Six-bilayer periodic structures in GaN grown on GaAs(001)

Mitsuru Funato, Teruki Ishido, Shizuo Fujita, and Shigeo Fujita
Department of Electronic Science and Engineering, Kyoto University, Kyoto 606-8501, Japan

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We have observed six-bilayer periodic structures in GaN grown on GaAs(001). The periodicity occurs along the zinc-blende(ZB)-[111]A direction, suggesting that it originates from stacking faults on close-packed planes. GaN grown on GaAs includes both ZB and wurtzite phases as a result of formation of stacking faults and the periodic structures are mostly located between these two crystalline phases. Based on this observation, possible layer stacking sequences are proposed, which are classified as 6H polytypes. © *2000 American Institute of Physics.* [S0003-6951(00)00303-X]

Zinc-blende (ZB) and wurtzite (W) are the most common polytypes of binary octet semiconductors.[1–3] The stable structure of GaN is wurtzite and devices including the light emitting diodes now available commercially have been fabricated with W–GaN.[4,5] On the other hand, by selecting proper substrates and growth conditions, the metastable ZB structure can also be grown epitaxially.[6–11] For example, there are many reports on the successful growth of ZB–GaN on cubic (001) substrates such as GaAs,[6–8] Si,[9] and 3C–SiC,[10,11] although inclusion of the W phase has not been completely eliminated. The polytypes so far found in GaN are W and ZB, and other structures such as 4H and 6H have not yet been observed. As is well known, however, some semiconductors such as ZnS and SiC exhibit surprisingly many (more than 200) polytypes,[12,13] depending on the growth parameters. This motivates us to investigate GaN in terms of polytypism. For this purpose, a theoretical study by Wright[14] provides an interesting clue; W is the most stable structure in the case of GaN, and this makes it energetically favorable to introduce stacking faults in ZB films because ZB faults on close-packed planes inevitably contain the lower-energy W stacking. Indeed, as long as we observed by transmission electron microscopy (TEM), ZB–GaN grown on GaAs(001) included a much greater number of stacking faults than W–GaN grown on $Al_2O_3(0001)$ did. It must be noted, here, that hexagonal polytypes consist of the mixture of the ZB and W stacking and, consequently, are more stable than the pure ZB structure. Therefore, it is reasonably assumed that various polytypes are formed in GaN layers grown on cubic substrates as a result of generation of stacking faults. In this study, we investigate GaN grown on GaAs(001) structurally and demonstrate the presence of polytypes other than ZB and W.

A GaN thin film was grown on a GaAs(001) substrate by atmospheric-pressure metalorganic vapor phase epitaxy (MOVPE). The gallium and the nitrogen source precursors were triethylgallium (TEGa) and dimethylhydrazine (DMHy), respectively. The GaAs substrate was etched in a solution of $H_2SO_4:H_2O_2:H_2O=5:1:1$ at 40 °C for 1 min. In order to remove the surface oxide, the GaAs substrate was thermally annealed at 600 °C for 10 min in a hydrogen ambient. Nitridation of the GaAs surface was not conducted. A GaN buffer layer about 20 nm thick was grown on GaAs at 600 °C under a V/III ratio of 100. Then a GaN layer was grown at a higher temperature of 795 °C with a V/III ratio of 50. Under those conditions, the growth rate was about 0.35 μm/h for both the low and high temperature grown layers.

From a crystallographic point of view, polytypism is a phenomenon whereby a compound exhibits a variety of periodic layered structures along the ZB-⟨111⟩ direction, which is equivalent to the hexagonal ⟨0002⟩ direction (*c* axis). For example, ZB (3C) is characterized by an $ABCABC\cdots$ sequence, whereas W (2H) by an $ABABAB\cdots$ sequence. In those notations, each letter stands for an ordered pair of cation and anion layers. Thus, in order to investigate polytypes in GaN on GaAs(001), (110) and $(1\bar{1}0)$ cross sections were observed by TEM operated at 200 kV. The indices of the cross sections were identified by carefully preparing the specimens so as not to lose the already-known crystalline orientation of the substrates. The electron diffraction (ED) pattern obtained from the (110) cross section, which includes information on stacking features of (111)B planes, shows only the fundamental diffraction spots of the ZB phase. On the other hand, in the ED pattern from the $(1\bar{1}0)$ cross section, many additional spots were observed. Therefore, discussion hereafter will be concentrated on the $(1\bar{1}0)$ cross section, that is, on the (111)A layer stacking.

In the bright field image shown in Fig. 1(a), stacking faults inclined in the (111)A planes can be seen. The microbeam ED patterns were observed at several regions labeled (1)–(3) in the schematic view [Fig. 1(b)] and are compared

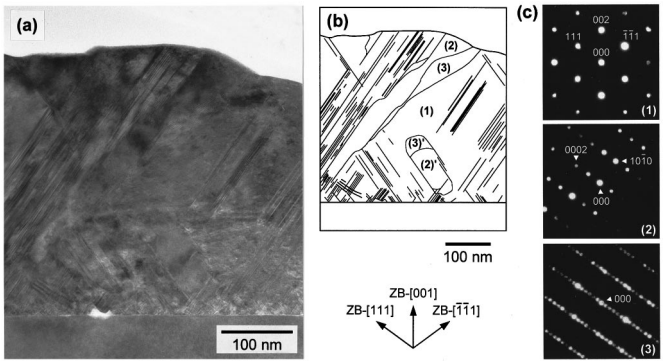

FIG. 1. (a) TEM bright field image of the $(1\bar{1}0)$ cross section of GaN grown on GaAs(001) and (b) its schematic view. The ED patterns shown in (c) were measured at the regions (1)–(3) in the schematic view, which indicate the presence of pure ZB, pure W, and a six-bilayer periodic structure, respectively.

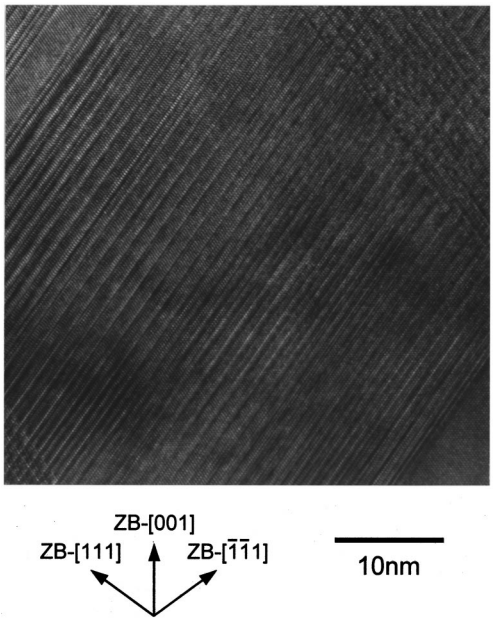

FIG. 2. High-resolution image of the region including the six-bilayer periodicity.

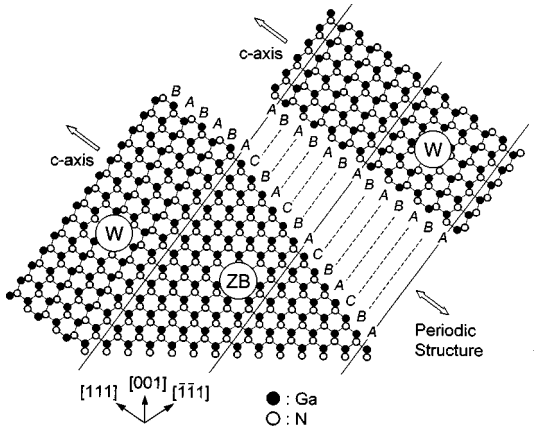

FIG. 3. Structural model for the formation of the periodic structure.

in Fig. 1(c). The ED patterns from the regions (1) and (2) prove that these regions consist of the pure ZB and W phase, respectively. It was confirmed that the ZB-[111] direction was parallel to the W-[0002] direction (*c* axis). On the other hand, the ED pattern from the region (3) shows satellite spots aligned in the ZB-[111] direction. The distance between the neighboring satellite spots is exactly 1/6 of that between 000 and ZB-111 diffraction spots. These findings indicate that the sample involves the periodic structure along the ZB-[111] direction with the periodicity of 6 times as thick as the ZB-{111} spacing. The ZB-{111} spacing, which is equal to the W-{0002} spacing, is the bilayer (monomolecular) spacing in the ⟨111⟩ direction, that is, 2.6 Å. Therefore, the period of the structure is estimated to be 15.6 Å. It should be noted that the period is almost always six bilayers, indicating that the closest-packing structure is preserved. In Fig. 1, other variants for the W phase and the periodic structure which orient the ZB-[$\bar{1}$11] direction are also found, for example, at the positions indicated as (2)′ and (3)′, respectively. In this study, regarding the periodic structures, the directions along which the periodicity occurs are denoted as the ''*c* axis.'' The *c* axis of the periodic structure is parallel to either the ZB-[111] or ZB-[$\bar{1}\bar{1}$1] direction. The layer thickness of the periodic structures along their *c* axis ranged from 50 to 100 nm and the fractional occupancy against the entire area of the cross section was estimated to be about 5%, though these structural parameters depend on growth conditions.

In order to identify the layer stacking sequence of the structure with six-bilayer periodicity, a high-resolution (HR) image was observed at the corresponding region. The result is shown in Fig. 2. In this region, the *c* axis of the periodic structure is parallel to the ZB-[111] direction and the periodicity spreads over 50 nm along the *c* axis. The HR image again confirms the periodicity of 15.6 Å, but we could not determine the stacking sequence due to the diffused spots, which are probably caused by strain induced distribution of atom positions within the specimen thickness for the TEM observation. The origin of this distribution is considered to be related to the formation mechanism of the six-bilayer periodic structures and will be discussed below in detail.

Let us consider plausible stacking sequences in the periodic structures. For this, it is critical to elucidate its origin. Referring to Fig. 1 again, it is found that the periodic structures are sandwiched between the ZB and W phases in the directions perpendicular to their *c* axes; the region (3) is between (1) and (2), while (3)′ is between (1) and (2)′. In other places, which are not shown in Fig. 1, the periodic structure was observed between two W variants with different orientations, that is, *c* axis∥ZB-[111] and ZB-[$\bar{1}\bar{1}$1]. However, this structure is essentially identical with the structures found in Fig. 1, in which the periodic structures are located between the ZB and W phases, because the ZB-{111} planes are equivalent to the W-{0002} planes. Therefore, we discuss the sandwich structure with ZB and W.

Figure 3 schematically illustrates this structural model. When the ZB and W phases are stacked along the *c* axis of the W phase, these regions may be separated by a single stacking fault due to the equivalency of ZB-{111} and W-{0002} as shown on the left-hand side of Fig. 3. On the other hand, when the stacking direction of ZB and W is perpendicular to the *c* axis as on the right-hand side of Fig. 3, spatial shifts of atom positions must occur. The layer stacking sequence along ZB-⟨111⟩ for ZB is $ABCABC\cdots$, while $ABABAB\cdots$ for W. Therefore, if ZB and W transform into each other directly, the difference of the latter four sequences (*CABC* for ZB and *ABAB* for W) brings the shift of the atoms in the corresponding sequences in the vicinity of the ZB–W interface, resulting in large strain. In order to avoid the introduction of the large strain, a transition region with the six-bilayer periodicity will be formed. The periodicity of six bilayer is derived from the complete agreement of the layer stacking sequences of ZB and W every six-bilayer stacking, as is deduced from the sequences of ZB ($ABCABC\cdots$) and W ($ABABAB\cdots$), or from Fig. 3.

As for the stacking sequences in the periodic structures, the sequences which induce much more strain than the direct transformation between ZB and W may be ruled out. For example, an $ACBCBC\cdots$ sequence is different by four sequences from both ZB and W, and therefore it will hardly appear. Furthermore, the experimental result that the closest-packing is maintained in the periodic structures as was

mention in the discussion with Fig. 1 allows us not to consider the stacking of the same sequence such as *AA*, *BB*, and *CC*. Taking these factors into account, it is found that possible sequences are $ABCBAC\cdots$, $ABCBAB\cdots$, and $ABABAC\cdots$. The $ABCBAC\cdots$ sequence differs by two sequences from both ZB and W. For the latter two, $ABCBAB\cdots$ and $ABABAC\cdots$, on the other hand, the deviation from ZB is counted as three sequences, while one sequence from W. Therefore, as the stacking sequences in the periodic structures, the transition of ZB($ABCABC\cdots$)$\leftrightarrow ABCBAC\cdots\leftrightarrow$($ABCBAB\cdots$ or $ABABAC\cdots$)$\leftrightarrow$W($ABABAB\cdots$) is a plausible candidate. It should be noted that those sequences do not need to appear with the similar fractional occupancy and that either sequence can dominate the periodic structure. In the case of Fig. 2, these sequences would be mixed and, consequently, we could not identify the stacking sequence uniquely.

In the above discussion, the sandwich structure was used as a structural model. In the actual crystal growth, however, the growth direction of the GaN layer ([001]) is different from the direction in which the periodicity occurs (ZB-[111]A). Therefore, it is not determined at the onset of the periodic structures on the ZB or W phase whether those are finally sandwiched by ZB and W. From this fact, the formation process of the six-bilayer structures is deduced as follows; when a driving force to be W is applied to the ZB phase, or vice versa, the periodic structure is formed and continues to grow unless it is terminated. An example of the driving force is atomically rough surfaces. Let us suppose that there is a hole which is surrounded with {111} planes on the outermost plane of the ZB phase. If an adatom is captured at the hole and is going to occupy the W sublattice on the ZB-(111) plane, the relation between the embedded atom and the ZB-$(\bar{1}\bar{1}\bar{1})$ plane realize the situation shown on the right-hand side of Fig. 3. Therefore, in this case, the periodic structure whose *c* axis is in the ZB-[111] direction will be formed. The periodic structure along ZB-$[\bar{1}\bar{1}\bar{1}]$ as well can appear via the same mechanism.

To summarize, the structural properties of GaN grown on GaAs(001) were investigated by TEM in terms of polytypism. It was revealed that there was the structure with six-bilayer periodicity along the ZB-[111]A direction, which is indicative of the presence of 6H polytypes. Its origin was attributed to the transformation of ZB$\leftrightarrow$W along the direction perpendicular to the *c* axis of the W phase. The present study demonstrates the possibility of the presence of many polytypes in GaN grown on GaAs(001).

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