

Magnetic Interface States and Finite-Size Effects

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Studies of the formation of a nonmagnetic/magnetic silver/iron interface by spin-polarized photoemission identify magnetic interface states showing discrete binding energies dependent on the number of atomic layers in the overlayer. The results for one layer of silver on iron are in good agreement with a full-potential linearized-augmented-plane-wave calculation and tight-binding modeling allows us to reproduce qualitatively the layer-dependent binding energies for one, two, and three layers of silver on iron. The interface states appear to be related to a minority surface resonance on the iron surface.

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In recent years there has been considerable interest in the properties of magnetic surfaces [1], thin films [2], and multilayers [3]. Much of the experimental work has been oriented towards understanding two-dimensional magnetic phenomena; testing predictions of enhanced magnetic moments at surfaces and in thin films [4], and understanding the properties that determine anisotropy in these films [5]. The technological drive for such experiments lies in the possibility of tailoring new materials for the recording and device industries. In early work [6] the magnetic thin films were covered with a nonmagnetic protective coating such as silver before making the magnetic measurements. Initial disagreement between experiments and theory, particularly in the hyperfine splittings, was resolved with calculations [7] showing that significant changes in the electronic structure occur at the interface. Such interfacial properties may also be important when many repeat units of these thin-film systems (i.e., multilayers) are grown. Indeed, recent theoretical work [8] has emphasized the interfacial properties as a possible explanation of the magnetic coupling in certain transition-metal multilayer systems, examples of which include iron/chromium [9,10] and iron/copper [11,12] superlattices. In such systems it is possible to achieve either ferromagnetic or antiferromagnetic coupling of adjacent ferromagnetic iron layers depending on the thickness of the intervening layer. The model is similar to a picture [13] which has already been used to describe the magnetic properties of rare-earth compounds and superlattices, where the Coulomb exchange interaction is of paramount importance. In the case of transition metals on the other hand, the hybridization interaction at the interface is assumed to be the dominant effect. The related giant magnetoresistance properties [10] of the Fe/Cr superlattices and the large enhancement of the Kerr rotation [12] in the Fe/Cu multilayers make these systems particularly interesting.

In this Letter we describe spin-polarized photoemission experiments that directly probe the electronic states at a magnetic/nonmagnetic metal interface formed by depositing silver on an iron substrate. We are able to demonstrate that the binding energy of the interface states are strongly layer dependent—as the silver thickness increases these states move up to and probably through the Fermi level. Spin-polarization analysis of the photoemitted

electrons shows that these localized interface states are magnetic. *Thus both the electronic and the magnetic properties of the interface may be modified by the presence of the nonmagnetic thin film.* Such effects may well need to be taken into account when the properties of overlayers and multilayers are being considered. By comparing our experiments with the results of tight-binding calculations we are able to show that the presence of the silver overlayers leads to the localization of a previously identified iron surface resonance [14] into the region of the interface. Similar observations have already been made for the Nb/Pd interface [15] where a Nb surface resonance again localizes in the interface and for the Pd/Fe interface [16] where a spin-split interface state in the Pd 4*d* bands has been reported. However, unlike in those studies, the present experiment finds a discrete new binding energy for the interface state as each layer of silver is deposited. These observations are qualitatively reproduced in our tight-binding modeling.

The spin-polarized photoemission experiments reported here were carried out on an apparatus which will be described in detail elsewhere [17]. Briefly, spin detection is achieved with a compact low-energy spin detector [18] and uses light provided by the U5 VUV undulator at the National Synchrotron Light Source. The angular resolution of the hemispherical analyzer was $\pm 1.5^\circ$ and the combined photon and analyzer energy resolution was 0.35 eV. The Fe(001) crystal was manufactured in the form of a picture frame with each leg along a $\langle 100 \rangle$ direction and magnetized using a coil wound around one leg. The crystal was cleaned by repeated argon-ion bombardment and annealing cycles. The surface contamination level was monitored initially using Auger electron spectroscopy and in the final stages using photoelectron spectroscopy. The surface crystallographic order was examined with low-energy electron diffraction (LEED).

The silver films were evaporated at room temperature and at a rate of approximately 0.25 monolayer (ML) per minute. The iron and silver Auger ratios were measured as an estimate of the coverage and the evaporations were monitored using a quadrupole mass spectrometer. LEED measurements showed a good sharp $p(1 \times 1)$ pattern at all coverages up to approximately 3 ML, after which the patterns became less sharp. As a result, in the following discussion we restrict our observations to the first three

monolayers.

The tight-binding calculations [19] were carried out for thirteen layers of iron and with one to four layers of silver (a total of 21 layers for the thickest films). A two-center nonorthogonal basis set was used, the parameters being taken from Papaconstantopoulos [20]. The silver-iron interaction parameters were taken as the mean of the iron and silver parameters [21] and where required the scaling scheme of Andersen and co-workers [20–22] was used. The on-site silver energies were also adjusted to align the silver and iron Fermi levels. The iron and silver lattice constants were taken as the bulk values and for the interfacial separation the mean of the iron and silver interlayer spacings was used following Fu and Freeman [23]. The calculations for a thirteen-layer iron film and the same film with a silver monolayer were compared with the results of a full-potential linearized-augmented-plane-wave (FLAPW) calculation [7,24] and found to be in good agreement. No attempt was made to adjust the parameters so as to fit the experimental observations as the principle aim was to examine trends.

Figure 1 shows the evolution of the spin-integrated angle-resolved photoemission spectra at normal emission

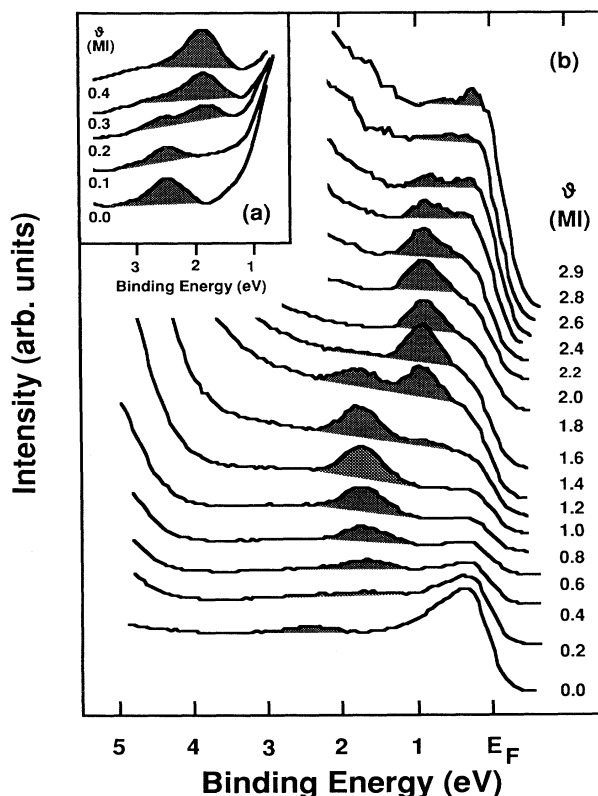


FIG. 1. Normal-emission angle-resolved photoemission spectra at a photon energy ($h\nu$) of 52 eV and p -polarized light ($\varphi_i = 70^\circ$), showing the evolution of the spectra with increasing silver overlayer thickness (ϑ) in monolayers (ML) for (a) the low coverage regime 0.0–0.4 ML and (b) coverages up to ~ 3 ML.

and 52-eV photon energy with increasing silver coverage. (For clarity the number of spectra shown has been limited, data were collected for every 0.1 ML of silver.) The region within the first 4 eV of the Fermi level includes the iron d bands and the silver s - p bands. For the bulk materials the photoemission spectra are characterized by a peaked structure near the Fermi level for iron and for silver by structureless intensity stretching from the Fermi level to the start of the silver d bands at ~ 4 -eV binding energy. The feature at 2.4-eV binding energy on the clean Fe(001) surface [Fig. 1(a)] has previously been identified as a minority-spin surface resonance [14]. As the silver coverage is increased this feature attenuates and is no longer observable at ~ 0.4 -ML silver coverage. However, after only ~ 0.2 -ML silver deposition a new feature at 1.7-eV binding energy is seen to coexist with the surface resonance. This new feature continues to increase in magnitude, maximizing at approximately 1-ML coverage [Fig. 1(b)]. As the second monolayer starts to form, the peak decreases in intensity and from 1.2 ML another feature at 1-eV binding energy is observed. The 1.7-eV peak, which we associate with a single monolayer film, continues to decrease in intensity. The peak at 1 eV we correlate with the 2-ML film since it peaks in intensity at 2-ML coverage and then decreases in intensity as the third layer is deposited. Although the features in successive layers are getting weaker, a new feature at approximately 0.3-eV binding energy is still seen to grow in and we associate this with the three-layer silver film. We assume that for higher coverages the peak would move through the Fermi level.

It is evident that for each silver/iron overlayer system, 1, 2, or 3 ML, there is a distinct electronic state associated with it. The attenuation of the intensity of the peaks as a function of coverage is consistent with their being states at the iron/silver interface, which is continuously buried. Since all these states have the same symmetry (as determined by their dependence on the polarization of the incident light) and the minority-spin surface resonance is attenuated [see Fig. 1(a)] on depositing silver rather than extinguished as in the case of oxygen absorption, we look for a common origin by investigating their spin character. Figure 2 shows that a dip in the spin polarization corresponding to the position of each of the overlayer states is observed; this is as a result of all the states being of minority character. The corresponding majority states are broader, weaker, and not so easily resolved from the substrate features. Consequently, in the following we will concentrate on the minority states. With increasing silver deposition the overall level of spin polarization is diminished and in a manner which is consistent with covering a magnetic substrate with a non-magnetic overlayer. Further, the observation that the states are magnetic lends support to the proposal that they are located in the interface rather than in the silver layer.

It should be noted that the iron d bands (Fig. 1) ap-

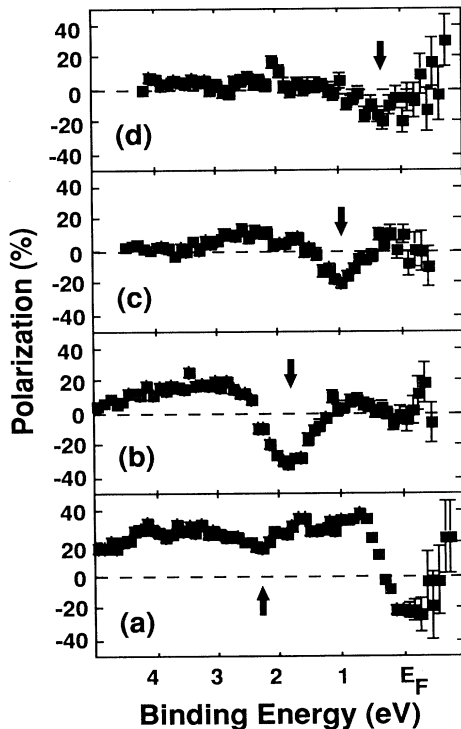


FIG. 2. Spin-polarization spectra taken at normal emission, $h\nu=52$ eV and $\varphi_i=70^\circ$ for (a) clean Fe(001) and with silver overlayers, (b) 1 ML, (c) 2 ML, and (d) 3 ML thick. The arrows mark the positions of the peaks in the photoemission spectra shown in Fig. 1 for each coverage.

pear to attenuate much more rapidly than one would expect for small silver coverages. This is largely due to the substantial surface contribution to the iron spectrum under these experimental conditions. For instance, a 0.1-L oxygen dose ($1 \text{ L} = 10^{-6}$ Torr) decreases the iron spectral intensity by $\sim 50\%$. At photon energies (e.g., $h\nu = 37$ eV) where the spectra are less dominated by surface features, the d bands are more prominent and the interfacial features are relatively weaker.

Several earlier experimental studies of thin-film growth have identified layer-dependent states in both silver [25] and alkali-metal overlayers [26]. The results of these experiments have been interpreted in terms of a phase model analogous to that used in the discussion of surface-state formation [27]. Thus the analysis involves a phase shift of $2kd$ within the thin film, or potential well, where d is the thickness of the film and k is the free electron wave number representing the state within the well. Although not included in the phase model the periodic structure within the well is reflected in the thicker silver films in that eventually the allowed states map the band states of the overlayer [25]. In the present study the films are still within the ultrathin regime where it is less obvious that the "bulk" band structure of the overlayer will play a role. However, it may be anticipated that the periodic structure of the film will still result in quantization effects dependent on the film thickness [28]. This could then

lead to states moving to or away from the Fermi level depending on the individual case. The initial iron surface resonance from which these states are derived involves d states as well as s and p states and does not therefore lend itself to a rigorous treatment within the phase analysis, which was originally demonstrated for s - p -derived states [27]. We therefore chose to compare our results with thin-film calculations and use a tight-binding description to discuss the layer dependence of the interface states.

The interfacial nature of the observed state for 1 ML of silver on iron can be confirmed by comparison with a FLAPW thin-film calculation [7,24]. A minority interface state (more than 67% of the character being in the silver and iron interfacial layers) is found; it has the correct symmetry and is at a binding energy of ~ 1.6 eV, which correlates well with the observed feature at ~ 1.7 -eV binding energy (Fig. 1). The FLAPW calculations for the uncoated iron surface find a minority surface resonance [14] localized in the outer two iron layers ($> 55\%$); the Ag/Fe interface state can be thought of as arising from a hybridization of the iron surface resonance, which is of s - p_z - d_z^2 character, with the silver bands of the same symmetry—the s - p band at a similar binding energy and the silver $4d$ bands at deeper binding energies. For the thicker silver coverages no first-principles calculation is available. However, our tight-binding results for one layer of silver on iron show qualitatively similar results to the FLAPW calculations; we find a state localized at the interface and at ~ 2 -eV binding energy. The tight-binding method allows us to extend our calculations to thicker silver films without carrying out prohibitively large first-principles calculations. The results for two layers of silver show an interfacial feature closer to the Fermi level than for 1 ML, as is observed experimentally; however, the calculated shift of ~ 0.3 eV is less than that observed (~ 0.7 eV). The difference probably reflects the increased importance of the s - p band in the thicker films and the poor treatment of these states in the tight-binding model. The two-layer state, although predominantly centered at the interface, is slightly less localized than for one layer, its weight extending into the outer (second) silver layer. This can be seen in Fig. 3 which shows the layer-resolved charge density for the interface states as determined from the tight-binding calculations. The calculations for three and four layers of silver show a similar trend, states with substantial weight at the interface are found and they successively move closer to the Fermi level. Beyond two layers significant intensity also develops in the outer silver layer (Fig. 3). This is most clearly observed for the four-layer film and reflects the formation of a silver surface band. The latter's orbital character is predominantly p_z and it appears to be related to the s - p_z surface resonance on silver which occurs approximately 1 eV above the Fermi level, as determined from a thirteen-layer silver tight-binding calculation [29] and from the application of the phase model [27].

In summary, both the experimental and theoretical

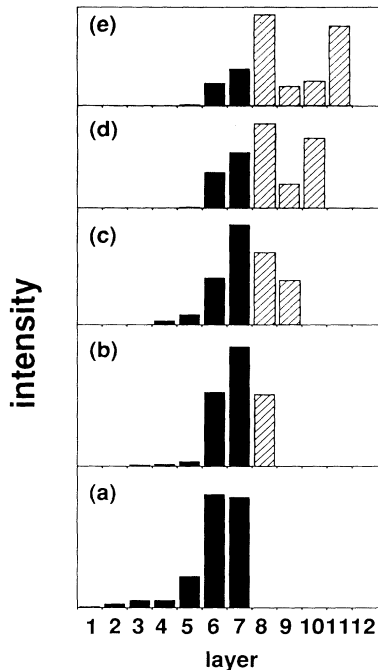


FIG. 3. The intensity per layer for (a) the minority surface resonance, and the minority interface states for (b) one layer, (c) two layers, (d) three layers, and (e) four layers of silver on iron as determined from the tight-binding modeling. The iron layers are shown in black and the silver is hatched. Layer 1 is the center of the slab and layer 7 is the outermost iron layer.

work are consistent with the conclusion that we have observed magnetic interface states. Their binding energy strongly depends on the thickness of the nonmagnetic overlayers and further they appear to be related to the surface properties of iron. The tight-binding modeling is qualitatively in agreement with the measurements, the movement of the interface states towards the Fermi level being reproduced. In addition, since there is appreciable intensity in the silver layers, for these minority-spin states, we can conclude that there are spin-dependent states on the silver sites. The observation that the interfacial electronic structure is related to the surface properties and that there are distinct size effects is of import to theoretical models which depend on the electronic structure at the interface.

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- [1] A. J. Freeman, C. L. Fu, S. Ohnishi, and M. Weinert, in *Polarized Electrons in Surface Physics*, edited by R. Feder (World Scientific, Singapore, 1985), Chap. 1.
 [2] *Magnetism in Ultrathin Films*, edited by D. Pescia, spe-

cial issue of *Appl. Phys. A* **49** (1989).

- [3] L. M. Falicov, D. T. Pierce, S. D. Bader, R. Gronsky, K. B. Hathaway, H. J. Hopster, D. N. Lambeth, S. S. P. Parkin, G. Prinz, M. Salamon, I. K. Schuller, and R. H. Victora, *J. Mater. Res.* **5**, 1299 (1990).
 [4] For example, H. J. Elmers, G. Liu, and U. Gradmann, *Phys. Rev. Lett.* **63**, 566 (1989).
 [5] B. T. Jonker, K.-H. Walker, E. Kisker, G. A. Prinz, and C. Carbone, *Phys. Rev. Lett.* **57**, 142 (1986); N. C. Koon, B. T. Jonker, F. A. Volkening, J. J. Krebs, and G. A. Prinz, *Phys. Rev. Lett.* **59**, 2463 (1987).
 [6] J. Tyson, A. H. Owens, J. C. Walker, and G. Bayreuther, *J. Appl. Phys.* **52**, 2487 (1981).
 [7] S. Ohnishi, M. Weinert, and A. J. Freeman, *Phys. Rev. B* **30**, 36 (1984).
 [8] Y. Wang, P. M. Levy, and J. L. Fry, *Phys. Rev. Lett.* **65**, 2732 (1990).
 [9] P. Grunberg, R. Schreiber, Y. Pang, M. B. Brodsky, and H. Sowers, *Phys. Rev. Lett.* **57**, 2442 (1986).
 [10] M. N. Baibich, J. M. Broto, A. Fert, F. Nguyen Van Dau, and F. Petroff, P. Eitenne, G. Creuzet, A. Friederich, and J. Chazelas, *Phys. Rev. Lett.* **61**, 2472 (1988).
 [11] B. Heinrich, Z. Celinski, J. F. Cochran, W. B. Muir, J. Rudd, Q. M. Zhong, A. S. Arrott, K. Myrtle, and J. Kirschner, *Phys. Rev. Lett.* **64**, 673 (1990).
 [12] W. R. Bennett, W. Schwarzacher, and W. F. Egelhoff, Jr., *Phys. Rev. Lett.* **65**, 3169 (1990).
 [13] Y. Yafet, *J. Appl. Phys.* **61**, 4058 (1987).
 [14] N. B. Brookes, A. Clarke, P. D. Johnson, and M. Weinert, *Phys. Rev. B* **41**, 2643 (1990).
 [15] X. Pan, P. D. Johnson, M. Weinert, R. E. Watson, J. W. Davenport, G. W. Fernando, and S. L. Hulbert, *Phys. Rev. B* **38**, 7850 (1988).
 [16] W. Weber, D. A. Wesner, G. Guntherodt, and U. Linke, *Phys. Rev. Lett.* **66**, 942 (1991).
 [17] P. D. Johnson, S. L. Hulbert, R. Klaffky, N. B. Brookes, A. Clarke, B. Sinković, and M. Kelly (to be published).
 [18] J. Unguris, D. T. Pierce, and R. J. Celotta, *Rev. Sci. Instrum.* **57**, 1314 (1986).
 [19] J. C. Slater and G. F. Koster, *Phys. Rev.* **94**, 1498 (1954).
 [20] D. A. Papaconstantopoulos, *Handbook of the Band Structure of Elemental Solids* (Plenum, New York, 1986).
 [21] J. D. Shore and D. A. Papaconstantopoulos, *Phys. Rev. B* **35**, 1122 (1987).
 [22] O. K. Andersen and O. Jepsen, *Physica (Amsterdam)* **91B**, 317 (1977); O. K. Andersen, W. Klose, and H. Nohl, *Phys. Rev. B* **17**, 1209 (1978).
 [23] C. L. Fu and A. J. Freeman, *Phys. Rev. B* **33**, 1611 (1986).
 [24] M. Weinert (private communication).
 [25] A. L. Wachs, A. P. Shapiro, T. C. Hsieh, and T.-C. Chiang, *Phys. Rev. B* **33**, 1460 (1986); T. Miller, A. Samsavar, G. E. Franklin, and T.-C. Chiang, *Phys. Rev. Lett.* **61**, 1404 (1988).
 [26] S. Å. Lindgren and L. Walldén, *Phys. Rev. Lett.* **59**, 3003 (1987); **61**, 2894 (1988).
 [27] N. V. Smith, *Rep. Prog. Phys.* **51**, 1227 (1988).
 [28] P. D. Loly and J. B. Pendry, *J. Phys. C* **16**, 423 (1983).
 [29] N. B. Brookes, Y. Chang, and P. D. Johnson (unpublished).