Anomalous perpendicular magnetoanisotropy in Mn₄N films on Si(100)

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Ferrimagnetic Mn₄N films were deposited on Si (100) substrate by dc reactive magnetron sputtering from sintered Mn target. Highly (002) textured Mn₄N ordered phase is formed in situ at studied substrate temperatures of 150–250 °C without further annealing. Anomalous perpendicular magnetoanisotropy exists in these face-centered cubic films with larger coercivity measured perpendicular to the film (2000–3000 Oe) than that parallel (1100–1300 Oe), as is the remanence. Coercivity in either direction decreases, while the saturation flux density (from 240 to 610 G) increases with increasing substrate temperature. The anomalous perpendicular magnetoanisotropy is attributed to (1) the stress-induced anisotropy due to in-plane tensile stress coupled with a reverse magnetostriction, and (2) the shape anisotropy due to columnar grain structure.

I. INTRODUCTION

In 1932 Ochsenfeld observed that manganese takes up nitrogen at about 1100 °C and gives it off again at 1300–1320 °C, and that the nitrided product has a Curie point of about 500 °C, a coercive force, Hc, of 200 Oe, an intrinsic induction of 200 G under an applied field of 600 Oe, and a remanence, Br, of 110 G.1

Although there was an argument that Mn₄N is ferromagnetic,1,2 according to the result of neutron diffraction in 1962, the Mn₄N compound was identified to be a ferrimagnetic material,3 which can be formulated as Mn(II)₆Mn(II)₃. It crystallizes in a perovskite-derived structure ABX₃: A is Mn(I) at the corner position, B is N at the body center, and X is Mn(II) at face centers of the cubic cell. Mn(I) has a large moment (3.53 μB at 300 K) with antiparallel spin alignment with respect to Mn(II) (~0.89 μB at 300 K), leading to a ferrimagnetic order of the lattice with a total magnetization at 300 K of 0.86 μB per formula unit.3

It is arduous to synthesize Mn₄N powder by traditional ceramic processes, because it requires high temperature (>925 K), long reaction time (>200 h), and precise atmosphere control.3 However, through the assistance of technology like sputtering, it is possible to obtain such films much more easily, because high temperature phases could be successfully deposited at low substrate temperatures. On the other hand, Mn₄N films were rarely studied. One report studied Mn₄N films prepared by facing target reactive sputtering and obtained a film with saturation flux density of 510 G and coercivity of less than 900 Oe.5 It is interesting to investigate again other synthesis methods and magnetic properties of such films. In this study, Mn₄N films have been prepared by dc reactive magnetron sputtering at low substrate temperatures on Si (100) substrate. Structure and magnetic properties of the films were studied.

II. EXPERIMENT

The Mn₄N films were prepared by dc reactive magnetron sputtering from sintered Mn (99.9%) target. The substrates used were Si (100). The vacuum system was pumped to the base pressure of 5×10⁻⁷ Torr. Ultrahigh purity Ar and N₂ gases were first mixed at a ratio of 80:40 seem, and the total pressure during deposition was set at 3 mTorr, controlled by a needle valve. The substrate temperature was varied from 150 to 250 °C. Distance between the target and the substrate was 3.5 cm.

The resultant films were examined by x-ray diffractometry (XRD) using Cu-Kα radiation at a scanning speed of 1°/min for phase identification. Hysteresis loop both perpendicular and parallel to the film plane were measured at room temperature by using a vibrating sample magnetometer with a maximum applied field of 20 kOe. The sign of magnetostriction coefficient was measured by a strain gauge. Microstructure of the films was observed by means of a scanning electron microscope (SEM). Stress of the films was measured by a strain gauge. Microstructure of the films was observed by means of a scanning electron microscope (SEM).

![FIG. 1. X-ray diffraction patterns of as-deposited Mn₄N films at various substrate temperatures shown.](image)

### TABLE I. Magnetic properties of Mn₄N vs substrate temperature (Tₛ, in °C). S is the squareness ratio, Hₛ, in Oe, Bₛ, in G.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tₛ (°C)</th>
<th>Hₛ (Oe)</th>
<th>Bₛ (G)</th>
<th>S₁</th>
<th>S₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>150</td>
<td>1333</td>
<td>3048</td>
<td>240</td>
<td>0.40</td>
</tr>
<tr>
<td>A2</td>
<td>175</td>
<td>1143</td>
<td>2476</td>
<td>200</td>
<td>0.35</td>
</tr>
<tr>
<td>A3</td>
<td>225</td>
<td>1143</td>
<td>2381</td>
<td>530</td>
<td>0.38</td>
</tr>
<tr>
<td>A4</td>
<td>250</td>
<td>1153</td>
<td>2020</td>
<td>610</td>
<td>0.37</td>
</tr>
</tbody>
</table>

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FIG. 2. Hysteresis loops measured perpendicular (⊥) and parallel (∥) to the film plane of a Mn,N film deposited at 225 °C.

Measured by a film stress measurement apparatus (FSM). Thickness of the films was measured by means of a stylus method.

III. RESULTS AND DISCUSSION

Films of fixed 1.2 μm thickness, as monitored by ex situ thickness measurements, were deposited on Si (100) at substrate temperature (T_s) of 150, 175, 225, and 250 °C, respectively, with a controlled deposition rate of 27 nm/min. Figure 1 shows the XRD patterns of films deposited on Si(100) substrates. The films exhibit a strong Mn,N (002) texture with distinguishable (001) superlattice reflection. The degree of ordering, estimated from the peak height ratio between (001) and (002) diffractions, is practically the same for all T_s. There are contaminative phases, MnO and α-Mn. The amount of MnO increases with T_s due to higher oxidation tendency for α-Mn on the substrate with residual oxygen. While the amount of α-Mn decreases with increasing T_s due to oxidation.

Magnetic properties of the films are shown in Table I. For an fcc structure, large magnetic anisotropy is not usually anticipated. However, it is not true for the deposited Mn,N films. Comparing the hysteresis loops of the films measured parallel (∥) to the film plane with those perpendicular (⊥) (see Fig. 2) the perpendicular coercivity (H_c⊥) and remanence (B_r⊥), hence the perpendicular squareness (S⊥) are always much larger than H_c∥, B_r∥, and S∥, for all substrate temperatures (T_s). Specifically, H_c⊥ can be 1.8–2.3 times higher than H_c∥. Due to much higher He values and larger squareness ratio in the perpendicular direction, the films deposited on Si(100) show apparently perpendicular magnetic anisotropy. Also it is found that saturation flux density (B_s) increases with increasing T_s. The film deposited at 250 °C has a B_s of 610 G, which is 34% of the theoretical value (1770 G). This discrepancy should arise from impurity phases (e.g., Mn and MnO) embedded in the films.

By FSM measurement, it was found that films show in-plane tensile stress, which increases with increasing substrate temperature, as shown in Table II. Further, by measuring with a strain gauge bonded on the film, it was confirmed that films deposited on Si(100) at various substrate temperatures have negative magnetostriction coefficient λ in the film plane, as shown in Fig. 3. However, precise magnetostriction was not possible by this method. Magnetoelastic anisotropy constant Ku can be calculated by the following formula.

\[ Ku = -\frac{3}{2}λσ \]  

since σ of the films is positive, the reverse magnetostriction makes a positive Ku, that is the perpendicular magnetoanisotropy.

Besides, microstructure observation of the films by SEM, as shown in Fig. 4, reveals that films are in fact composed of columnar grain structure which gives rise to the shape anisotropy that is proportional to the square of saturation magnetization. For the grain shown in Fig. 4, the aspect ratio is estimated to be 5.6, giving rise to a shape anisotropy constant Ks of, assuming the grain structure is perfect having a theoretical saturation magnetization,

\[ Ks = (Na - Nc)M_s^2 = 1.1 \times 10^3 \text{ ergs/cm}^3. \]

TABLE II. The in-plane stress of the films vs substrate temperature (T_s, in °C).

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_s</th>
<th>Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>150</td>
<td>622</td>
</tr>
<tr>
<td>A2</td>
<td>175</td>
<td>648</td>
</tr>
<tr>
<td>A3</td>
<td>225</td>
<td>667</td>
</tr>
<tr>
<td>A4</td>
<td>250</td>
<td>730</td>
</tr>
</tbody>
</table>

FIG. 3. Typical magnetostriction vs applied field of a Mn,N film.

FIG. 4. A typical SEM micrograph of a Mn,N film showing cross-sectional view of the film structure.
The contribution of the shape anisotropy to coercivity would be as high as 760 Oe, which is within the reasonable increment range as comparing the perpendicular coercivity to that parallel.

IV. CONCLUDING REMARKS

(1) Ferrimagnetic Mn₄N films with ordered structure and (002) texture can be successfully deposited at low substrate temperatures from 150 to 250 °C by using dc magnetron reactive sputtering from sintered Mn target onto Si(100) substrate without any further annealing.

(2) Anomalous perpendicular anisotropy exists in these films. The coercivity measured perpendicular to the film plane (2000 to 3000 Oe) is 1.8–2.3 times that measured parallel. The perpendicular magnetoanisotropy is attributed to the combined effects of (a) the stress-induced anisotropy caused by in-plane tensile stress coupled with a reverse magnetostriction, and (b) the shape anisotropy caused by columnar grain structure.

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