Supporting Information

Modification of Electrical and Magnetic Properties of Fe_3O_4 Epitaxial Thin Films by Nitrogen Substitution for Oxygen

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Contents

1. Change of T_N by nitrogen substitution

Figure S1 shows XRD patterns of a $Fe_3O_{4-y}N_y$ film before and after annealing at 500 °C for 1 hour in an UHV chamber (base pressure $<5\times10^{-8}$ Torr). Note that this annealing temperature (500 °C = 773 K) is lower than T_N of Fe_3O_4 (~860 K). After the annealing, diffraction peaks from impurity phase(s) appeared due to intermixing between the $Fe_3O_{4-y}N_y$ thin film and MgO substrate. According to the previous report on Fe_3O_4 film on MgO, similar intermixing might start at much lower temperature of 300-450 °C.[S1-S4]

In order to avoid the intermixing between the $Fe_3O_{4-y}N_y$ thin film and MgO substrate, we conducted *M*-*T* measurements below room temperature. Although large uncertainty is included, extrapolation of the *M*-*T* curves above 200 K (Fig. S2) suggested a tendency that nitrogen substitution reduced T_N.

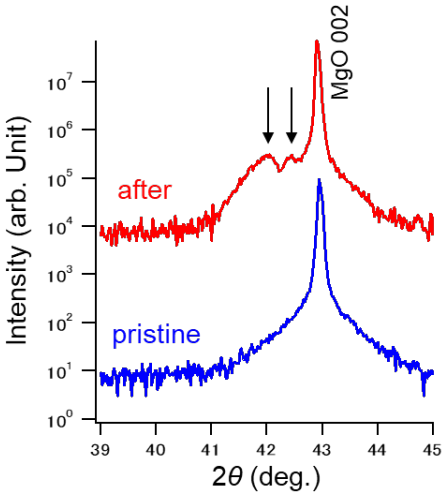

Figure S1. XRD patterns of a $Fe_3O_{4-y}N_y$ thin film (y=0.56) before and after the annealing. Arrows represent the diffraction from impurity phase(s).

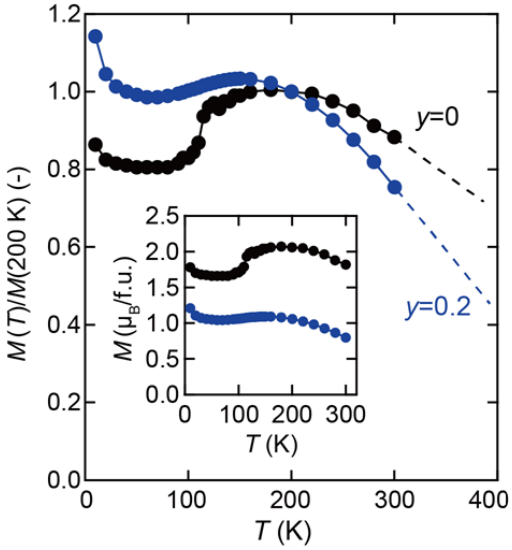

Figure S2. Normalized magnetization M(T)/M(200 K) vs temperature curves of $Fe_3O_{4-y}N_y$ thin films (y=0, 0.2) under field-cooled condition. A magnetic field of 1 kOe was applied along the in-plane direction. Dashed lines are visual guides for magnetization over 300 K. Inset shows the magnetization

without normalization.

Reference

[S1] Kim, Y. J.; Gao, Y.; Chambers, S. A. Selective Growth and Characterization of Pure, Epitaxial α-Fe_2O_3(0001) and Fe_3O_4(001) Films by Plasma-Assisted Molecular Beam Epitaxy. *Surf. Sci.* **1997**, *371*, 358.

[S2] Anderson, J. F.; Kuhn, M.; Diebold, U.; Shaw, K.; Stoyanov, P.; Lind, D. Surface Structure and Morphology of Mg-Segregated Epitaxial Fe_3O_4 (001) Thin Films on MgO (001). *Phys. Rev. B* **1997**, *56*, 9902.

[S3] Handke, B.; Haber, J.; Ślęzak, T.; Kubik, M.; Korecki, J. Magnesium Interdiffusion and Surface Oxidation in Magnetite Epitaxial Films Grown on MgO (100). *Vacuum* **2001**, *63*, 331.

[S4] N.T.H. Kim-Ngan, A.G. Balogh, J.D. Meyer, J. Brötz, S. Hummelt, M. Zając, T. Ślęzak, and J. Korecki, Nucl. Instruments Methods Phys. Res. B **2009**, *267*, 1484.

2. Physical properties of nitrogen rich $Fe_3O_{4-x}N_y$ thin films (y=0.6 and 0.8)

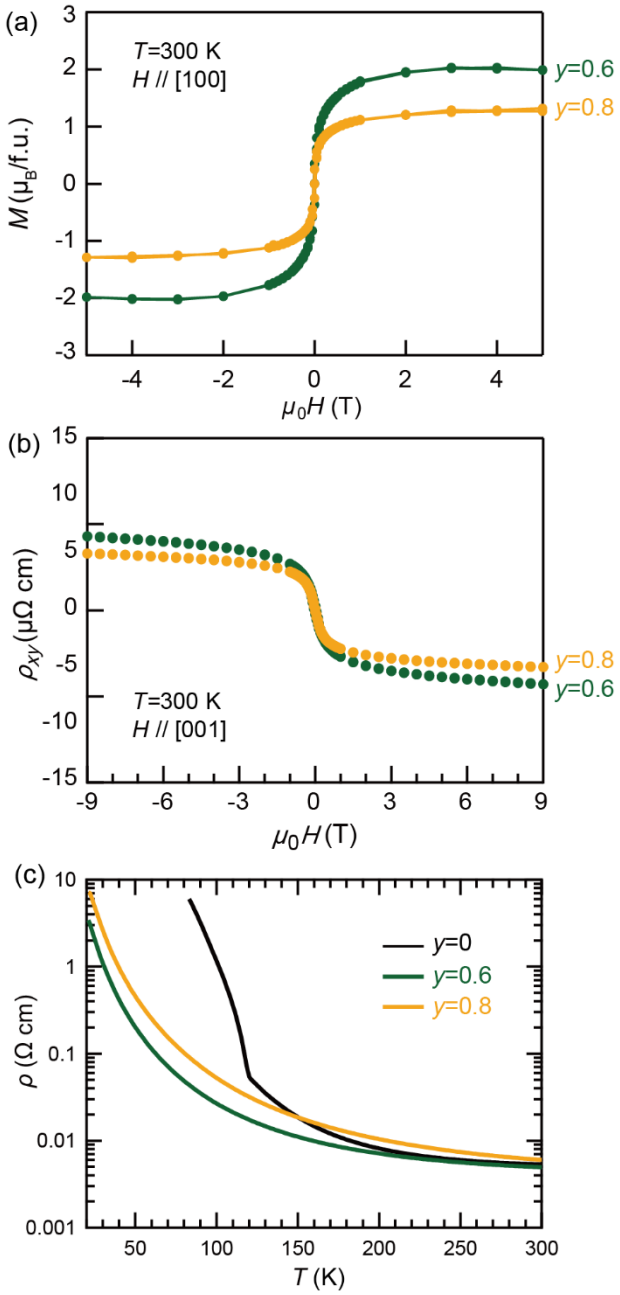

Figure S3. (a) In-plane magnetization vs magnetic filed curves at room temperature (300 K), (b) Hall resistivity ρ_{xy} at 300 K, and (c) ρ–T curves of the $Fe_3O_{4-y}N_y$ thin films.

3. DOSs under epitaxial strain

The crystal and electronic band structures of Fe_3O_4 and $Fe_3O_{3.5}N_{0.5}$ under the epitaxial strain from MgO substrate were calculated by using constrained structural optimization procedures. Firstly, we calculated the lattice constant of MgO using the GGA-PBE functional. The obtained value 4.251 Å was about 1% larger than the experimental value of 4.210 Å. Next, we optimized the out-of-plane lattice constant and atomic positions of Fe_3O_4 and $Fe_3O_{3.5}N_{0.5}$, where the in-plane lattice constant was fixed at that of MgO, as follows. We used the primitive cell (Fe_6O_8 or Fe_6O_7N) of which the lattice vector is:

$$(\mathbf{a}\quad\mathbf{b}\quad\mathbf{c}) = \frac{1}{2}\begin{pmatrix} 0 & a & a \\ a & 0 & a \\ c & c & 0 \end{pmatrix} \tag{1}$$

where a and c are the in-plane and out-of-plane lattice constants, respectively. In this constrained structure optimization, a was set to the double of MgO (8.502 Å), and c was optimized.

Table S1 compares the calculated c and lattice distortion ratio ($c/a - 1$) with the experimental values. The experimentally observed distortion ratio, c.a. −0.5%, was qualitatively reproduced by our calculations. Figures S4(c) and (d) in the main text show the density of states (DOS) profiles of strained Fe_3O_4 and $Fe_3O_{3.5}N_{0.5}$. The whole profiles are almost the same as those obtained by the strain-free calculations (Figures S4(a) and (b)), indicating that the tensile strain does not have a significant effect on the electronic conduction of $Fe_3O_{4-y}N_y$.

Table S1. Experimental (Exp.) and calculated (DFT) out-of-plane lattice constant, c, and distortion ratio, $c/a-1$. In-plane lattice constant a was fixed to the double of MgO ($a_{Exp.}$=8.420 Å and a_{DFT}=8.502 Å).

	$c_{Exp.}$ (Å)	$c_{Exp.}/a_{Exp.}-1$ (%)	c_{DFT} (Å)	$c_{DFT}/a_{DFT}-1$ (%)
Fe_3O_4	8.369	−0.61	8.456	−0.54
$Fe_3O_{3.6}N_{0.4}$	8.382	−0.45		
$Fe_3O_{3.5}N_{0.5}$			8.455	−0.55

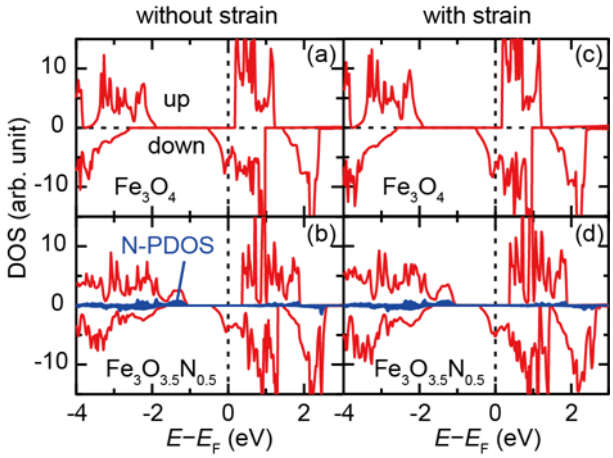

Figure S4. Spin-polarized electronic density of states (DOS) of (a, c) y = 0 (Fe_3O_4) and (b, d) y = 0.5 ($Fe_3O_{3.5}N_{0.5}$) (c, d) with and (a, b) without epitaxial strain. The blue lines in (b) and (d) correspond

to the partial DOS (PDOS) for nitrogen.