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Preparation of Co_2FeSn Heusler alloy films and magnetoresistance of Fe/MgO/Co_2FeSn magnetic tunnel junctions

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To obtain magnetic tunnel junctions (MTJs) composed of non-equilibrium alloy, Co_2FeSn films were prepared by atomically controlled alternate deposition at various substrate temperatures. X-ray diffraction patterns and Mössbauer spectra clarify that Co_2FeSn films in the Heusler alloy phase can be realized by growing at a substrate temperature of 250 °C or below. Phase separation into cubic CoSn, hexagonal CoSn and cubic CoFe phases occurs in films grown at substrate temperatures 300 °C or greater. Fe/MgO/Co_2FeSn MTJs were prepared with the Co_2FeSn layer grown at various substrate temperatures. The MTJs with the ferromagnetic Co_2FeSn layer grown at a substrate temperature of 250 °C showed tunnel magnetoresistance ratios of 72.2% and 43.5% at 2 K and 300 K, respectively. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3688324]

I. INTRODUCTION

Tunnel magnetoresistance (TMR) in magnetic tunnel junctions (MTJs) is of interest for use in spin electronic devices, e.g. read heads in hard disk drives and magnetic random access memory, etc.[1,2] One promising way to achieve high TMR ratio is to use highly spin-polarized materials as ferromagnetic electrodes of MTJs. Heusler alloys, which have the composition X_2YZ (X and Y: transition metals; Z: group III, IV or V element), are predicted to be highly spin-polarized materials[3,4] and have been used for MTJ electrodes.[5–7] Recently, TMR ratios of over 300% at room temperature were reported for MTJs with $Co_2FeAl_{0.5}Si_{0.5}$/MgO/$Co_2FeAl_{0.5}Si_{0.5}$ and Co_2FeAl/MgO/CoFe structures.[8,9] Large TMR effects may also be obtained in MTJs using new ferromagnetic alloys which have not yet been tested. Some Heusler-type alloys which cannot be fabricated in thermal equilibrium because of phase separation may show high spin-polarization. On the other hand, it is expected that thin films of non-equilibrium alloy can be fabricated using atomically controlled alternate deposition.[10] We have already demonstrated that Heusler alloy films prepared by this technique have more uniform magnetic environments than bulk alloys prepared by arc-melting.[11]

In this paper, we report fabrication of Co_2FeSn Heusler alloy films with an $L2_1$ ordered structure using atomically controlled alternate deposition. The physical properties of Co_2FeSn have not been experimentally studied so far, because it is difficult to fabricate Co_2FeSn alloy. Zhang *et al.* demonstrated that bulk $Co_2Mn_{1-x}Fe_xSn$ Heusler alloys with $x > 0.5$ prepared by arc-melting contain impurities such as Co_3Sn_2 and CoFe and tend to decompose when x increases.[12] Judging from these results, Co_2FeSn Heusler alloy cannot be fabricated by arc melting method because of phase separation. On the other hand, since Co_2FeSn contains ^{119}Sn and ^{57}Fe nuclei, local magnetism can be investigated using Mössbauer spectroscopy. Therefore, MTJs with a Co_2FeSn layer allows us to clarify the relation between local magnetism and TMR effects. X-ray diffraction patterns and Mössbauer spectra indicate that Co_2FeSn films in the Heusler alloy phase can be fabricated at substrate temperatures of 250 °C or below and that phase separation into cubic CoSn, hexagonal CoSn and cubic CoFe phases occurs in films grown at higher substrate temperatures. MTJs were also prepared with Co_2FeSn grown at various substrate temperatures. TMR measurements for Fe/MgO/Co_2FeSn MTJs, where the Co_2FeSn layer was grown at the substrate temperature of 250 °C, show the TMR ratios of 72.2% and 43.5% at 2 K and 300 K, respectively.

II. EXPERIMENTAL

Co_2FeSn films were prepared at various substrate temperatures, T_s on a Cr buffer layer grown on MgO (001) substrates using an electron beam deposition system. Co_2FeSn films 39 nm thick were grown by depositing one atomic layer of Co, and half an atomic layer of Fe and Sn alternately in a controlled manner. The compositions of the Co_2FeSn films were examined by an electron probe micro analyzer. The crystal structures were characterized by reflection high energy electron diffraction and X-ray diffraction (XRD) with Cu $K\alpha$ radiation. To obtain information on local magnetism and structures, ^{119}Sn and ^{57}Fe Mössbauer spectra were measured by means of conversion electron Mössbauer spectroscopy. The spectra were fitted with a magnetically split sextet with a distribution of magnetic hyperfine fields. MgO (5 nm)/Cr (30 nm)/Fe (20 nm)/MgO (2.4 nm)/Co_2FeSn (19.6 nm)/Co (25 nm)/Cr (1 nm) layered structures for MTJs were prepared on MgO (001) substrates. The bottom

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ferromagnetic Fe layer was deposited at room temperature and annealed at 350 °C to improve the crystallographic quality. After deposition of the MgO barrier layer at room temperature, the top ferromagnetic Co_2FeSn layer was prepared by depositing one atomic layer of Co, half an atomic layer of Fe and Sn alternately at substrate temperatures of 200, 250, 300 and 400 °C. The interface atoms at the Co_2FeSn layer on the MgO barrier were designed to be Co. The Co (25 nm) layer was deposited on the Co_2FeSn layer to reinforce an antiparallel configuration of magnetization between the lower Fe and upper Co_2FeSn layers. The layered structures were fabricated into MTJs comprising ellipse-shaped pillars with an in-plane size of several μm using photolithography and Ar ion etching. Magnetoresistance measurements were carried out using a standard dc four-probe method.

III. RESULTS AND DISCUSSION

Figure 1(a) shows θ-2θ XRD patterns of the Co_2FeSn films. The peaks at about 31° and 63° in each XRD pattern can be attributed to $L2_1$ Co_2FeSn (002) and Co_2FeSn (004) reflections. These peaks may also be from CoSn, CoFe and/or FeSn with B2 or A2 structure. The dependence of lattice parameters perpendicular to the plane of the films estimated from the position of the peaks around $2\theta = 31°$ on the substrate temperature is shown in Fig. 1(b). The lattice parameter varies from 5.90 Å to 5.81 Å with increasing substrate temperature. As clarified from the Mössbauer spectra discussed in the following paragraphs, Co_2FeSn in the Heusler phase

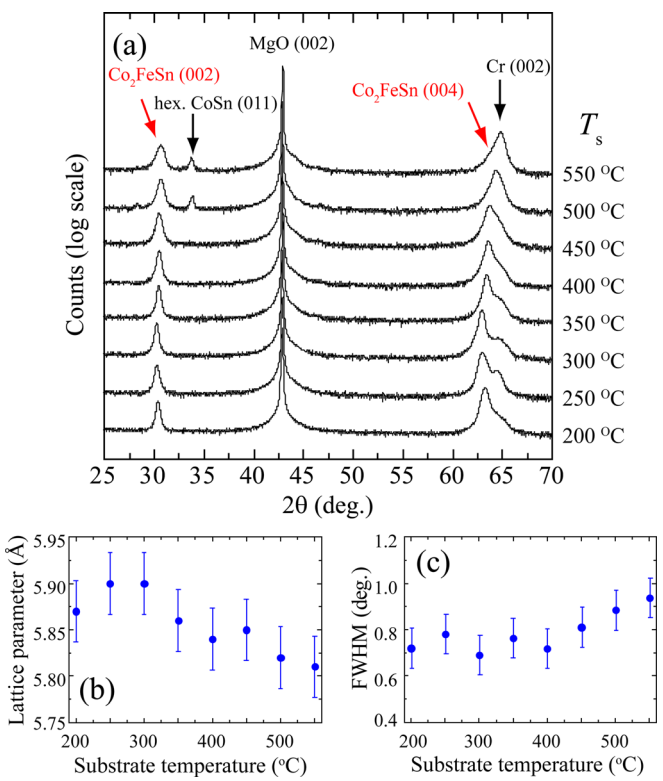

FIG. 1. (Color online) (a) X-ray diffraction patterns for Co_2FeSn films grown at various substrate temperatures, T_s. (b) Dependence of lattice parameter perpendicular to the plane of the prepared films on substrate temperature. (c) FWHM of rocking curve of the peaks at $2\theta = 31°$ as a function of substrate temperature.

becomes dominant when the growth temperature is under 250 °C. A peak from hexagonal CoSn (110) is observed at $2\theta = 33°$ for the films grown at $T_s \geq 500$ °C. The full widths at half maxima (FWHM) of ω-scan XRD of the peaks around $2\theta = 31°$ as a function of the substrate temperature are shown in Fig. 1(c). The degree of (001) epitaxy decreases a little for the Co_2FeSn films grown at $T_s \geq 450$ °C. This may be because an equilibrium hexagonal CoSn phase separated out in the films grown at $T_s \geq 450$ °C. From the intensity ratio of the Co_2FeSn (111) and (002) diffraction peaks in polar plots, the degree of $L2_1$ order of the Co_2FeSn films grown at around 250 °C is estimated to be about 16%.

Figure 2(a) shows ^{119}Sn conversion electron Mössbauer spectra, 2(b) shows distributions of hyperfine field at the ^{119}Sn sites, 2(c) ^{57}Fe conversion electron Mössbauer spectra and Fig. 2(d) shows distributions of hyperfine field at the ^{57}Fe sites. A broad peak is observed at fields higher than 10 T in the ^{119}Sn hyperfine-field distributions of the films deposited at $T_s \leq 400$ °C. Another peak is observed at around 2 T in the ^{119}Sn hyperfine-field distributions of the films grown at $T_s \geq 300$ °C. This peak becomes sharper with increasing substrate temperature. On the other hand, a single peak at around 35 T can be seen in the ^{57}Fe hyperfine-field distribution for all the Co_2FeSn films. The width of this peak becomes sharper with increasing substrate temperature.

The significant difference in ^{119}Sn hyperfine-field distributions as a function of growth temperature can be explained by phase separation in the Co_2FeSn films grown at high substrate temperatures. Judging from the ^{119}Sn Mössbauer spectra of bulk $Co_2Mn_{1-x}Fe_xSn$ Heusler alloys prepared by arc-melting,[12] the peak at around or above 10 T in Fig. 2(b) can be attributed to the $L2_1$-ordered Co_2FeSn Heusler alloy. The broad distribution in hyperfine field implies that the degree of $L2_1$ order is not particularly high, which is consistent with the estimation from the XRD patterns. For comparison with the Co_2FeSn films, non-equilibrium films of B2 CoSn alloy were prepared by atomically controlled alternate deposition at a substrate temperature of 100 °C. The ^{119}Sn Mössbauer spectrum and hyperfine-field distribution at the ^{119}Sn sites of the B2 CoSn film are shown in Fig. 3. There is a peak at around 2 T in the hyperfine-field distribution. The spectrum is similar to the spectra of the Co_2FeSn films grown at high substrate temperatures. Therefore, it can be concluded that phase separation into CoSn and CoFe occurs in the films grown at higher substrate temperatures. There is slight asymmetry in the profiles of ^{119}Sn Mössbauer spectra for the Co_2FeSn films grown at higher substrate temperatures. This is because not only B2 CoSn but hexagonal CoSn exists in these films.[13] We note that peaks from B2 FeSn[14] are not observed in the spectra.

On the other hand, the ^{57}Fe Mössbauer spectra for all the films show no significant differences. The peak at around 35 T in the hyperfine-field distribution at the ^{57}Fe sites in the films grown at low substrate temperatures is attributed to an ordered Co_2FeSn Heusler alloy. Because the Mössbauer spectrum of cubic CoFe also has a peak at around 35 T,[15] there is no significant difference in the ^{57}Fe Mössbauer spectra when phase separation occurs. Considering all the Mössbauer spectroscopic results, it is evident that Co_2FeSn films

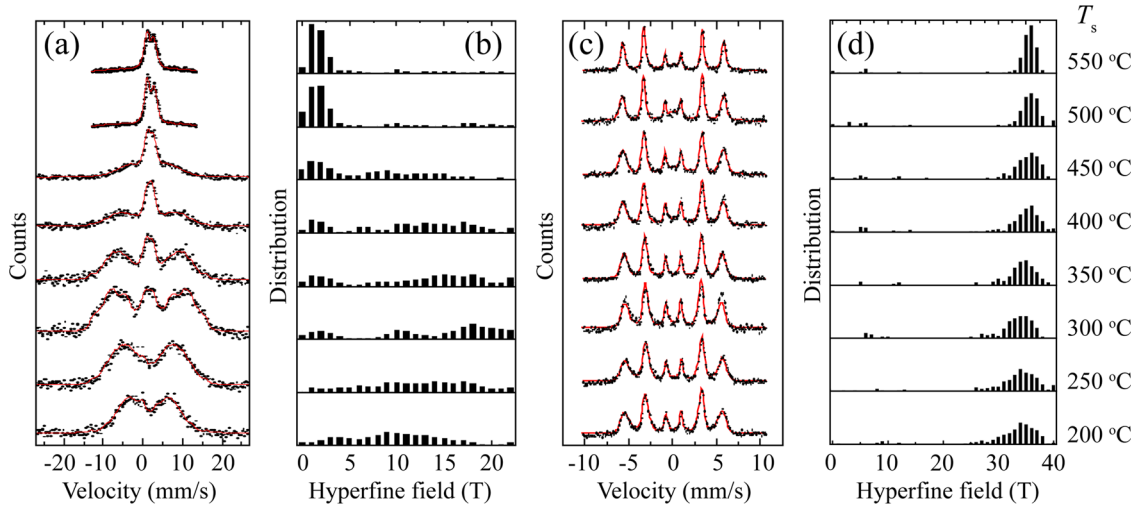

FIG. 2. (Color online) (a) ^{119}Sn conversion electron Mössbauer spectra and (b) hyperfine-field distributions at the ^{119}Sn sites of the Co_2FeSn films. (c) ^{57}Fe conversion electron Mössbauer spectra and (d) hyperfine-field distributions at the ^{57}Fe sites of the Co_2FeSn films.

in the Heusler alloy phase are obtained when the films are grown at a substrate temperature of 250 °C. Phase separation into hexagonal CoSn, cubic CoSn and cubic CoFe phases occurs in the films grown at higher substrate temperatures.

Since the conditions for making Co_2FeSn films in the Heusler alloy phase were determined, MTJs using the Co_2FeSn alloy as a ferromagnetic layer were prepared to measure their TMR. Figure 4 shows the θ-2θ XRD patterns of the MgO/Cr/Fe/MgO/Co_2FeSn/Co/Cr layered structures. Co_2FeSn (002), Co_2FeSn (004) and Fe (002) peaks are observed, indicating that the Co_2FeSn and Fe electrodes have been grown epitaxially with (001) orientation on the MgO (001) substrate.

Figure 5(a) shows magnetoresistance curves of the Fe/MgO/Co_2FeSn MTJs at a bias voltage of 1 mV at 300 K. TMR ratios of 25.5%, 43.5%, 27.0% and 11.0% are observed for MTJs with the Co_2FeSn layer grown at substrate temperatures of 200, 250, 300 and 400 °C, respectively. The resistance area product values of the MTJs are about 10^5 $\Omega\mu m^2$.

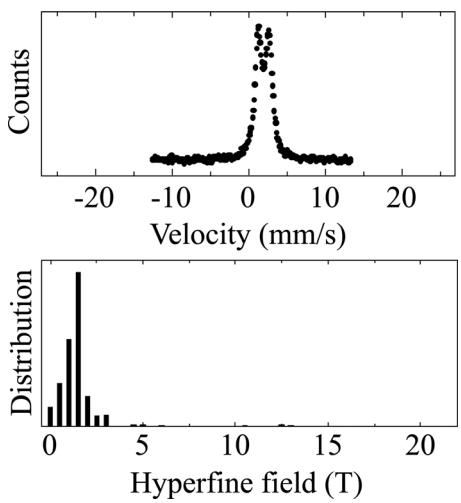

FIG. 3. ^{119}Sn conversion electron Mössbauer spectrum and hyperfine-field distribution at the ^{119}Sn sites of a B2 CoSn film fabricated by atomically controlled alternate deposition at a substrate temperature of 100 °C.

The largest TMR ratio is realized for the sample grown at 250 °C, where the Co_2FeSn layer has no second phases such as cubic CoSn and cubic CoFe. The TMR ratios of the MTJs with the Co_2FeSn layer grown at higher substrate temperatures become smaller. This may be because of phase separation into hexagonal CoSn, cubic CoSn and cubic CoFe phases and disorder of the crystal structure in the Co_2FeSn layers. It has been reported that TMR effect is suppressed by the existence of disordered phases in ferromagnetic layers of MTJs with Heusler alloys.[16,17] We have shown the relation between phases in the ferromagnetic layers of the MTJs and the suppression of TMR effect using Mössbauer spectroscopy. These results indicate that Mössbauer spectroscopy is applicable to optimize MTJs fabrication conditions.

The magnetoresistance at a bias voltage of 1 mV at 2 K for the MTJ with Co_2FeSn layer grown at a substrate temperature of 250 °C is shown in Fig. 5(b). The MTJ exhibits a TMR ratio of 72.2% at 2 K. The spin polarization of the Co_2FeSn layer estimated from the TMR ratio at 2 K is 0.55, assuming the spin polarization of Fe to be 0.48. Note that the band calculation of Co_2FeSn (Ref. 18) shows that Co_2FeSn has negative spin polarization at the Fermi level, whereas the spin polarization values observed experimentally are positive.

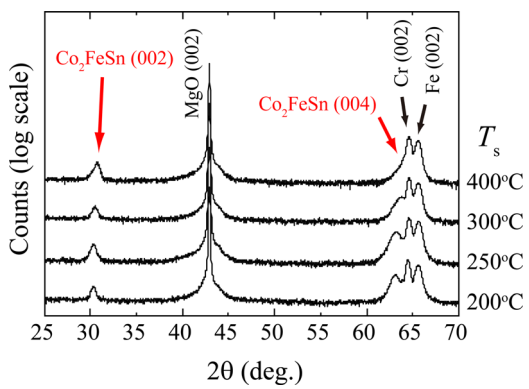

FIG. 4. (Color online) X-ray diffraction patterns for layered Fe/MgO/Co_2FeSn structures, where the Co_2FeSn layer was grown at various substrate temperatures T_s.

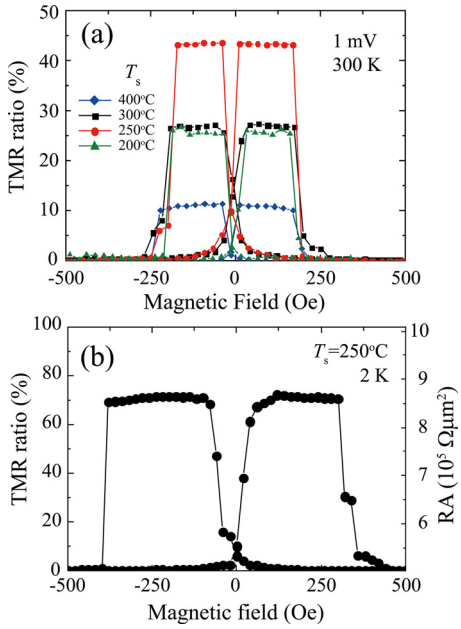

FIG. 5. (Color online)(a) Magnetoresistance curves at 300 K for Fe/MgO/Co_2FeSn MTJs, where the Co_2FeSn layer was grown at various substrate temperatures T_s. (b) Magnetoresistance curve at 2 K for an Fe/MgO/Co_2FeSn MTJ with the Co_2FeSn layer grown at 250 °C.

This difference in the sign of spin polarization between theoretical and experimental results can be attributed to the difference between the energy band of bulk Co_2FeSn and that at the Co_2FeSn interface with the MgO barrier. Some previous researches[19,20] demonstrated that the spin polarization at the ferromagnetic-electrode interfaces with the barrier rather than that of the bulk ferromagnetic electrodes dominates the spin polarization of tunneling electrons. In this way, we have succeeded in obtaining the TMR effect for MTJs with a non-equilibrium ferromagnetic layer.

IV. CONCLUSION

In this study, we fabricated Co_2FeSn films using atomically controlled alternate deposition at various substrate temperatures. X-ray diffraction patterns and Mössbauer spectra clarify that Co_2FeSn films in the Heusler alloy phase can be fabricated at substrate temperatures of 250 °C or below, and that B2 or hexagonal CoSn and B2 or A2 CoFe phases separate out at substrate temperatures of 300 °C or more. The MTJs with Fe/MgO/Co_2FeSn structure, where the Co_2FeSn layer was grown at a substrate temperature of 250 °C show TMR ratios of 72.2% and 43.5% at 2 K and 300 K, respectively. We have demonstrated that non-equilibrium material can be used as ferromagnetic layers for MTJs.

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