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Growth Process of GaN Layer on ZrB_2 Substrate by Gas Source Molecular Beam Epitaxy

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The surface structure of ZrB_2 substrate and direct growth processes of GaN on the ZrB_2 substrate with NH_3 gas source molecular beam epitaxy have been investigated by ***in-situ*** reflection high energy electron diffraction and atomic force microscopy. It is found that there is an effect of hydrogen gas irradiation onto the substrate on making clean and flat surface at a low temperature of 800℃. It has been observed that GaN layer is epitaxially grown on the ZrB_2 substrate. It is considered that ZrB_2 substrate has a high potentiality as an appropriate substrate for GaN growth.

Key words: GaN, NH_3, ZrB_2, MBE, RHEED

1. Introduction

The GaN and related compounds of AlGaN are promising materials for opto-electronic devices in the ultra violet-wavelength region [1-3]. Many GaN-based opto-electronic devices are demonstrated on sapphire and SiC substrate [4-6]. It is, however, difficult to obtain the high-quality GaN on a sapphire substrate with flat growing surface and low density of threading dislocation because of the large misfit of lattice constant and difference of the thermal coefficient [7-11]. Therefore, an appropriate substrate matching of the lattice constant and the thermal coefficient is required.

Zirconium diboride (ZrB_2) substrate has a hexagonal crystal structure with an C-plane lattice constant of 0.317 nm and a thermal coefficient of 5.9×10^{-6}[1/K] which are very close to those of GaN (0.319 nm and 5.6×10^{-6}[1/K])[12-14].

Recently, Otani *et. al.* have reported that single ZrB_2 bulk crystal was grown using a floating zone (FZ) method[13]. In this paper, we have investigated the initial growth process of GaN on $ZrB_2(0001)$ by NH_3 gas source molecular beam epitaxy (GS-MBE) with ***in-situ*** reflection high-energy electron diffraction (RHHED) system.

2. Experiment

A growth apparatus for GS-MBE equipment with a RHEED system was used for ***in-situ*** observation of the growth process of GaN epitaxy. Since details of apparatus equipment were reported previously [9], we describe only the outline. A growth chamber was evacuated by turbo molecular vacuum pumps, and the base pressure was of 1×10^{-10} Torr. ZrB_2 wafer was used as substrates after thermal annealing at a temperature of 800 ℃ with hydrogen irradiation onto the substrate. The substrate was set on sample holder and heated by directly passing a dc electric current through molybdenum electrodes.

The substrate temperature was measured by an optical pyrometer. NH_3 gas was introduced onto the substrate surface through a delivery stainless tube. The pressure of NH_3 gas during GaN growth was preciously controlled by a mass-flow controller in the range of 5×10^{-5} to 2×10^{-4} Torr. Growth rate of GaN epitaxy layer estimated from the growth condition is about 0.1 μm/h. The substrate surface and film growth processes in the initial stage were observed by ***in-situ*** the RHEED system operated at an acceleration voltage 10 kV and ex-situ atomic force microscopy (AFM). The diffraction patterns for GaN growth sequences were detected by digital still camera.

3. Results and Discussions

3.1 Clean surface of ZrB_2

We first investigated the surface morphology of the ZrB_2 substrate by the observation of AFM analysis. Figure 1 shows in-plane and cross sectional AFM images from (a) before and (b) after thermal annealing. It is found that there are micro scratches on the as-polished ZrB_2 substrate surface in Fig. 1 (a).

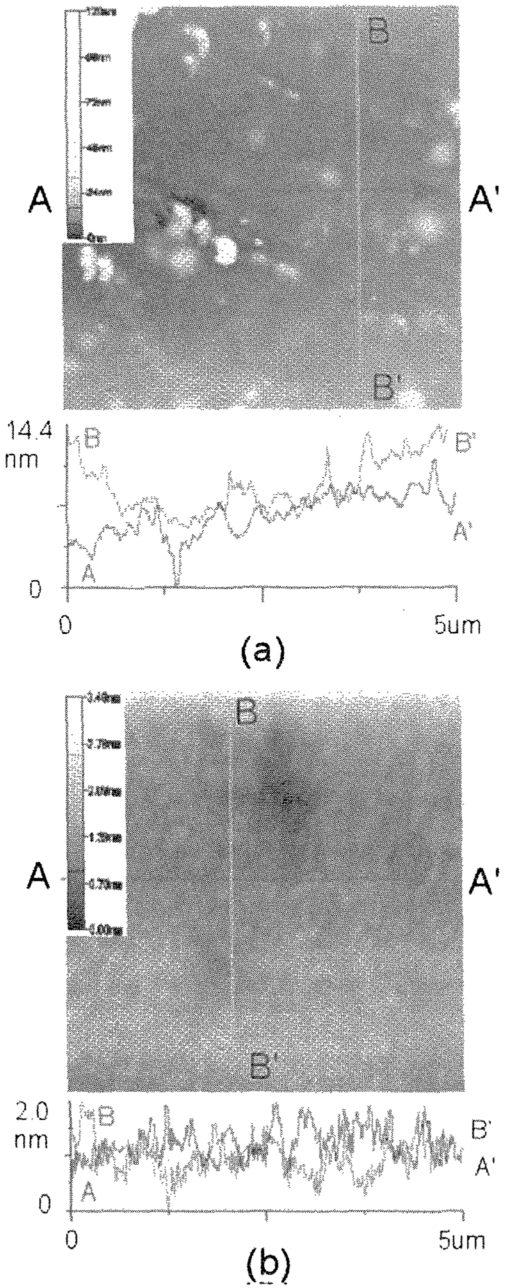

Fig. 1 In-plane AFM images taken from ZrB_2 substrate and the cross sectional images along the lines between A-A' and B-B' marked in the AFM images (a) before, and (b) after thermal annealing with hydrogen irradiation.

It is noticed that these scratches are clearly reduced by thermal annealing under hydrogen irradiation at a temperature of 800℃ for 60 min in the growth chamber as shown in Fig. 1(b). Furthermore, it is observed that the surface of the annealed substrate is covered with a scale-shaped structure. These results suggest that the scratches as the damage by polishing only remain in the surface adsorbed layer. Therefore, it is thought that there is no damage by polishing on the bare surface of the ZrB_2 substrate.

Figure 2 shows RHEED patterns taken from the ZrB_2 substrate (a) before and (b) after thermal annealing corresponding to Fig. 1 (a) and Fig. 1 (b), respectively. It is found that the RHEED pattern is changed from halo one to spot pattern meaning a formation of islands. It is considered that the adsorptive layer on the surface is effectively removed and the islanding structure is constructed by the thermal annealing at a temperature of 800℃ with hydrogen irradiation. These results are consistent with that of AFM observations.

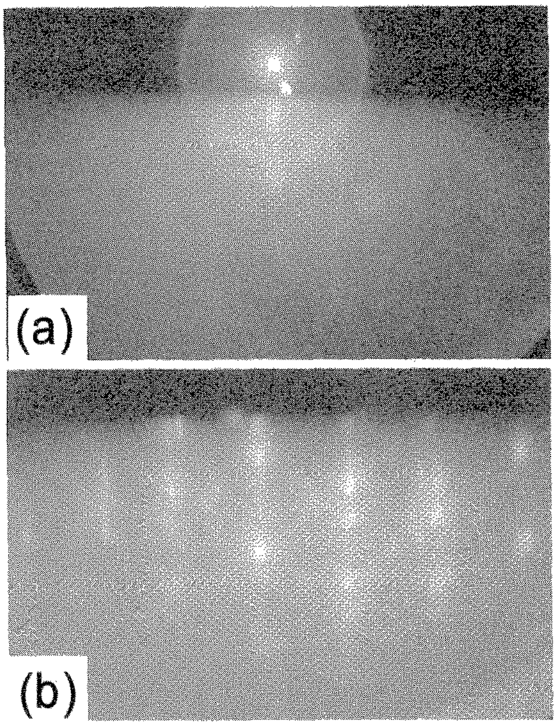

Fig. 2 ***In-situ*** RHEED patterns taken from ZrB_2 substrate (a)before and (b)after thermal annealing with hydrogen irradiation for 60 min.

3.2 GaN growth on ZrB_2 substrate

Figure 3 shows ***in-situ*** RHEED patterns from GaN films grown on ZrB_2 substrate at 800℃ for the initial stage. Growth times are (a) 10, (b) 20, (c) 40 and (d) 60 min. After thermal annealing with hydrogen irradiation, Ga molecular beam and NH_3 gas source is supplied onto ZrB_2 substrate at the same time following stopping of the hydrogen gas source. The diffraction pattern corresponding ZrB_2 changes to streaky one as starting GaN growth in Fig. 3 (a). As the proceeding the GaN growth, weak and broad diffraction intensities indicated by allows in Fig. 3 (b) are appeared at the growth time of 20min. This intensity becomes gradually strong as GaN growth shown in Fig. 3 (c) and 3 (d). On the other hand, the diffraction intensity from ZrB_2 becomes weak by degrees. Therefore, it is considered that the weak and broad streaks indicated by arrows are corresponding to growth of GaN layer.

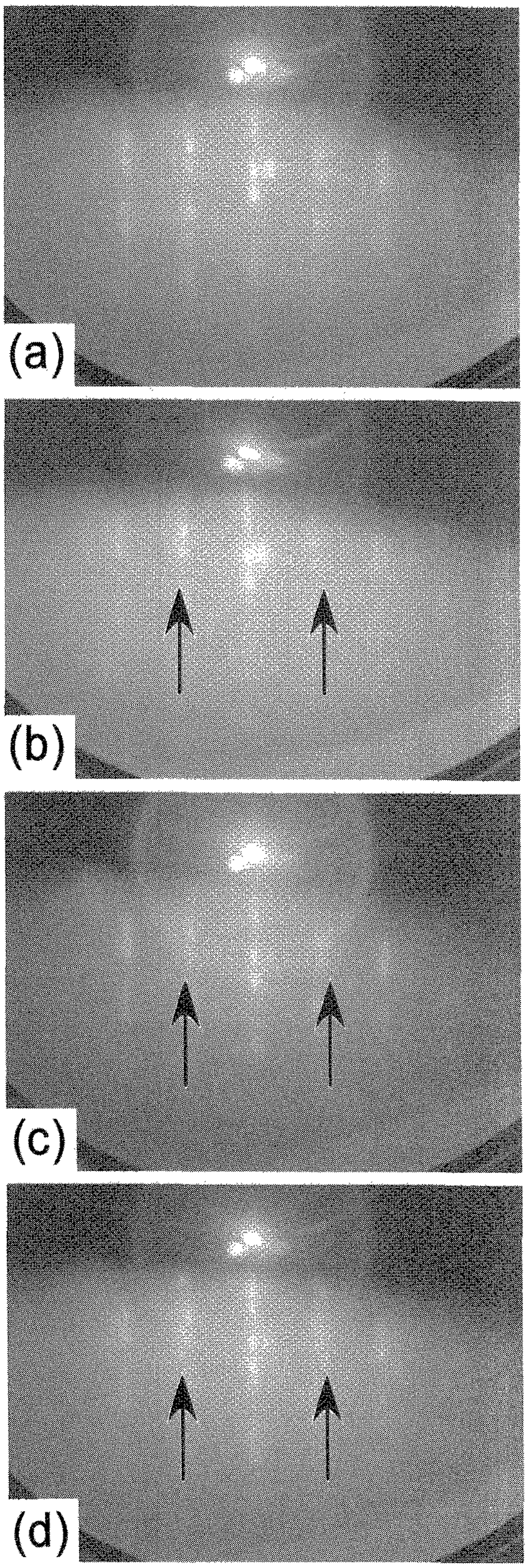

Fig. 3 ***In-situ*** RHEED patterns taken from GaN film grown on ZrB_2 substrate at 800 ℃ for the initial stage. Growth times are (a) 10, (b) 20, (c) 40 and (d) 60 min.

Figure 4 shows AFM and cross sectional image of GaN epilayer on the ZrB_2 substrate for 60 min. It is found that the scale-shaped structure is disappeared and many small GaN islands are formed on relatively flat and continuous growing base structure. In the case of GaN growth in sapphire substrate at 800℃ [9], continuous epilayer is not formed in the initial growth stage such as Fig. 4. This result suggests that ZrB_2 has closer affinity for GaN.

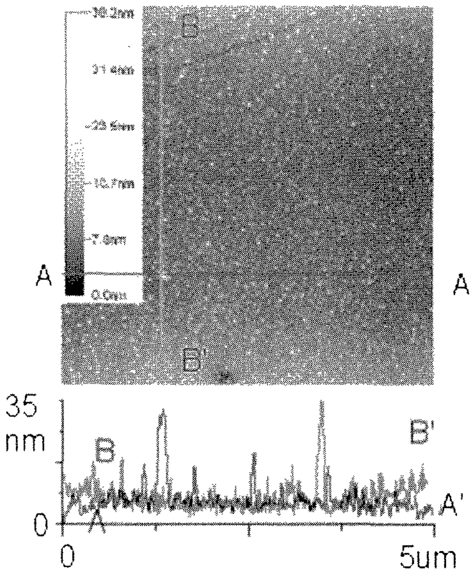

Fig. 4 In-plane and cross sectional AFM image of GaN epilayer on ZrB_2 for 60 min growth time.

Figure 5 shows change of the lattice spacing normalized by the initial one at 15 min growth time and the standard deviation for lattice constant measurement. The error bar corresponds to the standard deviations. The lattice constant is estimated from the distance between the GaN diffraction streaks indicated by arrows in Fig. 4. There are no measurements for 15 min initial stage of GaN growth because the intensity of the diffraction streaks form GaN is too weak to measure the spacing.

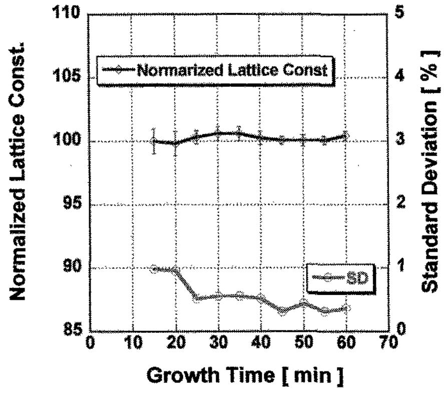

Fig. 5 Lattice spacing normalized by the initial one at 15 min growth time and the standard deviation for lattice constant measurement.

It is expected that the GaN diffraction intensity would be observed just inside of the diffraction form substrate because lattice constant of GaN is slightly smaller than that of the ZrB_2 substrate. It is, however, found that the diffraction intensity form GaN is appeared at the outside of the fundamental diffraction streaks of the substrate. It is thought that the ZrB_2 surface is still covered the thin oxide layer. So that, the normalized lattice spacing is estimated instead of real lattice constant. It is found that the lattice spacing of GaN epilayer is kept at relatively same value during the growth. From these results, it is considered that GaN epitaxial layer is grown on the ZrB_2 substrate directly without some buffer layer. It is concluded that ZrB_2 substrate has a high potentiality as an appropriate substrate for GaN growth.

4. Conclusions

The surface structure of ZrB_2 substrate and direct growth processes of GaN on the ZrB_2 substrate with NH_3 gas source molecular beam epitaxy have been investigated by ***in-situ*** reflection high energy electron diffraction and atomic force microscopy. It is found that the surface of the ZrB_2 substrate is effectively cleaned by thermal annealing at a low temperature of 800℃ with hydrogen gas irradiation onto the substrate. It has been observed that GaN layer is epitaxially grown on the ZrB_2 substrate and ZrB_2 substrate has closer affinity for GaN epitaxial layer. It is considered that ZrB_2 substrate has a high potentiality as an appropriate substrate for GaN growth.

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