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GROWTH MODE AND SURFACE RECONSTRUCTION OF GaN(000$\bar{1}$) THIN FILMS ON 6H-SiC(000$\bar{1}$)

XUE QI-ZHEN(薛其贞)[a], XUE QI-KUN(薛其坤)[a,b],
S. KUWANO[a], K. NAKAYAMA[a], and T. SAKURAI[a]
[a] *Institute for Materials Research, Tohoku University, Sendai* 980-8577, *Japan*
[b] *State Key Laboratory for Surface Physics, Institute of Physics, Chinese Academy of Sciences, Beijing* 100080, *China*

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Two-dimensional growth of GaN thin films on an atomically flat C-face 6H-SiC(000$\bar{1}$) surface prepared by ultra-high vacuum Si-etching is observed when using an AlN buffer layer in N plasma-assisted molecular beam epitaxy. Scanning tunneling microscopy and reflection high energy electron diffraction observations reveal a series of Ga-stabilized reconstructions which are consistent with those reported for an N-polar GaN(000$\bar{1}$) film. The result, including the effect observed previously for GaN thin film on Si-terminated 6H-SiC(0001), agrees with the polarity assignment of heteroepitaxial wurtzite GaN films on polar 6H-SiC substrates, i.e., GaN film grown on SiC(000$\bar{1}$) is $< 000\bar{1} >$ oriented (N-face) while that on SiC(0001) is $< 0001 >$ oriented (Ga-face).

Keywords: GaN, 6H-SiC, molecular beam epitaxy, scanning tunneling microscopy, X-ray diffraction, surface reconstruction
PACC: 8115, 6116P, 6110, 7300

I. INTRODUCTION

Wide band-gap III-V nitrides (Ga/In/Al/N) have attracted much interest because of their enormous application possibilities in short-wavelength optoelectronic devices.[1] Absence of a reversion symmetric center in the hexagonal GaN crystal gives rise to a freedom in its thin film polarity: The (000$\bar{1}$) polar surface terminated by a Ga-N bilayer known as the Ga polarity and the (000$\bar{1}$) polar surface terminated by an N-Ga bilayer known as the N polarity.[2,3] These two faces exhibit different structures, chemical compositions, and growth kinetics,[4–7] but all play important roles in fundamental studies and practical applications.[2] Although the bulk GaN now is available,[8,9] most GaN films are usually obtained by heteroepitaxy on dissimilar substrates, such as sapphire and SiC. With the present growth techniques, heteroepitaxial GaN films contain a high density of defects, which is even more severe in the case of the N-face GaN films.[6,7] These defects significantly deteriorate the performance of GaN-based electrical and optical devices,[10] and improving the quality of GaN materials has been a subject of extensive research efforts.

As far as the similar lattice constants and thermal expansion coefficients of SiC and GaN are concerned, SiC has several advantages over the sapphire often used for heteroepitaxy of GaN films. Recent studies show that smooth SiC surfaces prepared by chemical etching[11] or by hydrogen etching[12] result in nitride films with a lower density of defects and better crystallinity. On scratch-free and atomically flat 6H-SiC(0001), we have grown a reasonably good GaN film which enables us to study its surface structure in great detail by scanning tunneling microscopy (STM).[13,14] While many studies focused on GaN on the Si-face 6H-SiC(0001) substrate, there are only few reports[15] on the C-face 6H-SiC(000$\bar{1}$). On the other hand, both wurtzite GaN and hexagonal SiC are polar materials, and previous experiments[15–17] and theories[18] demonstrated that the GaN films exhibit a certain polarity when they form on SiC. Thus, it would be interesting to verify the polarity assignment by directly comparing surface reconstructions of GaN films grown on both Si- and C-faces of SiC. In this paper, it is reported about the first STM study on the clean surface of 6H-SiC(000$\bar{1}$) and GaN growth on it. With optimized AlN buffer layers, two-dimensional growth has been obtained. All films grown on this substrate were confirmed to be N-face.

† Corresponding author, E-mail:qkxue@aphy.iphy.ac.cn

Ⅱ. EXPERIMENTAL

Experiments are carried out in a molecular beam epitaxy (MBE) combined STM system. Research-grade-quality on-axis SiC(000$\bar{1}$) samples (n-type doped 2×10^{18}cm^{-3}, Cree Research Inc.) are used as substrate. Before loaded into the UHV chamber, the SiC wafers are degreased ultrasonically by acetone and methanol for 10 minutes. After overnight degassing at 650°C in UHV, the 6H-SiC substrates are cleaned by UHV annealing under an Si molecular beam (hereafter called Si etching). The Si molecular beam is supplied from a Si wafer which is heated up to ∼1100°C by direct current heating. The distance between the Si wafer and the SiC substrate is ∼10cm during annealing. Typically ten cycles of the Si etching process may result in a clean surface. The GaN film is grown by plasma-assisted solid source MBE, and a radio frequency EPI N plasma source is employed to activate N_2 molecules. The growth starts with approximately 1.0ML group-III metal deposition on the SiC(000$\bar{1}$) 2×2 surface. An AlN buffer layer (approximately 100Å thick) is deposited at a substrate temperature of ∼750°C for all the samples studied. This AlN buffer layers reduce the lattice mismatch (∼6%) between the GaN and 6H-SiC substrate, and can enhance the interface bonding between the epilayer and the sapphire substrate. Optimization of the buffer layer growth is achieved by a coordination of the Al/N flux ratio and the substrate temperature, by which a streaky RHEED pattern is usually resulted right after the buffer layer growth. Then the substrate temperature is lowered to 700°C and the GaN film is grown under Ga-rich conditions (Ga/N> 1) at a rate of ∼1000Å/h. The N plasma source is usually operated at 250W with a typical N pressure of 7.5×10^{-5}–1.0×10^{-4} Torr. The GaN films studied here have a thickness of approximately 5000Å. The samples are further characterized by ex-situ atomic force microscopy (AFM) and X-ray diffraction.

Ⅲ. RESULTS AND DISCUSSION

Figure 1(a) shows a typical surface of the as-supplied SiC(000$\bar{1}$) sample measured by AFM. The surface is very rough and consists of many hills/holes and randomly directed scratches caused by mechanical polishing. Atmospheric hydrogen etching of the 6H-SiC(0001) sample at high temperature (∼1600°C) was found to remove all surface scratches and result in a flat surface with large-scale terraces separated by regular steps.[12–14] Bernhardt *et al.*[20] applied the same technique to 6H-SiC(000$\bar{1}$) and obtained a smooth surface morphology detected by low energy electron diffraction observation. However, such high temperature hydrogen etching could easily damage the wafer due to the inhomogeneous heating. Si etching is relatively simple, can avoid graphitization, and achieve stoichiometric a surface,[21–23] which is chosen to prepare the clean 6H-SiC(000$\bar{1}$) surfaces in this study.

The large-scale STM image (Fig.1(b)) after UHV Si etching shows an atomically flat surface with large terraces (several thousands of angstrom wide) separated by randomly directed steps. Such a smooth morphology is even comparable to that of the well-developed Si or GaAs surfaces. No scratches are observed after careful sampling of the whole sample surface, suggesting that Si etching is sufficient to remove the mechanical damage. Two types of steps are observed, as shown in Fig.1(b). Step A is four Si-C bilayers high (4H, 10Å), whereas step B is two Si-C bilayers high (2H, 5Å). Several groups reported $\sqrt{3}\times\sqrt{3}$, 2×2, 3×3, and $2\sqrt{3}\times2\sqrt{3}$ reconstructions[20–24] for this surface, but our treatment usually leads to a 2×2 reconstruction decorated with randomly distributed bright dots, as shown in Fig.1(c). The 2×2 surface is prepared by annealing the sample under Si flux. Its structure is consistent to the Si-rich 2×2 phase reported by Bernhardt *et al.*[20] These dots are attributed to tunneling from carbon rest adatoms, because of the Si evaporation during annealing at higher temperatures. Note that in the case of the 6H-SiC(0001) substrate, sole Si etching could not remove all mechanical damage. This might be explained by the higher decomposition rate of the C-face of 6H-SiC. In addition, the step structure of the (000$\bar{1}$) surface is quite different from that of the (0001) surface prepared by hydrogen etching, where the steps are very straight and have the same height of six Si-C bilayers (6H, 15Å). The different appearance is consistent with the AFM observation of step structures on the as-grown 6H-SiC(0001) surfaces.[25,26] This result will be reported elsewhere.

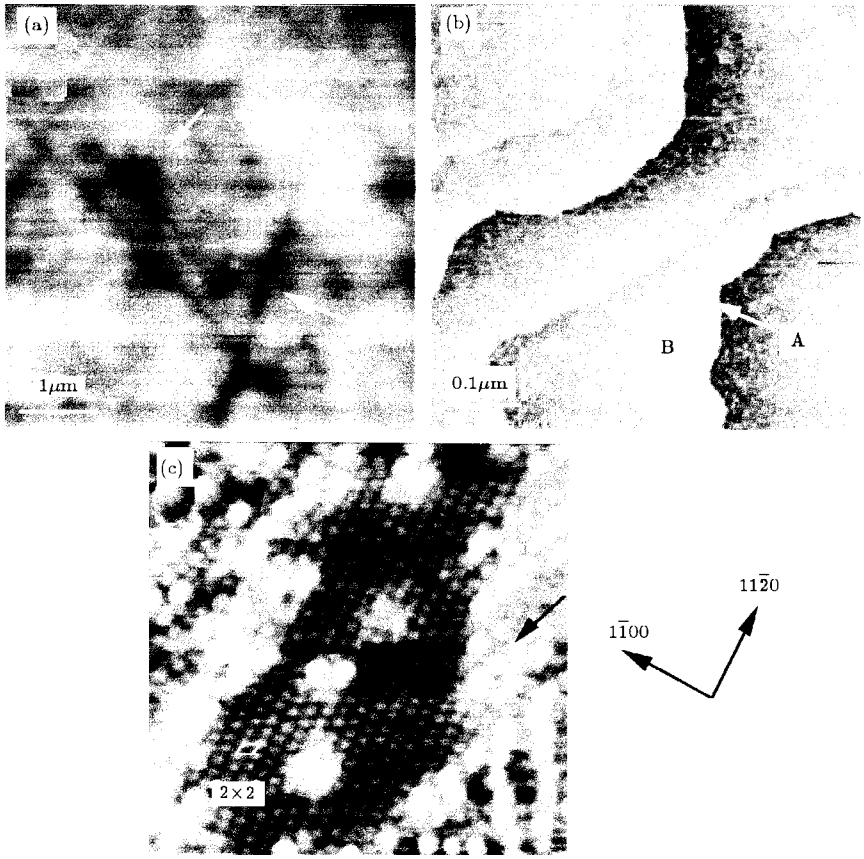


Fig.1. (a) 5μm×5μm AFM image of the as-supplied SiC (000$\bar{1}$) sample. The arrows indicate the scratches and holes resulting from mechanical polishing. The height difference between the bright and dark areas corresponds to 20 nm. (b) Filled-states STM image of 6H-SiC (000$\bar{1}$) after Si etching. The arrows A and B indicate the 4H and 2H steps, respectively. (c) 100Å×100Å filled-states STM image of a (2×2) reconstruction with carbon rest adatoms (bright spots, marked by an arrow). The sample bias V_s is –2.6V, and the tunneling current is 0.1nA.

On the clean SiC(000$\bar{1}$) substrate prepared by this method after 0.5μm thick GaN growth, the surface usually displays a sharp 1×1 RHEED pattern as shown in Fig.2(a). This streaky pattern reveals that the growth is two-dimensional. When a certain amount of Ga has been deposited on this 1×1 surface at 250°C followed by annealing at the same temperature for about 10 minutes, several reconstructions, such as Ga-stabilized 6×8, 6×6, $\sqrt{7} \times \sqrt{7}$, and 2×3 will develop depending on the amount of Ga supplied. This is summarized in Fig.3. Even though the RHEED pattern is streaky, the AFM measurements demonstrate that the whole surface morphology is not as uniform as the substrate, but characterized by irregularly shaped mesas with a flat top (Fig.4(a)). These mesas are 5–10nm high and isolated from each another. The boundaries between them are meandering. However, the AFM image of Ga-face GaN film on SiC(0001) shows that the surface is much smoother and featureless,[13] suggesting a higher lateral growth rate in case of the Ga-face.

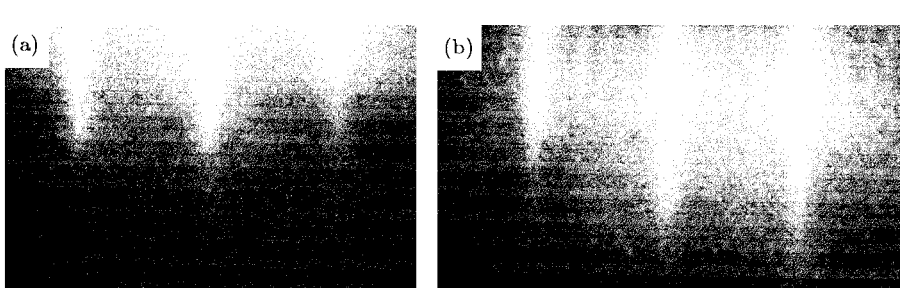


Fig.2. RHEED patterns along the [11$\bar{2}$0] azimuth of (a) an as-grown (1×1) surface, and (b) a (6×6) superstructure surface obtained by post-growth Ga deposition followed by annealing.

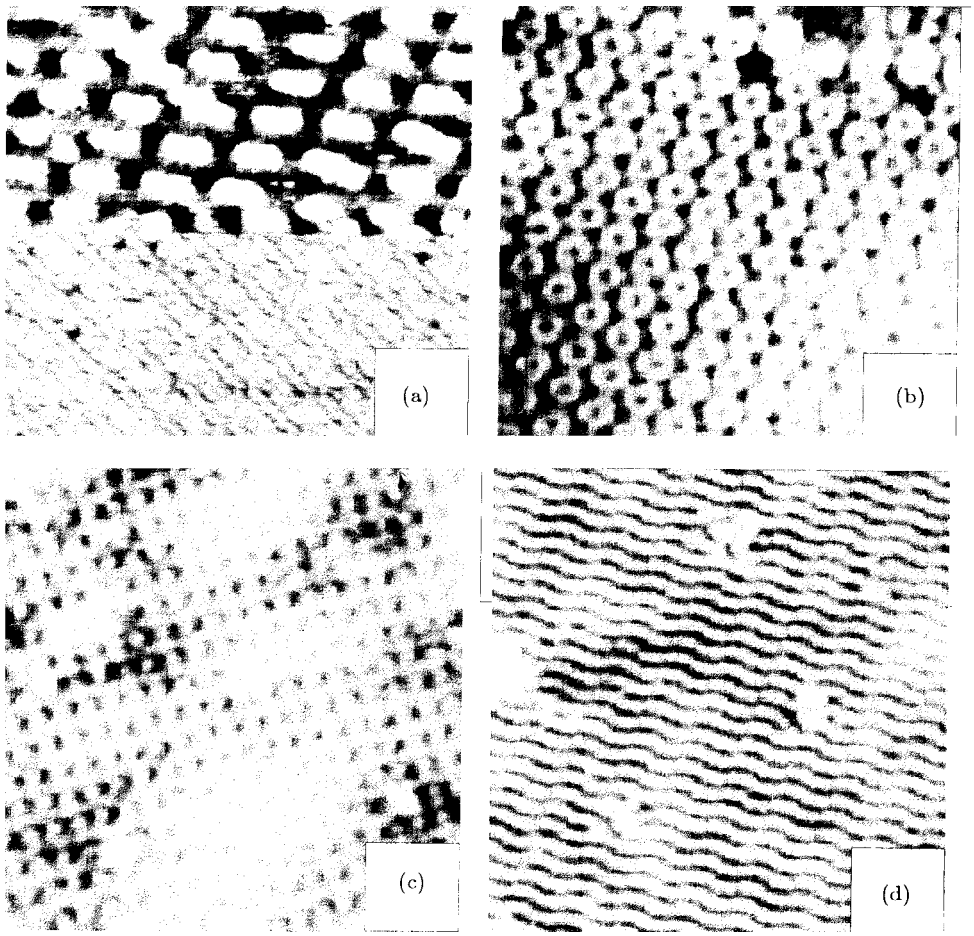


Fig.3. Summary of the reconstructions on the N-polar GaN $(000\bar{1})$ surface as a function of decreasing Ga coverage. (a) 6×8, (b)6×6, (c) $\sqrt{7} \times \sqrt{7}$, and (d) 2×3.

STM measurement reveals a typical terrace-plus-step surface morphology on top of the mesas, as shown in Fig.4(b). Interestingly, the steps have alternative single and double Ga-N bilayer heights along the crystallographic directions. As discussed by Xie *et al.*[27] there are two types of steps. The "A" step consists of the edge atoms with two dangling bonds, while the edge atoms at "B" step have only one dangling bond. Hence the more reactive "A" step grows faster than the "B" step and catches up with the "B" step of the sublayer, resulting in the double bilayer height steps (step bunching) as indicated in Fig.4(b). Together with the fact that there is no island nucleation on the terraces, this anisotropic growth behavior further supports the fact that the growth takes place in the two-dimensional step-flow mode as suggested by RHEED results.

Figure 4(c) shows an STM image of the 6×6 reconstruction whose RHEED pattern is indicated in Fig.2(b). Its ring-like donut structure is exactly same as that observed on the GaN $(000\bar{1})$ surface by Smith *et al.*[28] This is the first evidence of our films being N-face based on the polarity assignment by surface reconstructions.[29] Further confirmation is based on the molten KOH etching which makes the films quickly dissolve, agreeing well with the chemical property of the N face of GaN films.[2,3,29] In our previous study, a distinct series of surface reconstructions of 2×2, 4×4, 5×5, $\sqrt{7} \times \sqrt{7}$, $5\sqrt{3} \times 2\sqrt{13}$, and 10×10 were obtained on the Si-face SiC(0001) under similar preparation conditions,[14,30] where the epitaxial film is Ga-face. These results provides direct evidence of the polarity priority of wurtzite GaN grown on polar SiC substrates, which agrees well with Hellman *et al.*[2] This polarity priority can be attributed to the heavy ionicity of GaN and SiC.[16,18]

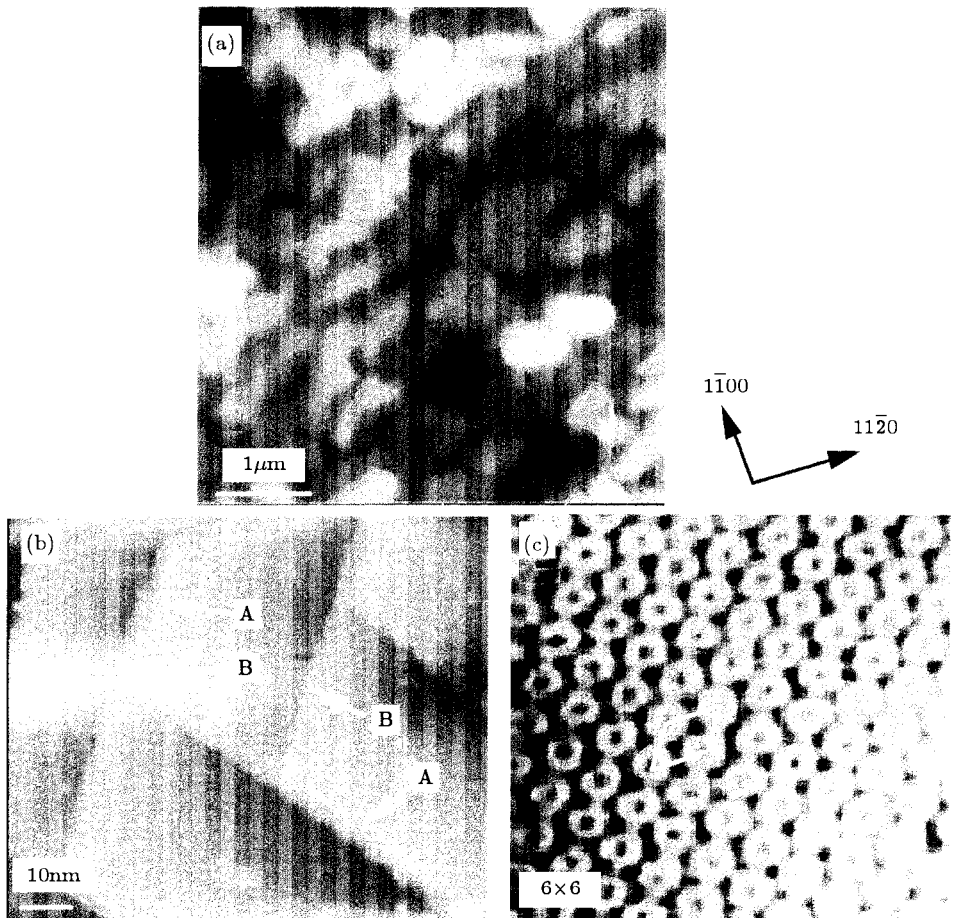


Fig.4. (a) 5μm×5μm AFM image of a 0.5μm thick GaN (000$\bar{1}$) film. The height difference between the bright and dark regions is around 115Å. (b) 1000Å×800Å STM image of the mesas surface shown in (a). The arrows indicate the 'A' and 'B' steps, implying anisotropic step flow growth. (c) 135Å×135Å filled-sates STM image of the GaN (000$\bar{1}$)-6×6 surface. V_s=–2.7V, I_t=0.1nA.

The crystalline quality of the GaN films is examined with XRD. The ω scan across the symmetric (0002) reflections exhibits a full width at half maximum (FWHM) of 500″. More detailed XRD and photoluminescence studies were reported elsewhere.[31] Note that the initial nucleation and the ratio of Ga/N could greatly influence the GaN epitaxial growth.[4–7] Further optimization of growth conditions can be expected to improve the film quality. In order to better understand the defects distribution and crystallinity of the GaN film, a corresponding cross-section transition electron microscopy study would be helpful.

IV. SUMMARY

To sum up, an atomically flat 6H-SiC (000$\bar{1}$) surface was prepared successfully by the UHV Si etching technique. Subsequent epitaxial growth of GaN films with AlN buffer layers essentially is two-dimensional. Observed reconstructions and chemical etching tests confirm that the present GaN film is N-face and provide the first direct evidence of the polarity assignment for the wurtzite GaN thin films on the polar hexagonal SiC substrate.

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