Influence of film composition in Co_2MnSi electrodes on tunnel magnetoresistance characteristics of Co_2MnSi/MgO/Co_2MnSi magnetic tunnel junctions

Takayuki Ishikawa (石川貴之), Hong-xi Liu (刘宏喜), Tomoyuki Taira (平智幸), Ken-ichi Matsuda (松田健一), Tetsuya Uemura (植村哲也), and Masafumi Yamamoto (山本眞史)[a)]
Division of Electronics for Informatics, Hokkaido University, Sapporo 060-0814, Japan

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Fully epitaxial Co_2MnSi (CMS)/MgO/CMS magnetic tunnel junctions (MTJs) with various values of Mn composition α in $Co_2Mn_\alpha Si$ electrodes were fabricated and the influence of α on the tunnel magnetoresistance (TMR) characteristics of these MTJs was investigated. MTJs with Mn-rich CMS electrodes showed TMR ratios, up to 1135% at 4.2 K and 236% at room temperature for $\alpha=1.29$, exceeding those of MTJs with CMS electrodes having an almost stoichiometric composition. A possible origin of the higher TMR ratios for α beyond 1.0 is a decreased density of gap states existing around the Fermi level in the half-metal gap caused by the suppression of Co_{Mn} antisites, where a Mn site is replaced by a Co atom, for Mn-rich CMS electrodes. © *2009 American Institute of Physics*. [doi:10.1063/1.3272926]

A highly efficient spin-polarized electron source is a key element for spintronic devices. Half-metallic ferromagnets (HMFs) are the most suitable materials for spin-polarized electron sources because they provide complete spin polarization at the Fermi level (E_F). Among HMFs, Co-based Heusler alloys are especially promising due to their high Curie temperatures, which are well above room temperature (RT). Recently, extensive studies have been conducted to apply these Co-based Heusler alloy thin films to spintronic devices.[1–8]

One Co-based Heusler alloy in particular, Co_2MnSi (CMS), has attracted interest[2,4,5,7] because of its theoretically predicted half-metallic nature with a relatively large energy gap of 0.4–0.8 eV for its minority-spin direction.[9,10] We recently developed fully epitaxial magnetic tunnel junctions (MTJs) with CMS thin films as both lower and upper electrodes and with a MgO tunnel barrier (CMS/MgO/CMS MTJs, hereafter CMS-MTJs).[11–13] Epitaxial layer structures with a CMS electrode and a MgO barrier are beneficial for creating highly spin-polarized current due to the potentially half-metallic nature of CMS electrodes and the coherent tunneling through the single-crystalline MgO barrier.[14–16] We have demonstrated relatively high tunnel magnetoresistance (TMR) ratios around 180% at RT and 700% at 4.2 K for CMS-MTJs.[11,13] Furthermore, we found strong evidence for the existence of interface states in the interfacial region of CMS electrodes facing a MgO tunnel barrier, as well as evidence of residual states in the bulk region of upper CMS electrodes, in both cases in the half-metal gap for minority spins around E_F from analysis of the dI/dV and d^2I/dV^2 characteristics of CMS-MTJs.[12,13]

The film composition of CMS electrodes used in our previous study[11–13] was $Co_2Mn_{0.91}Si_{0.93}$, a slightly Co-rich composition with respect to the stoichiometry (or a slightly Mn- and Si-deficient composition). Film composition deviation from the stoichiometry inevitably induces some kinds of structural defect. The influence of defects in CMS on the half-metallic electronic structure has been investigated theoretically.[17–20] It has been pointed out that the half-metallicity of CMS is lost through the formation of Co_{Mn} antisites, where a Mn site is replaced by a Co atom, because of the appearance of states in the half-metal gap (gap states).[17] Therefore, it is important to investigate experimentally the effect of structural defects possibly associated with nonstoichiometry in Co-based Heusler-alloy electrodes on their half-metallicity. Our purpose in the current study has been to clarify the influence of the CMS film composition on the TMR characteristics of fully epitaxial CMS-MTJs and to understand the origin of the observed composition dependence.

The fabricated MTJ layer structure was as follows: (from the substrate side) MgO buffer (10 nm)/CMS lower electrode (30 nm)/MgO barrier (2.0–3.0 nm)/CMS upper electrode (3–5 nm)/Ru (0.8 nm)/$Co_{90}Fe_{10}$ (2 nm)/IrMn (10 nm)/Ru cap (5 nm), grown on a MgO (001) single-crystal substrate. Each layer was successively deposited in an ultrahigh vacuum chamber (base pressure of $\sim 6\times10^{-8}$ Pa). The fabrication procedure for the MTJ layer structures, except for the CMS electrodes, was the same as in the case of CMS-MTJs previously reported.[11–13] In this study, the CMS electrodes were deposited by co-sputtering from a nearly stoichiometric CMS target and a Mn target to systematically vary the Mn composition in CMS. The film compositions of the CMS electrodes were determined to be $Co_2Mn_\alpha Si_\gamma$ ($\gamma=1.0\pm0.06$) by inductively coupled plasma optical emission spectroscopy with an accuracy of 2% for Co or Mn and 5% for Si. Hereafter, we denote $Co_2Mn_\alpha Si_\gamma$ ($\gamma=1.0\pm0.06$) by $Co_2Mn_\alpha Si$ using the mean value of 1.0 for Si composition γ. Note that the composition ratio of Co to Si was close to 2:1. We prepared CMS electrodes with values of Mn composition α ranging from 0.69 (Mn-deficient CMS) to 1.46 (Mn-rich CMS), including $\alpha=0.99$ (almost stoichiometric CMS). The layer structure was annealed *in situ* at 600 °C just after deposition of the

[a)]Author to whom correspondence should be addressed. Electronic mail: yamamoto@nano.ist.hokudai.ac.jp.

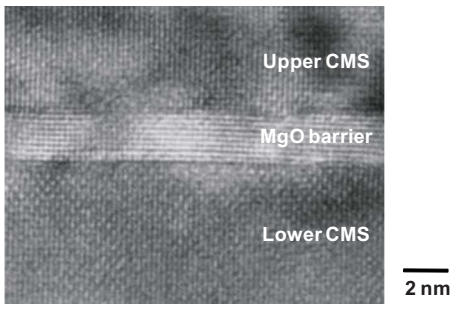

FIG. 1. (Color online) Cross-sectional high-resolution transmission electron microscope lattice image of a CMS/MgO (2.0 nm)/CMS MTJ layer structure with a film composition of $Co_2Mn_{1.29}Si_{1.06}$, along the [1$\bar{1}$0] direction of the CMS layers.

lower CMS electrode and at 550 °C just after deposition of the upper CMS electrode. We fabricated MTJs with the layer structure described above using photolithography and Ar ion milling. The fabricated junction size was 10×10 μm. After the fabrication, MTJs were annealed *ex situ* at 400 °C in a vacuum of 5×10^{-2} Pa under a magnetic field of 5 kOe to enable exchange biasing on the upper CMS electrode. We measured TMR characteristics of the fabricated MTJs using a dc four-probe method.

Figure 1 shows a cross-sectional high-resolution transmission electron microscope lattice image of a MTJ trilayer structure consisting of CMS/MgO/CMS with a film composition of $Co_2Mn_{1.29}Si_{1.06}$ (α=1.29), along the [1$\bar{1}$0] direction of the CMS layers. This image clearly shows that all the layers of the MTJ trilayer were grown epitaxially and were single crystalline. We also confirmed that extremely smooth and abrupt interfaces were formed. Furthermore, microbeam electron diffraction patterns with a beam diameter of 2.5 nm for CMS electrodes showed 111 spots, indicating the ordered-$L2_1$ structure for both the lower and upper CMS electrodes. It should also be noted that unknown spots were superimposed onto the $L2_1$ spots in some regions of the lower and upper CMS electrodes, indicating the coexistence of unidentified materials or structures in addition to the $L2_1$ structure.

Figure 2 shows the α dependence of the TMR ratios at 4.2 K and RT for fully epitaxial CMS-MTJs with $Co_2Mn_\alpha Si$. The error bars for the TMR ratios in the figure indicate the

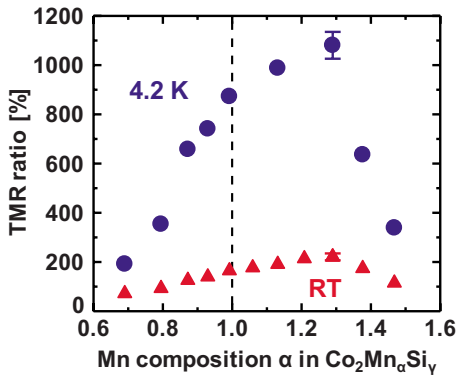

FIG. 2. (Color online) TMR ratios at 4.2 K and RT for $Co_2Mn_\alpha Si_\gamma$/MgO/$Co_2Mn_\alpha Si_\gamma$ ($\gamma=1.0\pm0.06$) MTJs as a function of Mn composition α ranging from 0.69 (Mn-deficient CMS) to 1.46 (Mn-rich CMS). The dotted line corresponds to an almost stoichiometric composition of CMS electrodes. The bias voltage was 1 mV at 4.2 K and 5 mV at RT.

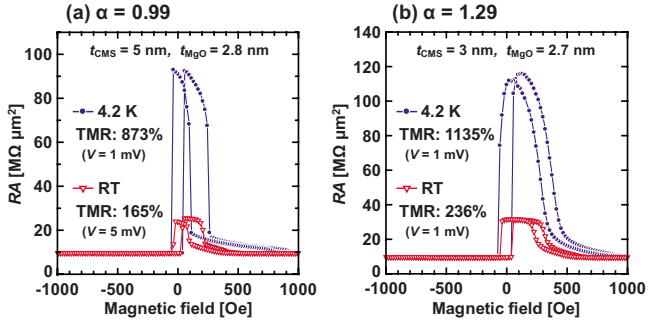

FIG. 3. (Color online) Typical TMR curves at 4.2 K and RT for $Co_2Mn_\alpha Si_\gamma$/MgO/$Co_2Mn_\alpha Si_\gamma$ ($\gamma=1.0\pm0.06$) MTJs with (a) almost stoichiometric CMS films having α=0.99 and (b) Mn-rich CMS films having α=1.29. t_{CMS} and t_{MgO} indicate the thickness of the upper CMS electrode and the MgO barrier, respectively.

range of observed TMR ratios for MTJs with different upper CMS electrode thicknesses of 3 and 5 nm. The TMR ratios at both 4.2 K and RT showed strong dependence on α in $Co_2Mn_\alpha Si$ electrodes. As shown in Fig. 2, the TMR ratios at 4.2 K and RT increased with increasing α for the range from 0.69 to 1.29 and then decreased with increasing α above 1.29. Most importantly, the TMR ratios were increasing even in the α range beyond 1.0, where α of 1.0 corresponds to an almost stoichiometric film composition of CMS, and the highest TMR ratios of 1135% at 4.2 K and 236% at RT were obtained for α of 1.29. Figure 3 shows typical TMR curves at 4.2 K and RT for fully epitaxial CMS-MTJs with almost stoichiometric CMS electrodes having α=0.99 [Fig. 3(a)] and with Mn-rich CMS electrodes having α=1.29 [Fig. 3(b)]. The MTJs with α of 1.29 showed TMR ratios of 1135% at 4.2 K and 236% at RT, exceeding those of 873% at 4.2 K and 165% at RT for MTJs with α of 0.99. Thus, higher TMR ratios were experimentally demonstrated at both 4.2 K and RT for fully epitaxial CMS-MTJs with off-stoichiometric, Mn-rich CMS electrodes with α up to 1.29 than for MTJs with almost stoichiometric CMS electrodes.

We will now discuss the possible origin of the observed α dependence of the TMR ratios of fully epitaxial CMS-MTJs with $Co_2Mn_\alpha Si$ electrodes. We consider the influence of possible defects in CMS electrodes with various values of α on the half-metallic electronic structure because nonstoichiometry induces some kinds of structural defect. As mentioned, a crucial effect of Co_{Mn} antisites on the half-metal gap structure of CMS has been found theoretically.[17,20] For example, Picozzi *et al.*[17] theoretically predicted that Co_{Mn} antisites induce gap states around E_F, resulting in a drastic reduction in the spin polarization of CMS. On the other hand, it is theoretically predicted that other structural defects, such as vacancies, Mn antisites, or Si antisites, do not critically affect the half-metal gap structure of CMS.[17–20] For Mn-deficient CMS ($\alpha<1$), possible induced defects include Co_{Mn} antisites, Si_{Mn} antisites, and Mn-site vacancies due to the deficiency in Mn atoms. Among these defects, Si_{Mn} antisites are the most likely to be induced because they have the lowest formation energy.[17,20] However, if only Si_{Mn} antisites occurred in the prepared CMS thin films having a Co:Si ratio of almost 2:1, Si-site vacancies would be created. Since the formation energy of a Si-site vacancy is much greater than that of a Co_{Mn} antisite,[17,20] Si_{Mn} antisites along with Co_{Mn} antisites were probably induced, rather than only Si_{Mn} antisites induced, for the Mn-deficient CMS. The formation of

Co_{Mn} antisites would lead to the appearance of gap states around E_F of the CMS electrodes, resulting in the deterioration of half-metallicity according to the theory.[17]

For Mn-rich CMS ($\alpha > 1$), on the other hand, Mn_{Co} antisites along with Mn_{Si} antisites would more likely be induced according to the theoretically calculated formation energies of possible defects for Mn-rich CMS. However, these defects would not critically affect half-metallicity. Importantly, the creation of Co_{Mn} antisites in Mn-rich CMS electrodes would be suppressed because a Mn_{Co} antisite has a much lower energy than a Co_{Mn} antisite. The suppression of Co_{Mn} antisite formation would lead to a decreased density of gap states around E_F for Mn-rich CMS. To put it briefly, Co_{Mn} antisites which are harmful to the half-metallicity of CMS would be suppressed with an increasing Mn composition, resulting in a decreased density of gap states around E_F of CMS electrodes.

We will now discuss the influence of gap states on the spin-dependent tunneling characteristics of CMS-MTJs. To do this, we will consider the tunneling processes for the antiparallel (AP) magnetization configuration for CMS-MTJs. First, we consider tunneling processes for AP at low temperatures and low bias voltages. Under these conditions, we can ignore the spin-flip scattering via magnons excited thermally or by hot electrons. Since the characteristic excitation energy of magnons in CMS-MTJs is about 4 mV,[13] our measurements of the TMR characteristics at 4.2 K and $V = 1$ mV were consistent with these conditions. The tunneling paths for AP are then restricted to two as follows: from the majority-spin (M-spin) band to minority-spin (m-spin) gap states or from m-spin gap states to the M-spin band. Therefore, a decrease in the density of gap states around E_F in CMS electrodes caused by the suppression of Co_{Mn} antisites leads to less tunneling conductance for AP, resulting in higher TMR ratios. Thus, the observed Mn composition dependence at 4.2 K is well explained. At RT, we must take into consideration tunneling processes that associate spin-flip scattering via thermally excited magnons. However, the tunneling processes involve m-spin gap states in the bulk region or m-spin interface states. Thus, the tunneling conductance for AP at RT would also decrease with a decrease in the gap states around E_F.

The observed further increase in the TMR ratios with increasing α beyond 1.0 suggests that Co_{Mn} antisites occur even for nearly stoichiometric CMS electrodes. This would probably be because CMS films deposited at RT and successively annealed *in situ* at 550–600 °C are films which do not reach a thermal equilibrium state. Thus, the suppression of Co_{Mn} antisites is a key to realizing high spin polarization for potentially half-metallic CMS films. Our experimental findings indicate that gap states existing around E_F that originate from Co_{Mn} antisites can be suppressed by using Mn-rich CMS films.

In summary, we investigated the TMR characteristics of fully epitaxial $Co_2Mn_\alpha Si/MgO/Co_2Mn_\alpha Si$ MTJs as a function of Mn composition α for CMS electrodes. MTJs with Mn-rich CMS electrodes exhibited TMR ratios of up to 1135% at 4.2 K and 236% at RT for $\alpha = 1.29$, higher than those of MTJs with almost stoichiometric CMS electrodes. The observed higher TMR ratios for MTJs with Mn-rich CMS electrodes can be explained by the suppression of Co_{Mn} antisites, which would cause a decreased density of gap states around E_F. In conclusion, our experimental findings suggest that the density of gap states existing around E_F can be reduced by appropriate control of defects through the film composition in potentially half-metallic Co-based Heusler alloys.

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