Ferromagnetic Co₃Sn₂S₂ thin films fabricated by co-sputtering

Kohei Fujiiwara¹, Junya Ikeda¹, Junichi Shiogai¹, Takeshi Seki¹,², Koki Takanashi¹,², and Atsushi Tsukazaki¹,²

¹Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
²Center for Spintronics Research Network (CSRN), Tohoku University, Sendai 980-8577, Japan

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We synthesized the magnetic Weyl semimetal candidate Co₃Sn₂S₂ as a thin film using the co-sputtering technique. By adjusting the film composition using a sulfur-rich SnS₁.₅ target with Co metal chips attached, we obtained highly crystallized, single-phase Co₃Sn₂S₂ films. The films showed a ferromagnetic transition around 180 K with perpendicular remanent magnetization. We observed the anomalous Hall effect with a tangent of Hall angle of 0.20 at 130 K, as previously reported for the bulk single crystals. Angular dependence measurements suggested that the magnetization reversal process governed by the domain wall motion leads to a large coercive field in the films.

SUPPLEMENTARY MATERIAL

Supplementary material for this article is available online.

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Fig. 1. (Color online) (a) Left: crystal structure of Co₃Sn₂S₂; right: Co kagome lattice viewed along the c-axis direction (Ref. 8). The gray lines represent the unit cell. (b) CoSn and CoS atomic ratios measured by energy-dispersive X-ray spectroscopy. Three Co–Sn–S films fabricated with SnS, SnS₁.₅, and SnS₂ targets are compared. The dashed line indicates the ideal CoSn and CoS atomic ratios for the shandite composition. The error bars are smaller than the symbol sizes. The inset shows a photograph of the SnS₁.₅ target with six Co metal chips attached.

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C₃Sn₂S₂ is one of the shandite compounds¹ and has been studied extensively because of its half-metallic properties below the ferromagnetic transition temperature Tₜ of 175 K.²–⁵ Very recently, the bulk single crystals were reported to show the anomalous Hall effect (AHE) with a tangent of Hall angle reaching 0.2, which is exceptionally large compared with those in known ferromagnetic materials.⁶–⁸ As schematically shown in Fig. 1, this compound has triangular-based alignment of magnetic cobalt atoms in the a–b plane, called the kagome lattice. According to first-principles calculations,⁹ Weyl nodes appear near the Fermi level owing to the kagome lattice topology cooperating with spin–orbit coupling. This specific band structure, enhancing the intrinsic AHE mechanism (Ref. 9), has triggered renewed interest in Co₃Sn₂S₂ as a promising candidate for magnetic Weyl semimetals.¹⁰–¹²

The magnetic Weyl semimetal is a new class of topological material, characterized by a pair of Weyl nodes with opposite spin chiralities.¹⁰–¹² It has been widely recognized in studies on three-dimensional topological insulators¹³–¹⁶ that precise control of the Fermi level into the bands with topological character is necessary for detecting phenomena specific to the surface states. The thin-film growth technique has offered effective approaches for this issue thanks to the availability of non-equilibrium processes and artificial structures.¹³–¹⁶ Although the fabrication of magnetic Weyl semimetal thin films remains to be developed, it will play an essential role in verifying theoretical proposals, e.g., the formation of Weyl nodes in multilayer structures,¹⁷,¹⁸) the emergence of the quantum AHE in ultrathin films,¹⁹,²⁰ as well as Fermi-level tuning by impurity doping or electrostatic doping using a field-effect device structure.¹³–¹⁶ For these thin-film-based experiments and future spintronics applications using Co₃Sn₂S₂, the growth of the high-quality films must be addressed. Here, we present ferromagnetic Co₃Sn₂S₂ thin films with a large tangent of Hall angle and perpendicular remanent magnetization fabricated using the co-sputtering technique.

Co₃Sn₂S₂ films were grown by radio-frequency magnetron sputtering on Al₂O₃ (0001) substrates. The three elements Co, Sn, and S were supplied from a single cathode by mounting Co metal chips on a SnS₃ target (x = 1.0, 1.5, and 2.0), as displayed in the inset of Fig. 1(b). The SnS and SnS₂ targets were made of single-phase tin sulfides, and the SnS₁.₅ target was composed of a mixture of them. Prior to deposition, the Al₂O₃ substrates were annealed at 1000 °C in air to obtain an atomically smooth surface. The Co–Sn–S films were deposited at 400 °C and capped with a 75 nm thick insulating SiO₂ layer, followed by annealing at 800 °C in a vacuum. The SiO₂ layer was used to suppress the evaporation of sulfur and tin sulfide during the post-annealing. The crystal structure and composition of the films were characterized by X-ray diffraction (XRD) using Cu Kα radiation and energy-dispersive X-ray spectroscopy,
respectively. Electrical and magnetic properties were measured with a physical property measurement system equipped with a sample rotator and a magnetic property measurement system (both from Quantum Design). For the electrical measurement, an indium solder was attached as the contact electrodes. To remove thermoelectric and geometric effects, the measured transverse Hall voltages were anti-symmetrized against the applied magnetic field.

In the present target setup, the composition ratio of Co to Sn could be controlled by the number and position of Co metal chips. To adjust the volatile sulfur content to be stoichiometric in the films, we examined the film composition using SnSₓ targets with different sulfur content. The deposition rates did not depend on the targets, and were approximately 6–7 nm min⁻¹. In Fig. 1(b), the Co/Sn and Co/S atomic ratios are compared between the Co–Sn–S films fabricated with the three targets. When the Co/Sn ratios are pre-adjusted to be about 1.5, the Co/S ratio becomes much larger (smaller) than 1.5 for the SnS (SnS₂) target due to the insufficient (excess) supply of sulfur. Using the SnS₁.₅ target, a nearly stoichiometric Co/S ratio is obtained. As seen in Fig. 2(a), the film fabricated with the SnS₁.₅ target exhibits the strongest Co₃Sn₂S₂ (0006) peak intensity with clear thickness fringes (see Fig. S1 in the supplementary material for wide-scan XRD patterns, available online at stacks.iop.org/JJAP/58/050912/mmedia). The c-axis length is estimated to be 13.16 Å, which agrees with the bulk value of 13.178 Å (JCPDS, PDF No. 01-084-7267 and Ref. 5). In contrast, the S-deficient film (SnS target) includes the impurity α-Co phase, and the S-excess film (SnS₂ target) shows a much weaker diffraction intensity. Their (0006) peaks appear at almost the same diffraction angles as that of the stoichiometric film (SnS₁.₅ target), implying that the c-axis length is not greatly affected by the sulfur content. These non-stoichiometric films may contain Co₃Sn₂S₂ as small domains with impurities and/or disordered phases. As displayed in Fig. 2(b), transmission electron microscopy observations captured the layered structure of Co₃Sn₂S₂ [Fig. 1(a)] in the film fabricated with the SnS₁.₅ target. By comparing fast Fourier transform diffraction patterns in Figs. 2(c) and 2(d), we determine the orientation relationship to be Co₃Sn₂S₂.
Fig. 4. (Color online) (a) \( \rho_{yx} \) versus \( \mu_0 H \) curves and (b) \( M_\parallel \) versus \( \mu_0 H \) curves of a 35 nm thick Co₃Sn₂S₂ film at \( T = 200, 150, \) and 100 K. (c) Magnetic field angular dependence of \( \rho_{yx} \) versus \( \mu_0 H \) curves at \( T = 150 \) K. See the inset of panel (d) for the definition of \( \theta_i \). The magnetic field direction is rotated in the \( y-z \) plane. The curves are shifted vertically for clarity. The gray lines denote the base lines (\( \rho_{yx} = 0 \)) for each curve. The \( \rho_{yx} \) versus \( \mu_0 H \) curve at \( \theta_i = 0^\circ \) is identical to that presented in panel (a). The filled black circles indicate the coercive fields \( \mu_0 H_c \). (d) \( \theta_i \) dependence of the normalized coercive field \( \mu_0 H_c / \mu_0 H_i \). \( \theta_i = 0^\circ \) at \( T = 150 \) K. The dashed curve represents the \( 1/\cos \theta_i \) function expected for the magnetization reversal process governed by domain wall motion. The inset depicts the setup for the angular dependence measurement (\( I \) current, \( V_{yx} \) transverse Hall voltage).

Although in-plane-rotated domains are partly detected in other view areas, these results demonstrate that the highly crystallized, single-phase Co₃Sn₂S₂ film with a nearly stoichiometric composition can be obtained with the co-sputtering technique. We hereafter focus on the magnetic and electrical properties of a 35 nm thick, nearly stoichiometric Co₃Sn₂S₂ film fabricated with the SnS₁.₅ target (the exact composition is Co₃.₀Sn₂.₀S₂.₂). Figure 3(a) shows the temperature (\( T \)) dependence of out-of-plane magnetization \( M_z \). We cooled the sample in a perpendicular magnetic field of \( \mu_0 H = 1 \) T so that the magnetization was aligned to the out-of-plane direction, and measured \( M_z \) under \( \mu_0 H = 10 \) mT on heating. A clear onset of \( M_z \) around 180 K, which is comparable to the bulk \( T_C = 175 \) K, indicates the ferromagnetic transition of the Co₃Sn₂S₂ film. The saturation magnetization of about 0.3 \( \mu_0 M / \rho \) is also consistent with those reported for bulk polycrystalline samples \(^{21-23} \) and single crystals \(^{4,6,7,23,24} \). According to a systematic study using S-deficient Co₃Sn₂S₂–₅ samples by Ref. 22, a slightly S-deficient condition is favorable for obtaining this ideal saturation magnetization. Therefore, the observation of 0.3 \( \mu_0 M / \rho \) in the slightly S-excess film (Co₃.₅Sn₂.₅S₂.₂) implies the different influence of sulfur off-stoichiometry on the magnetic properties in the film. The compositional dependence of the magnetic properties in Co–Sn–S films will be reported elsewhere. As shown in Fig. 3(b), the ferromagnetic transition is also observed as a kink in longitudinal electrical resistivity \( \rho_{xx} \). Figure 3(c) shows the \( T \) dependence of transverse Hall resistivity \( \rho_{yx} \) measured under \( \mu_0 H = 1 \) T. It is seen that \( \rho_{yx} \) increases below \( T_C \) and begins to decrease across the peak around 140 K. In Fig. 3(d), the tangent of Hall angle, \( \sigma_{yx} / \sigma_{xx} \), is plotted, where \( \sigma_{xx} \) and \( \sigma_{xy} \) are longitudinal electrical conductivity and transverse Hall conductivity given by \( \sigma_{xx} = \rho_{xx} / \rho_{xx} + \rho_{xx} \) and \( \sigma_{xy} = \rho_{xx} / \rho_{xx} + \rho_{xx} \), respectively (see Fig. S2 for the \( \rho_{xx} \) data at 1 T). The tangent of Hall angle reaches 0.20 at \( T = 130 \) K. Overall, these results are in excellent agreement with the bulk single-crystal behavior. \(^{6,7} \)

Figures 4(a) and 4(b) show \( \rho_{yx} \) and \( M_z \) versus \( \mu_0 H \) curves in an out-of-plane magnetic field, respectively. The clear hysteresis loops indicate that the easy magnetization axis is the out-of-plane \( c \)-axis direction; the coercive field \( \mu_0 H_c \) is comparable between \( \rho_{yx} \) and \( M_z \). Indeed, \( \mu_0 H_c \) is found to exceed 1 T at \( T = 150 \) K and further increase to about 5 T at

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$T = 100 \text{ K}$, two orders of magnitude larger than the bulk $\mu_0H_c$ of the order of 10 mT.\textsuperscript{6,7} This suggests that the dominant mechanism of magnetization reversal in the Co$_3$Sn$_2$S$_2$ film is different from that in the bulk. To gain insight into the magnetization process in the film, we measured the angular dependence of $\mu_0H_c$ at $T = 150 \text{ K}$, shown in Fig. 4(c). The measurement $T$ of 150 K was selected for tracking completely the enlargement of the $\mu_0H_c$ within our measurement limit of ±9 T. As depicted in the inset of Fig. 4(d), the magnetic field was applied to a direction tilted by $\theta_0$ to the $y$-direction from the normal of the film plane. At the regular AHE geometry ($\theta_0 = 0^\circ$), $\mu_0H_c$ is about 1.5 T, as indicated by the filled black circles in Fig. 4(c). With increasing $\theta_0$, $\mu_0H_c$ increases gradually. As summarized in Fig. 4(d), the $\theta_0$ dependence of $\mu_0H_c$ (normalized by $\mu_0H_c$ at $\theta_0 = 0^\circ$) obeys roughly the $1/\cos\theta_0$ function, which is characteristic of the magnetization reversal process governed by domain wall motion.\textsuperscript{25} Given the dominant role of domain wall motion, the increase of $\mu_0H_c$ at large $\theta_0$ is explained by the effective decrease in the projective component of the magnetic field along the out-of-plane direction ($\mu_0H \times \cos\theta_0$). For a comprehensive understanding of the large $\mu_0H_c$, it will be important to observe directly the domain nucleation and propagation processes by magnetic imaging techniques such as magnetic force microscopy.

In summary, we have fabricated thin films of the magnetic Weyl semimetal candidate Co$_3$Sn$_2$S$_2$ using the co-sputtering technique. By utilizing a sulfur-rich SnS$_{1.5}$ target, we achieved nearly stoichiometric Co$_3$Sn$_2$S$_2$ films with ferromagnetic behavior similar to that recently reported for the bulk single crystals.\textsuperscript{6,7} This study provides a platform for experiments on the electric field effect and quantum transport phenomena in Co$_3$Sn$_2$S$_2$ ultrathin films.\textsuperscript{10} In addition, the half-metallic properties of Co$_3$Sn$_2$S$_2$ could be useful in spintronics devices. These new challenges using Co$_3$Sn$_2$S$_2$ films will accelerate basic research and its applications as a magnetic Weyl semimetal candidate.

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**ORCID iDs** Kohei Fujiwara https://orcid.org/0000-0002-2164-2462

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