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ABSTRACT

Mn$_{x}$Sn$_{100-x}$ thin films with different compositions ($x=84, 80, 76,$ and $74$) were fabricated on MgO (111) substrates by radiofrequency magnetron sputtering at room temperature and their properties were evaluated. The samples crystallized into Mn$_3$Sn after thermal annealing at $400 \degree C$ or higher in vacuum. The Mn$_{80}$Sn$_{20}$ film showed only peaks of the (0001) family in out-of-plane XRD profiles, while the other films additionally showed other diffraction peaks indicating their polycrystalline structure. Cross-sectional transmission electron microscopy confirmed successful fabrication of highly c-plane orientated single-phased Mn$_3$Sn thin film in the $x=80$ sample. The sample possessed a weak ferromagnetic component in the film plane, whose magnitude was comparable with that of bulk Mn$_3$Sn. On the other hand, the out-of-plane magnetization curve had a linear response within $\pm 5T$. This magnetic anisotropy is the same as in bulk Mn$_3$Sn. The Hall curve measured with electric current (magnetic field) along the [01 $\bar{1}0$] ([0001]) axis indicated a negligibly small negative anomalous Hall effect (AHE). This response was also the same as in bulk Mn$_3$Sn. We thus concluded that the anisotropies of the magnetic properties and AHE of Mn$_3$Sn in a thin-film form are the same as those of bulk.

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I. INTRODUCTION

An anomalous Hall effect (AHE)\textsuperscript{1,2} with a significant amplitude, as strong as that of ferromagnetic materials, was observed in a bulk form of Mn$_3$Sn in 2015.\textsuperscript{3} Mn$_3$Sn is an antiferromagnetic material with a kagome lattice in its c-plane. The 120$\degree$-ordered Mn spins cancel each other in the kagome triangle,\textsuperscript{4–6} and a negligibly small spontaneous magnetic moment is induced with small canting from the triangle spin structure in the c-plane.\textsuperscript{7,8} The AHE in Mn$_3$Sn is exceedingly large compared with this small spontaneous magnetic moment. Since the AHE has been empirically confirmed to be related to the magnetic moment, this unconventional phenomenon has attracted significant attention. It is considered that the origin of the large AHE is related to the Berry-phase concept.\textsuperscript{9,10} Recent studies have revealed that the mechanism is crossing points near the Fermi energy in its band dispersion diagram. These points create Weyl fermions which behave like magnetic monopoles in momentum space\textsuperscript{12–14} and lead to a large Berry-curvature, which in turn results in the AHE. This is considered to be the reason why Mn$_3$Sn has a large AHE even though it is an antiferromagnetic material.\textsuperscript{15,16} The large AHE may have a prospect as a new approach to making spintronics devices. As an antiferromagnetic material, Mn$_3$Sn has no leakage of the magnetic field. Moreover, the Hall resistivity could be controlled by a small applied magnetic field of $\sim 0.03$ tesla. These
features may enable the development of high-performance spintronics devices, such as high-density magnetic random-access memories with small power consumption. Many studies have also been carried out with the purpose of applying the effect to practical devices. For these device applications, thin film fabrication techniques for Mn$_3$Sn are indispensable. We previously researched a way of fabricating Mn$_3$Sn thin films and studied the composition dependence of their magnetic and magneto-transport properties. We succeeded in fabricating polycrystalline Mn$_3$Sn thin films on Si/SiO$_2$ substrates by thermal annealing at 400 $^\circ$C or higher after sputtering deposition at room temperature and were able to obtain a large AHE in them. We also discovered that a Mn-rich composition was necessary to eliminate other phases (mainly, the Mn$_2$Sn phase) which degraded the AHE magnitude in the samples. On the other hand, the ratio of anomalous Hall resistivity to magnetic moment (anomalous Hall coefficient) was still small because the magnetic moment in the film was several times larger than in bulk Mn$_3$Sn. This might have been due to the grains in the polycrystalline thin films, whose crystal orientation is not suitable to show a large AHE. Thus, controlling the crystal orientation of grains in the whole film is essential for obtaining a larger value of AHE. However, there are not enough studies dedicated to the fabrication of orientated Mn$_3$Sn thin films and evaluation of their properties. In this research, we focused on MgO (111) substrate because of its small lattice mismatch with Mn$_3$Sn. The inter-atomic distance of the MgO (111) plane is 2.98 Å, and the length of the a-axis of Mn$_3$Sn is 2.83 Å. The purpose of this research was to examine epitaxial growth of c-plane-oriented Mn$_3$Sn thin films on MgO (111) substrate and to evaluate their magnetic and magneto-transport properties.

II. EXPERIMENTAL PROCEDURE

We employed the same fabrication conditions as for the polycrystalline samples in our previous study, except for the substrate and its surface treatment. Before depositions, MgO substrates were heated at 650 $^\circ$C for 30 minutes by a lamp heater in a vacuum chamber in order to remove the adsorbed moisture from the surface. 50-nm-thick Mn$_x$Sn$_{100-x}$ thin films were deposited by radiofrequency magnetron sputtering with co-deposition from the Mn and Sn targets at room temperature. Ar gas at 0.2 Pa pressure was used as a process gas. The film composition was changed by controlling each target’s power. Four kinds of sample were treated in this research ($x=84$, 80, 76, and 74). The compositions of the films were investigated by energy-dispersive X-ray spectrometry (EDS) after annealing at 500 $^\circ$C. Thermal annealing slightly changes the composition of the films. The measurement error of EDS was ±0.3 at%. To prevent oxidation, a 5-nm-thick Ta layer was stacked on top of the Mn$_x$Sn$_{100-x}$ alloy films. After the deposition, the films were annealed for one hour in a vacuum at various temperatures, $T_a = 200 – 500^\circ$C, to promote crystallization. The crystal structure was...
revealed by out-of-plane X-ray diffraction (XRD). For the samples showing highly-orientated peaks, in-plane XRD and transmission electron microscope (TEM) analysis were also carried out. Magnetic properties were investigated by using a superconducting quantum interference device (SQUID) magnetometer. To measure the Hall effect in the samples, a 100-μm wide Hall bar was fabricated with photolithography and an ion-milling technique.

III. RESULTS AND DISCUSSION

Figure 1 shows the out-of-plane (conventional 2θ-ω scan) XRD patterns of the samples that were annealed at various temperatures. The as-deposited samples and those annealed at 200°C did not indicate any peaks regardless of x. After annealing at 300°C, only the most Mn-poor sample in this study (Mn74Sn26) showed a peak around 2θ = 41° (Fig. 1(d)). The origin of this peak is considered to be the Mn2Sn phase,23,24 which is firstly crystallized phase from amorphous or nano-crystalline phase in the sample, which is the same as in Mn-deficient polycrystalline thin-film sample.17,18 A peak from Mn3Sn (0002)4,25 appeared in all samples after annealing at 400 or 500°C, and the peak from the Mn2Sn phase vanished from the Mn74Sn26 sample profile. The Mn80Sn20 film indicated the strongest Mn3Sn (0002) peak among the samples. In the spectra of the samples which were richer or poorer in Mn than in Mn80Sn20, Mn3Sn (20¯21) peaks were also obtained near 2θ = 42° (Figs. 1(a), (c), and (d)), indicating formation of a polycrystalline phase. These results mean that a Mn-rich composition is required for formation of a single phase and epitaxial growth of Mn3Sn thin films; the previous studies on polycrystalline Mn3Sn thin films reached similar conclusions.17,18

The crystallographic properties of the 500°C-annealed Mn80Sn20 sample were further investigated by making the following measurements. In-plane XRD (2θ-φ scan) profiles are shown in Fig. 2. In the case of a scattering vector parallel to MgO [110] (blue line), peaks from the Mn3Sn (11¯20)4,25 family were clearly observed. When the scattering vector was rotated 30° from the former configuration (red line), peaks from the Mn3Sn (10¯10)4,25 family were clearly

![Figure 2](image2.png)

![Figure 3](image3.png)
observed. Although the small peak near $2\theta_{K} = 56^\circ$ can not be assigned to either Mn$_3$Sn or Mn$_2$Sn, the above results indicate that the Mn$_3$Sn film was epitaxially grown on MgO (111) substrate. The mosaicity of the films was fairly small, less than 0.7\(^{\circ}\), which was determined from the half width at half maximum of the rocking curve ($\omega$ scan profile; not shown) of the Mn$_3$Sn (0002) diffraction peak.

Figure 3 shows the results of cross-sectional TEM analyses. The incidence direction of the electron beam was MgO [110]. A flat and continuous layer structure is shown in the bright field image (Fig. 3(a)). The high-resolution image (Fig. 3(b)) revealed that the Mn$_3$Sn film directly grew on the MgO substrate surface without any other phases at the interface, even though the interface was not atomically flat. In addition, there were scarcely any defects of the crystal lattice, such as grain boundary and dislocations, in the Mn$_3$Sn film. The electron diffraction patterns, in both Fig. 3(c) and (d), consisted of bright diffraction spots. It was thus revealed that the Mn$_3$Sn film was well crystallized and highly orientated on the MgO substrate. The epitaxial relationship can be concluded to be Mn$_3$Sn [1120] // MgO [110] (111).

Next, let us discuss the magnetic properties of the Mn$_3$Sn epitaxial thin film (the 500 \(^{\circ}\)C annealed Mn$_3$Sn$_{20}$ sample). Two kinds of magnetic curve at room temperature are present in Fig. 4. The red line indicates an in-plane magnetization curve, while the green line indicates an out-of-plane magnetization curve. The red line describes a small hysteresis loop in the low field (within 0.2 T) and a linear response in the high field, while the green line describes linear responses over the whole sweeping range in this measurement. These responses are the same as those of the bulk form of Mn$_3$Sn.\(^{3,7,8}\) The saturation magnetization of the weak ferromagnetic component is estimated to be 2.1 emu/cc from the in-plane hysteresis loop. This value is several times smaller than that of polycrystalline Mn$_3$Sn thin film\(^{7,8}\) and is comparable to that of bulk Mn$_3$Sn.\(^{3,7,8}\) Moreover, the in-plane magnetic susceptibility, which is also calculated from the magnetization curve, is approximately 4.1 emu/(cc·T) and is comparable to that of bulk.\(^{3,7,8}\) The magnetic susceptibility of the perpendicular to the plane is quite small compared with that of the bulk form of Mn$_3$Sn.\(^{3,7,8}\) Although the reason for this is unclear, the magnetic moments are strongly confined within the c-plane. Apart from the magnitude of the c-axis susceptibility, it turns out that the orientation dependences of the magnetic properties of Mn$_3$Sn epitaxial thin films are similar to those of bulk Mn$_3$Sn.\(^{3,7,8}\) Comparison of the magnetic properties is shown in Table I.

The results of the Hall effect measurement of the Mn$_3$Sn epitaxial thin film (the 500 \(^{\circ}\)C-annealed Mn$_3$Sn$_{20}$ sample) at room temperature are shown by the green line in Fig. 5. In this measurement, the electron current was along the [01\(\overline{1}\)0] axis, and the magnetic field was applied along the [0001] axis. The longitudinal resistivity was 226.4 $\mu$Ω·cm and was independent of the applied magnetic field. The Hall curve measured for the previously reported polycrystalline thin film with a magnetic field normal to the film plane\(^{1}\) is also shown in pink as a reference. The green line describes a negligibly small hysteresis loop in the low field region. When we take into account that a large AHE does not appear in the bulk single-crystal Mn$_3$Sn in this measurement configuration,\(^{1}\) it can be considered that the negligible hysteresis loop of the AHE was caused by the small tilting angle distribution of the Mn$_3$Sn (0002) axis from the film normal in the sample. Namely, the AHE in the c-plane oriented Mn$_3$Sn

![FIG. 4. Magnetization curves of the epitaxial Mn$_3$Sn thin film measured along the out-of-plane and in-plane directions at room temperature.](image-url)

![FIG. 5. Hall curves of the epitaxial (green line) and polycrystalline (pink line) Mn$_3$Sn thin film at room temperature. The electron current was in-plane ([01\(\overline{1}\)0] axis for the epitaxial film), and the magnetic field was applied perpendicular to the film plane ([0001] axis for the epitaxial film). Longitudinal resistivity of the epitaxial Mn$_3$Sn thin film is plotted as a light-blue line.](image-url)

| Table I. Magnetic properties. Comparison of the magnetic properties of Mn$_3$Sn in bulk and epitaxial thin film forms. |
|---------------------------------|---------------|---------------|
| Magnetization (emu/cc) | Susceptibility (emu/(cc·T)) |
|-----------------|---------------|
| Bulk ([H//[01\(\overline{1}\)0]) | 1.8 | 5.2 |
| Epi thin film (in-plane) | 2.1 | 4.1 |

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epitaxial thin films is the same as in the bulk. For practical device applications of Mn$_3$Sn, it might be necessary to determine the fabrication conditions for a- or m-plane oriented thin films in order to utilize its large AHE.

IV. SUMMARY

Highly c-plane oriented epitaxial Mn$_3$Sn thin films were successfully fabricated on MgO (111) substrates by thermal annealing at 400°C or higher after deposition at room temperature. The epitaxial relationship was Mn$_3$Sn [1120] //MgO [110] (111). It was concluded that control of the composition from stoichiometric to Mn-rich is necessary to fabricate single-phase Mn$_3$Sn epitaxial thin films. The fabricated epitaxial thin films possessed a weak ferromagnetic component in the c-plane whose magnitude was comparable to that of bulk. Negligibly small magnetic hysteresis and AHE were obtained in the c-plane oriented epitaxial thin film with a magnetic field along the c-axis. Namely, the anisotropies in the magnetic properties and AHE in the thin-film form of Mn$_3$Sn are the same as those in the bulk form.

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