Structural and magnetic properties of stoichiometric epitaxial CoO/Fe exchange-bias bilayers

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We present a detailed study of the magnetic and structural properties of the CoO/Fe bilayers by using a combination of x-ray diffraction (crystalline structure), Rutherford backscattering (chemical composition), and SQUID magnetometry (magnetic characterization) measurements. We prepared stoichiometric and single crystalline CoO thin films by a post-deposition annealing process in ultrahigh-vacuum conditions from sputter deposited hyperstoichiometric, polycrystalline CoO films. A simultaneous increase of the CoO crystalline quality and chemical phase purity has been achieved. Subsequently, the annealed CoO layers served as a template for the growth of epitaxial Fe films. The epitaxial relation between CoO and Fe was found to be of the Nishiyama-Wassermann type, where the Fe[001] direction is parallel aligned to the CoO[1-10] direction. The magnetic properties of CoO/Fe bilayers are strongly influenced by the stoichiometry of the antiferromagnetic CoO layer. Especially the blocking temperature is sensitive to the oxygen concentration within the CoO layer. While the blocking temperature of stoichiometric, epitaxial CoO/Fe exchange-bias bilayers almost equals the Néel temperature of bulk CoO, it is strongly reduced for superstoichiometric, polycrystalline CoO.

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I. INTRODUCTION

In a ferromagnet (F)/antiferromagnet (AF) bilayer system, the presence of the AF strongly influences the magnetic properties of the F via the exchange coupling at their common interface. Upon field cooling below the Néel temperatures (T_N) of the AF, the hysteresis loop of the F experiences a shift along the field axis and acquires an enhanced coercivity H_C . This so-called exchange-bias (EB) effect was discovered by Meiklejohn and Bean in 1956.¹ In the last decades it triggered numerous research activities due to its fascinating physical properties as well as its application in EB based spin valves.^{2,3} There are several theoretical models to describe the EB, which take particular imperfections into account such as interface roughness,⁴ randomly oriented polycrystalline AF grains,⁵ or diluted nonmagnetic impurities.^{6,7} Recently, Meiklejohn and Bean type of models have also shown detailed agreement with the experimental data.⁸⁻¹¹

CoO has extensively been used as a antiferromagnet in exchange-biased bilayers and multilayers. The main physical advantages of the choice of CoO as a AF are the easily accessible Néel temperature, which is close to room temperature (RT), the strong anisotropy and the simple NaCl-like crystal structure, which recommend it both for experimental as well as for theoretical studies. Due to the rich bulk Co-O phase diagram,^{12,14} exhibiting several oxide phases with distinct spin structures and Néel temperatures,^{15,16} special efforts must be taken to achieve phase purity. The desired stable, stoichiometric CoO phase crystallizes in the face-centered-cubic (fcc) NaCl structure with a lattice parameter of $a_{\text{CoO}}=4.26$ Å. The oxygen solubility range in this phase is rather large, so that superstoichiometric $\text{Co}_x\text{O}_{1+\delta}$ is stable at room temperature. It has been observed that the H_{EB} in Co/CoO samples can be increased by a factor of 3 if the CoO layer is diluted either by Mg or by overoxidation.⁶ At elevated temperatures however, the additional oxygen starts to leave the lattice. Above 1000 °C only the stoichiometric

phase is stable.¹⁷ Apart from the oxygen rich spinel-type Co_3O_4 phase, there are reports about low temperature CoO phases, which all transform to CoO at high temperatures with smaller lattice parameter but conserved structure.^{12-14,17,18} There are several procedures reported in the literature to grow thin CoO layers. Most of the experimental studies use natural oxidation or *in-situ* thermal oxidation of Co, resulting in a CoO top layer of about 25 Å.^{1,19-23} Thicker monocrystalline CoO can be achieved by reactive sputtering,²⁴⁻²⁷ magnetron sputtering techniques,²⁸ or by evaporating Co in O atmosphere by molecular beam epitaxy (MBE).²⁹⁻³¹

Due to their lattice parameters, we expect Fe (110) to grow epitaxially on single crystalline CoO(111) films. Iron crystallizes in the body-centered-cubic (bcc) structure with a lattice parameter of $a_{\text{Fe}}=2.864$ Å. In a hard sphere model, the resulting epitaxial relation is governed by the ratio $\alpha = \frac{d_{\text{bcc}}}{d_{\text{fcc}}}$ of the respective in-plane nearest-neighbor distances. For $0.88 < \alpha_{\text{KS}} < 0.96$ one expects the Kurdjumov-Sachs (KS) relation,³² where the $[1\bar{1}0]_{\text{fcc}}$ in-plane direction is parallel to the $[1\bar{1}1]_{\text{bcc}}$ direction, while for $0.83 < \alpha_{\text{NW1}} < 0.88$ and for $1.02 < \alpha_{\text{NW2}} < 1.19$ the Nishiyama-Wassermann (NW) relation³³⁻³⁵ for which $[1\bar{1}0]_{\text{fcc}} \parallel [001]_{\text{bcc}}$ is energetically more favorable.³⁶ The nearest-neighbor distances for both materials is $d_{\text{Fe}} = \frac{\sqrt{3}}{2} a_{\text{Fe}} = 2.48$ Å and $d_{\text{CoO}} = \frac{1}{\sqrt{2}} a_{\text{CoO}} = 3.01$ Å. Thus the ratio $\alpha = \frac{d_{\text{Fe}}}{d_{\text{CoO}}} = 0.83$ predicts epitaxial growth in the NW relation. Apart from the expected epitaxial growth the system CoO/Fe offers the opportunity to employ element specific magnetometry to study the AF and the F separately.²⁷

However, despite numerous magnetic studies and applications, a systematic growth study of Fe/CoO layers, including chemical analysis is still missing. We optimized the growth process of CoO(111) films in the Fe/CoO bilayer system by a systematic variation of the substrate temperature and the partial pressure of oxygen during reactive rf-sputter growth

of the CoO films followed by a post- (deposition) annealing step but prior to Fe deposition. Following this road, epitaxial, stoichiometric CoO/Fe bilayers can be prepared. The crystalline properties of the individual layers were investigated by x-ray diffraction (XRD). Additionally, the surface morphology was explored by atomic force microscopy (AFM). The structural measurements were complemented by Rutherford backscattering (RBS), which delivers the depth resolved chemical profile of the samples. Finally, the magnetic characterization was carried out by superconducting quantum interference device (SQUID) magnetometry.

II. INITIAL GROWTH AND CHARACTERIZATION OF THE CoO FILMS

The CoO layers were prepared by reactive rf sputtering of Co in a mixture of Ar (92%) and O₂ (8%) atmosphere on Al₂O₃(11 $\bar{2}$ 0) substrates. The total gas pressure was fixed at $p_{\text{tot}} = 5.3 \times 10^{-3}$ mbar and the partial oxygen pressure was set to $p_{\text{O}_2} = 4.0 \times 10^{-4}$ mbar. This value is the optimized result of a preliminary study,³⁷ where a series of samples were prepared by varying the partial oxygen pressure. For each sample, hysteresis loops were measured by SQUID magnetometry at 10 K as well as at room temperature. The dependence of the average magnetic moment as a function of the partial oxygen pressure indicated that, above a partial oxygen pressure of $p_{\text{O}_2} = 4 \times 10^{-4}$ mbar the ferromagnetic contribution to the hysteresis loop vanishes. Thus, we infer that the CoO layer was completely oxidized during the deposition process and no elementary and/or atomic Co was left in the CoO layer. Under this pressure condition we varied the temperature of the substrate from 250 °C to 500 °C during the deposition with the aim to optimize the structural properties of 200 Å thick CoO films. The deposition rate was kept constant at a value 0.1 Å/s.

AFM topographies of the resulting films, recorded with an AutoProbe AFM in contact mode, display uniform, flat surfaces. A typical $5 \times 5 \mu\text{m}^2$ area of the sample exhibits a root-mean-square (rms) roughness of 5 Å. X-ray characterization was employed to discern different structural phases by their respective lattice parameters. The measurements have been carried out at the high intensity wiggler beamline W1.1 of the HASYLAB synchrotron radiation facility in Hamburg, Germany. A four circle diffractometer was deployed at a fixed energy of 8048 eV ($\lambda = 1.5405$ Å) to investigate the in- and out-of-plane lattice parameter as well as the crystalline structure of the samples. For in-plane measurements we use surface scattering techniques with glancing incident and exit angles with respect to the surface.³⁸ For all these measurements the incident angle was kept constant, slightly above the critical angle for total external reflection of the top layer. The intensity of the exit beam was integrated over a wide range of exit angles via a broad detector window. With this setup the structural information is averaged over the entire thickness.

Figure 1 depicts out-of-plane radial scans of CoO films prepared at three different substrate temperatures. The two vertical lines indicate the bulk positions of the (111)-reflections of the low temperature CoO at 34.14° and of the

FIG. 1. Out-of-plane radial measurements of the as-prepared CoO films deposited at different growth temperatures. Vertical lines at $2\theta = 34.14^\circ$ and at $2\theta = 36.48^\circ$ mark the bulk positions for the CoO (111) reflections for both different temperature phases. All diffractograms were recorded at $E = 8048$ eV ($\lambda = 1.54$ Å).

high temperature CoO phase at 36.48°.^{12–14,17,18} Apart from the common substrate reflection at 37.76°, the diffractograms display two sets of reflections, one around 34° and one around 37.5°, whose angular position and intensity varies systematically with temperature. The rather broad peak at 34° can be identified as the (111)-reflection of the high temperature unstable CoO phase observed before.^{13,18} While this peak shows some fine structure at low growth temperature, it gradually vanishes at higher growth temperatures. The integrated intensity of the peak around 37.5° on the other hand increases with temperature, while its position shifts to lower angles. Even though this position differs clearly from the bulk position of the desired NaCl-like CoO (111)-reflection, we attribute this peak to the cubic CoO phase. The angular deviation can be explained by an out-of-plane lattice compression that decreases linearly with temperature from $\epsilon_z = 2.43\%$ for the sample grown at 250 °C to $\epsilon_z = 1.58\%$ for the one grown at 500 °C. Extrapolating this temperature dependence to higher temperatures, the compression will vanish at

FIG. 2. Distortion ϵ_z of the out-of-plane lattice parameter as a function of the growth temperature and linear extrapolation to a zero distortion state $\epsilon_z = 0$.

FIG. 3. (Color online) RBS spectrum of a 200 Å thick CoO film grown at 450 °C on an Al₂O₃ substrate recorded with a 2 MeV He⁺ ion beam under an incidence angle of 50° to the surface to prevent channeling.

about 940 °C. Figure 2 shows the measured data together with a linear fit.

The x-ray data clearly show the presence of at least two distinct structural CoO phases for all samples. There is a clear trend that higher growth temperatures lead to single phase CoO films and that the lattice parameter approaches the bulk value. However, XRD only senses crystalline ordered parts of the sample and may not detect randomly oriented nanocrystalline grains. Therefore we complemented the structural data by RBS to measure the chemical composition of the sample. RBS detects the energy loss of ions backscattered from the sample. There are two contributions to the energy loss: (1) inelastic scattering events with the nuclei of the sample itself, (2) energy loss of the ions by the electrons of the sample atoms. Therefore the energy of the scattered particle depends on the mass of the sample nucleus as well as on the depth of the scattering process. The scattering cross section is governed by the charge of the target nuclei. The energy distribution of the backscattered ions yields information about the area density of scattering centers in a certain sample depth. Knowing the exact sample thickness, it is possible to extract the number density of each constituent element within the system.³⁹ The RBS measurements were carried out at the tandem accelerator of the Ruhr-University in Bochum, Germany. In a standard routine, He⁺ ions with an energy of 2 MeV were used at an incident angle of 50° to avoid possible channelling effects. A silicon detector was positioned at an angle of 170° with respect to the incoming ion beam. All RBS spectra were normalized with respect to the incident beam.

A representative RBS random spectrum including the fit to the data is shown in Fig. 3. The spectrum was recorded for the sample grown at 450 °C. The yield at energies below 860 keV and 1280 keV represent backscattering from O and Al from the substrate, respectively. The O contribution from the CoO layer can clearly be distinguished from the substrate contribution by the yield below 860 keV. The Co backscattered yield is observed between 1700 keV and 1820 keV. The average stoichiometry of the CoO layer was determined by comparison between numerical simulations and the experimental data. In all model calculations, the thickness of the layer was kept constant and equal to the value determined from the small angle x-ray reflectivity (XRR) measurements, leaving only the Co/O ratio as a free parameter. The simulations nicely reproduce the Co backscattered yield, proving that the XRR data are reliable. Over the whole series it was necessary to assume a superstoichiometric Co₁O_{1+δ} of the sample in order to obtain satisfactory fits.

The deviation δ of the individual samples also decreases systematically with increasing growth temperature. From RBS data we obtain $\delta=0.75$ for the sample grown at 250 °C and $\delta=0.55$ for the sample grown at 500 °C. There is a clear tendency that higher growth temperatures favor the stoichiometric CoO phase, confirming the trend observed by XRD.

III. PREPARATION AND CHARACTERIZATION OF SINGLE CRYSTALLINE Fe FILMS ONTO ANNEALED CoO FILMS

We have first prepared a CoO film at a substrate temperature of 500 °C, which is the highest available temperature with the present sputtering setup. Afterwards the CoO film was annealed in an ultrahigh-vacuum system (base pressure 1.1×10^{-11} mbar) for 30 min at 1100 °C. The annealing temperature was chosen above the 940 °C estimated before to be the temperature where the out-of-plane distortion approaches zero. Additionally, it has been shown by Jauch *et al.*¹⁷ that for polycrystalline powder samples also the bulk phase diagram applies. Above 1000 °C higher oxides were reduced, additional O was removed and internal stresses were relieved.

After the annealing step the sample was cooled to 300 °C prior to the Fe deposition. The 210 Å thick Fe layer, serving as the ferromagnetic layer of the exchange-bias bilayer system was prepared by thermal evaporation from an effusion cell. To prevent the Fe layer from corrosion, all samples were capped with Pd film (50 Å) by *e*-beam gun deposition. Both layers were prepared at a growth rate of 0.5 Å/s.

FIG. 4. Out-of-plane (a) and in-plane (b) radial measurements of the final CoO/Fe sample. The out-of-plane scan was measured with a small off-set angle $\Delta\theta = 0.18^\circ$ in θ to reduce the intensity of the Al₂O₃ (11 $\bar{2}$ 0) substrate peak. Both scans were recorded at $E=8048$ eV ($\lambda=1.54$ Å).

FIG. 5. In-plane-360°-rocking-scan recorded on the sample described above at $E=8048$ eV ($\lambda=1.54$ Å). The scans were shifted for clarity along the intensity axis.

The x-ray analysis of the CoO/Fe clearly shows improved crystalline properties of the CoO layer as compared to the initial sample. Figure 4(a) (left-hand panel) depicts a radial out-of-plane scan. Four Bragg reflections are present in this scan. They can be identified as CoO(111) at 36.48° , Al_2O_3 ($11\bar{2}0$) at 37.76° , Pd (111) at 40.24° and Fe (110) at 44.78° , respectively. To suppress the dominating substrate reflection, the scan was recorded with a θ offset of 0.18° . Apart from CoO, no other cobalt oxide phases are present. The angular position of the CoO reflection matches exactly the bulk value. With the aim to manifest crystalline growth mode of the metallic layers mentioned above, we performed also an in-plane radial measurement. In Fig. 4(b) (right-hand panel) we recognize well separated in-plane Bragg reflections, confirming good in-plane order, crystallinity and epitaxial growth.

We compared the in-plane epitaxial relation of the CoO (111) film to the Fe (110) top layer using in-plane scattering techniques. To provide this measurement we set the in-plane detector angle 2θ to each one of the in-plane Bragg peaks depicted in Fig. 4(b). Then the sample was rotated (Φ axis) by 360° around the surface normal. The in-plane-360° scan recorded at a fixed detector angle $2\theta=61.5^\circ$, corresponding to the CoO($2\bar{2}0$) reflection, reveals six Bragg reflections equally separated by 60° , indicating the sixfold symmetry of the (111) zone axis of CoO, as seen in Fig. 5. Keeping the scattering vector constant at the value of the Fe (002) reflection and rotating the sample, six strong Bragg reflections 60° apart can be seen. They originate from the Fe layer. The sixfold CoO (111) surface offers three equivalent directions for the Fe (110) growth, exhibiting twofold symmetry. As a result, the Fe layer consists of three structural domains, rotated by 120° . Taking into account the different 2θ values of the CoO($2\bar{2}0$) and the Fe (002) reflections by plotting the intensity versus $\Phi-2\theta/2$, the iron reflections coincide exactly with the CoO reflections, confirming the parallel alignment of the CoO($2\bar{2}0$) and the Fe (002) directions. This confirms the expected Nishiyama-Wassermann epitaxial relation between the face-centered CoO and the body-centered cubic Fe lattice.^{33,34} The Fe layer itself also

FIG. 6. (Color online) RBS-spectra recorded for a 2 MeV He^+ ion beam under a incidence angle of 50° to the surface to prevent channeling of the post-annealed sample.

serves as a template for epitaxial Pd growth, as the Pd($2\bar{2}0$) reflections are aligned with respect to the Fe (002) reflections. We note a slight increase of mosaicity of the constituent layers of the sample, from the bottom to the top as the width of the rocking curves increases. Additionally we observed that the CoO lattice is rotated by about 27° with respect to the (0001) axis of the sapphire substrate, thus the complete epitaxial relation can be expressed as $\text{Al}_2\text{O}_3[1\bar{1}00] \parallel \text{CoO}[2\bar{2}0] \parallel \text{Fe}[002] \parallel \text{Pd}[2\bar{2}0]$. This is equivalent to $\text{Al}_2\text{O}_3[1\bar{1}00] \parallel \text{CoO}[1\bar{1}0] \parallel \text{Fe}[001] \parallel \text{Pd}[1\bar{1}0]$ and corresponds to the Nishiyama-Wassermann epitaxial relation.

The stoichiometry of the sample was again measured by RBS as described above. The resulting spectrum is represented in Fig. 6 together with the numerical simulation. In the recorded spectrum the ions backscattered from the thin Fe and Co layers could not be resolved due to their similar masses. However, as their respective thicknesses are well established by XRR, the oxygen content could be determined, proving a stoichiometric CoO layer. Obviously the annealing process removes superstoichiometric oxygen, eliminates unstable low-temperature phases, finally resulting in the pure NaCl-like cubic CoO phase.

The annealing process however also modifies the surface morphology. Figure 7 displays an atomic force microscopy (AFM) topography of a $1 \times 1 \mu\text{m}^2$ area of the annealed CoO surface prior to Fe deposition. The initial featureless, flat preannealed surface now exhibits 100-nm-sized structural domains. The height difference between two neighboring grains can be as large as 10 nm, while the rms roughness of a typical individual grain is about 2 nm. Obviously, the phase transitions and the removal of surplus oxygen is accompanied by a recrystallization and reorganization of the surface, leading to the formation of large, rough grains.

IV. MAGNETIC PROPERTIES

The magnetic properties of the CoO/Fe are quite complex. The bias field H_{EB} depends on the respective thickness of the constituent layers, it increases with decreasing Fe thickness^{2,22} and displays a peaklike behavior at reduced CoO thickness⁴⁰ with a reduced CoO anisotropy.³⁰ Details of

FIG. 7. AFM topography of the annealed CoO surface prior to Fe deposition. The image depicts a $1 \times 1 \mu\text{m}^2$ area of the sample. Structural domains with typical lateral size of 100 nm can clearly be seen. The height difference between two neighboring grains can be as large as 10 nm, while the rms roughness of a typical individual grain is about 2 nm.

the remagnetization process are governed by the interface properties and the angle between the external field applied during the initialization of the EB effect and the anisotropy axes of the system.⁴¹ In the following we focus on the blocking temperature (T_B), which is independent of the details mentioned above. It characterizes the transition of the F in an exchange-biased system from the biased to the unbiased state (AF in the paramagnetic state). The blocking temperature is inherently independent of the field cooling (FC) direction.

At low temperatures (10 K) all samples show a pronounced exchange-bias effect. Figure 8 displays the biased

FIG. 8. Hysteresis loops of a 210 Å thick Fe layer deposited on an as-prepared 330 Å thick CoO film. Filled symbols correspond to magnetization reversal after field cooling down to 10 K, open symbols show measurements at room temperature above the blocking and Néel temperature of the AF.

FIG. 9. Hysteresis loops of 210 Å thick Fe layers deposited on 330 Å thick CoO for the post-annealed CoO film. Filled symbols correspond to magnetization reversal after field cooling down to 10 K, open symbols show measurements at room temperature above the blocking and Néel temperature of the AF.

hysteresis loop of the as-prepared sample after cooling the sample in an external field of +9 kOe, together with the corresponding unbiased loop, measured at 300 K. The unbiased loop is symmetric with respect to the origin and is characterized by a small coercive field and a remanent magnetization of about $0.5M_{\text{sat}}$. At 10 K we observe a biased, square-shaped hysteresis loop, exhibiting a coercive field of $H_{c1} = -330$ Oe and $H_{c2} = +130$ Oe, respectively. In Fig. 9 the room temperature hysteresis loop of the post-annealed sample together with the hysteresis loop recorded at 10 K after field cooling are shown. The shift of the loop along the field axis and the increased coercivity ($H_{c1} = -665$ Oe and $H_{c2} = +360$ Oe) is clearly visible and results in an increased exchange bias field from $H_{\text{EB}} = -100$ Oe (as-prepared) to $H_{\text{EB}} = -150$ Oe (annealed). Thus, the exchange bias of the annealed sample is by 50 Oe higher than the corresponding value of the as-prepared one.

However, the most striking difference between the as-prepared and post-annealed sample is the change of the shape of the hysteresis loop. While the as-prepared sample shows a square shape, the hysteresis of the annealed sample has a more than doubled coercive field H_{c1} combined with a 25% reduced remanence. This results in a more rounded overall shape of the hysteresis for the post-annealed sample in comparison to the as-prepared case. We attribute these different shapes of the hysteresis loops and the increased coercivity by the modified interface structure of the post-annealed sample. In particular the increased roughness (see Fig. 7) in the post-annealed sample serves as pinning centers for the Fe layer, clearly seen in a comparison of the RT hysteresis between both samples. Details of the magnetic properties and the role of the interfacial roughness will be shown in a forthcoming paper.⁴²

The temperature dependence of the H_{EB} is depicted in Fig. 10. To exclude the reduction of H_{EB} due to training effects, at each data point (i.e., for each temperature), the sample was first heated to $T = 310$ K, which is about 20 K above the Néel temperature of bulk CoO. Subsequently, the sample was field cooled in a field of +9 kOe.⁴³

FIG. 10. (Color online) Temperature dependencies of the normalized exchange bias field for both samples. Open symbols correspond to the as-prepared sample, filled symbols to the post-annealed sample. Note the different blocking temperatures for both samples and the independence of the blocking temperature with respect to the field cooling direction.

To focus the discussion on the reduction of H_{EB} with increasing temperature and thus on the transition of the Fe layer from a biased to an unbiased state, we normalize each data set on its maximum exchange bias shift measured at 10 K [$H_{EB}(10\text{ K})$]. This allows to plot the decay of the biasing fraction of AF spins, independent of their absolute number. For both samples the normalized shift of H_{EB} decreases monotonically from its maximum value at low temperatures until it reaches zero at the blocking temperature T_B . The sample containing the as-prepared CoO layer exhibits a T_B of 240 K. While the magnitude of H_{EB} depend on the relative orientation of the anisotropy axis of the AF with respect to the applied cooling field and the shape of the hysteresis loop on the interface morphology, the blocking temperature T_B only depends on the stoichiometry of the antiferromagnet. For the sample containing the post-annealed CoO film, finite values of H_{EB} can be observed up to $T = 290\text{ K}$, which is close to the Néel temperature of bulk CoO [$T_N(\text{CoO}) = 291\text{ K}$]. The homogeneity range of CoO is rather broad and all stoichiometries ranging from Co_1O_1 , Co_3O_4 , to Co_2O_3 can exist simultaneously below 900°C .¹² On the other hand, the T_N for Co_1O_1 is at 291 K and the T_N for Co_3O_4 is at 34 K. Since the upper limit of the T_B is fixed by T_N , a deviation in the stoichiometry of CoO from Co_1O_1 to Co_3O_4 reduces the Néel temperature, thereby also reducing blocking temperature of the exchange-bias system. Therefore, as the observed blocking temperature reaches $T_N(\text{CoO})$, we conclude also from the magnetic data that the annealing leads to stoichiometric CoO films due to a removal of surplus oxygen. Thus, the magnetic data confirm the RBS data and the annealing process leads to stoichiometric CoO.

To verify the independence of the blocking temperature from the FC direction, we depicted the temperature dependence measurements of the as-prepared sample in two perpendicular geometries as shown in Fig. 10 where we clearly see an insensitivity of T_B on the FC direction.

In Fig. 11 we show the azimuthal dependence of H_{EB} magnitude on the FC direction for the sample containing the annealed CoO film. The angle Φ characterizes the FC direc-

FIG. 11. (Color online) H_{EB} magnitude dependence on field cooling direction for the first and second hysteresis. Note, for every direction we heat up the sample to room temperature and field cool it in 9000 Oe down to 10 K and measure the first and second hysteresis consecutively. The insets depict hysteresis loops for two orthogonal directions one close to the easy axis at 30° and the other one close to the hard axis at 300° .

tion and the direction of the applied field during the measurement of the hysteresis loop at the same time. Black dots represent the first and (red) triangles the second hysteresis after field cooling, respectively. We recognize in the H_{EB} dependence of the first hysteresis a twofold, i.e., a uniaxial anisotropy. Note that the uniaxial anisotropy can only be observed by successive FC from RT for all azimuthal angles. Rotation of the sample after one initial FC in only one azimuthal direction shows the usual unidirectional anisotropy field. Based on the investigations by Roth⁴⁴ the easy axis of

FIG. 12. (Color online) Small angle x-ray reflectivity curves for two identically prepared, isostoichiometric CoO films, deposited by dc sputtering on a -plane Al_2O_3 substrates. The increased roughness after the annealing process leads to a stronger decay of the reflected intensity with increasing angle. The inset shows two $1 \times 1\ \mu\text{m}^2$ representative AFM topographies of the respective samples. Note the different height scales of the two images.

FIG. 13. Temperature dependencies of the normalized exchange bias field for both isostoichiometric CoO/Fe samples. Open symbols correspond to the as-prepared sample, filled symbols to the post-annealed sample.

CoO is directed in $(\bar{1}\bar{1}7)$ and has a projection on the CoO(111) plane in $[\bar{1}\bar{1}0]$ which is perpendicular to CoO $[\bar{2}20]$ found in Fig. 5. Following this line of arguments we identify in Fig. 11 the easy axis of CoO along 0° and 180° where H_{EB} field is biggest. The angular dependence of H_{EB} for the second loop is dramatically reduced. The reason for the disappearance of the anisotropy field in the consecutive hysteresis is the training effect which also reduces the magnitude of H_{EB} with the number of loops cycles after the initial field cooling. From the shape of the hysteresis loops (insets of Fig. 11) we distinguish coherent rotation processes during all reversals in all directions of the sample.

Since it is known that Co_3O_4 is the only stoichiometric stable phase above 1100°C ,¹² post-annealing of an isostoichiometric CoO layer will not change the stoichiometry of this layer but may only increase the roughness of the CoO surface, as shown in Fig. 12.

To separate the interface morphology from the stoichiometric variation, we prepared two identical isostoichiometric and thus stoichiometrically stable CoO films. First, a CoO film was deposited on a Al_2O_3 ($11\bar{2}0$) substrate by dc magnetron sputtering using a CoO target. Subsequently, the sample was divided into two pieces. One-half piece was annealed as the previous samples (30 min at 1100°C). Prior to the Fe deposition, the surface roughness of both half-pieces was measured via XRR and their surface morphology was investigated by AFM. The post-annealed half-piece shows an enhanced rms roughness ($15 \text{ \AA}$), as compared to the virgin sample, exhibiting a rms roughness of about $4 \text{ \AA}$. In the XRR curves this leads to a stronger decay of the reflected intensity with increasing angle. While the AFM only probes the sample locally, XRR averages over the whole footprint area of several mm^2 . The XRR curves and the corresponding AFM micrographs are displayed in Fig. 12. Note especially the different height scale of the AFM images.

Finally, both half-pieces were covered simultaneously with Fe ($200 \text{ \AA}$) in the MBE system and protected with Pd ($50 \text{ \AA}$) against corrosion in ambient atmosphere. As before, the dependence of the normalized H_{EB} as a function of

temperature was recorded by SQUID magnetometry and is shown in Fig. 13. Similarly to the set of samples shown in Fig. 10, we observe again a smooth decrease of the normalized shift H_{EB} with increasing temperature with the limiting value $H_{EB}=0$ at the same blocking temperature $T_B \approx T_N(\text{CoO})=291 \text{ K}$ for both samples. Thus we confirm that the blocking temperature of thick CoO layers (thicker more than $100 \text{ \AA}$) is independent of the interface roughness but more sensitive on the stoichiometry of the CoO_x layer. The similar insensitivity of the blocking temperature on the interface roughness has been reported by Moran *et al.* in Ref. 43.

V. SUMMARY AND CONCLUSIONS

We have demonstrated a procedure to prepare single crystalline, epitaxial exchange-bias CoO/Fe bilayers on Al_2O_3 ($11\bar{2}0$) substrates. Reactive sputtering of Co in Ar/O atmosphere allows to prepare thick and atomically flat $\text{Co}_{1+\delta}$ films. Annealing the as-prepared CoO films in UHV at 1100°C removes the excess oxygen and leads to single crystalline CoO films that serve as a template for the growth of epitaxial Fe layers. The epitaxial relation was identified as the Nishiyama-Wassermann relation in which the $[1\bar{1}0]_{\text{fcc}}$ direction is parallel to the $[001]_{\text{bcc}}$ direction. On the other hand, the annealing process roughens the sample surface and submicron sized crystalline domains form at the surface. For the annealing process of the CoO film the bulk Co/O phase diagram applies. The improved structural and chemical phase purity could be verified by XRD and RBS, respectively.

The improved chemical purity and crystalline quality as well as the modified interface morphology influence the magnetic properties in two different ways. First, the epitaxial, stoichiometric CoO/Fe bilayers exhibit a blocking temperature which is close to the Néel temperature of bulk CoO, while in the superstoichiometric $\text{CoO}_{1+\delta}$ samples the exchange-bias effect vanishes for temperatures above 240 K , demonstrating the strong influence of the stoichiometry on the antiferromagnetic to paramagnetic phase transition in the $\text{CoO}_{1+\delta}$ layer. The interface morphology, on the other hand, determines the coercive fields, the shape of the hysteresis loops as well as the magnitude of the exchange-bias field. In agreement with work of Moran *et al.*,⁴³ the geometric structure of the AF/F interface has a strong influence on the magnitude of H_{EB} , leaving the blocking temperature unchanged. In the roughness regime of several hundred $\text{\AA}$ rms at the AF/F interface, the authors show an increase of H_{EB} with increasing roughness. We observe a contrary tendency of H_{EB} with roughness. However, roughness values in the present samples are two orders of magnitude lower as compared to the work presented in Ref. 43. These divergent results illustrate that the influence of interfacial roughness on the exchange bias is not unambiguous, as has also been discussed by Nogués and Schuller.^{2,45}

In summary, we have shown that only stoichiometric CoO exhibits the highest blocking temperature close to the Néel temperature. All other stoichiometries exhibit a blocking temperature, which is lower than this.

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