Time-resolved diffraction and photoelectron spectroscopy investigation of the reactive molecular beam epitaxy of Fe$_3$O$_4$ ultrathin films

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We present time-resolved high energy x-ray diffraction (tr-HEXRD), time-resolved hard x-ray photoelectron spectroscopy (tr-HAXPES) and time-resolved grazing incidence small angle x-ray scattering (tr-GISAXS) data of the reactive molecular beam epitaxy (RMBE) of Fe$_3$O$_4$ ultrathin films on various substrates. Reciprocal space maps are recorded during the deposition of Fe$_3$O$_4$ on SrTiO$_3$(001), MgO(001) and NiO/MgO(001) in order to observe the temporal evolution of Bragg reflections sensitive to the octahedral and tetrahedral sublattices of the inverse spinel structure of Fe$_3$O$_4$. A time delay between the appearance of rock salt and spinel-exclusive reflections reveals that first, the iron oxide film grows with Fe$_{1.3}$O rock salt structure with exclusive occupation of octahedral lattice sites. When this film is 1.1 nm thick, the further growth of the iron oxide film proceeds in the inverse spinel structure, with both octahedral and tetrahedral lattice sites being occupied. In addition, iron oxide on SrTiO$_3$(001) initially grows with none of these structures. Here, the formation of the rock salt structure starts when the film is 1.5 nm thick. This is confirmed by tr-HAXPES data obtained during growth of iron oxide on SrTiO$_3$(001), which demonstrate an excess of Fe$^{2+}$ cations in growing films thinner than 3.2 nm. This rock salt phase only appears during growth and vanishes after the supply of the Fe molecular beam is stopped. Thus, it can be concluded the rock salt structure of the interlayer is a property of the dynamic growth process. The tr-GISAXS data link these structural results to an island growth mode of the first 2–3 nm on both MgO(001) and SrTiO$_3$(001) substrates.

INTRODUCTION

Iron oxides grow in a variety of crystal structures and stoichiometries, and their electronic and magnetic properties vary significantly between these phases. Both hematite ($\alpha$-Fe$_2$O$_3$) and maghemite ($\gamma$-Fe$_2$O$_3$) are semiconductors and represent the iron oxides with the highest oxidation state, with all iron ions occurring in the Fe$^{3+}$ charge state [1,2]. $\alpha$-Fe$_2$O$_3$ crystallizes in a corundum structure [3] and is a canted antiferromagnet at room temperature with a Néel temperature $T_N = 683^\circ$C [4], while $\gamma$-Fe$_2$O$_3$ is ferrimagnet with a Curie temperature of $T_C = 620^\circ$C [5] and grows in a defect spinel structure [4]. Magnetite (Fe$_3$O$_4$) is a half-metallic ferrimagnet with a Curie temperature of $T_C = 580^\circ$C. It crystallizes in the inverse spinel structure ($a_{Fe_3O_4} = 8.396$ Å) and exhibits mixed valences of Fe$^{2+}$ and Fe$^{3+}$ cations [6]. Wüstite (Fe$_{1.4}$O) – a semiconducting antiferromagnet with a Néel temperature of $T_N = -75^\circ$C, crystallizing in the rock salt structure ($a_{FeO} = 4.332$ Å) [7,8] – represents the lowest oxidized polymorph. Wüstite is often found in a defect stoichiometry and typically denoted as Fe$_{1+\delta}$O, with $\delta$ ranging from 0.05 to 0.17 [7,9].

Because of this variability of their properties, thin films of iron oxides are often regarded as attractive for spintronics. For instance, magnetite is a long-standing candidate to contribute to all-oxide thin-film spintronic devices, as a source for spin-polarized currents [10–15], maghemite has been discussed as a magnetic tunnel barrier for spin-filter [16–18], and exchange bias has been observed in Fe/Fe$_{1.4}$O bilayers.

In order to effectively study thin-film-based spintronic devices, a detailed knowledge of the growth mechanism down to the monolayer level is necessary. The growth mechanism of Fe$_3$O$_4$ thin films has been frequently studied. Chang et al. investigated the cation stoichiometry of Fe$_3$O$_4$/MgO(001) for very thin films of few monolayers with x-ray absorption spectroscopy (XAS) and concluded that these ultrathin films dynamically redistribute during growth in order to avoid polarity [17]. It has also been reported on an iron-deficient wüstite layer of about 3 monolayers at the Fe$_3$O$_4$/MgO(001) interface observed by x-ray diffraction (XRD) [18].

Fe$_3$O$_4$ ultrathin films have been grown on a wide array of substrates. The most widespread choice is the rock salt crystal MgO(001), because doubling its lattice constant of $a_{MgO} = 4.212$ Å results in a small mismatch of 0.3% to Fe$_3$O$_4$ and grants pseudomorphic growth [17–25]. A drawback of MgO(001) substrates is the limitation of growth and annealing temperatures to 250$^\circ$C, as Mg starts to interdiffuse into the magnetite film at higher temperatures [26]. SrTiO$_3$(001) substrates, in contrast, crystallize in the perovskite structure and have a lattice constant of $a_{SrTiO_3} = 3.905$ Å and a mismatch of $-7.5\%$ to magnetite, offering the possibility to study strain effects on magnetite [27–31]. Different than on MgO, Fe$_3$O$_4$ can be grown on SrTiO$_3$ at elevated tempera-
cles with no risk of interdiffusion [30]. On SrTiO$_3$(001), Fe$_3$O$_4$ has been reported to grow in different orientations: for temperatures below 400$^\circ$C, it grows with a (001) orientation, while for temperatures of 700$^\circ$C and above, the more stable (111) orientation is favored [32,33]. Ultrathin film bilayers of Fe$_3$O$_4$ and NiO, on the other hand, are very interesting from a spintronic perspective, because the exchange bias between the ferrimagnetic magnetite and NiO, which is antiferromagnetic below its Néel temperature of $T_N = 250^\circ$C, can be exploited for magnetic tunnel junctions [34–38]. This effect causes an asymmetric hysteresis of the ferromagnetic film, with different switching fields depending on the direction of the external magnetic field.

In previous studies, Fe$_3$O$_4$ films were grown by reactive molecular beam epitaxy (RMBE) and subsequently investigated after growth [38,39]. XRD has been used to study thickness dependent structural properties while x-ray photoelectron spectroscopy (XPS) has been applied for electronic and chemical analysis. A more direct access to the growth process can be granted by simultaneously depositing the film and performing XRD [31] and XPS investigations. This is the route taken in this study. Fe$_3$O$_4$ ultrathin films are grown on Nb-doped SrTiO$_3$(001), MgO(001) and NiO/MgO(001) by RMBE, and time-resolved high-energy x-ray diffraction (tr-HEXRD) is used to observe the formation of Bragg peaks of the evolving Fe$_3$O$_4$ film which are specific to the order of octahedrally and tetrahedrally coordinated Fe cations during growth. Along with the tr-HEXRD, time-resolved grazing incidence small angle x-ray scattering (tr-GISAXS) data are recorded in order to monitor the growth mode of the films. Time-resolved hard x-ray photoelectron spectroscopy (tr-HAXPES) is employed to observe the development of the Fe 2p spectrum of Fe$_3$O$_4$/SrTiO$_3$ during the deposition in order to allow conclusions towards the different oxidation states of Fe through the entire film thickness.

### EXPERIMENTAL DETAILS

Synchrotron-based tr-HEXRD measurements utilize high energy x-rays in combination with large area 2D detectors to collect time-resolved diffraction data of dynamic processes, such as thin film growth [40] or catalytic processes [41]. In this study, we observe the intensity evolution of the Bragg reflections of Fe$_3$O$_4$ during the deposition of the films.

Our tr-HEXRD and tr-GISAXS measurements were performed at beamline P07/EH2 of PETRA III at Deutsches Elektronen-Synchrotron (DESY). A custom-designed UHV-deposition chamber was mounted on the diffractometer, in order to perform grazing-incidence diffraction with a glancing angle of $\theta = 0.03^\circ$ during the deposition of the thin films. The sample preparation followed the procedures in Refs. [38,39,42]. Before deposition, the MgO and the Nb-doped (0.05 wt%) SrTiO$_3$ substrates were annealed at 400$^\circ$C for one hour in an oxygen atmosphere of $p_{O_2} = 10^{-4}$ mbar. For the Fe$_3$O$_4$/NiO/MgO(001) sample, first a 5.6 nm thick NiO layer was grown by evaporating Ni from a metal target in an oxygen atmosphere of $p_{O_2} = 5 \times 10^{-6}$ mbar at 250$^\circ$C substrate temperature. Both the Fe$_3$O$_4$ films on NiO/MgO(001) and on MgO(001) were deposited by evaporating Fe under the same conditions as the NiO film. The Fe$_3$O$_4$/SrTiO$_3$(001) film was deposited in a reduced oxygen atmosphere of $p_{O_2} = 1 \times 10^{-6}$ mbar and a higher substrate temperature of 350$^\circ$C. Film thicknesses were controlled by calibrating the fluxes of the evaporators. Table I summarizes the final thicknesses $d_{Fe_3O_4}$ after growth and growth rates for the three investigated samples.

| sample | tr-HEXRD | tr-HAXPES |
|--------|----------|-----------|
| d$_{Fe_3O_4}$ (nm) | 18.9 ± 0.1 | 18.8 ± 0.3 |
| rate (nm/min) | 2.6 | 0.47 |

For the Fe$_3$O$_4$/NiO/MgO(001) and the Fe$_3$O$_4$/SrTiO$_3$(001) samples, a photon energy of 74 keV was used, and data were recorded on a Dectris Pilatus 3X CdTe 2D area detector. Before the start of the deposition, the samples were azimuthally aligned to an angle $\omega_{(111)}$ at which the Bragg condition for the substrate (111) reflection was fulfilled. During deposition, the samples were continuously azimuthally rotated between $\omega_{(111)} \pm 7^\circ$ with a rotation speed of 2$^\circ$/sec, in order to observe the development of the (22L)$_{Fe_3O_4}$ crystal truncation rod (CTR) during growth. The detector images obtained during each one of these 14$^\circ$-rotations were then summed up to obtain one reciprocal space map (RSM) every 12 seconds (cf. right half of Fig. II). After growth, the electronic structure of the samples was characterized in situ by XPS, using a Phoibos HSA 150 hemispherical analyzer and an Al Kα anode, in order to probe the stoichiometry of the grown iron oxide, and a RSM with a full rotation of 90$^\circ$ was recorded with a rotation speed of 0.5$^\circ$/sec.

For the Fe$_3$O$_4$/NiO/MgO(001) sample, we followed the same procedure, but using a photon energy of 72 keV and a Perkin-Elmer XRD1621 detector, with a rotation range of $\omega_{(111)} \pm 5^\circ$, and recorded one RSM every 28 seconds. Again, after growth a RSM with a full rotation of 90$^\circ$ was recorded.

### Table I. Thicknesses and deposition rates of the samples.

| sample | Fe$_3$O$_4$/NiO/MgO | Fe$_3$O$_4$/MgO | Fe$_3$O$_4$/SrTiO$_3$ | tr-HAXPES |
|--------|---------------------|----------------|---------------------|-----------|
| $d_{Fe_3O_4}$ (nm) | 18.9 ± 0.1 | 18.8 ± 0.3 |
| rate (nm/min) | 2.6 | 0.47 |
In order to obtain information on the temporal evolution of the stoichiometry of the different cations of Fe$_3$O$_4$ during the growth, we performed complimentary tr-HAXPES measurements during the growth of Fe$_3$O$_4$ films on SrTiO$_3$. To this end, we installed the same custom-designed UHV-deposition chamber used for the tr-HEXRD measurements at beamline P22 of PETRA III at DESY [43]. The samples were illuminated by an x-ray beam under a glancing angle of 3° to the surface normal, resulting in an information depth of about ID(95) = 16 nm [38].

The films were deposited in an oxygen atmosphere of $p_{O_2} = 5 \times 10^{-6}$ mbar at a substrate temperature of 400°C. One sample was deposited continuously up to a thickness of 18.8 nm, and one sample was deposited step-wise: After each spectrum taken during the deposition of 1.7 nm Fe$_3$O$_4$, the growth was stopped by interrupting the molecular beam, and a Fe 2p spectrum was measured with higher sampling time before the next deposition step. The photoelectron spectra of the Fe 2p were recorded by scanning from high to low binding energies. For the continuously deposited film, the spectra were recorded in 0.2 eV energy steps and an integration time of 0.1 sec/step, taking 60 seconds for a single spectrum, which means that the film thickness was increasing by 0.5 nm during each measurement. For instance, the first spectrum started recording at a binding energy of 760 eV and a film thickness of 0 nm, and ended at a binding energy of 690 eV with a film thickness of 0.5 nm. We used a linear scaling function on these spectra in order to account for the fact that the intensity of the Fe 2p increases with the film thickness. The step-wise deposited film in energy steps of 0.2 eV and an integration time of 0.2 sec/step, taking 120 seconds for a single spectrum. The deposition rates can be found in Tab. 1. Charge transfer multiplet (CTM) calculations of the XPS spectra of the three cation species in Fe$_3$O$_4$ have been performed using the method and parameter set of Fuji et al. [34].

RESULTS

Reciprocal space map of Fe$_3$O$_4$

Figure 1 shows a RSM of the as-grown Fe$_3$O$_4$/MgO sample, obtained by a full 90° azimuthal rotation. The right half shows recorded data and the left a schematic of the peak positions from MgO, SrTiO$_3$ and Fe$_3$O$_4$.

The goal of the tr-HEXRD measurements is to record the intensity evolution of the (222)$_{Fe_3O_4}$ and the (224)$_{Fe_3O_4}$ reflection. This endeavor is complicated by...
the close lattice match of MgO and Fe$_3$O$_4$: Fe$_3$O$_4$ has roughly double the lattice constant of MgO with a small lattice mismatch of only 0.3%, and consequently, Bragg reflections ($hKL$)$_{\text{MgO}}$ of MgO almost coincide with reflections (2$H$, 2$K$, 2$L$)$_{\text{Fe}_3\text{O}_4}$ of Fe$_3$O$_4$. This can be seen in the schematic RSM in Fig. 1 where black circles indicate the MgO reflections, and squares the reflections of Fe$_3$O$_4$. The intensity difference between the bright substrate reflections and the weaker film reflections is too high for the detector to record them simultaneously. For this reason, the MgO reflections had to be covered by semi-transparent beamstops on the detector. For instance, on the one hand, the (222)$_{\text{Fe}_3\text{O}_4}$ has to be blocked (see white disk in the RSM presented in the right half of Fig. 1) since it almost coincides with the (111)-reflection of MgO. On the other hand, the (224)$_{\text{Fe}_3\text{O}_4}$ is fully visible, since the corresponding substrate-related Bragg reflection (112)$_{\text{MgO}}$ is forbidden.

In contrast, the perovskite structure of SrTiO$_3$ has more allowed reflections, including the (112)$_{\text{SrTiO}_3}$, as illustrated by the green crosses in Fig. 1. But since its higher lattice mismatch of $-7.5\%$ to Fe$_3$O$_4$, the substrate reflections are well separated from the film reflection, making a direct observation of both the (222)$_{\text{Fe}_3\text{O}_4}$ and the (224)$_{\text{Fe}_3\text{O}_4}$ reflections possible.

Fe$_3$O$_4$/SrTiO$_3$

Information on the early growth stage can be collected by tr-HEXRD by analyzing the grazing incidence small angle x-ray scattering (GISAXS) data in the small angle region of the RSMs. Figure 2(a) shows the small angle region of an RSM taken at a film thickness of 1.1 nm. Two streaks parallel to the $q_{\parallel}$ direction are highlighted by black arrows. Their reciprocal space distance $\Delta q_\parallel$ is plotted as a function of film thickness in Fig. 2(c). They become first visible at a film thickness of about 0.5 nm, and then move gradually closer to each other along the $q_{\parallel}$ direction with increasing film thickness, until they eventually become indistinguishable and merge in the center at a thickness of about 2.2 nm. At a film thickness of 2.9 nm, two new streaks appear, highlighted by black dashed lines in Fig. 2(b). In the projection of the RSM, they are tilted by an angle of 55° from the $q_{\parallel}$ direction. Such streaks are characteristic for (111) facets and remain present for the rest of the growth process, including the finished film.

In order to gain insight into the growth dynamics of the Fe$_3$O$_4$/SrTiO$_3$ film, we used tr-HEXRD to monitor the evolution of the (222)$_{\text{Fe}_3\text{O}_4}$ and the (224)$_{\text{Fe}_3\text{O}_4}$ reflections, which are sensitive to the octahedral and tetrahedral order, respectively. Figure 3(a) shows how the intensity along the (22$L$)$_{\text{Fe}_3\text{O}_4}$-rod (white dashed box in Fig. 1) changes with the film thickness. The color scale corresponds to the intensity, the horizontal axis to the Miller index $L$ (parallel to $q_{\perp}$) and the vertical axis to the film thickness. For the thickness axis, we assumed a linear relation between deposition time and film thickness. In the color plot of Fig. 3(a), it can be seen that at the beginning of the growth, neither the (222)$_{\text{Fe}_3\text{O}_4}$ nor the (224)$_{\text{Fe}_3\text{O}_4}$ can be observed. After about 1 nm of growth, intensity is detected at the (222)$_{\text{Fe}_3\text{O}_4}$ position, and with a slight delay the (224)$_{\text{Fe}_3\text{O}_4}$ reflection appears. For better quantification, Fig. 3(b) shows the $L$-integrated intensity along the white dashed lines for the (222)$_{\text{Fe}_3\text{O}_4}$ and the (224)$_{\text{Fe}_3\text{O}_4}$ (cf. Fig. 3(a)) as a function of film thickness and deposition time for the full growth process, and Fig. 3(c) contains a close-up of the early growth stage. Here, the delay between the emergence of the (222)$_{\text{Fe}_3\text{O}_4}$ and the (224)$_{\text{Fe}_3\text{O}_4}$ can be determined to be $\Delta d = 1.25 \pm 0.12$ nm. It can also be seen that the (222)$_{\text{Fe}_3\text{O}_4}$ does not appear before a coverage of 1.55 nm has been reached.

The position of the (222)$_{\text{Fe}_3\text{O}_4}$ has been fitted to draw conclusions towards the lattice constant during growth.
deposition step. The violet, magenta and cyan spectra interrupted. Spectra were taken during and after each of 1
integration times (cf. Fig. 5(b)). It was grown in steps process, for which spectra could be recorded at higher This effect is even more obvious in a step-wise deposition films thicker than 3
3
.3 nm, a satellite feature at the high-energy side of the Fe 2p3/2 (purple and magenta arrows), which vanishes for both, films thicker than 5.1 nm and the spectrum taken during the interruption. This satellite is well known to be a charge-transfer satellite from Fe2+ cations on octahedral lattice sites. To illustrate this, Fig.5(e) shows CTM calculations of the Fe 2p spectrum for the three cation species in Fe3O4. The individual cation spectra show a distinct charge-transfer satellite between the Fe 2p3/2 and the Fe 2p1/2 lines at different energies. It is highlighted for the Fe2+ oct spectrum by a green arrow. Summing up the three spectra in a 1:1:1 ratio yields the Fe3O4 spectrum (black), which does not exhibit any apparent satellite structure between the Fe 2p main lines, because the satellites of the individual cation spectra overlap in such a way that they form a flat plateau. This shape is observed for the spectra during the third deposition step and in the interruption after the first deposition step in Fig. 5(b), and for film thicknesses higher than 3.8 nm in Fig. 5(a).

Additionally, we observe a chemical shift of about 0.5 eV for both Fe 2p main lines between the spectrum during the first deposition step on the one hand and the spectra recorded after the first and during the third step on the other hand, shown for the Fe 2p3/2 peak in the inset of Fig. 5(a). The spectrum taken during the second deposition step displays both a weaker satellite as well as an energy position in between the two other spectra.

Fe3O4/MgO and Fe3O4/NiO/MgO

For the Fe3O4 films deposited on MgO, an accordant evaluation of the tr-HEXRD data is slightly more difficult because the overlap of the (222)Fe3O4 and the (111)MgO reflections does not allow for an immediate observation of the (222)Fe3O4. Particularly, the region around the (111)MgO has to be blocked by a semi-transparent absorber, as can be seen in Fig. 1. Therefore, instead of the Bragg peak, we observe the intensity of the CTR at a position (2, 2, 2 − ε)Fe3O4 close to the (222)Fe3O4 reflection, with ε = 0.12. Analogous to Fig. 3(a), Fig. 6(a) shows a false color map of the diffracted intensity during the growth process of the Fe3O4 film on MgO. Before starting the growth process, again, there is no intensity at the (224)Fe3O4 position. Around the position of the (222)Fe3O4 (L ≃ 1.003 in Fig. 6(a)), however, no

![Figure 4](image_url)

**FIG. 4.** Evolution of (a) the in-plane scattering vector \( q_\| \) and (b) the out-of-plane scattering vector \( q_\perp \) of the film (222) reflection. Dashed horizontal lines indicate the expected scattering vectors for bulk Fe3O4 and bulk Fe1.8O. Dotted blue and red vertical lines indicate the thicknesses at which the (222) and the (224) reflections emerge, respectively.

Figures 4(a),(b) show the evolution of the in-plane component \( q_\| \) and the out-of-plane component \( q_\perp \) of the scattering vector of the (222)Fe3O4. Both components move from a smaller position at low film thicknesses to a larger position at thicker films. This corresponds to a progressive compression of the lattice parameters in both vertical and lateral direction for increasing film thickness. The dashed lines indicate the scattering vector components expected for bulk Fe3O4 and for bulk Fe1.8O. It can be seen that the position of the (222) reflection is close to the expected value for Fe1.8O at the beginning of the deposition, and settles close to the position expected for Fe3O4 when the film grows thicker.

In order to make further conclusions about the oxide phase in this early growth phase, we performed tr-HAXPES measurements of the growth of Fe3O4/SrTiO3 films. The results are shown in Fig. 5. Figure 5(a) shows the spectra recorded from the continuously deposited Fe3O4/SrTiO3 film. During the measurement of each spectrum, about 0.47 nm of Fe3O4 have been deposited. For the films below 1.4 nm thickness, the low signal-to-noise ratio makes it difficult to observe spectral features. However, for film thicknesses from 1.9 nm to 3.3 nm, a satellite feature at the high-energy side of the Fe 2p3/2 can be observed, highlighted by the arrows. For films thicker than 3.8 nm, this satellite disappears, and the region between the Fe 2p3/2 and the Fe 2p1/2 is flat. This effect is even more obvious in a step-wise deposition process, for which spectra could be recorded at higher integration times (cf. Fig. 5(b)). It was grown in steps of 1.7 nm. After each deposition step, the growth was interrupted. Spectra were taken during and after each deposition step. The violet, magenta and cyan spectra presented in Fig. 5(b) were recorded during the first three deposition steps, and had thicknesses of 1.7 nm, 3.4 nm and 5.1 nm after the end of the corresponding measurement, respectively. The orange spectrum was taken during the interruption after the first deposition step, at a film thickness of 1.7 nm. These deposition steps are illustrated in Fig. 5(d), with the step labels 1), 2) and 3) corresponding to the spectra in Fig. 5(b).

For the spectra recorded during the first two deposition steps (purple and magenta), a satellite can be seen on the high-energy side of the Fe 2p3/2 (purple and magenta arrows), which vanishes for both, films thicker than 5.1 nm and the spectrum taken during the interruption. This satellite is well known to be a charge-transfer satellite from Fe2+ cations on octahedral lattice sites. To illustrate this, Fig. 5(e) shows CTM calculations of the Fe 2p spectrum for the three cation species in Fe3O4. The individual cation spectra show a distinct charge-transfer satellite between the Fe 2p3/2 and the Fe 2p1/2 lines at different energies. It is highlighted for the Fe2+ oct spectrum by a green arrow. Summing up the three spectra in a 1:1:1 ratio yields the Fe3O4 spectrum (black), which does not exhibit any apparent satellite structure between the Fe 2p main lines, because the satellites of the individual cation spectra overlap in such a way that they form a flat plateau. This shape is observed for the spectra during the third deposition step and in the interruption after the first deposition step in Fig. 5(b), and for film thicknesses higher than 3.8 nm in Fig. 5(a).

Additionally, we observe a chemical shift of about 0.5 eV for both Fe 2p main lines between the spectrum during the first deposition step on the one hand and the spectra recorded after the first and during the third step on the other hand, shown for the Fe 2p3/2 peak in the inset of Fig. 5(a). The spectrum taken during the second deposition step displays both a weaker satellite as well as an energy position in between the two other spectra.
FIG. 5. (a) HAXPES data of the Fe 2p recorded during the continuous deposition of a Fe$_3$O$_4$/SrTiO$_3$ film. The data was smoothed by a Gaussian filter. (b) HAXPES data of the Fe 2p recorded during the step-wise deposition process of a Fe$_3$O$_4$/SrTiO$_3$ film [1] purple, 2) magenta and 3) cyan] and during an interruption of the deposition (orange), as illustrated in (d). At the end of the measurements during deposition, the films were 1.7 nm, 3.4 nm and 5.1 nm thick. (c) Close-up of the Fe 2p$_{3/2}$ region; violet and yellow lines indicate center of the peak in the respective spectrum. (d) Sketch of the step-wise deposition process, corresponding to the spectra in (b). (e) CTM calculations of the XPS spectra for the three cation species of Fe$_3$O$_4$, Fe$^{2+}_{\text{oct}}$ (green), Fe$^{3+}_{\text{oct}}$ (red) and Fe$^{3+}_{\text{tet}}$ (blue). Grey line is the sum of the Fe$^{2+}_{\text{oct}}$ and Fe$^{3+}_{\text{oct}}$ spectra, and the black line is the sum of all three spectra, representing the full Fe$_3$O$_4$ spectrum. Arrows in (a),(b) and (e) highlight the charge-transfer satellite characteristic for Fe$^{3+}$ cations.

We used the same procedure to analyze the Fe$_3$O$_4$/NiO/MgO sample. The intensity of the $(2,2,2-\epsilon)$Fe$_3$O$_4$ was analyzed at $\epsilon = 0.09$. The results are shown in Figs. 5(d)-(e). In Fig. 5(d), Laue oscillations caused by the finite thickness of the pre-deposited NiO film are visible already before the deposition of Fe$_3$O$_4$ starts. After start of the deposition, they are superimposed by the Laue-oscillations due to the Fe$_3$O$_4$ film, resulting in a Moiré pattern caused by the Laue-oscillations of the two films. As in the case of the Fe$_3$O$_4$/MgO sample, the intensity of the $(2,2,2-\epsilon)$Fe$_3$O$_4$ position starts oscillating immediately after the beginning of the deposition, while the intensity of the $(224)$Fe$_3$O$_4$ reacts with a delay of about $\Delta d = 10\pm3$ Å.

DISCUSSION

The GISAXS data of the Fe$_3$O$_4$/SrTiO$_3$ film suggest that the film starts to grow in islands. The two distinct vertical streaks observed in the early stage of the growth (cf. Fig. 2(a)) are an indicator for a cluster formation on the substrate surface, and their orientation parallel to the $q_{\perp}$ direction corresponds to the formation of islands of cylindrical or box shape. Their separation distance is a measure of the mean distance of the clusters, and has
been observed to decrease with growing film thickness (cf. Fig. 2c)), corresponding to a coarsening process due to, e.g., coalescence of smaller islands to bigger ones. From the film thickness at which the two streaks are not visibly separated anymore, we can conclude that a fully closed film is formed not before a coverage of 2 nm. The appearance of the second set of streaks at 2.9 nm, exhibiting a 55° tilt to the out-of-plane direction (cf. Fig. 2b)), is an indication for the formation of (111) facets [40]. This means that after the first layer is closed, the film continues to grow in (001) direction, but develops (111) facets on the surface, pointing towards pyramid-shaped islands on the surface. The development of (111) facets has been reported earlier for Fe₃O₄ films, and is related to the (111) surface being more stable than the (001) surface [33, 47]. The GISAXS data collected of the Fe₃O₄/MgO(001) film (not shown) displays initially the same behavior: the film grows islands which coalesce to a closed layer at a coverage of about 2 – 3 nm. However, no small angle signal indicating the formation of additional nanostructures such as (111) facets is observed. This suggests that the Fe₃O₄/MgO(001) film continues to grow in layer-by-layer mode.

While for the two samples grown on MgO(001), the (222)Fe₃O₄-reflection emerges immediately after begin of the deposition, for Fe₃O₄/SrTiO₃ the (222)Fe₃O₄ appears only after about 1.5 nm are grown already. This implies a lower initial ordering in films below a coverage of 1 nm deposited on SrTiO₃(001) than for films on MgO(001). Such a distorted interface layer of Fe₃O₄/SrTiO₃(001) has been reported before [31]. A possible explanation is that the competition between a (001) and a (111) orientation reported for Fe₃O₄/SrTiO₃(001) [22, 33] might cause different orientations for different islands, so that no Bragg peaks develop due to missing long range order during this growth stage. However, our data do not allow a clarification of the structure in this phase.

The most striking result for all three samples is the fact that after the (222)Fe₃O₄ reflections and their diffraction rods appear, the spinel-exclusive (224)Fe₃O₄ reflection follows only after the film has grown thicker by 1.1 ± 0.15 nm. The inverse spinel structure of Fe₃O₄ can be described as consisting of a cubic close-packed oxygen sublattice and two cation sublattices, one con-
taining the octahedrally coordinated $\text{Fe}^{2+/3+}_\text{oct}$ cations (B-sites) and one containing the tetrahedrally coordinated $\text{Fe}^{3+}_\text{tet}$ cations (A-sites). These sublattices give rise to different Bragg-reflections, some of which are exclusive to the spinel structure while others also occur in a rock salt phase [22]. Figure 7 shows the structure factors of the octahedral, tetrahedral and oxygen sublattices to the structure factor $|F_{\text{sublattice}}|^2$ of Fe$_3$O$_4$.

FIG. 7. Contributions of the octahedral, tetrahedral and oxygen sublattices to the structure factor $|F_{\text{sublattice}}|^2$ of Fe$_3$O$_4$.

Additionally, the position of the (222) reflection of the film agrees well with the expected position of the bulk (111)$_\text{Fe}_1\delta\text{O}$ reflection, and only relaxes towards the lattice constant of Fe$_3$O$_4$ when the film grows thicker. This suggests that iron oxide films which are grown under conditions that are well-known to grow in the Fe$_3$O$_4$ phase [19, 22, 30, 42, 48] begin to grow in a Fe$_1\delta\text{O}$ structure with exclusive occupation of octahedral lattice sites, and only after a certain thickness start to form the inverse spinel structure of Fe$_3$O$_4$ with Fe cations occupying also tetrahedral lattice sites, as well. We determine the thickness of this rock salt layer to be about 1 nm, as this is the thickness difference between the emergence of the two reflections consistent for all three samples. This corresponds to about 2–3 unit cells of Fe$_1\delta\text{O}$, or about 4–6 atomic layers [18]. We also want to emphasize that this finding is robust although the growth rates differ by almost an order of magnitude between the samples (cf. Tab. 1) and different substrates have been used. A similar effect has been reported earlier for Fe$_3$O$_4$/MgO(001) films deposited at low temperatures or low deposition rates [22]. It has been attributed to an iron-deficient rock salt structure which retains the same stoichiometry as Fe$_3$O$_4$.

In our tr-HAXPES data obtained for the growth of Fe$_3$O$_4$ on SrTiO$_3$(001), we observe a charge-transfer satellite at the high-energy side of the Fe 2P$_{3/2}$ and a chemical shift of the Fe 2P$_{1/2}$ and the Fe 2P$_{1/2}$ to about 0.5 eV lower energies for iron oxide films with thicknesses between ~1.5 nm to ~4 nm. Both, the satellite and the chemical shift in Figs. 5(a)-(c) are indicators for an excess of Fe$^{2+}$ cations. This also suggests a Fe$_{1.5}$O phase, consistent with the diffraction data. The chemical shift and the satellite are most pronounced for the 1.9 nm and the 1.7 nm-thick films in Figs. 5(a) and 5(b), respectively. They are weakened after the thickness is increased to 3.3 nm and 3.4 nm, and vanish at thicknesses of 3.8 nm and 5.1 nm. The information depth of our HAXPES measurements is about ID(95) = 16 nm, and therefore accesses the entire film thickness. However, the vanishing of the spectral features does not necessarily imply a vanishing of the Fe$^{2+}$-rich Fe$_{1.5}$O phase itself, but can also be attributed to its signal becoming invisible due to the Fe$_3$O$_4$ phase forming on top.

The tr-HAXPES data of the step-wise deposited film also reveal that the stoichiometry of the film changes when the growth is interrupted (cf. Fig. 5(b)). During deposition, the 1.7 nm film clearly shows a Fe$^{2+}$-charge-transfer satellite, also seen for the continuously deposited sample (cf. Fig. 5(a)). However, when the iron supply is cut, the 1.7 nm-thick film exhibits a spectrum characteristic for Fe$_3$O$_4$, and as soon as the deposition is continued, the satellite returns. This suggests that this Fe$_{1.5}$O phase is a transient phenomenon and exclusively occurs during the dynamic growth process, but further oxidizes to Fe$_3$O$_4$ when the deposition is stopped.

FIG. 8. Illustration of the growth stages at 1 nm, 2 nm, 2.5 nm and 4 nm for (a)-(d) Fe$_3$O$_4$/SrTiO$_3$(001) and (e)-(h) Fe$_3$O$_4$/MgO(001). FeO$_x$ denotes an iron oxide phase of unclear stoichiometry.
SUMMARY

In summary, the initial growth stage of Fe$_3$O$_4$/SrTiO$_3$(001) appears to occur in 3 steps, as illustrated in Fig. 8(a)-(d): First, the iron oxide film grows in disordered islands of unknown structure. Second, at a coverage of about 1.5 nm, as the islands become bigger, they predominantly form a rock salt structure and show an excess of Fe$^{2+}$, likely being a Fe$_{1.6}$O phase. Between a coverage of 2.2 nm and 3 nm, the first layer closes, and at about 2.8 nm the film finally starts to grow in an inverse spinel structure in [001] direction, developing (111) facets on the surface.

The stages of Fe$_3$O$_4$ films on MgO(001) and on NiO/MgO(001) are illustrated in Fig. 8(e)-(h). They start to grow in islands, too, and the first closed layer forms at a coverage of about 2−3 nm. However, the immediate appearance of the (222)Fe$_3$O$_4$ reflection after the begin of the deposition suggests that these islands immediately exhibit a well ordered rock salt structure. After a thickness of about 1 nm, they grow in the inverse spinel structure. It seems very likely that it is due to the formation of a Fe$_{1.4}$O layer before the Fe$_3$O$_4$ phase starts to grow for all three samples.

The tr-HAXPES measurements of Fe$_3$O$_4$/SrTiO$_3$(001) additionally reveal that the Fe$_{1.4}$O phase in the subnanometer range is only stable during the deposition process, but turns into a Fe$_3$O$_4$ phase when the deposition is interrupted. We therefore conclude that this is a strictly dynamic property of the growth process.

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[1] M. I. Litter and M. Á. Blesa, Can. J. Chem. 70, 2502 (1992)
[2] R. Grau-Crespo, A. Y. Al-Baitai, I. Saadounne, and N. H. D. Leeuw, J. Phys. Condens. Matter 22, 255401 (2010)
[3] L. Pauling and S. B. Hendricks, J. Am. Chem. Soc. 47, 781 (1925)
[4] R. M. Cornell and U. Schwertmann, The Iron Oxides: Structure, Properties, Reactions, Occurences and Uses, 2nd ed. (WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2003)
[5] A. U. Gehring, H. Fischer, M. Louvel, K. Kunze, and P. G. Weidler, Geochemical Journal International 179, 1361 (2009), https://academic.oup.com/gji/article-pdf/179/3/1361/6005703/179-3-1361.pdf
[6] J. M. D. Coey, Magnetism and magnetic materials, 1st ed. (Cambridge University Press, The Edinburgh Building, Cambridge CB2 8RU, UK, 2009).
[7] F. Koch and J. B. Cohen, Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater. 25, 275 (1969)
[8] P. D. Battle and A. K. Cheetham, J. Phys. C: Solid State Phys. 12, 337 (1979)
[9] G. S. Parkinson, Surf. Sci. Rep. 71, 272 (2016).
[10] J.-B. Moussy, J. Phys. D Appl. Phys. 46, 143001 (2013).
[11] J. M. D. Coey and C. L. Chien, MRS Bulletin 28, 720 (2003)
[12] M. Bises and A. Barthelemy, IEEE Trans. Electron Devices 54, 1003 (2007)
[13] I. Zutić, J. Fabian, and S. D. Sarma, Rev. Mod. Phys. 76, 323 (2004).
[14] J. A. Moyer, R. Gao, P. Schiffer, and L. W. Martin, Sci. Rep. 5, 10363 (2015).
[15] L. Marnitz, K. Rott, S. Niehorster, C. Klewe, D. Meier, S. Fabretti, M. Witzkiok, A. Krampf, O. Kuschel, T. Schemme, K. Kuepper, J. Wollschläger, A. Thomas, G. Reiss, and T. Kuschel, AIP Adv. 5, 041703 (2015)
[16] H. Yanagihara, M. Hasegawa, E. Kita, Y. Wakabayashi, H. Sawa, and K. Siratori, J. Phys. Soc. Jpn. 75, 054708 (2006)
[17] C. F. Chang, Z. Hu, S. Klein, X. H. Liu, R. Sutarto, A. Tanaka, J. C. Cezar, N. B. Brookes, H.-J. Lin, H. Hsieh, C. T. Chen, A. D. Rata, and L. H. Tjong, Phys. Rev. X 6, 041011 (2016)
[18] F. Bertram, C. Deiter, O. Hoeftert, T. Schemme, F. Timmer, M. Suendorf, B. Zimmermann, and J. Wollschläger, J. Phys. D Appl. Phys. 45, 395302 (2012)
[19] S. Celotto, W. Eerenstein, and T. Hibma, Eur. Phys. J. B 36, 271 (2003)
[20] P. van der Zaag, P. Bloemen, J. Gaines, R. Wolf, P. van der Heijden, R. van de Veerdonk, and W. de Jonge, J. Magn. Magn. Mater. 211, 301 (2000)
[21] F. Bertram, C. Deiter, K. Pflaum, M. Suendorf, C. Otte, and J. Wollschläger, J. Appl. Phys. 110, 102280 (2011).
https://doi.org/10.1063/1.3661655
[22] F. Bertram, C. Deiter, T. Schemme, S. Jentsch, and J. Wollschläger, J. Appl. Phys. 113, 184103 (2013)
https://doi.org/10.1063/1.4803894
[23] D. T. Margulies, F. T. Parker, M. L. Rudee, F. E. Spada, J. N. Chapman, P. R. Aitchison, and A. E. Berkowitz, Phys. Rev. Lett. 79, 5162 (1997)
[24] J. G. Tobin, S. A. Morton, S. W. Yu, G. D. Waddill, I. K. Schuller, and S. A. Chambers, J. Phys. Condens. Matter 19, 315218 (2007)
[25] S. K. Arora, H. Wu, H. Yao, W. Y. Ching, R. J. Choudhary, I. V. Shvets, and O. N. Myraosov, IEEE Trans. Magn. 44, 2628 (2008)
[26] N.-T. Kim-Ngan, A. Balogh, J. Meyer, J. Brötz, M. Zajac, T. Šlezak, and J. Korecki, Surf. Sci. 603, 1175 (2009)
[27] M. Monti, M. Sanz, M. Oujja, E. Rebollar, M. Castillejo, F. J. Pedrosa, A. Bollero, J. Camarero, J. L. F. Cuñado, N. M. Nemes, J. F. Mompean, M. Garcia-Hernández, S. Nie, K. F. McCarty, A. T. N'Diaye, G. Chen, A. K. Schmid, J. F. Marco, and J. de la Figuera, J. Appl. Phys 114, 223902 (2013).

[28] S. Kale, S. M. Bhagat, S. E. Lofland, T. Scabarozi, S. B. Ogale, A. Orozco, S. R. Shinde, T. Venkatesan, B. Hanney, B. Mercey, and W. Prellier, Phys. Rev. B 64, 205413 (2001).

[29] J. Rubio-Zuazo, L. Onandia, E. Salas-Colera, A. Muñoz Noval, and G. R. Castro, J. Phys. Chem. C 119, 1108 (2015).

[30] O. Kuschel, R. Buß, W. Spiess, T. Schemme, J. Wöllermann, K. Kuepper, T. Kuschel, J. Wollschlager, and K. Kuepper, Phys. Rev. B 94, 094423 (2016).

[31] O. Kuschel, W. Spiess, T. Schemme, J. Rubio-Zuazo, K. Kuepper, and J. Wollschlager, Appl. Phys. Lett. 111, 041902 (2017), https://doi.org/10.1063/1.4995408.

[32] R. Takahashi, H. Misumi, and M. Lippmaa, Cryst. Growth Des. 12, 2679 (2012).

[33] R. Takahashi, H. Misumi, and M. Lippmaa, Phys. Rev. B 78, 064427 (2008).

[34] J. Keller, P. Miltényi, B. Beschoten, G. Güntherodt, U. Nowak, and K. D. Usadel, Phys. Rev. B 66, 014431 (2002).

[35] C. Gatel, E. Snoeck, V. Serin, and A. Fert, Eur. Phys. J. B 45, 157 (2005).

[36] I. P. Krug, F. U. Hillebrecht, M. W. Haverkort, A. Tanaka, L. H. Tjeng, H. Gomonay, A. Fraile-Rodriguez, F. Nolting, S. Cramm, and C. M. Schneider, Phys. Rev. B 78, 064427 (2008).

[37] M. Pilard, O. Enser, S. Cherifi, B. Carvello, L. Roiban, B. Muller, F. Scheurer, L. Ranno, and C. Boeglin, Phys. Rev. B 76, 214436 (2007).

[38] K. Kuepper, O. Kuschel, N. Pathé, T. Schemme, J. Schmalhorst, A. Thomas, E. Arenholz, M. Gorgó, R. Ovsyannikov, S. Bartkowski, G. Reiss, and J. Wollschlager, Phys. Rev. B 94, 024401 (2016).

[39] T. Schemme, O. Kuschel, F. Bertram, K. Kuepper, and J. Wollschlager, Thin Solid Films 589, 526 (2015).

[40] M. Roelsgaard, Á.-C. Dippel, K. A. Borup, I. G. Nielsen, N. L. N. Broge, J. T. Röh, O. Gutowski, and B. B. Iversen, IUCrJ 6, 299 (2019).

[41] J. Gustafson, M. Shipilin, C. Zhang, A. Stierle, U. Hejral, U. Ruett, O. Gutowski, P.-A. Carlsson, M. Skoghundh, and E. Lundgren, Science 343, 758 (2014).

[42] J. Rodewald, J. Thien, T. Pohlmann, M. Hoppe, F. Timmer, F. Bertram, K. Kuepper, and J. Wollschlager, Phys. Rev. B 100, 155418 (2019).

[43] C. Schlueter, A. Gloskovskii, K. Ederer, I. Schostak, S. Piec, I. Sarkar, Y. Matveyev, P. Lömker, M. Sing, R. Claessen, C. Wiemann, C. M. Schneider, K. Medjanik, G. Schönhenne, P. Amann, A. Nilsson, and W. Drube, AIP Conf. Proc. 2054, 040010 (2019).

[44] T. Fujii, F. M. F. de Groot, G. A. Sawatzky, F. C. Voogt, T. Hibma, and K. Okada, Phys. Rev. B 59, 3195 (1999).

[45] G. Renaud, R. Lazzari, and P. Leroy, Surf. Sci. Rep. 64, 255 (2009).

[46] Z. Jang, “Theory of GISAXS,” Lecture (2014).

[47] G. S. Parkinson, P. Lackner, O. Gamba, S. Maß, S. Gerhold, M. Riva, R. Bliem, U. Diebold, and M. Schmid, Surf. Sci. 649, L120 (2016).

[48] G. Ketteler, W. Weiss, W. Ranke, and R. Schlögl, Phys. Chem. Chem. Phys. 3, 1114 (2001).