Study of the effect of annealing on the properties of Mn$_2$Ru$_x$Ga thin films

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Abstract—The effect of vacuum annealing thin films of the compensated ferrimagnetic half-metal Mn$_2$Ru$_x$Ga at temperatures from 250°C to 400°C is investigated. The 39.3 nm films deposited on (100) MgO substrates exhibit perpendicular magnetic anisotropy due to a small ∼ 1 % tetragonal elongation induced by substrate strain. The main change on annealing is a modification in the compensation temperature $T_{comp}$, which first increases from 50 K for the as-deposited film to 185 K after annealing at 250°C, and then falls to 140 K after annealing at 400°C. There are minor changes in the atomic order, coercivity, resistivity and anomalous Hall effect (AHE), but the net magnetization measured by SQUID magnetometry with the field applied in-plane or perpendicular-to-the-plane changes more significantly. It saturates at 20 kA·m$^{-1}$ to 30 kA·m$^{-1}$ at room temperature, and a small soft component is seen in the perpendicular SQUID loops which is absent in the square AHE hysteresis loops. This is explained by the half-metallic nature of the compound; the AHE probes only the 4c Mn sublattice that provides the spin-polarized electrons at the Fermi level, whereas the SQUID measures the sum of the oppositely-aligned 4c and 4a sublattice magnetisations.

I. INTRODUCTION

A dream material for spintronics would have low or zero spontaneous magnetization $M_s$, produce no stray fields but be 100 % spin polarised. This useful combination is possible in a fully compensated half metallic ferrimagnet, or a zero-moment half metal (ZHM). Such a material was envisaged by de Groot in 1983 [1] (he called it a half-metallic antiferromagnet, although the two sublattices cannot be crystallographically equivalent), but the first example Mn$_2$Ru$_x$Ga (MRG) was only discovered experimentally in 2014 [2].

In the solid solution between the ferrimagnetic end members Mn$_2$Ga and Mn$_2$RuGa, the extrapolated MRG net moment is found to change sign at $T = 0$ at $x = 0.5$, which corresponds to 21 valence electrons in the cubic L2$_1$ Heusler structure [2–5], as shown in Fig. 1. This demonstration opened a new field of spin electronics with no net moment, with potential applications in high frequency oscillators and spin-torque devices [6–11]. If MRG is to be integrated into a device manufactured using silicon-based CMOS technology, the MRG layer will have to be able to survive the relevant processing conditions without modification of properties, and must be smooth. A major concern is the potential diffusion of elements in and from the MRG layer [12]. It is also important to understand how the properties of MRG may change due to the annealing at various temperatures. More fundamentally, there is an opportunity to examine the relation between the net magnetization $M$ and Hall resistivity $\rho_{xy}$ for one sublattice in a half-metallic ferrimagnet [2]. Here we investigate the effect of magnetic annealing on the properties of the thin films of Mn$_2$Ru$_0.7$Ga, in the as-deposited state, and annealed in vacuum at temperatures up to 400°C. Under post-deposition annealing the MRG is able to maintain the high-quality, as-deposited surface roughness.

II. METHODOLOGY

A. Sample preparation

An epitaxial thin film of MRG was grown by DC magnetron sputtering, using our Shamrock sputtering system, on a 25 x 25 mm$^2$ (100) MgO substrate. The film was co-sputtered in argon from two 75 mm targets of Mn$_2$Ga and Ru onto the substrate maintained at 380°C. The chosen composition was Mn$_2$Ru$_0.7$Ga, which exhibits compensation below room temperature [2–4]. The film was capped in situ with a 3 nm layer of AlO$_x$ deposited at room temperature in order to prevent oxidation. The large sample was diced into four equal squares, and smaller pieces for subsequent treatment and measurements.

Pieces of the thin film were annealed in a vacuum of 10$^{-6}$ mbar in a perpendicular magnetic field of 800 mT for one hour. The annealing temperatures chosen were 250°C, 300°C, 350°C and 400°C. Provided the annealing temperature is kept below 400°C, the L2$_1$ crystal structure of MRG is maintained and Mn diffusion out of the film is minimized [13].
B. Structural properties

A Bruker D8 X-ray diffractometer with a copper tube emitting Kα1 X-rays with wavelength 154.06 pm and a double-bounce Ge [220] monochromator was used to determine the diffraction patterns of the thin films. Low angle X-ray reflectivity was measured using a Panalytical X’Pert Pro diffractometer, and thickness was found by fitting the interference pattern using X’Pert Reflectivity software with a least square fit.

C. Electrical properties

Longitudinal and Hall Resistivity were measured using the 4-point Van der Pauw method with indium contacts and an applied current of 5 mA.

D. Magnetic properties

Measurements of the magnetization with magnetic field applied perpendicular or parallel to the surface of the films was carried out using a 5 T Quantum Design SQUID. Hysteresis loops were measured in fields up to 5 T, at temperatures between 100 K and room temperature. These data were corrected for the diamagnetism of the substrate. Thermal scans in 30 mT after saturation of the magnetization at room temperature were used to determine the compensation temperatures of the annealed and unannealed films.

III. RESULTS

A. Structural Properties: Crystal Structure and Thickness

X-ray data on the films are shown in Fig. 2. Fitting the X-ray reflectivity in Fig. 2(a) gives a film thickness of 39.3 nm. There are no significant differences among four samples taken from different parts of the large film. The diffraction patterns in Fig. 2(b) of the as-deposited Mn2Ru0.7Ga film and samples annealed at 250 °C, 300 °C, 350 °C and 400 °C in the perpendicular magnetic field exhibit (002) and (004) reflections from the MRG, together with peaks from the MgO substrate. There are only small changes in the relative (002) and (004) peak intensities (I(002))/I(004) on annealing, in the range 0.11 to 0.14 (TABLE I). This small value is indicative of a high degree of atomic order in the L21 Heusler structure [3]. The broadening of the (002) reflection is consistent with the measured MRG film thickness. Peak shifts on annealing are very small, and the c parameter of 604.2 pm decreases by only about 0.6 pm (TABLE I).

A reciprocal space map of the as-deposited film, Fig. 2(a), confirms the c parameter, and shows a distribution of a parameters around the central value of 595.8 pm, which corresponds to that of MgO, to 604 pm. The map for the film annealed at 400 °C is very similar (Fig. 2(b)), showing that the crystal structure is practically unchanged by annealing. The ~1 % substrate-induced tetragonal expansion of the cubic L21 cell is responsible for the perpendicular magnetic anisotropy of the films.

B. Electrical Properties: Resistivity and Hall Angle

For Mn2Ru0.7Ga films, the calculated longitudinal ρ∥, and anomalous Hall ρ⊥ resistivity values show no significant variation on annealing. The Hall angle was 3.4%, and did not vary significantly from sample to sample. The almost perfectly-square anomalous Hall loops are shown in Fig. 3 where the coercivity is close to 450 mT, regardless of annealing temperature.

C. Magnetic properties

The compensation temperature of MRG is determined from thermal scans of the remanence after saturating in 5 T at room temperature and scanning in a small field of 30 mT, performed on three of the samples which are as-deposited MRG and MRG annealed at 250 °C and 400 °C. Data in Fig. 4 shows a compensation temperature Tcomp of about 50 K for the as-deposited, unannealed sample. There is a large Curie-law upturn coming from a few ppm of Fe2+ in the MgO substrate and the magnetization of the film therefore does not cross zero. Compensation shifts to 185 K for a sample annealed at 250 °C, and is at 140 K in the sample annealed at 400 °C (TABLE I).

Since the measurements are performed in a small magnetic field, it is expected that the small diamagnetic contribution may lead to an overestimation of Tcomp. The magnetic moment of the substrate was found to be about −24.5 pA · m² and the shift in Tcomp due to this moment is about 0.15 K, which is negligible.

In the room-temperature SQUID measurements (Fig. 5), the as-deposited sample exhibits a square perpendicular hysteresis loop with coercivity of 466 mT, but with clear signs of an easily-saturating component which was not seen in the AHE data of Fig. 4. The parallel magnetization also shows a small, easily-saturated in-plane component and the net magnetization approaches saturation in fields of order 5 T. The magnetocrystalline anisotropy constant Kn is given by Kn = 1/2μ0HsMs where μ0 is the permeability in vacuum, Hs is the anisotropy field and Ms is saturation magnetisation. Assuming an anisotropy field of 5 T and a net magnetization of 20 kA · m⁻¹, we find Kn to be 50 kJ · m⁻³. After annealing at 250 °C, the coercivity decreases and the hysteresis is squarer, although the shape of the loop changes with temperature. The easily-saturated component is larger and appears in the perpendicular loops of the films annealed.
Fig. 3. RSM of MgO (113) peak and (a) as-deposited MRG (204) peak and (b) MRG annealed at $T_a = 400^\circ$C peak. The lattice parameters are calculated with respect to the MRG unit cell.

Fig. 4. Anomalous Hall effect in MRG annealed at various temperatures. The data have been vertically centered.

Fig. 5. Temperature dependence of moment, measured at remanence (small applied field of 30 mT) of as-deposited MRG and MRG annealed at 250°C and 400°C.

| $T_a$ (°C) | $I_{\text{comp}}$ ($\mu$A) | $H_c$ (mT) | $H_{\text{AHE}}$ (mT) | $H_{\text{AHE}}/H_c$ | $T_{\text{comp}}$ (K) |
|-----------|-------------------|----------|-----------------|-----------------|-----------------|
| -         | 0.140             | 604.1    | 466             | 485             | 1.04            | 50              |
| 250       | 0.143             | 604.4    | 413             | 495             | 1.20            | 185             |
| 300       | 0.119             | 603.6    | 406             | 441             | 1.09            | -               |
| 350       | 0.145             | 603.8    | 432             | 475             | 1.10            | -               |
| 400       | 0.119             | 603.6    | 265             | 434, 207$^a$    | 1.64            | 140             |

$^a$After saturation in 5 T

at 300°C and 350°C, but vanishes in the film annealed at 400°C. There the coercivity is only 265 mT, or just over half of the original value, and strikingly different from that measured by AHE in smaller fields (TABLE I). The easily saturated in-plane component increases in magnitude with annealing, becoming almost equal to the out-of-plane moment.

The overall decrease in coercivity and the features of the hysteresis loops may be related to the variation in concentration of Ru across the thickness MRG film, with more Ru found closer to the capping layer as found by transmission electron microscopy [5]. This may contribute to the spread of $a$ in the reciprocal space maps.

IV. Discussion

Based on the X-ray results in Fig. 2(b), there seem to be only minor changes in the atomic order on annealing. However, it should be emphasized that the substrate temperature during deposition is 380°C, and the post-deposition annealing for an hour is mostly carried out at a lower temperature. The magnetic parameter most sensitive to annealing is $T_{\text{comp}}$. It is around 50 K in the as-deposited film, rising to 185 K after annealing at 250°C, and then falling back to 140 K. Since we are unlikely to significantly alter the Mn(4a) – Mn(4c) exchange coupling by annealing as the lattice parameters remain unchanged, these large variations in $T_{\text{comp}}$ must reflect small changes in manganese populations of the two sites. Initial annealing might be expected to modify the number of Ga/Mn(4a) antisites,
much as anisotropy. The compensation temperature can vary however by as <Ga or Ru atoms on the two different sites. The issue of the diffusion in the ferrimagnetic structure.

5 T closer to the coercivity, which exceeds that of the major loop (TABLE I). We must look for an explanation that is consistent with the near-compensated SQUID, which reflects the difference of the two sublattice moments, 5 T with the 4

is more complex and it reflects the misalignment of the 4a site moment detected by neutron diffraction [14]. The difference between the hysteresis measured by AHE (Fig. 4) and the sublattice magnetization (Fig. 4) is striking, especially in the different saturation fields in the two measurements, and if we measure the 4a (2b in the D0_22 structure) site moment detected by neutron diffraction [14]. The 4a (2b) site appears to have easy-cone anisotropy.

The difference in coercivity of the net magnetization (Fig. 3) and the 4c sublattice magnetization (Fig. 3) is striking, especially in the sample annealed at 400 °C. It must be pointed out that we have used different saturation fields in the two measurements, and if we measure the AHE loop in 5 T, we find a coercivity of 207 mT, which is closer to the 5 T SQUID result. It is unusual to find a minor loop coercivity, which exceeds that of the major loop (TABLE I). We must look for an explanation that is consistent with the near-compensated ferrimagnetic structure.

V. CONCLUSION

Our studies of the effects of annealing the compensated ferrimagnetic half metal have shown that the changes in lattice parameter are < 0.2 %, with minor modifications of the perpendicular anisotropy. The compensation temperature can vary however by as much as 130 K. Since T_{comp} depends on the balance between the two manganese sublattices, it is very sensitive to slight changes in site population due to redistribution of magnetic Mn and nonmagnetic Ga or Ru atoms on the two different sites. The issue of the diffusion is addressed elsewhere [12].

The 4c sublattice moment shows near-perfect square minor loops in the 1 T AHE measurements, but this does not persist after saturation in 5 T. The hysteresis of the net magnetization measured by SQUID, which reflects the difference of the two sublattice moments, is more complex and it reflects the misalignment of the 4a moment with the c axis. The minor changes in structure of MRG and its AHE measured in small fields bodes well for its use in devices annealed at temperatures up to 350 °C.

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