Effect of defects in Heusler alloy thin films on spin-dependent tunnelling characteristics of Co$_2$MnSi/MgO/Co$_2$MnSi and Co$_2$MnGe/MgO/Co$_2$MnGe magnetic tunnel junctions

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Effect of defects in Heusler alloy thin films on spin-dependent tunnelling characteristics of $\text{Co}_2\text{MnSi}/\text{MgO}/\text{Co}_2\text{MnSi}$ and $\text{Co}_2\text{MnGe}/\text{MgO}/\text{Co}_2\text{MnGe}$ magnetic tunnel junctions

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Abstract

Fully epitaxial magnetic tunnel junctions (MTJs) with Co-based Heusler alloy Co$_2$MnSi electrodes and a MgO tunnel barrier were fabricated with various values of Mn composition $\alpha$ for Co$_2$Mn$_{\alpha}$Si in Co$_2$Mn$_{\alpha}$Si/MgO/Co$_2$Mn$_{\alpha}$Si MTJs. The tunnel magnetoresistance (TMR) ratios at both 4.2 K and room temperature (RT) increased systematically with increasing $\alpha$ in Co$_2$Mn$_{\alpha}$Si electrodes from Mn-deficient compositions ($\alpha < 1$) up to a certain Mn-rich composition ($\alpha > 1$), demonstrating high TMR ratios of 1135% at 4.2 K and 236% at RT for MTJs with Mn-rich Co$_2$Mn$_{\alpha}$Si electrodes with $\alpha = 1.29$. Identically fabricated Co$_2$Mn$_{\beta}$Ge$_{\delta}$/MgO/Co$_2$Mn$_{\beta}$Ge$_{\delta}$ ($\delta = 0.38$) MTJs showed similar dependence of the TMR ratio on Mn composition $\beta$, demonstrating relatively high TMR ratios of 650% at 4.2 K and 220% at RT for $\beta = 1.40$. The Mn composition dependence of the TMR ratio at both 4.2 K and RT observed commonly for both Co$_2$MnSi/MgO/Co$_2$MnSi and Co$_2$MnGe/MgO/Co$_2$MnGe MTJs can be attributed to suppressed minority-spin in-gap states around the Fermi level for Mn-rich Co$_2$MnSi and Co$_2$MnGe electrodes.
1. Introduction

Manipulation of the spin degree of freedom of the conduction electrons in an electron device, or spintronics, has been extensively studied recently [1, 2]. Half-metallic ferromagnets feature an energy gap for one spin direction (mostly the minority-spin band) at the Fermi level ($E_F$), which provides complete spin polarisation at $E_F$ [3]. Because they exhibit complete spin polarisation at $E_F$, half-metallic ferromagnets are one of the key materials for ferromagnetic electrodes in spintronic devices [4]. Co-based Heusler alloys ($\text{Co}_2\text{YZ}$, where $Y$ is usually a transition metal and $Z$ is a main group element) are amongst the most extensively studied potentially half-metallic electrode materials. This is because half metallicity is theoretically predicted for several of these alloys [5–7] and because they have high Curie temperatures, which are well above room temperature (RT) [8]. Co-based Heusler alloy thin films have been applied for spintronic devices, including magnetic tunnel junctions (MTJs) [9–15] and giant magnetoresistance devices [16–19], and for spin injection from ferromagnetic electrodes into semiconductors [20, 21].

We have recently proposed and developed fully epitaxial MTJs with either a $\text{Co}_2\text{YZ}$ thin film as a lower electrode [12, 13, 22–24] or $\text{Co}_2\text{YZ}$ thin films as both lower and upper electrodes [25, 26], and with a MgO barrier in both cases, and demonstrated high tunnel magnetoresistance (TMR) ratios of up to 705% at 4.2 K and 182% at RT for fully epitaxial $\text{Co}_2\text{MnSi}/\text{MgO}/\text{Co}_2\text{MnSi}$ MTJs [26–28]. Fully epitaxial MTJ layer structures with $\text{Co}_2\text{YZ}$ thin films and a MgO barrier are advantageous for thoroughly utilising high spin polarisations of potentially half-metallic $\text{Co}_2\text{YZ}$ electrodes in terms of (1) preparing structurally high-quality single-crystal $\text{Co}_2\text{YZ}$ electrodes, (2) forming atomically flat and abrupt interfaces, and (3) ensuring that the interfacial region of the $\text{Co}_2\text{YZ}$ lower electrode facing the MgO barrier is not oxidised [29, 30] by the deposition of MgO barriers by electron beam evaporation. Epitaxial MTJs with $\text{Co}_2\text{YZ}$ electrodes and a MgO barrier also enable an enhancement of the tunnel conductance for the parallel magnetisation configuration as a result of coherent tunnelling of electrons of the majority-spin $\Delta_1$ channel.
Note that heterostructures consisting of a Heusler alloy upper electrode on a MgO tunnel barrier are common basic building blocks for $\text{Co}_2\text{YZ/MgO/Co}_2\text{YZ}$ MTJs and for layer structures for spin injection from a Heusler alloy electrode with a high spin polarisation into semiconductors through a MgO tunnel barrier [34]. Thus, the development of $\text{Co}_2\text{YZ/MgO/Co}_2\text{YZ}$ MTJs and clarification of key factors that determine their spin-dependent tunnelling characteristics would also be useful for constructing highly efficient spin-injection layer structures consisting of a semiconductor channel/MgO barrier/Heusler alloy upper electrode. In our previous papers [26–28], the film composition of the $\text{Co}_2\text{MnSi}$ electrodes used in the $\text{Co}_2\text{MnSi/MgO/Co}_2\text{MnSi}$ MTJs was $\text{Co}_{2.91}\text{Mn}_{0.93}\text{Si}_{0.93}$, which is slightly Co-rich with respect to the Mn composition (or slightly Mn-deficient with respect to the Co composition). Nonstoichiometry in $\text{Co}_2\text{YZ}$ inevitably leads to the introduction of defects in the $\text{Co}_2\text{YZ}$ host. The effect of defects in $\text{Co}_2\text{YZ}$ on spin-dependent electronic structures has been investigated theoretically [35–41]. Picozzi et al. predicted from first principles that half-metallicity in $\text{Co}_2\text{MnSi}$ and $\text{Co}_2\text{MnGe}$ is lost for $\text{Co}_{\text{Mn}}$ antisites, where a Mn site is replaced by a Co atom because of the appearance of minority-spin in-gap states just near $E_F$, while half-metallicity is retained for $\text{Mn}_{\text{Co}}$ antisites, where a Co site is replaced by a Mn atom [35].

In the present study, our purpose has been to experimentally clarify the effect of defects in Heusler alloy thin films of $\text{Co}_2\text{MnSi}$ (CMS) and $\text{Co}_2\text{MnGe}$ (CMG) possibly associated with nonstoichiometry on potentially half-metallic electronic structures. For this purpose, we investigate the TMR characteristics of CMS/MgO/CMS MTJs (CMS-MTJs) and CMG/MgO/CMG MTJs (CMG-MTJs) fabricated with various Mn composition values $\alpha$ and $\beta$ in the $\text{Co}_2\text{Mn}_\alpha\text{Si}$ and $\text{Co}_2\text{Mn}_\beta\text{Ge}_\delta$ ($\delta = 0.38$) electrodes. We introduce formula unit composition models for the nonstoichiometric CMS and CMG taking into consideration the theoretically predicted formation energies for various kinds of defects for $\text{Co}_2\text{MnSi}$ and $\text{Co}_2\text{MnGe}$ [35, 41]. We then, on the basis of the formula unit composition models, discuss the origin of the Mn composition dependence of the TMR ratio at both 4.2 K and RT observed commonly for both CMS-MTJs
and CMG-MTJs in terms of the effect of defects in the prepared CMS and CMG electrodes. We further examine the validity of the proposed formula unit composition model for the nonstoichiometric CMG films by investigating the saturation magnetization ($\mu_s$) per formula unit (f.u.) as a function of $\beta$ in the Co$_2$Mn$_\beta$Ge$_{0.38}$ electrodes.

This paper is organised as follows. Section 2 describes our experimental methods. Section 3 presents experimental results for the structural characterisation and TMR characteristics of CMS-MTJs and CMG-MTJs fabricated with various Mn compositions for the Co$_2$Mn$_\alpha$Si and Co$_2$Mn$_\beta$Ge$_\delta$ ($\delta = 0.38$) electrodes. Section 3 also presents the experimental saturation magnetization ($\mu_s$) per formula unit (f.u.) of Co$_2$Mn$_\beta$Ge$_{0.38}$ thin films at 10 K for various $\beta$ ranging from 0.67 to 1.40. Section 4 discusses a possible origin of the observed Mn composition dependence of the TMR ratio and $\mu_s$ in terms of the effects of defects possibly induced in nonstoichiometric CMS and CMG films. Section 5 summarises our results and concludes.

2. Experimental methods

The fabrication procedure for CMS-MTJs and CMG-MTJs was essentially the same as in the case of the exchange-biased CMS-MTJs previously reported [26], but in this study we intentionally varied the Mn compositions in the CMS (CMG) electrodes by co-sputtering from a CMS (CMG) target and a Mn target for both the lower and upper CMS (CMG) electrodes. We used a nearly stoichiometric CMS target and a stoichiometric CMG target. We determined the film composition of the prepared CMS or CMG film through an inductively coupled plasma analysis with an accuracy of 2% to 3% for each element, except Si, for which the accuracy was 5%. The film composition of the original CMS film prepared by sputtering from only a nearly stoichiometric CMS target was Mn-deficient Co$_2$Mn$_{0.69}$Si$_{1.01}$ and that of the original CMG film prepared by sputtering from only a stoichiometric CMG target was both Mn- and Ge-deficient Co$_2$Mn$_{0.67}$Ge$_{0.38}$. For CMS, the film composition was Co$_2$Mn$_\gamma$Si$_\gamma$ with $\gamma = 1.0 \pm 0.06$; i.e., the Co to Si
ratio was almost 2:1. For CMG, the film composition was Co$_2$Mn$_\gamma$Ge$_\delta$ with $\delta = 0.38$; i.e., Ge was strongly deficient. We prepared Co$_2$Mn$_\alpha$Si$_\gamma$ ($\gamma = 1.0 \pm 0.06$) electrodes with various values of $\alpha$ ranging from 0.69 to 1.46. We also prepared Co$_2$Mn$_\beta$Ge$_\delta$ ($\delta = 0.38$) electrodes with various values of $\beta$ ranging from 0.67 to 1.40.

The fabricated MTJ layer structure was as follows: (from the substrate side) MgO buffer (10 nm)/CMS or CMG (both 30 nm)/MgO barrier (2–3 nm)/CMS (3 or 5 nm) or CMG (10 nm)/Ru (0.8 nm)/Co$_{90}$Fe$_{10}$ (2 nm)/Ir$_{22}$Mn$_{78}$ (10 nm)/Ru cap (5 nm), grown on a MgO(001) substrate. Each layer was successively deposited in an ultrahigh vacuum chamber (with a base pressure of about $6 \times 10^{-8}$ Pa). The lower CMS (CMG) electrode was deposited at RT using magnetron sputtering and subsequently annealed in situ at 600 °C (500 °C) for 15 min. The MgO tunnel barrier was deposited by electron beam evaporation at RT. The deposition rate was 0.01 nm/s and the pressure during the deposition of the MgO tunnel barrier was about $6 \times 10^{-7}$ Pa. We fabricated CMS-MTJs with different upper CMS electrode thicknesses of 3 and 5 nm but typically 5 nm, and we fabricated CMG-MTJs with a fixed upper CMG electrode thickness of 10 nm. The upper CMS or CMG electrode was also deposited at RT. The MTJ trilayer was annealed in situ right after deposition of the upper CMS or CMG electrode at 550 °C for CMS-MTJs and 500 °C for CMG-MTJs. We fabricated MTJs with the layer structure described above using photolithography and Ar ion milling. The fabricated junction size was 10 µm × 10 µm. The magnetoresistance was measured with a magnetic field applied along the [110] axis of the Co$_2$YZ at 4.2 K and RT using a dc four-probe method. We defined the TMR ratio as $(R_{AP} - R_P)/R_P$, where $R_P$ and $R_{AP}$ are the respective resistances for the parallel (P) and antiparallel (AP) magnetisation configurations between the lower and upper electrodes. The bias voltage ($V$) was defined with respect to the lower electrode; i.e., electrons tunnel from the lower Co$_2$YZ electrode to the upper Co$_2$YZ electrode at a positive $V$.

The magnetic properties of Co$_2$Mn$_\gamma$Ge$_{0.38}$ thin films with various $\beta$ ranging from 0.67 to 1.40 were measured by using a superconducting quantum interference device magnetometer (Quantum Design
For the estimation of magnetization, the contribution from the MgO substrate was subtracted. To obtain the $\mu_s$ values per f.u., the film thicknesses of $\text{Co}_2\text{Mn}_{0.38}$ films were obtained through X-ray reflectivity measurements, and in-plane and perpendicular lattice constants, $a$ and $c$, were measured by a $\theta-2\theta$ scan with a four-circle X-ray diffractometer.

3. Experimental Results

3.1. Structural properties

First, we describe the structural properties of the fabricated CMS-MTJ layer structures with co-sputtered CMS films having a film composition of $\text{Co}_2\text{Mn}_{1.29}\text{Si}_{1.06}$.

Sharp streak patterns dependent on the electron injection direction were obtained by reflection high energy electron diffraction (RHEED) for each successive layer in a CMS-MTJ trilayer structure with co-sputtered $\text{Co}_2\text{Mn}_{1.29}\text{Si}_{1.06}$ films, clearly indicating that all the layers, including the CMS lower electrode, MgO tunnel barrier, and CMS upper electrode, grew epitaxially. We also observed 1/2-order superlattice reflections along the $[110]_{\text{CMS}}$ direction in the RHEED patterns for both the lower CMS electrode annealed at 600 °C and the upper CMS electrode annealed at 550 °C, showing that both had the $L2_1$ structure.

Figure 1(a) shows a cross-sectional high-resolution transmission electron microscope (HRTEM) lattice image of an MTJ layer structure consisting of CMS (30 nm)/MgO barrier (2 nm)/CMS (5 nm)/Ru (0.8 nm)/$\text{Co}_9\text{Fe}_{10}$ (2 nm)/$\text{Ir}_{52}\text{Mn}_{78}$ (10 nm)/Ru cap (5 nm) with co-sputtered $\text{Co}_2\text{Mn}_{1.29}\text{Si}_{1.06}$ films, along the $[1–10]$ direction of the CMS. This image clearly shows that all the layers of the CMS-MTJ trilayer were grown epitaxially and were single crystalline, as in the case of the MTJ layer structure with CMS films having a film composition of $\text{Co}_2\text{Mn}_{0.91}\text{Si}_{0.93}$ deposited from only a CMS target [28]. It also confirms that extremely smooth and abrupt interfaces were formed.
Next, we describe the structural properties of CMS/Ru/Co$_{90}$Fe$_{10}$/IrMn quadrilayers. The cross-sectional HRTEM lattice image (Fig. 1(a)) showed that all the layers of Ru, Co$_{90}$Fe$_{10}$, and IrMn were grown epitaxially on the single-crystal CMS upper electrode and were single crystalline, as with fully epitaxial, exchange-biased Co$_2$YZ/MgO-based MTJs previously reported [13, 23, 24].

Figures 1(b) and (c) show micro-beam electron diffraction patterns for the lower and upper CMS electrodes for a beam diameter of 2.5 nm, where 111 spots were observed, indicating the L2$_1$ structure for both the lower and upper CMS thin films prepared by co-sputtering. It should be noted that both the 111 spots, which are characteristic of the L2$_1$ structure, and the 002 spots, which are characteristic of the B2 and L2$_1$ structures, are clearer for the lower CMS electrode than for the upper CMS electrode, although the same beam diameter of 2.5 nm was used for both the lower and upper electrodes. This difference in the superlattice spot intensities suggests that the degree of order for the upper CMS electrode is lower than that for the lower CMS electrode, which is common to that observed for lower and upper CMS electrodes previously prepared by sputtering from only a CMS target [42]. It should also be noted that unknown spots were superimposed onto the Heusler L2$_1$ spots in some regions of the lower and upper CMS electrodes, indicating the coexistence of unidentified materials or structures in addition to the Heusler L2$_1$ structure. This was in contrast to the micro-beam electron diffraction patterns for CMS thin films used as both lower and upper electrodes with a film composition of Co$_2$Mn$_{0.91}$Si$_{0.93}$, which were deposited by sputtering with only a CMS target: those patterns showed only the L2$_1$ structure for any spot region [28].

Similarly, sharp streak patterns dependent on the electron injection direction were obtained for each successive layer in the CMG-MTJ trilayer structure with co-sputtered CMG films, clearly indicating that all the layers, including the CMG lower electrode, MgO tunnel barrier, and CMG upper electrode grew epitaxially (not shown).
3.2. Spin-dependent tunnelling characteristics of Co$_2$MnSi/MgO/Co$_2$MnSi MTJs as a function of Mn composition $\alpha$ in Co$_2$Mn$_{\gamma}$Si electrodes

We now describe the TMR characteristics of CMS-MTJs with Co$_2$Mn$_{\alpha}$Si$_{\gamma}$ ($\gamma = 1.0 \pm 0.06$) electrodes fabricated with $\alpha$ ranging from 0.69 to 1.46. Hereafter, we denote Co$_2$Mn$_{\alpha}$Si$_{\gamma}$ ($\gamma = 1.0 \pm 0.06$) by Co$_2$Mn$_{\alpha}$Si using the mean value of 1.0 for Si composition $\gamma$.

Typical TMR curves at 4.2 K and RT for a fabricated epitaxial CMS/MgO (2.7 nm)/CMS MTJ with Mn-rich Co$_2$Mn$_{1.29}$Si$_{1.06}$ electrodes are shown in Fig. 2(a). The thickness of the upper CMS electrode was 3 nm. The bias voltage was 1 mV at both 4.2 K and RT. Clear exchange-biased TMR characteristics were obtained with high TMR ratios of 1135% at 4.2 K and 236% at RT. These values are significantly better than previously reported TMR ratios of 705% at 4.2 K and 182% at RT for a CMS-MTJ with slightly Mn-deficient Co$_2$Mn$_{0.91}$Si$_{0.93}$ electrodes prepared by sputtering with only a CMS target [26, 28].

Figure 2(b) shows the TMR ratios at 4.2 K and RT for CMS-MTJs as a function of $\alpha$ ranging from 0.69 to 1.46, where both the lower and upper CMS electrodes, except those with $\alpha = 0.69$, were deposited by co-sputtering. The bias voltages were 1 mV at 4.2 K and 5 mV at RT. (The lowering of the TMR ratios measured at 5 mV was negligibly small compared to those measured at 1 mV at RT.) The error bars for the TMR ratios for $\alpha = 1.29$ indicate the range of observed TMR ratios for MTJs fabricated with different upper CMS electrode thicknesses ($t_{\text{upper-CMS}}$) of 3 and 5 nm. We found that the TMR ratios at both 4.2 K and RT showed strong dependence on $\alpha$. The TMR ratio at 4.2 K increased from 192% for Mn-deficient $\alpha = 0.69$ to 1135% for Mn-rich $\alpha = 1.29$. It then decreased for $\alpha$ beyond 1.29. Similarly, the TMR ratio at RT increased from 72% for Mn-deficient $\alpha = 0.69$ to 236% for Mn-rich $\alpha = 1.29$ and then decreased for $\alpha$ beyond 1.29.

Most importantly, the TMR ratios at both 4.2 K and RT increased with $\alpha$ even beyond $\alpha = 1.0$, where the film composition is close to the stoichiometric Co$_2$MnSi composition, and the maximum TMR ratios of 1135% at 4.2 K and 236% at RT were obtained for $\alpha = 1.29$. Thus, we experimentally found that the
TMR ratios for CMS-MTJs with nonstoichiometric, Mn-rich Co$_2$MnSi electrodes with a film composition of Co$_2$Mn$_{1.29}$Si$_{1.06}$ were higher than those for MTJs with almost stoichiometric Co$_2$MnSi electrodes.

Figure 3 shows $G_P/G_{AP}$ values at 4.2 K and RT that provided the TMR ratios (TMR ratio = $G_P/G_{AP} - 1$) shown in Fig. 2(b) for CMS-MTJs as a function of $\alpha$, where $G_P = 1/R_P$ and $G_{AP} = 1/R_{AP}$ are the respective tunnel conductances for P and AP. The $G_P/G_{AP}$ values at both 4.2 K and RT showed similar dependence on $\alpha$; i.e., $G_P/G_{AP}$ increased with increasing $\alpha$ from 0.69 to 1.29 and then decreased for $\alpha$ beyond 1.29 at both 4.2 K and RT. The origin of the dependence of the TMR ratio or equivalently of $G_P/G_{AP}$ on $\alpha$ is discussed in Section 4.

3.3. Spin-dependent tunnelling characteristics of Co$_2$MnGe/MgO/Co$_2$MnGe MTJs as a function of Mn composition $\beta$ in Co$_2$Mn$_{\beta}$Ge$_{0.38}$ electrodes

Next, we describe the TMR characteristics of CMG-MTJs with Co$_2$Mn$_{\beta}$Ge$_{0.38}$ electrodes fabricated with $\beta$ ranging from 0.67 (Mn-deficient CMG) to 1.40 (Mn-rich CMG). Figure 4(a) shows typical TMR curves at 4.2 K and RT for a CMG/MgO (2.5 nm)/CMG MTJ with co-sputtered Mn-rich Co$_2$Mn$_{1.40}$Ge$_{0.38}$ electrodes. The bias voltages were 1 mV at 4.2 K and 5 mV at RT. Clear exchange-biased TMR characteristics were obtained with relatively high TMR ratios of 650% at 4.2 K and 220% at RT.

Figure 4(b) shows TMR ratios at 4.2 K and RT for CMG-MTJs as a function of $\beta$ ranging from 0.67 to 1.40, where both the lower and upper CMG electrodes, except those with $\beta = 0.67$, were deposited by co-sputtering. The bias voltages were again 1 mV at 4.2 K and 5 mV at RT. As with the CMS-MTJs, the TMR ratios at both 4.2 K and RT showed strong dependence on $\beta$ in Co$_2$Mn$_{\beta}$Ge$_{0.38}$. The TMR ratio at 4.2 K increased from 276% for Mn- and Ge-deficient $\beta = 0.67$ to 650% for Mn-rich and Ge-deficient $\beta = 1.40$. Similarly, the TMR ratio at RT increased from 78% for $\beta = 0.67$ to 220% for $\beta = 1.40$.

Furthermore, as with the CMS-MTJs, the TMR ratios of CMG-MTJs at both 4.2 K and RT increased
with increasing $\beta$ even beyond $\beta = 1.0$, where $\beta = 1.0$ corresponds to the Co:Mn ratio of 2:1, and the maximum TMR ratios of 650% at 4.2 K and 220% at RT were obtained for $\beta = 1.40$ in the $\beta$ range up to 1.40 used in this study.

3.4. Saturation magnetization of nonstoichiometric $\text{Co}_2\text{Mn}_\beta\text{Ge}_{0.38}$ thin films

Figure 5(a) shows experimentally obtained $\mu_s$ values for $\text{Co}_2\text{Mn}_\beta\text{Ge}_{0.38}$ thin films at 10 K as a function of $\beta$, along with $Z_{t-24}$, where $Z_t$ is the total valence electron number per formula unit provided by the formula unit model for $\text{Co}_2\text{Mn}_\beta\text{Ge}_{0.38}$ discussed in section 4.3. The experimental $\mu_s$ values for $\beta$ ranging from 0.67 to 1.40 were larger than 5.0 $\mu_B$/f.u., which is the value theoretically predicted by the Slater-Pauling rule for stoichiometric, half-metallic $\text{Co}_2\text{MnGe}$ [7]. The experimental $\mu_s$ values increased with increasing $\beta$ from 6.06 $\mu_B$/f.u. for $\beta = 0.67$ to 6.63 $\mu_B$/f.u. for $\beta = 1.40$. This $\beta$ dependence of $\mu_s$ is discussed in section 4.3 on the basis of a formula unit model that includes antisite defects.

4. Discussion

4.1. Effect of defects on TMR ratios at low temperatures

Now we discuss the possible origin of the dependence of the TMR ratio, or equivalently of $G_p/G_{AP}$, on the Mn composition in CMS-MTJs and CMG-MTJs. In this section, we discuss the tunnelling mechanism at low temperatures and low bias voltages. Here, low temperatures mean that thermal energy $k_BT$ is much lower than the minimum magnon excitation energy $\hbar\omega_0$, and low bias voltages mean that $eV$ is lower than $\hbar\omega_0$. Considering that the characteristic energy for magnon excitation was typically 4 meV for fully epitaxial CMS-MTJs, as reported in our previous papers [27, 28], $V = 1$ meV used to measure the TMR ratio at 4.2 K was lower than the magnon excitation energy. Thus, we can ignore tunnelling processes that include spin-flip scattering via magnons excited thermally or excited by
hot electrons in the electrodes at 4.2 K. Then, the main tunnelling paths for AP at 4.2 K and $V = 1$ mV for MTJs with high-spin polarisations to be taken into consideration include (1) a tunnelling path from the majority-spin band in the emitter to minority-spin in-gap states in the bulk region of the collector directly or through minority-spin interface states in the interfacial region of the collector facing a MgO barrier and (2) a tunnelling path from minority-spin in-gap states in the bulk region of the emitter to the majority-spin band in the collector directly or through minority-spin interface states in the interfacial region of the emitter facing a MgO barrier. Therefore, the main factor that determines $G_{AP}$ at low $T$ and low $V$ is the density of minority-spin in-gap states at $E_F$ ($D_{gs}(E_F)$), and the $G_{AP}$ is proportional to $D_{gs}(E_F)$, i.e.,

$$G_{AP} \propto D_{gs}(E_F).$$  

Therefore, the TMR ratio in potentially half-metallic Co$_2$YZ-based MTJs at low $T$ and low $V$ is crucially dependent on $D_{gs}(E_F)$ and increases with decreasing $D_{gs}(E_F)$. For a more rigorous treatment, we must take into consideration the influence of coherent tunnelling (conservation of the electron wave vector parallel to the plane), and $D_{gs}(E_F)$ in Eq. (1) should be replaced by the partial density of minority-spin in-gap states at $E_F$ for which the tunnelling probability is higher due to the coherent tunnelling effect.

Nonstoichiometry in Co$_2$YZ generally induces defects. The effect of defects on half-metallicity for Co$_2$YZ has been investigated theoretically by first-principles calculations [35–41]. Picozzi et al. theoretically predicted that the Co$_{2n}$ antisites induce minority-spin in-gap states around $E_F$, resulting in reduced spin polarisations, while the Mn$_{2n}$ antisites retain the half-metallic character [35]. On the other hand, Galanakis et al. theoretically investigated the effect of disorder between Mn atoms and Si atoms for the Co$_2$Mn$_{1-x}$Si$_x$ system for both $x < 0$ (Mn-deficient side) and $x > 0$ (Mn-rich side) [37]. They reported that substituting Si for Mn, which is likely to occur for the Mn-deficient side, induces states just at the bottom edge of the minority-spin half-metal gap, while substituting Mn for Si, which is likely to occur for the Mn-rich side, pushes the unoccupied minority-spin states even higher in energy and the
half-metal gap becomes wider. Therefore, the disorder between Mn and Si atoms does not induce minority-spin in-gap states around $E_F$, and half-metallicity is thus retained. Furthermore, note that the Mn-rich side in the Co$_2$Mn$_{1+x}$Si$_{1-x}$ system is more favourable than the Mn-deficient side for stable half-metallicity because the half-metal gap is wider for the Mn-rich side.

Next, we consider possible defects induced by Mn-deficient nonstoichiometry in Co$_2$Mn$_\alpha$Si ($\alpha < 1$). According to the theoretically predicted formation energies of various defects induced in CMS [35, 41], Si$_{\text{Mn}}$ antisites are likely to be induced for the range $\alpha < 1$. This is because a Si$_{\text{Mn}}$ antisite has much lower formation energy than a Co$_{\text{Mn}}$ antisite and a vacancy at a Mn site. If only Si$_{\text{Mn}}$ antisites are induced, however, in the prepared Co$_2$Mn$_\alpha$Si thin film having a Co:Si ratio almost of 2:1, vacancies will be formed at Si sites. However, this possibility would be quite low because a Co$_{\text{Mn}}$ antisite has much lower formation energy than a vacancy at a Si site. Thus, it is most likely that Si$_{\text{Mn}}$ antisites are induced along with Co$_{\text{Mn}}$ antisites for the range $\alpha < 1$, resulting in the formula unit model Co$_2$[Mn$_{1-x}$Co$_x$Si$_y$]Si, where [Mn$_{1-x}$Co$_x$Si$_y$] represents the nominal Mn site. The Co:Mn:Si ratio in Co$_2$[Mn$_{1-x}$Co$_x$Si$_y$]Si must be equal to that in the representation of Co$_2$Mn$_\alpha$Si with a given $\alpha$ value. From this requirement, the values of $x$ and $y$ are determined. According to this model, the Co$_{\text{Mn}}$ antisite ratio $x$ decreases with increasing $\alpha$ in the range $\alpha < 1.0$ from $x = 0.17$ for $\alpha = 0.69$ to $x = 0$ for $\alpha = 1.0$.

Similarly, Mn$_{\text{Co}}$ antisites are likely to be induced for the range $\alpha > 1$. This is because a Mn$_{\text{Co}}$ antisite has much lower formation energy than other defects, including a vacancy at a Co site, a Mn$_{\text{Si}}$ antisite, and a vacancy at a Si site. If only Mn$_{\text{Co}}$ antisites are induced, however, vacancies will be formed at Si sites. However, this possibility would be quite low because a Mn$_{\text{Si}}$ antisite has much lower formation energy than a vacancy at a Si site. Thus, it is most likely that Mn$_{\text{Co}}$ antisites are induced along with Mn$_{\text{Si}}$ antisites for the range $\alpha > 1$, resulting in the formula unit model [Co$_{2-x}$Mn$_x$]Mn[Si$_{1-u}$Mn$_u$], where [Co$_{2-x}$Mn$_x$] and [Si$_{1-u}$Mn$_u$] represent the nominal Co and Si sites, respectively.

Given these considerations, we discuss the effect of defects on minority-spin in-gap states. For
Mn-deficient Co$_2$Mn$_\alpha$Si thin films ($\alpha < 1$), it is likely that Co$_{Mn}$ antisites are induced, as discussed above. Note that Co$_{Mn}$ antisites are most harmful for the half-metallicity of CMS and CMG, whereas Si$_{Mn}$ and Mn$_{Si}$ antisites do not affect the half-metallicity at all, as discussed above. Therefore, the observed lower TMR ratio or equivalently lower $G_P/G_{AP}$ for MTJs with Mn-deficient Co$_2$MnSi electrodes at 4.2 K (Figs. 2(b) and 3, respectively) would be due to induced Co$_{Mn}$ antisites, which result in increased $D_{gs}(E_F)$ and thereby lead to the increased $G_{AP}$.

With increasing $\alpha$ beyond 1, where $\alpha = 1$ corresponds to the Co:Mn ratio of 2:1, Mn$_{Co}$ antisites would be induced, while detrimental Co$_{Mn}$ antisites would be suppressed, as discussed above. Thus, the observed higher TMR ratio or equivalently higher $G_P/G_{AP}$ for MTJs with Mn-rich Co$_2$MnSi electrodes would be due to suppressed Co$_{Mn}$ antisites, which result in decreased $D_{gs}(E_F)$ and thereby lead to the decreased $G_{AP}$.

In this section, we have mainly discussed the dependence of the TMR ratio of CMS-MTJs on the Mn composition of Co$_2$MnSi electrodes. The discussion is also applicable to CMG-MTJs, considering that the effect of defects in Co$_2$MnGe hosts on the half-metallic gap structure is essentially the same, as suggested by the theoretical calculations [35]. The possible defects induced in nonstoichiometric, Ge-deficient Co$_2$Mn$_{\alpha}$Ge$_{0.38}$ thin films are discussed in detail in section 4.3.

Note that the proposed formula unit models for $\alpha < 1$ and $\alpha > 1$ for Co$_2$Mn$_\alpha$Si both provide the Co$_{Mn}$ antisite ratio $x = 0$ for $\alpha \geq 1.0$. This is because the models are based on the formation energies of various kinds of defects in the thermal equilibrium state. The increase in the TMR ratio or equivalently that of $G_P/G_{AP}$ with increasing $\alpha$ beyond $\alpha = 1$ for MTJs with CMS electrodes, however, suggests that Co$_{Mn}$ antisites were induced in CMS thin films even for $\alpha \geq 1.0$, indicating that CMS films prepared by sputtering at RT and subsequent annealing at around 500–600 °C do not reach a thermal equilibrium state. Our experimental findings indicate, however, that the concentration of detrimental Co$_{Mn}$ antisites decreases with increasing $\alpha$ beyond $\alpha = 1$ and hence the density of minority-spin in-gap states is reduced.
in Co₂MnSi electrodes. For the Co₂Mn₁₆Ge₀₃₈ thin films, we must also take into consideration that the Ge composition was strongly deficient with respect to the Co composition (See section 4.3).

4.2. Effect of defects on TMR ratios at room temperature

For tunnelling processes for AP at elevated temperatures, where $k_B T$ is comparable or larger than $\hbar \omega_0$, we must take into consideration tunnelling processes for AP that associate spin-flip scattering in the emitter or collector electrode via thermally excited magnons, including the following processes: (1) electrons are spin-flip scattered in the emitter from the majority-spin band to minority-spin in-gap states in the bulk region or minority-spin interface states by thermally excited magnons and then electrons tunnel to the majority-spin band of the collector and (2) electrons tunnel from the majority-spin band of the emitter to minority-spin interface states or minority-spin in-gap states in the bulk region of the collector and then electrons are spin-flip scattered in the collector to the majority-spin band by thermally excited magnons. This model takes into consideration both minority-spin interface states [27, 43] and minority-spin in-gap states in the bulk region of electrodes. These tunnelling processes increase $G_{AP}$ (or equivalently decrease $R_{AP}$) with increasing $T$ because the density of thermally excited magnons increases with increasing $T$.

Note that minority-spin in-gap states in the bulk region and minority-spin interface states are involved in these tunnelling processes. Therefore, $G_{AP}$ at finite $T$ and low $V$ would be proportional to the total density of minority-spin in-gap states at $E_F$ that is the sum of the density of minority-spin interface states at $E_F$ ($D_{if}(E_F)$) and $D_{gs}(E_F)$, and $G_{AP}$ at finite $T$ is expressed as

$$G_{AP} \propto [D_{if}(E_F) + D_{gs}(E_F)] \times [T\text{-dependent term}],$$

where the $T$-dependent term represents the effect of spin-flip scattering via thermally excited magnons. Here, we ignored the effect of magnons excited by hot electrons due to the finite $V$ at RT. The excess energy of $e|V|$ at RT for tunnelling electrons arising from the finite $V$ of 5 mV used for the measurements...
at RT may excite magnons in the collector region, but the TMR ratios measured at $V = 5$ mV were less than 1% lower than those measured at $V = 1$ mV (e|$| = 1$ meV is less than the characteristic magnon excitation energy of $\sim 4$ meV). This means that the effect of magnons excited by hot electrons with excess energy of up to 5 mV at RT can be ignored at RT in comparison with the effect of thermally excited magnons at RT ($k_B T \sim 26$ meV). In this sense, we could regard $V$ of up to 5 mV used here as being a low voltage. In a more rigorous treatment, however, the term $D_g(E_F) + D_{gs}(E_F)$ in Eq. (2) should also be replaced by the partial density of minority-spin in-gap states at $E_F$, including that of minority-spin interface states, for which the tunnelling probability is higher due to the coherent tunnelling effect.

The increase in $G_P/G_{AP}$ with increasing $\alpha$ for an $\alpha$ range of 0.69–1.29 at RT (Fig. 4(b)) can be explained by the decrease in $G_{AP}$ caused by the decrease in the total density of minority-spin in-gap states at $E_F$, i.e., $D_g(E_F) + D_{gs}(E_F)$. The minority-spin interface states at $E_F$ may include (1) intrinsic interface states investigated theoretically [44] and (2) extrinsic interface states influenced by structural defects at the interface. Therefore, $D_g(E_F)$, like $D_{gs}(E_F)$, is a quantity that changes with $\alpha$. Although we could not separate the contributions of $D_{gs}(E_F)$ and $D_g(E_F)$ to $G_{AP}$ at RT, it is certain that $D_{gs}(E_F)$ plays a role in determining the dependence of $G_P/G_{AP}$ on $\alpha$ at RT. As discussed in Section 4.1, $D_{gs}(E_F)$ decreases with the change from CoMn antisites for the Mn-deficient side to MnCo antisites for the Mn-rich side, resulting in the increase in $G_P/G_{AP}$ for $\alpha$ up to 1.29 also at RT through the term of $D_{gs}(E_F)$ in Eq. 2.

4.3. Defects induced in nonstoichiometric, Ge-deficient Co$_2$Mn$_{\theta}$Ge$_{0.38}$

We now discuss possible defects induced in the prepared nonstoichiometric, Ge-deficient Co$_2$Mn$_{\theta}$Ge$_{0.38}$ films. Note that the Co:Ge ratio in the prepared CMG films was 2:0.38, i.e., the Ge ratio was strongly deficient with respect to the Co ratio. According to the theoretically predicted formation energies of various kinds of defects for Co$_2$MnSi [41], with the assumption that the relative magnitude of these
formation energies for Co₂MnGe is essentially the same as that for Co₂MnSi, we introduce a formula unit composition model for strongly Ge-deficient CMG films with $\beta < \beta_c = 1.62$ as $\text{Co}_2[\text{Mn}_{1.62}\text{Co}_x][(\text{Ge}_{1.3}\text{Mn}_y]$ where $[\text{Mn}_{1.62}\text{Co}_x]$ and $[\text{Ge}_{1.3}\text{Mn}_y]$ represent the nominal Mn and Ge sites, respectively. The detailed reasons for this model are as follows: For Ge sites, MnGe antisites, where a Ge site is replaced with a Mn atom, are likely to be induced because a MnGe antisite has much lower formation energy than a vacancy at a Ge site and a CoGe antisite [41]. Thus, Ge sites are fully occupied by the normal Ge atoms and MnGe antisites. For Mn sites, CoMn antisites are likely to be induced because a CoMn antisite has lower formation energy than a vacancy at a Mn site [41]. Thus, the normal Mn atoms and CoMn antisites should occupy Mn sites. The Co:Mn:Ge ratio in $\text{Co}_2[\text{Mn}_{1.62}\text{Co}_x][\text{Ge}_{1.3}\text{Mn}_y]$ must be also equal to that in the representation of $\text{Co}_2\text{Mn}_{\beta}\text{Ge}_{0.38}$ with a given $\beta$ value. From this requirement, the values of $x$ and $y$ are determined. This model provides the total number of valence electrons per f.u. ($Z_t$) and the CoMn site ratio $x$ for a given $\beta$ ($< \beta_c$). The numbers of $Z_t$–24 are plotted in Fig. 5(a) and the $x$ values are plotted in Fig. 5(b), both as a function of $\beta$. This model provides respective formula units ranging from $\text{Co}_2[\text{Mn}_{0.377}\text{Co}_{0.623}][\text{Ge}_{0.498}\text{Mn}_{0.502}]$ (where $x$ is 0.62 and $Z_t = 31.75$) for $\text{Co}_2\text{Mn}_{1.67}\text{Ge}_{0.38}$ to $\text{Co}_2[\text{Mn}_{0.884}\text{Co}_{0.116}][\text{Ge}_{0.402}\text{Mn}_{0.598}]$ (where $x$ is 0.12 and $Z_t = 31.03$) for $\text{Co}_2\text{Mn}_{1.40}\text{Ge}_{0.38}$. Even at $\beta = 1.03$, for which the Co:Mn ratio is close to 2:1, the model provides a formula unit of $\text{Co}_2[\text{Mn}_{0.654}\text{Co}_{0.346}][\text{Ge}_{0.446}\text{Mn}_{0.554}]$ that features a still high $x$ value of 0.35 for $\text{Co}_2\text{Mn}_{1.03}\text{Ge}_{0.38}$. This is because the Ge ratio is strongly deficient for $\text{Co}_2\text{Mn}_{\beta}\text{Ge}_{0.38}$. For $\beta = \beta_c = 1.62$, the model predicts a formula unit of $\text{Co}_2\text{Mn}[\text{Ge}_{0.38}\text{Mn}_{0.62}]$, where $x$ becomes zero. Importantly, the ratio $x$ of the detrimental CoMn antisite at the Mn site considerably decreases with increasing $\beta$ from $x = 0.62$ for $\beta = 0.67$ to $x = 0.12$ for $\beta = 1.40$ with this formula unit model. Thus, this formula unit model derived by taking into account the formation energies of various defects at the thermal equilibrium state can reasonably explain the $\beta$ dependence of the TMR ratio observed for CMG-MTJs with $\text{Co}_2\text{Mn}_{\beta}\text{Ge}_{0.38}$ electrodes, i.e., the observed increase in the TMR ratio with increasing $\beta$ up to 1.40 is ascribed to a decrease in the CoMn antisite.
antisite ratio $x$, which causes a reduced density of minority-spin in-gap states around $E_F$. If we take into account that the Co$_2$Mn$_{\beta}$Ge$_{0.38}$ films were prepared by sputtering and subsequent annealing around 500°C, the films probably didn’t reach a thermal equilibrium state. Thus, the Co$_{\beta}$ antisite ratio $x = 0.12$ for $\beta = 1.40$ estimated by this formula unit model [Fig. 5(b)] should be regarded as the lower bound for $\beta = 1.40$ and the realistic $x$ value for $\beta = 1.40$ should be higher than this value.

We now examine the validity of this formula unit model by comparing the experimental $\beta$ dependence of $\mu_s$ at 10 K of Co$_2$Mn$_{\beta}$Ge$_{0.38}$ films with Slater-Pauling behavior of $\mu_s$ which is applicable for half-metallic Heusler alloys and predicts $\mu_s = Z_{\gamma}^{-24} [\mu_B/\text{f.u.}]$ for half-metallic Co$_2YZ$ alloys [7]. Although the experimental $\mu_s$ values were much smaller than the Slater Pauling values of $Z_{\gamma}^{-24}$ for $\beta < 1.0$, they approached the values given by $Z_{\gamma}^{-24}$ with increasing $\beta$ up to 1.40 as shown in Fig. 5(a), and the experimental $\mu_s = 6.63 \mu_B/\text{f.u.}$ for $\beta = 1.40$ is close to the Slater-Pauling value of 7.03 $\mu_B/\text{f.u.}$ for $\beta = 1.40$. These behaviors of the experimental $\mu_s$ are consistent with the formula unit model. First, the larger difference between the experimental $\mu_s$ and $Z_{\gamma}^{-24}$ for $\beta < 1.0$ is reasonable because the large Co$_{\beta}$Mn antisite ratio for $\beta < 1.0$ predicted by the formula unit model results in a certain density of minority-spin in-gap states around $E_F$ [35], leading to that the Slater-Pauling $\mu_s$ value is not a good approximation. However, the difference between the experimental $\mu_s$ and $Z_{\gamma}^{-24}$ deceases with increasing $\beta$ up to 1.40 because the Co$_{\beta}$Mn antisite ratio $x$ decreases with increasing $\beta$ beyond $\beta = 1.0$ according to the formula unit model. Because of the relatively small value of $x = 0.12$ for $\beta = 1.40$, the experimental $\mu_s$ of Co$_2$Mn$_{\beta}$Ge$_{0.38}$ with $\beta = 1.40$ was in relatively good agreement (within 6%) with the Slater-Pauling $\mu_s$ for $\beta = 1.40$. The difference between these two values, i.e., the smaller experimental $\mu_s$ than the Slater-Pauling $\mu_s$ for $\beta = 1.40$ is reasonable if we take into account that the Co$_2$Mn$_{\beta}$Ge$_{0.38}$ film with $\beta = 1.40$ still contains at least the 12% Co$_{\beta}$Mn antisite ratio at a Mn site. In summary, it was shown that the formula unit model based on the formation energies of various kinds of defects reasonably explains the observed dependence of $\mu_s$ on $\beta$. This finding supports our interpretation that the Mn composition
dependence of the TMR ratio observed universally for both CMS-MTJs and CMG-MTJs is due to suppressed minority-spin in-gap states around $E_F$ which are caused by the decreased Co$_{Mn}$ antisites in Mn-rich CMS and CMG electrodes.

5. Conclusion

We investigated the TMR characteristics of CMS/MgO/CMS MTJs and CMG/MgO/CMG MTJs fabricated with various Mn compositions $\alpha$ and $\beta$ in Co$_2$Mn$_{\alpha}$Si and Co$_2$Mn$_{\beta}$Ge$_{0.38}$ electrodes. We obtained higher TMR ratios for CMS/MgO/CMS MTJs with Mn-rich Co$_2$MnSi electrodes and for CMG/MgO/CMG MTJs with Mn-rich Co$_2$MnGe$_{0.38}$ electrodes and we observed high TMR ratios of 1135% at 4.2 K and 236% at RT for MTJs with Mn-rich Co$_2$Mn$_{\alpha}$Si electrodes with $\alpha = 1.29$. The observed lower TMR ratio for MTJs with Mn-deficient Co$_2$MnSi or Co$_2$MnGe$_{0.38}$ electrodes was explained by induced Co$_{Mn}$ antisites, which resulted in an increased density of minority-spin in-gap states around $E_F$ and thereby led to increased tunnel conductance for AP. On the other hand, the observed higher TMR ratio for MTJs with Mn-rich Co$_2$MnSi or Co$_2$MnGe$_{0.38}$ electrodes was explained by suppressed Co$_{Mn}$ antisites, which caused a reduced density of minority-spin in-gap states around $E_F$ and thereby led to decreased tunnel conductance for AP. It was shown that the picture of suppressed Co$_{Mn}$ antisites with increasing Mn composition in Co$_2$Mn$_{\alpha}$Si and Co$_2$Mn$_{\beta}$Ge$_{0.38}$ films is consistent with the formula unit composition models introduced by taking into account the theoretical formation energies of various kinds of defects induced in Co$_2$MnSi and Co$_2$MnGe. It was found that the formula unit model for Ge-deficient Co$_2$Mn$_{\beta}$Ge$_{0.38}$ films qualitatively explains the observed $\beta$ dependence of the saturation magnetization per formula unit at 10 K, supporting the validity of the formula unit models for Co$_2$Mn$_{\alpha}$Si and Co$_2$Mn$_{\beta}$Ge$_{0.38}$ films. In conclusion, our experimental findings suggest that the density of minority-spin in-gap states can be reduced by appropriately controlling defects in Co$_2$MnSi and Co$_2$MnGe electrodes. Nonstoichiometry is inevitable, to various degrees, in Co$_2$YZ thin films, which are
mostly prepared by magnetron sputtering. Our findings, however, suggest that detrimental Co$_{\text{Mn}}$ antisites can be suppressed by preparing Co$_2$MnZ films with a Mn-rich composition.

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Figure captions

Figure 1. (a) Cross-sectional HRTEM lattice image of an MTJ layer structure consisting of CMS (30 nm)/MgO barrier (2 nm)/CMS (5 nm)/Ru (0.8 nm)/Co$_{90}$Fe$_{10}$ (2 nm)/Ir$_2$Mn$_{78}$ (10 nm)/Ru cap (5 nm) with CMS films with a film composition of Co$_{2}$Mn$_{1.29}$Si$_{1.06}$ grown on a MgO-buffered MgO substrate, along the [1–10] direction of the CMS, where the lower CMS electrode was annealed in situ at 600 °C after it was deposited at RT while the MTJ layer structure was annealed in situ at 550 °C after deposition of the upper electrode. (b) Electron diffraction pattern for the lower CMS electrode (30 nm). (c) Electron diffraction pattern for the upper CMS electrode (5 nm). The electron-beam diameter was 2.5 nm.

Figure 2. (Colour online) (a) Typical TMR curves at 4.2 K and RT for a CMS/MgO (2.7 nm)/CMS MTJ with Mn-rich Co$_{2}$Mn$_{1.29}$Si$_{1.06}$ electrodes. The junction size was 10 µm × 10 µm. The bias voltage was 1 mV at both 4.2 K and RT. (b) TMR ratios at 4.2 K and RT for Co$_{2}$Mn$_{a}$Si$_{y}$/MgO/Co$_{2}$Mn$_{a}$Si$_{y}$ (y = 1.0 ± 0.06) MTJs as a function of $a$ ranging from 0.69 (Mn-deficient CMS) to 1.46 (Mn-rich CMS). The bias voltages were 1 mV at 4.2 K and 5 mV at RT.

Figure 3. (Colour online) $G_P/G_{AP}$ values at (a) 4.2 K and (b) RT that provided the TMR ratios (TMR ratio = $G_P/G_{AP}$ −1) shown in Fig. 3 for CMS-MTJs as a function of $a$. The right vertical axes show normalized $G_P/G_{AP}$ values, where $G_P/G_{AP}$ values were normalized by the respective mean values for $a$ = 1.29 at 4.2 K and RT.

Figure 4. (Colour online) (a) Typical TMR curves at 4.2 K and RT for a CMG/MgO (2.5 nm)/CMG MTJ with Mn-rich Co$_{2}$Mn$_{1.40}$Ge$_{0.38}$ electrodes. The junction size was 10 µm × 10 µm. (b) TMR ratios at 4.2 K and RT for Co$_{2}$Mn$_y$Ge$_{0.38}$/MgO/Co$_{2}$Mn$_y$Ge$_{0.38}$ MTJs as a function of $β$ ranging from 0.67 (Mn- and Ge-deficient CMG) to 1.40 (Mn-rich and Ge-deficient CMG). The bias voltages were 1 mV at 4.2 K and
5 mV at RT for both (a) and (b).

Fig. 5. (a) Experimentally obtained $\mu_s$ values (open circles) for $\text{Co}_2\text{Mn}_\beta\text{Ge}_{0.38}$ thin films at 10 K and $Z_t - 24$ (solid circles) as a function of $\beta$ ranging from $\beta = 0.67$ to 1.40, where $Z_t$ is the total valence electron number per formula unit provided by the formula unit model $\text{Co}_2[\text{Mn}_{1-x}\text{Co}_x][\text{Ge}_{1-y}\text{Mn}_y]$ for $\text{Co}_2\text{Mn}_\beta\text{Ge}_{0.38}$ with $\beta < 1.62$. (b) $\text{Co}_{\text{Mn}}$ antisite ratios $x$ provided by the formula unit model $\text{Co}_2[\text{Mn}_{1-x}\text{Co}_x][\text{Ge}_{1-y}\text{Mn}_y]$ for $\text{Co}_2\text{Mn}_\beta\text{Ge}_{0.38}$ with $\beta < 1.62$ as a function of $\beta$ ranging from $\beta = 0.67$ to 1.40.
Figure 1
Figure 2

(a) $\text{Co}_2\text{Mn}_{1.29}\text{Si}_{1.06}$

- $t_{\text{MgO}} = 2.7$ nm
- $10 \times 10 \mu\text{m}^2$
- $V = 1 \text{ mV}$

RA (M$\Omega$µm$^2$)

- 4.2 K
  - TMR: 1135%
- RT
  - TMR: 236%

(b) $\text{Co}_2\text{Mn}_\gamma\text{Si}_\gamma (\gamma = 1.0 \pm 0.06)$

- 4.2 K
- RT

TMR ratio (%)

Mn composition $\alpha$
Figure 3
Figure 4
Figure 5

(a) $\text{Co}_2\text{Mn}_\beta\text{Ge}_{0.38}$

(b) $\text{Co}_2[\text{Mn}_{1-x}\text{Co}_x][\text{Ge}_{1-z}\text{Mn}_z]$