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## Negative spin polarization at the Fermi level in Fe<sub>4</sub>N epitaxial films by spin-resolved photoelectron spectroscopy

Keita Ito,<sup>1</sup> Kazuaki Okamoto,<sup>2</sup> Kazunori Harada,<sup>1</sup> Tatsunori Sanai,<sup>1</sup> Kaoru Toko,<sup>1</sup> Shigenori Ueda,<sup>3</sup> Yoji Imai,<sup>4</sup> Taichi Okuda,<sup>5</sup> Koji Miyamoto,<sup>5</sup> Akio Kimura,<sup>2</sup> and Takashi Suemasu<sup>1,a)</sup>

<sup>1</sup>*Institute of Applied Physics, University of Tsukuba, Ibaraki 305-8573, Japan*

<sup>2</sup>*Graduate School of Science, Hiroshima University, Hiroshima 739-8526, Japan*

<sup>3</sup>*Synchrotron X-ray Station at SPring-8, National Institute for Materials Science (NIMS), Hyogo 679-5148, Japan*

<sup>4</sup>*National Institute of Advanced Industrial Science and Technology (AIST), Ibaraki 305-8565, Japan*

<sup>5</sup>*Hiroshima Synchrotron Radiation Center, Hiroshima University, Hiroshima 739-0046, Japan*

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We evaluated the valence band structures of 10-nm-thick ferromagnetic Fe<sub>4</sub>N epitaxial films on SrTiO<sub>3</sub>(001) substrates at room temperature using spin-resolved photoelectron spectroscopy. Negative spin polarization is confirmed at the Fermi level. The experimentally obtained photoelectron spectra are well explained by first-principles calculations based on the pseudopotential method. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4733327>]

### I. INTRODUCTION

Ferromagnetic Fe<sub>4</sub>N is a promising material for application in high performance spintronic devices. Fe<sub>4</sub>N has been extensively studied for magnetic recording media.<sup>1,2</sup> It has a cubic perovskite lattice structure, wherein a nitrogen atom is located in the body center of the fcc-Fe lattice. Spin polarization of the density of states (DOSs) ( $P$ ) at the Fermi level ( $E_F$ ) and spin asymmetry of the electrical conductivity ( $\beta$ ) was calculated to be  $-0.6$  and  $-1.0$ , respectively.<sup>3</sup> A recent theoretical calculation predicts that Co<sub>4</sub>N has a larger negative polarization than Fe<sub>4</sub>N.<sup>4</sup> In particular, a fully negative spin polarization ( $P = -1.0$ ) at  $E_F$  is predicted for Co<sub>3</sub>FeN.<sup>5</sup> We therefore expect that (Co,Fe)<sub>4</sub>N alloy is very promising for application in spintronics devices. We have previously measured the  $\beta$  values of Fe<sub>4</sub>N and pure Fe using point contact Andreev reflection (PCAR) and confirmed that Fe<sub>4</sub>N has a larger  $\beta$  than Fe.<sup>6</sup> We also measured spin and orbital magnetic moments of epitaxial Fe<sub>4</sub>N and Co<sub>4</sub>N films using x-ray magnetic circular dichroism.<sup>7,8</sup> An inverse tunnel magnetoresistance (TMR) ratio of  $-75\%$  was reported in a CoFeB/MgO/Fe<sub>4</sub>N magnetic tunnel junction (MTJ),<sup>9</sup> and negative anisotropic magnetoresistance was observed in Fe<sub>4</sub>N films.<sup>10-12</sup> These results are thought to originate from the negative  $P$  and  $\beta$  in Fe<sub>4</sub>N.

The  $P$  value of material can be evaluated from a TMR ratio using Julliere's formula.<sup>13</sup> However, it is very sensitive to interface states at the ferromagnet/insulator interfaces in MTJ,<sup>14-16</sup> making it difficult to determine the  $P$  value. Also, the sign of  $\beta$  cannot be determined from a conductance curve in the PCAR measurement.<sup>17-19</sup> In contrast, spin-resolved photoelectron spectroscopy (SRPES) is an effective means to directly observe the spin-polarized DOS of ferromagnetic materials.<sup>20-23</sup> Dedkov *et al.* and Wang *et al.* showed that the values of  $P$  in half-metallic materials such as Fe<sub>3</sub>O<sub>4</sub> and Co<sub>2</sub>MnSi by SRPES.<sup>20,21</sup> The spin-resolved electrical struc-

tures at surfaces of Eu/Gd(0001) and YCo<sub>2</sub>/W(110) were also directly observed.<sup>22,23</sup> However, there have been no reports about SRPES measurements on Fe<sub>4</sub>N, (Co,Fe)<sub>4</sub>N, and Co<sub>4</sub>N films. In this study, we grew 10-nm-thick Fe<sub>4</sub>N films on SrTiO<sub>3</sub>(STO)(001) substrates by molecular beam epitaxy (MBE) and evaluated its spin dependent electronic structure near  $E_F$  using hard x-ray photoelectron spectroscopy (HX-PES) and SRPES.

### II. EXPERIMENTAL METHOD

A CaF<sub>2</sub>(1 nm)/Fe<sub>4</sub>N(10 nm) layered structure was grown epitaxially by an ion-pumped MBE system. First, an Fe<sub>4</sub>N layer was formed on the STO(001) substrate by supplying 5N-Fe and radio frequency NH<sub>3</sub> plasma, simultaneously. Detailed growth procedures for Fe<sub>4</sub>N are described in our previous report.<sup>24</sup> After the growth of the Fe<sub>4</sub>N layer, a CaF<sub>2</sub> capping layer was formed at room temperature (RT), in order to prevent oxidation of the Fe<sub>4</sub>N layer. The CaF<sub>2</sub> capping layer has a large energy band gap of 12.1 eV (Ref. 25) and thereby does not influence photoelectron spectroscopy measurements. The crystalline quality of the Fe<sub>4</sub>N layer was characterized by reflection high-energy electron diffraction (RHEED) and  $\theta$ - $2\theta$  x-ray diffraction (XRD). HX-PES measurements were performed at the undulator beamline BL15XU (Ref. 26) of SPring-8 in Japan. The valence band (VB) structures of Fe<sub>4</sub>N were measured by HX-PES with a photon energy of 5953 eV and overall energy resolution of 230 meV. The angle of incident light was 89° relative to the surface normal. We also calculated the spin-polarized DOS of Fe<sub>4</sub>N using the CASTEP (Ref. 27) code based on the density-functional theory in describing the electron-electron interaction, a pseudopotential description of the electron-core interaction, and a plane-wave expansion of the wavefunction, and compared them with experimentally obtained VB spectra. After the CaF<sub>2</sub> capping layer was removed by Ar ion sputtering (1-2 keV), and a clean Fe<sub>4</sub>N surface was obtained, spin-resolved VB structures near  $E_F$  were measured by SRPES. The SRPES measurements

<sup>a)</sup>Author to whom correspondence should be addressed: Electronic mail: suemasu@bk.tsukuba.ac.jp.

were carried out at the Hiroshima Synchrotron Radiation Center.<sup>28</sup> Samples were excited by an unpolarized He I $_{\alpha}$  resonance line ( $h\nu = 21.2$  eV), and the overall energy resolution was 110 meV. The angle of incident light was 50° relative to the surface normal. Both HX-PES and SRPES measurements were performed at RT.

### III. RESULTS AND DISCUSSION

Figure 1 shows the  $\theta$ - $2\theta$  XRD pattern of the sample. The diffraction peaks of Fe $_4$ N (002) and (004) planes were observed. The inset shows the observed streaky RHEED pattern of the Fe $_4$ N layer along STO[110]. These results mean that the Fe $_4$ N layer was epitaxially grown on the STO substrate. From the XRD peak positions, we confirmed that the grown layers were almost strain-free Fe $_4$ N.

Figures 2(a) and 2(b) show the calculated partial DOSs of Fe 3*d*, Fe 4*s*, Fe 4*p*, N 2*s*, and N 2*p* states, and total DOSs of majority and minority spins in Fe $_4$ N, respectively. The VB structures mainly consist of the Fe 3*d* state, and the N state is dominant in the structures located at  $-7$  and  $-17$  eV. The negative spin polarization near  $E_F$  is expected from Fig. 2(b). These features are in good agreement with the electrical VB structures derived by first-principle calculations.<sup>3,4,29–31</sup>

Figures 3(a) and 3(b) show the expected photoelectron spectra of Fe 3*d* and 4*s* states using the partial DOS of Fe $_4$ N multiplied by the photo-ionization cross-sections at a photon energy of 6 keV (Ref. 32) and the HX-PES VB photoelectron spectrum, respectively. In the wide HX-PES spectra, peak structures from Sr and Ti were observed (not shown), which indicates the substantially large probing depth. The contribution of N 2*s* and 2*p* states in the HX-PES spectrum should be negligibly small if their low photoionization cross sections are taken into account. We were not able to calculate the photoelectron spectrum of Fe 4*p* state because there have been no report so far on the photo-ionization cross-sections of Fe 4*p* state at a photon energy of 6 keV. We can see that the structures labeled A-F in Fig. 3(b) were well fitted to those labeled *a-f* in Fig. 3(a), although the overall structure differs slightly to each other. Structures B-E mainly consist of the Fe 3*d* state, and structures F and G are explained by the Fe 4*s* state. It is difficult to attribute the structure H,

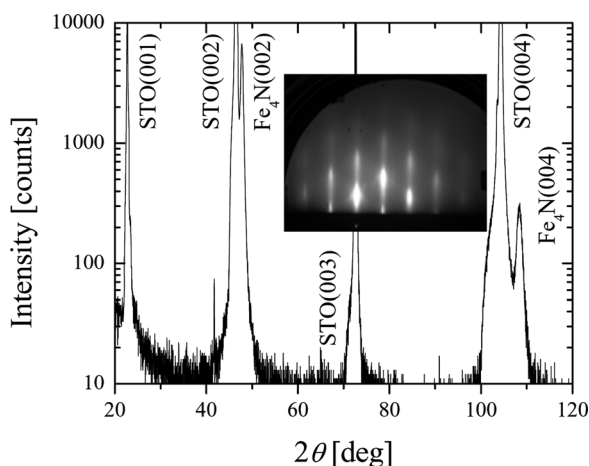


FIG. 1.  $\theta$ - $2\theta$  XRD and RHEED patterns of sample.

located at  $-12.5$  eV in Fig. 3(b), to Fe $_4$ N. We think that this structure is related to other Fe-N phases in the Fe $_4$ N layers.

Figure 4 shows the Auger electron spectroscopy (AES) spectra, obtained using an incident electron energy of 3 keV, measured before and after removing the CaF $_2$  capping layer by Ar ion sputtering. The AES spectra were normalized by the signal intensity of Fe (*LMM*; 702 eV). Before the sputtering, intense signals corresponding to C (*KLL*; 269 eV) and O (*KLL*; 511 eV) were observed, in addition to those of Fe (*LMM*; 595, 648, and 702 eV), Ca (*LMM*; 292 eV), and F (*KLL*; 651 eV), as shown by the red curve. These C and O signals originate from contamination on the sample surface. After the sputtering (blue curve), the signals corresponding to Ca, F, C, and O disappeared and the signal for N (*KLL*; 384 eV) appeared instead. The Fe signal remained unchanged. These results confirmed the cleanliness of the sputtered sample surface of the Fe $_4$ N layer. SRPES measurements were subsequently performed without exposure to air.

Figure 5(a) shows the spin-resolved photoelectron spectra around  $E_F$  measured by SRPES. The flat background signals due to secondary electrons caused by the He II resonance line ( $h\nu = 40.8$  eV) were removed from raw spectra. Peak structures labeled A' and A'' appear at  $-0.75$  eV in the majority spin state (red marks) and  $-0.45$  eV in the minority spin state (blue marks), respectively. These structures correspond to the structure A in Fig. 3(b), and agree with the calculated total DOS shown in Fig. 2(b). Figure 5(b) presents the spin polarization  $P$  near  $E_F$  deduced from Fig. 5(a), that

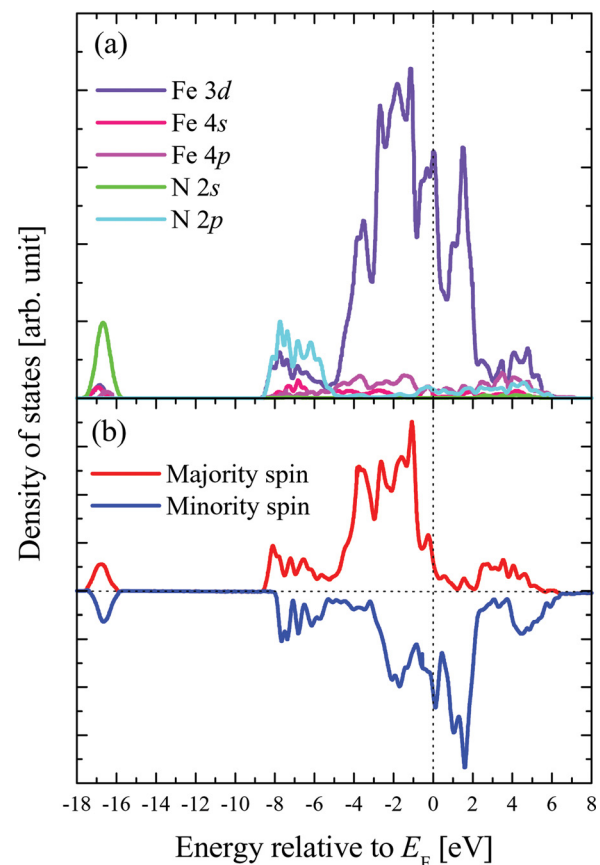


FIG. 2. (a) Calculated partial DOSs for Fe 3*d*, Fe 4*s*, Fe 4*p*, N 2*s*, and N 2*p* states and (b) total DOSs of majority and minority spins in Fe $_4$ N.

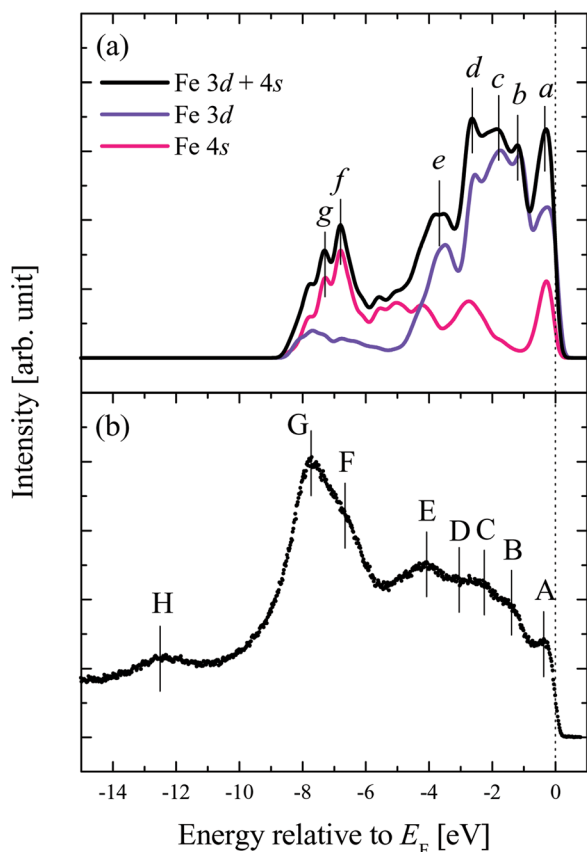


FIG. 3. (a) Calculated photoemission spectra for Fe 3d and Fe 4s states in Fe<sub>4</sub>N. (b) HX-PES spectrum for Fe<sub>4</sub>N measured at photon energy of 5953 eV.

is, the majority spin states minus the minority spin states, divided by their sum. As shown in the figure,  $P$  value is approximately  $-0.2$  at RT, being clearly negative at  $E_F$ . We should note here that the  $P$  value is slightly shifted to the positive upward region in the wide range of energy due to the positive background signals. Therefore, it can be safely stated that Fe<sub>4</sub>N has a negative  $P$  at  $E_F$ . In general, secondary electrons excited from ferromagnetic material have positive  $P$  because the number of excited electrons with majority spin is dominant in total. In our case, secondary electrons excited by He I<sub>α</sub> resonance line attribute to the background signals. In this work, we chose to adopt almost strain-free Fe<sub>4</sub>N epi-

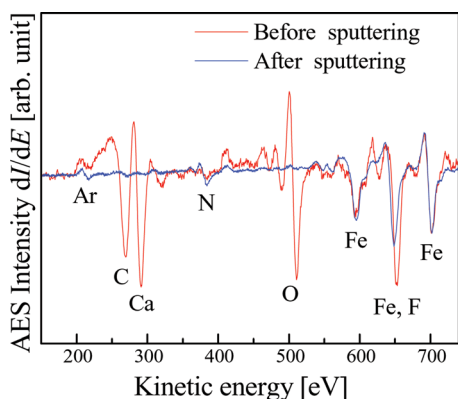


FIG. 4. AES spectra of the sample (a) before (red curve) and (b) after (blue curve) removing the CaF<sub>2</sub> capping layer by Ar ion sputtering.

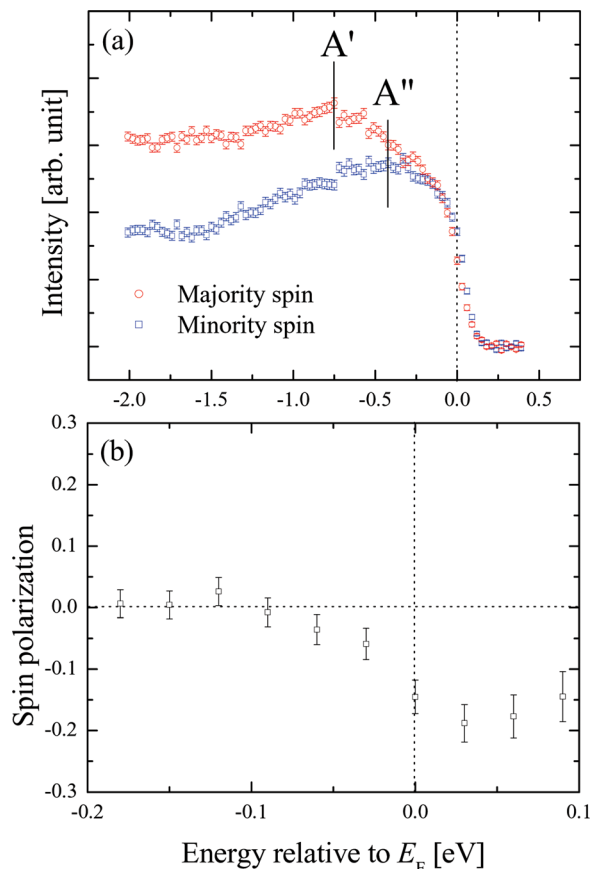


FIG. 5. (a) SRPES spectra of majority (red marks) and minority (blue marks) spin states for Fe<sub>4</sub>N. (b) Spin polarization of Fe<sub>4</sub>N deduced from Fig. 5(a).

taxial layers for SRPES measurements. We do not have enough data to discuss the influence of crystalline quality of Fe<sub>4</sub>N on SRPES spectra. However, the SRPES spectra shown in Fig. 5(a) are attributed to the intrinsic properties of Fe<sub>4</sub>N. Thus, we speculate that the observed SRPES spectra themselves are not so much affected by the crystalline quality of Fe<sub>4</sub>N as far as the interatomic distances in Fe<sub>4</sub>N are not modified by something like strain and vacancies.

#### IV. SUMMARY

CaF<sub>2</sub>(1 nm)/Fe<sub>4</sub>N(10 nm)/STO(001) was grown by MBE, and the VB structures of Fe<sub>4</sub>N were characterized by photoelectron spectroscopy. Structures observed in the HX-PES spectra were explained by the calculated photoemission spectra of Fe 3d and 4s states in Fe<sub>4</sub>N. In the SRPES measurement,  $P$  was estimated having negative sign at  $E_F$  in spite of a positive shift due to secondary electrons.

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