CO Adsorption Effects on the Magnetism and Surface Structure of Fe/Cu(001)*

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Effects of CO adsorption on the magnetic properties of Fe films on Cu(001) were studied at 100 K as a function of the film thickness. CO adsorption does not affect the magnetic property of 2 ML Fe film but induces the spin reorientation transition from perpendicular to in-plane magnetization for 4 ML Fe film. It also causes the apparent decrease of magnetization, which is attributed to the reduction in surface magnetization by analyses of depth-resolved XMCD spectra. The reduction of the magnetization can be originated from a reconstruction of the surface structure of the films. It was suggested that the surface structures of the 4 ML Fe film are changed to a bcc-like structure upon CO adsorption, while the structure of the 2 ML Fe film could not change by CO adsorption because its magnetization is unchanged. [DOI: 10.1380/ejssnt.2008.233]

Keywords: X-ray absorption spectroscopy; Iron; Carbon monoxide; Magnetic films

I. INTRODUCTION

Atomic and magnetic properties of Fe thin films on Cu(001) have been extensively studied as a prototypical case of magnetic thin films [1]. Fe/Cu(001) films exhibit three characteristic regimes: regime I ( < 4 ML), II (5–11 ML), and III (> 12 ML). We focused on regime I, which exhibits a distorted fcc structure, and perpendicular magnetization with a ferromagnetic coupling throughout the film.

In this article, we report the effects of CO adsorption on the magnetism [2] and structure of Fe/Cu(001) magnetic thin films. The magnetic state of a 2 ML Fe film is not affected by CO adsorption, while a 4 ML Fe film changes the magnetic properties drastically. The direction of magnetization rotates from perpendicular to in-plane, and the surface two layers loses the spin magnetic moment by CO adsorption. In the latter part of this article, we report the different desorption and/or dissociation behaviors of CO molecules on 2 ML and 4 ML Fe films on Cu(001) studied by XPS, and the difference of surface structures between CO adsorbed 2 ML and 4 ML Fe films. CO molecules on 4 ML Fe films go to dissociate more than those on 2 ML Fe films. It is suggested that the surface of 4 ML Fe film has a bcc-like structure, while that of 2 ML Fe film maintains an fcc structure.

II. EXPERIMENTAL

Our experiments were performed at BL-7A and BL-11A of the Photon Factory at the Institute of Materials Structure Science, High Energy Accelerator Research Organization equipped with an ultrahigh vacuum chamber (a base pressure of 3×10^-8 Pa). Fe/Cu(001) films were...
prepared in the chamber at room temperature. The film thickness was monitored with in situ reflection high energy electron diffraction (RHEED) observations. Fe films of 2 and 4 ML were prepared.

Conventional and depth-resolved x-ray magnetic circular dichroism (XMCD) measurements [3] were carried out at 100 K with normal (90°) and grazing (30°) x-ray incidence, which are referred to as “NI” and “GI” hereafter. The sample was magnetized by a magnetic filed pulse of about 700 G oriented along the x-ray propagation direction generated by pulsed current through a coil, and the measurements were performed at remnant conditions. Fe L-edge x-ray absorption spectra (XAS) were measured with the field antiparallel and parallel to the fixed photon helicity and XMCD spectra were obtained from the difference of the two spectra. After each clean film measurement, the film was dosed with 5 L CO, and the CO adsorbed films were studied in the same way.

XPS measurements were performed with another ultrahigh vacuum chamber upon annealing from low temperature to 450 K. This chamber is equipped with a hemispherical analyzer, GAMMADATA-SCIENTA SES-2002. Carbon 1s and oxygen 1s XPS were recorded one after another with the x-ray of 630 eV.

III. RESULTS AND DISCUSSION

A. Magnetic properties

Fe L-edge XMCD spectra of Fe(2 and 4 ML)/Cu(001) are shown in Fig. 1(a) and 1(c). These XMCD spectra indicate that the both films have perpendicularly magnetized, since XMCD signal for NI geometry is about twice as large as that for GI geometry. The spin magnetic moments were obtained to be about $m_s = 2.4 \mu_B$ for the two films by applying the sum rules [4, 5].

Fe L-edge XMCD spectra of CO adsorbed Fe 2 and 4 ML films are shown in Fig. 1(b) and 1(d). The XMCD spectra of the 2 ML Fe film are not changed upon CO adsorption. In contrast, the XMCD spectra of CO/Fe(4 ML)/Cu(001) exhibit almost no signal for NI geometry, but significant signal for GI geometry. These features directly indicate in-plane magnetization of the film. Thus, the CO adsorption rotates the easy axis of magnetization of the 4 ML film from perpendicular to in-plane.

The obtained spin magnetic moment of CO/Fe(4 ML)/Cu(001) was 1.1 $\mu_B$, which is about a half of that of Fe(4 ML)/Cu(001), 2.4 $\mu_B$. This apparent decrease of $m_s$ is considered to be the disappearance of $m_s$ of the top two layers. The probing depth (effective electron escape depth) dependence of $m_s$ of the film was obtained by the analysis of the depth-resolved XMCD spectra, as shown in Fig. 2. The spin magnetic moment decreases with decreasing the probing depth, directly indicating that the moment is small near the surface. This probing depth dependence was analyzed with a simple model, which is composed of the top two layers and bottom two layers as shown in Fig. 2. The top two layers have little magnetic moment (0.17 $\mu_B$), while the bottom two layers exhibit a moment of 2.31 $\mu_B$. These complex magnetic phases can be interpreted by assuming that CO adsorption kills ferromagnetic coupling of surface layers, while the Cu(001) substrate always keeps ferromagnetic coupling of adjacent two layers [2].

B. CO desorption and dissociation by annealing

Figure 3 shows C 1s XPS of CO/Fe(2 ML)/Cu(001) and CO/Fe(4 ML)/Cu(001) taken during annealing from 200 K to 450 K. The peak at about 285.3 eV is attributed to molecular CO species [6, 7]. This peak was large before annealing, decreased with annealing, and disappeared at around 350 K. The other peak at 282.3 eV corresponds to atomic carbon. This peak increased during annealing. The series of these spectra exhibit CO desorption from Fe film surface and CO dissociation into atomic carbon and oxygen by heating the samples from 200 K to 450 K.

A bigger peak of atomic carbon is seen in the spectra of CO/Fe(4 ML)/Cu(001) (Fig. 3(b)) than in those of CO/Fe(2 ML)/Cu(001) (Fig. 3(a)). It is concluded that CO dissociation more easily occurs on 4 ML Fe compared to 2 ML Fe.
FIG. 3: C 1s XPS taken during annealing from 200 K to 450 K: (a) CO/Fe(2 ML)/Cu(001) and (b) CO/Fe(4 ML)/Cu(001). The CO peak at 285.3 eV was decreasing, while the atomic carbon peak at 282.3 eV was increasing upon annealing.

FIG. 4: O 1s XPS taken during annealing from 200 K to 450 K: (a) CO/Fe(2 ML)/Cu(001) and (b) CO/Fe(4 ML)/Cu(001). The CO peak of 531.3 eV was decreasing, while the atomic oxygen peak of 530.0 eV was increasing.

FIG. 5: C 1s XPS peak intensity of (a) CO/Fe(2 ML)/Cu(001) and (b) CO/Fe(4 ML)/Cu(001). Solid squares (■) represent CO peak intensities, and open circles (○) atomic carbon. The dashed line represents the onset of atomic C intensities for CO/Fe(2 ML)/Cu(001), and the dotted line for CO/Fe(4 ML)/Cu(001).

O 1s XPS recorded during annealing under the same condition as C 1s XPS are shown in Fig. 4. Peaks at 530.0 and 531.3 eV, respectively, correspond to atomic oxygen and CO [6, 7]. The peak at 531.3 eV decreased during annealing, while that at 530.0 eV increased. Atomic oxygen peaks of CO/Fe(4 ML)/Cu(001) (Fig. 4(b)) are bigger than that of CO/Fe(2 ML)/Cu(001) (Fig. 4(a)), which is consistent with the C 1s results.

These C 1s and O 1s XPS indicate that CO molecules desorb and dissociate on the Fe surface upon annealing to 450 K. In addition, CO molecules on 4 ML Fe dissociate easier than those on 2 ML Fe. It has been reported that Atomic carbon and oxygen are yielded from the dissociation of CO molecules adsorbed on “lying down” bridge sites on bcc Fe surface, while desorbed CO molecules come from upright CO molecules adsorbed on fcc Fe surface [8]. Here, more atomic carbon and oxygen are observed on 4 ML Fe than on 2 ML Fe after annealing at 450 K. Thus, there were more CO molecules which were on “lying-down” bridge sites on 4 ML Fe than on 2 ML Fe. We can conclude that the CO-adsorbed surface of 4 ML Fe has more bcc-like structures than that of 2 ML Fe.

Figure 5 shows C 1s XPS peak area intensities of CO and atomic C for CO/Fe(2 ML)/Cu(001) and CO/Fe(4 ML)/Cu(001). In the both plots, CO intensities gradually decreased from about 200 K, and had completely gone at around 350 K. Atomic C intensities increased from around room temperature and almost saturated at around 350 K. The atomic C XPS intensity of CO/Fe(2 ML)/Cu(001) got the onset of the increase at
around 290–300 K, while that of CO/Fe(4 ML)/Cu(001) started to increase at around 250–260 K. The XPS intensity of atomic C started to increase at lower temperature for CO on 4 ML Fe than on 2 ML Fe. CO dissociation occurs at lower temperature on 4 ML Fe than 2 ML Fe.

**IV. CONCLUSION**

In conclusion, the effects of CO adsorption on the magnetism and surface structure of Fe(2 and 4 ML)/Cu(001) were studied at 100 K. The magnetism of the 2 ML Fe film is not affected by CO adsorption. In contrast, the 4 ML Fe films change their magnetism drastically. The direction of magnetization rotates from perpendicular to in plane. In addition, the two surface layers lose the spin magnetic moment upon CO adsorption and consequently only the bottom two layers have magnetization. These complex magnetic phases can be interpreted by assuming that CO adsorption kills ferromagnetic coupling of surface layers, while the Cu(001) substrate always keeps ferromagnetic coupling of adjacent two layers [2].

Atomic carbon and oxygen XPS peaks were larger on the 4 ML Fe film than on the 2 ML Fe film after annealing at 450 K. In addition, the onset temperature of the dissociation of CO was lower in the 4 ML Fe film than in the 2 ML Fe film. We can conclude that the CO-adsorbed surface of the 4 ML Fe film has a bcc-like structure, while that of the 2 ML Fe film maintains an fcc structure.

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