Direct Observation of Spin-Split Electronic States of Pd at the Pd(111)/Fe(110) Interface

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(Received 10 December 1990)

A spin-split interface state in the Pd 4*d* band of epitaxial Pd(111) films on Fe(110) has been identified in spin-resolved and spin-integrated photoemission. It is most pronounced for Pd thicknesses between 1 and 2 atomic layers (AL), with an exchange splitting of about 130 ± 50 meV that is inverted compared to that of Fe. Bulklike states of Pd(111) at Pd thicknesses between 1.5 and 2.7 AL also appear spin polarized, but without a resolvable exchange splitting. Above 2.7-AL Pd thickness no spin polarization attributable to Pd is evident.

PACS numbers: 75.70.Ak, 75.50.Rr, 75.70.Cn

Stacking ultrathin magnetic layers with nonmagnetic spacer layers in metallic multilayers [e.g., Co/Pt (Ref. 1)] yields novel magnetic properties different from those of the bulk, such as strong out-of-plane anisotropies, giving rise to remanent magnetization perpendicular to the layer plane. In view of the promising applications of such multilayers as high-density, magneto-optical storage media, the role of interface anisotropies is presently under intense investigation, mainly from a structural point of view (e.g., the changes in anisotropy upon interface sharpening[2]). While first-principles calculations of magnetic anisotropies in thin-film structures are being increasingly pursued,[3] the electronic structure at the interface itself has so far not been investigated experimentally.

Magnetometry measurements of multilayers incorporating interfaces of Pd with Ni,[4] Fe,[5,6] and Co (Ref. 7) have been interpreted in terms of an induced magnetic polarization of Pd at the interface. Similarly, magnetic polarization is predicted for a Pd(100) substrate covered by an Fe monolayer.[8] Brillouin light-scattering measurements in Fe(110) films as a function of coverage with Pd, Pt, or Ag overlayers show the largest change in the spin-wave frequencies near 1 atomic layer (AL) of Pd or Pt. In contrast, there is a much weaker effect for Ag.[9] This is interpreted as a change in surface anisotropy of the Fe film upon coating with Pd or Pt and as possible evidence for a magnetic polarization of these overlayers. This finding prompted our choice of the Pd(111)/Fe(110) system for an electronic structure study by means of spin-resolved and spin-integrated photoemission spectroscopy.[10] We report here the first direct observation of a spin-split interface state at the interface Pd(111)/Fe(110) and its development with increasing Pd thickness.

Two different experimental setups were used. Spin- and angle-resolved photoemission spectra were recorded with unpolarized He I radiation ($h\nu = 21.2$ eV, light incident at 30° to the surface normal approximately along the $[1\bar{1}0]$ azimuth). Energy and angle resolutions were 100 meV and ±3°, respectively (details are given elsewhere[11]). Samples were remanently magnetized in the Fe(110) film plane along the $[1\bar{1}0]$ direction, which is the easy magnetization axis (instead of [001] for bulk Fe) for film thicknesses below a critical value in the range 50–100 Å (25–50 AL of Fe).[12,13] The spin-integrated, angle-resolved photoemission measurements were performed at the synchrotron radiation facility BESSY, Berlin. The combined energy resolution (photons plus electrons) was 250 meV, the angle resolution ±1°. In both systems films were electron-beam evaporated *in situ* on W(110) substrates; the thickness was monitored by quartz microbalances. Preparation of clean, epitaxial Fe(110) films on W(110) is well established and described elsewhere.[14] Bulklike Fe films ~18 AL thick were grown at a rate of ~0.7 AL/min at 450-K substrate temperature; Pd evaporation on the Fe film followed at low rates of ~0.2 AL/min at room temperature to avoid intermixing.

Pd grows epitaxially in (111) planes on Fe(110) (Ref. 9) in the "Kurdjumov-Sachs" mode.[15] A slight azimuthal rotation of the Pd(111) plane relative to the Fe(110) substrate (~ ±5°) and some compression (~1%) yields a commensurate structure with a coincidence (ten Pd on eleven Fe) along the Fe [111] crystal direction.[9] This generates satellites near the Fe reflexes in low-energy electron diffraction at submonolayer Pd coverages, suggesting patches with essentially bulk (111)-plane structure. At the low growth rates used, at least the first two layers grow layer by layer, as revealed by kinks in the straight lines of the Fe and Pd Auger intensities as a function of Pd coverage.[10] We assume a

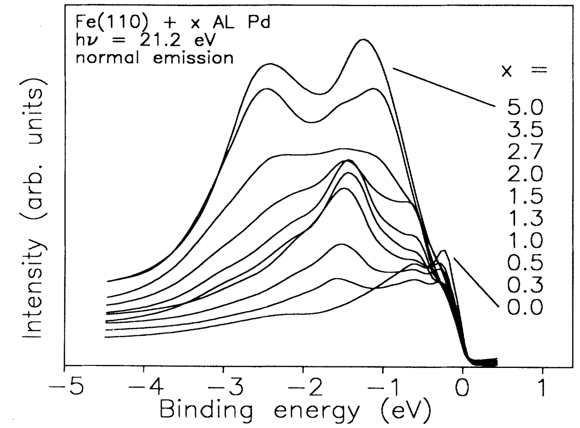

FIG. 1. Spin-integrated EDC's for various Pd overlayer thicknesses (in AL) on Fe(110). Spectra are plotted on the same absolute intensity scale.

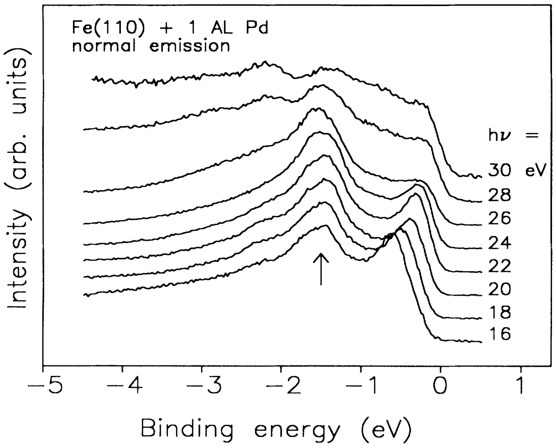

FIG. 2. Spin-integrated EDC's for a 1-AL Pd overlayer on Fe(110) measured at various photon energies. Spectra are arbitrarily scaled to have the same maximum intensity and are shifted vertically for clarity.

spacing between the Pd layers identical to that of bulk Pd(111) (2.25 Å) and give the Pd thickness in AL (1 AL of Pd≡2.25 Å).

Figure 1 shows spin-integrated energy distribution curves (EDC's) of the valence band of clean ($x=0$) and Pd-covered Fe(110), taken in the spin-resolved photoemission apparatus. Binding energies here and below are given relative to the Fermi energy E_F. Generally, as Pd coverage grows, structures of the EDC for clean Fe (bottom curve in Fig. 1—see also the spin-resolved EDC for $x=0$ in Fig. 3) are rapidly buried under increasingly intense Pd-induced features. Even at low Pd coverages a structure emerges near -1.5 eV due to Pd $4d$ states, not surprising in light of their large photoionization cross section relative to Fe.[16] The binding energy is similar to that for 1 AL of Pd on transition metals.[17-19] This state shifts little with increasing Pd coverage, and is present as a weak shoulder for 3.5-AL Pd. Significantly, the intensity saturates around 1.5-AL Pd. Further increase of intensity at -1.5 eV with Pd coverage above 1.5 AL is caused by the superposition of two other states emerging at lower and higher binding energies. These states evolve to bulklike structures at larger Pd coverages ($x \geq 3.5$), for which the EDC approaches that of bulk Pd(111).[20] The saturation of intensity suggests interface character for the state at -1.5 eV. One observes similar behavior in the system Cu/Ru(0001), in which, however, the interpretation is easier because the interface state is isolated from the bulklike states.[21]

More information on the Pd state at -1.5 eV comes from the photon energy dependence of its binding energy. Figure 2 shows valence-band EDC's as a function of $h\nu$ for a 1-AL Pd film on Fe(110) taken at BESSY (normal emission, light incidence angle of 65° to the surface normal along the [001] azimuth). The peak at -1.5 eV shifts by <100 meV for photon energies from 16 to 30 eV (see Fig. 2, arrow). Thus, the state disperses little when the perpendicular component of the photoelectron wave vector $k_\perp$ changes. In contrast, the Fe state near E_F and bulklike Pd states of thick Pd films (not shown) exhibit stronger dispersion with $k_\perp$. Other experiments in off-normal emission show significant dispersion of the interface state when the parallel wave-vector component $k_\parallel$ changes,[10] as expected for a two-dimensional electronic state confined in the normal direction.

Figure 3 shows spin-resolved EDC's at Pd coverages of 0, 1, 2, and 5 AL. For clean Fe ($x=0$) our results agree with earlier spin-resolved photoemission experiments on the same system,[22] and also with experimentally (spin-integrated and angle-resolved photoemission)[23] and theoretically[24] determined bulk Fe band structures. The band symmetry assignments shown are based on a comparison with these earlier investigations.[22-24]

Turning next to the 5-AL-thick Pd film we observe two bulklike Pd features at -1.2 and -2.4 eV, which dominate both spin directions. The only difference is a uniform, slightly higher intensity for the majority-spin channel caused by the background of positive Fe spin polarization. Thus there is no evidence for spin-polarized Pd states at a Pd coverage of 5 AL.

For a Pd thickness of 1 AL the interface state shows different peak positions for the two spin channels: -1.55 eV in the minority-spin channel and -1.4 eV in the majority-spin channel. Thus, we find an exchange splitting of the interface state which is inverted compared to that of Fe at the same k point. Here it is important to note that the minority-spin peak has only a small, structureless background, while the majority-spin peak overlaps the Fe $\Sigma_{4\uparrow}$ state (see the spectrum for $x=0$ in Fig. 3). We used various background-subtraction schemes to try to isolate a "true" Pd signal. This subtraction generally shifts the majority-spin peak

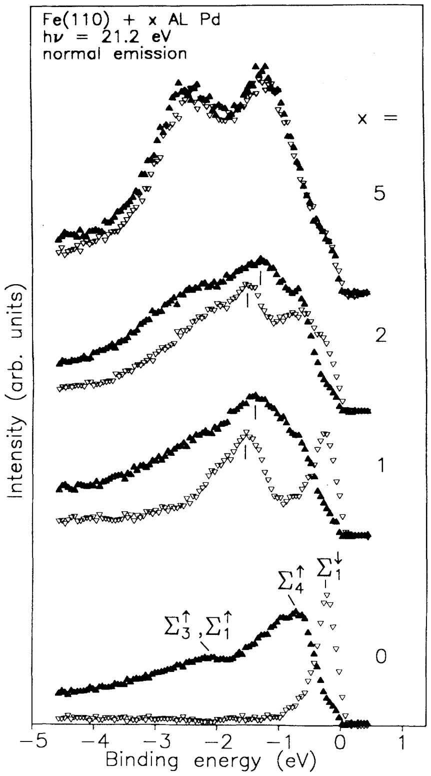

FIG. 3. Spin-resolved EDC's for various Pd overlayer thicknesses (in AL) on Fe(110). Spectra are plotted on the same absolute intensity scale, but each spin-resolved pair is shifted vertically for clarity. Solid symbols correspond to the majority-spin direction and open symbols to the minority-spin direction.

slightly (by ≤ 50 meV) to more negative binding energy. Nevertheless, an inverted exchange splitting of 130 ± 50 meV remains when all film thicknesses for which this peak is discernible (i.e., up to about 2.7-AL Pd) are analyzed. As a check that the inverted exchange splitting in Pd is not confined to only one particular k point, we also measured spin-resolved EDC's in off-normal emission (emission angle 11°) in approximately the [001] azimuth. The value of $k_{\parallel}$ corresponds to about one-fourth of the way to the surface Brillouin-zone boundary. Here the interface state is clearly resolvable; its spin-resolved components are essentially identical to those at normal emission.

Between 1 and 2 AL new structures appear in the EDC at −0.7 and −2.2 eV, on either side of the interface state. These evolve to the bulklike Pd structures at higher coverages and probably arise from second-layer Pd atoms. Especially for the −0.7-eV state, the spectra suggest spin polarization, since structures in the two spin channels differ considerably after background compensation (e.g., by subtraction of the 1-AL spectrum from the 2-AL spectrum). An exchange splitting is difficult to estimate because these states partially overlap the interface state; however, a high minority-spin channel intensity at −0.7 eV (and, after background subtraction, possibly also at −2.2 eV) does suggest negative spin polarization. In other spin-resolved EDC's (not shown), additional Pd-induced features obtained between 2.7 and 3.5 AL no longer differ appreciably for the two channels, consistent with unpolarized states. Thus, we assert that Pd in at least the first layer, and possibly in the second as well, is spin polarized by Fe. For comparison, calculations[8] show that 1 AL of Fe on a Pd(100) substrate induces a magnetic moment in two Pd layers. 1 AL is also the Pd coverage range for which Brillouin light-scattering measurements[9] show the largest effects. At 3.5 AL (not shown in Fig. 3) and, certainly, at 5 AL no Pd polarization is evident.

An apparently *inverted* exchange splitting of the interface state relative to the Fe exchange splitting is surprising in light of magnetometry results showing net *positive* induced Pd moments at interfaces.[4-7] However, both the magnetometry and the spin-resolved photoemission results are consistent with a spin-resolved density-of-states (DOS) calculation of a pseudomorphic Pd monolayer on a three-layer Fe(100) slab by Huang *et al.*[25] by a self-consistent, localized-orbital method. While these authors find a small Pd polarization of $+0.36\mu_B$ (i.e., a Pd moment parallel to that of the Fe), the spin-resolved DOS of Pd is strongly distorted from that expected for an exchange-split band structure. No obvious exchange shifting of the calculated minority-spin DOS of Pd to lower binding energy relative to the majority-spin DOS of Pd is evident. Rather, between E_F and −2 eV, the prominent DOS structures are a minority-spin peak near −1.8 eV and a majority-spin peak near −1.2 eV, apparently inversely split compared to the Fe substrate layers (see Fig. 3 of Ref. 25). In contrast, the minority-spin DOS of an Fe slab is essentially a replica of the majority-spin DOS, exchange shifted to lower binding energy relative to the latter. Huang *et al.* invoke hybridization of Fe and Pd d states across the interface to explain the strong distortion.[25] This agrees qualitatively with our results, assuming the interface state contributes significantly to the DOS of Pd in the binding-energy range between E_F and −2 eV. Quantitative differences between experiment and theory may arise from the different film structures in the calculations [Pd(100)] and the experiment [Pd(111)]. Other predictions by Huang *et al.*[25] of a weak DOS of the Pd monolayer near E_F and a small charge transfer across the interface (we observe a work function change of only −50 meV for 1-AL Pd) are also consistent with our results.

In summary, we observe a spin-split interface state in the first Pd layer of Pd(111)/Fe(110). Spin polarization probably extends to the second Pd layer, but not further. The interface state exhibits an inverted exchange splitting compared to that of Fe, possibly due to strong Pd-Fe hybridization, in qualitative agreement with a spin-resolved DOS calculation.[25] Our direct spectroscopic information thus corroborates the magnetometric findings of magnetically polarized Pd.[4-7] Such interface states and their magnetic polarization must be important for the magnetic anisotropies at interfaces, especially in light of the apparent extreme sensitivity of magnetic anisotropies to details of the electronic structure.[3]

We thank T. Ditzinger, Ch. Lunau, H. Neddermeyer, and the BESSY staff for their assistance with the spin-integrated measurements, which are supported by Bundeministerium für Forschung und Technologie (BMFT) Projects No. 05 332 AAI and No. 05 432 AAB. We also benefited from helpful discussions with P. Baumgart, M. Gruyters, J. V. Harzer, K.-P. Kämper, D. Kerkmann, R. Lorenz, D. Pescia, F. Schumann, and R. L. Stamps.

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