

Chemisorption-induced change in thin-film spin anisotropy: Oxygen adsorption on the $p(1 \times 1)\text{Fe}/\text{Ag}(100)$ system

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Magneto-optical techniques are used to explore the magnetic anisotropy of ultrathin (1–3 monolayer) epitaxial Fe films on Ag(100) when exposed to oxygen. Small doses of oxygen produce striking changes in the spin anisotropy of bilayer magnetic films: the preferred spin orientation changes from perpendicular to the surface to an in-plane orientation. Low-energy electron-diffraction analysis indicates the oxygen adsorption is accompanied by significant structural changes in the film. The structural changes are consistent with recently observed effects of adsorbed gases on metal epitaxy. While some of the observed effects can be reconciled with the established thickness dependence of thin-Fe-film magnetic properties by assuming oxygen-induced quenching, and taking into account the structural changes of the film that accompany oxygen adsorption, the primary effect (oxygen-induced change of preferred spin direction) appears to be produced by electronic effects that govern the surface-anisotropy parameter. Previous disagreements between results obtained by spin-polarized photoemission and magneto-optical techniques are resolved.

I. INTRODUCTION

The magnetic properties of thin epitaxial Fe films on Ag(100) surfaces have been explored by various experiments^{1–6} and first-principles calculations.^{7–12} Spin-polarized photoemission experiments¹ failed to detect in-plane spin polarization in films having thicknesses below 2.5 monolayers (ML), suggesting that they were either nonmagnetic or that the remanent magnetization (\mathbf{M}_r) was perpendicular to the surface. The interesting possibility of perpendicular spin orientation in ultrathin magnetic films stimulated several additional experiments on the Fe/Ag(100) system and on similar capped thin-film systems. Ferromagnetic resonance studies² of Au-capped epitaxial Fe films of 2-, 3-, 5-, 17-, and 28-ML thicknesses indicated that, in films less than or equal to 2 ML thick, \mathbf{M}_r was perpendicular to the surface. Conversion-electron Mössbauer spectroscopy³ of capped Fe films on Ag(100) indicated that, at 15 K, 1- and 2.4-ML films had \mathbf{M}_r out of the film plane, and, at 5.5 ML, \mathbf{M}_r was in the film plane with an out-of-plane component at 300 K. More recent spin-polarized photoemission studies⁴ of uncapped epitaxial films have suggested that remnant perpendicular magnetization exists only for film thickness between 3.5 and 5 ML at 30 K, and that, above 100 K, no perpendicular remanence exists for any of the film thicknesses studied (0.8, 1.5, 3.5, 5, and 10 ML). Magneto-optical Kerr-effect studies⁵ contradict this result, finding remnant polar magnetization at 100 K for 1- and 2-ML films.

An accurate theoretical understanding of the magnetic anisotropy in ultrathin film systems remains a difficult challenge. The origin of magnetic anisotropy in bulk three-dimensional (3D) ferromagnetic materials is the spin-orbit interaction.¹³ In ultrathin films, the direction of \mathbf{M}_r is governed by a competition between the surface anisotropy, described by the surface-anisotropy constant

K_{us} , and the dipole-demagnetizing energy (shape anisotropy).¹¹ The spin-orbit component of the anisotropy energy, K_{us} , arises primarily from details of the electronic structure,¹² especially in regions near band crossings and near the Fermi energy. Slight alterations of the physical environment of the magnetic atoms in local-spin-density calculations can have large effects on total-energy differences among various spin states. The subtle energy differences, which determine the spin anisotropy, are also extremely sensitive to the convergence associated with computational parameters (i.e., the k -point mesh). These factors render calculations of magnetic anisotropy in ultrathin films very difficult. In addition, the dipole demagnetizing energy, which always favors in-plane magnetization, can apparently be affected by film morphology.^{14,15} This presents an additional experimental challenge to investigators wishing to address magnetic anisotropies in ultrathin films.

In spite of these difficulties, a few first-principles calculations of ultrathin magnetic films, including effects of spin orbit coupling,^{10–12} have been carried out. These studies predict anisotropy constants for selected free-standing magnetic monolayers as well as the layer dependence of the surface-anisotropy constant for ultrathin films. The system most extensively studied consists of Fe layers grown on Ag(100). This system appears to offer attractive features for systematic analysis of ultrathin-film magnetic phenomena. First-principles calculations for epitaxial $p(1 \times 1)\text{Fe}$ films on Ag(100) surfaces suggest that the electronic coupling between film and substrate is relatively weak^{7–9} and at the same time predict a variety of novel effects. A 40% enhancement of the magnetic moment per atom for monolayer and bilayer Fe films on Ag(100) was predicted to occur with a small reduction in moment of the second layer, i.e., $2.94\mu_B(S)$, $2.63\mu_B(S-1)$. Corresponding calculations^{10–12} including spin-orbit effects predicted that, for a monolayer of

Fe having a lattice constant governed by epitaxy onto Ag(100), the total spin-anisotropy energy is minimized if the magnetization is allowed to orient perpendicular to the surface. The calculations also predicted that for films thicker than 2-ML the shape-anisotropy contribution begins to dominate, forcing the magnetization at zero applied field to lie in the plane. These calculations, therefore, are consistent with the experimental detection of ferromagnetism in ultrathin Fe films on Ag(100), and also with the novel (perpendicular) magnetic anisotropy observed in the 1- and 2-ML films by the magneto-optical Kerr-effect studies.

Although there is general agreement between the various experiments that ultrathin Fe films on Ag(100) are ferromagnetic and that below 3-ML novel magnetic anisotropy exists (specifically, perpendicular anisotropy), several important discrepancies exist between the various experimental results. For example, the spin-polarized photoemission results⁴ suggest that remanent perpendicular anisotropy at 30 K does not persist below 3.5 ML or above 5 ML, and that above 100 K there is no perpendicular remanence for any film thickness. Magneto-optical Kerr-effect studies⁵ disagree with these results, finding a perpendicular easy axis at 30 K for 1-ML films, and perpendicular remanence at 100 K. There are also significant experimental contradictions among studies of film growth of Fe on Ag(100) that are discussed later. It is clear that additional studies of this system are justified based on its novel properties and the fundamental discrepancies between existing experiments.

In the present work, we have continued to study the magnetic properties of ultrathin epitaxial Fe films on Ag(100) and have also explored the modifications in magnetic properties of this system resulting from the chemisorption of oxygen on the magnetic layer. Our experiments show that trace amounts of surface oxygen cause significant changes in Kerr-effect signals that can only be due to changes in the thin-film magnetism. Submonolayer oxygen coverage causes the magnetic easy direction of bilayer films to change from perpendicular to the surface to an in-plane direction. This dramatic effect accounts for the disagreement between the polarized-electron spectroscopy results (which were contaminated with a few at. % O) and the magneto-optical Kerr-effect results. The results also suggest that caution should be used in drawing conclusions about ultrathin-film magnetic anisotropy in capped film systems in relation to calculations for inequivalent (uncapped) systems. The results presented clearly show that low levels of surface contamination can dramatically affect the magnetic behavior of ultrathin films.

II. EXPERIMENTAL DETAILS

A description of our experimental apparatus, including analysis of our Kerr-effect polarimeter sensitivity and a discussion of $p(1\times 1)\text{Fe}/\text{Ag}(100)$ sample-preparation techniques, has been reported.¹⁵ Our previous work on the Fe/Ag(100) system, as well as work by others,^{4,6,14,15} has shown that bcc Fe grows pseudomorphically on fcc Ag(100), and that the growth mode is complex and

dependent on substrate temperature as well as substrate morphology. The surface net of Ag(100) ($a = 4.09 \text{ \AA}$) accommodates the γ -Fe lattice ($a = 2.87 \text{ \AA}$) rotated 45° with a mismatch of only 0.7%. This suggests that stress resulting from the lattice mismatch between film and substrate will be minimal. The surface energy of Fe ($\sigma_{\text{Fe}} = 2550 \text{ mJ/m}^2$) is considerably larger than that of Ag ($\sigma_{\text{Ag}} = 1250 \text{ mJ/m}^2$). From these parameters, simple thermodynamical arguments¹⁶ lead to the prediction that Fe should nucleate and grow initially on Ag in what is known as the Volmer-Webber mode, in which islands of uniform height and several layers thickness form before complete wetting of the surface occurs. This prediction appears to be qualitatively correct at low coverage, although most experimental evidence obtained during growth of Fe films on Ag(100) suggests that nearly layer-by-layer growth occurs after several monolayers have been deposited.

Films used in the experiments reported here were prepared and studied *in situ* at pressures below 1×10^{-10} Torr. The 1-cm-diam \times 1-mm-thick Ag(100) crystals were aligned by x-ray Laue techniques and cut to an accuracy exceeding $\pm 1^\circ$. The surface step density of the substrate was probed by low-energy electron-diffraction (LEED) spot analysis, which indicated terrace widths comparable to or greater than the instrument transfer width (about 150 \AA^{-1}). The Fe films were deposited at substrate temperatures ranging from 100 to 300 K by electron-beam heating of a 2-mm-diam high-purity (99.999%) Fe wire. Film and substrate purity was determined using Auger-electron spectroscopy (AES), and film growth (typically 0.25 ML/min) was monitored on the sample in real time by AES and by a quartz microbalance placed approximately at $\frac{1}{10}$ the source-to-sample distance. Quoted film-thickness values are believed accurate to approximately 10%.

Before discussing our magneto-optical Kerr-effect measurements, it is useful to briefly review what is known about the growth behavior and structure of Fe thin films on Ag(100). Li *et al.*¹⁷ have recently reported a LEED study of this system, including an explicit discussion of the apparent contradiction between growth behavior deduced from observations of reflection high-energy electron-diffraction (RHEED) oscillations, and from other techniques, including LEED and Auger analysis. The LEED analysis by Li *et al.*¹⁷ indicates that the growth of Fe on Ag(100) at low coverage is neither layer by layer (Frank-van der Merwe) nor of Stranski-Krastanov type. LEED intensity calculations for a $p(1\times 1)\text{Fe}$ one-layer equivalent structure on Ag(100) yielded only poor fits with experimental data for any reasonable parameter variations of the Fe-Ag distance. LEED measurements of subsequent film growth (> 1 ML) suggested complex behavior in the 2–5-ML range characterized by poor-quality LEED spots and the disappearance of structure in I - V curves. Film growth above 5-ML thickness was characterized by a return of well-defined LEED spots and meaningful I - V spectra.

Since island growth should not be accompanied by RHEED oscillations, and the deterioration of LEED spots and simultaneous failure of $I(V)$ analysis suggests

the loss of long-range order in three- to five-layer Fe films grown on Ag(100), there is clearly a contradiction in the conclusions based on the RHEED and LEED analyses of film growth.

The growth mode of Fe on Ag(100) was initially reported¹⁸ to be the Stranski-Krastanov mode, in which the first few (in this case three) atomic layers grow layer by layer and succeeding layers by island nucleation and growth. In a RHEED oscillation study of the growth, Egelhoff and Jacob¹⁹ observed that when Fe is grown on Ag(100) at 300 K, the first RHEED oscillation was missing, but was present when film growth was carried out at 100 K. Forward-scattering studies (also by Egelhoff¹⁹) of Fe films at low coverage ($\ll 1$ ML) grown at 300 K indicate the presence of some second-layer atoms, but less than that occurs for Fe on Cu(100). Forward-scattering experiments using an Fe layer grown at 100 K and having a thickness defined by one RHEED oscillation indicated approximately 30% of the Fe atoms occupied second-layer sites.

RHEED oscillation studies by Heinrich *et al.*^{2,20} also initially observed the absence of a first oscillation, but later Fe-film-growth studies on more precisely aligned Ag(100) surfaces ($\Delta\theta < 0.5^\circ$) observed the first RHEED oscillation in films grown at 300 K. The RHEED oscillations suggested layer-by-layer growth starting at 1 ML of at least a nine-layer Fe film at 77 K and of five- or six-layer films at 300 K. Heinrich *et al.*²⁰ stress the importance of the quality of the surface and the method of surface preparation in determining the initial growth mode of Fe on Ag(100). Using Fe "whiskers" (which exhibit nearly perfect surfaces) as a standard, they have found that carefully aligned ($\pm 0.25^\circ$) and electropolished Ag(100) surfaces yield Fe-film-growth properties similar to that found in the homoepitaxy of Fe on Fe-whisker surfaces. These results suggest the substrate morphology, specifically the surface step density, plays an important role in the initial film nucleation and growth of Fe on Ag(100). Later, we will show that our Ag(100) surfaces are apparently smooth enough to yield growth properties generally corresponding to those reported by Heinrich *et al.*²⁰

III. MAGNETO-OPTICAL KERR-EFFECT RESULTS

We first present the magnetic effects observed in our experiments, and then return to issues pertaining to the thin-film structure. Figure 1 displays hysteresis curves obtained using the magneto-optical Kerr effect that illustrate the temperature and thickness dependence of the magnetic anisotropy of $p(1 \times 1)$ Fe on Ag(001). The magnetic properties of clean $p(1 \times 1)$ Fe on Ag(100) have been discussed in our previous publications.⁵ We find that the transformation from perpendicular to parallel spin orientation determined by magneto-optical Kerr-effect measurements occurs at 2 ML (as predicted theoretically). This transformation does not seem to be strongly dependent on temperature (as can be judged from Fig. 1) and does not seem to be strongly dependent on minor variations in the film morphology—specifically small variations in the step density of the growth template. The rel-

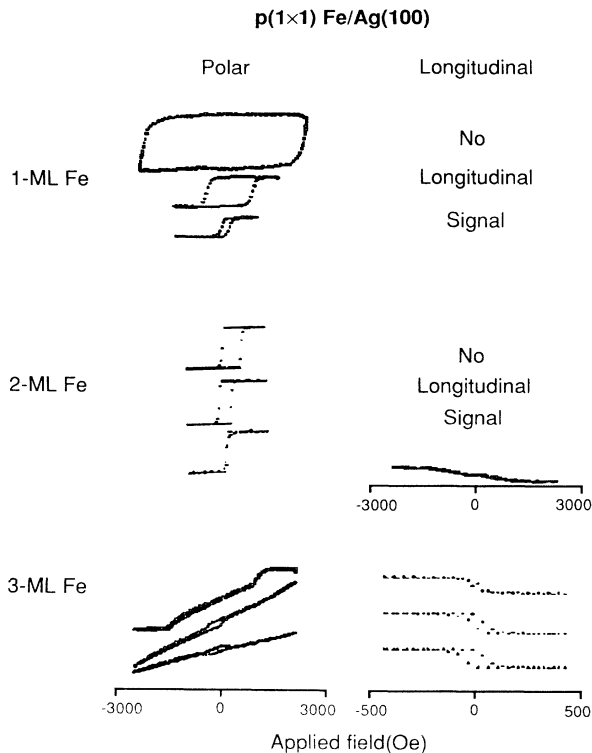


FIG. 1. Left panel: polar configuration (applied field perpendicular to the surface) magneto-optical Kerr-effect loops for $p(1 \times 1)$ Fe on Ag(001) as a function of thickness and temperature. Top, middle, and bottom loops for each film thickness correspond to 35, 100, and 300 K, respectively. Right panel: corresponding results for longitudinal configuration (applied magnetic field parallel to surface and in the plane of incident light).

ative insensitivity of the transformation from parallel to perpendicular magnetic anisotropy will be used later to argue that small structural modifications of the Fe film which accompany oxygen adsorption probably do not account for the dramatic oxygen-induced change in magnetic anisotropy observed in 2-ML Fe films on Ag(100).

Figure 2 displays the effects of oxygen dose on hysteresis loops for 2-ML Fe films grown on Ag(100) at ~ 100 K. Three distinct types of oxygen-dose experiments were performed on several 1.5- and 2-ML films. In one type of experiment, the direction of applied magnetic field was held fixed in either the polar configuration or the longitudinal configuration and a hysteresis loop was taken at 2-min intervals while the thin Fe film was exposed to 1×10^{-9} Torr oxygen. The oxygen pressure was determined using a Varian UHV-24 gauge uncorrected for oxygen and the oxygen dose in langmuirs ($1 \text{ L} = 1 \times 10^{-6} \text{ Torr sec}$) is indicated in the left panel of Fig. 1. In a second type of experiment, the magnet was rotated between polar and longitudinal configurations every 2 min and hysteresis loops were measured for the same sample in both configurations during oxygen exposure. This procedure verified the reproducibility of the results and showed that the sample-to-sample variation of results was within experimental error. The amplitudes of all

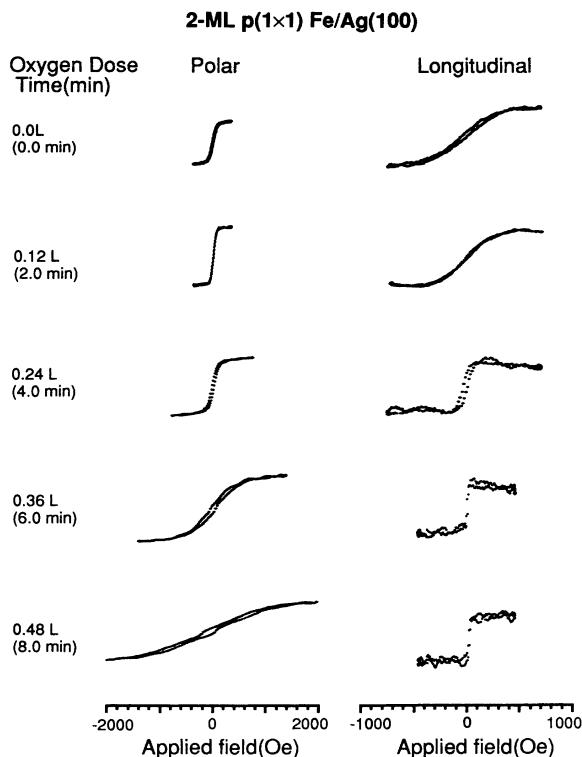


FIG. 2. Left panel: polar configuration (applied magnetic field perpendicular to surface) magneto-optical Kerr-effect hysteresis loops for 2-ML $p(1 \times 1)$ Fe on Ag(100) as a function of oxygen dose in langmuirs ($1 \text{ L} = 1 \times 10^{-6}$ Torr sec) and time in minutes. Right panel: corresponding results for longitudinal configuration (applied magnetic field parallel to surface and in the plane of incident light). All hysteresis loops have been normalized to the same height to emphasize shape differences in the loops resulting from oxygen adsorption.

loops (vertical axis) in Fig. 2 have been normalized to unity, but the applied field dependence of all loops in each column (horizontal axis) is plotted on the same scale. This permits direct visual comparison of the dependence on oxygen coverage of the hysteresis-loop properties (shape) and coercive force.

Magnetic saturation of the clean 2-ML films occurs when ± 100 -Oe polar fields are applied, or when ± 1000 -Oe longitudinal fields are applied. Clearly, clean 2-ML $p(1 \times 1)$ Fe films on Ag(100) at 300 K exhibit a “perpendicular” magnetic easy axis. The same film, after being exposed to a 0.48-L dose of oxygen, exhibits an in-plane easy axis: magnetic saturation occurs when ± 20 -Oe longitudinal fields are applied, or when ± 2000 -Oe polar fields are applied. Clearly, low concentrations of chemisorbed oxygen cause a dramatic change in the magnetic anisotropy of 2-ML $p(1 \times 1)$ Fe films on Ag(100).

Figure 3 displays, in greater detail, the dependence of the field required to saturate 2-ML $p(1 \times 1)$ Fe films either parallel (H_{\parallel}) or perpendicular (H_{\perp}) to the surface as a function of oxygen dosage in langmuirs. Figure 4 displays the corresponding Kerr-effect amplitude dependence on oxygen dosage. The absolute surface concentration of oxygen at a 1.0-L oxygen dose is also indicated in Figs. 3 and 4. The surface-oxygen concentration was ob-

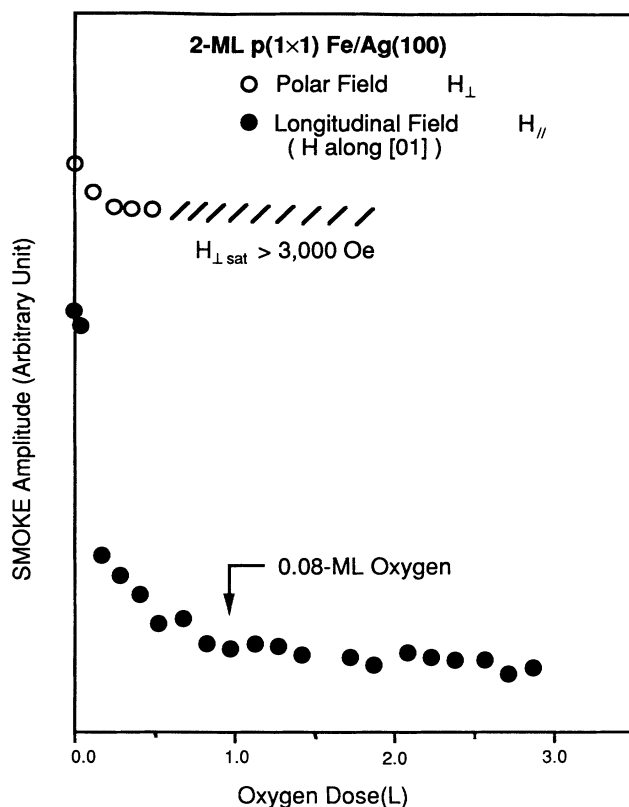


FIG. 3. Oxygen-dose dependence of surface magneto-optical Kerr-effect (SMOKE) amplitude for 2-ML $p(1 \times 1)$ Fe on Ag(100). Arrow indicates dose at which an 8 at. % oxygen coverage occurs.

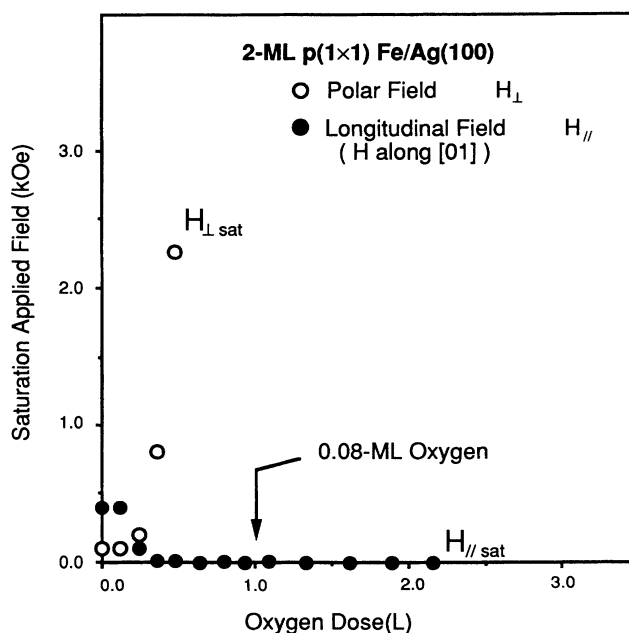


FIG. 4. Oxygen-dose dependence of fields required to saturate a $p(1 \times 1)$ Fe film on Ag(100) in the polar (H_{\perp} to film surface) and longitudinal (H_{\parallel} to film surface) configurations. Arrow indicates dose at which an 8 at. % oxygen coverage occurs.

tained by monitoring the Fe(703), Ag(351), and O(503) Auger intensities as a function of time while exposing a 2-ML $p(1 \times 1)$ Fe film to oxygen at 1×10^{-9} Torr, just as in the Kerr-effect studies. The oxygen-dose dependence of these Auger line intensities is shown in Fig. 5. The oxygen concentration was estimated by comparing Auger peak intensities using relative cross-section data.²¹ The results displayed in Figs. 3 and 4 show that the rapid decrease in Kerr-effect amplitude observed in the longitudinal configuration occurs over the same oxygen-coverage range that accompanies the rapid change in the field required to saturate the film. These changes occur at surface-oxygen concentrations below 10%.

It is useful to compare our measurements of the dose dependence of surface-oxygen concentration at a 2-ML $p(1 \times 1)$ Fe film with corresponding results for a bulk Fe(100) surface. Figure 5, therefore, compares our measured Auger intensities for Ag(351), Fe(703), and O(503) versus oxygen dose with surface-oxygen-concentration results obtained by others for bulk Fe(100). For a given dose, we find that oxygen concentration at the thin-film Fe surface is lower by a factor of 2 compared with the bulk Fe(100) surface. Figure 5 establishes the approximate oxygen coverage of $p(1 \times 1)$ Fe on Ag(100) after a 1-L exposure to be 8 at. %.

Two facts are immediately apparent from Figs. 3 and 4. First, the polar magneto-optical Kerr-effect amplitude is not significantly affected by oxygen dose ($0 \leq \Theta \leq 0.5$ L), even though the field required to saturate the film in-

creases significantly. Second, the longitudinal magneto-optical Kerr-effect signal is dramatically reduced, primarily in the coverage range $0 \leq \Theta \leq 0.5$ L, and above $\Theta = 0.5$ L there is little change. In the same coverage range, where the greatest decrease in longitudinal magneto-optical Kerr-effect signal occurs, the field required to saturate the film also decreases dramatically.

The effects displayed in Figs. 2–4 reflect changes in magnetic properties of the 2-ML $p(1 \times 1)$ Fe films resulting from the low-coverage chemisorbed layer of oxygen, not from the oxygen itself. It has been shown by spin-polarized photoemission that the $2p$ orbitals of $p(1 \times 1)$ O on a (bulk) Fe(100) surface²² are polarized (exhibit exchange splitting throughout the two-dimensional Brillouin zone). Similar effects have been observed for oxygen on thin Fe films grown on W(100).²³ However, direct contributions to magneto-optical Kerr-effect signals from a magnetically polarized oxygen layer (especially at coverages below 10%) are expected to be very small. Interband optical excitations involving the O $2p$ orbitals at ~ 6.0 eV binding energy are not possible at the laser wavelength, $\lambda = 6328$ Å, used in our magneto-optical Kerr-effect measurements, and spin-orbit effects in oxygen are much smaller than in Fe. Contributions from these effects can be ruled out.

IV. LEED ANALYSIS

Our magneto-optical Kerr-effect studies of oxygen-induced changes in magnetic behavior of $p(1 \times 1)$ Fe thin films on Ag(100) were accompanied by LEED analysis of the substrate, of the prepared films, and of structural changes in the film resulting from oxygen exposure. It is not unreasonable to expect significant structural changes in a metastable thin-film structure resulting from oxygen adsorption. Egelhoff and Steigerwald²⁴ have observed that deliberately adsorbed gases can favorably affect the epitaxial growth of metals on metals. In many cases, chemisorbed oxygen (and other strongly bound atoms) were found to move to the growing surface without affecting the degree of epitaxial ordering, and at the same time, tended to suppress undesirable effects such as interdiffusion and agglomeration. We have not studied effects of oxygen on the film during film growth of Fe on Ag(100), but have carried out both LEED intensity versus voltage (I - V) and spot-profile analyses of the substrate, and of the thin-film structures before and after exposure to oxygen. These LEED studies detected significant structural changes in the Fe thin films that accompany the changes in their magnetic behavior described in Sec. V and illustrated in Figs. 2–4.

It is reasonable to rule out direct changes in the LEED spot profiles due to scattering from the oxygen atoms. The highest oxygen-surface concentration of relevance in the present discussion is below 10 at. %. In addition, inspection of the atomic-scattering intensities²⁵ for various atoms over the typical energy range used in LEED studies (50–200 eV) reveals the scattering intensity for oxygen atoms to be significantly lower than that of transition- and noble-metal atoms above 100 eV. No evidence of an ordered oxygen layer at higher coverage (as reported on

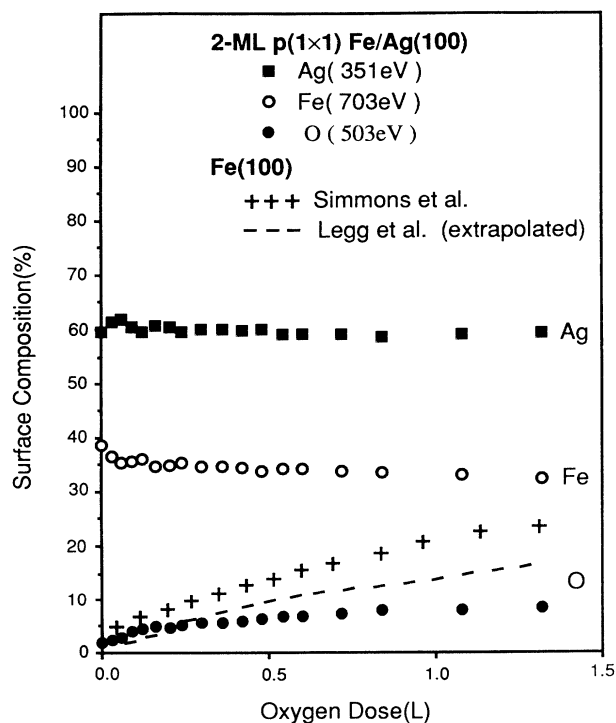


FIG. 5. Auger-spectroscopy results for oxygen up-take by a 2-ML $p(1 \times 1)$ Fe film on Ag(100) compared with corresponding published results for bulk Fe surfaces: plus signs (+), Simmons *et al.* (Ref. 26); dashed line, Legg *et al.* (Ref. 27). The surface "composition" was calculated from Auger peak intensities using sensitivity factors.

bulk Fe surfaces^{26–29}) was observed in our LEED studies; therefore, it is likely that, at low coverage, oxygen atoms chemisorb at random sites, and therefore do not contribute directly to diffracted-beam intensities. Based on this, one can argue that any significant changes in spot profiles that occur at low oxygen coverages represent structural changes in the metal film rather than scattering from the oxygen atoms.

Our LEED studies of Fe epitaxial growth on Ag(100) generally reproduced what has been reported by Li *et al.*¹⁷ both qualitatively and quantitatively, with the exception that frequently we were able to obtain good I - V curves for 2-ML $p(1\times 1)$ Fe films. In this sense, we believe that our results also agree with findings of Heinrich *et al.*²⁰ in the 1–3-ML thickness range. Our magneto-optical Kerr-effect results reported in Figs. 2–4 were not found to depend significantly on the quality of LEED I - V curves, only on the oxygen coverage. We did observe some deterioration of the quality of LEED patterns, specifically beam broadening accompanied by an increased diffuse background, over the Fe coverage range $0 \leq \theta \leq 3$ ML, as reported by Li *et al.*¹⁷ At 1-ML coverage, our I - V curves for (11) beams resemble those reported by Li *et al.*, but we are also able to obtain good I - V curves at 2 ML. For the purpose of the present work, we

limit our attention to changes in LEED spot profiles that accompany the adsorption of oxygen at low coverage on the 2-ML $p(1\times 1)$ Fe films.³⁰

Figure 6 displays a sequence of LEED beam spot profiles that were obtained during Fe-film growth on Ag(100) and during subsequent adsorption of oxygen. The LEED spot displayed in the upper left panel establishes the instrument response at 165 eV. This spot was obtained using a precisely aligned (0.1°) Si(111)7×7 surface having terrace widths exceeding 1000 Å. The spot profile corresponds to an instrument transfer width of approximately 150 \AA^{-1} . The upper right panel displays (11)-beam spot intensity contours for a 2-ML Fe film on Ag(100) prior to oxygen exposure.

The spot profile and width of beams from the clean Ag(100) surface (not shown) were comparable to the spot shown (upper left panel), which established the instrument response function. Therefore, the clean Ag(100) surface had average terrace widths of $\sim 100 \text{ \AA}$ or slightly greater. This result was expected based on Laue photographs of the crystal taken during alignment and polishing. Spot profiles from the 2-ML $p(1\times 1)$ Fe film grown on the Ag(100) substrate are considerably broader (at least by a factor of 3), suggesting that the Fe layer consists of two-dimensional islands having average widths of ~ 30 – 50 \AA . The spots from the 2-ML film were observed to broaden and narrow slightly as the electron-beam energy was varied, which is a manifestation of in-phase and out-of-phase scattering conditions for the islands. This behavior further supports the hypothesis of island-structure formation.

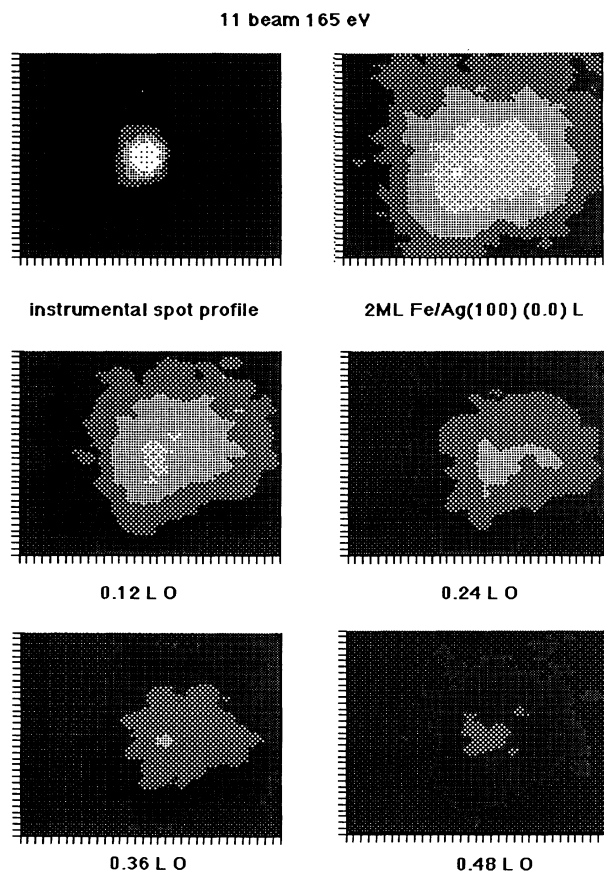


FIG. 6 Spot profiles of a 2-ML $p(1\times 1)$ Fe film on Ag(100) after film growth (upper right panel) and after exposure to various oxygen doses (lower four panels). Upper left panel: instrument response function obtained from a precisely aligned Si(111) surface.

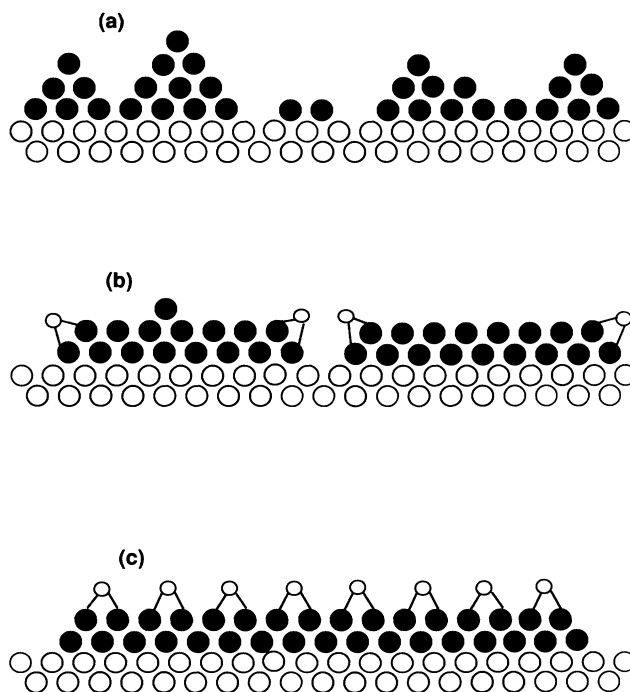


FIG. 7. Model illustrating how oxygen atoms, acting as a surfactant, can increase the order of a thin-film structure. Upper panel: film structure prior to oxygen adsorption. Center panel: low-coverage oxygen increases island size. Lower panel: saturated coverage.

The remaining four panels show that the spot profiles are not stable under oxygen adsorption. After exposure of the film to 0.12 L O, the LEED spot size decreases slightly, suggesting additional order and larger island sizes. Subsequent oxygen doses result in a significant reduction of spot size (by approximately 30%), suggesting that the average island size is increased. Many sets of LEED data at different energies were found to exhibit the same behavior. These effects are interpreted as resulting from physical changes in the size distribution of the Fe islands at the surface induced by chemisorbed oxygen.

The apparent oxygen-induced spreading of Fe islands is not unreasonable based on the previously described work of Egelhoff and Steigerwald.²⁴ One can view the chemisorbed oxygen atoms as acting as surfactants, reducing the surface energy of the film and thus promoting wetting. Figure 7 illustrates how oxygen atoms could affect the film structure in a manner consistent with the LEED results presented in Fig. 5.

V. DISCUSSION

The experimental facts presented in Secs. III and IV can be summarized as follows. Fe films grown on Ag(100) at temperatures between 80 and 300 K form epitaxial island structures similar to the idealized illustration in Fig. 7(a). Higher growth or annealing temperatures promote interdiffusion, which is accompanied by irreversible changes in magnetic properties. The Fe clusters are in good registry with the Ag(100) substrate, but the atomic-scale thickness varies in a manner that is consistent with an average terrace width of 30–50 Å at film thickness of 2 ML. The sticking probability of oxygen on these thin-film structures is approximately 50% lower than on a bulk Fe surface, and detectable structural changes (increase in island size) accompanies oxygen adsorption, even at oxygen surface concentrations of 5 at. % or less.

Oxygen affects the $p(1 \times 1)$ Fe film magnetic properties in two ways: it reduces the magneto-optical Kerr-effect amplitudes in both perpendicular (small change) and longitudinal (large change) applied-field configurations, and it dramatically changes $H_{\perp \text{sat}}$ and $H_{\parallel \text{sat}}$, the applied fields required to bring the film to magnetic saturation perpendicular or parallel to the surface.

While a detailed understanding of the oxygen-induced changes in magnetic behavior demonstrated in Figs. 2–4 may require electronic-structure calculations, some of the changes are consistent with what is known about (1) the layer-dependent magnetic properties of $p(1 \times 1)$ Fe on Ag(100),⁵ and (2) the structural changes that accompany an oxygen dose and how these microstructural changes may affect the magnetic properties of the films. Strong polar magneto-optical Kerr-effect signals are observed in 1- and 2-ML films. The 1-ML films require a significantly higher value of H_{\perp} to magnetically saturate the film (refer to Fig. 1). If a low coverage of chemisorbed oxygen increases the average terrace width of nominal 2-ML films, but also partially quenches the top-layer moments, one could imagine the net effect would be to significantly increase the saturation field (due to a reduced effective film thickness) while not greatly affecting the Kerr-effect am-

plitude (the decrease due to moment quenching being partially compensated by the increase in effective 2-ML-thick area).

The same structural-change arguments can also partially account for the decrease in longitudinal magneto-optical Kerr-effect amplitude—which is presumably associated with regions of the film which exceed 3-ML thickness prior to the oxygen dose. These regions would tend to support in-plane magnetization prior to an oxygen dose, but would revert to perpendicular magnetization either due to structural changes or partial quenching of the top-atom-layer magnetic moment by oxygen. This behavior also favors small changes in Kerr-effect amplitude for H_{\perp} and larger ones for H_{\parallel} .

Cochran *et al.*³¹ have recently reported Brillouin-scattering and ferromagnetic resonance experiments that address anisotropies in ultrathin fcc Fe(001) films grown on Cu(001), including experiments which indirectly probe the effects of surface roughness on the ultrathin-film magnetic anisotropy. These studies showed that growing a few monolayers of Cu on the Cu(001) substrate prior to growth of the Fe(001) layer yielded higher (perpendicular) uniaxial anisotropy. Related work reported by Heinrich *et al.*⁶ also suggests that a decrease in the density of atomic steps increases the perpendicular anisotropy parameter, K_{us} . This conclusion was based on studies of 3-ML Fe films grown on both conventional Ag(001) surfaces and on ultrasmooth Ag(001) surfaces prepared by epitaxy starting with a very smooth (001) facet of an Fe whisker. From these results, it appears that if film morphology dominates the magnetic behavior, the larger terrace widths produced by oxygen chemisorption should *not* force the remanent magnetization into the plane, as observed in our experiments.

Pappas *et al.*³² have studied the magnetic properties of ultrathin Fe films on Cu(001) using spin-polarized secondary-emission spectroscopy. These studies also addressed the effect of oxygen coverage on the magnetic anisotropy, finding an abrupt transition from perpendicular to parallel magnetization at a critical oxygen coverage. In these experiments, the “clean-surface” transition from perpendicular to in-plane magnetism occurs at ≈ 6 ML (at 100 K), while our experiments for Fe on Ag(001) indicate a transition at 3 ML. An oxygen dose of 3–6 ML applied to the Fe films on Cu(001) yields a transition from perpendicular to parallel magnetization at approximately 0.5 L; the corresponding transition for a 2-ML Fe film on Ag(001) occurs at approximately 0.25 L—which we have determined to correspond to a surface concentration of approximately 2 at. % O.

VI. CONCLUSIONS

The disagreement between spin-polarized photoemission measurements⁴ and magneto-optical Kerr-effect measurements⁵ of magnetic anisotropy in thin Fe films on Ag(001) are resolved by the results presented in this paper. Some of the polarized-electron experiments were carried out with oxygen contamination of ~ 5 at. % O, and this level of contamination has been shown to dramatically affect the magnetic anisotropy of Fe thin

films on Ag(001).

While very low oxygen contamination (~ 5 at. % or less) of 2-ML Fe films grown on Ag(100) produce significant (30%) changes in the average terrace widths, it is unlikely that these morphological effects drive the dramatic changes in magnetic anisotropy. The predicted effect of a smoother surface (based on other experiments described in Sec. V) is to increase the surface-anisotropy parameter, which should increase the tendency of the film to adopt a perpendicular magnetization direction; just the opposite is observed. While a smoother (more uniform) thin film may also yield a higher demagnetizing-energy contribution to the total magnetic anisotropy (which would favor an in-plane magnetic alignment), there is no experimental evidence that this is a strong effect. Supporting this view is the previously mentioned critical-thickness insensitivity of the transformation from perpendicular to parallel anisotropy for films having step densities differing by an amount comparable to the oxygen-induced changes (30%).

Heinrich *et al.*⁶ have deduced the separate contributions to the ultrathin-film anisotropy parameter K_{us} for Fe on Ag(001) from the Fe/vacuum interface, for the Fe/Ag interface, and for an Fe/Au interface. These

values are $K_{us} = 0.96, 0.63,$ and 0.30 erg/cm², respectively. A total surface anisotropy for an Fe/Ag film (obtained by adding the two interface values) equal to $K_{us} = 1.6$ erg/cm² is predicted to support perpendicular magnetization in films to ~ 7 ML thickness. We find that oxygen-free Fe films on our best Ag(001) surfaces (150-Å terrace widths) revert to parallel-spin alignment at about 2 ML. Clearly, higher-quality substrates and films will be required to test the absolute accuracy of these values of K_{us} . However, Heinrich *et al.*⁶ did observe a very large reduction in K_{us} (to 1.0 erg/cm²) when a clean 14.2-ML Fe film was oxidized to 6 at. %. This result is consistent with the abrupt transition from perpendicular to parallel magnetization we observe at very low (2 at. %) oxygen coverage. Therefore, all results appear to suggest that the thin-film anisotropy of Fe on Ag(001) is dominated by spin-orbit contributions (electronic rather than structural effects) at the Fe/vacuum interface.

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11 beam 165 eV

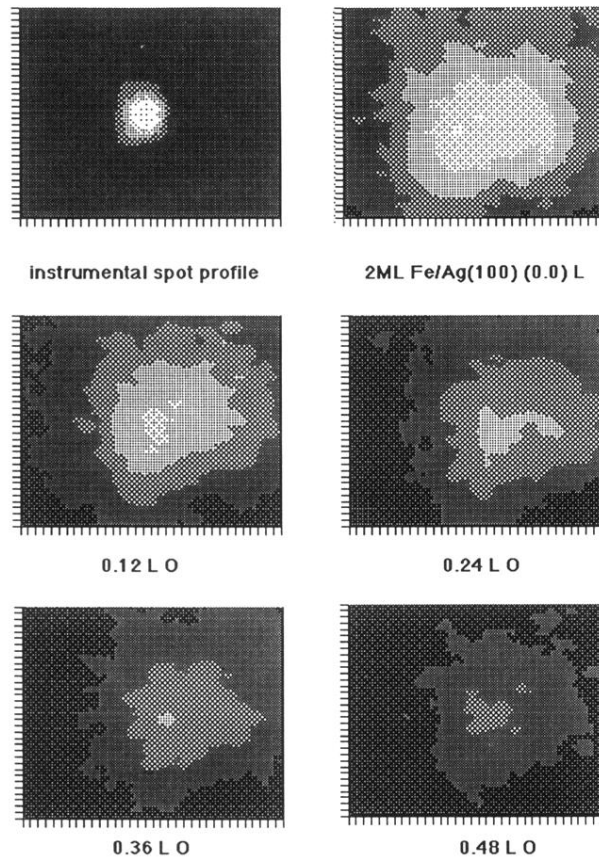


FIG. 6 Spot profiles of a 2-ML $p(1 \times 1)$ Fe film on Ag(100) after film growth (upper right panel) and after exposure to various oxygen doses (lower four panels). Upper left panel: instrument response function obtained from a precisely aligned Si(111) surface.