

Structural versus Magnetic Properties at the Surface of Fe Films during Oxygen-Assisted Homoepitaxial Growth

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The correlation between structural and magnetic properties at the surface of Fe films deposited on Fe(001)- $p(1 \times 1)$ O has been investigated in real time during growth by He reflectivity (R_{He}), spin polarized metastable deexcitation spectroscopy (SPMDS), and spin resolved adsorbed curve spectroscopy (ACS). Surface oxygen acts as a surfactant for Fe growth as demonstrated by the well-resolved oscillations of R_{He} . The asymmetries measured both by SPMDS and ACS, sensitive to the spin polarization of occupied and unoccupied density of states, respectively, oscillate in phase with R_{He} . This demonstrates a strict correlation between morphology and the intensity of magnetization at surface.

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The investigation of magnetic properties at surfaces and of thin films has attracted much attention in recent years as the reduced dimensionality induces novel effects of great interest both from a fundamental and a technological point of view [1]. In these systems the connections between magnetic properties and geometrical structure are particularly interesting and are extensively investigated. Paradigmatic is the case of thin Fe films grown on Cu(001), which show a variety of different magnetic phases [2].

Here we present clear evidence of a direct relationship between structural order and magnetic properties at surfaces during the epitaxial growth of Fe thin films. We have deposited Fe in the presence of surface oxygen. In particular, we have studied the growth of Fe on a well-ordered Fe(001)- $p(1 \times 1)$ O phase. This phase has been extensively studied [3], and it shows large spin-dependent effects in electron spectroscopies [4,5], which are in turn related to the surface magnetic properties.

Investigation of structural properties has been performed by He diffraction, while electronic and magnetic properties have been investigated by means of spin-polarized metastable deexcitation spectroscopy (SPMDS) and spin-resolved adsorbed current spectroscopy (ACS). As a result of this combined study, we find that during the growth of Fe, oxygen atoms segregate to the surface acting as surfactants and induce a quasi-ideal layer-by-layer growth. He reflectivity presents in fact a strong oscillating behavior as a function of the amount of Fe deposited on the surface, with maxima corresponding to the completion of each new monolayer (ML). The large spin dependent asymmetries observed in both SPMDS and ACS oscillate with the same periodicity. Structural and magnetization parameters are thus measured in real time during the growth, yielding a strict

correlation between reflectivity (surface order) and asymmetry (magnetization).

The physical processes of SPMDS have been described in a number of papers which delve deeply into the quenching mechanisms of metastable He atoms (He^*) at surfaces [6,7] and the information on the effective, spin-selected density of the occupied states which can be obtained from this spectroscopy [8,9]. On the contrary, ACS probes the band structure at energies above the Fermi level, yielding information on the unoccupied electron states [10]. Spin resolution, as achieved by measuring the absorption of a beam of spin polarized electrons [5,11], gives access to the study of their spin character.

The main characteristics of the experimental apparatus for He scattering and SPMDS have been described elsewhere [9]. Here we recall that He^* atoms are produced with high efficiency in a discharge source. In the beam, besides He^* , He atoms in the ground state are also present allowing helium diffraction and deexcitation measurements to be performed at the same time. Measurements are performed in an ultrahigh-vacuum (UHV) system with pressure $p < 10^{-10}$ mbar. The sample is magnetized at saturation in-plane, along the [001] direction of the Fe lattice, by means of a current pulse through a coil. All magnetic measurements are then taken at room temperature in a magnetic field of 0.5 G, which provides the quantization axis for the spin polarization of He^* [12].

ACS measurements have been taken in a different UHV apparatus equipped with standard surface characterization techniques [5,13]. The target adsorbed current spectra are recorded by measuring the electron current running to ground while a collimated and transversely polarized electron beam [13] impinges on the sample at normal incidence. In this case, spectra are taken in magnetic remanence, after having magnetized at saturation the sample. Absolute calibration of the incident beam polarization was

performed in a separate experiment by Mott scattering [13].

In both experiments, a clean and ordered Fe(001) surface is obtained by *in situ* epitaxial growth of a single crystal Fe film on a clean MgO(001) substrate [14]. The clean Fe(001) surface is then exposed to research grade oxygen (10–30 L; 1 L = 10^{-6} Torr s) and successively flash heated at 900 K for a few seconds. This procedure [4] leaves a well-ordered structure, as demonstrated by the observation of well-resolved helium diffraction peaks and a sharp primitive 1×1 [$p(1 \times 1)$] low-energy electron diffraction (LEED) pattern. The x-ray photoelectron spectroscopy (XPS) analysis for coverage determination was also found in agreement with previous data [3]. On such a well-characterized surface, Fe films are finally deposited at room temperature, with rates ranging from 0.25 to 1 monolayer/min (ML/min), as monitored by a calibrated quartz microbalance or by He reflectivity. During deposition, exploiting an electron bombardment evaporation cell, the pressure remains below 2×10^{-10} mbar.

The growth of Fe on the Fe(001)- $p(1 \times 1)$ O substrate was monitored by observing the helium reflectivity $R_{\text{He}}(t)$ that, because of its strong dependence on the surface defect density, provides an effective way to determine the characteristics of the growth [15]. $R_{\text{He}}(t)$ is shown in Fig. 1 (continuous line) and it exhibits strong and regular oscillations during Fe deposition, proving that the growth proceeds in a layer-by-layer mode. Note that this is at variance with the case of room temperature Fe/Fe(001) growth. The homoepitaxial growth of Fe is characterized by an exponential decrease of the He reflectivity which clearly indicates a disordered 3D growth, as previously observed by other methods [16]. This difference is due to the surfactant action of the oxygen atoms, which migrate to the surface during the growth. A similar action of surface

oxygen was first observed in the case of the growth of Fe and Ni on Cu(100) [17].

The occupied electronic states have been investigated by SPMDS. In the interaction of He^* atoms with the surface of a 3d ferromagnetic metal, the metastable atoms deexcite with almost unit probability through a two step process. In the first step, the 2s electron of He^* tunnels into an empty state of the metal, leaving the atom in an ionic state (resonant ionization). In the second step, the hole in the 1s level of He^+ is filled by an electron from the valence band of the metal, while a second electron of the solid is emitted in vacuum [Auger neutralization, (AN)]. This spectroscopy is surface specific because AN is effective at a distance of a few angstroms outside the surface plane, so that SPMDS is sensitive to electronic states which spill out into vacuum at that distance [9]. If the incoming atoms are spin polarized, one can define the asymmetry $A(E)$ as

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

where $I_{\uparrow(\downarrow)}(E)$ are the energy distribution curves of electrons ejected from the surface following the interaction of spin-polarized He^* atoms with polarization parallel (\uparrow) or antiparallel (\downarrow) to the magnetization direction of the sample, and P is the polarization degree of the He^* beam. The theoretical bases which allow one to calculate $I(E) = \frac{1}{2}[I_{\uparrow}(E) + I_{\downarrow}(E)]$ and $A(E)$ as

$$I(E) = \int_0^{\infty} d\varepsilon n\left(\frac{E - E_{\text{max}}}{2} - \varepsilon\right) n\left(\frac{E - E_{\text{max}}}{2} + \varepsilon\right), \quad (2)$$

$$A(E) = -\frac{\int_0^{\infty} d\varepsilon m\left(\frac{E - E_{\text{max}}}{2} - \varepsilon\right) n\left(\frac{E - E_{\text{max}}}{2} + \varepsilon\right)}{\int_0^{\infty} d\varepsilon n\left(\frac{E - E_{\text{max}}}{2} - \varepsilon\right) n\left(\frac{E - E_{\text{max}}}{2} + \varepsilon\right)} \quad (3)$$

are thoroughly discussed elsewhere [9]. In Eqs. (2) and (3), $n(E) = \rho_{\uparrow}(E) + \rho_{\downarrow}(E)$ and $m(E) = \rho_{\uparrow}(E) - \rho_{\downarrow}(E)$ are the surface density of states (DOS) and the magnetization density (DOM), respectively, while E_{max} is the maximum kinetic energy of the emitted electrons. $\rho_{\uparrow(\downarrow)}(E)$ are the spin-selected density of states with majority (minority) character which can be obtained by the fit of the experimental data [$I^{\text{exp}}(E)$ and $A^{\text{exp}}(E)$] with the aid of Eqs. (2) and (3).

$n(E)$ and $m(E)$ for the Fe(001)- $p(1 \times 1)$ O surface are shown as continuous lines in Figs. 2(a) and 2(b), respectively. The peak in the DOS at $E_b \approx 6$ eV is due to O_{2p} states, while the shoulder at lower binding energies can be ascribed to Fe_{3d} states. Oxygen atoms are ferromagnetically coupled to the iron substrate and their majority and minority states exhibit an exchange splitting $\Delta E = 0.44 \pm 0.05$ eV. As discussed in Ref. [18], these findings are in good agreement with previous results on the same phase either obtained by *ab initio* calculations [19] or by spin polarized photoemission [4].

Concerning the empty states, spin-resolved ACS data on the Fe(001)- $p(1 \times 1)$ O surface have been already reported

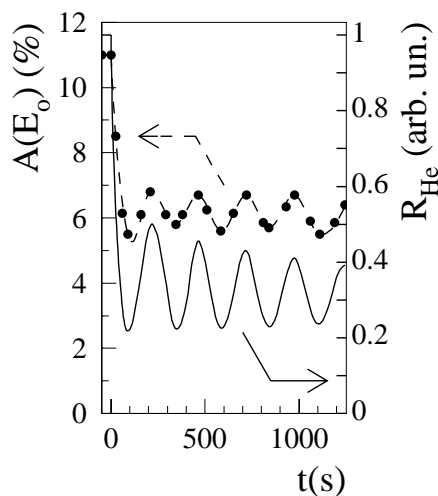


FIG. 1. Fe growth on Fe(001)- $p(1 \times 1)$ O at room temperature. He reflectivity (R_{He} , continuous line) and SPMDS asymmetry $A(E_0)$ at $E_0 \approx 11.5$ eV (dots) as function of deposition time. The dashed line is a guide for the eye.

and discussed at a qualitative level on the basis of band structure of clean Fe(001) [5,20]. Briefly, the essential feature is the presence of an energy gap in the 4–10 eV region above the vacuum level. At these energies the incoming electrons cannot couple with states inside the crystal, do not enter the solid, and are strongly reflected, leading to a deep valley in the adsorbed current curve [10]. Moreover, since the energy gaps for minority- and majority-spin electrons are different, spin asymmetries arise in the spectra [11,20]. This effect is monitored by measuring spin-resolved ACS. A spin asymmetry is defined as in Eq. (1), where now I_{\uparrow} and I_{\downarrow} represent the ac intensities for primary electrons with magnetic moment parallel or antiparallel to sample magnetization, and P is the polarization of the primary electron beam. In the 4–8 eV region, the incoming beam energy lies between the majority and minority H_{15} levels of the Fe band structure. Thus minority-spin electrons can enter the crystal while the majority-spin ones are reflected, giving rise to negative values of A . The opposite occurs above 10 eV, i.e., where the beam energy crosses the H_{12} levels of the bulk band structure, and A changes sign (see the inset of Fig. 3). The spin-dependent asymmetry is large ($A = -12.5\%$ at 6 eV kinetic energy), so that this effect can be exploited in electron polarimetry [20].

The high sensitivity of the experimental apparatus allowed us to perform real-time measurements of the magnetic properties during the growth of Fe on the Fe(001)- $p(1 \times 1)$ O substrate. In particular, the measurement of the spin asymmetries at a fixed energy takes only a few seconds. The SPMDS asymmetry was measured at a kinetic energy of the emitted electrons $E_0 \approx 11.5$ eV, in correspondence with the largest value of $A(E)$ for the starting Fe(001)- $p(1 \times 1)$ O surface. The results, reported as dots in Fig. 1, exhibit an oscillating behavior in perfect phase with helium reflectivity: a clear indication of a correlation between surface magnetic properties and surface structure. In order to clarify whether these oscillations are a consequence of order-magnetism correlation or growth-induced, time-dependent surface composition (or both), films of different thickness obtained by interrupting iron deposition in correspondence of a given minimum (or maximum) of $R_{He}(t)$ were investigated. As an example, the effective densities of states and of magnetization are reported in Figs. 2(a) and 2(b), respectively, where dotted (dashed) lines refer to measurements taken in correspondence of the first maximum (minimum) of the He reflectivity. Considering first the density of states $n(E)$ [Fig. 2(a)], it is seen that upon Fe deposition the contribution of O_{2p} states decreases ($E_b \approx 6$ eV), while there is a simultaneous increase of the Fe states ($E_b \approx 2$ eV). However, a comparison between the intensities of the O_{2p} peaks for the ordered [maximum of $R_{He}(t)$] and disordered [minimum of $R_{He}(t)$] surface shows that, after deposition of 0.5 Fe ML, there is no further detectable variation of the oxygen contributions [21]. More in general, as deposition proceeds, the whole density of

state does not exhibit any significant variation. This clearly shows that the surface composition remains fairly constant during the growth, while the surface undergoes a cyclic variation of the defect density. Considering the $m(E)$ curve [Fig. 2(b)], we observe that its shape remains unchanged upon iron deposition while the intensities of both O_{2p} and Fe_{3d} contributions decrease. However, by comparing measurements performed under minimum and maximum order, we observe that the behavior is not monotonic, but shows well-defined oscillations in phase with the helium reflectivity. A similar oscillating behavior is found in ACS, as shown in Fig. 3, where we present the evolution of the spin-dependent asymmetry as a function of the amount of deposited Fe. Measurements have been collected at a fixed energy (6 eV above the vacuum level), corresponding to the maximum absolute value of the asymmetry for the Fe(001)- $p(1 \times 1)$ O surface (see inset of Fig. 3). It is seen that as soon as Fe is deposited on the surface the asymmetry decreases to about half of its initial value, and then an oscillating behavior takes place in very much the same way as in the He reflectivity curve. The periodicity of the oscillations matches up with the completion of successive deposited layers, as measured by the calibrated thickness monitor. This is a further independent confirmation of the relationship between surface order and spin-dependent properties. Moreover, upon annealing, the SPMDS and the ACS asymmetries recover to the initial value of the Fe(001)- $p(1 \times 1)$ O surface. This can be related to surface reordering as also indicated by LEED observations. In fact, the LEED

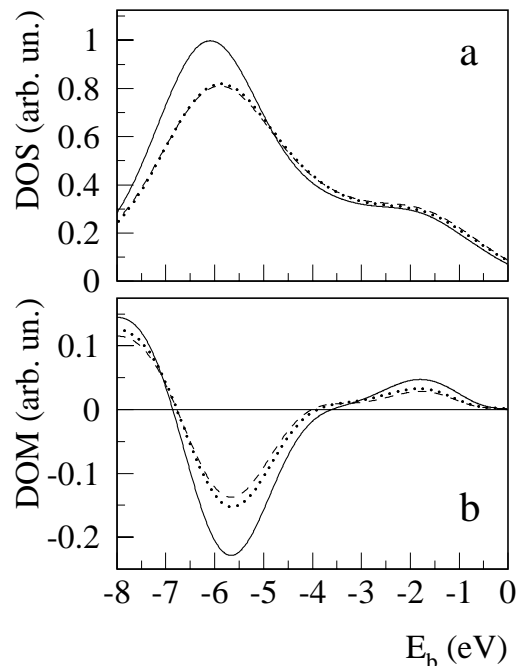


FIG. 2. Density of states (DOS) and density of magnetization (DOM) as obtained from SPMDS data. Continuous line: Fe(001)- $p(1 \times 1)$ O; dotted line: first minimum of Fig. 1; dashed line: first maximum of Fig. 1.

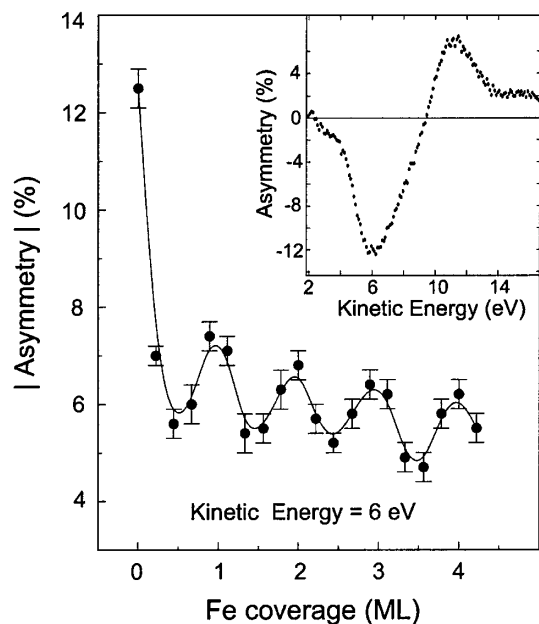


FIG. 3. Asymmetry at $E_k \approx 6$ eV from ACS data as a function of Fe deposition. The asymmetry $A(E_k)$ for the Fe(001)- $p(1 \times 1)$ O substrate is shown in the inset.

pattern becomes diffuse during deposition and becomes sharp again upon annealing.

In summary, we have shown that oxygen atoms act as surfactants in the growth of iron. While the room temperature homoepitaxial growth of iron proceeds in a disordered fashion (He reflectivity decreases exponentially with film thickness), the presence of oxygen induces a layer-by-layer growth as demonstrated by the oscillating behavior of the He reflectivity. An analysis of the surface density of states shows that, following the deposition of the first half monolayer of iron, the surface composition remains unchanged.

During the growth of iron on the Fe(001)- $p(1 \times 1)$ O substrate, we could measure in real time both structural and magnetization parameters obtaining a correlation between reflectivity (surface order) and asymmetry (magnetization). This then allows one to conclude that the oscillating behavior of the magnetization we observe is due to the oscillating behavior of the surface order and that the spin polarization of the electronic states at surfaces (both occupied and unoccupied) is strongly affected by the long range order at the surface.

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