ISSN 1063-7850, Technical Physics Letters, 2012, Vol. 38, No. 4, pp. 336–339. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © V.A. Vikulov, V.V. Balashev, T.A. Pisarenko, A.A. Dimitriev, V.V. Korobtsov, 2012, published in Pis'ma v Zhurnal Tekhnicheskoi Fiziki, 2012, Vol. 38, No. 7, pp. 73–80.

The Effect of Synthesis Temperature on Structural and Magnetic Properties of Fe_3O_4 Films Grown on the SiO_2/Si(001) Surface

V. A. Vikulov*, V. V. Balashev, T. A. Pisarenko, A. A. Dimitriev, and V. V. Korobtsov

Institute of Automation and Control Processes, Far East Branch,
Russian Academy of Sciences, Vladivostok, 690041 Russia
School of Natural Sciences, Far Eastern Federal University, Vladivostok, 690950 Russia
**e-mail: vikulov@mail.dvo.ru*

Received November 23, 2011

Abstract—Magnetite (Fe_3O_4) films have been deposited on a SiO_2/Si(001) surface at various temperatures by reactive sputtering of iron in oxygen. The influence of the synthesis temperature on the structure and magnetic properties of Fe_3O_4/SiO_2/Si(001) samples have been studied by the methods of reflection high-energy electron diffraction, atomic force microscopy, Raman spectroscopy, and vibrating sample magnetometry. An optimum substrate temperature for the formation of polycrystalline films with the best magnetic characteristics has been determined.

DOI: 10.1134/S1063785012040141

Magnetite (Fe_3O_4) is characterized by a large spin polarization of electrons and a high Curie temperature (580°C), which makes this compound a promising material for hybrid device structures in spintronics [1, 2]. The growth of thin Fe_3O_4 film can be performed by various methods, including pulsed laser ablation [3], molecular beam epitaxy [4], and RF sputtering [5]. Recently, we have demonstrated the possibility to obtain homogeneous polycrystalline Fe_3O_4 films on thin buffer SiO_2 layers by reactive sputtering of iron in oxygen. However, the experiments were performed at a fixed temperature (T_{dep}) of the SiO_2/Si(001) substrates [6].

As is known, the temperature of synthesis (deposition) significantly influences the structure of Fe_3O_4 films and, hence, their structure-dependent magnetic characteristics [7]. For this reason, the present study was aimed at determining the influence of the deposition temperature on the structure and magnetic properties of Fe_3O_4 films synthesized on tunneling-transparent buffer SiO_2 layers by reactive sputtering of iron in oxygen.

The substrates were cut from *n*-type (001)-oriented single-crystalline Si wafers with a resistivity of 4.5 Ωcm, on which a thin (1.5 nm thick) SiO_2 layer was formed by wet chemical treatment. The experiments on the synthesis of Fe_3O_4 films were performed in an ultrahigh-vacuum setup equipped with attachments for the reflection high-energy electron diffraction (RHEED) and spectral ellipsometry measurements. The temperature of substrates for Fe_3O_4 film synthesis was varied in the range from 200 to 400°C with a 50°C step. The film thickness as determined from the results of ellipsometric measurements was about 50 nm, The experimental conditions have been described in more detail elsewhere [6].

The structure and phase compositions of the obtained films were studied by RHEED. The RHEED patterns from films grown at various deposition temperatures T_{dep} in the indicated interval showed diffraction fringes typical of polycrystalline magnetite films with [311] texture [6]. The sharpness of this pattern increased with T_{dep}, which was indicative of a growth in the grain size. This conclusion was also confirmed by the data of atomic force microscopy (AFM). Figure 1a shows the typical AFM image of a Fe_3O_4 film obtained on a Solver-P47 instrument (NT MDT Co.). As can be seen, the sample surface exhibits a "granular" structure with microcavities, the lateral dimensions of which are comparable with the sizes of grains (see the inset to Fig. 1a). An analysis of these AFM images showed that the density of microcavities amounted to 3.5×10^9 cm^{-2} in a film deposited at $T_{dep} = 200$°C and decreased by a factor of 2–3 in the films grown at higher temperatures. The depth of these microcavities in the films synthesized at various T_{dep} did not exceed 20 nm at a total film thickness of 50 nm. Accordingly, it was believed that the films had no through pores and possess continuous structures. As T_{dep} was increased from 200 to 400°C, the average grain size and rms roughness of the surface increased by a factor of ~2.5 and 3, respectively (Fig. 1b). The surface density of grains monotonically decreased from 3.0×10^{11} to 5.0×10^{10} cm^{-2} with the deposition temperature increasing in the indicated interval.

More detailed information about the phase composition of synthesized films was obtained using the method of Raman spectroscopy (RS). The Raman spectra were measured in a range of 190–900 cm^{-1} on an Ntegra Spectra instrument (NT MDT Co.) at room temperature with excitation by Ar$^+$ laser radiation at a wavelength of 488 nm. The probing radiation power at the sample surface was 8 mW. According to published data [8], a single-crystalline Fe_3O_4 is characterized by five active Raman modes: A_{1g} (ω = 669 cm^{-1}); E_g (ω = 410 cm^{-1}); and $3T_{2g}$ (ωT_{2g}^1 = 193 cm^{-1}, ωT_{2g}^2 = 540 cm^{-1}, and ωT_{2g}^3 = 300 cm^{-1}). The spectral range under consideration can also display intense peaks corresponding to the A_{1g} modes of other iron oxides (228 and 447 cm^{-1} for α-Fe_2O_3, 695 cm^{-1} for γ-Fe_2O_3) [9].

Figure 2 shows the Raman spectra of a Si substrate and the samples synthesized at various temperatures. As can be seen, the spectra of films grown at $T_{dep} >$ 250°C display an intense peak at 669 cm^{-1}. The characteristic magnetite modes E_g, T_{2g}^2, and T_{2g}^3 are not manifested because of their weak intensity and the overlap with the characteristic modes of silicon at 520 and 303 cm^{-1}. The peaks observed in the region of 669 cm^{-1} were decomposed into Lorentzian components. An analysis of the results showed the presence of a certain amount of γ-Fe_2O_3 in the films formed at T_{dep} = 200°C, which disappeared in the films grown at higher temperatures. The peak half-width (FWHM) of the A_{1g} mode of Fe_3O_4 decreases when T_{dep} is increased from 200 to 300°C and then remains unchanged with the further growth in the temperature of synthesis (see table in the inset to Fig. 2). Taking into account that A_{1g} mode is related to the structure of Fe_3O_4 [10], the observed decrease in the peak half-width with increasing T_{dep} can be related to a structural ordering in the grains.

Information of the effect of the temperature of synthesis on the magnetic properties of Fe_3O_4 films was obtained from an analysis of the magnetic hysteresis loops (Fig. 3a) measured by the induction technique on a vibrating sample magnetometer. It was established that the obtained Fe_3O_4 films were magnetically isotropic. As T_{dep} was increased, the coercive field (H_c) exhibited a slight decrease from 305 Oe (at T_{dep} = 200°C) to 270 Oe (at T_{dep} = 400°C), the effective saturation magnetization (M_{eff}) exhibited a 1.5-fold increase in this temperature interval, and the loop squareness (M_r/M_s) exhibited a maximum at T_{dep} = 300°C (Fig. 3b). Note that the observed H_c values are comparable with the coercive fields of polycrystalline magnetite films obtained by other methods [11, 12].

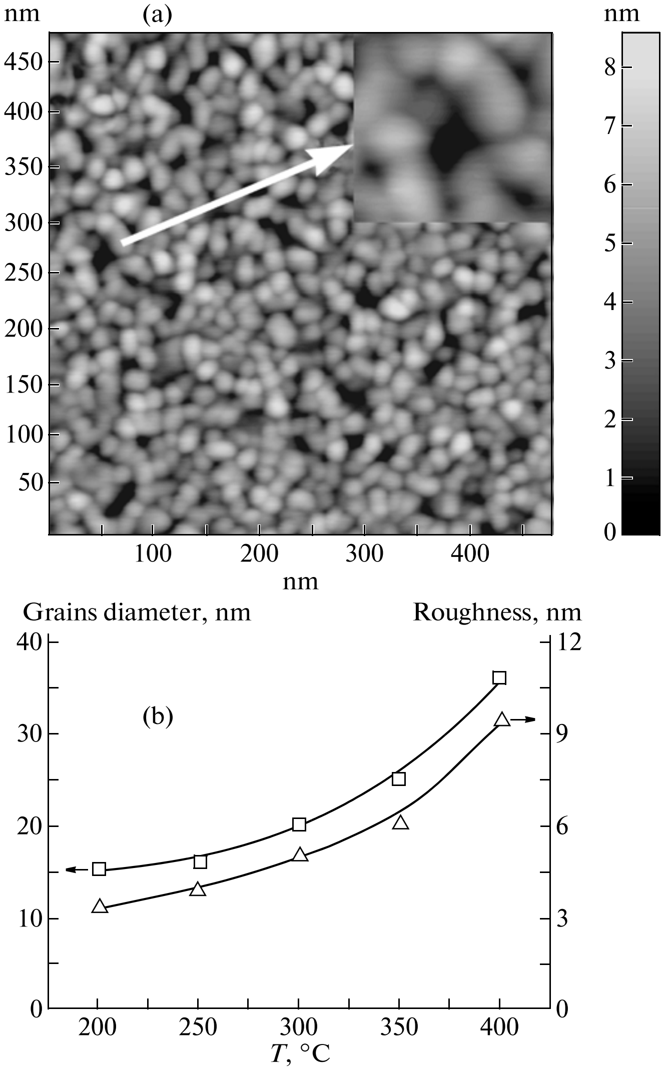

Fig. 1.(a) AFM image of Fe_3O_4 film grown at T_{dep} = 300°C (the inset shows the typical image of microcavities); (b) plot of the average grain size and rms surface roughness vs. synthesis temperature.

Malyutin et al. [13] showed that the coercivity of nanocrystalline films can be represented as a sum of contributions related to the grain boundaries (H_v), grain size (H_K), surface roughness (H_s), surface relief (H_{ms}), and pores (H_w):

$$H_c = (H_v^{3/2} + H_K^{3/2} + H_s^{3/2} + H_{ms}^{3/2} + H_w^{3/2})^{2/3}.$$

The character of various H_c components, depending on the grain size, variance of the easy axes, crystallographic anisotropy, film thickness, and the average depth and diameters of microcavities was considered in [13]. The effect of parameters of the surface roughness, including the rms amplitude (h) and lateral period (l), on the H_c value was studied in [14]. Since our Fe_3O_4 films are considered to be structurally continuous, the main contributions to H_c can be due to

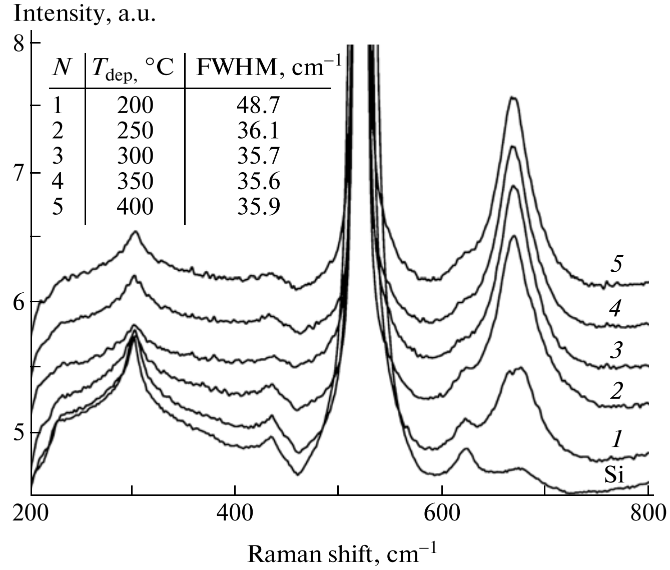

Fig. 2. Raman spectra of Fe_3O_4 film grown on SiO_2/Si substrates at various T_{dep} (°C): (*1*) 200, (*2*) 250, (*3*) 300, (*4*) 350, and (*5*) 400 (for the sake of clarity, the spectra are shifted along the ordinate axis). The inset gives data on the full width at half maximum (FWHM) of the A_{1g} peak.

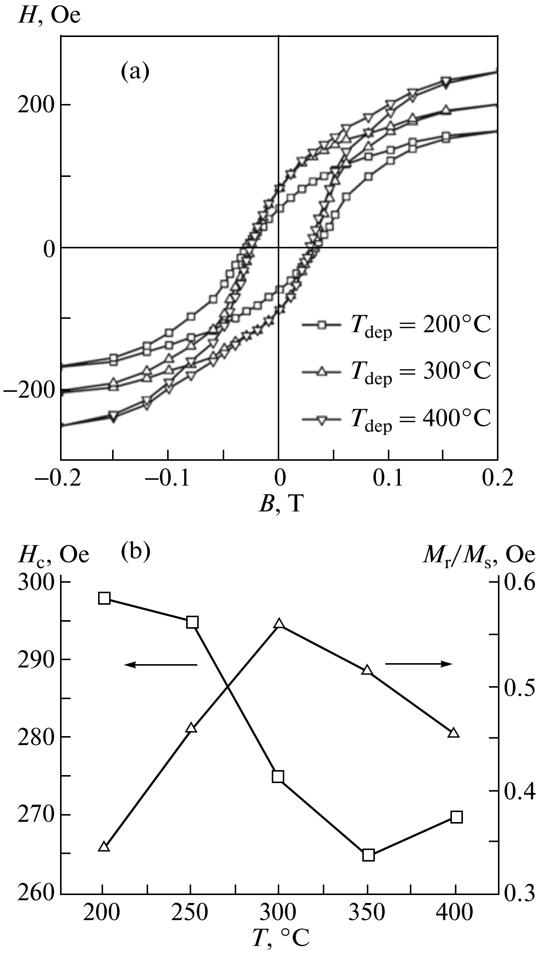

Fig. 3. (a) Hysteresis loops of Fe_3O_4 films grown on the $SiO_2/Si(001)$ surface at various temperatures T_{dep} and (b) plots of the coercive field H_c and reduced remanent magnetization M_r/M_s vs. T_{dep}.

H_K, H_{ms}, and H_s. The H_K value increases with the grain size, while H_s and H_{ms} decrease because of variations in the $(h/l)^{4/3}$ ratio and a decrease in the density of microcavities, respectively. It is a change in the ratio of H_s and H_{ms} that accounts for a decrease in H_c. An increase in M_s can be related to a decrease in the volume fraction of grain boundaries in the film with increasing grain size, since the effective magnetization is a sum of the magnetization of grains (M_s) and their boundaries (M_{gb}):

$$M_{eff}V = M_sV_g + M_{gb}V_{gb},$$

where V_g, V_{gb}, and V are the volumes of grains, grain boundaries, and the film, respectively [15]. The reduced remanent magnetization reaches a maximum for the films formed at $T_{dep} = 300$°C. This result can be explained by the fact that, in films grown at temperatures below 300°C, the phase composition and structure change so that the remanent magnetization M_r increases faster than the effective saturation magnetization M_s, In contrast, at $T_{dep} > 300$°C, the value of M_r remains constant while M_s increases due to a decrease in the amount of defects in the film volume.

Thus, the present investigation demonstrated the possibility of growing continuous polycrystalline Fe_3O_4 films with pronounced (311) texture of grains on SiO_2/Si substrates by the reactive sputtering of iron in oxygen in a range of substrate temperatures from 200 to 400°C. It has been shown that an increase in the temperature of synthesis leads to a structural ordering of grains in the film. The dependence of the remanent magnetization on the film deposition temperature exhibits a maximum at $T_{dep} = 300$°C.

Acknowledgments. The authors are grateful to Prof. L.A. Chebotkevich for fruitful discussions and Dr. E.A. Chusovitin for his help in conducting AFM measurements.

This work was supported in part by the Far East Branch of the Russian Academy of Sciences (project nos. 09-III-A-02-023 and 09-I-OFN-057), the Ministry of Education and Science of the Russian Federation ("Program in Support for Leading Scientific Schools," project no. NSh-46342010.2), and the Russian Foundation for Basic Research (project no. 11-02-98523-r_vostok_a).

REFERENCES

1. A. Yanase and K. Siratori, J. Phys. Soc. Jpn. **53**, 312 (1984).
2. N. Tsuda, K. Nasu, A. Fujimori, and K. Siratori, *Electronic Conduction in Oxides* (Springer-Verlag, Berlin, 1991).
3. M. Ziese et al., J. Magn. Magn. Mater. **290–291**, 1116 (2005).
4. Y. Zhou, C. McEvoy, R. Ramos, and I. V. Shvets, J. Appl. Phys. **99**, 081111 (2006).
5. Hong Yan, Ming Zhang, and Hui Yan, J. Magn. Magn. Mater. **321**, 2340 (2009).
6. V. V. Balashev, V. V. Korobtsov, T. A. Pisarenko, and L. A. Chebotkevich, Tech. Phys. **56**, 1501 (2011).
7. A. Zukova, A. Teiserskis, Y. K. Gun'ko, et al., Appl. Phys. Lett. **96**, 172502 (2010).
8. J. L. Verbe, Phys. Rev. **9** (12), 5236 (1974).
9. I. Chamritski and G. Burns, J. Phys. Chem. B **109**, 4965 (2005).
10. Shailja Tiwari, D. M. Phase, and R. J. Choudhary, Appl. Phys. Lett. **93**, 234108 (2008).
11. D. Tripathy A. O. Adeyeye, and C. B. Boothroyd, J. Appl. Phys. **99**, 081105 (2006).
12. J. Tang, K.-Y. Wang, and W. Zhou, J. Appl. Phys. **89** (11), 7690 (2001).
13. V. I. Malyutin, V. E. Osukhovskii, A. A. Ivanov, L. A. Chebotkevich, I. V. Lobov, and Yu. D. Voroviev, Phys. Status Solidi (a) **93**, 585 (1986).
14. S. P. Li, A. Samand, W. S. Lew, Y. B. Xu, and J. F. C. Bland, Phys. Rev. B **61** (10), 6871 (2000).
15. S. V. Vonsovskii, *Magnetism* (Moscow, 971) [in Russian].

Translated by P. Pozdeev