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Correlation between Crystallographic Alignment of Self-induced GaN Nanowires and Features of Si(111) Nitridation

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Formation and spatial ordering of self-induced GaN nanowires grown by molecular beam epitaxy on a spatially pre-nitridazed Si(111) substrate have been studied. It was found the close correlation between Si substrate nitridation parameters and crystallographic alignment of NWs. Conditions for NWs nucleation and in- plane orientation are predefined by a structural anisotropy of silicon nitride nanolayer. Mechanism of NWs orderly emergence suggested.

Keywords: GaN, Nanowires, Si (111), Crystallographic alignment, Nitridation.

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1. INTRODUCTION

Gallium nitride (GaN) is a wide-bandgap semiconductor that has been under intense development because of already shown promise for realizing high-power, -frequency and optoelectronic devices [1]. GaN is grown most often on sapphire (Al_2O_3), silicon carbide (SiC), and silicon (Si) substrates. The lattice mismatch between GaN and these substrates leads to high dislocation densities in films, especially in the case of Si substrate. Despite these difficulties there is strong interest in combining the advantages of GaN properties with the technological advantages of Si substrates.

The strong influence of lattice mismatch on GaN crystal quality, grown on Si substrate, can be avoided by the growth of one-dimensional GaN nanowires (NWs). GaN NWs mostly on Si(111) surface are extensively studied due to their perfect structural characteristics in comparison with planar epitaxial layers. This allows creation of new electronic devices with improved parameters.

There has been significant research devoted to the study of the growth and properties of GaN NWs in recent years. However, despite of increasing number of publication in this field, many issues are still unclear. One of them is the mechanism of in-plane crystallographic orientations of self-induced GaN NWs grown on Si(111) substrate.

In general, III-nitride layers on Si(111) or Al_2O_3(0001) grow in the wurtzite *c*-plane (0001) orientation. The in-plane crystallographic orientation of GaN on *c*-plane sapphire corresponds to lattice mismatch of about ~ 14% [2]. For planar GaN/Si(111) epitaxial structure, the in-plane crystallographic orientation I of GaN corresponds to lattice mismatch of about ~ 17% (Fig. 1). However, another possibility of the in-plane crystallographic orientation II of GaN corresponding to lattice mismatch of about ~ 4.1% (Fig. 1) were shown previously for self-induced GaN NWs formed on thin intermediate Al(Ga)N layers pre-deposited on Si(111) substrates [3]. These results correlate well with two in-plane orientations of 2D AlN [4] and thick epitaxial AlN layers [5] on Si(111).

On the other hand, the in-plane crystallographic alignment of self-induced GaN NWs on bare Si(111) substrate corresponds to orientation I [6, 7], like for planar GaN/Si(111) epitaxial structure. It is also shown that the very thin silicon nitride (Si-N) buffer layer is formed between GaN and substrate [6-8]. Moreover, it was shown that the substrate nitridation process has strong influence on the in-plane arrangement of GaN NWs [7] and on properties of GaN layers [8, 9]. Thus, the reason of different in-plane crystallographic orientation of self-induced GaN NWs on AlN and SiN buffres on Si(111), as well as role of Si(111) pre-nitridation before NWs growth, require more detailed investigation.

In this work, the mechanism responsible for in-plane arrangement of self-induced GaN NWs grown by plasma-assisted molecular beam epitaxy (PAMBE) on Si(111) substrate was investigated.

2. EXPERIMENTAL

The investigated GaN NWs were grown by PAMBE on Si(111) substrates at ~ 760°C under highly nitrogen-rich conditions. The growth time of the NWs was 120 min. The growth started by deoxidation of Si(111) substrate until a clear 7 × 7 reflection high-energy electron diffraction pattern appear. Then, the substrate was exposed to a nitrogen flux for 30 min at the nitridation temperature ~150°C (LT substrate) and ~ 850°C (HT substrate).

We investigated both nitridazed Si(111) substrates, as well as GaN NWs array grown on them. The samples were examined *ex-situ* by using a high-resolution x-ray diffraction (HRXRD) PANalytical X'Pert Pro MRD XL, scanning electron microscope (SEM) Hitachi SU-70 and an atomic force microscope (AFM) NanoScope IIIa Dimension 3000™.

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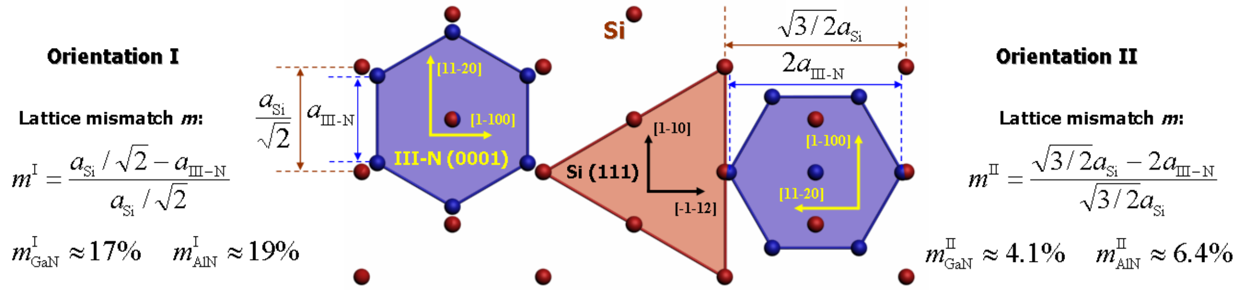

Fig. 1 – Sketches of the interfacial planes of III-N(0001) and Si(111) corresponding to orientation I with lattice mismatches for GaN (~ 17%) and for AlN (~ 19%); corresponding to orientation II with lattice mismatches for GaN (~ 4.1%) and for AlN (~ 6.4%)

3. RESULTS

At first, we investigated the GaN NWs array grown on LT and HT Si(111) substrates. The structural parameters and crystallographic orientation of GaN NWs were determined by HRXRD. The NWs out-of-plane orientation distribution (tilt) and lateral correlation length ($D^{||}$), as well as vertical correlation length ($D^{\perp}$) and microstrain ($\varepsilon^{\perp}$) were analyzed by Williamson–Hall plots from symmetric 0002, 0004 and 0006 ω and ω-2θ scans, respectively. The similar values of $D^{||} \sim 9 \pm 2$ nm and $D^{\perp} \sim 290 \pm 10$ nm were found for GaN NWs on LT and HT substrate. For both samples GaN NWs grow along the c-axis normal to the Si(111) surface with tilt ~ 2.7±0.1°. The fluctuation of the c lattice constant within NWs (average microstrain) is about $\varepsilon^{\perp} \sim 5 \times 10^{-5}$ for LT and HT substrate nitridation.

X-ray diffraction pole figures of Si(220) and GaN(10-12) reflections were measured in order to define the crystallographic orientation of GaN NWs with respect to the substrates (Fig. 2). For HT substrate (Fig. 2b), the GaN six-fold symmetry coincide with Si threefold symmetry which mean that the NWs have their in-plane [11-20] directions aligned with [1-10] Si directions (orientation I, Fig. 1). For LT substrate the in-plane orientation of GaN NWs is random (Fig. 2a). The only weak broad maxima appear in the [0111] directions. Thus, the GaN NWs are crystallographically aligned and disorderly distributed at HT and LT substrate nitridation, respectively.

The SEM images (Fig. 3) reveal variation in NW's surface density for LT and HT substrate processing 200 NWs/um^{-2} at 19% coverage and 250 NWs/um^{-2} at 30% coverage, respectively. Diameters of wires have lognormal distribution with maximum near 27 nm in the both cases, which correlate well with HRXRD results. 2D Fourier analysis of the SEM images (inserts, Fig. 3) clearly illustrates the changes in the long-range order of NWs on the substrate with increasing of nitridation temperature. In the first case (LT), all directions on the substrate are equal, and in the second case (HT) - the probability of the NWs location along the six radially symmetric preferred directions significantly increases. This means that the features of substrate nitridation should define the NWs odering processes.

Further, we investigated the morphology of LT and HT Si(111) substrates. Fig. 4 illustrates an AFM study of Si(111) surface evolution under nitridation process at increasing temperature. Initial epi-ready silicon wafer has a randomly rough surface with a typical roughness near ~ 0.2 nm (Fig. 4a). This surface covered by some nano-patterned Si-N layer after LT processing (Fig. 4b). Weak terraces running perpendicular to the [11-2] direction appear. This can be explained by charge distributions anisotropy of the Si(111)-7 × 7 surface [10], and features of its reaction with N atoms at low temperature [11].

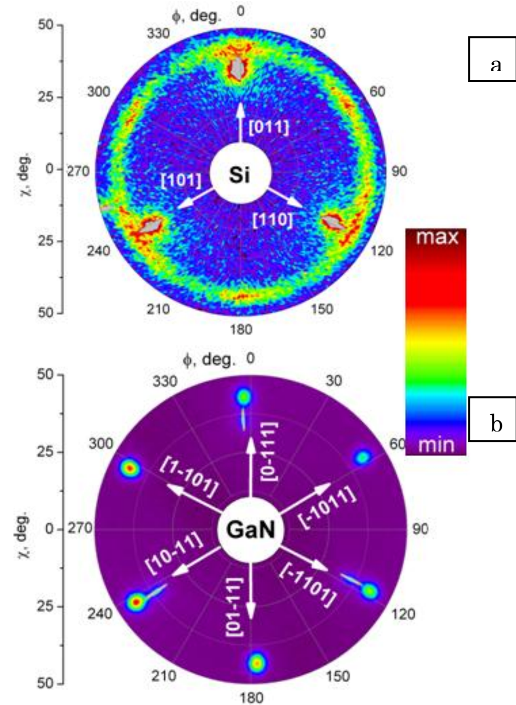

Fig. 2 – X-ray diffraction Si(220) and GaN(10-12) pole figures of LT (a) and HT (b) samples

Drastic transformation of surface takes place after HT processing (Fig. 4c). The pattern of overlapped triangular Si-N plateaus with characteristic lateral dimensions of ~ 150±50 nm formed. They are separated by narrow trenches of about ~ 2 nm in-depth and a width from ~ 10 to ~ 90 nm. The shape of plateaus demonstrates the fragments of the flat facets with angles of 60 and 120° crystallographically binded to the silicon substrate. The plateaus growth strongly prefers proceeding along the [11-2] directions on Si (111). This correlates well with the previous results, where the reactions of N atoms with the clean Si(111)-7 × 7 surface at high temperature were studied [12, 13]. The misorientation of plateaus characterized by surface normal histogram (Fig. 4f). Vertical inclination angles of plateaus surface ranged within 0-7°, mainly. There is

clear visible six-fold symmetry of azimuthal orientation of surface normales caused by boundaries of plateaus and three-fold symmetry of histogram central part which reflects deviations of plateaus plane from vertical.

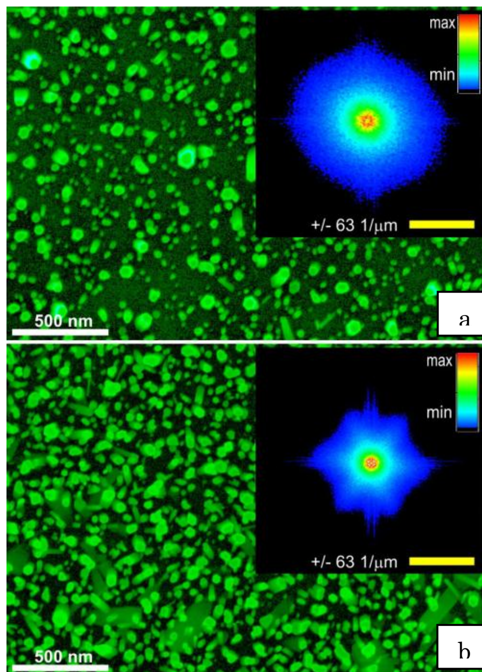

Fig. 3 – Contrasted SEM images of GaN NWs grown on LT (a) and HT (b) Si(111) substrates. Inserts show 2D FFT of corresponding SEM images

Surface normales distribution do not excide 2° in the case of LT processing and has some tails (up to 5°) caused by terraces anisotropy (Fig. 4e). Thus, during LT processing the nitridation of Si(111)-7x7 surface is gradual (layer-by-layer), while during HT processing at the surface appear anisotropic-oriented Si-N plateaus.

Comparing the results, presented in Fig. 3a and Fig. 4e, it can be concluded that on the smooth surface of Si-N (at LT) nucleation and orientation of GaN NWs are random (chotic). On the contrary, the symmetry of histogram in Fig. 4f and 2D FFT in Fig. 3b allows us to assume the close relationship between substrate pattern symmetry and symmetry in NWs distribution over surface. Furthermore, detailed 3D surface mapping of the HT sample with sheared GaN NWs (Fig. 5) detects the same orientation of NW's facets. NW's are localized on rises (elevations) mainly. In the case of HT, it is proposed that NW nucleation is governed by the facets of Si-N plateaus acting as their preferred nucleation sites.

Thus, in our opinion, the key moment to the ordered nucleation of NWs is the presence of oriented facets, which forces (impose) common to all NWs in-plane orientation and the anisotropy of their density on the substrate. Indeed, in conditions of excess nitrogen the most important are kinetics of gallium atoms. The last flow down to the boundaries (facets) and corners of the plateaus where form flatly faceted two-dimensional nuclei. These fragments grow toward the center of the plateau by step-flow mechanism with preservation of the local hexagonal symmetry.

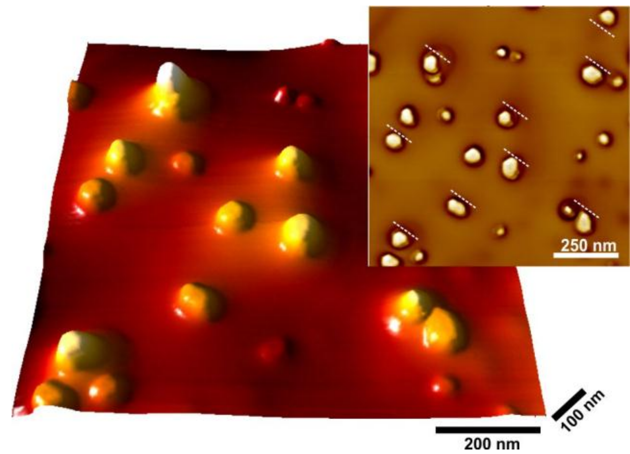

Fig. 5 – 3D AFM image of sheared GaN NWs grown on the HT nitridated Si substrate. Insert shows corresponding AFM phase contrast image. Parallel white dashed lines are shown as eye-guide to illustrate the same orientation of NW's facets

Independence of NWs dimensions from the features of the Si-N layer testify that the transition from two-dimensional to the vertical growth depends only on thermodynamical reasons (parameters of growth). But their spatial orientation depends mainly on geometrical parameters of Si-N layer.

Indeed, in case of HT substrate the facets of Si-N plateaus and (1-100) of GaN NWs have the same orientations along the [11-2] Si directions so that the [11-20] GaN direction corresponds to [1-10] Si direction (orientation I, Fig. 1). In case of LT substrate there are no preferred NW nucleation sites on the smooth surface of Si-N, which results in random in-plane orientation of GaN NWs. Moreover, the average level of GaN NWs microstrain is independent on their in-plane orientation. This fact also indicates non-influence of the Si (111) substrate (field of strain) on GaN NWs in-plane crystallographic alignment.

4. DISCUSION AND CONCLUSIONS

To clarify role of Si-N layer let us discuss the growth features of GaN and AlN on Si (111) substrate. As it was mentioned above, the two possible crystallographic alignment of growing AlN were observed. The direct growth of III-N layers on Si causes the Si-N buffer layer at the interface due to the high reactivity of Si and N [14]. Since the Al-N binding energy is much higher than the Ga-N binding energy [15], we suppose that "clear" AlN/Si and AlN/SiN/Si interface regions can be formed during AlN deposition on Si surface. But the only GaN/SiN/Si interface is formed during GaN deposition on Si surface. For "clear" AlN/Si interface, the in-plane crystallographic alignment of AlN relative to Si(111) corresponds to the direction of minimum lattice mismatch ~ 6.4% (orientation II). Formation of Si-N buffer layer leads only to the in-plane crystallographic orientation I for both GaN and AlN. This is why we observe two in-plane orientations for GaN NWs with AlN buffers [3], as well as for epitaxial layers [5] and 2D AlN [4] deposited directly on Si(111).

The growth of III-N layers on pre-nitridazed Si excludes reaction between III-atoms and Si because Si-N layer plays role of diffusion barrier. As a result, for both

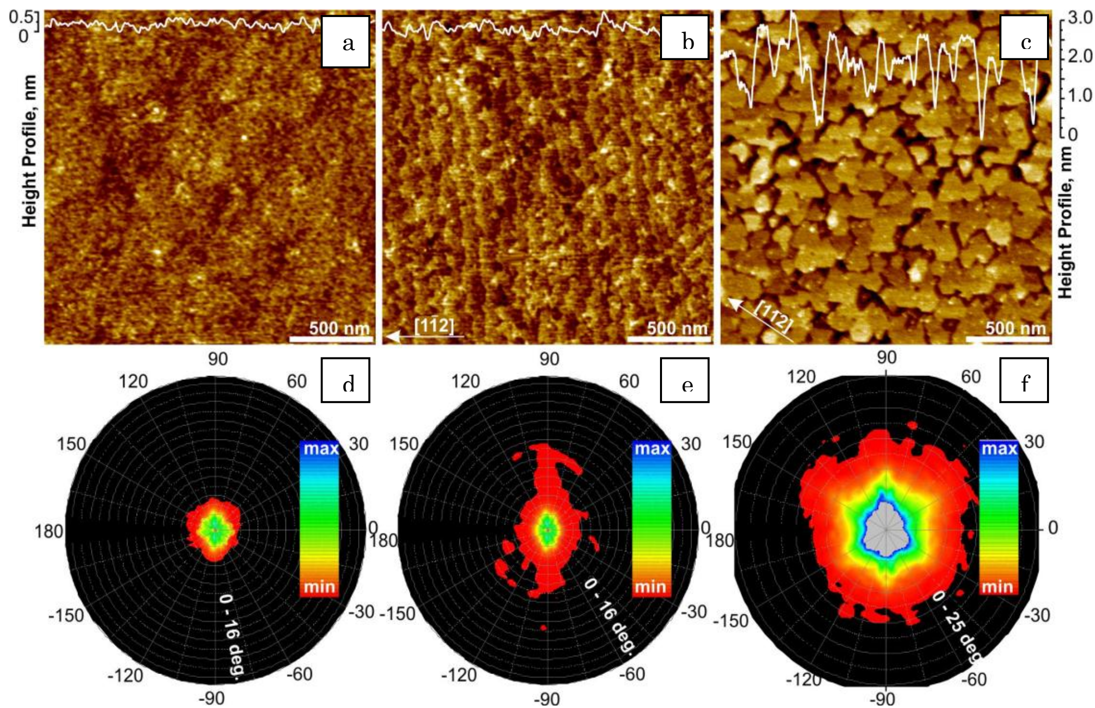

Fig. 4 – AFM images of substrates: silicon (111) epi-ready wafer (a), LT (b) and HT (c) Si(111) substrates. Typical surface cross-sections are shown as white lines. Corresponding 3D histograms of the surface normal orientation are shown in d-f. Azimuthal data reflects in-plane orientation and radial data correspond to the surface normal inclination angles

both GaN and AlN deposited on SiN/Si substrate the in-plane crystallographic orientation I is mostly observed. There are many hypotheses on the influence of Si-N buffer layer on the in-plane crystallographic alignment of self-induced GaN NWs [3, 6-8, 16]. Most of them are based on the crystallinity, stoichiometry or discontinuities of Si_3N_4 interlayer; despite cross-sectional transmission electron microscopy of Ga(Al)N/SiN/Si interface explicitly shows that the Si-N buffer layer is amorphous. There is no doubt that the Si-N formed at high nitridation temperature of Si is a mixture of the crystalline and amorphous phases. However, as it was shown in [17], crystalline Si_3N_4 buffer layer must be amorphized to allow GaN NW nucleation. This hampers explanation of crystal orientation transfer of the Si substrate to the grown GaN NWs through the amorphous Si-N layer. In our opinion, despite the very thin Si-N layer (~ 2 nm), the Si (111) substrate has no influence on the spatial ordering of the self-induced GaN NWs. Only features of Si-N surface morphology can influence on the spatial ordering of the self-induced GaN NWs, by creating preferred NW nucleation sites on Si-N surface.

In summary, it is shown that one of the ways to control the spatial ordering of the self-induced GaN NWs can be the formation of nano-structured silicon nitride substrate. Anisotropic orientation of Si-N plateau facets, which were influenced by silicon substrate, forces (impose) prevailing in-plane orientation of NWs and the anisotropy of their surface density.

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