Electronic structures and magnetic moments of Co3FeN thin films grown by molecular beam epitaxy

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<th>Authors</th>
<th>Ito Keita, Sanai Tatsunori, Zhu Siyuan, Yasutomi Yoko, Toko Kaoru, Honda Syuta, Ueda Shigenori, Takeda Yukiharu, Saitoh Yuji, Imai Yoji, Kimura Akio, Suemasu Takashi</th>
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We evaluated electronic structures and magnetic moments in Co$_3$FeN epitaxial films on SrTiO$_3$(001). The experimentally obtained hard x-ray photoemission spectra of the Co$_3$FeN film have a good agreement with those calculated. Site averaged spin magnetic moments deduced by x-ray magnetic circular dichroism were 1.52 $\mu_B$ per Co atom and 2.08 $\mu_B$ per Fe atom at 100 K. They are close to those of Co$_4$N and Fe$_4$N, respectively, implying that the Co and Fe atoms randomly occupy the corner and face-centered sites in the Co$_3$FeN unit cell. © 2013 AIP Publishing LLC.

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3d transition metal ferromagnetic nitrides, composed of abundant elements, have received significant attention for applications in magnetic recording media and spintronics devices. The spin-polarization of electrical conductivity in Fe$_4$N was calculated to be $-0.50$, and the spin-polarization of density of states ($P$) at the Fermi level ($E_F$) to be $-0.60$. Larger $|P|$ of 0.88 ($P < 0$) was also theoretically predicted in Co$_3$FeN. However, it is difficult to form stoichiometric Co$_4$N films because the body-centered N atoms tend to be deficient. In our previous work, the diffraction intensity of Co$_3$FeN(001) was very weak in the x-ray diffraction (XRD) measurements on Co$_4$N films. According to the x-ray extinction rule, the diffraction peak of Co$_3$FeN(001) is absent when the body-centered N atoms are absent. Thus, we have paid more attention to ternary alloys Co$_3$Fe$_{1-x}$N. Among Co$_3$Fe$_{4-x}$N, first-principles calculation showed that Co$_3$FeN has larger $|P|$ of 0.75 ($P < 0$) than Fe$_4$N when Fe atoms are located at the corner (I) sites, and Co atoms at the face-centered (II) sites in the anti-perovskite unit cell as shown in Fig. 1. Epitaxial growth of Co$_3$Fe$_{4-x}$N films has been achieved on SrTiO$_3$ (STO)(001) substrates by molecular beam epitaxy (MBE) and on TiN/Si(001) using magnetron reactive sputtering. The diffraction peak of Co$_3$FeN(001) was observed in the XRD patterns, which means that a nitrogen atom is located at the body center of the unit cell of Co$_3$FeN. However, there have been no experimental reports on the electronic structure and magnetic moments of Co and Fe atoms in these Co$_3$FeN layers. Theoretical studies about what happens when the Co and Fe atoms are located differently from the above-mentioned ideal case have yet to be investigated. In this study, we aim to measure the magnetic moments of Co and Fe atoms, and valence band (VB) structures in Co$_3$FeN films, and compare them with those expected theoretically in order to discuss the Fe and Co sites in the Co$_3$FeN. We calculated the spin-polarized partial density of states (DOSs) of Co$_3$FeN. Here, we set Co atoms at sites I and II, and Fe atoms at site II, and used the CASTEP code based on the density-functional theory (DFT) in describing the electron-electron interaction, a pseudopotential description of the electron-core interaction, and a plane-wave expansion of the wave function. As for the method of approximation to the exchange-correlation term of the DFT, we used a spin-polarized Perdew-Wang Generalized Gradient Approximations (GGA-PW). The DOS curves were obtained by broadening discrete energy levels using the Gaussian smearing function of 0.07 eV full-width at half-maximum on a grid of $k$-points generated by the Monkhorst–Pack scheme. The pseudopotential used is the ultrasoft pseudopotential generated by the scheme of Vanderbilt. Kinetic cutoff energy for expansion of wave-functions and spacing of sampled $k$-points in the reciprocal space were set to be 400 eV and 0.5 nm$^{-1}$, respectively, which correspond to $24 \times 24 \times 24$ Fast-Fourier Transformation and $7 \times 7 \times 7$ mesh parameters (the number of the sampled $k$-points from the irreducible part of the Brillouin zone are 172), respectively. These values have been confirmed to be sufficient to obtain well-converged results. We also calculated the value of the magnetic moments for each atom in the ordered Co$_3$FeN by using the Bader analysis and the VASP package with the projected-augment wave pseudopotential and a spin-polarized GGA-PW method. The optimized lattice structure, a cutoff value of the plane waves of 400 eV and the $k$-points sampling of $11 \times 11 \times 11$ are used for the calculation of the charge density with VASP package. In our

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framework of first-principle calculations, we cannot take into account thermal effects at the finite temperature to the DFT calculation.

Hard x-ray photoemission spectroscopy (HAXPES) and x-ray magnetic circular dichroism (XMCD) measurements were performed in the CaF$_2$(2 nm)/Co$_3$FeN(10 nm) layered structure grown on the STO(001) substrate using MBE. Details of epitaxial growth procedures of Co$_3$FeN films are shown in Ref. 5. HAXPES measurements were performed at the undulator beamline BL15XU$^{14}$ of SPring-8 in Japan. We measured VB structures of the Co$_3$FeN film at 300 K using incident light with a photon energy of 5953 eV and overall energy resolution of 230 meV. The angle of incident light was 88° relative to the surface normal. The CaF$_2$ capping layer has a large band gap energy (12.1 eV),$^{15}$ and therefore the VB of CaF$_2$ is located far below that of Co$_3$FeN. This means that the contribution of the CaF$_2$ layer to the measured VB spectrum can be neglected.$^{16}$ Obtained VB spectrum was compared with the photoemission spectrum deduced from the results of the above mentioned first-principles calculation. XMCD measurements were performed at the undulator beamline BL23SU$^{17}$ of SPring-8. We measured x-ray absorption spectra (XAS) and XMCD spectra at Co and Fe $L_{2,3}$-edges using the total electron yield method and deduced orbital ($m_{\text{orb}}$) and spin ($m_{\text{spin}}$) magnetic moments per Co and Fe atoms in the Co$_3$FeN film. Circularly polarized x-rays were incident perpendicular to the sample surface at 100 and 300 K. External magnetic fields of ±3 T were applied to Co$_3$FeN[001] direction (perpendicular to the sample surface) during measurements, and we used their averaged spectra for analysis of magnetic moments to ensure the accuracy of the measurement. 3 T was enough to saturate the magnetization of the sample. On the basis of the obtained magnetic moments, we estimated positions of Co and Fe atoms in the Co$_3$FeN unit cell.

Figure 2 indicates the calculated spin-polarized partial DOSs of the modeled Co$_3$FeN. We deduced $P$ to be −0.63 at $E_F$, which means that $|P|$ is decreased when the Co and Fe atoms are located differently from the ideal case shown in Ref. 4.

Figure 3(a) shows the VB spectrum of the Co$_3$FeN film measured by HAXPES, and Fig. 3(b) exhibits the calculated photoemission spectra of Co 3$d$, 4$s$, and Fe 3$d$, 4$s$ states and their summation in Co$_3$FeN. These calculated spectra were deduced from the calculated partial DOSs of Co$_3$FeN multiplied by the photo-ionization cross-sections at a photon energy of 6 keV.$^{18}$ We did not take the N 2$s$ and 2$p$ states into account because those photoemission intensities were negligibly small, and we were not able to calculate the Co and Fe 4$p$ states because there have been no reports so far on the photo-ionization cross-sections of these states.$^{16}$ Structures labeled A-D in Fig. 3(a) correspond to those labeled a-d in Fig. 3(b). Structures A-C mainly consist of the Co 3$d$ state, and structure D is explained by the Co 4$s$ state.

The obtained VB spectrum was well fitted to the simulated
spectrum using the first-principles calculation. However, it is difficult to discuss the sites of Co and Fe atoms in the Co$_3$Fe$_N$ film just by comparing the observed VB spectra with those calculated. As reported in Ref. 19, the difference in the whole shape of VB structures between ordered and disordered metal alloys is very small.

Figures 4(a) and 4(b) display the XAS and XMCD spectra at Co $L_{2,3}$-edges in the Co$_3$Fe$_N$ film at 300 K, respectively. Distinct MCD signal was observed at Co $L_{2,3}$-edges. In Fig. 4(a), we can see the satellite peaks by approximately 2–3 eV higher than the main peaks of $L_{2,3}$-edges, which are also observed in the reported XAS spectra of Fe$_4$N and Co$_4$N films. We considered that these satellite peaks were attributed to atoms located at the face-centered sites. Details of this examination will be reported elsewhere. Figures 5(a) and 5(b) present the XAS and XMCD spectra at Fe $L_{2,3}$-edges in the Co$_3$Fe$_N$ film at 300 K, respectively. The structure of F $K$-edge is attributed to the CaF$_2$ capping layer. Distinct MCD signal was observed at Fe $L_{2,3}$-edges, which have the same sign as those of Co $L_{2,3}$-edges. This means that ferromagnetic order is created between Co and Fe atoms. We also note here that there are small satellite peaks by approximately 2–3 eV higher than the main peaks of Fe $L_{2,3}$-edges. The site-averaged $m_{\text{orb}}$ and $m_{\text{spin}}$ per Co and Fe atoms of the sample were deduced by applying magneto-optical sum-rules analysis. The backgrounds of the XAS spectra were removed by subtracting the two step function from the raw XAS spectra. The electron hole numbers of 3$d$ orbital ($N_h$) of Co and Fe in the sample were determined to be $2.43 \pm 0.23$ and $4.31 \pm 0.70$, respectively, from the XAS spectra of the sample by referring to the standard XAS spectra of hcp-Co and bcc-Fe, and $N_h$ values in hcp-Co (2.49) and bcc-Fe (3.39). The site-averaged $m_{\text{orb}}$, $m_{\text{spin}}$, and sum of them ($m_{\text{total}}$) of the sample are summarized in Table I. The reported values of the magnetic moments of Co$_4$N and Fe$_4$N are also shown for comparison. The $m_{\text{total}}$ value per Co atom was evaluated to be $1.44 \pm 0.13 \mu_B$ at 300 K and $1.51 \pm 0.17 \mu_B$ at 100 K. For Fe atom, it was deduced to be $1.84 \pm 0.20 \mu_B$ at 300 K and $1.96 \pm 0.16 \mu_B$ at 100 K. In Table I, magnetic moments corrected by taking the saturation effect are listed in parentheses. We used the correction factors in case that the light is incident normal to the film plane with the 10-nm-thick Co and Fe films, shown in Ref. 28. We estimated the saturation magnetization of the sample to be 1210 emu/cc at 300 K, using deduced $m_{\text{total}}$. This value is a little smaller than 1310 emu/cc obtained by a superconducting quantum interface device magnetometer at 300 K. We think that the deduced magnetic moments from the XMCD measurement are underestimated. The $m_{\text{spin}}$ values are calculated to be $1.97$ and $1.49 \mu_B$, respectively, for Co atoms in Co$_4$N at I and II sites, and the $m_{\text{spin}}$ values to be $3.07$ and $2.03 \mu_B$, respectively, for Fe atoms in Fe$_4$N at I and II sites. The $m_{\text{spin}}$ values for Co and Fe atoms in CoFe$_3$N are calculated to be $1.76$ and $2.32 \mu_B$, in case that Co atoms are located at I sites, and Fe atoms at II sites. This means that $m_{\text{spin}}$ values are enhanced at I sites, but are decreased at II sites, due to the band hybridization between 3$d$ orbit of II site atoms and 2$p$ orbit of nitrogen atoms. We calculated the $m_{\text{spin}}$ values for Co and Fe atoms to be $1.41$ and $3.09 \mu_B$, respectively, in the ordered Co$_3$Fe$_N$. However, the deduced site-averaged $m_{\text{spin}}$ values of Co and Fe atoms in the Co$_3$Fe$_N$ film from the XMCD measurements are close to those in Co$_4$N and Fe$_4$N, respectively.
implies that both Co and Fe atoms are located at both I and II sites in the Co$_3$Fe$_N$ film. In order to obtain high spin-polarized Co$_3$Fe$_N$, optimization of the growth conditions is required to prevent the disorder of Co-Fe atoms in the Co$_3$Fe$_N$ film.

In summary, the first-principles calculation showed that the $|P|$ value at $E_F$ is decreased when the Co and Fe atoms are located differently from the ideal case. HAXPES and XMCD measurements for the MBE-grown Co$_3$Fe$_N$ film were performed and those VB structure and magnetic moments were evaluated. Line shape of the observed photoemission spectrum was well fitted to the calculated spectrum based on the DOSs of Co$_3$Fe$_N$. Magnetic moments per Co and Fe atoms in the Co$_3$Fe$_N$ film deduced by sum-rules analysis were close to those in Co$_4$N and Fe$_4$N, respectively. These results show that the Co and Fe atoms occupy both the corner and face-centered sites in the Co$_3$Fe$_N$ film.

The authors thank Professor T. Oguchi of Osaka University for private discussions. The HAXPES measurements were performed at SPring-8 BL15XU, NIMS (Proposal No. 2012A4806). The XMCD measurements were performed at XMCD Station at SPring-8 BL23SU, JAEA (Proposal Nos. 2012B3804 and 2013A3880). K. Ito and T. Suemasu also thank Dr. N. Ota and Professor K. Asakawa of the Tsukuba Nano-Tech Human Resource Development Program at the University of Tsukuba for useful discussions.

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### TABLE I. Orbital, spin, and total magnetic moments of Co and Fe atoms in Co$_x$Fe$_{3-x}$N deduced by XMCD and theoretical calculations. Corrected moment values of samples after taking the saturation effect into account are listed in parentheses.

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<th>$m_{orb}$</th>
<th>$m_{spin}$</th>
<th>$m_{total}$</th>
<th>Method</th>
<th>Reference</th>
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<td>1.44 ± 0.13</td>
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<tr>
<td></td>
<td>(corrected)</td>
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<td>(~1.47)</td>
<td>(~1.62)</td>
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<tr>
<td></td>
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<td>XMCD</td>
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</tr>
<tr>
<td></td>
<td>(corrected)</td>
<td>(~0.16)</td>
<td>(~1.91)</td>
<td>(~2.07)</td>
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<tr>
<td></td>
<td>(corrected)</td>
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<td>(~1.70)</td>
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