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Magnetite (Fe₃O₄) is a popular magnetic oxide material that has been used in a great number of applications, including electric motors, electromagnets, transformers, video and audio adapters, magnetic inks, and biomedical agents. Moreover, in thin-film form it has recently attracted interest from the spintronics research field where its nearly half-metallic magnetoresistive structure is explored for spin injection into semiconductors and magnetoresistive structures. Films of Fe₃O₄ have been grown on MgO, Al₂O₃, Si, GaAs, and other substrates using various deposition techniques including molecular beam epitaxy, pulsed-laser deposition, rf and reactive dc magnetron sputtering, e-beam deposition, and ion beam deposition (IBD). The resulting magnetic properties vary considerably due to differences in crystalline texture, stoichiometry, surface morphology, film strain, and lattice defects. Another possible route to tailor the properties of Fe₃O₄ films is the use of a magnetic field during deposition. While this option has not been explored intensively, reports on magnetron-sputtered films indicate that relative modest fields of 30–35 mT can already modify the remanent magnetization and saturation field. This anomalous magnetic field effect does not drastically alter the crystalline texture of Fe₃O₄ on MgO(001), and thus the lattice mismatch between film and substrate is small. Consequently, it is impossible to detect the Fe₃O₄(004) reflection at an expected angle of 43.05° in a conventional θ-2θ x-ray diffraction scan as it overlaps with the more intense MgO(002) substrate peak at 42.90°. For this reason, x-ray diffraction analysis of Fe₃O₄ films on MgO(001) was conducted by tilting the sample at a ψ angle of 15.79°, which corresponds to the angle between the (001) and (115) lattice planes. In this configuration, unstrained Fe₃O₄ films exhibit a single (115) reflection at a 2θ angle of about 56.93°. Figure 1 shows a summary of the x-ray diffraction results on Fe₃O₄ films that were grown at different temperatures and with and without an external magnetic field. The measurements clearly demonstrate that the films are single crystalline. The position of the (115) reflection is shifted to higher angles (57.1°–57.4°) with respect to bulk Fe₃O₄ indicating compressive out-of-plane lattice strain in all films. The amount of lattice strain depends nonmonotonously on deposition temperature and it correlates with the variation in film thickness. The application of a 1 T magnetic field during film growth does not drastically alter the crystalline texture of Fe₃O₄ on MgO(001) as illustrated by the negligible changes in the position and width of the (115) reflection for each deposition temperature [black and red data in Fig. 1(b)]. The ψ scan of the (115) reflection exhibits four peaks of similar intensity which is typical for fully epitaxial films with an in-plane out-of-plane lattice strain.
Fe₃O₄[100]/MgO[100] alignment. All films are gray metallic in color and their electrical resistivity corresponds closely to that of bulk Fe₃O₄ at room temperature.

Figure 1(d) shows selected scanning electron microscopy (SEM) images of Fe₃O₄ films on MgO(001). The film grown at 450 °C (not shown) is smooth and its surface consists of small particle aggregates with an average size of 25–35 nm. The films that were grown at 550 and 600 °C possess a similar surface morphology with slightly larger aggregates (40–50 nm). The application of a 1 T field during growth does not affect the Fe₃O₄ films grown below 550 °C, but slightly increases the surface roughness at 600 °C. We therefore conclude that the application of a 1 T magnetic field during PL MOCVD of Fe₃O₄ does not drastically modify the crystalline texture and the surface morphology.

The magnetic properties of the films were measured using a superconducting quantum interference device (SQUID). Magnetic characterization of the Fe₃O₄ films was carried out at 300 K in a maximum in-plane magnetic field of 1 T. The hysteresis curve of some of the Fe₃O₄/MgO(001) samples was also measured in an out-of-plane magnetic field. The magnetic properties are summarized in Table I and SQUID results for films that were grown at 550 °C are shown in Fig. 2. The magnetic hysteresis curves of Fe₃O₄ films on MgO(001) are rounded and tilted and the remanent and saturation magnetization are small if no magnetic field is used. The application of a 1 T field during film growth drastically alters the magnetic response of the films. The largest effects are obtained at a deposition temperature of 550 and 600 °C where the saturation magnetization increases by 150%–220% and the enhancement of the remanent magnetization is even larger. The saturation magnetization for the film grown at 600 °C is 457×10⁴ A/m, which is close to the Fe₃O₄ bulk value of 471×10⁴ A/m. The magnitude of the field-induced modifications is unprecedented and somewhat surprising as they do not correlate with clear changes in crystalline texture, surface morphology, and film thickness. To test if an enhancement of film magnetization is only obtained during Fe₃O₄ film growth, we also grew some films without applied magnetic field and subsequently cooled them down to room temperature in 1 T. In this case, a much smaller increase in the remanent and saturation magnetization is observed as illustrated by the triangles in Fig. 2 for a deposition temperature of 550 °C. This clearly demonstrates that field-induced changes in the magnetic properties are only partly thermally activated after deposition and thus depend mostly on alterations during the PL MOCVD growth process.

The large influence of deposition temperature and applied magnetic field indicates a significant modification of the magnetic microstructure. Other studies on Fe₃O₄/MgO(001) have shown that the magnetic response is strongly influenced by the formation of antiphase boundary

Table I. Summary of magnetic properties of PL MOCVD-grown Fe₃O₄ films on MgO(001).

<table>
<thead>
<tr>
<th>Deposition temperature</th>
<th>Mₛ (10⁴ A/m)</th>
<th>Mₘ (10⁴ A/m)</th>
<th>μ₀Hₘ (mT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450, 0 T</td>
<td>82</td>
<td>35</td>
<td>10.0</td>
</tr>
<tr>
<td>450, 1 T</td>
<td>107</td>
<td>48</td>
<td>10.0</td>
</tr>
<tr>
<td>500, 0 T</td>
<td>166</td>
<td>102 (25.1</td>
<td>8.3 (18.5)</td>
</tr>
<tr>
<td>500, cool down 1 T</td>
<td>159</td>
<td>94 (27.1</td>
<td>14.5 (22.0)</td>
</tr>
<tr>
<td>500, 1 T</td>
<td>181</td>
<td>115 (33.1</td>
<td>12.0 (21.0)</td>
</tr>
<tr>
<td>550, 0 T</td>
<td>191</td>
<td>26 (35.1</td>
<td>4.7 (13.0)</td>
</tr>
<tr>
<td>550, cool down 1 T</td>
<td>233</td>
<td>52</td>
<td>9.0</td>
</tr>
<tr>
<td>550, 1 T</td>
<td>430</td>
<td>161 (124.1</td>
<td>11.8 (18.5)</td>
</tr>
<tr>
<td>600, 0 T</td>
<td>296</td>
<td>32 (59.1</td>
<td>5.2 (15.3)</td>
</tr>
<tr>
<td>600, 1 T</td>
<td>457</td>
<td>70 (47.1</td>
<td>3.5 (6.0)</td>
</tr>
</tbody>
</table>

FIG. 2. (Color online) (a) In-plane and (b) out-of-plane hysteresis curves of Fe₃O₄ films grown at 550 °C without (squares) and with (squares) an external magnetic field of 1 T. The triangles illustrate the effect of cooling in a 1 T field. The insets show a magnification of the same data for small magnetic field.
(APB) networks.\textsuperscript{6,8,14,15} APBs form during the initial stages of film growth when neighboring islands with different Fe$_3$O$_4$ symmetry coalesce. Coupling across APBs has been found to vary from ferromagnetic to antiferromagnetic and this can lead to highly complicated magnetic behavior including local out-of-plane moments, superparamagnetism, reduced film magnetization, and saturation fields that can be two orders of magnitude larger than the anisotropy field of bulk Fe$_3$O$_4$. Figure 3 shows plan view transmission electron microscopy (TEM) images of a Fe$_3$O$_4$ film that was grown without magnetic field and subsequently cooled in 1 T (left) and a film that was grown and cooled in 1 T magnetic field (right). The magnetic response of these films corresponds to the triangles and squares curves in Fig. 3(a), respectively. The main TEM images of Fig. 3 were recorded near the [001] direction using dark field contrast and the (220) reflection. Under these conditions, APBs with out-of-plane shift vectors of the $a/2[011]$ type are imaged as dark bands. Obviously, the Fe$_3$O$_4$ film that was grown without an external magnetic field exhibits a high density of APBs with irregular shapes. The domain size varies from a few nanometers to about 30 nm and this closely mimics results on magnetron-sputtered Fe$_3$O$_4$ films.\textsuperscript{14,15} The application of a 1 T magnetic field during the PI MOCVD growth process drastically reduces the formation of APBs and this results in domains of about 50–100 nm. Moreover, the APBs now coexist with a network of lattice dislocations. This is particularly clear in the inset of Fig. 3, which shows an area with a high density of lattice dislocations and no APBs. TEM analysis of this sample therefore suggests that lattice dislocations are formed because strain relaxation via APBs is no longer sufficient. This contrasts with the results on Fe$_3$O$_4$ films that are grown without magnetic field. In the latter case, a dense network of APBs accommodates most of the film stress.

The TEM images of Fig. 3 provide a possible explanation for the anomalous magnetic field effects during Fe$_3$O$_4$ film growth. If no field is applied during PI MOCVD, many APBs are formed. Magnetic coupling across the APBs is disturbed and this leads to a complicated magnetic microstructure and reduced film magnetization. Growth in a 1 T external magnetic field, on the other hand, suppresses the formation of APBs. As a result, the magnetic microstructure is more uniform and the saturation magnetization approaches the Fe$_3$O$_4$ bulk value.

In conclusion, we have demonstrated that high-quality Fe$_3$O$_4$ films can be successfully grown using a single-step PI MOCVD growth process with a Fe(tmhd)$_3$ precursor. As one of the main results, it was shown that the application of a 1 T magnetic field during Fe$_3$O$_4$ film growth significantly alters the magnetic properties without major changes in crystalline texture, surface morphology, and film thickness. This anomalous behavior is explained by a reduction in APBs as illustrated by TEM analysis. The ability to improve the magnetic properties by an effective suppression of APB formation during Fe$_3$O$_4$ growth opens up new approaches toward the fabrication of functional thin magnetic films in external magnetic field.

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