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Surface Science 377-379 (1997) 481-486

surface science

# Surface magnetism of an ultrathin Fe/Ag(100) film: influence of O<sub>2</sub> and CO adsorption

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Received 1 August 1996; accepted for publication 15 October 1996

## Abstract

The influence of adsorption of O<sub>2</sub> and CO on the surface magnetism of a 10 ML film of Fe grown at 120 K on Ag(100) has been investigated by spin polarized metastable deexcitation spectroscopy. The extreme surface sensitivity of this spectroscopy allows us to study the effects of adsorption from exposures as low as ~0.1 L. Oxygen adsorbs dissociatively at 120 K and the O<sub>2p</sub> states are spin polarized. At this low temperature, oxidation starts from exposures of the order of 1 L and above 3-4 L a non-magnetic oxide layer is formed. CO adsorbs molecularly at T=120 K and then dissociates above room temperature. Following dissociation, carbon atoms do not have any effect on the spin polarization of oxygen and iron states at the surface.

**Keywords:** Adatoms; Atom-solid interactions, scattering, diffraction; Carbon monoxide; Iron; Magnetic films; Magnetic measurements; Magnetic phenomena; Oxygen; Silver

## 1. Introduction

The magnetism of thin films has been extensively studied both theoretically and experimentally in recent years. Due to the low dimensionality of these systems, unique properties such as the thickness-dependent spin anisotropy and the enhancement of magnetic moments at surfaces are observed [1].

In particular, the modifications in the magnetism of thin films induced by the adsorption of atoms and molecules cover an area of great interest. Concerning iron, many experimental investigations have been carried out for chemisorbed species like

carbon monoxide [2], oxygen [3] and sulfur [4]. Obviously, to study these effects the availability of a probe sensitive to the first layer of the sample is of primary importance, particularly when one is interested in low-exposure effects.

Here, we study surface magnetism by measuring the electron emission induced by deexcitation at surfaces of spin-polarized metastable helium atoms He\* (SPMDS) [5,6], a technique which has proved to be extremely surface sensitive.

The deexcitation at surfaces of an atom in a metastable electronic excited state may occur in two different ways depending on the value of the ionization potential  $E^*$  of the atom as compared to the surface work function  $\Phi$ , and on the presence of adsorbates on the surface [7,8]. In particular, for 3d ferromagnetic clean metals  $E^* < \Phi$  and the metastable deexcites through a two-step process. First, the 2s electron of the atom tunnels in an

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empty state of the metal, leaving the incoming atom in an ionic state (resonant ionization, RI), then the hole in the 1s level of the ion is filled by an electron of the valence band of the metal, while a second electron of the solid is emitted in vacuum (auger neutralization, AN). The AN step is effective at a distance of  $\sim 2\text{--}3 \text{ \AA}$  outside the surface plane, then being sensitive to the electronic states which spill into vacuum at that distance [6,7,9].

If the incoming metastable atoms are spin-polarized, we can extract information on the convolution of the spin-selected density-of-states by introducing the asymmetry:

$$A(E) = \frac{1}{P} \frac{I_{\downarrow}(E) - I_{\uparrow}(E)}{I_{\downarrow}(E) + I_{\uparrow}(E)}, \quad (1)$$

where  $P$  is the polarization degree of the  $\text{He}^*$  atoms impinging on the surface and  $I_{\downarrow(\uparrow)}(E)$  are the energy distributions of the ejected electrons following the interaction of  $\text{He}^*$  atoms with polarization parallel ( $\uparrow$ ) or anti-parallel ( $\downarrow$ ) to the magnetization direction of the sample.

Completely different is the case when the tunneling process (RI) is inhibited either because  $E^* > \Phi$  or because of the presence of adsorbates. In this case  $\text{He}^*$  deexcites in only one step, named Penning or Auger deexcitation (AD): an electron coming from the valence band of the solid fills the hole in the 1s level of  $\text{He}^*$  while the electron in the 2s level is emitted in vacuum [8].

If  $\text{He}^*$  is spin polarized, the energy distribution of the emitted electrons reflects directly the spin-resolved surface density-of-states at the distance where this process is effective ( $\sim 5 \text{ \AA}$  outside the surface plane [7]).

In this paper we present a study, using the SPMDS technique, of the magnetic properties of a 10 ML iron film grown on Ag(100) at  $T = 120 \text{ K}$ . In particular we report the modifications to surface magnetism induced by the exposure, also at  $T = 120 \text{ K}$ , to  $\text{O}_2$  and CO. Chemisorption and magnetic properties have been extensively studied on single-crystal iron surfaces and films and the motivations of the present investigation can be summarized as follows.

Oxygen is known to chemisorb dissociatively and to form several ordered structures which depend both on coverage and on the crystallo-

graphic face. Most of the available literature concerns room-temperature chemisorption and high-temperature oxidation while little is known about the low-temperature regime, particularly for the formation of oxidized phases and the effects on magnetic properties.

CO chemisorbs on the low-temperature Fe(100) surface in a tilted geometry at low exposures. A second state, characterized by a vertical geometry of adsorption, is observed at higher exposures. Upon annealing above room temperature, CO partly desorbs and partly dissociates leaving O and C atoms randomly adsorbed on the surface.

Here, we will compare the results on the spin polarization of oxygen-derived states following dissociation of  $\text{O}_2$  or CO.

## 2. Experimental details

The experimental results have been obtained in an apparatus which has been described elsewhere [10]. In the present experiment the Fe film (10 ML) was grown at  $T = 120 \text{ K}$  on the Ag(100) substrate and adsorption experiments were performed at the same temperature. The temperature of growth and deposition was chosen in order to minimize the amount of silver segregated at the surface and, for the same reason, no annealing of the film was attempted. From previous studies, in fact, we know that for a 10 ML film grown at  $T = 120 \text{ K}$  the amount of silver on the surface layer is below 2% [11] and that annealing temperatures as low as 300 K are sufficient to start the segregation of silver atoms to the surface [12].

As the surface of the iron film is disordered, we were not able to observe He (ground state) diffraction patterns and to detect ordered overlayers as adsorption proceeds. For this reason we do not have any mean to calibrate the coverage and therefore we will present the experimental data as a function of exposures  $\Theta$  in langmuir units ( $1 \text{ L} = 10^{-6} \text{ Torr} \cdot \text{s}$ ).

## 3. Results and discussion

We start the discussion by presenting the data relative to oxygen chemisorption. The energy

distribution curves (EDC's) are reported in Fig. 1A as a function of oxygen exposures while asymmetries (Eq. (1)) are shown in Fig. 1B. All spectra were recorded for the same intensity of the incoming He\* beam so that the EDC's and the asymmetries are fully comparable. Inspection of Fig. 1 shows that oxygen strongly modifies both the spectrum and the asymmetry.

The data on the clean iron film have been

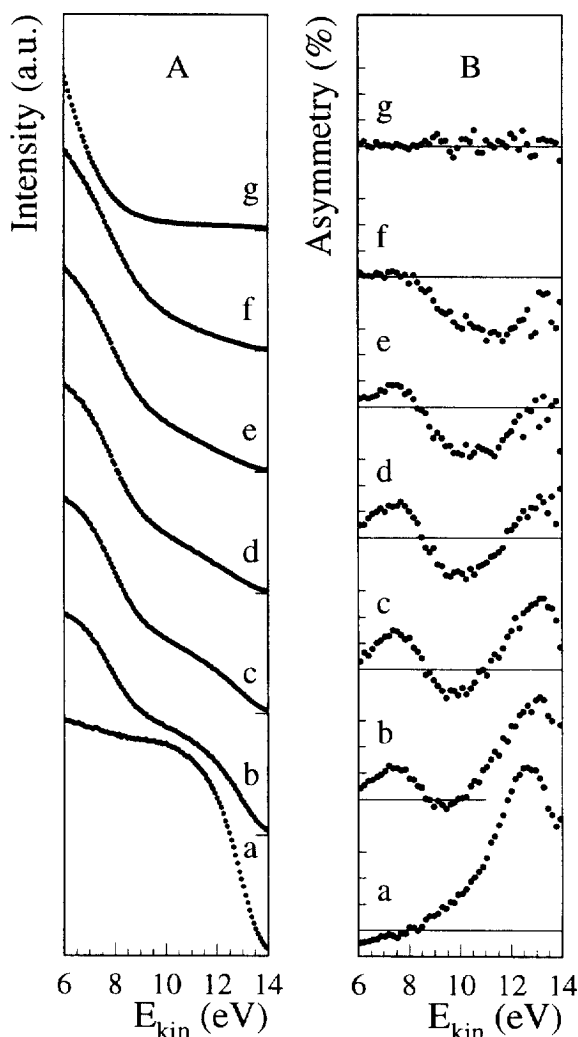


Fig. 1. Dependence on oxygen exposure of (A) energy distribution curves of electrons produced in the deexcitation of He\*; (B) asymmetry (Eq. (1)) calculated from the EDC's obtained with spin-polarized He\*. (a) Fe/Ag film; (b)  $\Theta_{\text{O}_2} = 0.45$  L; (c) 0.7 L; (d) 1.0 L; (e) 1.2 L; (f) 1.7 L; (g) 4 L.

thoroughly discussed elsewhere [10] and here we observe that the spectrum shows a steep rise at high kinetic energies due to the convolution of iron states near the Fermi edge (curve a of Fig. 1A). Near  $E_F$ , the density-of-states of iron is dominated by d states [13] but the high sensitivity of He\* to states extending into vacuum results in an enhanced sensitivity to less localized states such as the s-p ones. In the absence of accurate calculations for the Auger neutralization process (AN step), we cannot at present disentangle the two contributions.

Turning to the asymmetry (curve a of Fig. 1B), we observe a wide, positive structure centered near the maximum of the kinetic energy ( $E_{k,\text{max}}$ ) which corresponds to states near  $E_F$ . According to the definition of  $A(E)$  and to the theory of Penn and Apell [9], a positive structure of  $A(E)$  can be related to a predominance of minority spin states. This finding is in agreement with theoretical [13,14] and experimental data [15].

As the film is exposed to oxygen, up to 1.2–1.7 L we observe a decrease of the EDC near  $E_{k,\text{max}}$  with the appearance of a steep rise at  $E_k \approx 8$  eV. According to Sesselmann et al. [8], the derivative of the spectrum with respect to energy gives the main features of the effective density-of-states  $n(E)$  entering in the deexcitation process. The behaviour of the EDC's can then be interpreted as due to a reduction of  $n(E)$  near  $E_F$  and to the appearance of new states at  $E_B = E_{k,\text{max}} - E_k \approx 6.5$  eV. This value compares well with the energy position of the  $\text{O}_{2p}$  states as observed by photoemission [4] so that we can assign this feature in the EDC's to oxygen-induced states.

The behaviour of  $A(E)$  with  $\Theta_{\text{O}_2}$  is even richer. As  $\Theta_{\text{O}_2}$  increases, the positive structure at high  $E_k$  decreases and a second positive peak appears at  $E_{k,\text{max}} - E_k \approx 6.5$  eV, corresponding to the rise in the EDC. The intensity of this structure goes through a maximum at  $\Theta_{\text{O}_2} \approx 0.7$  L and then vanishes at higher exposures. Between the two positive maxima of  $A(E)$ , a negative minimum appears at  $E_k \approx 9.5$  eV which gradually broadens, moves towards higher  $E_k$  with increasing exposures and finally becomes the only feature of  $A(E)$  at  $\Theta_{\text{O}_2} \approx 1.2$ –1.7 L.

Qualitatively, these results are similar to the

ones measured by SPMDS on oxygen adsorbed on Fe(110) films grown on W [16] and GaAs [17] substrates. The main quantitative differences are the intensity of  $A(E)$ , which is lower here, and the amount of oxygen required to modify the asymmetry, lower in the present experiment by almost one order of magnitude.

Concerning the peak of  $A(E)$  at  $E_B \simeq 6.5$  eV, we observe that it already appears at the lowest exposure and corresponds to the oxygen-induced states in the EDC. It can then be interpreted as the spin polarization of  $O_{2p}$  states, in agreement with photoemission [4] and theoretical data [18] on the  $O(1 \times 1)$  overlayer on Fe(100). Its sign indicates a predominance of minority states.

The appearance of the negative minimum as exposure increases means that the majority spin component overcomes the minority one for states near  $E_F$ . Turning to the EDC's, we observe that in the same range of exposures the density-of-states near  $E_F$  decreases. At present we could speculate that there is a charge transfer from iron to oxygen states which leaves behind iron states having a majority character. This statement, which obviously requires further investigations, is in qualitative agreement with the calculations of Huang and Hermanson [18]. In the 0–4 eV (binding energy) range, in fact, the density-of-states on the adlayer (relevant in a SPMDS experiment) was found to be lower than the one on the clean iron surface with a predominance of majority spin states.

Finally, if we move to high exposures, we observe that for  $\Theta > 3$ –4 L,  $A(E)$  vanishes and the EDC changes its shape drastically (see curves g of Fig. 1A and B).

At the same coverages, the UPS spectrum (not shown here) closely resembles the one measured on an oxidised surface [19]. Even at this low temperature, then, relatively high exposures of oxygen start to form an oxide layer which is magnetically dead as observed by metastable atoms.

Returning to the peak of  $A(E)$  at  $E_B \simeq 6.5$  eV, we observe that the same feature was also detected in SPMDS experiments on the Fe/W [16] and the Fe/GaAs [17] clean systems, and on the Fe/Ag(100) film either grown at room temperature

[20] or after a moderate annealing of the film grown at  $T = 120$  K [12].

This feature could then be attributed to oxygen contamination, though a sizable partial pressure of oxygen in a UHV apparatus seems unlikely. However, oxygen could also derive from dissociation of CO, a molecule which is certainly present particularly when filaments for thermionic emission are used in deposition sources or sample heaters. In order to clarify this point, we have performed preliminary experiments on the adsorption of CO at  $T = 120$  K on the surface of the Fe/Ag(100) film. The surface was saturated at  $T = 120$  K with CO after an exposure of 5.4 L and the measured EDC is typical of the AD deexcitation mechanism. CO adsorption inhibits the ionization process of the RI+AN mechanism, consistently with a vertical geometry of adsorption; a geometry that, at high exposures on a low-temperature Fe(100) surface, is in agreement with previous work [2]. Concerning the asymmetry measured on this system, we can anticipate that we observe a spin polarization of the  $4\sigma$ ,  $5\sigma$  and  $1\pi$  states of CO with a predominance of majority states (negative asymmetry).

Annealing of the film leads to the dissociation of CO and the results obtained at  $T = 420$  K are reported in Fig. 2 (full dots). In the same figure, the results obtained after an oxygen dosing of 1 L at  $T = 120$  K are also reported for comparison (open dots, same as curves d of Fig. 1A and B). We observe some differences in the EDC's (upper panel of Fig. 2), perhaps due to the presence of C atoms following the dissociation of CO or, more likely, to the segregation of silver to the surface. The two asymmetries are instead indistinguishable (lower panel of Fig. 2) so that we can conclude that the maximum of the asymmetry at  $E_{k,\max} - E_k \simeq 6.5$  eV observed in iron films deposited on GaAs and W is probably due to the spin polarization of  $O_{2p}$  states derived from CO dissociation.

The analysis of the Fe/Ag case is complicated by the fact that  $O_{2p}$  and silver d states occur at the same energy and that a spin-resolved photoemission study on an Ag overlayer on Fe(100) did show that the d states of silver are spin polarized [21]. However, the shape analysis of  $A(E)$  suggests

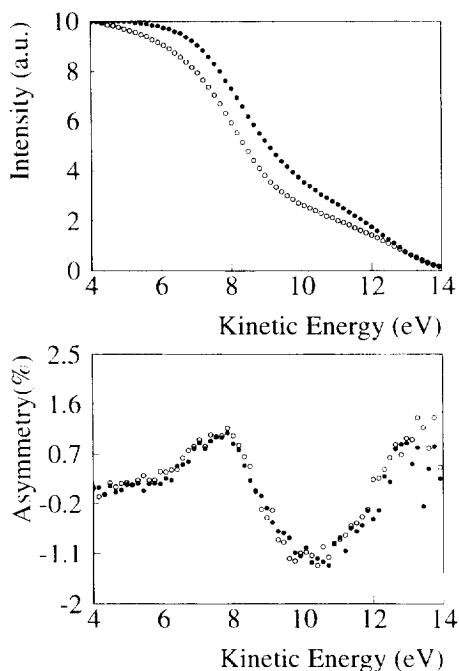


Fig. 2. Comparison between energy distribution curves (upper panel) and asymmetries (lower panel) for an oxygen exposure of 1 L (open dots) and a CO exposure of 5.4 L at  $T=120$  K and then annealed at  $T=420$  K (full dots).

that, even in the case of Fe/Ag, a strong contribution to this peak derives from CO dissociation.

Finally, we would also like to observe from the lower panel of Fig. 2, that the presence of C atoms does not seem to have any effect on  $A(E)$  and therefore on the spin polarization of iron and oxygen states at a surface.

#### 4. Conclusion

In summary, we have studied the effect on surface magnetism of  $O_2$  and CO adsorption on a 10 ML film of iron grown at  $T=120$  K on a Ag(100) substrate.

Oxygen was found to chemisorb atomically on the iron film with a spin polarization of the  $O_{2p}$  states. At exposures higher than 3–4 L, the surface is covered with an oxidized film as obtained by the shape of the EDC and by UPS data. The asymmetry vanishes so that this layer is magneti-

cally dead as seen by  $He^*$ . The oxidation process is already active at lower exposures as the feature of  $A(E)$  attributed to the spin polarization of  $O_{2p}$  states starts to decrease at  $\Theta_{O_2} \simeq 1$  L. Surface disorder could play a significant role in this respect and could also be the reason for the discrepancy we observe with respect to previous SPMDS data on Fe/GaAs and Fe/W systems. In fact we measure a lower asymmetry and a higher sticking coefficient, as the exposures we need are lower by almost one order of magnitude.

CO chemisorbs in a molecular state at  $T=120$  K, at high exposures ( $\Theta_{CO} \simeq 5.4$  L) gives rise to a Penning spectrum, and the  $4\sigma$ ,  $5\sigma$  and  $1\pi$  molecular states are spin polarized. Annealing above room temperature leads to CO dissociation as observed both by the shape of the EDC and by the asymmetry. In particular the spin polarizations of the  $O_{2p}$  states following dissociation are absolutely equivalent to the ones derived from  $O_2$  dissociation. This demonstrates that the presence of C atoms does not affect the spin polarization of oxygen and iron states at surfaces and permits us to interpret a feature observed in previous SPMDS works as due to contamination of CO.

Work is in progress to extract from the reported data the spin-selected density-of-states by the application of a model which was successfully applied to the study of the clean Fe/Ag film.

#### References

- [1] Magnetism in Ultrathin Films, Ed. D. Pescia, Appl. Phys. A 49 (1989) (special issue).
- [2] N.B. Brookes, A. Clarke and P.D. Johnson, Phys. Rev. Lett. 63 (1989) 2764.
- [3] B. Sinkovic, P.D. Johnson, N.B. Brookes, A. Clarke and N.V. Smith, Phys. Rev. Lett. 65 (1990) 1647.
- [4] A. Clarke, N.B. Brookes, P.D. Johnson, M. Weinert, B. Sinkovic and N.V. Smith, Phys. Rev. B 41 (1990) 9659.
- [5] F.B. Dunning, C. Rau and G.K. Walters, Comm. Solid State Phys. 12 (1986) 17.
- [6] M. Onellion, M.W. Hart, F.B. Dunning and G.K. Walters, Phys. Rev. Lett. 52 (1984) 380.
- [7] H. Hagstrum, Phys. Rev. 96 (1954) 336; 139A (1965) 526; 150 (1966) 495.
- [8] W. Sesselmann, B. Woratschek, J. Kupperts, G. Ertl and H. Haberland, Phys. Rev. B 35 (1987) 1547.
- [9] D. Penn and P. Apell, Phys. Rev. B 41 (1990) 3303.

- [10] M. Salvietti, R. Moroni, P. Ferro, M. Canepa and L. Mattera, *Phys. Rev. B* 54 (1996) 14758.
- [11] M. Canepa, E. Magnano, A. Campora, P. Cantini, M. Salvietti and L. Mattera, *Surf. Sci.* 352–354 (1996) 36.
- [12] M. Salvietti, R. Moroni, M. Canepa, P. Ferro and L. Mattera *J. Magn. Magn. Mater.*, in press.
- [13] S. Ohnishi, A. J. Freeman and M. Weinert, *Phys. Rev. B* 28 (1983) 6741.
- [14] R. Wu and A.J. Freeman, *J. Appl. Phys.* 73 (1993) 6739.
- [15] B.T. Jonker, K.H. Walter, E. Kisker, G.A. Prinz and C. Carbone, *Phys. Rev. Lett.* 57 (1986) 142.
- [16] M. Getzlaff, D. Egert, P. Rappolt, M. Wilhelm, H. Steidl, G. Baum and W. Raith, *Surf. Sci.* 331–333 (1995) 1404.
- [17] M.S. Hammond, F.B. Dunning, G.K. Walters and G.A. Prinz, *Phys. Rev. B* 45 (1992) 3674.
- [18] H. Huang and J. Hermanson, *Phys. Rev. B* 32 (1985) 6312.
- [19] D.E. Eastman and J.L. Freeouf, *Phys. Rev. Lett.* 34 (1975) 395;  
C.F. Brucker and T.N. Rhodin, *Surf. Sci.* 57 (1976) 523.
- [20] M. Salvietti, R. Moroni, M. Canepa and L. Mattera, *J. Electron Spectrosc. Relat. Phenom.* 76 (1995) 677.
- [21] N.B. Brookes, Y. Chang and P.D. Johnson, *Phys. Rev. B* 50 (1994) 15330.