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Magnetic properties of nanocrystalline Fe_3O_4 films

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Nanocrystalline magnetite Fe_3O_4 films of about 180 nm thick have been deposited on Si(100) substrates by pulsed laser deposition. Zero-field-cooled magnetization shows clearly the Verwey transition near 120 K by an abrupt change, which is absent from the field-cooled magnetization. This is correlated to its hysteresis curves where the loops remain open until a high field of 2 T. The magnetization does not saturate in field 2 orders of magnitude higher than its coercive field. Such behaviors may result from the existence of antiphase domains. Antiphase boundaries inside the grains are clearly observed with transmission electron microscopy. Negative magnetoresistance of about 12% has been observed near 120 K in a field of 9 T. © 2001 American Institute of Physics. [DOI: 10.1063/1.1358350]

Pulsed laser deposition (PLD) is an attractive method for preparation of a variety of films.¹ It is a highly versatile tool for a range of thin films from nanocomposite to epitaxial growth.² A few of the characteristic features of PLD are stoichiometric transfer, growth from an energetic beam, reactive deposition, and its simplicity to operate. Highly nanocrystalline or cluster-assembled films have been produced by PLD. PLD has also been used to form other exotic hybrid or composite thin films containing normally incompatible materials that could be difficult to synthesize otherwise.³

There has been increased interest in the half-metallic magnetite Fe_3O_4 as its highly spin polarized nature (supposedly ~100%) is desirable for tunneling magnetoresistance based device applications.⁴ PLD has been successfully used recently to grow Fe_3O_4 films by several groups. Epitaxial Fe_3O_4 films were prepared on MgO ,⁵ SrTiO_3 , and $\alpha\text{-Al}_2\text{O}_3$ ⁶ substrates by the technique. Polycrystalline Fe_3O_4 films have also been prepared using PLD⁷ and other techniques, for example, reactive dc sputtering on Si substrate.⁸ The average grain size of these polycrystalline films is about a few micrometers.

Another interesting aspect of thin film Fe_3O_4 is that the magnetization does not saturate in fields 2 orders of magnitude higher than its bulk anisotropy field.⁹ This may be due to the presence of antiphase boundaries in single crystal films, across which the exchange coupling is altered.¹⁰ So far, antiphase boundaries have been observed in sputtered and MBE epitaxial Fe_3O_4 films grown on MgO substrates only.¹¹

We have prepared nanocrystalline Fe_3O_4 films of average grain size 50 nm on Si substrates by PLD and report in this article some of the important features found in the films.

Fe_3O_4 films of about 180 nm thick were deposited on Si (100) substrates by PLD. The $\alpha\text{-Fe}_2\text{O}_3$ target used for laser ablation was prepared by pressing high purity $\alpha\text{-Fe}_2\text{O}_3$ powders (99.998%) into a pellet and sintered at 1000 °C for 2 h.

A focused beam of KrF excimer laser ($\lambda = 248$ nm) was used for the deposition. The repetition rate was 12 Hz and the Si substrate was heated to 350 °C. Prior to the deposition, an unfocused laser beam was rastered across the Si substrate in a vacuum of 3×10^{-6} Torr to clean the substrate surface.

Glancing angle x-ray diffraction data were collected with a Philips X'Pert diffractometer using $\text{Cu } K\alpha$ radiation. Figure 1 shows the diffraction pattern of the Fe_3O_4 film. The lattice constant $a = 0.8392(2)$ nm is close to the powder diffraction (Card No. 19-629) value. Transmission electron microscopy (TEM) was done with a JEOL Model 2010 TEM. Figure 2(top) is a plane-view TEM image of the Fe_3O_4 film. The average grain size is 50 nm. This is much smaller than those in the polycrystalline films mentioned earlier, which is in micrometers.

It is evident from the micrograph that within each single crystal grain it is not uniform. This is due to the presence of antiphase domains in the PLD nanocrystalline Fe_3O_4 films. The TEM image made using (220) reflection shows antiphase domains within each single crystal grain, see Fig.

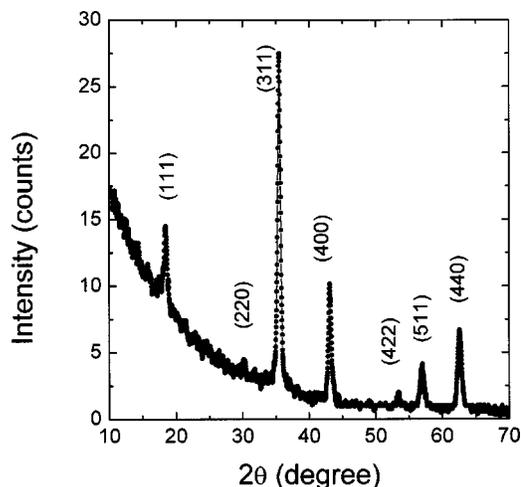


FIG. 1. Glancing angle x-ray diffraction pattern of a nanocrystalline Fe_3O_4 film.

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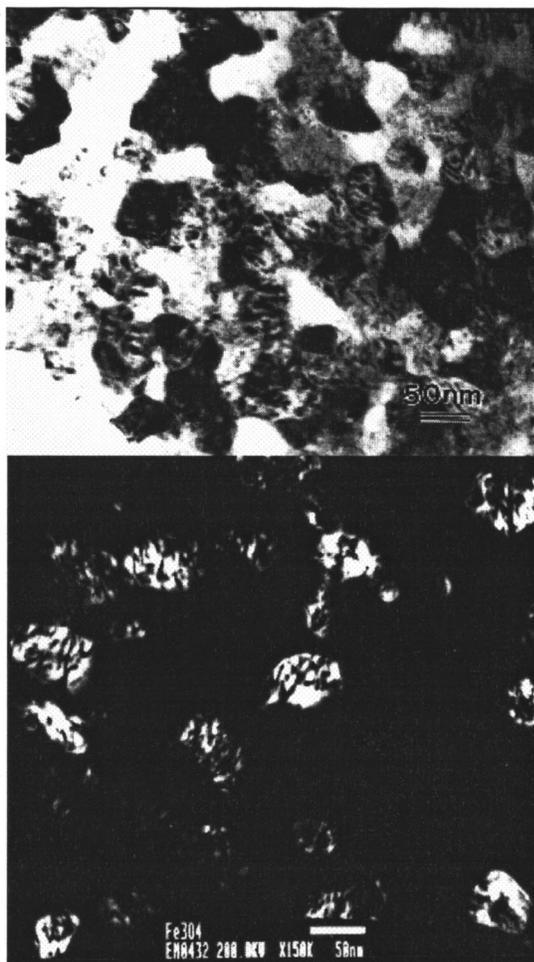


FIG. 2. (Top) A plane view of TEM of the nanocrystalline Fe₃O₄ film. (Bottom) TEM image made with 220 reflection that shows antiphase domains in a single crystal.

2(bottom), where sharp contrast between the neighboring antiphase domains is seen.¹² Our results suggest the antiphase domains also exist in Fe₃O₄ films deposited on Si substrates, not exclusively on MgO substrates as originally thought.^{11,12}

Magnetization data obtained with a Quantum Design superconducting quantum interference device is shown in Fig. 3 as a function of temperature. A magnetic field of 500 Oe was used for both the zero-field-cooled (ZFC) and field-cooled (FC) measurements. ZFC data clearly show the Verwey transition at about 120 K with the characteristic sharp drop. One of the unique features of the PLD nanocrystalline films is the absence of the sharp drop in the FC data below the Verwey transition in a field of 500 Oe. An abrupt drop is usually observed in FC runs in applied fields up to several kOe in bulk and epitaxial films.^{9,13} We will discuss this feature in conjunction with the magnetic hysteresis curves later.

The resistance of the sample measured with a standard four-probe method is also shown in Fig. 3. The change in the resistance at the Verwey transition is not as sharp as those observed in some single crystal samples and relatively thick epitaxial films, but is similar to the relatively thin (≤ 50 nm) films.⁷ For comparison, the resistance of a bulk-like 660 nm thick Fe₃O₄ film is also shown (data taken from Ref. 7).

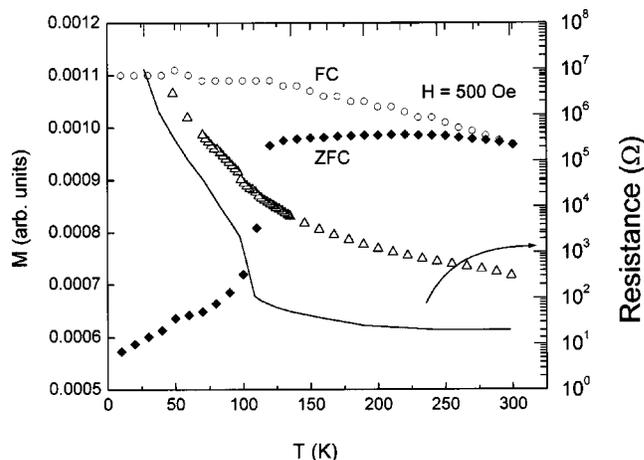


FIG. 3. Magnetization of the nanocrystalline Fe₃O₄ film as a function of temperature measured under FC and ZFC conditions. Also shown are the resistance of the nanocrystalline Fe₃O₄ film (Δ) and the resistance of a bulk-like 660 nm thick Fe₃O₄ film (—) (data taken from Ref. 7).

Strain, size effects, and possible small departure from the precise Fe₃O₄ stoichiometry might be responsible for the observed broadening.^{14,15}

The temperature dependence of the coercivity H_c and remanence M_r of the Fe₃O₄ nanocrystalline films is shown in Fig. 4. The remanence increases from 140 to 195 emu/cm³ as temperature decreases from 300 to 5 K. A plateau forms just below the Verwey transition which is consistent with the single crystal data.¹⁴ The coercivity is 275 Oe at 300 K and increases very slowly from 300 to 120 K. Then it undergoes a rapid increase at the Verwey transition and reaches 750 Oe at 5 K. The abrupt increase in coercivity is associated with a change of anisotropy due to the Verwey transition where a structural change from cubic to monoclinic occurs.^{16,17}

As mentioned earlier, the FC magnetization shows no anomaly at the Verwey transition in a field of 500 Oe. This is consistent with the hysteresis data shown in Fig. 5, inset, where the three curves measured at 100, 120, and 140 K,

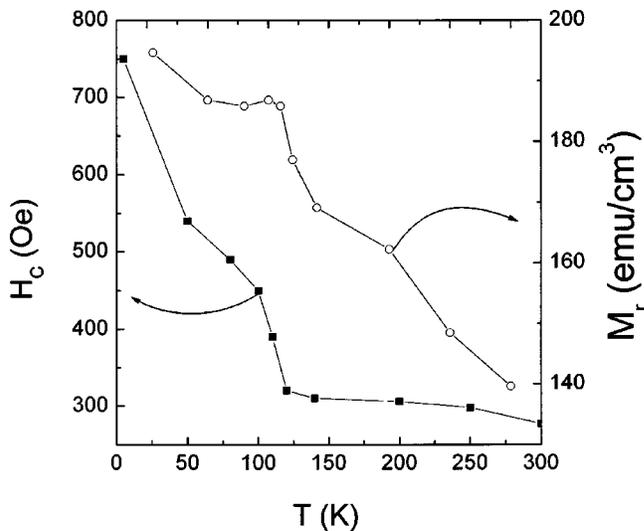


FIG. 4. Temperature dependence of coercivity H_c and remanence M_r of the Fe₃O₄ film.

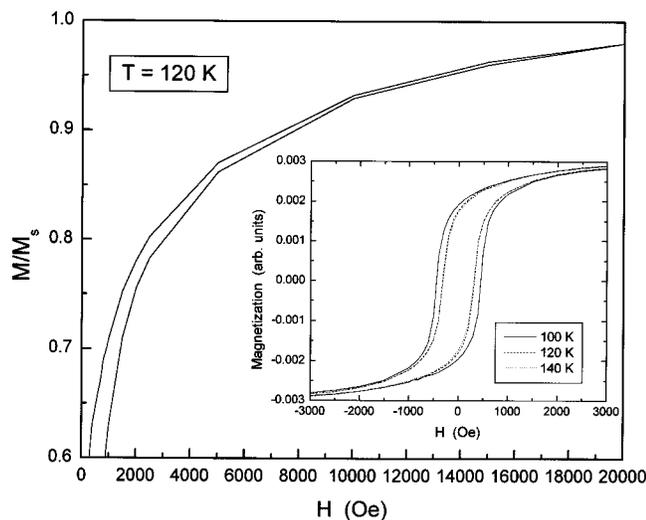


FIG. 5. Hysteresis curve at 120 K that shows open loop and unsaturated magnetization at 20 kOe. (Inset) Low field hysteresis curves at 100, 120, and 140 K, respectively.

respectively, lie almost on top of each other at $H \geq 500$ Oe as the field decreases. An important point to make is that the magnetization does not saturate at 2 T and the hysteresis loop does not close until 2 T. Figure 5 shows the portion of the hysteresis curve from 0 to 2 T at 120 K. High saturation field has been observed in epitaxial films⁹ and explained as the consequence of disturbed exchange coupling across antiphase boundaries.¹⁰ The open loop is unique to the PLD nanocrystalline films. This open loop and the lack of saturation at such high field suggest the existence of an additional anisotropy beyond the bulk value, and it is most likely caused by the presence of antiphase boundaries.

Magnetoresistance (MR) of the film was measured in a Quantum Design physical property measurement system up to a maximum magnetic field of 9 T. The magnetic field was applied perpendicular to the film. Figure 6 shows the MR $= [R(H) - R(0)]/R(0)$ of the film at 90, 130, and 300 K. The MR is about 5% at 300 K and 12% near the Verwey transition. The data also indicate the MR exhibits a peak at the Verwey transition as the temperature is varied. These results are similar to those of the epitaxial films.^{5,6}

Coey *et al.* reported negative MR of pressed Fe_3O_4 powders and polycrystalline films prepared by reactive dc sputtering.⁸ The grain sizes of the sputtered film were about 1–2 μm . The MR ($\sim 1.0\%$ at room temperature and 0.5 T) was attributed to the intergranular transport of spin polarized electrons.¹⁸ On the other hand, comparison between epitaxial and polycrystalline films⁷ suggests minimal contribution from the electron transport across grain boundaries. Our study does not address specifically whether the spin-dependent intergranular transport plays a dominant role in the observed negative MR, however the connection, if any, between the MR and possible existence of antiphase domains should be explored. It has been argued that the antiphase boundaries may become immobile magnetic domain walls.¹⁰ It is of interest to study the MR due to pinned domain walls as their thickness can become smaller than the spin diffusion length and give large MR.

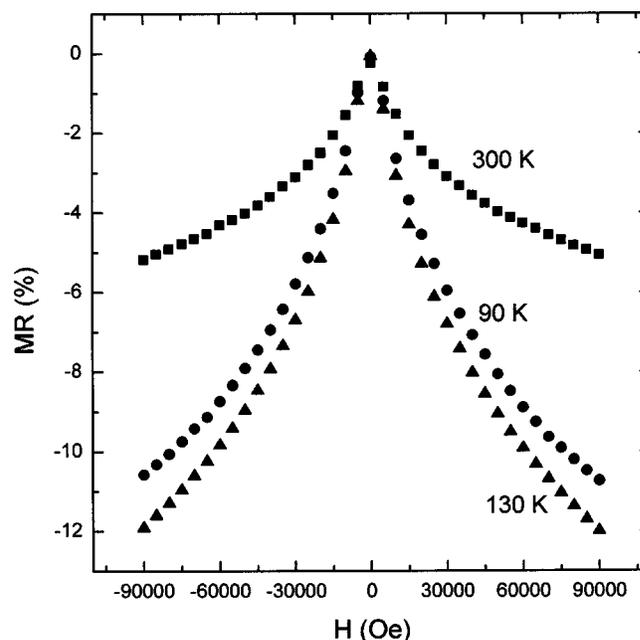


FIG. 6. Magnetoresistance as a function of magnetic field at 90, 130, and 300 K, respectively.

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