Opposite spin reorientation transitions driven by a magnetic orbital moment: Ultrathin Ni films on Cu surfaces

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We observed two opposite spin reorientation transitions (SRT), perpendicular to in-plane magnetization and vice versa, in ultrathin Ni films grown on clean and preoxidized Cu(001) surfaces covered with Cu overlayers. The magneto-optical Kerr effect measurement shows that the Cu capping stabilizes perpendicular magnetization for the clean surface and in-plane magnetization for the preoxidized surface. Correspondingly, the x-ray magnetic circular dichroism measurement elucidates that upon Cu capping the Ni orbital moment is suppressed for clean Cu(001) and enhanced for preoxidized Cu(001). These clearly contrasting findings can be explained by the fact that oxygen atoms act as a surfactant; oxygen always locates at the surface even after Ni and Cu deposition. The present results clearly demonstrate that the modification of the in-plane orbital moment drives the SRT, which is sensitive to interfacial interaction.

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I. INTRODUCTION

The magnetization easy axis for nanoscale magnetic thin films is strongly governed by surface/interface magnetic anisotropy. The surface anisotropy is sensitive to chemical modifications such as the adsorption of gases and metals, which switches the magnetization easy axis, a phenomenon known as spin reorientation transition (SRT). Except for the shape anisotropy, the origin of the magnetic anisotropy is attributed to the spin-orbit coupling $\boldsymbol{L}\cdot\boldsymbol{S}$ (Ref. 1). Thus, the change of the orbital moment is essential for the SRT.

For ultrathin films, several studies have been reported concerning the orbital magnetic moment that induces SRT upon the surface modification. Phenomenologically, the anisotropy of thin films, K, is expressed as

$$K = 2\pi M^2 - K_V - K_i/d, \tag{1}$$

where M is the sample magnetization, K_V the intrinsic volume anisotropy, K_i the surface/interface anisotropy for both sides of the film, and d the film thickness. This phenomenological equation implicitly contains various structural and electronic effects in the thin film: strain, expansion, and orbital magnetic moment. A negative value of K means that the perpendicular magnetization anisotropy (PMA) is stable. The surface/interface modification changes the K_i and SRT occurs when the K changes its sign. Experimental investigations of the change of a magnetization easy axis were first performed using x-ray magnetic circular dichroism (XMCD) for the Co/X (X=Pd, Pt, and Ni) multilayers[2] and Au/Co/Au thin film.[3] A linear scaling between the magnetic anisotropy and the orbital moment was obtained for the Co/X multilayers. Following these experiments, many investigations were carried out to reveal the relationship between the orbital moment and the magnetic anisotropy.[4] However, for thin films exhibiting SRT by the modification of surfaces/interfaces, the interrelation between the macroscopic anisotropy energy and the spin-orbit coupling remains experimentally ambiguous. This is partly because the spin-orbit coupling in the spin reorientation is difficult to evaluate due to the tiny change of the orbital moment.

Ni/Cu(001) is one of the most investigated magnetic thin films. This film shows a thickness-dependent SRT from in-plane to out-of-plane magnetization at $d_c \sim 10$ ML (Ref. 5). The PMA is stabilized via the volume anisotropy term due to its strained structure. Surface modifications of Ni/Cu(001) by adsorbates (H_2, CO, and Cu) change the surface anisotropy, resulting in a shift of the critical thickness, d_c. The adsorbates always shift d_c to a thinner region, because the surface anisotropy in this system strongly favors in-plane magnetization and the adsorbates suppress the surface anisotropy.[6]

In this paper, we present combined XMCD and *in situ* magneto-optical Kerr effect (MOKE) results for the Cu capping effects in the Ni films grown on clean and preoxidized Cu(001). The two Ni films exhibit opposite SRT upon Cu capping; the critical thickness is reduced for Ni on clean Cu(001), while it becomes larger for preoxidized Cu(001) upon Cu capping. This is due to the fact that oxygen atoms always locate at the surface. It should be noted that, despite the fact that the chemical bond between O and Ni is much stronger than that between O and Cu, oxygen favorably locates at the surface even after the Cu capping. From the macroscopic and microscopic points of view, we show that the decrease in the surface/interface anisotropy energy is accompanied by the reduction of the orbital moment and vice versa, and that the hysteresis loss, which can be proportional to the uniaxial magnetic anisotropy, also follows the variation of the orbital moment.

II. EXPERIMENTAL

Experiments were performed in two separate ultrahigh vacuum chambers, one for MOKE and another for XMCD measurements. The operating pressures were less than 2×10^{-10} Torr. Both the chambers were equipped with low-energy electron-diffraction (LEED) and reflection high-energy electron-diffraction (RHEED) optics, and the LEED

equipments were also used to take Auger electron spectra (AES). A Cu(001) sample was cleaned by repeated cycles of Ar^+ sputtering at 1 keV and subsequent annealing at 825 K. Carbon contamination was removed by annealing the sample at 600 K in 2×10^{-8} Torr of NO gas. After this cleaning, the sample showed a 1×1 LEED pattern with low background, and by using AES the contamination (mainly carbon) was below 2%. The sample was oxidized by exposing 1000 L O_2 (1 L=1×10^{-6} Torr s) at 500 K. Ni and Cu were deposited from commercial evaporators, and the pressure was maintained at below 5×10^{-10} Torr for Ni and 2×10^{-9} Torr for Cu deposition. The sample temperature was kept at 300 K for Ni film growth and 90 K for Cu capping, respectively. The Ni coverage was calibrated by the observation of the RHEED oscillation, while the Cu coverage was measured by AES.

The MOKE experiment was performed using a diode laser (635 nm) with an available magnetic field of 2500 G. The laser was focused onto the sample ($\phi\sim0.2$ mm) with the incident angle of 45° for both longitudinal and polar configuration. The XMCD measurement was done using the circularly polarized synchrotron radiation from BL4B at UVSOR (a bending magnet station). During the XMCD measurement, a magnetic field of 1000 G was applied, large enough to saturate the sample magnetization along the easy axis. The circularly polarized x rays were obtained using the symmetric upper and lower parts (±0.4 mrad) from the orbital plane. By using the thick Co film as a standard specimen, we evaluated the polarization as 0.70, where the energy resolution $\Delta E/E$ was 10^{-3}. We took all the x-ray absorption spectra (XAS) by monitoring the total electron yield, and simultaneously we measured the intensity of the incident x ray (I_0) with a Au-coated *W* mesh placed in front of the sample. We obtained the circularly polarized XAS spectra by division of the total yield spectra with the I_0 current measured simultaneously, subsequent preedge linear background subtraction, and normalization with the edge jumps. The XMCD spectra were recorded with the reversal of the magnetic field and the helicity of x rays. The MOKE and XMCD measurements were done at 90 K, far below the Curie temperature for the 5-ML Ni films ($T_c>300$ K). For the films with the in-plane magnetization easy axis, the magnetic field is applied along the [110] direction, which is the easy axis for Ni/Cu(001).[7]

III. RESULT AND DISCUSSION

First, we show structural results for the growth of the Ni films and the Cu capping effect of Cu/Ni/Cu(001) with and without preoxidized treatment using LEED and AES. As is well shown in Refs. 8 and 9, the oxygen acts as a surfactant and stays at the surface during the Ni film growth. The oxygen's upcoming behavior is demonstrated well in the AES plot (Fig. 1), where the intensity of the O-*KLL* Auger electrons is constant during Ni growth. Furthermore, during the Cu capping, ~10 ML, the oxygen AES intensity is again constant, clarifying that the oxygen stays at the surface. Figures 1(a)–1(d) show the evolution of the LEED pattern. The LEED changes from the $(2\sqrt{2}\times\sqrt{2})R45°$ pattern of

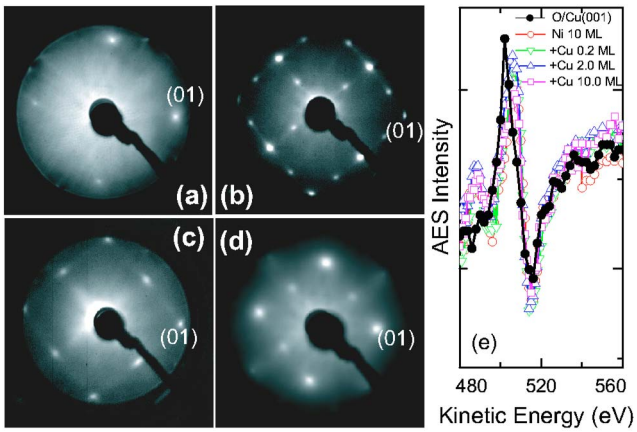

FIG. 1. (Color online) Evolution of the LEED pattern [(a)-(d)] and the AES intensity (e) during the Ni growth on Cu(001): (a) $p(1\times1)$ for Cu(2 ML)/Ni(10 ML)/Cu(001), (b) $p(2\sqrt{2}\times\sqrt{2})R45°$ for O/Cu(001), (c) $c(2\times2)$ for Ni(5.5 ML)/O/Cu(001), and (d) $c(2\times2)$ for Cu(2 ML)/Ni(5.5 ML)/O/Cu(001). (e) O-*KLL* AES intensities as a parameter of Cu capping thickness.

O/Cu(001) to $c(2\times2)$ upon the deposition of Ni, and finally the $c(2\times2)$ pattern survives after the 2-ML Cu capping. The oxygen forms missing rows on Cu(001) when it is adsorbed at a high substrate temperature, while the oxygen atoms are adsorbed on hollow sites with a low temperature.[10] The $c(2\times2)$ pattern observed on Cu/Ni/O/Cu(001) indicates that the O atoms adsorb on hollow sites and the oxygen acts as a surfactant for the additional Cu capping even at 90 K. The LEED and AES results clearly show that after the Cu capping both the interfaces of the Ni films are essentially identical.

The structural results suggest that the Ni thin films Cu/Ni/Cu(001) and Cu/Ni/O/Cu(001) have the same magnetic properties for more than 1-ML Cu capping, and that no oxygen layer is inserted in the magnetic film. The chemical bond between O and Ni should be much stronger than the O-Cu bond, and thus the upturn of the oxygen atoms during the Ni growth is reasonable. However, it should be emphasized that during the Cu capping the oxygen atoms are again brought up to the surface. This implies that the stable site of the oxygen atoms is always on the surface, overcoming the energy loss concerning the O-Cu chemical bond instead of the O-Ni one.

Figure 2(a) shows the polar-MOKE intensities (P-MOKE) as a function of Ni film thickness on clean Cu(001) and subsequent Cu capping thickness. With increasing Ni thickness, the Ni film shows SRT around 9 ML from in-plane to perpendicular magnetization, in agreement with the previous works.[6] Upon Cu capping, the perpendicular magnetization region is extended to lower Ni coverage, indicating that the energy of the surface (vacuum/Ni interface) anisotropy is smaller than that of the Cu/Ni interface anisotropy. Figure 2(b) shows the P-MOKE intensities as a function of Ni film thickness on preoxidized Cu(001). With increasing Ni thickness, the Ni film shows a SRT around 5 ML from in plane to perpendicular.[7] Upon Cu capping the critical thickness shifts to a higher Ni coverage side, indicating that the O/Ni interface anisotropy energy is larger than the Cu/Ni one. The

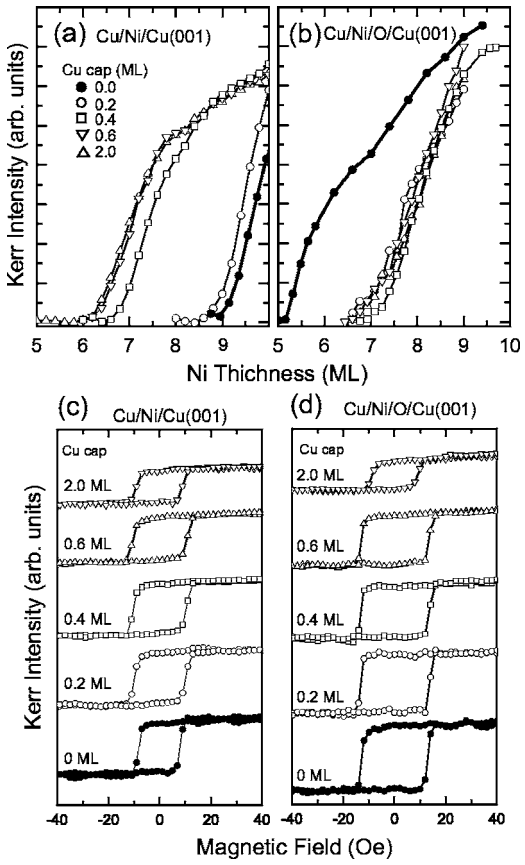

FIG. 2. (a) Polar-MOKE intensity (perpendicular magnetization) for various Cu capping thicknesses onto the Ni film without oxygen measured in remanence. The data was taken on a wedged Ni film. (b) The same as (a), but measured for the Ni film grown on the preoxidized surface. (c) Magnetic hysteresis loops using the longitudinal Kerr effect (in-plane magnetization) measured on Cu/Ni(5.5 ML)/Cu(001). (d) The same as (c), but on Cu/Ni(4.8 ML)/O/Cu(001).

P-MOKE result shows that we can control the direction of SRT upon Cu capping using differently prepared Ni films.

Figures 2(c) and 2(d) show the hysteresis curves by the longitudinal MOKE (L-MOKE) for the Ni films (5.5 and 4.8 ML) deposited onto Cu(001) and preoxidized Cu(001) surfaces. The magnetic hysteresis curves show almost 100% remanence, and thus the magnetization easy axis is in plane, indicating the presence of a single magnetic domain. The Kerr intensity is roughly proportional to the magnetization, and thus the Cu capping reduces the Kerr intensity. The coercivity also changes, and this change is attributed to the modification of the magnetic anisotropy.

Figures 3(a) and 3(b) show the Ni L-edge XMCD spectra for the Cu/Ni/Cu(001) and Cu/Ni/O/Cu(001) surfaces at a grazing (60°) x-ray incidence, which probes the projection of the in-plane component of the magnetic moments. For Cu/Ni/Cu(001), the L_3-edge signal decreases with increasing Cu capping thickness. Since the magnetic orbital moment is derived from the area difference between the L_2 and L_3 XMCD spectra, the reduction in the L_3 edge directly demonstrates a decrease in the in-plane orbital moment. On the other hand, for Cu/Ni/O/Cu(001), the L_3-edge signal increases with the Cu thickness. These opposite results are in good accordance with the opposite magnetic stabilizations for the Ni films obtained by the MOKE measurements (Fig. 2).

In Fig. 3, we found that the XMCD spectrum from Ni/O/Cu(001) without Cu capping has a different shape from other spectra. While the 3.3-eV satellite in the L_3 edge is clearly observed in Ni/Cu(001) and Cu/Ni/Cu(001), it is not clearly seen in Ni/O/Cu(001). Theoretically, the $3d^8$ configuration reduces the pronounced satellite of 3.3 eV (Ref. 11), leading to the reduction of the orbital moment. With the oxygen atoms on the surface, a charge transfer from Ni $3d$ to O $2p_z$ is expected,[10] while the Cu capping does not alter the electronic configuration of Ni due to the nature of metallic bondings. The charge transfer in Ni/O/Cu(001) increases the population of the Ni $3d^8$ state. Therefore, the O-covered Ni film has a smaller orbital moment compared to the other films studied. However, for Ni films grown on preoxidized Cu(001) and Cu(110) in the PMA region, the XMCD spectra show the 3.3-eV satellite.[12] The films used in Ref. 12 are slightly thicker than the films in our study. Thus there is a possibility that the thinner film and the glacing x-ray incidence to detect the in-plane magnetization enhances the surface contribution to the XMCD spectra. Further studies will be needed to clarify the precise reasons for this result.

Figure 3(c) shows the XMCD spectra for the Cu/Ni(10.5 ML)/Cu(001) taken at normal x-ray incidence. The easy axis is normal to the surface regardless of the capped Cu thickness. The Cu capping does not change the $L_{2,3}$-edge signals, and thus the orbital moment along the surface normal is constant upon Cu capping. The invariance of the orbital moment indicates that the Cu capping effectively modifies the band structures of Ni that are responsible for the in-plane orbital moment. This is typical for surface adsorption, since the surface capping hinders the motion of the electron orbitals perpendicular to the surface, which exhibit in-plane orbital moments.[13] The orbital moment normal to the surface is not relevant to the Cu capping that induces SRT.

The exact magnetic anisotropy is defined by the area difference between the magnetization curves for the easy and hard magnetization axes. The area surrounding the hysteresis curves determines the hysteresis loss, which is approximately the product of the coercivity and magnetization for the films showing the 100% remanence. The hysteresis loss is closely related to the magnetic anisotropy because the increased magnetic anisotropy makes it difficult to flip the magnetization. The Ni films in this experiment are single crystals, and their magnetic structures are approximately regarded as a single domain with its uniaxial anisotropy, K_u, along the surface normal. The magnetic hysteresis curve for the films with uniaxial anisotropy and a single magnetic domain consists of a rectangle shape with its coercive field proportional to K_u (Ref. 14). For the Ni films studied, the variation of the hysteresis loss upon Cu capping represents the change of K_u of the films in the simple model described above, $\Delta B \cdot H \propto \Delta K_u + \delta$, where δ contains modifications of

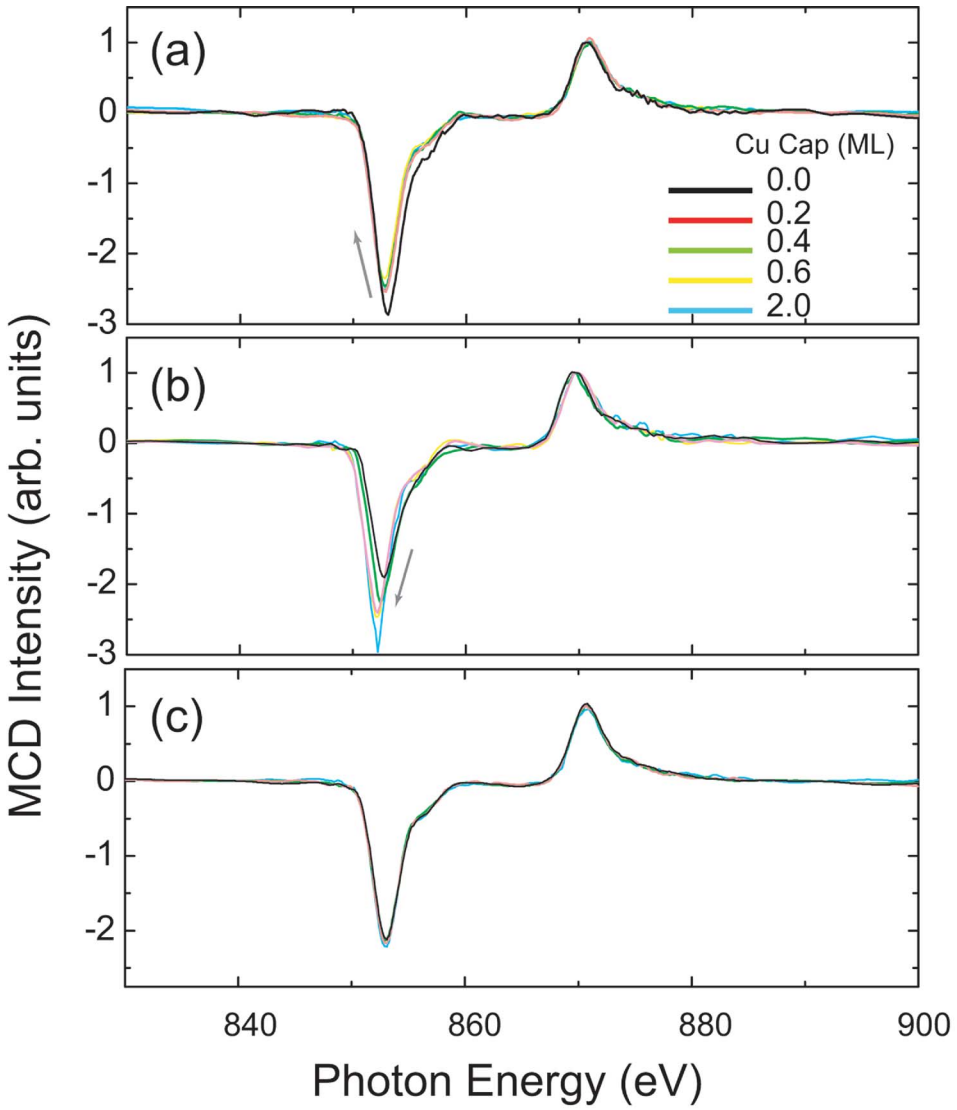

FIG. 3. (Color) XMCD spectra of Ni $L_{2,3}$ edge for (a) Cu (x ML) / Ni (5.5 ML) / Cu(001) and (b) Cu (x ML) / Ni(4.8 ML)/O/Cu(001) taken at grazing x-ray incidence (60°), and (c) Cu(x ML)/Ni(10.5 ML)/Cu(001) taken at normal x-ray incidence. All the MCD spectra are normalized at the L_2 edge.

shape and volume anisotropies, which exhibit smaller changes compared to the interface anisotropy.

Figure 4 shows the variation of the hysteresis loss and the orbital moment upon Cu capping derived from the sum rule.[15] The figure clearly shows that for both Ni/Cu(001) and Ni/O/Cu(001) the hysteresis loss and orbital moment vary in a similar manner: reduced in-plane magnetic anisotropy is associated with an increase in the orbital magnetic moment in the clean Ni/Cu(001) film, and the opposite situation is true for the oxidized Ni film. The simple relation between the hysteresis loss and magnetic anisotropy, $\Delta B \cdot H \propto \Delta K_u + \delta$, is approximately adequate to the present case since the Ni films grow in a pseudomorphic manner with high anisotropy and in a single magnetic domain. Bruno[16] derived theoretically the anisotropy energy originating from the spin-orbit energy, $E_{SO} = \xi(m_{orb}^{\perp} - m_{orb}^{\parallel})/4\mu_B$, where ξ is the spin-orbit coupling constant, and $m_{orb}^{\parallel}$ and $m_{orb}^{\perp}$ are the in- and out-of-plane orbital moments, respectively. Although we have not measured $m_{orb}^{\perp}$ for the Ni film with the in-plane easy axis, the measurement for the Ni film of 10.5 ML shows the imperceptible change of $m_{orb}^{\perp}$ upon Cu capping, which is supported by a previous study on SRT.[17] The results of LEED (Ref. 18) and scanning tunneling microscopy[19] exclude the structural and morphological change less than 12 ML. Thus, it is plausible to assume that the out-of-plane component of the orbital moment in the in-plane magnetization region is also not significantly influenced by Cu capping. Combined with the scaling relation between the hysteresis loss and the orbital moment, this result indicates that a linear relation holds between the magnetic anisotropic energy and the orbital moment. The finding that the modifications of the clean Ni films are opposite to those of the preoxidized Ni films reinforces the conclusion that the in-plane orbital moment governs the magnetic anisotropy as well as the SRT on the Ni films.

IV. CONCLUSIONS

In summary, we have prepared Ni ultrathin films on clean and preoxidized Cu(001). These Ni films show the opposite magnetic stability, perpendicular and parallel to the surface, upon Cu capping. This stabilization is connected to the macroscopic surface magnetic anisotropy such that the oxygen reduces the surface/interface anisotropy of the Ni films more effectively than a vacuum or Cu layer. The XMCD measure-

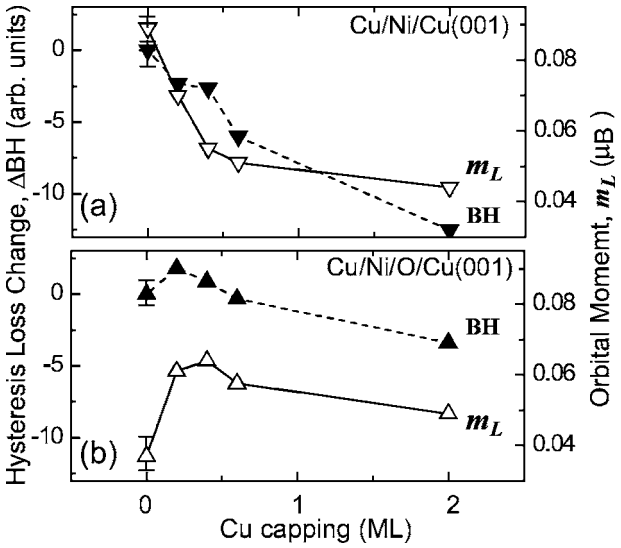

FIG. 4. Comparison between the hysteresis loss changes (open symbols) from MOKE and the orbital magnetic moment (filled symbols) from XMCD for (a) Cu(x ML)/Ni(5.5 ML)/Cu(001) and (b) Cu(x ML)/Ni(4.8 ML)/O/Cu(001). The plots demonstrate a one-to-one correspondence between the hysteresis loss and orbital magnetic moment.

ment for ~5 ML Ni films shows that the orbital moment is larger when the films gain more in-plane anisotropy, and it also gradually changes with the Cu capping. The reduction (enhancement) of the orbital magnetic moment within the plane leads to the instability (stability) of the in-plane magnetic anisotropy for the Ni film on Cu(001), which is in agreement with the direction of SRT. Our results directly demonstrate that the microscopic origin of the anisotropy change and SRT lies in the orbital magnetic moment, and we show that the magnetic anisotropy obtained from the MOKE measurement has a clear relation with the orbital magnetic moment during Cu capping. The control of the magnetic anisotropy and SRT through the orbital magnetic moment using various adsorbates has a potential to establish nanoscale spin arrangements.

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