Journal of Magnetism and Magnetic Materials 421 (2017) 336–339

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Growth and characterization of $MnAu_2$ films

S.F. Cheng *, K.M. Bussmann

Naval Research Laboratory, Washington, DC, 20375 USA

ARTICLE INFO

Article history:
Received 26 February 2016
Received in revised form
12 May 2016
Accepted 2 August 2016

Keywords:
Helical spin
$MnAu_2$
Sputtered film
Structure

ABSTRACT

$MnAu_2$ films ranging from 60 to 200 nm thickness are deposited by co-sputtering from elemental targets. X-ray diffraction confirmed these films to be nearly single phase with tetragonal lattice parameters of $a=0.336$ nm and $c=0.872$ nm that compare well to the bulk values of $a=0.336$ nm and $c=0.876$ nm. The density of the films is analyzed using x-ray reflectivity to be 14.95 g/cm^3 and within experimental error of previously determined value of 15.00 g/cm^3. The films grown on c-plane sapphire, (100)MgO and (100) MgF_2 are randomly oriented polycrystalline, while the films grown on *a*-plane sapphire, (111)MgO and (111)Si/(0001)AlN showed that the (110) plane is parallel to the film plane and there are three sets of domains in equal amount differing by 60° in-plane rotation. Magnetic order is found to become paramagnetic near 360 K which is in close proximity to the bulk value. There are deviations in the slope of hysteresis loops observed at 10 K around 10 kOe that indicate complex magnetic switching.

1. Introduction

The tetragonal $MnAu_2$ intermetallic compound is of the $MoSi_2$ structural prototype and shows spiral magnetic ordering below 363 K [1]. Mn forms atomic planes separated by two layers of Au that propagate in the *c*-direction of the unit cell. Spins within a particular Mn atomic plane are aligned ferromagnetically but successive planes are rotated relative to each other forming a spin spiral along the c-axis. The rotation angle between consecutive Mn planes varies with temperature, from 60° at 5 K to 40° at 250 K [2]. Theoretical understanding of the spiral state is viewed as a competition between the short-range antiferromagnetic exchange and a long-range ferromagnetic interaction induced by the polarization of Au bands that result in the spiral state as most energetically favorable [3]. The helical spin structure can be overcome with the application of magnetic field to enforce ferromagnetic alignment. At room temperature, the helical spin structure can be transitioned to a fan like state at about 10 kOe and aligned in a ferromagnetic configuration at around 30 kOe [4].

A GMR value of about 10% at 300 K and 70 kOe was reported in bulk $MnAu_2$ as a result of the metamagnetic transition from a spiral to a ferromagnetic structure, making this material an interesting candidate for GMR devices [5]. The threshold magnetic field (H_{th}) of the metamagnetic transition can be reduced by alloying to render it more suitable for device applications. With 5 at% substitution of Fe for Mn, it displays a ferromagnetic behavior and no metamagnetic transition is observed between 10 and 300 K [6]. Cr substitution decreases the magnetic ordering temperature T_N, the threshold field H_{th}, and the helical angle [2]. However, for up to 15% of Cr substitution a metamagnetic transition is observed suggesting that the helical configuration remains the ground state. *Ab initio* calculations suggests two different kinds of metamagnetic phase transition for the Fe and Cr alloyed $MnAu_2$ [7]. Hydrostatic compression was found to lower H_{th} while increasing T_N in $MnAu_2$ [8]. The increase in T_N is explained as the result of pressure decreasing the distance between the Mn atoms that lie in the basal planes, leading to an increase in the in-plane ferromagnetic interaction and consequently the increase in T_N. The magnetic behavior of $MnAu_2$ is thus influenced by a complex matrix of magnetic field, temperature, alloy composition and pressure.

Most of the studies on this alloy system have focused on bulk, polycrystalline materials prepared by casting or melt-spinning [2,6]. Here we report the results of our work using dc magnetron sputtering to deposit $MnAu_2$ film onto a selection of substrates. Our goal is the growth of single phase $MnAu_2$ film with the tetragonal c-axis perpendicular to the film plane that allows for modulation of the spiral wavevector via strain or charge dosing mechanisms and for the development of low-power magnetoelectric control of non-volatile memory devices.

2. Experiments

All Mn–Au films were prepared using DC magnetron sputtering

* Corresponding author.
E-mail address: shufan.cheng.ctr@nrl.navy.mil (S.F. Cheng).

http://dx.doi.org/10.1016/j.jmmm.2016.08.007
0304-8853/

in an AJA International Inc. sputtering chamber with base pressure less than 3×10^{-8} Torr. The sputtering guns are in a confocal geometry with ~15° of incidence angle and ~15 cm of distance between substrate and the gun. The films were prepared by co-sputtering from Mn and Au targets and the composition was controlled by adjusting the sputtering power of the guns. Mn–Au films ranging from 60 to 200 nm thickness were deposited between 573 and 773 K at 3 m Torr of Ar gas pressure on single crystal substrates of c-Al_2O_3, a-Al_2O_3, (100)MgO, (111)MgO, (001) MgF_2 and PVDNC coated (0001)AlN on (111)Si, purchased from commercial sources. Fused silica and Si/Si_3N_4 substrates were also used to grow reference samples.

Surface ordering of the films was examined by RHEED in the sputtering chamber after growth. The alloy composition was characterized using the Thermo Scientific Quant'X x-ray fluorescence system. Phase analysis was done using x-ray diffraction with Cu radiation by a PANalytical Inc. X'Pert MRD. Film thickness and density was measured using x-ray reflectivity and structural and orientation information were determined using pole figure and rocking curve measurements. Magnetic properties were characterized using a MicroSense VSM up to 20 kOe and 413 K. Low temperature and high magnetic field measurements were performed using the Quantum Design MPMS SQUID-based magnetometer. Surface morphology and roughness were also characterized using Digital Instruments (Bruker) atomic force microscope.

3. Results and discussions

3.1. Characterization of crystal structure

The Mn–Au films were deposited onto varieties of substrates at elevated temperatures. The bottom curve in Fig. 1 shows a phase scan of a 200 nm Mn–Au film grown on fused silica at 773 K using the sputtering power of 22 and 76 W for Au and Mn respectively. The diffraction pattern confirms it as a randomly oriented polycrystalline film with a single phase of $MnAu_2$ with tetragonal lattice parameters of $a=0.336$ nm and $c=0.872$ nm. This is in good agreement with the bulk values of $a=0.336$ nm and $c=0.876$ nm [9]. The density of the films was analyzed using x-ray reflectivity to be 14.95 g/cm^3 and also agrees well with the previously determined x-ray density of 15.00 g/cm^3 [9]. The Mn–Au film grown on Si/Si_3N_4 substrate using the same deposition conditions showed similar x-ray results as that of on fused silica. Films ranging from Au-rich to Mn-rich were deposited at 773 K at 22 W power to the gold source and the Mn sputtering power varied between 62–84 W. Higher Au concentration causes the formation of a second phase of monoclinic Au_5Mn_2 while cubic (or nearly cubic) MnAu compound presents as the secondary phase for the Mn-rich films. Substrate temperature was found to have a small effect on the film composition caused by the variation of sticking coefficients and re-evaporation of sputtered species that could be compensated by adjustments to the sputter gun power.

Several single crystal substrates were used to grow textured films. MgF_2 was chosen for the proximity of the $MnAu_2$ a-parameter to MgF_2 $a/\sqrt{2}=0.327$ nm with the goal of obtaining c-axis texture. It was found, however, that $MnAu_2$ films grown on c-plane sapphire, (100)MgO and (100)MgF_2 resulted in polycrystalline order with little or no texture. In contrast, the $MnAu_2$ films on a-plane sapphire, (111)MgO and (111)Si/(0001)AlN were found to be highly (110) textured with the (110) parallel to the film plane. The top curve in Fig. 1 shows the diffraction pattern of a 190 nm $MnAu_2$ film grown at 673 K on (111)MgO. As can be seen, only the (111) and (222) peaks of MgO and (110) and (220) peaks of $MnAu_2$ are present. Higher growth temperature gives sharper lines in the RHEED patterns indicating better ordering but we chose to use

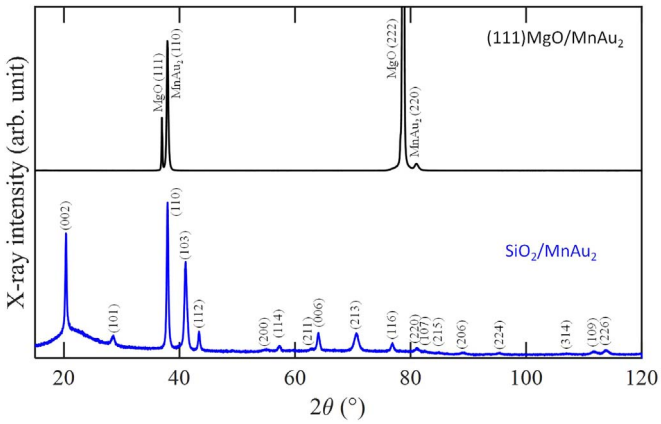

Fig. 1. The 2 theta–theta x-ray diffraction patterns (Cu Kα radiation) of the $MnAu_2$ film on fused silica substrate and on (111)MgO.

673 K as the growth temperature to avoid elemental evaporation. The rocking curve measurements using high resolution optics give full width half maximum (FWHM) of the $MnAu_2$ (110) peak as 2.29°, 2.30° and 2.60° on (111)MgO, c-AlN and a-Al_2O_3, respectively. The FWHM value for the substrates (111)MgO, (0002)AlN and (110)Al_2O_3 are measured for comparison as 0.0185°, 0.9607° and 0.0158°, respectively.

Fig. 2a–c shows the (200) pole figures of the $MnAu_2$ films deposited on (111)Si/c-AlN, (111) MgO and a-Al_2O_3. All three figures show six high intensity peaks 60° apart at 45° tilt from the axis normal to the film plane. For (110) oriented single crystal $MnAu_2$ film there should only be two diffraction spots for the (200) pole figures. We thus can conclude that all three films are highly (110) textured but they are short of being single crystal by having three sets of in-plane domains that differ by 60° rotation. Fig. 2d–f shows the (10 $\bar{1}$ 2) pole of AlN, (200) pole of MgO, and (30 $\bar{3}$ 0) pole of Al_2O_3. From those we can deduce the following orientation relationship: (110)$MnAu_2$//(0001)AlN and [1 $\bar{1}$ 0]$MnAu_2$//[0 $\bar{1}$ 10]AlN; (110)$MnAu_2$//(111)MgO and [1 $\bar{1}$ 0]$MnAu_2$//[$\bar{1}$1 2]MgO; (110) $MnAu_2$//(11 $\bar{1}$ 0)Al_2O_3 and [1 $\bar{1}$ 0]$MnAu_2$//[1 $\bar{1}$ 00]Al_2O_3.

3.2. Magnetic properties

Fig. 3a shows the M vs. T curves of a polycrystalline 190 nm $MnAu_2$ film on Si/Si_3N_4 substrate, measured from 5 to 300 K with the MPMS SQUID magnetometer at an applied field of 50 kOe and 3 kOe. The field direction is perpendicular to the film normal. The zero-field cooled 50 kOe curve shows only ferromagnetic characteristics, indicating that the film is fully polarized at this field and for this temperature range. At 3 kOe, the zero-field cooled M vs. T response shows a broad maximum near 240 K which indicates an antiferromagnetic behavior. Fig. 3b shows the M vs. T curves of a different piece of the same film measured using a VSM (allowing for higher temperature measurements) with the applied field of 10 kOe, 3 kOe and 300 Oe. We subtract the diamagnetic signal deriving from the sample rod and substrate from the data. We find that above room temperature, the magnetization decreases monotonically with increasing temperature and transition to a paramagnetic state near 360 K as expected from similar measurements on bulk samples [1].

Fig. 4 shows the M vs. H curves of the Si/Si_3N_4/190 nm $MnAu_2$ polycrystalline film at 10, 100 and 300 K measured by SQUID without background correction. The magnetic field direction is perpendicular to the film normal. The curve at 10 K did not show a sharp metamagnetic transition with applied field. However, it does show a small slope discontinuity at about 10 kOe. The saturation magnetization is calculated to be 22.3 emu g^{-1} at 10 K. The