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ABSTRACT

Cu$_2$Sb-type intermetallic compound, MnAlGe, is known to exhibit uniaxial magnetocrystalline anisotropy and relatively small saturation magnetization, which are suitable for spintronic applications, e.g. spin-transfer phenomena requiring small critical current density. Ge-concentration dependence of the crystal structures, saturation magnetization, $M_s$, and perpendicular magnetic anisotropy, $K_u$, was investigated for MnAlGe films prepared onto silicon substrates with a thermally oxidized amorphous layer. For the stoichiometric and Ge-rich samples, the films exhibited (001)-texture with perpendicular magnetization. The maximum values of $M_s$ and $K_u$ were 270 emu/cm$^3$ and $4.8 \times 10^6$ erg/cm$^3$, respectively, which were comparable values with those reported for bulk and epitaxially grown films in literatures.

INTRODUCTION

Cu$_2$Sb-type intermetallics, (XX')Z, form a crystal structure shown in Figure 1 which is a tetragonal C38 phase of the space group P4/nmm, No. 129. For typical compounds, the Z atom is a 3d-transition metal, the X' atom is a 3d-transition metal or a group 13 element in the periodic table, and Z atom is a group 15 element. The atomic positions are the Wyckoff 2a (000), (1/2 1/2 0), 2c (0 1/2 0), (1/2 0 1/2), and 2c (0 1/2 0), (1/2 0 1/2), for X, X', and Z atoms, respectively. Magnetism of Mn-based intermetallics, such as Mn$_2$Sb, (Mn-Cr)Sb, and CuMnAs showing the Cu$_2$Sb-type crystal structure varies with the composition, 1-9 and the itinerant nature of electrons has been of interest. 10 Among the materials, equiatomic MnAlGe is known to exhibit small magnetic tunnel junctions with the (001)-orientation for large tunnel magnetoresistance. 11,12 The crystal structure and magnetic properties of MnAlGe in film form have been investigated intensively for epitaxially grown samples, and the dependence on film compositions was reported. 13,14 On the other hand, correlations between magnetic properties and the chemical order of the compounds have not been investigated systematically. In addition, for the poly-crystalline MnAlGe films, although the literature reported perpendicular magnetization, 15 the details for crystal structures and quantitative magnetic properties has been unclear. In this study, Ge concentration dependence is investigated in poly-crystalline Mn-Al-Ge films.

EXPERIMENTAL PROCEDURES

Film samples were deposited using ultra-high-vacuum magnetron sputtering system with base pressure less than $3 \times 10^{-7}$ Pa.
The films were deposited onto thermally oxidized silicon substrates. The stacking structure was as follows: Substrate | Mn-Al-Ge 100 nm | MgO 2 nm | Ta 3 nm. Co-sputtering technique was used for the deposition of Mn-Al-Ge layer with an Mn-Al alloy target and a Ge target, and four series of samples were prepared with different Ge concentration including no Ge sample, Mn-Al, as summarized in Table I. All layers were deposited at room temperature, and after depositing capping layers consisting of MgO | Ta, post-annealing was carried out using a vacuum furnace. The annealing temperatures were in the range of 200 – 500 °C and changed in 100 °C increments. The crystal structures were characterized using x-ray diffraction, XRD, for the out-of-plane and in-pane configurations. In addition, XRD measurements for the grazing incidence angle were also carried out around the 011 and 112 diffractions. The magnetization curves were measured by using vibrating sample magnetometer, VSM. The maximum applied fields were 25 kOe and 90 kOe for the measurements with the perpendicular-to-plane and in-plane directions, respectively. All measurements were carried out at room temperature.

### RESULTS AND DISCUSSION

The out-of-plane and in-plane XRD profiles are shown in Figure 2. Diffractions from the Cu$_2$Sb-type structure are marked by ▼, and the diffraction indexes are shown on the top of the graphs. The diffractions from the silicon substrates and an unknown phase are marked by ▽ and ∗, respectively. The annealing temperatures are 400 °C for the no-Ge and Ge-poor samples (Fig. 2(a–d)), and 500 °C for the stoichiometric and Ge-rich samples (Fig. 2(e–h)), which are optimum annealing temperatures showing maximum $M_s$ as it is discussed in the following part except for Ge-poor samples showing no hysteresis loop for all the annealing temperatures. In the XRD profiles, the no-Ge sample exhibits a 111 diffraction which is clearly seen for the out-of-plane geometry shown in Fig. 2(a). Although the intensity is very weak, a tiny diffraction is also seen for the in-plane geometry (Fig. 2(b)). The 111 diffraction is possibly from the face-centered cubic, fcc, or face-centered tetragonal, fct, structure. With a small Ge concentration, the Ge-poor sample exhibits several weak diffraction peaks from the Cu$_2$Sb-type structure and possibly from the fcc or fct structure. On the other hand, the stoichiometric and Ge-rich samples clearly exhibit diffraction peaks from the Cu$_2$Sb-type structure and possibly from the fcc or fct structure. The 111 diffraction is possibly from the face-centered cubic, fcc, or face-centered tetragonal, fct, structure. With a small Ge concentration, the Ge-poor sample exhibits several weak diffraction peaks from the Cu$_2$Sb-type structure and possibly from the fcc or fct structure. On the other hand, the stoichiometric and Ge-rich samples clearly exhibit diffraction peaks from the Cu$_2$Sb-type structure and possibly from the fcc or fct structure.

![FIG. 1. A schematic crystal structure of the Cu$_2$Sb type material “(XX)Z.”](image)

![FIG. 2. XRD profiles of Mn-Al-Ge films with different Ge-concentration for (a, c, e, g) out-of-plane configuration, and (b, d, f, h) in-plane configuration. The diffraction indexes are noted on the top of graphs. Marks of ▼, ▽, and ∗ represent diffraction peaks of the Cu$_2$Sb-structure, unknown phase, and the silicon substrates, respectively. Annealing temperatures are 400 and 500 °C for (a – d) and (e – h), respectively.](image)

**TABLE I. Compositions and the stoichiometry of the film samples.**

| Sample       | Composition (at.%) | Stoichiometry |
|--------------|--------------------|---------------|
| No-Ge        | Mn$_{58.8}$Al$_{42.0}$ | Mn$_{1.16}$Al$_{0.84}$ |
| Ge-poor      | Mn$_{41.7}$Al$_{58.3}$Ge$_{24.3}$ | Mn$_{1.25}$Al$_{0.72}$Ge$_{0.73}$ |
| Stoichiometric | Mn$_{35.9}$Al$_{30.0}$Ge$_{34.0}$ | Mn$_{1.08}$Al$_{0.90}$Ge$_{1.02}$ |
| Ge-rich      | Mn$_{31.7}$Al$_{26.8}$Ge$_{41.4}$ | Mn$_{0.95}$Al$_{0.81}$Ge$_{1.24}$ |
(001)-texture. Note that an unknown diffraction peak is also observed in the out-of-plane XRD profile of the Ge-rich sample. The annealing temperature dependence exhibited negligibly small difference in the XRD patterns in the temperature range of 300 - 500 °C, however, no diffraction peak was observed in all samples annealed at 200 °C for which no hysteresis loop was observed in magnetization curves measurements.

Lattice parameters for c-axis (out-of-plane), a-axis (in-plane), and c/a ratio are summarized as a function of the annealing temperature for stoichiometric and Ge-rich samples in Figure 3. The lattice parameters were not evaluated for no-Ge or Ge-poor samples, because diffraction peaks were very weak and insufficient to determine both values for the c- and a-axes quantitatively. Concerning the stoichiometric samples, the lattice parameter of c-axis slightly increase with the annealing temperature, while a-axis exhibits nearly no change, and as a result, c/a ratio slightly increases. The trend is similar for the Ge-rich samples with that of the stoichiometric samples, however, the change of c-axis is relatively large. The annealing temperature dependence of lattice parameters is possibly caused by relaxation of strain which was, e.g., induced during sputtering process, and an increase of volume fraction of the Cu₂Sb phase. Compared with values in a bulk sample \(^4\) and calculated values, as the value is smaller (larger) for c-(a)-axis, which results in the relatively small c/a ratio for the present film samples, and the deviation from the literature values is larger in the Ge-rich samples than that in the stoichiometric samples.

Relative integrated diffraction peak intensities of \(I_{001}/I_{002}\) and \(I_{011}/I_{112}\) are summarized as a function of the annealing temperature in Figure 4. Simulation values for a fully ordered MnAlGe with the Cu₂Sb-type structure are also indicated using broken lines in the figure, for which the calculated energetically stable lattice parameters in Ref. 11 were used. Here, the ratio of \(I_{001}/I_{002}\) depends on the layer-by-layer chemical order of the Mn- and the (Al-Ge)-layers in the Cu₂Sb-type structure. On the other hand, the ratio of \(I_{011}/I_{112}\) depends on the chemical order between the Al sites and the Ge sites in the plane. Note that the integrated peak intensities also depend on the values of \(u_k\) and \(v_c\), however, possible changes of \(u_k\) and \(v_c\) are neglected in the following discussion because of no experimental values due to the limited XRD peaks for the present film samples. Although all \(hkl\) diffractions are allowed for the present P-lattice in the Bravais family even in case of the disordered situation, those specified diffraction intensity ratios become weak because of different atomic scattering factors. For the stoichiometric samples, the values of \(I_{001}/I_{002}\) exhibit nearly no change between the annealing temperatures of 300 and 400 °C, and it slightly increases at 500 °C. Regarding \(I_{011}/I_{112}\) for the stoichiometric samples, the values increase with the annealing, for which the difference is relatively large between the data points at 300 and 400 °C. These results suggest that the chemical order for the (001)-planes were slightly increased by the annealing at 500 °C, while the chemical order insides the Al-Ge planes were drastically promoted by the annealing at 400 °C. On the other hand for the Ge-rich samples, both values of \(I_{001}/I_{002}\) and \(I_{011}/I_{112}\) increase with the annealing temperature, suggesting that both chemical order for (001)-planes and Al-Ge sites were improved by the annealing over 300 °C.

Magnetization curves are shown in Figure 5. The annealing temperatures were 400 °C for Fig. 5(a, b), and 500 °C for Fig. 5(c, d). Magnetization curves for all samples including other annealing temperatures are shown in Figure S1 of supplementary material. For the no-Ge sample, hysteresis loops are observed for both perpendicular-to-plane, \(\perp\), and in-plane, \(\parallel\) directions showing similar coercivity...
and the squareness, each other. The trend is similar for other annealing temperatures of no-Ge samples, however, $M_s$ was less than 100 emu/cm$^3$ (Fig. S1(e)). For the Ge-poor sample, no-hysteresis is observed for both perpendicular and in-plane directions, which were nearly the same for other annealing temperatures (Figs. S1(b, f, j, n)). The reason is unclear for no hysteresis in the Ge-poor samples, however, the reduction of Curie temperature and/or the cancelation of spin moments might happen considering the very week XRD patterns suggesting a small volume fraction of the Cu$_2$Sb-type structure as well as a possible mixture of the fcc/ict phase. On the other hand, although finite coercivity is found in the in-plane magnetization curves, both stoichiometric and Ge-rich samples clearly exhibit perpendicular magnetization. From the magnetization curves, $M_s$ and the effective perpendicular magnetic anisotropy energy, $K_u^\text{eff}$ were evaluated. In this study, $K_u^\text{eff}$ was calculated from the area enclosed by the perpendicular-to-plane and in-plane magnetization curves. Using the $K_u^\text{eff}$, the perpendicular magnetic anisotropy energy, $K_u$, of films is defined as $K_u = K_u^\text{eff} + 2\pi M_s^2$.

The values of $M_s$ and $K_u$ are summarized as a function of the annealing temperature in Figure 6 for the no-Ge (only $M_s$ values are shown), stoichiometric and the Ge-rich samples. For the no-Ge samples, $M_s$ values exhibit maximum at the annealing temperature of 400 °C and decreases at 500 °C. The drop of $M_s$ at the high-temperature annealing is possibly caused by an appearance of another phase than the ferromagnetic r-phase in Mn-Al which is a meta-stable phase. For the stoichiometric and Ge-rich samples, both $M_s$ and $K_u$ increase with the annealing temperature, and the stoichiometric samples exhibit larger values for all the temperature range. The maximum values of $M_s$ and $K_u$ are 270 emu/cm$^3$ and 4.8 × 10$^6$ erg/cm$^3$, respectively, for the stoichiometric sample annealed at 500 °C. These maximum values are comparable with those for a single-crystalline bulk and an epitaxially grown MnAlGe film reported in literatures.$^{10,18}$

Regarding correlations between the magnetic properties and the integrated diffraction intensity ratios shown in Fig. 4, firstly in the Ge-rich samples, $I_{001}/I_{112}$ closely correlates with both $M_s$ and $K_u$. In addition, for the stoichiometric samples, enhancements of $M_s$ and $K_u$ from the annealing temperatures of 400 to 500 °C possibly correspond to the small increase of $I_{001}/I_{112}$. On the other hand, regarding the ratios of $I_{011}/I_{112}$, even though the values increase with the annealing temperature, no clear correlation is seen in the magnetic properties: Relatively large $M_s$ and $K_u$ were also achieved in the samples annealed at 300 °C especially in the stoichiometric sample, for which the Al-Ge sites are considered to be nearly random. These experimental results suggest that the order of the (001)-planes is crucial for the magnitude of the Mn-moment and anisotropy, which is reasonable because it was reported that the Mn atoms present strong itinerant nature when those locate at the Wyckoff 2a positions, while the nature of the electron changed when those locate at the 2c positions.$^7$

**SUMMARY**

Ge-concentration dependence of crystal structures, $M_s$, and $K_u$ were investigated for poly-crystalline MnAlGe films onto thermally oxidized silicon substrates. The films clearly exhibited the Cu$_2$Sb-type structure with (001)-orientation for the stoichiometric and Ge-rich samples, while other samples with no-Ge and Ge-poor concentration exhibited weak XRD peaks with no particular orientation. Hysteresis loops showing the perpendicular
magnetization were achieved in the stoichiometric and the Ge-rich samples. The maximum values of $M_s$ and $K_u$ of 270 emu/cm$^3$ and $4.8 \times 10^6$ erg/cm$^3$, respectively, were achieved in the stoichiometric sample, which were comparable with those reported in single-crystalline bulk and the epitaxially grown film samples in the literatures.

SUPPLEMENTARY MATERIAL

See a supplementary material for magnetization curves for all samples in this study.

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