Epitaxial Growth of Mg\textsubscript{x}Ca\textsubscript{1-x}O on GaN by Atomic Layer Deposition

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Abstract: We demonstrate for the first time that a single-crystalline epitaxial Mg\textsubscript{1-x}Ca\textsubscript{x}O film can be deposited on gallium nitride (GaN) by atomic layer deposition (ALD). By adjusting the ratio between the amounts of Mg and Ca in the film, a lattice matched Mg\textsubscript{x}Ca\textsubscript{1-x}O/GaN(0001) interface can be achieved with low interfacial defect density. High resolution X-ray diffraction (XRD) shows that the lattice parameter of this ternary oxide nearly obeys Vegard’s Law. An atomically sharp interface from cross-sectional transmission electron microscopy (TEM) confirmed the high quality of the epitaxy. High temperature capacitance-voltage characterization showed that the
film with composition $\text{Mg}_{0.25}\text{Ca}_{0.75}\text{O}$ has the lowest interfacial defect density. With this optimal oxide composition, a $\text{Mg}_{0.25}\text{Ca}_{0.75}\text{O}/\text{AlGaN}/\text{GaN}$ metal-oxide-semiconductor high-electron-mobility (MOS-HEMT) device was fabricated. An ultra-high on/off ratio of $10^{12}$ and a near ideal $\text{SS}$ of 62mV/dec was achieved with this device.

KEYWORDS: Epitaxy, dielectric, GaN, MOS-HEMT, magnesium calcium oxide

The wide implementation of solar energy and fast development of electrical vehicles both require more efficient power electronic devices working under high voltage (>600V), high temperature (>100 °C) and high frequency conditions. Currently, Si-based power devices could not meet these demands due to the small band gap (1.1 eV) and low breakdown field of Si. GaN could replace Si for future power applications because of its higher band gap (3.4eV) and higher breakdown field. However, unlike Si, the interface trap density between GaN and its native oxide (Ga$_2$O$_3$) is huge, which prevents high efficiency modulation of GaN devices. Many alternative dielectrics, such as HfO$_2$, Al$_2$O$_3$, SiO$_2$, Sc$_2$O$_3$, etc, have been employed as dielectrics on GaN in various studies. However, GaN devices with a low defect interface and high quality dielectric have not been achieved with any material.

Recently, our group demonstrated that ALD can grow lanthanum oxide epitaxially on
gallium arsenide (GaAs) (111)A surfaces, and that the density of interfacial defects is remarkably low.\textsuperscript{7} Although the (0001) surface of GaN wurtzite structure has an atomic structure similar to the (111)A surface of GaAs, it is more challenging to apply the same strategy to GaN due to the lack of any lattice matched oxide. We have also reported ALD-Sc\textsubscript{2}O\textsubscript{3} growth on AlGaN/GaN based HEMT devices.\textsuperscript{5} Due to the large lattice mismatch between Sc\textsubscript{2}O\textsubscript{3} and the substrate (~9\%), epitaxial growth could not be achieved. MgO and CaO, both have relatively high dielectric constants (MgO 9.8, CaO 11.8) and large band gaps (both 7~8 eV), and thus might be suitable gate oxides for GaN. Moreover, the GaN lattice size lies between those of the MgO and CaO lattices (mismatch -6.5\% for MgO and +6.5\% for CaO). Therefore, by tuning the composition of Mg\textsubscript{x}Ca\textsubscript{1-x}O, a lattice match with GaN substrates can be achieved. Hellman et al.\textsuperscript{8} demonstrated that epitaxial Mg\textsubscript{1-x}Ca\textsubscript{x}O can be grown by molecular beam epitaxy (MBE) on MgO substrates. Later, Paisley et al.\textsuperscript{9} and Ren et al.\textsuperscript{10} reported that epitaxial Mg\textsubscript{0.5}Ca\textsubscript{0.5}O can be grown on GaN with the same method. Measurements on HEMTs with MBE-fabricated MgCaO insulators showed improved gate-lag.\textsuperscript{11} However, MBE is not applicable to large substrates needed for cost-effective industrial processing. Thus a more scalable and lower cost method to deposit epitaxial Mg\textsubscript{x}Ca\textsubscript{1-x}O is highly desirable.

In this work, we demonstrate that atomic layer deposition (ALD) can form Mg\textsubscript{x}Ca\textsubscript{1-x}O epitaxially on GaN(0001). Cross sectional transmission electron microscopy (TEM)
determined the relationship of this heteroepitaxy to be

$$(111)\times[011]Mg_xCa_{1-x}O\parallel GaN(0001)\times[11-20]$$. High-resolution X-ray diffraction
(HRXRD) and electron diffraction (ED) showed that the lattice constants of
$Mg_xCa_{1-x}O$ with different compositions are close to the predictions of Vegard’s Law.
Capacitance-voltage (C-V) measurements were employed to study the interfacial
defects and $Mg_{0.25}Ca_{0.75}O$ showed the lowest density of defects. Additionally, an
ultra-high on/off ratio of $10^{12}$ and a near-ideal subthreshold swing of 62mV/dec were
achieved with $Mg_{0.25}Ca_{0.75}O$ as a gate oxide of GaN MOS-HEMT. This is the first
demonstration of epitaxial $Mg_xCa_{1-x}O$ in a GaN/AlGaN/GaN MOS-HEMT device.
The results show that the $Mg_xCa_{1-x}O$ dielectric is promising for applications in
high-frequency and power electronics.

ALD of $Mg_xCa_{1-x}O$ was carried out in a home-built tubular reactor$^{12}$.

Bis($N,N'$-diisopropylacetamidinato)calcium(II) dimer$^{13}$,
bis($N,N'$-di-sec-butylacetamidinato)magnesium$^{14}$ and $H_2O$ were used as calcium,
magnesium and oxygen sources, respectively. Structural formulas for the Mg and Ca
precursors are shown in Fig. 1. Three different precursor dosing ratios, namely
Mg:Ca=1:1, Mg:Ca=1:2 and Mg:Ca=1:3, were employed. The compositions of the
resulting films were determined by Rutherford Backscattering Spectroscopy (RBS) to
be $Mg_{0.72}Ca_{0.28}O$, $Mg_{0.51}Ca_{0.49}O$ and $Mg_{0.25}Ca_{0.75}O$, respectively. The detailed growth
conditions are summarized in supporting information. The depositions below a
substrate temperature of 290 °C were not well crystalized while carbon impurity can be detected at above 330 °C. Therefore, an optimal growth temperature is determined to be 310 °C. The film growth rates with different dosing ratios and the corresponding compositions are summarized in Table 1. For all three compositions, the growth rates are slightly smaller than a linear combination of the MgO and CaO growth rates, and the Mg contents are higher than their corresponding dosing ratio in the 1:1 and 1:2 cases. This indicates that the MgO cycle might have a hindering effect on the reaction of the CaO deposition cycle. Although MgO and CaO are nearly immiscible at equilibrium below 2000 °C, this solid mixture is kinetically stable up to about 600 °C.

One powerful method to examine the epitaxial film quality is cross-sectional TEM imaging. Figure 2 summarizes the cross-section TEM images of three different MgₓCa₁₋ₓO/GaN samples. Since GaN and MgₓCa₁₋ₓO have different crystal structures, their lattice patterns in TEM are different. The GaN region shows a distinctive three atomic line periodicity pattern in the vertical direction while MgₓCa₁₋ₓO does not have this feature. All three samples show sharp interfaces without any interfacial layer. The nearly perfect single crystal lattices in Fig. 2 a and b confirmed the high quality of epitaxy of Mg₀.₂₅Ca₀.₇₅O and Mg₀.₅Ca₀.₄O on GaN. On the other hand, the grain boundaries in Fig. 2 c indicate that a highly textured Mg₀.₇₂Ca₀.₂₈O film is formed on GaN. The well-defined film spots in the diffraction pattern (Fig. S2) also confirmed
the high quality of epitaxial Mg$_{0.25}$Ca$_{0.75}$O and Mg$_{0.51}$Ca$_{0.49}$O films while the Mg$_{0.72}$Ca$_{0.28}$O film has some textured features. Moreover, from the diffraction pattern, the zone axis of the GaN substrate in these TEM images is [11-20], while the film zone axis can be determined as [011]. Therefore, the epitaxial relation between the film and substrate is (111)×[0-11] Mg$_x$Ca$_{1-x}$O //GaN(0001)×[11-20].

In order to study the lattice mismatch between Mg$_x$Ca$_{1-x}$O film and GaN substrate, coupled 2θ-ω HRXRD scans were employed. Both GaN(0004) and Mg$_x$Ca$_{1-x}$O(222) peaks are seen in all three samples (Fig. 3 a). The absence of MgO and CaO peaks indicates that phase separation into the two binaries has not occurred. The Mg$_x$Ca$_{1-x}$O(222) peak shifts to lower 2θ position as the Ca content increases. Both measured lattice constants and the calculated lattice constants based on Vegard’s Law are plotted in Fig. 3 b. Assuming a fully relaxed hetero-epitaxial relation at the interface and considering the epitaxial relationship between the film and the substrate, the out-of-plane lattice mismatch can be defined as: \( \frac{(a_{\text{MgCaO(222)}} - a_{\text{GaN(0004)}})}{a_{\text{GaN(0004)}}} \). The mismatch is -1.2% for Mg$_{0.72}$Ca$_{0.28}$O, +2.4% Mg$_{0.51}$Ca$_{0.49}$O and +3.1% for Mg$_{0.25}$Ca$_{0.75}$O. Similar lattice mismatch values obtained from in-plane FFT analysis of TEM cross-sectional images also confirmed the relaxed interface. (Fig. S8) Despite the larger lattice mismatch, Mg$_{0.51}$Ca$_{0.49}$O and Mg$_{0.25}$Ca$_{0.75}$O show nearly perfect epitaxy while Mg$_{0.72}$Ca$_{0.28}$O, with a smaller mismatch, exhibits a textured structure. Such results indicate that there might be factors other than mismatch affecting the
epitaxial quality.

Although MgO and CaO are immiscible with each other below 2000 °C, previous reports have shown that Mg$_x$Ca$_{1-x}$O can be grown by MBE at lower temperature without phase separation. In order to examine the microscopic crystallinity and phase composition of the Mg$_x$Ca$_{1-x}$O films deposited by this ALD method, transmission electron microscopy (TEM) was employed. As shown in supporting information, the ring diffraction pattern in Fig. S1 (b) clearly indicates that film is polycrystalline on SiNx. The relative positions between different diffraction rings in the electron diffraction pattern are in accord with the FCC standard pattern. This indicates that the Mg$_x$Ca$_{1-x}$O shares the same rock salt structure with MgO and CaO. Additionally, the values of the lattice spacings lie in between the corresponding spacings in MgO and CaO, showing that the Mg$_x$Ca$_{1-x}$O film is a uniform alloy of the two components without phase separation.

In summary of the above structural characterizations, Mg$_x$Ca$_{1-x}$O films deposited by ALD were proved to be epitaxial on GaN by both TEM and XRD. Cross sectional TEM revealed near perfect epitaxy of Mg$_{0.51}$Ca$_{0.49}$O and Mg$_{0.25}$Ca$_{0.75}$O on GaN. However, although a smaller lattice mismatch was found in Mg$_{0.72}$Ca$_{0.28}$O/GaN, the epitaxy was not as perfect as for the other two compositions. Therefore lattice mismatch might not be the only parameter affecting the quality of epitaxy.
Mg$_x$Ca$_{1-x}$O/GaN MOS-capacitor devices were fabricated to examine the electrical performance by capacitance-voltage and conductance-voltage measurements. Since GaN has a wide band gap of 3.4eV, a room temperature CV does not effectively probe defects near the middle of the bandgap. Therefore, the MOS-capacitors were measured at 150 °C as well as at room temperature. Due to the hydroscopic nature of Mg$_x$Ca$_{1-x}$O, 5 nm of Al$_2$O$_3$ were deposited as a capping layer to keep moisture away from the Mg$_x$Ca$_{1-x}$O layer. An amorphous Al$_2$O$_3$/GaN MOS was also prepared for comparison. A “top-to-top” capacitor structure was used to measure the capacitance due to the insulating sapphire substrate under the GaN (Fig. S3). In this measurement, the positive probe is placed in contact with the gate electrode while the negative probe is in contact with the large area of GaN covered by aluminum metal. Since the gate has a serial connection with the large area, the measured capacitance is given by 

$$\frac{1}{C_m} = \frac{1}{C_g} + \frac{1}{C_I},$$

where $C_m$ is the capacitance measured by the LCR meter, $C_g$ is the capacitance of the gate and $C_I$ is the capacitance of the larger area. Since $C_I \gg C_g$, the measured capacitance is dominated by the gate: $C_m \approx C_g$.

The measured room temperature and high temperature CV curves from three Mg$_x$Ca$_{1-x}$O/GaN samples as well as an Al$_2$O$_3$/GaN sample are summarized in Fig. 4. In room temperature studies (Fig. 4 a, b and c), very small (<6%) frequency dispersion can be seen in the depletion region for all three Mg$_x$Ca$_{1-x}$O samples, while
there is a 20% dispersion in the same region in the Al$_2$O$_3$/GaN sample (Fig. 4 d). In the absence of interface traps, dispersion should not occur. Therefore the reduced dispersion in the three Mg$_x$Ca$_{1-x}$O samples compared to the Al$_2$O$_3$ sample qualitatively indicates that the epitaxial film did reduce the number of interfacial traps. Due to the low interfacial trap density, a numerical value for $D_{it}$ could not be extracted from the room temperature CV measurements. During the CV measurement, the Fermi level is moved deeper in the band gap at a higher temperature; thus defect information can be obtained over a wider range of energies within the band gap.$^{18}$ In the CV data taken at 150 °C (Fig. 4 e, f, g and h), the frequency dispersion remained relatively small (<6%) for all three Mg$_x$Ca$_{1-x}$O samples while the dispersion in Al$_2$O$_3$/GaN is as large as 100%. The smaller frequency dispersion at high temperature indicates that the Mg$_x$Ca$_{1-x}$O film effectively reduced the interfacial trap density near the midgap region compared to Al$_2$O$_3$. In order to measure the $D_{it}$ values quantitatively, the conductance method was employed since the Terman method is considered less sensitive$^{19}$ and the Gray-Brown method is not applicable to III-V semiconductors.$^{20}$ The detailed measurement procedure and conductance data are summarized in the supporting information(Fig. S5).$^{18}$ The measured values of $D_{it}$ are summarized in Fig. 4 i. Two of the samples with epitaxial films show the lowest $D_{it}$ values, while the textured sample has about one order of magnitude higher interfacial trap density. Although the lattice mismatch of the Mg$_{0.25}$Ca$_{0.75}$O sample is slightly larger than that of the other two Mg$_x$Ca$_{1-x}$O samples, the measured $D_{it}$ level is the lowest ($\sim 5 \times 10^{12}$ eV$^{-1}$cm$^{-2}$). One possible explanation is that during the early ALD
cycles, the Ca growth rate is smaller than that of the Mg. Thus the Ca content near the interface is lower than in the bulk Mg₅Ca₁₋₅O film. Another possible explanation is that a trace amount of Mg(OH)₂ may also cause interfacial traps, while adding more Ca content may help reduce the number of hydroxyl groups and therefore reduce the Dᵣ level. The dielectric constant of the Mg₀.₂₅Ca₀.₇₅O film derived from the CV measurement is 10, which is close to the permittivities of MgO and CaO.

The ultimate goal of developing this material is implementing MgₓCa₁₋ₓO into GaN MOS-HEMT devices with unprecedented oxide/semiconductor interface quality. A schematic cross section of such a device is shown in Fig. 5 a. The fabrication process is summarized in supporting information. The Mg₀.₂₅Ca₀.₇₅O film was used as the gate dielectric in this study due to its lower Dᵣ. The gate oxide stack is Al₂O₃(5nm)/Mg₀.₂₅Ca₀.₇₅O(10nm)/GaN. Well-behaved Iₓ-Vₓ, and linear-scale Iₓ-Vgs curves (Fig. 5 b and d) show the good control capability of the GaN MOS-HEMT. Fig. 5 c shows the transfer characteristics in a log-scale plot at Vₓ=1 V and 5 V, respectively. This device possesses an ultra-high on/off ratio 10¹² due to the high quality interface. Thus the channel can be shut off completely. This value is two orders of magnitude higher than those HEMT devices with Al₂O₃ passivation.²¹ In addition to the ultra-high on/off ratio, the GaN MOS-HEMT also possesses a near ideal subthreshold swing (SS) of 62 mV/dec, further confirming the high quality interface between GaN and the Mg₀.₂₅Ca₀.₇₅O layer.²² The successful implementation
of the Mg$_{0.25}$Ca$_{0.75}$O into a GaN MOS-HEMT shows that it’s promising for use in GaN MOS technology.

Epitaxial Mg$_x$Ca$_{1-x}$O films have been successfully grown on GaN [0001] surfaces using ALD for the first time. The crystallographic relationship of this hetero-epitaxy has been studied in detail. Moreover, the potential of applying this unprecedentedly high-quality dielectric film has been evaluated with C-V characterization, revealing that the density of defects is affected by not only the lattice mismatch but also by the composition of the film. Mg$_{0.25}$Ca$_{0.75}$O is found to provide the interface with the fewest traps and the MOS-HEMT made from it exhibits an ultra-high on/off ratio of $10^{12}$ and a near ideal SS of 62 mV/dec. Thus we believe this epitaxial Mg$_x$Ca$_{1-x}$O film can provide improved high-frequency and high-power electronics in the future.
Table 1. Summary of ALD growth rates, compositions and lattice constants of different Mg\textsubscript{x}Ca\textsubscript{1-x}O films. The composition was measured by Rutherford back scattering (RBS). Lattice constants of Mg\textsubscript{x}Ca\textsubscript{1-x}O (222) were measured by HRXRD. MgO and CaO (222) lattice constants were from Crystallography Open Database.

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<th>Lattice constant (nm)</th>
<th>Vagard’s Law prediction (nm)</th>
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<td>0.1213</td>
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Figure 1. Structures of the metal precursors. (a) bis(N,N'-di-sec-butylacetamidinato)magnesium; (b) bis(N,N'-diisopropylacetamidinato)calcium(II) dimer.
Figure 2. Cross-sectional TEM of Mg$_x$Ca$_{1-x}$O films grown on GaN(0001) surface. (a) Mg$_{0.25}$Ca$_{0.75}$O/GaN; (b) Mg$_{0.51}$Ca$_{0.49}$O/GaN; (c) Mg$_{0.72}$Ca$_{0.28}$O/GaN, grain boundaries can be found between each region labeled with letters. The enlarged grain boundary between region A and B shows both darkness contrast as well as pattern difference. Region B is showing a three line repeating pattern, which indicates two different orientation grains are overlapping together. Similar pattern can also be found in regions D and E.

![Figure 2](image)

Figure 3. Lattice constant study by HRXRD. (a) HRXRD study of Mg$_x$Ca$_{1-x}$O/GaN film. The black vertical line is the peak position of GaN(0004) diffraction. The dashed lines represent the peak positions of the Mg$_x$Ca$_{1-x}$O (222) diffractions; (b) Vegard’s Law predicted lattice constant vs XRD measured poly-crystalline Mg$_x$Ca$_{1-x}$O (222) lattice constants. The green dashed line is the lattice constant that matches the GaN(0004) lattice.

![Figure 3](image)
Figure 4. C-V measurements for Mg$_x$Ca$_{1-x}$O/GaN and Al$_2$O$_3$/GaN samples. The frequency ranges of all samples are from 1kHz to 1MHz. (a) 20°C Al$_2$O$_3$(5nm)/Mg$_{0.25}$Ca$_{0.75}$O(15nm)/GaN; (b) 20°C Al$_2$O$_3$(5nm)/Mg$_{0.51}$Ca$_{0.49}$O(15nm)/GaN; (c) 20°C Al$_2$O$_3$(5nm)/Mg$_{0.72}$Ca$_{0.28}$O(15nm)/GaN; (d) 150°C Al$_2$O$_3$(5nm)/Mg$_{0.25}$Ca$_{0.75}$O(15nm)/GaN. (e) 150°C Al$_2$O$_3$(5nm)/Mg$_{0.51}$Ca$_{0.49}$O(15nm)/GaN; (f) 150°C Al$_2$O$_3$(5nm)/Mg$_{0.72}$Ca$_{0.28}$O(15nm)/GaN; (g) 20°C Al$_2$O$_3$(20nm)/GaN for comparison; (h) Al$_2$O$_3$(20nm)/GaN; (i) Dit summary of four samples determined by the conductance method: Al$_2$O$_3$(20nm)/GaN (light blue star ), Al$_2$O$_3$(5nm)/Mg$_{0.72}$Ca$_{0.28}$O(15nm)/GaN (blue circles ), Al$_2$O$_3$(5nm)/Mg$_{0.51}$Ca$_{0.49}$O(15nm)/GaN (green down triangle ) and Al$_2$O$_3$(5nm)/Mg$_{0.25}$Ca$_{0.75}$O(15nm)/GaN (red up triangles ).
Figure 5. MOS-HEMT device performance characterization. a) Schematic of the Mg$_x$Ca$_{1-x}$O MOS-HEMT device; b) Transfer characteristics of the Mg$_{0.25}$Ca$_{0.75}$O/GaN/AlGaN/GaN MOS-HEMT device; c) I-V characteristics comparison between two different source drain voltage; d) Conductivity and current vs gate voltage study. Solid lines represent $V_{DS} = 5$ V, dashed lines represent $V_{DS} = 1$ V.
Supporting Information

Methods, TEM diffraction patterns of MgxCa1-xO/GaN, MOS-HEMT and MOS-capacitor fabrication, AC conductance method to extract $D_n$.

Acknowledgements

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References


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Table of Content Figure

![Graph of GaN device characteristics](image.png)

On/off: 10^12

- SS = 62 mV/dec

- Red line: V_DS = 5V
- Blue line: V_DS = 1V

5nm
Epitaxial Growth of Mg$_x$Ca$_{1-x}$O on GaN by Atomic Layer Deposition

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XRR/XRD

Mg$_x$Ca$_{1-x}$O grown on thermal oxide (300nm SiO$_2$/Si) wafers was characterized by XRD and XRR for lattice spacing and thickness respectively. Each thermal oxide wafer was cleaned of organic contamination by exposure to UV light in air (UV-ozone treatment) for 5 min before being loaded into the deposition chamber. Both XRR and XRD characterization was performed with a Bruker D8 Discover system.
Deposition conditions for ALD

The magnesium and calcium precursors were kept in sealed bubblers at 110 °C and 140 °C respectively in two separate ovens, and were delivered into the reaction chamber with controlled volumes of N₂ carrier gas. The deposition was performed at a substrate temperature of 310 °C. The dosing sequence was [(Ca-H₂O)ₙ-(Mg-H₂O)₁]ₙ. Each metal precursor dose was followed by a water dose. The composition was adjusted by varying the dosing ratio between the Mg and Ca cycles. The GaN substrates were treated with UV-Ozone for 5min then followed with 20% ammonium hydroxide soaking for 20min prior to ALD deposition. The water contact angle on newly received GaN substrate was 70°. This hydrophobic surface was due to the adsorbed organic compounds. After removal of organic contamination by UV-Ozone treatment, the contact angle decreased down to 18° since the surface was turned into Ga₂O₃. The contact angle of GaN surface further decreased to 9° after ammonium hydroxide treatment. This was because the ammonium hydroxide could effectively remove the Ga₂O₃ and expose the clean and highly hydrophilic GaN surface for deposition. Such surface is highly favorable for a Frank–van der Merwe (layer-by-layer) growth in ALD.

FIB/TEM

Transmission electron microscopy (TEM) images were taken with a JEOL-2100 TEM at the Harvard Center for Nanoscale Systems (CNS). The TEM cross-section sample preparation was done with a FEI Helios 660 focused ion beam (FIB) system.

Top view TEM of Mg₀.₂₅Ca₀.₇₅O/Si₃N₄ membrane and its diffraction pattern in Fig. S1 confirmed that no phase separation into MgO and CaO occurred.
Figure S1. (a) Top view of Mg$_{0.25}$Ca$_{0.75}$O/Si$_3$N$_4$ membrane. (b) TEM diffraction pattern of the area in (a).

In the cross section TEM diffraction patterns (Fig. S2), as Mg content increases, the MgCaO (-200) and (-111) diffraction spots shift farther from the center of the pattern. This trend is accord with the HRXRD results shown in Fig 2. The MgCaO (111) diffraction spots are overlapped with the GaN (0002) spot.

Figure S2. TEM diffraction pattern of cross sectional Mg$_x$Ca$_{1-x}$O/GaN interface sample. The zone axis is GaN [-1 -1 2 0]. (a) Mg$_{0.25}$Ca$_{0.75}$O/GaN; (b) Mg$_{0.51}$Ca$_{0.49}$O/GaN; (c) Mg$_{0.72}$Ca$_{0.28}$O/GaN.

RBS

Rutherford Backscattering Spectroscopy (RBS) was done at the Department of Physics and Astronomy, Rutgers University.
MOS-capacitor

Epi-layers GaN (5µm thick) grown on sapphire substrates were purchased from MTI with resistivity of 0.02 Ω • cm. The GaN wafers were treated with UV-ozone for organic removal and then soaked for 20 min in 20% aqueous ammonium hydroxide to remove native oxides. After pretreatment the samples were patterned into circular capacitors by photo lithography. 300nm Al metal was then deposited onto the dielectric and the remaining photoresist with thermal evaporation. After lift-off overnight, the “top-to-top” capacitor structure was formed as shown in Fig. S3

![Figure S3. MOS-capacitor for CV measurement. (a) Top view of the MOS-capacitor. (b) Side view of the MOS-capacitor.](image)

MOS-HEMT

The AlGaN/GaN MOS-HEMT structure was grown on a Si (111) substrate, consisting of, a 5-nm Al₂O₃ capping layer, a 10-nm Mg_{0.25}Ca_{0.75}O epitaxial oxide, a 2-nm GaN capping layer, a 17-nm Al_{0.26}Ga_{0.74}N barrier, a 1-nm AlN spacer, a GaN channel, and a 800 nm GaN buffer. Device fabrication started with mesa isolation by Cl₂/BCl₃ etching to a depth of 80 nm. Then, Ohmic contacts were formed by depositing Ti/Al/Ni/Au (20/100/40/50 nm) followed by 775 °C rapid thermal anneal in N₂ atmosphere. The sheet resistance (R_{SH}) and contact resistance (R_{C}) were determined to be 480 Ω/□ and 0.3 Ω-mm through transfer length method (TLM). Then gate oxides were deposited by ALD. The gate metal is formed by deposition of Ni/Au (30/50 nm) with lift-off process. Electrical measurements were performed with a Keysight E4980A LCR meter.
**MOS-HEMT measurement conditions**

I<sub>DS</sub>-V<sub>DS</sub>: The V<sub>DS</sub> is swept from 0 to 10 V and the V<sub>GS</sub> is stepped from 5 V to -5 V with -0.5 V as the step.

I<sub>DS</sub>-V<sub>GS</sub>: The V<sub>GS</sub> is swept from 4 V to -5.5 V with -0.05 V as a step at V<sub>DS</sub>=1 V and 5 V.

**AC conductance method to extract D<sub>it</sub>**

The AC conductance method is one of the most sensitive methods to determine D<sub>it</sub>. The equivalent circuits of the MOS capacitor are as following in Fig S4:

![Equivalent circuits of MOS capacitor](image)

**Figure S4.** Equivalent circuits of MOS capacitor; (a) an equivalent circuit model of the MOS capacitor, (b) the measured circuit, (c) the simplified circuit of (a).

The extracted D<sub>it</sub> can be expressed by the following equation:

\[ D_{it} = \frac{2.5}{q} \left( \frac{G_p}{\omega} \right)_{\text{max}} \]

where \( G_p/\omega \) is

\[ \frac{G_p}{\omega} = \frac{\omega (G_m - G_t) C_{ox}^2}{G_m^2 + \omega^2 (C_{ox} - C_m)^2} \]

\( C_{ox} \), \( C_m \), \( G_m \) and \( G_t \) are oxide capacitance, measured capacitance, measured conductance, and measured oxide tunnel conductance, respectively.
Figure S5. $G_p/\omega$ vs. frequency at 150 °C. (a) Al$_2$O$_3$(5nm)/Mg$_{0.25}$Ca$_{0.75}$O(15nm)/GaN. (b) Al$_2$O$_3$(5nm)/Mg$_{0.51}$Ca$_{0.49}$O(15nm)/GaN. (c) Al$_2$O$_3$(5nm)/Mg$_{0.72}$Ca$_{0.28}$O(15nm)/GaN. (d) Al$_2$O$_3$(20nm)/GaN;

The trap energy level within the bandgap can be expressed as:

$$\Delta E = kT \times \ln\left(\frac{e^{V_T/N}}{2\pi}\right)$$

where $k$, $T$, $\sigma$, $V_T$, $N$, and $f$ are Boltzmann constant, temperature, trap capture cross section, thermal velocity, conduction band density, and conductance peak corresponding frequency, respectively.

XPS

X-ray photoelectron spectroscopy (XPS) was taken by a Thermo Scientific K-alpha system. In Fig S6, the absence of Ga and N signals from substrate in Mg$_{0.25}$Ca$_{0.75}$O/GaN indicates that the surface of GaN is fully covered by MgCaO film. Since the penetration depth of XPS and the film thickness in this case were both about 10 nm, any missing areas of the film would result in detectable substrate signals. Therefore, the absence of substrate signal indicates that the film is uniformly covering the GaN surface.

Figure S6. XPS spectrum of bare GaN (green) and Mg$_{0.25}$Ca$_{0.75}$O(10nm)/GaN (red).
AFM study is done with an Asylum MFP-3D AFM System. The similar RMS values obtained from before and after the deposition indicate that the film has uniform thickness.

![AFM images]

**Figure S7.** (a) GaN surface, RMS = 0.37 nm; (b) Mg_{0.25}Ca_{0.75}O(10nm)/GaN surface, RMS = 0.47 nm

**FFT analysis of crosssectional TEM images.**

Fast Fourier Transform (FFT) analysis is employed to study the in-plane lattice mismatch. By measuring the lateral distance of corresponding spots in the FFT images with pixel as unit, the in-plane lattice mismatch can be calculated with \((L_{\text{sub}} - L_{\text{film}})/L_{\text{film}}\). The error range of in-plane mismatch from FFT is about ±1% due to the limited image resolution. The results show that the in-plane mismatch is in good agreement with the out-of-plane mismatch.

<table>
<thead>
<tr>
<th>Film composition</th>
<th>Mg_{0.25}Ca_{0.75}O</th>
<th>Mg_{0.49}Ca_{0.51}O</th>
<th>Mg_{0.77}Ca_{0.23}O</th>
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</thead>
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<td><img src="image2" alt="FFT images" /></td>
<td><img src="image3" alt="FFT images" /></td>
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<tr>
<td>FFT of GaN substrate</td>
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<td><img src="image5" alt="FFT images" /></td>
<td><img src="image6" alt="FFT images" /></td>
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<tr>
<td>Lateral distance of film</td>
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<td>107p</td>
<td>64p</td>
</tr>
<tr>
<td>Lateral distance of Sub</td>
<td>108p</td>
<td>110p</td>
<td>63p</td>
</tr>
<tr>
<td>FFT lattice mismatch</td>
<td>+ 3.8%</td>
<td>+ 2.8%</td>
<td>-1.5%</td>
</tr>
<tr>
<td>XRD lattice mismatch</td>
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<td>+ 2.4%</td>
<td>-1.2%</td>
</tr>
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</table>

**Figure S8.** Fast Fourier Transform analysis of MgCaO/GaN crosssection TEM images. The original images are from Fig 2. * “p” stands for pixels in the image.
Reference