Synchrotron studies of laser MBE grown iron oxide epitaxial layers on GaN(0001)

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Hybridization of semiconductor and magnetic materials into a single heterostructure is believed to provide vast opportunities in design of novel functional spintronic devices. The nanometer thick epitaxial films of four iron oxides (Fe3O4, α-Fe2O3, γ-Fe2O3 and multiferroic metastable ε-Fe2O3) exhibiting drastically different crystal structure, electric and magnetic properties have been recently stabilized on GaN(0001) using Laser MBE growth technique. The present work is focused on the synchrotron X-ray diffraction, X-ray absorption spectroscopy and X-ray magnetic circular dichroism studies of the iron oxide on GaN films aimed at confirmation of their crystalline quality and adequate magnetic structure.

1 Introduction

Hybrid heterostructures combining closely spaced semiconducting and magnetic layers are promising candidates to be used in design of functional spintronic devices. Unlike diluted magnetic semiconductors, the hybrid heterostructures allow separate control over the magnetic and electrical properties. Insulating properties and reasonable optical transparency of the magnetic layer in the visible range would be welcome in the optoelectronic ferroic-semiconductor devices. The simple formula iron oxides are suitable candidates for magnetic layer material in the discussed hybrid heterostructures. The iron oxides including Fe3O4 and a number of Fe2O3 polymorphs make up a big family of magnetically ordered materials exhibiting a rich variety of outstanding physical properties presenting interest for technological applications and fundamental studies. Ferrimagnetic Fe3O4 (magnette) is known for the intriguing Verwey metal-insulator transition. Ferrimagnetic γ-Fe2O3 (maghemite) is the close relative of magnetite with slightly smaller magnetization and insulating properties. Hematite (α-Fe2O3) deserves interest for the Morin transition from the antiferromagnetic to a weak ferromagnetic state. The metastable ε-Fe2O3 not existing in bulk has been only few times crystallized in the form of epitaxial layers [1, 2, 3]. This intriguing material shows very high magnetocrystalline anisotropy with coercivity values exceeding 2 T and exhibits multiferroic properties.

In the present work GaN was chosen as the semiconductor widely used in numerous devices such as bright blue LEDs, HEMT transistors for high-power, high-frequency and high radiation resistant applications. Placing a ferroic film next to the active zone of the GaN-based devices is supposed to add new functionality to these devices [4,5] including spin injection into GaN.

Recently the possibility to stabilize four different iron oxide phases - Fe3O4, α-Fe2O3, γ-Fe2O3 and ε-Fe2O3 - in the form of epitaxial layers on GaN substrate by Laser MBE has been reported [6]. The orange tint insulating antiferromagnetic ε-Fe2O3 phase nucleates in oxygen at intermediate temperature and is the most stable one. The ochre tint insulating metastable ε-Fe2O3 polymorph nucleates in oxygen at higher temperature and exhibits properties of a hard ferrimagnet with the magnetization lying in-plane and coercivity exceeding 1 T. Magnetite films are grown in nitrogen exhibiting gray metallic tint and being conductive at RT due to half metal nature of Fe3O4. The close to rectangular in-plane magnetization curves measured for magnetite films show coercivity of 600 Oe. Maghemite γ-Fe2O3 films are produced by annealing magnetite layers in oxygen. The Fe3O4 – γ-Fe2O3 transformation is accompanied by the film color change from gray to ochre, drop of conductivity and slight decrease of the magnetization. To grow thick γ-Fe2O3 layers the growth / oxidation procedure has to be repeated multiple times as the Fe3O4 oxidation affects only the top 20 nm of the film.

In the present report we present the results of synchrotron studies performed on the iron oxide on GaN layers. The X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) studies have been performed at PF to clarify the influence of the laser MBE technological parameters on the growth process, as well as on the crystal and magnetic structure of the resulting iron oxide films.

2 Experiment

The iron oxide films having thickness of 40-60 nm were grown in Ioffe Institute on the prefabricated GaN (0001) / Al2O3 (0001) substrates by Laser MBE using the KrF excimer laser to ablate Fe3O4 target. Depending on the particular iron oxide phase the growth was performed at 600 – 800°C in either oxygen or nitrogen atmosphere at a pressure of 0.02 – 0.2 mbar. Preliminary structural studies have been performed in situ by high-energy electron diffraction (RHEED) 3D reciprocal space mapping [7] to confirm epitaxial stabilization of each particular phase. The in-plane magnetization curves have been measured by MOKE and VSM to confirm the expected magnetic properties. XRD measurements have been carried out at BL3A beamline. The dedicated software has been developed by the authors to carry out 3D reciprocal space mapping at BL3A using the Pilatus 100K detector. The 3D mapping data visualization, processing and modeling is carried out in a unified way for both X-ray and electron diffraction data. XAS and
XMCD studies have been carried out at BL16 beamline at room temperature.

3 Results and Discussion

Fig. 2 shows intensity profiles taken along the specular rods for ~40 nm films of the four different iron oxide phases grown on GaN. The profiles have been precisely aligned using the Al$_2$O$_3$ and GaN substrate reflections as a reference. Reflection indexing was facilitated knowing the epitaxial relations extracted from our preliminary RHEED studies:

\[ \begin{align*}
\alpha\text{Fe}_2\text{O}_3 \; (001) \parallel \; \text{GaN}(001); \alpha\text{Fe}_2\text{O}_3 \; [110] \parallel \; \text{GaN}[1 \bar{0} \bar{1}] \\
\epsilon\text{Fe}_2\text{O}_3 \; (001) \parallel \; \text{GaN}(001); \epsilon\text{Fe}_2\text{O}_3 \; [100] \parallel \; \text{GaN}[0 \bar{1}0] \\
\gamma\text{Fe}_2\text{O}_3 \; (111) \parallel \; \text{GaN}(001); \gamma\text{Fe}_2\text{O}_3 \; [1 \bar{1} \bar{2}] \parallel \; \text{GaN}[1 \bar{0} \bar{1}] \\
\text{Fe}_3\text{O}_4 \; (111) \parallel \; \text{GaN}(001); \text{Fe}_3\text{O}_4 \; [1 \bar{1} \bar{2}] \parallel \; \text{GaN}[1 \bar{0} \bar{1}] 
\end{align*} \]

The given epitaxial relations help in clarifying why the four iron oxides having so different lattice structure and lattice parameters grow epitaxially on GaN. The iron oxide lattice basically consists of closely packed frame of oxygen atoms with iron atoms sandwiched in between the oxygen planes in octahedral and tetrahedral slightly distorted sites (Fig. 1). GaN has a similar lattice structure with closely packed frame of nitrogen atoms and Ga atoms in between. Our diffraction studies confirm that the different iron oxides nucleate on GaN so that the oxygen lattice in between. Our diffraction studies confirm that the four iron oxides having so different lattice structure and lattice parameters grow epitaxially on GaN. The iron oxide lattice may be rotated around surface normal by 180 deg in addition to the epitaxial relations discussed above. Related to GaN (0001) surface symmetry have been found mapping. A number of equivalent epitaxial relations GaN have been studied by XRD 3D reciprocal space mapping. A number of equivalent epitaxial relations have been found in addition to the epitaxial relations discussed above. Placed over hexagonal GaN (0001) surface the iron oxide lattice may be rotated around surface normal by 180 deg for \( \alpha\text{Fe}_2\text{O}_3 \), \( \gamma\text{Fe}_2\text{O}_3 \), \( \text{Fe}_3\text{O}_4 \), and by ±120 deg for \( \epsilon\text{Fe}_2\text{O}_3 \).

A noteworthy feature of the shown profiles is the highly asymmetrical shape of the GaN peak slopes. This is an evidence of interference between crystal truncation rods of the flat GaN (0001) surface and the transition layer. This kind of interference often results in noticeable shift of the film peak maximum and can be used to estimate the distance at the interface. Interestingly there exists a small but noticeable difference between \( \gamma\text{Fe}_2\text{O}_3 \) and \( \text{Fe}_3\text{O}_4 \) intensity profiles. Magnetite and maghemite are known to crystallize in the same cubic lattice with lattice parameters rather close to each other. The only difference (besides iron oxidation state) is the presence of octahedral vacancies in the \( \gamma\text{Fe}_2\text{O}_3 \) lattice. According to the presented XRD profiles, the \( \text{Fe}_3\text{O}_4 \) to \( \gamma\text{Fe}_2\text{O}_3 \) transformation is accompanied by slight decrease of the (111) interlayer distance (see the 555 reflection) due to Fe diffusion from the layer to the surface where the reaction with oxygen takes place.

The lattice parameters extracted from the specular profiles are:

- \( \alpha\text{Fe}_2\text{O}_3 \): \( a=8.37 \; \text{Å} \) (tabular value \( a=8.33 \; \text{Å} \) for \( \gamma\text{Fe}_2\text{O}_3 \)), \( c=9.481 \; \text{Å} \) (tabular value \( c=9.471 \; \text{Å} \) for \( \alpha\text{Fe}_2\text{O}_3 \))
- \( \gamma\text{Fe}_2\text{O}_3 \): \( a=8.53 \; \text{Å} \) (tabular value \( a=8.40 \; \text{Å} \) for \( \text{Fe}_3\text{O}_4 \)), \( c=13.708 \; \text{Å} \) (tabular value \( c=13.747 \; \text{Å} \) for \( \gamma\text{Fe}_2\text{O}_3 \))
- \( \text{Fe}_3\text{O}_4 \): \( a=9.481 \; \text{Å} \) (tabular value \( a=9.471 \; \text{Å} \) for \( \epsilon\text{Fe}_2\text{O}_3 \)).

The tendency is that the iron oxide lattice is slightly expanded perpendicular to the surface.

The off specular reflections of the iron oxide films on GaN have been studied by XRD 3D reciprocal space mapping. A number of equivalent epitaxial relations related to GaN (0001) surface symmetry have been found in addition to the epitaxial relations discussed above. Placed over hexagonal GaN (0001) surface the iron oxide lattice may be rotated around surface normal by 180 deg for \( \alpha\text{Fe}_2\text{O}_3 \), \( \gamma\text{Fe}_2\text{O}_3 \), \( \text{Fe}_3\text{O}_4 \), and by ±120 deg for \( \epsilon\text{Fe}_2\text{O}_3 \).
Interestingly the εFe₂O₃ off-specular reflections were found to be elongated along [100] in-plane direction. An example is shown in Fig. 3 representing a reciprocal space cut carried out parallel to the surface through εFe₂O₃ (113) and εFe₂O₃ (112) off-specular reflections. When reciprocal lattice nodes of two/three orientational domains coincide, reflections have four- or six-ray stars. The observed reflection elongation is probably due to disorder caused by coexistence of the three orientational domains. Presumably anti-phase boundaries are formed upon island coalescence with different orientation or phase shift. The latter is favored by the fact that εFe₂O₃ surface cell is 6 times larger than that of the GaN (Fig. 3d).

![XRD Maps](image)

**Fig. 3:** Off-specular XRD maps. Reciprocal space cuts parallel to the surface showing star-like shapes of εFe₂O₃ (113) (a) and εFe₂O₃ (112) (b) reflections. Reciprocal space cut perpendicular to the surface showing the Laue oscillations on the streak passing through εFe₂O₃ (112) reflection (c). Schematic explanation of stacking fault formation principle (d).

**XMCD and XAS results**

X-ray absorption spectroscopy (XAS) is known to be a highly appropriate tool to investigate core level atomic structure responsible for oxidation state and crystallographic environment of individual atoms. With circular polarized light it is possible to probe the atom selective magnetization. The L₂,₃ spectra of transition metals are usually dominated by the dipole-allowed 2p to 3d transitions. They consist of L₃ and L₂ main peaks resulting from spin-orbit coupling. Each of the main peaks is further split by crystal field (εₚ, ε₂). This splitting provides a highly sensitive tool to probe the coordination environment and the corresponding magnetization.

The Fe L₂,₃ XAS spectra measured in the iron oxide films grown on GaN are shown in Fig. 4a. They can be compared to the reference spectra adopted from [8, 9, 10] and shown in Fig. 4b. In all the studied samples the L₁ peak exhibits two major components: a larger peak at 709.5 eV and a smaller satellite at 708 eV. This spectral shape is characteristic of iron oxides as opposed to the metallic iron [11].

**Fig. 4:** XAS and XMCD spectra obtained from the iron oxide epitaxial films on GaN. Reference data adopted from [8,9,10] is shown for comparison.

In thick 40 nm αFe₂O₃ film the splitting is most pronounced originating from the pure octahedral coordination of Fe³⁺ ions in hematite [8,11,12]. In 40 nm γFe₂O₃ and εFe₂O₃ films the L₁ splitting is less pronounced in agreement with earlier studies of these materials: γFe₂O₃ [8, 12] and εFe₂O₃ [9]. While the separation between the 708 eV and 709.5 eV components is the same as in αFe₂O₃, the intensity drop between the peaks becomes less pronounced due to the presence of a Fe³⁺ T₃ line right in the middle between the two O₃ peaks. Interestingly the same shape of L₁ edge as in γFe₂O₃ and εFe₂O₃ is observed during the onset of αFe₂O₃ growth (measured in a 5 nm film) indicating the presence of T₄ sites. Noteworthy the non-hematite nature of the few nm thick transition layer formed between the GaN substrate and the pure αFe₂O₃ phase is also confirmed by our diffraction measurements. It is noteworthy that in the only one existing paper describing the XAS of εFe₂O₃ [9] the
The XAS spectra obtained in this work for the exotic εFe₂O₃ phase was similar to that of γFe₂O₃. Interestingly in εFe₂O₃ nanoparticles showed aFe₂O₃-like absorption. The XMCD spectra of the ferromagnetic iron oxide films on GaN allowed visualization of the sublattice specific magnetization behavior being in good agreement with the known results for bulk aFe₂O₃, γFe₂O₃ and nanoparticulate εFe₂O₃.

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