Journal of Magnetism and Magnetic Materials 439 (2017) 236–244

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Research articles

Contribution from Ising domains overlapping out-of-plane to perpendicular magnetic anisotropy in Mn_4N thin films on MgO(001)

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ARTICLE INFO

Article history:
Received 18 January 2017
Received in revised form 17 February 2017
Accepted 26 March 2017
Available online 16 April 2017

Keywords:
Manganese anti-perovskite
Magnetic force microscopy
Molecular beam epitaxy
Perpendicular magnetic anisotropy

ABSTRACT

Single phase ε-Mn_4N thin and ultrathin films are grown on MgO(001) using molecular beam epitaxy. Reflection high-energy electron diffraction and *out-of-plane* X-ray diffraction measurements are taken for each sample in order to determine the *in-* and *out-of-plane* strain for each sample. Vibrating sample magnetometry and superconducting quantum interference device measurements, which are performed on the thin and ultrathin films respectively, are used to plot the magnetization of each sample versus both *in-* and *out-of-plane* $\vec{\mathbf{H}}$-fields and to determine the magnitude of perpendicular magnetic anisotropy in these films. Three significant components of perpendicular magnetic anisotropy are observed in these films and are attributed to sample strain (1 component) and shape (2 components). Among these components, the most significant component ($0.8-4.9\ \frac{\mathrm{Merg}}{\mathrm{cm}^3}$) is identified as a second term of shape anisotropy, which possesses a negative linear relationship with sample thickness over the range from 9 nm to 310 nm. Atomic (magnetic) force microscopy measurements show the presence of a surface localized magnetic polarization (22–82%), which increases with decreasing thickness, when the net magnetizations of the films are zero. The second term of shape anisotropy as well as the surface localized polarization, which each depend on sample thickness, are each regarded as a consequence of Ising domains overlapping *out-of-plane* in these films.

1. Introduction

Manganese anti-perovskites [Mn_3AX (A: transition metal or semiconducting element, X: N or C)] have shown a wide range of magnetic properties including spin-glass behavior, piezomagnetic effect, giant magnetoresistance, and magnetocaloric effect [1–4]. In particular, the Mn_3AX material ε-Mn_4N exhibits potential applications in dilute magnetic semiconductors, spin-injection contacts, magnetoresistive devices, microwave shielding, electrochemical capacitors, the synthesis of water-purifying catalysts and as a Cu diffusion barrier in silicon chip manufacturing [5–11]. This wide range of applications is supported by the many practical aspects of the material. These aspects of ε-Mn_4N include a high Néel temperature ($T_N = 738$ K) and temperature/chemical stability as well as suitability for growth on a myriad of substrates, such as technologically relevant semiconductors (Si and GaN) and metals (Cu and Al) [12–21]. One property of ε-Mn_4N [perpendicular magnetic anisotropy (PMA)] can be linked with three of the applications of ε-Mn_4N (spin-injection contacts, magnetoresistive devices, and microwave shielding) [7,22–24].

Initial studies into ε-Mn_4N PMA by Ching et al. indicate that grain size and strain both affect PMA [15–17]. Since then, multiple studies arguing that the strain term is the primary component of PMA in ε-Mn_4N have been put forward [7,19,24,25,29]. This is supported by the experimental and theoretical evidence that lattice distortions and temperature changes mediate transitions among many different types of magnetism (non-magnetic, multiple antiferromagnetic/ferrimagnetic orderings, and even mixtures of these types) in ε-Mn_4N [8,14,26–31]. This evidence indicates that strain has a significant role in the magnetic properties of ε-Mn_4N.

On the other hand, an association between columnar grain structure and PMA in ε-Mn_4N is found by Ching et al. [17] In addition, measurements from Yuping et al. demonstrate a strong dependence of magnetic permeability and microwave absorption on ε-Mn_4N grain size [23]. Together these two studies suggest that grain size, and therefore shape anisotropy, in addition to strain play an important role in the magnetic properties of ε-Mn_4N. For this reason, additional study of the effect of shape anisotropy on

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http://dx.doi.org/10.1016/j.jmmm.2017.03.079
0304-8853/

PMA in ε-Mn_4N while taking care to consider the effect of strain is of particular interest.

In this study, Mn_4N thin films of varying thickness (t = 9–310 nm) and tetragonal strain (differences between *out-of-* and *in-plane* Cauchy strain from 2.3×10^{-3} to -15.5×10^{-3}) are grown on MgO(001). The influence of strain and shape anisotropy on PMA are investigated for each sample and it is found that the shape is the most significant factor of PMA in each case. In addition, the strain component is found to have a significant contribution, which is 11–63% the size of the shape contribution, in each case. The focus on shape anisotropy leads to the consideration of two terms of shape anisotropy. Among these samples, the first term of the shape anisotropy, which is due to the energy of a single magnetic dipole, is responsible for an effect ranging only 5–6% the size of the total PMA. On the other hand, in these thin films a second order (dipole-dipole) term of shape anisotropy is found to be the most significant component of PMA. It is predicted that this second shape term is a significant component of PMA in films with t up to ~360 nm. This second shape term is found to be primarily due to the energy inherent in a domain shape attributed to a dipole-dipole interaction, which is mediated by the internal (molecular) magnetic fields produced by opposing Ising domains.

2. Procedure

All sample growths were performed in a custom designed ultra-high vacuum molecular beam epitaxy system [32]. Thin samples (#1 and #2), which were 310 ± 33 nm and 106 ± 12 nm thick respectively, were grown with the method outlined for high-purity ε-Mn_4N on MgO(001) growth in our previous work [6]. One or more annealing step(s) using a substrate temperature of 772 °C were used in addition to the previous method on the ultra-thin samples (#3 and #4), which were each 9 ± 1 nm thick.

Reflection high-energy diffraction (RHEED) is actively used *in situ* with a 20 keV incident electron beam energy in order to monitor surface structure as well as the lattice values parallel to the sample plane during growth. Lattice measurements based on the RHEED streak spacings are calibrated using the post-annealing MgO substrate streak spacings as a reference for each growth. *Out-of-plane* X-ray diffraction (XRD) measurements are taken *ex situ* using Cu K_α X-rays in order to determine the bulk crystal structure and the lattice values normal to the sample plane. A growth rate calibration is performed using Rutherford backscattering spectrometry (RBS) to determine Mn flux from the Mn deposition over time for one test sample. The thicknesses of samples #1 and #2 are known by using the same growth rate as the test sample for different known times. On the other hand, the thicknesses of #3 and #4 are determined individually using separate RBS measurements so that any Mn lost during annealing step(s) is accounted for.

Vibrating sample magnetometry (VSM) and superconducting quantum interference device (SQUID) measurements are performed on the thin and ultrathin films, respectively, in order to determine magnetic hysteresis, as well as the anisotropic magnetic field (H_K) and saturation magnetization (M_S). The diamagnetic signal from the MgO substrate is subtracted from the VSM or SQUID measurement for each sample using the VSM measurement of a blank MgO substrate as a reference.

Atomic (magnetic) force microscopy is performed using a Park Scientific CP AFM/MFM head retrofitted with a new controller system by Anfatec Inc., which is operated *ex situ* to obtain information about the topographical and magnetic properties of the sample. The magnetic polarization states in proximity to the surface of the samples are measured using MFM in a method similar to that of Park et al. [33] The magnetic polarization $\left(P = \frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow}\right)$ is determined for each sample by using the distributions of the magnetic contrast in MFM images of each sample as an approximation of the distribution of magnetization states in the sample. These distributions of magnetic contrast are normalized to the range of the distribution. Then, the relative number of states in the distribution above compared to below zero magnetic polarization is found and used to calculate $P = \frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow}$. A Fisher Scientifc FS60 Ultrasonic Cleaner was used to vibrate the samples for ~ 10 min intervals in order to remove any net magnetic polarization in the samples.

3. Results and discussion

3.1. Ultrathin ε-Mn_4N growth and strain control

The steps of growth, which involve annealing and regrowth, for samples (#3 and #4) can be followed in Fig. 1. The first two steps follow the method of our previous work by annealing an MgO(001) substrate [RHEED image shown in Fig. 1(a)] and then depositing a Mn_xN_y thin film [RHEED image shown in Fig. 1(b)] [6]. Thirdly, the sample is annealed at 772 °C, which is found to remove Mn_xN_y material from the sample while at the same time the Mn_xN_y is annealed towards a higher phase purity of ε-Mn_4N.

In the initial growth (first step) of samples #3 and #4, some undetermined Mn_xN_y phase and/or mix of Mn_xN_y phases, which cannot be identified from RHEED (the only *in situ* measurement available), are grown. Removal of some of the Mn_xN_y material is confirmed in RBS measurements, which find the finished samples to be thinner than expected based on the known Mn flux and total time of growth.

Among the phases of the Mn_xN_y system, 2× streaks are the unique signature for ε-Mn_4N [18]. Therefore, an increase in ε-Mn_4N phase purity is observed in the appearance of 2× streaks in Fig. 1(c) after an annealing step (second step) when there were previously no 2× streaks as in Fig. 1(b). Annealing from Mn_xN_y to ε-Mn_4N is in agreement with the observation of Suzuki et al., in which the tetragonal phases of the Mn_xN_y system could all be annealed into ε-Mn_4N [34].

The second step (annealing) is concluded just as inner first order streaks (4.21 Å) begin to reappear alongside the outer first order Mn_xN_y streaks (3.93 Å) along the MgO[100] direction as seen in Fig. 1(c). The spacing of the inner first order streaks matches the streak spacing of MgO[100] [18]. The outer first order streaks (3.93 Å) in Fig. 1(c) are identified as ε-Mn_4N streaks because of the signature 2× streaks corresponding to them.

In the third step (regrowth), high phase purity ε-Mn_4N is deposited to the desired t on what is expected to be a mostly ε-Mn_4N template at 641 °C for samples #3 and #4. High temperature annealing of Mn_xN_y thin films has the potential to introduce ζ-phase grains into the samples [6]. However, the high ε-Mn_4N phase purity of each finished sample (#1 through #4) is confirmed through the three methods established in our previous work; namely, a single set of 1st order streaks with corresponding bright 2× streaks along MgO[100] in RHEED as seen in Fig. 1(d), the presence of only the ε-Mn_4N peak among the known MgO substrate peaks (and no other significant peaks such as ζ peaks) in XRD as seen in Fig. 1(f)/(g), and the presence of a single uniform morphology with magnetic contrast throughout in AFM/MFM images [6].

In a previous study, if Mn_xN_y grains other than ε-Mn_4N were grown in the nucleation step, these Mn_xN_y grains would continue to grow alongside ε-Mn_4N grains when growth conditions favored ε-Mn_4N phase purity [6]. Therefore, it is expected that if the ultra-thin samples (#3 and #4) are grown on a template, which has Mn_xN_y phase grains alongside ε-Mn_4N grains, then Mn_xN_y grains would be present throughout the sample. However, the ε-Mn_4N phase purity of the samples has been confirmed by RHEED, XRD