TOPICAL REVIEW

Highly spin-polarized materials and devices for spintronics*

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Abstract

The performance of spintronics depends on the spin polarization of the current. In this study half-metallic Co-based full-Heusler alloys and a spin filtering device (SFD) using a ferromagnetic barrier have been investigated as highly spin-polarized current sources. The multilayers were prepared by magnetron sputtering in an ultrahigh vacuum and microfabricated using photolithography and Ar ion etching. We investigated two systems of Co-based full-Heusler alloys, Co2Cr1−xFexAl(x) (CCFA(x)) and Co2FeSi1−xAlx (CFSA(x)) and revealed the structure and magnetic and transport properties. We demonstrated giant tunnel magnetoresistance (TMR) of up to 220% at room temperature and 390% at 5 K for the magnetic tunnel junctions (MTJs) using Co2FeSi0.5Al0.5 (CFSA(0.5)) Heusler alloy electrodes. The 390% TMR corresponds to 0.81 spin polarization for CFSA(0.5) at 5 K. We also investigated the crystalline structure and local structure around Co atoms by x-ray diffraction (XRD) and nuclear magnetic resonance (NMR) analyses, respectively, for CFSA films sputtered on a Cr-buffered MgO (001) substrate followed by post-annealing at various temperatures in an ultrahigh vacuum. The disordered structures in CFSA films were clarified by NMR measurements and the relationship between TMR and the disordered structure was discussed. We clarified that the TMR of the MTJs with CFSA(0.5) electrodes depends on the structure, and is significantly higher for L21 than B2 in the crystalline structure. The second part of this paper is devoted to a SFD using a ferromagnetic barrier. The Co ferrite is investigated as a ferromagnetic barrier because of its high Curie temperature and high resistivity. We demonstrate the strong spin filtering effect through an ultrathin insulating ferrimagnetic Co-ferrite barrier at a low temperature. The barrier was prepared by the surface plasma oxidization of a CoFe2 film deposited on a MgO (001) single crystal substrate, wherein the spinel structure of CoFe2O4 (CFO) and an epitaxial relationship of MgO(001)[100]/CoFe2(001)[110]/CFO(001)[100] were induced. A SFD consisting of CoFe2/CFO/Ta on a MgO (001) substrate exhibits the inverse TMR of −124% at 10 K when the configuration of the magnetizations of CFO and CoFe2 changes from parallel to antiparallel. The inverse TMR suggests the negative spin polarization of CFO, which is consistent with the band structure of CFO obtained by first principle calculation. The −124% TMR corresponds to the spin filtering efficiency of 77% by the CFO barrier.

Keywords: Heusler alloys, magnetic tunnel junctions, spin filters, Co-ferrites, spin polarization, nuclear magnetic resonance

(Some figures in this article are in colour only in the electronic version.)

* Invited paper.
1. Introduction

The performance of spintronics depends on the spin polarization of the current. Therefore, a highly spin-polarized current source is strongly desired in spintronics. A promising method for this purpose is to take advantage of coherent tunneling in magnetic tunnel junctions (MTJs) with a MgO (001) barrier, in which the giant tunnel magnetoresistance (TMR) has been demonstrated theoretically and experimentally [1–4]. The second method for obtaining highly spin-polarized current is the use of half-metallic ferromagnets (HMFs) [5], which exhibit a semiconductor behavior with a band gap at the Fermi level \(E_F\) for one spin direction, while the other spin band shows typical metallic behavior and thus has 100% spin polarization at \(E_F\). Among some kinds of HMFs, Co-based full-Heusler alloys have been increasingly investigated since the observation of large TMR at room temperature (RT) using a Co\(_2\)Fe\(_{0.8}\)Cr\(_{0.6}\)Al (CCFA) [6] electrode in the MTJs [7]. The third method is the usage of the spin filtering devices (SFDs). Several device structures have been reported to filter out the one spin direction effectively from an unpolarized current in the SFDs since the first observation of spin filtering using a magnetic semiconductor in a SFD [8]. In the case of using a ferromagnetic barrier in SFDs, up- and down-spin electrons see different potential barrier heights from each other because of the spin-dependent barrier height due to the exchange splitting of the ferromagnet. Since the tunneling probability depends exponentially on the barrier height, electrons with one spin direction can tunnel through a ferromagnetic barrier much easier than electrons with the other spin direction, which can lead to very efficient spin filtering and thus a large TMR. In this article, we report two sources for highly spin-polarized current, half-metallic Co-based full-Heusler alloys and a SFD with a ferrimagnetic CoFe\(_2\)O\(_4\) barrier.

2. Half metallic full-Heusler alloys

2.1. Review of crystallographic and electronic structures and magnetism

2.1.1 Crystallographic structure. A schematic representation of the density of states of a half-metal is shown in figure 1, where 100% spin polarization is seen at the Fermi level. Therefore these compounds have a fully spin-polarized current and are useful for spin injection with high efficiency and thus for maximizing the efficiency of spintronics devices. Some kinds of half metals have been theoretically predicted, such as Fe\(_2\)O\(_3\), CrO\(_2\), (La, Sr)MnO\(_3\) perovskites, double perovskites, zinc-blende-type CrAs and Heusler alloys. Heusler alloys, in particular, are promising materials for spintronics applications, because a number of them have been predicted to be HMFs. There are two distinct families of Heusler alloys, one of which has the form of \(XYZ\) and crystallizes in the \(\text{Cl}_b\) structure [9]. This family is known as the half-Heusler alloys, that consist of fcc sublattices occupied by the three atoms X, Y and Z and a vacant site in the \(\text{Cl}_b\) structure. The second family of Heusler alloys is the so-called full-Heusler alloys that possess an \(X_2YZ\) formula with the \(\text{L}_2\) structure, as shown in figure 2 [10]. The \(\text{L}_2\) structure for the full-Heusler alloys is similar to the \(\text{Cl}_b\) structure, however, the vacant site in the \(\text{Cl}_b\) structure is occupied by atom X. Therefore, full-Heusler alloys, which we discuss here, are more stable than half-Heusler alloys in structure and thus will be useful for practical applications. Magnetic and magneto-optical properties of full-Heusler alloys have been investigated by Buschow and van Engen for bulk materials [11].

2.1.2 Electronic structure. The first theoretical prediction of half-metallicity in full-Heusler alloys was for Co\(_2\)MnSi and Co\(_2\)MnGe [12]. They are both strong ferromagnets with high Curie temperatures above 600 K, and they show very little disorder [9]. Each Mn or sp atom (Si or Ge) has eight Co atoms as first neighbors, sitting in octahedrally symmetric positions, while each Co has four Mn and four sp atoms as first neighbors and thus, the symmetry of the crystal is reduced to the tetragonal one. The Co atoms occupying the

![Figure 1. Schematic representation of the DOS for a half metal.](image1)

![Figure 2. \(\text{L}_2\) crystalline structure of full-Heusler alloys.](image2)
two different sublattices are chemically equivalent, because the environment of one sublattice is the same as that of the second one but rotated by 90°. Although in the L2₁ structure the Co atoms are sitting on second-neighbor positions, their interaction is important in explaining the magnetic properties of these compounds, as shown in the following.

Calculated spin-resolved densities of states (DOS) are shown for some Co–Mn based full-Heusler alloys in figure 3 [13], which shows each gap in the minority spin band. The gap is indirect with the maximum of the valence band at Γ point, and is the minimum of the conduction band at the X point. The Co atoms are ferromagnetically coupled to the Mn spin moments and they possess a spin moment that varies from ~0.7 to 1.0µB. In contrast, the sp atom has a very small negative moment that is one order of magnitude smaller than that of Co atoms. The total spin moment $M_t$ is related to the total number of valence electrons $Z_t$ by a simple relation: $M_t = Z_t - 24$, as shown below.

2.1.3 Origin of gap. Here, we explain the band gap in the minority band of Co-based full-Heusler alloys referring to Galanakis et al [13]. Here the four sp-bands are located far below the Fermi level and thus are not relevant to the gap. In Co₂MnGe, for example, Co atoms form a simple cubic lattice and the Mn atoms occupy the body centered sites and have 8 Co atoms as nearest-neighbors (NNs) as seen in figure 2. Although the distance between the Co atoms is a second neighbor distance, the hybridization between these atoms is qualitatively very important. The 5 orbitals are divided into the twofold degenerate $e_g$ and three degenerate $t_{2g}$ bands, which hybridize between the Co atoms and form energy bands, as illustrated schematically in figure 4 [13], where $e_g$ or $t_{2g}$ denote bonding orbitals and $e_u$ and $t_{1u}$ denote antibonding orbitals. These Co–Co orbitals hybridize with Mn d-orbitals, inducing energy bands, as shown in the right-hand part of figure 4. In these energy bands, all 5 Co–Mn bonding bands are occupied and all 5 Co–Mn antibonding bands are empty, and the Fermi level falls in between the 5 nonbonding Co bands, such that three $t_{1u}$ bands are occupied and the two $e_u$ bands are empty. Thus, in total, eight minority d bands are filled and seven are empty. The maximum moment of the full-Heusler alloys is therefore $7 \mu_B$ per unit cell, if all majority d-states are occupied.

2.1.4 Slater–Pauling behavior. Figure 5(a) shows total spin magnetic moments for full-Heusler alloys as a function of the total number of valence electrons [13]. The dashed line represents the half metallicity rule: $M_t = Z_t - 24$. This rule arises from the fact that the minority band contains 12 electrons per unit cell (figure 4): 4 occupy the low-lying $s$ and $p$ bands of the sp element and 8 the Co-like minority d bands ($2 \times e_g$, $3 \times t_{2g}$ and $3 \times t_{1u}$), as shown in figure 4. Many of the calculated results coincide with the Slater–Pauling curve, which is in agreement with the experimental results.

2.1.5 Effect of structural defects on half-metallicity. The formation energies for four different defects in Co₂MnSi and Co₂MnGe are calculated by the GGA-FLAPW method, and the results are shown in table 1 [14]. The formation energy for the Mn antisite defect in both Heusler alloys is the minimum ($\Delta E = 0.33$ eV). This considerably small value suggests that this kind of defect is likely to be found in Co₂MnSi and Co₂MnGe. The total DOS is calculated for ideal and defective Co₂MnSi [14] as shown in figure 6, including the (a) Mn antisite and (b) Co antisite defects. This figure indicates that half-metallicity is maintained with Mn antisite defects, while Co antisite defects destroy the half-metallicity owing to a very sharp peak located just in proximity to $E_F$. The other Co–Mn and Mn–Si swap defects do not destroy half-metallicity [14].

2.2. Experiments with Co-based full-Heusler alloys

Co-based full-Heusler alloys have high Curie temperatures and are promising for practical applications. The L₂₁ structure
for Co₂YZ transforms into the B2 or A2 structure depending on its atomic site disorder. The spin polarization of Co-based full-Heusler alloys has been believed to be sensitive to the site disorder, as shown above [14]. Relatively large TMR has been reported for Co-based full-Heusler alloys such as Co₂FeAl (CFA) [15], Co₂MnSi (CMS) [16] and CFSA [17] in MTJs. In particular, CMS has been demonstrated to possess a high spin polarization of up to 0.86 at low temperature [16]. However, the spin polarization of CMS is temperature sensitive and becomes low at RT, resulting in 90% TMR at RT. Recently, we developed a new Heusler alloy, Co₂FeSi₀.₅Al₀.₅ (CFSA), and obtained a significantly large TMR of 175% at RT [18], which indicates a good temperature dependence of TMR.

Table 1. Formation energy (in eV) and total magnetic moments (in μ₀) for different defects in Co₂MnSi and Co₂MnGe.

|             | Co₂MnSi | Co₂MnGe |
|-------------|---------|---------|
| ΔE          | 0.80    | 0.33    |
| Mₜ          | 38.01   | 38.00   |
| Mₜ½         | 0.84    | 0.33    |
| Mₜ½         | 38.37   | 38.00   |

Figure 5. (a) Calculated total spin moments for full Heusler alloys. The dashed line represents the Slater–Pauling behavior. (b) Schematic band structure for explaining the Z₁ – 12 rule for total magnetization [13].

Figure 6. (a) Total DOS for defective (solid line) and ideal (dashed line) Co₂MnSi with (a) Mn antisite and (b) Co antisite defects in Co₂MnSi [14].

In the investigations described above the Heusler alloys were employed only for the bottom electrode on a MgO (001) substrate, because a highly ordered B2 or L2₁ structure of the Heusler alloys is difficult to form on the amorphous AlOₓ barrier used, although it is easily fabricated on a single crystal MgO (001) substrate or a metallic buffer layer such as Cr. Recently, we successfully fabricated a CFSA film on a MgO barrier with a good interface, and obtained the giant TMR of 220% at RT for a spin-valve-type MTJ with CFSA full-Heusler films for top and bottom electrodes and a MgO barrier, formed on a Cr-buffered MgO (001) single crystal substrate [19]. In this work we first review the structure of the Co-based Heusler alloy films and their TMR of the MTJ, studied by our group. We then investigate more details of the TMR using CFSA electrodes and discuss the relationship between the TMR and the structure of CFSA.

2.3. Experimental method

MTJs with a stacking structure of Heusler alloy/MgO(001)/AlOₓ (15 nm)/Ir₂₂Mn₇₈ (30 nm)/Co₇₅Fe₂₅ (3 nm)/Cr (3 nm) were fabricated on Cr-buffered MgO (001) substrates. The films are prepared using a deposition system with the combination of magnetron sputtering and electron beam...
(EB) deposition at the base pressure of $2 \times 10^{-7}$ Pa. In the former system the bottom Heusler alloy films are deposited by using sputtering from stoichiometric compositions of the Heusler targets at an ambient substrate temperature followed by post annealing or at heated substrate temperatures. Other films on the Heusler films are sputtered-deposited at an ambient substrate temperature. For the latter system, on the other hand, the lower CFSA electrode is formed by sputtering from a stoichiometric Heusler target at an ambient substrate temperature and then annealed at 400 °C in the same chamber. The Ar pressure during sputtering is 0.1 Pa and the typical sputtering rate was 0.03 nm s$^{-1}$ for CFSA, which yields the best smooth surface morphology and the B2 structure of CFSA. The MgO barrier is deposited from MgO grains by EB evaporation. The pressure during evaporation is under $5 \times 10^{-6}$ Pa and the typical evaporation rate is 0.01 nm s$^{-1}$. The upper CFSA electrode is sputtered on the MgO barrier, followed by the deposition of antiferromagnetic Ir$_{22}$Mn$_{78}$ at RT, which is used to exchange bias the upper ferromagnetic layer. Finally a Ta cap layer is deposited at RT.

The MTJs were patterned into $8 \times 8 \mu m^2$ by the conventional EB lithography and Ar ion etching. The patterned MTJs were annealed at temperatures around 350–500 °C for 1 h in a high vacuum by applying a 2 kOe magnetic field. The crystalline structure was investigated by x-ray diffraction (XRD, Rigaku ATX-G) with a Cu-Kα source for both $\theta - 2\theta$ (out-of-plane) and $\phi - 2\theta$ (in-plane) scans. The film roughness was evaluated by atomic force microscopy (AFM) and x-ray reflectivity measurements. Magnetic properties were measured using a vibrating sample magnetometer (VSM) from 5 K to RT. Nuclear magnetic resonance (NMR) measurement was carried out for $^{59}$Co nuclei in Heusler alloy films on Cr-buffered MgO (001) by the spin echo method at a low temperature in order to investigate the local structure around the Co atoms. The magnetoresistance measurement of the MTJs was performed by a conventional dc four-point technique.

2.4. Results

2.4.1 $Co_xCr_{1-x}Fe_xAl$ [20]. Figure 7(a) shows XRD patterns obtained with the Cu-Kα source for the 100 nm thick $Co_xCr_{1-x}Fe_xAl$ films with different Fe concentrations deposited on thermally oxidized Si (SiO$_2$) substrates at RT. The patterns show clear peaks indicative of a polycrystalline nature and are characterized by a lack of diffractions from the (111) superlattice line identifying the L2$_1$ structure. Also, the intensity of the (200) superlattice reflection corresponding to the B2 structure becomes weak with increasing Fe content and disappears for $x = 1$. Therefore, it is suggested that the B2 structure for $x = 0$ tends to transform into the A2 structure with increasing Fe content. As a measure of the degree of the ordering of the B2 structure, the (200) reflection intensity relative to that of the (220) peak is shown in the inset of figure 7(a), along with the theoretical data. The experimental intensity is lower than the theoretical one for even $x = 0$, suggesting an imperfect B2 structure. The lattice constants measured from data in figure 7(a) are shown in figure 7(b) as a function of $x$. The values for bulk $Co_2CrAl$ and $Co_2FeAl$ with the L2$_1$ structure are also shown. The lattice constant decreases with increasing $x$ owing to the transformation from the B2 to the A2 structure. The lattice constant of $Co_2FeAl$ with the A2 structure is significantly lower than that of the $Co_2FeAl$ with L2$_1$ structure.

Figure 8 shows the x-ray reflectivity for the 100 nm thick $CCFA(x)$ deposited at RT and elevated temperatures. The as-deposited film exhibits a periodic pattern in a wide diffraction angle, suggesting a flat layer structure, while the films deposited at elevated temperatures exhibit a rapid decrease in the reflectivity intensity, particularly for the films deposited above 773 K, indicating a rough surface. The flat layer structure of the $Co_2(Cr_{1-x}Fe_x)Al$ films deposited at a
lower substrate temperature is a key factor in obtaining large TMR in MTJs.

The normalized magnetization-temperature curves below RT are shown in figure 9(a) for the CCFA(x) films, which were annealed at an appropriate temperature depending on x after the deposition at RT. The curves reveal that the Curie temperature in CCFA(x) monotonically increases with increasing Fe content. Magnetic moments per formula unit at 5 K are shown as a function of x in figure 9(b). The theoretical values calculated for the L2₁ structure assuming the Slater–Pauling curve are also shown by the dotted line. It is noted that the obtained magnetic moments are significantly lower than the theoretical values for the L2₁ structure, particularly for higher Cr content. For example, the magnetic moment per formula unit at 5 K is 1.1 μ₄B for Co₃CrAl in this study, which is significantly smaller than the theoretical value of 2.96 μ₄B for bulk Co₃CrAl with the L2₁ structure, where the magnetic moments of Co and Cr are 0.76 and 1.54 μ₄B, respectively [21]. This may be attributed to the Cr atoms occupying the Co sites, as theoretically suggested by Miura et al [22], who predicted the Cr atoms occupying the Co atom sites in the L2₁ structure to be antiferromagnetically coupled with the Cr atoms at the right positions. This means that our CCFA films do not form the perfect B2 structure but contain the disordered A2 structure. It is, however, difficult to estimate the degree of disorder in the B2 structure from XRD measurements. The (200) superlattice reflection line intensity for the B2 structure is written as \[ F(200) = 4|2f_0 - (f_{Al} + f_X)|, \] where \( f_i \) is the average scattering factor for the atoms on the i-sublattice and X is either Cr or Fe. The \( f_i \) values for the Co, Cr and Fe atoms are nearly the same because the atomic numbers are close to each other. Thus, the x-ray intensity cannot be changed by the replacement of Co by either Cr or Fe. A detailed study of the magnetic structure of our CCFA(x) samples is desirable using EXAFS and XMCD, which are useful for the investigation of the local structure and site-resolved magnetic moments.

Magnetoresistance was measured for the spin-valve-type MTJs consisting of CCFA(x)(20 nm)Al(1.2)-Oₓ/CoFe(3 nm)/IrMn(15 nm)/Ta(60 nm) deposited on a MgO (001) substrate. The CCFA(x) grows epitaxially with the B2 structure on a MgO (001) substrate when deposited above 473 K. The TMR significantly depends on the quality of the tunnel barrier, which is affected by the roughness of the underlayer upon which the barrier is formed. The MgO (001) substrate significantly improves the roughness of the CCFA(x) deposited at elevated temperatures, compared with the SiO₂ substrate. The TMRs at RT and 5 K for the junctions with a CCFA(x) electrode deposited on a MgO (001) substrate are shown in figure 10 as a function of x, in which the CCFA(x) films are deposited at 673 K and the other films constructing the junction are deposited at RT. The obtained large TMR is caused by the smooth surface of the CCFA(x) film owing to the deposition on a MgO (001) single crystal substrate. Fe substitution significantly increases the TMR, because the TMR obtained with the Co₃CrAl film is only 13% at 5 K. The maximum TMR of
83% at 5 K was obtained for x = 0.6, which results in a spin polarization $P = 0.59$, if $P = 0.5$ for CoFe is applied in the Julliere equation for TMR [23]. The value of $P = 0.59$ corresponds to 88% of the theoretical value reported in [21]. It is notable that the large TMR is obtained using a Heusler alloy with the B2 structure containing a disorder, because the spin polarization is very sensitive to the atomic site disorder of half-metallic alloys. Recently, Miura et al [22] predicted that the Co–Cr-type disorder, in which some of Cr atoms occupy Co atom sites, significantly decreases the spin polarization, while the spin polarization is negligibly affected by the Cr–Al-type disorder. Taking into account these results, our CCFA($x$) films have the possibility of containing the Co–Cr-type disorder, which is not contradictory to the smaller magnetization than that in the case of the L21 structure shown in figure 9(b).

The maximum TMR at $x = 0.6$ obtained may be due to the contributions of both the decreased Co–Cr-type disorder, as seen in figure 9(b), and the decreasing spin polarization with increasing Fe content. The larger TMR and magnetization may be obtained if the CCFA($x$) film with the B2 structure could be fabricated without the Co–Cr-type disorder.

The TMR curves exhibiting 52 and 83% at RT and 5 K, respectively, are shown for a junction with a Co$_2$(Cr$_{0.4}$Fe$_{0.2}$)Al electrode in figure 11. The curves are typical ones for a spin-valve, and the TMR is based on the antiparallel alignment of the magnetizations between the Co$_2$(Cr$_{0.4}$Fe$_{0.2}$)Al and CoFe layers in a low magnetic field, corresponding to the small coercive force of Co$_2$(Cr$_{0.4}$Fe$_{0.2}$)Al, followed by the parallel alignment of the magnetizations in a large field.

2.4.2 Co$_2$FeAl. Co$_2$FeAl thin film exhibits almost the same magnetization as the theoretical value, as described in the previous section. Thus, we investigated it in more detail. Figure 12(a) shows XRD patterns for 50-nm-thick Co$_2$FeAl deposited on SiO$_2$ substrates at various temperatures. The films exhibit the B2 structure when deposited at temperatures above 473 K, because the (200) superlattice diffraction line can be observed in the films, while the films deposited below 473 K have the A2 structure because there is no diffraction line from (200). The diffraction intensity of (200) relative to that of (220) in the inset is close to almost the theoretical value for films deposited above 573 K. Figure 12(b) shows the x-ray reflectivity for the same Co$_2$FeAl films as in figure 12(a). The films deposited at temperatures below 473 K exhibit a periodic pattern within a wide diffraction angle, suggesting a flat layer structure, while the films deposited above 473 K exhibit a rapid decrease in reflectivity intensity, indicating a rough surface. The AFM image of the film deposited at 773 K, shown in figure 12(c), also exhibits a rough surface with Ra = 1.05 nm, owing to grain growth.

We have investigated the TMR for the MTJ consisting of SiO$_2$ sub/Co$_2$FeAl(20 nm)/Al(1.2 nm)-O$_x$/Co$_{57}$Fe$_{25}$(3 nm)/IrMn(10 nm)/Ta(60 nm), using Co$_2$FeAl films deposited at various substrate temperatures, in which the other films, except for Co$_2$FeAl, were deposited at RT. The junction was annealed at 498 K in a magnetic field for the exchange
biasing of Co$_{75}$Fe$_{25}$ film using an IrMn antiferromagnet. TMR at RT is shown in figure 13 as a function of the substrate temperature ($T_s$). The resistance area (RA) product of the junction is also shown in the figure. The large TMR of 51% is obtained for as-deposited Co$_2$FeAl with the A2 structure. When the substrate temperature is increased, the TMR first increases and then decreases, taking the maximum of 54% in the case of A2 structure for $T_s = 473$ K, while RA monotonically decreases with increasing $T_s$. The decrease of TMR above $T_s = 473$ K, where the Co$_2$FeAl electrode has the B2 structure, may be due to the surface roughness of the Co$_2$FeAl films, as shown in figure 12. The A2 and B2 structures can be identified from $^{59}$Co NMR spectra, which are shown in figure 14, measured at 4.2 K for Co$_2$FeAl films on a SiO$_2$ substrate. The spectrum for the A2 structure shows the pattern characterized by a broad maximum at around 180 MHz due to the random distribution of Co, Fe and Al atoms. In contrast, the B2 structure exhibits the distinctive 7 resonance peaks in a frequency range of 50–300 MHz. The peaks correspond to the Fe and Al atoms distributed with different ratios on the 8 NN sites around a Co atom site. The highest resonance frequency of around 290 MHz corresponds to the 8 NN sites occupied by 8 Fe, the peak at around 270 MHz corresponds to 7 Fe + 1Al, and so on. There is no resonance frequency for 8 Al atoms surrounding a Co atom, because the corresponding CoAl is nonmagnetic. The resonance frequency around 180 MHz due to the random distribution of Co, Fe and Al atoms is reasonable considering that the highest probability for the

Figure 12. (a) XRD patterns and (b) x-ray reflectivity of Co$_2$FeAl films deposited on SiO$_2$ substrates at various temperatures. (c) AFM image of Co$_2$FeAl deposited on SiO$_2$ substrates at 773 K.

Figure 13. TMR and resistance-area (RA) product at RT as a function of substrate temperature for junctions with Co$_2$FeAl electrode deposited on SiO$_2$ substrates.

Figure 14. $^{59}$Co NMR spectra for Co$_2$FeAl films with A2 and B2 structures on SiO$_2$ substrates.
random distribution of Fe and Al atoms in B2 occurs when the proportions of the two atoms are the same.

We also investigated Co$_2$FeAl films deposited on a MgO (001) substrate. Figure 15(a) shows the in-plane and out-of-plane XRDs for 20-nm-thick Co$_2$FeAl films deposited on MgO substrates at various temperatures. All the films grew epitaxially with the (001) orientation. The (200) intensity relative to that of (400) increases with increasing temperature (figure 15(b)), although the intensity is significantly below the theoretical one. We have investigated the (111) orientation of the films by the in-plane $\phi$-scan in the (111) plane. The (111) intensity is observed only in the film deposited at 773 K, and not in the films deposited below 673 K. The (111) intensity, however, is very weak compared with the theoretical one, thus the L2$_1$ structure may be limited to a small region of the Co$_2$FeAl film deposited at 773 K. The surface roughness of the Co$_2$FeAl films deposited on MgO (001) substrates is negligibly affected by the substrate temperature, as shown in the (a) x-ray reflectivity spectra and (b) AFM image for the film deposited at 773 K in figure 16. This is in contrast to the films on SiO$_2$ substrates shown in figure 12, that exhibit rougher surfaces with increasing substrate temperature.

Figure 16(a) shows TMR as a function of the substrate temperature for the MgO (001) sub./Co$_2$FeAl(20 nm)/Al (1.2 nm)-O$_x$/Co$_{75}$Fe$_{25}$ (3 nm)/IrMn (10 nm)/Ta(60 nm) junctions, as well as that on the SiO$_2$ substrate shown in figure 13. The TMR for the junctions on the MgO (001) substrate does not depend on the substrate temperature, which is consistent with the nearly same surface roughness of the Co$_2$FeAl films for all substrate temperatures investigated, as shown in figure 16. The temperature dependence of the TMR is shown in figure 17(b), compared with that on a SiO$_2$ substrate ($T_s = 773$ K). Both Co$_2$FeAl films have the B2 structure. The temperature dependence of the TMR is more generous for the junction on a MgO substrate than that on a SiO$_2$ substrate, which may be due to the smaller barrier roughness of the former. The obtained TMR at 5 K for the MgO substrate is about 75%, which leads to the spin polarization of 56.2% for the Co$_2$FeAl film with the B2 structure, or 93% of the theoretical spin polarization of 60.7% [24]. The nearly theoretical value of the TMR obtained is notable because the experimentally obtained spin polarization for the Heusler alloy is generally small compared with the theoretical one. The reason behind of this attainment may be the highly ordered B2 structure of the Co$_2$FeAl films on the MgO (001)
substrate, as demonstrated by the NMR measurement shown in figure 14. It is also noted that the A2 structure of Co$_2$FeAl leads to nearly the same TMR as the B2 structure.

We could not obtain the Co$_2$FeAl film with the L2$_1$ structure by either substrate heating or annealing after the film deposition. The theoretical calculation yields the spin polarization of 84.5% for L2$_1$-Co$_2$FeAl [24], which can lead to the TMR of over 100% at RT. Thus, the L2$_1$ structure is strongly desired to be fabricated for the Co$_2$FeAl film. For bulk Co$_2$FeAl, the L2$_1$ structure may be obtained by heat treatment above 700 K after annealing at a higher temperature above 1373 K [25].

2.4.3 Co$_2$FeSi. Recently, Co$_2$FeSi with the L2$_1$ structure was demonstrated to be half-metallic with 100% spin polarization by first-principles calculation [26]. Experimentally it has been verified that Co$_2$FeSi crystallizes in the L2$_1$ structure in the bulk by quenching after annealing at a high temperature [26] or in the film deposited on a GaAs substrate [27]. We deposited Co$_2$FeSi films on SiO$_2$ and MgO (001) substrates without a buffer layer with substrate heating or annealing after the deposition at RT. All the films on the SiO$_2$ substrate exhibited the A2 structure, while the films on a MgO (001) substrate had different structures depending on the heat treatment conditions, as shown in table 2. The L2$_1$ structure can be realized by adopting substrate heating above 473 K or in the film deposited on a GaAs substrate. The lattice constant of the Co$_2$FeSi films was 0.567 nm, which is nearly the same as that of the bulk, 0.564 nm [26]. The surface roughness of the Co$_2$FeSi film investigated by the x-ray reflectivity analysis is larger than that of the Co$_2$FeAl film with higher substrate heating temperature than the post deposition annealing temperature, where both films are deposited on the MgO (001) substrate. This may be due to the larger lattice misfit between Co$_2$FeSi and MgO compared with that between Co$_2$FeAl and MgO, where the lattice constant of Co$_2$FeAl is 0.573 nm.

Table 2. Crystal structures of Co$_2$FeSi films deposited on a MgO (001) substrate heated at various temperatures or annealed after the deposition at RT.

| Temperature (k) | Crystal structure |
|----------------|-------------------|
| as-depo        | A2                |
| Post anneal    | A2                |
|                | B2                |
|                | L2$_1$            |
| Substrate heating | 473 L2$_1$     |
|                | 573 L2$_1$        |
|                | 673 L2$_1$        |
|                | 773 L2$_1$        |

Figure 18. In-plane (200) rocking curves for Co$_2$FeSi and Co$_2$FeAl thin films deposited on a MgO(100) substrate at 773 K.
2.4.4 Co$_2$FeSi$_{1-x}$Al$_x$. We demonstrated that in Co$_2$FeAl films, the L$_2_1$ structure is difficult to form, but highly ordered B2 can be fabricated, which provides nearly the same TMR as the theoretical prediction, although the film is not half-metallic. On the other hand, in Co$_2$FeSi, L$_2_1$ is easily formed, but the TMR using L$_2_1$-Co$_2$FeSi is significantly small compared with the theoretical prediction for the half-metallicity. Thus, we investigated Co$_2$FeSi$_{1-x}$Al$_x$ in order to clarify the effective differences between Co$_2$FeAl and Co$_2$FeSi and the composition dependence of the TMR. We also noted that the Fermi level position in the gap of the minority spin band can be controlled by replacing Si with Al, because the valence electron numbers are different between Si and Al atoms by one. The Fermi level position in the minority band gap is very important for obtaining the large TMR using half-metallic ferromagnets [28], because spin flip tunneling easily occurs, leading to the reduction of TMR, when the Fermi level is near the gap edge. The most desirable Fermi level position is at the midpoint in the gap.

Figure 19 shows the TMR at RT as functions of temperatures of substrate heating ($T_s$) and annealing ($T_a$) after deposition at RT for MgO(001)/Co$_2$FeSi/AlO$_x$/CoFe/IrMn/Ta junctions.

The TMR will be improved by optimizing the preparation conditions of the junction and/or by using a buffer layer to reduce the lattice misfit between the Co$_2$FeSi film and MgO (001) substrate.

Figure 20. TMR curves at RT (a) and 5 K (b) for the MTJ with a Co$_2$FeSi electrode. (c) Temperature dependence of TMR and RA.
decreases with increasing \( T_a \) and then increases steeply with \( T_a \) above 500°C, while it is significantly improved by using the Cr-buffer layer, which may be due to the improvement of the lattice misfit by the Cr metal layer.

Figure 23 shows TMR at RT as a function of post-annealing temperature for junctions with CFSA electrodes with different MgO layer thicknesses. It reveals high sensitivity of TMR to MgO thickness \( t_{\text{MgO}} \) [19]. The TMR first increases and then decreases with increasing \( T_a \) and becomes a maximum of 220% at around \( T_a = 430–450 \)°C for \( t_{\text{MgO}} = 1.7 \) nm, in which CFSA on a Cr buffer layer shows the L2₁ structure, as seen in figure 21(b). The TMR curves at RT and 5 K are shown for \( T_a = 430 \) °C (a) and 500°C (b) in figure 24. The former shows the exchange-biased spin-valve-type of junction with the TMR of 390% at 5 K, corresponding to 81% spin polarization calculated by Julliere model, while the latter exhibits not-exchange-biased type of junction, which may be due to the Mn interdiffusion from the IrMn layer at the higher temperature. Thus the TMR reduction at \( T_a \) higher than 450°C for \( t_{\text{MgO}} = 1.7 \) nm in figure 23 will be attributed to Mn interdiffusion, and hence CFSA may have potentially a higher spin polarization than 81%.

Figure 25 shows the cross-sectional transmission electron micrograph (TEM) of the multilayer prepared under the same fabrication conditions as the MTJ with 220% TMR at low (a) and high (b) magnifications. The low-magnification image indicates good morphology of the MTJ structure with a smooth interface between CFSA and the MgO barrier. The high-resolution image reveals a high degree of epitaxy of both the upper and lower CFSA and the MgO barrier. However, there is degradation in the MgO barrier, such as crystalline structure distortion and an extra atomic plane. This degradation originates from the lattice misfit of 4.5% between MgO and the top CFSA, which leads to the strong MgO thickness dependence of TMR shown in figure 23. Namely, the surface of the MgO barrier on CFSA becomes rough with increasing \( t_{\text{MgO}} \), which affects the structure of the upper CFSA and degrades the spin polarization, as seen in the TMR reduction with increasing \( t_{\text{MgO}} \) from 1.7 to 2.5 nm. The TMR reduction with increasing MgO thickness is not consistent with the coherent tunneling effect for the TMR [1, 2]. Thus, the large TMR obtained using CFSA electrodes and a MgO barrier may be based on the high spin polarization of CFSA, indicating that CFSA may be a promising material for used in various spintronics devices.
The XRD intensity for the (111) orientation for $T_a = 450 \, ^\circ$C in figure 21, providing the maximum TMR of 220% at RT, is very weak compared with that for $T_a = 500 \, ^\circ$C. This suggests that the corresponding L2$_1$ structure is highly disordered. Here we investigate the disorder in the L2$_1$ CFSA films using NMR for $^{59}$Co nuclei [29]. The NMR frequency is proportional to the hyperfine field on atomic nuclei, which is dependent on the local environment around the atoms. Therefore, NMR is useful for investigating the site disorder. Figure 26(a) shows the local environment around Co in

![Local environment around Co in L2$_1$Co$_2$FeAl](image)

Figure 26. (a) Local structure around Co atom in L2$_1$-Co$_2$FeAl. (b) $^{59}$Co NMR spectrum in bulk L2$_1$-Co$_2$FeAl.

![NMR for Bulk Co$_2$FeAl](image)

Figure 25. Cross-sectional TEM with low and high magnifications of the multilayer prepared under the same fabrication condition as the MTJ with 220% TMR.

![Cross-sectional TEM with low and high magnifications of the multilayer](image)

Figure 24. TMR curves at RT and 5 K for junctions with CFSA electrodes with post-annealing at (a) 430 $^\circ$C and (b) 500 $^\circ$C.
L2₁-CO₂FeAl, in which a CO atom has 4 Fe and 4 Al NN atoms and 6 Co next-nearest-neighbor (NNN) atoms. Figure 26(b) is the ⁵⁹Co NMR spectrum for bulk CO₂FeAl with L₂₁, which exhibits a main peak at around 193 MHz and subsidiary peaks at frequencies both higher and lower than the main peak. The main peak originates from the ordered L₂₁ structure. It is inferred from the XRD in figure 21 and NMR in figure 27(a), that the L₂₁ structure for Tₐ = 450 °C giving 220% TMR at RT is more disordered than 15%. Thus, a greater TMR than the present record may be realized by improving the degree of ordering in L₂₁-CFSA.

3. Spin filtering using Co-Ferrite barrier

3.1. Introduction

In a SFD used as a source for spin-polarized electrons, a ferromagnetic tunnel barrier is used to generate a polarized current in spin-filter tunneling, called the spin-filter effect, shown schematically in figure 28. This is in contrast to the conventional spin-dependent tunneling using a ferromagnetic metal and a nonmagnetic barrier. In such a ferromagnetic barrier, exchange splitting of the conduction band creates two different tunnel barrier heights, a lower one for spin-up electrons (φₚ) and a higher one for spin-down electrons (φ₈). In general, spin is conserved during the tunneling process. Therefore, for a given barrier thickness (d), the tunneling current density J depends exponentially on the corresponding barrier height [30]:

\[ J \propto \mu \exp(-\frac{\phi^2}{d}) \]

Thus, even with modest differences in barrier heights, the tunneling probability for spin-up electrons is much greater than that for spin-down electrons, resulting in the spin polarization of tunneling current.

The most striking difference between the SFD and the MTJ is the bias voltage dependence of the TMR. In the SFD with increasing bias voltage the TMR increases linearly and then decreases at high voltage, as shown schematically in figure 29 [31]. At low voltage the tunneling probability for spin-up channel is higher than that for the other, while at high voltage, this tunneling probability increases for both channels; thus the conductance ratio G¹/G⁰ tends to unity, and hence the TMR decreases. In contrast, the TMR for the MTJ is known to decrease monotonically with increasing voltage. Moodera et al [8] first reported SFDs with ferromagnetic semiconductor barriers, Eu calcogenides. They obtained a spin-filtering efficiency as high as 86% at 0.4 K using EuS for a ferromagnetic barrier. However, Eu calcogenides have
low Curie temperatures ($T_c$), thus, the spin-filtering effect has not been observed at RT [32, 33]. For practical use SFDs are required to work at RT. The low $T_c$ is the fatal problem in the case of using Eu calcogenides. Recently, SFDs with a (La, Sr)MnO$_3$ electrode and ferromagnetic oxide barriers, such as BiMnO$_3$ [34] and NiFe$_2$O$_4$ [35], have also been studied. Although NiFe$_2$O$_4$ has a high $T_c$, the spin-filtering effects are observed only at low temperatures, not RT because of the low $T_c$ of the (La, Sr)MnO$_3$ electrode. In order to observe the spin-filtering effect at RT, a ferromagnetic insulating barrier with high $T_c$ and a high-$T_c$ ferromagnetic electrode should be applied. Table 3 lists the properties of the known spin-filter materials [36] including our recent results [37].

In this work, we focus on a Co-ferrite (CFO) as the ferromagnetic barrier material. CFO is one of the spinel ferrites and is believed to be mostly of the inverse spinel kind with divalent Co ions occupying predominantly the octahedral sites. It has high $T_c$ (~800 K) and high resistivity (~$10^7$ $\Omega$cm), suggesting it to be a promising candidate for the ferromagnetic barrier. The spin-resolved DOS has been calculated for bulk CFO with the inverse spinel structure as shown in figure 30 [38]. This exhibits a band gap of 0.8 eV for the spin-down electrons, which is lower than that for the spin-up electrons, accompanied with exchange splitting $\Delta E_x = 1.28$ eV. This structure suggests that the tunneling probability for spin-down electrons is much greater than that for spin-up electrons, which results in negative spin polarization of tunneling current.

### Table 3. Spin-filter materials studied up to now.

| Material | Magnetic behavior | $T_c$ (K) | Moment ($\mu_B$) | Structure (a nm) | $E_F$ (eV) | $2\Delta E_x$ (eV) | $P$ (%) | Reference |
|----------|------------------|-----------|-----------------|------------------|-----------|-----------------|--------|-----------|
| EuO      | FM               | 69.3      | 7.9             | Fcc 0.514        | 1.12      | 0.54            | 29     | [32]      |
| EuS      | FM               | 16.6      | 7.9             | Fcc 0.596        | 1.65      | 0.36            | 86     | [34]      |
| EuSe     | AFM              | 4.6       | 7.9             | Fcc 0.619        | 1.80      | –               | 100    | [33]      |
| BiMnO$_3$| FM               | 105       | 3.6             | Perovskite       | –         | –               | 22     | [34]      |
| NiFe$_2$O$_4$ | Ferri-M | 850  | 2.0             | Spinel           | 1.2       | –               | 22     | [35]      |
| CoFe$_2$O$_4$ | Ferri-M | 796  | 3.0             | Spinel           | 1.28      | –               | 77     | [37]      |

Figure 29. Schematic of bias voltage dependence of TMR in a spin filter.

Figure 30. Calculated DOS for Co ferrite with inverse spinel structure.

#### 3.2. Experimental method

In fabricating the SFD, single crystal substrates such as MgO (001) are useful for obtaining a flat interface. However, very thin spinel ferrite films on a MgO (001) substrate exhibit anomalous magnetic properties [39, 40] because of the antiphase domain boundary formation. Thus, we used the CoFe$_2$ surface oxidation method to obtain a thin CFO barrier layer [41]. CoFe$_2$ thin films were prepared on MgO (001) substrates by magnetron sputtering with a CoFe$_2$ target. The incident power, Ar gas pressure, and substrate temperature were controlled at 1.7 W cm$^{-2}$, 1.0 Pa and RT, respectively, during sputtering. The thickness of CoFe$_2$ was fixed at 20 nm. The surface of the deposited CoFe$_2$ thin film was oxidized by reverse sputtering. The incident power and substrate temperature during oxidization were 50 W and 523 K, respectively. The partial pressures of both Ar and O$_2$ gasses were 0.75 Pa. Oxidation time was fixed at 900 s for the evaluation of the film properties and 600 s for SFDs. The base pressures in the sputtering and oxidation chambers were below $2 \times 10^{-7}$ and $1 \times 10^{-5}$ Pa, respectively.

#### 3.3. Results and discussion

Figure 31(a) shows the in-plane XRD pattern for the 900-s-oxidized CoFe$_2$ films. The CoFe$_2$ underlayer deposited on a MgO (001) substrate is highly oriented in the (001) plane. The peaks corresponding to CFO (220) and (440) planes are clearly observed in addition to that of (200) CoFe$_2$. The $\phi$ scan in the CFO (440) plane is also shown in the inset of figure 31(a). Four sharp peaks having a 4-fold symmetry are observed, indicating a single-crystalline CFO thin film. The lattice parameters of CoFe$_2$ and CFO thin films are identified as 0.285 and 0.828 nm, respectively. The differences in the
Figure 31. (a) In-plane XRD pattern for surface-oxidized CoFe₂ thin films on MgO (001) single crystal substrates (oxidation time is 900 s). The inset shows φ scan on Co-ferrite 440 plane. (b) Electron diffraction pattern and (c) cross-sectional TEM image for MgO(001)/CoFe₂/Co-ferrite.

lattice parameters from that of the bulk are $-0.35\%$ for CoFe₂ and $-1.2\%$ for CFO thin films, while the lattice parameter of the MgO substrate is 0.415 nm. The electron diffraction pattern and the stacking structure observed by TEM are shown in figures 31(b) and (c), respectively. They reveal the layered structure of CFO and CoFe₂ on the MgO (100) substrate and an epitaxial relationship of CoFe₂[110]/CFO [100] in the (001) plane.

Figure 32 shows the hysteresis loops for the nonoxidized CoFe₂ films and those oxidized for 300, 600 and 900 s at 523 K with the magnetic field applied parallel to the MgO [001] direction; the magnetization is normalized by each film area. For the nonoxidized CoFe₂ film, the thickness of which was designed to be 20 nm, the saturation magnetization ($M_s$) is estimated to be $\sim 1500$ emu cm$^{-3}$, which is about 77% of the bulk value (1950 emu cm$^{-3}$). After the surface plasma oxidation, the magnetization decreases and coercivity ($H_c$) increases with increasing oxidation time. This is understood from the formation of CFO having a lower magnetic coupling between CoFe₂ and CFO becomes 2.1 [42].

The $H_c$ of CFO increases with increasing oxidation temperature and becomes as high as 900 Oe at 673 K (not shown). The magnetization in the hysteresis loop of figure 32 decreases with increasing negative field and exhibits two inflection points, A and B, which correspond to the $H_c$ values of soft CoFe₂ and hard CFO, respectively. The gradual decrease of the magnetization in the second quadrant suggests weak magnetic coupling between CoFe₂ and CFO films with different coercivities. The thicknesses of the films in the CoFe₂/CFO bilayer are estimated to be 17.1 and 14.0 nm for CoFe₂ and CFO, respectively, from the cross-sectional TEM in figure 31(c). Assuming that sputter etching of the film surface is negligible and volume increase due to the oxidation results only in a thickness increase, the theoretical thickness ratio between bulk CoFe₂ and CFO becomes 2.1 [42]. Using this ratio, the thicknesses of the oxidized CoFe₂ and the original CoFe₂ are estimated to be 6.7 and 23.8 nm, respectively.

TMR versus field curve (top) at 5 mV and the magnetization curve (bottom) are shown in figure 33 for a SFD consisting of CoFe₂/CoFe₂-Oₓ,900 s/Ta(10 nm) on a MgO (001) single crystal substrate, which were measured at RT. Both the TMR and magnetization curves correspond well to the higher resistance for the parallel magnetization configuration than for the antiparallel magnetization configuration between the CoFe₂ electrode and the CFO barrier, demonstrating the inverse TMR. The TMR value is very small, $-0.13\%$, at RT. However, the TMR curve was not changed for the different field directions applied in the plane, which rules out anisotropic magnetoresistance.
In order to investigate whether the spin-dependent tunneling contributes to TMR, we measured the TMR curves at low temperatures [37]. Figure 34(a) shows the current density ($J$)–voltage ($V$) curve and figures 34(b) and (c) show TMR curves for (b) a major loop at 5 K with the bias voltage of 5 mV and (c) a minor loop at 10 K with the bias voltage of 1 mV. The $J$–$V$ curve clearly exhibits a nonlinear behavior, suggesting that CFO acts a tunneling barrier. The barrier height and barrier thickness estimated using the Simmons equations [30] are 0.18 eV and 4.5 nm, respectively. This barrier thickness is significantly smaller than the 14 nm observed in figure 31(c), suggesting a nonuniform barrier thickness and interfacial roughness. The major loop in figure 34(b) indicates a TMR of approximately $-20\%$ at 5 mV bias voltage and a large coercivity of about 800 Oe for the CFO film at 5 K. The parallel magnetization alignment between the CoFe$_2$ electrode and the CFO barrier also exhibits higher resistance than that in the case of the antiparallel alignment, indicating inverse TMR, as shown at RT in figure 33. The TMR at 1 mV bias voltage is $-124\%$ at 10 K, as seen in figure 34(c). By applying this value to the Jullièvre model [23] with 50% spin polarization of the CoFe$_2$ electrode, we obtain 77% spin polarization for the CFO, which is comparable to the 80% spin polarization attained by conductive AFM for CFO films [43]. In CFO, the bottom of the conduction band is significantly lower for spin-down electrons than for spin-up electrons [37], therefore, the tunneling probability for the spin-down electrons is much higher than that for the spin-up electrons with negative spin polarization, resulting in the inverse TMR.

We also measured the temperature dependence of the RA product and TMR at 1 mV bias voltage for the junction in figure 34, but results are not shown. The RA of the order of $10^7 \Omega \mu m^2$ at 10 K strongly decreases with increasing temperature above 50 K and takes a low value of the order of $10^2 \Omega \mu m^2$ at RT, which is characteristic of the tunneling process. TMR, on the other hand, decreases more steeply with increasing temperature above 10 K, being $-16$ and $-0.1\%$ at 50 K and above 100 K, respectively. The cause of the stronger temperature dependence of the TMR is not clear at this stage, but may be attributed to the interface roughness and/or defective CFO barrier with a small barrier height. This temperature dependence also induces the tunneling upon the thermal excitation of the spin-up electrons into their corresponding majority spin conduction band, if conduction band splitting is small with respect to $k_B T$. The bias voltage dependence of TMR is also very strong, resulting in TMR of

Figure 33. Tunneling magnetoresistance at (a) RT and (b) 5 K for spin filter consisting of CoFe$_2$/CoFe$_2$-O$_{2x}$(600 s)/Ta(5 nm) on a MgO (001) single crystal substrate. The bias voltage is 5 mV.

Figure 34. (a) Current density ($J$) – voltage ($V$) curve at 1 kOe (parallel state) at 10 K. The circles represent experimental data and solid line is curve fitted using Simmons equations. (b) Major R–H curve at 5 K and 5 mV and (c) minor R–H curve at 10 K and 1 mV for SFD consisting of CoFe$_2$(20 nm)-O$_{2x}$(900 s)/Ta(10 nm) on a MgO (001) single-crystal substrate.
−124% at 1 mV and −20% at 5 mV, and may also have same origin as the strong temperature dependence of the TMR. However, a detailed discussion involving magnon excitation effects is required to understand these strong temperature and bias voltage dependences.

4. Summary

We have investigated the structural, magnetic and transport properties of the Co$_2$(Cr$_{1-x}$Fe$_x$)$_3$Al, Co$_2$FeSi and Co$_2$FeSi$_{0.5}$Al$_{0.5}$ full-Heusler alloy films prepared using an ultrahigh-vacuum magnetron sputtering system on thermally oxidized Si and MgO (001) substrates. Co$_2$(Cr$_{1-x}$Fe$_x$)$_3$Al films do not show the L2$_1$ structure as expected for the bulk, but exhibit the B2 and A2 structures, depending on the Fe concentration and heat treatment conditions; the B2 structure tends to form with increasing Fe concentration. Both the magnetic moment and the Curie temperature monotonically increase with increasing Fe content. The A2 structure decreases the magnetic moment in Cr-containing systems, which may be due to the Co–Cr-type disorder involved. The spin-valve-type tunneling junctions consisting of Co$_2$Cr$_{1-x}$Fe$_x$Al (1.2 nm)/CoFe (3 nm)/IrMn (15 nm) on a MgO (001) substrate exhibited the maximum TMR value of 52 and 83% at RT and 5 K, respectively, for $x = 0.6$. In contrast, although the Co$_2$FeSi films on a MgO (001) substrate can easily be fabricated with the L2$_1$ structure, the maximum TMR obtained using a Co$_2$FeSi electrode with the L2$_1$ structure is 60% at 5 K, which is significantly smaller than the expected value for the half-metallic L2$_1$-Co$_2$FeSi. The TMR, however, may be improved in the future by optimizing the junction fabrication conditions.

Co$_2$FeSi$_{0.5}$Al$_{0.5}$ (CFSA) Heusler alloy films can provide a giant TMR of up to 220% at RT and 390% at 5 K for the MTJ, corresponding to the spin polarization of 0.81 at 5 K. We have investigated the crystalline structure and disordering by XRD and NMR analyses, respectively, for the sputtered CFSA films on a Cr-buffered MgO (001) substrate followed by post annealing at various temperatures in an ultrahigh vacuum. The disordered structure was clarified and the relationship between TMR and the disordered structure was discussed. It was revealed that the TMR of the MTJs with L2$_1$-CFSA electrodes is significantly higher than that of MTJs with B2-CFSA electrodes.

We prepared CoFe$_2$O$_4$ (CFO) thin films by surface oxidation of (001)-oriented CoFe$_2$ films deposited on MgO (001) single crystal substrates. The CFO films have a spinel structure and an epitaxial relationship with the CoFe$_2$ underlayer. The magnetizations of CoFe$_2$ and CFO films reverse with weak magnetic coupling between them and with different coercivities. The SFDs fabricated with a CFO barrier and a nonmagnetic Ta electrode show nonlinear I–V curves and the spin-filtering effect with the inverse TMR of −124% at 10 K, corresponding to a 77% spin-filtering effect of the CFO barrier. The TMR is significantly temperature sensitive and is only −0.13% at RT.

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