Supplementary Information: Thermal phase design of ultrathin magnetic iron oxide films: From Fe$_3$O$_4$ to $\gamma$-Fe$_2$O$_3$ and FeO

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1 Characterization of structural and magnetic properties

We grow a series of ultrathin magnetite Fe$_3$O$_4$ films, i.e. 2 nm, 4 nm and 38 nm on two different oxide substrates, SrTiO$_3$ (001) and yttria-stabilized zirconia (001) (YSZ). We characterized the heterostructures using different techniques, and present the X-ray diffraction (XRD) and magnetic measurements via vibrating sample magnetometry (VSM) in the following.

Fig. 1 (a) and (c) show the XRD pattern of Fe$_3$O$_4$ 38 nm thick films grown on SrTiO$_3$ and YSZ, respectively. The XRD pattern in Fig. 1 (a) confirms the epitaxial growth of Fe$_3$O$_4$ (100) on SrTiO$_3$ (100). In Fig. 1(c) the growth of Fe$_3$O$_4$ (111) on YSZ (100) reveals the formation of fringes which refer to a high quality of the crystalline structure of the magnetite film.

A clear indication for the stoichiometric quality of the magnetite thin films is by determining the Verwey temperature $T_V$. Fig. 1(b) and (d) show the magnetization vs. temperature (M(T)) curves of Fe$_3$O$_4$ 38 nm thick films grown on SrTiO$_3$ and YSZ, respectively. In particular, the first and second derivatives of the magnetization curves is utilized to determine $T_V$ and the transition width $\Delta T_V$. The curves show a strong decrease for the magnetization around 120 K referring to the Verwey transition. This observation thereby confirms the stoichiometry of the magnetite thin films.

After optimizing the growth parameters and confirming the high quality of the 38 nm thick Fe$_3$O$_4$ films by the different characterization methods grown on SrTiO$_3$ (for more details see our previous work$^1$) and on YSZ, also ultrathin films of 2 nm and 4 nm are grown on both SrTiO$_3$ and YSZ substrates.

2 HAXPES

In order to ensure that the kinetics of the thermal annealing experiment is not playing a role for our analysis, we performed the following test experiments: We annealed a film of 4 nm at 600 °C in UHV for 90 min, and took HAXPES spectra every 30 min. No changes occur in the spectra as depicted in Fig. 2.

All HAXPES have been analyzed quantitatively by a linear combination fitting of the elemental spectral weights, as shown in Fig. 3(a) and (b). In particular, we calculate the Fe, Fe$^{2+}$ and Fe$^{3+}$ cation ratios with respect to the annealing temperature, and thereby conclude on the chemical phase ratio.

To exclude any cations diffusion, we conducted HAXPES to a 38 nm thick film grown on SrTiO$_3$ substrate. Figure 4 shows the survey spectra of the films annealed at different temperature up to 700 °C in comparison to Fe 2p core level spectra of SrTiO$_3$ substrate as a reference for possible cations diffusion from the underlying substrate.

3 Thermodynamics calculations

Under thermal annealing, the iron oxide films undergo transitions into different chemical phases, for which the three equilibrium equations are given below:

$$\begin{align*}
\text{1} & \quad 3\text{Fe}_2\text{O}_3 \rightleftharpoons 2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2 \\
\text{2} & \quad \text{Fe}_3\text{O}_4 \rightleftharpoons 3\text{FeO} + \frac{1}{2}\text{O}_2 \\
\text{3} & \quad \text{FeO} \rightleftharpoons \text{Fe} + \frac{1}{2}\text{O}_2
\end{align*}$$

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**Fig. 1** (a) and (c) Out-of-plane x-ray diffraction $\theta-2\theta$-scans of the Fe$_3$O$_4$ (004)/SrTiO$_3$ (002) and the Fe$_3$O$_4$ (222)/YSZ (002) reflections, respectively for films 38 nm thick. (b) and (d) Magnetic detection of Verwey transition of 38 nm thick film: $M(T)$, the first and second derivatives for the magnetization curve to detect $T_V$ and $\Delta T_V$ of films grown on SrTiO$_3$ and YSZ, respectively.

**Fig. 2** Fe 2p core level HAXPES spectra for 4nm/STO films annealed at 600 °C in UHV for 30, 60 and 90 min.
Fig. 3 (a) and (b) Fitting example for films annealed at 500 °C of thickness 2 nm and 38 nm, respectively.
Fig. 4 Survey spectra for 38 nm film grown on SrTiO$_3$ substrate annealed in different temperature. In dotted line, a Ti 2p core level spectra of SrTiO$_3$ substrate.
The classical van ’t Hoff analysis for the phase equilibria reads as

$$\ln(K) = -\frac{\Delta G^0}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R},$$

whereby $R$ is the gas constant, $\Delta G^0$ is the change of Gibbs free energy, $\Delta H$ is the change of the enthalpy and $\Delta S$ of the entropy. $K$ the equilibrium constant of the equilibria according to [1] and [2] and [3], respectively. $K$ is directly related to the Fe, Fe$^{2+}$ and Fe$^{3+}$ cation ratios as shown below, which we determined from the HAXPES peak fitting analysis.

From the first equilbirium [1]

$$3[2Fe^{3+} + 3O^{2-}] \rightleftharpoons 2[Fe^{2+} + 2Fe^{3+} + 4O^{2-}] + \frac{1}{2}O_2,$$

we derive

$$K_1 = \frac{[Fe^{3+}]^3 [O^{2-}]^3}{[Fe^{2+}]^2 [Fe^{3+}]^2 [O^{2-}]^2} p_{O_{eff}}^{-\frac{1}{2}},$$

where, $p_{O_{eff}}$ is the effective oxygen pressure $p_{O_{eff}}$ of the heterostructure, i.e substrate, film and atmosphere. We reorganize the equation to

$$K_1 = \frac{[Fe^{3+}]^2 [O^{2-}]^2}{[Fe^{2+}]^3} p_{O_{eff}}^{-\frac{1}{2}} = K_{red \frac{3}{2}} \times p_{O_{eff}},$$

For the second equilibrium [2] we derive

$$Fe^{2+} + 2Fe^{3+} + 4O^{2-} \rightleftharpoons 3[Fe^{2+} + 3O^{2-}] + \frac{1}{2}O_2,$$

$$K_2 = \frac{[Fe^{2+}]^3 [O^{2-}]^3}{[Fe^{2+}] [Fe^{3+}]^2 [O^{2-}]^4} p_{O_{eff}}^{-\frac{1}{2}},$$

$$K_3 = \frac{[Fe^{2+}]^2 [O^{2-}]^2}{[Fe^{3+}]^3} p_{O_{eff}}^{-\frac{1}{2}} = K_{red \frac{3}{2}} \times p_{O_{eff}},$$

For the third equilibrium [3] we derive

$$Fe^{2+} + O^{2-} \rightleftharpoons Fe^{0} + \frac{1}{2}O_2,$$

$$K_3 = \frac{[Fe^{0}]}{[Fe^{2+}] [O^{2-}]^2} p_{O_{eff}}^{-\frac{1}{2}} = K_{red \frac{3}{2}} \times p_{O_{eff}},$$

As first approximation we neglect the effective oxygen pressure and calculate $K_{red}$. Then we calculated the enthalpy ($\Delta H$) and the entropy ($\Delta S$) according to equation [4] for all the samples, as shown in Table [1].

Secondly, we calculated the effective oxygen pressure $p_{O_{eff}}$,

$$\frac{1}{2} p_{O_{eff}} = e^{\frac{\Delta G^0}{K_{red}}}$$

with $\Delta G^0$ being a function of temperature. For the three relevant redox processes 1, 2 and 3, we calculated $\Delta G^0$ as follows:

$$\Delta G^0_{1} (T) = 2G^0_{Fe_2O_4}(T) + \frac{1}{2}G^0_{O_2} - 3G^0_{Fe_3O_4}(T)$$

$$\Delta G^0_{2} (T) = 3G^0_{FeO}(T) + \frac{1}{2}G^0_{O_2} - G^0_{Fe_2O_4}(T),$$

$$\Delta G^0_{3} (T) = G^0_{Fe}(T) + \frac{1}{2}G^0_{O_2} - G^0_{FeO}(T).$$
Table 1 Thermodynamics parameters calculated from \( \ln(K_{red}) \) vs. \( 1/T \).

<table>
<thead>
<tr>
<th>Film</th>
<th>Reaction</th>
<th>Enthalpy ( \Delta H ) (kJ/mol)</th>
<th>Entropy ( \Delta S ) (J/molK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 nm/STO ①</td>
<td></td>
<td>35.32±1.9</td>
<td>53.5±4.5</td>
</tr>
<tr>
<td>2 nm/STO ②</td>
<td></td>
<td>55.11±6.8</td>
<td>96.2±11.9</td>
</tr>
<tr>
<td>2 nm/STO ③</td>
<td></td>
<td>47.19±4.3</td>
<td>42.1±4.7</td>
</tr>
<tr>
<td>4 nm/STO ①</td>
<td></td>
<td>25.64±2.1</td>
<td>32.6±4.2</td>
</tr>
<tr>
<td>4 nm/STO ②</td>
<td></td>
<td>57.52±22.97</td>
<td>82.5±33.5</td>
</tr>
<tr>
<td>4 nm/STO ③</td>
<td></td>
<td>....</td>
<td>....</td>
</tr>
<tr>
<td>4 nm/YSZ ①</td>
<td></td>
<td>22.02±3.3</td>
<td>31.1±7.98</td>
</tr>
<tr>
<td>4 nm/YSZ ②</td>
<td></td>
<td>53.29±3.9</td>
<td>101.7±7.6</td>
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<tr>
<td>4 nm/YSZ ③</td>
<td></td>
<td>145.8±33.4</td>
<td>176.8±43.1</td>
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<tr>
<td>38 nm/STO ①</td>
<td></td>
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</tr>
<tr>
<td>38 nm/STO ②</td>
<td></td>
<td>31.16±2</td>
<td>74.2±3.8</td>
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<tr>
<td>38 nm/STO ③</td>
<td></td>
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<td>....</td>
</tr>
</tbody>
</table>

\[ G_{Fe_2O_3}^0(T), G_{Fe_3O_4}^0(T), G_{FeO}^0(T), G_{Fe}^0(T) \text{ and } G_{O_2}^0 \text{ are calculated from the NIST database}\text{.} \] Table 2 shows the standard values of the different iron oxides for the Gibbs formation energy, enthalpy and entropy calculated at room temperature.

Table 2 Standard thermodynamics parameters calculated at room temperature.

<table>
<thead>
<tr>
<th></th>
<th>( G^0 ) (kJ/mol)</th>
<th>( \Delta f H^0 ) (kJ/mol)</th>
<th>( S^0 ) (J/molK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(_2)O(_3)</td>
<td>-851.55</td>
<td>-863.21</td>
<td>87.28</td>
</tr>
<tr>
<td>Fe(_3)O(_4)</td>
<td>-1164.21</td>
<td>-1163.34</td>
<td>145.17</td>
</tr>
<tr>
<td>FeO</td>
<td>-290.15</td>
<td>-286.74</td>
<td>60.72</td>
</tr>
<tr>
<td>Fe</td>
<td>-20.54</td>
<td>-12.4</td>
<td>27.31</td>
</tr>
</tbody>
</table>

The respective Gibbs formation energy for each equilibrium as function of temperature and the values at room temperature are given in Table 3.

Table 3 The calculated Gibbs formation energy of the three equilibria at room temperature.

<table>
<thead>
<tr>
<th></th>
<th>( \Delta G_{①}^0 ) (kJ/mol)</th>
<th>( \Delta G_{②}^0 ) (kJ/mol)</th>
<th>( \Delta G_{③}^0 ) (kJ/mol)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>256.996</td>
<td>324.513</td>
<td>300.356</td>
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</table>

Notes and references
