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Epitaxial relationship between wurtzite GaN and β-Ga_2O_3

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The epitaxial relationship between wurtzite GaN and monoclinic β-Ga_2O_3 is studied by transmission electron microscopy. GaN is grown on β-Ga_2O_3 by molecular beam epitaxy without any low-temperature buffer layer, obtaining *c* plane GaN on *a* plane β-Ga_2O_3. The effect of the surface nitridation, which is necessary for the epitaxial growth, is analyzed at the atomic level. The lattice mismatch has a minimum of 2.6% for the in-plane epitaxial relationship $\langle 0\ 1\ 1\rangle_{Ga_2O_3} \| \langle 1\ 0\ \bar{1}\ 0\rangle_{GaN}$. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2745645]

In the last years, β-Ga_2O_3 is attracting attention as a transparent conductive substrate.[1,2] At present, sapphire is the most widely used substrate for the deposition of Ga nitrides, although it is insulating and has a large effective lattice mismatch (LM) to GaN (13%). For light-emitting diodes and laser diodes with large current densities a vertical diode structure is preferable, and therefore conductive substrates are strongly requested. SiC polytypes, in spite of being electrically conductive and having a relatively small LM to GaN, 3.8% and 3.5% for 4*H* and 6*H*, respectively, exhibit two disadvantageous features. On the one hand, micropipes are still present, impeding a full use of the wafers. On the other hand, the incorporation of N as *n*-type dopant leads to SiC coloration, brown and green for 4*H* and 6*H* SiC, respectively, so that optical losses have to be considered.

β-Ga_2O_3 belongs to the monoclinic system, space group $C2/m$.[3] The lattice parameters are $a=12.23$ Å, $b=3.04$ Å, and $c=5.80$ Å and $\beta=103.7°$. It exhibits the largest band gap among the transparent conductive oxides with $E_g=4.8$ eV.[4] Despite its cleavage nature, we have succeeded to cut and polish 1 in. wafers,[5] which are transparent in the visible wavelength region and *n*-type conductive (resistivity $\approx 0.02\ \Omega$ cm). Therefore, β-Ga_2O_3 compromises the transparency of sapphire with the conductivity of SiC. Preliminary studies on the growth of Ga nitrides on β-Ga_2O_3 by the metal-organic-vapor-phase-epitaxy technique, using a low-temperature (LT) buffer layer, have been already shown.[1] The blue emission from a gallium nitride multiquantum well after a vertical current injection has been reported.

In this letter, we investigate at the atomic level how GaN can be grown epitaxially on β-Ga_2O_3 in spite of the difference in crystal structure. For it, *c* plane GaN was grown on an effectively nitridized *a* plane β-Ga_2O_3 substrate without any LT buffer layer by the rf-plasma-assisted molecular beam epitaxy (MBE) technique.[2] The interface was analyzed by cross-section transmission electron microscopy (TEM).

β-Ga_2O_3 substrates were prepared from single crystals grown by the floating zone technique, as described in detail elsewhere.[5] The deposition took place in a MBE chamber with a base pressure of 7×10^{-7} Pa. An effective nitridation of the *a* surface prior to the deposition was carried out by introducing NH_3 into the chamber for few minutes, while keeping the substrate temperature close to 800 °C.[2] 7*N* Ga was evaporated from a Knudsen cell at 910 °C, while elemental N was supplied by a rf ion-radical beam operating at 350 W. During the growth of GaN the substrate temperature was kept at about 815 °C, according to a pyrometer pointing to the substrate, and the chamber pressure was constant at 7×10^{-3} Pa. The growth time was 60 min. It should be noted that no LT buffer layer, which is commonly used for the epitaxial growth on other substrates, was deposited.

TEM was carried out with a JEM-3010, under an acceleration voltage of 300 kV. The cross section of the sample was prepared parallel to the *b* plane of the β-Ga_2O_3 substrate, and the TEM-diffraction images were taken along the *b* axis of the substrate, fixing the sample orientation.

The cross-section TEM micrograph of a 400 nm thick GaN epilayer is shown in Fig. 1. Two differentiated parts can be distinguished. In the first one, at the interface with the substrate, horizontal dislocations are predominant. These are caused by a lateral stress that can be attributed to the in-plane LM, as it will be explained later. Above this first 200 nm GaN relaxes—the horizontal dislocations disappear—and only vertically propagating dislocations can be observed.

Electron-diffraction patterns of Fig. 2 were taken at the positions a, b, and c of Fig. 1, related to the substrate, the interface, and the GaN layer, respectively. Figure 2(a) corre-

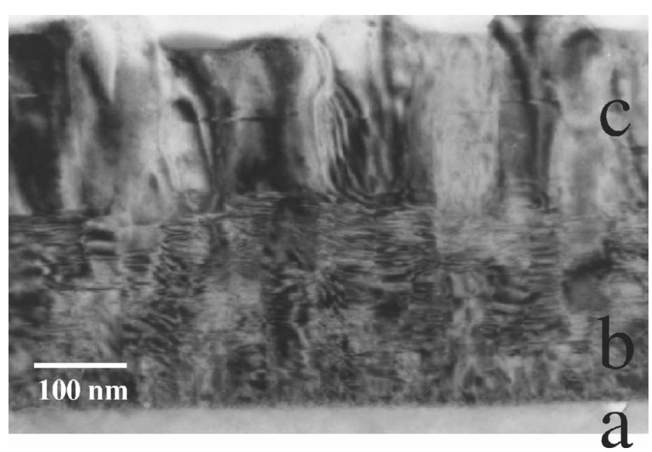

FIG. 1. Cross-section TEM micrograph of GaN on β-Ga_2O_3 by MBE without any LT buffer layer. Substrate, interface, and epilayer locations used for electron diffraction (see Fig. 2) are indicated by a, b, and c, respectively.

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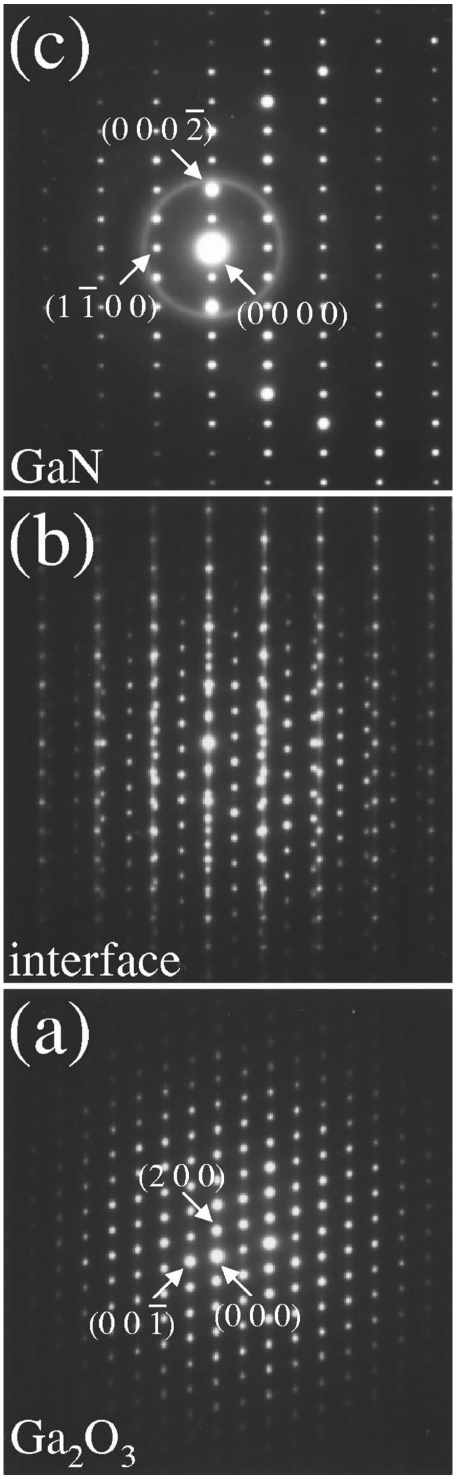

FIG. 2. Electron-diffraction patterns at the three locations indicated in Fig. 1, all taken under the same sample orientation.

sponds to β-Ga_2O_3 $[0\ \bar{1}\ 0]$ zone axis, while Fig. 2(c) to GaN $[1\ 1\ \bar{2}\ 0]$ zone axis, although the image asymmetry indicates a deviation angle of $\approx 1°$. This result agrees with the one obtained previously by glancing-incidence in-plane x-ray diffraction,[2] where following in-plane epitaxial relationship (ER) was proposed: $\langle 0\ 1\ 0\rangle_{Ga_2O_3} \| \langle 1\ 1\ \bar{2}\ 0\rangle_{GaN}$ and $\langle 0\ 0\ 1\rangle_{Ga_2O_3} \| \langle 1\ \bar{1}\ 0\ 0\rangle_{GaN}$. Close to the interface, diffraction spots from the substrate and the epilayer overlap, yielding to the diffraction pattern of Fig. 2(b), which will be discussed below in detail (see Fig. 6).

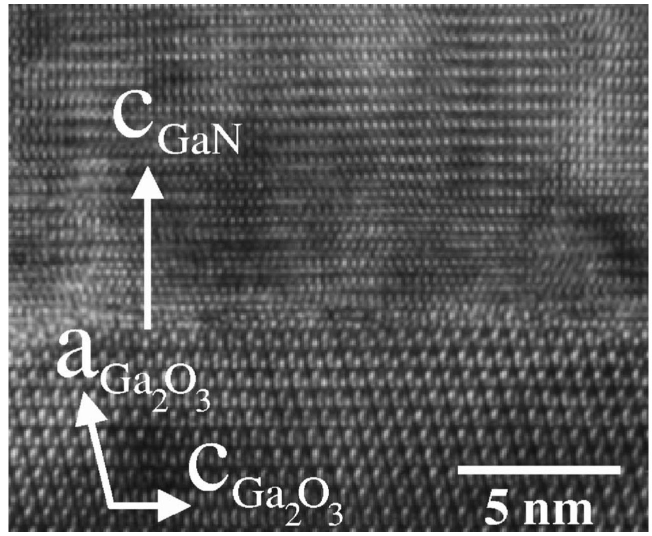

FIG. 3. High-resolution TEM micrograph of the GaN/Ga_2O_3 interface along the $[0\ \bar{1}\ 0]$ zone axis of β-Ga_2O_3.

A high-resolution micrograph of the GaN/Ga_2O_3 interface is shown in Fig. 3. Along the *a* axis, a half lattice spacing of 5.9 Å for the main {2 0 0} β-Ga_2O_3 cleavage plane can be readily resolved. Also, a lattice spacing of 5.6 Å is observed for the secondary {0 0 1} β-Ga_2O_3 cleavage plane. The interface between both compounds is smooth, suggesting that the surface nitridation prior to the GaN deposition does not induce a reaction in the depth, but just an atomic rearrangement at the surface, as suggested previously by the streak patterns of reflection high energy electron diffraction (RHEED).[2]

In order to gain insight into the effect of surface nitridation, precondition for the epitaxial growth,[2] it is necessary to consider the atomic structure of the substrate surface. Figure 4(a) shows the perspective view along the *b* axis, so that the {2 0 0} cleavage plane is easily recognizable by the weakly bonding oxygen atoms in the $O_{(3)}$ site. On the other

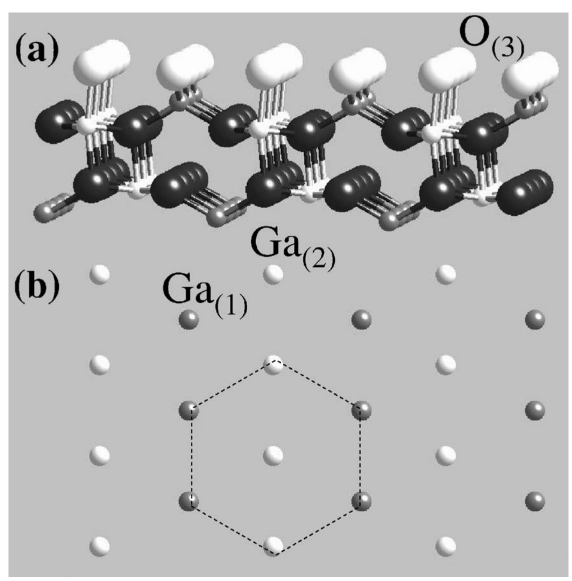

FIG. 4. β-Ga_2O_3 atomic structure. (a) Projection along the *b* axis, $O_{(3)}$ atoms are linked to the {2 0 0} plane. (b) Projection perpendicular to the *a* plane, showing the hexagonal-like arrangement of the Ga atoms bonded to $O_{(3)}$.

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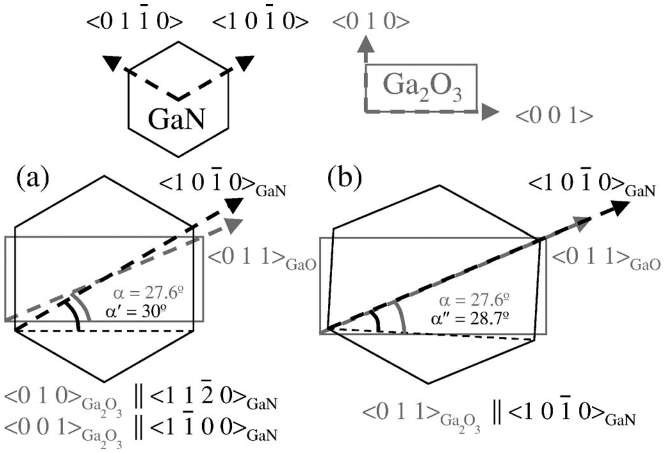

FIG. 5. Schematic of the ER between *c* plane wurtzite GaN and *a* plane β-Ga_2O_3. (a) Initial observation and (b) refined model with a stressed and reoriented GaN at the interface. The LM minimum of 2.6% is given at 1° tilted angle with respect to case (a).

hand, Fig. 4(b) shows the projection perpendicular to the *a* plane (along the ⟨201⟩ direction), where for the sake of clarity only the gallium atoms bonded to $O_{(3)}$ are shown ($Ga_{(1)}$ and $Ga_{(2)}$ sites). As indicated by a doted polygon, these are in an almost regular hexagonal arrangement, which is very similar to that of gallium atoms in wurtzite GaN. Therefore, taking into account the RHEED and high-resolution TEM results, it is reasonable to assume that during the nitridation process O from the uppermost surface will be substituted by N. During this substitution, the surface would reconstruct to a *n*-polarlike GaN surface, on which GaN can be deposited quasihomoepitaxially, without any LT buffer layer.

Due to the difference in crystal structure a nonuniform in-plane stress of the GaN epilayer occurs. In the following we consider the LM between the sixfold symmetric GaN epilayer and the twofold symmetric β-Ga_2O_3 substrate. For the ER given above and which is shown schematically in Fig. 5(a), an ≈5% LM between β-Ga_2O_3 and GaN is calculated: a 4.9% tensile stress parallel to the *c* axis, in contrast to a 4.8% compressive one parallel to the *b* axis. This anisotropic stress seems actually unlikely and therefore we estimate instead the LM caused by a minimum distortion, which is shown in Fig. 5(b). In this case, the ER is given by $\langle 0\ 1\ 1\rangle_{Ga_2O_3} \| \langle 1\ 0\ \bar{1}\ 0\rangle_{GaN}$ and the LM becomes as small as 2.6%. Thus, if the nucleation layer is stressed by this 2.6% reoriented, as shown in Fig. 5(b), then the GaN epilayer should be tilted 1 ° from the initially proposed in-plane ER of Fig. 5(a). This hypothesis agrees with the observed deviation of the electron-diffraction pattern of GaN in Fig. 2(c), which was taken under fixed sample orientation, i.e., along the *b* axis of the substrate.

In order to confirm that the tilting angle is not an artifact caused by some sample bendings during the preparation of the cross section, we examine the electron-diffraction pattern directly at the interface. In Fig. 6, negative of Fig. 2(b), we distinguish between the diffraction spots originated from the substrate and from the epilayer by red circles and blue triangles, respectively. It is seen that the diffraction pattern from the substrate is symmetric, while the one from the GaN epilayer deviates from the symmetry direction, as visualized by white arrows. Figure 2(b) represents the combination of the electron-diffraction patterns of Figs. 2(a) and 2(c), and it proves the slight tilting of the GaN layer relative to the β-Ga_2O_3 substrate, in accordance with the scheme of Fig. 5(b).

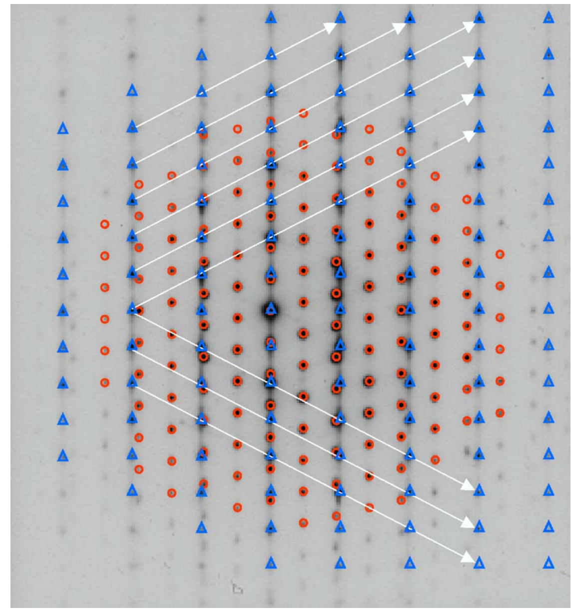

FIG. 6. (Color online) Electron-diffraction pattern at the interface [Fig. 2(b)] differentiating the reflections from β-Ga_2O_3 (red circles) to GaN (blue triangles). The asymmetric distribution of the GaN spots is indicated by white arrows.

Summarizing, it is shown that *c* plane wurtzite GaN can be grown quasihomoepitaxially on *a* plane β-Ga_2O_3 substrate after an effective surface nitridation. The in-plane mismatch is as small as 2.6%, compressive along the *b* axis and tensile along the *c* axis of β-Ga_2O_3, for the in-plane ER $\langle 0\ 1\ 1\rangle_{Ga_2O_3} \| \langle 1\ 0\ \bar{1}\ 0\rangle_{GaN}$. These results indicate that in spite of the difference in crystal structure, β-Ga_2O_3 can be used as a transparent and conductive substrate for Ga nitride based devices.

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