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SPIN POLARIZED PHOTOEMISSION STUDIES OF SURFACES AND THIN FILMS

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ABSTRACT

Spin polarized photoemission is used to study the magnetic states associated with the clean iron (001) surface. These studies reveal evidence for a minority spin surface state in agreement with first principles calculation. Studies of the same surface with silver and chromium epitaxial overlayers reveal evidence for interface states derived from the states found on the clean surface. In the case of the silver overlayer the binding energy of this state is found to be dependent on the layer by layer thickness of the overlayer. With chromium overlayers the binding energy for the same interface state does not show the same thickness dependence. However a second interface state is observed immediately below the Fermi level.

INTRODUCTION.

In recent years there has been a marked increase in research activity in the general area of surface magnetism including the magnetic properties of surfaces [1], thin films [2] and multilayers [3]. Much of the work in the latter area has been motivated by the observation that in certain transition metal multilayers, an example being the Fe/Cr system, alternate ferromagnetic layers may be made to align either parallel or anti-parallel depending on the thickness of the intervening layer [4]. Further in the same systems enhanced magnetoresistance effects have also been observed [5]. The period of the oscillations is not easily explained by a simple RKKy type interaction and hence several explanations have been proposed for the phenomena. One model proposes that the oscillations in the coupling reflect size quantization of hole states trapped in the nonmagnetic medium between the layers [6]. An alternative model relies on coupling of states localized in the interface through hybridization with conduction electrons in the intervening layer [7]. Clearly a better knowledge of the spin dependent electronic structure of these materials will be of benefit in any attempt to elucidate the correct mechanism.

Spin polarized photoemission with the capability of identifying two and three dimensional electronic states represents an excellent tool for such studies. The technique is however limited by the mean free path or escape depth of the photoelectrons. This limitation makes it more difficult to study directly the multilayer systems. However the interfaces may be studied by growing them in situ using molecular beam epitaxial growth methods.

In this paper we describe spin polarized photoemission experiments, which examine the magnetic structure of the clean iron (001) surface and modifications to this structure through the growth of thin film overlayers of silver and chromium. We are able to show that, as predicted, magnetic surface states or resonances exist at the iron (001) surface. With the deposition of epitaxial overlayers these states appear to become more localized in the interface region.

Fig.1 Schematic diagram of the apparatus used for spin polarized photoemission. Upper level: light from the U5 undulator excites photoelectrons which are detected by a hemispherical electron spectrometer. This analyser is coupled via an exit lens to a spin detector. Lower level: arrangement of the spin detector of the type described by Unguris et al. (ref. 9). G1 and G2 represent energy selecting retard grids. Four discrete anodes collect the scattered electrons as indicated at the lower left side.

As the thin film grows the interface states are found to be continuously sensitive to the changing boundary conditions, particularly in the case of the iron-silver interface where each newly deposited silver layer results in a discrete new binding energy for the state. For the chromium-iron interface two new states are observed with one state sitting immediately below the Fermi level.

EXPERIMENTAL.

The experiments described in this paper were carried out on a spin polarized photoemission facility [8] established on the U5 UV undulator at the

NSLS. Shown schematically fig. 1, a commercial hemispherical electron spectrometer, equipped with a low energy spin detector of the type described by Unguris et al. [9] is mounted on a goniometer allowing the full flexibility of angle resolved measurements. Measurement of a spin dependent asymmetry in the scattering of low energy, 150 eV, electrons from a polycrystalline gold target is used to determine the polarization of the photoemitted electrons. The low efficiency or figure of merit of the spin detector, 10^{-4} , is more than compensated for by the high photon flux available from the undulator. The experimental chamber is also equipped with Low Energy Electron Diffraction (LEED) and Auger Electron Spectroscopy (AES) for surface characterization.

Fcc silver and bcc chromium have a nearly perfect lattice match for growth on a bcc iron (001) substrate, the appropriate interatomic spacings being 2.88, 2.86 and 2.87 Å respectively. The metal overlayers were produced from electron beam evaporators with deposition rates monitored by both AES and by evaporating directly into a quadrupole mass spectrometer. Silver films were deposited on an iron (001) substrate at room temperature but in order to study the same interface it was found to be necessary to evaporate iron films on a silver

Fig.2. Photoemission spectra recorded for emission along the surface normal from the clean surface and the same surface following exposure to 0.1L of oxygen. Solid and open triangles indicate the spin resolved majority and minority spin spectra respectively. The incident photon energy was 52 eV with an angle of incidence corresponding to p polarized light.

(001) substrate at a lower temperature of approximately 160 K. Chromium films were evaporated on the iron substrate at the slightly elevated temperature of 70 C. Thin iron films were subsequently deposited on these chromium films at room temperature.

RESULTS.

Studies of the clean Fe(001) surface, fig. 2, reveal evidence for a minority spin surface resonance at the center of the zone, approximately 2.7 eV below the Fermi level. As evidenced in fig. 2, the surface designation reflects the sensitivity of the state to adsorption or contamination. Comparison with first principles calculations shows this state to be largely d in character but with some admixture of s and p states [10]. At the center of the zone, where no absolute bandgap exists, the state is essentially a bulk band "resonating" in the surface region. Farther out in the zone, at the X point, a band gap exists and it becomes a surface state. Fig. 3 shows charge density plots for the state at the center and edge of the zone [11], clearly demonstrating the difference in localization between the two points. Although predicted theoretically, no majority counterpart for this state is clearly observed. However the calculations suggest that such a state may possibly be dispersed over a larger range of binding energies.

Deposition of silver on this surface quenches the minority surface peak but a new feature is observed at a lower binding energy [12]. Shown in fig. 4, the latter peak is observed to undergo a maximum in intensity at a silver coverage corresponding to one monolayer, as calibrated by AES. LEED studies of this overlayer system show a good $p(1 \times 1)$ pattern throughout the initial growth. The new peak observed in the photoemission spectrum, fig. 4, is identified with an

Fig. 3 Calculated charge density plots for the minority surface resonance at the center of the zone and for the same state at the zone boundary where it falls within a bulk band gap

Fig. 4 Photoemission spectrum recorded along the surface normal following the deposition of 1ML of silver on the Fe(001) surface. For comparison the spectrum recorded from the clean surface is also shown. IS indicates the interface state and SR the surface resonance on the clean surface. Note that the two spectra, both recorded with an incident photon energy of 52 eV, are not normalized with respect to each other.

interface state predicted in a first principles calculations for this overlayer system [13].

With subsequent growth of the silver thin film, the "interface" state is observed to move towards the Fermi level in a series of discrete steps, fig. 5, each step reflecting the layer by layer growth. Spin polarization analysis indicates that in all cases the interface state is of minority spin character [12] and thus suggests that the state is derived from the minority spin surface state observed on the clean surface. The interface state is also observed when an iron monolayer is deposited on a silver (001) surface [14]. However in that case the state is less well resolved and it is not possible to detect any movement reflecting subsequent layers. The experimentally observed dispersion of the Ag/Fe(001) interface state away from the center of the zone is in reasonable accord with the predictions of the calculation [14].

Chromium overlayers deposited on Fe(001) again result in the formation of an interface state derived from the surface state associated with the substrate, fig. 6 [15]. However unlike the silver overlayers the presence of chromium now causes the surface resonance to move further from the Fermi level rather than towards it with the absolute magnitude of the shift being smaller than that observed for silver. The spin integrated spectra of fig. 6 also show an increase in

Fig. 5. Photoemission spectra recorded along the surface normal from a series of silver coverages deposited on Fe(001). The different coverages are indicated. The incident photon energy is 52 eV and the angle of incidence corresponds to p-polarized light.

the intensity of emission immediately below the Fermi level. A spin polarized spectrum, fig. 7, recorded following the deposition of one monolayer of chromium shows the interface state at a binding energy of 2.7 eV to be entirely of minority spin character, identical to the interface states observed for the silver overlayers. The spin resolved spectrum shows that the new intensity appearing below the Fermi level is also of minority character. Both the spectra in fig. 6 and the spectrum in fig. 7 are recorded with the light at an angle of incidence corresponding to p polarization. We note that in this photon energy range near the center of the zone a peak below the Fermi level is found in the minority spectrum of clean iron. However in that case, because of the symmetry of the initial state, the intensity is a maximum for s polarized rather than p polarized incident light.

With thicknesses of chromium beyond 2.0 Å the spin integrated spectra in fig. 6 show the evolution of the peak at approximately 3.0 eV binding energy into

Fig. 6. Spin integrated photoemission spectra recorded from Cr deposited on Fe(001) as a function of Cr coverage. The incident photon energy is 52 eV and the angle of incidence corresponds to p-polarized light.

the chromium surface resonance equivalent to that observed on the clean iron surface. Interestingly, a spin polarized photoemission study of this feature shows no particular polarization indicating that if the Cr(001) surface is ferromagnetic as calculated [16], the presence of steps and terraces masks any possible observation [17].

As noted in the introduction, other experiments have previously shown that iron overlayers deposited on the chromium films may show a parallel or antiparallel magnetic alignment with the iron substrate depending on the thickness of the intervening chromium layer [4]. Figure 7 shows spin resolved photoemission spectra recorded from iron films, 3.3 and 3.9 Å thick, grown on chromium films 3.2 and 3.9 Å thick, respectively. These spectra clearly show the reversal of polarization associated with the antiparallel alignment on the thicker chromium layer. They also provide some indication that the local moment on the iron for the two systems must be similar in that exchange split counterparts are placed at approximately the same binding energies of 0.5 and 2.5 eV.

DISCUSSION.

The sensitivity to the presence of adsorbates of the minority feature observed in the spin resolved spectra, fig.1, and the close agreement to calculation supports its identification as a surface state. As noted above, the state is a resonance rather than a pure surface state. Such a state is also predicted in a simple tight binding calculation using a nonorthogonal basis set [12]. The latter

Fig. 7. Spin polarized photoemission spectrum recorded from approximately one monolayer of chromium on Fe(001). The photon energy for this spectrum is 52 eV and the angle of incidence corresponds to p-polarized light.

calculation is a layered scheme with parameters taken from the tabulations, fitted to bulk calculations, provided by Papaconstantopoulos [18]. The modelling was extended to thin overlayers by scaling the respective parameter sets according to the scheme of Andersen [19]. Using such a method a calculation for a silver monolayer on iron (001) found an interface state in close agreement with both experiment and first principles calculation.

The tight binding simulation suggests that with the formation of the interface, a state is formed with 70% of its weight on the surface iron atoms and 30% on the silver monolayer. On the silver side the state has approximately 50% d character, the rest being s and p character. At the same time the modelling indicates that with the formation of the interface, the state becomes more localized within the surface layers of the iron substrate. Thus the decay of the resonant state back into the bulk of the material is reduced. A similar phenomena was previously observed in an inverse photoemission study of an unoccupied interface state in the Nb(110)/palladium interface [20]. In that study it was also shown theoretically that the presence of the palladium tended to localize a niobium surface resonance into the interface region.

Simulations of the chromium monolayer find that, as in the case of silver, the clean iron surface resonance is both localized and shifted by the presence of the overlayer. In agreement with the experiment the interface state is now at a higher rather than lower binding energy. The calculation now finds that the chromium component of the interface state is nearly 80% d in character. This increase in the d component probably reflects the fact, unlike silver, the chromium has unfilled d bands. At the same time the modelling also finds another interface state pulled down below the Fermi level. Unlike the higher binding

Fig. 8. Spin polarized photoemission spectra recorded from thin iron films of thickness approximately 3.5 Å grown on different thicknesses of chromium. As in previous spectra the photon energy is 52 eV and the angle of incidence corresponds to p-polarized light. The different thicknesses of chromium are indicated in the two panels.

energy interface state, which is d_{z^2} in character this second state has d_{xz} character. It is derived from an unoccupied surface state sitting immediately above the Fermi level on the clean iron surface.

To summarize, for both the silver and chromium films the presence of the overlayer appears to localize states within the interface, at least in terms of the decay length into the substrate. These magnetic states, having a well defined spin character, also have weight on the overlayer sites. However it is difficult on the basis of the present experiments to make any quantitative statements regarding the possible existence or size of magnetic moments on the overlayer atoms. In the case of silver, the interface states show well defined binding energies reflecting the thickness of the overlayer film. Thus the presence of the overlayer modifies both the electronic and magnetic properties of the interface. Any modelling that reflects the electronic structure of the interface should allow for the possibility of such changes. One further consideration is the probability of a distinct face dependence for the surface states and surface resonances from which the interface states are derived.

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REFERENCES.

1. A.J. Freeman, C.L. Fu, S. Ohnishi and M. Weinert, Chapter 1 in "Polarized Electrons in Surface Physics", Ed. by R. Feder, (World Scientific, Singapore 1985).
2. "Magnetism in Ultrathin Films", Special Issue of Appl. Phys. A49, Ed. D. Pescia (1989).
3. L.M. Falicov, D.T. Pierce, S.D. Bader, R. Gronsby, 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. P. Grunberg, R. Schreiber, Y. Pang, M.B. Brodsky, and H. Sowers, Phys. Rev. Lett. 57,2442 (1986).
5. M.N. Baibich, J.M. Broto, A. Fert, F. Nguyen Van Dau, F. Petroff, P. Etienne, G. Creuzet, A. Friederich, and J. Chazelas, Phys. Rev. Lett. 61,2472 (1986).
6. D.M. Edwards and J. Mathon, to be published.
7. Y. Wang, P.M. Levy and J.L. Fry, Phys. Rev. Lett. 65,2732 (1990).
8. P.D. Johnson, S.L. Hulbert, R. Klaffky, N.B. Brookes, A. Clarke, B. Sinkovic, N.V. Smith, M.J. Kelly, D.T. Pierce, R. Celotta and M.R. Howells, to be published.
9. J. Unguris, D.T. Pierce and R.J. Celotta, Rev. Sci. Instr. 57, 1314 (1986)
10. N. Brookes, A. Clarke, P.D. Johnson and M. Weinert, Phys. Rev. B 41, 2643 (1990).
11. M. Weinert, private communication.
12. N. Brookes, Y. Chang and P.D. Johnson, submitted to Phys. Rev. Lett.
13. S. Ohnishi, M. Weinert and A.J. Freeman, Phys. Rev B 30, 36 (1984).
14. N. Brookes, Y. Chang, P.D. Johnson and M. Weinert, to be published.
15. Y. Chang, N. Brookes and P.D. Johnson, to be published.
16. e.g. P.H. Victora and L.M. Falicov, Phys. Rev B 31, 7335 (1985).
17. S. Blugel, D. Pescia and P.H. Dederichs, Phys. Rev B 39, 1392 (1989); R. Wiesendanger, H.-J. Guntherodt, G. Guntherodt, R.J. Gambino and R. Ruf, Phys. Rev. Lett. 65,247 (1990).
18. D.A. Papaconstantopoulos, "Handbook of the Band Structure of Elemental Solids", (Plenum Press 1986).
19. O.K. Andersen and O. Jepsen, Physica B 91, 317 (1977).
20. 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).

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