Stabilization of metastable expanded face-centered-tetragonal manganese

Stabilization of Metastable Expanded Face-Centered-Tetragonal Manganese

J. T. Kohlhepp* and W. J. M. de Jonge

Eindhoven University of Technology, Department of Applied Physics and center for NanoMaterials (cNM), P.O. Box 513, 5600 MB Eindhoven, The Netherlands

(Received 16 December 2005; published 12 June 2006)

The structural and magnetic properties of Mn prepared on single crystalline face-centered-tetragonal (fct) Co(001) were investigated. Mn grows coherently up to at least 50 monolayers (ML) and adopts a metastable expanded fct(001) phase [$c/a = 1.055(5)$]. This new fct-Mn phase was recently predicted theoretically by Hafner and Spišák [Phys. Rev. B **72**, 144420 (2005)]. Studies of magnetic Mn/Co interface exchange interactions prove the room temperature antiferromagnetic state for thicknesses above 2.5 ML. The magnetic anisotropy of the thin Mn is high enough to induce a significant exchange anisotropy for Mn thicknesses as low as 6 ML. The potential of fct-Mn to become a novel model system for systematic studies on the exchange interactions at antiferromagnet/ferromagnet interfaces is discussed.

DOI: 10.1103/PhysRevLett.96.237201 PACS numbers: 75.70.Cn, 75.30.Gw, 81.15.Hi

Introduction.—The stabilization of nonequilibrium crystal structures at room temperature and under ambient pressure, by constraining a material to the lattice of a single-crystal substrate, is one of the outstanding achievements of modern solid state physics [1]. It was mainly driven by the fact that these structures provide the chance to observe properties which are unavailable in bulk materials, and was primarily made possible by the development and rapid improvement of sophisticated ultrahigh vacuum deposition and characterization techniques. An epitaxy-stabilized nonequilibrium structure can even be a so-called metastable (MS) structure, if the substrate lattice matches a structure possessing a local minimum of the free energy of the deposited material.

Recently it was recognized by Hafner and Spišák [2]—using *ab initio* spin-density functional techniques—that two energetically, almost degenerate face-centered-tetragonal (fct) ground states exist for the MS γ phase of Mn. Interestingly, these states differ only slightly in their axial ratios, being either *contracted* ($c/a = 0.945$) or *expanded* ($c/a = 1.048$). While both are predicted to be antiferromagnets (AFM) with collinear spin structures, the spin directions are expected to differ pronouncedly, being layered (001) out-of plane for the former, or $c(2 \times 2)$ (001) in-plane compensated for the latter MS structure. Thus, a small change of the axial ratio induces a dramatic change in the AFM spin structure. This predestines fct-Mn as a highly interesting material for fundamental studies on the exchange interactions at AFM/ferromagnet (FM) interfaces, which should distinctly depend on the exact interface spin arrangements.

In fact, the layered AFM phase was experimentally inferred from an extrapolation of high-temperature quenched manganese-rich FeMn bulk alloy crystals to a pure Mn content already three decades ago [3]. An axial ratio of $c/a = 0.946$ was found in these studies, which is in excellent agreement with the predicted value. However, so far the expanded MS structure and its magnetic properties could not be identified.

From the results presented in [2] a room temperature (RT) in-plane lattice constant of $a = 3.66$ Å is estimated for expanded fct-Mn [4], which is quite close to Cu ($a = 3.615$ Å). Unfortunately, the growth of Mn on Cu(001) is known to be complex, ill defined, and moreover, accompanied by serious interdiffusion problems [1]. In this Letter we propose a promising alternative for the stabilization of expanded fct-Mn, namely, contracted fct-Co(001) which is primarily based on the following arguments: (i) It is now well established that thin Co layers can be grown pseudomorphic on Cu(001) with a quality corresponding to a virtually perfect Co structure [5]. It was also shown that a strained fcc phase with an almost thickness independent strain up to at least 80 monolayer (ML) is adopted by Co [6]. Only very small partial strain relief sets in above 15–20 ML, which means, that the in-plane lattice constant of Cu is essentially preserved in the Co. (ii) Co has a much higher surface energy as Cu as well as Mn, making a complete wetting of the Co and a layer-by-layer growth mode more likely. (iii) And last, but not least, STM studies have shown that the surface of a 20 ML Co(001)-film is reasonable flat, exposing only four different atomic levels [7]. This provides us with a well-defined and Mn-overlayer thickness independent surface morphology, making—in contrast to a nonmagnetic substrate—systematic Mn-thickness dependent studies of magnetic interface interactions possible.

In this Letter we present structural and magnetic results giving evidence that (i) expanded fct-Mn(001) can be prepared on fct-Co(001) with a high structural quality, (ii) that it is indeed a MS phase, and (iii) that it is antiferromagnetically ordered at RT already for thicknesses as low as 2.5 ML.

Experimental.—Mn/fct-Co(001) bilayers were grown on Cu(001) single crystals in a VG-Semicon V80M multichamber-MBE working at a base pressure of 8×10^{-12} mbar. During evaporation of the layers the pressure never rose above 5×10^{-11} mbar. Such low pressures were a prerequisite for the creation of clean and high-

quality Mn-films and Mn/Co interfaces. The Cu(001) substrates were treated by several sputter and anneal procedures until a clean and atomically flat surface was achieved, which was routinely checked by scanning tunneling microscopy (STM), low energy electron diffraction (LEED), x-ray photoelectron (XPS), and Auger electron spectroscopy (AES).

The layers were deposited at substrate temperatures of 50 °C with typical growth rates of 1 ML/min and 2 ML/min for Co and Mn, respectively. Depending on the exact experiment, either homogeneous or wedge-shaped Mn overlayers were prepared. The thickness of the Co films was kept at 20 ML throughout the whole study, in order to ensure consistency and a decent magnetic response. The Mn evaporation rate was accurately calibrated using a combination of STM, AES, and LEED; for the latter the intensity of the $c(2 \times 2)$ spots formed at $\frac{1}{2}$-ML coverage of Cu(001) with Mn was monitored. Thus, one Mn-ML is defined as the amount of Mn atoms necessary to cover the surface of Cu(001) completely assuming pseudomorphic growth. The rates were checked throughout the deposition using quartz microbalances.

The magnetic properties of the bilayers were characterized by longitudinal magneto-optical Kerr effect (MOKE) measurements using a focused HeNe laser beam (70 μm diameter) and employing polarization modulation and lock-in techniques.

Structure.—LEED patterns of different Mn film thicknesses grown on 20 ML Co(001)/Cu(001) are depicted in Fig. 1. No change of the spot positions with respect to the Cu(001) substrate (not shown here) are observed for uncovered 20 ML Co(001) [Fig. 1(a)], confirming again the (at least very close to) pseudomorphic growth. In agreement with an earlier study [8], but in contrast with another paper [9], no indication of the formation of a $c(2 \times 2)$ ordered surface alloy was found in the thickness range between 0 and 1 ML [Fig. 1(b)], which might be explained by different vacuum and/or growth conditions used in the experiments. However, Mn-thickness dependent angular resolved AES and XPS studies [7] suggest that extensive alloy formation in the initial stage of Mn growth is unlikely. Further increasing the Mn-overlayer thickness keeps the fourfold symmetry and the positions of the LEED spots unaltered. Beyond 50 ML the LEED spots are quickly disappearing and a high background is observed, possibly indicating a structural change to α-Mn. Complementary STM and AES measurements show that the Mn grows up to about 10–15 ML in a close to a layer-by-layer fashion onto strained Co(001), consequently followed by an increasingly roughened and disordered surface topography, explaining the enhanced background and the broadened spots observed in Fig. 1(d) [7].

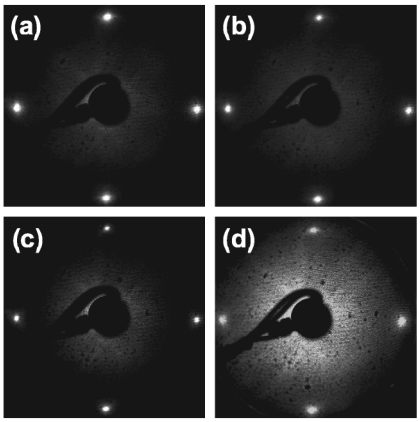

FIG. 1. LEED patterns of Mn grown on 20 ML Co/Cu(001); measured at RT with $E_{kin} = 67$ eV: (a) 0 ML Mn, (b) $\frac{1}{2}$ ML Mn, (c) 5 ML Mn, and (d) 20 ML Mn.

An elegant and direct way to identify *tetragonal* distortions by a direct measurement of the axial ratio c/a, is to use x-ray photoelectron diffraction (XPD) to monitor angular shifts of forward scattering enhancements (FSE) along low index crystallographic directions [10]. For our system we utilized FSE along the fcc[101] and fcc[112] directions [Figs. 2(a) and 2(c)] to determine c/a of the Mn films. In order to avoid any experimental artifacts, we employed for these experiments large Cu(001) crystals (20 mm diameter). One third of the Cu surface area was left uncovered [fcc-Cu(001) reference], one-third was covered with 20 ML Co [fct-Co(001) check], and the last third was finally used for the Mn(001)/Co(001)/Cu(001) samples, which ensured that the angle-dependent measurements could be performed under identical experimental

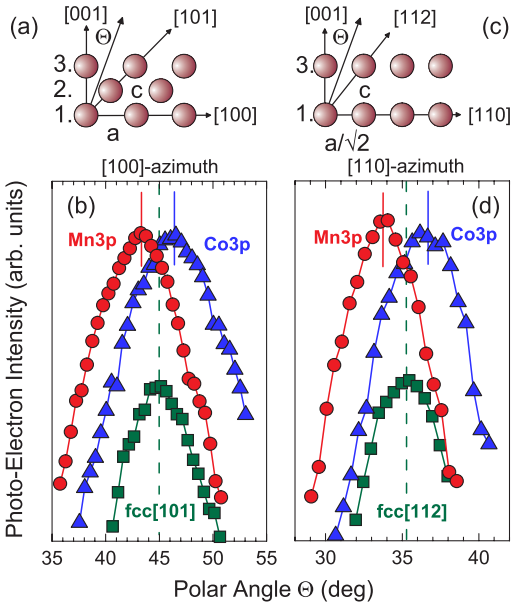

FIG. 2 (color online). Angle resolved Cu3p (squares), Co3p (triangles), and Mn3p (circles) XPS intensities measured around the (b) [101]- and (d) [112]-forward scattering directions of uncovered Cu(001), 20 ML Co/Cu(001), and 8 ML Mn/20 ML Co/Cu(001). In (a) and (c) the experimental geometries defining the polar angles Θ are depicted for polar rocking scans along the [100] and [110] azimuths, respectively.

conditions. In this way, the Cu(001) regions could also serve as a reference for the exact determination of the FSE angles, knowing that for undistorted fcc-Cu, these have to appear at 45° and 35.26° for the [101] and [112] directions, respectively.

For 20 ML Co(001) shifts to higher polar angles with respect to the Cu peaks are observed in both forward scattering directions [Figs. 2(b) and 2(d)], indicating a contracted fct phase. The axial ratio can easily be calculated from these shifts, resulting in a $c/a = 0.956(4)$ from an average over the FSE shifts of several independently prepared samples. This is in excellent agreement with the results of kinematical LEED, NMR, and x-ray diffraction studies of identical Co films [6].

On the other hand, for 8 ML Mn/Co(001) shifts to lower polar angles are observed, indicating now, that the Mn adopts indeed an expanded fct phase on Co(001)/Cu(001). The axial ratio [$c/a = 1.055(5)$] is found to be Mn-thickness independent, at least in the range studied with XPD (3–25 ML), suggesting a metastable low-strain phase of Mn. As mentioned in the introduction, such a locally stable expanded state is predicted by a recent theoretical calculation [2]. The slightly higher axial ratio found in our study, compared to the calculated $c/a = 1.048$, can tentatively be explained by the additional small tetragonal distortion originating from the elastic reaction of Mn on the forced pseudomorphic growth on the Co template, because of the somewhat larger equilibrium in-plane lattice constant of expanded fct-Mn with respect to fct-Co/Cu(001).

Magnetic properties.—A direct proof of the predicted AFM state in expanded fct-Mn films is far from trivial. Methods routinely used for the identification of bulk AFMs, like for instance neutron diffraction, are not sensitive enough to achieve conclusive results. However, by exploiting characteristic features of exchange interactions at AFM/FM interfaces, like, e.g., enhanced switching fields (coercivity H_C) and/or unidirectional shift fields (exchange bias H_E) observed for AFMs grown onto FMs in the presence of a magnetic field [11], valuable information about the magnetic state of fct-Mn is obtained.

Indeed, expanded fct-Mn is antiferromagnetic even at RT as demonstrated by several experimental results: 20 ML Co(001) covered with 5 ML fct-Mn(001) exhibits a fivefold enlarged H_C [Fig. 3(a)]. For larger Mn thicknesses not only H_C is enhanced, but simultaneously small loop shifts antiparallel to the growth-field and unshifted hard-axis magnetization loops perpendicular to the growth-field directions [Fig. 3(b)] are detected. All these characteristics are expected from elementary exchange bias theories for the interaction of an FM (Co) with an AFM (Mn) [11].

As a matter of fact, for fct-Co(001) external growth fields are not necessary to achieve a finite H_E. Fct-Co(001) is an FM with a biaxial magnetic anisotropy having magnetic easy axes along the four in-plane ⟨110⟩ directions. A zero-field grown, or alternatively a demagnetized Co(001)-film, forms magnetic domains where the

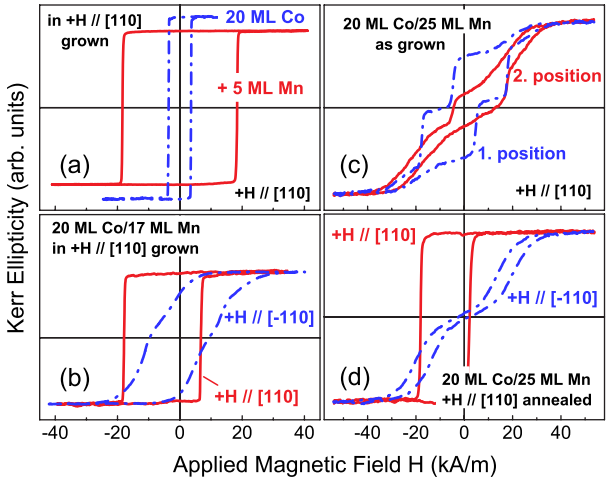

FIG. 3 (color online). Room temperature longitudinal MOKE hysteresis loops of 20 ML Co/Cu(001) covered with different Mn thicknesses. In (a) and (b) the bilayers were grown in a magnetic field aligned parallel to the [110] easy-axis direction of the Co film, in (c) the bilayer was grown without a field and locally measured at different positions on the sample, and in (d) the same bilayer was heated to 170 °C and field cooled.

magnetization of each domain is aligned along one of the easy directions. The remnant field of a domain locally defines the symmetry direction of the exchange anisotropy (H_E antiparallel to remnant field), hence, depending on the particular domain state, four different unidirectional H_E directions should be observable. This behavior is demonstrated by the MOKE loops depicted in Fig. 3(c). At laser position 1 a symmetric double hysteresis curve with a distinct hard-axis component is observed, which can be interpreted by a superposition of the four different and equally distributed bias directions sampled by the laser spot. Also unequal bias distributions can be observed at a second position, demonstrating the influence of the exact domain state of the as grown Co film on the spin ordering at the Mn/Co interface. However, heating this bilayer to 170 °C followed by a field-cool process to RT recovers a homogenous unidirectional exchange anisotropy direction, indicating a blocking temperature somewhere between RT and 170 °C for this Mn thickness [see Fig. 3(d)].

In order to study the apparent thickness dependence of the exchange interaction, and especially to determine the onset of the AFM state in expanded fct-Mn in more detail, we have grown several wedge-shaped Mn layers on top of 20 ML Co(001). In Fig. 4 the results for two of these measurements are plotted. A significantly decreased H_C—already for small amounts of Mn at the interface—is observed, however, this decrease is completed at 1 ML Mn, suggesting an interface effect. A changed magnetic interface anisotropy due to the proximal Mn is a likely explanation for this. For both wedges, H_C starts to rise at around 2.5 ML, indicating the onset of AFM order in Mn at RT. Consequently, H_C displays a sharp maximum at around

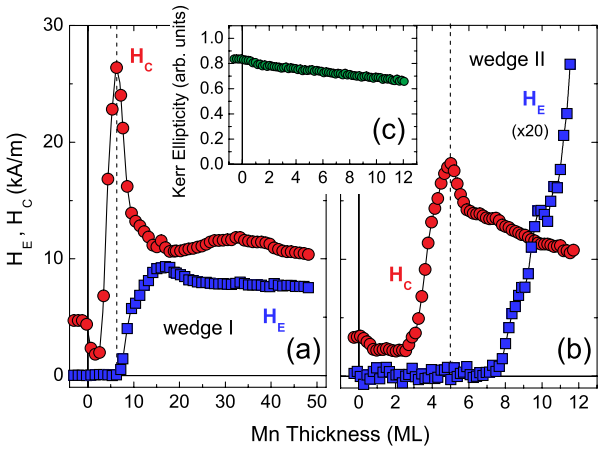

FIG. 4 (color online). Room temperature values of H_C and H_E versus the fct-Mn(001) thickness as measured by local MOKE measurements on two Mn(001)-wedge/20 ML Co(001) bilayer samples. For wedge II a more shallow wedge was grown on another Cu(001) crystal (note here the 20-fold zoom of the H_E data). Inset (c) shows the Mn-thickness dependence of the saturation Kerr ellipticity for wedge II.

5–6 ML and converges to a value of 10 kA/m, which is about 3 times the value observed without Mn.

H_C maxima are often associated with the onset of exchange anisotropy [11], which apparently seems to be the case for wedge I as well, because distinct loop shifts are observed beyond 6 ML Mn, matching well with the H_C-peak value [Fig. 4(a)]. However, this seems to be fortuitous, because in general such a coincidence could not be confirmed by us, as can, e.g., be seen in high resolution measurements using a different wedge [Fig. 4(b)]. While a H_C peak was observed around 4–7 ML in all of our wedge studies, no systematic correlation between the exact positions of these peaks and the onset of H_E could be found; also the H_C enhancement (defined as the value in the peak with respect to the value observed for >20 Mn-ML) showed a large variation (from 20% up to 300%). Currently, the real origin of the enhancements is actually still not known.

Basically, a finite exchange bias is expected to be observable only if uncompensated AFM spins are available at the interface, and when the magnetic anisotropy of the AFM is strong enough to avoid irreversible rotations of these AFM interface spins. For an expanded fct-Mn(001) surface a compensated collinear in-plane spin structure is expected [2]. Indeed, the Mn-overlayer thickness dependence of the saturation Kerr ellipticity is not oscillating [see Fig. 4(c)], which rather suggests a compensated than a layered AFM structure. However, an interface is rarely completely ideal, rather a distinct amount of defects, steps, and other inhomogeneities are found, giving rise to an altered interface spin structure with a small amount of uncompensated spins. Nevertheless, from H_E found at Mn thicknesses above 20 ML an exchange anisotropy energy of $J = 50\ \mu J/m^2$ is estimated. However, this value depends on the sample used, resulting in slightly different values as could be expected by a defect dictated effect.

While we could successfully prove the AFM state of expanded fct-Mn(001), we have at the moment no unambiguous proof for the proposed in-plane compensated spin structure at the interface. More dedicated future experiments are needed for this.

Conclusions.—We have demonstrated that high-quality antiferromagnetic expanded fct-Mn(001) films can be grown on strained fct-Co(001). The fct-Mn(001)/fct-Co(001) system has a the potential to become a powerful model system for systematic and well-defined studies of exchange interactions at AFM/FM interfaces. In comparison to other exchange anisotropy systems [11], it has several advantages; e.g., (i) both FM and AFM are made of single elements and are metals, (ii) it is single crystalline, coherently grown, adopts a relative simple crystal structure, and possesses a well-defined interface, (iii) and the interface spin structure of expanded fct-Mn(001) is predicted to be collinear and confined to the (001) plane.

Earlier, bct-Mn(001)/Fe(001) was proposed as a similar AFM/FM model system [12]. However, very recent experimental and theoretical investigations have shown that this system is far more complex than initially suggested [2,13]. Furthermore, no exchange bias was reported. Future theoretical investigations have to show if Mn/Co(001) has indeed the potential to become a real model system with simple and interesting properties.

*Corresponding author.
Electronic address: j.t.kohlhepp@tue.nl

[1] M. Wuttig and X. Liu, *Ultrathin Metal Films* (Springer Verlag, Berlin, Heidelberg, 2004).
[2] J. Hafner and D. Spisák, Phys. Rev. B **72**, 144420 (2005).
[3] Y. Endoh and Y. Ishikawa, J. Phys. Soc. Jpn. **30**, 1614 (1971).
[4] By division of $a_{exp} = 3.796$ Å by $a_{calc} = 3.632$ Å of contracted fct-Mn, an empirical correction constant $A = 1.045$ is found; assuming that the c/a axial ratios are correctly calculated, but the lattice constants systematically underestimated by this factor A, $a = 3.66$ Å ($a_{calc} = 3.506$ Å) is estimated for expanded fct-Mn.
[5] H. Wieldraaijer, W. J. M. de Jonge, and J. T. Kohlhepp, Phys. Rev. Lett. **93**, 177205 (2004).
[6] H. Wieldraaijer, W. J. M. de Jonge, and J. T. Kohlhepp, Phys. Rev. B **72**, 155409 (2005).
[7] J. T. Kohlhepp and W. J. M. de Jonge (unpublished).
[8] W. L. O'Brien and B. P. Tonner, Phys. Rev. B **50**, 2963 (1994).
[9] B.-C. Choi, P. J. Bode, and J. A. C. Bland, Phys. Rev. B **58**, 5166 (1998).
[10] S. A. Chambers, Adv. Phys. **40**, 357 (1991).
[11] J. Nogués and I. K. Schuller, J. Magn. Magn. Mater. **192**, 203 (1999).
[12] U. Schlickum *et al.*, Phys. Rev. Lett. **92**, 107203 (2004).
[13] C. Grazioli *et al.*, Phys. Rev. Lett. **95**, 117201 (2005).