Real-time monitoring of the structure of ultra thin Fe$_3$O$_4$ films during growth on Nb-doped SrTiO$_3$(001)

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In this work thin magnetite films were deposited on SrTiO$_3$ via reactive molecular beam epitaxy at different substrate temperatures. The growth process was monitored in-situ during deposition by means of x-ray diffraction. While the magnetite film grown at 400°C shows a fully relaxed vertical lattice constant already in the early growth stages, the film deposited at 270°C exhibits a strong vertical compressive strain and relaxes towards the bulk value with increasing film thickness. Furthermore, a lateral tensile strain was observed under these growth conditions although the inverse behavior is expected due to the lattice mismatch of -7.5%. Additionally, the occupancy of the A and B sublattices of magnetite with tetrahedral and octahedral sites was investigated showing a lower occupancy of the A sites compared to an ideal inverse spinel structure. The occupation of A sites decreases for a higher growth temperature. Thus, we assume a relocation of the iron ions from tetrahedral sites to octahedral vacancies forming a deficient rock salt lattice.

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In the rising fields of spintronics and spin caloritronics materials with highly spin-polarized carriers are required for applications based on magnetoresistive effects or on spin-injection. For this purpose, the material class of half-metals provides ideal properties with one metallic and another semiconducting or insulating spin channel. Here, magnetite (Fe$_3$O$_4$) is one of the intensively studied half-metals due to a predicted 100% spin polarization at the Fermi level and a high Curie temperature of 858 K, making thin magnetite films, on one hand, particularly suitable for room temperature spintronic applications. On the other hand, multilayers of magnetite and platinum enhance the efficiency of thermal generation of spin currents based on the Seebeck effect making Fe$_3$O$_4$ attractive in spin caloritronics as well.

Magnetite has a bulk lattice constant of 8.3963 Å and crystallizes in the inverse spinel structure, where eight tetrahedral (A) sites of the bulk unit cell are only occupied by Fe$^{3+}$ cations while 16 octahedral (B) sites are equally shared by Fe$^{2+}$ and Fe$^{3+}$ cations. At about 120 K bulk magnetite undergoes the so-called Verwey transition, which results in a two-orders-of-magnitude decrease in conductivity and a reduction from cubic to monoclinic crystal symmetry leading to a spontaneous ferroelectric polarization and, thus, multiferroicity. However, for thin magnetite films this unique transport and magnetic properties as well as structural parameters are strongly influenced by the interaction between the film and the substrate.

In this study the influence of the substrate temperature on the growth behavior of thin magnetite films deposited on 0.05% Nb-doped SrTiO$_3$(001) was investigated. For this system the lattice mismatch between Fe$_3$O$_4$ and SrTiO$_3$ amounts to -7.5%. Film preparation and characterization were carried out at beamline BM25 of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). BM25 is a bending magnet beamline with a double crystal monochromator consisting of two parallel Si(111) crystals to produce monochromatic beam. The endstation is equipped with a 2S + 3D diffractometer and an ultra-high vacuum (UHV) chamber. The UHV chamber includes thermal evaporation sources, a sample heating device, a LEED (low energy electron diffraction) optics and an x-ray source with a dual Ti/Mg anode and an electrostatic cylinder-sector analyzer to perform x-ray photoelectron spectroscopy (XPS) and LEED. The base pressure in the UHV chamber was 10$^{-10}$ mbar. The set-up design allows to use the sample heating and evaporator and to perform x-ray diffraction (XRD) measurements during growth. For XRD experiments a NaI detector was used.

Prior to deposition, the SrTiO$_3$(001) substrates were annealed at 400°C in 1 × 10$^{-4}$ mbar of O$_2$ for 1 h in order to remove carbon contamination and get well-defined surfaces. The crystal surface quality and the chemical cleanliness was controlled after each preparation step in situ by XPS (Mg K$_α$1/2, $\hbar\nu = 1253.6$ eV) and LEED. XPS shows no carbon contamination and LEED reveals quadratic surface symmetry and sharp diffraction spots for the cleaned SrTiO$_3$ substrates. Afterwards, thin magnetite films were grown via reactive molecular beam epitaxy (RMBE) (thermal evaporation from pure metal rod in 5 × 10$^{-6}$ mbar oxygen) at two different substrate temperatures of 270°C and 400°C. Additionally, for the sample grown at 400°C the annealing was continued for 30 min after the evaporation was stopped. The resulting film thicknesses were measured by means of x-ray reflectivity (XRR). The thickness was determined to be (25.5 ± 0.3) nm and (10.2 ± 0.3) nm for the film grown at 270°C and 400°C, respectively. Hence, the used deposition rate for both samples was (1.65 ± 0.1) Å/min. Di-
rectly after deposition Fe\(2\text{p}\) photoelectron spectra were recorded for both films (not shown here). They show no apparent charge transfer satellites, indicating neither an excess of Fe\(^{2+}\) nor Fe\(^{3+}\) ions. Further, the Fe\(2\text{p}_{3/2}\) and Fe\(2\text{p}_{1/2}\) main peaks are located at binding energies of 710.6 eV and 723.6 eV corresponding to the well-known values for Fe\(\text{O}_4\)\(^{19}\). In addition, LEED measurements show a \((\sqrt{2} \times \sqrt{2})R45^\circ\) superstructure (not shown here) for both films typical for well ordered magnetite surface\(^{21,22}\). Combining the results from XPS and LEED we can conclude that both iron oxide films have Fe\(\text{O}_4\) stoichiometry and surface structure.

X-ray diffraction measurements were performed during the deposition of iron oxide at an interval of 3-4 min. Scans along the \((00L)\) crystal truncation rod \((\text{CTR})\) were recorded in \(\theta - 2\theta\) geometry close to the Sr\(\text{TiO}_3\)(002)\(_P\) and Fe\(3\text{O}_4(004)\)_S Bragg reflections. Here, index \(P\) and \(S\) denote the indexing for perovskite type \((\text{SrTiO}_3)\) and spinel type \((\text{Fe}_3\text{O}_4)\) bulk unit cells, respectively. Since magnetite has almost doubled bulk lattice constant compared to Sr\(\text{TiO}_3\) the Fe\(3\text{O}_4(004)\)_S reflection is located close to the Sr\(\text{TiO}_3\)(002)\(_P\) Bragg peak but at lower \(L\) values.

Fig. 1 shows the evolution of the Fe\(3\text{O}_4(004)\)_S Bragg peak for the sample grown at 400°C. In this measurement an intense substrate peak located at \(L = 2\) and a much broader Bragg peak at \(L \approx 1.86\) corresponding to the Fe\(3\text{O}_4(004)\)_S reflection are visible. The CTR shows no Laue fringes indicating an inhomogeneous crystalline structure of the film (e.g. inhomogeneous thickness, grains etc.). With increasing exposure time the intensity of the Fe\(3\text{O}_4(004)\)_S reflection increases while the peak width is decreasing. The substrate peak was fitted by a Lorentzian shaped function and the magnetite peak by a Gaussian shaped function to characterize the growth properties. Due to low peak intensity, it was only possible to fit the data beyond 15 min deposition time (equivalent to 2.6 nm film thickness). The temporal evolution of the vertical layer distance obtained from the positions of the magnetite diffraction peaks are depicted as a function of the exposure time in Fig. 2(a). The layer distance remains constant at a value of \((210.2 \pm 0.2)\) pm during the whole deposition and annealing period. This value coincides with the value expected for bulk magnetite at 400°C taking into account thermal expansion\(^{24}\). After cooling to room temperature \((\text{RT})\) the resulting layer distance of the magnetite film also coincides within the error tolerance with the bulk value of magnetite\(^{14}\). Consequently, the magnetite film deposited at 400°C grows fully relaxed already at early stages, despite the lattice mismatch between film and substrate of -7.5%.

Fig. 2(b) shows the full width at half maximum (FWHM) and the peak intensity (inset) of the Fe\(3\text{O}_4(004)\)_S reflection extracted from curve fitting. The vertical grain size of the individual steps during the deposition and annealing process was estimated from the FWHM using the Scherrer formula\(^{25}\).

\[
\text{FWHM} = \frac{A}{t - t_0},
\]
Here, $t_0$ indicates the starting point of ordered growth. In accordance with the result for the FWHM, the peak intensity follows a parabolic law for $t > t_0$ (cf. inset of Fig. 2(b)). From the fit of the evolution of the FWHM and intensity of the Fe$_3$O$_4$(004)$_S$ peak an interlayer of 1.0-1.5 nm thickness was determined. Here, we assume a high density of point defects and misfit dislocations within this interlayer leading to a fast strain relaxation and, subsequently, the growth of an ordered fully relaxed magnetite film on top.

During the subsequent annealing process ($t > 65 \text{ min}$) the decrease of the FWHM is negligible while the intensity shows a significant increase pointing to a higher ordering of the magnetite film. The resulting increase of the vertical grain size of only 0.5-0.8 nm is too small compared with the strong increment of the intensity. Thus, the strong increase in the intensity during the annealing indicates a lateral ordering of the magnetite film. Nevertheless, comparing the vertical grain size calculated by the Scherrer equation and the film thickness obtained from the XRR we estimate a residual distorted interface layer of ≤1 nm.

The evolution of the Fe$_3$O$_4$(004)$_S$ Bragg peak for the sample grown at 270°C is depicted in Fig. 3 showing an increase in intensity but a decrease in the peak width with increasing exposure time. Here also, no Laue fringes are visible near the Bragg peak pointing to an inhomogeneous crystalline order of the magnetite film. In contrast to the film grown at 400°C, the Bragg peak shifts to lower $L$ values over the deposition time. For detailed analysis the substrate peak was also fitted by a Lorentzian and $L$ values over the deposition time. For detailed analysis the Scherrer equation and the film thickness obtained from the XRR we estimate a residual distorted interface layer of ≤1 nm.

In Fig. 3(a) the vertical lattice constant as a function of the exposure time is presented. This sample shows a strong strain relaxation behavior towards the bulk value with increasing deposition time. However, considering the thermal expansion coefficients the bulk value is not completely reached. The vertical lattice distance increases from (207.8 ± 0.2) pm after deposition of 3 nm to a value of (209.7 ± 0.2) pm at the end of the deposition. After cooling down to room temperature the vertical layer distance amounts to (209.1 ± 0.2) pm, which corresponds to a vertical compressive strain of -0.4 %.

The lateral lattice constant was determined by measuring the Fe$_3$O$_4$(400)$_S$ Bragg reflection along the (H00) direction at room temperature to analyze the structure in more detail (cf. inset of Fig. 3). The obtained lateral layer distance of (210.2 ± 0.2) pm exceeds the bulk value of magnetite by 0.14 %. Thus, the Fe$_3$O$_4$ film grown on SrTiO$_3$ at 270°C exhibits vertical compressive and lateral tensile strain. These results are not expected for magnetite on SrTiO$_3$ since the doubled lattice constant of SrTiO$_3$ (3.905 Å) is smaller compared to the lattice constant of magnetite (8.3963 Å). Therefore, one expects the inverse behavior, namely lateral compression and vertical tension, due to the lattice mismatch of -7.5 %. The origin of this effect for magnetite deposited at 270°C on SrTiO$_3$ is still under discussion. However, auxetic behavior of this magnetite film, like it was proposed for...
TABLE I: Magnitude of the structure factors for the Bragg peaks of the (22L) CTR. Fe$_3$O$_4$ describes an ideal magnetite crystal and Fe$_{0.75}$O an defective rock salt like lattice with the same stoichiometry as magnetite but without tetrahedrally coordinated iron ions. $\varepsilon$ denotes the parameter of disorder calculated following Eq. 2.

| $F_{222}$   | $F_{224}$   | $F_{226}$   | $F_{222}$ (exp.) | $F_{224}$ (exp.) | $F_{226}$ (exp.) | $F_{222}$ (theo.) | $F_{224}$ (theo.) | $F_{226}$ (theo.) |
|------------|------------|------------|------------------|------------------|------------------|------------------|------------------|------------------|
| 122.9      | 122.9      | 127.8      | 137.7            | 122.9            | 138.4            | 145.7            | 116.0            | 144.2            |
| 279.1      | 0          | 0.146      | 239.8            |                  |                  |                  |                  |                  |

The film grown at 270°C shows a slightly lower value of $\varepsilon = 0.095$ and, thus, a higher occupancy of the tetrahedral sites compared to the results reported by Bertram et al. for a well-ordered magnetite film grown at 250°C on MgO which could only be obtained for higher growth rates of 3.2 Å/s. Despite the fully relaxed growth and a higher deposition temperature the film grown at 400°C exhibits a lower ordering of the tetrahedral sublattice ($\varepsilon = 0.146$) compared to magnetite film grown at 270°C.

In summary, the growth process of two magnetite films deposited on SrTiO$_3$ (001) at 270°C and 400°C was monitored by measuring (00L) CTRs during deposition. The magnetite film grown at 270°C exhibits a vertical compressive strain and relaxes continuously over the entire growth process. Additionally, a lateral tensile strain is obtained excluding auxetic behavior. Due to a lattice mismatch of -7.5% and, thus, anticipated lateral compressive and vertical tensile strain, this contradicts the behavior expected due to lattice mismatch and requires further investigations. In contrast, for the sample grown at 400°C we assume a strong strain relaxation within the very first few layers followed by a fully relaxed growth regime. However, magnetite grown at 400°C shows a lower ordering of the sublattices due to a lower occupancy of the A sites compared to the sample deposited at 270°C. This points to a relocation of the iron ions from tetrahedral sites to octahedral vacancies forming a deficient rock salt lattice.

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