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Radio-frequency MBE growth of cubic GaN on BP(001)/Si(001) hetero-structure

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Zincblende gallium nitride (c-GaN) was grown on zincblende boron monophosphide (BP)/silicon (001) using radio-frequency plasma-assisted molecular-beam epitaxy (RF-MBE). In spite of near perfect lattice-match coordination between c-GaN and BP, the initial nucleation of c-GaN was 3D island formation due to imperfect wetting. Using cross-sectional electron backscatter diffraction pattern (x-EBSD), it was found that dislocations were eliminated with an increase of epilayer thickness of c-GaN, and finally 99.4% c-GaN (001) was achieved. The (2x2) and (4x1) reconstructions of the surface of almost pure c-GaN (001) were confirmed by reflection high-energy electron diffraction (RHEED) under arsenic-contamination-free conditions.

1 Introduction

Cubic (zincblende) group III-nitrides (c-AlN, c-GaN, and c-InN) and related alloys have drawn lots of attention because they are more environmentally friendly, have higher electron mobilities, smoother cleavage surfaces, and greater ease of p-type doping than hexagonal (wurtzite) III-nitrides. This is due to the cubic phase having a higher crystal symmetry than the hexagonal phase. Cubic GaN has been grown on various substrates such as zincblende silicon carbide (3C-SiC) [1–6], gallium arsenide [7–9], Si [10, 11] and magnesium oxide [12] using epitaxy techniques. Boron monophosphide (BP) has wide indirect band-to-band gap (4.25 eV) [11], a zincblende structure with a lattice constant of 4.538 Å (300 K), and nearly the same thermal expansion coefficient as c-GaN (5 - 6.2 x 10^{-6} K^{-1} (800 K) [12–15]. Therefore BP is a near-perfect lattice-matched material to c-GaN (mismatch of 0.3 % at 300 K). The heterostructure between GaN and BP was first studied by Izumiya et al. [16]. They demonstrated an h-GaN/BP structure using organo-metalic chemical vapour deposition (MOCVD) on Si (001) [16]. The first c-GaN/BP on Si (001) using MOCVD was reported from Nishimura et al. [17]. However, except for the coordination of plane is GaN (001) || BP(001) from XRD (X-ray diffraction) measurement, little is known about c-GaN/BP/Si(001). To grow meta-stable c-GaN, molecular beam epitaxy (MBE) method is a suitable epitaxial technique because MBE allows deposition at low substrate temperature and has precise control of both the interface smoothness and the composition of alloy crystals. Moreover, the use of source materials is more economical with MBE compared to MOCVD. In this paper, we will present the successful growth of high-quality c-GaN growth on BP/Si (001) using radio frequency plasma assisted MBE (RF-MBE). Despite the arsenic-free condition that we used to grow our c-GaN on BP/Si (001), the reconstruction of c-GaN showed (2x2) and (4x1) patterns.

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2 Experimental

All c-GaN growth were performed using a V.G. 80H MBE system equipped with an RF source (Arios IRFS) [4, 18]. A 2-inch BP/Si (001) substrate was prepared by Showa Denko K.K. [19]. Prior to loading into MBE system, BP/Si (001) was treatment as follows: 1) a 10-min ultrasonic clearing with acetone; 2) a 5-min rinse in deionized (DI) water; 3) a 1-min dip into a 0.5 % HF aqueous solution; 4) a 5-min rinse in DI water. To investigate the thermal stability of BP under ultrahigh vacuum, BP/Si(001) was heated to 760 ^{o}C and held for 30 min. The surface temperatures were measured by a thermocaouple calibrated by Al/Si eutectic phase transition (577 ^{o}C) [20]. A built-in quadrupole mass spectrometer was employed for the analysis of residual presence of boron (B) and phosphorus (P) caused by thermal decompositon of BP. After thermal cleaning, a low temperature (LT) buffer layer was deposited 10 ML at 350–500 ^{o}C using LT-MEE (migration enhance epitaxy). Then the substrate temperature was increased to 600 ^{o}C. Finally, the bulk growth of c-GaN was performed. The growth time and thickness of c-GaN films were 3–7 hours, 1.3–2.5 μm, respectively. The Ga source (99.99999 %) was loaded in a conventional K-cell. The Ga flux was maintained at 1.01–1.03 x 10^{-4} Pa (BEP). The flow rate of nitrogen gas (99.9999 %) was kept at 2.0 sccm. The process pressure of the growth chamber was 6.8 x 10^{-3} Pa during c-GaN growth. In situ RHEED was employed to examined the surface structure of c-GaN epilayer. Heterostructure of c-GaN epilayer on BP/Si (001) was observed using high-resolution cross-sectional transmission electron microscope (x-TEM). XRD analysis was used to estimate the purity of c-GaN. The microscopic analysis of crystallographic orientation distribution inside c-GaN epilayer was performed using cross-section electron backscatter diffraction (x-EBSD).

3 Results and discussion

3.1 Reconstruction and thermal stability of BP under UHV

Figure 1 shows a RHEED pattern of a BP epilayer on Si (001) at 760 ^{o}C after the test of thermal stability had been performed at 760 ^{o}C. This (2x2) reconstruction could be seen at ~500 ^{o}C. However, taking account into the nature of heteroepitaxy on Si, the formation of anti-phase-domain (APD) can not be negligible. Thus, this (2x2) reconstruction might be caused by (1x2) and (2x1) double domain. The presence of residual Both B and P was not detected using Q-Mass analysis.

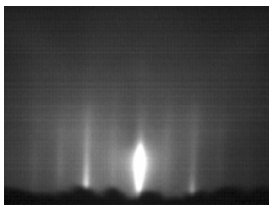

Fig. 1 RHEED reconstruction of BP/Si (001).

3.2 c-GaN growth on BP/Si (001)

Figure 2 shows RHEED pattern just after 10 ML c-GaN deposition. The x-TEM image also indicated that high density of stacking fault (SF) was inserted during LT-MEE (Fig. 3) despite the near-perfect coordination between c-GaN and BP. Ito et al. predicted that 65 nm pure c-GaN (001), where pure c-GaN (001) means c-GaN (001) without any SFs and h-GaN inclusion via SF, would be grown on BP (001) from energetic stability calculation [21]. However, we could not obtain 2D c-GaN on BP (001) at the early stage. One possibility of this disagreement is due to the surface roughness of BP epilayer. The effect from a cavity of BP epilayer was found in Fig. 3. However, SFs could be confirmed at the very smooth region of a BP surface. According to Phillips, the ionicity of BP and GaN are only f_i = 0.006 and f_i =0.500, respectively [22]. BP is a very covalent material whereas c-GaN is a semi-ionic material. Hence, this large mismatch of ionicity between c-GaN and BP is the origin of initial 3D growth.

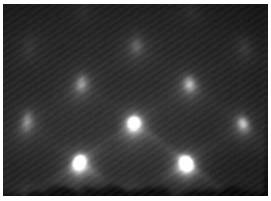

Fig. 2 RHEED pattern of 10 ML c-GaN using LT-MEE. The azimuth of electron beam was [1-10].

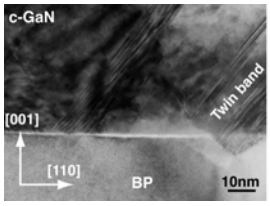

Fig. 3 HRTEM image of c-GaN. High density of SF and twin feature can be confirmed.

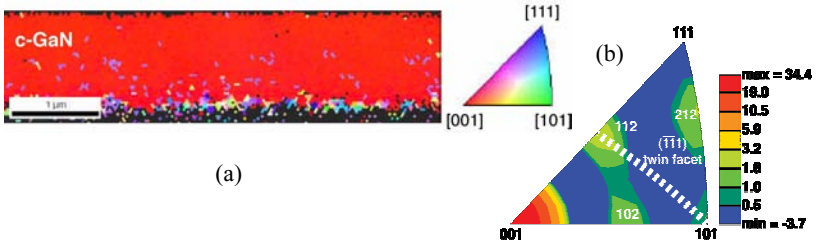

Fig. 4 Cross-sectional EBSD analysis for 1.3 μm c-GaN epilayer on BP/Si (001). (a) Left: Crystal direction mapping. The orientation distribution is corresponding to color distribution. (b)Right: IPFW of (a).

Figure 4a shows the purity analysis results of cross-sectional 1.3 μm thick c-GaN epilayer using x-EBSD method. From the analysis of crystal direction mapping, only 75.6 % of c-GaN was epitaxialy grown at the early stage of c-GaN growth including the nucleation layer grown by LT-MEE (0–300 nm). As growth proceeded, the purity of the c-GaN epilayer increased (e.g., the region from 500 to 800 nm thick: 96.7 %, the region from 1000 to 1300 nm thick: 99.4 %). Figure 4b shows an inverse pole figure mapping (IPFM) result of the same c-GaN. Surely not only {111} and {-1-11} twin feature were confirmed, but {212} high-index orientation feature was also confirmed. These irregularities against (001) orientation were mainly confirmed at the early stage of c-GaN growth by LT-MEE. Hence, the purity of c-GaN (001) epilayer on BP (001) improved according to the increase of the thickness of c-GaN epilayer, and 1.0 μm thickness of c-GaN epilayer was required to obtain pure c-GaN (001) surface. Figure 5a shows the (2x2) reconstruction obtained from 1.3 μm of c-GaN epilayer grown under slightly Ga excess condition. In the similar way, (2x2) RHEED reconstruction was obtained from 2.5 μm of c-GaN epilayer grown under slightly Ga excess condition (Fig. 5b). The (4x1) RHEED reconstruction was ascertained from 2.5 μm of c-GaN epilayer grown under unity III/V ratio (Fig. 5c). The (2x2) structure of c-GaN is thought to be due to arsenic (As) dimers derived from the presence of As from the background [23, 24]. However, we have never used As and never loaded any GaAs after overhaul and cleaning of our MBE machine. Needless to say, we replaced all As-contaminated components. Hence our (2x2) structure is not clearly due to As. The same group III material P had a possibility to work the same effect of As. As described above, the presence of residual P, caused by thermal decomposition of BP layer, was not confirmed (see Section 3.1). From x-EBSD analysis, the surface of c-GaN/BP (001) was confirmed as an almost pure c-GaN surface. Thus, (2x2) structure of pure c-GaN(001) surface exists. However, the possibility that this (2x2) reconstruction was caused from a (1x2)+(2x1) double domain as mentioned in 3.1 cannot be negligible. In our experiments, a unity condition led to a (4x1) structure whereas a slightly Ga excess condition led to (2x2) reconstruction. Thus, III/V ratio plays crucial role to define the surface reconstruction of pure c-GaN. Figures 6a and 6b show the comparison of θ–2θ and ω locking curve profiles between BP and 1.3 μm c-GaN. The FWHM values of ω locking curve were 30.34 arcmin for c-GaN epilayer and 28.52 arcmin for BP. 1.3 μm c-GaN was slightly inferior to BP in terms of mosaicity. This is partially due to the lower substrate temperature growth for c-GaN. Purity analysis for c-GaN epilayer based on XRD was performed [25]. 1.3 μm c-GaN was estimated 98.23 %, and this value agreed with x-EBSD analysis.

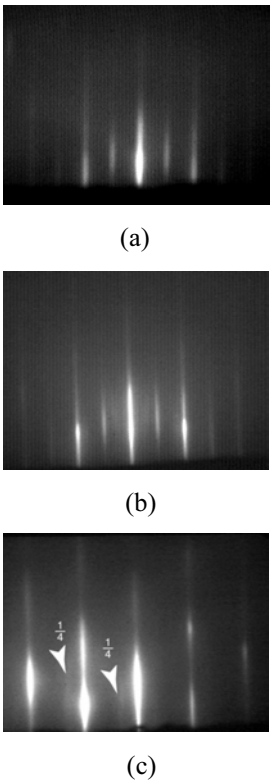

Fig. 5 RHEED images of c-GaN epilayers. (a) 1.3-μm-thick layer, (b) 2.5-μm-thick layer, (c) 2.5-μm-thick. (a) and (b) were grown under Ga BEP was kept at 1.03x 10^{-4} Pa, (c) was grown under 1.01x10^{-4} Pa corresponding to stoichiometric condition.

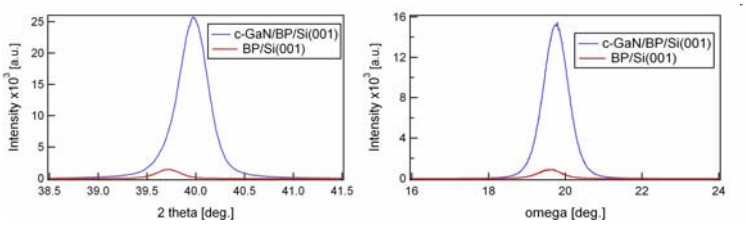

Fig. 6 θ–2θ (a) and ω (b) XRD profiles of c-GaN/BP/Si (001) and BP/Si (001), respectively. ω FWHM values: 30.34 arcmin for c-GaN and 28.52 arcmin for BP, 2θ FWHM values: 14.12 arcmin for c-GaN, and 11.45 arcmin for BP.

4 Conclusions

We demonstrated c-GaN epitaxy on BP/Si (001) substrate by RF-MBE. Despite the near perfect lattice-match condition between c-GaN and BP, 3D island growth was dominant at the early stage of c-GaN using LT-MEE.This is due to imperfect wetting between c-GaN and BP. According to the x-EBSD analysis, we grew a 99.4 % c-GaN (001) surface and the disorientation of c-GaN (001) was improved according to the increase of the thickness of c-GaN epilayer. We demonstrated the (2x2) RHEED reconstruction of c-GaN (001) grown under a slightly Ga-excess condition without As contamination. In contrast, a (4x1) reconstruction was observed from c-GaN (001) grown under stoichiometric condition.

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