Epitaxial stabilization of a monoclinic phase in Y$_2$O$_3$ films on c-plane GaN

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**Abstract**

Nanometer-thick Y$_2$O$_3$ films were grown epitaxially on GaN (0 0 0 1) using molecular beam epitaxy (MBE). The structures of the oxide films were studied in situ by reflection high energy electron diffraction (RHEED) during the growth and ex situ by high resolution X-ray diffraction using synchrotron radiation. At atmospheric pressure, Y$_2$O$_3$ exists in either cubic or hexagonal structure. For the first time, the high-pressure monoclinic phase of Y$_2$O$_3$, stabilized by epitaxy, was prepared and preserved under atmospheric pressure. The electrical characterization carried out on the Y$_2$O$_3$/GaN metal-oxide-semiconductor (MOS) capacitors showed a leakage current density of $\sim 3 \times 10^{-6}$ A/cm$^2$ at 1.5 MV/cm, which remained almost the same after 800°C annealing. A dielectric constant of ~20 and a hysteresis of ~250 mV were deduced from the capacitance–voltage (C–V) curves for the epitaxial monoclinic Y$_2$O$_3$.

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1. Introduction

Rare-earth oxide/semiconductor hetero-structures have always received scientific and technological interest. For example, rare-earth oxides are attractive as alternative gate dielectrics for SiO$_2$ due to their high dielectric constants and large conduction band offsets with Si [1–5]. High-quality crystalline rare-earth oxides of Si with good thermal stability and lower gate leakage than SiO$_2$ have been successfully demonstrated [6]. Yttrium sesquioxide thus exhibits similar physical properties and has often been employed for the similar applications as rare-earth oxides. Gd$_2$O$_3$, La$_2$O$_3$, and Y$_2$O$_3$ have been applied to GaAs [7–10], GaN [11–13], and Ge [14–16], respectively, as gate dielectrics for pursuing low capacitance equivalent thickness (CET) and high performance device. Among them, crystalline Gd$_2$O$_3$ has effectively passivated GaAs surface, thus opening up a new era for GaAs metal-oxide-semiconductor field-effect transistors (MOSFETs) [7]. Moreover, a single crystal Gd$_2$O$_3$ layer on GaN yielded a high dielectric constant of 24 with a low CET of 0.5 nm [13]. Previous work demonstrated that Y$_2$O$_3$ passivates GaAs [9,17] and Ge [16] surface without the need of an interfacial layer.

At atmospheric pressure, Y$_2$O$_3$ has two polymorphs: cubic and hexagonal. The cubic (C) phase with the bixbyite structure is the most stable one at room temperature, which transforms at ~2600 K to the more closely packed hexagonal (H) phase [18]. Monoclinic (M) Y$_2$O$_3$ is a high-pressure phase, which exists only when C-Y$_2$O$_3$ is compressed beyond ~10 GPa. Above ~19 GPa M-Y$_2$O$_3$ starts to transform into the H-Y$_2$O$_3$. In the decompression process, H-Y$_2$O$_3$ can reversibly transform back to M-Y$_2$O$_3$. However, the cubic to monoclinic structure phase transition is irreversible; the meta-stable monoclinic phase remains when the pressure is lowered down and is preserved at ambient pressure [19]. It was also reported that M-Y$_2$O$_3$ could only be converted from H-Y$_2$O$_3$ in the decompression process and was, however, not formed during the compression of C-Y$_2$O$_3$ [20].

In this work, Y$_2$O$_3$ films were epitaxially grown on GaN using molecular beam epitaxy (MBE). For the layers with thickness greater than ~3 nm, the Y$_2$O$_3$ films display a monoclinic structure. This is the first time that the monoclinic phase Y$_2$O$_3$ is stabilized at ambient conditions without undergoing a high pressure treatment. The structural and electrical properties of the Y$_2$O$_3$ epi-film were thoroughly studied and presented.

2. Experimental

GaN epitaxial layer of 0.3 μm thickness and n-type doping ($5 \times 10^{17}$ cm$^{-3}$) was grown on c-plane sapphire substrate buffered...
with a 1.5 μm thick GaN layer. The GaN surface yielded a (1 x 1) reflection high-energy electron diffraction (RHEED) pattern with clear Kikuchi lines, as displayed in Fig. 1(a). The patterns in left and right panels of Fig. 1 were taken along the GaN <1120> and <1010> directions, respectively. Y2O3 was then deposited on GaN (0 0 0 1) surface by electron beam evaporation from a pure Y2O3 compact powder target, with a substrate temperature maintained at 660 °C. In situ RHEED was employed to monitor the evolution of surface structure during the deposition. During the growth of Y2O3, the RHEED patterns were streaky all the time and remained (1 x 1) until the weak (4 x 2) reconstruction feature, as illustrated in Fig. 1(b), appeared. Since Y2O3 tends to absorb moisture, an Al2O3 cap was then deposited to protect Y2O3 beneath [21]. Detailed structural characterization was performed by high resolution X-ray diffraction (XRD) using synchrotron radiation at wiggler beamline BL17B1 of the National Synchrotron Radiation Research Center (NSRRC), Taiwan.

Parts of the samples were subsequently rapid-thermal-annealed (RTA) to 800 °C for 30 s in helium to reduce the traps caused by the e-beam bombardment during deposition. For electrical measurements, TiN dots of 100 μm in diameter were then deposited as metal gate electrodes by RF sputtering. After oxide patterning by lithography and wet etching, Ti (30 nm)/Al (120 nm) was deposited on GaN as an ohmic contact. The capacitance–voltage (C–V) and the electrical leakage density–electrical field (J–E) characteristics were measured using Agilent 4284 and 4156 C, respectively.

3. Results and discussion

Fig. 2(a) shows the XRD radial scans along the surface normal across GaN (0 0 0 2) and (0 0 0 4) reflections taken from two Y2O3 samples of different thicknesses. The abscissa is in the units of GaN reciprocal lattice unit along the L axis, i.e. \(2\pi/c(GaN)=1.2118 \text{ Å}^{-1}\). In addition to the GaN and sapphire Bragg reflections from the substrate, the broad peaks centered at 0.88, 1.77, 2.64, and 3.54 rlu GaN are designated to be (2 0 1) and the corresponding high order reflections of M-Y2O3. The thickness fringes, particularly pronounced in the regions near M-Y2O3 (4 0 2) and (8 0 4) reflections, reveal the sharp interface and good crystalline quality of the oxide layers. From the period of the thickness fringes, the thicknesses of the oxide layers were derived to be 3.9 and 8.0 nm. The radial scans along the lateral direction across the GaN (1 1 2 0) reflection are shown in the inset. Two broad peaks originating from the oxide layer were observed and their corresponding inter-planar spacings are close to those of M-Y2O3 (3 ± 13) and (0 ± 20) reflections. Azimuthal phi scans across these M-Y2O3 peaks showed 6-fold symmetry.

To further characterize the crystalline structure of the oxide layer, we also conducted two-dimensional reciprocal space
mapping around various reflections, which reveal that each M-Y$_2$O$_3$ peak actually has several other reflections nearby as illustrated in Fig. 2(b). The position of every reflection agrees with the simulation results assuming that the oxide layer consists of six rotational domains with $\{201\}$ normal and their $\{010\}$ axes aligned with the 6-fold degenerate GaN $\langle11\bar{2}0\rangle$ directions. By fitting the angular position of many reflections, the lattice parameters of the M-Y$_2$O$_3$ layer were determined to be $a = 13.995$ Å, $b = 3.526$ Å, $c = 8.569$ Å, and $\beta = 100.27^\circ$, which are different from the values ($a = 13.91$ Å, $b = 3.483$ Å, $c = 8.593$ Å, and $\beta = 100.15^\circ$) of a monoclinic phase Y$_2$O$_3$ obtained under a high pressure [22]. Our measured lattice constants are close to the values, $a = 14.1191$ Å, $b = 3.5174$ Å, $c = 8.6958$ Å, and $\beta = 100.279^\circ$, calculated based on the density functional theory (DFT) and the projector augmented wave (PAW) pseudo-potentials method [23]. The volume per formula unit, 69.346 Å$^3$, falls between those of the cubic (74.523 Å$^3$) and hexagonal (68.560 Å$^3$) phases, consistent with the anticipated trend.

According to the thermal phase diagram of Y$_2$O$_3$ [18], the cubic and the hexagonal phases exist, respectively, at room temperature and temperatures above $\sim 2600$ K. Unlike Gd$_2$O$_3$ and many other rare-earth oxides, in which cubic, hexagonal, and monoclinic phases exist in different temperature ranges under atmospheric pressure [12,24], no monoclinic phase of Y$_2$O$_3$ exists at ambient pressure. Bulk M-Y$_2$O$_3$ can only be obtained by a high pressure treatment through a phase transition either from C-Y$_2$O$_3$ under compression or from H-Y$_2$O$_3$ under decompression [19,20]. In contrast, the monoclinic phase of Y$_2$O$_3$ thin film has been obtained with epitaxy at atmospheric pressure using MBE and exhibits very good thermal stability as shown below.

The radial scans taken from the samples before and after 800 °C RTA are illustrated in Fig. 3, with Fig. 3(a) and (b) displaying the scans along surface normal and lateral direction across GaN $\langle11\bar{2}0\rangle$ reflection of the sample with 3.9 nm thick oxide layer. The squares and circles depict, respectively, the data before and after 800 °C annealing.

![Fig. 3. Radial scans along (a) surface normal and (b) lateral direction across GaN (11\bar{2}0) reflection of the sample with 3.9 nm thick oxide layer. The squares and circles depict, respectively, the data before and after 800 °C annealing.](image)

![Fig. 4. $J$–$E$ curves for as deposited and 800 °C annealed TiN/Al$_2$O$_3$/M-Y$_2$O$_3$/GaN MOS capacitors. The hysteresis $C$–$V$ curve at 100 kHz is shown in the inset.](image)

4. Conclusion

Previously, cubic 1.6–10 nm thick single crystal Y$_2$O$_3$ films were epitaxially grown on Si (1 1 1) using MBE with structures approaching their perfection [25]. Moreover, epitaxial stabilization makes it possible to obtain the nonexistent compounds in the form of thin epitaxial films. Here, we have fabricated nanometer-thick monoclinic Y$_2$O$_3$ films, which do not exist in the phase diagram and were only obtained under high pressure for the bulk Y$_2$O$_3$. The oxide layers exhibit a high dielectric constant, small hysteresis and good thermal stability. These properties strongly favor the application of the Y$_2$O$_3$ as a gate dielectric on GaN for the advanced MOS technologies.

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