Stability and capping of magnetite ultra-thin films.

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Ultrathin films of Fe₃O₄ have been grown epitaxially on nearly lattice matched MgO(001). The stability of 4 nm thick films in ambient air and under annealing in an oxygen atmosphere at 200°C has been studied. By magneto-optical and Raman measurements we can confirm the presence of the Fe₃O₄ phase and the formation of a maghemite top layer passivating the Fe₃O₄ thin film. In a second step we are able to demonstrate that this top layer oxidation in ambient air can be prevented by a 2 nm thick magnesium ferrite passivation layer, while a thicker 20 nm MgO layer prevents oxidation even at elevated temperatures.

Magnetite is a material used for its ferromagnetic properties in magnetic data storage and ferrofluids. Its basic electrical, optical and crystallographic properties at room temperature are well characterised. For applications of magnetite, in-plane devices with controlled stoichiometry and crystallinity are typically required. The control over the magnetite properties in thin film form, and reliable measurements of thin film properties are complicated due to top layer oxidation of the films upon air exposure. While Fe₃O₄ is stable at room temperature, the top layers of thin film samples can be further oxidized forming maghemite (γ-Fe₂O₃). Therefore, understanding the issues of oxidation of ultra thin films of magnetite and finding ways of preserving the film stoichiometry under ambient air is important.

This oxidation of ultra-thin magnetite layers grown on nearly lattice matched MgO(001) by plasma assisted molecular beam epitaxy (MBE, Model: DCA MBE M600) is investigated here. Fe₃O₄ is grown at 520 K by e-beam evaporation of iron. Protective layers of MgFe₂O₄ are grown at 520 K by e-beam co-evaporation of metallic iron and ceramic MgO. MgO capping layers were grown at room temperature. Reactive oxygen was supplied by an electron cyclotron resonance plasma source (Oxford Scientific OSPrey) operating at 30 mA in 3×10⁻⁶ mbar oxygen partial pressure.

Due to a strong dependency of thin film Fe₃O₄ properties on film thickness, it is crucial to compare the effect of different capping layers on identical Fe₃O₄ films. For this reason a single Fe₃O₄ layer was grown first, which was subsequently covered by MgFe₂O₄ and MgO using shadow masks. This resulted in samples with the same original Fe₃O₄ layer and 4 patches: (a) Uncovered 4 nm thick Fe₃O₄, the same film capped by (b) 2 nm MgFe₂O₄, (c) 20 nm MgO, and (d) 2 nm MgFe₂O₄ and 20 nm MgO. Reference samples of 20 nm MgO and 2 nm MgFe₂O₄ were also produced to exclude the possibility that a magneto-optical Kerr effect (MOKE) or Raman signals originate from these layers.

To assess the crystallographic phase and the amount of surface oxidation, Raman spectra of the samples have been measured with the 488 nm Ar-line in a Renishaw inVia micro Raman system using z(x₀₀₁, x₀₀₁) scattering geometry and polarisation. Magnetite can be identified by its characteristic A₁g mode at 665 cm⁻¹, which shifts to higher wavenumber in thin film form due to the presence of substrate induced strain or anti phase boundaries. The surface oxidized phase, which we could identify as γ-Fe₂O₃, has a split peak of the same symmetry, where the larger component is found at 720 cm⁻¹. The differently capped structures have been measured within 2 days of initial exposure to ambient air as well as subsequently in the following 2 months. As shown in Fig. 1, the uncapped samples already show a broader initial Fe₃O₄ A₁g mode compared to any of the capped structures, and within the first two months...

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the uncapped sample after O$_2$ air. Such an asymmetry could arise from strain gradients between the peaks at higher and lower energy ($I_2/I_1$), and line broadening ($\Gamma$) are also given. The peak ratio can be used to estimate the thickness of the $\gamma$-Fe$_2$O$_3$ top layer.

Table I compares the results of the peak fit of the $A_{1g}$ mode and estimation of the over layer oxidation based on a shape analysis of the mode. For the fully capped samples, peaks were fully symmetric Lorentzian shaped and only a single peak has been fitted. For all other layers, a double peak structure was used with a shared Lorentzian width. The intensity ratio between the peaks at higher and lower energy ($I_2/I_1$), and line broadening ($\Gamma$) are also given. The peak ratio can be used to estimate the thickness of the $\gamma$-Fe$_2$O$_3$ top layer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_{1g}$ (cm$^{-1}$)</th>
<th>$I_2/I_1$</th>
<th>$\Gamma$ (cm$^{-1}$)</th>
<th>$d_{\gamma$-Fe$_2$O$_3$} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 nm Fe$_3$O$_4$ uncapped</td>
<td>666, 708</td>
<td>0.8</td>
<td>40</td>
<td>1.3</td>
</tr>
<tr>
<td>after 2 months</td>
<td>661, 708</td>
<td>1.2</td>
<td>156</td>
<td>2.2</td>
</tr>
<tr>
<td>after O$_2$ anneal</td>
<td>667, 713</td>
<td>1.9</td>
<td>57</td>
<td>4</td>
</tr>
<tr>
<td>with MgFe$_2$O$_4$ cap</td>
<td>672, 704</td>
<td>0.2</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>after 2 months</td>
<td>670, 704</td>
<td>0.4</td>
<td>53</td>
<td>0.4</td>
</tr>
<tr>
<td>after O$_2$ anneal</td>
<td>673, 716</td>
<td>1.4</td>
<td>48</td>
<td>2.7</td>
</tr>
<tr>
<td>with MgO cap</td>
<td>668, 704</td>
<td>0.3</td>
<td>45</td>
<td>-</td>
</tr>
<tr>
<td>after 2 months</td>
<td>669, 709</td>
<td>0.2</td>
<td>57</td>
<td>-</td>
</tr>
<tr>
<td>after O$_2$ anneal</td>
<td>670, 705</td>
<td>0.2</td>
<td>48</td>
<td>-</td>
</tr>
<tr>
<td>with full cap</td>
<td>675</td>
<td>0</td>
<td>48</td>
<td>-</td>
</tr>
<tr>
<td>after 2 months</td>
<td>675</td>
<td>0</td>
<td>51</td>
<td>-</td>
</tr>
<tr>
<td>after O$_2$ anneal</td>
<td>675</td>
<td>0</td>
<td>49</td>
<td>-</td>
</tr>
<tr>
<td>50 nm thick Fe$_3$O$_4$</td>
<td>665</td>
<td>0</td>
<td>42</td>
<td>-</td>
</tr>
</tbody>
</table>

The importance of the protection of ultra-thin Fe$_3$O$_4$ films is immediately evident. The uncapped sample already has a $\sim$1.3 nm thick $\gamma$-Fe$_2$O$_3$ formed after air exposure, which increases to $\sim$2 nm after prolonged exposure. Any electrical or magnetic measurements on such films are already greatly affected as more than a quarter of the material is not magnetite anymore.

To demonstrate this effect we measured the polar magneto optical Kerr effect (MOKE) of the thin film samples spectroscopically. Details of the spectrometer and magnet are described elsewhere. The MOKE spectra of thin films are dominated by a superposition of the actual magneto-optical properties of the magnetic material, the overall reflectivity of the layered stack, and the thickness of the magnetic layer. Already for a layer thickness below 100 nm, a reduction in Kerr rotation is typically expected. Consequently the Kerr rotation in the ultrathin Fe$_3$O$_4$ films will be substantially lower than in thicker magnetite films or bulk magnetite. The MOKE spectra in infrared MOKE signal is qualitatively expected in an ultra-thin film. The remaining quantitative differences in the ultra-violet (UV) are caused by the presence of the MgO cap and a modification of the dielectric function of the Fe$_3$O$_4$ itself due to the quantum confinement effects in an ultra-thin film.

The spectroscopic MOKE measurements are not only sensitive enough to quantify the Kerr effect of just a 3 nm thick film, we can even observe and understand the differences introduced by the surface oxidation. Figure 2b shows the changes in the MOKE spectra for the 4 nm uncapped samples during prolonged air exposure and after O$_2$ annealing. Most prominently the characteristic
and γ are surface oxidized and transformed into FeO4 layers. The initial oxidation after even just 1 day of exposure to air is limited to approximately 1 nm. On the timescale of months the γ-FeO4 layer gets thicker. Annealing in an oxygen atmosphere accelerates this process. The introduction of an even thinner MgFeO4 capping layer can prevent the initial oxidation, while caps of 20 nm of MgO fully protect the FeO4 thin films. Best results have been achieved by a combination of thin MgFeO4 cap and the MgO cap. While protecting samples with MgO is not a problem for optical measurements, it poses a problem in electrical measurements, or if the FeO4 is to be used as conductive or spin injecting buffer layer. In this case MgFeO4 capping can be used as an alternative, as long as samples are processed within a couple of days after the growth.

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![FIG. 2](image_url)  
**FIG. 2.** a) Polar MOKE measurements of an capped 3 nm and uncapped 50 nm thick FeO4 layer on MgO(001) at a magnetic field of 250 mT. The optical model qualitatively describes the differences between the 3 nm and 50 nm thick sample due to the changes on overall reflection of the layer stack. b) effect of air exposure and O2 annealing on the MOKE of an uncapped 4 nm thick sample at 125 mT.

![FIG. 3](image_url)  
**FIG. 3.** MOKE spectra of 4 nm thick FeO4 capped with a) 2 nm MgFeO4 and b) a combination of 2 nm MgFeO4 and 20 nm MgO. Both caps maintain the MOKE signal in the infrared typically seen for FeO4. The large difference between the two types of caps is caused by interference effects in the thicker, transparent MgO layer as shown in the optical model.

In conclusion, we have demonstrated that uncapped ultra thin FeO4 layers are not stable in ambient air but are surface oxidized and transformed into γ-FeO4. The initial oxidation after even just 1 day of exposure to air is limited to approximately 1 nm. On the timescale of months the γ-FeO4 layer gets thicker. Annealing in an oxygen atmosphere accelerates this process. The introduction of an even thinner MgFeO4 capping layer can prevent the initial oxidation, while caps of 20 nm of MgO fully protect the FeO4 thin films. Best results have been achieved by a combination of thin MgFeO4 cap and the MgO cap. While protecting samples with MgO is not a problem for optical measurements, it poses a problem in electrical measurements, or if the FeO4 is to be used as conductive or spin injecting buffer layer. In this case MgFeO4 capping can be used as an alternative, as long as samples are processed within a couple of days after the growth.

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16. F. Bourgeois, P. Gerhard, H. Renevier, C. Leclere, and G. Feuil-


22A. M. Jubb and H. C. Allen, ACS Applied Materials & Interfaces 2, 2804 (2010).


