Electronic structure and magnetic anisotropy of Co/Au(111): A spin-resolved photoelectron spectroscopy study

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We have measured spin- and angle-resolved photoemission spectra of Co thin films epitaxially grown on the Au(111) substrate and investigated their electronic and magnetic properties. At the Co/Au(111) interface, we observed strong mixing between Au $5d$ and Co $3d$ states resulting in the spin polarization of Au $5d$ states and the increase of Co $3d$ orbitals parallel to the surface, which causes the perpendicular magnetic anisotropy of Co films. The electronic structure of Co thin films in a low-coverage region is different from that of bulk hcp Co and it becomes closer to those of the bulk as film thickness increases. The reorientation of the magnetization direction was observed at about 6 ML, the origin of which is qualitatively explained by the relaxation of the atomic distance of Co perpendicular to the surface.

I. INTRODUCTION

Epitaxially grown magnetic thin films in a monolayer regime have attracted many interests because they embody magnetic properties with low dimensionality such as perpendicular magnetic anisotropy (PMA), enhanced magnetic moments at surface, etc.,[1] which have been considered to play a prominent role in developing future magnetic data-storage media. The interest in epitaxial grown Co films and Co/Au multilayers are due to their peculiar magnetic properties; giant magnetoresistance, oscillatory behavior of interlayer magnetic coupling, and PMA.[2–4] Since the magnetic properties of the systems depend on details of geometric structures, many studies have been performed using various experimental techniques, which are accessible to their structural and magnetic properties. In a Co/Au(111) system, a large lattice mismatch ($\sim$14%) between Co and Au(111) causes the characteristic growth mode of Co films. The features of the growth mode of Co were observed in detail by ion scattering experiments,[5] scanning tunneling microscopy (STM),[6–9] low-energy electron diffraction (LEED), and Auger electron spectroscopy (AES).[8,10] An x-ray diffraction study[11,12] suggests the structure of Co films to be a hexagonal structure. The investigation by STM (Ref. 6) showed that evaporated Co starts to nucleate at a kink of the reconstructed Au(111) surface with a zigzag pattern and forms flat islands with a hexagonal closed-packed (hcp) structure and then the islands become coreleased and connected to one another to form film domains.

Magnetically, the polygonal Co islands are of two atomic layers in the low-coverage region and show superparamagnetism at low temperature.[9] The magnetization direction depends on the film thickness and changes from perpendicular to parallel to the surface at a certain thickness (about 6 ML),[13] which is due to the dominant contribution of surface and interface terms to an anisotropy energy. A recent study of the magnetic anisotropy of the Co film in Co/Au/Cu(111) trilayer configuration[14] shows that PMA is strongly influenced by the expansion of the in-plane lattice of Co. This suggests the connection between the structure and the electronic, and hence, the magnetic properties of Co films at the interface. However, only a few experimental works were devoted to directly observe the electronic structures of Co films on Au and their interfaces, so far. Angle-resolved photoemission spectra of Co/Au(111) (Ref. 15) show that the surface electronic states of Au(111) are diminished by the growth of Co layers. The analyses of the Au $4f$ core-level spectra show a possible interdiffusion between Co overlayers and the substrate.[16] The relationship between morphological information and electronic states causing the characteristic ferromagnetism of Co film has not been fully understood.

In this paper, we present spin-and angle-resolved photoemission spectra (SARPES) of a Co/Au(111) system in order to demonstrate the spin-dependent electronic structures in a monolayer regime and to investigate the thickness dependence of the electronic and magnetic properties of Co films.

II. EXPERIMENT

The SARPES measurements were carried out at the undulator beamline BL-19A of the Photon Factory using a spin- and angle-resolved photoelectron spectrometer consisting of a hemispherical electron energy analyzer and a compact retarding type Mott detector.[17] A Au single crystal was cleaned by repeated cycles of Ar ion bombardment and annealing at 550 °C. The reconstructed clean Au(111) surface was confirmed by clear LEED patterns and the existence of surface electronic states in the valence-band photoemission spectra. The Co film was evaporated at room temperature by an electron bombardment of a high-purity Co wire in the vacuum below 4×10^{-10} Torr with a growth rate of 0.1–0.2 ML/min. The cleanliness of the Co film was confirmed by AES before and after every SARPES measurement. Since the growth mode is not a layer-by-layer one but a formation of islands as has been observed by STM measurements,[6] the thickness presented below indicates an averaged one within the area measured by SARPES. We have estimated the Co film thickness by the Auger intensity ratio of Co MVV (53 eV) to Au NVV (69 eV), which was normalized to the disappearance thickness of out-of-plane magnetization of 6 ML.[13]

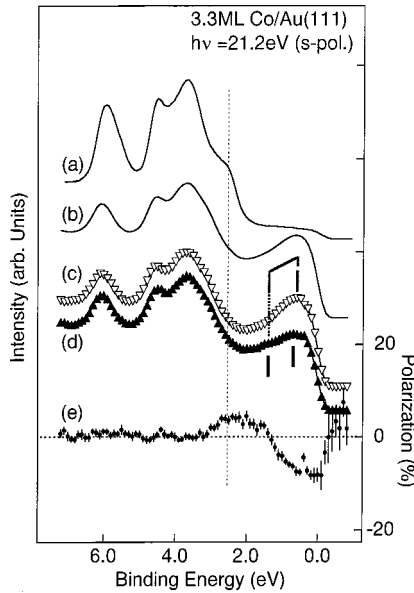In SARPES measurements, samples were magnetized re-

FIG. 1. Spin-resolved photoemission spectra and the spin polarization for a 3.3 ML Co film deposited on Au(111) substrate measured in normal emission at the photon energy of 21.2 eV. Photoemission spectrum for a clean surface of Au(111) is indicated in the solid line (a). (b) shows the spin-integrated spectra of 3 ML Co film deposited on Au(111). The majority- (c) and minority- (d) spin spectra are plotted by solid markers and open triangles, respectively. (e) shows spin polarization perpendicular to the surface.

manently by applying a magnetic field (below ~0.1 T) along the direction parallel or perpendicular to the sample surface. We have adopted s-polarized incident light and collected photoelectrons emitted normal to the sample surface. The photon energies of 21.2 and 28 eV were selected, so that the observed SARPES could be compared with previous observations using a He discharge lamp[15] and those corresponding to the electronic states at the Γ point in the Bruillouin zone (BZ), respectively. The energy resolution of the observed spectra was 0.3 and 0.15 eV at excitation energies of 21.2 and 28 eV, respectively.

III. RESULTS AND DISCUSSION

Figure 1 shows SARPES and the spin polarization of Co/Au(111) in the low-coverage region (3.3 ML) together with the spectrum of clean Au(111). They were measured at room temperature with an excitation energy of 21.2 eV with applying the magnetic field perpendicular to the surface. In the Au(111) spectrum [Fig. 1(a)], the prominent structures at the binding energies around 6 and 4 eV are originated from $5d$ valence bands of e_g and t_{2g} symmetries, respectively. The shoulder discernible at about 2.5 eV is a surface resonance state derived from upper $5d$ bands.[18] The surface electronic states, which was observed previously near the Fermi level,[15,18] did not appear in the spectrum, since the photoelectron excitation from the state is not allowed by s-polarized light. Upon Co deposition, a new broad feature appears within 2 eV from the Fermi level, which dominates over Au valence bands as the Co thickness increases.
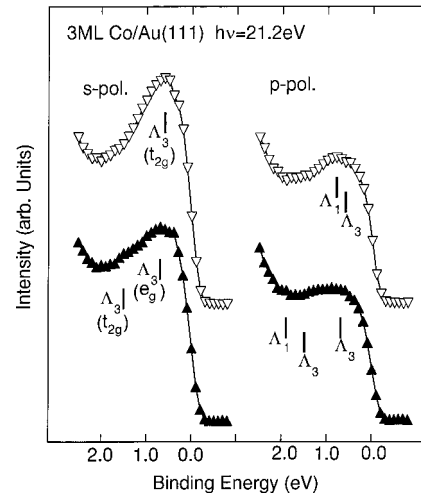

FIG. 2. Spin-resolved photoemission spectra of Co/Au(111) with the film thickness of 3 ML measured with s- (left) and p-polarized light (right) at 21.2 eV. Majority- and minority-spin spectra measured with p-polarized light consist of both Λ_1 and Λ_3 symmetry bands.

The remarkable point in the figure is that the shoulder at the Au $5d$ bands is diminished after Co deposition [Fig. 1(b)] and shows a considerably large positive spin polarization perpendicular to the surface, while the main Au $5d$ bands do not acquire a noticeable transport polarization due to the traveling of the photoelectrons through the magnetic Co film.[19–21] Since the Au $5d$ states are almost fully occupied at the initial state, the observation indicates that the Co deposition alters the surface resonant states derived from the upper $5d$ states and causes the charge transfer from the Au $5d$ occupied states to the Co $3d$ empty states at the Au/Co interface. This leads the occupancy difference between the majority- and minority-spin electrons, and hence, the positive spin polarization in the upper $5d$ states. The main origins of the negligibly small transport polarization effect are considered that the spin-dependent inelastic scattering probability is small for photoelectrons through a thin film of Co with a small number of unoccupied $3d$ states and that the inelastic mean free path is relatively large for photoelectrons with kinetic energy below 30 eV.[20,21]

The excitation energy of 21.2 eV probes the electronic states at the quarter point of the Γ-L line in the fcc BZ,[22] and only the fcc Λ_3 symmetry states are observable by s-polarized light. To investigate the electronic structures of the Co $3d$ originated valence states, we have assigned the energy positions of the peaks on the basis of a second derivatives of the energy distribution curves of both spins. In the majority-spin spectrum, a distinct peak at the binding energy of 0.7 eV and a broad peak at 1.4 eV are assigned as Λ_3 symmetry upper and lower bands, respectively. The conspicuous peak in the minority-spin spectrum corresponds to the lower Λ_3 band, which is the exchange partner of the Λ_3 band in the majority spectrum. The assignment of the features was confirmed by the polarization dependence of the SARPES (Fig. 2). The observed spectra measured with p-polarized light show both Λ_1 and Λ_3 bands in the
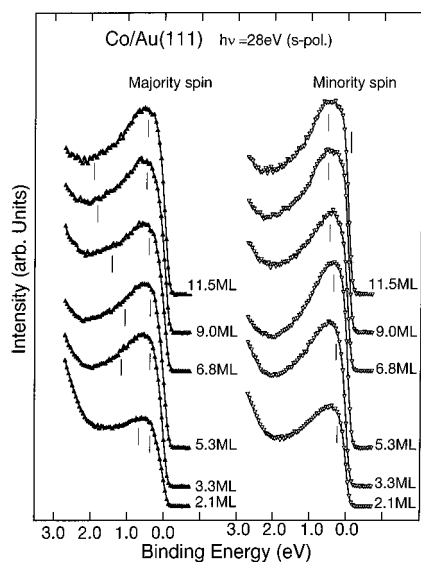
FIG. 3. Spin-resolved photoemission spectra of Co/Au(111) of various Co film thicknesses. The spectra have been measured in normal emission mode with excitation energy of 28 eV. The majority- and minority-spin spectra are arranged on the left and right side in the figure, respectively. Vertical bars indicate the binding energies of the spectral features obtained by the least square fitting procedure.

majority- and minority-spin spectra.

Figure 3 shows the thickness dependence of SARPES observed with an excitation energy of 28 eV, which corresponds to the valence states at Γ point in the BZ. In the figure we show spectral features with a binding energy below 3 eV to investigate the evolution of Co $3d$ bands. The spectra with the Co thickness below 6 ML and above it have been measured by applying the magnetic field along [0001] and [$10\bar{1}0$] direction, respectively. We could not observe SARPES for the Co films with a thickness below 2 ML, which implies that there was no remanent magnetization in the Co film at room temperature. The specific range of the Co film thickness with PMA is comparable with the previous reports[13] within the limitation of errors of the measured thickness originated from the characteristic growth mode of Co on Au(111) substrate. In the present paper, we have neglected the effects originated from the magnetic grain structures that have been observed by microscopic techniques,[23] since the spin-dependent electronic structures are averaged ones within the area measured by SARPES.

In Fig. 3, two spectral features are observed in each majority-spin spectrum. The feature at lower-binding energy corresponds to e_g states and the one at higher-binding energy to t_{2g} states. The binding energies of both features show thickness dependence; the binding energy of the upper-band peak slightly increases from 0.37 to 0.46 eV and the binding energy of the lower band changes from 0.69 to 1.92 eV as the film thickness increases from 2.1 to 12 ML. In the minority-spin spectra, the observed peaks correspond to the lower $3d$ band. Its binding energy increases from 0.23 to 0.54 eV with an increase of the Co thickness. For the Co film with a thickness over 7 ML, an additional feature appears
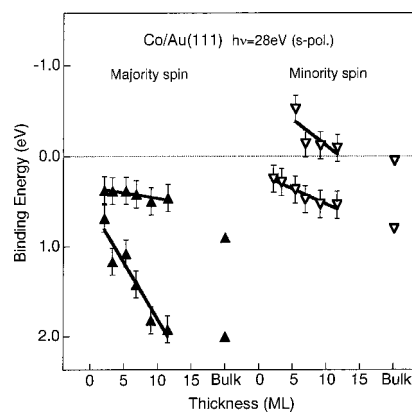

FIG. 4. Thickness dependence of the spectral features in the majority- and minority-spin spectra. The binding energies for bulk Co is obtained from Ref. 24.

near the Fermi level and its binding energy and spectral intensity increase with the film thickness. Figure 4 shows the thickness dependence of the binding energies of the spectral features in the majority- and minority-spin spectra in Fig. 3. The binding energies were obtained by a least-square-fitting method adopting the experimental energy resolution of 0.15 eV and the Fermi distribution function at room temperature. In the figure, the binding energy of the lower band shows more obvious thickness dependence than that of the upper band. The majority- and minority-spin spectra observed for the Co films thicker than 12 ML reveal spectral features of those of bulk hcp Co(0001) (Ref. 24) and we did not observe further thickness dependence in the SARPES.

So far, the magnetic anisotropy of thin films and multilayers have been studied by magneto-optical Kerr effects,[25] magnetic linear and circular dichroism,[26,27] etc. The origin of the reorientation of magnetization direction was considered due to the demagnetizing field caused by the roughness of the interface,[28] to spin-orbit interaction,[29,30] or to the relaxation of lattice mismatch between the film and the substrate.[4,13,31] In order to discuss the relationship between our experimental results and the magnetic anisotropy, we have considered two aspects; magnetoelastic and magnetocrystalline anisotropy. Recently, Murayama *et al.*[14] have studied the magnetic properties of Co/Au/Cu(111) system with varying the thickness of Au and showed that PMA of the Co film increases with increase of the in-plane Co lattice constant. The result suggests that the strain induced in the Co at the interface plays a significant role in the phenomenon and that the reorientation of the magnetization direction of Co film could be understood as a result of the restoration of the strain. In Fig. 3, the intensity and the width of Co $3d$ states increase with an increase of the film thickness. Since the probing depth of the SARPES in the present paper is about 3 ML or less, the observed spectra represent the electronic structure of the Co within a few layers from the surface. The observed thickness dependence of the electronic structure implies that the density of the Co valence states in the topmost few layers vary with the film thickness, the origin of which is possibly due to the relaxation of the lattice constant of the Co film. Since the STM and XAFS (Ref. 32)

TABLE I. Experimentally observed binding energies of Co films at the Γ point in the BZ together with those obtained previously for bulk and thick (20 ML) films on Cu(111).

		Upper band			Lower band		
		$\Gamma_{12\uparrow}$	$\Gamma_{12\downarrow}$	Δ_{ex}	$\Gamma_{25\uparrow}$	$\Gamma_{25\downarrow}$	Δ_{ex}
Bulk Co(0001)		0.9	0.05	0.85	2.0	0.8	1.2
Thick film Co/Cu(111)		1.0	$>E_F$		2.1	0.7	1.4
Co/Au(111)	2.1 ML	0.37	$>E_F$		0.69	0.23	0.46
	11.5 ML	0.46	−0.09	0.55	1.92	0.54	1.38

studies showed that the structure of Co on Au(111) was hcp and the in-plane lattice constant did not vary with Co film thickness, it is reasonable to regard that the relaxation of the lattice distance of Co occurs in the direction perpendicular to the surface and the restoration to the lattice constant of bulk Co causes the thickness dependence of the electronic structure. In the momentum space, the relaxation causes the restoration, i.e., the shrink of the reciprocal lattice along the Γ-L direction in the BZ and hence, leads to the increase of the density of states observed by SARPES with a certain energy and momentum resolution. The magnetic thin film of Ni/Cu(111) (Ref. 33) was actually observed to be in a strained structure, which is considered to cause the reorientation of the magnetization direction due to the magnetoelastic anisotropy.

On the basis of the results of XMCD experiments, Weller *et al.*[26] have shown that PMA of Co films could be understood in respect to the spin-orbit coupling between $3d$ electrons in Co, i.e., magnetocrystalline anisotropy. According to the perturbation theory treated by Bruno,[29] they showed that in the low-coverage region, the easy magnetization axis directs perpendicular to the surface due to the larger contribution of in-plane $3d_{xy}$ and $3d_{x^2-y^2}$ orbitals than those from the out-of-plane orbital to the magnetic moment of Co. As the film thickness increases, the increasing contribution of the out-of-plane orbitals ($3d_{yz}$ and $3d_{zx}$) leads to redirect the easy magnetization axis parallel to the surface. The explanation implicitly assumed that the modification of electronic structures occurs at the Co/Au interface and as the film thickness increases, the valence band with $3d_{zx}$ and $3d_{yz}$ symmetry states would shift from unoccupied to occupied states. According to the first-principle calculation of the electronic structure of Co/Cu(111), Zong *et al.*[34] pointed out that the hybridization of out-of-plane Co $3d_{yz}$ and $3d_{zx}$ states with Cu $3d$ states at the interface results the upward shift in energy and plays an essential role in PMA of the Co film. However, we cannot simply apply their results to the Co/Au(111) system as they suggested. Since the shoulder structure of Au $5d$ derived band is diminished and the upper $5d$ bands show positive spin polarization, there exists a strong contribution of in-plane Au $5d$ orbitals to the hybridization, which results the spin polarization of Au $5d$ states perpendicular to the surface. To interpret the microscopic origin of PMA of Co ''at the thin end,'' we have to consider not only the in-plane Co $3d$ states but also in-plane Au $5d$ states.

We could not observe PMA, but in-plane magnetization for Co films thicker than 6 ML, above which both majority- and minority-spin spectra show broad features. Especially,

we have observed the clear evidence of a new feature appeared near the Fermi level in the minority spectra. This additional feature corresponds to the upper Λ_3 band and mainly consists of out-of-plane Co $3d_{yz}$ and $3d_{zx}$ states. In Fig. 4, the binding energy of this band increases with an increase of the film thickness. This implies the increase of the occupancy of this band and the increase of the in-plane orbital moment. Hence, the relaxation of the Co atomic distance perpendicular to the surface causes the increasing contribution of $3d_{yz}$ and $3d_{zx}$ states with the film thickness to the Co valence states, which leads to the reorientation of the PMA occurred at the Co/Au(111) interface.

In Table I, we present the experimentally observed binding energies of the spectral features at the Γ point in the BZ together with previously observed ones. The exchange splittings of upper and lower bands increase with increasing thickness and reach to those obtained from SARPES of thick (20 ML) Co/Cu(111) film[35] and those of bulk.[24] However, the discrepancy still exists between the present results evaluated from SARPES and those in the previous works. The exchange splitting of the upper bands (0.55 eV) for thick (11.5 ML) film are smaller compared with the one reported for the bulk, while the exchange splitting of the lower bands (1.38 eV) is comparable to the one for the bulk. Since we did not observe a further increase of the exchange splitting energies with increasing film thickness over 12 ML, the discrepancy between present results and those of previously reported is partly due to the uncertainty which inevitably is included in the line-shape analysis to separate the spin-integrated spectra into majority- and minority-spin ones.

In conclusion, we have measured the thickness dependence of the SARPES spectra of Co films grown on Au(111) surface. At Co/Au(111) interface, the strong mixing between Au $5d$ and Co $3d$ states results in the increase of the $3d$ orbitals parallel to the surface, and it takes a part of the perpendicular magnetic anisotropy of Co films. The origin of the reorientation of PMA observed at about 6 ML Co film is qualitatively explained that the lattice distance of the Co in the few layers from the surface relaxes along the direction perpendicular to the surface as the film thickness increases.

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