Interface structure of half-metallic Heusler alloy Co$_2$MnSi thin films facing an MgO tunnel barrier determined by x-ray magnetic circular dichroism

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Using x-ray absorption spectroscopy and x-ray magnetic circular dichroism, we performed an element-specific investigation of the spin magnetic moments of Mn and Co of Co$_2$MnSi ultrathin layers grown on an Fe underlayer to stabilize the ferromagnetism and facing an MgO barrier. The experimentally observed dependence of the spin magnetic moments of Mn and Co on the Co$_2$MnSi layer thickness in the ultrathin region is qualitatively in good agreement with the one theoretically obtained for a MnSi-terminated interface of the Co$_2$MnSi layer facing an MgO barrier. This clarification would provide a strong basis for further advancement of applications of half-metallic Heusler alloy electrodes into spintronic devices.

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I. INTRODUCTION

Spintronic devices that manipulate the spin degree of freedom of the electron are being extensively studied, which could lead to future electron devices featuring nonvolatility and reconfigurability. Half-metallic ferromagnets (HMFs) are characterized by an energy gap for one spin direction, providing complete spin polarization at the Fermi level, which is usually a transition metal and $Z$ is a main-group element. In particular, Co$_2$MnSi, has attracted much interest because of its high Curie temperature of 985 K.

For magnetic tunnel junctions (MTJs) with half-metallic electrodes, Mavropoulos et al. theoretically predicted a crucial role of the minority-spin interface states at the half-metallic electrode/oxide junction in spin-dependent tunneling characteristics for antiparallel (AP) magnetization alignment. Furthermore, Co$_2$YZ layers in epitaxial Co$_2$YZ/MgO heterostructures with the (001) basal plane have two possible terminated interfaces with an MgO barrier, i.e., the YZ- and Co-terminated interfaces. It has been predicted by first-principles calculations that the interfacial spin polarization of Co$_2$MnSi facing an MgO barrier strongly depends on the terminated interface structure of Co$_2$MnSi at Co$_2$MnSi/MgO junctions. Thus, identifying the interface structure at Co$_2$YZ/MgO junctions with well-controlled interfaces is essential. We have recently proposed and developed fully epitaxial MTJs with Co$_2$YZ alloy electrodes in combination with an MgO(001) barrier and demonstrated a high tunneling magnetoresistance (TMR) ratio of up to 1135% at 4.2 K with a substantially decreased one of 236% at room temperature (RT) for epitaxial Co$_2$MnSi-MgO/Co$_2$MnSi MTJs. The strong temperature ($T$) dependence of the TMR ratio for epitaxial Co$_2$MnSi-MgO MTJs. Similar $T$ dependence of the TMR ratio was observed also for Co$_2$MnSi/AlO$_x$/Co$_2$MnSi MTJs. On the basis of the dynamical mean-field theory, Chioncel et al. attributed the strong $T$ dependence of the TMR ratio to nonquasiparticle states, which appear in the half-metallic gap of Co$_2$MnSi and degrade the spin polarization remarkably with increasing $T$. In recent hard x-ray photoelectron spectroscopic measurements, however, no distinct $T$ dependence has been observed for the valence band of Co$_2$MnSi. We therefore need an alternative explanation of the $T$ dependence of the TMR ratio observed in the MTJs with Co$_2$MnSi electrodes. Ishikawa et al. experimentally suggested the critical role played by interface states for minority spins existing around $E_F$ of Co$_2$MnSi electrodes facing an MgO barrier to explain the spin-dependent $dI/dV$ versus $V$ characteristics. On the other hand, recent high-angle annular dark-field scanning-transmission electron-microscopy measurements suggest that the terminating interface of the Co$_2$MnSi layer facing an MgO barrier consists of the layer next to the Co layer, including site disorder between the first two atomic layers at the junction, where the MgO barrier was deposited by magnetron sputtering. Given this background, in order to further advance the applicability of half-metallic Co$_2$YZ into spintronic devices, it is essential to develop a means for determining nondestructively the interface structure and clarify the structural, electronic, and magnetic properties of the interfacial region between Co$_2$YZ electrodes and tunneling barrier.
Our objective in the present study was to elucidate the interface structure of Co₂MnSi electrodes facing an MgO barrier by experimental investigation along with a theoretical analysis. For this purpose, we performed an element-specific investigation of the spin magnetic moments \(m_{\text{spin}}\) of Mn and Co of Co₂MnSi in the interface region facing an MgO barrier by means of x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD), which are very effective techniques for exploring the electronic and magnetic states of the interface region of ferromagnetic thin films facing an oxide or semiconductor. To specifically measure the interfacial region by XAS and XMCD, we prepared ultrathin Co₂MnSi layers facing an MgO barrier with Co₂MnSi thicknesses \(t\) down to one monolayer, where one monolayer of Co₂MnSi consists of a Co plane and a MnSi plane and corresponds to half the unit cell of Co₂MnSi. To stabilize the ferromagnetic order of the ultrathin Co₂MnSi layers, the Co₂MnSi layers were grown on an Fe underlayer. The experimentally obtained dependence of \(m_{\text{spin}}\) of Mn and Co of Co₂MnSi in the Fe/CMS \(t\)/MgO as a function of \(t\) was analyzed theoretically, taking into consideration the influence of both interfaces with the lower Fe layer and upper MgO barrier.

II. EXPERIMENTAL

The sample layer structure was as follows: (from the substrate side) MgO buffer (10 nm)/Fe underlayer (50 nm)/Co₂MnSi \(t\)/MgO barrier (2 nm)/Ru cap (2 nm), grown on an MgO(001) single-crystal substrate, where \(t\)=177 ML (50 nm), 4 ML (1.13 nm), 2 ML (0.565 nm corresponding to a unit cell), and 1 ML (0.283 nm). The preparation of the samples is described in detail elsewhere. The Co₂MnSi film was deposited at RT by magnetron sputtering and subsequently annealed in situ at 325 °C for 15 min. To ensure there would be no Fe diffusion into the ultrathin Co₂MnSi film, we used a relatively low annealing temperature of 325 °C. The MgO barrier was deposited at RT by electron-beam (EB) evaporation. The composition of the Co₂MnSi films used in this study was determined as Co₂Mn_{0.9}Si_{0.1}, which was slightly Co rich against the Mn and Si composition. From in situ reflection high-energy electron diffraction (RHEED) observations, we confirmed that all the layers in the Fe/Co₂MnSi/MgO with \(t\)=2 and 1 ML grew epitaxially with the (001) basal plane as in the case for \(t\)=4 ML. We also observed 1/2-order superlattice reflections along the [110]CMS direction in the RHEED patterns for these films annealed at 325 °C, indicating that the Co₂MnSi film with \(t\)=2 and 1 ML had the L₂₁ structure as that for \(t\)=4 ML did. XAS and XMCD spectra were measured at RT with the total electron yield method by using circularly polarized synchrotron radiation at the KEK Photon Factory (BL-11A). The degree of circular polarization of incident light was set to 87% (±4%). XAS spectra for opposite magnetic-field directions were acquired consecutively with the photon helicity fixed. XMCD is defined as the difference between the two spectra with the photon helicity parallel (\(\mu_+\)) and antiparallel (\(\mu_-\)) to the 3d majority-spin directions.

III. RESULTS

A. X-ray magnetic circular dichroism spectra

Figure 1 shows XAS and XMCD spectra for Fe/Co₂MnSi \(t\)/MgO at the Co-L₂₃ and Mn-L₂₃ edges for \(t\)=2 and 1 ML. The XAS and XMCD intensities were normalized by the Co-L₂₃ (Mn-L₂₃) XAS peak total intensity, i.e., \(\mu_+\) and \(\mu_-\), with a linear background subtracted in the XAS. We first describe how the XAS and XMCD spectrum at the Co-L₂₃ changes with decreasing \(t\). In the referenced XAS spectrum for \(t\)=4 ML in Ref. 25, a small distinct shoulder appeared at the higher photon energy (about 3 eV) side of the Co-L₁ peak, which is characteristic of Co₃YZ with the L₂₁ structure. The shoulder structure became weaker and the Co-L₃ peak width became smaller for \(t\)=2 ML [Fig. 1(a)] than those for \(t\)=4 ML. For \(t\)=1 ML, the shoulder structure disappeared and a much narrower Co-L₃ peak was observed [Fig. 1(b)], reflecting the significant interfacial effect and some possible structural disorder in the ultrathin 1-ML-thick Co₂MnSi film. We then describe how the XAS and XMCD spectrum at the Mn-L₂₃ changes with decreasing \(t\). For \(t\)=4 ML in Ref. 25, a broad structure appeared in the XAS and XMCD spectra in the higher photon energy (about 2~10 eV) region of the Mn-L₃ XAS peak and a doublet structure appeared in the Mn-L₂ region in the XAS spectrum, which are characteristic of Co₂YZ with the L₂₁ structure. The broad structure in XAS spectra, however, disappeared for \(t\)=2 and 1 ML [Figs. 1(c) and 1(d)], reflecting a considerable interfacial effect. For these Co₂MnSi films with \(t\) ranging from 4 to 1 ML, XMCD signals were noticeably observed, which implies the existence of substantial magnetic moments on Co and Mn, even for \(t\)=1 ML with an assist from the molecular field of the Fe.
The values of the averaged respective theoretical Co2MnSi film with characteristic multiplet structures of CoO magnetic moment of Mn for Fe of Co and Mn atoms deduced from the XMCD spectra observed for Fe/Co2MnSi (t ML)/MgO layer structures with thickness t of 1, 2, 4, and 177 ML (50 nm).

<table>
<thead>
<tr>
<th>t (ML)</th>
<th>$m_{\text{spin}}$ ($\mu_B$)</th>
<th>$m_{\text{orb}}$ ($\mu_B$)</th>
<th>$m_{\text{spin}}$ ($\mu_B$)</th>
<th>$m_{\text{orb}}$ ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>177$^a$</td>
<td>1.16 ± 0.1</td>
<td>0.02 ± 0.1</td>
<td>2.95 ± 0.1</td>
<td>0.08 ± 0.1</td>
</tr>
<tr>
<td>4$^a$</td>
<td>1.25</td>
<td>0.06</td>
<td>3.35</td>
<td>0.05</td>
</tr>
<tr>
<td>2</td>
<td>1.37</td>
<td>0.18</td>
<td>3.92</td>
<td>0.28</td>
</tr>
<tr>
<td>1</td>
<td>1.48</td>
<td>0.15</td>
<td>2.74</td>
<td>0.03</td>
</tr>
</tbody>
</table>

$^a$References 25 and 26.

underlayer. The Mn-edge XMCD signal for t = 1 ML [Fig. 1(d)], however, is smaller than those of the Co2MnSi films with t = 4 and 2 ML, which indicates a reduction in the magnetic moment of Mn for t = 1 ML. The absence of the characteristic multiplet structures of CoO (Ref. 20) and MnO (Ref. 25) in the XAS spectrum and the noticeably observed XMCD signals for all Co2MnSi films also rule out the possibility of oxidation of Co and Mn atoms.

For a more precise analysis of the XAS and XMCD spectra, we used the sum rules,29 from which one can evaluate $m_{\text{spin}}$ and the orbital magnetic moment ($m_{\text{orb}}$) of Mn and Co as

\[
m_{\text{orb}} = -\frac{4}{3} q n_b \mu_B, \tag{1}
\]

\[
m_{\text{spin}} + 7m_{\text{orb}}^2 = -\frac{6p - 4q}{r} n_b \mu_B, \tag{2}
\]

where r is the XAS energy integral, $r = \int_{L_{\text{edge}}} L_{\text{edge}} (\mu_+ - \mu_-) d\omega$, q is the XMCD energy integral over the $L_{2,3}$ edges, and p

\[
z_f L_{\text{edge}} (\mu_+ - \mu_-) d\omega.
\]

The p is the XMCD energy integral over the $L_{\text{edge}}$ edge, expressed as $p = \int_{L_{\text{edge}}} (\mu_+ - \mu_-) d\omega$, and $m_{Tz}^2 = (T_z) \mu_B / \hbar$ with $(T_z)$ being the expectation value of the intraatomic magnetic dipole operator.28 For the evaluation of $m_{\text{spin}}$ and $m_{\text{orb}}$ of Co and Mn in Co2MnSi films using the bare spin sum rules because a correction factor of Mn in Co2MnSi with the $L_{2,3}$ structure is not accurately known.

The obtained experimental $m_{\text{spin}}$ and $m_{\text{orb}}$ values of Co and Mn for Co2MnSi films with t = 2 and 1 ML and with t = 4 ML and t = 177 ML (50 nm) (Refs. 25 and 26) as references are listed in Table I, and the experimental $m_{\text{spin}}$ values are plotted in Fig. 2. Most importantly, the experimental $m_{\text{spin}}$ values of both Co and Mn considerably increased with decreasing t from 4 to 1 ML with the exception of the decreased $m_{\text{spin}}$ value of Mn for t = 1 ML. Although slight increases in these values for t = 4 ML compared with those for t = 177 ML have been observed (8% and 14% increases for Co and Mn, respectively),26 we found that the $m_{\text{spin}}$ values definitely increase with decreasing t for samples with t = 2 and 1 ML except for the $m_{\text{spin}}$ value of Mn for t = 1 ML. These behaviors clearly demonstrate interfacial effects in these heterostructures. The $m_{\text{spin}}$ value of Co increased with decreasing t from 1.16$\mu_B$ for t = 177 ML to 1.48$\mu_B$ for t = 1 ML (a 28% increase). In addition, the $m_{\text{spin}}$ value of Mn increased with decreasing t from 2.95$\mu_B$ for t = 177 ML to 3.92$\mu_B$ for t = 2 ML (a 33% increase) while it dropped to 2.74$\mu_B$ for t = 1 ML.

On the other hand, the $m_{\text{orb}}$ values for Co and Mn were very small for t = 4 and 177 ML [0.02–0.06$\mu_B$ and 0.05–0.08$\mu_B$, respectively]. This indicates that the orbital

![FIG. 2. (Color online) Experimental $m_{\text{spin}}$ for (a) Co and (b) Mn of Co2MnSi films in Fe/Co2MnSi (t)/MgO layer structures as a function of t for B = 3 T at RT (solid circles), where the experimental $m_{\text{spin}}$ values are normalized by their respective experimental values for the Co2MnSi film with t = 177 ML (50 nm) [$m_{\text{bulk}}$ (experiment for t = 177 ML) = 1.16$\mu_B$ for Co and 2.95$\mu_B$ for Mn]. Theoretically calculated values of the averaged $m_{\text{spin}}$ ($m_{\text{orb}}$) of Co and Mn in the Fe(001)/Co2MnSi (t)/MgO layer structures with the MnSi/MgO interface (solid triangles) and Co/MgO interface (open triangles) are also shown as a function of t, where the theoretical $m_{\text{spin}}$ values are normalized by their respective theoretical $m_{\text{spin}}$ values for bulk Co2MnSi [$m_{\text{bulk}}$(theory) = 0.935$\mu_B$ for Co and 3.31$\mu_B$ for Mn).]
magnetic moments are quenched due to the cubic symmetry in Co2MnSi with the L21 structure, though these values are larger than the theoretically predicted ones of about 0.02μB for Co and about 0.008μB for Mn in bulk Co2MnSi with the L21 structure. However, except for the m_{orb} value of Mn for t=1 ML, some increases in the m_{orb} values of Co and Mn were observed when t was further decreased to 2 and 1 ML, as shown in Table I. The increased m_{orb} values have also been observed for Co2MnSi thin films grown on GaAs(001) substrates. Comparing the t dependence of m_{spin} and that of m_{orb}, the former is more distinct. Furthermore, the accuracy of the m_{spin} values is higher that of the m_{orb} values because of their one-order higher values. Thus, the t dependence of m_{spin} is more suitable than that of m_{orb} for comparisons with theoretical analyses that take interfacial effects at both sides into account.

B. First-principles calculation

To reveal the terminated interface structure of Co2MnSi layers facing an MgO barrier through comparison with the experimental results, we performed first-principles calculations for supercells consisting of Fe, Co2MnSi, and MgO, using the density-functional theory within the generalized-gradient approximation for the exchange-correlation energy. We adopted plane-wave-basis sets along with the ultrasoft pseudopotential method using the quantum code ESPRESSO. The spin-orbit interaction and the noncollinear spin structures were neglected in our calculations. The number of k points was taken to be 10x10x1 for all cases, and Methfessel-Paxton smearing with a broadening parameter of 0.01 Ryd was used. The cut-off energy for the wave function and charge density was set to 30 and 300 Ryd, respectively. The Fe(001)/Co2MnSi (t)/MgO (t=1–4 ML) layer structure was constructed in a tetragonal supercell. We prepared the supercell containing eight atomic layers of bcc-Fe, 1–4 ML of Co2MnSi and eight atomic layers of MgO. The in-plane lattice parameter of the supercell was fixed at 0.399 nm, which corresponds to \(a_0/\sqrt{2}\), where \(a_0=0.565\) nm is the lattice constant of the bulk Co2MnSi.

Figures 3(a) and 3(b) show schematic representations of Fe(001)/Co2MnSi (4 ML)/MgO layer structures with the MnSi/MgO interface and the Co/MgO interface, respectively. Figures 3(c) and 3(d) show the local \(m_{spin}\) projected on to each atomic sphere in the structures as a function of distance from the Co2MnSi/MgO interface. As can be seen in Figs. 3(c) and 3(d), the local \(m_{spin}\) of Mn at the MnSi/MgO interface increases compared with that in the interior region of the Co2MnSi layer, while the local \(m_{spin}\) of Co at the Co/MgO interface decreases compared with that in the interior region of the Co2MnSi layer, as reported in a previous theoretical work.

At the MnSi/MgO interface, as shown schematically in Fig. 3(a), the difference in the covalent bond radius between Si (0.111 nm) and Mn (0.139 nm) causes relaxation of the interfacial structure. The Si atom moves away from the MgO side and only the Mn atom makes a bond with the O atom. In our previous study, we showed that this relaxation thermodynamically stabilizes the MnSi/MgO interface rather than the Co/MgO interface. However, the relaxation weakens the local bonding between the Co2MnSi layer and the MgO layer, causing dangling bonds for the interfacial atoms. Since electrons in the dangling bond states are energetically unstable, they tend to localize in order to reduce the exchange-correlation energy, which is associated with the increase in the local \(m_{spin}\) of the interfacial Mn atom. This increase is achieved by a charge transfer from the minority-spin to the majority-spin states. On the other hand, at the Co/MgO interface, the interfacial Co atom makes a strong bond with the O atom. The strong bonding causes charge transfer from the Co layer to the MgO layer owing to the large electron affinity of O atoms. We confirmed that \(E_F\) of the local density of states (LDOS) of Co at the Co/MgO interface shifts toward the lower energy side compared to that in bulk Co2MnSi (see Fig. 2 of Ref. 14). Since bulk Co2MnSi has no minority-spin state at \(E_F\), reduction in the occupied states in the interfacial LDOS is significant for the majority-spin states, resulting in the decrease in the local \(m_{spin}\) of Co at the Co/MgO interface.

Next, we discuss the magnetic properties of the Fe(001)/Co2MnSi interface. The local \(m_{spin}\) of Co at the Fe/Co interface (1.27μB) is larger than that of Co in bulk Co2MnSi (0.935μB), as shown in Fig. 3(c), because the \(m_{spin}\) of Co in bulk Co2MnSi is smaller than that in B2-type CoFe (1.72μB). Furthermore, the local \(m_{spin}\) of Mn at the Fe/MnSi
interface (2.63\(\mu_B\)) is smaller than that of Mn in bulk Co\(_2\)MnSi (3.31\(\mu_B\)), as shown in Fig. 3(d). Since the Fe/MnSi interface can be seen locally as Fe\(_3\)MnSi, the local \(m_{\text{spin}}\) of Mn at the Fe/MnSi is close to the \(m_{\text{spin}}\) of Mn in bulk Fe\(_2\)MnSi (2.83\(\mu_B\)) rather than that of Mn in bulk CMS.

The theoretically calculated values of the averaged \(m_{\text{spin}}\) of both Co and Mn on the interface structure of half-metallic Heusler alloys can be seen locally as Fe\(_3\)MnSi, the local \(m_{\text{spin}}\) of Mn at the Fe/MnSi is close to the \(m_{\text{spin}}\) of Mn in bulk Fe\(_2\)MnSi (2.83\(\mu_B\)) rather than that of Mn in bulk CMS.

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