

Single-phase hexagonal GaN grown on AlAs/GaAs(001)

Mitsuru Funato,^{a)} Teruki Ishido, Atsushi Hamaguchi, Shizuo Fujita, and Shigeo Fujita
 Department of Electronic Science and Engineering, Kyoto University, Kyoto 606-8501, Japan

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This letter describes successful growth of single-phase *hexagonal* GaN (*h*-GaN) layers on *cubic* GaAs(001) nominally singular substrates with the assistance of thin AlAs intermediate layers. The crystallographic relationship between *h*-GaN and GaAs is extracted from a pole figure to be *h*-GaN[0001]||GaAs[001] in the growth direction and *h*-GaN[1010]||GaAs[110] in the in-plane direction. In a photoluminescence spectrum measured at 20 K, excitonic emission from the *h*-GaN layer is detected at 3.47 eV. © 2000 American Institute of Physics. [S0003-6951(00)05328-6]

GaN, which is now in practical applications in the field of optoelectronics, has mostly been grown on sapphire(0001) substrates.¹ On the other hand, there is an increasing interest in other substrates such as Si and GaAs because of the larger wafer size, higher conductivity, and advanced technology of these substrates.^{2–8} Among a number of candidate substrates, GaAs possesses an advantage from the viewpoint of the thermal expansion coefficients; the thermal expansion coefficients of GaAs and GaN are 5.7×10^{-6} (Ref. 9) and $5.59 \times 10^{-6} \text{ K}^{-1}$,¹⁰ respectively. The difference between them is much smaller than those with other substrates such as Si, 3C-SiC, and sapphire, which may prevent the generation of cracks. This encourages us to use GaAs as a substrate for the GaN growth. There have already been many reports on the growth of hexagonal GaN (*h*-GaN) and cubic GaN (*c*-GaN) on the GaAs substrates.^{4–8} Basically, *h*-GaN is grown on GaAs(111) and *c*-GaN is grown on GaAs(001) as is deduced from the crystallographic relationship. In contrast, this letter demonstrates that *c*-oriented *h*-GaN is grown on GaAs(001) if an AlAs thin layer is inserted between GaN and GaAs(001). Since the lattice parameters of GaAs and AlAs are almost the same, and since no remarkable difference in their surface structures has been seen, the observed result is interpreted by the difference of the surface chemistry of GaAs and AlAs.

The samples were grown by atmospheric-pressure metalorganic vapor phase epitaxy. On the GaAs(001) substrate, a 20-nm-thick AlAs layer was grown at 700 °C using trimethylaluminum (TMAI) and tertiarybutylarsine (TBAs) as source precursors. The molar flow ratio of TBAs/TMAI was 10 and the growth rate was 900 nm/h. Atomic force microscopy (AFM) observation proved that the surface structure of AlAs thus obtained was quite similar to that of GaAs and consisted of monolayer steps ($\sim 0.3 \text{ nm}$) and atomically flat terraces. Therefore, the influences of the surface structures on the crystalline structures of GaN can be neglected in this study. Then, 0.3- μm -thick GaN was successively grown using triethylgallium (TEGa) and dimethylhydrazine (DMHy). The growth was initiated by simultaneously supplying those precursors to avoid nitridation, which may affect surface structures and influence the crystalline structure.⁶ The growth temperature was ranged from 500 to 700 °C, at which deg-

radation of the AlAs surfaces does not occur. The typical molar flow ratio of DMHy/TEGa was 100 and the growth rate was 280 nm/h.

First of all, GaN was grown directly on the GaAs(001) substrate. It was confirmed by x-ray diffraction measurements using Cu $K\alpha_1$ radiation as an x-ray source that the GaN layers were in the cubic phase with *c*-GaN[001]||GaAs[001], though the inclusion of the hexagonal phase could not completely be eliminated. This is similar to many past reports.^{6–8} On the other hand, when an AlAs thin layer (20 nm) was inserted between the GaAs substrate and GaN, GaN was no longer in the cubic phase but in the hexagonal phase with the orientation relation of *h*-GaN[0001]||GaAs[001], which was assessed by the following manner. Figure 1 shows an x-ray diffraction pole figure of GaN grown on AlAs/GaAs(001) at 600 °C. In the figure, χ refers to the angle between the GaAs surface [(001) plane] and the plane under measurement. The diffractions from *h*-GaN{1011}, *c*-GaN{002}, and GaAs{115} planes were measured successively without changing the experimental configurations. As a result, the six-fold *h*-GaN 1011 diffractions were detected at $\chi = 62^\circ$, but no *c*-GaN 002 dif-

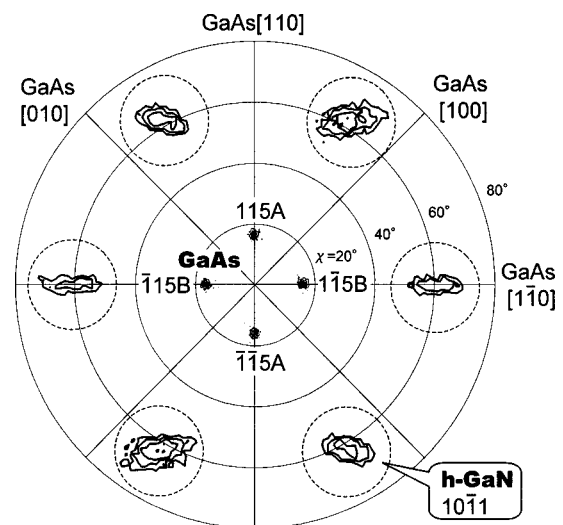


FIG. 1. Pole figure of GaN grown on AlAs/GaAs(001) at 600 °C. The diffractions from *h*-GaN{1011}, *c*-GaN{002}, and GaAs{115} planes were measured successively without changing the experimental configurations and all results are shown together. Isointensity contour levels at 2^n ($n = 0, 1, 2, 3, \dots$) cps.

^{a)}Electronic mail: funato@kuee.kyoto-u.ac.jp

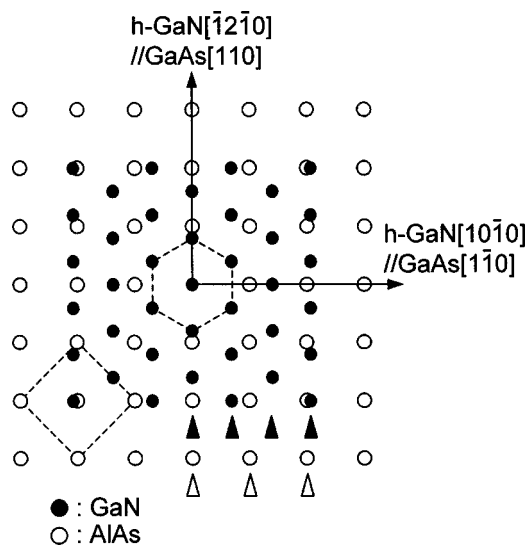


FIG. 2. Schematic view of the in-plane crystallographic relationship in GaN/AlAs/GaAs(001). Hexagon and square indicated by the dotted lines represent *h*-GaN and cubic GaAs lattices, respectively. Closed arrowheads designate the *h*-GaN{1010} planes, while open arrowheads the GaAs{110} planes.

fractions. Two important conclusions can be extracted from these results: (1) the grown film is single-phase *h*-GaN and (2) its *c* axis is parallel to the GaAs[001] direction (i.e., growth direction). The latter was extracted in the following way. The observed value of χ indicates that the angle between the *h*-GaN{1011} planes and the GaAs(001) plane is 62° . On the other hand, a plane in *h*-GaN forming an angle of 62° to {1011} is (0001). Therefore, *h*-GaN(0001) is parallel to GaAs(001), that is, *h*-GaN[0001]||GaAs[001]. Further information obtained from the pole figure is that the GaAs 115B and 115B diffractions and two GaN 1011 diffractions are on a straight line. This provides the additional conclusion that a pair of parallel *h*-GaN{1010} planes [(1010) and ($\bar{1}0\bar{1}0$), for example] are parallel to the GaAs(110) and ($\bar{1}10$) planes.

By summarizing the results of the pole figure measurement, the in-plane crystallographic relationship involved in GaN/AlAs/GaAs(001) can schematically be drawn as Fig. 2. Since the AlAs layer is sufficiently thin to grow coherently, lattice points are exactly the same as those in GaAs. As seen, *h*-GaN[$\bar{1}2\bar{1}0$]||GaAs[110] as well as *h*-GaN[1010]||GaAs[110] is satisfied, which is a desirable configuration because those four planes can be cleaved. Now, a question arises what causes such a crystallographic relationship. We consider that a reason is strain. Twice the GaAs{110} spacing [=7.9950 Å at room temperature (RT)] is well commensurate with three times the *h*-GaN{1010} spacing (=8.2853 Å at RT), which is indicated by arrowheads in Fig. 2. Therefore, the epitaxial relationship takes place so as to make those planes parallel, while minimizing the strain.¹¹ Geometrically, *h*-GaN[1010]||GaAs[110] is equivalent to *h*-GaN[1010]||GaAs[110], but the former did not occur. This is probably due to the anisotropic bond configuration of AlAs; for the (001) surface of AlAs, the orientation of the Al dangling bonds has projection along [110], while that of the As dangling bonds has projection along [110], which suggests that the bonds between Al and N

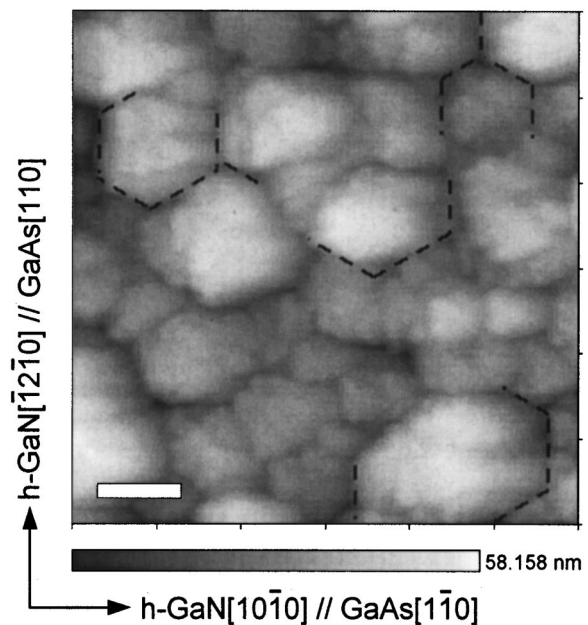


FIG. 3. Surface AFM image of *h*-GaN grown on AlAs/GaAs(001). The dotted lines were drawn so as to be parallel to the sides of the hexagon in Fig. 2. Marker represents 100 nm.

align nitrogen atoms along AlAs[110] and lead to *h*-GaN[1010]||GaAs[110].

This crystallographic relationship is reflected on the surface. Figure 3 shows an AFM image of *h*-GaN grown on AlAs/GaAs. Many hillocks are observable. The dotted lines in the figure were drawn so as to be parallel to the sides of the hexagon in Fig. 2. Relatively good agreement between the dotted lines and the sides of the hillocks suggests that those consist of *h*-GaN{1010} planes. Since {1010} is a singular plane of hexagonal crystals, that may appear at the growth front and, consequently, the sides of the hillocks became parallel to {1010}.

The experimental finding that the crystalline structures of GaN varied depending on the underlying layers is analogous to Cd(Mn)Te on GaAs.^{12–14} On a clean GaAs(001) substrate, [111]-oriented CdTe is grown with the crystallographic relationship of CdTe[211]||GaAs[110].¹³ Since cubic {111} planes are equivalent to hexagonal {0002} planes, the crystallographic relationship in CdTe/GaAs(001) is the same as that in *h*-GaN/AlAs/GaAs(001) revealed here. In contrast, on a GaAs(001) substrate whose surface is perturbed in some way, [001]-oriented CdTe is grown. This perturbation could be the result of a very thin layer of residual oxide¹³ for example, or the presence of a monolayer of adsorbed Te.¹⁴ What the examples of Cd(Mn)Te/GaAs(001) tell us is that the surface electronic states of an underlying layer play a crucial role in determining the crystalline orientation of the “epitaxial” layer. Actually, in this study, both the AlAs and GaAs surfaces were atomically flat, and furthermore, nitridation which can modify the surface structures was not conducted, as mentioned previously. Therefore, the present result that *c*-GaN is grown on GaAs(001), while *h*-GaN on AlAs/GaAs(001) must be interpreted in terms of the difference in chemistry of the GaAs and AlAs surfaces. Another interesting experimental result we found is that *h*-GaN can be grown even on AlAs covered with thin (<5 nm) GaAs

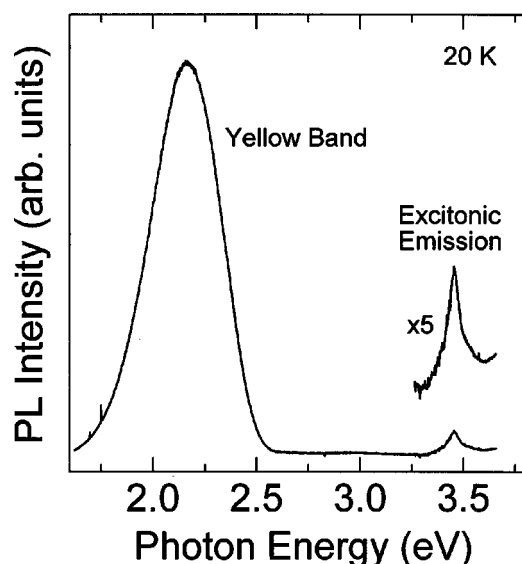


FIG. 4. PL spectrum of *h*-GaN grown on AlAs/GaAs(001) at 900 °C. The measurement was carried out at 20 K under the excitation by a He–Cd laser.

(the details will be given elsewhere).¹⁵ On the basis of those results, we consider that the surface electronic structure determines the crystalline phase and orientation of GaN and that the interface atom itself is not essential.

Finally, the photoluminescence (PL) properties of *h*-GaN on AlAs/GaAs(001) are shown. The measurements were conducted at 20 K with a He–Cd laser (325 nm) as an excitation source. PL was detected using a cooled charge coupled device in conjunction with a 50 cm monochromator. In the earlier discussions, GaN has been grown at relatively low temperatures (500–700 °C) in order to avoid degradation of the AlAs surface. However, those layers did not exhibit PL. Therefore, on such GaN, whose thickness was reduced to 20 nm, 1.1- μ m-thick GaN was grown at a higher temperature.¹⁶ Tentative (not optimized) growth conditions were a growth temperature of 900 °C, a V/III ratio of 25, and a growth rate of 1.1 μ m/h. Figure 4 shows a PL spectrum of GaN grown under those conditions. Although the spectrum is dominated by the yellow band emission peaking at 2.15 eV, the emission is also detected at 3.47 eV. In bulk *h*-GaN, donor bound excitons emit at 3.4709 eV,¹⁷ and therefore, the emission observed in this study will be related to excitons. Further improvement of the PL properties is expected by optimizing the growth conditions.

In summary, *c*-oriented *h*-GaN was successfully grown on the GaAs(001) substrate with the assistance of the AlAs thin layer. The crystallographic relationship between *h*-GaN and GaAs was clarified from the pole figure measured by x-ray diffraction. PL was observed at 3.47 eV and was attributed to excitonic emission.

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¹¹A preliminary calculation showed that the observed crystallographic relationship (*h*-GaN[1010]||GaAs[110]) minimized the mean distance between GaN and AlAs lattice points at early stages of the growth. This suggests that strain as well is minimized by *h*-GaN[1010]||GaAs[110].

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