Surface Science 454–456 (2000) 875–879
surface science
www.elsevier.nl/locate/susc

Study of the growth and the magnetism of ultrathin films of Cr on Fe

R. Moroni, F. Bisio, M. Canepa, L. Mattera *

Unità INFM and CFSBT, Dipartimento di Fisica, Università di Genova, via Dodecaneso 33, I-16146 Genova, Italy

Abstract

The surface magnetic properties of ultrathin Cr films grown on an O/Fe/Ag(100) substrate have been studied by means of spin polarized metastable de-excitation spectroscopy. The presence of oxygen on top of the Fe film inhibits the segregation of Ag and strongly reduces Fe/Cr intermixing. The magnetization of the outermost Cr layer is zero immediately after its deposition, whereas, upon annealing up to 500 K, a net magnetization is observed which reverse its direction as a function of the film thickness already from a 3 ML thick film. The magnetization reversal is in agreement with the layered antiferromagnetic structure of Cr clearly observed for thicker films. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Chromium; Growth; Iron; Magnetic measurements; Magnetic surfaces; Oxygen

The magnetic properties of surfaces and thin films are the object of a strong interest because of the great variety of phenomena observed in systems with low dimensionality [1].

Chromium, with its layered antiferromagnetic structure and its incommensurate spin-density wave, is particularly interesting [2]. Since Allan's prediction of a ferromagnetic phase at the Cr(100) surface characterized by high localized magnetic moments [3], considerable efforts have been devoted to the experimental determination of the magnetic state of this surface [4].

The first attempts to identify the magnetization at the Cr(100) surface gave controversial results [5–7]. The disagreement between theoretical and experimental results can be attributed to the fact that real surfaces are not perfectly flat as assumed in the calculations. In fact, the presence of terraces separated by single steps can explain the absence of a net macroscopic magnetic moment at surface.

Recently, the magnetic properties of thin Cr films have also been investigated because giant magnetoresistance effects, which may have important technological applications, have been observed in Fe films separated by thin Cr layers [8]. The net magnetization at the surface of Cr films grown on Fe(100) has been investigated by means of scanning electron microscopy with polarization analysis (SEMPA) [9] and inelastic polarized electron scattering (SPEELS) [10]. Apart from the conflicting results concerning the phase of the antiferromagnetic ordering of the Cr layers, both SEMPA and SPEELS experiments observe a delayed onset of the antiferromagnetic ordering which becomes clear from the fifth layer on. The suppression of a clear antiferromagnetic ordering up to the fourth layer can be attributed to the Cr–Fe intermixing revealed by STM experiments [11].

---

* Corresponding author. Fax: +39 10 311 066.
E-mail address: mattera@fisica.unige.it (L. Mattera)

PII: S0039-6028(00)00137-0

In this experiment, we investigate the magnetic state at the surface of the above-described system and the role played by growth conditions and Cr–Fe alloying in films with thickness smaller than 5–6 ML. We use spin polarized metastable de-excitation spectroscopy (SPMDS) to investigate the surface magnetism of ultrathin films of Cr grown on Fe. SPMDS exploits the electron emission induced by the de-excitation at the surface of spin-polarized metastable helium atoms [12–14]. This technique is surface specific as it is sensitive to the electronic states which spill out into vacuum at a distance of about 2–3 Å from the surface plane [15–17]. Obviously, the surface specificity is particularly suitable for the measurement of the magnetization of the outermost layer of the Cr film and it is essential in the study of ultrathin films.

The surface magnetization can be related to the experimentally measured asymmetry

$$A^{\mathrm{expt}}(E)=\frac{1}{P}\frac{I_{\downarrow}^{\mathrm{expt}}(E)-I_{\uparrow}^{\mathrm{expt}}(E)}{I_{\downarrow}^{\mathrm{expt}}(E)+I_{\uparrow}^{\mathrm{expt}}(E)}. \tag{1}$$

In Eq. (1), P is the polarization degree of the metastable helium atom beam impinging on the surface and $I_{\downarrow(\uparrow)}^{\mathrm{expt}}(E)$ are the experimental energy distributions of electrons ejected following de-excitation of metastable atoms with polarization antiparallel (↓) or parallel (↑) to the magnetization vector at the surface.

In order to extract quantitative information on surface magnetism, we apply a model thoroughly described elsewhere [14]. The model allows the calculation, from the experimental quantities $I_{\downarrow(\uparrow)}^{\mathrm{expt}}(E)$, of the *effective* spin-selected densities of states $\rho_{\uparrow(\downarrow)}(E)$ with majority (minority) character. The effective density of magnetization $m(E)=\rho_{\uparrow}(E)-\rho_{\downarrow}(E)$ and of charge $n(E)=\rho_{\uparrow}(E)+\rho_{\downarrow}(E)$ can then be easily obtained. As shown in Ref. [14], the best fit of the experimental quantities depends critically on the choice of $\rho_{\uparrow(\downarrow)}(E)$ so that $m(E)$ and $n(E)$ can be obtained with high accuracy.

The experimental apparatus in which surface magnetism is investigated by means of SPMDS and surface morphology by means of (ground state) He reflectivity R_{He} [18] has been described in detail elsewhere [14].

The substrate on which Cr films are grown is obtained by evaporating 20 ML of Fe on the (100) surface of a silver single crystal prepared by means of successive cycles of sputtering with Ne^{+} at 3 keV followed by annealing at 700 K. In order to minimize the amount of silver segregated at surface, the iron film was deposited on the Ag(100) substrate held at 120 K [14]. Successive deposition of Cr on this substrate does not lead to a magnetic surface (the asymmetry is zero) irrespective of the thickness of the chromium layer. This can be understood by observing that the Fe surface on which Cr growth takes place is rough (R_{He} is vanishingly small) and it cannot be annealed [19] in order to avoid segregation of silver to the surface layer. Consequently, the Cr film deposited on such a surface is also rough and, being composed by a *large* number of terraces of different thickness, it is characterized by a surface magnetization which averages to zero.

Oxygen is known to improve the surface order of Fe films and to act as a surfactant for the growth of Fe [20]. In fact, although the homoepitaxial growth of iron is of 3D type [21,22], the growth of Fe on O(1 × 1)-Fe(100) proceeds in a layer-by-layer mode, the surface composition remaining unchanged during the deposition.

In an attempt to improve the surface order of the Fe/Ag(100) substrate, the Fe surface was exposed to oxygen (7 L; 1 L $=10^{-6}$ Torr s) at room temperature and subsequently annealed at 500 K. He diffraction measurements indicate the formation of a O(1 × 1) phase although more disordered than that obtained on the Fe/MgO substrate (the intensity of the first order diffraction peaks is lower).

The presence of oxygen on top of the Fe film inhibits the segregation of Ag to the surface. The presence of silver on the surface can be excluded by examining the SPMDS energy distribution curves and by comparing them to those measured as a function of the annealing temperature for Fe/Ag(100) [19]. Ion backscattering measurements are under way in order to determine the in-depth concentration of Ag.

As in the case of the Fe deposition on O(1 × 1)-Fe(100), also on this substrate, R_{He} exhibits oscillations during further deposition of iron and the total density of states of the surface does not change.

On this $O(1\times 1)$-Fe/Ag substrate, the asymmetry exhibits the same shape as that measured for $O(1\times 1)$-Fe/MgO [23] although its intensity is lower (4–5% compared with 12%). The observation of a lower asymmetry can be related either to an increased disorder or to the presence of Ag dissolved in the Fe film (or both). Work is in progress to clarify this point.

On the $O(1\times 1)$-Fe/Ag(100) substrate held at room temperature, Cr films of different thickness have been evaporated by electron bombardment of a rod at a deposition rate of 0.3 ML min^{-1}. The thickness of the film and the deposition rate have been determined by monitoring the oscillations of R_{He} during the growth process. The oscillations are strongly damped and three oscillations only are detected, a clear indication of a 3D growth.

Measurements performed after having interrupted the growth in correspondence of the third maximum of R_{He}, show that the asymmetry is zero, an indication of the absence of a net magnetization at surface. This is consistent with the low value of R_{He}, a clear indication of a disordered surface.

A better structural order is obtained upon annealing at 500 K. After the annealing, R_{He} recovers to values similar to those detected on the initial $O(1\times 1)$-Fe/Ag(100) substrate. The SPMDS asymmetry measured on the annealed 3 ML Cr film is shown in Fig. 1a (dots): the high values of $A(E)$ provide evidence that the surface exhibits a net magnetization.

One more monolayer of Cr was then deposited at room temperature. During deposition, a reduction of the helium reflectivity is observed without any oscillation. Immediately after deposition, the net magnetization of the surface is zero. Following a further annealing at 500 K, the asymmetry shown in Fig. 1b is observed. The figure clearly shows that the asymmetry changes sign from 3 to 4 ML and that the shape of $A(E)$ is quite similar in the two cases. The different intensities are probably due to a different surface morphology of the two films determined by a different density of terraces. The change of sign of the asymmetry, and therefore of the magnetization, is in agreement with the layered antiferromagnetic structure of Cr previously observed for larger thicknesses [9,10].

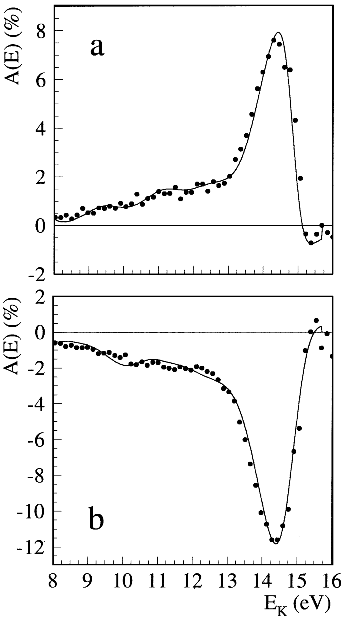

Fig. 1. Asymmetry for 3 ML (a) and 4 ML (b) Cr films deposited on $O(1\times 1)$-Fe/Ag(100) at room temperature and annealed at 500 K. The experimental data, measured at room temperature, are represented by dots whereas the continuous lines provide the fit to the data (see text).

The experimental data obtained by means of SPMDS for the 3 and 4 ML thick films have been analyzed by using the model mentioned above (continuous lines in Fig. 1). The corresponding majority (minority) density of states for the 3 ML film are reported as dashed (dotted) lines in Fig. 2 where the total density of states $n(E)=\rho_{\uparrow}(E)+\rho_{\downarrow}(E)$ is also shown (continuous line).

Four features are clearly visible in the density of states. The shoulder at lower binding energy ($E_{\mathrm{b}}\approx 1$ eV) can be attributed to Cr d states in agreement with theoretical calculations [24] and ARUPS data [25]. Moreover the spin-selected density of states shows a predominance of the states with majority character at this binding energy again in agreement with theoretical calculations [24]. According to the results of Ref. [26], the features at $E_{\mathrm{b}}\approx 5$ eV and $E_{\mathrm{b}}\approx 7$ eV can be attributed to states of oxygen chemisorbed on the

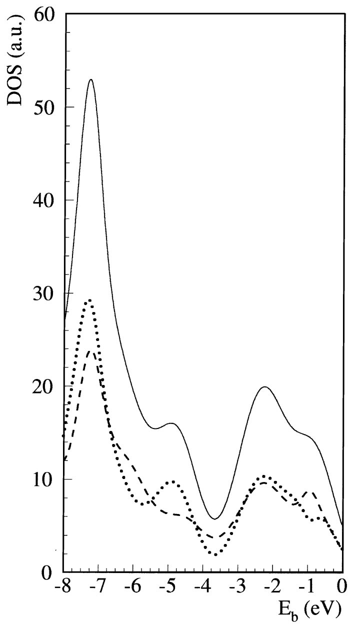

Fig. 2. Majority density of states $\rho_\uparrow(E)$ (– – –), minority density of states $\rho_\downarrow(E)$ (···) and total density of states $n(E)=\rho_\uparrow(E)+\rho_\downarrow(E)$ (—) obtained from the fit of the experimental data relative to the 3 ML Cr film.

surface and the peak at $E_b \approx 2.5$ eV can be attributed to a Cr state induced by the presence of oxygen. The oxygen-induced states definitely exhibit a spin polarization as can be observed in Fig. 2.

We observe that the ARUPS data of Ref. [26] were obtained by exposing the (100) surface of a chromium single crystal to oxygen so that the good agreement between the states detected on O/Cr(100) [26] and on Cr/O(1 × 1)-Fe/Ag allows us to relate the above-mentioned states to the presence of oxygen, excluding any effect induced by the presence of Fe. Furthermore, the oxygen-induced states of the O/Fe/Ag system ($E_b \approx 6$ eV) [27] are absent, which allows one to exclude the presence of areas uncovered by Cr.

The analysis of the 4 ML film (not shown here) provides equivalent results concerning $\rho_{\uparrow(\downarrow)}(E)$ and $n(E)$, with the role of the majority and minority components being obviously reversed.

Finally we observe that the analysis of the surface density of states of the 3 ML film before and after annealing shows that oxygen contributions are already present at the surface of the as-grown film, but that they do increase upon annealing. Concerning iron, at present we cannot exclude its presence at the surface, although we observe that its contribution to the density of states near the Fermi edge seems to be minor, if any.

In conclusions, we find that the net magnetization of the outermost Cr layer is zero immediately after its deposition. After the annealing of the film up to 500 K, the asymmetry increases to about 10% and it oscillates in sign as a function of the thickness of the Cr film starting already from a 3 ML thick film.

The data available at present indicate that oxygen does not act as a surfactant for the growth of Cr on Fe (at least not to the extent it does for the homoepitaxial growth of Fe [20]) but that it seems to reduce strongly the Cr–Fe intermixing.

Several questions are still open such as the role of oxygen and the influence of annealing on the structure and the magnetic properties of Cr film. Work is in progress to clarify the previous points and to determine the effect of oxygen on the growth conditions, on Cr–Fe intermixing and on the formation of the Cr/Fe interface. The presence of the antiferromagnetic order in 1 and 2 ML thick films is currently under investigation.

Acknowledgements

This work has been supported by the Italian Ministry of University and Scientific and Technological Research through the MURST-Cofin97 Project n. 9702178261_003.

References

[1] J.A.C. Bland, B. Heinrich (Eds.), Ultrathin Magnetic Structures Vols. I and II Springer, Berlin, 1994.
[2] E. Fawcett, Rev. Mod. Phys. 60 (1988) 209.
[3] G. Allan, Surf. Sci. 74 (1978) 79.
[4] H. Dreyssé, C. Demangeat, Surf. Sci. Rep. 28 (1997) 65 and references cited therein.
[5] F. Meier, D. Pescia, T. Schreiber, Phys. Rev. Lett. 48 (1982) 645.
[6] C. Carbone, S.F. Alvarado, Phys. Rev. B 36 (1987) 2433.

[7] L.E. Klebanoff, S.W. Robey, G. Liu, D. Shirley, Phys. Rev. B 30 (1984) 1048.
[8] M.N. Baibich, J.M. Broto, A. Fert, F. Nguyen Van Dau, F. Petroff, P. Etienne, G. Creuzet, A. Friederich, J. Chazelas, Phys. Rev. Lett. 61 (1988) 2472.
[9] J. Unguris, R.J. Celotta, D.T. Pierce, Phys. Rev. Lett. 69 (1992) 1125.
[10] T.G. Walker, A.W. Pang, H. Hopster, S.F. Alvarado, Phys. Rev. Lett. 69 (1992) 1121.
[11] A. Davies, J.A. Stroscio, D.T. Pierce, R.J. Celotta, Phys. Rev. Lett. 76 (1996) 4175.
[12] F.B. Dunning, C. Rau, G.K. Walters, Comments Solid State Phys. 12 (1986) 17.
[13] M. Onellion, M.W. Hart, F.B. Dunning, G.K. Walters, Phys. Rev. Lett. 52 (1984) 380.
[14] M. Salvietti, R. Moroni, P. Ferro, M. Canepa, L. Mattera, Phys. Rev. B 54 (1996) 14 758.
[15] H. Hagstrum, Phys. Rev. 96 (1954) 336.
[16] H. Hagstrum, Phys. Rev. 139A (1965) 526.
[17] H. Hagstrum, Phys. Rev. 150 (1966) 495.
[18] R. Kunkel, B. Poelsema, L.K. Verheij, G. Comsa, Phys. Rev. Lett. 65 (1990) 773.
[19] M. Salvietti, R. Moroni, M. Canepa, P. Ferro, L. Mattera, J. Magn. Magn. Mater. 165 (1997) 230.
[20] F. Bisio, R. Moroni, M. Canepa, L. Mattera, R. Bertacco, F. Ciccacci, Phys. Rev. Lett. 83 (1999) 4868.
[21] J.A. Stroscio, D.T. Pierce, R.A. Dragoset, Phys. Rev. Lett. 70 (1993) 3615.
[22] P. Bonanno, M. Canepa, P. Cantini, R. Moroni, L. Mattera, S. Terreni, Surf. Sci. 454–456 (2000) 697, these proceedings.
[23] R. Moroni, F. Bisio, M. Canepa, L. Mattera, Surf. Sci. 433–435 (1999) 676.
[24] R.H. Victoria, L.M. Falicov, Phys. Rev. B 31 (1985) 7335.
[25] L.E. Klebanoff, R.H. Victora, L.M. Falicov, D.A. Shirley, Phys. Rev. B 32 (1985) 1997.
[26] J.C. Peruchetti, C. Pirri, D. Bolmont, G. Gewinner, Solid State Commun. 59 (1986) 517.
[27] P. Ferro, R. Moroni, M. Salvietti, M. Canepa, L. Mattera, Surf. Sci. 407 (1998) 212.