BL-16A/2014G725, BL-3A/2014G726, BL-3A/2016G684

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

Sergey Suturin[1,*], Alexander Korovin[1], Masao Tabuchi[2] and Nikolai Sokolov[1]
[1] Ioffe Institute, 26 Polytechnicheskaya, 194021 St. Petersburg, Russia
[2] Synchrotron Radiation Research Center, Nagoya University, Nagoya, Japan

Hybridization of semiconducting 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 (Fe_3O_4, αFe_2O_3, γFe_2O_3 and multiferroic metastable εFe_2O_3) 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 Fe_3O_4 and a number of Fe_2O_3 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 Fe_3O_4 (magnetite) is known for the intriguing Verwey metal-insulator transition. Ferrimagnetic γFe_2O_3 (maghemite) is the close relative of magnetite with slightly smaller magnetization and insulating properties. Hematite (αFe_2O_3) deserves interest for the Morin transition from the antiferromagnetic to a weak ferromagnetic state. The metastable εFe_2O_3 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 - Fe_3O_4, αFe_2O_3, γFe_2O_3 and εFe_2O_3 - in the form of epitaxial layers on GaN substrate by Laser MBE has been reported [6]. The orange tint insulating antiferromagnetic αFe_2O_3 phase nucleates in oxygen at intermediate temperature and is the most stable one. The ochre tint insulating metastable εFe_2O_3 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 Fe_3O_4. The close to rectangular in-plane magnetization curves measured for magnetite films show coercivity of 600 Oe. Maghemite γFe_2O_3 films are produced by annealing magnetite layers in oxygen. The Fe_3O_4 – γFe_2O_3 transformation is accompanied by the film color change from gray to ochre, drop of conductivity and slight decrease of the magnetization. To grow thick γFe_2O_3 layers the growth / oxidation procedure has to be repeated multiple times as the Fe_3O_4 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) / Al_2O_3 (0001) substrates by Laser MBE using the KrF excimer laser to ablate Fe_2O_3 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_2O_3 and GaN substrate reflections as a reference. Reflection indexing was facilitated knowing the epitaxial relations extracted from our preliminary RHEED studies:

αFe_2O_3 (001) || GaN(001); αFe_2O_3 [110] || GaN[1-10]
εFe_2O (001) || GaN(001); εFe_2O_3 [100] || GaN[1-10]
γFe_2O_3 (111) || GaN(001); γFe_2O_3 [11-2] || GaN[1-10]
Fe_3O_4 (111) || GaN(001); Fe_3O_4 [11-2] || GaN[1-10]

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 planes are aligned parallel to the surface and the O-O-O triangles within the oxygen planes are aligned with respect to the N-N-N triangles in the GaN(0001) planes (Fig. 1). In this way the 7% lateral lattice matching between the film and the substrate is achieved.

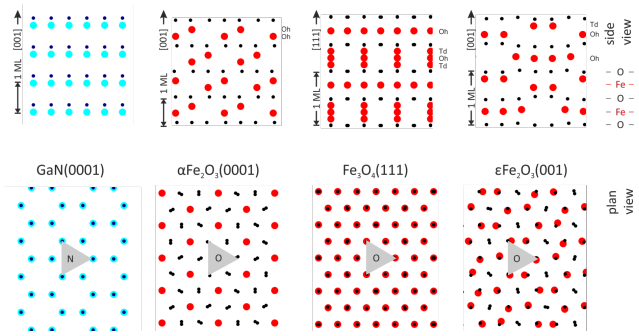

Fig. 1: Lattice matching between GaN(0001), αFe_2O_3 (0001), εFe_2O_3 (001), Fe_3O_4 (111) and γFe_2O_3 (111).

The different arrangement of the O_h and T_d iron sites as well as the different stacking order of the oxygen planes (AB-AB in αFe_2O_3, ABC-ABC in Fe_3O_4 / γFe_2O_3, ABCA-ABCA in εFe_2O_3) account for slightly different distances between the oxygen planes and slightly shifted specular reflections for different oxides. In all oxides except αFe_2O_3 the monolayer consists of two oxygen planes leading to twice higher reflection frequency.

Interestingly our diffraction data shows the presence of a few nanometers thick non-hematite layer presumably located at the interface of αFe_2O_3 / GaN film. This is evidenced by the presence of the two bumps approximately at the position of εFe_2O_3 (004) and εFe_2O_3 (008) reflections on the specular XRD profile of αFe_2O_3 film in Fig. 2. One can assume that the transition layer between GaN and αFe_2O_3 is a rich in stacking faults mixture of αFe_2O_3 and εFe_2O_3 phases. This layer is likely responsible for the non-zero MOKE signal in the otherwise supposed to be antiferromagnetic αFe_2O_3 layers.

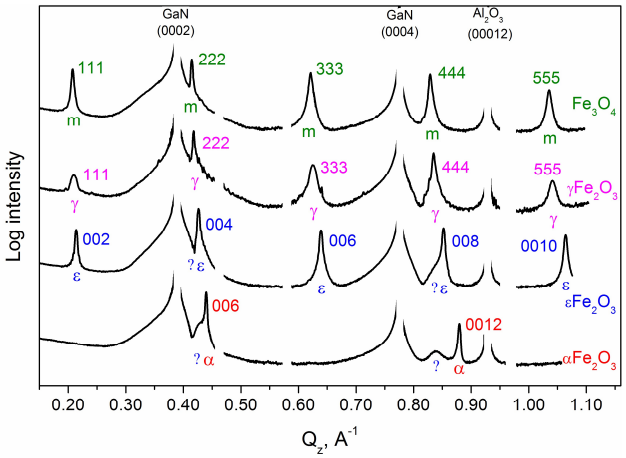

Fig. 2: XRD specular intensity profiles measured in epitaxial iron oxide layers on GaN(0001).

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 γFe_2O_3 and Fe_3O_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 oxydation state) is the presence of octahedral vacancies in the γFe_2O_3 lattice. According to the presented XRD profiles, the Fe_3O_4 to γFe_2O_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: a=8.37 Å (tabular value a=8.33 Å) for γFe_2O_3; a=8.53 Å (tabular value a=8.40 Å) for Fe_3O_4, c=13.708 Å (tabular value c=13.747 Å) for αFe_2O_3, and c=9.481 Å (tabular value c=9.471 Å) for εFe_2O_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 αFe_2O_3, γFe_2O_3, Fe_3O_4 and by ±120 deg for εFe_2O_3.

Interestingly the εFe_2O_3 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 εFe_2O_3 (113) and εFe_2O_3 (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 εFe_2O_3 surface cell is 6 times larger than that of the GaN (Fig. 3d).

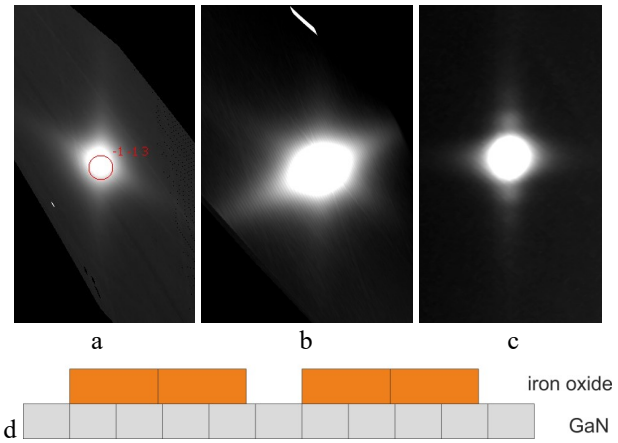

Fig. 3: Off-specular XRD maps. Reciprocal space cuts parallel to the surface showing star-like shapes of εFe_2O_3 (113) (a) and εFe_2O_3 (112) (b) reflections. Reciprocal space cut perpendicular to the surface showing the Laue oscillations on the streak passing through εFe_2O_3 (112) reflection (c). 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 L_{23} spectra of transition metals are usually dominated by the dipole-allowed 2p to 3d transitions. They consist of L_3 and L_2 main peaks resulting from spin-orbit coupling. Each of the main peaks is further split by crystal field (e_g, t_{2g}). This splitting provides a highly sensitive tool to probe the coordination environment and the corresponding magnetization.

The Fe L_{23} 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 L_3 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].

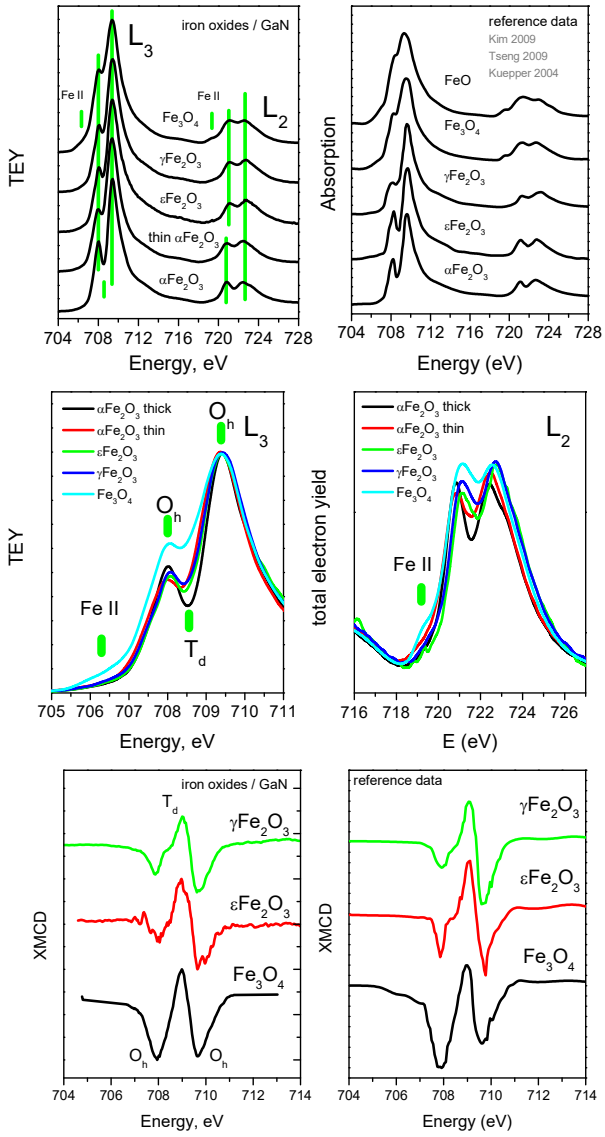

Fig. 4: XAS and XMCD spectra obtained from the iron oxide epitaxial films on GaN. Reference data adopted from [8,9,10] is shown for comparison.

In thick 40 nm αFe_2O_3 film the splitting is most pronounced originating from the pure octahedral coordination of Fe^{III} ions in hematite [8,11,12]. In 40 nm γFe_2O_3 and εFe_2O_3 films the L_3 splitting is less pronounced in agreement with earlier studies of these materials: γFe_2O_3 [8, 12] and εFe_2O_3 [9]. While the separation between the 708 eV and 709.5 eV components is the same as in αFe_2O_3, the intensity drop between the peaks becomes less pronounced due to the presence of a Fe^{III} T_d line right in the middle between the two O_h peaks. Interestingly the same shape of L_3 edge as in γFe_2O_3 and εFe_2O_3 is observed during the onset of αFe_2O_3 growth (measured in a 5 nm film) indicating the presence of T_d sites. Noteworthy the non-hematite nature of the few nm thick transition layer formed between the GaN substrate and the pure αFe_2O_3 phase is also confirmed by our diffraction measurements. It is noteworthy that in the only one existing paper describing the XAS of εFe_2O_3 [9] the

spectrum is more like in αFe_2O_3 with high contrast L_3 splitting while our data show resemblance to γFe_2O_3. The latter seems more natural as unlike in αFe_2O_3 in εFe_2O_3 the T_d iron sublattice is known to exist in addition to the three distorted O_h sublattices. In contrast to the pure trivalent oxides, the Fe_3O_4 films exhibit an extra shoulder at 706.5 eV and a considerably higher satellite at 709.5 eV. These features are known to be characteristic of O_h Fe^{II} sites in magnetite [11, 13, 12, 14, 15]. The shape of the L_2 peaks in the studied iron oxide films bears some similarity to the L_3 peak exhibiting the Fe^{II} low energy shoulder in Fe_3O_4 and a better resolved satellite in αFe_2O_3.

XMCD measurements have been carried out to investigate magnetic nature of the individual Fe sublattices within the iron oxide films on GaN allowing comparison to the known properties of the corresponding bulk materials. Not surprisingly no dichroic signal has been detected in the expected to be aniferromagnetic (at least far from the GaN interface) αFe_2O_3 films. As for the other three ferrimagnetic iron oxides, their corresponding XMCD spectra are shown in Fig. 4e. The general trend is that in the iron oxides the L_3 XMCD spectra are dominated by the two negative peaks corresponding to the Fe magnetic moments in O_h sites aligned parallel to the field and a positive peak in between the O_h peaks corresponding to the Fe magnetic moments in T_d site aligned antiparallel to the field. In the pure Fe^{III} oxides (γFe_2O_3, εFe_2O_3) the higher energy O_h peak is dominant (see reference spectra in Fig. 4f adopted from [8, 9]). In the mixed II / III Fe_3O_4 the low energy peak is higher and wider due to the presence of O_h Fe^{II} ions [14, 16]. The net magnetization in ferromagnetic iron oxides results in antiparallel alignment of the octahedral and tetrahedral Fe sites. In contrast to the XMCD spectra of metallic iron for which the L_3 peaks measured at opposite light helicities show different heights, in iron oxides these peaks are slightly shifted in energy. The ratio between the occupation of the tetrahedral and octahedral sites can be in principle determined by the ligand field multiplet analysis of the XMCD shape.

Conclusion

We have applied XRD, XAS and XMCD synchrotron methods to study Fe_3O_4, αFe_2O_3, γFe_2O_3 and εFe_2O_3 iron oxide films epitaxially deposited onto GaN(0001) surface by means of Laser MBE. The structural studies have confirmed that the thick films are mostly single phase and have lattice orientation characterized by alignment of closely packed oxygen planes parallel to the GaN(0001) substrate surface. The presence of a non-hematite transition layer have been detected in αFe_2O_3 films in the vicinity of the interface. Interestingly in εFe_2O_3 layers the reflections were found to be considerably elongated along the [100] direction. This is supposed to be due to columnar structure of εFe_2O_3 films whereas the individual columns are separated by the antiphase boundaries. The XAS spectra measured in the studied iron oxides were found to be characteristic of the particular phases, giving additional proof of the phase purity. Interestingly the XAS spectrum obtained in this work for the exotic εFe_2O_3 phase was similar to that of γFe_2O_3 is contrast to the known result from [9] where the εFe_2O_3 nanoparticles showed αFe_2O_3-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 αFe_2O_3, γFe_2O_3 and nanoparticulate εFe_2O_3.

Acknowledgement

The authors wish to acknowledge V. V. Lundin for providing GaN / Al_2O_3 wafers, the beamline staff at PF and for kind assistance in conducting experiments. Beamtime at PF was granted for projects 2014G726, 2014G725, 2016G684. Support for this work has been received from Government of the Russian Federation (Program P220, project No.14.B25.31.0025) and from Nagoya University.

References

[1] L. Corbellini *et al*., *Sci. Rep.* **7(1)**, 3712 (2017).
[2] T. M. N. Thai *et al*., *J. Appl. Phys.* **120(18)**, 185304 (2016).
[3] M. Gich *et al*., *Adv. Mater.* **26(27)**, 4645 (2014).
[4] L. Hao et.al., Thin Solid Films, **520(7)**, 3038 (2012).
[5] Zhang *et.al., Sem. Sci. Tech.*, **25(3)**, 035011 (2010).
[6] S.M. Suturin *et al*., 24th Int. Symp. "Nanostructures: Physics and Technology", Saint Petersburg, 37 (2016)
[7] S. M. Suturin *et al*., *J. Appl. Crystallogr.,* **49(5)**, 1532, (2016).
[8] D. H. Kim *et al*., *Phys. Rev. B.* **79(3)**, 2 (2009).
[9] Y.-C. Tseng *et al*., *Phys. Rev. B*, **79(9)**, 94404 (2009).
[10] K. Kuepper *et al*., *Phys. Status Solidi* **201(15)**, 3252, (2004).
[11] T. Regan *et al*., *Phys. Rev. B* **64(21)**, 1 (2001).
[12] D. Peak *et al*., *Environ. Sci. Technol.* **46(6)**, 3163 (2012).
[13] J. Chen *et al*., *Phys. Rev. B* **69(8)**, 85107 (2004).
[14] W. Q. Liu *et al*., *Appl. Phys. Lett.* **104(14)**, (2014).
[15] D. J. Huang *et al*., *Phys. Rev. Lett.* **93(7)**, 77204 (2004).
[16] P. K. J. Wong *et al*., *Phys. Rev. B* **81(3)**, (2010).

* suturin@mail.ioffe.ru