

# Heteroepitaxy of $\text{La}_2\text{O}_3$ and $\text{La}_{2-x}\text{Y}_x\text{O}_3$ on GaAs (111)A by Atomic Layer Deposition: Achieving Low Interface Trap Density

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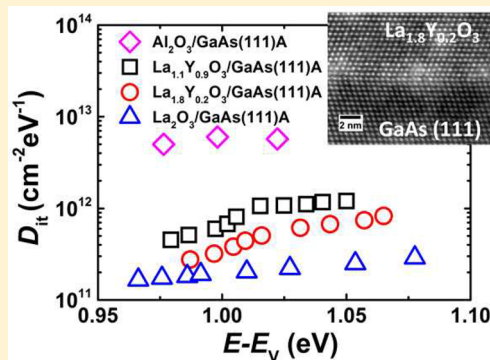
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**S** Supporting Information

**ABSTRACT:** GaAs metal–oxide–semiconductor devices historically suffer from Fermi-level pinning, which is mainly due to the high trap density of states at the oxide/GaAs interface. In this work, we present a new way of passivating the interface trap states by growing an epitaxial layer of high- $k$  dielectric oxide,  $\text{La}_{2-x}\text{Y}_x\text{O}_3$ , on GaAs(111)A. High-quality epitaxial  $\text{La}_{2-x}\text{Y}_x\text{O}_3$  thin films are achieved by an ex situ atomic layer deposition (ALD) process, and GaAs MOS capacitors made from this epitaxial structure show very good interface quality with small frequency dispersion and low interface trap densities ( $D_{it}$ ). In particular, the  $\text{La}_2\text{O}_3/\text{GaAs}$  interface, which has a lattice mismatch of only 0.04%, shows very low  $D_{it}$  in the GaAs bandgap, below  $3 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$  near the conduction band edge. The  $\text{La}_2\text{O}_3/\text{GaAs}$  capacitors also show the lowest frequency dispersion of any dielectric on GaAs. This is the first achievement of such low trap densities for oxides on GaAs.

**KEYWORDS:** Epitaxy, thin films, field-effect transistors, gallium arsenide



High-mobility InGaAs metal–oxide–semiconductor field-effect transistors (MOSFETs) have shown promising performance compared to Si-based devices for high-speed complementary MOS (CMOS) logic applications. However, GaAs MOS devices suffer from Fermi-level pinning, which is mainly due to the high trap density of states at the oxide/GaAs interface.<sup>1,2</sup> In this work, we present a new way of passivating the interface trap states by growing an epitaxial layer of high- $k$  dielectric oxide,  $\text{La}_{2-x}\text{Y}_x\text{O}_3$ , on GaAs(111)A, which effectively reduces the trap density and minimizes the frequency dispersion of capacitance.

For GaAs MOS structures, usually the dielectric oxide is either amorphous or polycrystalline, and therefore a high density of dangling bonds exists at the oxide/GaAs interface. These dangling bonds form interface states in the midgap,<sup>3</sup> which trap carriers and produce a large frequency dispersion of capacitance and Fermi-level pinning. GaAs MOS devices with epitaxial dielectric layers should have a low interface trap density of states ( $D_{it}$ ), since a perfect epitaxial interface is supposed to have no dangling bonds. Also, contrary to polycrystalline oxides, a perfect epitaxial oxide should contain no grain boundaries,<sup>4</sup> which preserves the desired features of the low leakage current and uniformity. However, growing epitaxial oxides on GaAs is rather challenging, since GaAs is neither chemically stable nor thermally stable. GaAs can be oxidized easily to form low quality surface oxides that compromise the interface quality,<sup>5</sup> and GaAs starts to lose As over 400 °C.<sup>6</sup> Hong et al.<sup>7,8</sup> have demonstrated a method of using in situ electron beam evaporation to grow epitaxial

(Ga,Gd)<sub>2</sub>O<sub>3</sub> or Gd<sub>2</sub>O<sub>3</sub> layers on GaAs(100) with the epitaxial relationships  $(110)_{\text{Gd}_2\text{O}_3} // (100)_{\text{GaAs}}$ ,  $[001]_{\text{Gd}_2\text{O}_3} // [011]_{\text{GaAs}}$ , and  $[\bar{1}10]_{\text{Gd}_2\text{O}_3} // [01\bar{1}]_{\text{GaAs}}$ . Their capacitance–voltage measurements do show a significant decrease in  $D_{it}$ ,<sup>8</sup> which suggests the importance of epitaxy in reducing interfacial defects.<sup>9</sup> However, the frequency dispersion of the capacitance was still fairly large,<sup>8</sup> and the drive current of the inversion-mode MOSFETs made from (Ga,Gd)<sub>2</sub>O<sub>3</sub>/GaAs was less than 1 mA/mm.<sup>10</sup> This may be due to the relatively large in-plane mismatch between Gd<sub>2</sub>O<sub>3</sub> and GaAs (1.9 and –3.9% in the [011] and [01 $\bar{1}$ ] directions of GaAs, respectively). Getting MOSFETs even of this quality also requires that there is no air-break between growth of the GaAs and the oxide, so that complex multichamber MBE systems are necessary. Several follow-up structural analyses of Gd<sub>2</sub>O<sub>3</sub>/GaAs(100)<sup>11–13</sup> revealed that perfect strained epitaxy only occurs in the first few layers. When the oxide film thickness exceeds ~3 nm, the Gd<sub>2</sub>O<sub>3</sub> film starts to relax by generating misfit dislocations, so that the film is no longer perfectly epitaxial.<sup>8</sup> Unfortunately, simply substituting Gd<sub>2</sub>O<sub>3</sub> with other lanthanide sesquioxides cannot accommodate the mismatch simultaneously in two orthogonal in-plane directions, since the in-plane lattice spacing of Gd<sub>2</sub>O<sub>3</sub> is greater than GaAs in one direction but smaller in the other. Very recently, epitaxial growth of cubic high- $k$  oxide,

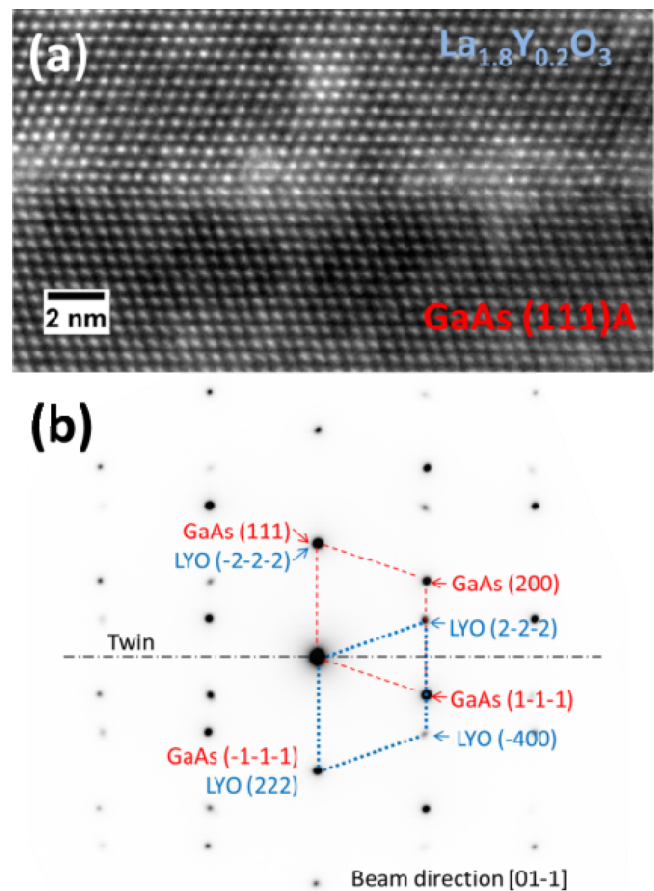
Received: November 8, 2012

Revised: December 15, 2012

LaLuO<sub>3</sub> on GaAs(111)A has been achieved by an ex situ atomic layer deposition (ALD) process in our group.<sup>14</sup> The heteroepitaxial relationship was found to be (111)<sub>LaLuO<sub>3</sub></sub>//(111)<sub>GaAs</sub> ( $a_{\text{LaLuO}_3} \approx 2a_{\text{GaAs}}$ ) with a relaxed interface.<sup>14</sup> Since the (111) plane has a 3-fold symmetry, the in-plane mismatch between oxide and GaAs can be simultaneously engineered with lanthanide sesquioxides that have appropriate cation sizes. Initial electrical characterizations showed quite promising results, as the MOS capacitors made from epitaxial ALD LaLuO<sub>3</sub>/GaAs showed an order of magnitude reduction in interface trap density ( $D_{\text{it}} \sim 7 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ ) compared with amorphous ALD Al<sub>2</sub>O<sub>3</sub>/GaAs ( $\sim 8 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ ).<sup>14</sup> But, still LaLuO<sub>3</sub> has a fairly large lattice mismatch with respect to GaAs (-3.8%), and another concern is that Lu is one of the rarest elements on earth, which would be problematic for large scale fabrication.

In this work, we report an ALD process for depositing another high-*k* oxide, La<sub>2-x</sub>Y<sub>x</sub>O<sub>3</sub>, epitaxially on GaAs(111)A. The *k*-value of La<sub>2-x</sub>Y<sub>x</sub>O<sub>3</sub> was reported as high as 27,<sup>15</sup> and the terrestrial elemental abundance of Y is much higher than Lu. The ternary oxide, La<sub>2-x</sub>Y<sub>x</sub>O<sub>3</sub>, can be considered as a mixture of La<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub>. The lattice constant of cubic La<sub>2</sub>O<sub>3</sub> is very slightly larger than 2 times the GaAs lattice constant, while the lattice constant of cubic Y<sub>2</sub>O<sub>3</sub> is ~6% smaller than that of La<sub>2</sub>O<sub>3</sub>. Therefore, we can adjust the lattice constant of the ternary compound, La<sub>2-x</sub>Y<sub>x</sub>O<sub>3</sub>, to study the effect of mismatch by varying the ratio of La and Y. As an ALD process grows films in a layer-by-layer manner, the compositional ratio of these two cations can be tuned by varying the ratio of La<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> cycles. A high-resolution X-ray structural analysis indicates a high-quality heteroepitaxy of La<sub>2-x</sub>Y<sub>x</sub>O<sub>3</sub> on GaAs(111)A. Electrical measurements on MOS capacitors show a promisingly small frequency dispersion of capacitance and a low  $D_{\text{it}} \sim 2 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$  in the GaAs bandgap close to the conduction band edge. In addition, our process tolerates an air-break between growth of the GaAs and ALD of the epitaxial oxide. ALD is known to produce uniform films over large areas with good reproducibility,<sup>16</sup> so we believe that this process is very promising for large scale manufacturing.

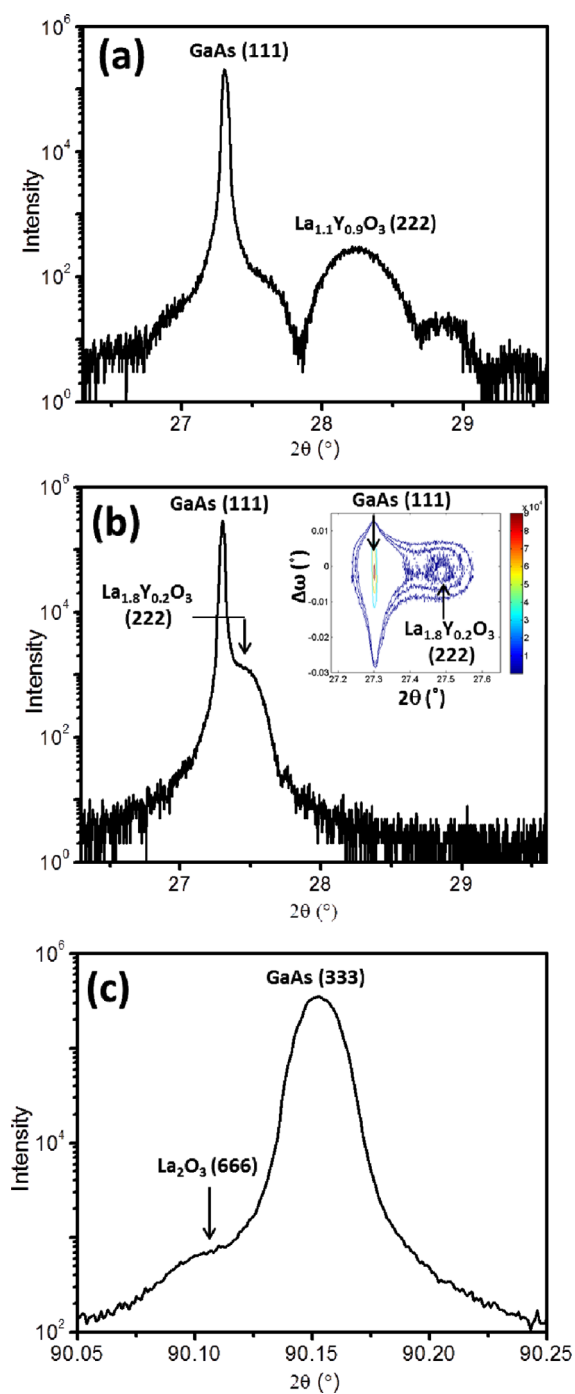
La<sub>2-x</sub>Y<sub>x</sub>O<sub>3</sub> films were grown by ALD from precursors including lanthanum tris(*N,N'*-diisopropylformamidate), yttrium tris(*N,N'*-diisopropylacetamidate) and H<sub>2</sub>O in a home-built tube reactor. In particular, pure La<sub>2</sub>O<sub>3</sub> or pure Y<sub>2</sub>O<sub>3</sub> films can be made by using the corresponding single metal precursor source. When films were deposited on amorphous SiN<sub>x</sub> substrates, the as-deposited pure La<sub>2</sub>O<sub>3</sub> and pure Y<sub>2</sub>O<sub>3</sub> films were polycrystalline in their cubic phases, respectively. But alloying these two oxides did not form a polycrystalline film on amorphous SiN<sub>x</sub>, on which the La<sub>1.1</sub>Y<sub>0.9</sub>O<sub>3</sub> film was almost amorphous (Supporting Information Figure S1). However, when La<sub>2-x</sub>Y<sub>x</sub>O<sub>3</sub> films were grown on GaAs (111)A, the as-deposited films, including La<sub>2</sub>O<sub>3</sub>, La<sub>1.8</sub>Y<sub>0.2</sub>O<sub>3</sub>, La<sub>1.1</sub>Y<sub>0.9</sub>O<sub>3</sub>, and Y<sub>2</sub>O<sub>3</sub> were all well crystallized and, in fact, they were highly epitaxial due to induction by the substrates. Cross-sectional transmission electron microscopy (TEM) of La<sub>2-x</sub>Y<sub>x</sub>O<sub>3</sub>/GaAs interfaces indicates a cube-on-cube epitaxy with a twin boundary relation at the interface, and the interface is atomically abrupt with no interlayer. A representative TEM image of a La<sub>1.8</sub>Y<sub>0.2</sub>O<sub>3</sub>/GaAs(111)A sample is shown in Figure 1a. The twin boundary relation at the oxide/GaAs was also confirmed by the selective area electron diffraction pattern as shown in Figure 1b, where the two sets of diffraction patterns



**Figure 1.** (a) Cross-sectional TEM image of La<sub>1.8</sub>Y<sub>0.2</sub>O<sub>3</sub>/GaAs(111)A interface, and (b) the corresponding electron diffraction pattern with the electron beam aligned along the [011] direction of GaAs. (“La<sub>1.8</sub>Y<sub>0.2</sub>O<sub>3</sub>” is labeled as “LYO” in the diffraction pattern.).

belonging to cubic-phase La<sub>1.8</sub>Y<sub>0.2</sub>O<sub>3</sub> and GaAs are well aligned vertically. In particular, the diffraction spot of GaAs (111) overlaps with the La<sub>1.8</sub>Y<sub>0.2</sub>O<sub>3</sub> (222) spot, suggesting that the cubic lattice constant of La<sub>1.8</sub>Y<sub>0.2</sub>O<sub>3</sub> is very close to twice that of GaAs. However, TEM does not have enough resolution to determine precisely the small difference between their lattice constants. Therefore, high-resolution X-ray diffraction (HRXRD) was used to investigate the detailed epitaxial structures.

Coupled  $2\theta$ - $\omega$  HRXRD scans were performed for the oxide/GaAs(111)A samples. The peaks from the GaAs substrate were used as the internal references, and the oxide/GaAs lattice mismatch, which is defined as  $(a_{\text{oxide}} - 2a_{\text{GaAs}})/2a_{\text{GaAs}}$ , was calculated from the relative shift of the oxide peak with respect to the GaAs peak, assuming a fully relaxed heteroepitaxy relation at the interface.<sup>14</sup> For the La<sub>1.1</sub>Y<sub>0.9</sub>O<sub>3</sub>/GaAs sample, the coupled  $2\theta$ - $\omega$  scan clearly shows both peaks of the GaAs(111) and La<sub>1.1</sub>Y<sub>0.9</sub>O<sub>3</sub>(222) reflections, as shown in Figure 2a. The corresponding  $\omega$  rocking curves of GaAs(111) and La<sub>1.1</sub>Y<sub>0.9</sub>O<sub>3</sub>(222) reflections have a similar shape with the same full width at half-maximum of  $\sim 32^\circ$  (Supporting Information Figure S3). This indicates a high quality heteroepitaxy of La<sub>1.1</sub>Y<sub>0.9</sub>O<sub>3</sub>/GaAs over a large area (several mm<sup>2</sup>). The  $2\theta$  angle of the La<sub>1.1</sub>Y<sub>0.9</sub>O<sub>3</sub> (222) peak was found to be  $0.958^\circ$  greater than that of the GaAs(111) peak, which corresponds to a lattice mismatch of  $-3.32\%$  for La<sub>1.1</sub>Y<sub>0.9</sub>O<sub>3</sub> with respect to GaAs. For the La<sub>1.8</sub>Y<sub>0.2</sub>O<sub>3</sub>/GaAs sample, the



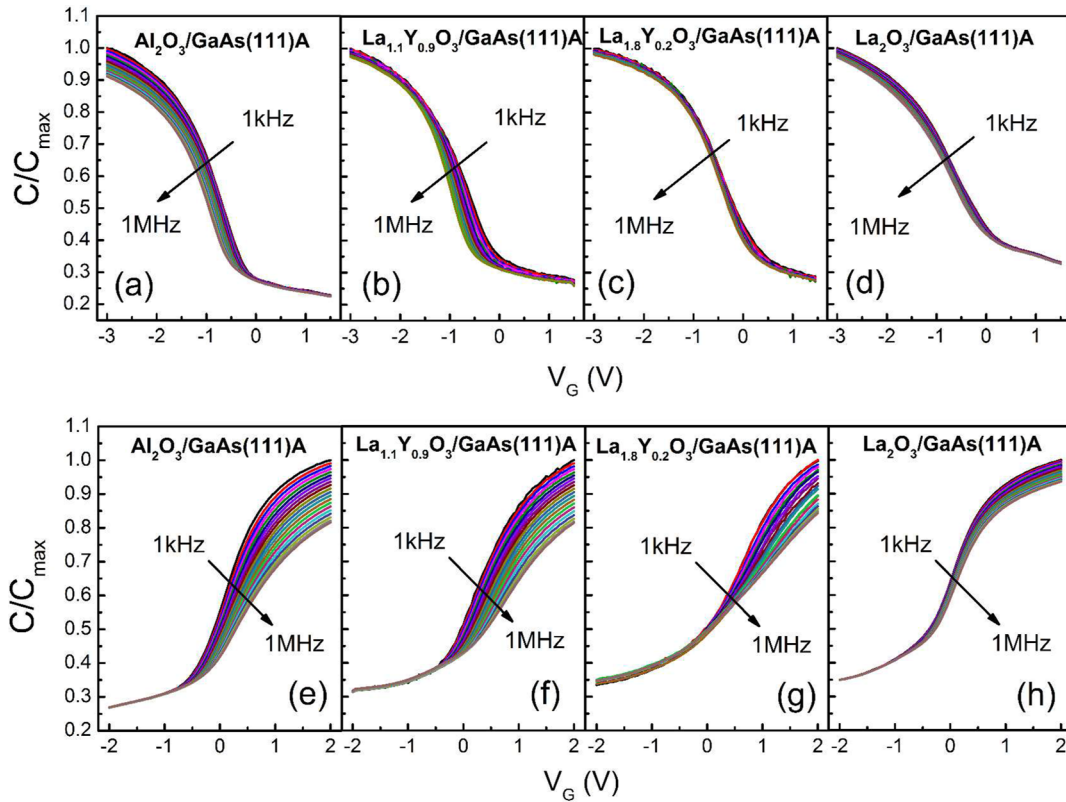
**Figure 2.** HRXRD coupled  $2\theta$ - $\omega$  scans of (a)  $\text{La}_{1.1}\text{Y}_{0.9}\text{O}_3$ , (b)  $\text{La}_{1.8}\text{Y}_{0.2}\text{O}_3$ , and (c)  $\text{La}_2\text{O}_3$  on GaAs(111)A. The scans of (a) and (b) were performed around the GaAs (111) reflection, and the scan of (c) was performed around the GaAs (333) reflection. The inset of (b) shows the  $2\theta$ - $\Delta\omega$  reciprocal space map around the GaAs(111) peak for the  $\text{La}_{1.8}\text{Y}_{0.2}\text{O}_3/\text{GaAs}$  sample.

$2\theta$ - $\omega$  scan (Figure 2b) shows that the peaks of GaAs(111) and  $\text{La}_{1.8}\text{Y}_{0.2}\text{O}_3$ (222) are much closer, indicating  $\text{La}_{1.8}\text{Y}_{0.2}\text{O}_3$  has a smaller lattice mismatch to GaAs. Thus, we performed a  $2\theta$ - $\Delta\omega$  reciprocal space mapping (RSM) on this sample, and the RSM contour is plotted in the inset of Figure 2b, where the contour levels are chosen to highlight the peaks. The  $2\theta$  angle of the  $\text{La}_{1.8}\text{Y}_{0.2}\text{O}_3$  (222) peak was found to shift by  $+0.18^\circ$  from the GaAs(111) peak, indicating a lattice mismatch of  $-0.64\%$

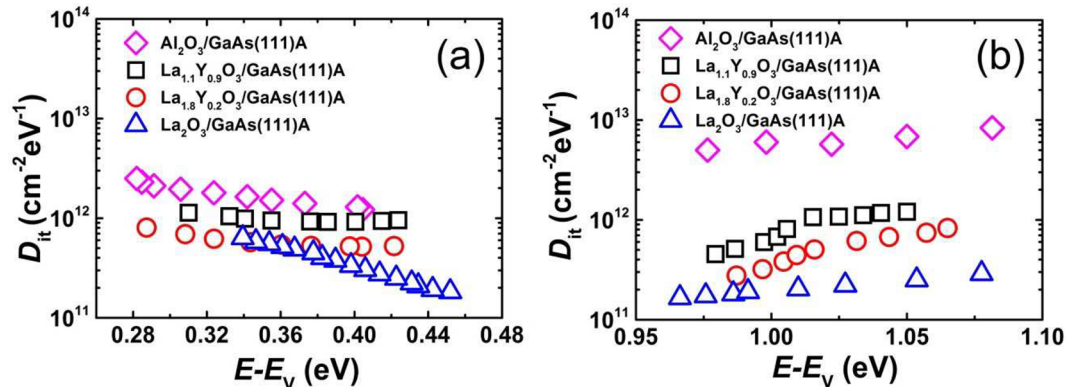
for  $\text{La}_{1.8}\text{Y}_{0.2}\text{O}_3$  with respect to GaAs. As for the  $\text{La}_2\text{O}_3/\text{GaAs}$  sample, the peaks of GaAs(111) and  $\text{La}_2\text{O}_3$ (222) in the  $2\theta$ - $\omega$  scan were found to be entirely overlapping with each other (Supporting Information Figure S4). Therefore, we performed another  $2\theta$ - $\omega$  scan around the GaAs(333) reflection to determine the mismatch with greater sensitivity. As shown in Figure 2c, the  $2\theta$  angle of the  $\text{La}_2\text{O}_3$ (666) peak was only  $\sim 0.046^\circ$  smaller than that of the GaAs(333) peak, suggesting a much smaller lattice mismatch of only  $+0.04\%$  for  $\text{La}_2\text{O}_3$  with respect to GaAs.

In summary of the above structural analysis, both of the TEM and HRXRD results suggested a high-quality heteroepitaxy relation of  $\text{La}_{2-x}\text{Y}_x\text{O}_3/\text{GaAs}(111)\text{A}$  ( $x = 0, 0.2$ , and  $0.9$ ) with smaller lattice mismatch for higher La-content oxide. The measured lattice mismatch approximately follows Vegard's law (Supporting Information Figure S6). In addition, we also found that pure  $\text{Y}_2\text{O}_3$  on GaAs(111)A is also epitaxial (Supporting Information Figure S5). Therefore we believe that epitaxy can be achieved for mixed  $\text{La}_{2-x}\text{Y}_x\text{O}_3$  oxides with any La/Y ratio. This epitaxial relation is quite similar to the  $\text{LaLuO}_3/\text{GaAs}(111)\text{A}$  case, where the  $\text{LaLuO}_3$  film was grown by a similar ALD process in our lab.<sup>14</sup>

Since epitaxial  $\text{La}_{2-x}\text{Y}_x\text{O}_3/\text{GaAs}$  structures are expected to provide a better interface quality with a lower interface trap density for electrical devices, we fabricated the corresponding  $\text{La}_{2-x}\text{Y}_x\text{O}_3/\text{GaAs}$  MOS capacitors to examine the electrical properties. Both p-type and n-type MOS capacitors of  $\text{La}_{2-x}\text{Y}_x\text{O}_3/\text{GaAs}(111)\text{A}$  ( $x = 0, 0.2$  and  $0.9$ ) were fabricated and characterized by capacitance-voltage ( $C$ - $V$ ) and conductance-voltage ( $G$ - $V$ ) methods. Due to the hygroscopic nature of  $\text{La}_{2-x}\text{Y}_x\text{O}_3$ , an in situ ALD capping layer of  $6.5$  nm  $\text{Al}_2\text{O}_3$  was deposited right after the deposition of  $\text{La}_{2-x}\text{Y}_x\text{O}_3$  on GaAs(111)A. Capacitors with only amorphous ALD  $\text{Al}_2\text{O}_3$  as the dielectric material ( $\text{Al}_2\text{O}_3/\text{GaAs}(111)\text{A}$ ) were also fabricated for comparison. The  $C$ - $V$  response was measured at room temperature with the frequency of the small AC signal ranging from  $1$  kHz to  $1$  MHz. Figure 3 shows the normalized  $C$ - $V$  curves measured on these capacitors. A general trend for the frequency dispersion is that the capacitors with amorphous  $\text{Al}_2\text{O}_3$  dielectric show the largest frequency dispersions compared with the capacitors with epitaxial  $\text{La}_{2-x}\text{Y}_x\text{O}_3$  dielectric. Among these  $\text{La}_{2-x}\text{Y}_x\text{O}_3$  capacitors, those with smaller lattice-mismatch  $\text{La}_{2-x}\text{Y}_x\text{O}_3$  (higher La content) show smaller frequency dispersion. For p-type GaAs MOS capacitors, the frequency dispersion in the accumulation region ( $\Delta C/C_{\text{max}}$ ) is reduced from  $7.6$  to  $\sim 2\%$  by replacing the amorphous  $\text{Al}_2\text{O}_3$  with epitaxial  $\text{La}_{2-x}\text{Y}_x\text{O}_3$  as the dielectric ( $2.5, 1.9$ , and  $2.6\%$  for  $x = 0.9, 0.2$  and  $0$ , respectively), and with a better lattice-matched oxide,  $\text{La}_2\text{O}_3$ , the dispersion in the depletion region ( $V_G \sim 0$ ) is further reduced. A similar trend was also observed for the n-type GaAs MOS capacitors:  $\text{Al}_2\text{O}_3$  shows the largest frequency dispersion of  $19.0\%$  in the accumulation region, and  $\text{La}_{1.1}\text{Y}_{0.9}\text{O}_3$ ,  $\text{La}_{1.8}\text{Y}_{0.2}\text{O}_3$ , and  $\text{La}_2\text{O}_3$  show decreasing frequency dispersions of  $18.6, 15.6$ , and  $9.9\%$ , respectively. We also measured the  $D_{\text{it}}$  by the conductance-voltage method (Supporting Information Figure S7).<sup>17</sup> The distribution of  $D_{\text{it}}$  within the GaAs band gap is plotted in Figure 4. Consistent with the  $C$ - $V$  results, the interface of the amorphous  $\text{Al}_2\text{O}_3/\text{GaAs}$  showed much larger interface trap density compared to the epitaxial  $\text{La}_{2-x}\text{Y}_x\text{O}_3/\text{GaAs}$  interfaces. Among these epitaxial  $\text{La}_{2-x}\text{Y}_x\text{O}_3/\text{GaAs}$  devices, the  $\text{La}_2\text{O}_3/\text{GaAs}$  capacitor with a lattice-almost-matched interface showed the smallest  $D_{\text{it}}$  on the order of  $10^{11}$   $\text{cm}^{-2}$   $\text{eV}^{-1}$ , and in particular the interface trap



**Figure 3.**  $C-V$  characteristics of p-type and n-type GaAs MOS capacitors with stacks of (a,e) Ni/8 nm  $\text{Al}_2\text{O}_3/\text{GaAs}(111)\text{A}$ , (b,f) Ni/6.5 nm  $\text{Al}_2\text{O}_3/7.5$  nm  $\text{La}_{1.1}\text{Y}_{0.9}\text{O}_3/\text{GaAs}(111)\text{A}$ , (c,g) Ni/6.5 nm  $\text{Al}_2\text{O}_3/7.5$  nm  $\text{La}_{1.8}\text{Y}_{0.2}\text{O}_3/\text{GaAs}(111)\text{A}$ , and (d,h) Ni/6.5 nm  $\text{Al}_2\text{O}_3/9$  nm  $\text{La}_2\text{O}_3/\text{GaAs}(111)\text{A}$ , respectively.



**Figure 4.**  $D_{it}$  distribution in the GaAs band gap obtained on both (a) p-type and (b) n-type MOS capacitors with  $\text{Al}_2\text{O}_3/\text{GaAs}(111)\text{A}$ ,  $\text{La}_{1.1}\text{Y}_{0.9}\text{O}_3/\text{GaAs}(111)\text{A}$ ,  $\text{La}_{1.8}\text{Y}_{0.2}\text{O}_3/\text{GaAs}(111)\text{A}$  and  $\text{La}_2\text{O}_3/\text{GaAs}(111)\text{A}$  as the interfaces, respectively.

density in the upper half of the band gap is below  $3 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$  in the whole region measured. Notice that typically the  $D_{it}$  close to the conduction band edge is quite high for other oxides on GaAs, and those traps severely pin the Fermi level. The traps hinder the Fermi level from moving away from the center of the bandgap up to the conduction band edge, preventing the realization of high-performance inversion-mode GaAs MOSFETs. With a lattice-matched  $\text{La}_2\text{O}_3$  dielectric layer, a very good interface with low trap density was achieved. The decreasing trend of  $D_{it}$  with smaller lattice mismatch indicates the importance of matching the lattice constant of the oxide with GaAs. In addition, the  $k$ -values of  $\text{La}_{1.1}\text{Y}_{0.9}\text{O}_3$ ,  $\text{La}_{1.8}\text{Y}_{0.2}\text{O}_3$ , and  $\text{La}_2\text{O}_3$  were estimated from the capacitance to be 20, 22, and 16, respectively. The above excellent electrical results show

that the epitaxial  $\text{La}_{2-x}\text{Y}_x\text{O}_3$  is a very promising gate dielectric candidate material for future high-performance GaAs MOS devices. In addition, we believe that the strategy of using epitaxial dielectrics can also be extended to other substrate material systems, such as Ge, InP, and InGaAs.<sup>18</sup>

**Conclusions.** In this letter, we demonstrated an ex situ ALD process for growing epitaxial  $\text{La}_{2-x}\text{Y}_x\text{O}_3$  on GaAs(111)A. High-quality epitaxy of  $\text{La}_{2-x}\text{Y}_x\text{O}_3/\text{GaAs}(111)\text{A}$  was achieved for  $x = 0$  (i.e., pure  $\text{La}_2\text{O}_3$ ), 0.2, and 0.9. GaAs MOS capacitors made from this epitaxial structure showed very good interface quality with small frequency dispersion and low interface trap densities. In particular, the  $\text{La}_2\text{O}_3/\text{GaAs}$  interface, which has a lattice mismatch of only 0.04%, showed very low  $D_{it}$  in the GaAs bandgap, below  $3 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$  near the conduction band

edge. The  $\text{La}_2\text{O}_3/\text{GaAs}$  capacitors also showed the lowest frequency dispersion of any dielectric on GaAs. This is the first achievement of such low trap densities for oxides on GaAs. We believe that these new results will expand the nearly 50 year research on the oxide/GaAs interface to an unprecedented level.

**Methods.**  $\text{La}_2\text{O}_3$  and  $\text{La}_{2-x}\text{Y}_x\text{O}_3$  films were grown by ALD from precursors including lanthanum tris( $N,N'$ -diisopropylformamidate), yttrium tris( $N,N'$ -diisopropylacetamidate), and  $\text{H}_2\text{O}$  in a home-built tube reactor. The pure  $\text{La}_2\text{O}_3$  films were deposited by alternately supplying the La precursor vapor and water at a deposition temperature of 385 °C, and the ternary  $\text{La}_{2-x}\text{Y}_x\text{O}_3$  oxides were deposited by repeatedly growing one or multiple cycles of  $\text{La}_2\text{O}_3$  followed by one or multiple cycles of  $\text{Y}_2\text{O}_3$  at 300 °C. Details of these ALD processes can be found in our previous publications.<sup>19,20</sup> The exposures of the La and Y precursors were estimated to be 0.003 Torr s and the exposure of  $\text{H}_2\text{O}$  was 0.06 Torr s in each cycle. After each  $\text{H}_2\text{O}$  pulse, the chamber was purged under nitrogen flowing for 80 s to minimize the amount of water and/or hydroxyl groups trapped in the oxide films,<sup>21</sup> as they considerably degrade the crystallinity and permittivity and cause large frequency dispersion.<sup>15</sup> By controlling the cycle ratio of  $\text{La}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ , the elemental composition of the ternary oxide  $\text{La}_{2-x}\text{Y}_x\text{O}_3$  (i.e.,  $x$ ) can be tuned. In this Letter, two cycle ratios of  $(\text{La}/\text{Y})_{\text{cyc}} = 1:3$  and  $3:1$  were used, and their compositional ratios, which were determined by Rutherford backscattering spectroscopy, were  $(\text{La}/\text{Y})_{\text{comp}} = 1.1:0.9$  and  $1.8:0.2$ , respectively. Before depositing  $\text{La}_{2-x}\text{Y}_x\text{O}_3$  on the GaAs(111)A substrates, all the GaAs substrates were first dipped into a 3 M HCl solution to remove the native oxide and then soaked in a 10%  $(\text{NH}_4)_2\text{S}$  solution for 20 min for sulfur-passivation. Cross-sectional TEM images were taken with JEOL 2100. HRXRD spectra were taken by a Bruker D8 HRXRD with the incident beam  $\text{Cu K}\alpha 1$  being monochromated by a Ge (022)  $\times 4$  asymmetric monochromator. Because of the hygroscopic nature of  $\text{La}_{2-x}\text{Y}_x\text{O}_3$ , all the films for HRXRD analysis were capped by a 6 nm in situ ALD  $\text{Al}_2\text{O}_3$  layer before being taken out from the deposition chamber. For characterizing the electrical properties, n-type and p-type GaAs(111)A wafers with doping concentration of  $5\text{--}7 \times 10^{17} \text{ cm}^{-3}$  were used as the substrates. To fabricate MOS capacitors, either 7.5 nm  $\text{La}_{2-x}\text{Y}_x\text{O}_3$  (for  $x = 0.9$  and  $0.2$ ) or 9 nm  $\text{La}_2\text{O}_3$  was first deposited on the GaAs substrates, and then an in situ ALD layer of 6.5 nm  $\text{Al}_2\text{O}_3$  was deposited on top to prevent the hygroscopic  $\text{La}_{2-x}\text{Y}_x\text{O}_3$  from being exposed to air. All the  $\text{La}_{2-x}\text{Y}_x\text{O}_3/\text{GaAs}$  capacitors were subjected to rapid thermal annealing (RTA) at 800 °C for 30 s in  $\text{N}_2$  ambient. Capacitors with amorphous ALD  $\text{Al}_2\text{O}_3$  as the dielectric material (Ni/8 nm  $\text{Al}_2\text{O}_3/\text{GaAs}(111)\text{A}$ ) were fabricated for comparison. The  $\text{Al}_2\text{O}_3/\text{GaAs}(111)\text{A}$  capacitors were subjected to RTA at 600 °C for 30 s in  $\text{N}_2$  ambient. Ni/Au circular electrodes for MOS capacitors were patterned by a lift-off process with a diameter of 150  $\mu\text{m}$ . The capacitance–voltage/conductance–voltage measurements were carried out at room temperature by using an HP4284A precision LCR meter with frequency varying from 1 kHz to 1 MHz.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

TEM images and electron diffraction patterns for  $\text{La}_{2-x}\text{Y}_x\text{O}_3$  deposited on amorphous  $\text{SiN}_x$ , schematic illustration of  $\text{La}_{2-x}\text{Y}_x\text{O}_3/\text{GaAs}$  lattice overlay, additional HRXRD scans

including  $\omega$  rocking scans for  $\text{La}_{1.1}\text{Y}_{0.9}\text{O}_3$ , coupled  $2\theta\text{--}\omega$  scans for  $\text{La}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ , Vegard's law plot, frequency-dependent conductance–voltage plots and an extended  $D_{\text{it}}$  plot of  $\text{La}_{1.8}\text{Y}_{0.2}\text{O}_3/\text{GaAs}$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The lanthanum and yttrium amidinate precursors were supplied by the Dow Chemical Company. This work was performed in part at Harvard University's Center for Nanoscale Systems (CNS), a member of the National Nanotechnology Infrastructure Network (NNIN). The work at Purdue University is partly supported by the Air Force Office for Scientific Research (AFOSR), monitored by Dr. James C. M. Hwang.

## ■ REFERENCES

- (1) *Fundamentals of III-V Semiconductor MOSFETs*; Oktyabrsky, S., Ye, P. D., Eds.; Springer: New York, 2010.
- (2) del Alamo, J. A. *Nature* **2011**, *479* (7373), 317–323.
- (3) Wang, W. C.; Xiong, K.; Wallace, R. M.; Cho, K. J. *Phys. Chem. C* **2010**, *114* (51), 22610–22618.
- (4) Shubhakar, K.; Pey, K. L.; Kushvaha, S. S.; O'Shea, S. J.; Raghavan, N.; Bosman, M.; Kouda, M.; Kakushima, K.; Iwai, H. *Appl. Phys. Lett.* **2011**, *98*, 7.
- (5) Hinkle, C. L.; Milojevic, M.; Brennan, B.; Sonnet, A. M.; Aguirre-Tostado, F. S.; Hughes, G. J.; Vogel, E. M.; Wallace, R. M. *Appl. Phys. Lett.* **2009**, *94*, 16.
- (6) Tsao, J. Y.; Brennan, T. M.; Klem, J. F.; Hammons, B. E. *J. Vac. Sci. Technol., A* **1989**, *7* (3), 2138–2142.
- (7) Hong, M.; Passlack, M.; Mannaerts, J. P.; Kwo, J.; Chu, S. N. G.; Moriya, N.; Hou, S. Y.; Fratello, V. J. *J. Vac. Sci. Technol., B* **1996**, *14* (3), 2297–2300.
- (8) Hong, M.; Kwo, J.; Kortan, A. R.; Mannaerts, J. P.; Sergent, A. M. *Science* **1999**, *283* (5409), 1897–1900.
- (9) Hill, R. J. W.; Moran, D. A. J.; Xu, L.; Haiping, Z.; Macintyre, D.; Thoms, S.; Asenov, A.; Zurcher, P.; Rajagopalan, K.; Abrokwhah, J.; Droopad, R.; Passlack, M.; Thyne, I. G. *IEEE Electron Device Lett.* **2007**, *28* (12), 1080–1082.
- (10) Ren, F.; Hong, M.; Hobson, W. S.; Kuo, J. M.; Lothian, J. R.; Mannaerts, J. P.; Kwo, J.; Chu, S. N. G.; Chen, Y. K.; Cho, A. Y. *Solid-State Electron.* **1997**, *41* (11), 1751–1753.
- (11) Sowwan, M.; Yacoby, Y.; Pitney, J.; MacHarrie, R.; Hong, M.; Cross, J.; Walko, D. A.; Clarke, R.; Pindak, R.; Stern, E. A. *Phys. Rev. B* **2002**, *66*, 20.
- (12) Kortan, A. R.; Hong, M.; Kwo, J.; Mannaerts, J. P.; Krajewski, J. J.; Kopylov, N.; Steiner, C.; Bolliger, B.; Erbudak, M. *J. Vac. Sci. Technol., B* **2001**, *19* (4), 1434–1438.
- (13) Hong, M.; Lu, Z. H.; Kwo, J.; Kortan, A. R.; Mannaerts, J. P.; Krajewski, J. J.; Hsieh, K. C.; Chou, L. J.; Cheng, K. Y. *Appl. Phys. Lett.* **2000**, *76* (3), 312–314.
- (14) Liu, Y.; Xu, M.; Heo, J.; Ye, P. D.; Gordon, R. G. *Appl. Phys. Lett.* **2010**, *97*, 16.
- (15) Zhao, Y.; Kita, K.; Kyuno, K.; Toriumi, A. *Appl. Phys. Lett.* **2006**, *89*, 25.

- (16) Kessels, W. M. M.; Putkonen, M. *MRS Bull.* **2011**, *36* (11), 907–913.
- (17) Lin, D.; Brammertz, G.; Sioncke, S.; Fleischmann, C.; Delabie, A.; Martens, K.; Bender, H.; Conard, T.; Tseng, W. H.; Lin, J. C.; Wang, W. E.; Temst, K.; Vatomme, A.; Mitard, J.; Caymax, M.; Meuris, M.; Heyns, M.; Hoffmann, T. *IEEE Int. Electron. Dev. Mtg. Tech. Dig.* **2009**, 1–4.
- (18) Urabe, Y.; Miyata, N.; Ishii, H.; Itatani, T.; Maeda, T.; Yasuda, T.; Yamada, H.; Fukuhara, N.; Hata, M.; Yokoyama, M.; Taoka, N.; Takenaka, M.; Takagi, S. *IEEE Int. Electron. Dev. Mtg. Tech. Dig.* **2010**, 6.5.1–6.5.4.
- (19) de Rouffignac, P.; Park, J.-S.; Gordon, R. G. *Chem. Mater.* **2005**, *17* (19), 4808–4814.
- (20) Wang, H.; Wang, J.-J.; Gordon, R.; Lehn, J.-S. M.; Li, H.; Hong, D.; Shenai, D. V. *Electrochem. Solid State Lett.* **2009**, *12* (4), G13–G15.
- (21) Kwon, J.; Dai, M.; Halls, M. D.; Langereis, E.; Chabal, Y. J.; Gordon, R. G. *J. Phys. Chem. C* **2009**, *113* (2), 654–660.