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Surface magnetic canting of iron films

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The magnetization direction of α-Fe thin films was investigated by means of quantum-beat spectroscopy using nuclear resonant scattering in the glancing-incidence regime and conversion-electron Mössbauer spectroscopy (CEMS). The CEMS results show that the mean magnetization of the films is in plane. Quantum-beat data, on the other hand, reveal that perpendicular components are present in the magnetization at the film surfaces, indicating that the magnetization cants from the in-plane to the perpendicular direction near the surfaces.

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The magnetization direction of bulk materials is essentially determined by magnetocrystalline anisotropy originating from spin-orbit interaction. According to Néel, surfaces possess particular magnetic anisotropy,[1] which is caused by modification of the spin-orbit interaction reflecting the modified crystal field due to the broken symmetry at surfaces. In this regard, the magnetization direction of ultrathin films of ferromagnetic materials has been thoroughly investigated under various conditions of temperature, thickness, shape, roughness, etc.[2–7] The magnetization direction of Fe films changes from in plane to perpendicular depending on the film thickness.[8,9] The film magnetization is nevertheless not necessarily uniform: The magnetization direction could be altered at surfaces as compared to the bulk due to the surface magnetic anisotropy, which is called surface magnetic canting.[10] Such surface magnetic canting has been theoretically suggested for Fe films.[11] The experimental evidence of surface magnetic canting, on the other hand, is very rare to date, only indirectly suggested for the surface of Gd(0001).[12]

A powerful tool to investigate the magnetism of solids is Mössbauer spectroscopy, which probes the Zeeman splitting of relevant nuclei.[13] With the use of synchrotron radiation (SR), the hyperfine structure of a nucleus can be measured as quantum beats in the time spectrum of x-ray emission associated with nuclear resonant excitation.[14] The quantum-beat frequency reflects the energy difference between the two excited levels of the relevant nuclei.[15] Two advantages of SR quantum-beat spectroscopy are the probing depth and the polarization. In the glancing-angle reflection regime, the probing depth of the incident photon can be varied on a nanometer scale by changing the glancing angle. Since the SR light is linearly polarized, the selection rule for Δm (m is the magnetic quantum number) limits the possible transitions depending on the polarization direction with respect to the magnetization direction, which allows us to distinguish the magnetization direction of samples.[16–18]

In the present Rapid Communication, we have investigated the magnetization of ^{57}Fe thin films with SR quantum-beat spectroscopy in the reflection regime and conversion-electron Mössbauer spectroscopy (CEMS) using a conventional radioactive isotope. Whereas the magnetization is in-plane deep in the films, the magnetization cants into the surface normal direction near the film surfaces.

The samples used in the present work are Fe films with a thickness of 20 nm. Two samples were fabricated on $Fe_xSi_{1-x}/Si(111)$ [sample (a)] and $SiO_2/Si(111)$ [sample (b)] by evaporating iron of 20 nm enriched with ^{57}Fe nuclei at 95% at room temperature in an ultrahigh vacuum chamber (base pressure of 2×10^{-8} Pa). The deposited amount of iron was monitored by a quartz oscillator. The $Fe_xSi_{1-x}/Si(111)$ substrate was prepared by depositing iron of 2.4 nm on clean Si(111)7×7 followed by annealing at 820 K for 6 h.[19] The $SiO_2/Si(111)$ substrate was prepared by annealing the as-installed Si(111) at 600 K for 1 h, where the native oxide layer was maintained and the iron silicide formation was blocked upon Fe film formation.[20] With the x-ray reflectivity measurement,[21] the roughness of the sample surface was evaluated to be 4.5 and 0.47 nm for samples (a) and (b), respectively.

After sample preparation, glancing-angle dependence of the quantum beat was *in situ* measured at the BL09XU beamline of SPring-8. The linearly polarized SR beam with an energy of 14.4 keV and an energy width of 3.5 meV irradiated the sample surface with its electric polarization parallel to the surface, and the reflected beam was detected by an avalanche photodiode (APD) set in the specular-reflection direction. The time spectra of x rays emitted from the sample were collected by a time-to-amplitude converter, where the event signal and the reference timing signal from the storage ring were used as the stop and start signals, respectively. The azimuthal-angle dependence of the quantum beat was, on the other hand, measured *ex situ* at the PF-AR NE1A beamline of KEK at an energy width of 6.5 meV (14.4 keV) after exposure of the samples to air. The quantum-beat frequency was analyzed by means of the maximum entropy method. Note that the experimental results *ex situ* measured at PF-AR were essentially the same as those obtained by the *in situ* measurements at SPring-8 under the same experimental conditions.

After the quantum-beat experiments, furthermore, CEMS was conducted with a conventional ^{57}Co radioactive source,

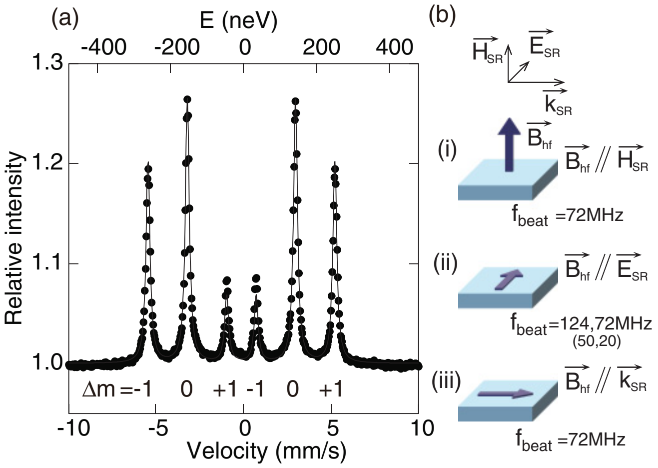

FIG. 1. (Color online) (a) Conversion electron Mössbauer spectrum (CEMS) taken for ^{57}Fe film of 20 nm grown on $SiO_2/Si(111)$ [sample (b)]. The γ ray with 14.4 keV from the ^{57}Co source irradiated the sample in the surface normal direction. (b) Relation of the magnetization direction ($\mathbf{B}_{hf}$) with the SR magnetic polarization ($\mathbf{H}_{SR}$), and expected quantum-beat frequencies.

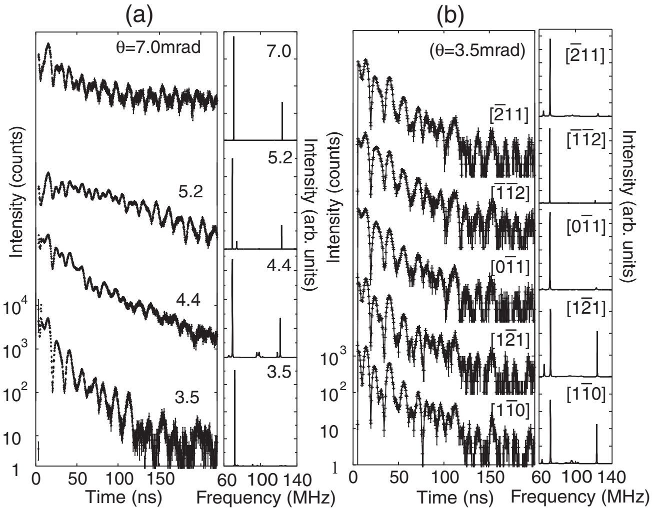

FIG. 2. The time spectra of the nuclear resonant x ray (left-hand panel) reflected from the ^{57}Fe film (20 nm) on $^{57}Fe_xSi_{1-x}/Si(111)$ and the frequency spectra of the quantum beats (right-hand panel). (a) The spectra taken at various glancing angles with SR incidence along $[11\bar{2}]$ of the Si(111) substrate. (b) The spectra taken at various azimuthal directions at a glancing angle of 3.5 mrad.

where the γ ray was incident to the sample surface in the surface normal direction. The spectra corresponding to iron oxides were not detected in the spectra.

Figure 1(a) shows a typical CEMS taken for sample (b). The six lines correspond to the excitations of $\Delta m = \pm 1,0$ between the Zeeman-splitted ground and first-excited states. The magnetic field and the isomer shift of both iron films are evaluated to be 33 T and -0.11 mm/s, in agreement with those of the ferromagnetic state of α-Fe, and the linewidth is analyzed to be the same for the six lines within the experimental accuracy. If we fit the theoretical formula[16,17] to the spectrum of Fig. 1(a), the mean magnetization of the ^{57}Fe film on the assumption that the magnetization is spatially homogeneous is evaluated to be almost in the in-plane direction with a slight out-of-plane component. It should be noted that the CEMS signal from a deeper region of a sample is significantly enhanced as compared to that from a shallower region due to the effect of secondary-electron emission.[22] Therefore, a quantitative analysis of the magnetization direction based on CEMS is essentially difficult for samples with depth-dependent magnetization, as the sample in the present study. The probing depth of CEMS under the present experimental condition is larger than a film thickness of 20 nm.[23] Note that the spectrum taken for sample (a) is essentially the same as Fig. 1(a) except for the paramagnetic component of the iron-silicide layer.[24,25]

Figure 1(b) illustrates the quantum-beat frequencies expected for a particular magnetization direction ($\mathbf{B}_{hf}$) with respect to the SR magnetic polarization (H_{SR}) under the present experimental condition. The allowed transitions are restricted to $\Delta m = 0$ for $\mathbf{B}_{hf} \parallel \mathbf{H}_{SR}$ and $\Delta m = \pm 1$ for $\mathbf{B}_{hf} \perp \mathbf{H}_{SR}$ among the six excitations in Fig. 1(a). While one quantum-beat component with a frequency of 72 MHz is present in the cases of $\mathbf{B}_{hf} \parallel \mathbf{H}_{SR}$ and $\mathbf{B}_{hf} \parallel \mathbf{k}_{SR}$, another beat component with a frequency of 124 MHz appears when $\mathbf{B}_{hf} \perp \mathbf{H}_{SR}$.[18] Although another component of 52 MHz is also expected to appear, this component is suppressed in the total-reflection regime.[26]

Figure 2(a) shows the time spectra of the nuclear resonant x-ray and corresponding frequency spectra taken for sample (a) at various glancing angles. The SR irradiated the sample along the $[11\bar{2}]$ direction of Si(111). The spectra reveal clear oscillations originating from the quantum beat of the Zeeman-splitted nuclear levels. In the frequency spectra of Fig. 2(a), two beat frequencies of 69–72 and 124 MHz are observed. Whereas only one quantum-beat frequency of 72 MHz is observed at a low glancing angle of 3.5 mrad, the two beat components with 72 and 124 MHz are present at higher glancing angles. The left-hand and right-hand panels of Fig. 2(b) show the time spectra of the nuclear resonant x-ray and frequency spectra taken for sample (a) at various azimuthal angles with the glancing angle fixed at 3.5 mrad. A quantum-beat frequency of 72 MHz is intensely observed at azimuthal directions of $[0\bar{1}1]$, $[\bar{1}\bar{1}2]$, and $[\bar{2}11]$. On the other hand, two quantum-beat frequencies of 72 and 124 MHz are observed at azimuthal directions of $[1\bar{1}0]$ and $[1\bar{2}1]$.

Figures 3(a) and 3(b) show the time spectra of the nuclear resonant x-ray and corresponding frequency spectra taken for sample (b) at various glancing angles and azimuthal angles, respectively. As clearly seen in the frequency spectra, only one quantum-beat component is present at a frequency of 70–72 MHz at all glancing angles and azimuthal angles, which is in remarkable contrast to the results for sample (a).

The present quantum-beat data allow us to identify the depth-dependent magnetization direction in the Fe films. Two quantum-beat components with frequencies of 124 and 72 MHz are observed at higher glancing angles for sample (a). This implies that an in-plane magnetization component is present in the film as illustrated in Fig. 1(b), and that the in-plane magnetization is mainly along the $[1\bar{1}0]$ direction (perpendicular to the x-ray incidence direction of $[11\bar{2}]$) of Si(111). As the glancing angle is reduced, on the other hand, the 124-MHz component is reduced in intensity and only

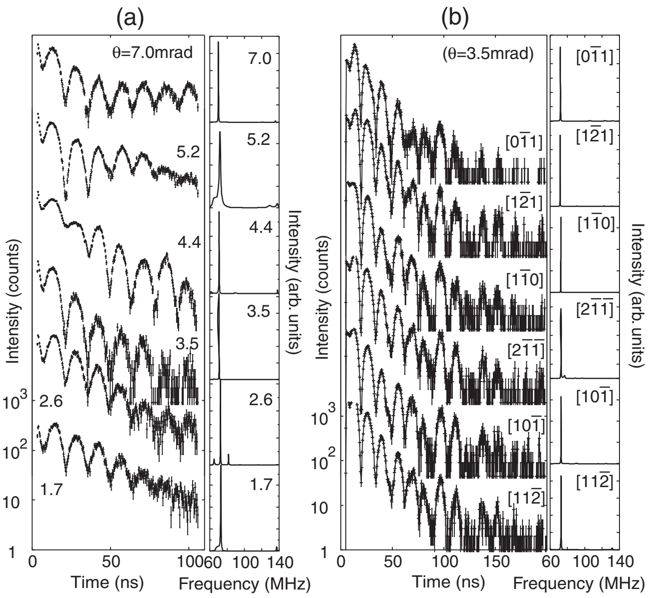

FIG. 3. The time spectra of the nuclear resonant x ray (left-hand panel) reflected from the ^{57}Fe film (20 nm) on SiO$_2$/Si(111) and the frequency spectra of the quantum beats (right-hand panel). (a) The spectra taken at various glancing angles with SR incidence along [1$\bar{1}$0] of the Si(111) substrate. (b) The spectra taken at various azimuthal directions at a glancing angle of 3.5 mrad.

the quantum beat with a frequency of 72 MHz is observed at glancing angles of lower than 3.5 mrad, as shown in Fig. 2(a). This indicates that the magnetization direction at the near-surface region is different from the deeper region, corresponding to the case of either (i) or (iii) in Fig. 1(b). When the azimuthal angle is changed at $\theta = 3.5$ mrad, the quantum-beat component with 123 MHz appears in [1$\bar{1}$0] and [1$\bar{2}$1], as shown in Fig. 2(b), which implies that an in-plane magnetization component is present in the near-surface region. From the azimuthal dependence data, the magnetization direction is expected to mainly point to the [$\bar{1}\bar{1}$2] direction. The intensity ratio of the two beat components, on the other hand, is different from the value expected from the complete in-plane magnetization. Therefore, it can be concluded that sample (a) mainly has an in-plane magnetization as an entire film, and has a perpendicular magnetization component in the near-surface region. This agrees with the easy-magnetization axis of an iron film on Si(111) reported in a previous study:[27] The easy-magnetization axis switches from $\langle 1\bar{1}0\rangle$ to $\langle 11\bar{2}\rangle$ as the Fe film thickness is increased.[27]

The results for sample (b) are more remarkable. In all azimuthal angles at a glancing angle of 3.5 mrad, only one quantum-beat component is present at a frequency of 72 MHz, as shown in Fig. 3(b). If an in-plane magnetization component were present, the 124-MHz component would appear in any of the spectra. The in-plane magnetization component is estimated to be less than 3%. It is noted that the probing depth for ^{57}Fe of the x ray around the nuclear resonant excitation energy is shallower than 2 nm at $\theta = 3.5$ mrad.[28,29] Therefore, we can unambiguously conclude that the magnetization in the near-surface region of sample (b) is perpendicular to the surface. It should be emphasized that the mean magnetization direction of the film is in plane, as confirmed by the CEMS measurement shown in Fig. 1(a).

Both samples have in-plane magnetization deep in the film, and a perpendicular component in the near-surface region. The internal magnetic field for the perpendicular components agrees with the bulk value within the experimental accuracy, as estimated from the quantum-beat frequency. Whereas sample (a) has both in-plane and perpendicular magnetization components in the near-surface region, the magnetization fully cants to the perpendicular direction for sample (b). The roughness of sample (b) is as small as 0.47 nm, therefore this particular magnetic structure of the iron film should be caused by the surface magnetic anisotropy due to the broken symmetry as predicted by theory.[11] Regarding sample (a), two possible magnetization structures can be conceived: The magnetization fully cants to the perpendicular direction as sample (b) in the shallower surface region or the surface magnetization points to an inclined direction with respect to the surface normal direction. Since the roughness of sample (a) is 4.5 nm, furthermore, both roughness and surface magnetic anisotropy would contribute to the presence of the perpendicular magnetization component.

In conclusion, depth-dependent magnetization of Fe thin films grown on Si substrates was investigated by synchrotron radiation quantum-beat spectroscopy and CEMS. Whereas the Fe films reveal predominantly an in-plane magnetization, the magnetization cants toward the surface normal direction in the near-surface region. This work is a definite experimental verification of the surface magnetic canting in an itinerant ferromagnetic-material, which has been predicted theoretically.

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