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ABSTRACT

$\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ thin films with varying Ni amount ($0 \leq x \leq 1.5$) were deposited on $\text{MgO}(001)$ via reactive molecular beam epitaxy. The growth process was monitored during film deposition by means of X-ray diffraction. All prepared films exhibit a well-ordered structure with complete vertical crystallinity throughout the whole film growth and flat surfaces of the final films independent of the Ni amount. An enhancement of the vertical compression in the initial growth continuously decreases up to a film thickness of 8 nm. During further growth, all films exhibit residual and constant vertical compression with lateral adaption of the final films to the substrate lattice, as observed by high energy surface X-ray diffraction experiments. Hard X-ray photoelectron spectroscopy measurements of the final films reveal increasing $\text{Fe}^{3+}:\text{Fe}^{2+}$ ratios for higher Ni content and point to additional NiO agglomerations within the films exceeding the stoichiometric Ni amount of $x = 1$.

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Transition metal ferrites are in the focus of current research due to several intriguing properties, resulting from the competition of spin, charge, and orbital degrees of freedom. In particular, most ferrites exhibit high Curie temperatures T_c and significant magnetic moments, making them extremely interesting in the fields of spin caloritronics¹ and spintronics.^{2–4}

In the latter, spin-filter applications with the capability of generating highly spin-polarized currents are aimed to be realized. Here, NiFe_2O_4 (NFO) as an insulating and ferrimagnetic transition metal ferrite with a high T_c of 865 K represents a promising material.^{5–7} Since the structural quality of the tunneling barrier and its interfaces crucially influences the spin-filter efficiency⁷ and is important for the transmission of spin currents, ferrites have to be prepared as thin films with low defect densities for high-quality spintronic and spin caloritronic devices.

In addition, the chemical composition of ferrites, i.e., the cationic ratio, can have significant impact on their structural, chemical, magnetic, and electronic properties.^{8–11} Thus, in this work, $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ thin films with varying Ni content ($0 \leq x \leq 1.5$) are grown on $\text{MgO}(001)$ via reactive molecular beam epitaxy. $\text{MgO}(001)$ with a lattice constant of $a_{\text{MgO}} = 421.2$ pm is used as a substrate due to the small

lattice mismatches of only 0.3% and 1% compared to the halved lattice constants of Fe_3O_4 ($a_{\text{Fe}_3\text{O}_4} = 839.6$ pm) and NiFe_2O_4 ($a_{\text{NFO}} = 833.9$ pm), respectively. With this, a minimization of strain-induced defects and structural disorder is aimed for in order to obtain well-ordered ultrathin NFO films.

Film preparation and characterization were carried out at beamline I07 of the Diamond Light Source (DLS). Here, the endstation is equipped with an ultra high vacuum (UHV) chamber mounted on a 2 + 3 circle diffractometer with a hexapod sample stage and a two-dimensional PILATUS 100k detector. This setup enables X-ray diffraction (XRD) experiments during and after film growth without breaking the vacuum. The $\text{MgO}(001)$ substrates used in this study were purchased from CrysTec GmbH, exhibiting a surface orientation tolerance of less than 0.1° . Prior to film deposition, the substrates have been cleaned by heating at 400°C for 1 h in a molecular oxygen atmosphere of 1×10^{-4} mbar. The films were deposited by thermal co-evaporation of Ni and Fe from pure rods heated by electron bombardment in a diluted molecular oxygen atmosphere of 5×10^{-6} mbar. The substrate temperature was held at 250°C to obtain optimal growth conditions,¹² while suppressing Mg diffusion into the ferrite films.^{13,14} The material flux was controlled by adjusting the ion current

of each evaporator. For XRD measurements during film deposition, the cleaned substrate surface was aligned in the X-ray beam to perform scans along the (00L) crystal truncation rod (CTR) across the MgO(002) and the emergent ferrite (004) Bragg conditions in $\theta - 2\theta$ geometry with a photon energy of 20 keV. Additionally, film thicknesses were determined at beamline I07 after deposition by means of X-ray reflectivity (XRR) (not shown here). All final NFO films exhibit comparable thicknesses between 14.8 and 18.6 nm (cf. Table I).

After film preparation, surface sensitive high energy surface X-ray diffraction (HESXRD) experiments were performed at beamline P07-EH2 of PETRA III at the Deutsches Elektronen-Synchrotron (DESY). For these measurements, an X-ray energy of 102 keV was used. The diffraction pattern was collected with a two-dimensional PerkinElmer XRD 1621 flat panel detector. To record reciprocal space maps, the samples are illuminated by the X-ray beam at a fixed angle of 0.03° during a continuous azimuthal rotation of 90° with $0.5^\circ/\text{s}$. Afterward, processing of the detector images was applied that each pixel of the processed image only consists of the highest detected intensity throughout the measurement. By this, a reciprocal space map is obtained as a projection of CTRs and Bragg reflections from the film and the substrate, which intersect with the detector plane during rotation.^{15,16}

Furthermore, the final film composition was analyzed by hard X-ray photoelectron spectroscopy (HAXPES) at beamline P09 of PETRA III at DESY. Here, a photon energy of 5948 eV was used. The cationic Ni amount x in the prepared $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ films was determined by integrating the background corrected intensities underneath the Ni $2p_{1/2}$ and Fe $2p$ spectra (cf. Fig. 5), considering the respective differential photoionization cross sections from Trzhaskovskaya *et al.*¹⁷ In total, four different films have been prepared with Ni amounts of $x = 0$ (Fe_3O_4), $x = 0.75$, $x = 1.20$, and $x = 1.50$.

The temporal evolution of the (00L) CTR across the MgO(002) and NFO(004) Bragg peaks during film growth is depicted in Fig. 1 exemplarily for the film with $x = 1.20$. Here, the film thickness D during deposition is obtained by calibrating the final film thickness to the monitored exposure during film growth. For the first growth stages below ~ 1 nm thickness, only the substrate Bragg reflection at $L = 2$ is clearly visible. For higher coverages, an additional peak at slightly higher L values arises, which can be attributed to the NFO(004) film Bragg reflection. Due to finite size effects, this peak is broad with only low intensity at the early growth stages, while the peak width decreases and its intensity increases for higher coverages, as it is expected for crystalline film growth. The arising NFO(004) film reflection is accompanied by the emergence of Laue fringes (marked by the dashed lines in Fig. 1), indicating well-ordered crystalline film growth with smooth

FIG. 1. Evolution of the (00L) CTR across the MgO(002) and NFO(004) Bragg peaks during film growth for a Ni amount of $x = 1.20$. The single scans were interpolated with each other to follow the evolution of the Laue fringes (dashed lines). Several selected scans are depicted for clarity (solid lines). The vertical crystallite size $D_{\text{cryst}}^{\text{vert}}$ (depicted in the inset) coincides with the total film thickness D (marked by a dashed line), meaning completely crystalline growth in the vertical direction.

interfaces during the whole deposition process. These observations for the $\text{Ni}_{1.2}\text{Fe}_{1.8}\text{O}_4$ film are representative for all prepared NFO films.

For each XRD scan, analysis of the diffraction data was performed using calculations based on full kinematic diffraction theory. From these calculations, the vertical layer distance d_{vert} (defined as the monolayer distance in the [001] direction) and the number N_{ML} of NFO monolayers (ML) are extracted, both determining the vertical crystallite size $D_{\text{cryst}}^{\text{vert}} = N_{\text{ML}}d_{\text{vert}}$ depicted in the inset of Fig. 1 exemplarily for the NFO film with $x = 1.20$. Here, completely crystalline growth in vertical direction is observed during the whole deposition process, since the vertical crystallite size coincides with the film thickness (indicated by a dashed line in the inset of Fig. 1). This behavior is observed for all prepared NFO films (not shown here), stating completely crystalline films in vertical direction independent of the Ni amount x .

In addition, the evolution of the vertical layer distance d_{vert} for each film is depicted in Fig. 2. For reference, the bulk layer distances of Fe_3O_4 and NFO at the elevated deposition temperature of 250°C , determined by their respective thermal expansion coefficients,^{18,19} are shown as well. All films exhibit vertical compression throughout the whole deposition process. This type of strain in the vertical direction is expected, considering an expansion of the lateral layer distance d_{lat} (defined as the monolayer distance in the [100] or [010] direction) due to an adaption of the film to the substrate lattice (as verified by

TABLE I. Vertical layer distance d_{vert} , interface distance d_{IF} , film roughness σ_{film} , and the number of NFO monolayers N_{ML} obtained by the analysis of XRD data via the kinematic diffraction theory. Film thicknesses D are listed as well.

x	d_{vert} (pm)	d_{IF} (pm)	σ_{film} (Å)	N_{ML}	D (nm)
0	208.6	207.4	0.3	70	15.1
0.75	207.3	202.0	0.9	86	18.6
1.20	206.5	200.7	0.9	74	15.2
1.50	206.8	198.9	1.1	68	14.8

HESXRD; see below). Based on elastic theory for continuum, d_{vert} for homogeneous tetragonally (in-plane) distorted films is related to d_{lat} via²⁰

$$\frac{\Delta d_{\text{vert}}}{d_{\text{vert}}} = \frac{2\nu}{\nu - 1} \frac{\Delta d_{\text{lat}}}{d_{\text{lat}}}, \quad (1)$$

with ν as the Poisson ratio. Assuming complete lateral adaption of the Fe_3O_4 film ($\nu = 0.356$ ²¹) to the MgO lattice during deposition, the vertical strain of $\Delta d_{\text{vert}}/d_{\text{vert}} = -0.4\%$ would be expected, considering respective thermal expansion coefficients of Fe_3O_4 and MgO .^{18,22} Here, for the magnetite film, the residual strain of $\Delta d_{\text{vert}}/d_{\text{vert}}^{\text{Fe}_3\text{O}_4} = -0.7\%$ is obtained above 4 nm thickness, which is slightly larger but close to the expected value. For stoichiometric NiFe_2O_4 ($\nu = 0.338$ ²¹), Eq. (1) predicts $\Delta d_{\text{vert}}/d_{\text{vert}} = -1.0\%$, which is in accordance with the values obtained for the NFO films with a constant strain above 8 nm [$\Delta d_{\text{vert}}/d_{\text{vert}}^{\text{NFO}} = (-1.1 \pm 0.2)\%$]. Further, the critical thickness D_c , above which defects as, i.e., misfit dislocations are incorporated into the film to release strain, can be estimated following the model of Matthews and Blakeslee²³ via

$$\frac{D_c}{b} = \frac{(1 - \nu \cos^2 \alpha) \left(\ln \left(\frac{D_c}{b} \right) + 1 \right)}{2 \pi f (1 + \nu) \cos(\lambda)}, \quad (2)$$

which already provided consistent results for the $\text{Fe}_3\text{O}_4/\text{NiO}$ bilayers on $\text{MgO}(001)$.²⁴ Here, b is the magnitude of the Burgers vector, f is the lattice mismatch, $\alpha = 90^\circ$ is the angle between the Burgers vector and the dislocation line, and $\lambda = 45^\circ$ is the angle between the Burgers vector and the direction normal to the dislocation line and within the plane of the interface. Following this model, critical thicknesses D_c of 104 and 27.4 nm are obtained for magnetite ($b_{\text{Fe}_3\text{O}_4} = 296.8$ pm) and stoichiometric NFO ($b_{\text{NFO}} = 294.8$ pm) on $\text{MgO}(001)$, respectively. Here, the Burgers vectors $b = a_0/4\langle 110 \rangle$ were assumed (a_0 : ferrite lattice constant) allowing for dislocation dissociation in the ferrite films

to obtain the lowest D_c possible.²⁵ However, both values are well above the prepared film thicknesses and therefore in good agreement with the observed residual strain in the final films.

Though for low coverages below 4 nm, even larger compressive strain is observed. This observation could be correlated with the presence of antiphase boundaries (APBs), which are assumed to have an impact on strain, as already proposed in former studies,^{26,27} where APBs lead to, i.e., constant strain far beyond the critical film thickness. In particular, Arora *et al.*²⁶ proposed an altered elastical behavior with additional tensile strain components due to the APBs in Fe_3O_4 films on $\text{MgO}(001)$, which, in turn, would enhance the lateral strain in addition to the lattice mismatch, resulting in a stronger vertical compression, as observed here. Since the APB density in ferrites decreases with an increasing film thickness,^{28,29} additional strain components due to APBs could explain the observed enhanced strain in the ultrathin ferrite films. Additionally, the vertical layer distance generally decreases with an increasing Ni content (see the inset of Fig. 2). For films above 8 nm thickness, which exhibit a constant strain throughout further growth, this decrease is observed up to a Ni amount of $x = 1.2$, whereas the layer distance of the film with $x = 1.5$ is again slightly increased.

After film deposition, XRD measurements with a higher resolution and a wider range in L were conducted, as the coverage and, thus, the shape of the (00L) CTR do not change anymore during the scan. These measurements are shown in Fig. 3 in addition to the respective kinematic diffraction theory calculations. The models show excellent agreement with the data for all films with varying Ni content. The resulting fit parameters are listed in Table I. For the Fe_3O_4 film ($x = 0$), the Laue fringes are damped stronger than for the Ni containing films due to a higher interface roughness, resulting from a rougher substrate surface. In contrast, the film surface roughness σ_{film} is the lowest for magnetite, while it tends to slightly increase with an

FIG. 2. Vertical layer distance d_{vert} during the growth of each $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ film with varying Ni amount x . The dashed lines serve as guides to the eye. Bulk layer distances for Fe_3O_4 and NFO at the deposition temperature of 250°C are shown for reference. The inset shows the evolution of d_{vert} for three exemplary film thicknesses dependent on the Ni content x .

FIG. 3. XRD measurements after film deposition of the different NFO films with varying Ni content x . The solid lines represent the calculations based on full kinematic diffraction theory.

increasing Ni content. Still, low film roughnesses of up to only 1.1 Å point to flat surfaces with very low defect densities for all films. In addition, the position of the (004) film Bragg peak increases for a Ni content up to $x = 1.2$ (meaning a decreasing vertical layer distance d_{vert}), while it slightly decreases again for the highest Ni amount of $x = 1.5$ (meaning a slight increase in d_{vert}). Moreover, the interface distance d_{IF} (the distance between the topmost substrate and the first film monolayer in [001] direction) is smaller than both the layer distance of the MgO(001) substrate and the ferrite film. In addition, it decreases with an increasing Ni amount from ~ 207 pm for Fe_3O_4 to ~ 199 pm for $x = 1.5$. Due to the well-ordered film structure with complete crystallinity in vertical direction, the number N_{ML} of NFO monolayers used in the models only deviate by ± 4 ML (corresponding to one NFO unit cell) compared to the total film thickness D (as determined by XRR).

In addition, HESXRD measurements were conducted in a grazing incident geometry to obtain not only vertical but also lateral layer distances d_{lat} of the films after deposition. Figure 4 shows the projection of the 3D reciprocal volume on the $\sqrt{H^2 + K^2}$ vs L plane for the film with a Ni content of $x = 1.20$. With this diffraction pattern, the position of the spinel type NFO film reflections (denoted by index S) in relation to the reflections of the rock salt type MgO substrate (index RS) were determined by peak fitting in lateral ($\sqrt{H^2 + K^2}$) and vertical (L) scattering directions. In total, 14 reflexes (positive and negative parallel scattering directions) were considered in the analysis. The results are depicted in the inset of Fig. 4. Comparing the vertical layer distances derived from XRD (denoted as $d_{\text{vert}}^{\text{XRD}}$ in the inset of Fig. 4) and HESXRD, respectively, both analyses reveal similar values. However, due to thermal expansion, the values obtained by XRD

FIG. 4. Reciprocal space map in vertical (L) and lateral ($\sqrt{H^2 + K^2}$) scattering directions measured by HESXRD for an exemplary NFO film with a Ni amount of $x = 1.20$. Theoretical positions of the diffraction rods of the substrate are indicated by solid lines. Bragg reflections of the rock salt type MgO substrate (index RS) are covered to protect the detector. Spinel type reflections of the NFO film are denoted by index S. Vertical (d_{vert}) and lateral layer distances (d_{lat}) determined by the analysis of HESXRD data for the different NFO films with varying Ni amount x are shown in the inset. The vertical layer distance $d_{\text{vert}}^{\text{XRD}}$ resulting from XRD analysis and bulk values for NFO, NiO, Fe_3O_4 , and MgO are shown additionally.

deviate to slightly higher values, as XRD measurements were conducted at 250°C sample temperature compared to room-temperature HESXRD measurements. Nevertheless, the layer distance evolution depending on the Ni content is the same in both measurements. In particular, the slight increase in d_{vert} for the NFO film with the highest Ni amount of $x = 1.5$ is confirmed by both measurements, resembling the rise of the bulk layer distance from NiFe_2O_4 to NiO (marked by the dashed lines in the inset of Fig. 4). In addition, HESXRD analysis reveals tensile strain in lateral direction, as the lateral layer distances match the one of the MgO substrate, resulting from lateral adaption of the film to the substrate lattice. Thus, as we do not observe any relaxation of the Ni ferrite films independent of the Ni content, the films are homogeneously strained and their structure is tetragonally distorted without the incorporation of strain releasing defects. Complete crystallinity with high interface and film quality as seen in XRD measurements confirms this assumption.

HAXPES measurements of the Ni 2p and Fe 2p core level spectra after film deposition are depicted in Figs. 5(a) and 5(b), respectively. The shape of the Ni 2p spectra with its satellites ~ 7 eV above the main spin-orbit split Ni $2p_{3/2}$ and Ni $2p_{1/2}$ peaks [cf. Fig. 5(a)] closely resembles the reported Ni 2p spectra for NiFe_2O_4 according to the presence of Ni^{2+} cations.³⁰ In addition, NFO films with Ni contents of $x \geq 1.2$ exhibit a small shoulder at the high binding energy side of the Ni $2p_{3/2}$ peak [cf. the inset of Fig. 5(a)]. As this shoulder is ascribed to a screening process of electrons originating from neighboring NiO_6 clusters,³¹ its appearance indicates the presence of NiO agglomerations in NFO films exceeding the stoichiometric Ni amount ($x > 1$). In addition, a low binding energy shoulder of the Fe $2p_{3/2}$ peak, resulting from the presence of Fe^{2+} cations, decreases for higher Ni content and vanishes for $x \geq 1.2$ [cf. the inset of Fig. 5(b)]. This behavior is accompanied by an increase in the Fe^{3+} satellite at a binding energy of ~ 718.9 eV,³² stating increasing $\text{Fe}^{3+}:\text{Fe}^{2+}$ ratios with a higher Ni content in the NFO films.

FIG. 5. (a) Ni 2p and (b) Fe 2p HAXPES measurements of all prepared NFO films with varying Ni content x . For better comparison, the Ni $2p_{3/2}$ and Fe $2p_{3/2}$ (scaled to the maximum) core levels are explicitly shown in the insets of (a) and (b), respectively.

In summary, four $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ films with different Ni amounts ($0 \leq x \leq 1.5$) and similar thicknesses [(16.7 ± 1.9) nm] were deposited on $\text{MgO}(001)$ substrates and structurally characterized *in situ* by means of XRD during film growth. All films exhibit complete crystallinity in vertical direction and high crystalline quality throughout the whole deposition process. Enhanced vertical compression at low coverages is observed up to a thickness of ~ 8 nm and can be attributed to APB-induced strain. Thicker films exhibit residual but constant vertical compression. In addition, HESXRD measurements reveal lateral tensile strain in the final films due to lateral lattice matching of the film to the substrate lattice. The observed strain in both vertical and lateral directions with a homogeneous tetragonal distortion of the film lattice is in accordance with the significantly higher critical film thicknesses upon which strain releasing defects would be incorporated. Consequently, these films are assumed to exhibit less defects, confirmed by complete crystallinity and high crystalline quality with flat surfaces observed by XRD analysis. HAXPES measurements reveal an increasing $\text{Fe}^{3+}:\text{Fe}^{2+}$ ratio for higher Ni content as expected for the gradual substitution of Fe^{2+} by Ni^{2+} cations with increasing Ni amount. Moreover, the results point to a formation of lattice matched NiO agglomerations in NFO films exceeding the stoichiometric Ni content of $x = 1$. However, high crystalline quality and extremely low surface roughness make the prepared NFO films promising for the application in spintronic and spincaloritronic devices. In addition, the existent strain in ultrathin NFO films with varying Ni content is assumed to be valuable for tailoring physical characteristics as, i.e., magnetic and electronic properties, to match specific purposes of spintronic and spincaloritronic applications.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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