Cr adsorption effect of magnetic property of Fe/Cu(001)∗

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Epitaxial growth of iron on Cu(001) below 11 ML shows a perpendicular magnetic anisotropy. The sub-monolayer Cr adsorbed fct Fe/Cu(001) have been investigated by x-ray absorption spectroscopy and x-ray magnetic circular dichroism (XMCD) to understand the element specific magnetic properties and the electronic states. It is found that the XMCD signal has been clearly observed in the Cr $L_{2,3}$ edge, which indicates the anti-parallel magnetic moment in the adsorbed Cr atom to that of the Fe layer. The smaller remnant magnetization for the larger amount of Cr has been observed for both 2.5 and 7.4 ML Fe films, where their magnetizations disappear upon the 0.4 and 0.2 ML Cr adsorption at 185 K, respectively. This behavior is turned out to be caused by the suppression of the Curie temperature. It is also found that the modification of the magnetic property for 7.4 ML Fe is similar to that for 2.5 ML. [DOI: 10.1380/ejssnt.2006.345]

Keywords: Chromium; Iron; Magnetic films; X-ray absorption spectroscopy; Magnetic phenomena

I. INTRODUCTION

It is expected that peculiar magnetic properties emerge in the ultra-thin films, which are much different from those in bulk materials due to a reduced dimensionality. There have been so far a lot of studies on the magnetic thin films, motivated not only by the fundamental interest in the relationship between the structure and magnetism but also by the possible application to magnetic and magneto-optic storage technologies. The physical properties of the magnetic films are sensitive to the film thickness, growth condition, film morphology and electronic band structure. Among them, Fe is one of the most studied elements because the magnetic properties are strongly linked with the structure. It is well known that a body-centered-cubic (bcc) Fe is ferromagnetic at room temperature, while for a face-centered-cubic (fcc) Fe, which exists only above 1184 K in the bulk, a non-magnetic, anti-ferromagnetic and ferromagnetic states are energetically degenerate around a lattice constant of 3.6 Å from a theoretical point of view [1, 2]. The fcc like Fe can be realized in a thin film form by means of an epitaxial growth at room temperature on some of the fcc metal substrates.

The ultra-thin Fe films are typically fabricated on Cu(001) single crystal substrate, where the lattice constant of fcc Fe closely matches with that of Cu. In this case, the magnetic properties strongly depend on the preparation method and condition. The film growth at room temperature induces nearly a layer-by-layer mode [3–9], while for the growth at low temperature (~100 K) the roughness is enhanced and morphological changes of the surface occur with increasing thickness [10–15]. Fe/Cu(001) film grown at room temperature exhibits three different structural and magnetic phases [8]. Up to 5 ML (region I), the films show the ferromagnetic character with forming the face-centered-tetragonal (fct) structure, as clarified by surface magneto-optical Kerr effect (SMOKE) combined with a quantitative $I$-$V$ analysis of low energy electron diffraction (LEED-IV) [3]. In contrast, the 5~11 ML Fe films (region II) show the antiferromagnetism with spin density wave (SDW), forming the unstrained face-centered-cubic (fcc) lattice covered...
with the ferromagnetic fct double layer [6, 7, 16]. These Fe films exhibit a perpendicular magnetic anisotropy below 11 ML. Above 11 ML (region III), the films are modified to bcc structure with in-plane magnetic anisotropy.

It is expected that the transition metal atom adsorption can modify the magnetism of these Fe films. The modification of magnetic properties and electronic structure of fct-Fe upon a transition metal atom adsorption has not been elucidated except for several studies. Pierce, et al. have reported the spin reorientation transition form the perpendicular to in-plane direction of Fe/Cu(001) induced by Co capping layer [17–19]. Vollmer, et al. have observed the reduction of the Curie temperature ($T_C$) for Fe/Cu(001) covered with 1 ML Cu [20].

In this paper, we report on the investigations of the submonolayer Cr atoms adsorbed fct Fe/Cu(001) by means of the Fe and Cr $L_{2,3}$ core excited soft x-ray absorption (XAS) spectroscopy and its x-ray magnetic circular dichroism (XMCD) in order to understand the magnetic properties and interface electronic states. It is known that the core XAS is a powerful technique to study the valence electronic states of magnetic materials. We can obtain the information of the element specific electronic structure with tuning the photon energy for each core level absorption edge of each element. The XMCD in the core XAS spectrum provides us with the spin and orbital magnetic moments with use of the magneto-optical sum rule [21, 22].

II. EXPERIMENTAL

Experiments were performed in an ultrahigh-vacuum system with a base pressure lower than $1.0 \times 10^{-8}$ Pa. Prior to deposition, a Cu(001) single crystal substrate was prepared by several cycles of Ar ion bombardment and annealing to 800 K. A cleanliness of the surface was checked by the Auger electron spectroscopy (AES) and a sharp (1×1) reflection high-energy electron diffraction (RHEED) and a low-energy electron diffraction (LEED) patterns (Fig. 2(a)). In this research, all of the Fe films were grown at room temperature (296 K) and the Cr atoms were deposited at 185 K after taking the XMCD spectrum of bare Fe. The pressure in the chamber was kept below $2.0 \times 10^{-8}$ Pa during evaporation. The Fe films were grown by e-beam evaporation of the Fe wire (99.999% purity) at a rate of about 0.2 ML/min onto a single-crystal Cu(001) surface. The set-up of the film growth is schematically shown in Fig. 1(a). The Fe film thickness was controlled by the RHEED oscillations (Fig. 1(b)). The RHEED patterns appearing on the fluorescent screen were recorded during the Fe deposition every a few seconds by a CCD camera connected to a computer for data storage and analysis. This method allows a real-time monitoring of film growth. The film thickness was also checked by the AES spectra. After the film growth, we have observed the LEED patterns for the fct Fe films as shown in Figs. 2(b), (c) and (d). The LEED patterns for Fe films in the region I show (4×1) and (5×1)
superstructures depending on the Fe coverage, while a (2 × 1) reconstruction is observed for 6.0 ML Fe (region II), with strong fundamental spots and weak extra spots neighbored, which is in agreement with the former works [15, 16]. The Cr deposition on the Fe/Cu(001) was carried out by the e-beam evaporation from a well out-gassed Cr pieces. The deposition rate was carefully calibrated by a quartz microbalance.

The experiments were conducted at the beam line 14 of Hiroshima Synchrotron Radiation Center, which provides us with the circularly polarized soft x-ray beam. The XAS and XMCD spectra were measured in situ after the film growth, in order to prevent the films from the surface contamination and to ensure the cleanness of the films surface. The XAS spectra were measured by means of the total photoelectron yield method by directly detecting the sample drain current. The XMCD spectra were obtained by changing the direction of the sample magnetization with a fixed photon helicity. The samples were magnetized by a pulsed magnetic field of 0.2 T and the XAS spectra were measured for the remanently magnetized films. The photon energy resolution and the circular polarization were set to ΔE = 0.5 eV and P_C = 0.7 for the Fe L_{2,3} edge, respectively. In the present paper, the XMCD spectrum is defined as μ_− (dashed line) and μ_+ (solid line) respectively.

III. RESULTS AND DISCUSSION

The XAS and XMCD spectra for 0.1 ML Cr adsorbed 2.5 ML Fe film grown on Cu(001) in the Fe L_{2,3} core excitation region are shown in Fig. 3(a). Here, the sample temperature was set to 185 K. The incident angle of circularly polarized light was chosen to be normal to the sample surface due to the perpendicular magnetic anisotropy as schematically shown in Fig. 3(c). The Fe L_3 and L_2 core absorption edges are located at \( h\nu = 710 \text{ eV} \) and 723 eV, respectively. The XMCD spectrum shows a negative sign on the lower \( h\nu \) side of L_3 core absorption edge, a small positive sign on the higher \( h\nu \) side of L_3 edge, and a positive sign at the L_2 edge. Figure 3 (b) shows Cr L_{2,3} XAS and XMCD spectra. It is noticed that a clear XMCD signal is also recognized for the Cr L_{2,3} edge. The XAS spectra show that the μ_- (dashed line) is larger than that for μ_+ (solid line) in the L_3 core absorption region, whereas μ_- is smaller than μ_+ in the L_2 region. In addition, the spectral weight of μ_+ shifts to higher energy compared to that of μ in both L_3 and L_2 regions. As a result, the observed Cr L_{2,3} XMCD signal shows a positive-negative feature with increasing \( h\nu \) at the L_3 edge and a negative sign at the L_2 edge. We can see in Figs. 3(a) and (b) that the sign of the XMCD signal at the
FIG. 3: The XAS and XMCD spectra for (a) Fe $L_{2,3}$ and (b) Cr $L_{2,3}$ edges of 0.1 ML Cr adsorbed 2.5 ML Fe/Cu(001) at 185 K. (c) The schematic image of the experimental geometry. (d) The schematic figure of the magnetic moments of Fe and Cr layers with anti-ferromagnetic coupling.

The $L_{2,3}$ edge is just opposite to that at the Fe $L_{2,3}$ edge. These results indicate that $z$ component of the magnetic moment of the Cr atom is aligned anti-parallel to that of the Fe as described schematically in Fig. 3(d). The observed anti-parallel coupling of the magnetic moments between the Cr and Fe layers has been also found for the bcc Cr/Fe multilayer system with an in-plane easy magnetization axis [23, 24]. However, the anti-ferromagnetic coupling with perpendicular magnetic anisotropy as in the present case has not been observed so far.

Next, we will show the XMCD spectra depending on the amount of the adsorbed Cr atoms. Figure 4 (a) shows the Fe $L_{2,3}$ XMCD spectra taken at 185 K of Cr/Fe (2.5 ML) in the Cr nominal thickness region of 0∼0.4 ML. It is found that the peak intensity of the XMCD spectra decreases with increasing the amount of Cr atoms, while the line shapes of Fe $L_{2,3}$ XAS and XMCD spectra are not influenced by the Cr adsorption. From these XMCD spectra we have plotted the integrated intensity of the $L_3$ XMCD signal as a function of the Cr layer thickness as shown by the filled circles in Fig. 4(b). Note that the integrated intensity is thought to be nearly proportional to the magnetization. We find in Fig. 4(b) that the perpendicular component of the Fe magnetization is gradually suppressed with Cr adsorption and disappears at 0.4 ML Cr at 185 K. No vertical component of magnetization has been found by further deposition up to 1.5 ML (not shown). The suppression of the perpendicular magnetization could be caused by a spin reorientation transition (SRT) from the perpendicular to in-plane magnetic anisotropy. So we have tried to measure the XMCD spectra also for the in-plane magnetized films. In this case, the direction of the irradiated light is 45° off from the direction of magnetization (surface normal). No in-plane component has been found from the XMCD spectra for 0, 0.2 and 0.4 ML Cr/2.5 ML Fe. Thus the reduction of perpendicular magnetization cannot be attributed to SRT.

We have measured the temperature dependence of XMCD spectra in order to illustrate the reduction of the perpendicular magnetization. Figure 5 shows the integrated intensities of the Fe $L_3$ XMCD signals for 0 (filled circle) and 0.3 ML (filled triangle) Cr/3.0 ML Fe as a function of temperature. Since these plots in Fig. 5 can be regarded as magnetization vs. temperature ($M$-$T$ curve) of the Fe layer. We found from these $M$-$T$ curves that...
and in-plane components of magnetization, respectively. We find that the vertical component of magnetization for the 7.4 ML Fe disappears with 0.2-0.3 ML Cr adsorption at 185 K. Since the in-plane magnetization has not been observed with Cr adsorption, the SRT from perpendicular to in-plane magnetization can not be the reason for the reduced magnetization. The topmost double layer in the region II is considered to be ferromagnetic with fct structure situated on the anti-ferromagnetic inner layers [8]. It is thought that the ferromagnetic double layer in the magnetization of the bare Fe is in agreement with the reported results by means of SMOKE technique [25]. In contrast, for 0.3 ML Cr adsorbed Fe, the remanent magnetization drops around T = 150-200 K. We can conclude that the disappearance of the perpendicular magnetization is caused by a reduction of a Curie temperature $T_C$

We have also measured the XAS and XMCD spectra for 7.4 ML Fe/Cu(001) (region II) as shown in Fig. 6. We can recognize that the overall line shape of the XMCD spectrum for 7.4 ML Fe is similar to that for 2.5 ML Fe. Note that the XMCD intensity is smaller than that for the region I because the ferromagnetically alive layers exist only at the surface and sub-surface. In Fig. 7(a) are shown the XMCD spectra for several amounts of Cr on 7.4 ML Fe film in the thickness range of 0 - 0.3 ML. Figure 7(b) represents the integrated intensity of the observed Fe $L_3$ XMCD spectra as a function of Cr thickness. The filled and open triangles are for the perpendicular
the region II is quite similar to that in the region I. In a similar way of the 2.5 ML Fe film, the disappearance of the ferromagnetism in the 7.4 ML Fe film might be caused by the reduction of \( T_C \). We notice that the critical Cr thickness to lead the disappearance of the ferromagnetism for the 7.4 ML Fe is smaller than that for the 2.5 ML Fe. Recently, Amemiya, et al. have proposed the anti-ferromagnetic interface coupling between the spin in the double ferromagnetic surface layer and that of the 3rd layer corresponding to the 1st layer of the internal fcc film by means of the depth-resolved XMCD, where the internal film shows the spin density wave below 200 K [26]. According to their interpretation, the effective ferromagnetic layer thickness for 7 ML can be 1 ML because of the cancellation between the spins in the second and third layers. As \( T_C \) is generally suppressed if the film thickness is thinner [27], we propose that the ferromagnetism for the 7.4 ML Fe easily disappears compared with that for the 2.5 ML Fe upon Cr adsorption at 185 K, since the effective ferromagnetic layers for the 7.4 ML Fe are thinner than that for the 2.5 ML Fe in the present experiment.

IV. SUMMARY

In summary, the modification of surface and interface magnetism of Fe/Cu(001) covered with the sub-monolayer Cr atoms has been explored through the Fe and Cr \( L_{2,3} \) XAS and XMCD spectra. We have found that the Cr 3d magnetic moment is aligned, which are anti-parallel to the Fe moments. We have observed the reduced remnant magnetization for both 2.5 (region I) and 7.4 (region II) ML Fe films with increasing Cr amount and the magnetization disappears upon the 0.4 and 0.2 ML Cr adsorption at \( T = 185 \) K, respectively, which can be attributed to the suppression of Curie temperature due to a degraded dimensionality of the ferromagnetic layers.

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