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Enhancement of $L2_1$ order and spin-polarization of Heusler alloy Co_2MnSi thin film by Ag alloying

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ABSTRACT

We report enhancement of $L2_1$ order and the resultant improvement of spin polarization of Co_2MnSi (CMS) Heusler alloy thin films by a small amount of Ag alloying ($x_{Ag} \leqslant 4.5$ atomic (at.) %). The degree of $L2_1$ order in CMS increases with x_{Ag}(=2.7 at.% and 4.5 at.%), which shows a positive correlation with the magnitude of negative anisotropic magnetoresistance ratio, suggesting the enhancement of spin polarization. Since the benefit of Ag-doping was confirmed even at low annealing temperature around 350 °C, this method could be useful for processing spintronic devices using Heusler alloys at relatively low annealing or substrate temperature.

Ferromagnetic (FM) materials with high Curie temperature and large spin polarization are expected to work as spin polarized electric current and spin current sources in various spintronic devices [1]. The theoretical predictions of 100% spin polarization in FM and ferrimagnetic Heusler alloys have stimulated research on half-metallic materials as well as the development of devices using them. Among various FM Heusler alloys, Cobalt-based Co_2YZ (Y = Mn, Fe, and Z = Si, Ge, Al, etc.) Heusler alloys [2] are the most promising material because of their high Curie temperatures well above room temperature (RT). High magnetoresistance (MR) ratios and large spin accumulation signals reflecting the half-metallicity of Co-based Heusler alloys have been clearly demonstrated in current perpendicular to plane giant magnetoresistance (CPP-GMR) [3–9], tunneling magnetoresistance (TMR) [10–13] and non-local spin-valve (NLSV) devices [14–16] using Co_2MnSi (CMS), $Co_2Fe(Al_{0.5}Si_{0.5})$, $Co_2(Fe_{0.4}Mn_{0.6})Si$ (CFMS), $Co_2Fe(Ga_{0.5}Ge_{0.5})$ (CFGG), and Co_2FeSi as FM electrodes. Especially in the CPP-GMR devices using CFMS and CFGG, MR ratios over 50% at room temperature were reported, which are one order of magnitude higher than those using conventional FMs such as CoFe or NiFe. In addition, recent careful investigation of the spin-polarization in CMS thin film using photoemission spectroscopy revealed exceptionally large spin-polarization of about 93% at RT [17]. Therefore, the promise of Co_2MnZ and Co_2FeZ Heusler alloys for developing practical spintronic devices was clearly recognized owing to recent extensive studies on those alloys.

Although the $L2_1$ structure is the most stable phase, full-Heusler compounds X_2YZ often contain B2 and A2 disorder, in which (Y, Z) and (X, Y, Z) are substituted by each other. The half-metallic band gap sensitively changes depending on the degree of chemical disorder [18]; hence, obtaining high degree of $L2_1$ order is essential to achieve the half-metallicity at room temperature. Although the half-metallic band gap in the $L2_1$ structure is theoretically predicted to be preserved in the B2 structure in some of Co_2FeZ and Co_2MnZ-types alloys, significant improvement of ΔRA with increasing the degree of $L2_1$-order by post-annealing above 500 °C was reported in the CFMS/Ag/CFMS [5] and CFGG/Ag/CFGG [7] tri-layer structures.

Recently, the CPP-GMR devices using Heusler alloys regained strong interest as a potential alternative for the MgO based TMR sensors for read head applications in hard disk drives (HDD) due to the low device resistance obtained from the all metallic layers structure [19]. However, ΔRA of beyond 10 mΩ μm^2 must be obtained at low annealing temperature below 350 °C in practical devices due to the poor thermal tolerance of a permalloy shield. The dilemma is that annealing at high temperatures over 500 °C is often required to attain a high degree of $L2_1$-order from A2-disordered films deposited by industrial sputtering systems. Therefore, the enhancement of spin polarization by improving $L2_1$-order and the reduction of ordering temperature are crucial issues for the development of spintronic devices using Heusler alloys.

The alloying additions of insoluble elements such as Ag, Au, and Cu has been established as an effective method for the reduction of

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kinetic ordering temperature of $L1_0$ ordered FePt perpendicular thin films and granular media [20–22]. In such a process, the alloying element enhances the kinetics of $L1_0$ ordering while it is rejected from FePt during heat treatment. Hence the alloying addition of insoluble elements to Heusler alloy is worth examining for enhancing the $L2_1$-ordering in Heusler alloy thin films; however, no systematic studies were reported to date. According to the equilibrium binary phase diagrams [23], Ag has little solubility with Co and Si. Therefore, the purpose of this study is to investigate the effect of Ag alloying on the enhancement of $L2_1$-order as well as the reduction of ordering temperature in Co_2MnSi, and the resultant change in spin polarization.

Ag-alloyed Co_2MnSi thin films, denoted as CMS(Ag), were grown on (001) oriented MgO single crystalline substrates by the co-sputtering method with CMS and Ag targets using a ultra-high vacuum (UHV) magnetron sputtering system. A mesh was installed on the top of the Ag target to decrease the deposition rate of Ag. First, the MgO substrate was annealed at 600 °C to achieve a clean and flat surface. Then, 50-nm thick CMS(Ag) epitaxial films with Ag concentration (x_{Ag}) of 0, 2.7 and 4.5 at.% were grown on the MgO-substrates with and without Cr/Ag buffer layers. Cr (10 nm)/Ag (100 nm) buffer layers, which is a widely-used underlayer structure for (001)-oriented epitaxial Heusler alloy-based CPP-GMR devices [24], were deposited at room temperature (RT) and post annealed at 300 °C to improve the surface morphology and reducing the lattice mismatch (<2%). In this study, the heat treatment for CMS(Ag) thin films was carried out at two different approaches, one was room temperature (RT) deposition with subsequent post-deposition annealing, T_{ann} from 300 to 600 °C for 30 min, and the other was the deposition at the elevated substrate temperatures, T_s = 250 °C, and 300 °C. Finally a 10 nm Ru was deposited as a capping layer. Crystal structure and microstructure of the CMS(Ag) thin films were investigated by X-ray diffraction (XRD), high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM), and energy-dispersive X-ray spectroscopy (EDS) techniques. The actual amount of doped Ag was analyzed by inductively coupled plasma (ICP) mass spectroscopy. In order to investigate the spin-polarization of CMS(Ag) films qualitatively, anisotropic magnetoresistance (AMR) was measured by using physical properties measurement system (PPMS), since the negative AMR ratio has been demonstrated to be a fingerprint of half-metallicity in a theoretical study by Kokado et al. [25] followed by recent experimental verifications [26,27]. It was clearly proven in the systematic study on AMR in various Co_2FeZ and Co_2MnZ films that there is a monotonic positive relationship between the magnitude of negative AMR ratio and spin-polarization of conduction electron [27].

XRD measurement results of Ag-alloyed CMS thin films deposited directly on MgO(100) substrates are presented in Fig. 1(a)–(f). In the case of pure CMS (x_{Ag} = 0), the CMS film with chemical composition of Co ~ 47.2 at.%, Mn ~ 26.4 at.%, and Si ~ 26.4 at.% was amorphous up to T_{ann} = 400 °C as shown in Fig. 1(b), and was crystalized above 400 °C. The detection of (004) fundamental and (002) B2 superlattice peaks for T_{ann} = 500 °C and 600 °C indicates the epitaxial growth of CMS. The broadening of CMS peaks along the χ-direction in two dimensional ($\chi - 2\theta$) XRD image in Fig. 1(a) corresponds to the broadening of rocking curve as shown in the inset to Fig. 1(b) for CMS(400) peak at T_{ann} = 600 °C. A large full width at half-maximum (FWHM) in the rocking curve about 11.7° suggests that the (001) oriented CMS layer is strained because of a relatively large lattice mismatch between CMS and MgO. Interestingly, the peak broadening to the χ-direction notably decreases with increasing x_{Ag} as shown in Fig. 1(c)–(f), and a minimum FWHM about 1.3° was observed for x_{Ag} = 4.5 at.% at T_{ann} = 600 °C (inset of Fig. 1(f)). These results clearly indicate that the Ag alloying strongly decrease the strain of the epitaxially grown CMS film with MgO substrate after annealing, i.e., substantially improves structural quality of CMS films. The ratio of $L2_1$-superlattice I(111) and fundamental I(400) peak intensities, reflecting the degree of $L2_1$ order in CMS, is plotted in Fig. 2(a) as a function of T_{ann}. In the case of x_{Ag} = 0 at.%, no considerable enhancement of $L2_1$ order has been detected with T_{ann} over 500 °C. However, the $L2_1$ order increases monotonically with T_{ann} for x_{Ag} = 2.7 at.%, and the I(111)/I(004) ratio becomes almost twice of that for x_{Ag} = 0 at.% at T_{ann} = 600 °C. For x_{Ag} = 4.5 at.%, CMS is amorphous up to T_{ann} = 500 °C; however, the $L2_1$ order also dramatically enhances when it crystallized at T_{ann} = 600 °C. Therefore, we can conclude that Ag-alloying is effective to enhance the $L2_1$-order in CMS and improves the crystallinity.

Furthermore, we have measured AMR ratios of CMS(Ag) thin films for a qualitative evaluation of the spin-polarization [25–27]. AMR ratios measured at 300 K and 10 K are plotted as a function of I(111)/I(400) peak intensities ratio for corresponding $L2_1$ order in Fig. 2(b). The maximum values of AMR −0.23% at 10 K, and −0.18% at 300 K observed for the highest $L2_1$-oredered film with x_{Ag} = 2.7 at.%, reveals a clear positive correlation between the magnitude of negative AMR ratios and the I(111)/I(400) ratios, i.e., the degree of $L2_1$ order. The AMR effect in principle originates from the s–d scattering of the conduction electrons, that is the s-states with localized d-states that are hybridized by spin–orbit interactions in ferromagnetic metals. According to a recent theoretical report by Kokado et al. [25] the AMR ratio should be negative when the dominant scattering is from $s\uparrow \rightarrow d\uparrow$ or $s\downarrow \rightarrow d\downarrow$. Since the density of states of either up- or down-spin channel is absent at the Fermi level in half-metals, the sign of the AMR ratio should also be negative due to $s\uparrow \rightarrow d\uparrow$ or $s\downarrow \rightarrow d\downarrow$ scattering. Experimentally, Yang et al. [26] reported the variations in the remanent density of states at the Fermi level and the change of the sign of AMR from positive to negative by tuning the half-metallic gap in $Co_2Fe_xMn_{1-x}Si$. Sakuraba et al. [27] also reported a clear correlation between negative AMR and the position of the Fermi level from the band gap edges in various Heusler compounds Co_2MnZ and Co_2FeZ (Z = Al, Si, Ge, Ga) in terms of the number of valence electrons. Therefore, both the sign and magnitude of AMR ratio are sensitive to the density of states at Fermi level. The possible reason for the increase of the magnitude of negative AMR ratio with the degree of $L2_1$ order is considered to be due to the suppression of the remanence density of states at Fermi level by the formation of a distinct half-metallic band gap in $L2_1$-ordered CMS. Therefore, the enlargement of magnitude of negative AMR ratio indicates the enhancement of spin-polarization of conduction electron in Ag alloyed CMS.

In addition, we have studied the properties of Ag-alloyed CMS films prepared on Cr/Ag buffer layers with both T_{ann} and T_s. The ratios of I(111)/I(004) peak intensities are summarized in Fig. 3 as a function of T_{ann} (/T_s). Compared to the CMS(Ag) films that were directly deposited on MgO-substrates, Fig. 1, the deposition of CMS (Ag) thin films on buffer layers reduces the crystallization temperature significantly down to 350 °C. For x_{Ag} = 0 at.%, the CMS film was epitaxially grown with a slight $L2_1$-order even without post-deposition annealing, and the degree of $L2_1$ order gradually increases with T_{ann} > 300 °C. In contrast, for x_{Ag} = 2.7 and 4.5 at.%, CMS(Ag) films are amorphous up to 300 °C and 350 °C, respectively; however, the $L2_1$ order dramatically increases on crystallization of CMS. The improvement of $L2_1$-order by Ag-alloying was clearly confirmed even at relatively low T_{ann} ~ 350–400 °C, which is very important for the usage of this technique in practical applications such as HDD read sensors. The maximum I(111)/I(004) in CMS at T_{ann} = 600 °C for x_{Ag} = 4.5 at.% is about double as that for x_{Ag} = 0 at.%, thus the degree of $L2_1$-order S_{L2_1}, which is usually defined by the root of I(111)/I(004), becomes almost 40% lar-