Heteroepitaxy of single-crystal $LaLuO_3$ on GaAs(111)A by atomic layer deposition

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We demonstrate that $LaLuO_3$ films can be grown epitaxially on sulfur-passivated GaAs(111)A substrates by atomic layer deposition (ALD). Transmission electron microscopy and x-ray diffraction analyses reveal that the oxide film exhibits a cubic structure with a lattice mismatch of -3.8% relative to GaAs. The epitaxial layer has a high degree of crystalline perfection and is relaxed. Electrical characterizations performed on this structure show interfaces with a low interface state density of $\sim 7\times 10^{11}$ cm^{-2} eV^{-1}. The measured dielectric constant is around 30, which is close to its bulk crystalline value. In contrast, ALD $LaLuO_3$ is polycrystalline on GaAs(100) and amorphous on Si(111). © *2010 American Institute of Physics*. [doi:10.1063/1.3504254]

Lanthanum lutetium oxide ($LaLuO_3$) has been widely studied as an alternative gate dielectric to replace silicon dioxide for metal-oxide-semiconductor field-effect transistors (MOSFETs). Single crystals of this oxide have a high dielectric constant ($\kappa\sim 30$) and a large optical band gap (5.6 eV).[1] $LaLuO_3$ films have been grown by several physical and chemical methods. Epitaxial cubic $LaLuO_3$ thin films were grown on Si(111) by molecular beam epitaxy (MBE) at 700 °C (Ref. 2) and orthorhombic $LaLuO_3$ on both $SrTiO_3$ and $SrRuO_3$(100) by pulsed-laser deposition at temperatures higher than 600 °C.[3] Amorphous films were also made on Si by these techniques at relatively lower temperatures (<450 °C).[4–6] We have reported that high-quality amorphous $LaLuO_3$ thin film grew by atomic layer deposition (ALD) on H-terminated Si(100) at 300 °C and showed promising electrical results.[7]

The aggressive scaling of MOSFETs has created interest in using high mobility III–V channel materials to replace traditional strained Si. However, it has been challenging to form dielectrics that can passivate III–V surfaces with a low interface state density (D_{it}).[8] Several dielectrics have been investigated. For example, epitaxial cubic Gd_2O_3 ($\kappa\sim 10$) was deposited by MBE to passivate GaAs(100) surfaces and a low D_{it} was obtained.[9] Epitaxial perovskite $SrTiO_3$ was grown by MBE on GaAs(100) with sharp interfaces and a high κ but a low D_{it} was not found.[10] However, these deposition techniques are not considered as commercially practical processes. Therefore, many efforts have been made to study oxides such as amorphous Al_2O_3 and HfO_2 on GaAs made by ALD (Refs. 11–13) but the κ values of these materials are relatively low and the structures need lower D_{it}. The work presented here deposits $LaLuO_3$ dielectrics by ALD on sulfur-passivated GaAs substrates. $LaLuO_3$ films were grown epitaxially on GaAs(111)A by a low-temperature ALD process. Both high κ and low D_{it} were obtained together by a commercially practical process.

$LaLuO_3$ thin films were deposited from the precursors including lanthanum tris(N,N'-diisopropylformamidinate), lutetium tris(N,N'-diethylformamidinate), and H_2O in a horizontal gas flow reactor. The deposition temperature was fixed at 350 °C. The deposition was done by repeatedly growing one cycle of La_2O_3 followed by one cycle of Lu_2O_3. The metal precursors were delivered with high-purity nitrogen assist. The exposures of the La and Lu precursors were estimated to be around 0.003 Torr s and the exposure of H_2O was about 0.06 Torr s in each cycle. The chamber was purged under nitrogen for 40 s and 60 s after the metal precursor and H_2O pulse, respectively. Such a long purging time minimized the number of hydroxyl groups trapped in the film. N-type GaAs(111)A wafers with carrier concentration around 5×10^{17} cm^{-3} were used as substrates. GaAs(100) and Si(111) wafers were also studied for comparison. Before deposition, all GaAs substrates were passivated by first dipping into an $HCl:H_2O=1:1$ solution to remove the native oxide and then soaking in a 20% $(NH_4)_2S$ solution for 10 min at room temperature for S-passivation. Si wafers were dipped in 5% HF solution for 10 s before deposition. The deposition rate was 0.2 nm for a complete cycle of $LaLuO_3$. The composition ratio of La:Lu was about 1:1 estimated by Rutherford backscattering spectroscopy. For electrical characterizations, all samples were capped with 6 nm ALD-Al_2O_3 and subjected to rapid thermal anneal at 700 °C in N_2 ambient for 30 s. Ni/Au circular electrodes for MOS capacitors were patterned by a lift-off process with a diameter of 150 μm.

Figure 1 shows a cross-sectional transmission electron microscopy (TEM) micrograph of $LaLuO_3$/GaAs(111)A and the inset corresponds to its in-plane selected area electron diffraction pattern. The magnified image of the interface is shown at the bottom. The sample for cross-sectional TEM image has 12 nm $LaLuO_3$ deposited on GaAs by 60 complete $LaLuO_3$ cycles. The electron beam is oriented along the ⟨110⟩ direction of the GaAs substrate. The oxide is uniform in thickness and is approximately 35 monolayers thick. As shown in Fig. 1, a twin relationship is observed between the oxide and underlying GaAs substrate at the common $(1\bar{1}\bar{1})$ interface. Similar epitaxial relations were found in $(La_xY_{1-x})_2O_3$ and $(La_xLu_{1-x})_2O_3$ (cubic) on silicon (111)

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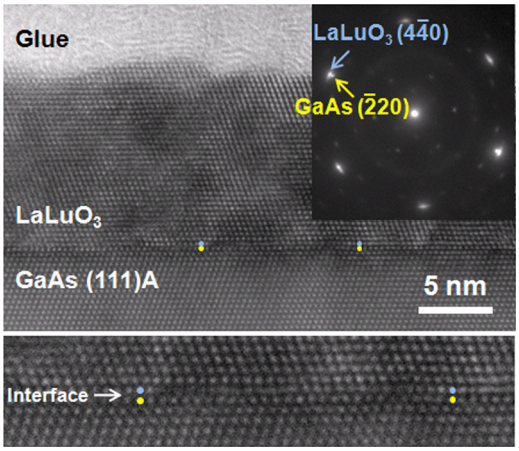

FIG. 1. (Color online) Cross-sectional TEM micrograph of the $LaLuO_3$/GaAs(111)A heterostructure. The magnified image at the interface is shown at the bottom. The inset shows the selected area diffraction pattern in the 111 pole of the substrate.

grown by MBE.[2,14] By carefully examining the interface, it is found that a metal atom of $LaLuO_3$ sits right on top of a lattice point of GaAs every 28 columns (see marks). This shows that despite the lattice mismatch between $LaLuO_3$ and GaAs, the oxide layer is mostly relaxed. The diffraction pattern was taken from a sample with 45 nm of $LaLuO_3$ and shows that the arrays of ⟨440⟩ diffraction spots from $LaLuO_3$ are nearly superimposed on those ⟨220⟩ from GaAs. The structure of $LaLuO_3$ is identified as a cubic phase.

The epitaxial growth of cubic $LaLuO_3$ film on GaAs(111)A was further confirmed by high-resolution x-ray diffraction (HRXRD) measurements. Figure 2(a) shows the omega-two theta scan for the $LaLuO_3$ layer on GaAs(111)A. The $LaLuO_3$(222) reflection is shifted from the GaAs(111) peak by 0.63°. The lattice constant (a_{oxide}) is estimated to be ~10.86 Å. For cube-on-cube epitaxy, the resulting mismatch is −3.8% compared to GaAs (a=5.65 Å), where the mismatch is defined as (a_{oxide}-2a)/2a. This indicates that the epitaxial film is relaxed with no strain, which is consistent with the TEM observation. The well-defined thickness fringes at both sides of the $LaLuO_3$(222) peak indicate a high degree of crystalline uniformity over a large area. Figure 2(b) shows the omega scan for the $LaLuO_3$(222) reflection. The full width at half maximum is 16.5 arc sec, where 1 arc sec is 1/3600°. This value is equal to the value of 16.2 arc sec for the GaAs(111) substrate peak (not shown here), indicating that the quality of the epitaxial ALD-$LaLuO_3$ layer is comparable to that of the GaAs substrate.

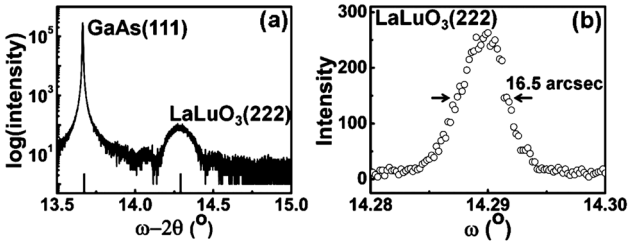

FIG. 2. (a) High-resolution x-ray omega-two theta scan for $LaLuO_3$ film on GaAs(111)A. (b) The rocking curves of the $LaLuO_3$(222) peak.

The electrical properties of $LaLuO_3$/GaAs(111)A were also characterized. Capacitance-voltage (C-V) curves were measured on MOS capacitors with 6 nm Al_2O_3/10 nm $LaLuO_3$/n-GaAs(111)A stack under different frequencies and temperatures. Since Fermi-level unpinning was reported on ALD Al_2O_3/GaAs(111)A system,[12] a capacitor with 8 nm Al_2O_3/n-GaAs(111)A was measured for comparison. ALD Al_2O_3 was confirmed to be amorphous on GaAs(111)A by cross-sectional TEM studies. As shown in Figs. 3(a) and 3(b), $LaLuO_3$/GaAs(111)A has a smaller frequency dispersion of 9% on the accumulation side and a smaller flatband shift of 0.2 V between 1 MHz and 1 kHz, compared with 13% and 0.64 V in Al_2O_3/GaAs(111)A. These comparisons indicate that there are fewer electronic defects at the $LaLuO_3$/GaAs(111)A interface than at the Al_2O_3/GaAs(111)A interface. C-V curves showed little difference among six pads of each capacitor sample and did not change after two months. From the conductance measurement, D_{it} of $LaLuO_3$/GaAs(111)A was estimated as $\sim 7 \times 10^{11}$ $cm^{-2}\,eV^{-1}$, which is an order of magnitude lower than that of Al_2O_3/GaAs(111)A ($\sim 8 \times 10^{12}$ $cm^{-2}\,eV^{-1}$), as shown in Fig. 3(c). Another capacitor with amorphous 10 nm $LaLuO_3$/2 nm Al_2O_3/n-GaAs(111)A stack was prepared to compare the κ values of crystalline and amorphous $LaLuO_3$, since $LaLuO_3$ was found to be amorphous with ALD Al_2O_3 underneath. The κ value of crystalline $LaLuO_3$ was extracted to be 29–30 from the accumulation capacitance at 1 kHz, which is close to the value of $LaLuO_3$ crystal,[1] while the κ value of amorphous $LaLuO_3$ was estimated to be 25–26. These results demonstrate that a high-quality epitaxial $LaLuO_3$ film on GaAs(111)A has superior electrical properties.

In contrast, $LaLuO_3$ formed as polycrystalline on S-passivated GaAs(100), as can be seen from the cross-sectional TEM image of Fig. 4(a). Electron diffraction and XRD analysis both indicate that the polycrystalline structure

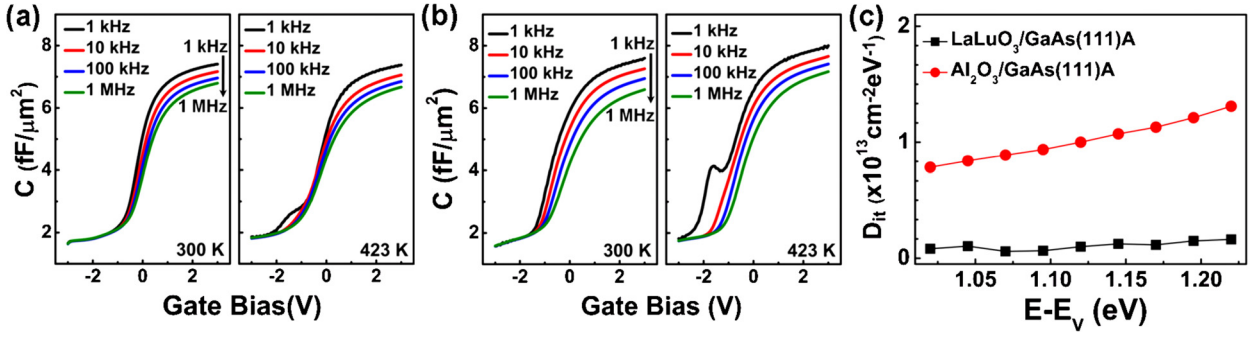

FIG. 3. (Color online) [(a) and (b)] Capacitance-voltage (C-V) characteristics of 6 nm Al_2O_3/10 nm $LaLuO_3$/n-GaAs(111)A and 8 nm Al_2O_3/n-GaAs(111)A, respectively. (c) D_{it} vs band gap energy.

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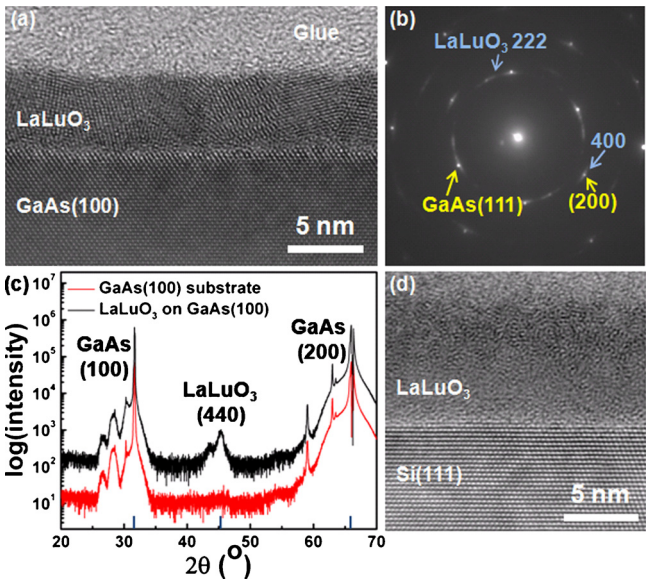

FIG. 4. (Color online) (a) Cross-sectional TEM image of the $LaLuO_3$/GaAs(100) stack. (b) Electron diffraction pattern on a cross-sectional TEM sample of $LaLuO_3$/GaAs(100) stack. (c) XRD two theta-omega scan of a $LaLuO_3$/GaAs(100) sample and a bare GaAs(100) substrate for comparison. (d) Cross-sectional TEM image of the $LaLuO_3$/Si(111) stack.

is (110) preferentially oriented [Figs. 4(b) and 4(c)]. This orientation can be explained by the model proposed by Yoshimoto *et al.*[15] The model claimed that for oxide epitaxy, the first species to bond with the substrate is oxygen and the growth orientation of the oxide is determined by the spacing between O atoms. In the case of $LaLuO_3$/GaAs(100), the spacing between the dangling bonds on the GaAs(100) surface is ~3.99 Å and the average distance between O atoms in the $LaLuO_3$(001) plane is ~2.72 Å (−30% mismatch). In the (110) plane the spacings are 3.84 Å (−3.8% mismatch) and 2.72 Å (−30% mismatch). Thus better matching is found with the (110) plane, with two possible (110) domain orientations, resulting in a polycrystalline structure with (110) preferential orientation at lower temperatures.[14,15] This structure is in accord with our observation of polycrystalline $LaLuO_3$ on GaAs(100). Epitaxy is favored for $LaLuO_3$/GaAs(111) because the spacing between the dangling bonds on the GaAs(111) surface is ~3.99 Å and between O atoms in the (111) plane of $LaLuO_3$ is ~3.84 Å, providing a small mismatch of −3.8% and one unique domain orientation. Besides, the slow growth rate of ALD-$LaLuO_3$ can also be an important factor for epitaxy. The rate is estimated as one monolayer for two complete cycles of $LaLuO_3$ (210 s/cycle). This could provide enough time for adatoms to arrange themselves into their lowest energy configuration and thus form cube-on-cube epitaxy.

Figure 4(d) shows that $LaLuO_3$ formed an amorphous phase on Si(111), although the substrate has a similar surface configuration with GaAs(111)A and a very small (0.18%) mismatch with $LaLuO_3$. This finding is explainable by considering the interface reactions between oxide and substrates. Based on enthalpy formation calculations, La_2O_3 and Lu_2O_3 in contact with Si are found to be unstable against silicate formation.[16] Our previous studies have shown that a very thin silicate layer is formed during the initial growth by using *in situ* Fourier transform infrared spectroscopy.[17] The amorphous interfacial layer disturbs the ordering of Si(111), which leads to random orientation of O atoms. In contrast, the fact that an epitaxial single crystal $LaLuO_3$ film forms on GaAs(111)A suggests the absence of any amorphous interlayer before initiation of epitaxial oxide growth.

In summary, heteroepitaxial $LaLuO_3$ on S-passivated GaAs(111)A was achieved by a very low-temperature ALD process. TEM and XRD analyses confirmed that $LaLuO_3$ has a cubic structure with good crystallinity and no strain in the oxide. Epitaxial $LaLuO_3$ on n-GaAs(111)A demonstrated well-behaved C-V curves with a low D_{it} of 7×10^{11} eV^{-1} cm^{-2} and a high κ value of 30. Different crystalline structures of $LaLuO_3$ on GaAs(111)A, GaAs(100), and Si(111) were explained by the spacing of first absorbing oxygen atoms on the substrates. ALD $LaLuO_3$ could be a promising high-κ candidate for future III–V technology.

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