Structural Characteristics of Nanometer Thick Gd$_2$O$_3$ Films Grown on GaN (0001)

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ABSTRACT: High-quality Gd$_2$O$_3$ epi-films 5–20 nm thick have been grown on GaN (0001) using molecular beam epitaxy. A detailed structural investigation was carried out by in situ reflection high energy electron diffraction, cross sectional transmission electron microscopy, and X-ray scattering using a synchrotron radiation source. The films consist of the high-temperature monoclinic (m) phase with six rotational domains, which can be easily mistaken for the hexagonal phase. All the domains follow the m-Gd$_2$O$_3$ (201)/(020) || GaN (0001) <1120> orientational relationship.

Introduction

GaN has been intensively studied for high-power devices in high electron mobility transistors (HEMTs).1–2 Owing to its wide energy band gap (3.4 eV) which alleviates the adverse effects like drain-induced barrier lowering (DIBL) and band-to-band tunneling (BTBT), GaN combining with novel dielectrics with high $\kappa$ is now also being considered as a channel candidate for complementary metal-oxide-semiconductor (CMOS) devices beyond the 15 nm node technology.

In order to achieve a self-aligned process, a gate dielectric/GaN sustainable to implant activation is needed. In other words, no thermal degradation is acceptable with rapid thermal annealing (RTA) up to at least 1100 °C for 5 min. Much research effort has been devoted to high $\kappa$ dielectrics on GaN, including Sc$_2$O$_3$,3 Ga$_2$O$_3$(Gd$_2$O$_3$),6,7 Al$_2$O$_3$,8,9 MgO,10,11 HfO$_2$,12 and Gd$_2$O$_3$.13,14 Among them, single-crystal Gd$_2$O$_3$ with the high-temperature hexagonal phase stabilized by GaN substrate has been demonstrated.13 The Gd$_2$O$_3$ layer exhibited a low interfacial density of states ($D_s$) with GaN and a high dielectric constant $k \sim 24$, low electrical leakage currents, and excellent thermal stability, and thus is a promising contender for the gate dielectrics on GaN.

According to the phase diagram, bulk Gd$_2$O$_3$ has four polymorphs, cubic C-type, monoclinic B-type, hexagonal A-type, and cubic X-type structures, which exist at temperature $T < \sim 1300$ K, 1300–2450 K, 2450–2650 K, and $> \sim 2650$ K, respectively.15 Cubic (c) phase Gd$_2$O$_3$, the stable phase at room temperature, is the most commonly observed one. Because of its unique spectral properties, including large Stokes shifts, narrow emission bandwidths, long fluorescence lifetimes and upconversion phenomena, c-Gd$_2$O$_3$, in particular rare-earth doped Gd$_2$O$_3$, have received more and more attention for biological applications, such as luminescent labels for immunoassays and reporters for optical detection and visualization of antibody arrays,16,17 and for solid-state light emitting devices as upconverting phosphor.18,19 For these applications, Gd$_2$O$_3$ of powder form consisting of nanosized crystallines is adopted. Another major application of Gd$_2$O$_3$ is high-$k$ gate dielectrics for CMOS devices. Gd$_2$O$_3$ epitaxial growth has been demonstrated on various semiconductor substrates. MBE grown Gd$_2$O$_3$ with the most stable cubic bixbyite structure$^{20–24}$ was found to grow on GaAs, Si, and Ge substrates with various orientations. One rare exception is the case reported on Ge (001) at a specific growth condition, where the structure of the Gd$_2$O$_3$ layer underwent a phase transition from the cubic phase with (110) normal to the monoclinic phase with dominant (100) normal and then back to the cubic phase as the layer thickness increased.24

Both monoclinic and hexagonal phases of Gd$_2$O$_3$ have higher $k$ values than that of c-Gd$_2$O$_3$ and are also more compatible in symmetry with the substrates of hexagonal symmetry. On c-plane GaN, high temperature hexagonal phase with c-plane normal and in-plane orientation locking with the substrate has been reported.13,25 Recently, we also observed the existence of a Gd$_2$O$_3$ layer with monoclinic structure,14 which can be easily mistaken for the hexagonal one; these oxide films exhibit good electrical properties and excellent thermal stability with GaN. In this work, we have thoroughly studied the structures of the (201) oriented monoclinic Gd$_2$O$_3$ films grown by MBE on GaN (0001) surface. The detailed structural characteristics clearly distinguished from their counterpart of the hexagonal phase are given.

Experimental Section

Micron-thick n-type GaN (0001) grown by metal–organic chemical vapor deposition (MOCVD) on 2-in. c-plane (0001) sapphire was used as the substrate for oxide growth. The surface of the GaN layer was determined to be Ga-polar. After heating to 700 °C in UHV for surface cleaning, the reflection high energy electron diffraction (RHEED) pattern of the GaN surface changed from a weak (1 × 1) to a bright (2 × 2) reconstructed pattern with Kikuchi arcs, indicating a clean GaN
surface free of contaminations or native oxides. Gd$_2$O$_3$ was then deposited on GaN (0001) by molecule beam epitaxy (MBE) in a multichamber ultrahigh vacuum (UHV) system using electron beam evaporation from a powder-packed and sintered Gd$_2$O$_3$ at a substrate temperature of 700°C. The samples were in situ annealed under partial oxygen ambient (∼10^{-8} Torr) during cooling for 10–20 min to repair the oxygen deficiency defects in the bulk of the films.

Synchrotron X-ray scattering measurements were performed at wiggler beamline BL17B1 at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. The incident X-rays were monochromatized to energies in the range of 7–12 keV by a Si (111) double-crystal monochromator. The dimensions of the beam size are typically 2 mm × 0.3 mm (H × V) at the sample position. With two pairs of slits between sample and detector, the typical resolution was set to about 5-10 Å^-1. High-resolution X-ray measurements were carried out in single-crystal geometry with a six-circle diffractometer.

Results and Discussion

A (1 × 1) oxide RHEED pattern appeared right after the initial oxide deposition, which superimposed with the reconstructed (2 × 2) pattern from the GaN underneath. After ∼5 nm of deposition, the pattern changes to a reconstructed (3 × 2) streaky pattern and remains unvaried upon further deposition. In this work, the majority of the presented data were taken from the sample with a 10 nm thick oxide layer, which represents the typical structure of samples with Gd$_2$O$_3$ thickness larger than ∼5 nm. The RHEED patterns of clean GaN surface and after Gd$_2$O$_3$ deposition, taken along two orthogonal directions are shown in Figure 1. The invariance of the patterns after 60° rotation against surface normal and a ratio of 31/2 between the separation of main streaks taken along GaN [1010] and [2110] directions indicate that the Gd$_2$O$_3$ layer has a structure of 6-fold symmetry.

To examine the layer orientation and crystalline quality, we performed high-resolution X-ray scattering measurements. Figure 2 illustrates the intensity profile of a specular scan, in which the abscissa is in units of GaN reciprocal lattice units along the ĉ axis (rilu$_{\text{GaN}} = 2\pi/c_{\text{GaN}} = 1.212$ Å^-1). The intense sharp peaks centered at 2 and 2.4 rlu$_{\text{GaN}}$ are GaN (0002) and sapphire (0006) Bragg reflections, respectively. The broad peaks centered at 0.87 and 1.74 rlu$_{\text{GaN}}$ originate in the Gd$_2$O$_3$ layer. The interplanar spacing corresponding to the peak centered at 1.74 rlu$_{\text{GaN}}$, 0.298 nm matches closely the d-spacing of the (402)$_m$ reflection of the monoclinic (m) phase and the (0002)$_h$ reflection of the hexagonal (h) phase Gd$_2$O$_3$. Because the (201)$_m$ reflection is allowed but the (0001)$_h$ reflection is forbidden, the presence of the peak located at 0.87 rlu$_{\text{GaN}}$ implies that the Gd$_2$O$_3$ film has a monoclinic structure, inconsistent with the hexagonal structure implied by the RHEED observation. Besides, it is noted that pronounced oscillations, known as the thickness fringe, appear in the range of l < 2 rlu$_{\text{GaN}}$, which signifies smooth and sharp surface/interfaces and good crystalline quality of the grown film. From the fringe period 0.0511 rlu$_{\text{GaN}}$, we derived the layer thickness to be 10.2 nm. From the full width at half-maximum (fwhm) of the two Gd$_2$O$_3$ peaks, 0.535 and 0.569 nm^-1, we obtained the structural coherent length along the growth
direction to be ∼10 nm. The agreement between the two numbers manifests that the atomic arrangement of oxide film remains coherent throughout the entire layer thickness. We also measured the θ-rocking curve of the peak. The narrow peak width 0.09°, slightly larger than that of the GaN (0002) reflection 0.07°, again reveals the good crystalline quality of the grown film.

In order to clarify the structure of the oxide layer, we carried out a series of measurements on the off-normal reflections. For simplicity, the reference frame based on the Gd$_2$O$_3$ hexagonal phase structure with (0001) normal is adopted. Shown in Figure 3 is the intensity distribution of scattered X-rays of an azimuthal cone scan across Gd$_2$O$_3$\{10$ar{1}$$\bar{1}$\}_h reflections; six evenly spaced peaks with their angular positions coinciding with that of GaN \{10$\bar{1}$$\bar{1}$\} reflections were observed. This result agrees with the hexagonal characteristics and the orientational locking between h-Gd$_2$O$_3$ and wurtzite GaN substrate reported previously.\textsuperscript{25} However, every peak is split into more than two maxima in the tip, which was also observed in the azimuthal scans across other reflections, for example, (11$ar{2}$2)$_h$. Moreover, we performed rod scans, scans along the surface normal, along Gd$_2$O$_3$ (10$ar{1}$)$_h$ and (202)$_h$ crystal truncation rods with $l$ varying from 1 to 4 (not shown).

Figure 3. Azimuthal cone scan against the surface normal across h-Gd$_2$O$_3$ \{1101\}_h reflections. Six evenly spaced peaks delineate the 6-fold symmetry of the structure. However, the split line shape is unexpected.

Again, we found split peaks at the expected position for the Bragg peaks associated with hexagonal phase oxide. Two dimensional mesh scans reveal that each reflection is actually consistent with a cluster of peaks, whose number and interpeak spacing depend on the Miller index of the reflection. Obviously, the Gd$_2$O$_3$ layer is not the hexagonal phase.

Carefully examining the atomic arrangement of hexagonal phase of rare earth sesquioxide Gd$_2$O$_3$, we found that it consists of slabs made of OGd$_4$ tetrahedra with the Gd atoms (circles in blue) taking the corner sites and the O (large circles shaded area in Figure 4. Those slabs are stacked on top of each other, separated by a layer of ionic oxygen O$_2$\textsuperscript{2-},\textsuperscript{27} and parallel to the (0001)$_h$ basal plane as illustrated in Figure 4a, in which the (11$\bar{2}$0)$_h$ plane is parallel to the plane of paper. In contrast, the monoclinic phase of Gd$_2$O$_3$ can be described as a deformation of the hexagonal one subjected to a shear distortion and the (0001)$_h$ axis is tilted by ∼3.7° toward the [1$\bar{1}$00]$_h$ direction. In the monoclinic reference frame, the slabs are parallel to the (201)$_m$ plane, as illustrated in Figure 4b, where the plane of paper represents the (010)$_m$ plane. The slight difference in the atomic arrangement between the hexagonal and monoclinic structures leads to the great similarity in their diffraction patterns. Shown in Figure 5a is the surface projection of the m-Gd$_2$O$_3$ quasi-surface reflections, which lie on a plane tilted by a few degrees from the sample surface. The peaks form deformed hexagons stretched along the [010]$_m$ direction and the pattern has a plane of mirror symmetry in the $h$-$l$ plane, marked by the dashed line in Figure 5a. Surface projections of the three reciprocal lattice vectors (a*, b*, and c*) as well as the Miller index associated with each peak are also marked on the pattern. The filled and empty circles denote the diffraction peaks located on/above and below sample surface, respectively. As a comparison, the hexagons corresponding to the lattice of h-Gd$_2$O$_3$ and two vectors [1$\bar{1}$00]$_h$ and (11$\bar{2}$0)$_h$ are also outlined in blue. The projection of the m-Gd$_2$O$_3$ diffraction pattern on the $h$-$l$ plane, which is perpendicular to the b* axis, is illustrated in Figure 5b.

Figure 4. Atomic arrangement of (a) hexagonal and (b) monoclinic Gd$_2$O$_3$ viewed along [1$\bar{1}$20]$_{hh}$ and [010]$_m$ directions, respectively. The red circles denote O atoms and the blue circles represent Gd atoms, of which the solid/larger ones are lying on the plane of paper and the dashed/smaller ones are at either above or below the paper plane. The projection of the lattice basis vectors are also outlined in the figures.

Figure 5. Azimuthal cone scans of the GaN (0002) and Gd$_2$O$_3$ \{1101\}$_h$ ((a) and (c)) reflections. The (202)$_h$ crystal truncation rods are also marked on the pattern. The filled and empty circles denote the diffraction peaks located on/above and below sample surface, respectively.
in which the dotted line represents the surface plane which is parallel to the (201)\textsubscript{m} plane. All the diffraction peaks noted in Figure 5a lie on the plane defined by the (101)\textsubscript{m} and (010)\textsubscript{m}, which is depicted by the dashed line in Figure 5b and makes an angle of ~3.7° with the surface plane.

Even though the diffraction pattern of \textit{m-}Gd\textsubscript{2}O\textsubscript{3} is very similar to that of \textit{h-}Gd\textsubscript{2}O\textsubscript{3}, it will not yield an azimuthal scan with 6-fold symmetry. To account for the experimental observation, we attributed the 6-fold symmetry to the coexistence of six rotational domains with their [010]\textsubscript{m} aligned with the 6-fold degenerate <11\textsubscript{2}0> directions of the underlying GaN (0001) surface. The projection of superimposed diffraction pattern onto the plane defined by (0001)\textsubscript{h} and (1\textsubscript{1}2\textsubscript{0})\textsubscript{h} in reciprocal space is illustrated in the bottom of Figure 6a, in which a spot of different color represents reflection originating from different domains. In the area near (1\textsubscript{1}2\textsubscript{2})\textsubscript{h}, as marked by the red circle, three peaks exist. The corresponding mesh scan indeed shows three maxima, as illustrated in the top of Figure 6a on which the corresponding Miller indices associated with the monoclinic phase are noted. As indicated by the Miller indices, each peak represents two reflections with opposite k value. Some pairs of reflections are azimuthally separated, which can be resolved in the pole figure, and the others coincide. For example, according to the calculations the pair of (7\textsubscript{1}1) and (7\textsubscript{1}1) are ~7° apart in azimuthal angle but the (4\textsubscript{2}2) reflection coincides with the (4\textsubscript{2}2). Both results are confirmed by our experimental observations shown in Figure 7, where \(\chi\) and \(\phi\) denote the polar and azimuthal angle, respectively. Similarly, the mesh scan near (1\textsubscript{1}0\textsubscript{1})\textsubscript{h} together with the simulated diffraction pattern projected onto the plane expanded by (0001)\textsubscript{h} and (1\textsubscript{1}0\textsubscript{0})\textsubscript{h} in reciprocal space are depicted in Figure 6b, where four peaks were clearly resolved. All the experimental results agree with the simulated peak positions and confirm that the oxide thin film indeed has the

**Figure 5.** (a) Surface projection of the quasi-surface reflections of \textit{m-}Gd\textsubscript{2}O\textsubscript{3} with (201)\textsubscript{m} normal. The reciprocal lattice of the \textit{h-}Gd\textsubscript{2}O\textsubscript{3} is outlined by the dashed hexagons as a comparison. (b) Side view of the allowed reflections of \textit{m-}Gd\textsubscript{2}O\textsubscript{3} with the surface normal pointing upward and (010)\textsubscript{m} pointing out of the paper. The solid and empty circles denote the reflection on/above and below the sample surface, respectively.

**Figure 6.** (a) Reciprocal space map (RSM) near \textit{h-}Gd\textsubscript{2}O\textsubscript{3} (1\textsubscript{1}2\textsubscript{2})\textsubscript{h} are shown on the top panel. The simulated diffraction patterns of \textit{m-}Gd\textsubscript{2}O\textsubscript{3} with six rotational domains projecting onto the same plane in reciprocal space are displayed in the bottom, in which the encircled region corresponds to the region shown on top. Reciprocal lattice points marked by different colors originate from different domains. Similarly, 2D RSM taken near \textit{h-}Gd\textsubscript{2}O\textsubscript{3} (1\textsubscript{1}0\textsubscript{1})\textsubscript{h} together with the simulated patterns are illustrated in (b).
monoclinic structure with six rotational domains. After the Miller index of each reflection is properly identified, the lattice constants are determined to be \( a = 13.965 \) Å, \( b = 3.595 \) Å, \( c = 8.787 \) Å, and \( \beta = 101.34^\circ \) by least-squares-fitting the angular position of the reflections. The derived molar volume 43.394 \( \text{cm}^3 \text{ mol}^{-1} \) is very close to the value reported by Zinkevich (43.403 \( \text{cm}^3 \text{ mol}^{-1} \)).

A high resolution cross sectional TEM image of the \( \text{Gd}_2\text{O}_3 \) /GaN interface with zone axis along GaN \([11\bar{2}0]\) is shown in Figure 8. The interface is atomically sharp and no amorphous interfacial layer is present. Regions of slightly different atomic arrangement can be identified in the \( \text{Gd}_2\text{O}_3 \) layer, in agreement with the conclusion of multirotational domains drawn from X-ray scattering results.

Monoclinic phase is seldom observed in MBE grown \( \text{Gd}_2\text{O}_3 \) epi-layer. The previous study on a 3.2-nm-thick \( \text{Gd}_2\text{O}_3 \) layer grown under a similar condition revealed that the oxide layer has hexagonal structure, which is stabilized by the epitaxy with GaN substrate. In light of the monoclinic phase being energetically more favorable than the hexagonal phase at low temperatures and the mild atomic rearrangement between the two structures, we attributed the formation of the monoclinic phase as a means to minimize the total energy as the layer thickness exceeds a critical value. We also found that the monoclinic oxide films exhibit excellent thermal stability. Upon RTA at 1100 °C for 5 min in helium ambient, the line widths of the diffraction peaks become slightly narrower implying a slight increase of domain size. Besides that, no obvious structural change was detected.

**Figure 7.** Section of pole figures taken near (a) \((\overline{7} \pm 17)_{\text{m}}\) and (b) \((\overline{7} \pm 22)_{\text{m}}\) reflections. The red lines note the azimuthal angle aligned with GaN \([11\bar{2}0]\) and equivalently \( m-\text{Gd}_2\text{O}_3 \) \([010]\).

**Figure 8.** High-resolution cross sectional TEM micrograph of the region near \( \text{Gd}_2\text{O}_3 /\text{GaN} \) interface. The zone axis is along GaN \([11\bar{2}0]\). The dashed line marks the \( \text{Gd}_2\text{O}_3 /\text{GaN} \) interface.

**Conclusion**

High-\( \kappa \) oxide \( \text{Gd}_2\text{O}_3 \) epitaxial films of thickness 5–20 nm have been successfully grown on GaN (0001) substrates. The thorough structural investigation reveals that on \( c \)-plane GaN, \( \text{Gd}_2\text{O}_3 \) adopts the high temperature monoclinic phase with \((201)_{\text{m}}\) surface normal. Six rotational domains with \( \text{Gd}_2\text{O}_3 [020]_{\text{m}} \) aligned with GaN \(<11\bar{2}0>\) coexist, resulting in the misleading 6-fold symmetry observed in electron diffraction patterns. Although the \( m-\text{Gd}_2\text{O}_3 \) layer exhibits high dielectric constant and thermal stability, the hexagonal phase has even better properties and is more desirable. Proper control of the growth conditions and layer thickness to prohibit the development of the monoclinic phase and retain the hexagonal phase is important to further improve the performance of \( \text{Gd}_2\text{O}_3 \) gate dielectrics.

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