

Thermal stability and structure of ultrathin Co/Fe₂O₃ films on the Cu(110) surface

Christian Pflichtsch, Laurens K. Verheij,^{a)} Rudolf David, and René Franchy
Institut für Schichten und Grenzflächen (ISG 3), Forschungszentrum Jülich, D-52425 Jülich, Germany

(Received 24 April 2001; accepted for publication 24 October 2001)

The thermal stability of very thin Co(0.9 nm \approx 7 ML)/Fe₂O₃(1 nm) double layers, deposited on Cu(110), was studied by Auger electron spectroscopy, thermal energy helium atom scattering, and low energy electron diffraction. Ordering of the double layer requires annealing to 400–450 K. After annealing, the film consists mainly of Co(110). Part of the Co(110) surface shows a (3 \times 1) reconstruction which could be related to the presence of oxygen floating on the Co film. In addition, evidence was found for the presence of *c*(2 \times 2) reconstructed domains of fcc Co(100). The Co/Fe₂O₃ double layer is essentially stable up to 400 K. Above this temperature, the Co and Fe₂O₃ start to mix, resulting in segregation of Fe₂O₃ to the surface at around 700 K. Similar as in the case of the single layer system Fe₂O₃/Cu(110), copper is found to diffuse towards the surface at temperatures > 600 K, but the surface itself remains covered by iron oxide up to 1100 K. Already below 1000 K, Co is completely dissolved in the bulk of the copper crystal. © 2002 American Institute of Physics. [DOI: 10.1063/1.1428093]

I. INTRODUCTION

Double layers consisting of an antiferromagnetic Fe₂O₃ film and a ferromagnetic Co or CoFe alloy film are promising materials for new spin valve concepts.^{1–4} For the magnetic performance of the double layer, important properties are the order in the two layers, the matching between the crystal structures of the layers, and the thermal stability with respect to mixing of the two films. In the present work we report a study on growth, ordering, and stability of Co/Fe₂O₃ double layers deposited on Cu(110), studied with Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and thermal energy helium atom scattering (TEAS). Previously, we have considered Fe/Fe₂O₃ double layers deposited on Cu(110).⁵ We were able to prepare such double layers with an ordered epitaxial bcc α -Fe film on top of the, about 1 nm thick, Fe₂O₃ layer. Yet we had to conclude that Fe/Fe₂O₃ double layers are not very stable. At low temperatures ($T < 200$ K), evidence was found for a reaction between the oxide and the Fe film, occurring at the interface between the two layers. More complete mixing of the two films, also involving atoms further away from the interface, seems to start at 400 K. About the same temperature appeared to be necessary for ordering of the Fe film.

One may expect that Co/Fe₂O₃ double layers are more stable than Fe/Fe₂O₃ double layers with respect to reduction of the oxide because the heat of formation of cobalt oxides ($\Delta H_f = 237.9$ kJ/mol for CoO and 891 kJ/mol for Co₃O₄)⁶ is lower than the heat of formation of iron oxides ($\Delta H_f = 272$ kJ/mol for FeO, 824.2 kJ/mol for Fe₂O₃, and 1118.4 kJ/mol for Fe₃O₄).⁶ In contrast to the reaction of Fe and Fe₂O₃ into Fe₃O₄, which is clearly exothermic ($\Delta H = 58.4$ kJ/mol), the energy, which is released when Co reacts

with Fe₂O₃ into CoO and Fe₃O₄ ($\Delta H = 2.1$ kJ/mol), is very little. Therefore this energy seems to be insufficient to compensate for the strain resulting from the mismatch between the reaction products CoO and Fe₃O₄ and the Co and Fe₂O₃ layers. With respect to diffusion, cobalt and iron seem to behave similarly. Cobalt and iron, deposited on clean Cu(110), start diffusing into the bulk of the copper substrate around 450 K.^{7,8} With a Fe₂O₃ layer between the metallic film and the copper substrate, diffusion of Cu to the surface will be delayed because the Fe₂O₃/Cu(110) interface is stable up to about 600 K.⁹ Below this temperature mixing of the oxide and the metallic film is found for Fe/Fe₂O₃ double layers.⁵ However, one may expect that Co/Fe₂O₃ double layers behave differently because of the different reactivity of Co and Fe with respect to oxygen.

II. EXPERIMENT

The present investigation on the growth and stability of Co/Fe₂O₃ double layers deposited on Cu(110) was performed in an UHV-helium scattering apparatus with a base pressure of 5×10^{-11} mbar. The system is equipped with a supersonic helium nozzle beam with a quadrupole mass spectrometer as the detector, a four-grid LEED optics, and an AES spectrometer. The He scattering measurements (TEAS), which are reported here, were performed at a He beam energy of 24.4 meV and at a total scattering angle of $\theta_i = \theta_f + \theta_j = 90^\circ$, where θ_i is the angle of incidence and θ_f the exit angle, both measured with respect to the surface normal. In the diffraction spectra the scattered He intensity is shown as a function of the in-plane component of the wave vector transfer $q_{||} = |\mathbf{k}|(\sin \theta_i - \sin \theta_f)$, where $|\mathbf{k}|$ is the absolute value of the wave vector of the incoming atoms. More details about the experiment and about the apparatus can be found elsewhere.^{5,7–12}

Co was evaporated onto the Fe₂O₃/Cu(110) substrate by electron impact heating of a cobalt rod. During evaporation,

^{a)} Author to whom correspondence should be addressed; electronic mail: l.verheij@fz-juelich.de

the pressure in the main chamber did not rise appreciably (less than 2×10^{-10} mbar). The calibration of the Co evaporator was performed by monitoring the deposition of Co on $\text{O}(2 \times 1)\text{Cu}(110)$, a system for which Co grows in the layer by layer mode.^{8,13,14} The epitaxial Fe_2O_3 film is prepared by depositing a 0.6 nm thick iron film on the $\text{Cu}(110)$ surface at 130 K, annealing the film to 240 K in order to create a smooth and well-ordered fcc $\gamma\text{-Fe}$ film and freeze the film to below 150 K.¹⁰ By oxidizing the Fe film at 130 K and annealing the sample to 700 K, an ordered (0001) Fe_2O_3 film is formed. With TEAS a (21×6) superstructure is observed showing that the surface of the Fe_2O_3 film is distorted. The distortion is considered to be a corrugation perpendicular to the surface due to the misfit between the hexagonal Fe_2O_3 lattice and the Cu lattice, i.e., the surface still has symmetry properties characteristic for the $\text{Cu}(110)$ surface. In addition a small inplane distortion seems present.⁹ The $\text{Fe}_2\text{O}_3/\text{Cu}(110)$ surface is stable up to 700 K. Above this temperature the oxide changes into FeO .⁹

III. RESULTS

A. Thermal stability

A cobalt film with a thickness of about 0.9 nm, corresponding to ~ 7 ML fcc $\text{Co}(110)$, was deposited on the $\text{Fe}_2\text{O}_3/\text{Cu}(110)$ surface at 130 K. The deposition was monitored by specular He scattering. The specular intensity was found to decrease exponentially. A decay rate constant (or "initial decay rate") of $0.68 \text{ nm}^2/\text{Co atom}$ was observed, which can be interpreted as the cross section for diffuse scattering of helium atoms from Co adsorbed on $\text{Fe}_2\text{O}_3/\text{Cu}(110)$.^{15,16} This value is about 10% smaller than the cross section for Fe adsorbed on this surface.⁵ After deposition of 0.9 nm of Co, the surface is completely disordered as far as can be seen by TEAS and LEED.

The thermal stability of the Co film was investigated by slowly heating the sample while monitoring the chemical composition of the film by AES and the order of the film by TEAS. It was not possible to use the low energy Auger transitions of iron between 46 and 52 eV to characterize the chemical state of the iron atoms,^{5,17-19} because of the proximity of the AES transition of cobalt at 53 eV. Therefore, the high energy AES transitions at 775 eV (cobalt), 513 eV (oxygen), 703 eV (iron), and 920 eV (copper) were measured as a function of the sample temperature. Since the 775 eV transition of cobalt almost coincides with one of the minor AES transitions of Cu (at 776 eV), a correction had to be applied to obtain the intensity of the cobalt AES transition. A constant fraction, one-tenth, of the 920 eV copper AES transition was subtracted from the Co signal.

Figure 1 shows the normalized peak-to-peak amplitudes of the copper and cobalt AES transitions as a function of the sample temperature. The heating rate in the AES measurements is 4 K/min. Concentrating first on the interface between the copper substrate and the $\text{Co}/\text{Fe}_2\text{O}_3$ double layer, one can see that intermixing at this interface is essentially absent below ~ 600 K. Above this temperature, the copper AES signal increases, indicating that Cu starts to diffuse towards the surface. The stability of the interface between the

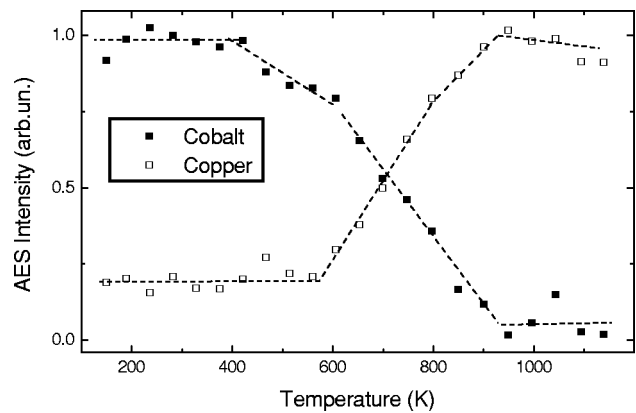


FIG. 1. Annealing (4 K/min) of a 0.9 nm Co film [~ 7 ML $\beta\text{-Co}(110)$] deposited on $\text{Fe}_2\text{O}_3/\text{Cu}(110)$ at 130 K monitored with AES (peak-to-peak amplitudes). Closed squares: cobalt [I(768 eV)-I(775 eV)], open squares: copper [I(914 eV)-I(920 eV)]. The dashed lines are drawn to guide the eye.

substrate and the $\text{Co}/\text{Fe}_2\text{O}_3$ double layer can be attributed to the oxide. For $\text{Fe}/\text{Fe}_2\text{O}_3$ and Fe_2O_3 films deposited on $\text{Cu}(110)$ we also found that the Cu AES signal started to increase around 600 K,^{5,9} whereas for a Co film deposited on clean $\text{Cu}(110)$, intermixing is observed already at 450 K.⁸

The interface within the double layer, between Co and Fe_2O_3 , is found to become unstable at a lower temperature than the substrate/double layer interface. The cobalt AES signal starts to decrease at about 400 K, indicating that the cobalt and the oxide layer are already mixing between 400 and 600 K. The intermixing of the double layer in this temperature range is confirmed by the increase observed for the oxygen and iron AES signals shown in Fig. 2. Essentially no intermixing of the Co and Fe_2O_3 layers is found below ~ 400 K. This is different from the behavior found for $\text{Fe}/\text{Fe}_2\text{O}_3$ double layers on $\text{Cu}(110)$. The oxygen AES signal measured for $\text{Fe}/\text{Fe}_2\text{O}_3/\text{Cu}(110)$ (dotted curve in Fig. 2), reproduced from Ref. 5, indicates that the Fe and Fe_2O_3

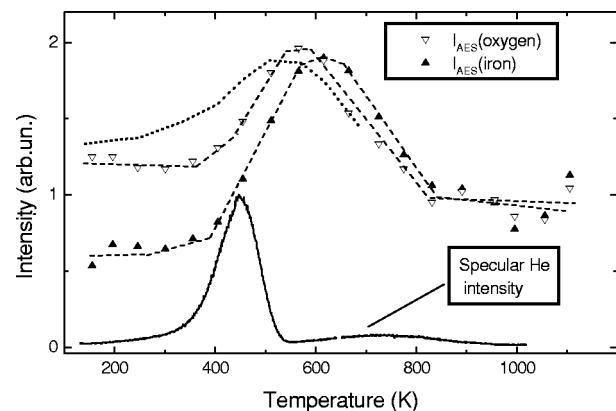


FIG. 2. Annealing of a 0.9 nm Co film [~ 7 ML $\beta\text{-Co}(110)$] deposited on $\text{Fe}_2\text{O}_3/\text{Cu}(110)$ at 130 K monitored with AES (peak-to-peak amplitudes) and specular helium scattering ($q_{\parallel}=0$). In the AES measurements the heating rate is 4 K/min. Open triangles: oxygen [I(508 eV)-I(513 eV)], closed triangles: iron [I(696 eV)-I(703 eV)]. In the specular He scattering measurement the heating rate is 20 K/min (solid line). For comparison we have also drawn the oxygen AES signal measured when heating a $\text{Fe}/\text{Fe}_2\text{O}_3$ double layer deposited on $\text{Cu}(110)$ (Ref. 5) (dotted curve). The dashed lines are drawn to guide the eye.

layers start mixing already below 200 K. The observation in Fig. 2 of a maximum of the oxygen and iron AES signals around 600 K confirms that the surface changes completely above this temperature. Between 600 and 900 K the cobalt disappears (Fig. 1), it probably diffuses into the bulk of the Cu crystal. Also some of the oxygen and the iron disappears into the bulk or desorbs, but similar to a Fe/Fe₂O₃ double layer on Cu(110), a non-negligible amount of both species remains present up to 1100 K. Though we cannot exclude that a small amount of copper diffuses onto the Co layer, this seems unlikely because Cu diffusion through the Fe₂O₃ film is not observed for the Fe₂O₃/Cu(110) and Fe/Fe₂O₃/Cu(110) systems.

B. Surface structure

As discussed above, we are interested not only in the thermal stability of the Co/Fe₂O₃ double layer on Cu(110) with respect to mixing, but also in the ordering of the two layers. The ordering in the double layer during annealing was monitored by specular helium scattering. To allow a direct comparison between the mixing and the ordering behavior, we have plotted in addition the specular He intensity ($q_{\parallel} = 0$) in Fig. 2. One should note that the heating rate in this measurement was five times faster than in the Auger study (because of experimental reasons). Already at 160 K the specular intensity increases with temperature. However, the major increase takes place between 300 and 450 K, i.e., order in the double layer is essentially created in this temperature range. It can be seen in Fig. 2 that there is some overlap between the temperature ranges in which ordering of the double layer (~ 300 –450 K) and intermixing (~ 400 –600 K) takes place, but the overlap is even smaller than suggested by this figure because of the higher heating rate in the He scattering measurement. The overlap is certainly much smaller than in the case of a Fe/Fe₂O₃ double layer on Cu(110). The stability of a Fe/Fe₂O₃ double layer with respect to intermixing is worse than that of a Co/Fe₂O₃ double layer (see above), but ordering of the Fe/Fe₂O₃ double layer was found to occur at a 100 K higher temperature.⁵ In spite of the large overlap between the temperature ranges for ordering and mixing in the case of Fe/Fe₂O₃ thin films, an ordered bcc α -Fe(100) surface on top of the Fe/Fe₂O₃/Cu(110) sample could be formed.⁵ Consequently, preparing a stable Co/Fe₂O₃ double layer on Cu(110) with an ordered Co surface on top is quite simple. At around 730 K, a second, shallow maximum of the specular intensity is found, indicating the formation of a different structure than that found at 450 K.

After annealing the Co/Fe₂O₃/Cu(110) sample to 440 K and subsequent cooling to 130 K, we found LEED images showing a (1×1) pattern relative to the Cu(110) substrate, with additional weak spots which cannot be interpreted in terms of a structure bearing a simple relation to the (110) surface (see Fig. 3). The simplest interpretation of the weak spots would be to assume a $c(2 \times 2)$ superstructure of a fcc (100) surface. The annealed Co/Fe₂O₃/Cu(110) surface was also investigated by TEAS. Figure 4 shows diffraction spectra measured along the $[1\bar{1}0]$ and the $[001]$ direction of the

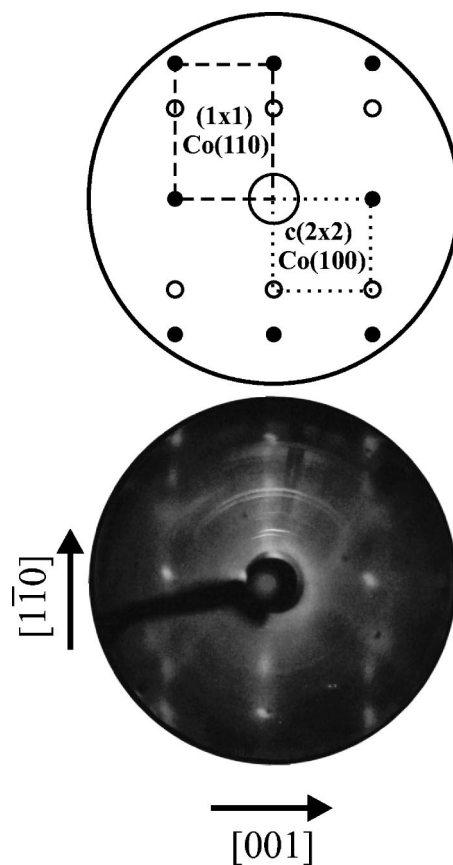


FIG. 3. LEED pattern of a 0.9 nm Co film deposited on Cu(110) at 130 K and subsequently annealed to 440 K (20 K/min). The LEED pattern is measured at 130 K. The primary energy of the electrons is 67 eV. The schematic image shows the observed spots and the reciprocal unit cells of a (1×1) Co(110) and a $c(2 \times 2)$ reconstructed Co(100) surface. [Note that the $[110]$ axis of the (100) lattice is rotated over 45° with respect to the $[110]$ axis of the (110) lattice.]

Cu(110) substrate. In addition to the integer order diffraction peaks, broad $\pm 1/3$ order diffraction peaks are found in the $[1\bar{1}0]$ direction. At the position expected for the $\pm 2/3$ order diffraction peaks in the $[1\bar{1}0]$ direction, we observe scattered intensity above the background level, i.e., there could be He intensity diffracted into the $\pm 2/3$ order, but the peaks

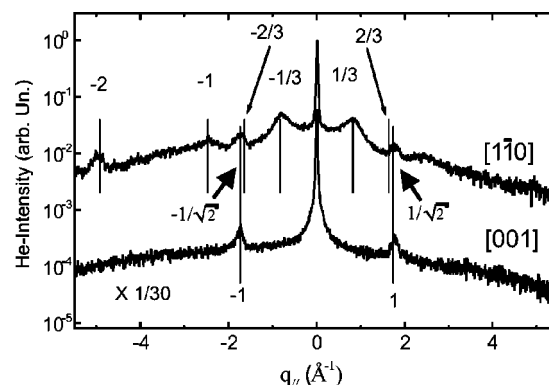


FIG. 4. TEAS spectra measured in the Cu- $[001]$ and $[1\bar{1}0]$ direction on Co(0.9 nm)/Fe₂O₃(1 nm)/Cu(110) annealed to 440 K. The He beam energy was 24.4 meV. The measurements were performed at 130 K. The lower curve ($[100]$ -direction) is multiplied by a factor of 1/30.

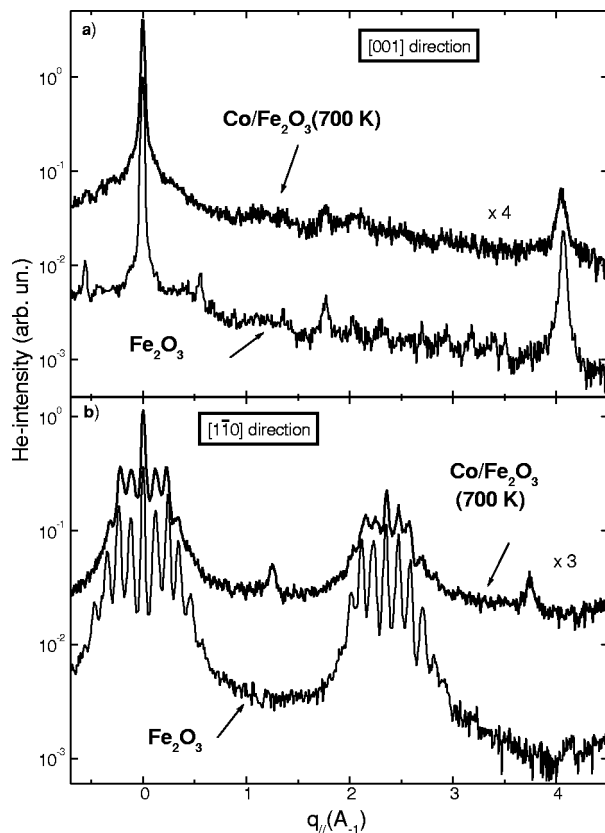


FIG. 5. TEAS spectra measured on Co(0.9 nm)/Fe₂O₃(1 nm)/Cu(110) annealed to 730 K (upper curve), and on Fe₂O₃/Cu(110) (lower curve). The measurements were performed at 130 K. (a) Spectra in the Cu-[001] direction, the upper curve (Co/Fe₂O₃) is multiplied by a factor of 4. (b) Spectra in the Cu-[110] direction, the upper curve (Co/Fe₂O₃) is multiplied by a factor of 3.

which are observed are clearly shifted with respect to this position. They agree better with the value of q_{\parallel} , characteristic for the first order diffraction peak in the [001] direction. This indicates that the cobalt film consists of a mixture of two domains, both crystallized in a fcc lattice, but one with a (110) orientation and a surface showing a (3×1) superstructure, and the other with a (100) orientation and a surface with a $c(2 \times 2)$ superstructure.

After annealing the Co/Fe₂O₃ double layer to 730 K, the structure of the surface changes drastically. Helium diffraction spectra measured on Co/Fe₂O₃/Cu(110), after annealing to 730 K, are very similar to spectra measured on Fe₂O₃/Cu(110). In the [001] direction [Fig. 5(a)] all the diffracted beams found on the Co/Fe₂O₃ double layer are also seen on the Fe₂O₃ film, though one peak, at $\pm 0.55 \text{ \AA}^{-1}$, is missing on Co/Fe₂O₃. In the [110] direction [Fig. 5(b)] the diffraction patterns are also very similar. Around $q_{\parallel} = 0 \text{ \AA}^{-1}$ and around $q_{\parallel} = \pm 2.4 \text{ \AA}^{-1}$ bunches of diffraction peaks are found for both surfaces. In addition, on the Co/Fe₂O₃ double layer, diffraction peaks are observed at ± 1.24 and $\pm 3.73 \text{ \AA}^{-1}$. These peaks can be interpreted as the 1/2 and 3/2 order diffraction peaks corresponding to a (2×1) superstructure of a fcc (110) Co surface. Note that the integer order peaks are also present (in both directions), but they are also part of the diffraction pattern of the Fe₂O₃

film. Accordingly, we conclude that, after annealing to 730 K, the Co/Fe₂O₃/Cu(110) surface essentially consists of Fe₂O₃, though some fcc (110) domains of cobalt seem to remain present up to this temperature. With LEED we found for this surface essentially the same diffraction pattern as on the Fe₂O₃ film,⁹ though the observed diffraction features are somewhat more diffuse. Upon annealing the Co/Fe₂O₃ double layer to 1000–1050 K, the surface structure changes further in the same way as it was observed before for a thin iron oxide film deposited on the Cu(110) surface. Both with LEED and with TEAS diffraction patterns were observed on Co/Fe₂O₃/Cu(110) after annealing to more than 1000 K, which are practically identical to those reported before for iron oxide deposited on Cu(110) and annealed to more than 1000 K, and which were interpreted as being due to diffraction from FeO/Cu(110).⁹ Since the half-order diffraction spots [Fig. 5(b)] are not seen after annealing to 1000 K, it is not plausible to interpret the (2×1) superstructure in terms of an oxidized Cu layer on top of the Co film.

IV. CONCLUSION AND DISCUSSION

In conclusion, we have shown that an epitaxial cobalt film can be grown on Fe₂O₃/Cu(110). This film was prepared by depositing cobalt at 130 K and annealing the sample to 440 K. Part of the film is pseudomorphic with the Cu(110) substrate, showing a (3×1) superstructure. In addition, there seem to be some fcc Co(100) domains in which the [100] direction is aligned parallel to the [001] direction of the Cu(110) substrate. Apparently the corrugation of the Fe₂O₃ film⁹ is such that the direction and atomic distance of the [001] substrate rows are still clearly felt by Cu atoms deposited on the oxide surface. The fact that evidence for (100) domains is found in addition to (110) domains reconstructed in the $[1\bar{1}0]$ direction would then indicate that the directional information of the $[1\bar{1}0]$ axis is preserved on the oxide surface, but that the formation of regular $[1\bar{1}0]$ rows is not favored. A (3×1) reconstruction of a fcc Co(110) surface has been observed before, but only in the presence of oxygen floating on top of the Co/Cu(110) surface.^{8,13,14} Without oxygen, a (1×1) structure of Co(110) was found on Co/Cu(110), but with first order diffraction peaks in the $[1\bar{1}0]$ direction having very low intensities. A reasonable agreement is obtained between the intensities of the diffraction peaks in our study and the intensities observed for the reconstructed (3×1) and unreconstructed (1×1) Co/Cu(110) surfaces reported in Ref. 13 by assuming that our Co/Fe₂O₃/Cu(110) surface consists of (1×1) Co(110) whereof 10%–30% is covered by patches of oxygen which induce locally a (3×1) reconstruction. A $c(2 \times 2)$ reconstructed Co(100) film, i.e., the same as we find, is also found when cobalt is deposited on carbon contaminated W(110) (two-dimensional tungsten carbide)^{20,21} or on carbon contaminated Cu(100).²²

The Co/Fe₂O₃ double layer is stable with respect to intermixing. No evidence is found for mixing at or close to the interface of the double layer below $\sim 400 \text{ K}$, as is observed in the case of Fe/Fe₂O₃ double layers.⁵ With respect to the thermal stability of the Co/Fe₂O₃/Cu(110) system, it was

found that the $\text{Co/Fe}_2\text{O}_3$ double layer is stable up to about 400 K, whereas mixing of the deposited films with the substrate is found to occur above 600 K. The stability up to 600 K with respect to mixing with the substrate is probably due to the $\text{Fe}_2\text{O}_3/\text{Cu}(110)$ interface. For both iron and iron oxide films deposited on clean $\text{Cu}(110)$, the copper AES signal starts to increase at around 600 K when the sample is slowly heated,^{5,7,9} whereas for the $\text{Co/Cu}(110)$ interface, mixing has been observed above 450 K.⁸ At first sight the thermal stability of the $\text{Co/Fe}_2\text{O}_3$ double layer seems to be similar to that of the $\text{Fe/Fe}_2\text{O}_3$ double layer. In both cases most of the intermixing of the layers takes place between 400 and 600 K. However, in the case of the $\text{Fe/Fe}_2\text{O}_3$ double layer, not only the atoms in the layers are mixing, but the atoms in the two layers also react with each other, i.e., the iron in the oxide is reduced by the iron in the metallic layer. In the case of the $\text{Co/Fe}_2\text{O}_3$ double layer the layers are only mixing, but the chemical nature of the oxide does not change as is evidenced by the observation that the surface of the sample mainly consists of Fe_2O_3 after heating to 730 K. Finally, we found that intermixing of the double layer is very slow in the temperature range in which the surface of the $\text{Co/Fe}_2\text{O}_3$ double layer orders. It is therefore possible to prepare an ordered $\text{Co/Fe}_2\text{O}_3$ double layer on $\text{Cu}(110)$ which still shows a relatively sharp interface between Co and Fe_2O_3 .

ACKNOWLEDGMENT

This work was supported by the HGF project "Magnetoelectronics."

¹N. Hasegawa, A. Makino, F. Koike, and K. Ikarashi, IEEE Trans. Magn. **32**, 4618 (1996).

- ²Y. Kawawake, Y. Sugita, M. Satomi, and H. Sakakima, J. Appl. Phys. **85**, 5024 (1999).
- ³Y. Kawawake, Y. Sugita, M. Satomi, and H. Sakakima, J. Appl. Phys. **87**, 6983 (2000).
- ⁴Y. Sugita, Y. Kawawake, M. Satomi, and H. Sakakima, Jpn. J. Appl. Phys., Part 1 **37**, 5984 (1998).
- ⁵C. Pflitsch, L. K. Verheij, R. David, and R. Franchy, J. Appl. Phys. **90**, 1215 (2001).
- ⁶D. R. Lide and H. P. R. Frederikse, *CRC Handbook of Chemistry and Physics*, 5-5 (1998).
- ⁷C. Pflitsch, R. David, L. K. Verheij, and R. Franchy, Surf. Sci. **468**, 137 (2000).
- ⁸C. Tölkes, *Berichte des Forschungszentrum Jülich* (1998), Vol. 3614.
- ⁹C. Pflitsch, L. K. Verheij, R. Franchy, and R. David, Surf. Sci. **488**, 32 (2001).
- ¹⁰C. Pflitsch, R. David, L. K. Verheij, and R. Franchy, Europhys. Lett. **53**, 388 (2001).
- ¹¹K. Kuhnke, *Berichte des Forschungszentrums Jülich* (1991), Vol. 2490.
- ¹²K. Kuhnke, K. Kern, R. David, and G. Comsa, Rev. Sci. Instrum. **65**, 3458 (1994).
- ¹³C. Tölkes, R. David, K. G. Tschersich, G. Comsa, and P. Zeppenfeld, Europhys. Lett. **46**, 589 (1999).
- ¹⁴C. Tölkes, R. Struck, R. David, P. Zeppenfeld, and G. Comsa, Phys. Rev. Lett. **80**, 2877 (1998).
- ¹⁵B. Poelsema and G. Comsa, *Scattering of Thermal Energy Atoms* (Springer, Berlin, 1989).
- ¹⁶F. Farias and K. H. Rieder, Rep. Prog. Phys. **61**, 1575 (1998).
- ¹⁷C. Ruby and J. Fusy, Appl. Surf. Sci. **99**, 393 (1996).
- ¹⁸V. S. Smentkowski and J. T. Yates, Jr., Surf. Sci. **232**, 113 (1990).
- ¹⁹M. Seo, J. B. Lumsden, and R. W. Staehle, Surf. Sci. **50**, 541 (1975).
- ²⁰H. Pinkvos, H. Poppa, E. Bauer, and J. Hurst, Ultramicroscopy **47**, 339 (1992).
- ²¹A. Bettac, J. Bansmann, V. Senz, and H. H. Meiwes-Broer, Surf. Sci. **454-456**, 936 (2000).
- ²²A. Clarke, G. Jennings, R. F. Willis, P. J. Rous, and J. B. Pendry, Surf. Sci. **187**, 327 (1987).