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**MAGNETISM  
AND FERROELECTRICITY**

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## Self-Propagating High-Temperature Synthesis and Magnetic Features of Fe–Al<sub>2</sub>O<sub>3</sub> Granulated Films

V. G. Myagkov\*, K. P. Polyakova\*, G. N. Bondarenko\*\*, and V. V. Polyakov\*

\* Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences,  
Akademgorodok, Krasnoyarsk, 660036 Russia

\*\* Institute of Chemistry and Chemical Technology, Siberian Division, Russian Academy of Sciences,  
Krasnoyarsk, 660036 Russia  
e-mail: miagkov@iph.krasn.ru

Received April 18, 2002

**Abstract**—The classical solid-phase reaction between Fe<sub>2</sub>O<sub>3</sub> and Al layers in thin films is initiated. It is shown that, in the reaction products, Fe granulated films are formed in the Al<sub>2</sub>O<sub>3</sub> nonconducting matrix. Analysis of the reaction equation demonstrates that the volume fraction of iron in the granulated films is less than the percolation threshold. This determines the magnetic properties of iron clusters in a superparamagnetic state. It is assumed that the nanocrystalline microstructure exists in thin films after solid-phase reactions proceeding under conditions of self-propagating high-temperature synthesis. © 2003 MAIK “Nauka/Interperiodica”.

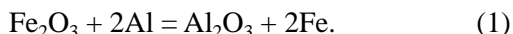
### 1. INTRODUCTION

Granulated films consisting of ferromagnetic nanoclusters contained in a nonconducting matrix have been intensively studied in recent years, because they exhibit very interesting properties, such as giant magnetoresistance [1], giant anomalous Hall effects [2], specific optical properties [3], and quantum-confinement effects [4]. From the practical point of view, these films can be used as media for magnetic and magneto-optical recording [5, 6]. Granulated magnetic films that contain nanoclusters of Fe, Ni, Co, and their alloys in SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> matrices have been the main subject of recent investigation in this field. A conventional method of producing metallic nanoclusters inside a nonconducting matrix in thin films is codeposition of a metal and an insulator onto a substrate. In this case, the nanoclusters are randomly distributed over the matrix and their size depends on the conditions of thermal annealing and deposition. However, the successive deposition of a metal and an insulator can result in self-organization in the formation of metallic nanoclusters [7]. The development of new techniques for preparing granulated samples is very important, because this makes it possible to extend the range of structural characteristics determining the physical properties of nanocomposites.

The purpose of this work was to investigate Fe nanogranulated films formed inside the Al<sub>2</sub>O<sub>3</sub> matrix.

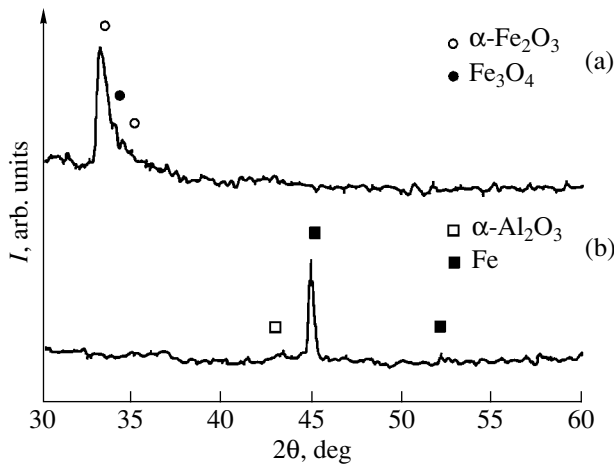
### 2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The preparation procedure is based on initiating the classical solid-phase reaction in thin films:

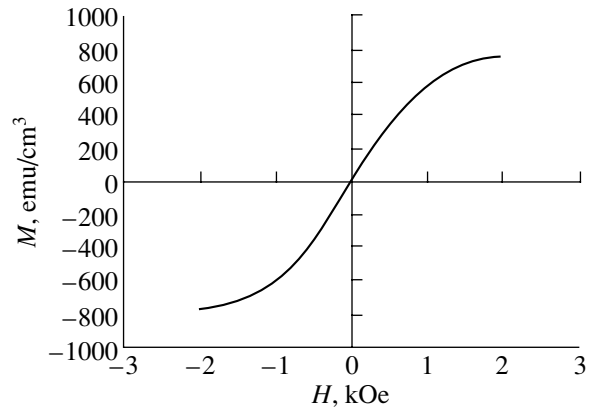


Earlier [8, 9], it was demonstrated that solid-phase reactions in bilayer thin films at high heating rates proceed under conditions of self-propagating high-temperature synthesis. The self-propagating high-temperature synthesis in thin films proceeds in the form of a surface combustion wave. This process is characterized by the initiation temperature  $T_0$ . In our case, the reagents for reaction (1) were bilayer and multilayer Al/Fe<sub>2</sub>O<sub>3</sub> film samples, which were prepared by dc ion-plasma sputtering through successive deposition of Fe<sub>2</sub>O<sub>3</sub> and aluminum layers without vacuum deterioration. The targets used in producing Al and Fe<sub>2</sub>O<sub>3</sub> films were prepared in the form of wafers cut respectively from monolithic aluminum and a conducting ceramic coating of iron oxide, which was obtained by plasma deposition [10].

The films were evaporated on glass substrates at a temperature of ~320 K in an argon atmosphere at a pressure of  $5 \times 10^{-2}$  Pa. The evaporation rate was 0.3 nm/s for aluminum and 0.2 nm/s for iron oxide. The total thicknesses of the aluminum and iron oxide films lay within the ranges 15–50 and 40–120 nm, respectively. The samples obtained were heated at a rate no less than 20 K/s in order to initiate the wave of self-propagating high-temperature synthesis. For bilayer film samples, the solid-phase reaction proceeded at temperatures above the initiation temperature  $T_0 \sim 800$  K under conditions of self-propagating high-temperature synthesis. The front of the propagation of high-temperature synthesis, which was observed visually, is typical of self-propagating high-temperature synthesis in thin films [8, 9]. For multilayer film samples, the observation of the front of self-propagating high-temperature synthesis was hampered. For this rea-



**Fig. 1.** X-ray diffraction patterns of the [Al(20 nm)/Fe<sub>2</sub>O<sub>3</sub>(40 nm)] × 4 multilayer film: (a) initial sample and (b) sample after thermal annealing at a temperature of 800 K for 10 min.



**Fig. 2.** Magnetization curve for the [Al(20 nm)/Fe<sub>2</sub>O<sub>3</sub>(40 nm)] × 4 multilayer film after thermal annealing at a temperature of 800 K for 10 min. The magnetization is given per unit volume of iron.

son, these samples were subjected to thermal annealing through heating to a temperature 10–20 K higher than the initiation temperature  $T_0$  and heat treatment at this temperature for 50 min (the time required for completing the reaction and subsequent annealing).

### 3. RESULTS AND DISCUSSION

Figure 1a shows a typical x-ray diffraction pattern for the [Al(20 nm)/Fe<sub>2</sub>O<sub>3</sub>(40 nm)] × 4 multilayer film sample prior to the solid-phase reaction. This pattern contains reflections attributed to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The formation of Fe<sub>3</sub>O<sub>4</sub> in small amounts is also possible in the initial samples. The absence of reflections attributed to aluminum implies that aluminum is in an amorphous or finely crystalline state. After the solid-phase reaction (Fig. 1b), reflections from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> disappear and the reflections assigned to iron and amorphous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> appear in the x-ray diffraction pattern. The presence of the reflections associated with Fe(110) in the x-ray diffraction patterns, along with other weak reflections or their complete absence, indicates that iron nanocrystallites are characterized by a preferred orientation of the (110) plane aligned parallel to the substrate surface. The size distribution of nanoclusters and the relative volume of the metallic fraction  $x$  are important factors responsible for the magnetic properties of granulated materials. It follows from the reaction equation that  $x_r = 0.365$ . This value is less than the percolation threshold  $x_p$ . For many granulated systems that contain metallic nanoclusters in a dielectric matrix, the percolation threshold is estimated as  $x_p = 0.5$ – $0.6$  [11]. This suggests that the metallic nanoclusters are separated from each other. The separation of iron nanoclusters is confirmed by a high resistivity of the samples, namely,  $\rho = 10^{-6}$ – $10^{-4}$   $\Omega$  m, which is typical of metallic clusters

in a nonconducting matrix below the percolation threshold.

The size of iron grains in the direction perpendicular to the sample surface was determined from the broadening of the diffraction peak of Fe(110) according to the Scherrer formula. The mean grain size was found to be 28 nm. As was shown by Chen *et al.* [12], particles with a smaller size exist in a one-dimensional state. Under the assumption that the iron cluster in other directions has the same size, the cluster should exhibit a magnetic single-domain structure. In this case, the sample can be treated as an ensemble of single-domain particles and its behavior can be described in terms of the Stoner–Wohlfahrt theory. The magnetization curve for an ensemble of single-domain particles has the form of a hysteresis loop with the following parameters:  $M_r = 0.5M_S$  and  $H_c = 0.958$  K/ $M_S$  (see, for example, [13]). Figure 2 depicts a typical magnetization curve for Fe–Al<sub>2</sub>O<sub>3</sub> films obtained as a result of reaction (1). The absence of a hysteresis loop permits us to assume that the iron clusters predominantly occur in the superparamagnetic state. A similar hysteresis curve, which can be considered as a superposition of magnetization curves for iron nanoclusters in superparamagnetic and magnetic states, was observed earlier for Co–Ag granulated films [14]. The coexistence of the superparamagnetic and magnetic states can also be observed in ferromagnetic nanoclusters inside a nonconducting matrix [15]. The critical size below which the iron nanoclusters in the Al<sub>2</sub>O<sub>3</sub> matrix are in the superparamagnetic state is approximately equal to 10 nm [12]. This suggests that the size distribution of iron nanoclusters in the samples under investigation is rather broad and covers sizes from several to tens of nanometers. It should be noted that no hysteresis loop is observed even at a temperature of 77 K. It follows that the blocking temperature  $T_B$

for iron nanoparticles in the superparamagnetic state is below this temperature.

The reaction products are formed solely at the front of self-propagating high-temperature synthesis. The characteristic reaction time is determined from the formula  $t = \tau/V_f^2$  where  $\tau$  is the thermal diffusivity of the bilayer film sample and  $V_f$  is the front velocity at the initiation temperature of self-propagating high-temperature synthesis. Let us assume that  $\tau$  is determined by the thermal diffusivity of the metal oxide; i.e.,  $\tau \sim (1-5) \times 10^{-7}$  m<sup>2</sup>/s and  $V_f \sim 1 \times 10^{-2}$  m/s [8, 9]. As a result, the characteristic reaction time is estimated as  $t = (1-5) \times 10^{-3}$  s. Under the assumption that the reaction proceeds in the solid phase at a temperature close to the melting point of the metal and that the diffusion coefficient is determined to be  $D \sim 10^{-12}-10^{-14}$  m<sup>2</sup>/s, the size of metallic clusters is estimated as  $r \sim \sqrt{Dt} = (3-70)$  nm. This estimate is in good agreement with the aforementioned sizes of iron nanoclusters formed as a result of reaction (1). The dependence of the front velocity of self-propagating high-temperature synthesis  $V_f$  on the substrate temperature  $T_S$  ( $T_S > T_0$ ) follows a law close to the Arrhenius law. Consequently, this velocity should determine the size distribution function and the mean size of iron nanoparticles. Therefore, the microstructure can be controlled both by varying the substrate temperature  $T_S$  upon initiating the self-propagating high-temperature synthesis in Al/Fe<sub>2</sub>O<sub>3</sub> bilayer films and by choosing the conditions of subsequent heat treatment. In turn, the microstructure determines the magnetic properties of Fe–Al<sub>2</sub>O<sub>3</sub> granulated films.

Note that the nanocrystalline microstructure should be predominant after passing the wave of self-propagating high-temperature synthesis in all the samples containing more than two phases in the reaction products. In particular, similar microstructure and magnetic properties are observed in Fe–TiO<sub>2</sub> films after the solid-phase reaction between Ti and Fe<sub>2</sub>O<sub>3</sub> layers.

#### 4. CONCLUSIONS

It was demonstrated that the solid-phase reactions proceeding under conditions of self-propagating high-temperature synthesis can be used for preparing granulated media. Specifically, the Fe–Al<sub>2</sub>O<sub>3</sub> granulated films were obtained after the solid-phase reaction

between Al and Fe<sub>2</sub>O<sub>3</sub> layers. Analysis of the reaction equation proved that the volume fraction of iron is less than the percolation threshold. In the studied samples, the (110)-textured iron nanoclusters are in superparamagnetic and magnetic states.

#### ACKNOWLEDGMENTS

This work was supported by the Krasnoyarsk Regional Foundation for Research, project no. 11F001C.

#### REFERENCES

1. S. Mitani, S. Takahashi, K. Takahashi, *et al.*, Phys. Rev. Lett. **81** (13), 2799 (1998).
2. A. B. Pakhomov, X. Yan, and Y. Xu, J. Appl. Phys. **79** (8), 6140 (1996).
3. A. N. Drachenko, A. N. Yurasov, I. V. Bykov, *et al.*, Fiz. Tverd. Tela (St. Petersburg) **43** (5), 897 (2001) [Phys. Solid State **43**, 932 (2001)].
4. B. Raquet, M. Goiran, N. Negre, *et al.*, Phys. Rev. B **62** (24), 17144 (2000).
5. S. H. Liou and C. L. Chien, Appl. Phys. Lett. **52** (6), 512 (1988).
6. Z. S. Jiang, G. J. Jin, J. T. Ji, *et al.*, J. Appl. Phys. **78** (1), 439 (1995).
7. D. Babonneau, F. Petrov, J.-L. Maurice, *et al.*, Appl. Phys. Lett. **76** (20), 2892 (2000).
8. V. G. Myagkov and L. E. Bykova, Dokl. Akad. Nauk **354** (6), 777 (1997).
9. V. G. Myagkov, V. S. Zhigalov, L. E. Bykova, and V. K. Mal'tsev, Zh. Tekh. Fiz. **68** (10), 58 (1998) [Tech. Phys. **43**, 1189 (1998)].
10. A. A. Lapeshev, V. N. Saunin, S. V. Telegin, *et al.*, Zh. Tekh. Fiz. **70** (5), 130 (2000) [Tech. Phys. **45**, 653 (2000)].
11. C. L. Chien, J. Appl. Phys. **69** (8), 5267 (1991).
12. C. Chen, O. Kitakami, and Y. Shimada, J. Appl. Phys. **84** (4), 2184 (1998).
13. M. Prutton, *Thin Ferromagnetic Films* (Butterworths, Washington, 1964; Sudostroenie, Leningrad, 1967).
14. S. Honda, M. Nawate, M. Tanaka, and T. Okada, J. Appl. Phys. **82** (2), 764 (1997).
15. Y. Xu, B. Zhao, and X. Yan, J. Appl. Phys. **79** (8), 6137 (1996).

*Translated by N. Korovin*