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Citation: *Journal of Applied Physics* **89**, 7398 (2001); doi: 10.1063/1.1358831

View online: <http://dx.doi.org/10.1063/1.1358831>

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Granular growth of Fe_3O_4 thin films and its antiphase boundaries prepared by pulsed laser deposition

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Fe_3O_4 thin film prepared by pulsed laser deposition on Si (100) substrate has been investigated by transmission electron microscopy from plane and cross-sectional views. The thin film, which shows a spinel structure as characterized by selected-area diffraction, is about 180 nm thick with granular growth of particle size about 50 nm. High resolution electron microscopy observations indicate reduced thickness of the native SiO_2 layer between the thin film and Si due to rastering of the substrate surface by an unfocused laser beam before the deposition. By using a 220 diffraction spot in two beam condition near the $\langle 001 \rangle$ axis of a single Fe_3O_4 grain, antiphase boundaries (APBs) inside the grains could be clearly resolved. The existence of APBs in the thin film is consistent with the magnetic experiments including an open hysteresis loop and unsaturated magnetization in relatively high magnetic fields. This study suggests that APBs are not unique to Fe_3O_4 films grown on MgO substrates. © 2001 American Institute of Physics. [DOI: 10.1063/1.1358831]

There has been a recent surge in interest in magnetic spinel Fe_3O_4 due to its highly spin polarized nature, which is desirable for tunneling magnetoresistance based device applications.^{1,2} Epitaxial Fe_3O_4 thin films have also shown several anomalous magnetic properties, such as much larger saturation field than bulk single crystals, superparamagnetic behaviors, and local out-of-plane magnetic moments in zero field, etc.³⁻⁵ Antiphase boundaries (APBs), across which the oxygen sublattice is continuous and the cations are displaced by vectors $1/4a\langle 110 \rangle$ or their combinations,⁵ have been found in epitaxially grown Fe_3O_4 thin films on MgO, and the anomalous magnetic behaviors in these thin films are attributed to the cation exchange coupling across the APBs.^{4,5}

Epitaxial Fe_3O_4 films have been shown to successfully grow on MgO,⁶ SrTiO_3 , and Al_2O_3 (Ref. 7) substrates. Polycrystalline Fe_3O_4 films have also been deposited by using different techniques, such as pulsed laser deposition (PLD)⁸ and dc sputtering on Si substrates.⁹ The average grain size of these polycrystalline films is typically several microns. APBs have been observed in Fe_3O_4 epitaxially grown on MgO substrates only, possibly due to the unique lattice match between the two, where the lattice constant of the spinel structure is nearly twice as large as that of MgO.^{4,5} In this article, we report a transmission electron microscopy (TEM) study of granular growth of a Fe_3O_4 thin film with grain size about 50 nm. The film was deposited by PLD on a Si substrate with the native SiO_2 partially removed, and APBs have also been observed. The APBs play an important role in the magnetic behaviors of the film.

PLD is considered one of the most effective methods for preparation of a variety of oxide films due to the unique features of stoichiometric transfer, direct growth from an energetic beam, and its simplicity of operation.¹⁰ In this study, Fe_3O_4 films of about 180 nm thick were deposited on Si substrates by PLD. An $\alpha\text{-Fe}_2\text{O}_3$ 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 applied 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. After the deposition, the heater was switched off and the film was cooled down to room temperature at a rate of 10 °C/min. Transmission electron microscopy observation was performed using JEOL 2010 with EDAX DX prime energy dispersive spectroscopy (EDS). The plane-view sample was prepared by grinding, polishing, and dimpling the Si substrate, then back side ion milling was applied until electron perforation. The cross-sectional sample was prepared by the conventional sandwich technique with the foil surface normal to the $\langle 110 \rangle$ Si substrate.¹¹

Figure 1 is a selected-area diffraction pattern from a cross-sectional sample. The corresponding rings, denoted by arrows, are the 111, 220, and 311 of the spinel structure with $a = 0.839$ nm; this indicates the successful synthesis of the Fe_3O_4 thin film. Some of the strong diffraction spots are from Si [110] substrate. Figure 2(a) is a dark-field cross-

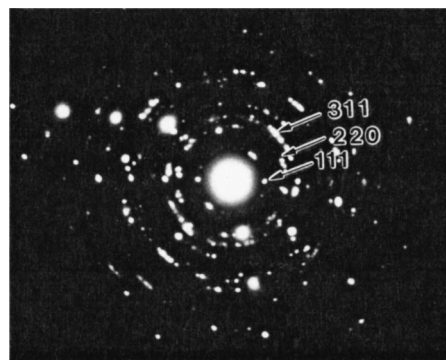


FIG. 1. Electron diffraction pattern of Fe_3O_4 taken from cross-sectional view. The strong spots are from Si [110] substrate. The rings can be indexed as typical spinel Fe_3O_4 structure.

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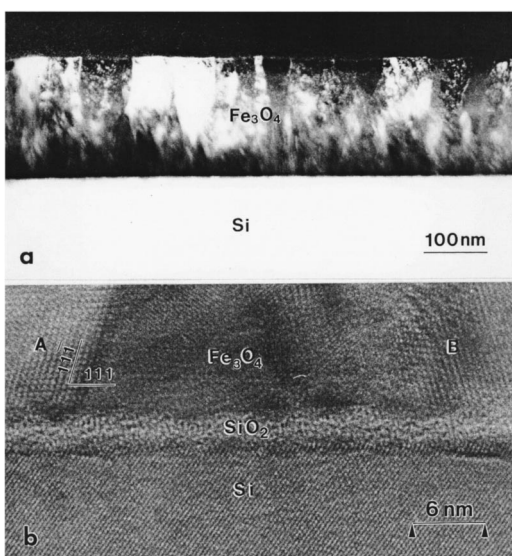


FIG. 2. (a) Dark-field cross-sectional TEM micrographs of the thin film, showing columnar growth Fe_3O_4 grains. (b) HREM image of the interface between Si and the substrate. The (111) planes of grains A and B were found parallel to the substrate surface.

sectional micrograph of Fe_3O_4 thin film. The Si substrate appears as white contrast and the columnar grain growth is clearly seen perpendicular to the surface of the Si substrate. The thickness of the thin film is about 180 nm. By looking at the interface of the thin film and substrate from the high resolution electron microscopy (HREM) image in Fig. 2(b), we have found a thinner native SiO_2 amorphous layer (only 1.5 nm thick) compared to our previous results (2.3 nm) without laser rastering.¹² Some Fe_3O_4 grains prefer growing with {111} plane parallel to the Si (100) substrate as denoted A and B in Fig. 2(b).

Figure 3(a) is a plane-view micrograph which shows that the thin film has granular growth with grain sizes varying from 30 to 80 nm. The microdiffraction patterns also confirm the Fe_3O_4 spinel structure while EDS analysis verifies the Fe_3O_4 composition. Most grains appear in bright or dark contrast due to different orientations. Carefully looking at some grains, we can find some bright and dark bands inside the grains. By putting a 3 nm spot to the bright or dark bands of single grains and detecting with EDS, one does not observe much change in the composition as a function of crystal orientation. This means both the composition and crystalline structure inside the grains are homogeneous. Dislocation lines are not observed by tilting the grains to different orientations. In the reported epitaxial thin films the APBs have been frequently observed close to the $\langle 001 \rangle$ direction by using the 220 reflection to obtain an image.^{4,5} The bright and dark bands are due to the antiphase domains separated by an APB across which the oxygen sublattice is continuous and that of the cations is not. The bright and dark bands can be observed due to out-of-plane shift vectors. In our case, by tilting one grain to the [001] direction using a microdiffraction pattern and then obtaining the two beam condition by using a 220 diffraction spot, the different sizes of bright and dark bands are clearly seen as shown in Fig. 3(b). Some moiré fringes can be seen at the edge of the grain which are

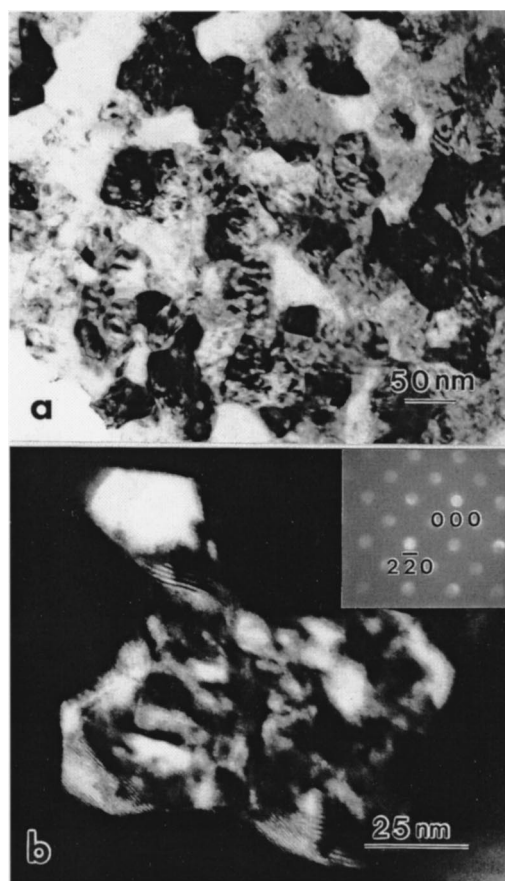


FIG. 3. (a) Plan-view micrograph shows bright and dark bands inside the grains. (b) A single grain taken using 220 diffraction in two beam condition along [001] direction. The APBs can be seen and the inset is a [001] microdiffraction pattern. The moiré fringes come from the overlapping of the grain with nearby grains.

generated from the overlapping of nearby grains, however, we did not observe any fringes inside the grains. The left upper side fringes in Fig. 3(b) come from the overlapping of another small grain with the grain we observed. The APBs also disappeared by imaging with the 004 diffraction spot. This phenomenon can also be observed in other grains. Margulies *et al.*⁴ suggest that the APBs in Fe_3O_4 results from the intrinsic growth mechanism on MgO substrates and their presence is independent of preparation techniques. The existence of APBs in Fe_3O_4 grown on the Si substrate with amorphous SiO_2 native layer as shown in this study suggests another mechanism for their formation. Although the exact mechanism needs to be studied, APBs may be intrinsic to Fe_3O_4 independent of the substrate as well as preparation method.

Similar to the epitaxial films, the shape of the antiphase domains is irregular. The sizes of the antiphase domains in our film range from 5 to 15 nm. The density of APBs is hard to estimate due to the different orientations of each grain. But the substrate temperature as well preparation method does affect the density of APBs. In the epitaxial films, the average size of antiphase domain has been found to range from 30 nm, for the sputter deposited film at 500 °C, to 300 nm, for the molecular beam epitaxially grown film at 225 °C.^{4,5} In our case the film was deposited at 350 °C by the

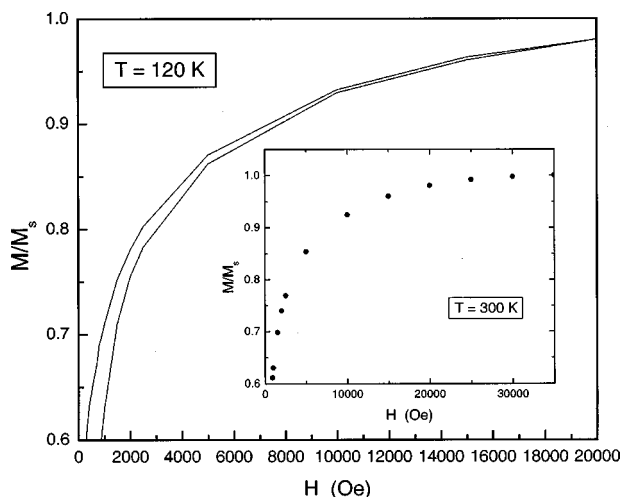


FIG. 4. Magnetic hysteresis loop at 120 K. The inset is the magnetization curve measured at 300 K. Note there is an open loop and lack of saturation at high field.

more energetic PLD. The density of APBs is comparable and even higher than the sputter deposited films. The substrate temperature may also affect the APB density.

The existence of APBs in our Fe_3O_4 film is supported by the magnetic measurements. Figure 4 shows a portion of the magnetic hysteresis loop of the Fe_3O_4 thin film at 120 K. The inset is the magnetization curve measured at a higher temperature (300 K) and to a higher field. An important point to make is that the magnetization does not saturate until ~ 3 T, which is two orders of magnitude higher than its coercive field, and the hysteresis loop remains open until ~ 2 T. The high saturation field is a consequence of disturbed exchange coupling across the APBs, which has been observed in the epitaxial films as mentioned earlier. The open loop at high field is unique to our PLD nanocrystalline films.¹² This open loop and the lack of saturation at such high field suggest the existence of additional anisotropies beyond the bulk values,

which is consistent with the observation of APBs in the sample.

In summary, granularly grown Fe_3O_4 thin films on a Si (100) substrate using the PLD method were studied by TEM. The average grain size is about 50 nm with columnar growth. The SiO_2 amorphous native layer is reduced by rastering the substrate surface using an unfocused laser beam before deposition. Antiphase domains ranging from 5 to 15 nm were also observed by TEM in our granularly grown thin film. Magnetic measurements suggest that the open hysteresis loop and high saturation field are the consequence of disturbed exchange coupling across the APBs. The APBs found in thin film on Si substrates imply the existence of APBs might be intrinsic to Fe_3O_4 independent of the substrate as well as preparation method.

The authors gratefully acknowledge the support by AMRI through DARPA Grant No. MDA972-97-1-0003.

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