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Increasing spin polarization in Fe$_3$O$_4$ films by engineering antiphase boundary densities

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We present a systematical study on the evolution of antiphase boundary (APB) densities in Fe$_3$O$_4$ films, which were prepared by pulsed laser deposition and post annealing at different temperatures. By measuring the electron-phonon coupling parameter and using Allen’s formula, we evaluate the films’ antiphase boundary densities, which show a decreasing tendency with increasing annealing temperature. Consequently, a 50% increase of spin polarization in Fe$_3$O$_4$ films is achieved, and a 110% increase of the magnetoresistance ratio was found in 900°C annealed Fe$_3$O$_4$ films compared to the as-grown sample. This work could contribute to the effective manipulation of APB densities and spin polarization in Fe$_3$O$_4$ films, which is desirable for the application of spintronics devices based on Fe$_3$O$_4$ films. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4979586]

The complex and intriguing properties of half metallic magnetite (Fe$_3$O$_4$), especially on the nanoscale, have attracted tremendous attention in both fundamental physics and practical applications of spintronics.$^{1–3}$ The theoretical 100% spin polarization at the Fermi level and appropriate conductivity enable Fe$_3$O$_4$ to be an ideal spin source for semiconductors, benefiting the integration into modern information technologies to realize the next generation spintronics devices such as spin field effect transistors (SFETs).$^{4,5}$ More importantly, the high Curie temperature of Fe$_3$O$_4$ is desirable in room temperature spintronics applications and advantageous compared with other half metallic materials such as La$_{0.5}$Sr$_{0.5}$MnO$_3$.$^6$ These fascinating properties have triggered intensive studies on Fe$_3$O$_4$ in the past few decades, and various spin dependent effects such as the spin Seebeck effect,$^7$ spin filtering effect,$^8$ and gate voltage-induced phase transition$^9$ have been exploited.

However, some spin transport properties of Fe$_3$O$_4$, which are critical for the application of Fe$_3$O$_4$ in spintronics, are still under controversy. For instance, the experimentally reported magnetoresistance (MR) data are quite inconsistent, and the spin polarizations determined from MR measurements are much lower than that of the theoretical prediction.$^{10}$ Recent works indicate that the MR in Fe$_3$O$_4$ films is associated with the relative spin orientation between adjacent nanograins, and film defects such as antiphase boundaries (APBs) might be the main factor for the reduced spin polarization in Fe$_3$O$_4$.$^2$ It is suggested that APBs induce an antiferromagnetic coupling between adjacent structure domains, thereby affecting the electrical and magnetic properties of the films immensely.$^{11}$ However, owing to the atomic scale structure of APBs, the precise manipulation and determination of APB densities are still challenging, and detailed experimental evidence which links the evolution of APBs to the change of spin polarization in Fe$_3$O$_4$ films is needed.

In this paper, we demonstrate that the APBs in Fe$_3$O$_4$ films can be dramatically decreased by a post annealing process, which prominently enhances the MR and gives rise to an increased spin polarization by 50% in Fe$_3$O$_4$. The evolution of APBs in Fe$_3$O$_4$ films was investigated by evaluating the electron-phonon coupling parameter from Lorentzian fitting of Raman modes. The MR measurements were performed in a four-point-probe configuration and they verified the enhancement of spin polarization in annealed Fe$_3$O$_4$ films. Furthermore, the evolution of structure, morphology, and magnetostatic properties of the Fe$_3$O$_4$ films is also discussed.

As-grown Fe$_3$O$_4$ thin films were prepared on a Si (100) substrate using an Fe$_2$O$_3$ target in a pulsed laser deposition (PLD) system. Before deposition, the Si (100) substrate was chemically cleaned successively with acetone, ethanol, and distilled water in an ultrasonic bath to remove impurities. Fe$_3$O$_4$ films were deposited on the surface-treated substrate at a substrate temperature of 600°C with a base pressure of 2.0 × 10$^{-4}$Pa. The pulse repetition rate was adjusted at 10 Hz, and 5000 laser pulses with a pulse energy of 300 mJ were utilized to grow 50 nm thick films. To investigate the evolution of APB defects, two of the prepared Fe$_3$O$_4$ films were annealed for 1 h in the same vacuum chamber at temperatures of 750°C and 900°C, respectively.

Fig. 1(a) shows the X-ray diffraction (XRD) patterns of as-grown and annealed Fe$_3$O$_4$ films at different annealing temperatures, where only diffraction peaks of the {111} crystallographic planes are detected, indicating the oriented growth of these films. Furthermore, the full width at half maximum (FWHM) of the diffraction peak is significantly decreased by annealing treatment, manifesting the growth of nanograins in annealed samples.

Fig. 1(b) shows the Raman spectra of as-grown and annealed Fe$_3$O$_4$ films in the spectral range of 100–900 cm$^{-1}$. We observed three modes in the spectra: the strongest A$_{1g}$ mode, T$_{2g}$ (2) mode, and T$_{2g}$ (3) mode for all films. It should...
be noted that the mode positions for all samples (see Table I) are close to those of pure Fe₃O₄ films reported previously, which can be readily distinguished from maghemite ones at 720, 500, and 350 cm⁻¹.¹² The result indicates that the Fe₃O₄ phase can still be maintained even if the films were vacuum annealed at a temperature of 900 °C.

In the Fe₃O₄ system, the structural property and the electronic property are relevant to the A₁g mode (symmetric stretch of oxygen atoms along the Fe-O bond) and T₂g mode (symmetric and asymmetric bending of oxygen with respect to Fe), respectively.¹³ It has been reported that the presence of APBs would affect the local electric network, thereby giving rise to an increased electron-phonon coupling parameter (λ), which can be estimated from the measured linewidths and peak positions of the Raman modes.¹¹,¹³ In Figs. 1(c) and 1(d), we fitted the A₁g and T₂g(3) modes, respectively, with Lorentzian line shapes, and the fitted line shape parameters are given in Table I. Using Allen’s formula, for an mth phonon, the FWHM (Γₘ/ω) and frequency (ω) of a Raman mode are related as¹⁴

\[
\Gamma_m/\omega^2 = \left(\frac{2\pi}{\hbar g_m}\right)\lambda_m N(E_F),
\]

where g_m is the degeneracy of the mth mode and N(E_F) is the density of states at the Fermi level. The calculated value of N(E_F) = 3 states/eV per Fe at room temperature is used to estimate λ. For the A₁g mode, the values of the calculated λ are almost constant, indicating a similar structure for all samples. As for the T₂g(3) mode, we observe a distinct decrease of calculated λ from 0.81 to 0.52 due to the annealing treatment of the Fe₃O₄ film, and the calculated value of λ ~ 0.52 for the 900 °C annealed Fe₃O₄ film is close to the bulk value (λ ~ 0.5) of magnetite, indicating the effective reduction of APBs in the Fe₃O₄ film.

Figure 2 shows the atomic force microscopy (AFM) and magnetic force microscopy (MFM) images of the films. A smooth surface is observed in the as-grown Fe₃O₄ film consisting of fine grains, as shown in Fig. 2(a). However, rough surfaces composed of many bulged particles are observed in the annealed films, especially for the 900 °C annealed Fe₃O₄ film. The observed bulged particles could be the coalescence of nanograins during the annealing process as the high temperature can stimulate the migration of grain boundaries, thereby increasing the nanograin size in annealed films.¹⁵ In addition, the coefficient of thermal expansion mismatch between the substrate and film could also give rise to the

<table>
<thead>
<tr>
<th>Mode</th>
<th>A₁g</th>
<th>T₂g(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃O₄ films</td>
<td>ω (cm⁻¹)</td>
<td>Γ/ω (eV)⁻¹</td>
</tr>
<tr>
<td>As-grown</td>
<td>665.6</td>
<td>0.75</td>
</tr>
<tr>
<td>750 °C annealed</td>
<td>665.2</td>
<td>0.74</td>
</tr>
<tr>
<td>900 °C annealed</td>
<td>663.1</td>
<td>0.76</td>
</tr>
</tbody>
</table>
generation of bulged particles.\textsuperscript{16} The corresponding MFM images shown in Figs. 2(d)–2(f) demonstrate complex multi-domain configurations in all films. The magnetic contrast of the MFM images is slightly enhanced in the annealed Fe$_3$O$_4$ films, indicating probably a larger out-of-plane magnetization component,\textsuperscript{17} which is reasonable as the film normal corresponds to the [111] crystallographic orientation, i.e., the easy axis of magnetization in magnetocrystalline anisotropy of magnetite, and the enhanced (111) orientation for annealed films has been confirmed by XRD analysis.

The in-plane field dependences of the magnetization (M-H curves) for all samples were measured by using a vibrating sample magnetometer (VSM) at room temperature, as shown in Fig. 3(a). The saturation magnetization (Ms) and coercivity (Hc) for all samples were determined from the M-H curves, and both increase with increasing annealing temperature, as shown in Fig. 3(b). The increased saturation magnetization might be ascribed to the increase of Fe$^{2+}$ due to the induced oxygen deficiency in the vacuum annealing process, as net magnetic moment in Fe$_3$O$_4$ is mainly arising from Fe$^{2+}$. Moreover, the growth of nanograins in the annealed samples could also give rise to the increase of Ms and Hc.

Magneto-transport measurements of the Fe$_3$O$_4$ films were performed with current in plane geometry. We define MR as $\frac{\rho(H) - \rho(Hc)}{\rho(Hc)}$ as the maximum resistance occurs at the coercive field, where $\rho(H)$ and $\rho(Hc)$ are the resistances under the applied magnetic field and at the coercive field, respectively. The room temperature MR curves for the Fe$_3$O$_4$ films are shown in Fig. 3(c), which manifests a significant enhanced MR effect with increasing annealing temperature. The room temperature MR ratio of the 900°C annealed Fe$_3$O$_4$ film under a field of 10 kOe is around 3.2%, which is 2.1 times the value of the as-grown Fe$_3$O$_4$ film. Fig. 3(d) shows the temperature dependence of MR behaviors of our samples. It can be seen that the MR increases with decreasing temperature for all samples, and we ascribe this to the increased magnetic anisotropy with decreasing temperature.\textsuperscript{18}

As shown in Figs. 4(a)–4(c), the low-field butterfly shaped MR curves of all the samples follow the relation for a granular tunneling system described as $MR = A(M/MS)^2$, where $A$ is a constant and $M$ is the magnetic moment. The magnetic moment is proportional to the thickness of the film, and the coercivity is a function of the grain size and the anisotropy field. The in-plane field dependence of the magnetization (M-H curves) for all samples were measured by using a vibrating sample magnetometer (VSM) at room temperature, as shown in Fig. 3(a). The saturation magnetization (Ms) and coercivity (Hc) for all samples were determined from the M-H curves, and both increase with increasing annealing temperature, as shown in Fig. 3(b). The increased saturation magnetization might be ascribed to the increase of Fe$^{2+}$ due to the induced oxygen deficiency in the vacuum annealing process, as net magnetic moment in Fe$_3$O$_4$ is mainly arising from Fe$^{2+}$. Moreover, the growth of nanograins in the annealed samples could also give rise to the increase of Ms and Hc.

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where $A$ is the spin-dependent scattering coefficient, $M$ is the global magnetization, and $M_s$ is the saturation magnetization. The MR curves can be well fit by choosing $A = -0.8$, $-1.2$, and $-1.7$ for as-grown, 750°C, and 900°C annealed Fe$_3$O$_4$ films, indicating a typical granular tunneling conduction mechanism in all our films. Moreover, an unsaturated and linearly increased MR behavior at high fields can be observed for all samples. A similar phenomenon has also been reported in other Fe$_3$O$_4$ films and can be interpreted by a model of spin-polarized transport across atomically sharp APBs. Correspondingly, the observed unsaturated MR behavior at high fields might also indicate the presence of APBs in our films.

By calculation of $P$ from $MR = P^2/(1 + P^2)$ for the granular ferromagnets, spin polarizations ($P$) for the Fe$_3$O$_4$ films are obtained. As shown in Fig. 4(d), the temperature dependence of the spin polarization for all films manifests a similar behavior to that of MR. At 300 K, the spin polarization of the as-grown Fe$_3$O$_4$ film is only 12.3%, which is increased to 17.8% for the 900°C annealed sample. The deviation of spin polarization between the as-grown and annealed Fe$_3$O$_4$ films becomes more evident at low temperature, as the spin polarizations at 100 K for as-grown and 900°C annealed Fe$_3$O$_4$ films are 16.1% and 24.2%, respectively. Based on the aforementioned Raman analysis, we ascribe the enhanced MR and spin polarization in the annealed Fe$_3$O$_4$ film to the decreased APBs, as the electron-phonon coupling strength is reduced in the annealed Fe$_3$O$_4$ film. Although the spin polarization of annealed Fe$_3$O$_4$ films is significantly increased compared with that of the as-grown film and previous reports on Fe$_3$O$_4$ films, it is still far below the expected value of half metallic Fe$_3$O$_4$ (100%), especially at room temperature. The deterioration of spin polarization is partly due to the unsaturated MR effect even at 10 kOe, and the spin scattering at grain boundaries also weakens the MR effect, thereby reducing the spin polarization in Fe$_3$O$_4$ films.

In summary, we demonstrate that the spin polarization in Fe$_3$O$_4$ can be significantly increased by engineering APB densities in the films via a post annealing process. The evolution of APBs in Fe$_3$O$_4$ films was evaluated by estimating the electron-phonon coupling parameter ($\lambda$) from fitting the line shapes of Raman modes. We found that $\lambda$ was decreased with increasing annealing temperature, indicating the effective reduction of APBs in the Fe$_3$O$_4$ film. The influence of APB densities on the spin polarization of Fe$_3$O$_4$ films was investigated by magneto-transport property measurements, which verified that 50% increase of spin polarization can be achieved by reducing the APB density in Fe$_3$O$_4$ films. The results contribute to the understanding of MR and spin polarization related to APBs in Fe$_3$O$_4$ films and could be beneficial for the application of spintronics devices based on Fe$_3$O$_4$ films.

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