**Abstract:** Our research activities during the last eight years from 2006 to 2013, with the grant supports from Nano National programs, NSC, Taiwan and AOARD, have been pushing the material limits of III-V InGaAs and GaN metal-oxide-semiconductor (MOS) systems using high $\kappa$ dielectrics. In the third year of the funding, with the capabilities of atomic-scale probing and manipulating the high $\kappa$ oxides/semiconductors interfaces, we have established the correlations between electronic structures and electrical properties essential to understand the Fermi level pinning/unpinning mechanism of the interfaces between metal/oxide and oxide/semiconductor. We have successfully continuously kept our world-leading expertise of high-$\kappa$ dielectric growth on InGaAs by achieving world record drain current of 1.8 mA/$\mu$m, transconductance of 0.80 mS/$\mu$m, and low sub-thresholds in a self-aligned inversion-channel InGaAs metal-oxide-semiconductor field-effect transistor of 1 $\mu$m gate length. *In-situ* ultra-high vacuum deposited Y$_2$O$_3$ and HfO$_2$ and atomic-layer-deposited (ALD) Al$_2$O$_3$ and HfO$_2$ 2-3 mono-layers thick on freshly grown In$_{0.53}$Ga$_{0.47}$As, with an Al$_2$O$_3$ cap, were employed as a gate dielectric.

Furthermore, high quality nm-thick Gd$_2$O$_3$ and Y$_2$O$_3$ (rare-earth oxide, R$_2$O$_3$) films have been epitaxially grown on GaN (0001) substrate by molecular beam epitaxy (MBE). The R$_2$O$_3$ epitaxial layers exhibit remarkable thermal stability at 1100$^\circ$C, uniformity, and highly structural perfection. Structural investigation was carried out by *in-situ* reflection high energy electron diffraction (RHEED) and *ex-situ* X-ray diffraction (XRD) with synchrotron radiation. In the initial stage of epitaxial growth, the R$_2$O$_3$ layers have a hexagonal phase with the epitaxial relationship of R$_2$O$_3$ (0001) $\|//GaN(0001)$\|$[1 1 0]$. With the increase in R$_2$O$_3$ film thickness, the structure of the R$_2$O$_3$ films changes from single domain hexagonal phase to monoclinic phase with six different rotational domains, following the R$_2$O$_3$ (-201) $\|//GaN (0001)$\|$[1 1 0]$ orientational relationship. The structural details and fingerprints of hexagonal and monoclinic phase Gd2O3 films have also been examined by using electron energy loss spectroscopy (EELS). Approximate 3-4 nm is the critical thickness for the structural phase transition depending on the composing rare earth element.

**Introduction:** Hetero-epitaxy between two dissimilar materials has been the key for producing artificial structured materials, the building blocks for new sciences, novel devices and advanced technologies.

Particularly, the epitaxial growth among oxides and semiconductors has always been scientifically intriguing and technologically relevant. One notable example is the successful growth of single crystal GaN on sapphire and Si(111), which has led to the recent commercialization of solid state lighting and high power devices. The growth of single crystal Gd$_2$O$_3$ on GaAs(001) is another example, leading to the first...
### ABSTRACT

Our research activities during the last eight years from 2006 to 2013, with the grant supports from Nano National programs, NSC, Taiwan and AOARD, have been pushing the material limits of III-V InGaAs and GaN metal-oxide-semiconductor (MOS) systems using high $k$ dielectrics. In the third year of the funding, with the capabilities of atomic-scale probing and manipulating the high $k$ oxides/semiconductors interfaces, we have established the correlations between electronic structures and electrical properties essential to understand the Fermi level pinning/unpinning mechanism of the interfaces between metal/oxide and oxide/semiconductor. We have successfully continuously kept our world-leading expertise of high-$k$ dielectric growth on InGaAs by achieving world record drain current of 1.8 mA, transconductance of 0.80 mS, and low sub-thresholds in a self-aligned inversion-channel InGaAs metal-oxide-semiconductor field-effect transistor of 1.8 $k$ gate length. In situ ultra-high vacuum deposited Y$_2$O$_3$ and HfO$_2$ and atomic-layer-deposited (ALD) Al$_2$O$_3$ and HfO$_2$ 2-3 mono-layers thick on freshly grown In$_{0.53}$Ga$_{0.47}$As, with an Al$_2$O$_3$ cap, were employed as a gate dielectric.

### SUBJECT TERMS

CMOS, Magneto-optical imaging, Nanotechnology, Indium Gallium Arsenide
demonstration of inversion-channel GaAs metal-oxide-semiconductor field-effect-transistors (MOSFETs), timely for the ultimate complementary MOS (CMOS) technology.\textsuperscript{10,11}

Gd$_2$O$_3$ and Y$_2$O$_3$ of cubic phase were found to grow epitaxially on Si, Ge, and GaAs. The lattice constants of cubic Gd$_2$O$_3$ and Y$_2$O$_3$ are 10.8 and 10.6 Å, respectively, which are approximately twice those of GaAs, Si, and Ge, being 5.65, 5.43, and 5.65 Å, respectively. The oxides deposited on Si(111) exhibit the same (111) surface normal.\textsuperscript{12} The oxides deposited on the (001) oriented GaAs,\textsuperscript{6} Si,\textsuperscript{13} and Ge\textsuperscript{14}, however, have (011) parallel with the (001) normal of the semiconductors. The in-plane lattice spacing of the oxide (011) does not match well with those of GaAs,\textsuperscript{15} Si,\textsuperscript{13,16} and Ge,\textsuperscript{17} indicating the bond arrangement and the energy consideration at the oxide/semiconductor interfaces are more critical than the crystalline symmetry.

Besides the epitaxial growth, an effective passivation of high dielectrics on semiconductor has been intensively studied as higher device performance demands smaller device sizes and thinner gate dielectrics. GaN and its related compounds, which have been used for high-temperature high-power RF electronics because of the large critical breakdown fields and high saturation velocities,\textsuperscript{18} are now being considered for the post Si CMOS. Recently, GaN MOSFETs have been demonstrated using MgO,\textsuperscript{19,20} Al$_2$O$_3$,\textsuperscript{21} HfO$_2$,\textsuperscript{22} and Ga$_2$O$_3$(Gd$_2$O$_3$)\textsuperscript{23} as the gate dielectrics. For pushing the GaN MOS technology, the equivalent oxide thickness (EOT) of the gate dielectric is required to be much less than 1 nm.\textsuperscript{11} Therefore, the dielectric constant of the gate dielectric has to be enhanced. Moreover, self-aligned inversion-channel GaN MOSFETs may require the gate dielectric to be of single crystal as amorphous films tend to form poly-crystalline resulting from the high temperature source/drain (S/D) dopant activation process; the gate dielectric needs to sustain rapid thermal annealing (RTA) process up to 1100°C for at least 5 mins.\textsuperscript{24} High-quality hexagonal phase Gd$_2$O$_3$ with good crystallinity has been successfully deposited on c-plane GaN and shows excellent electrical properties.\textsuperscript{25,26} More recently, the monoclinic Gd$_2$O$_3$ and Y$_2$O$_3$ layers consisting of six different rotational domains on GaN have also been reported.\textsuperscript{27-29} The monoclinic phase of rare earth oxides is not energetically favorable under ambient condition. The presence of these non-ambient phases is attributed to epitaxial stabilization.

In this work, we have systematically scaled down the thickness of the molecular beam epitaxy (MBE) deposited Gd$_2$O$_3$ and Y$_2$O$_3$ on GaN from 10-20 nm to 1-2 nm. With decreasing layer thickness to 2-4 nm, the structure of the rare-earth oxides changes from monoclinic phase to hexagonal phase. There are great similarities on the structural properties between Gd$_2$O$_3$ and Y$_2$O$_3$. The discussion will, therefore, focus on Gd$_2$O$_3$. The structural characterizations were performed by high resolution X-ray diffraction (HRXRD) with synchrotron radiation.

Results and Discussion: The RHEED pattern of the starting GaN surface was a streaky reconstructed (2 × 2) along GaN <11\overline{2}0> and <1\overline{1}0\overline{1}0>, respectively. With the Gd$_2$O$_3$ thickness larger than 0.8 nm, the patterns turned to a streaky (1 × 1) and with the thickness increasing to >5 nm, a reconstructed (3 × 2) appeared, which remained unvaried all the way to 20 nm;\textsuperscript{28} The patterns remained streaky during the growth, indicating two-dimensional growth. From the systematic X-ray diffraction study as will be discussed later, the initial growth of Gd$_2$O$_3$ has yielded a hexagonal phase with surface normal (0001) and in-plane axes of Gd$_2$O$_3$ being parallel to the corresponding axes of GaN.

The X-ray diffraction scans along the surface normal of the Gd$_2$O$_3$ samples with different oxide thickness are shown in Fig. 1. The intense sharp peaks of GaN (0002), GaN (0004) and sapphire (0006) reflections are, respectively, centered at 2.0, 4.0, and 2.395 rlu$_{GaN}$, the reciprocal lattice unit of GaN along its c-axis with 1 rlu$_{GaN}$ = 2n/c$_{GaN}$ = 1.212 Å$^{-1}$. The oxide peaks are those with the periodic thickness fringes, which are caused by the interference between the X-rays reflected by the top surface and buried interface. The presence of the
The scans along surface normal alone would not provide the off-normal crystallographic information, which is needed for accurately determining the symmetry of the oxide films and the alignment between the oxides and the substrates. Lateral radial scans were thus performed along the GaN in-plane \(<1\bar{1}20>_{\mathrm{H}}\) direction, shown in Fig. 2. The measurements were performed in the grazing incidence diffraction geometry by keeping the surface normal almost perpendicular to the vertical scattering plane. For the Gd$_2$O$_3$ layers of thickness less than 4 nm, in addition to the narrow GaN \(<1\bar{1}20>\) reflection centered at 1 rlu$_{\text{GaN}}$, the reciprocal lattice unit of GaN along the lateral direction with the magnitude of $4\pi / (\sqrt{3}d_{\text{GaN}})$ = 2.274 Å$^{-1}$, a broad peak appears at 0.855 rlu$_{\text{GaN}}$. Both peaks exhibit 6-fold symmetry in azimuthal $\phi$ scans against the surface normal (not shown), revealing the hexagonal crystalline structure. The broad peak was indexed as the H-Gd$_2$O$_3$ \((1\bar{1}20)_{\mathrm{H}}\) reflection, which is aligned with the GaN \((1\bar{1}20)\) reflection. For the samples with Gd$_2$O$_3$ thickness greater than 4 nm, the oxide peak splits into two broad peaks, centered at 0.835 and 0.88 rlu$_{\text{GaN}}$, respectively. Even though their azimuthal scans also have 6 evenly spaced peaks, each peak further splits (not shown). The observed 6-fold symmetry and peak splitting can be accounted for by the coexistence of 6 rotational domains of M-Gd$_2$O$_3$ with \((201)_{\mathrm{M}}\) normal and each domain has its [020]$_{\mathrm{M}}$ axis aligned with one of the 6-fold symmetric GaN \(<1\bar{1}20>\) direction. The two peaks at 0.835 and 0.88 rlu$_{\text{GaN}}$ in Fig. 2 are indexed as \((3\pm 13)_{\mathrm{M}}\) and \((0\pm 20)_{\mathrm{M}}\), respectively.

To further verify the crystalline structure of the hetero-epitaxial system, we performed reciprocal space mapping (RSM) around Gd$_2$O$_3$ \((1\bar{1}01)_{\mathrm{H}}\) reflection in the GaN \(/h/\) plane. A clean oval-shape peak was obtained from the thin layers with thickness less than 4 nm, as illustrated in Fig. 3(a), (b) and (c), indicating that H-Gd$_2$O$_3$ possesses only one domain. The reduction in the profile elongation along the \(/\) direction reflects the increase of vertical structural coherence length associated with the increasing layer thickness. As the thickness increases beyond 4 nm, the peak profile gradually evolves into a cluster of 4 peaks. According to the model of \((\bar{2}01)_{\mathrm{M}}\) oriented M-Gd$_2$O$_3$ with six rotational domains, the four maxima in the RSM shown in Fig. 3(d), (e), and (f) are associated with the Gd$_2$O$_3$ \((40\bar{1})_{\mathrm{M}}, (3\pm 10)_{\mathrm{M}}, (\bar{1}\pm 12)_{\mathrm{M}}\) and \((003)_{\mathrm{M}}\) reflections, in the order of increasing \(/\) value, belonging to six different rotational domains. The evolution of the Gd$_2$O$_3$ reflection from a single maximum to four peaks in the RSM shown in Fig. 3 as the oxide thickness increases attest the structural transition from the hexagonal to the monoclinic phase and the critical thickness is...
By fitting the angular positions of many reflections, we derived the lattice parameters of the hexagonal phase to be \( a = b = 3.75 \text{ Å} \) and \( c = 5.94 \text{ Å} \), similar to the results of ab initio energetic calculations based on the density functional theory (DFT) and projector augmented wave (PAW) pseudo-potentials method. Similarly, the monoclinic phase lattice constants are determined to be \( a = 13.965 \text{ Å} \), \( b = 3.595 \text{ Å} \), \( c = 8.787 \text{ Å} \), and \( \beta = 101.34^\circ \). According to the phase diagram, bulk Gd\(_2\)O\(_3\) exists in three polymorphic forms: cubic (\( Ia\overline{3} \)), monoclinic (\( C2/m \)), and hexagonal (\( P\overline{3}m1 \)) at temperature below \( \sim 2500 \text{K} \) and the cubic phase with the bixbyite structure is the one stable at the ambient condition. Both the cubic and monoclinic phases have been reported existing at room temperatures. The hexagonal phase only exists at high pressure or high temperature. It is thus difficult to accurately determine the strain state of the hexagonal phase oxide layers because of the lack of ambient condition data to compare with. Nevertheless, the lattice parameters of H-Gd\(_2\)O\(_3\) layer remained practically unchanged and their values are close to the theoretical prediction, implying the lattice is nearly fully relaxed.

**Summary:** Gd\(_2\)O\(_3\) and Y\(_2\)O\(_3\) epi-layers on GaN (0001) have the hexagonal phase with their thickness less than a critical value \( t_c (3\sim4 \text{ nm}) \), as stabilized by epitaxy. The hexagonal to monoclinic phase transition occurs as thickness exceeds \( t_c \). The stabilization of the hexagonal phase at a few nm-thick with high thermal stability, a high dielectric constant, and a low interfacial density of states strongly favors the application of single crystal Gd\(_2\)O\(_3\) and Y\(_2\)O\(_3\) as gate dielectrics for advanced GaN MOS devices with low EOT.

**References:**


30. JCPDS cards (No 42-1465)

Fig. 1: XRD longitudinal scans along surface normal of samples with different Gd2O3 layer thickness.
Fig. 2: Intensity distributions of in-plane radial scans along GaN \([11\bar{2}0]_H\) direction for Gd$_2$O$_3$ samples with thickness from 1.5 to 20 nm.

Fig. 3: The 2D reciprocal space maps in the GaN /h/ plane near the Gd$_2$O$_3$ (10\overline{1}1)$_H$ reflection for the samples with a (a) 1.5 nm, (b) 2.2 nm, (c) 3.2 nm, (d) 4.3 nm, (e) 10 nm, and (f) 20 nm thick Gd$_2$O$_3$ epi-layer.
List of Publications:

Publications (SCI)


Conference presentations (Invited)


4. "Overview of III-V Activities at National Taiwan University", M. Hong and J. Kwo, T. J. Watson Research Center IBM, October 2, 2012


8. "50 years of research/development of oxides on InGaAs leading to ultimate CMOS", M. Hong, Institute of Physics, Academia Sinica, Taipei, November 27, 2012.


12. "Pushing the material limit and physics novelty in high k's/high carrier mobility

15. "Realization of III-V MOSFETs using High k Gate Dielectrics on InGaAs Semiconductors", J. Kwo and M. Hong, the 2013 Asia-Pacific Radio Science Conference (AP-RASC’13), Howard International House, Taipei, Taiwan, September 3-7, 2013.

16. "Pushing the ultimate CMOS and more – a physicist’s role”, Dept. Physics, National Chung Hsing University, Taichung, September 27, 2013.


Conference presentations (Contributed)


7. "DLTS Measurement for low midgap interfacial trap density in In₀.₅₃Ga₀.₄₇As MOSCAPs by in-situ atomic-layer-deposited HfO₂ passivation”, C. A. Lin (林俊安), M. C. Hsieh (謝孟謙), C. L. Tsai (蔡哲倫), Y. H. Chang (張宇行), T. D. Lin (林宗達), J. F. Chen (陳振芳), M. Hong (洪銘輝), and J. Kwo (郭瑞年), ROC Annual Physical Meeting, 中華民國物理學會年會,
National Dong-Hwa University, Hua-Lien, Taiwan, Jan. 29-31, 2013.

8. "Investigation of MBE-grown In$_{0.53}$Ga$_{0.47}$As (001) 4x2 surface and in-situ ALD TEMA-Hf dosed surface by STM", Y. C. Liu (劉有騏), M. L. Huang (黃懋霖), T. D. Lin (林宗達), Y. T. Liu (劉雅婷), W. C. Lee (李威縉), H. Y. Lin (林孝于), W. W. Pai (白偉武), M. Hong (洪銘輝), and J. Kwo (郭瑞年), ROC Annual Physical Meeting, 中華民國物理學會年會, National Dong-Hwa University, Hua-Lien, Taiwan, Jan. 29-31, 2013.


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