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Growth of atomically smooth AlN layers on Si(111) substrates through an amorphous Si_xN_y layer by plasma-assisted molecular beam epitaxy

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The study focuses on the growth of AlN layers on Si(111) substrates using plasma-assisted molecular beam epitaxy. The influence of the substrate temperature on the crystalline quality of the AlN layers is systematically investigated. It is demonstrated that the predeposition of an amorphous Si_xN_y layer on the Si(111) surface followed by the deposition of approximately ~ 2 monolayers of Al allows one the formation of AlN layer with a surface roughness as less as 0.43 nm at a layer thickness of 170 nm. The results are of interest for the monolithic integration of III-N optoelectronic and radio frequency devices with silicon-based technologies.

Keywords: Aluminum nitride, molecular beam epitaxy, semiconductors, silicon.

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III-V semiconductor compounds play a critical role in the production of optoelectronic components [1], and III-N semiconductor compounds have recently attracted increasing interest [2]. The potential to adjust the band gap width within the range from ~ 5.9 to ~ 0.7 eV and the direct-gap electronic structure of (In, Ga)N and (Al, Ga)N materials allow one to design optoelectronic devices operating in various spectral ranges, including ultraviolet (disinfection), visible, and telecommunication ones [3]. Moreover, in contrast to classical III-V semiconductor-based components, devices based on III-N materials maintain stable operation under extreme conditions even when a significant number of structural defects are present.

The development of techniques for synthesis of III-N semiconductor materials on silicon substrates is one of the critical research problems in this field. The difficulty lies in compensating for the mismatch of lattice parameters and thermal expansion coefficients between Si and III-N materials. One possible way to solve this problem is to form AlN buffer layers on Si substrates in advance. However, the task of growing AlN layers on silicon presents certain difficulties. Specifically, direct growth of single-crystal AlN layers on (111) silicon is infeasible due to Al−Si interdiffusion [4]. A significant suppression of such interdiffusion may be achieved by pre-treating the Si(111) surface with nitrogen plasma, which induces the formation of a thin „barrier" layer of Si_xN_y on the silicon surface. It is important here to determine the advantages of synthesis of crystalline Si_3N_4 or amorphous Si_xN_y prior to AlN growth. The approach of several research groups is to grow intentionally a Si_3N_4 layer (1.5−2 nm [5]) and then form a wetting Al layer ~ 1.5 ML in thickness on the Si_3N_4 surface. Other groups try to avoid nitriding the Si surface, largely for the reason that it may cause the formation of amorphous Si_xN_y, which may result in a high density of defects in AlN and failure of epitaxial growth. In one of the latest studies [6], the issue of influence of Si(111) surface treatment on the properties of formed AlN layers was investigated in the process of synthesis by ammonia molecular-beam epitaxy.

In the present study, we examine an approach to the formation of AlN layers on the surface of amorphous Si_xN_y by molecular-beam epitaxy with nitrogen plasma activation. This method has an advantage in providing lower growth temperatures (compared to gas-phase methods), which helps circumvent some of the problems caused by the mismatch of lattice parameters and thermal expansion coefficients of the silicon substrate and nitride layers on it. Specifically, one may form thin (up to 1 μm) layers without preliminary synthesis of a complex and thick thermal compensation buffer layer and avoid cracking of the epitaxial layer in the process of cooling (even delicate) after growth. The influence of the substrate growth

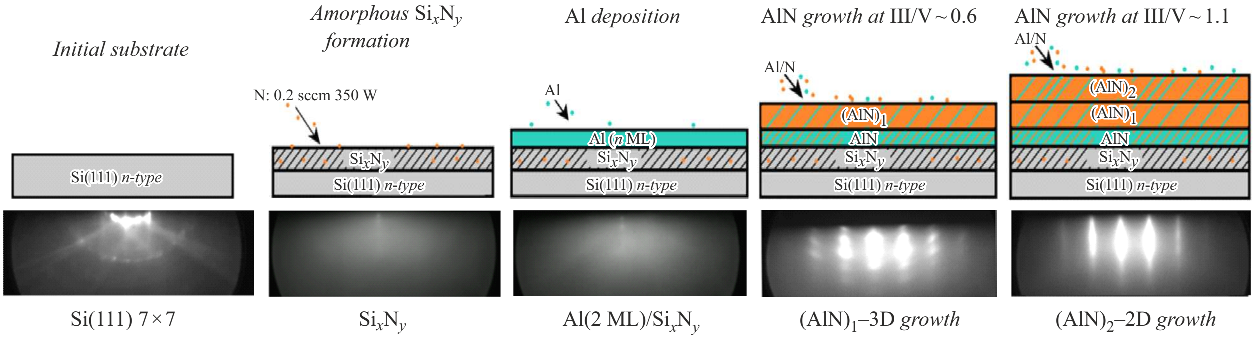

Figure 1. Schematic diagram of the stages of formation of an AlN layer on a Si(111) substrate and RHEED patterns corresponding to each stage.

temperature (T_s) on the structural properties of the formed AlN layers is investigated. The statistics of defect formation on the surface of grown AlN layers is analyzed as a function of substrate temperature. It is demonstrated that smooth AlN layers with a roughness down to 0.43 nm may be grown on a thin pre-formed amorphous Si_xN_y layer with ~ 2 ML of deposited Al.

Growth experiments were performed in a Riber Compact 12 molecular-beam epitaxy setup fitted with an Addon RF600 nitrogen plasma source and effusion sources of Ga, In, and Al. A reflection high-energy electron diffraction (RHEED) system and an infrared pyrometer pre-calibrated against the reconstructed Si(111) 7×7 to 1×1 were used to monitor the state and temperature of the substrate surface during growth. KEF 0.002-0.004 *n*-type Si wafers were used as the initial substrate. The crystalline orientation of the substrate surface corresponded to (111) with a misorientation of 4° in the [110] direction. Prior to the introduction into the growth chamber, the substrate was treated in a solution of hydrofluoric acid with a concentration of 47.5 % (high purity; „NevaReaktiv") for 40 s and rinsed with deionized water for 60 s. The substrate was then loaded into the growth chamber and annealed at a temperature of 920 °C for 20 min. Following annealing, the substrate temperature was reduced to 620 °C (according to pyrometer measurement data). It can be seen from the RHEED patterns (Fig. 1) that the silicon surface after annealing corresponded to the 7×7 reconstruction. The growth stages of AlN and the RHEED patterns corresponding to each stage are shown in the same figure. When the temperature was stabilized at 620 °C, the nitrogen plasma source was initiated at a power of 350 W and a nitrogen flux of 0.2 sccm, and the substrate was treated in nitrogen plasma for 20 min. A thin amorphous Si_xN_y layer was formed as a result, which is evidenced by the lack of any reflections in the RHEED pattern. At the next stage (without nitrogen plasma), Al was deposited on the formed Si_xN_y layer for 6 s, which nominally corresponded to ~ 2 ML. The RHEED pattern corresponded to the one observed at the previous stage of growth. The substrate temperature was then raised to growth levels. It was claimed in several studies (see [7] and references therein) that heating to high temperatures (characteristic of AlN epitaxy) leads to the formation of a thin barrier and, at the same time, seed AlN layer due to the breaking of Si–N bonds and the formation of Al–N bonds. Processing with the plasma nitrogen source before high-temperature growth contributes to complete binding of Al adatoms with N. In this connection, plasma was initiated again at the growth temperature (similar to the previous stage), and AlN growth was carried out at a III/V flux ratio of ~ 0.7 for 10 min. The three-dimensional RHEED dot pattern confirms the formation of AlN under nitrogen-enriched growth conditions (Fig. 1). Here and elsewhere, the flux ratio is indicated without account for desorption of adatoms from the surface. Nitrogen-enriched conditions were maintained to avoid accumulation of excess Al on the growth surface. However, nitrogen-enriched growth leads to high surface roughness; therefore, the growth was interrupted after the formation of a continuous AlN barrier layer with a thickness of ~ 10 nm, the Al source temperature was raised, and the AlN layer was grown (after temperature stabilization) in metal-enriched conditions with a III/V flux ratio of ~ 1.1. The linear RHEED pattern is indicative of the formation of a continuous AlN layer (Fig. 1). The duration of this growth stage was 2.5 h. When the growth process was completed, the AlN surface was nitrided for 10 min. A series of experiments with AlN growth temperature (T_s) varying from 805 to 845 °C were carried out. The thickness of grown AlN layers was ~ 170 nm.

The structural properties of samples were examined using a Zeiss SUPRA 25 (Germany) scanning electron microscope (SEM) and the RHEED method. Raman spectra were measured with a Horiba Jobin-Yvon LabRAM HR800 spectrometer fitted with a 532 nm laser pump source. The optical system provided an opportunity to focus the laser beam into a spot approximately 1 μm in diameter with an optical power of ~ 6 mW. In order to perform statistical analysis of the formed surface defects (droplets, (Al, Si)N crystallites, and other types of inhomogeneities), the surface of samples was examined with a Leica INM 100 high-resolution semi-automatic optical microscope. The

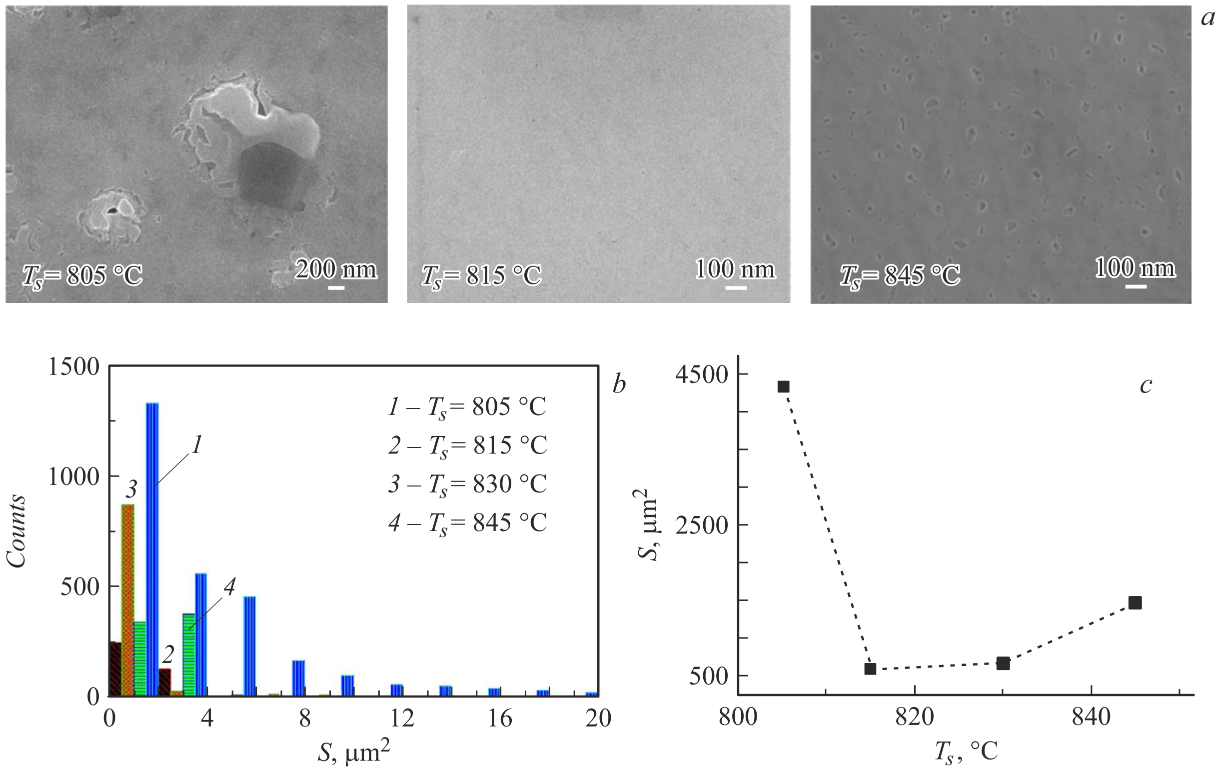

Figure 2. *a* — SEM images of the sample surface with typical defects arising at low, optimum, and high substrate growth temperatures; *b* — distributions of surface defects by occupied area for each of the grown samples; and *c* — dependence of the total area occupied by surface defects on substrate growth temperature. A color version of the figure is provided in the online version of the paper.

surface roughness of samples was studied by atomic force microscopy (AFM) using an NT-MDT NTEGRA THERMA (Zelenograd, Russia) setup.

Figure 2, *a* shows SEM images of the surface of layers grown at temperatures of 805, 815, and 845 °C. At 805 °C, a non-uniform AlN layer consisting mostly of Al droplets and (Al, Si)N crystallites is formed. The formation of (Al, Si)N is attributable to the fact that the eutectic temperature of the Al−Si system is 577 °C [8], which is significantly lower than the growth temperature (805 °C). Therefore, excess aluminum on the substrate surface interacts with silicon atoms, inducing the formation of this phase. Even at a III/V ratio of ~ 0.7 at the initial stages of growth, excess Al emerges as a result of significant elastic stresses due to the mismatch of lattice parameters of AlN and Si, which leads to rupture of Al−N bonds. As the substrate temperature increases, excess aluminum is desorbed from the surface, which helps suppress the formation of inhomogeneities of this type. As Al evaporation intensifies with an increase in temperature, the process of Al droplet formation in metal-enriched growth (III/V ~ 1.1) gets suppressed. The number of surface defects in the AlN layer is minimized under these growth conditions, and they take the form of mesopores only. With an increase in temperature to 845 °C, the number of mesopores increases significantly due to the intensification of Al desorption from the surface and, consequently, to the reinforcement of nitrogen-enriched growth conditions (Figs. 2, *b, c*). (Al, Si)N structures do not form at temperatures of 830 °C and above.

Figure 3 shows the results of measurements of the structural properties and surface roughness of the sample grown at the optimum substrate temperature (815 °C). The crystalline quality and internal stresses of the grown layer were determined by analyzing the Raman spectrum. Figure 3, *a* presents the measured spectrum. Dashed and dotted lines correspond to the AlN modes and two-phonon scattering from the Si substrate, respectively (see [9] and references therein). The primary peak, $E_2(high)$, corresponds to a Raman shift of $653\,\mathrm{cm}^{-1}$ [8,9], and its half-width is $7.5\,\mathrm{cm}^{-1}$, which is comparable with earlier data on the growth of AlN on Si [6,9]. The $E_2(high)$ mode is shifted to the red side by $\sim 3.76\,\mathrm{cm}^{-1}$ relative to its position in unstressed AlN layers ($\sim 657.4\,\mathrm{cm}^{-1}$) [10], indicating the presence of tensile stresses, which are likely to be attributable to the mismatch in lattice parameters between AlN and the Si substrate, in the layer. In a linear approximation, the magnitude of tensile stresses may be estimated based on the shift of Raman mode $E_2(high)$ as $\Delta\omega = K\sigma$, where K is a constant that assumes a value of $3.39\,\mathrm{cm}^{-1}$/GPa for AlN layers on Si [6,11,12]. According to this estimate, the magnitude of internal tensile stresses (σ) is 1.1 GPa, which is typical of AlN layers on Si [6,9]. The sample surface roughness measured using five maps $2 \times 2\,\mu$m in size was 0.43 nm (Fig. 3, *b*). Such low surface

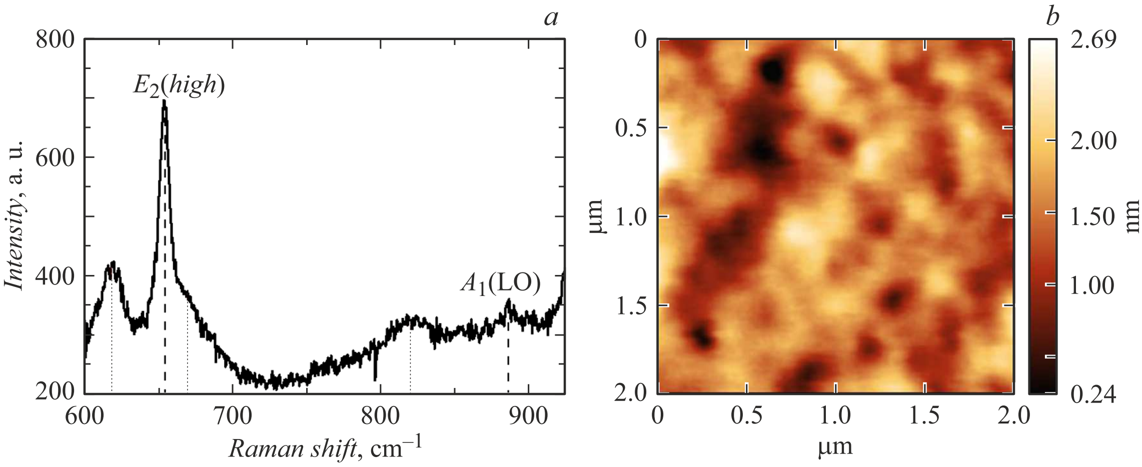

Figure 3. *a* — Raman spectrum of the sample grown at 815 °C. Dashed lines correspond to AlN, while dotted lines correspond to the Si substrate. *b* — Typical AFM map of the sample surface.

roughness levels hold promise for subsequent fabrication of heterostructures with a sharp interface based on layers of binary and ternary (Al, Ga, In)N compounds and their use as efficient optoelectronic and radioelectronic devices.

The study revealed the efficiency of application of a pre-formed amorphous Si_xN_y layer with deposited Al in synthesis of epitaxial AlN layers on Si(111) substrates by molecular-beam epitaxy with nitrogen plasma activation. Optimization of the substrate temperature provided an opportunity to obtain thin (170 nm) single-crystal AlN layers with low surface roughness (0.43 nm). However, such layers are subject to internal tensile stresses, which reach 1.1 GPa in magnitude. The obtained results may be of interest for further development of methods for monolithic integration of optoelectronic and radioelectronic devices based on III-N semiconductor materials with silicon.

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Conflict of interest

The authors declare that they have no conflict of interest.

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