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# Perpendicular magnetic anisotropy associated with strain relaxation in Ru/Co/Ru(0001): Anomalous relation of atomic and magnetic structures

J. Miyawaki,[1,2] D. Matsumura,[1,3] H. Abe,[1,4] T. Ohtsuki,[1] E. Sakai,[1] K. Amemiya,[5,6,*] and T. Ohta[7]

[1]*Department of Chemistry, Graduate School of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan*

[2]*Soft X-ray Spectroscopy Laboratory, RIKEN SPring-8 Center, Sayo, Sayo, Hyogo 679-5148, Japan*

[3]*Kansai Photon Science Institute, Japan Atomic Energy Agency, Sayo, Sayo, Hyogo 679-5148, Japan*

[4]*Department of Chemistry, Faculty of Science and Technology, Keio University, Yokohama, Kanagawa 223-8522, Japan*

[5]*Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Ibaraki 305-0801, Japan*

[6]*Japan Science and Technology Agency, CREST, Kawaguchi, Saitama 332-0012, Japan*

[7]*SR Center, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan*

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Atomic structure and magnetic anisotropy of Ru/Co/Ru(0001) were studied by Co *K*-edge extended x-ray absorption fine structure and Co $L_{III,II}$-edge x-ray magnetic circular dichroism. The Co/Ru(0001) films exhibit in-plane magnetization in a thickness range of 1–15 ML. The Co film shows a large expansion of the in-plane Co-Co bond length at the initial stage of the growth, leading to a large strain. Upon Ru capping on the Co/Ru(0001) film, the strain is relaxed and a spin reorientation transition (SRT) occurs from in-plane to out-of-plane magnetization. These results contradict the conventional understanding of magnetic anisotropy in which perpendicular magnetic anisotropy (PMA) is believed to be enhanced by the strain in the film. The estimation of magnetic anisotropy constants revealed that the SRT is induced by a large PMA at the Co/Ru interface in the Ru capped films, as well as a large in-plane magnetic anisotropy at the vacuum/Co and/or Co/Ru interfaces in the Co bare films.

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Magnetic thin films have been extensively studied in recent decades because of their various peculiar magnetic properties such as perpendicular magnetic anisotropy (PMA) and interlayer exchange coupling.[1–3] Among many ferromagnetic/nonmagnetic metal systems, Ru/Co/Ru(0001) shows PMA, as well as a strong magnetic interlayer exchange coupling.[4–9] Moreover, interesting magnetic properties based on a unique Co growth mode on a Ru(0001) substrate were reported.[10,11] Although the origin of the interlayer coupling is believed to be basically understood, few studies were dedicated to the atomic structure[7,12–14] and the magnetic anisotropy.[15,16]

PMA in Co films has been attributed to a large strain, an in-plane expansion of Co, and to the contribution of the interface between Co and nonmagnetic metals. Efforts have been made to connect the atomic structure with magnetic anisotropy by estimating the magnetoelastic anisotropy energy from the strain in the films.[17–21] The atomic structure has usually been investigated by low-energy electron diffraction (LEED) or reflection high-energy electron diffraction (RHEED). Only the lateral strain can be estimated by these techniques, however, so that the effects of the vertical strain have been neglected or just speculated so far. Moreover, the structural changes in the magnetic film upon capping with nonmagnetic overlayer cannot be investigated due to the surface sensitivity of LEED and RHEED and the lack of element specificity.

In this work, we have investigated the atomic structure and magnetic anisotropy of Co thin films on a Ru(0001) single crystal and the effects of the Ru capping by means of extended x-ray absorption fine structure (EXAFS) and x-ray magnetic circular dichroism (XMCD). Owing to the element specificity and bulk sensitivity of fluorescence-yield EXAFS, the atomic structure of Co films can be directly determined even after Ru capping. Moreover, polarization dependence of EXAFS allows us to separately determine the strain in both the lateral and vertical directions. The EXAFS analyses show a large in-plane expansion of the Co films at the initial stage of the film growth, which is drastically relaxed upon Ru capping. The changes in magnetic anisotropy constants are estimated by using the obtained structural parameters. It is revealed that the spin reorientation transition (SRT) to PMA upon Ru capping is attributed to a large PMA at the Co/Ru interface in the Ru capped films and to a large in-plane magnetic anisotropy at the vacuum/Co and/or Co/Ru interface in the Co bare films.

All the samples were prepared in an ultrahigh-vacuum chamber according to the following procedure. A Ru(0001) single crystal was cleaned by repeated cycles of $Ar^+$ sputtering (2 keV) and subsequent annealing at ~1470 K. Co films were deposited on Ru(0001) at the substrate temperature of 363 K with the electron-bombardment evaporation method. The thickness of the Co films was controlled by monitoring the oscillatory intensity of a RHEED spot and the Co deposition rate was ~0.2 ML/min. Ru/Co/Ru(0001) samples were prepared by the subsequent deposition of Ru at 363 K. The deposition rate of Ru was calibrated by the homoepitaxial growth on Ru(0001).

The Co *K*-edge EXAFS spectra were measured at BL-7C of the Photon Factory in the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-PF). All the spectra were recorded in the fluorescence-yield mode with a solid-state detector. To examine a crystallographic anisotropy in the Co thin films, EXAFS spectra were taken at grazing incidence (GI) of the x rays ($\theta$=30°) and normal incidence (NI, $\theta$=90°), where $\theta$ is the angle be-

 

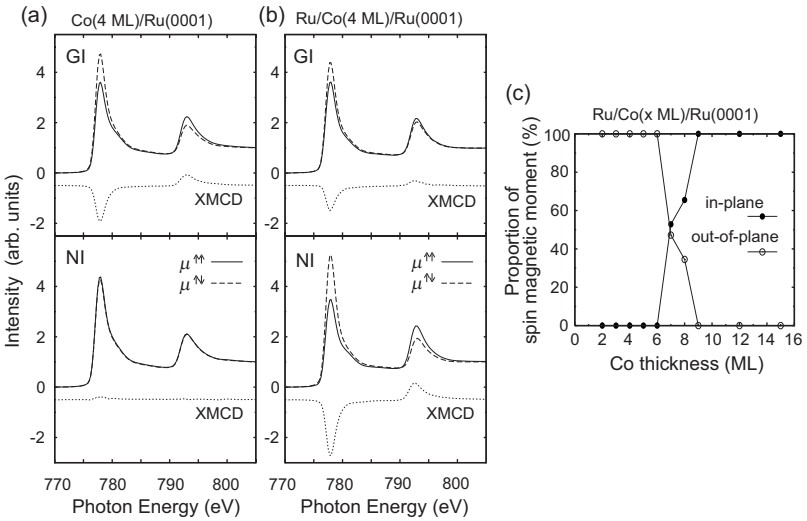


FIG. 1. Co $L_{III,II}$-edge circularly polarized x-ray absorption (solid and dashed lines) and XMCD difference (dotted line) spectra of 4 ML Co/Ru(0001) (a) before and (b) after 5 MLE-Ru capping, and (c) proportion of in-plane and out-of-plane magnetizations in Ru(5 MLE)/Co($x$ ML)/Ru(0001) films.

tween the direction of the incident x-ray beam and the sample surface. All the measurements were performed at 120 K.

The Co $L_{III,II}$-edge XMCD spectra were taken at BL-7A of KEK-PF. All the spectra were recorded in the partial electron yield mode with a microchannel plate detector. The XMCD spectra were obtained by reversing the magnetization of the films by the pulse magnetic field of ~0.1 T along the x-ray propagation direction, and the remanent magnetization was examined. For the detection of the direction of magnetization, XMCD measurements were performed at GI ($\theta$ =30°) and NI ($\theta$=90°).

Figure 1 shows Co $L_{III,II}$-edge circularly polarized and XMCD difference spectra of a 4 ML Co film taken before and after capping by 5 monolayer-equivalent (MLE) Ru. In the as-deposited film, a strong XMCD signal is observed only at GI. This directly implies the in-plane magnetization since the XMCD intensity is proportional to the magnetic component parallel to the incident x rays. Upon capping with Ru, the XMCD signal appears at NI, indicating that an SRT to PMA occurs. Figure 1(c) shows the proportion of in-plane and out-of-plane magnetizations for as-deposited and 5 MLE-Ru-capped Co thin films, which is obtained from the incidence-angle dependence of the XMCD signals. Although Co films show only in-plane magnetization before Ru capping, the films between 2 and 6 ML exhibit PMA after Ru capping. It should be mentioned that El Gabaly *et al.*[11] reported PMA at 2 ML Co thickness without any capping layer, which seems to contradict with our results. The substrate temperature during the film growth was 460 K in their experiments, however, leading to a different film structure with that in the present study.

Figure 2 shows Fourier transform of the Co $K$-edge EXAFS function for as-deposited Co thin films. The first nearest-neighbor (NN) shell was analyzed, and the curve-fitting results for the Co-Co bond length are plotted in Fig. 3. The detailed analysis procedures are described elsewhere.[22] The in-plane bond length for the 1 ML sample (2.663 Å) is much larger than that of bulk Co (2.49–2.51 Å) and is almost equal to that of bulk Ru (2.70 Å). This indicates that the first Co layer grows coherently with the Ru substrate, which induces a large strain in the Co film. This strain is gradually relaxed with increasing Co thickness up to 6 ML. These results are in good agreement with RHEED studies.[7,12] Note here that the observed Co-Co bond length is the average over the whole film so that one cannot simply distinguish whether the first (bottom) layer retains the large in-plane expansion during further film growth. The precise EXAFS analyses for the 2 ML sample show, however, that the difference in the in-plane bond lengths of the first and second layers is rather small, suggesting a structural change in the whole film.

Next, the effects of Ru capping were examined. A series of Fourier transforms with increasing Ru coverage on Co(3 ML)/Ru(0001) are shown in Fig. 4. The change in the Co-Co bond length is estimated as shown in Fig. 5. The strain in the

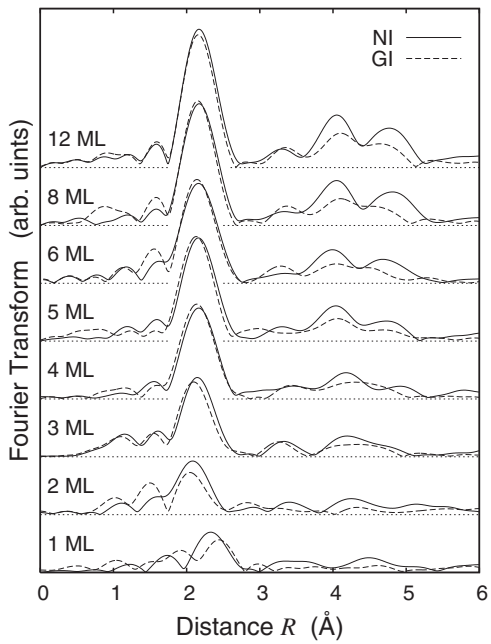


FIG. 2. Fourier transform of the EXAFS function, $k^2\chi(k)$, of Co/Ru(0001) for different Co thicknesses at NI (solid lines) and GI (dashed lines). The windows in the Fourier transformation are from ~3.4 to ~12.0 Å$^{-1}$.

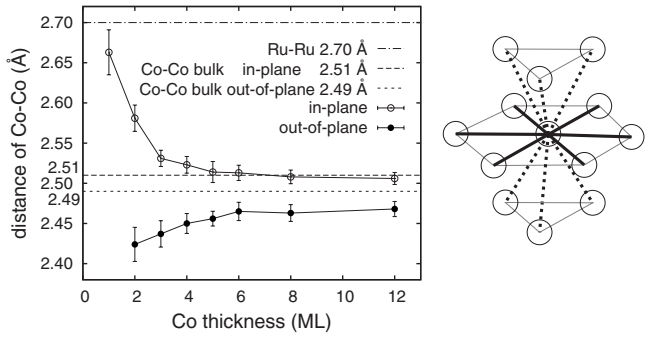


FIG. 3. In-plane and out-of-plane Co-Co distances of Co/Ru(0001) as a function of the Co thickness. The in-plane and out-of-plane bonds are depicted as thick and dotted lines, respectively.

as-deposited 3 ML Co thin film is relaxed by Ru capping and finally vanishes with 4 MLE-Ru capping. Although the same result was also obtained from the 2 ML sample, the Co-Co bond length is not affected by the Ru capping in the 6 ML sample (figures not shown). This is consistent with the fact that the as-deposited 6 ML Co film has no in-plane strain (see Fig. 3).

It should be emphasized here that the Ru substrate induces a large strain in the Co film, while Ru capping reduces the strain. This might be due to the lower surface free energy of Co compared to Ru.[23] At the initial stage of the film growth, Co wets the Ru substrate so as to reduce the surface free energy, leading to a coherent growth with a large strain. As the Co thickness increases or the film is capped with Ru, the strain in the Co film is relaxed because the coherent growth no longer reduces the surface free energy.

It seems surprising that the SRT to PMA is associated with the relaxation of the strain because it contradicts with the conventional understanding of PMA in which PMA is believed to be enhanced by the strain in the film. Finally, magnetic anisotropy of the Co/Ru(0001) and Ru/Co/Ru(0001) films is discussed by using the obtained structural parameters. The uniaxial magnetic anisotropy constant of a hcp Co film including shape anisotropy is given by

$$K_{\mathrm{eff}} = -2\pi M_s^2 + K_{\mathrm{me}} + K_{\mathrm{cr}} + K_i/t, \tag{1}$$

where $M_s$ is saturation magnetization of Co, $t$ is film thickness, and $K_i$ is the interface magnetic anisotropy constant,

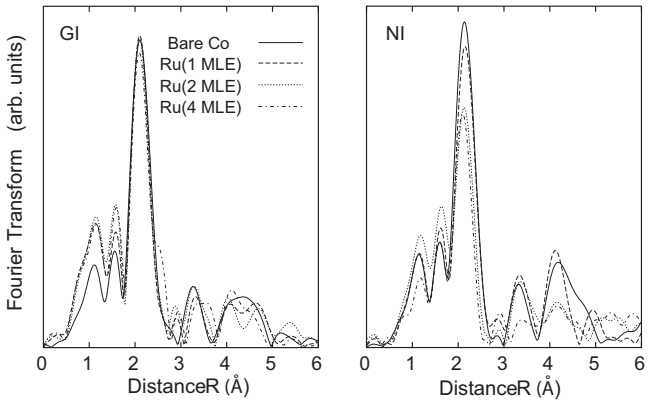


FIG. 4. Fourier transform of $k^2\chi(k)$ of Ru/Co(3 ML)/Ru(0001) for different Ru coverages.

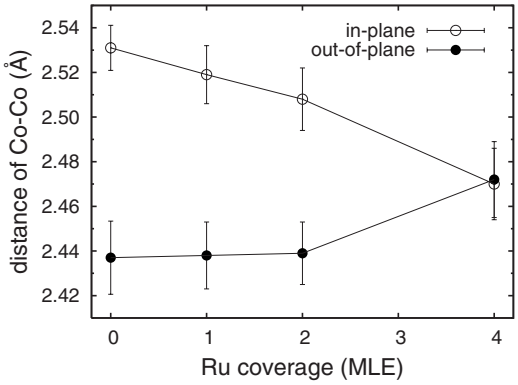


FIG. 5. In-plane and out-of-plane Co-Co distances of Ru/Co (3 ML)/Ru(0001) as a function of the Ru coverage.

expressed as $K_{\mathrm{surf}}+K_{\mathrm{Co/Ru}}$ and $K^{\mathrm{top}}_{\mathrm{Co/Ru}}+K^{\mathrm{bottom}}_{\mathrm{Co/Ru}}$, respectively, for Co/Ru and Ru/Co/Ru. Here, $K_{\mathrm{surf}}$ and $K_{\mathrm{Co/Ru}}$ represent the magnetic anisotropy constants at the Co/vacuum and Co/Ru interfaces, respectively, and $K_{\mathrm{me}}$ is magnetoelastic anisotropy and $K_{\mathrm{cr}}$ is magnetocrystalline anisotropy for an unstrained hcp Co, $6.2\times10^5$ J/m$^3$.[17] $K_{\mathrm{me}}$ is directly related to the atomic structure by using the in-plane strain, $\varepsilon_{11}$ and $\varepsilon_{22}$, and out-of-plane one, $\varepsilon_{33}$,[18,19]

$$K_{\mathrm{me}} = -B_1\varepsilon_{22} - B_2\varepsilon_{33} - B_3(\varepsilon_{11}+\varepsilon_{22}). \tag{2}$$

Here, we can safely assume that $\varepsilon_{11}=\varepsilon_{22}$ and adopt the reported values[18] for bulk hcp Co, $B_1=0.81\times10^7$ J/m$^3$, $B_2=2.90\times10^7$ J/m$^3$, and $B_3=-2.82\times10^7$ J/m$^3$. Note here that the sign of these coefficients is opposite to that in the literature[18] due to the opposite definition of the anisotropy constants.

Figure 6(a) shows in-plane and out-of plane strains, $\varepsilon_{11}$ ($=\varepsilon_{22}$) and $\varepsilon_{33}$, respectively, which are defined by $\varepsilon_{11}=a/2.51-1$ and $\varepsilon_{33}=c/4.07-1$, where $a$ and $c$ are the in-plane and out-of-plane lattice constants. Since Co atoms are tetragonally bonded between the layers, $a$ and $c$ are calculated from the in-plane and out-of-plane bond lengths, $R_\parallel$ and $R_\perp$, as $a=R_\parallel$ and $c=2\sqrt{R_\perp^2-R_\parallel^2/3}$. By using the obtained strains, $K_v=K_{\mathrm{me}}+K_{\mathrm{cr}}$ is estimated from Eq. (2), which is shown in Fig. 6(b). $K_v$ is large in the Co/Ru films especially in the thin-film region due to the large in-plane expansion and out-of-plane compression, while it is relatively small in the Ru capped films.

Then we estimate the overall magnetic anisotropy, $K_{\mathrm{eff}}$. First, let us consider the Ru capped films. The strain in the Co film is relaxed upon Ru capping so that all the films exhibit almost the same atomic structure regardless of the thickness. Therefore, we use the average of $K_v$ for the 2, 3, and 6 ML Co films, $4.6\times10^5$ J/m$^3$. Then the interface contribution, $K_i$, is determined so as to reproduce the critical Co thickness ($\sim$7 ML) for the SRT. By using the saturation magnetization for bulk hcp Co ($M_s=1.787$ $\mu_B$, corresponding to $-2\pi M_s^2=-1.27\times10^6$ J/m$^3$), $K_i=1.2$ mJ/m$^2$ is obtained. The simulated magnetic anisotropy, $K_{\mathrm{eff}}\cdot t$, is also indicated in Fig. 6. Since PMA is realized when $K_{\mathrm{eff}}\cdot t>0$, the observed PMA below $\sim$7 ML Co thickness is reproduced.

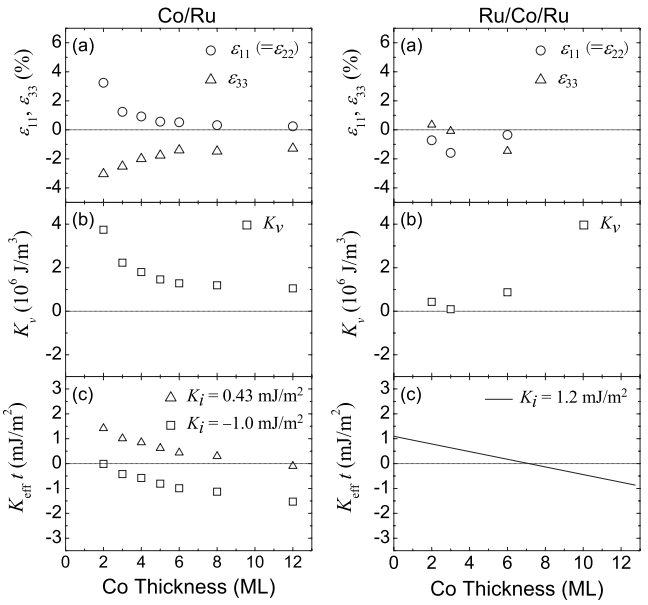


FIG. 6. (a) In-plane and out-of-plane strains, $\varepsilon_{11}$ and $\varepsilon_{22}$, (b) volume part of magnetoelastic anisotropy, $K_v = K_{me} + K_{cr}$, calculated from the strains, and (c) effective anisotropy constant $K_{eff} \cdot t$.

For the bare Co/Ru(0001) films, the obtained strain at each Co thickness is used since the atomic structure strongly depends on the Co thickness. We cannot determine $K_i$ ($=K_{surf}+K_{Co/Ru}$), however, because no PMA is observed over the whole thickness range. Moreover, $K_i$ might depend on the film thickness due to the structural changes. Since $K_{surf} = -0.17$ mJ/m$^2$ was reported[24] for Co/Au(111), we first adopt this value and $K_{Co/Ru} = (K^{top}_{Co/Ru} + K^{bottom}_{Co/Ru})/2$, leading to $K_i = 0.43$ mJ/m$^2$. The simulated curve does not explain observed in-plane magnetization in the thin-film region. In order to reproduce the in-plane magnetization down to 2 ML Co, we must assume a large in-plane magnetic anisotropy at the vacuum/Co and/or Co/Ru interfaces, $K_i < -1.0$ mJ/m$^2$, indicating that the changes in interface anisotropy upon Ru capping is essential for the SRT. It should be emphasized here that even $K_{Co/Ru}$ can be changed by Ru capping due to the large structural changes in the Co films. In fact, El Gabaly *et al.*[11,25] reported that a structural change during the Co evaporation at 460 K induces two SRT, which suggests that the structure of the Co/Ru interface plays an important role in SRT.

In summary, we have measured Co *K*-edge EXAFS and Co $L_{III,II}$-edge XMCD spectra of Co/Ru(0001) and Ru/Co/Ru(0001). PMA is observed only for the Ru capped films in the thickness range of 2–6 ML. Co grows coherently on Ru(0001) with a large strain at the initial stage of the film growth, but the strain is relaxed by Ru capping. The magnetic anisotropy constants were estimated by using the obtained structural parameters, and the SRT is attributed to a large PMA at the Co/Ru interface in the Ru capped films, and to a large in-plane magnetic anisotropy at the vacuum/Co and/or Co/Ru interfaces in the bare Co films.

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*kenta.amemiya@kek.jp

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