# Publishing pitaxial engineering of polar $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> for tunable two-dimensional electron

### gas at the heterointerface

Sung Beom Cho<sup>1,\*</sup> and Rohan Mishra<sup>1,2,\*</sup>

<sup>1</sup>Department of Mechanical Engineering and Materials Science, Washington University in St.

Louis, St. Louis, Missouri 63130, United States

<sup>2</sup>Institute of Materials Science and Engineering, Washington University in St. Louis, St. Louis,

Missouri 63130, United States

\*To whom all correspondence should be addressed: cho.s@wustl.edu, rmishra@wustl.edu

#### Abstract

We predict the formation of a polarization-induced two-dimensional electron gas (2DEG) at the interface of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> and CaCO<sub>3</sub>, wherein the density of the 2DEG can be tuned by reversing the spontaneous polarization in  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub>, for example, with an applied electric field.  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> is a polar and metastable ultra-wide band-gap semiconductor. We use density-functional theory (DFT) calculations and coincidence-site lattice model to predict the region of epitaxial strain under which  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> can be stabilized over its other competing polymorphs and suggest promising substrates. Using group-theoretical methods and DFT calculations, we show that  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> is a ferroelectric material where the spontaneous polarization can be reversed through a non-polar phase by using an electric field. Based on the calculated band alignment of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> with various substrates, we show the formation of a 2DEG with a high sheet charge density of 10<sup>14</sup> cm<sup>-2</sup> at the interface with CaCO<sub>3</sub> due to the spontaneous and piezoelectric polarization in  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub>, which makes the system attractive for high-power and high-frequency applications.



Ga<sub>2</sub>O<sub>3</sub> is emerging as an attractive semiconductor for high-power switching applications due to its high breakdown field and ultra-wide band gap <sup>1-4</sup>. Amongst the various polymorphs of Ga<sub>2</sub>O<sub>3</sub>,  $\beta$ -phase has received the most attention due to its stable form under ambient conditions and the ease of growing large single crystals <sup>5-7</sup>. Recently, carrier confinement and formation of a two-dimensional electron gas (2DEG) has been experimentally demonstrated at the interface of Ga<sub>2</sub>O<sub>3</sub> with a wider band gap alloy (Al<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> by using modulation doping with silicon<sup>8</sup>, which enables Ga<sub>2</sub>O<sub>3</sub>-based devices to simultaneously operate at high-power and highfrequencies <sup>9-11</sup>. However, as modulation doping results in a modest 2DEG density of ~10<sup>12</sup> cm<sup>-2</sup> compared to 2DEG density of ~10<sup>13</sup> cm<sup>-2</sup> at AlGaN/GaN interface <sup>12</sup>. Furthermore, mobility degradation of 2DEG is unavoidable due to impurity scattering. Those has led to a search for alternative ways to generate 2DEG in Ga<sub>2</sub>O<sub>3</sub> <sup>13</sup>

Recently, ferroelectric hysteresis has been reported in thin films of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub>, which is a metastable polymorph <sup>14</sup>. Contrary to 2DEG formation in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, the spontaneous polarization of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> can open a path to achieve 2DEG with high mobility and, possibly, higher sheet charge density without doping. While there have been numerous attempts to grow  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> on various substrates <sup>16,17</sup>, they have been unsuccessful to grow single-phase thin films that are free of defects <sup>18</sup>. This is primarily due to a lack of understanding of the stability of the competing phases of Ga<sub>2</sub>O<sub>3</sub> under epitaxial strain. Very recently,  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> thin films have been stabilized on (001) Al<sub>2</sub>O<sub>3</sub> substrates by using tin dopants during growth <sup>19</sup>; however the formation of a 2DEG was not reported. This is because the formation of a 2DEG at the interface of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub>, also requires a specific band alignment and the knowledge of its spontaneous and piezoelectric polarization constants, all of which are currently missing.



In this Letter, we have investigated the energy landscape of various Ga<sub>2</sub>O<sub>3</sub> polymorphs under epitaxial strain by combining coincident-site lattice models (CSL) with first-principles density-functional theory (DFT) calculations. We have identified the lattice parameter of the substrates that minimize the epitaxial strain of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> with respect to other competing phases and recommend a list of commercially available substrates to grow phase-pure  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> without doping. By using group-theoretical methods, we show  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> is ferroelectric and the polarity of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> can be switched with an external electric field. Furthermore, by calculating the band alignment of the various lattice-matched substrates, we identify CaCO<sub>3</sub> to be particularly promising as it allows the formation of a 2DEG in  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> due to polarization-induced charges. Finally, we show that an electric field can be used to switch the spontaneous polarization in  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> to obtain a large charge density of  $10^{14}$  cm<sup>-2</sup>. Therefore, by stabilizing an ultrawide band gap semiconducting ferroelectric and an electric-field tunable 2DEG, our work paves a way to achieve a new generation of devices.

DFT calculations were performed using the VASP package <sup>20</sup> and projector augmentedwave potentials<sup>21</sup>. The plane-wave basis set was expanded to a cutoff energy of 520 eV to remove Pulay stress during the structural optimization. The structural optimization was truncated after the Hellmann-Feynman forces were under 0.001 eV/Å. The *k*-point meshes were sampled using Morkhorst-Pack method with grids of  $6 \times 6 \times 2$  for  $\alpha$ -,  $13 \times 4 \times 4$  for  $\beta$ -, and  $6 \times 4 \times 4$  for the transformed cell of  $\varepsilon$ -phase under epitaxial strain, respectively.<sup>23</sup> The 3*d*, 4*s*, 4*p* states of Ga and 2*s*, 2*p* states of O are taken as valence state and the exchange-correlation energy of valence electrons was described using the Perdew, Burke, and Ernzerhof (PBE) functional.<sup>22</sup> As the PBE is known to overestimate the lattice constants, to maintain consistency, we have used PBEoptimized lattice constants for all the substrate candidates, which are shown in Supplemental

**blishing** erial Table S3 <sup>24</sup> Regarding the polarization calculation, we used the Berry-phase method with a *k*-points grid of 6×4 with 16-point strings<sup>25</sup>. To evaluate the dielectric, piezoelectric and stiffness constants, we employed density functional perturbation theory with an increased cutoff energy of 700 eV and the same k-point grids of the PBE calculation<sup>26</sup>. The band gaps and electron affinities were calculated using the Heyd-Scuseria-Ernzerhof (HSE) hybrid functionals with a mixing parameter of 0.35 and 0.15 to fit the experimental band gaps of β-Ga<sub>2</sub>O<sub>3</sub> (Eg = 4.9 eV) and CaCO<sub>3</sub> (Eg = 6.0 eV), respectively <sup>27.30</sup>. Due to the lack of experimental measurements of the band gap of high-quality ε-Ga<sub>2</sub>O<sub>3</sub>, combined with the similar theoretical band gap of ε-Ga<sub>2</sub>O<sub>3</sub> and β-Ga<sub>2</sub>O<sub>3</sub> calculated using PBE (0.06 eV difference), we have used  $\alpha$  = 0.35 to calculate the band gap of ε-Ga<sub>2</sub>O<sub>3</sub>. The *k*-points grid of substrate candidates were sampled with a density of 2000 *k*-points per reciprocal atom, which is consistent to that of the other Ga<sub>2</sub>O<sub>3</sub> (104) and of ε-Ga<sub>2</sub>O<sub>3</sub> (010) surface with the macroscopic electrostatic potential averaging technique for a slab thicker than 25 Å and with 20 Å vacuum <sup>31, 32</sup>.

An orthorhombic  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> belongs to the *Pna*2<sub>1</sub> space group that is a subgroup of hexagonal *P63mc*. It implies that the orthorhombic lattice can be expressed with a basis transformation from the hexagonal lattice. The calculated a = 5.13 Å and b = 8.81 Å lattice parameters of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> have a ratio of  $1.718 \approx \sqrt{3}$  that also corresponds to the ratio of the two diagonals of the rhombohedral lattice. According to CSL theory <sup>33</sup>, the epitaxial interface should be constrained such that a repeating unit is formed where the lattice sites of the film and the substrate coincide. Therefore, the (001) plane is promising as it can satisfy the CSL conditions for epitaxial growth on a hexagonal substrate (Supplemental Material Fig. S1). On the other hand,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> does not have a coincidence lattice with hexagonal substrate for small epitaxial strains.



**shime** reported preferred orientation of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> on hexagonal substrates is the ( $\overline{2}$ 01) plane, which has calculated in-plane lattice vectors of 3.09 Å for [010] direction and (14.98 Å) for [10 $\overline{1}$ ] direction, needs at least 7% strain to fit hexagonal constraints. Furthermore, the large difference of the two in-plane vectors in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> requires a large CSL leading to a number of dangling bonds.  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> can, instead, form a CSL with a smaller unit cell on a hexagonal substrate. This is beneficial to stabilize metastable  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> over stable  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. We have also considered the CSL of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>, which is less stable compared to the  $\varepsilon$  and  $\beta$  phases in the bulk form <sup>5</sup>, but has a hexagonal structure and could be expected to be stabilized on hexagonal substrates. The crystal structure of the  $\alpha$ ,  $\beta$ , and  $\varepsilon$ -phases of Ga<sub>2</sub>O<sub>3</sub> are shown in Figure 1a.

**Table 1.** Calculated commercially-available substrates whose lattice mismatch with  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> is under ±3%. The lattice constants and the resulting strain have been calculated using PBE calculation.

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_	Substrate	Lattice constant (Å)	Strain
_	α-Fe <sub>2</sub> O <sub>3</sub>	5.066	-1.19%
	LiTaO3	5.19	1.23%
	CaCO <sub>3</sub>	5.06	-1.31%
$\sim$	LiNbO <sub>3</sub>	5.212	1.65%
$\mathbf{Q}$	<i>h</i> -BN	2.512	-2.01%
	α-SiO <sub>2</sub>	5.024	-2.04%

We have calculated the energy of the preferred orientation of  $\alpha$ ,  $\beta$ , and  $\varepsilon$ -phases of Ga<sub>2</sub>O<sub>3</sub> on hexagonal substrates as a function of varying lattice constant of the substrate, as shown in Figure 1b. For epitaxial stabilization of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub>, on hexagonal substrates, it should have the lowest energy amongst the three competing phases. Furthermore, the lattice mismatch with the



**blishing** trate should be small, usually within ±3% in the case of oxides <sup>34</sup>, to avoid formation of defects caused by strain relaxation. With these constraints, we find hexagonal substrates matching the smallest CSL with  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> and having lattice constant between (4.97 – 5.12) Å to be most promising. Based on the calculated phase diagram under epitaxial strain, we find previously used substrates to grow epitaxial  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> either impose strains over 3 % or the  $\alpha$  or  $\beta$  phases are expected to be most stable, which explains the poor quality of the deposited thin films (See Supplemental Material) <sup>18</sup>. Based on identified region of stability of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub>, we searched the, Materials Project database <sup>35</sup>, and suggest promising substrates in Table 1. We find nonpolar substrates, such as  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub>, *h*-BN, SiO<sub>2</sub> are also commercially available. As discussed below, we find CaCO<sub>3</sub> is particularly promising to induce 2DEG in  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> due its large band gap of 6.0 eV and favorable band alignment <sup>27</sup>.

We now focus on identifying the polar properties of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> and examine whether it is indeed possible to obtain ferroelectric switching to explain the hysteretic behavior reported in recent experiments <sup>36</sup>. Bulk  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> belongs to the non-centrosymmetric *Pna*2<sub>1</sub> space group Using Berry-phase calculations, we find  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> has a spontaneous polarization (*P*<sub>SP</sub>) of 23  $\mu$ C/cm<sup>2</sup> oriented along the *c*-axis, which is in good agreement with a recent theoretical report <sup>13</sup>. The calculated *P*<sub>SP</sub> of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> is ten times larger than that of pyroelectric wide band gap semiconductor GaN (2.9  $\mu$ C/cm<sup>2</sup>) <sup>37</sup>. To switch the dipole moment in  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> to the opposite direction, a transition through an intermediate centrosymmetric (non-polar) supergroup of the *Pna*2<sub>1</sub> space group is required. Using group-theoretical techniques, as implemented in the Pseudo and Amplimodes programs in the Bilbao crystallographic server <sup>38-40</sup>, we have identified *Pnna*, *Pecn*, *Pbcn*, and *Pnma* as the four centrosymmetric supergroups from which *Pna*2<sub>1</sub> can be obtained with minimal atomic distortion. Amongst them, we find the transition from *Pbcn* to



**shing** 2<sub>1</sub> space group involves the smallest displacement of all atoms along the  $\Gamma_3^-$  polar phonon mode and has the smallest energy barrier (E<sub>b</sub>) of 0.95 eV, as shown in Figure 2 (see Supplementary materials Figure S2 for other transition pathways). This is a relatively large activation barrier comparable to that of GaFeO<sub>3</sub> (1.05 eV), which shows a high ferroelectric to paraelectric transition temperature of 1368 K <sup>41</sup>. Such a high activation barrier is expected to stabilize the polarization against thermally activated random dipole switching even at high temperatures during operation, which makes  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> an attractive ferroelectric semiconductor with an ultrawide band gap.

In addition to  $P_{SP}$ , the use of an epitaxial strain to stabilize  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> is expected to induce piezoelectric polarization ( $P_{PE}$ ). For a non-polar substrate, the termination of polarization at the substrate/ $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> interface will induce a charge density ( $\sigma$ ) with contributions from both  $P_{SP}$  and  $P_{PE}$  that can be expressed by <sup>42</sup>:

$$\sigma = P_{\rm SP} + P_{\rm PE} = P_{\rm SP} + e_{31}\epsilon_1 + e_{32}\epsilon_2 + e_{33}\epsilon_3, \tag{1}$$

where  $e_{33}$  and  $e_{31}$  are the piezoelectric constants,  $\epsilon_1$  and  $\epsilon_2$  are the two in-plane strains and  $\epsilon_3$  is the out-of-plane strain on  $\epsilon$ -Ga<sub>2</sub>O<sub>3</sub> due to the substrate. The out-of-plane strain can be obtained using the elastic constants of  $\epsilon$ -Ga<sub>2</sub>O<sub>3</sub>:  $\epsilon_3 = -\epsilon_1 c_{13}/c_{33} - \epsilon_2 c_{23}/c_{33}$ . The calculated piezoelectric and elastic constants are shown in Table 2. We find that the piezoelectric constants are comparable to III-V semiconductors. For instance,  $e_{33}$  and  $e_{31}$  in GaN are 0.73 and -0.49, respectively <sup>37</sup>. Due to the magnitude of  $e_{31}$  and  $e_{33}$ , even small epitaxial strains can produce a large  $P_{\text{PE}}$ .

Table 2 Calculated piezoelectric constants and elastic constants of bulk ε-Ga<sub>2</sub>O<sub>3</sub>.

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Publishing	(μC/cm <sup>2</sup> )	$e_{32} (\mu C/cm^2)$	<i>e</i> <sub>33</sub> (µC/cm <sup>2</sup> )	<i>c</i> <sub>31</sub> (GPa)	<b>c</b> <sub>32</sub> (GPa)	c33 (GPa)	
	9.5	7.9	-16.3	125	125	207	

We use CaCO<sub>3</sub> as the substrate and calculate the charge density at the interface with  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub>. CaCO<sub>3</sub> imposes a compressive strain of 1.4 %, which leads to  $P_{PE} = -49 \ \mu\text{C/cm}^2$ , which has an opposite sign to that of  $P_{SP}$  (23  $\mu$ C/cm<sup>2</sup>) and points towards the substrate. While  $P_{PE}$  is fixed by the choice of the substrate,  $P_{SP}$  is switchable by an external electric field. Thereby, depending on the orientation of  $P_{SP}$  in  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub>, the total polarization can be varied from -26  $\mu$ C/cm<sup>2</sup> ( $P_{PE} + P_{SP}$ ) to -72  $\mu$ C/cm<sup>2</sup> ( $P_{PE} - P_{SP}$ ). The corresponding sheet charge density ( $\sigma$ ) varies between 1.6×10<sup>14</sup> cm<sup>-2</sup> and 4.4×10<sup>14</sup> cm<sup>-2</sup>, respectively, which is higher than the density of present at AlGaN/GaN <sup>42</sup> and modulation-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>/Si:(Al<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> heterojunctions <sup>9-11</sup>. Furthermore, the ferroelectric nature of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> allows modulation of the charge density with an external electric field.

To identify the conditions under which the above calculated interface charges are expected to be mobile as opposed to being fixed, we have analyzed the band alignment and potential shift for different  $P_{SP}$  and thickness of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> films on the CaCO<sub>3</sub> substrate. The polarization in  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> is associated with an internal electric field and potential-shift along the [001] direction. Based on the calculated dipole moment in an unit cell of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub>, the potential-shift can be estimated as <sup>43-45</sup>:

$$\Delta V = -4\pi e \, \frac{(P_{SP} + P_{PE})c}{\varepsilon}.$$
(2)



**Publishingre**, c is the lattice vector along [001] direction (9.424 Å) of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> and  $\varepsilon$  is its calculated static dielectric constant (13.2). The potential shift  $\Delta V$  of pristine  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> without any strain (PPE=0) is -1.98 V/nm. The potential shift  $\Delta V$  of strained  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> on CaCO<sub>3</sub> substrate is 2.23 V/nm for  $P_{PE} + P_{SP}$  and 6.17 V/nm  $P_{PE} - P_{SP}$ . Therefore, it depends on the direction of  $P_{SP}$ . which can be controlled with an external electric field. With an optimal band alignment between the two materials, the large potential shift can be exploited such that the electrons from the valence band of CaCO<sub>3</sub> spontaneously ionize and spillover to the conduction band of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> to form a mobile 2DEG at the interface, as shown in Figure 3. We have calculated band alignment between  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> and the CaCO<sub>3</sub> substrate based on their bulk band gap, electron affinity, and potential shift. We find that the two materials form a staggered gap of 2.86 eV at the heterointerface (Supplemental Material), where the band alignment is determined by the Anderson rule without considering the polarity <sup>46</sup>. Figure 3 shows the schematic band alignment at the *ε*-Ga<sub>2</sub>O<sub>3</sub>(001)/CaCO<sub>3</sub>(0001) interface and the different spontaneous polarization and thickness of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> under which a mobile 2DEG is expected to form. The direction of the total polarization is always towards the substrate as it is determined by  $P_{PE}$ , regardless of the direction of  $P_{SP}$ . For a thin layer of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> (< 2.7 nm), if  $P_{SP}$  is parallel to  $P_{PE}$  (i.e.,  $P_{PE} + P_{SP}$ ), the strong field of 6.17 V/nm drives the conduction band of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> above the valence band of CaCO<sub>3</sub>. This results in ionization of the valence electrons of CaCO<sub>3</sub> and a mobile 2DEG on the  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> side. On the other hand, when the  $P_{SP}$  is switched such that it is antiparallel to  $P_{PE}$  (i.e.,  $P_{PE}$  –  $P_{SP}$ , the interface charges are confined to the valence band of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> and are expected to be immobile. For *ɛ*-Ga<sub>2</sub>O<sub>3</sub> films with thickness above 2.7 nm, mobile 2DEG are expected for both the directions of  $P_{SP}$ ; however, the sheet charge density can be tuned between  $1.6 \times 10^{14}$  cm<sup>-2</sup> and  $4.4 \times 10^{14}$  cm<sup>-2</sup> with an external electric field. We would like to point that the exact sheet charge

blishides sity and the critical thickness for the formation of 2DEG will also depend on the quality of the heterointerface, including the presence of defects and intermixing as is observed in the 2DEG formed at the LaAlO<sub>3</sub>/SrTiO<sub>3</sub> heterointerface <sup>47-49</sup>.

In conclusion, we have investigated a pathway to stabilize metastable, polar  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> using epitaxial strain and have identified promising substrate candidates. We have also calculated possible switching pathways for  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> and predict it to be a ferroelectric wide band gap semiconductor. Furthermore, we predict the formation of 2DEG at the interface of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> with CaCO<sub>3</sub> substrates with a sheet charge density that is two orders of magnitude higher than that obtained using modulation doping in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>/(Al<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub>. Due to the ferroelectric nature of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub>, we show that the interface 2DEG density can be modulated using an external electric field, which opens a pathway to design new device architectures. The polarization-induced 2DEG in  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> is also expected to result in devices that can simultaneously operate at high-power and high frequencies.

## **Supplementary Material**

See supplementary material for the choice of CSL, the effect of PBE functional, and the further substrate candidates for the epitaxial growth.

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**Figure 1 (a)** Atomic structure of  $\alpha$ ,  $\beta$ , and  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> along the preferred lattice orientation on a hexagonal substrate. Green and red atoms represent Ga and O, respectively. The yellow plane represents the growth plane. (b) Strain energetics on a hexagonal (001) substrate and cubic (111) substrate. The shaded box highlights the region where the epitaxial strain on  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> along [100] direction is under 3% and  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub> is more stable than the two other polymorphs.





**Figure 2**. The activation energy and spontaneous polarization along the transition path of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub>. The figures on the right show the atomic structure of the polar states with opposite direction of the dipole moment and the intermediate non-polar phase.



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**Figure 3** Band alignment at the  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub>(001)/CaCO<sub>3</sub>(0001) interface. Below the critical thickness of  $\varepsilon$ -Ga<sub>2</sub>O<sub>3</sub>, which is 2.7nm (a) mobile 2DEG are expected to form with  $P_{\text{PE}} - P_{\text{SP}}$ , but not for (b)  $P_{\text{PE}} + P_{\text{SP}}$ . (c) Above the critical thickness, mobile 2DEG will form even for  $P_{\text{PE}} + P_{\text{SP}}$ .





