In the present study we have successfully introduced an epitaxial MgO buffer between the ε-Fe₂O₃ and GaN layers to eliminate Ga migration into the iron oxide film. The resulting structural and magnetic properties of the fabricated heterostructure were probed by complementary x-ray diffraction (XRD), x-ray reflectometry (XRR), vibrating sample magnetometry (VSM), and polarized neutron reflectometry (PNR). An outcome of the epitaxial stabilization of ε-Fe₂O₃ on the MgO buffer is a technological advantage that provides further opportunities to integrate the promising epsilon ferrite into epitaxial Fe [4,25–28], Fe₃O₄ [29–33], α-Fe₂O₃ [31,32,34], and γ-Fe₂O₃ [31,33] heterostructures and superlattices grown on MgO substrates.

The substrates used in this work were commercial sapphire Al₂O₃ (0001) wafers with a 3-μm-thick Ga terminated MgO buffer.

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The magnetic-on-semiconductor heterostructures attract a lot of interest nowadays due to the vast opportunities they provide for designing novel functional spintronic devices for magnetic memory applications and bio-inspired computing [1–7]. Placing a multiferroic layer with controllable magnetization/polarization in contact with a semiconductor adds the functionality of controlling optical, electronic, and magnetic properties of the heterostructure by applied voltage [8–11]. One of the rare examples of material with spontaneous room-temperature magnetization and electric polarization is the metastable iron(III) oxide polymorph ε-Fe₂O₃ [12–15]. Quite recently, the crystalline layers of ε-Fe₂O₃ have been successfully synthesized on a number of oxide substrates [12,16–20] and GaN(0001) [21]. The structural and magnetic properties of the iron oxide films drastically depend on the composition of the neighboring buffer layer, the chosen substrate, and the growth temperature. The feasibility to synthesize as much as four different iron oxide phases: ε-Fe₂O₃, Fe₃O₄, α-Fe₂O₃, and γ-Fe₂O₃ on GaN(0001) has been recently demonstrated [21]. It has been shown that stabilization of the ε-Fe₂O₃ phase requires elevated growth temperature that leads to formation of a few nanometer-thick Ga-rich magnetically soft transition layer at the interface between the iron oxide film and the GaN substrate [22]. Later on, a very similar Ga/Fe substitution phenomena have been observed in yttrium iron garnet (YIG) films grown at above 700 °C onto a gadolinium gallium garnet (GGG) [23]. Although Pn₃aGa₂Ga-substituted epsilon-ferrite GaFeO₃ is isostructural to ε-Fe₂O₃ [24] and promotes further growth of the desired phase, its magnetic ordering temperature and coercivity field are somewhat lower than those of ε-Fe₂O₃ [14]. This can potentially reduce the magnetoelectric and magneto-optical performance of the functional devices based on the ε-Fe₂O₃/GaN heterostructures.

In the present study we have demonstrated epitaxial stabilization of the metastable magnetically hard ε-Fe₂O₃ phase on top of a thin MgO(111) buffer layer grown onto the GaN (0001) surface. The primary purpose to introduce a 4-nm-thick buffer layer of MgO in between Fe₂O₃ and GaN was to stop thermal migration of Ga into the iron oxide layer. Though such migration and successive formation of the orthorhombic GaFeO₃ was supposed earlier to be a potential trigger of the nucleation of the isostructural ε-Fe₂O₃, the present work demonstrates that the growth of single crystalline uniform films of epsilon ferrite by pulsed laser deposition is possible even on the MgO capped GaN. The structural properties of the 60-nm-thick Fe₂O₃ layer on MgO/GaN were probed by electron and x-ray diffraction, both suggesting that the growth of ε-Fe₂O₃ is preceded by formation of a thin layer of γ-Fe₂O₃. The presence of the magnetically hard epsilon ferrite was independently confirmed by temperature dependent magnetometry measurements. The depth-resolved x-ray and polarized neutron reflectometry reveal that the 10 nm iron oxide layer at the interface has a lower density and a higher magnetization than the main volume of the ε-Fe₂O₃ film. The density and magnetic moment depth profiles derived from fitting the reflectometry data are in a good agreement with the presence of the magnetically degraded γ-Fe₂O₃ transition layer between MgO and ε-Fe₂O₃. The natural occurrence of the interface between magnetoelectric ε- and spin caloritronic γ-iron oxide phases can enable further opportunities to design novel all-oxide-on-semiconductor devices.

The substrates used in this work were commercial sapphire Al₂O₃ (0001) wafers with a 3-μm-thick Ga terminated MgO buffer.
GaN (0001) layer grown on top by means of metalorganic vapor-phase epitaxy (MOVPE). The GaN surface showed a step-and-terrace surface morphology (Fig. 1) as confirmed by atomic force microscopy (AFM). The oxide layers were grown by pulsed laser deposition (PLD) from MgO and Fe₂O₃ targets ablated using a KrF laser. The crystallinity and epitaxial relations of the grown layers were controlled by in situ high energy electron diffraction (RHEED) reciprocal space three-dimensional (3D) mapping. With this technique [35] one obtains a 3D reciprocal space map from a sequence of conventional RHEED images taken during the azimuthal rotation of the sample. Thus the obtained sequence of the closely spaced spherical cuts through the reciprocal space and can be then compiled into a uniform 3D map and shown in the easy interpreted form of planar cuts and projections. The side cuts and plan views of the reciprocal space maps obtained at each growth stage are shown in the same scale in Fig. 2. The expected positions of the reciprocal lattice nodes are indicated with circles on the the left halves of the maps.

The 4-nm-thick MgO layer was deposited onto GaN in 0.02 mbar of oxygen at the substrate temperature of 800 °C. As confirmed by atomic force microscopy (Fig. 1), the MgO coverage on GaN is smooth and sufficiently uniform to serve as a diffusion barrier. The epitaxial relations extracted from RHEED are as follows: GaN(0001) || MgO(111); GaN[1 1 10] || MgO ± [1 1 2] (Fig. 2). The two possible MgO orientations arise due to the symmetry reduction occurring at the interface: from GaN(0001) C₆ to MgO(111) C₃. Reflections on the RHEED map of MgO are streaky corresponding to the semiplat surface.

A 60-nm-thick iron oxide layer was grown onto the surface of MgO(111) in 0.2 mbar of oxygen at the substrate

FIG. 1. Atomic force microscopy images of the surface morphology at consecutive growth stages (from bottom to top): GaN, MgO/GaN, and ε-Fe₂O₃/MgO/GaN.

FIG. 2. In situ reflection high-energy electron diffraction maps obtained at consecutive growth stages: MgO/GaN, γ-Fe₂O₃/MgO/GaN, and ε-Fe₂O₃/γ-Fe₂O₃/MgO/GaN. Shown in the same scale are the side cuts (top) and plan view projections (bottom) of the reciprocal space. The modeled reflection positions are shown with circles.
temperature of 800 °C following the approach described in our previous report [21]. It was discovered that unlike when grown directly on GaN, the iron oxide layer on MgO nucleates in gamma rather than in epsilon phase. Upon deposition of 3–5 nm of iron oxide, the RHEED reciprocal space maps start showing a distinct 2 × 2 pattern of streaks characteristic for the spinel γ-Fe₂O₃ lattice (Fig. 2) oriented with the [111] axis perpendicular to the surface and the [11 − 2] axis parallel to MgO [11 − 2] and GaN[1 − 10]. The diffraction map remains streaky corresponding to the still flat surface.

The preference of the γ-Fe₂O₃ over ε-Fe₂O₃ is naturally related to the cubic symmetry of both lattices. The phase choice mechanisms for the Fe₂O₃/MgO(111) system might be similar to those of the Fe₂O₃/MgO (001) system where γ-Fe₂O₃ is known to be the dominant phase [31,36,37]. It is noteworthy that a thin γ-like transition layer was also observed during the nucleation of α- and ε-Fe₂O₃ directly on GaN [21]. Though the diffraction patterns of that layer bore resemblance to FeO, the spacing between the adjacent (111) reflections of MgO as they considerably overlap with those of γ-Fe₂O₃. The few nanometer surface roughness measured by AFM (Fig. 1) is small because of the larger surface cell and the lack of the equivalent cubic symmetry of both lattices. The in-plane periodicity in GaN is about 8.5% larger than in Fe₂O₃ [21]. The observed in-plane and out-of-plane reflection widths may be used to judge on the strain relaxation and minimal crystallographic domain size in the grown films. The strain relaxation if present would involve a distribution of lattice parameters in the system and would cause reflection broadening that is proportional to the magnitude of the wave vector Q. Even if such a broadening is present in our system, it is below the experimental resolution as all the observed reflections are of the same shape and width. Such an effect can be attributed to the finite size of the coherent crystallographic domains within the crystal lattice and is typical for the nanostructured samples. Measuring the in-plane and out-of-plane reflection widths (see the insets in Fig. 3) one can conclude that the minimal coherent domains of ε-Fe₂O₃ are shaped as (width × height) 14×35 nm² columns (in agreement with Ref. [22]) while those of γ-Fe₂O₃ look like 33 × 10 nm² disks. The reduced coherent thickness of ε-Fe₂O₃ film suggests that a transition layer with a mixed lattice structure exists at the γ-Fe₂O₃/ε-Fe₂O₃ interface. The lateral coherence between the adjacent nucleation sites is substantially reduced because the surface cell of the iron oxides is larger than that of MgO. Compared to γ-Fe₂O₃ the coherent domain of ε-Fe₂O₃ is smaller because of the larger surface cell and the lack of the
The magnetometry measurements were carried out using a Quantum Design PPMS vibrating-sample magnetometer (VSM). The magnetic field was applied in the sample plane along the [100] easy magnetization axis of one of the three ε-Fe₂O₃ domains. Figure 4 shows the hysteresis loops measured in the temperature range of 5–400 K and corrected for the linear diamagnetic contribution of the substrate. The observed values of saturation magnetization were about 130 emu/cm³ at T = 5 K and 100 emu/cm³ at T = 400 K which is consistent with what was reported for ε-Fe₂O₃ nanoparticles [38] and ε-Fe₂O₃ thin film grown on SrTiO₃ (STO) [12], YSZ [19,39], and GaN [22], and predicted from ab initio calculations [15].

The wasp-waist magnetization loops shown in Fig. 4(a) are typical for ε-Fe₂O₃ films and nanoparticles and can be qualitatively decomposed to hard and soft component loops [Fig. 4(b)] by subtracting 2M_{soft}/\pi \arctan(B/B_{sat}) from temperature-independent M_{sat} = 71 emu/cm³ and B_{sat} = 62 mT. These parameters were unambiguously derived from manual optimization aimed at making the remaining hard component smooth and monotonous in the vicinity of zero magnetic field.

The value of M_{sat} = 71 emu/cm³ observed for the soft magnetic component is in general agreement with the presence of γ-Fe₂O₃ sublayer buried below the main layer of ε-Fe₂O₃ as observed by XRD, RHEED, and PNR. The magnetization plotted in Fig. 4(b) is normalized to the total film thickness of 70 nm. Taking into account the reported values of M_s = 300–400 emu/cm³ for γ-Fe₂O₃/MgO, the soft loop can be attributed to a layer of γ-Fe₂O₃ having thickness of 12–14 nm. This is comparable though slightly higher than the thickness estimated from RHEED and PNR (see the details below).

The hard component hysteresis loops show a large saturation field of 1.2–1.8 T characteristic of ε-Fe₂O₃. The coercive field gradually increases as the sample is cooled down from 0.27 T at 400 K to 0.66 T at 5 K. The loop shape is typical for the system with three uniaxial domains at 120 deg to each other. At saturation the magnetization is collinear to the field in all three domains M_{f,\text{sum}} = 3M_s. From saturation to zero field the magnetization gradually decreases to 2/3 M_{f,\text{sum}} as the the magnetization in the two noncollinear domains returns to the equilibrium state at 120 deg to the field. From this state the magnetization reversal is gradually completed towards the negative saturation. Notably, the magnetic phase transition to an incommensurate state that is often observed in ε-Fe₂O₃ nanoparticles, as dramatic shrinkage of the loop at T ≈ 100–150 K [40–43], has not been observed in ε-Fe₂O₃ films—neither on GaN nor on the other substrates. The absence of a sharp phase transition in films can be caused by the variation of the magnetic properties across the film depth. Thus, a temperature-dependent investigation of the depth resolved magnetic structure of ε-Fe₂O₃ films by neutron or resonant x-ray diffraction is highly desired to address this issue.

The XRR measurement was performed on the Panalytical X’Pert PRO x-ray diffractometer at room temperature using Cu Kα (1.5406 Å) radiation to determine the electron scattering length density (SLD) profile ρ_z of the film as a function of distance from the GaN surface z. The specular reflectance was measured in the range of incident angles between 0.5 and 3.5 deg covering the Q_z range from 0.075 to 0.5 Å⁻¹.

The neutron reflectometry experiments were performed at the D17 setup [44,45] (ILL, Grenoble, France) in polarized time-of-flight mode. Sample temperature and magnetic field were controlled by an Oxford Instruments 7 T vertical field cryomagnet equipped with single-crystalline sapphire windows. Neutrons with wavelengths of 4–16 Å were used to ensure the constant polarization of P_l > 99%. Three different incident angles (0.8, 1.5, and 3.7 deg) were chosen to access the Q_z range from 0.017 to 0.17 Å⁻¹. Intensity of the reflected beam was collected by a two-dimensional ⁴He position-sensitive detector. The data was integrated using a method taking into account the sample curvature or beam divergence [44,46]. Non-spin-flip reflectivities R⁺ and R⁻,
where \( + \) (\( - \)) denotes the incident neutron spin alignment parallel (antiparallel) to the direction of applied magnetic field, were acquired without polarization analysis. The detailed description of the reflectometry techniques can be found elsewhere [47,48].

Figure 5(a) shows x-ray reflectivity (room temperature) and neutron reflectivity (\( T = 5 \) K) curves plotted as a function of momentum transfer \( Q_z \). The neutron reflectivity curves were measured at the characteristic characteristic points of the \( M(B) \) loop marked as (1–4) in Fig. 4. The PNR curves shown in Fig. 5(a) are measured in applied magnetic fields of \( B = 0.025 \) T (state 1 in remanence) and \( B = 2 \) T (state 3 in saturation). The XRR and PNR curves were simultaneously fitted using GenX software [49]. The simplest model, for which the fitting routine converges, corresponds to a stack consisting of the GaN substrate, the MgO buffer, the transition iron oxide layer with an unspecified density, and the GaN film. The depth profiles of the x-ray (\( \rho_x \)) and nuclear neutron (\( \rho_r \)) scattering length densities (SLDs) extracted from the refined model are shown in Fig. 5(b).

The magnetization profile of the heterostructure is encoded in the dependence of the spin-asymmetry ratio \(( R^+ - R^- )/( R^+ + R^- )\) on \( Q_z \). Fitting it against the model gives the depth profile of the magnetic contribution to the neutron SLD \( \rho_m(\AA^2) \) which can be converted to magnetization \( M \) (emu/cm\(^3\)) using the following formula: \( M = 3505 \times 10^5 \rho_m \) [50]. The measured and fitted spin-asymmetry ratios are shown in Fig. 5(c) for the two magnetic states 2 and 3 on the lower branch of the hysteresis loop (see Fig. 4): with partially switched magnetization \(( B = 0.5 \) T before and \( B = 0.025 \) T after magnetization reversal, and back to the positive remanence)

FIG. 5. (a) Measured (symbols) and fitted (solid lines) x-ray and neutron reflectivity curves as a function of momentum transfer (\( Q_z \)) on a logarithmic scale. The curves are shifted along the vertical axis for clarity. (b) X-ray scattering length density (SLD) \( \rho_x \) (green line), and neutron nuclear SLD \( \rho_r \) (red line) of \( \epsilon \)-Fe\(_2\)O\(_3\)/MgO/GaN film as a function of the distance from the GaN layer surface (\( z \)) obtained from the fitting routine. X-ray SLD \( \rho_x \) is given in the units of the classical electron radius \( r_e \). (c) PNR spin-asymmetry ratio \(( R^+ - R^- )/( R^+ + R^- )\) at applied magnetic field \( B = 2 \) T and \( B = 0.5 \) T after magnetization reversal obtained from experimental data (symbols) and fitted models (solid curves). (d) Neutron magnetic SLD \( \rho_m \) profile at \( B = 2 \) T, \( B = 0.025 \) T before and at \( B = 0.025 \) T, \( B = 0.5 \) T after magnetization reversal, corresponding to the characteristic points (1–4) of the \( M(B) \) loop shown in Fig. 4.
as shown in Fig. 5(d) the magnetization of the softer interface layer is switched between $B = 0.025 \text{T}$ (state 1) and $B = 0.5 \text{T}$ (state 2) and reaches saturation at 70 emu/cm$^3$ \(\epsilon\-Fe_2O_3\) layer observed by VSM. The magnetization of the much harder \(\epsilon\-Fe_2O_3\) layer switches somewhere between $B = 0.5 \text{T}$ (state 2) and $B = 2 \text{T}$ (state 3). As the magnetically hard component of the hysteresis loop is not completely closed in the maximum applied positive of 2 T [Fig. 4(b)], the PNR curves measured at $B = 2 \text{T}$ (state 3) and $B = 0.025 \text{T}$ (state 4) belong to the minor branch of the hysteresis. Magnetization of 56 emu/cm$^3$ \(\gamma\-Fe_2O_3\) is found at $B = 2 \text{T}$, which is slightly smaller that the saturation moment. Going back to positive remanence of the minor loop (state 4), the magnetization of both interface and bulk layers start slowly decreasing (faster for the interface layer).

Sequential switching of interface \(\gamma\) and main \(\epsilon\) layers in principle reflects a steplike shape of the hysteresis loops observed by VSM magnetometry (Fig. 4). It must be noted that the maximum magnetization for \(\epsilon\-Fe_2O_3\) layer derived from PNR is about twice lower than the highest reported values for \(\epsilon\-Fe_2O_3\) but in good agreement with the maximum magnetization observed in the decomposed VSM loop shown in Fig. 4(b). The maximum magnetization of the \(\gamma\-Fe_2O_3\) layer derived from PNR is about 5 times lower than the expected 300–400 emu/cm$^3$ reported for \(\gamma\-Fe_2O_3/MgO\) layers [31,36,37], and cannot completely explain the soft-magnetic component observed by VSM. Magnetic degradation of the transition \(\gamma\-Fe_2O_3\) layer can be possibly explained by the size effect [51], epitaxial strain [52–54], or large number of the antiphase boundaries [55,56] between the nanocolumns in the plane of the layer and at the interface with main \(\epsilon\-Fe_2O_3\) film.

The much higher magnetization of the soft magnetic component observed in VSM suggests that another soft magnetic phase is likely present in the sample that cannot be distinguished in the PNR experiment. Similar effect was also observed in \(\epsilon\-Fe_2O_3\) grown directly on GaN [22]. The most plausible candidates are homogeneously distributed minor fractions of polycrystalline \(\gamma\-Fe_2O_3\) and Fe$_3$O$_4$ [57–59] not pronounced in XRD data. Again, one must also take into account the columnar structure of the \(\epsilon\-Fe_2O_3\) films containing considerable concentration of the antiphase boundaries. As was pointed out in Ref. [60] the antiphase boundaries in iron oxides may account for the soft magnetic behavior. The magnetic moments located in minor phase fractions of small volume, or at the antiphase boundaries in the sample plane that cannot be resolved with PNR, which is a laterally averaging technique, because the disordered moments at boundaries and minor phase fractions are highly diluted, but integrated into the magnetization measured by VSM. We suggest that the deposition of small (\(\mu\text{m}\) scale) iron particulates ejected from the PLD target is the most plausible scenario, that have been also observed for other PLD films [61–63].

In conclusion, we have demonstrated the possibility to epitaxially grow single crystal \(\epsilon\-Fe_2O_3\) thin film on MgO(111) surface by pulsed laser deposition. In contrast to the previously investigated nonbuffered \(\epsilon\-Fe_2O_3/GaIn(0001)\) system, where the interfacial GaFeO$_3$ magnetically degraded layer was reported to form due to Ga diffusion [22] from GaN, the \(\epsilon\-Fe_2O_3/MgO/GaN\) system has advantage of exploiting the diffusion blocking MgO barrier. Though formation of the orthorhombic GaFeO$_3$ was supposed earlier to be a potential trigger of the nucleation of the isostructural \(\epsilon\-Fe_2O_3\), the present work demonstrates that the growth of single crystalline uniform films of epsilon ferrite by pulsed laser deposition is possible even without the aid of Ga. Still the aid of Ga seems important as on GaN the \(\epsilon\-Fe_2O_3\) layer could be nucleated with a transition layer of few angstrom thickness while on MgO the growth of \(\epsilon\-Fe_2O_3\) film is preceded by nucleation of a 10-nm-thick layer of another iron oxide phase. A complimentary combination of electron and x-ray diffraction, x-ray reflectometry, and polarized neutron reflectometry techniques allowed unambiguous identification of this phase as \(P4_132\) (\(P4_132\) cubic \(\gamma\-Fe_2O_3\)). This phase is known to show magnetoelectric functionality [64] and spin Seebeck effect [65] and can enable further opportunities to design the novel all-oxide heterostructure magnetoelectric and spin caloritronic devices.

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