Valence Band Photoemission Study of Co/Pd Multilayer

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We report the photoemission (PES) studies for the Co/Pd multilayer. The Co $3d$ PES spectrum of Co/Pd exhibits two interesting features, one near the Fermi energy, E_F, and another at ~ 2.5 eV below E_F. the Co $3d$ peak near E_F of Co/Pd is much narrower than that of the bulk Co, consistent with the enhanced Co magnetic moment in Co/Pd compared to that in the bulk Co. The Co $3d$ feature at ~ -2.5 eV resembles the Pd valence band structures, which suggests a substantial hybridization between the Co and Pd sublayers. The Co $3d$ PES spectrum of Co/Pd is compared with the existing band structures, obtained using the local spin density functional calculations. A reasonable agreement is found concerning the bandwidth of the occupied part of the Co $3d$ band, whereas a narrow Co $3d$ peak near E_F seems not to be described by the band structure calculations.

I. INTRODUCTION

Artificially structured multilayers(ML), consisting of magnetic layers a monolayer thick and intervening non-magnetic ones, have recently attracted much attention as model samples for studying interface magnetism and also as new materials which do not exist in nature[1]. Ferromagnetic/non-ferromagnetic ML's such as Co/Pd and Co/Pt show perpendicular magnetic anisotropy when the Co-sublayer thickness is less than a few monolayers[2-5]. These ML systems appear to be promising candidates for high-density magneto-optical(MO) media, due to their high corrosion and oxidation resistance, and enhanced Kerr effects at shorter-wavelength lasers[6-8].

The origin of the magnetic anisotropy is not well understood yet, even though the anisotropy of these systems is considered to be primarily attributable to the surface/interface contribution[3, 4].

The magnetic anisotropy should be closely related to the electronic structures of the system. A few theoretical studies concerning electronic and magnetic structure of Co/Pd and Co/Pt have been reported[9, 10]. But only few experimental studies concerning electronic structures, such as photoelectron spectroscopy(PES), have been reported yet, probably due to the difficulties in *in situ* preparation of the ML samples and simultaneous surface measurements.

In this paper we report photoemission studies of Co/Pd. We have investigated Co/Pd with a particular interest in the extent of the hybridization between Co and Pd states and its effect on their electronic structures. We have determined the Co and Pd partial densities of states(PDOS) by making use of the minimum in the Pd $4d$ photoionization cross-sectionn around $h\nu \sim 120$ eV. the so-called Cooper minimum[11]. Cooper minimum arises from the vanishing of the matrix

elements for electron transitions to final states at that photon energy[12].

II. EXPERIMENTAL DETAILS

The Co/Pd multilayers with a few atomic layers of Co were prepared onto a Si substrate at room temperature[13]. The prepared multilayer consists of 17 bilayers of alternationg ~3 Å-thick Co-and ~8 Å-thick Pd-sublayers, terminated with a Pd top sublayer which is very stable to oxidation. Pd and Co films, both of which are ~300 Å-thick, are similarly prepared to be used as reference materials for this study. X-ray diffraction(XRD) measurements indicate that the prepared Co/Pd has a superlattice structrue with sharp interfaces and with alternating fcc Pd(111) and fcc Co(111) layers, and that the pure Pd film has the fcc(111) texture.

The photoemission measurements were performed at the Synchrotron Radiation Center of the University Wisconsin-Madison, on the Ames/Montana beamline. All the samples were measured at room temperature in a vacuum better than 4×10^{-11} Torr. The measured surfaces were obtained by mild sputtering of the *ex situ* prepared samples. Co/Pd was cleaned by sputtering using Ar-ions at about 500 eV in order to minimize the roughness of the surface due to sputtering, whereas the Pd and Co films were sputtered at ~1 keV. The cleanness of the sample surface was monitored by the oxygen $2p$ emission which appears at ~6 eV below the Fermi level(E_F) in the energy distribution curve (EDC) with the photon energy of $h\nu = 21.2$ eV. For Co/Pd and the Pd film, no detectable O $2p$ emission is observed after sputtering. A commercial double-pass cylindrical-mirror analyzer(CMA) was used to analyze the photoelectrons. The overall instrumental resolution is 0.2 eV at $h\nu$ ~20 eV and 0.4 eV at $h\nu$ ~150 eV, respectively, for the spectra presented in this paper. The Fermi level of the system was determined from the valence-band spectrum of a sputtered Cu sample. The EDC'S for each sample were normalized to the incident pho-

ton flux and also to the transmission function of the CMA[14].
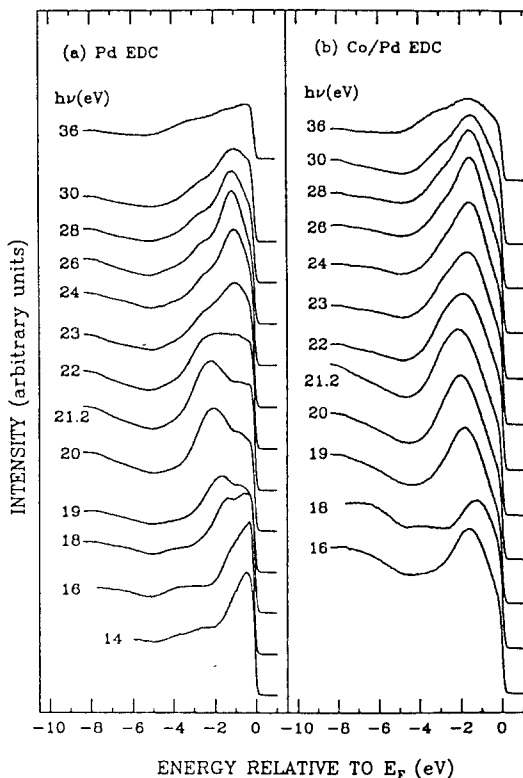
III. RESULTS AND DISCUSSION

Fig. 1. (a) Energy distribution curves(EDC) for Pd withe $h\nu$ between 14 and 36 eV, and (b) EDC's for the Co/Pd multilayer with $h\nu$ between 16 and 36 eV.

Fig. 1(a) and (b) show the valence band EDC's of the Pd film and Co/Pd, respectively, at $h\nu$ between 14 and 36 eV. It is interesting that peaks in the EDC's of the Pd film show dispersions as $h\nu$ varies. Our data in Fig. 1(a) are qualitatively similar to the angle-resolvd PES results of Pd(111)[15, 16] which were compared with the band structure calculations[17]. Considering that the Pd film has the fcc(111) texture, and that the detected electrons are mainly those of normal emission[18], the measured Pd surface seems to represent the

fcc Pd(111). The EDC's on Pd(111) [15] exhibit sharper features than ours, probably because of the rough surface of our sample and the contribution from the glancing angle emission in our data.

Valence band EDC's of Co/Pd in Fig. 1(b) also show a dispersion-like behavior with hv. The variation in the EDC's of Co/Pd is smaller than that of the Pd film, which probably reflects the loss of translational symmetry in Co/Pd due to the Co interlayer. This figure suggests that our PES spectra of Co/Pd can be considered to represent the intrinsic electronic structures of Co/Pd. This conjecture may be further supported by the fact that our PES spectra of the Co/Pd multilayer are different from those of the Co-Pd alloy film[19] as well as those of the Pd Co dilute alloy(Pd : host, Co : impurity)[20].
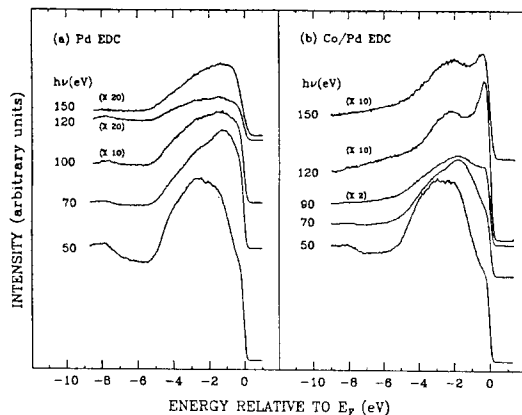

Fig. 2. (a) EDC's for the Pd film with hv over 50-150 eV, and (b) similarly for Co/Pd.

Fig. 2(a) shows EDC's of the Pd film with hv over 50-15 eV. Analysis of the Pd $4d$ photoionization cross section for the Pd film yields that the overall hv dependence is qualitatively similar to that in literature, but that the size of the suppression in the Pd $4d$ cross section at the minimum is larger than in literature[11, 21, 22]. The discrepancies may be due to the differences between bulk and film as well as due to the

uncertainties associated with normalization The valence band line shape in Fig. 2(a) changes slightly from $hv = 50$ eV to 70 eV, whereas it does not change much for hv above 70 eV. This may be because the momentum uncertainty becomes larger at higher hv [23, 24], so that the valence band spectrum begins to represent the density of states (DOS) as hv increases. In fact, our valence band PES spectra of the Pd film with hv above 70 eV are similar to that obtained using X-ray photoemission spectroscopy(XPS) [25, 26].

Fig. 2(b) shows EDC's of Co/Pd with hv over 50-150 eV, in comparison with Fig. 2(a) For hv below 90 eV, where the Co $3d$ cross sections are negligible with respect to the Pd $4d$ cross sections[20] and so Pd d emissions are dominant, EDC's of Co/Pd are similar to those of the Pd film. The well-known Cooper minimum in the Pd $4d$ photoionization cross section is clearly seen around $hv = 120$ eV. Consequently, the sharp structure near E_F in the EDC's of Co/Pd with hv around 120 eV is taken to originate from Co $3d$ states.

Fig. 3(a) compares the valence band spectra of the Pd film and Co/Pd, taken at $hv = 70$ eV where Pd $4d$ emissions are dominant. The purpose of this figure is to show the ecperimentally determined Pd d partial density of states(PDOS) in Co/Pd. The large energy scale features of the Co/Pd PES spectrum are similar to those of the Pd film, suggesting that Pd d electronic structures of Co/Pd are not much different from those of the Pd film. This finding is consistent with the Pd $3d$ core level PES studies[27], in which the Pd $3d$ spectrum of Co/Pd is found essentially identical with that of the Pd film, implying that the average local environment of Pd is nearly the same in Pd and Co/Pd. on the other hand, there are some differences : (i) The Pd d bandwidth of Co/Pd is slightly larger than that of Pd, which probably reflects the compression of the lattice constant in Co/Pd($\sim$3.8 Å) relative to that of the bulk Pd fcc lattice (3.89 Å). (ii) The emission near E_F in Co/Pd is smaller than that in Pd. These differences may be important in understanding the
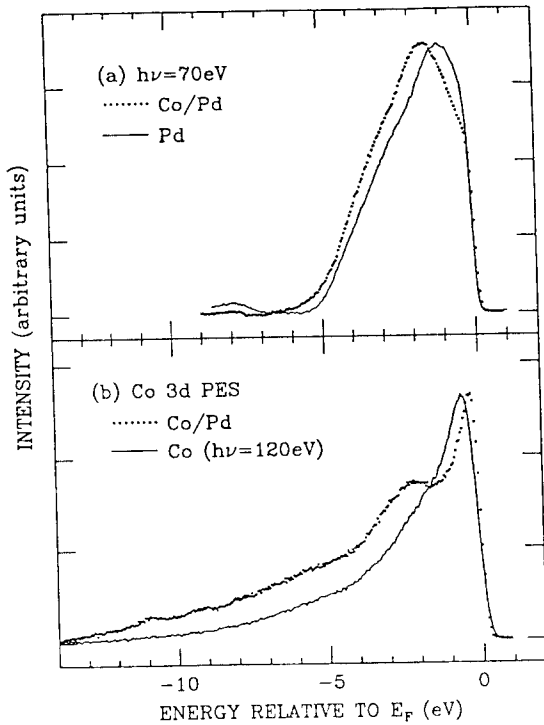
Fig. 3. (a) Comparison of the valence band spectra of Co /Pd and the Pd film, taken at $hv = 70$ eV, where Pd 4d emissions are dominant. (b) Comparison of the Co 3d spectrum of Co /Pd and the Co film. See the text for the details.

induced magnetic moment of Pd in Co /Pd [9, 10], which will be discussed later.

It is possible to extract the Co 3d spectral weight in Co /Pd by subtracting the spectrum at the Pd 4d Cooper minimum from that well away from the Cooper minimum. It is necessary to scale the former by a factor, α, to account for the non-Co 3d emission. We have chosen $hv = 70$ eV and 120 eV, respectively, and have used $\alpha = 0.02$, which is determined from the hv dependence of the valence band PES of the Pd film, As discussed in Fig. 2(a), the magnitude of this factor is smaller than the value in literature[21, 22]. Since we have used a consistent normalization scheme for both the Pd film and Co /Pd, the errors associated with our normalization would be cancelled in extracting the Co 3d spectrum.

Fig. 3(b) compares the extracted Co 3d spectrum of Co /Pd (dots) with the PES spectrum of the pure Co film(solid lines) at $hv = 120$ eV. Before we discuss the Co 3d features, we should mention two experimental artifacts. First, the PES spectrum of the Co film was obtained from a somewhat oxidized surface. Nevertheless, at $hv = 120$ eV where the O 2p cross section is negligible with respect to the Co 3d cross section, our Co PES spectrum is nearly the same as that of clean Co in literature[28, 29]. Secondly, a weak feature was observed in a wide scan for Co /Pd, at the binding energy corresponding to the Si 2p level [30], but not for the Co film. Thus the unusually long tail in the extracted Co 3d PES of Co /Pd, which extends almost down to −15 eV, is likely to be due to the s/p emissions from the Si substrate [31], as compared to the PES studies on the amorphous Si [30].

The major findings of Fig. 3(b) are as follows: (i) The Co 3d peak of Co /Pd at low binding energy is narrower and located closer to E_F than that of the Co film. (ii) There is a broad shoulder about 2.5 eV below E_F in Co /Pd, in contrast to bulk Co [32]. The narrowing of the Co 3d bands near E_F may be a consequence of the stretched lattice of Co /Pd(the nearest neighbor Co-Co distance, d_{Co-Co} $\simeq 2.70$ Å)[33],which makes Co more atomic-like, compared to that of the bulk Co($d_{Co-Co} \simeq 2.5$ Å) [34]. This narrowing, implying enhancement of the DOS near E_F, can be ascribed to the origin of the enhanced Co spin polarization than in bulk[9, 10] and may play an important role in determining the magnetic anisotropy of this system. Another feature, a shoulder at ~ −2.5 eV, resembles the Pd valence band features(see Fig. 3(a)), suggesting tht there is a substantial hybridization between the Co and neighboring Pd sublayers.

Figure 4 compares the Co 3d PES of Co /Pd with the calculated layer projected density of states (LDOS) onto the Co layer in Co /Pd (111). Three curves are scaled arbitrarily. The experimental Co 3d PES (in dots) is that of Fig. 3(b), from which some fraction of the emission around −10eV
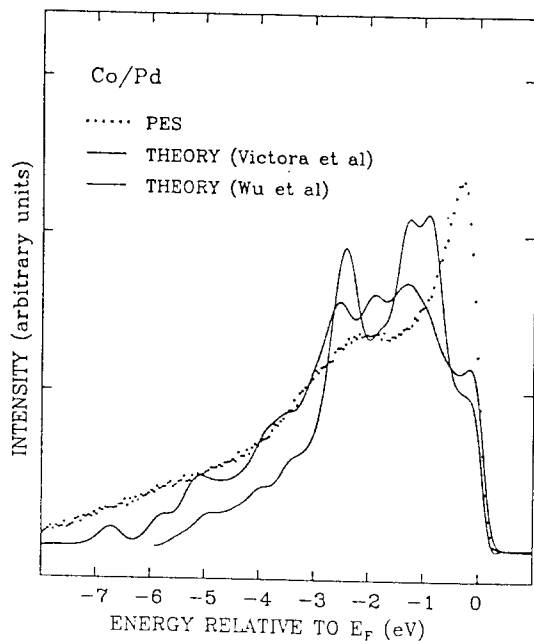
Fig. 4. Comparison of the experimental Co $3d$ PES spectrum of Co/Pd (dots) and the theoretical Co $3d$ LDOS taken from Victora et. al. (thick solid lines) and from Wu et. al.(light solid lines) for Co/Pd(111).

has been subtracted in order to eliminate the contribution from the Si substrate. Both of two theoretical results are obtained from the local spin density functional (LSD) calculations. Light solid lines denot the Co LDOS obtained by Wu et al. [9], in which Co/Pd (111) is simulated by 5 Pd (111) layer slabs covered by a Co monolayer on each side. Thick solid lines denote the Co LDOS which is obtained by Victora et al. [10] for an fcc supercell with 1-Co layer/4-Pd layers along the (111) direction. In this comparison, the occupied parts of the theoretical Co $3d$ majority and minority spin LDOS are summed because our experimental PES spectra are not spin-resolved. Then they are broadened by a Gaussian of 0.3 eV at FWHM(full width at half maximum) to simulate the instrumental resolution, whereas the lifetime broadening and the matrix element effects are ignored.

For systems with strong correlations, the experimental bandwidths are considerably less than the one electron bandwidths, obtained from band structure calculations, in general. Fig. 4 shows that the theoretical bandwidths of the occupied parts of the Co $3d$ LDOS are comparable to that of the experiment, suggesting that Co $3d$ correlation effects are rather weak in Co/Pd. In contrast, a sharp peak near E_F, observed in the experimental Co $3d$ PES spectrum, is missing in both of the theoretical Co $3d$ LDOS. It is not trivial to assign spin character to a specific peak in our Co $3d$ PES, but theoretical results might be used as a guide for spin-identification of the experimental features. According to the spin and layer projected DOS in both of the theoretical calculations, there is a high and narrow minority Co $3d$ band peak just above E_F, while the Co LDOS below∼ −1 eV is mainly due to the majority Co $3d$ spin bands which are substantially hybridized with Pd $4d$ bands. Therefore a broad shoulder at −2.5 eV may originate from the majority Co $3d$ spin states hybridized with Pd $4d$ states. A sharp and narrow peak just below E_F is difficult to be identified as the specific spin character at the moment since there is no corresponding LDOS in the theoretical results [9, 10].

Remember that the general features of the Pd $4d$ PES of Co/Pd are similar to that of the Pd film (see Fig. 3(a)). even though there are differences such as smaller intensity near E_F and larger Pd $4d$ bandwidth in Co/Pd. These differences may be important in understanding the induced magnetic moment of Pd in Co/Pd since the band structure calculations [9] predict that major differences in the Pd LDOS between Pd(111) and Co/Pd(111) will occur near E_F. However, such small-size differences observed in experiments may not be taken too seriously at the moment, considering experimental uncertainties as well as rather large-size discrepancy between experiment and theory as the following. We have found that the width of the Pd $4d$ LDOS [9, 10] by ∼1 eV for both the Pd film and Co/Pd(not shown in this paper), which is taken to reflect Pd $4d$ correlation effects in both the Pd film and Co/Pd.

Ⅳ. CONCLUSIONS

The EDC's of both the Pd film and Co/Pd show dispersions at low photon energies, suggesting that the measured surfaces probably represent the intrinsic features corresponding to the fcc (111) texture. The Co $3d$ PES of Co/Pd shows two interesting features : (i) The bandwidth of the peak near E_F is narrower than that of the Co film. This narrowing is consistent with the enhanced Co spin polarization in Co/Pd compared to that in the bulk Co. (ii) Another shoulder-like feature, at ∼ −2.5 eV, resembles the Pd valence band structures, suggesting a substantial hybridization between the Co and Pd sublayers. A reasonable agreement is found between the PES spectra and LSD band structure calculations in some aspects : First, the theoretical bandwidths of the occupied Co $3d$ LDOS are comparable to the experimental Co $3d$ bandwidths. Secondly, the feature around ∼ −2.5 eV. observed in the Co $3d$ PES of Co/Pd, is well predicted and explained by the band theory. On the other hand, the narrow Co $3d$ peak near E_F in the Co $3d$ spectrum of Co/Pd, which may play an important role in determining the magnetic properties of Co/Pd, is not described by band structure calculations.

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[32] These findings are somewhat similar to those of the Co 3d PES studies of the Pd̲Co dilute alloy (see Ref. 20), but different in that the Co 3d peak near E_F of our Co /Pd multilayer is much (i) sharper, (ii) narrower, and (iii) located closer to E_F than that of the Pd̲Co alloy.

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광전자분광법을 이용한 Co /Pd 다층박막의 전자구조연구

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광전자분광법 (Photoelectron Spectroscopy : PES) 을 이용하여, 차세대 광자기 기록매체로 유망한 Co /Pd 다층박막의 전자구조를 연구하였다. Co /Pd 다층박막의 Co $3d$ 전자 PES 스펙트럼에서는 페르미 에너지 (E_F) 근처에 폭이 좁은 피이크가 관찰되었고, 아울러 E_F로부터 약 2.5 eV 아래에 폭이 넓은 피이크도 관찰되었다. 그 중 E_F 근처에 위치한 피이크의 폭은 bulk Co $3d$ 전자 PES 스펙트럼에서의 피이크폭에 비하여 훨씬 좁았는데, 이러한 차이는 Co 자기모멘트가 Co /Pd 다층박막에서 bulk Co 에 비하여 증진되는 현상과 일치한다. 한편 E_F 아래 2.5 eV에 위치한 피이크는 Pd의 valence band 구조와 유사함이 발견되었는데, 이는 Co 단층과 Pd 단층간에 상당한 상호작용 (hybridization)이 있음을 나타낸다고 볼 수 있다. Co /Pd 다층박막에 대하여 실험적으로 결정한 Co $3d$ 전자 PES 스펙트럼을 국재스핀밀도함수이론을 이용하여 얻은 이론적 전자구조 계산결과와 비교하였다. 이상의 비교에 의하면 밴드이론계산에 의한 Co $3d$ 밴드폭은 실험과 잘 일치하였으나, PES 스펙트럼에서 관찰되어진 E_F 근처의 폭이 좁은 피이크는 밴드이론이 잘 기술하지 못함이 발견되었다.