Spin-Polarized Photoemission Study of Epitaxial Fe(001) Films on Ag(001)

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The electronic and magnetic character of epitaxial Fe films on Ag(001) has been studied as a function of Fe coverage by spin- and angle-resolved photoemission. At coverages well below a monolayer, the spectra exhibit a local spin-split electronic state. Although spectra for films in the monolayer coverage range display electronic structure in close agreement with calculated monolayer-film critical-point energies, no spin polarization is observed up to 2.5 monolayers. Thicker films approach the spin-split electronic structure and spin polarization of bulk Fe(001).

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A fundamental problem of magnetism is at what dimension long-range ferromagnetic order occurs. The question of whether two-dimensional ferromagnetism is possible was raised long ago.[1] Powerful computational methods have since been developed to investigate the electronic and magnetic structure of ultrathin films within the local-density approximation.[2-4] Recent calculations describing the spin-resolved band structure and consequent magnetic character of epitaxial Fe monolayers on Ag(001) predict an enhanced magnetic moment for one[3,4] or two[4] such Fe monolayers (ML). This is believed to be due to a decrease in coordination number and an increase in nearest-neighbor spacing experienced by the atoms comprising the monolayer, and a lack of hybridization between the electronic states of the overlayer and substrate. These studies thus address fundamental aspects of the formation and interplay between the electronic and magnetic character of a system.

Spin-polarized angle-resolved photoelectron spectroscopy is well suited for investigating such effects, as it provides an independent identification and decomposition of spin-split emission features for samples exhibiting ferromagnetic order. An additional fundamental question addressed in most studies of magnetic surface layers or thin films is a determination of the onset of long-range magnetic order as a function of temperature or film thickness. There is strong evidence to suggest that the exchange splitting alone *cannot* be taken as an indication of spontaneous magnetization or as a measure of long-range ferromagnetic order.[5-7] Since spin-polarized angle-resolved photoelectron spectroscopy measures the net polarization of the photoelectrons, it provides a direct measure of long-range magnetic order (or absence thereof) required to address the predictions of enhanced moments.

In this Letter, we report the results of spin- and angle-resolved photoemission studies of Fe films epitaxially grown *in situ* on Ag(001). The epitaxial system of Fe on Ag is well suited for these studies, since Ag has only very weak (*sp*) emission between the Fermi energy E_F and ≅3.5-eV binding energy, the energy range over which emission from the prominent Fe $3d$ bands occurs. With use of a photon energy of $h\nu = 60$ eV to minimize the photoelectron escape depth, optimum surface sensitivity is achieved. Use of this photon energy also permits direct comparison with previous work on bulk Fe(001) samples.[8]

The experiments were conducted on the TGM1 beam line of the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung (BESSY) synchrotron radiation facility. Details of the spin- and angle-resolving electron spectrometer have been described in detail elsewhere.[8] The total energy resolution was 0.4 eV at $h\nu = 60$ eV, including the linewidth of the normally incident, *s*-polarized light. Data were taken for normal emission with an angular acceptance cone of ±3°. Electron spin polarization was measured by means of a 100-keV Mott detector.

The Fe films were epitaxially grown on a Ag(001) film approximately 150 Å thick, which was previously grown *in situ* on an Fe(001) signal crystal (4×6 mm^2, 0.5 mm thick). An in-plane ⟨100⟩ axis (the normal easy-magnetization axis for bulk Fe) which lay along the long axis of the crystal was aligned parallel to the spin-sensitive direction of the Mott detector. All depositions were performed at room temperature in ultrahigh vacuum (base pressure of 2×10^{-10} Torr) and monitored by a quartz-crystal monitor. An absolute calibration for the incident Fe flux as measured by the quartz monitor was obtained from x-ray fluorescence measurements of Fe films deposited on GaAs substrates.[9] Sample cleanliness was verified with ultraviolet photoemission spectroscopy and Auger-electron spectroscopy, and the single-crystal structure and orientation of the films verified with low-energy electron diffraction (LEED). LEED showed the Ag films to be well ordered and oriented to the (001) face, as expected, although the beams were slightly broader than that of the bulk Fe(001) substrate. Upon Fe deposition at a rate of 1 ML/min, a clear (1×1) pattern is maintained as reported by Smith, Padmore, and Norris.[10] The sample was magnetically poled after each Fe deposition along the in-plane ⟨100⟩ axis parallel to the spin-sensitive direction of the Mott detector by placing it in a small magnetizing coil and applying current pulses to the coil.

Smith, Padmore, and Norris[10] have demonstrated the layer-by-layer nature of the growth of the first three monolayers of Fe on Ag(001) by observing breaks in the plot of the Fe and Ag Auger-electron-spectroscopy signals versus deposition time. They (erroneously) conclude, however, that such growth produces fcc Fe through a miscalculation of lattice mismatch.[11] Since there is only a 0.8% mismatch between the fcc Ag(001) and bcc α-Fe(001) surface nets after a 45° rotation, there is little reason to suspect formation of the thermodynamically unfavored γ-Fe (fcc) phase, for which the lattice mismatch is 12%.[11] Indeed, the spin-resolved photoelectron energy distribution curves (EDC's) obtained here for thicker films ($\theta \geq 5$ ML) exhibit structure characteristic of the bands along Γ-Δ-H as obtained from bulk bcc α-Fe(001) single-crystal data.[8]

Since the magnetic character of the film is expected to be intimately connected with film morphology, it is essential to confirm the mode of film growth. We have done so by plotting the ratio of the ultraviolet-photoemission-spectroscopy Fe $3d$ emission peak near E_F to the Ag $4d$ peak as a function of coverage, and comparing these data with curves calculated by use of the analysis of Ossicini, Memeo, and Ciccacci.[12] We find good agreement with the layer-by-layer mode for at least the first three Fe monolayers, confirming the results of Smith, Padmore, and Norris. This permits a direct comparison with calculated results which assume one and two complete monolayers.[3,4] We note that the LEED beams become significantly broader with further coverage, suggesting island formation beyond 3 ML as noted by Smith, Padmore, and Norris.[10]

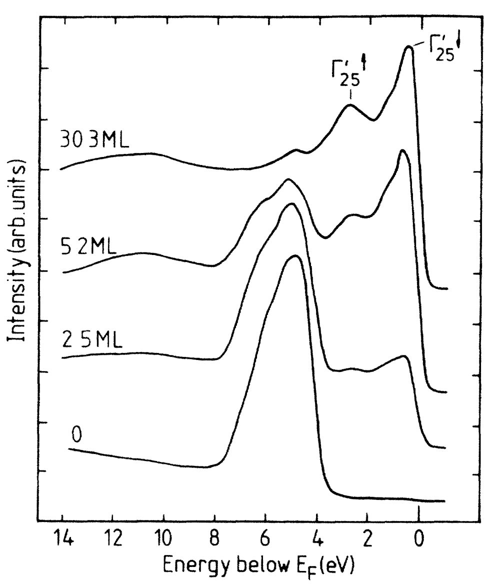

FIG. 1. Energy distribution curves for different coverages of Fe on Ag(001) taken at 60-eV photon energy for normal emission and s-polarized light. Coverages are given in equivalent Fe(001) monolayers.

In Fig. 1 we display a series of energy distribution curves for different Fe coverages, beginning with the clean Ag(001) substrate. The Ag(001) EDC is dominated by a broad peak at 4–7-eV binding energy (BE) due to strong emission from the Ag $4d$ bands. A plateau of relatively weak intensity due to Ag sp emission extends to E_F. Fe deposition results in a strong increase in emission, easily distinguished from that of the Ag, between $\simeq 3.5$-eV BE and E_F. Emission structure in this region develops significantly with Fe coverage, as shown in Fig. 2, where the Ag contribution has been subtracted. For the lowest coverage studied (0.15 ML), the Fe contribution displays two overlapping peaks of equal intensity, one just below E_F and the other at $\simeq 2.3$-eV BE. These peaks remain approximately equal in intensity until 0.45-ML Fe coverage, where emission at E_F has become larger. With increasing coverage, the peak at E_F becomes more prominent relative to the peak at 2.3-eV BE. For coverages between 0.95 and 2.5 ML, we observe a weak additional structure at 3-eV BE. The in-plane spin polarization P $[P \equiv (I_\uparrow - I_\downarrow)/(I_\uparrow + I_\downarrow)]$[8] was found to be very low for all films up to 2.5-ML coverage. The spin-averaged EDC and spin-polarization data for a 2.5-ML film are shown in Fig. 3(a); the spin polarization is zero within experimental error. Spin-resolved EDC's for such films are, of course, nearly identical to the spin-averaged EDC.

The spin-averaged EDC's shown in Fig. 1 show a significant increase in emission intensity at E_F between 2.5 ML (no spin polarization detected) and 5.2 ML—the next coverage studied, and the first coverage for which spin polarization was observed. In Fig. 3(b) we show spin-resolved EDC's for the 5.2-ML film (no Ag contribution subtracted). In this case, the majority-spin EDC consists of two peaks of nearly equal intensity, one at $\simeq 2.6$-eV and the other at $\simeq 0.6$-eV BE, while the minority-spin EDC is dom-

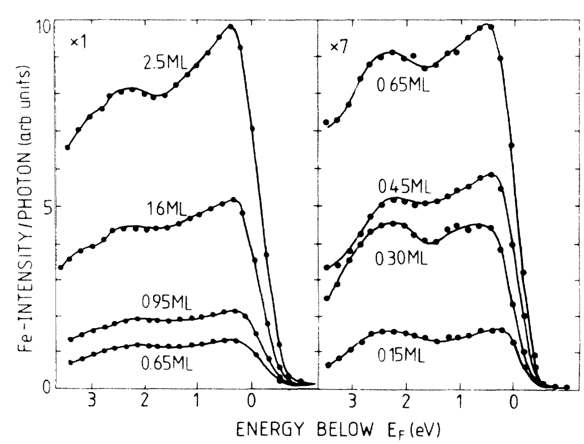

FIG. 2. Difference EDC's for Fe on Ag(001) for the same experimental conditions as in Fig. 1.

inated by a single strong peak at 0.3-eV BE.

Little change occurs in the EDC's up to 30 ML, the thickest film studied. Note that some Ag signal at $\simeq$ 5-eV BE is still apparent at 30-ML coverage (Fig. 1), further evidence that growth beyond the first three monolayers proceeds via island formation, as noted earlier.[10] These thicker films are not of particular interest in this study, and since the mode of film growth beyond 3 ML is not expected to produce uniform, well-ordered films, their electronic and magnetic character is expected to be somewhat different from that obtained for a good single-crystal surface.[8]

The range of Fe coverages studied here may be roughly divided into three regimes. For the lowest coverages ($\theta \leq 0.3$ ML), the Fe atoms exist as isolated atoms or 2–3-atom clusters on the Ag substrate, and the Newns-Anderson chemisorption model[13] should apply. Self-consistent calculations are available for comparison for the related problem of Fe impurities in Ag,[14] which exhibit a spin-split d resonance (virtual bound state) with a majority-spin local density of states at 2.14-eV BE. 50% of the minority-spin local density of states is unoccupied, with a peak at 0.07 eV above E_F. We may thus identify the two peaks in the low-coverage data with the two local-density-of-states peaks of this impurity model. The relatively large width of these peaks is attributed to clustering or lifetime broadening.

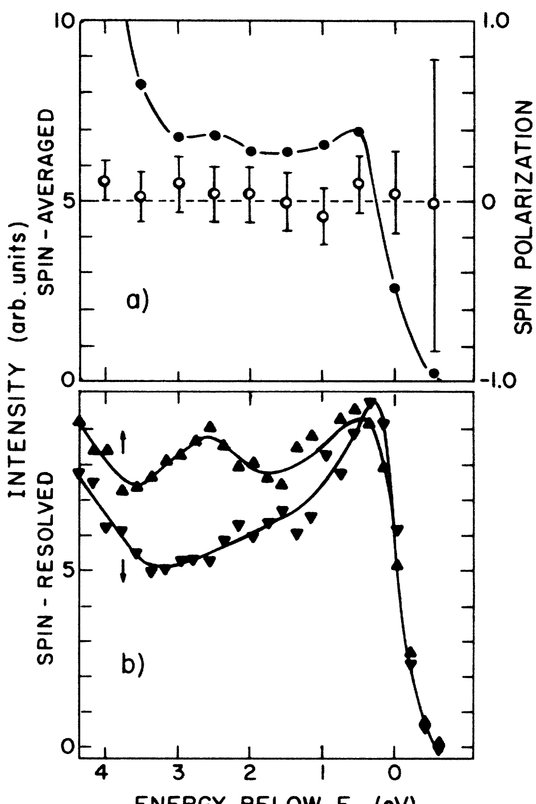

FIG. 3. (a) Spin-averaged EDC (closed circles) and spin-polarization data (open circles) for a 2.5-ML Fe film on Ag(001). (b) Spin-resolved EDC's for a 5.2-ML Fe film; upward pointing triangles indicate majority-spin contribution (downward, minority spin). No Ag contribution has been subtracted in either (a) or (b).

For Fe coverages in the monolayer regime (0.65 to 2.5 ML), we compare the data with the calculated band structure of Richter, Gay, and Smith[3] for an Fe ML on Ag(001). For the two-dimensional system formed by the Fe monolayer, the normal component of the momentum is undefined, and only in-plane band dispersions are allowed. In a nominally normal emission geometry, we confine ourselves to emission from states with very small values of $k_{\parallel}$, i.e., states near the Γ point. For the experimental conditions used, we expect to observe states which are odd with respect to reflection in the mirror plane perpendicular to the surface.[5,15] For these coverages we observe a weak structure at 3 eV in addition to the more well developed peak at 2.3-eV BE. Both peaks are attributed to the calculated majority spin states at Γ.[3] The peak observed near E_F may be identified with the calculated minority-spin critical point at 0.8 eV.[3] In contrast with the predictions of an enhanced magnetic moment for one[3,4] or two[4] monolayers, we observe no net in-plane spin polarization (no long-range ferromagnetic order) up to 2.5 ML, even though an exchange-split electronic structure is inferred from the data.

With increasing Fe deposition, one may reasonably expect contributions from initial states dispersing along the Γ-Δ-H direction (the surface normal) from approximately 3-ML coverage on, since the normal component of the momentum is now a meaningful parameter, and states with significant $k_\perp$ are well defined. In addition, surface states and resonances localized in the first two layers of bulk Fe(001) have been predicted to occur at Γ just below E_F and at 2.3-eV BE (odd states, minority spin), and at 0.8- and 2.3-eV BE (odd states, majority spin).[16] These surface bands have been observed by Turner and Erskine,[15] but are difficult to distinguish from bulk states in normal emission because the critical-point energies are very similar. The appearance of a net in-plane spin polarization indicating long-range ferromagnetic order at 5 ML appears to be associated with the development of emission intensity at E_F (Fig. 1). These data are similar to those observed previously for the bulk Fe(001) surface,[8] except that the peaks are broader and the background is stronger. This structure is consistent with emission from bulklike initial states dispersing along Γ-Δ-H[17,18] broadened by surface contributions. The spin-resolved EDC shown in Fig. 3(b) clearly resolves the emission intensity within 1 eV of E_F into two components: a broad majority-spin contribution at 0.6 eV attributed to the $\Gamma_{12'\uparrow}$ initial state (which for perfect experimental conditions is dipole forbidden), and a sharper minority-spin feature just below E_F due to the $\Gamma_{25'\downarrow}$ band.[8] The majority-spin feature at 2.6-eV BE is attributed to emission from the $\Gamma_{25'\uparrow}$ initial state. Only minor variations in intensity are observed in these features up to 30 ML, the thickest film studied. We regard the stronger background and the higher amplitude of the dipole-forbidde $\Gamma_{12'\uparrow}$ peak relative to the observed intensities in bulk sample studies[8] as an indication that the crystalline structure of these thicker films is not yet as good as bulk Fe(001). This is consistent with the formation of islands after completion of three complete monolayers, as noted earlier. The onset of a net in-plane spin polarization indicative of spontaneous magnetization or long-range ferromagnetic order at 5 ML is therefore associated with the development of states characteristic of the bulk Fe(001) surface, including states dispersing along the surface normal (Γ-Δ-H). The film has thus made a transition from surface-dominated two-dimensional behavior to a bulklike character.

The most striking result of this study is the absence of a net in-plane spin polarization up to 2.5-ML coverage, contrary to what one might expect from the theoretical predictions of enhanced magnetic moments for one- or two-monolayer films.[3,4] Although an exchange-split electronic structure may be inferred from a comparison of the data with calculation,[3] the absence of polarization indicates that such films cannot be magnetized remanently along the $\langle 100 \rangle$ axis at room temperature. This could be caused either by a film anisotropy significantly different from that in the bulk, or by a film Curie temperature T_C near or below room temperature. Experimental examples for both possibilities can be found in the literature. It has been shown that T_C of monolayer films of Co on Cu(111) is lower than for bulk Co,[19] although the exchange splitting exhibits little temperature dependence.[7] We were unable to cool our samples below room temperature to test this hypothesis. Such a large reduction in T_C (from 77 °C to near room temperture), however, would be very noteworthy, and is without experimental precedent. Recent measurements by Bader, Moog, and Grunberg[20] for Fe on Au(100) indicate substantial T_C values [$\gtrsim 0.5 T_C$(bulk)] for comparable Fe coverages. Alternatively, a strong surface anisotropy may force the moment to lie perpendicular to the surface, as observed for monolayer films of NiFe or Co on Cu(111).[19] Rado has pointed out, for example, that crystal faces having a threefold or higher symmetry axis normal to the plane have their surface anisotropy axis parallel to the surface normal.[21] In addition, with such a easy-magnetization axis, demagnetizing effects would tend to produce antiparallel domains, resulting in a zero net moment on a macroscopically averaged scale as sampled in a photoemission measurement. Neither effect (reduced T_C or surface anisotropy) is inherently included in the local-spin-density formalism on which the calculations[3,4] are based. Therefore, although the calculations are capable of predicting a magnitude for the magnetic moment, they are unable to specify a direction or temperature dependence.

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Note added.—Anisotropy calculations by Gay and Richter for a free-standing Fe(001) monolayer at the Ag lattice constant indicate that the easy axis is perpendicular to the surface[22] as suggested by this study.

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