Surface antiferromagnetic coupling of Fe/Cu(001) induced by NO adsorption studied by means of depth-resolved XMCD method

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Abstract. Effects of NO adsorption on the magnetism of Fe(2 and 4 ML)/Cu(001) films have been studied. XMCD spectra have been measured for the films before and after NO adsorption. The bare 4 ML Fe film is magnetized perpendicularly, and $m_{\text{eff}}$ is 2.5 $\mu_B$. However, the NO adsorbed 4 ML Fe film exhibits in-plane magnetization and shows $m_{\text{eff}}$ of 1.2 $\mu_B$, which is about a half of $m_{\text{eff}}$ of the bare film. The apparent fifty percent reduction of $m_{\text{eff}}$ can be attributed to an idea that $m_{\text{eff}}$ of 1 ML aligns in the opposite direction to that of the other 3 MLs'. This antiferromagnetic coupling between the topmost layer and the other layers is suggested by the careful analyses of the depth resolved XMCD spectra.

1. Introduction
Fe thin films on Cu(001) have been extensively studied for their atomic and magnetic properties as a prototypical case of magnetic thin films [1, 2, 3, 4, 5, 6, 7, 8, 9, 10]. Fe/Cu(001) films change their atomic and magnetic structures as a function of the thickness. In the film thickness less than 4 monolayers (ML), the film exhibits a distorted fcc structure (face centered tetragonal, fct) and a ferromagnetic coupling among the whole film with perpendicular magnetization. Recently, a bcc-like reconstruction at the surface was reported by scanning tunneling microscope observations, and such a reconstruction was suggested to be the origin of the ferromagnetic coupling [10, 11, 12]. In the film thickness above 5 ML, some extraordinary atomic and magnetic structures have been reported [13, 14, 15], though they do not directly concern the present study.
The effects of atomic and molecular adsorption on magnetic thin films have been studied [16, 17, 18, 19, 20, 21]. J. Hong et al. studied the oxygen surfactant effects on spin reorientation transition (SRT) of Ni/Cu(001) films [16]. The presence of O on Ni/Cu(001) causes some lattice expansion and buckling, as well as changes in the electronic structures caused by the O–Ni interaction, leading to the change of surface magnetic anisotropy. The adsorption of CO molecules drastically affect the magnetic properties of the films. T. Tanabe et al. reported that CO molecules on Fe/Cu(001) films initially adsorbs on the bridge sites and on the on-top sites with increasing coverage [20, 21]. First-principles calculations of clean and CO adsorbed Fe/Cu(001) films have been performed by D. Spišák and J. Hafner [18]. They found that the magnetic moments of Fe films are substantially reduced. We have also reported the CO adsorption effects on the magnetism of the Fe/Cu(001) films [22, 23]. SRT occurs from perpendicular to in-plane magnetization. Moreover, the depth-resolved x-ray magnetic circular dichroism (XMCD) measurements revealed that the surface layer(s) loses the magnetic moment upon CO adsorption.

NO molecule, which has one more electron than CO, is expected to interact more strongly with the magnetic thin films, since it has an unpaired electron. Thus, it is interesting to study NO adsorption effects on thin film magnetism. J. Stöhr et al. reported orientation of chemisorbed CO and NO on Ni(001) studied by means of surface absorption fine structure (SAFS) measurements [24], which are nowadays called near edge x-ray absorption fine structure (NEXAFS) measurements. The tilt angles of the molecules have been reported to be 0° with an experimental uncertainty of 10°. That is, the molecular axes of the molecules are oriented along the sample surface normal. NO chemisorption and reactions on metal surfaces have been reviewed by W. A. Brown and D. A. King [25], and NO adsorption on Cu should be in a molecular form and NO dissociation should not occur. On Fe, there are no data, but one can expect molecular adsorption.

In this contribution, we report the effects of NO adsorption on the magnetic properties of Fe(2 and 4 ML)/Cu(001) magnetic thin films. An antiferromagnetic coupling between the surface layer and the other layers was suggested in NO/Fe(4 ML)/Cu(001) by using the depth-resolved XMCD [26]. SRT occurred from perpendicular to in plane upon NO adsorption.

2. Experiment
All of our experiments were performed at BL-7A 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 films were deposited at room temperature by an electron-beam evaporation on a Cu(001) single crystal, which was cleaned by repeated cycles of Ar⁺ sputtering of 1.5 keV and annealing at ∼900 K. The film thickness was monitored with in situ reflection high energy electron diffraction (RHEED) observations.

XMCD measurements were carried out at remanent conditions at 120 K with synchrotron radiation, which is ~80% circularly polarized. The sample was magnetized using a pulsed current through a coil (~700 Gauss), where the magnetic field was oriented along the x-ray propagation direction. Fe L-edge x-ray absorption spectra (XAS) were measured with the field parallel and antiparallel to the fixed photon helicity, and XMCD spectra were obtained from the difference of the two spectra. The direction of magnetization was examined using the incidence angle dependence of the XMCD spectra taken at normal (90°) and grazing (30°) incidences, which are hereafter referred to as “NI” and “GI”. Depth-resolved XMCD measurements [26] were performed by an imaging-type microchannel plate detector in the partial electron yield mode, applying a retarding voltage of 500 V in order to collect the Fe LMM Auger electrons. The probing depth was controlled by varying the electron detection angle. After each clean film measurement, the film was dosed with NO 5 L (1.3×10⁻⁵ Pa, 50 s) and the NO adsorbed films were studied in the same way as that of the clean films. Nitrogen K-edge NEXAFS spectra were
3. Results and Discussion

First, NO adsorption states are briefly mentioned. Nitrogen $K$-edge NEXAFS spectra are shown in figure 1. Solid, dotted, and dashed line spectra represent spectra measured in NI, MI, and GI geometry, respectively. Most NO molecules adsorbed on Fe films molecularly. Few dissociation of NO molecules occurred at low temperature, $\sim$120 K, in this study. We might neglect atomic N species, which are appeared as the shoulder structure at 397 eV in the spectra.

There are the other two distinct peaks. The first sharper peak at 399.5 eV and second broader one at 413 eV are attributed to the absorption from 1s to $\pi^*$ orbital and so called $\sigma^*$ shape resonance, respectively. The $\pi^*$ peak shows its largest intensity for NI measurement and its smallest one for GI. In contrast, the $\sigma^*$ shape resonance peak shows the opposite tendency. These features indicate that NO molecules adsorbed in rather standing posture on the surface. This is similar to the case of NO/Ni(001), in which an upright NO orientation was reported [24].

Next, we go on to the magnetic properties of this system. Figure 2 shows conventional XMCD spectra of Fe 2 and 4 ML films on Cu(001) recorded before and after NO adsorption. The clean 2 and 4 ML Fe films had perpendicular magnetization. The NI XMCD intensity of the clean Fe(2 ML)/Cu(001) film is larger than the double of the GI XMCD intensity of that. This peculiar behavior is due the insufficiency of the applied magnetic field to saturate the magnetization for the GI measurement. The Fe(2 ML)/Cu(001) film has a relatively large coercive field and a strong perpendicular magnetic anisotropy. In the Fe(4 ML)/Cu(001) film, the XMCD intensity of the NI spectrum is twice as large as that of GI spectrum, and the film had perpendicular magnetization. Effective spin magnetic moments, $m_{\text{eff}}$, were obtained by applying sum rules [27, 28] to the spectra shown in figure 2. Both of the clean 2 and 4 ML Fe films were revealed to have $m_{\text{eff}}$ of 2.5 $\mu_B$.

NO adsorption on the films caused the anomalous behaviors to the XMCD signals. The NO/Fe(2 ML)/Cu(001) exhibited no XMCD signals in the NI nor GI spectra. On the other hand, there are significant XMCD signals in the GI spectrum of the NO/Fe(4 ML)/Cu(001) film, though no XMCD signals can be seen in the NI spectrum of the film. These XMCD spectra indicate that the NO/Fe(4 ML)/Cu(001) film exhibited in-plane magnetization. NO adsorption induces the SRT from perpendicular to in plane, and decreases $m_{\text{eff}}$ to be 1.2 $\mu_B$, which is about a half of $m_{\text{eff}}$ of the clean film.

A possible origin of the SRT is attributed to a decrease of perpendicular magnetic anisotropy (PMA) upon NO adsorption. D. P. Pappas et al. studied oxygen adsorption on Fe(5.5 ML)/Cu(001) films and concluded that small amounts of oxygen ($\sim$0.5 ML) caused an SRT to in plane magnetization [29]. It was stated that the Fe–vacuum interface, or topmost layer,
A mechanism of the apparent decrease of $m_{\text{eff}}$ will be discussed. Here, it is difficult to draw a conclusion only from the completely gone XMCD signals of the 2 ML case. It is good for us to focus on the discussion on the 4 ML case first, and to be back to the 2 ML case. The fifty percent reduction of $m_{\text{eff}}$ of the 4 ML film upon NO adsorption should be attributed to the ideas that $m_{\text{eff}}$ of the half of the film disappeared, or that magnetization of a certain 1 ML of the 4 ML aligns in the opposite direction to the others (antiferromagnetic coupling). The depth-resolved XMCD measurements were carried out in order to clarify the depth profile of the magnetic structure of this system and to reveal the reason why the apparent fifty percent reduction of the magnetization was observed for the NO/Fe(4 ML)/Cu(001) film.

The depth-resolved XMCD technique gives us a series of XMCD spectra at different probing depths. The series of XMCD spectra, which were measured for the NO adsorbed 4 ML film, were analyzed by using the sum rules [27, 28]. The probing depth dependences of $m_{\text{eff}}$ were obtained, and are shown in figure 3. The plot was fitted by the following equation, which describes the $m_{\text{eff}}$ of 4 ML film at a certain probing depth,

$$m_{\text{eff}}(x) = \frac{\sum_{i=1}^{4} m_{\text{eff}}^{i} \cdot \exp\left(-\frac{(i-1)a}{x}\right)}{\sum_{i=1}^{4} \exp\left(-\frac{(i-1)a}{x}\right)}$$

where $m_{\text{eff}}^{i}$ ($i = 1$ to 4) and $a$ represent the $m_{\text{eff}}$ of the $i$th layer and the interlayer distance, respectively. The interlayer distance was fixed to 1.8 Å.

The fitting procedure for the NO/Fe(4 ML)/Cu(001) has given us the result of $(m_{\text{eff}}^{1}, m_{\text{eff}}^{2}, m_{\text{eff}}^{3}, m_{\text{eff}}^{4}) = (-2.4, 2.3, 2.3, 2.6) \mu_B$. The fitting curve is drawn in figure 3.
Effective spin magnetic moment ($\mu_B$)
Probing depth (Angstrom)

Figure 3. The probing depth dependence of $m_s^{\text{eff}}$ of the NO/Fe(4 ML)/Cu(001) film. The solid line is the fitting curve of the surface antiferromagnetic coupling model. The dashed line corresponds to the situation of the surface demagnetized model.

as a solid curve. When we take the average of these $m_s^{\text{eff}}$, it goes to be $1.2 \mu_B$. This is in very good agreement with the $m_s^{\text{eff}}$ obtained by conventional XMCD measurements.

It should be emphasized here that the negative $m_s^{\text{eff}}$ is obtained. The negative value of $m_s^{\text{eff}} = -2.4 \mu_B$ indicates that the topmost layer is magnetized in the opposite direction to the other layers. In other words, the surface antiferromagnetic coupling is induced by NO adsorption.

The fitting results could, however, contain errors, and we consider another candidate model in order to estimate errors in the fitting result. Another candidate is the model that the surface 2 ML’s magnetization is disappeared. We call this model the surface demagnetized model hereafter. The average of the magnetization of the film for the surface demagnetized model should be almost the same as the surface antiferromagnetic coupling case, which is the fitting result of our study. Therefore, the result obtained above is compared to the following fitting with the surface demagnetized model.

In fact, the magnetic structures of the CO/Fe(3 and 4 ML)/Cu(001) films have been described by the surface demagnetized model [22, 23]. In the case of CO adsorption on Fe(4 ML)/Cu(001), the surface two layers lose the magnetization, and consequently only the bottom two layers have magnetization. Here, we make a fitting of the probing depth dependence of $m_s^{\text{eff}}$ using this model. The fitting result of $(m_s^{\text{eff}}_{1}, m_s^{\text{eff}}_{2}, m_s^{\text{eff}}_{3}, m_s^{\text{eff}}_{4}) = (0, 0, 2.2, 2.2) \mu_B$ is also shown in figure 3 as a dashed line. The fitting result of the simple disappearance of $m_s^{\text{eff}}$ in the surface two layers is barely in the range of the error bars, and the surface demagnetized model cannot be entirely denied for the magnetic structure of the NO/Fe(4 ML)/Cu(001) film. It can be, however, recognized that the fitting curve of the surface antiferromagnetic model exactly stays in the middle of the errors bars. The surface antiferromagnetic model is more plausible than the surface demagnetized model.

Thus, adsorbed NO induced surface antiferromagnetic coupling has been found to be the good model to express the apparent fifty percent reduction of the magnetization in the NO/Fe(4 ML)/Cu(001) film. In addition, the antiferromagnetic coupling is suggested for the NO/Fe(2 ML)/Cu(001) film by analogy with the NO/Fe(4 ML)/Cu(001) cases. If the antiferromagnetic coupling is realized for the NO/Fe(2 ML)/Cu(001) film, the averaged magnetization, which is measured by the conventional XMCD method, should be zero. Actually, no apparent magnetization was observed in the present study, and the antiferromagnetic coupling model is a good model to explain the XMCD results of the NO/Fe(2 ML)/Cu(001) film. A decrease of $T_c$ and/or an increase of $H_c$ could not be, however, excluded from the causes of the complete lack of XMCD signals of the NO/Fe(2 ML)/Cu(001) film.
The adsorbed NO induced surface antiferromagnetic coupling could be attributed to an electron interaction between the NO molecules and the Fe films, such as electron donation from NO or back donation from Fe. One should also consider some surface structure reconstruction, as it has been pointed out for the CO/Fe/Cu(001) films [22, 23]. Further investigations are required to clarify the origin of the surface antiferromagnetism.

4. Summary

NO adsorption effects on the magnetic properties of Fe(2 and 4 ML)/Cu(001) films have been reported. NO molecules adsorb in rather standing posture on Fe/Cu(001) at 120 K. It is suggested that the antiferromagnetic coupling at the surface is induced by NO adsorption. Adsorbed NO molecules make the magnetization of the topmost layer align in the opposite direction to that of the other layers. In addition, the SRT occurs from perpendicular to in plane. The antiferromagnetic coupling at the surface of NO/Fe(2 and 4 ML)/Cu(001) is suggested by the present contribution, but the origin should be carefully investigated further.

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