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Kinetics and thermodynamics of Si(111) surface nitridation in ammonia

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ABSTRACT

Kinetics and thermodynamics of Si(111) surface nitridation under an ammonia flux at different substrate temperatures are investigated by reflection high-energy electron diffraction. Two different stages of the nitridation process were revealed. The initial stage is the fast (within few seconds) formation of ordered two-dimensional SiN phase, occuring due to the topmost active surface Si atom (Si^{surf}) interaction with ammonia molecules. It is followed by the late stage consisting in the slow (within few minutes) amorphous Si_3N_4 phase formation as a result of the interaction of Si atoms in the lattice site (Si^{inc}) with chemisorbed ammonia molecules. It was found that the ordered SiN phase formation rate decreases, as the temperature increases. The kinetic model of the initial stage was developed, in which the ordered SiN phase formation is the two-dimensional phase transition in the lattice gas with SiN cells. The enthalpy of the active surface Si atom generation on the clean Si(111) surface was estimated to be about 1.5 eV. In contrast, the amorphous Si_3N_4 phase formation is the normal (thermally activated) chemical process with the first-order kinetics, whose activation energy and pre-exponential factor are 2.4 eV and 10^8 1/s, respectively.

1. Introduction

Silicon nitride (Si_3N_4) films are widely used for microelectronic applications due to their unique properties, including the high resistivity (10^{16} Ω cm) and the electrical breakdown limit (10 MV/cm) which is higher than that of most other dielectric films utilized in microelectronics [1]. As the scaling of very large-scale integrated circuits (VLSI) continues into the nanometer range to achieve higher levels of integration and performance, the ultrathin Si_3N_4 films became increasingly important for replacing silicon dioxide (SiO_2) as the gate dielectric material [2,3]. The highly motivated activity has been recently devoted to the fabrication and investigation of hybrid silicon nitride–graphene (HSiNG) devices that combine properties of the both materials which would greatly expand the range of possible device applications, combining desirable mechanical, optical and dielectric properties of silicon nitride with electrical and optical properties of graphene [4–8]. The graphene on Si_3N_4 ultrathin layers can be used for nanoelectromechanical systems, detectors, high-frequency graphene transistors and graphene-based nanophotonic devices [4–8]. Moreover, the fabrication of the nanophotonic Si_3N_4 circuits as well as the graphene flakes is compatible with standard complementary metal–oxide–semiconductor processing. Recently large-area uniform graphene-like thin films grown by chemical vapor deposition directly on silicon nitride were demonstrated [9]. The Si_3N_4 layers on graphene were also used as the gate dielectric [10].

Another interesting field of investigations is connected with the epitaxial growth of III-Nitrides (GaN, AlN and InN) on the Si(111) substrate, which could lead to the integration of optoelectronic devices with Si-based circuits. The improvement of both III-Nitride/Si interfaces and III-Nitride epitaxial layers, occurring as a result the ordered phase formation of silicon nitrides on silicon surfaces, was demonstrated [11–15]. These achievements boost the interest to the investigation of the high quality silicon nitride ultrathin layers formation.

Nitridation of the silicon surface, i.e. exposure of the surface to active nitrogen at high temperatures, is one of the ways for the formation of ultrathin silicon nitride layers. As a rule, the Si_3N_4 films formed on the silicon surface are amorphous [14–19]. The kinetics of Si(111) surface nitridation leading to the amorphous phase formation has been studied by several groups [16–19]. Experimental data were obtained mainly by ellipsometric measurements for the films with thicknesses in the range from 20 to 60 Å, i.e. for the late stage of the nitridation process, whereas the kinetics of initial nitridation stage was not investigated. Since the

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late nitridation stage is determined by the diffusion of reagents through previously formed Si_3N_4 films, while the initial nitridation stage is limited by surface reactions, it is impossible to extrapolate the kinetics data acquired on the late stage towards the initial stage. Moreover, the processes on the late stage strongly depend on the properties of Si_3N_4 films formed at the initial stage. In previous investigations the questionably very low values of activation energy of nitridation was found (for example, 0.23 eV [17] and 0.35 eV [18]). These low values do not correspond to activation energies of reactions between chemical components (silicon crystal and ammonia) or other processes, such as reagent diffusion through the layer.

It has been established that the initial stage of Si(111) surface nitridation at high temperatures leads to the ordered phase rather than amorphous Si_3N_4 phase formation [15,20]. The (8 × 8) reconstruction of the nitridated Si(111) surface was discovered by van Bommel et al. in 1967 [21]. Later, the atomic structure of the ordered Si_3N_4-(8 × 8) phase was investigated by several groups [15,22–24]. However, different aspects of its formation were not clarified so far. For example, a model of the (8 × 8) reconstruction, in which the Si(111) surface is covered by an ordered silicon nitride layer with Si_5N_3 composition, was proposed by Bauer et al. [22]. At the same time, the observation of the (8 × 8) reconstruction was also explained by a β-Si_3N_4 phase formation on the Si(111) surface [11,15,23,24]. Moreover, multiple authors [23,24] assumed that the β-Si_3N_4 crystal film with the thickness of 20–40 Å can be epitaxially grown on Si(111) substrates during nitridation under ammonia flux. The surface morphology evolution of nitridated Si (111) was investigated by low-energy electron microscopy (LEEM) in [22]. It was shown that silicon nitride layers are formed through the nucleation and growth of two-dimensional islands of the (8 × 8) phase.

In this work the kinetics and mechanisms of initial nitridation stages of the Si(111) surface under ammonia flux in the wide temperature range of 750–1150 °C are investigated in details by reflection high-energy electron diffraction (RHEED). A kinetic model of the silicon surface nitridation is proposed, as well as some thermodynamics aspects of the process are discussed.

2. Experimental

Experiments were carried out in a Riber CBE-32 machine. First, Si(111) substrates were ex situ chemically treated according to a procedure described elsewhere [25]. Then, the substrates were outgassed at 450 °C during 2 h in the preparatory vacuum chamber. The atomically clean and smooth Si(111) surface with the well-ordered (7 × 7) reconstruction was prepared by annealing at 1200 °C under ultrahigh vacuum conditions (see Fig. 1). At the temperature above 830 °C the initial surface structure exhibited a (1 × 1) RHEED pattern in agreement with the well known (7 × 7)→(1 × 1) phase transition occurring on the Si(111) surface. The sample surface was exposed to the ammonia flux of 10 sccm at different temperatures (750–1150 °C). RHEED with the primary electron beam energy of 11 keV was used for in situ studying of the nitridation process. The entire RHEED pattern during the ammonia treatment of the samples was monitored by a CCD-based system. The intensity evolution of RHEED spots from Si and silicon nitride was measured and analyzed. The surface morphology of SiN-(8 × 8) phases was investigated using scanning tunneling microscope (STM) manufactured by Omicron.

3. Results and discussion

The nitridation is started by the onset of ammonia flux onto the clean Si(111) substrate heated to various temperatures above 750 °C. At 750–830 °C, this results in the fast disappearance of the Si(111)-(7 × 7) RHEED pattern and in the decrease in the fundamental silicon spots intensity, as shown in Fig. 2. At temperatures above 830 °C, the intensities of initial (1 × 1) fundamental spots are also dropped after the ammonia introduction.

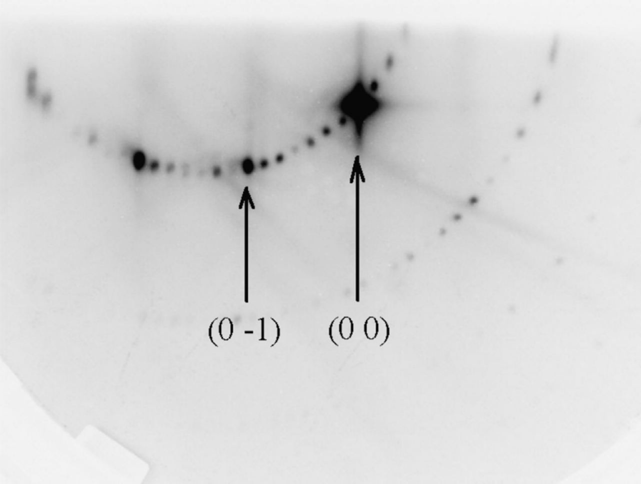

Fig. 1. RHEED pattern of the Si(111) surface with the (7 × 7) reconstruction. Arrows point to the fundamental spots.

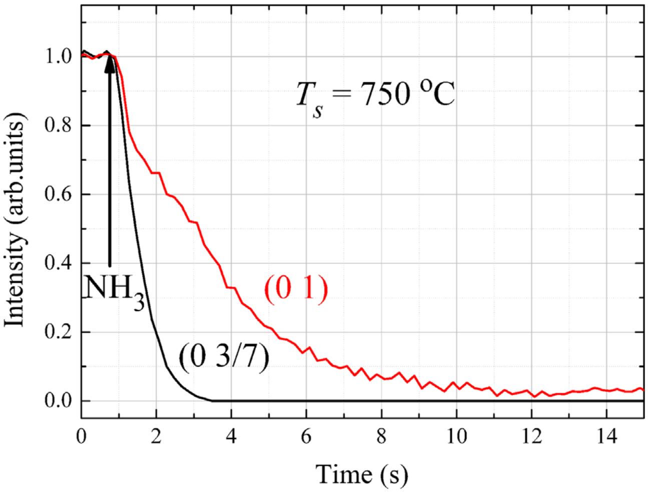

Fig. 2. Behavior of the (0 1) and (0 3/7) RHEED spots intensities from the sample under NH_3 flux. The arrow shows the moment of ammonia introduction.

Two different stages of the silicon nitridation were distinguished using RHEED during each experimental run: namely, the fast stage of an (8 × 8) phase formation and the following slow process of amorphous Si_3N_4 phase appearance while the growth parameters (ammonia flux and substrate temperature) were kept constant. The ordered (8 × 8) structure appears within a few seconds under ammonia flux for the all used temperatures. We denote the ordered ammonia-induced surface phase as a SiN-(8 × 8). The amorphous phase formation was accompanied by the total disappearance of diffraction spots in the RHEED pattern within several minutes.

Let us consider the both nitridation stages in more detail. At comparatively low temperatures (< 900 °C), the nitridation during first several seconds leads to the faint diffraction pattern of the SiN-(8 × 8) structure with the low intensity of elongated diffraction spots or streaks, as shown in Fig. 3(a). The nitridation at high temperatures (> 1000 °C) within approximately 5–6 s leads to the SiN-(8 × 8) structure with the bright and narrow fractional spots arranged along the Laue-circles [Fig. 3(b)].