/j.jcrysgro.2016.02.007

[14] D. Milakhin, T. Malin, V. Mansurov, Y. Maidebura, D. Bashkatov, I. Milekhin, S. Goryainov, V. Volodin, I. Loshkarev, V. Vdovin, A. Gutakovskii, S. Ponomarev, K. Zhuravlev. Surf. Interfaces, **51**, 104817 (2024). DOI: 10.1016/j.surfin.2024.104817

[15] A. Ishizaka, Y. Shiraki. J. Electrochem. Soc., **133** (4), 666 (1986). DOI: 10.1149/1.2108651

[16] V. Mansurov, Y. Galitsyn, T. Malin, S. Teys, D. Milakhin, K. Zhuravlev. Appl. Surf. Sci., **571**, 151276 (2022). DOI: 10.1016/j.apsusc.2021.151276

[17] V.G. Mansurov, Y.G. Galitsyn, T.V. Malin, S.A. Teys, K.S. Zhuravlev, I. Cora, B. Pecz. In: 2D Materials (p. 31). IntechOpen (2018). DOI: 10.5772/intechopen.81775

[18] V. Mansurov, T. Malin, S. Teys, V. Atuchin, D. Milakhin, K. Zhuravlev. Crystals, **12** (12), 1707 (2022). DOI: 10.3390/cryst12121707

[19] V. Mansurov, T. Malin, V. Golyashov, D. Milakhin, K. Zhuravlev. Appl. Surf. Sci., **640**, 158313 (2023). DOI: 10.1016/j.apsusc.2023.158313

[20] D.D. Bashkatov, T.V. Malin, V.G. Mansurov, D.S. Milakhin, K.S. Zhuravlev. *2023 IEEE 23rd Int. Conf. of Young Professionals in Electron Devices and Materials (EDM), 2022*, Technical Digest (Novosibirsk, Russian Federation, 2023) p. 200. DOI: 10.1109/EDM58354.2023.10225173

[21] P.D. Desai. J. Phys. Chem. Ref. Data, **15** (3), 967 (1986). DOI: 10.1063/1.555761

[22] A.V. Latyshev, A.L. Aseev, A.B. Krasilnikov, S.I. Stenin. Surf. Sci., **213** (1), 157 (1989). DOI: 10.1016/0039-6028(89)90256-2

[23] Y.F. Zhao, H.Q. Yang, J.N. Gao, Z.Q. Xue, S.J. Pang. Surf. Sci., **406** (1–3), L614 (1988). DOI: 10.1016/S0039-6028(98)00237-4

[24] H. Uchida, S. Watanabe, H. Kuramochi, J. Kim, K. Nishimura, M. Inoue, M. Aono. Phys. Rev. B, **66** (16), 161316 (2002). DOI: 10.1103/PhysRevB.66.161316

[25] T. Sato, S.I. Kitamura, M. Iwatsuki. J. Vac. Sci. Technol. A, **18** (3), 960 (2000). DOI: 10.1116/1.58228

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