Magnetic and transport properties of epitaxial thin film MgFe₂O₄ grown on MgO (100) by molecular beam epitaxy

Han-Chun Wu¹,², Ozhet Mauit³, Cormac Ó Coileáin²,³, Askar Syrlybekov⁴, Abbas Khalid³, Anas Mouti², Mourad Abid², Hong-Zhou Zhang³, Mohamed Abid² & Igor V. Shvets³

¹School of Physics, Beijing Institute of Technology, Beijing, 100081, P. R. China, ²KSU-Aramco Center, King Saud University, Riyadh 11451, Saudi Arabia, ³CRANN, School of Physics, Trinity College, Dublin 2, Ireland.

Magnesium ferrite is a very important magnetic material due to its interesting magnetic and electrical properties and its chemical and thermal stability. Here we report on the magnetic and transport properties of epitaxial MgFe₂O₄ thin films grown on MgO (001) by molecular beam epitaxy. The structural properties and chemical composition of the MgFe₂O₄ films were characterized by X-Ray diffraction and X-Ray photoelectron spectroscopy, respectively. The nonsaturation of the magnetization in high magnetic fields observed for M (H) measurements and the linear negative magnetoresistance (MR) curves indicate the presence of anti-phase boundaries (APBs) in MgFe₂O₄. The presence of APBs was confirmed by transmission electron microscopy. Moreover, post annealing decreases the resistance and enhances the MR of the film, suggesting migration of the APBs. Our results may be valuable for the application of MgFe₂O₄ in spintronics.

Results
Sample preparation and characterization. MgFe₂O₄ thin films, with different thicknesses, were grown on (100) oriented MgO single crystal substrates in an oxygen–plasma-assisted molecular beam epitaxy (MBE) system. The base pressure of the system is better than 5 × 10⁻¹⁰ Torr. The substrates were chemically cleaned prior to insertion into the growth chamber and then cleaned in situ by annealing at 600°C in ultra-high vacuum.
(UHV) for 1/2 hour followed by further annealing in \(1 \times 10^{-3}\) Torr oxygen for 2 hours. Co-deposition was used to grow the thin films, i.e., material fluxes were produced by e-beam evaporation of separate pure MgO and metallic Fe sources. The growth rates for Fe and MgO were set to 0.6 Å/s and 0.3 Å/s, respectively. During growth, the substrate temperature was maintained at 300°C and the plasma source was operated with an oxygen partial pressure of \(2 \times 10^{-2}\) Torr and a current of 30 mA. After deposition, the samples were annealed at 300°C, with the same oxygen partial pressure, for 3 hours. Reflection high energy electron diffraction (RHEED) was employed to establish the growth mode. RHEED patterns for the MgO substrate and MgFe\(_2\)O\(_4\) thin films (Fig. 1a and 1b) show vertical lattice rods and sharp Kikuchi lines, representative of a well-ordered and smooth surface, demonstrating the epitaxial growth of the MgFe\(_2\)O\(_4\) films on MgO substrates. The structural properties and chemical composition were further investigated using a high resolution XRD system and XPS. Figure 1c shows the full range XRD, from 10 to 100 degrees, for a 114 nm thick MgFe\(_2\)O\(_4\) film on a MgO substrate. Only the (200) and (400) peaks for the MgO substrate and the (008) and (004) peaks for the MgFe\(_2\)O\(_4\) film are observed indicating the epitaxial growth of the MgFe\(_2\)O\(_4\). The peak positions for MgO (400) and MgFe\(_2\)O\(_4\) (008) located at 93.88° and 94.47° respectively, which are consistent with the well-established values. X-ray photoemission spectroscopy compositional analysis of the surface of the MgFe\(_2\)O\(_4\) film is shown in Figure 1d. The Mg 2p and Fe 3p peaks have been consistently energy shifted to align the C 1s peak position to a binding energy (BE) of 284.7 eV. The XPS characterization indicates the atomic ratio of Mg : Fe is around 1 : 2. To investigate the interface between MgO and MgFe\(_2\)O\(_4\), Figure 1e presents a low-magnification high angle angular dark field (HAADF) STEM image showing the whole thickness of a MgFe\(_2\)O\(_4\) thin film (bright) on a MgO substrate (dark). The interfaces are sharp and defect free which further confirms MgFe\(_2\)O\(_4\) films were epitaxially grown on the MgO substrates. A selected area electron diffraction (SAED) pattern of the interface between MgO and MgFe\(_2\)O\(_4\) is shown in Fig. 1f. The red circles highlight the SAED spots for
MgFe₂O₄ only and the blue circles highlight the SAED spots for the MgO and MgFe₂O₄. A small lattice mismatch is observed indicating the high quality of the epitaxial thin film.

**Magnetic and transport properties.** The magnetic properties of the MgFe₂O₄ thin films were investigated by means of a PPMS (Quantum Design). Temperature dependent M (H) loops of a 114 nm thick MgFe₂O₄ thin film are displayed in Fig. 2a. The external magnetic field is applied in the film plane along [100] direction. It is clear that the film is ferromagnetic in nature at all the temperatures. The coercivity increases with decreasing temperature. The measured magnetization at 300 K and at 1 T is around 115 emu/cm³, which is larger than the value reported for MgFe₂O₄ nano pillars but smaller than the value for MgFe₂O₄ grown on sapphire substrates. Interestingly, the magnetization does not saturate in a field of 1T for all temperatures. Figure 2b shows M (H) loops for the same 114 nm thick MgFe₂O₄ thin film measured at room temperature with the external magnetic field applied along [100] and [110] directions. A significant difference between the M (H) loops for the two field directions is clearly observed. At room temperature, for a 114 nm thick MgFe₂O₄ thin film, with the field along the [100] direction, the coercivity field is 127 Oe. While when the field is along the [110] direction, the coercivity field increases to 216 Oe. Moreover, the M (H) loop for the field along [110] is much squarer than for field applied along [100]. It is clear that the easy axis, for the films grown, is along the [110] direction and hard axis is along the [100] direction. Figure 3a shows the magnetoresistance curves of a 114 nm thick MgFe₂O₄ thin film on a MgO substrate measured at different temperatures, where MR is defined as MR = (R(H)/R(0) - 1. The transport properties of MgFe₂O₄ were measured using the conventional four-probe method in the PPMS (Inset of Fig. 3a). A bias current of 4 µA was applied between the two outer contact electrodes along the [100] direction of the MgO substrate and a Keithley 2400 was used to measure the voltage drop. The external field was applied along the current direction. From Figure 3a, one can clearly see that the resistance shows a linear response to the external field at all temperatures. The MR ratio as a function of temperature is summarized in Figure 3b. It should be noted that the MR ratio increases with decreasing temperature. A MR ratio of ~0.55% was obtained at room temperature and a MR of ~3% was achieved at 80K. We would like to mention here that the shape of the MR curves is independent of temperature.

**Discussion**

Presence of APBs. The observed very large saturation field and negative linear MR can be attributed to and explained by the presence of antiphase boundaries, which are natural defects occurring during growth. The existence of APBs has been verified in numerous systems, for example, magnetite on MgO substrates, Ba₀.₆Sr₀.₄TiO₃ on (001) MgO, Ba(Zr,Ti)O₃ on (001) MgO, and etc. The reported anti-phase boundaries in epitaxial Fe₃O₄ films grown on MgO substrates is a consequence of lattice parameter of Fe₃O₄ (8.397 Å) being almost twice of that of the MgO substrate (4.213 Å), and its spinel structure being of lower symmetry (Fd3m) than that of MgO (Fm3m). The presence of these APBs defects in Fe₃O₄ contributes to unusual magnetic and transport properties, such as the magnetization non-saturation even at very high field, super-paramagnetic behavior in Fe₃O₄ films, miscompensation of the spin moments at the surface and at the APBs contribute a giant magnetization, a greater MR response across the AF-APBs, and a large transversal MR. Similar to Fe₃O₄, MgFe₂O₄ has a lattice parameter of (8.38 Å) and its spinel structure is of lower symmetry (Fd3m).

---

**Figure 2** | (a) M (H) loops of a 114 nm thick MgFe₂O₄ film measured at different temperatures with an in-plane magnetic field applied along the [100] direction. (b) M (H) loops of a 114 nm thick MgFe₂O₄ film measured at room temperature with an in-plane magnetic field applied along the [100] and [110] directions.

**Figure 3** | (a) MR curves for a 114 nm thick MgFe₂O₄ film after annealing with oxygen for 3 hours, measured at different temperatures. The magnetic field is applied in the film plane along the [100] direction. Inset: Schematic drawing of the setup used to measure the MR. (b) MR ratio as a function of temperature under a field of 2T. Inset: Schematic drawing of spin structure disturbance due to an AF-APB with and without an in-plane external field.
symmetry (Fd-3m). Therefore APBs are expected to form during growth of MgFe$_2$O$_4$ on MgO. To confirm the existence of the APBs, we show in Figure 4a a dark field cross-sectional HRTEM image of a 114 nm MgFe$_2$O$_4$ thin film on a MgO substrate. Several APBs are clearly visible. To highlight their presence, some APB domains are marked with dotted blue lines. Notably, MgFe$_2$O$_4$ is a partially inverse spinel. Thus, the spin configuration for atoms separated across APBs will be in a non-collinear configuration which means the spin states will be at least partially antiparallel. Therefore, the observed very large saturation field and negative linear MR in MgFe$_2$O$_4$ can be explained by the presence of AF-APBs. APB induced MR has been also observed in Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ and Ba(Zr,Ti)O$_3$ films on MgO substrates. As can be done for Fe$_3$O$_4$, we schematically drew the spin structure disturbance due to the presence of AF-APBs, with and without an in-plane external field, as the inset of Figure 3a. The external field aligns the spins far from the boundary and the spins at the APBs rotate by an angle of $\psi_{AF}$ (marked in the inset of Figure 3b), where $\psi_{AF}$ is the angle between the spins at the left side of the APB and the external field. We can write the conductivity of the film as $\rho = \rho_0 (1-t_0^2 \cos^2 \psi_{AF})$, where $\rho_0$ is due to spin-dependent scattering at the interface without an external field and the second term is dependent on the MR effect. The MR ratio for MgFe$_2$O$_4$ is around half that for Fe$_3$O$_4$, for the same thickness, indicating the AF APBs in MgFe$_2$O$_4$ are not as sharp as those in Fe$_3$O$_4$ and the exchange stiffness for the AF exchange interaction at the boundaries is not as strong as for Fe$_3$O$_4$. The underlying reason is that MgFe$_2$O$_4$ is a partially inverse spinel. $\psi_{AF}$ may not be zero in the absence of an external field. According to Ref. 14, the equation $M = Ms (1-b/Hn)$ can be used to describe the approach towards saturation, of the magnetization (M) as a function of field, a value for the exponent (n) near 0.4 was obtained for MgFe$_2$O$_4$. This value is smaller than that for Fe$_3$O$_4$ (0.5) but it is almost the same as for NiFe$_2$O$_4$ films.

To study effect of strain on APB formation, we prepared 4 sets of MgFe$_2$O$_4$ films in different strain states. The thicknesses of those 4 sets of MgFe$_2$O$_4$ films are around 114 nm (S1), 100 nm (S2), 90 nm (S3), and 60 nm (S4), respectively. Figure 4b shows XRD spectra for those 4 sets of MgFe$_2$O$_4$ films. To calculate the strain for those films, first the out-of-plane lattice constant $a_\perp$ is calculated with $a_\perp = d_{hkl} \sqrt{h^2 + k^2 + l^2}$, where $d_{hkl}$ is the spacing of lattice planes with the Miller indices (hkl), $\theta$ is the corresponding Bragg angle of the films, $\lambda$ the wavelength of X-rays used, and $n$ is an integer. The calculated out-of-plane lattice constants $a_\perp$ are 8.379 Å (S1), 8.377 Å (S2), 8.373 Å (S3), and 8.368 Å (S4), respectively. Thus, the corresponding strains for the films (ε) are 0.1%, 0.07%, 0.03%, and 0.004%, respectively, which can be calculated from $\varepsilon = \frac{a_0 - a_\perp}{a_0}$. Where $a_0$ is the lattice constant of MgFe$_2$O$_4$ (8.38 Å). Figure 4c shows R-T curves for those 4 sets of MgFe$_2$O$_4$ films. The resistivity of the films decreases with decreasing strain. The underline physics is that the APB domain size increases with decreasing strain. To confirm this, we estimated the APB domain size $d$ from the XRD data using $d = \frac{0.9 \lambda}{B \cos \theta}$, where $B$ is the half-width value of the XRD peaks. The estimated APB domain sizes for those 4 sets of MgFe$_2$O$_4$ films are 12 nm, 18 nm, 21 nm, and 29 nm, respectively. The strain as a function of grain size is summarized in Fig. 4d. One can see that with decreasing the strain, the APB domain size increases which results in the decrease in the resistivity.

**Effect of post annealing on electrical properties of MgFe$_2$O$_4$.** To investigate the effect of post annealing, in the presence oxygen, on the
electrical properties of MgFe$_2$O$_4$ films, Figure 5a shows R-T curves for an as-grown 114 nm thick MgFe$_2$O$_4$ film (black line) and after annealing in an oxygen partial pressure of $2 \times 10^{-5}$ Torr at 300 °C for 3 hours (red line). Post annealing significantly decreases the resistance of the samples. At room temperature, the resistance for an as-grown sample was 5200 Ω which decreased to 2600 Ω after annealing. Post annealing also reduces the activation energy ($E_a$) of the sample. The R-T plots were fitted with the relationship $R(T)=R_0 \exp(-E_a/k_BT)$. The activation energies for the as-grown sample and the sample after annealing were 76.4 meV and 67.1 meV, respectively. We also measured the MR of the as-grown sample and the sample after annealing were 76.4 meV and 2600 meV after annealing. Post annealing also increases the APB domain size and decreases the resistance and activation energy of the films$^{31}$. Therefore, it is reasonable to believe that APBs in MgFe$_2$O$_4$ can also migrate during annealing. Figure 5c shows XRD data for the as-grown 114 nm thick MgFe$_2$O$_4$ film (black line) and after annealing in an oxygen partial pressure of $2 \times 10^{-5}$ Torr at 300 °C for 3 hours (red line). The half-width value of the MgFe$_2$O$_4$ peak decreases after annealing, indicating an increase in the APB domain size. Another possible reason is that post annealing may modify the oxygen vacancies and nanodomain structures in MgFe$_2$O$_4$ which also will affect the resistivity and MR of the sample$^{27,28}$.

In summary, we investigated the magnetic and transport properties of epitaxial MgFe$_2$O$_4$ thin films grown on MgO (001) substrates. Large saturation fields and a linear negative MR were observed indicating the presence of APBs in MgFe$_2$O$_4$. The existence of APBs was further directly confirmed by HRSTEM characterization. The migration of APBs was also discussed. Our results may be valuable for the future application of MgFe$_2$O$_4$ in spintronics.

**Methods**

MgFe$_2$O$_4$ thin films with different thicknesses were grown on MgO (100) oriented single crystal substrates using an oxygen–plasma-assisted molecular beam epitaxy system. Co-deposition was used to grow the thin films. MgFe$_2$O$_4$ films in different strain states were prepared by controlling the film thickness. The magnetic and transport properties were examined by means of a physical property measurement system (PPMS, Quantum Design). X-ray photoelectron spectrometry measurements were performed in an Omicron Nanotechnology Spectroscopy system equipped with an Ar ion miller in the preparation chamber.

![Figure 5](image-url)
Acknowledgments

This work was supported by Beijing Institute of Technology Research Fund Program for Young Scholars, Science Foundation of Ireland (SFI) under Contract No. 06/IN.1/191, National Plan for Science and technology (Nos. NPST 1598-02 and NPST 1466-02) of King Abdulaziz City for Science and Technology. H.C.W., M.A.A., and M.O.A. thank Saudi Aramco for the financial support (project no. 6600028398). O. M. and A. S. acknowledge the financial support by the Bolashak Program funded by the Kazakhstan government.

Author contributions

H.C.W. and M.O.H.A. conceived the study. O.M., A.S. and C.C. grew the sample. H.C.W. performed the magnetic and transport measurements. A.K., A.M. and H.Z.Z. carried out the STEM measurements. M.O.U. and I.V.S. gave scientific advice. H.C.W. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Additional information

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Wu, H.-C. et al. Magnetic and transport properties of epitaxial thin film MgFe$_2$O$_4$ grown on MgO (100) by molecular beam epitaxy. Sci. Rep. 4, 7012; DOI:10.1038/srep07012 (2014).

This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder in order to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by-nc-nd/4.0/